Thermo-reversible binding of multivalent ions by surfactant self-assembly
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Thermo-reversible binding of multivalent ions by surfactant self-assembly

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Summary

Multivalent ions have to be removed from aqueous streams for a number of reasons, ranging from toxicity to the formation of salt depositions in process installations. Current methods to remove multivalent ions are based on ion exchange technology. A major disadvantage of ion exchange technology is the environmentally unfriendly regeneration of the ion exchange resins. For an effective regeneration large amounts of acid or caustic are required, which results in large waste streams. A way to obtain a more efficient ion removal process is to employ reversible multivalent ion binding mechanisms.

In this thesis carboxylic acid end standing (CAE) surfactants have been used for this purpose. CAE surfactants are Pluronic surfactants (i.e. polyethylene-polypropylene-polyethylene block copolymers) that are modified by reaction with succinic anhydride to obtain surfactants comprising carboxylic end groups. Like Pluronic surfactants, CAE surfactants show thermo-reversible aggregation behavior. Above the critical micellization temperature (CMT) CAE surfactants form micellar aggregates, and as a result of the modification they can bind multivalent cations. Lowering the temperature to a value below the CMT will release the cations from the micelles. The synthesis, chemical stability and polydispersity of the CAE surfactants have been discussed. Also, some general recommendations are given for the development of an environmentally feasible scaling up procedure for the synthesis of CAE surfactants.

The metal binding behavior of different CAE surfactants, like CAE-85, CAE-64 and CAE-81, have been studied with isothermal titration calorimetry (ITC), conductometry, differential scanning calorimetry (DSC), and dynamic light scattering (DLS). ITC has been used to obtain a binding isotherm for calcium ions to the CAE micelles. The Poisson-Boltzmann theory is used to derive a relation between the measured heat effects in ITC and the cation binding. ITC has also been used to study the effect of different parameters, including pH, ionic strength, surfactant concentration, ion valence, and temperature on the binding of cations to CAE surfactants. The results for the fractional binding to the CAE-85 system are quantified by fitting two isotherm models to the experimental data. It can be
concluded that ITC can effectively be used to study the binding of mono- and multivalent ions in ionic micellar solutions.

To overcome the drawbacks of conductometric analysis, a second method to determine the binding behavior of monovalent and divalent counterions in CAE surfactant systems has been developed. Different conductometric methods, including the use of Eisenberg plots and conductivity excess, are combined. With this approach qualitative and quantitative information is obtained about surfactant systems with respect to the binding of counterions and competition between monovalent and multivalent counterions. With respect to the micellization behavior, the influence of pH and salt additives on the CMT and the cloud point of the CAE surfactants have been determined. It appears that the cloud point and CMT of CAE surfactants are more sensitive to changes in pH and ionic strength as compared to the CMT and the cloud point of non-modified Pluronic surfactants.

Micellar-enhanced ultrafiltration (MEUF) is used to demonstrate the thermo-reversibility of the calcium binding to CAE-85 micelles. Furthermore, ultrafiltration experiments show that phenanthrene and calcium can be removed simultaneously from an aqueous stream by CAE surfactants. Both contaminants can be separated from the CAE-85 micelles by thermal regeneration. Additionally, solubilization experiments have been performed that show the influence of phenanthrene on the calcium binding and on the membrane fouling behavior of the CAE-85 surfactant. The fouling behavior of CAE-85 and Pluronic P85 on cellulose acetate (CA) and polyether sulfone (PES) membranes has been determined by performing hysteresis experiments. No fouling has been observed on CA membranes for both surfactants, while on PES membranes fouling has been detected.

Scale formation on membranes is the main bottleneck to enhance the water recovery in membrane water purification processes. CAE surfactants seem to be a promising alternative for conventional antiscalants, because of the thermo-reversible regeneration behavior. An economical evaluation is given for the implementation of CAE surfactants as an antiscalant or as an ion exchanger in an industrial scale RO membrane process. The process configurations have been evaluated using a scaling model and are compared with reference base cases to minimize the influence of estimation errors. The use of CAE-85 as an antiscalant seems to be the most feasible option, because it has lower treatment costs and a higher water recovery as compared to the base case. The degree of heat integration, the
method of surfactant immobilization and the binding capacity of the CAE surfactant are the key factors to obtain a feasible process.

The various results for the three CAE surfactants, which differ in hydrophobic-hydrophilic balance, provide directions for the development of new CAE surfactants for different temperature-responsive applications. The functionality of thermo-reversible surfactants can be changed in different ways. A higher binding capacity can be obtained by synthesizing surfactants with more carboxylic groups along the surfactant chain. By using a different anionic group, like the sulfonate group, micelles with stronger binding affinity for divalent cations might be obtained. Synthesizing surfactants with cationic terminated amine end groups allows for the binding of anions. The use of CAE surfactants as antiscalant or as reversible ion exchangers in combination with membrane technology seems to be the logical first step in the development of new feasible separation applications on industrial scale as well as on a household level. Considering the versatile features of thermo-reversible self-assembly, the long-term perspective of end group modified Pluronic surfactants seems promising.
Samenvatting

Meerwaardig geladen ionen moeten verwijderd worden uit waterige stromen vanwege hun toxiciteit of de mogelijkheid tot vorming van zoutafzettingen in procesinstallaties. De huidige technieken om meerwaardig geladen ionen te verwijderen zijn vaak gebaseerd op ionenwisseling. Een van de belangrijkste nadelen van ionenwisselaars is de milieu-onvriendelijke methode van regenereren. Bij deze methode zijn grote hoeveelheden zuur en/of base vereist om de gebonden meerwaardige ionen van de ionenwisselaar los te maken, met als gevolg dat er enorme zoute afvalstromen worden geproduceerd. Nieuwe reversibele ionbinding mechanismen zijn gewenst om efficiëntere processen te verkrijgen om deze ionen te verwijderen.

In dit proefschrift worden carboxylzuur eindstandige (CAE) surfactants gebruikt voor dit doel. CAE surfactants zijn Pluronic surfactants (polyethyleen-polypropyleen-polyethyleen blokcopolymeren) die zijn gemodificeerd door een reactie met barnsteenzuur, zodat surfactants met negatief geladen eindgroepen worden verkregen. CAE surfactants vertonen net zoals Pluronic surfactants thermisch reversibel aggregatiegedrag. Boven de kritische micellizatietemperatuur (CMT) vormen CAE surfactants micellen die als gevolg van de modificatie meerwaardig geladen kationen kunnen binden. Bij het verlagen van de temperatuur tot onder de CMT geraken deze kationen weer vrij in oplossing doordat de micellen uit elkaar vallen tot gewone surfactant moleculen. De synthese, de chemische stabiliteit en de polydispersiteit van de CAE surfactants worden bekeken in dit proefschrift. Verder worden enkele algemene aanbevelingen gedaan ten aanzien van de ontwikkeling van een opschalingsprocedure voor de CAE surfactant synthese.

Het bindingsgedrag van metaalionen aan verschillende CAE surfactants, zoals CAE-85, CAE-64 en CAE-81, is bestudeerd met isothermal titration calorimetry (ITC), geleidbaarheidsmetingen, differential scanning calorimetry (DSC) en lichtverstrooing (DLS). ITC metingen zijn gebruikt om een isotherm af te leiden voor de binding van calcium ionen aan CAE micellen. Hierbij wordt de Poisson-Boltzmann theorie gebruikt om een relatie te verkrijgen tussen de gemeten ITC warmte-effecten en de bindingsparameters van de kationen. De ITC techniek is ook gebruikt om het effect te meten van verschillende
parameters, waaronder de pH, de ionensterkte, de surfactantconcentratie, de temperatuur en het type kation, op de binding van kationen aan CAE micellen. Er kan geconcludeerd worden dat ITC een geschikte techniek is om informatie te vergaren over de binding van ionen aan miceloppervlakken.

Om de nadelen van conductometrische analyse te omzeilen, is een nieuwe methode ontwikkeld om het interactiegedrag van eenwaardige en meerwaardige ionen in CAE surfactant systemen te onderzoeken. Verschillende geleidbaarheidsmethoden, waaronder het gebruik van Eisenberg grafieken en de bepaling van de ‘conductivity excess’ zijn met elkaar gecombineerd. Met deze methode is kwalitatieve en kwantitatieve informatie verkregen over surfactant systemen met betrekking tot de binding van tegenionen en de competitie tussen eenwaardige en meerwaardige tegenionen. De invloed van de pH en de ionensterkte op het cloud point en op de CMT van de micel is bekeken. Het cloud point en de CMT van CAE surfactants zijn gevoeliger voor veranderingen in de pH of in de ionensterkte vergeleken met het cloud point en CMT van Pluronic surfactants.

Micellaire ultrafiltratie (MEUF) is gebruikt om de thermoreversibiliteit van de calciumbinding aan CAE-85 micellen aan te tonen. Verder is aangetoond dat zowel fenantreen als calcium gelijktijdig kunnen worden verwijderd uit een waterige oplossing door het gebruik van CAE surfactants. Beide watervervuilende componenten kunnen van de CAE-85 micellen worden gescheiden door thermisch regeneratie. Om tot dit resultaat te komen zijn er solubilizatie experimenten uitgevoerd die de invloed van fenantreen op de binding van calcium en op het membraanvervuilingsgedrag van CAE-85 laten zien. De vervuilende werking van CAE-85 en Pluronic P85 is bestudeerd op cellulose acetaat membranen (CA) en polyether sulfon (PES) membranen door middel van het uitvoeren van druk hysterese experimenten. Geen vervuiling (fouling) werd geconstateerd op CA membranen voor beide surfactants, in tegenstelling tot de PES membranen die wel vervuilden.

Zoutvorming op membranen is de belangrijkste bottle-neck wanneer het gaat om het vergroten van de wateropbrengst in drinkwater producerende processinstallaties gebaseerd op membraantechnologie. CAE surfactants lijken een goed alternatief te bieden voor conventionele antiscalants, door het mogelijk maken van een thermisch reversibele regeneratie. Er is een economische evaluatie uitgevoerd met betrekking tot de implementatie
van CAE surfactants als antiscalant dan wel als ionenwisselaar in een industrieel membraan proces. De procesconfiguraties zijn geëvalueerd met behulp van een scalingsmodel en worden vergeleken met referentie situaties om de invloed van fouten in de schattingen van parameters te beperken. Het gebruik van CAE-85 als een alternatieve antiscalant lijkt de meest haalbare optie, omdat de zuiveringskosten laag blijven en de opbrengst van zuiver water groot is vergeleken met de uitgangssituatie. De mate van warmteintegratie, de manier van surfactant immobilizatie en de totale bindingscapaciteit van de surfactant zijn de sleutelfactoren om te komen tot een economisch haalbaar proces.

De resultaten die behaald zijn voor de verschillende CAE surfactants, welke verschillen in de balans tussen hydrofobe en hydrofiele bloklengte, verschaffen mogelijkheden voor de ontwikkeling van diverse CAE surfactants voor nieuwe temperatuur reguleerbare toepassingen. De functionaliteit van thermo-reversibele surfactants kan aangepast worden op verschillende manieren. Een hogere bindingscapaciteit kan worden verkregen door het synthetizeren van surfactants met meer zuurgroepen aan de keten. Door het plaatsen van een andere anionische eindgroep, zoals de sulfonaat groep, kan een sterkere binding worden verkregen. Door surfactants te synthetizeren met kationische amine eindgroepen wordt de mogelijkheid verkregen om meerwaardige anionen te binden. Het gebruik van CAE surfactants als antiscalant of als reversibele ionenwisselaar in combinatie met membraantechnologie lijkt de eerste logische stap in de ontwikkeling van nieuwe haalbare scheidings applicaties zowel op industriële schaal als voor huishoudelijke toepassingen. Wanneer men de veelzijdige eigenschappen van thermo-reversibele surfactants in acht neemt dan lijkt het lange termijn perspectief voor eindgroep gemannipuleerde Pluronics veelbelovend.
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Chapter 1

Introduction to CAE surfactants for thermo-reversible binding of multivalent cations

Abstract

Multivalent ions have to be removed from aqueous streams for a number of reasons, ranging from toxicity to the formation of salt depositions in process installations. Current methods to remove multivalent ions are based on ion exchange technology. A major disadvantage of ion exchange technology is the environmentally unfriendly regeneration of the ion exchange resins. For an effective regeneration large amounts of acid and/or caustic are required, which results in large waste streams. One way to obtain a more efficient ion removal process is to make use of a reversible binding mechanism. In this Chapter carboxylic acid end standing (CAE) surfactants are introduced. Above the critical micellization temperature the CAE surfactants form micellar aggregates that can bind multivalent cations. Lowering the temperature to a value below the critical micellization temperature will release the cations from the micelles. With this feature the CAE surfactants may be used as thermally regenerable ion binders. The use of CAE surfactants as antiscalant or as reversible ion exchangers in combination with membrane technology seems to be the first step in the development of new separation applications. The Chapter concludes with a brief overview of the contents of this thesis.
1.1 Ion binding

Binding of multivalent cations is relevant for many phenomena occurring in aqueous environments. Wastewater streams resulting from e.g. metal processing industries, photographic industries, and refineries, contain (heavy) metal ions that have to be removed \[1, 2\]. Hardness ions, like calcium and barium, are undesired, because these cations cause salt deposition in process installations and on membrane surfaces \[3\]. Furthermore, other metal ions have to be removed for reasons of toxicity \[4\]. Nowadays, the most common techniques to remove ions are ion exchange \[5-8\], electrodialysis \[9, 10\], activated carbon adsorption \[11\], micellar-enhanced ultrafiltration (MEUF) \[12-16\] and polyelectrolyte ultrafiltration (PEUF) \[17-19\]. However, the major drawback in most ion binding systems is the difficult regeneration of the polymer or resin, because of the strong binding interaction of the cations with the functional groups of the binding material. The regeneration stage, which commonly consists of a treatment with acid or caustic, will often lead to undesired waste streams \[6, 20, 21\]. Moreover, with the growing interest for biophysical systems (e.g. for drug delivery, the binding to lipid bilayers and ion pumping) the interest for binding systems with specific ion interactions has increased \[16, 22, 23\]. The ion binding properties of the binding material are determined by its molecular architecture. An adequate choice of the molecular architecture can lead to ion binding systems with a tuneable uptake and release behavior to control the rate and the amount of cation binding.

1.2 Counterion binding to polyelectrolytes and surfactant aggregates

Polyelectrolytes are the main building blocks for many ion exchange resins. A polyelectrolyte, like polyacrylic acid (PAA), has a long polymer backbone that contains many charged groups. The charged groups of the polyelectrolyte, that are relatively close together, need to be stabilized by counterions. For polyelectrolytes the binding of monovalent counterions is mainly electrostatic of nature and is called condensation. Multivalent ions often will bind considerably stronger as compared to monovalent ions because of the higher ion charge and the tendency to bind more specifically \[24\]. However, when polyelectrolytes are dissolved in a solution the more hydrophobic nature of the multivalent ions can result in precipitation of the polymer. In surfactant-based separation processes, like micellar-enhanced
ultrafiltration (MEUF), micelles are used to remove metal ions through interaction of the charged micelle surface with the oppositely charged metal ion. Surfactant aggregates or micelles have a highly dynamic structure, and in the case of ionic surfactant systems this results in a less well-defined monovalent counterion binding. However, most ionic surfactants need the hydrophilicity of the ionic head group to stay soluble in an aqueous solution. Therefore, the stronger binding of multivalent ions as compared to monovalent ions will in most situations lead to precipitation of the surfactant.

The difference in structure between micelles and polyelectrolytes results in different theoretical descriptions for counterion binding. In the case of polyelectrolytes often the two-state approximation is used \[^{[24]}\], i.e. counterions are either bound or free in solution. For surfactant systems double layer or triple layer models \[^{[25, 26]}\] are used, where the distribution of counterions around micelles can be divided in several layers. A bulk layer, a diffuse layer where the counterion concentration decreases with distance from the micellar surface, and a Stern layer (triple layer models) that accounts for the bound counterions, can be distinguished (Figure 1.1).

![Figure 1.1: Schematic picture of the distribution of ions and the electrical potential around a micelle of anionic surfactant molecules, based on the so-called triple layer model. The double layer model is similar to the triple layer model, except for the absence of a Stern layer.](image-url)
The presence of ions and the binding of ions by aggregates or resins will have a considerable effect on the properties of the solution \cite{27}. Several experimental techniques, like e.g. conductometry and surface tension measurements, are based on the changes in solution properties to measure the degree of counterion binding. Conductometry can be used to determine the thermodynamic micellization parameters combined with mass action modeling \cite{28}.

1.3 Surfactants and micellar systems

1.3.1 Surfactants
Surfactants are molecules that consist of a lyophobic tail and a lyophilic head group. Surfactants can aggregate into micelles or more complex aggregates like rods and discs. This is an entropy-driven process; above a certain concentration and temperature, aggregation of the surfactant unimers is more favorable, because the entropy of the water molecules that surround the lyophobic tail increases. In these aggregates the lyophobic segments form a core surrounded by a shell of highly solvated lyophilic segments that extend into the continuous aqueous phase. The formation of surfactants aggregates takes place at the critical micellization concentration (CMC) and is often accompanied by a clear transition in several physical properties of the surfactant solution, like surface tension and conductivity \cite{35,36}.

Figure 1.4: Typical shapes of a micellar aggregate: (a) spherical, (b) cylindrical rod shaped and (c) disc shaped.
The shape of the aggregate depends highly on the surfactant concentration and chemical structure of the surfactant. The most common shapes in this respect are spheres, disc like structures or cylindrical rods (Figure 1.4).

In general, three classes of surfactants can be distinguished: anionic, cationic and nonionic surfactants. In the case of ionic surfactants the lyophilic head groups contain a negative charge for anionic surfactants and a positive charge for cationic surfactants. These charged head groups have electrostatic interactions with counterions of the opposite charge. Also, it is known that most surfactants can solubilize hydrophobic compounds into the lyophilic core and can therefore be used as an impurity removal agent in aqueous process applications.

The combined hydrophobic and hydrophilic nature of surfactants makes them indispensable for a great variety of technological and biological applications as functional detergents, (de)wetting agents, emulsifiers, dispersants, stabilizers or defoamers.

### 1.3.2 Triblock copolymer surfactants

Polyethylene oxide polypropylene oxide polyethylene oxide (PEO-PPO-PEO) triblock copolymer surfactants are a specific group of nonionic surfactants. This group of surfactants is commercially available as Pluronics (BASF) or Synperonics (ICI) and these high molecular weight surfactants are well documented in literature. The main feature of these Pluronic surfactants is the ability to show temperature dependent aggregation behavior. Lowering the temperature will increase the CMC dramatically. Therefore, in Pluronic systems it is more convenient to use the critical micellization temperature (CMT) instead of the CMC. The CMT is the transition temperature above which the Pluronic surfactants will form aggregates. Above the cloud point (CP), which is another transition temperature, nonionic surfactants will start to separate into two phases, because of a decreased solubility and increased intermicellar interactions.

Pluronic surfactants are available with different CMT and CP, depending on the molecular weight and the ratio of the ethylene oxide (EO) and propylene oxide (PO) parts. In this work three Pluronic surfactants are used, i.e P85, L64 and L81. The features of these surfactants are shown in table 1.1
Table 1.1: Composition and some phase transition properties of Pluronic surfactants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>EO</th>
<th>PO</th>
<th>$M_w$ [g/mol]</th>
<th>CMT [$^\circ$C]</th>
<th>CP 1.0 wt% [$^\circ$C]</th>
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</thead>
<tbody>
<tr>
<td>P85</td>
<td>52</td>
<td>39</td>
<td>4568</td>
<td>29.5</td>
<td>85</td>
</tr>
<tr>
<td>L64</td>
<td>26</td>
<td>30</td>
<td>2918</td>
<td>31.5</td>
<td>58</td>
</tr>
<tr>
<td>L81</td>
<td>6</td>
<td>43</td>
<td>2792</td>
<td>N.A.</td>
<td>20</td>
</tr>
</tbody>
</table>

1.4 Principle of thermo-reversible ion binding

Contrary to most ionic surfactants, nonionic polymeric surfactants can be dissolved in water in high concentrations in the presence of multivalent cations \(^29\). This feature is applied in binding processes of multivalent ions to aggregates of mixtures of ionic and nonionic surfactants, where the nonionic surfactants increase the solubility of the so-called mixed micelles \(^30-32\).

To allow for the reversible binding of multivalent cations in the aqueous shell of micelles, Pluronic P85 (EO\(_{26}\)–PO\(_{39}\)–EO\(_{26}\)) has been modified with succinic anhydride yielding a high molecular weight (MW = 4748 g/mol) triblock copolymer with carboxylic acid end standing (CAE) groups \(^33\). This polymer is denoted as CAE-85. The chemical structure of a CAE-85 surfactant molecule is shown in Figure 1.2.

![Figure 1.2: Chemical structure of the CAE-85 surfactant.](image)

The large fraction of ethylene oxide (EO) in the CAE-85 surfactant will assure that the surfactant remains soluble up to high concentrations of multivalent ions. The proposed mechanism of switchable multivalent ion binding to the CAE-85 based on temperature is shown in Figure 1.3.
Initially, at temperatures below the CMT the CAE-85 surfactant and the multivalent cations are present in solution as unimers or “free molecules”. The affinity of isolated carboxylic acid groups for multivalent cations is very low \[34\]. Increasing the temperature above the CMT brings the charged carboxylic acid groups present on different surfactant chains together, thus allowing for the sequestering of the multivalent cations. Subsequent lowering of the temperature to values below the CMT will release the bound cations, because the micellar structure breaks up. With the feature of thermo-reversible ion binding CAE surfactants can be applied as regenerable ion exchangers.

1.5 CAE surfactants in membrane processes

1.5.1 Basic principles of membrane technology
A membrane is a semi-permeable barrier, which selectively permits passage of one or more components of a mixture. The feed stream will be divided by the membrane into the retentate and a permeate stream, see Figure 1.4. In pressure driven aqueous membrane processes a distinction is made between micro-, ultra-, nanofiltration and reverse osmosis depending on the pore size of the membrane \[39\]. In particular, reverse osmosis membranes have the smallest pore size and need a trans membrane pressure of at least 10 bar as the driving force. Ultrafiltration membranes have a pore size in the order of a few nanometers and need a trans membrane pressure of 1 to 5 bar.
1.5.2 Micellar enhanced ultrafiltration (MEUF)

Ionic micellar systems are frequently used for the removal of metal ions in MEUF processes \[^{[13, 14]}\]. Anionic surfactants are added to an aqueous feed stream that is polluted with metal ions. In micellar form the surfactants are able to coordinate with the metal ions. The micelles with the bound metal ions are retained by a membrane. In MEUF processes the micelles are regenerated by removing the metal ions using additional chemical recovery steps \[^{[40]}\].

1.5.3 Scaling and antiscaling

In water purification processes clean water is produced from surface water, ground water or seawater using reverse osmosis membranes \[^{[3]}\]. Depending on the source, the feed water contains different amounts and types of organic solutes and dissolved ions. During water production the concentration of ions in the retentate stream of subsequent membrane modules will increase, and at a certain point the concentration of the low solubility salts, like \( \text{BaSO}_4 \) and \( \text{CaSO}_4 \), will exceed the solubility limit. Salt particles will be formed and will precipitate on the membrane surface, decreasing the water permeation flux, see Figure 1.5. The process of deposition of the formed salts on the membrane surface is called scaling \[^{[3]}\].
Two scaling mechanisms can be distinguished. In the mechanism of bulk precipitation the particles are formed in the solution at supersaturated conditions and will deposit on the membrane surface. With the surface precipitation mechanism, supersaturated conditions are obtained near the membrane surface by concentration polarization, resulting in the formation of small solid particles on the membrane surface.

To prevent scaling, usually antiscalants are added to the (feed) water stream before the ‘scaling sensitive’ stage of the membrane process. Antiscalants are additives that act like crystallization inhibitors and therefore will delay the formation of salt particles \((41)\). In this way the induction time for salt precipitation is extended. The interaction between the antiscalants and the salt ions is irreversible, and in general antiscalants have to be disposed after single use, so that the use of antiscalants is associated with large waste streams. This implies that for the development of environmentally friendly water purification processes, a new type of regenerable water softeners is indispensable. In this respect, thermo-reversible CAE surfactants might be a promising alternative for the use of antiscalants.

### 1.6 Outline of thesis

This thesis focuses on the binding of (multi)valent cations in thermo-reversible anionic CAE surfactant systems. The synthesis of the CAE surfactant, the physico-chemical aspects of the binding process, and the practical application of the CAE surfactant in a membrane system are discussed. First, in Chapter 2 the synthesis and characterization of the CAE-85 surfactant is described. In Chapter 3 a method is developed in order to derive a binding isotherm for multivalent ions to CAE micelles using experimental isothermal titration calorimetry (ITC) heat change data. This method is based on a theoretical triple layer model for the distribution of counterions in micellar systems. In Chapter 4 ITC measurements are used to study the influence of several parameters, like pH, ionic strength, cationic species, temperature and surfactant concentration on the binding of cations. In Chapter 5 the conductivity method of Pochard \((24)\), originally used to study counterion binding in polyacrylic acid systems, has been used to study counterion binding and competition effects between counterions in CAE surfactant systems. The phase behavior of the CAE surfactants in comparison with the Pluronic surfactants will be discussed in Chapter 6. The influence of pH and additives on the CMT and the cloud point is studied using differential scanning calorimetry (DSC) and
dynamic light scattering (DLS). The mixed micelle interactions between CAE surfactants and Pluronic surfactants are discussed as well. In Chapter 7 the application of the CAE surfactant in a micellar enhanced ultrafiltration setup is demonstrated. The solubilization of phenanthrene in CAE micelles and fouling behavior of CAE surfactants on cellulose acetate and polyether sulfone membranes have been studied in order to determine the possibility for simultaneous removal of calcium cations and phenanthrene in a MEUF application using CAE surfactants. Also, the reversibility of the counterion binding is demonstrated using ultrafiltration experiments. In Chapter 8 the economical evaluation for a design of a reverse osmosis membrane water purification process is presented, in which the CAE surfactant is implemented as an antiscalant or as an ion binder. Different process configurations are studied using experimental antiscaling data. Finally, in Chapter 9 the different results are combined to give a mechanistic picture of counterion binding to CAE micelles. Furthermore, the (dis)advantages of using CAE surfactants and possible future applications are evaluated.

It has to be noted that the setup of this thesis is such that each individual Chapter can be read independently. Consequently, some information is repeated in different Chapters of the thesis.

1.7 References

Introduction to CAE surfactants for thermo-reversible binding of multivalent cations


Chapter 2

Synthesis and characterization of CAE surfactants

Abstract

The synthesis of carboxylic acid end standing (CAE) surfactants is described. Gel permeation chromatography (GPC) and potentiometry are applied to characterize the starting materials and the products. Furthermore, the CAE-85 surfactant has been discussed in terms of chemical stability and polydispersity. Finally, some general recommendations are given for a feasible large-scale synthesis to produce larger amounts of the CAE surfactant.
2.1 Introduction

Carboxylic acid end standing (CAE) surfactants are synthesized by the reaction of succinic anhydride with a Pluronic surfactant (PEO-PPO-PEO triblock copolymer) in order to obtain a high molecular weight surfactant with anionic end groups. First a general synthesis procedure is described for the end group modification of Pluronic surfactants, followed by the characterization of the starting material using GPC. The characterization includes the determination of the polydispersity and the molecular weight distribution of the surfactant. To check if all acidic impurities are removed from the product a titration with NaOH has been performed. Furthermore, the chemical stability of the CAE surfactant in water and the effects of the surfactant polydispersity on the functionality of the CAE surfactant are discussed. Finally, some recommendations are given to scale-up the synthesis procedure from lab scale to pilot scale.

2.2 Synthesis of CAE surfactants

The synthesis procedure for Pluronic P85 is given as a general description, which can be used as a starting point for the modification of different Pluronic surfactants. In the synthesis of the CAE-85 surfactant, Pluronic P85 (BASF) is purified by dissolving it in diethyl ether (20 wt% solution). It is important that the ether is free of peroxides to avoid the formation of side products. The cloudy solution is clarified by sedimentation in a centrifuge (3000 rpm, 30 min), followed by precipitation in pentane of 5 °C by slow addition. The precipitate is left at 5 °C for two hours followed by a cold filtration. In the case of liquid Pluronic surfactants precipitation with pentane is not possible and the solvents have to be removed by evaporation.

Succinic anhydride is recrystallized from toluene (10 wt% solution) at 95 °C. The insoluble fraction consists mainly of succinic acid and is filtered above a hot and dry filter. Hexane is added to crystallize the succinic anhydride, which will crystallize in the form of long needles. Drying of the product should occur at room temperature at vacuum conditions (elevated temperatures may lead to sublimation).
The purified P85 is dissolved in toluene (23 wt% solution). Water is separated from the toluene by azeotropic distillation with a Dean Stark trap. Next, the succinic anhydride is added to the reaction mixture that is under a blanket of dry argon to prevent contact with oxygen. The reaction is performed for two hours at 90 °C and two hours at 110 °C, respectively.

After the reaction, the toluene is evaporated, and the oily product is dissolved in water (20 wt% solution). An excess of Na₂CO₃ is added to decompose the unreacted succinic anhydride until a pH of 10.5-11 is reached. Carbon dioxide is formed during the addition of Na₂CO₃ and the solution becomes viscous. Then the solution is left for 1 hour and is acidified back with diluted sulphuric acid to a pH value of 2. Again carbon dioxide is formed. Subsequently, the solution is saturated with hydrated Na₂SO₄. The solution is then extracted with butanol for three times. The collected extracts are washed several times with a saturated solution of Na₂SO₄ and are dried overnight above a layer of anhydrous Na₂SO₄.

The next step is to remove the butanol as far as possible through vacuum distillation and to redissolve the product in diethyl ether (10 wt% solution). The cloudy solution is clarified by sedimentation in a centrifuge (6000 rpm, 10 min). After evaporation of the diethyl ether the product is redissolved in toluene to remove final impurities (mainly salts). The salts are removed by filtration over a Büchner funnel and the toluene is evaporated. Finally, the product is redissolved in diethyl ether (20 wt% solution), followed by precipitation with an equal amount of pentane at 5 °C. The final product is obtained after a cold filtration at 5 °C and is dried at vacuum conditions at room temperature. In the case of liquid Pluronic surfactants the product is not dissolved into diethyl ether in the last step, but is mixed directly with hexane. The cloud can be removed by sedimentation and the hexane should be evaporated. The final product will then become a viscous liquid.

2.3 Characterization of thermo-reversible CAE surfactants

2.3.1 Purification of Pluronics

Pluronic surfactants are polydisperse polymer surfactants and can contain a large quantity of impurities (up to 15 wt%) [5]. The main impurity is an amount of polyethylene oxide blocks. In the synthesis procedure as described above, the Pluronics are purified to remove most impurities. Gel permeation chromatography (GPC) was used to determine the purity, the
molecular weight, and the degree of polydispersity. In Figure 2.1a the GPC results are shown for purified P85. The average molecular weight, $M_w$, is equal to 4568 g/mol and the degree of polydispersity, $D$, was equal to 1.43. No impurity peaks were observed in the GPC graph, so no large impurities are present in the purified P85 surfactant.

![Graph showing GPC results for purified P85](image1.png)

Figure 2.1 (a): Gel permeation chromatography results for purified P85.

![Graph showing pH-curve for base titration](image2.png)

Figure 2.1 (b): pH-curve for a base titration of a 1.0 wt% CAE-85 solution with 0.5 M NaOH.

### 2.3.2 Potentiometric titration of CAE-85 surfactant

After the synthesis a titration of a 1.0 wt% CAE-85 solution with 0.5 M NaOH was performed in order to determine the amount of acid groups and to check if the modified surfactant was free of succinic anhydride. Succinic anhydride will react with water to form a succinic acid, which will result in a too high amount of acid groups in the solution.
(> 5.0 *10^{-3} \text{ mol/L}). From Figure 2.1b it can be calculated that a negligible amount of succinic acid is detected in the solution and therefore it can be concluded that the removal of succinic acid by the washing steps of the synthesis is successful. The composition and molecular weight of the three CAE surfactants, i.e. CAE-85, CAE-64 and CAE-81, are given in table 2.1.

Table 2.1: Composition and molecular weight of CAE surfactants \cite{2}.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>EO</th>
<th>PO</th>
<th>$M_w$ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE-85</td>
<td>52</td>
<td>39</td>
<td>4768</td>
</tr>
<tr>
<td>CAE-64</td>
<td>26</td>
<td>30</td>
<td>3102</td>
</tr>
<tr>
<td>CAE-81</td>
<td>6</td>
<td>43</td>
<td>3039</td>
</tr>
</tbody>
</table>

2.4 Chemical features of CAE surfactants

2.4.1 Chemical stability of CAE surfactants in water

CAE surfactants have a high solubility in water, up to 20 wt%, but have a reduced chemical stability in aqueous environments as compared to Pluronic surfactants. The reaction of the hydroxyl end groups of the Pluronic surfactants with succinic anhydride to form CAE surfactants is an esterification reaction. Esters can undergo acid and base promoted hydrolysis \cite{6}. In the base promoted hydrolysis (see figure 2.2) the salt will be formed which causes the equilibrium to shift to the right. This shift will be less pronounced in an acidic environment, and this means that in solutions with a high pH the CAE surfactant is more sensitive to chemical degradation.

![Figure 2.2: Schematic representation of the base-promoted ester hydrolysis of the CAE surfactant.](image)

When hydrolysis occurs in the CAE surfactant solutions, this can be observed by a continuous decrease in the pH or a continuous increase in conductivity. In practice,
hydrolysis occurs in CAE surfactants solutions at pH values above 7.5. At acidic conditions, at pH values between 2 and 7, no significant degradation of the ester was observed during various experiments.

2.4.2 Influence of polydispersity

From GPC measurements a polydispersity index of 1.43 was found for the Pluronic P85 surfactant after purification. This has a clear consequence for the behavior of the polymer in water and on the functionality of the triblock copolymer. It is known that all (pseudo) phase transitions, like the critical micellization temperature or the sphere-to-rod transition, of the Pluronic surfactants are influenced by the polydispersity. The distribution in the molecular mass of the copolymers and the difference in ethylene oxide to propylene oxide ratio will broaden the phase transition. This is a disadvantage when CAE surfactants are used in practical applications, where a well-defined thermal responsive functionality is desired with a sharp transition. One way to reduce the degree of polydispersity is to alter the synthesis procedure of the starting material, the Pluronic triblock copolymers.

2.4.3 Recommendations for scale-up of the synthesis procedure

In this Chapter the synthesis procedure is described for the lab-scale synthesis of the CAE-85 surfactant. Several aspects have to be considered in order to scale up the synthesis of CAE-85 to pilot scale or industrial scale and to come to an environmentally benign process.

In the purification step of Pluronic P85, diethyl ether is used as a solvent. Diethyl ether cannot be used on industrial scale as a solvent, because it has a high volatility and it is extremely inflammable. However, in this purification step Pluronic P85 has to be separated from the main impurity, i.e. free PEO blocks (about 12 wt%). Consequently, a solvent is needed in which Pluronic P85 has a good solubility and in which PEO has a poor solubility. This requires a delicate choice for the solvent, as the chemical difference between P85 and PEO is not very large. A more suited solvent in the scaling up of this step may be toluene, because it is already used in the reaction step.

After the reaction of succinic anhydride with the P85 surfactant the unreacted anhydride has to be converted into succinic acid in order to prevent the presence of anhydride in one of the consecutive work-up steps. In the final product an impurity that consists of succinic anhydride will function as an acid when the product is dissolved in water, which has a
negative influence on a number of properties. The hydrolysis of succinic anhydride in the reaction mixture will normally take place spontaneously when it is dissolved into water. However, to assure that all anhydride will be converted, in the lab-scale procedure described above, the conversion of succinic anhydride is forced into the desired direction by adding Na$_2$CO$_3$ as a base (with the formation carbon dioxide), followed by the addition of diluted H$_2$SO$_4$ to neutralize the solution to a pH value of 2. Considering the fact that the hydrolysis of succinic anhydride takes place spontaneously in an excess of water after some time, this option will be preferred on a larger scale over the addition of Na$_2$CO$_3$ and diluted H$_2$SO$_4$.

Another difficulty in the scale up is the saturation of the aqueous mixture with Na$_2$SO$_4$ to salt out the CAE-85 surfactant from the solution. The high solubility of Na$_2$SO$_4$ in water (about 16.2 g per 100 mL at 20 °C) means that a large amount of salt is needed to obtain the desired result. To reduce the amount of Na$_2$SO$_4$ needed, the aqueous solution should be concentrated as much as possible by vacuum distillation. However, the solution should not become too viscous. The use of a Na$_2$SO$_4$ solution for washing of the butanol extracts can be minimized by using a small amount of saturated solution, while the contact time between the two liquids increases.

Finally, in the work-up procedure various solvents are used, i.e. butanol for the extraction of the polymer, toluene for the removal of impurities and pentane or hexane for the precipitation of the polymer. To reduce the amount of solvent that has to be evaporated an efficient (filtration) method to remove the impurities could improve the synthesis procedure to be applied on a larger scale.

### 2.5 Conclusions

A successful synthesis route for the modification of triblock copolymers has been developed. In general, the synthesis procedure can be applied to all ‘forms’ of the Pluronics at room temperature, including the paste, liquid and the flakes form. The procedure to synthesize about 25 g of CAE-85 surfactant is discussed in detail. Two techniques are described, i.e. gel permeation chromatography (GPC) and potentiometry to characterize the product and starting materials.

It can be concluded that hydrolysis of the ester occurs at acidic and caustic conditions, but no significant effect was observed in a pH range of 2 to 7. Furthermore, it can be concluded that
the degree of polydispersity for Pluronic surfactants will be retained in the CAE surfactants. A disadvantage of the high degree of polydispersity is the widening of the (pseudo) phase transitions, like the CMT and the sphere-to-rod transitions. For the scale-up of the synthesis procedure of CAE-85 the main problems will be the use of volatile solvents and the addition of large amount of salts.

2.6 References

Chapter 3

Binding of counterions in thermo-reversible surfactant systems studied with isothermal titration calorimetry

Abstract

An approach is presented to determine the binding of counterions to ionic micelles with thermal reversible properties. The binding of multivalent ions to carboxylic acid end group (CAE) modified Pluronic surfactants is studied experimentally using isothermal titration calorimetry (ITC). The main feature is that these CAE surfactants form aggregates that can bind multivalent ions reversibly without precipitation. As a consequence of the thermo-reversible binding properties more conventional methods using conductometry have some drawbacks in evaluating the binding parameters for CAE surfactant systems. For the binding of calcium ions to the CAE micelles an isotherm has been obtained from one single ITC experiment. It can be concluded that ITC is a relatively fast technique to study counterion interactions in surfactant systems.
3.1 Introduction

The distribution of counterions in ionic surfactant systems is a subject of extensive research [1-4]. It is noted that most studies reported in literature describe surfactants with monovalent counterions. However, the distribution of multivalent ions around micellar aggregates is studied only to a limited extent [5, 6]. This is probably the result of the fact that most ionic surfactants precipitate in the presence of multivalent ions.

Recently an ionic surfactant has become available that can bind multivalent ions reversibly. In particular, it has been demonstrated that calcium ions bind to carboxylic acid end standing (CAE) micelles [7]. Stable CAE-85 micelles, modified Pluronic P85 surfactants [8], are obtained above the critical micellization temperature (CMT) of 33 °C. Above the CMT binding of divalent ions takes place, while below the CMT no binding of divalent ions to the CAE-85 surfactant unimers takes place. Traditionally, the binding characteristics of ionic micellar systems are studied using conductivity [9], ellipsometry [10], surface tension measurements [11] or small-angle X-ray scattering (SAXS) [12-14]. SAXS provides good qualitative and quantitative results for counterion binding systems, but its relatively low accessibility for many research groups and difficult theoretical interpretation makes this technique less useful for the fast screening of counterion binding systems in different experimental conditions.

With respect to the CAE surfactants conductivity and surface tension methods suffer from some drawbacks, partly due to the fact that the Pluronic-based CAE surfactants have a (very) low critical micellization concentration (CMC) above the CMT. In this work isothermal titration calorimetry (ITC) is used to study the binding of calcium to the CAE-85 micelles. ITC is widely used to study heat effects for different type of interactions [15], ranging from binding phenomena [16, 17] to the aggregation of surfactants [18, 19].

The main advantage of using ITC is that from a single titration experiment the amount of counterions bound to the CAE-85 micelles is obtained as a function of the total concentration of counterions. A procedure is given to relate the heat effects from ITC to adsorption (or binding) parameters, using a description for the electrostatic potential around the CAE micelle.

The electric double layer [20-24] in colloid systems is often described using the Poisson-Boltzmann (PB) theory combined with the Debye- Hückel approximation [25-29]. In general,
two approaches are used to describe the distribution of ions in ionic micellar systems. The first approach is the so-called double layer model, or Gouy-Chapman model \cite{30, 31} and the second approach is the triple layer model \cite{32, 33}. The surface of a micelle consists of a flexible and dynamic layer, because surfactant molecules are moving in and out of the micelle. Therefore, counterions can partly penetrate the surface layer, and this affects the interactions between the surfactant head groups and the distribution of the ions around the micelle. In the double layer model the counterion distribution is described by dividing the area around the micelle into a diffuse layer, near the surface, and a bulk layer. In the diffuse layer the highest concentration of counterions is observed at the micellar surface, and the concentration decreases exponentially according to the PB theory \cite{34}. The bulk phase has a uniform counterion distribution. Use of this model often results in a counterion concentration at the micellar surface that is unrealistically high \cite{32}.

![Figure 3.1: Schematic picture of the distribution of ions and the electrical potential around a micelle of anionic surfactant molecules.](image)

To avoid this problem triple layer models were developed, in which a Stern layer was introduced between the micellar surface and the diffuse layer to account for specific adsorption and binding effects \cite{32, 33}, see Figure 3.1. Rathman and Scamehorn \cite{33} introduced two different descriptions of the Stern layer. The counterions in the Stern layer were modeled
either as ‘mobile’ within this layer or as ‘localized’ on certain surfactant head groups. In the model for mobile adsorption the counterions are free to move within the Stern layer, whereas for localized adsorption specific binding is assumed.

In the following, first, the interpretation of the ITC titration data obtained for the binding of calcium to a CAE-85 surfactant system is given. Second, the ITC heat change data is connected to the binding parameters using a theoretical description for the effective binding enthalpy. Finally, the obtained calcium isotherm is fitted using two standard adsorption/binding isotherm models.

3.2 Experimental

3.2.1 CAE Surfactants

The carboxylic acid end standing (CAE-85) surfactant was synthesized by modifying Pluronic P85 surfactant ($\text{EO}_{39}\text{-PO}_{52}\text{-EO}_{39}$) with succinic anhydride to obtain a high-molecular weight anionic surfactant with temperature sensitive micellization behavior \cite{7} (see Figure 3.2).

![Figure 3.2: Chemical structure of CAE-85 surfactant.](image)

3.2.2 Isothermal titration calorimetry

Experiments were performed using a MicroCal VP-ITC (Isothermal Conductivity Calorimetry) apparatus with a cell volume of 1.4431 mL. The experimental procedure consisted of adding 70 injections of 4 $\mu$L of a calcium chloride salt solution (30.0 mmol/L) to the sample cell, which contains solutions of CAE-85 surfactant (5.0 mmol carboxylate groups/L) or solutions of P85. Both solutions have a pH value of 6, adjusted with NaOH. In all experiments the reference cell was filled with demineralized water. Before each experiment the temperature was equilibrated at the desired value.
3.3 Results and discussion

3.3.1 ITC data interpretation

In Figure 3.3 a typical result for the heat change, $\Delta Q$, obtained from ITC is given as a function of the amount of calcium added. Only in the experiment for CAE-85 at 50 °C a significant heat effect is observed. The observed heat change $Q_{obs}$ decreases with an increase in the amount of calcium added, in terms of the molar ratio, $r$. The molar ratio is the defined as the amount of calcium added divided by the amount of surfactant end groups.

![Figure 3.3: Observed heat change per injection, $Q_{obs}$, as a function of the molar ratio, $r$, of added calcium per CAE-85 carboxylate group. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 and P85 solutions with a 30 mmol/L CaCl$_2$ solution.](image)

In ITC experiments where counterions will bind to micelles, the observed heat change can be divided into three heat contributions, according to:

$$\Delta Q = Q_{obs} = Q_{mix} + Q_{int} + Q_{mic}$$  \hspace{1cm} (3.1)

The mixing heat, $Q_{mix}$, is the result of the mixing of the diluted CaCl$_2$ solution and the surfactant solution, and usually this quantity is exothermic. Here, $Q_{mix}$ is neglected in the calculations because it is a very small value compared to the interaction heat $Q_{int}$. This assumption can be justified when it is noted that in the experiment for P85 at 50 °C no heat effect is observed, while the value for the mixing heat for P85 at 50 °C should be close to the
value for the mixing heat of CAE-85 at 50°C. The interaction heat or displacement heat $Q_{int}$ consists of the hydration heat and dissociation heat for the sodium ion that is released from the micellar surface and the dehydration heat and binding heat for the calcium ions that will bind to the micellar surface. However, when dealing with the exchange of monovalent ions with multivalent ions $Q_{int}$ predominantly is determined by the (de)hydration heat of the multivalent ion. $Q_{mic}$ is the micelle conformation heat and includes all structural changes of the micellar aggregate due to the titration. These changes of the micelle structure are mainly driven by a gain in free energy to obtain the most favorable conformation.

When no (pseudo)-phase transitions occur in the operational window of the experiment, which would be expressed by a sudden change in the heat change data during the experiment, it can be assumed that $Q_{mic}$ and $Q_{int}$ are related to each other. I.e. the only reason for both quantities to change is the increasing amount of calcium and chloride in solution. From this it can be concluded that the observed heat change $Q_{obs}$ solely is an effect coming from the interaction of the micelle with the calcium and chloride ions. More than that, because no heat effect is observed for P85 at 50 °C, $Q_{obs}$ can only be the result of the binding interaction of the calcium cation with the anionic head groups of CAE-85 and the structural changes due to that specific interaction.

Taking these considerations into account, it is assumed that one calcium ion will bind on average to two carboxylic groups and the exchange reaction of calcium and sodium will be as follows (electrostatic binding):

$$2[Na^+]_b + [Ca^{2+}]_f \leftrightarrow 2[Na^+]_f + [Ca^{2+}]_b$$

(3.2)

with the subscripts $b$ and $f$ as notations for the bound and free state of the ions. The smallest possible heat change is defined by the amount of calcium added per injection during an ITC experiment. This is generally expressed as a change in the fractional binding, $\Delta \theta$, according to:

$$\Delta Q = q C_{s,m} V \Delta H \Delta \theta$$

(3.3)
with \( q \) the number of binding sites for calcium per carboxylate group \( (q = 0.5) \), \( C_{s,m} \) the total molar concentration of carboxylate groups, \( \Delta H \) is the ‘effective’ binding enthalpy, and \( V \) is the volume of the ITC sample cell \( (V = 1.44 \text{ mL}) \). The fractional binding or surface occupancy, \( \theta \), for calcium bound to the CAE-85 micelle is defined as:

\[
\theta = \frac{2[Ca(\text{COO})_2]}{[\text{COOH}]_{\text{tot}}} \tag{3.4}
\]

It has to be noted that the ‘effective’ binding enthalpy, \( \Delta H \), is not solely the reaction enthalpy of the reaction, given in Eq. (3.2), but it also includes the enthalpy change that originates from the structural change of the micelles due to the binding of calcium.

In order to calculate the \( \Delta \theta \) from Eq. (3.3), a value for the ‘effective’ binding enthalpy has to be found. When it is assumed that the ‘effective’ binding enthalpy of each calcium ion that binds to the micelle is constant and independent of the surface occupancy, then the binding can be described by a Langmuir isotherm. Using Eq. (3.3) to calculate \( \theta \) with a constant \( \Delta H \) results in the most conservative binding isotherm for the binding system.

However, because in practice each bound calcium ion will decrease the effective charge of the micelle with as a result that the ‘driving force’ for calcium binding decreases. During the titration the electrical potential the cations experience will decrease, and consequently for each additional calcium ion the ‘binding affinity’ will be lower. For this reason the effective binding enthalpy, \( \Delta H \), will not be constant but will be a decreasing function of the amount of calcium added. From the fact that the equilibrium distribution of the different ions around the CAE-85 micelle is completely determined by the electrical potential and from the fact that the reorganization of the CAE-85 micelles to minimize the free energy is related to the degree of fractional binding of calcium ions, it is proposed that the ‘effective’ binding enthalpy, \( \Delta H \), can be directly proportional to the ‘effective’ electrical potential, according to:

\[
\Delta H(C) = \gamma \Psi(C) \tag{3.5}
\]

where \( \gamma \) is an empirical constant and \( \Psi \) is the ‘effective’ electrical potential. The definition of the ‘effective’ electrical potential will be given later on in this Chapter. The parameter \( \gamma \) can
be obtained by evaluating $\Delta H$ and $\Psi$ at the point that no calcium is added to the solution. For $\Delta H$ this means extrapolation of the curve in Figure 3.3 to $r = 0$. In the following a theoretical description is given to derive an equation for $\Psi$.

### 3.3.2 The use of the Poisson-Boltzmann theory

To describe the electrical potential of the diffuse layer around the CAE-85 ionic micelles, as a function of the distance from the micelle and the concentration of the electrolytes, the Poisson-Boltzmann equation for planar interfaces, assuming point-charges, is used \(^{25, 34}\):

\[
\frac{d^2 \psi}{dx^2} = \frac{-4\pi e}{\epsilon} \sum_i z_in_i(x) \\
= \frac{-4\pi e}{\epsilon} \sum_i z_in_i^b \exp\left(\frac{-z_i e \psi(x)}{kT}\right) \tag{3.6}
\]

with $\psi$ the electrical potential, $x$ the spatial coordinate, $e$ the elemental charge, $\epsilon$ the dielectric constant in the diffuse layer, $z$ the valence of the species, $n_i^b$ the number density of the species in the bulk, $k$, the Boltzmann constant, and $T$ the absolute temperature.

It is known that in the case of systems with divalent counterions the PB theory has its limitations \(^{25, 38}\) and can lead to errors. Typically, the error is in the order of 20-30 \% \(^2\). However, there are a number of reasons why the PB theory is used in this work. First, only a semi-quantitative description of the ‘effective’ electrical potential is needed. The effective potential, $\Psi$, is scaled by the empirical parameter $\chi$ and only a description for the decay of the electric potential is required. Second, the high-molecular weight CAE micelles have a relatively low surface charge density, because there is low amount of charged end groups per CAE micelle surface area. Combined with a low ionic strength this makes the error, arising from using the PB theory with the Debye-Hückel approximation less pronounced. Additionally, charge reversal effects \(^{23}\), which might occur in divalent counterion systems with high charge densities, are neglected here because of the low charge densities present in the CAE system. Third, as compared to conventional surfactant systems CAE-85 micelles are large aggregates (~15 nm), which makes the use for the PB solution for a planar system more appropriate. Fourth, as compared to the most conservative situation in which the $\Delta H$ is constant, the extension with the dependence on the electrical potential will most likely result
in a more accurate binding isotherm, even when the PB theory is used. Fifth and finally, for mathematical convenience and to demonstrate the possibility of the ITC technique as an analytical tool the PB theory will be the most convenient approach.

These considerations imply that the underestimation of the absolute micellar surface potential, which in general is the case when using the PB theory, does not lead to a significant error in the results for the binding of divalent cations using the ITC methodology. Although any improved description for the electrical potential probably will result in a more accurate binding isotherm.

3.3.3 Theoretical description for the 'effective' electrical potential

For the binding of divalent ions the CAE micelles the solution for the potential is given as function of space coordinate $x$ and ion concentration $C$ by:

$$
\psi(x, C) = \frac{4\pi \sigma}{\epsilon \kappa} \exp(-\kappa x)
$$

(3.7)

with $\kappa$ the reciprocal of the Debye-length.

The details of the derivation of Eq. (3.7) are given in Appendix A and B. Equation (3.7) is obtained using the following steps, the linearized PB theory is applied using the Debye-Hückel approximation. No well-defined Stern layer is chosen, and it is assumed that all bound cations are in a layer between $x=d$ and $x=0$, see Figure 3.1. The following boundary conditions were taken: for $x \to \infty$ that $\psi=0$ and for $x=0$ that $\psi=\psi_0$.

The next step is to relate the electrical potential, $\psi$, to the surface charge density, $\sigma$. Contrary to low molecular weight ionic surfactants, the CAE micelles do not have a sharp interface between the surfactant head groups and the surrounding water. As a consequence, binding will take place throughout the whole micellar corona and no well-defined Stern layer exists. The potential at $x=0$ is now taken as the surface potential of the micelle (see Figure 3.1).

In micellar solutions the surface charge density is not constant during the addition of electrolytes, because of the highly dynamic nature of the micellar surface. Especially in the case of binding, i.e. specific binding (complexation of the counterion with the surfactant end groups) and electrostatic binding, the surface charge density will decrease as a function of the
fractional binding or surface occupancy. Assuming that the surface charge density at $x=0$ depends linearly on the amount of free carboxylate groups, gives\textsuperscript{[35]}:

\[
\sigma = \frac{\xi \eta_{agg}}{A_{mic}} e (1 - \theta)
\]

\[
= \tau e (1 - \theta)
\]

with $\tau$ a geometric parameter, and $\eta_{agg}$ the aggregation number of the surfactant, $A_{mic}$ the micellar surface, $\xi$ the number of carboxylate groups per surfactant molecule ($\xi = 2$ for CAE surfactants).

From the ITC measurements the heat change, $\Delta Q$, is obtained as a function of the calcium concentration, and not as a function of the space coordinate. This means that $\Delta Q$ is an average over the entire volume of the sample cell, for a given calcium concentration. To determine the binding isotherm ($\theta$ as a function of $r$), from Eq. (3.3) and the experimental heat change, the dependence of the binding enthalpy on the concentration and on the fractional binding is needed. In order to obtain a relation for the electrostatic potential that depends only on the concentration, the values for the space coordinate should be accounted for. This is achieved by integration of Eq. (3.7) over space. This gives a new quantity, i.e. an ‘effective potential’ $\Psi$ [Vm], with as result:

\[
\Psi(C) = \frac{4\pi \sigma}{\varepsilon \kappa} \int_{0}^{\infty} \exp(-\kappa x) dx
\]

\[
= \frac{4\pi \sigma}{\varepsilon \kappa^2}
\]

(3.9)

**3.3.4 Binding isotherms**

A numerical solution for the isotherm is obtained by solving Eqs. (3.3), (3.5), (3.8) and (3.9) simultaneously (using Matlab 6.1). The result for the calcium isotherm obtained from the ITC data for the heat change (shown in Figure 3.3) is depicted in Figure 3.4.

So far, the presented description is based on an experimental approach using ITC data to describe the binding of divalent ions. To obtain a quantitatively description, two isotherm
models are used to relate the counterion adsorption to macroscopic binding parameters. The first model is the Langmuir-Freundlich (LF) isotherm:

\[ \theta = \frac{(K[Ca])^v}{1 + (K[Ca])^v} \]  \hfill (3.10)

and the second model is the localized binding (LB) model \(^{33}\):

\[ \theta = \frac{K[Ca] \exp\left(\frac{-z_{ca}e\psi_0}{kT}\right)}{1 + K[Ca] \exp\left(\frac{-z_{ca}e\psi_0}{kT}\right)} \]  \hfill (3.11)

with \( K \) a binding constant, \( v \) the degree of heterogeneity, and the subscript \( f \) refers to the free calcium.

![Figure 3.4: Binding isotherm derived from experimental ITC data shown in Figure 3.3, and binding isotherms obtained from a fit with the Langmuir-Freundlich model and the localized binding model.](image)

It is noted that in both models two binding parameters are optimized. In the LF model these are \( K \) and \( v \), in the LB model these are \( K \) and \( \tau \) (see Eq. (3.8)). It is seen in Figure 2.4 that both models are in good agreement with the experimental result obtained from the ITC data. The results of the fits (using Matlab 6.1) with Eqs. (3.10) and (3.11) to the experimental data in Figure 3.4 are given in Table 3.1.
For the binding of calcium to the CAE-85 micelles a nonlinear dependence on the total calcium concentration is observed. This indicates that the binding seems to be mainly electrostatic and that there is a minor contribution of specific binding. For \( r \) equal to 0.5, which corresponds to a calcium concentration of about \( 3.1 \times 10^{-3} \) mol/L, \( \theta \) is equal to about 0.31. For systems with strong binding, in general a linear increase can be observed until complete coverage at \( r = 0.5 \). This is the case, for example, for the binding of calcium to polyacrylic acid (PAA)\(^{[36]} \). The main reason for this difference lies in the dynamic nature of the CAE micellar system. The probability that two carboxylate groups will be close enough together to bind one calcium cation decreases with an increase in molar ratio. From the fact that two carboxylate groups are required for coordination in combination with the relative low surface charge density it follows that only at a very high molar ratio full surface coverage with calcium will be obtained.

Table 3.1. Results for the isotherm parameters obtained from a fit with Eq. (3.10) and Eq. (3.11) to the data given in Figure 3.4.

<table>
<thead>
<tr>
<th>Model</th>
<th>( K ) [L mol(^{-1})]</th>
<th>( \nu ) [-]</th>
<th>( \tau ) [10(^{16}) m(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF</td>
<td>339.8</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>LB</td>
<td>131.1</td>
<td>-</td>
<td>1.44</td>
</tr>
</tbody>
</table>

3.4 Conclusions

A procedure has been developed to obtain the binding isotherm from experimental enthalpy changes measured with ITC for divalent ions in CAE surfactant system. To obtain the isotherm, the effective binding enthalpy, which is not constant in micellar systems, is related in a linear manner to the ‘effective’ electrostatic potential. A second order approximation of the PB theory is used to give a description of the electrostatic potential as function of ion concentrations. The procedure presented here, combining experimental heat data from ITC with the theoretical description, provides a general method to obtain insight in the binding characteristics of multivalent ions in ionic surfactant systems.
3.5 References

Appendix A: Binding model

To describe the electrical potential of the diffuse layer around the CAE-85 ionic micelles, as a function of the distance from the micelle and the concentration of the electrolytes, the Poisson-Boltzmann equation for planar interfaces, assuming point-charges, is used:

\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi e}{\varepsilon} \sum_i z_i n_i(x)
\]

\[
= -\frac{4\pi e}{\varepsilon} \sum_i z_i n^b_i \exp\left(-\frac{z_i e \psi(x)}{kT}\right)
\]

(A.1)

with \(\psi\) the electrical potential, \(x\) the spatial coordinate, \(e\) the elemental charge, \(\varepsilon\) the dielectric constant in the diffuse layer, \(z\) the valence of the species, \(n^b_i\) the number density of the species in the bulk, \(k\), the Boltzmann constant, and \(T\) the absolute temperature.

Integration of Eq. (A.1) (see Appendix B) and using the boundary condition for \(x \to \infty\) that \(\psi = 0\) gives the so-called Gouy-Chapman expression \([25]\):

\[
\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{\varepsilon} \sum_i n^b_i \left(\exp\left(-\frac{z_i e \psi}{kT}\right) - 1\right)
\]

(A.2)

In order to obtain an analytical description a Taylor series approximation for Eq. (A.2) is used. This approximation is known as the Debye-Hückel approximation \([25, 37]\) Pluronic based surfactants have an extremely low CMC (above the CMT), typically in the order of \(10^{-7}\) mol/L, and it is assumed that there are no CAE-85 surfactant unimers present in the solution.

For the CAE-85 surfactant system with sodium counter ions and calcium chloride as the (additional) asymmetrical electrolyte, the second-order approximation for the exponential contributions results in:
\[
\left(\frac{d\psi}{dx}\right)^2 = \left(\frac{8\pi kT}{\varepsilon}\right) \left[ \left(\frac{-e}{kT}\right) \left[ n_{Na}^b z_{Na} + n_{Cu}^b z_{Cu} + n_{Cl}^b z_{Cl} + n_{s,m}^b z_{s,m} \right] \right] \psi + \ldots \\
+ \left(\frac{-e}{kT}\right)^2 \left(\frac{1}{2}\right) \left[ n_{Na}^b z_{Na}^2 + n_{Cu}^b z_{Cu}^2 + n_{Cl}^b z_{Cl}^2 + n_{s,m}^b z_{s,m}^2 \right] \psi^2 
\]

(A.3)

where the subscript \(s,m\) refers to the end groups of the CAE-85 surfactant in the micelles.

The first-order term is always equal to zero, because of electro-neutrality in the bulk, and Eq. (A.3) reduces to:

\[
\left(\frac{d\psi}{dx}\right)^2 = \kappa^2 \psi^2 
\]

(A.4)

with the reciprocal of the Debye-length, \(\kappa\), equal to:

\[
\kappa^2 = \frac{4\pi N_m e^2}{\varepsilon k T} \sum_i C_i z_i^2 \\
= \frac{8\pi N_m e^2}{\varepsilon k T} I 
\]

(A.5)

and \(I\) the ionic strength and \(C\) the molar concentration of the ions.

From Eq. (A.4) the negative root was chosen, because of the fact that the derivative has the opposite sign of the electrical potential. The final result reads:

\[
\frac{d\psi}{dx} = -\kappa \psi 
\]

(A.6)

The solution of Eq. (A.6) describes the electrical potential as function of the space coordinate, \(x\), and the various ion concentrations for (a)symmetrical electrolytes. Eq. (A.6) is applicable for multicomponent systems with a low surface potential.

The surface charge density at \(x=0\) is given by:
\[ \sigma = -\frac{\varepsilon}{4\pi} \left. \frac{d\psi}{dx} \right|_{x=0} \quad (A.7) \]

To obtain the micellar potential, \( \psi_0 = \psi(x = 0) \), as a function of the surface charge density and the concentration for an ionic micellar system with asymmetrical electrolytes, Eq. (A.6) is combined with Eq. (A.7), which yields:

\[ \sigma = \frac{\varepsilon}{4\pi} \kappa \psi_0 \quad (A.8) \]

In the following, Eq. (A.6) will be used to describe the spatial distribution of the potential. Solving Eq. (A.6) with the boundary conditions, for \( x \to \infty \) that \( \psi = 0 \) and for \( x=0 \) that \( \psi = \psi_0 \), gives:

\[ \psi = \psi_0 \exp(-\kappa x) \quad (A.9) \]

Combining Eqs (A.8) and (A.9) yields the relation for the electrical potential as function of the space coordinate, \( x \), and the concentration, \( C \):

\[ \psi(x, C) = \frac{4\pi \sigma}{\varepsilon \kappa} \exp(-\kappa x) \quad (A.10) \]

It is noted that the reciprocal of the Debye-length, \( \kappa \), is a function of the concentration, see Eq. (A.5).

In the case that binding of calcium ions to CAE-85 micelles occurs and the total bulk concentrations are low, the contribution of the bound calcium ions to the ionic strength will vanish. As a result, the change in the concentration of the calcium ions cannot be neglected. Therefore, the ionic strength will become a function of the fractional binding, and reads:

\[ I = \frac{1}{2} \left( C_{Na}^{b} z_{Na}^{2} + (C_{Ca}^{b} - 0.5 \theta C_{Na}^{b}) z_{Ca}^{2} + C_{Cl}^{b} z_{Cl}^{2} + (1 - \theta) C_{Na}^{b} z_{Na}^{2} \right) \quad (A.11) \]
Appendix B: Integration of the Poisson-Boltzmann equation

The Poisson-Boltzmann equation is given by:

\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi e}{\varepsilon} \sum_i z_i n_i(x) \\
= -\frac{4\pi e}{\varepsilon} \sum_i z_i n_i^h \exp\left(-\frac{z_i e \psi(x)}{kT}\right)
\]  

(B.1)

In order to obtain an expression for the electrostatic potential in the diffuse double layer a general solution needs to be found for differential equation (B.1). A solution is obtained by integration of Eq. (B.1) with the following procedure. The left hand side of Eq. (B.1) can be written as:

\[
\frac{d^2 \psi}{dx^2} = \frac{d}{d\psi} \cdot \frac{d\psi}{dx} \cdot \frac{d\psi}{dx} 
\]

(B.2)

The next step is to set \( p = \frac{d\psi}{dx} \), and Eq. (B.2) becomes:

\[
\frac{d^2 \psi}{dx^2} = p \frac{dp}{d\psi} 
\]

(B.3)

Combining Eqs. (B.1) and (B.3) results in the following relation:

\[
\int_0^p p \, dp = \int_0^\psi \left(-\frac{4\pi e}{\varepsilon} \sum_i z_i n_i^h \exp\left(-\frac{z_i e \psi(x)}{kT}\right)\right) \, d\psi 
\]

(B.4)

After integration this gives:

\[
\left[ \frac{1}{2} p^2 \right]_0^p = \left[ \frac{4\pi kT}{\varepsilon} \sum_i n_i^0 \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \right]_0^\psi 
\]

(B.5)
Using the boundary condition that \( p = 0 \) at \( \psi = 0 \), recalling that \( p = \frac{d\psi}{dx} \) and substitution of this in Eq. (B.5) gives the final result:

\[
\left( \frac{d\psi}{dx} \right)^2 = \frac{8\pi kT}{\varepsilon} \sum_i n_i \exp\left( -\frac{z_i e \psi}{kT} \right) - 1
\]  

Equation (B.6) gives a general description of the electrostatic potential, where no assumptions are made regarding the valency of the ions.
Chapter 4

Parametric study of the cation binding to CAE-85 surfactant systems studied with isothermal titration calorimetry

Abstract

Binding of multivalent ions to ionic micelles has been studied using isothermal titration calorimetry. In particular, isotherms are presented for multivalent cations bound to thermo-reversible carboxylic acid end standing (CAE) surfactant systems. The effect of different parameters, including pH, ionic strength, surfactant concentration, ion valence, and temperature on the binding has been investigated. A comparison is made between the binding of divalent cations to the CAE-85 surfactant and to polyacrylic acid (PAA). The results for the fractional binding for the CAE-85 system are quantified by fitting two isotherm models to the experimental data. It can be concluded that ITC can be used to study the binding of mono- and multivalent ions in ionic micellar solutions.
4.1 Introduction

There is an increasing interest for (macro)molecular architectures and assemblies with well-defined properties to deal with specific binding of metal ions\textsuperscript{[1, 2]}. This is important in many processes, ranging from biomedical applications to large-scale water purifications. Especially, the extent of controlling the binding and release behavior of these ions is an important subject in various research areas\textsuperscript{[3]}.

In this respect, a new class of surfactants has been developed that is capable of binding multivalent ions in a reversible way by means of a temperature shift\textsuperscript{[4]}. These so-called CAE surfactants are obtained by modifying Pluronic surfactants (PEO-PPO-PEO block copolymers)\textsuperscript{[5, 6]} with succinic anhydride to yield carboxylic end standing (CAE) surfactants. The CAE surfactants form anionic micelles with affinity for binding of cations above the critical micellization temperature (CMT)\textsuperscript{[7]}. Lowering the temperature below the CMT will break up the micellar structure resulting in the release of the cations. The CAE surfactants are the first anionic surfactants that are highly soluble in the presence of hardness ions, like calcium or barium, and that have a sharp CMT instead of a concentration dependent micellization behavior, typically observed for low molecular weight ionic surfactant systems.

In this work, the potential of the CAE surfactants to bind multivalent is demonstrated using isothermal titration calorimetry (ITC). ITC is a widely used technique to investigate interactions in mixed micelle systems\textsuperscript{[8-10]} and to study electrostatic interactions\textsuperscript{[11]}, e.g. in cation-polyacrylic acid systems\textsuperscript{[12, 13]}. The main advantage of ITC is the ability to measure small heat effects with a high accuracy. Only a small sample volume (in the order of 1 mL) is needed, which can be analyzed relatively fast. The binding behavior of CAE-85, which is a modified Pluronic P85, is studied for different parameters like pH, temperature, ionic strength, surfactant concentration, valence of the cation, and for different cationic species. The results will be presented using isotherms describing the amount of adsorbed cations on the micelles as a function of the amount of cations added. First, the data analysis for the ITC measurements will be discussed using the binding of calcium in the CAE surfactant system. Second, the characteristics of the binding process and the influence of different parameters will be evaluated using different cationic species. Finally, a comparison will be made between the binding results obtained for the CAE-85 surfactant system and for polyacrylic acid, which is known to be a good metal ion binder.
4.2 Experimental

4.2.1 Synthesis of CAE-85 surfactant

The carboxylic acid end standing (CAE-85) surfactant was synthesized by modifying Pluronic P85 surfactant (EO_{39}-PO_{52}-EO_{39}) with succinic anhydride to obtain a high-molecular weight anionic surfactant with temperature sensitive micellization behavior, see Figure 4.1.

In the synthesis of the CAE-85 surfactant \textsuperscript{[4]}, Pluronic P85 surfactant was purified by dissolving the polymer into diethyl ether. The cloudy turbidity was removed in a centrifuge, followed by precipitation of the surfactant in cold pentane. Purified P85 was then dissolved into toluene from which the water present in the toluene has been removed by azeotropic distillation.

The reaction was started by addition of succinic anhydride and was performed for four hours at 90 °C. After the reaction toluene was evaporated and the product was dissolved in water, followed by addition of sodium carbonate until pH>9 and diluted sulphuric acid until pH<2, respectively. The product was then extracted with butanol and dried overnight above a layer of anhydrous sodium sulphate. The product was redissolved in diethyl ether, followed by precipitation with an equal amount of pentane. The final product was obtained after filtering and drying under vacuum conditions at room temperature.

![Figure 4.1: Chemical structure of CAE-85 surfactant.](image)

4.2.2 Polyacrylic acid

The molecular weight of polyacrylic acid (PAA) used in the experiments was about 2000 g/mol.
4.2.3 Isothermal titration calorimetry (ITC)

The ITC experiments were performed using a MicroCal VP-ITC apparatus with a cell volume of 1.4431 mL. The experimental procedure consisted of adding 70 injections of 4 µL of metal chloride salt solution to the sample cell, which contains solutions of CAE-85 surfactant, Pluronic P85 surfactant, or polyacrylic acid. In all experiments the reference cell was filled with demineralized water. Before each experiment the temperature was equilibrated at the desired value.

During the titration the addition of small, well-known amount of reactant into a well-stirred sample cell will cause small changes in temperature. The resulting absorbed or evolved heat is measured very accurately. The difference in heat between the sample cell and the reference cell to keep both cells at the same temperature is obtained, and this is a measure for the cumulative enthalpic change in the sample cell.

4.3 Theoretical background

4.3.1 Counterion association

In general, counterion association appears primarily because of the strong electrical field created by the head groups of the micelle (electrostatic contribution), in which the valency of the counterion is the most important parameter. For this reason divalent ions will bind better than monovalent ions. However, counterions also associate because of certain specific interactions between the surfactant and counterion (specific contribution). These specific interactions are due to differences between counterions, like size, ease of hydration, possibility for hydrogen bonding, and contact ion pair formation with head groups.

In the case of a polyacrylic acid (PAA) system, monovalent counterions are only electrostatically bound, which is called condensation. However, calcium cations can form strong bidentate complexes with the carboxylate groups of PAA, because of strong specific interactions\cite{14}.

In micellar systems it is very likely that strong specific interactions will lead to precipitation of the surfactant, because the head group will become more hydrophobic in the case of complex formation\cite{15, 16}. The high molecular weight ionic CAE surfactants are highly soluble in the presence of divalent cations, because the hydrophilic ethylene oxide block of the surfactant is large enough to avoid precipitation. The contribution of the electrostatic and
specific binding in surfactant systems will depend on several properties, like the degree of surface coverage, type of end group, and on the dynamics of the (backbone) structure. For the electrostatic binding it is assumed that it resembles an adsorption process with a dynamic equilibrium, i.e. exchange of cations is possible. Micelles are dynamic systems, and this means that in the case of CAE-85 the probability for two carboxylate groups to be close enough together to bind one calcium cation will be lower as compared to the probability in rigid polymer structures, like for PAA systems. Therefore, the specific binding in CAE systems, where one divalent cation can be associated with two carboxylate groups, is weaker than the complexation in PAA systems. In general, multivalent cation binding to the CAE micelles occurs through both mechanisms.

However, from the heat effects obtained in the ITC measurements it is difficult to distinguish between the electrostatic binding contribution and the specific binding contribution. In order to relate the heat effects observed in ITC to the amount of ions bound to the CAE-85 micelles, a theoretical framework is required that describes the distribution of the ions around the micelles. The starting point is the triple-layer model \[^{17, 18}\] that describes the ion distribution around the micelle using a Stern layer, a diffuse layer, and a bulk phase, see Figure 4.2. The Stern layer contains all bound cations.

*Figure 4.2: Schematic picture of the distribution of ions and the electrical potential around a micelle of anionic surfactant molecules described by the triple layer model.*
For our purposes the following assumptions are made. Two carboxylate groups are needed to bind a single divalent cation, the surface charge density, \( \sigma \) (at \( x=0 \)), depends linearly on the amount of free carboxylate groups, and the two-state approximation can be used. The two-state approximation makes a distinction between the bound cations in the Stern layer and the free cations in the diffuse and bulk layer. The electrostatic potential between the Stern layer and diffuse layer, i.e. the surface potential \( \psi_0 \), is not only determined by the amount of cations bound to the micelle but also by the ion concentration in the diffuse layer. During an ITC experiment the ion concentration increases and, therefore, the electrical potential decreases, which immediately implies that the ‘binding affinity’ for cations will decrease upon addition of divalent cations. As a consequence the molar reaction enthalpy of binding, \( \Delta H_r \), will decrease, because it mainly consists of an electrostatic energy contribution, with the potential as a driving force. Contrary to low molecular weight ionic surfactants, the CAE micelles do not have a sharp interface between the surfactant head groups and the surrounding water. As a consequence, binding will take place throughout the whole micellar corona and no well-defined Stern layer exists. Nevertheless, it is assumed that all bound cations are in the ‘Stern layer’ between \( x=d \) and \( x=0 \).

4.3.2 Data analysis of the ITC experiments

In an ITC experiment the heat change of each successive injection is measured. The ITC software corrects for volume and concentration changes due to titrating liquid into the titration cell. The total heat change, \( Q \), is a summation of the heat changes of all injections and can be defined as:

\[
Q = \sum \Delta Q = n \theta [-\text{COO}^-]_{tot} \Delta H_r V
\]  

where \( n \) is the total number of binding sites per molecule, surface or surfactant head group, \( V \) is the active cell volume, and \( \Delta H_r \) is the molar reaction enthalpy of binding. The fractional counterion binding or surface coverage, \( \theta \), is described by:

\[
\theta = \frac{2[Dii(COO)_{2}]}{[-\text{COO}^-]_{tot}}
\]  

(4.2)
where \([Di(COO)_2]_\text{tot}\) is the bound divalent concentration and \([-COO^-]_\text{tot}\) is the total concentration of binding sites. The divalent cation mass balance is given by:

\[
[Di^{2+}]_\text{tot} = [Di^{2+}]_f + n \theta [-COO^-]_\text{tot}
\] (4.3)

where the subscript \(f\) refers to the unbound divalent ions.

The standard ITC procedure consists of combining Eqs. (4.1) to (4.3) with the Langmuir model, Eq. (4.4), to describe the measured heat change data.

\[
\theta = \frac{K[Di^{2+}]_f}{1 + K[Di^{2+}]_f}
\] (4.4)

The measurement of a cumulative enthalpy change is a disadvantage of the ITC technique. The observed heat effect, \(Q_{\text{obs}}\), is a summation of various enthalpic contributions, which complicates the interpretation of the data.

In the following the binding of calcium to the CAE-85 micelles will be used to discuss the analysis of the ITC results. In particular, a solution of surfactant R-COONa, with R-COO\(^-\) the anionic surfactant and Na\(^+\) the monovalent counterion, is titrated with a calcium chloride solution. It is assumed that the binding of Ca\(^{2+}\) will take place onto the micelles without precipitation of the polymer surfactant, and the binding ratio Ca\(^{2+}\):R-COO\(^-\) is taken as 1:2.

The observed heat change of the titration can be defined as:

\[
Q_{\text{obs}} = Q_{\text{mix}} + Q_{\text{diss}} + Q_{\text{hyd},Na} + Q_{\text{hyd},R-COO} + Q_{\text{dehyd},R-COO} + Q_{\text{dehyd},Ca} + Q_{\text{bind}} + Q_{\text{mic}}
\] (4.5)

with \(Q_{\text{mix}}\) the mixing heat, \(Q_{\text{diss}}\) the dissociation heat of R-COONa, \(Q_{\text{hyd},Na}\) the sodium ion hydration heat, \(Q_{\text{hyd},R-COO}\) the hydration heat of the surfactant head group, \(Q_{\text{dehyd},R-COO}\) the dehydration heat of the surfactant head group, \(Q_{\text{dehyd},Ca}\) the calcium ion dehydration heat, \(Q_{\text{bind}}\) is the binding heat, and \(Q_{\text{mic}}\) is the micelle conformation heat. The quantities \(Q_{\text{dehyd},R-COO}\) and \(Q_{\text{hyd},R-COO}\) have opposite signs and will cancel each other. Equation (4.5) will then become:
During the titration, the hydration heat, $Q_{\text{hyd,Na}}$, and the dehydration heat, $Q_{\text{dehyd,Ca}}$, depend only on the fractional binding, $\theta$, and are defined as:

$$Q_{\text{hyd,Na}} = \theta \Delta H_{\text{hyd,Na}} [-\text{COO}^-]_{\text{tot}}$$ (4.7)

$$Q_{\text{dehyd,Ca}} = 0.5 \theta \Delta H_{\text{dehyd,Ca}} [-\text{COO}^-]_{\text{tot}}$$ (4.8)

The standard molar hydration enthalpy of the sodium ion, $\Delta H_{\text{hyd,Na}}$, and the standard molar dehydration enthalpy of the calcium ion, $\Delta H_{\text{dehyd,Ca}} (= -\Delta H_{\text{hyd,Na}})$, are constants at isothermal conditions and are given in literature $^{[19]}$. Hydration enthalpies are always exothermic and, therefore, dehydration enthalpies are considered to be always endothermic. The charge and the ionic radius of the cation mainly determine the value of the hydration enthalpy. The higher the charge and the smaller the ionic radius, the more exothermic the molar hydration enthalpy will be, see Table 4.1.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$R_i$ [Å]</th>
<th>$R_h$ [Å]</th>
<th>$\Delta H_{\text{hyd}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium K$^+$</td>
<td>1.49</td>
<td>2.79</td>
<td>-334</td>
</tr>
<tr>
<td>Sodium Na$^+$</td>
<td>1.17</td>
<td>2.36</td>
<td>-416</td>
</tr>
<tr>
<td>Barium Ba$^{2+}$</td>
<td>1.49</td>
<td>2.82</td>
<td>-1332</td>
</tr>
<tr>
<td>Calcium Ca$^{2+}$</td>
<td>1.00</td>
<td>2.42</td>
<td>-1602</td>
</tr>
<tr>
<td>Magnesium Mg$^{2+}$</td>
<td>0.72</td>
<td>2.09</td>
<td>-1949</td>
</tr>
<tr>
<td>Zinc Zn$^{2+}$</td>
<td>0.74</td>
<td>2.10</td>
<td>-2070</td>
</tr>
<tr>
<td>Copper Cu$^{2+}$</td>
<td>0.71</td>
<td>2.11</td>
<td>-2123</td>
</tr>
<tr>
<td>Lanthanum La$^{3+}$</td>
<td>1.17</td>
<td>2.53</td>
<td>-3312</td>
</tr>
</tbody>
</table>

The mixing heat, $Q_{\text{mix}}$, is the result of mixing the diluted CaCl$_2$ solution and the surfactant solution, and usually this quantity is exothermic and considerably smaller than the hydration heat. Therefore, $Q_{\text{mix}}$ is neglected in the calculations. The mixing heat will become important in experiments where the interaction energy, $Q_{\text{int}}$, see Eq. (4.9), is small. The binding heat,
\( Q_{\text{bind}} \) is the heat that evolves when calcium is bound to the CAE-85 surfactant molecules in the micelle. The binding of cations and anions is energetically favorable, which makes this term exothermic. In general, the binding enthalpy is likely to become more exothermic when the ionic radius of the cation decreases \(^{[12]}\). In this respect, calcium should bind weaker than e.g. zinc or copper, as indicated by the values in Table 4.1.

Contrary to the binding energy, \( Q_{\text{bind}} \), the dissociation heat, \( Q_{\text{diss}} \), will give an endothermic contribution to the observed heat change, because energy is required to split a bound ion pair into separate ions. The total interaction heat, \( Q_{\text{int}} \), which is often referred to as the displacement energy, can then be defined as:

\[
Q_{\text{int}} = Q_{\text{diss}} + Q_{\text{dehyd,Na}} + Q_{\text{dehyd,Ca}} + Q_{\text{bind}}
\]  \( (4.9) \)

Combining Eqs (3.6) and (3.9) then gives:

\[
Q_{\text{obs}} = Q_{\text{mix}} + Q_{\text{int}} + Q_{\text{mic}}
\]  \( (4.10) \)

where \( Q_{\text{mic}} \) is the micelle conformation heat and includes all structural changes of the aggregate due to the titration. These changes of the micelle structure are mainly driven by a gain in free energy to obtain the most favorable conformation. In general, these enthalpic contributions are smaller than the interaction energy, \( Q_{\text{int}} \), however, these enthalpic contributions become more important when other micellar transitions come into play.

In the case of PAA, the micellar conformation heat, \( Q_{\text{mic}} \), can be replaced by the conformation heat of PAA, \( Q_{\text{con}} \). In practice, \( Q_{\text{con}} \) consists of chain stretching and contracting heats. In an ideal situation \( Q_{\text{mic}} \) and \( Q_{\text{mix}} \) are much smaller then \( Q_{\text{int}} \) and the observed heat change \( Q_{\text{obs}} \) becomes equal to \( Q_{\text{int}} \), according to Eq. (4.10). For an ideal situation, the total molar binding reaction enthalpy \( \Delta H_r \) can then be calculated directly from the experimental data using Eq. (4.1).

4.3.3 Binding parameters.
To quantify the binding in the CAE-85 surfactant system, two isotherm models are used to determine the binding parameters. The first model is the Langmuir-Freundlich model (LF):
The second model is the localized binding (LB) model \[^{17, 22}\]:

\[
\theta = \frac{(K[Ca])^v}{1 + (K[Ca])^v}
\]  

(4.11)

\[
\theta = \frac{K[Ca]e^{\frac{-ze_{a}e\psi_{0}}{kT}}}{1 + K[Ca]e^{\frac{-ze_{a}e\psi_{0}}{kT}}}
\]  

(4.12)

4.4 Results and discussion

In Figure 4.3 an example is given of a standard ITC-plot corresponding to an ideal complexation reaction, where the complexing ligand is added to a substrate in the sample cell. For a standard ITC procedure, the curve for \(Q_{obs}\) can be described by a Langmuir model, and the binding parameters \(n\), \(K\), and \(\Delta H\) are obtained from Eqs. (4.1) to (4.4). In this example \(n\) is equal to 1, because each substrate molecule has one single binding site. For the reaction enthalpy \(\Delta H\), a value of 10000 cal/mol has been taken, and for the binding constant \(K\), in the Langmuir model, a value of \(7.5\times 10^4\) has been taken. In this ideal case, \(n\) is given by the value of the molar ratio at the inflection point of the curve. The intersection of the curve with the y-axis corresponds to \(\Delta H\). In the ideal case, \(\Delta H\) is constant, like for example for the complexation of calcium to PAA, because the local surface charge density at the PAA macromolecule is constant.

However, in practice the heat change curve is the result of cumulative energetic effects. All other enthalpic effects not directly related to the complexation reaction will disturb the ideal behavior, and this results in a different shape for the heat change curve as a function of the molar ratio. Consequently, different values for the parameters \(n\), \(K\) en \(\Delta H\) are obtained from the ITC procedure, and these parameters are no longer directly related to the binding process. However, it is noted that in most cases the slope of the curve is a measure for the binding strength.
In ionic micellar systems the binding of cations to the micelle will induce some reorientation of the surfactant molecules in the micelle to obtain the energetically most favorable conformation. As a consequence of this reorganization, the local surface charge density of the micelle is not constant during the titration of ions to the surfactant system. The surface charge generates an electrical potential around the micelle that is the major driving force for binding. In particular, during the addition of cations both the potential and the driving force for binding decrease. Each extra cation experiences a weaker binding and as a consequence $\Delta H_r$ will decrease during the titration. For a proper description of the binding process in micellar systems this change in $\Delta H_r$ should be taken into account. For the description of the multivalent ion binding in the CAE surfactant systems the model presented in Chapter 3 is used.

### 4.4.1 ITC results of CAE-85 and P85

In Figure 4.4 the observed heat change is plotted for the titration of a 1 wt% CAE-85 solution and of a 1 wt% Pluronic P85 solution with a calcium chloride solution at two temperatures. The pH of the surfactant solutions was adjusted with NaOH to a value of 5.7. To be able to compare the experiments between P85 and CAE-85, it is assumed in the calculation of the molar ratio that P85 has also 5.0 mmol/L acid groups, where in reality P85 molecules have no binding sites. The surfactants are polydisperse and are therefore compared on a weight base.
It is seen that for the titration of P85 with the calcium chloride solution at 25 °C (below CMT) and 50 °C (above CMT) almost no net heat ($Q_{\text{obs}}=0$) is produced. Despite a very small mixing heat effect no binding effect can be seen. For the titration of CAE-85 at 25 °C the titration curve is similar to the P85 curves, indicating that no significant interaction occurs between calcium and the carboxylate end groups. However, for the situation with the CAE-85 surfactant at 50 °C a decreasing curve is observed, indicating a significant endothermic heat effect. This effect is not seen for the P85 solutions at 50 °C, and can, therefore, only be a result of the presence of the anionic CAE-85 micelles.

Figure 4.4: Observed heat change per injection, $Q_{\text{obs}}$, as a function of the molar ratio, $r$, of added calcium per CAE-85 carboxylate group. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 and P85 solutions with a 30 mmol/L CaCl$_2$-solution.

The observed heat effect can be split into two contributions, i.e. $Q_{\text{int}}$ and $Q_{\text{mic}}$, according to Eq. (4.10). The mixing heat, $Q_{\text{mix}}$, can be neglected because this is not observed during the experiment with P85 at 50 °C, and for the experiments with P85 and CAE-85 performed at 25 °C. It is known from literature [12] that the binding reaction of divalent ions is driven by a gain in free energy caused by the partial desolvation of the divalent ions and ionic head groups. In the case of binding, the (absolute) value of the endothermic contribution of $Q_{\text{dehyd,Ca}}$ is larger than the exothermic contribution of $Q_{\text{bind}}$. Therefore, $Q_{\text{int}}$ has a positive (endothermic) value. This indicates that the divalent binding contribution dominates the monovalent dissociation contribution. In practice, it is not possible to distinguish between $Q_{\text{int}}$
and \( Q_{mic} \), because these contributions are coupled. It is assumed that \( Q_{mic} \) is much smaller than \( Q_{out} \), because otherwise a contribution of \( Q_{mic} \) would have been observed for P85 as well. When it is assumed that a single calcium ion binds to two surfactant head groups then \( Q_{obs} \) should decrease to zero at a molar ratio, \( r \), of 0.5. From Figure 4.4 it follows that the curve for CAE-85 at 50 °C converges to zero at a molar ratio larger than 0.5. This suggests that the binding is not of a specific nature, but mainly electrostatic.

### 4.4.2 Binding of mono-, di- and trivalent ions to CAE-85

The next step is to determine the difference in binding characteristics between mono-, di-, and trivalent cations in the CAE-85 micellar system. Several ITC experiments have been performed at 50 °C with CAE-85 solutions that have been titrated with metal chloride solutions with a different valency. The alkaline earth metal ions calcium, barium and magnesium and the transition-metal ions zinc and copper have been used as a divalent cation, and an experiment has been performed using lanthanum chloride to test the affinity for trivalent ions. In all experiments the pH of the solutions was about 5.7. It has to be noted that, in this work, all heat effects measured with ITC are displacement heats relative to the system where sodium is the counterion.

From Figure 4.5a it can be concluded that heat effects are observed for all monovalent and multivalent cations.

![Figure 4.5a](image.png)

**Figure 4.5 (a):** Observed heat change per injection, \( Q_{obs} \), as a function of the molar ratio, \( r \), of added counterion per CAE-85 carboxylate group, \( r \). Results are for the titration of 1.0 wt% (6.19 mmol carboxylate groups/L for all experiments except for Mg\(^{2+}\) and Ba\(^{2+}\) (5.0 mmol/L)) CAE-85 solutions with 10 mmol/L metal chloride solutions of different cations.
Figure 4.5 (b): Fractional binding, $\theta$, calculated from measured heat data, as a function of the molar ratio, $r$.

In case of potassium this means that ITC can be used to measure displacement heat between different monovalent cations. The divalent cations Ca$^{2+}$, Ba$^{2+}$, and Mg$^{2+}$ have similar heat curves, and the same holds for Cu$^{2+}$ and Zn$^{2+}$. The heat effect observed for the transition metal ions are higher than the heat effects observed for the alkaline earth metal ions. A disadvantage of the graphs for $Q_{obs}$ as a function of the molar ratio is that no good comparison between different situations is possible. Binding isotherms, the fractional binding as a function of the molar ratio, provide a better way to compare the results obtained for different experimental conditions. In Figure 4.5b the isotherms for different cations are compared. Eventually potassium has the highest fractional binding, at a molar ratio of $r=1$ the fractional binding is about 0.6. This means that the distribution of potassium and sodium cations over the carboxylate groups is 60% and 40%, respectively. The reason that potassium has a higher affinity than sodium can be found in the higher dissociation constant of KCl, as compared to NaCl.

Furthermore, for the divalent ions initially the fractional binding is higher than the fractional binding for potassium. At a molar ratio of about unity the fractional binding for potassium becomes higher. Also, the fractional binding curves for the divalent ions do not follow the sequence, which is expected from the ionic radius (Table 4.1). Normally, for ions with an equal valence, for electrostatic interactions smaller ions will bind better than larger ones. Most likely the order observed for the fractional binding of divalent cations is a result of a
difference in specific interactions between the carboxylate groups and the various divalent cations. For the binding of a divalent ion to the micelle two carboxylate groups are required for coordination, and the probability that two carboxylate groups will be close enough together to bind one calcium cation decreases with an increase in molar ratio. Therefore, to obtain complete surface coverage with divalent cations is more difficult as compared to, for example, potassium. From the fact that two carboxylate groups are required for coordination in combination with the relatively low surface charge density it follows that only at a very high molar ratio full surface coverage with calcium will be obtained.

Lanthanum has the highest values for $Q_{\text{obs}}$, which is the result of the higher charge of the ion. Overall, there are only small differences in binding strength between the different ions, which confirms that the binding of (multivalent) cations to CAE-85 micelles is mainly determined by a charge compensating mechanism (electrostatic contribution) and to a lesser extent caused by specific interactions. It is noted that for lanthanum in the iterative numerical procedure large changes in the Debye length give rise to some difficulties in calculating the isotherm. This is also the case for the experiments where the ionic strength has been varied and for the experiment with 10 wt% surfactant concentration.

### 4.4.3 Influence of ionic strength on cation binding

The ionic strength has a considerable influence on the binding capacity of the CAE-85 micelles for divalent metal ions. For high monovalent ion concentrations the Debye-length or the double layer thickness decreases in systems with charged particles \(^{23}\). This means that in the solutions with a high ion concentration the ions will screen the effective charge of ionic micelles, and the electrical potential and the driving force for binding will be reduced. To study the influence of the ionic strength, several ITC experiments have been performed with 1.0 wt% CAE-85 solutions using different concentrations of KCl to adjust the ionic strength. From Figure 4.6 it can be concluded that indeed a lower heat effect is obtained with an increase in ionic strength. This indicates that there is a significant effect of the concentration of monovalent ions on the amount of binding of divalent cations. Specific binding effects would be influenced less by the ionic strength. Therefore, it can again be concluded that the binding of calcium to CAE-85 is mainly electrostatic of nature.
Figure 4.6: Observed heat change per injection, $Q_{\text{obs}}$, as a function of the molar ratio, $r$, of added calcium per CAE-85 carboxylate group. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 solutions with a 30 mmol/L CaCl₂ solution at various ionic strengths.

4.4.4 Influence of pH on calcium binding to CAE-85 micelles

The CAE-85 surfactant has two end standing (carboxylic) acid groups, and this means that there should be an influence of the pH on the binding capacity. At low pH the binding capacity of the CAE-85 surfactant is expected to be similar to that of P85, which is almost negligible. The binding of calcium to the CAE-85 aggregates has been measured at 50 °C for four different values of the pH, see Figure 4.7. It is seen that $Q_{\text{obs}}$ increases when the pH is increased, as a result of a larger amount of deprotonated carboxylic groups that have an interaction with calcium. Therefore, the total interaction energy $Q_{\text{int}}$ increases. From Figure 4.4a it also follows that at low pH (pH=3.47) there is no electrostatic interaction between calcium and the CAE-85 micelles, and the system behaves similar to the unmodified P85 surfactant. In terms of fractional binding, the amount of calcium bound to the CAE-85 micelles increases with an increase in pH, see Figure 4.7b. It is noted that in the definition of fractional binding and molar ratio always the total concentration of end groups is used and not the concentration of deprotonated acid groups.
Parametric study of the cation binding to CAE-85 surfactant systems studied with isothermal titration calorimetry

Figure 4.7 (a): Observed heat change per injection, $Q_{\text{obs}}$, as a function of the molar ratio, $r$, of added calcium per CAE-85 carboxylate group. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 solutions with a 10 mmol/L CaCl$_2$ solution, and the pH was adjusted with a 0.5 M NaOH solution.

Figure 4.7 (b): Fractional binding, $\theta$, calculated from measured heat data, as a function of the molar ratio, $r$.

4.4.5 Influence of surfactant concentration on the calcium binding to CAE-85 micelles

At a certain surfactant concentration intermicellar interactions come into play and this could have an influence on the binding characteristics. In Figure 4.8 the results of the titration with a calcium chloride solution, at 25 °C and 50 °C, to a CAE-85 solution with a concentration of 0.1 wt%, 1.0 wt%, and 10 wt% are given.
From Figure 4.8a it follows that, as expected, at 25 °C there is no net heat effect observed, while at 50 °C the heat effect clearly increases with an increase in CAE-85 concentration. It is noted that $Q_{obs}$ is the observed energy per mol calcium added. This means that for the experiment with the 10 wt% CAE-85 surfactant solution both the amount of carboxylate groups and the amount of calcium is 100 times higher than in the experiment with the 0.1 wt% CAE-85 surfactant solution. The fact that the heat change is relatively higher with the lower surfactant concentration can be explained by the larger amount of work, which is
required to overcome the larger distance between cation and micelle surface. On the other hand, from Figure 4.8b can be seen that the fractional binding is higher for the 1.0 wt% experiment. This is due to the fact that the probability for a calcium ion to find two carboxylate groups is larger at higher surfactant concentration.

### 4.4.6 Influence of temperature on the calcium binding to CAE-85 micelles

ITC experiments have been performed where calcium chloride solutions are titrated to CAE-85 solutions at different temperatures above the CMT, which is about 32 °C. In Figure 4.9a it is seen that the curves obtained at 40 °C, 45 °C, and 50 °C have some overlap, indicating that for these temperatures the heat effect is approximately the same. The result obtained at 55 °C and 60 °C is somewhat lower, as compared to the result obtained at the lower temperatures. At 55 °C and 60 °C a clear drop in the observed heat effect occurs, for 60 °C this happens at a molar ratio between 0.12 and 0.15. The most logical explanation for this sudden drop is the occurrence of a sphere-to-rod micelle transition. It is known from literature [24] that most Pluronics have such a transition, occuring at about 65 °C for the unmodified P85. In the presence of salts this transition shifts to lower temperatures, and here it is assumed that the presence of the carboxylic end-groups in the CAE-85 surfactant has only a limited effect.

![Figure 4.9 (a): Observed heat change per injection, Q_{obs}, as a function of the molar ratio of added calcium per CAE-85 carboxylate group, r. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 solutions with a 10 mmol/L calcium chloride solution at different temperatures.](image-url)
Figure 4.9 (b): Fractional binding, \( \theta \), calculated from measured heat data, as a function of the molar ratio, \( r \).

At 45 °C and 50 °C the fractional binding is almost the same, see Figure 4.9b. The fact that the fractional binding at the lowest temperature studied, i.e. 40 °C, shows a different behavior might be a result of the fact that the micellization process occurs over a temperature range. In the case of the CAE-85 surfactant the temperature of 40 °C falls in this range. Full micellization has not yet occurred, therefore, fewer binding sites are available. The occurrence of a sphere-to-rod transition lowers the binding isotherms for 55 °C and 60 °C and these isotherms are therefore more difficult to interpret, because the heat effect does not solely originate from binding effects.

4.4.7 ITC results for polyacrylic acid

PAA is known as a good calcium binder, binding calcium as a strong bidentate complex \([14]\). In Figure 4.10a results are shown for the titrations of PAA where the titrant is a calcium or barium chloride solution. The experiments have been performed at 25 °C and 50 °C, and at pH values where the carboxylic groups are protonated (pH=3.5) or deprotonated (pH=5.8). PAA has no temperature transition, like CAE-85, and it is to be expected that at all temperatures binding of calcium and barium occurs. However, at low pH both the carboxylic groups of CAE-85 and of PAA will be in a protonated state and there are no free binding sites. It is expected that in this case there is no binding of the divalent cations.
From Figure 4.10a it follows that at both temperatures indeed no heat effect is observed for the experiments carried out at low pH. In all the other PAA experiments a clear heat effect is observed, although the PAA curves have a different shape as compared to the curve for CAE-85 at 50 °C. A steep negative slope and a maximum are present in the PAA curves. The steep negative slope indicates strong bidentate binding of the divalent cations to PAA. The presence of a maximum in the curves can be explained by taking a change in chain conformation of PAA into account. The PAA chain is fully stretched at complete deprotonation, and when the divalent ions are bound to the carboxylate groups of PAA the distance between the carboxylate charges will become smaller and the chain will collapse into a random coil conformation. This is an exothermic process ($Q_{con}<0$), because of the higher conformational freedom of the monomer units in the coil conformation. It seems that the slopes of the different curves are almost the same. However, when the experiments of PAA with calcium and barium at the two different temperatures are examined, the higher temperature curves have a higher maximum than the low temperature curve. This can be understood when the binding process is considered to be endothermic, and therefore an increase in temperature results in an increased heat effect.

Figure 4.10 (a): Observed heat change per injection, $Q_{obs}$, as a function of the molar ratio, $r$, of added divalent ion per CAE-85 carboxylate group, $r$. Results are for the titration of 1.0 wt% (5.0 mmol carboxylate groups/L) CAE-85 and polyacrylic acid (MW=2000 g/mol) solutions with 30 mmol/L CaCl$_2$ or BaCl$_2$ solutions.
Furthermore, the lower binding energy of the barium ions, as compared to the calcium ions, can be related to the larger ionic radius and consequently a smaller hydration enthalpy of the barium ions (Table 4.1). It is noted that for all the PAA experiments in Figure 4.10a the inflection point is not at 0.5. This discrepancy might be the result of the additional conformation energy, $Q_{con}$, which makes the determination of $Q_{int}$ more difficult.

![Figure 4.10 (b): Fractional binding, $\theta$, calculated from measured heat data, as a function of the molar ratio, r.](image)

In Figure 4.10b a comparison is made between the results obtained for PAA and for the CAE-85 surfactant systems. There is not a large difference between the four isotherms obtained for the experiments with PAA. For the CAE-85 surfactant system a lower binding fraction of calcium is obtained as compared to PAA.

### 4.4.8 Binding parameters

The results for the binding parameters obtained from a fit with the two models, Eqs. (4.11) and (4.12), are summarized in Tables 4.2 and 4.3. Results for the binding of calcium to the CAE-85 micelles are given in Table 4.2, and in Table 4.3 results for the binding of the different cations to the CAE-85 micelles at different temperatures are given.

In the two models it assumed that the maximum amount of counterions that can be bound is equal to the total number of binding sites, where the valence of the counterions is taken into account.
Table 4.2: Binding parameters for the Langmuir-Freundlich model and localized binding model for experiments where CAE-85 is titrated with a calcium chloride solution at 50 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>wt% CAE-85</th>
<th>$K_{LF}$ [L/mol]</th>
<th>$v$ [-]</th>
<th>$K_{LB}$ [L/mol]</th>
<th>$\tau$ [10^{16} 1/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.34</td>
<td>1</td>
<td>27.8</td>
<td>0.38</td>
<td>10.5</td>
</tr>
<tr>
<td>2</td>
<td>5.40</td>
<td>1</td>
<td>619.3</td>
<td>0.62</td>
<td>300.4</td>
</tr>
<tr>
<td>3</td>
<td>10.0</td>
<td>1</td>
<td>1571.7</td>
<td>0.73</td>
<td>915.2</td>
</tr>
<tr>
<td>4</td>
<td>5.82</td>
<td>0.1</td>
<td>1225.4</td>
<td>0.44</td>
<td>314.8</td>
</tr>
</tbody>
</table>

Table 4.3: Binding parameters for the Langmuir-Freundlich model and localized binding model for experiments, where CAE-85 is titrated with metal chloride solutions at different temperatures. In all experiments 1.0 wt% solutions of CAE-85 were used with a pH value of about 5.8.

<table>
<thead>
<tr>
<th>Cation</th>
<th>T [°C]</th>
<th>$K_{LF}$ [L/mol]</th>
<th>$v$ [-]</th>
<th>$K_{LB}$ [L/mol]</th>
<th>$\tau$ [10^{16} 1/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca^{2+}</td>
<td>40</td>
<td>199.9</td>
<td>0.48</td>
<td>46.1</td>
</tr>
<tr>
<td>2</td>
<td>Ca^{2+}</td>
<td>45</td>
<td>359.9</td>
<td>0.56</td>
<td>171.4</td>
</tr>
<tr>
<td>3</td>
<td>Ca^{2+}</td>
<td>50</td>
<td>339.8</td>
<td>0.61</td>
<td>131.1</td>
</tr>
<tr>
<td>4</td>
<td>Ca^{2+}</td>
<td>55</td>
<td>49.7</td>
<td>0.36</td>
<td>16.7</td>
</tr>
<tr>
<td>5</td>
<td>Ca^{2+}</td>
<td>60</td>
<td>0.23</td>
<td>0.14</td>
<td>1.82</td>
</tr>
<tr>
<td>6</td>
<td>Ba^{2+}</td>
<td>50</td>
<td>672.5</td>
<td>0.62</td>
<td>290.4</td>
</tr>
<tr>
<td>7</td>
<td>Mg^{2+}</td>
<td>50</td>
<td>567.5</td>
<td>0.66</td>
<td>307.6</td>
</tr>
<tr>
<td>8</td>
<td>Zn^{2+}</td>
<td>50</td>
<td>355.2</td>
<td>0.62</td>
<td>133.3</td>
</tr>
<tr>
<td>9</td>
<td>Cu^{2+}</td>
<td>50</td>
<td>287.6</td>
<td>0.57</td>
<td>85.4</td>
</tr>
<tr>
<td>10</td>
<td>K⁺</td>
<td>50</td>
<td>918.1</td>
<td>0.87</td>
<td>738.6</td>
</tr>
</tbody>
</table>

This means that for all situations it is assumed that $\theta=1$ for $r \rightarrow \infty$. However, for a number of situations, like for low pH, it seems that not the total theoretical amount of binding sites is available for binding. As a result, the fractional binding converges to a value lower than unity. This should be taken into account when the values of Tables 4.2 and 4.3 are used to make a quantitative comparison with other systems used for the binding of divalent ions.

### 4.5 Conclusions

Isothermal titration calorimetry has been used to study the binding of different cations to CAE-85 micelles. It can be concluded that the CAE-85 micelles have a reasonable affinity for binding cations. The binding process is controlled by temperature; below the CMT of the CAE-85 surfactant virtually no binding of multivalent ions occurs.
From the results for calcium, it follows that the fractional binding increases with an increase in pH and with an increase in CAE-85 surfactant concentration. For temperatures where full micellization has taken place, i.e. above 40 °C, temperature has a minor influence on the binding of calcium to the CAE-85 micelles. For temperatures above 55 °C a deviation is observed in the heat curve, which can be explained by a sphere-to-rod transition. The results for the fractional binding of the divalent cations do not follow the sequence of the ionic radius, and the differences between the binding of the divalent ions are most likely the result of small differences in specific interactions.

From a comparison between the binding to CAE-85 and PAA it can be concluded that the CAE-85 surfactant system binds divalent ions weaker than PAA. However, it can also be concluded that the CAE-85 micelles form a binding system with an on/off mechanism that responds to a moderate temperature stimulus. This reversible binding of multivalent ions in CAE surfactant systems offers attractive opportunities for processes requiring a controlled binding and release behavior.

4.6 References

Chapter 5

Conductometric analysis of the binding behavior of counterions in CAE-85 surfactant systems

Abstract

The binding of monovalent and divalent counterions in a surfactant system with a temperature dependent micellization process has been studied using conductometry. The binding isotherm of calcium to thermo-reversible carboxylic acid end standing (CAE) micelles has been determined. These CAE surfactants, modified Pluronic P85, are capable of binding multivalent ions only above the critical micellization temperature. The critical micellization concentration of these CAE surfactant systems is too low to be used for the determination of micellization parameters using conventional conductometric methods. An approach has been developed where different conductometric methods, including the use of Eisenberg plots and conductivity excess, are combined. In general, with this approach qualitative and quantitative information can be obtained about surfactant systems with respect to binding of counterions and competition between monovalent and multivalent counterions.
5.1 Introduction

The binding of metal ions is important in various applications, like biomedical, environmental, and industrial processes \(^{[1,2]}\). In particular, controlling the binding and release behavior of metal ions is subject of extensive research \(^{[3]}\). In this respect, a new class of surfactants has been developed that is capable of binding multivalent ions in a reversible way. These so-called CAE (carboxylic acid end standing) surfactants \(^{[4]}\) are obtained by modifying the hydroxyl end groups of Pluronic (polyethylene oxide - polypropylene oxide - polyethylene oxide) block copolymers with succinic anhydride to form carboxylic acid end standing polymer surfactants. Similar to standard Pluronics \(^{[5]}\), the CAE surfactants have a critical micellization temperature (CMT). Reversible binding of the ions to the CAE surfactant aggregates is realized by means of a temperature shift \(^{[4]}\). Above the CMT the CAE surfactants form anionic micelles with a high affinity for multivalent cations, while below the CMT the micellar structure will breakup resulting in the release of the cations. As a result of the good solubility of the CAE surfactants, these are the first anionic surfactants that are highly soluble in the presence of hardness ions, like calcium or barium, and that have a temperature dependent micellization behavior instead of a more concentration dependent micellization behavior.

A proper understanding of the binding behavior of cations to anionic micelles requires a combined experimental and theoretical approach. Conventional methods, like conductometry \(^{[6,7,8]}\) and surface tension analysis \(^{[9]}\), used to study the binding behavior of (multivalent) cations to anionic micellar systems are based on a clear transition associated with a concentration dependent micellization process. Conductivity measurements are difficult to use when dealing with anionic surfactants that have a temperature-dependent micellization transition, because the conductivity depends strongly on the temperature. The fact that Pluronic-based surfactants have an extremely low critical micellization concentration (CMC), implies that no realistic data for the CAE surfactants can be obtained below the CMC. This means, in turn, that theoretical descriptions \(^{[10,11]}\) like mass action modeling cannot be used, because they are based on a comparison between conductivity data above and below the CMC. For Pluronic based surfactant systems, with a temperature sensitive critical micellization process, an alternative approach has to be developed to determine the micellization parameters.
In the following, the binding of monovalent and divalent ions to aggregates of CAE surfactants is studied using a conductivity method that has been applied to study ion binding to polyacrylic acid, as proposed by Pochard \cite{12, 13} and De Jong \cite{14}. Different experimental conductivity results, like conductivity excess and Eisenberg plots are discussed, and a detailed description of the binding behavior is given based on the two-state approximation. The experimental results obtained for the CAE surfactant are compared with results obtained for polyacrylic acid (PAA).

5.2 Experimental

5.2.1 CAE surfactants

The carboxylic acid end standing (CAE-85) surfactant was synthesized by modifying Pluronic P85 surfactant (EO\textsubscript{39}-PO\textsubscript{52}-EO\textsubscript{39}) with succinic anhydride to obtain a high-molecular weight anionic surfactant with temperature sensitive micellization behavior, see Figure 5.1. In the synthesis of the CAE-85 surfactant \cite{4}, Pluronic P85 surfactant (EO\textsubscript{39}-PO\textsubscript{52}-EO\textsubscript{39}) was purified by dissolving the polymer into diethyl ether. The cloudy turbidity was removed in a centrifuge, followed by precipitation of the surfactant in cold pentane. Purified P85 was then dissolved into toluene from which the water present in the toluene has been removed by azeotropic distillation.

The reaction was started by addition of succinic anhydride and was performed for four hours at 90 °C. After the reaction toluene was evaporated and the product was dissolved in water, followed by addition of sodium carbonate until pH>9 and diluted sulphuric acid until pH<2, respectively. The product was then extracted with butanol and dried overnight above a layer of anhydrous sodium sulphate. The product was redissolved in diethyl ether, followed by precipitation with an equal amount of pentane. The final product was obtained after filtering and drying under vacuum conditions at room temperature.

*Figure 5.1: Chemical structure of CAE-85 surfactant.*
5.2.2 Polyacrylic acid
The molecular weight of polyacrylic acid used in the experiments was about 2000 g/mol.

5.2.3 Conductometric analysis
All conductometric experiments were performed using a QiS M320 conductometer with a QiS QC203T epoxy/graphite conductivity cell. The cell constant was periodically checked and calibrated by a 0.01 M KCl solution. The solution temperature was kept constant (+/- 0.1 °C) with a Lauda C6 CP thermostat.

5.3 Theoretical background

5.3.1 Counterion binding
In micellar systems counterion association takes place because of the electrical field created by the head groups of the micelle. The electrostatic interaction is mainly determined by the valence of the counterion, and divalent ions bind stronger than monovalent ions [15]. Association of counterions occurs also because of certain specific interactions between the surfactant and the counterion. These specific interactions are a result of the differences between counterions, like a difference in size, ease of hydration, possibility for hydrogen bonding, and the formation of contact ion pairs with the surfactant head groups [16]. For most micellar systems the surfactant head group becomes too hydrophobic in the presence of divalent ions and the strong specific interaction will lead to precipitation of the surfactant. In the case of the CAE surfactant, the good solubility and dynamic nature of the micelle will prevent the occurrence of strong bidentate complexation.

In the case of a PAA system at high pH, monovalent counterions are partly electrostatically bound, a phenomenon known as condensation [12, 13]. Divalent calcium cations will form strong bidentate complexes with the carboxylate groups of PAA, because of strong specific interactions.

5.3.2 Two-state approximation
The counterion distribution around the micelle can be described using a Stern layer and a so-called ‘diffuse layer’. The Stern layer consists of the ‘bound’ counterions. In the diffuse layer the counterion concentration shows an exponential decrease according to the Poisso-
Boltzmann equation \[^{[17]}\], with the highest concentration at the micellar surface \[^{[18-20]}\]. This distribution is often simplified by using the two-state approximation \[^{[21]}\]. In this case the cations are either in a bound state (i.e. bound to the micelle) or are free in the bulk solution.

### 5.3.3 Conductivity theory

For a surfactant solution above its CMC or CMT the conductivity is determined by the contribution of monovalent counterions and the surfactant head groups. For CAE surfactants the CMC is very low, and therefore the contribution of the unimers (free surfactants) to the conductivity of a micellar solution can be neglected. The conductivity, \( K_p \), for a CAE surfactant solution can then be written as \[^{[12, 13]}\]:

\[
K_p = f_{p,0} C_p \lambda_p + f_{M,0} C_M \lambda_M = f_{M,0} C_p (\lambda_M + \lambda_p)
\]

(5.1)

where \( C \), \( \lambda \), and \( f \) are the concentration, the equivalent molar conductivity, and the free fraction of the monovalent counterion (\( M \)) or deprotonated carboxylic groups of the polyion or surfactant molecules (\( p \)). The subscript 0 indicates that no additional salt is present in the solution. When there are no additional salts present, the concentration of the surfactant, \( C_p \), is equal to the concentration of the monovalent ions, \( C_M \), and the fraction of unbound polymer, \( f_{p,0} \), is equal to the fraction of free monovalent ions, \( f_{M,0} \). In the case that a divalent chloride salt is added, e.g. \( \text{CaCl}_2 \), with conductivity, \( K_{di} \):

\[
K_{di} = C_{di} \lambda_{di} + C_{Cl} \lambda_{Cl} = C_{di} (\lambda_{di} + 2\lambda_{Cl})
\]

(5.2)

the total conductivity, \( K_T \), becomes:

\[
K_T = f_p C_p \lambda_p + f_M C_p \lambda_M + f_{di} C_{di} \lambda_{di} + 2C_{di} \lambda_{Cl}
\]

(5.3)

For the binding of divalent cations to the macromolecule, the total conductivity, \( K_T \), is expected to be smaller than the sum of \( K_p \) and \( K_{di} \) upon mixing.
This loss in conductivity occurs as a result of complexation of two charged groups. This difference is called the conductivity excess, $K_E$, and is defined as:

$$K_E = K_{di} + K_p - K_T$$  \hspace{1cm} (5.4)

Combining Eqs. (5.1) to (5.4) yields the following relation for the conductivity excess:

$$K_E = C_p (\lambda_p + \lambda_M) (f_{M,0} - f_M) + C_{di} (1 - f_{di}) (\lambda_{di} + 2\lambda_p)$$  \hspace{1cm} (5.5)

In Eq. (5.5), the first term on the right-hand side is related to the gain in conductivity as a result of the release of monovalent cations, and the second term is related to the loss of conductivity because of the binding of divalent ions to the polymer.

### 5.3.4 Equivalent molar conductivity at different temperatures

The conductivity is very sensitive to changes in temperature. Usually the values of equivalent molar conductivity of ions are only tabulated for a temperature of 25 °C \[22\]. At elevated temperatures molecules tend to move faster, which results in a higher conductivity. The equivalent molar conductivity at higher temperatures can be calculated from the ion diffusion coefficients. The Stokes–Einstein relation, Eq. (5.6), is used to determine the diffusion coefficient, $D$, of an ion as a function of temperature. It is assumed that the ionic radius, $r$, is independent of temperature. The Stokes-Einstein relation is given by:

$$D = \frac{kT}{6\pi\eta r}$$  \hspace{1cm} (5.6)

where, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ the viscosity of the medium.

The equivalent molar conductivity, $\lambda$, can be determined from the diffusivity by introducing the following equation (Einstein relation) for the ion mobility \[22, 23\].
where $z$ is the ionic charge, $F$ is the Faraday constant, and $R$ is the gas constant.

The equivalent molar conductivity is a function of the ionic strength according to Kohlrausch’s law \[^{[23]}\]. For the CAE surfactant systems low ionic strengths are used, and therefore this dependence can be neglected.

### 5.4 Results and discussion

#### 5.4.1 Temperature dependence of CAE-85 conductivity

First, the dissociation behavior of CAE micellar aggregates is studied using conductivity in the presence of only monovalent ions. The CMT can be determined from a difference in conductivity above and below the CMT. The molar conductivity of a solution, $\Lambda$, is defined as the ratio of the conductivity to the concentration of the solute, i.e. the polymer or surfactant groups:

$$
\Lambda = \frac{K}{C_p}
$$

**Figure 5.2 (a):** Molar conductivity as function of temperature of a 0.5 wt% CAE-85 solution. The concentration of carboxylate groups, $C_p$, is equal to $3.07 \times 10^{-3}$ mol/L and the pH is equal to 5.4.
In Figure 5.2 the molar conductivity of a 0.5 wt% CAE-85 solution, with sodium as the counterion, is shown as a function of temperature. The molar conductivity increases linearly with temperature, however, the slope of the conductivity is different above and below the CMT. The CMT is now given by the intersect of the two slopes. In the case of the CAE-85 surfactant a CMT of about 33 °C is obtained from the $\Lambda$-plot. This value for the CMT is in good agreement with results obtained with differential scanning calorimetry (DSC) experiments [9].

According to Eq. (5.1), below the CMT the conductivity is mainly determined by the contributions of the surfactant (carboxylate) end groups and the sodium counterion. When the temperature is increased, but remains below the CMT, the only change in the molar conductivity is caused by an increase in $\lambda_p$ en $\lambda_M$.

In the $\Lambda$ versus $C$ plots for conventional ionic surfactant systems [6, 7] the slope of the curve above the CMC is lower than the slope of the curve below the CMC. This is mainly a result of the condensation effect. Contrary to conventional ionic surfactant systems, a higher slope above the CMT is observed in the case of the CAE-85 surfactant. Furthermore, the difference in slope above and below the CMT is relatively small, which makes conductivity experiments with this surfactant more difficult. To check if the slope in the conductivity below the CMT is not too low as a result of incomplete dissociation of the CAE-85 surfactant, the logarithm of the molar conductivity is plotted as function of the reciprocal temperature in Figure 5.2b.
According to Walden’s rule\textsuperscript{[24, 25]}, the molar conductivity is related to the dynamic viscosity of the solution and the temperature by:

\[
\ln(\Lambda) = Q - \frac{E_v}{R} \frac{1}{T}
\]  

(5.9)

where \(E_v\) is the viscosity activation energy and \(Q\) is a constant.

At complete dissociation of the CAE-85 surfactants the temperature dependency of the molar conductivity is only a function of the viscosity of the solution, and \(E_v\) is almost equal to the value for pure water (17.80 kJ/mol). When the dissociation is incomplete, larger activation energy effects are expected, because counterions are being released when the temperature is increased. From the data in Figure 5.2b an activation energy of 17.78 kJ/mol is obtained, which is very close to the value of pure water. From this it can be concluded that there are no temperature dependent binding effects below the CMT. Most likely this implies complete dissociation of the ionic CAE-85 surfactant molecules.

From Figure 5.2a it follows that for the CAE-85 surfactant the slope of the conductivity above the CMT is higher than the slope of the conductivity below the CMT. Apparently, the conductivity in the presence of micelles is higher than the conductivity of in the case of the surfactant unimer solution. This is not caused by the increase in temperature, because then the slope of the conductivity below and above the CMT would have been the same. This increase in (slope of the) conductivity is a result of enhanced freedom of the sodium and the carboxylate groups in the case of the micelles. Below the CMT the most likely configuration of the CAE-85 surfactant unimers is a randomly coiled formation, where some shielding of the carboxylate groups occurs. Above the CMT there are two effects that enhance the conductivity. First, for the micelles there is an ‘ordered’ configuration, where the hydrophobic PPO block is located in the core and the hydrophilic PEO block with the carboxylate groups form the corona of the micelle. In general, the corona is stretched out into the aqueous surroundings, and as a result there is an enhanced contribution of the carboxylate groups to the conductivity. Furthermore, the volume occupied by the micelles, at 0.5 wt\%, is smaller then the volume occupied by the coiled formation of surfactant unimers. This means that the mobility of the sodium ions in the presence of the micelles is higher than in the case
of the surfactant unimer solution, and this higher mobility also results in an enhanced contribution to the conductivity.

5.4.2 Binding affinity of calcium counterions

The next step is to determine to what extent conductometric measurements can be used to evaluate calcium binding to the CAE-85 micelles. This implies determining the conductivity effect of the displacement of sodium ions by calcium ions. The absolute changes in conductivity as a result of complexation or binding are small, and are hard to distinguish from the changes caused by the temperature-viscosity dependence. In the case that calcium chloride is added to a CAE-85 surfactant solution it is difficult to determine the CMT from a difference in conductivity below and above the CMT. Addition of calcium diminishes the already small changes in conductivity observed for sodium even more. A way to circumvent this is to subtract the results of a reference experiment with sodium chloride from the results obtained for the experiment with calcium chloride.

Figure 5.3 shows the conductivity difference $\Delta K (=K_{exp,Na} - K_{exp,Ca})$ calculated for two experiments with a 0.5 wt% CAE-85 solution, in which sodium chloride and calcium chloride are added, respectively. For the [carboxylate group]:[divalent counterion charge] a ratio equal to 1.0:1.0 and equal to 1.0:0.5 was taken. Below the CMT no binding of calcium to the CAE-85 surfactants is expected and the difference between the sodium and calcium experiments arises from the fact that both ions have a different equivalent conductivity, $\lambda$, which is slightly higher per unit charge for calcium as compared to sodium.

It is noted that both ions have (almost) the same linear dependence of the conductivity with temperature, indicated by $\lambda(T)/\lambda(T=25 \, ^\circ C)$. This is confirmed by the results presented in Figure 5.3. With an increase in temperature, a negative value for $\Delta K$ with a negative slope is observed. Above the CMT the slope of the conductivity has a positive value, which indicates that the total conductivity of the calcium ions decreases relative to that of the sodium ions. The only explanation for this phenomenon is a loss of conductivity as a result of the binding of calcium ions to the CAE-85 micelles.
For a better understanding of the calcium binding to the CAE-85 micelles an experiment has been carried out at 50 °C, where a 1.0 wt% solution of CAE-85 is titrated with a CaCl$_2$ solution. The conductivity excess, $K_E$, from this experiment has been calculated using Eq. (5.4) and the results are plotted in Figure 5.4 as well as results for calcium binding to PAA. Pochard [12, 13] and de Jong [14] found that in the case of PAA, the excess conductivity increases linearly until almost full coverage of the carboxylate groups by calcium ions has been reached, which corresponds to a molar ratio $r (=C_{di}/C_p)$ in the order of
0.4 to 0.5. At full coverage, the excess conductivity becomes constant, because no further loss of conductivity takes place by the addition of more calcium. The linear dependence of the excess conductivity on the calcium concentration can be explained by a constant molar equivalent conductivity, \( \lambda_p \), of the carboxylate groups on the PPA chain. This means that there is no influence of calcium binding on the molar equivalent conductivity of the free carboxylate groups.

For the CAE-85 system the excess conductivity is a non-linear function of the calcium concentration over the whole range studied (up to \( r \) equal to unity), see Figure 5.4. The conductivity excess for the CAE-85 system shows a behavior characteristic for a binding isotherm. For \( r > 0.5 \) the calcium ions still have an electrostatic interaction with the CAE-85 micelles. The fact that initially no linear dependence is observed for the excess conductivity indicates that \( \lambda_p \) decreases with an increase in calcium concentration.

### 5.4.3 The role of monovalent ions in the CAE-85 system

The condensed monovalent cations stabilize the PAA chain and it is also known that in conventional anionic surfactant systems some monovalent counterion binding occurs for reasons of stability. Pochard \(^{12, 13}\) and de Jong \(^{14}\) showed that there is no difference in condensation behavior between the various alkali cations for PAA polyelectrolytes. To study the contribution of the monovalent counterions to the conductivity, CAE-85 solutions have been titrated with NaOH, KOH, and LiOH. The molar conductivity results for these three solutions are plotted as a function of the neutralization degree together with a PAA reference in Figure 5.5a.

For each of the four curves in Figure 5.5a an initial decrease in conductivity is observed, which is a result of the neutralization of free protons (H\(^+\) in solution) caused by the self-ionization of the macromolecule. For all cases, after the minimum the conductivity smoothly increases with an increase in ion concentration. For the CAE-85 system the conductivity shows a linear behavior, while the conductivity for PAA tends to have a decreasing slope until full neutralization (\( \alpha = 1 \)), where the neutralization degree, \( \alpha \), is defined as:

\[
\alpha = \frac{[\text{COO}^-]}{C_p}
\]  

(5.10)
The point where the slope starts to decrease, $\alpha$ of about 0.5, marks the beginning of condensation of monovalent ions on the PAA chain $^{[12, 13, 27]}$. The concentration of free monovalent ions reaches a maximum at that point, and binding of monovalent ions occurs when more base is added. However, this effect is not observed for the three CAE-85 experiments, in which each curve shows a linear conductivity increase from the minimum until the neutralization point.

Figure 5.5 (a): Molar conductivity, $\Lambda$, as a function of the neutralization degree, $\alpha$, for 1.0 wt% CAE-85 solutions with different alkali hydroxides. The concentration of free carboxylate groups, $C_p$, is equal to $5.1 \times 10^{-3}$ mol/L for CAE-85 and $7.3 \times 10^{-3}$ mol/L for PAA at $\alpha=1$.

Figure 5.5 (b): Eisenberg plot of 1.0 wt% CAE-85 solutions at 50 °C using CaCl$_2$ with molar ratios $r$ from 0 to 0.75.
From this it is concluded that no effective condensation takes place on the CAE-85 micelles. Apparently no cation layer is needed to stabilize the CAE-85 micelle, and the counterions are only present to fulfill electro-neutrality. An explanation for this phenomenon can be found in the molecular structure of the CAE-85 micelle, which is based on the triblock copolymer EO\textsubscript{39}-PO\textsubscript{52}-EO\textsubscript{39}. The molecular weight of the CAE-85 surfactants is 4748 g/mol, and the two anionic carboxylate end groups constitute only a small part of the CAE-85 surfactant molecule. These end groups have a very small influence on the micellization behavior of the CAE-85 surfactant, because Pluronic surfactants form already stable micelles. The small effect of the carboxylate end groups on the critical micellization temperature has been confirmed by differential scanning calorimetry (DSC) studies\textsuperscript{[4]}. The sharp increase in slope beyond \( \alpha = 1.0 \) is a result of the OH\textsuperscript{-} ions. At this point there are no longer free protons available to neutralize the OH\textsuperscript{-} ions, and therefore the OH\textsuperscript{-} ions start to contribute to the conductivity.

To evaluate the influence of the addition of divalent cations on the behavior of the monovalent ions an Eisenberg plot has been constructed (Figure 5.5b). In this graph the molar conductivity \( \Lambda_T \) is plotted as a function of the monovalent molar equivalent conductivity \( \lambda_M \) with \( M = \text{Li}^+, \text{Na}^+, \) and \( \text{K}^+ \) (see Table 5.1) for different molar ratios of divalent cations \( r \). When no divalent cations are added \( (r=0) \), \( C_{di} \) is equal to zero, and Eq. (5.3) in combination with Eq. (5.8) becomes:

\[
\Lambda_T = f_p \lambda_p + f_M \lambda_M
\]  

(5.11)

Table 5.1: Equivalent ionic molar conductivities\textsuperscript{[22, 28]} at 25 °C and 50 °C. The values at 50 °C are calculated from the values at 25 °C by means of Eqs. (5.6) and (5.7).

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \lambda_{eq}^{[22, 28]} ) [S cm(^2)/mol]</th>
<th>( \lambda_{eq} ) [S cm(^2)/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>50.08</td>
<td>81.62</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>38.66</td>
<td>62.96</td>
</tr>
<tr>
<td>K(^+)</td>
<td>73.48</td>
<td>119.73</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>118.97</td>
<td>193.72</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>76.31</td>
<td>124.26</td>
</tr>
</tbody>
</table>

From Eq. (5.11) it follows that the slope of an Eisenberg plot is equal to the free fraction of monovalent cations, \( f_M \) (or \( f_{M,0} \) when \( r \) is zero). At 25 °C a value of 0.96 for \( f_{M,0} \) was found,
which is close to unity and this confirms that full dissociation takes place below the CMT. A value of 0.67 for $f_{M,0}$ was found at 50 °C, which means that the monovalent ion contribution of the conductivity is reduced by almost 33% when CAE-85 micelles are present. In the absence of a condensation effect, this value of 0.67 for $f_M$ can only be explained by a reduction in mobility of the monovalent ions by the high micelle density in the 1 wt% solution at 50 °C, as compared to the mobility of the monovalent ions in the surfactant unimer solution at 25 °C. Apparently, the intermicellar effects for the 1 wt% solution are considerable larger than for the 0.5 wt% solution, as presented in Figure 5.2a.

Another feature observed in Figure 5.5.b is that when divalent cations are added to the surfactant solution ($r>0$), the slope of the Eisenberg plot hardly changes. This is contrary to results obtained for the PAA system [12, 13], where the slope of the curves increases to a value of unity for $r=0.5$. This increase in slope occurs because condensed monovalent cations are being displaced by divalent cations. The fact that for the CAE-85 system a constant slope is observed for different values of $r$, indicates that the conductivity of the monovalent cations does not depend on the presence of divalent cations. This is another indication that no condensation occurs in the CAE-85 micellar system.

### 5.4.4 Determination of binding isotherms

For the binding of (divalent) ions to PAA the two-state approximation is a valid assumption, which makes it possible to calculate the binding isotherms from $f_{di}$ for calcium quite accurately using Eq. (5.5). However, Eq. (5.5) cannot be used to calculate the isotherm for calcium binding to CAE-85 micelles, because no condensation effect is observed. More generally, there is almost no noticeable conductivity effect caused by the monovalent cations with varying calcium concentration. A description for the binding isotherm for calcium on CAE-85 can be obtained from the excess conductivity with the following four steps.

First, Eqs (5.1) to (5.4) are combined to re-write the excess conductivity as:

$$K_E = C_M \lambda_M (f_{M,0} - f_M) + C_{di} \lambda_{di} (1 - f_{di}) + C_p \lambda_p (f_{p,0} - f_p)$$  \hspace{1cm} (5.12)

Second, the two-state approximation is used only for the divalent cations. The influence of the monovalent cations is considered to be constant as determined from the Eisenberg plots.
This means that $f_M$ and $f_{M,0}$ are equal, and as a result the first term on the right hand side of Eq. (5.12) vanishes.

Third, as $f_{p,0}$ and $\lambda_p$ are difficult to determine experimentally, it is convenient to introduce an effective $f_p$ and an effective $\lambda_p$, according to:

$$f_{p,\text{eff}} = \frac{f_p}{f_{p,0}}$$

$$= 1 - 2(1 - f_{di})r$$

$$\lambda_{p,\text{eff}} = \lambda_p f_{p,0}$$

In practice $f_{p,0}$ is most likely to be lower than unity, because there is a restriction on the mobility of the carboxylate groups. All contributions arising from this are accounted for by $\lambda_p$, which becomes the effective equivalent molar conductivity $\lambda_{p,\text{eff}}$.

Fourth and finally, only divalent cations are able to bind to the free carboxylate groups, which means that $f_{p,\text{eff}}$ is related to $f_{di}$ by Eq. (5.13a).

Applying these four steps results in the following expression for the conductivity excess:

$$K_E = C_a \lambda_{di} (1 - f_{di}) + 2C_p \lambda_{p,\text{eff}} (1 - f_{di}) r = (1 - f_{di})(\lambda_{di} + 2\lambda_{p,\text{eff}})C_p r$$

In order to calculate a binding isotherm for calcium to CAE-85 the bound fraction of divalent cations, $1-f_{di}$, is related to the fractional binding occupancy:

$$\theta = 2(1 - f_{di})r$$

$$= 1 - f_{p,\text{eff}}$$

Combining Eq. (5.14) and Eq. (5.15) gives the following relation for the fractional binding occupancy:
Conductometric analysis of the binding behavior of counterions in CAE-85 surfactant systems

\[ \theta = \frac{2K_E}{(\lambda_{di} + 2\lambda_{p,eff})C_p} \]  

(5.16)

The only unknown parameter in Eq. (5.16) is \( \lambda_{p,eff} \), which is very difficult to determine as function of divalent cation concentration when dealing with surfactant systems. However, at 50 °C with \( r=0 \), \( \lambda_{p,eff} \) can be obtained from the conductivity data plotted in Figure 5.2a and use of Eq. (5.1). From the Eisenberg plot it was determined that \( f_{M,0} = 0.67 \text{ S cm}^2/\text{mol} \), this gives for \( \lambda_{p,eff} \) a value of 66.01 S cm\(^2\)/mol.

![Figure 5.6: Binding isotherm(s) of calcium on CAE-85 obtained from conductivity analysis, using two approximations for the effective equivalent conductivity, \( \lambda_{p,eff} \).](image)

It is likely that \( \lambda_{p,eff} \) will decrease as a function of \( C_{di} \) because the addition and binding of divalent cations will induce ordering of the carboxylate end groups, which will result in an overall lower mobility of the remaining free carboxylate end groups. It is not known how \( \lambda_{p,eff} \) decreases as a function of the fractional binding occupancy, \( \theta \). Therefore, two extreme cases are considered. The two resulting binding isotherms are plotted in Figure 5.6. One curve is constructed with the assumption of a constant \( \lambda_{p,eff} \) with the value of 66.01 S cm\(^2\)/mol, whereas for the other curve it is assumed that \( \lambda_{p,eff} \) has a starting value of 66.01 S cm\(^2\)/mol and decreases linearly to zero as a function of the divalent cation concentration. The actual isotherm will lie between these two extreme cases, however, a good indication of the amount of calcium bound to the micelles is obtained, because the two cases are
reasonably close together. It is seen that for the two cases the fractional binding occupancy coincide until \( r = 0.3 \). This indicates that the isotherm is mainly determined by the molar conductivity of calcium. The isotherm obtained for the decreasing \( \lambda_{p,\text{eff}} \) is somewhat higher then the isotherm obtained with the constant \( \lambda_{p,\text{eff}} \). It is not likely that the \( \lambda_{p,\text{eff}} \) will vanish completely for high molar ratios \(^{[29]}\), therefore it is to be expected that the result for the constant \( \lambda_{p,\text{eff}} \) gives a quite accurate isotherm.

### 5.5 Conclusions

The conductivity method of Pochard \(^{[12, 13]}\) and De Jong \(^{[14]}\), originally used for PAA systems, has been applied to the CAE-85 surfactant system in order to obtain information about the binding behavior of calcium and sodium cations.

First, for the CAE-85 micelles no condensation effect has been observed for the monovalent cations. This is a result of the low surface charge density caused by the relatively small amount of carboxylate groups with respect to the size of the micelle.

Second, a reduction in monovalent counterion conductivity has been observed when micelles are present. This is a result of a reduction in the mobility of the monovalent counterions, because of the high micelle density in the solution.

Third, a higher slope above the CMT in the conductivity / temperature plot has been observed. This indicates that an ordering of the carboxylate end groups occurs, from a more shielded position below the CMT to a more free position in the micellar corona. The high molecular weight of the surfactant, i.e. length of the PEO and PPO blocks, causes shielding of the end groups and monovalent cations, which reduces the total conductivity. This results in a higher \( \lambda_p \) above the CMT.

Furthermore, a binding isotherm has been constructed for the binding of calcium to CAE-85 micelles from the conductivity excess data assuming a two-state approximation. Two (limiting) cases have been considered to describe \( \lambda_{p,\text{eff}} \) as a function of \( \theta \), and these two cases set the maximum and minimum values for the binding isotherm. Until a molar ratio \( r = 0.3 \) the isotherms coincide for the two cases.

As a result of the low surface charge density, calcium cations are bound moderately by the CAE-85 surfactant aggregates, and the aggregates have almost no affinity for monovalent
ions. In general, with the conductivity method used in this work qualitative and quantitative information can be obtained for ionic surfactant systems with respect to binding of and competition between counterions.

5.6 References

Chapter 6

Micellar behavior of carboxylic acid end group modified Pluronic surfactants

Abstract

The micellar behavior of three different carboxylic acid end standing (CAE) surfactants has been characterized, using conductometry, differential scanning calorimetry, isothermal titration calorimetry, and dynamic light scattering. The CAE surfactants are modified high molecular weight Pluronic (PEO-PPO-PEO triblock copolymer) surfactants. The influence of pH and salt additives on the critical micellization temperature (CMT) and the cloud point of the CAE surfactants have been studied. It can be concluded that the cloud point and CMT of CAE surfactants are more sensitive to changes in pH and ionic strength than the Pluronic surfactants. Isothermal titration calorimetry has been used to study the interactions in mixed (nonionic-ionic) micelles consisting of Pluronic and CAE surfactants. The various results for the three CAE surfactants, which differ in hydrophobic-hydrophilic balance, provide directions for the development of CAE surfactants with desired properties for temperature responsive applications, ranging from binding of multivalent hardness ions to controlled release.
6.1 Introduction

Recently a new class of surfactants has been developed, i.e. carboxylic acid end standing (CAE) surfactants [1]. These surfactants are synthesized by reaction of Pluronic surfactants (poly ethylene oxide – poly propylene oxide - poly ethylene oxide block copolymers) [2-4] with succinic anhydride to obtain high molecular weight anionic surfactants. The main feature is that these anionic CAE surfactants have a temperature dependent micellization transition. Aggregates of these CAE surfactants are capable of binding multivalent ions above the critical micellization temperature (CMT), while below the CMT no binding occurs to the unimers. This feature makes the CAE-surfactant interesting in many (separation) processes, e.g. as a temperature dependent ion exchanger. In a previous study the binding of cations to CAE-85 micelles has been reported (see Chapter 3 and 4) [1].

Although Pluronic surfactants have a high molecular weight, it is to be expected that modification of these polymers by attaching relatively small ionic extensions to the end groups will result in a considerable change of the phase behavior. In general, there is a large influence of the solution properties, like ionic strength, pH and type of electrolyte, on the phase behavior of surfactants [5-8]. Different techniques are being used to study the phase behavior of unmodified Pluronic surfactants [9-13].

In this work, the phase behaviour of different CAE-surfactants, CAE-85, CAE-64 and CAE-81, modified Pluronic P85, L64, and L81, has been studied. The presence of a CMT has been investigated using conductometry. Differential scanning calorimetry (DSC) has been used to study the dependence of the CMT on different salt additives and on the pH. Cloud point measurements have been performed for two of the CAE-surfactants, using different salt additives and different pH. Dynamic light scattering (DLS) has been used to investigate the effect of the surfactant modification on the size of the micelles. Finally, isothermal titration calorimetry (ITC) has been used to obtain the calcium binding capacity of the three CAE surfactants, and to study mixed (nonionic - ionic) micelles of Pluronic and CAE surfactants.
6.2 Experimental

6.2.1 CAE surfactants

The carboxylic acid end standing (CAE-85) surfactant was synthesized by modifying Pluronic P85 surfactant (EO\textsubscript{39}-PO\textsubscript{52}-EO\textsubscript{39}) with succinic anhydride to obtain a high-molecular weight anionic surfactant with temperature sensitive micellization behavior, see Figure 6.1.

In the synthesis of the CAE-85 surfactant \textsuperscript{[1]}, the Pluronic P85 surfactant (EO\textsubscript{39}-PO\textsubscript{52}-EO\textsubscript{39}) was purified by dissolving the polymer into diethyl ether. The cloudy turbidity was removed in a centrifuge, followed by precipitation of the surfactant in cold pentane. Purified P85 was then dissolved into toluene from which the water present in the toluene was removed by azeotropic distillation.

The reaction was started by addition of succinic anhydride and was performed for four hours at 90 \degree C. After the reaction toluene was evaporated and the product was dissolved in water, followed by addition of sodium carbonate until pH>9 and diluted sulphuric acid until pH<2, respectively. The product was then extracted with butanol and dried overnight above a layer of anhydrous sodium sulphate. The product was redissolved in diethyl ether, followed by precipitation with an equal amount of pentane. The final product was obtained after filtering and drying under vacuum conditions at room temperature.

![Chemical structure of CAE surfactant](image)

*Figure 6.1: Chemical structure of CAE surfactant. The values of p and q are given in Table 6.1.*

Three CAE surfactants were synthesized using Pluronic P85, L64, and L81 as the starting material. P85 is a paste at 25 \degree C, while L81 and L64 are liquids at room temperature. The difference in physical state induces minor changes in the synthesis procedure of the three different CAE surfactants.

In Table 6.1 the number of ethylene oxide (EO) groups, \( p \), the number of propylene oxide (PO) groups, \( q \), and the molecular weight of the CAE surfactants are given.
Table 6.1: Composition of CAE surfactants synthesized.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>p</th>
<th>q</th>
<th>$M_w$ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE-85</td>
<td>26</td>
<td>39</td>
<td>4768</td>
</tr>
<tr>
<td>CAE-64</td>
<td>13</td>
<td>30</td>
<td>3102</td>
</tr>
<tr>
<td>CAE-81</td>
<td>3</td>
<td>43</td>
<td>3039</td>
</tr>
</tbody>
</table>

6.2.2 Experimental methods

In all the different experiments the pH of the surfactant solutions was adjusted to a higher pH using NaOH and to a lower pH using HCl.

6.2.3 Conductometric analysis

All conductometric experiments were performed using a QiS M320 conductometer with a QiS QC203T epoxy/graphite conductivity cell. The cell constant was periodically checked and calibrated by a 0.01 M KCl solution. The solution temperature was kept constant (+/- 0.1 °C) with a Lauda C6 CP thermostat.

6.2.4 Differential scanning calorimetry (DSC)

Experiments were performed using a Pyris Diamond DSC, type APP010, from Perkin Elmer Instruments. Aluminium pans of 50 µL with caps containing the sample or the reference material, usually water, were used. For each sample multiple temperature scans were made from 5 °C to 60 °C with a scanning rate of 20 °C/min. The determination of the onset temperature was performed using software from Perkin Elmer Series.

6.2.5 Cloud point measurements

The clouding behavior of the CAE-surfactants was determined by slow heating of 5 mL samples using a Lauda C6 CP thermostat (+/- 0.1 °C). At each temperature the samples were equilibrated before further heating. The first steady sign of turbidity, by visual detection, was taken as the cloud point. In general, it can be said that the accuracy of the cloud point measurements is lower for the CAE-surfactants, as compared to Pluronic surfactants, because the CAE surfactants have a less sharp cloud point transition.
6.2.6 Isothermal titration calorimetry (ITC)
Experiments were performed using a MicroCal VP-ITC apparatus with a cell volume of 1.4431 mL. The experimental procedure consisted of adding 70 injections of 4 µL of a calcium chloride salt solution to the sample cell, which contained solutions of CAE surfactant. In all experiments the reference cell was filled with demineralized water. Before each experiment the temperature was equilibrated at the desired value. To obtain a binding isotherm from the heat change data the procedure of Chapter 3 was followed. In the mixed micelle experiments the surfactant concentration in the sample cell was in all cases $2.16 \times 10^{-3}$ mol/L and the syringe surfactant concentration was $16.7 \times 10^{-3}$ mol/L.

6.2.7 Dynamic light scattering (DLS)
Dynamic light scattering experiments were performed with a Coulter N4 plus Submicron Particle Sizer apparatus. The scattered light was correlated with a size distribution program (SDP) using the CONTIN routine. All measurements were performed at a 90° scattering angle. In general, it can be said that the accuracy of the measurements is lower for the CAE-surfactants as compared to the Pluronic surfactants.

6.3 Theoretical background

6.3.1 Critical micellization temperature (CMT)
Low molecular surfactant molecules will aggregate to form micelles at a certain concentration, i.e. the critical micellization concentration (CMC). When a surfactant monomer is dissolved in water, the water molecules around the hydrophobic tail of the surfactant become more structured and, therefore, the entropy of the water molecules will decrease. The transfer of surfactant unimers from solution into the micelle is often an endothermic process. However, during the micellization process the ‘original’ structure of the water will be restored. This means that the water entropy will increase and this will overcome the entropy loss due to the localization of the hydrophobic surfactant chains, and overall micellization is dominated by the entropy contribution.

For Pluronic based surfactants, i.e. PEO-PPO-PEO block copolymers, the micellization process is more complex. At lower temperatures the block copolymers are relatively less hydrophobic and will appear in solution as unimers, even at high concentrations. When the
temperature is increased to above the critical micellization temperature (CMT), the PEO-PPO-PEO based surfactants will start to form micelles, even at very low polymer concentrations. This can be explained by the fact that water becomes a poorer solvent for polyethylene oxide (lower critical solution temperature (LCST) of about 100 °C) and polypropylene oxide (LCST of about 10 °C) at higher temperatures. Ethylene oxide and propylene oxide monomers can both be in a polar or a nonpolar state. At low temperatures the polar conformation dominates over the nonpolar state, because this is favorable from an enthalpic point of view. When the temperature is increased the entropy contribution will become more important and more EO and PO monomers will change to the nonpolar state and become less soluble. The contribution of the more hydrophobic PPO block is more important in this case, and at a certain temperature this results in clustering of the PPO blocks of the Pluronic based surfactant molecules into micellar aggregates. Therefore, the CMT is mainly determined by the length of the PPO block of the Pluronic surfactant. As a result of the polydispersity of these surfactants the micellization process occurs over a temperature range and does not have a sharp transition at a given temperature.

6.3.2 Cloud point
The change in polarity of the EO and PO parts continues at higher temperatures, even when complete micellization has occurred. In general, Pluronic based surfactants form spherical micelles at temperatures just above the CMT, and a spherical-to-rod transition will take place at higher temperatures \cite{2}. The dehydration of the EO part continues with a further increase in temperature, and there is a temperature where the polymer surfactant becomes insoluble in water and phase separation will occur. This temperature is called the cloud point, because of the sudden increase in solution turbidity above that temperature. Most Pluronic surfactants have a cloud point temperature, which can vary between 10 °C and 90 °C depending on the length of the PPO and PEO blocks.

6.3.3 Salt additives
The addition of salts to a Pluronic based surfactant solution has a clear effect on the different aspects of the phase behavior, including CMT and cloud point. The salting in/out behavior caused by ions is a well-known effect \cite{5,14-16}, and is usually explained by the direct effect of the ion hydration on the hydration of the polymer surfactant. Strongly hydrated ions, or
structure-making ions (kosmotropes), disturb the hydration of the surfactant and will cause a salting out mechanism. This will lead to a decrease in CMT and cloud point. On the other hand, poorly hydrated ions, or structure-breaking ions (chaotropes), will disturb the bulk water structure and improve the water structure around the surfactant. This will result in a salting-in mechanism, i.e. an enhanced solubility of the polymer surfactant, resulting in an increase in CMT and cloud point. These mechanisms are more pronounced for anions than for cations. The ability of ions to change the phase behavior in colloidal systems in this way is also called the polarization effect, and in general, this will follow the Hofmeister series \(^{[17-21]}\). However, new insights indicate that the presence of ions in water does not change the bulk water structure \(^{[22, 23]}\), but only the structure of the water molecules in the first hydration shell of the ions. The Hofmeister effects would then be the result of macromolecule-ion interactions and first hydration shell-ion interactions, instead of solely polarization effects. In this case poorly hydrated ions will interact with the macromolecule by direct binding and surface tension effects. Furthermore, different mechanisms for chaotropes and kosmotropes can be distinguished \(^{[22, 23]}\).

6.4 Results and discussion

6.4.1 Dependence of CMT on pH and on additives

In low molecular ionic surfactant systems, such as sodium dodecyl sulfate (SDS), conductometry is a well-proved technique to determine the critical micellization concentration \(^{[24]}\). For low molecular ionic surfactant systems, the slope of the conductivity as function of the surfactant concentration above the CMC is lower than the slope below the CMC. As a result of counterion binding above the CMC, the conductivity per surfactant molecule is reduced. This method can also be used to determine the CMT for CAE surfactants, but the conductivity should be plotted as function of temperature instead of the surfactant concentration. In Figure 6.2 the total conductivity for 0.5 wt% solutions of CAE-85, CAE-64 and CAE-81 is plotted as function of temperature. For CAE-85 and CAE-64 a change in slope is observed, which indicates the presence of a CMT. For the CAE-85 surfactant this is at about 34 °C and for the CAE-64 surfactant this is at about 35 °C. In both cases the CMT is about 3 to 4 °C higher, as compared to the ‘corresponding’ Pluronic surfactants P85 and L64.
Figure 6.2: Conductivity as function of temperature for 0.5 wt% CAE-85, 0.5 wt% CAE-64 and 0.5 wt% CAE-81 solutions with a pH of about 6. The CMT is given by the intersection of the slopes at low and high temperatures.

This increase can be explained by the high solubility of the modified (CAE) surfactants caused by the presence of the ionic charge. For the CAE-81 surfactant no change in the slope can be observed. It is noted that the slope of the conductivity of CAE-81 is the same as the slope obtained for the CAE-85 and CAE-61 below the CMT. It can therefore be concluded that the CAE-81 has no CMT in the temperature range investigated.

Figure 6.3 (a): DSC results for a 1 wt% CAE-85 solution as function of the pH.
As a second technique, differential scanning calorimetry (DSC) has been used to measure the CMT of a CAE surfactant solution. For Pluronic based surfactants the micellization enthalpy is relatively low, and therefore a high accuracy is required. For this reason it was not possible to measure the CMT of the CAE-64 surfactant. In Figure 6.3a the CMT of the CAE-85 is given as a function of the pH and in Figure 6.3b the CMT is given as a function of the ionic strength. At low pH the carboxylic acid groups of CAE-85 are protonated, and the CAE-85 surfactant can be considered as ‘nonionic’. With an increase in pH, the carboxylic acid groups will deprotonate and the CAE-85 surfactant head groups will become anionic.

**Figure 6.3 (b):** DSC results for the CMT of P85 and CAE-85 at different pH values as function of the ionic strength with CaCl$_2$ as an additional electrolyte.

**Figure 6.4 (a):** DSC results for the CMT of P85 and CAE-85 at a pH value of 3.5 as function of the ionic strength with CaCl$_2$, BaCl$_2$ and NaCl as the additional electrolytes.
The anionic head groups are more hydrophilic because of the charge, with as a result that the solubility and the CMT of the CAE-85 surfactant both increase. This increase of the CMT continues until the full neutralization point at pH of 7 is reached.

In Figure 6.3b the results for the CMT of the CAE-85 and the P85 surfactant are given as function of the ionic strength, which is adjusted with CaCl$_2$. Furthermore, the CMT of the CAE-85 surfactant is given for three different pH values. Besides the difference in ‘starting values’ at the y-axis, as a result of the difference in pH, the slopes of the four different series are approximately the same. This indicates that modification of the P85 surfactant has almost no effect on the micellization behavior. This can be explained by the fact that the PPO block mainly determines the micellization behavior. The influence of different electrolytes on the CMT of CAE-85 at low pH is shown in Figure 6.4a. It follows that the CMT decrease or the salting out effect on the CAE-85 follows the order NaCl > BaCl$_2$ > CaCl$_2$. This is opposed to what is to be expected from the Hofmeister series. It is noted that the anion, which is chloride in all cases, has a substantially larger influence on the salting out mechanism of the surfactant than the cation. However, in Figure 6.4 the main difference is caused by the cations, which interact with the ether groups of the polymer surfactant, and where divalent cations have a stronger interaction than monovalent cations $^5$. This means that the decrease in ionic strength is larger for divalent ions, with as a result that in the case of Pluronic based surfactants the
salting-out behavior of divalent cations will be weaker as compared to the salting-out behavior of monovalent cations.

In Figure 6.4b results for the CMT at high pH are shown. From a comparison with Figure 6.4a it follows that the results obtained at a higher pH show the same behavior as obtained for low pH. In both cases, the CMT decreases with an increase in ionic strength. The decrease of the CMT in the presence of NaCl is larger than the decrease of the CMT in the presence of CaCl$_2$. However, when the behavior of the CMT is examined at low ionic strength and with a pH equal to 10.0 a clear difference between CAE-85 and P85 can be seen. The CMT of P85 shows a linear dependence on the ionic strength. In the CAE-85 system a clear transition is seen: initially the CMT shows a sharp decreasing behavior, followed by a slope that resembles the slope of the P85 system. The shielding of the carboxylic charges of the surfactant by the calcium ions makes the head group more hydrophobic, resulting in a larger decrease of the CMT as compared to the P85 case. At the ionic strength where all charges are screened, i.e. at 2.5*10$^{-3}$ mol/L, the CAE-85 behaves in a similar way as the P85.

6.4.2 Dependence of cloud point on pH and on additives

Only for a few ionic surfactants, in particular for anionic surfactants with a large hydrophobic cation, a cloud point (CP) has been reported $^{[25, 26]}$. On the other hand, most nonionic surfactants with PEO blocks, including the Pluronic surfactants display a cloud point. The behavior of the CAE surfactants can be changed from nonionic to anionic by increasing the pH, and in this respect, applications of CAE surfactants related to the cloud point seem promising. The presence of anionic carboxylate groups will have a clear influence on the clouding behavior of the Pluronic based surfactants. In Table 6.2 results for CP measurements are given for both the CAE surfactants and the unmodified Pluronics at low pH, i.e. in the protonated form. For each CAE surfactant a substantial decrease in CP is observed, which is also highly dependent on the actual surfactant concentration. Contrary to the small difference between the CMT observed for the CAE and the Pluronic surfactants (Figure 6.3b), a considerable difference is obtained between the CP for the CAE and the Pluronic surfactants.
Table 6.2: Measured cloud points for Pluronics P85, L64 and L81 solutions and for CAE surfactants CAE-85, CAE-64 and CAE-81 solutions.

<table>
<thead>
<tr>
<th>Conc. [wt%]</th>
<th>P85</th>
<th>CAE-85</th>
<th>L64</th>
<th>CAE-64</th>
<th>L81</th>
<th>CAE-81</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1 (0.1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1 (0.1)</td>
</tr>
<tr>
<td>CP [°C]</td>
<td>85</td>
<td>60 (81)</td>
<td>58</td>
<td>25</td>
<td>20</td>
<td>8 (30)</td>
</tr>
</tbody>
</table>

This difference in CMT and CP can be explained by considering the clouding mechanism. The clouding behavior is largely determined by the type of head group of the surfactant, and in turn this determines the intermicellar interactions. The micellization behavior is mainly determined by the length of the PPO block. Modification with succinic anhydride makes the head group more hydrophobic at low pH, resulting in a considerable decrease in CP.

The CP of the CAE-85 surfactant as a function of the pH is shown in Figure 6.5. For all cases, a large increase in CP is observed when the pH is increased, which is a similar behavior as observed for the CMT (see Figure 6.4). For the case with no additional electrolyte the CP vanishes when the surfactant becomes anionic. However, a cloud point depression can be obtained by adding salts to the surfactant solution. Screening of the charged head group will make the surfactant more hydrophobic, resulting in a decrease in CP.

Contrary to the behavior observed for the CMT with salt additives, the CP depression follows the Hofmeister series, i.e. CaCl₂ > BaCl₂ > NaCl. For the case of 0.5 M NaCl a small deviation from this behavior is observed at a pH of 3.5.

Figure 6.5: Cloud point results for a 1 wt% CAE-85 solution as function of the pH with NaCl, CaCl₂, and BaCl₂ as salt additives.
Figure 6.6: Cloud point results for CAE-81 at a pH value of about 6 as function of the ionic strength with NaCl, CaCl$_2$, and MgSO$_4$ as additional electrolytes.

The hydrophobic Pluronic L81 has a low CP of about 20 °C. In this case, the unimer surfactants will not form micelles, but will immediately separate into two phases at the cloud point. After modification of the L81 to CAE-81 no CMT was observed, which was confirmed by conductivity measurements (see Figure 6.2). From Table 6.2 and Figure 6.6 it follows that for the hydrophobic CAE-81 the modification has a considerable influence on the clouding behavior. At low pH the nonionic CAE-81 has a CP of 8 °C, and at a pH of 6 the CP has disappeared. The CP decreases significantly in the presence of the different salts, already at low ionic strength. Again these results follow the Hofmeister series, which explains the large decrease of the CP with the addition of MgSO$_4$. In this case, both the cation and the anion are good kosmotropes.

The results of the CP measurements for CAE-85 and P85 are depicted in Figure 6.7. The CAE-85 seems to be less sensitive for cloud point depression as compared to CAE-81. This is the result of the more hydrophilic nature of the CAE-85 surfactant. From this it can be concluded that hydrophilic Pluronic based surfactants are less sensitive than the hydrophobic ones for cloud point depression. The results for CAE-85 and P85 follow the Hofmeister series, and it can be noted that not a large difference is observed between calcium and barium cations. However, in the case of NaCl at a pH value of 3.55 a larger cloud point depression is observed, as compared to other pH values. The explanation here can be found in the
competition of cations. A 1.0 wt% CAE-85 surfactant solution has a pH of 3.55. To obtain other pH values the pH is adjusted by adding NaOH or HCl.

Figure 6.7 (a): Cloud point results for P85 and CAE-85 at a pH value of 3.55 as function of the ionic strength with CaCl$_2$, BaCl$_2$ and NaCl as the additional electrolytes.

Figure 6.7 (b): Cloud point results for CAE-85 at pH values of 10.0, 3.55 and 2.38 as function of ionic strength with CaCl$_2$, BaCl$_2$ and NaCl as the additional electrolytes.

When it is assumed that cations will have some interaction with the ether groups of the surfactant molecules, the extra cations will be located near the ether groups. Barium and calcium ions experience some competition from the extra H$^+$ and Na$^+$ in the cases that the pH is adjusted, which makes it more difficult for barium and calcium to bind to the ether groups.
Therefore, because the (free) concentration of barium and calcium is higher, a larger CP depression is observed for the solutions with a pH of 2.38 and a pH of 10.0. For the situation with a pH value of 3.55 barium and calcium cations will bind better to the surfactant chain, and therefore the decrease of the CP will be less pronounced. As a result a reversed trend as compared to the Hofmeister series is obtained.

In general, it can be concluded that the CP of the CAE-surfactants is (very) sensitive to the addition of salts, similar to the behavior observed for the Pluronic surfactants. The CAE surfactants in anionic form have the possibility to show clouding behavior, even in the presence of salts like NaCl.

6.4.3 Determination of micelle size with dynamic light scattering

Micellar aggregates are dynamic structures, because surfactant monomers are exchanged between the aqueous surrounding and the micelles. Therefore, the micellar aggregates are sensitive to a change in solution properties of the unimers. A considerable amount of data is available about the size and structure of Pluronic surfactants, as function of various parameters \(^2\). In Figure 6.8a a comparison is made between the micellar size of P85 and CAE-85 aggregates obtained using dynamic light scattering. The diameter of P85 and CAE-85 aggregates is shown as function of the calcium concentration. With no calcium the diameter of the P85 micelle is about 16.2 nm, which is in agreement with values reported in the literature \(^2\). When only a small amount of calcium chloride is added to the solution, the P85 micelle shrinks to a shape with a diameter of 13.8 nm. The difference in polarity between the PEO head groups of the P85 surfactants and the aqueous solution with the calcium cations increases. It is known that the size of Pluronic micelles will increase when the CP is approached. The addition of calcium chloride stimulates the dehydration of the surfactant unimers and, therefore, depresses the CP. As a result, the size of the 85 micelles increases with an increase in calcium concentration to about 16.7 nm at a calcium concentration of 0.4 mol/L. The results for the diameter of the CAE-85 micelles at 20 °C, which is below the CMT, and at 50 °C, which is above the CMT are given in Figure 6.8b. At 20 °C no CAE-85 micelles are presented. At 50 °C the diameter of the CAE-85 micelle is about 15 nm, and independent of the pH. The result for the CAE-85 micelle at a pH of 3.5 is consistent with the results for the P85 micelles, see Figure 6.8a.
6.4.4 Counterion binding studied with ITC

In order to determine the capacity of the CAE-surfactant for the binding of divalent cations, ITC has been used to determine the binding isotherms for calcium bound to CAE-85 and CAE-64 micelles (see Chapter 3) [1]. The results for the binding isotherm of calcium at 45 °C are given in Figure 6.9. A binding isotherm for CAE-81 could not be obtained because of the absence of a transparent micellar phase. At 45 °C the CAE-81 solution is above its cloud point, and this two-phase system makes an interpretation of the heat change data difficult.

Figure 6.8 (a): Diameter of the P85 micelle as function of the added calcium concentration obtained with DLS.

Figure 6.8 (b): Diameter of the CAE-85 micelle as function of pH obtained with DLS at a temperature of 20 °C and 50 °C. The calcium chloride concentration is 15.3 mmol/L.
Micellar behavior of carboxylic acid end group modified Pluronic surfactants

Figure 6.9: Isotherms for the binding of calcium to 1.0 wt% CAE-64 ($1.0 \times 10^{-3}$ mol/L) and 1.0 wt% CAE-85 ($6.19 \times 10^{-3}$ mol/L) solutions at 45°C. The pH value of the solutions was around 6. The molar ratio $r$ is defined as the amount of calcium added per CAE-85 acid group.

From Figure 6.9 it can be concluded that the two CAE-surfactants have approximately the same binding behavior for calcium cations. A slightly lower binding isotherm has been obtained for the CAE-64 micelles, as compared to the CAE-85 micelles. The CAE-64 surfactant has a lower molecular weight, as compared to the CAE-85 surfactant, with as a consequence that in a 1 wt% solution there are more carboxylic end groups for CAE-64 than for CAE-85. On a weight base this means that the absolute binding capacity for calcium cations is higher for CAE-64.

6.4.5 Mixed micelle interactions studied with ITC

ITC is often used to measure interactions between surfactants in mixed micellar systems [27-29]. Here, mixed (nonionic - ionic) micelles of P85 and CAE-85 are being studied using ITC. In Figure 5.10a the results for the titration of a P85 surfactant solution to a solution of P85 micelles and to a solution of CAE-85 micelles are shown. In both experiments the heat data of a reference experiment is subtracted from the measured data. The reference experiment is the same experiment without the presence of calcium. The molar ratio $z$ is defined as the amount of added mol surfactant per mol surfactant in the sample cell before the start of the injections.
For the P85 solution titrated with P85 a small exothermic heat effect is observed. This is caused by the dilution of a concentrated P85 solution, from the syringe, in the sample cell, which contains a solution with a lower concentration P85. This heat effect becomes smaller during the titration because the concentrations of P85 in the sample cell solution and in the syringe solution converge to the same value. For the case that a concentrated P85 solution is titrated to a CAE-85 surfactant solution at low pH almost the same heat change curve is observed as for the case where the concentrated P85 solution has been titrated to a P85 solution. It can be concluded that the behavior of the modified CAE-85 surfactant at low pH resembles the behavior of the P85 surfactant. A larger difference is seen when the P85 solution is titrated to a CAE-85 solution at high pH. At high pH the end groups of the CAE-85 are deprotonated, and a considerable difference exists between the CAE-85 and P85 surfactant. As a result of this difference the formation of mixed micelles is less favorable, i.e. endothermic.

Initially, P85 surfactants unimers will be incorporated in the CAE-85 micelle without affecting the micellar structure. This results in a constant heat change, until a molar ratio, $r$, of 0.4. At this point, micelles are being formed that contain predominantly P85, and the heat change starts to decrease until no net heat effect will be observed. For the final situation, the solution in the sample cell and the solution in the syringe will converge to the same composition. From the results shown in Figure 6.10a it can be concluded that the intermicellar interactions increase considerably when the end groups of the Pluronic-based surfactant are charged.

In Figure 6.10b mixed micelles of P85 and CAE-85 are studied in the presence of calcium. For the two experiments a reference experiment was performed without calcium and this data was subtracted from the heat change data for the experiments with calcium. The heat effects shown in Figure 6.10b can be attributed solely to the presence of calcium chloride. An exothermic heat effect is seen when a solution of P85 is titrated to a solution of CAE-85 with calcium. This exothermic effect is a result of the release of the calcium from the CAE-85 micelles, because the hydration enthalpy of calcium is exothermic. At a certain point, all calcium cations are released while the P85 unimers start to dominate the composition of the mixed micelles. For the situation where CAE-85 is titrated to a solution of P85 with calcium initially no calcium will be bound. With the increase in CAE-85 surfactant concentration, calcium will have an increasing electrostatic interaction with the mixed micelles. This is an
endothermic effect, because the dehydration of the calcium cation is the dominant contribution. At a certain point, calcium will no longer contribute to the measured heat effect, because all calcium ions are bound to the CAE-85. The formation of the CAE-85 micelles will become the dominant factor for the measured heat effect, which again converges to zero.

Figure 6.10 (a): ITC heat change data for solution of P85 and CAE-85 at low pH titrated with P85 at 50°C, and for CAE-85 micelles at high pH titrated with P85 at 50°C, as a function of the molar ratio, z.

Figure 6.10 (b): ITC heat change data for solutions of P85 and CAE-85 at high pH and in the presence of calcium (molar ratio r=0.5) at 50 °C, as a function of the molar ratio, z.

Comparing Figure 6.10a and 6.10b it follows that below a molar ratio, z, of about 0.4 the observed behavior is predominantly determined by mixed micelles, while at higher values of z the contribution of the homogeneous micelles become the dominate behavior.
6.5 Conclusions

The phase behavior of three different CAE-surfactants, CAE-85, CAE-64, and CAE-81, has been studied using various experimental techniques, and a comparison is made with the unmodified Pluronics surfactants. Conductivity has been used to determine the CMT of the CAE-85 and CAE-64. For the CAE-81 no CMT could be obtained, because of its hydrophobic nature. The CMT of CAE-85 seems to be slightly affected by pH changes, where the addition of salts has about the same effect on the CMT of CAE-85 and P85. DSC has been used to study the effect of pH and additives on the CMT. A small pH effect is observed for the CMT of CAE surfactants. Contrary to the CMT the cloud point changes considerably for the CAE surfactants as compared to the Pluronic surfactants. The cloud point of the CAE-surfactants is very sensitive to changes in pH, because of the carboxylate end group. It can be concluded that the effect of salts on the cloud point will increase as the hydrophobicity of the Pluronic-based surfactant increases. DLS has been used to determine the micellar size of the Pluronic-based surfactants. The modification of the Pluronic surfactants has almost no effect on the micellar diameter. From the ITC measurements it follows that the binding capacity for calcium is larger for CAE-64 than for CAE-85, when compared on a weight base, although there is not a larger difference in the binding strength. It can be concluded that ITC is a useful technique to measure surfactant-surfactant interactions, which can provide detailed information about the phase behavior Pluronic-based surfactant systems.

By choosing a proper hydrophobic - hydrophilic balance of the starting Pluronic, CAE surfactants can be synthesized with different properties, which can be tuned by the solution properties, like pH and ionic strength. Understanding of the phase behavior of these CAE surfactants, like the pH dependency, will open new possibilities for temperature responsive applications. Furthermore, the CAE surfactants are the first ionic surfactants that show clouding behavior upon the addition of simple acids and salts like e.g. HCl or NaCl.
6.6 References

Abstract

Metal ions can be removed using thermo-reversible carboxylic acid end standing (CAE) surfactants in micellar-enhanced ultrafiltration (MEUF) processes avoiding the formation of waste salt, as in ion exchange processes, because this surfactant can be regenerated by means of a temperature switch. The thermo-reversibility of the calcium binding to CAE-85 has been demonstrated in an ultrafiltration experiment. Furthermore, the simultaneous removal of phenanthrene and calcium has been studied by performing solubilization experiments that show the influence of phenanthrene on the calcium binding and on the membrane fouling behavior of the CAE-85 surfactant. The fouling behavior of CAE-85 and Pluronic P85 has been studied on cellulose acetate (CA) and polyether sulfone (PES) membranes by performing pressure hysteresis experiments. No fouling has been observed on CA membranes for both surfactants, while on PES membranes fouling has been detected. Overall, the results show that with CAE surfactants new membrane separation processes can be developed that lead to a substantial reduction in the amount of waste salt.
7.1 Introduction

In micellar enhanced ultrafiltration (MEUF) processes a surfactant system is combined with an ultrafiltration (UF) membrane in order to remove (toxic) ions \cite{1-8}, organics \cite{9, 10} or both pollutants simultaneously \cite{11-13} from (dilute) aqueous systems. The surfactants are added to the feed stream of the membrane process. The head groups of ionic micelles can bind ions \cite{14} of opposite charge and hydrophobic organic compounds can be solubilized in the core of the micelles. In a MEUF process the micelles will be retained by the UF membrane, and therefore also retention of the bound ions and solubilized organics will occur. In general, membrane processes are advantageous because of the low energy consumption, and relatively low cost MEUF processes can be developed \cite{15, 16}. The main disadvantage of MEUF is that the surfactant needs chemical treatment before it can be reused \cite{17-19}. The addition of these chemicals will lead to the production of a substantial amount of waste.

Recently, a new class of surfactants has been developed, i.e. carboxylic acid end standing (CAE) surfactants \cite{20}. These surfactants are synthesized by reaction of high molecular weight Pluronic surfactants (PEO-PPO-PEO block copolymers) \cite{21} with succinic anhydride to obtain anionic surfactants. The main feature of the anionic CAE surfactants is that they have a temperature dependent micellization transition. These CAE surfactants have the ability to bind divalent counterions only above a certain temperature, i.e. the critical micellization temperature (CMT), while no binding takes place to the CAE unimers. With this feature CAE-surfactants are interesting for different (separation) processes, e.g. as a temperature dependent ion exchanger that can be regenerated by a temperature-shift.

For efficient MEUF processes the fouling of the membrane by the surfactants has to be minimized \cite{22-24}. The interactions between Pluronic surfactants and different membranes have been studied to some extent \cite{10}, and are expressed in terms of adsorption and fouling.

In this work, first the fouling behavior of CAE-85 and Pluronic P85 is compared, based on resistance measurements with a continuous UF membrane installation consisting of two cross flow membrane modules. Two types of membranes have been investigated, i.e. a regenerated cellulose acetate (CA) membrane and a more hydrophobic polyether sulfone (PES) membrane (see Figure 7.1). The resistance measurements have been performed using a pressure hysteresis method. In the experiments the effect of pH, temperature, and flow velocity on the total flow resistance of the membrane has been studied. Second, ultrafiltration
experiments have been carried out to study the reversibility of the calcium cation binding to CAE-85 aggregates. To verify if the calcium concentration in the permeate is lower at temperatures above the CMT as compared to temperatures below the CMT, the concentration in the permeate has been analyzed by colorimetric titration \[^{[25]}\]. Finally, the solubilization capacity of CAE-85 aggregates for phenanthrene has been investigated. The simultaneous removal of calcium and phenanthrene has been studied by performing MEUF experiments.

![Chemical structure of cellulose acetate and polyether sulfone](image)

*Figure 7.1: Chemical structure of cellulose acetate (left) and polyether sulfone (right).*

### 7.2 Experimental

#### 7.2.1 Calcium analysis by colorimetric titration

The total amount of calcium in a solution was determined by colorimetric titration with ethylenediaminetetraacetic acid (EDTA) using o-cresolphthalein complexone as an indicator \[^{[25]}\]. The following procedure was used. A sample of a few milliliters was taken (calcium concentration of sample should be between \(10^{-2}\) and \(10^{-4}\) mol/L) and was put in a 100 mL flask. Two milliliters of an ammonia buffer solution (25 mL \(\text{NH}_3\) and 7.5 g \(\text{NH}_4\Cl\) in \(1\) L water) and 2.5 mL indicator solution (about 30 mg o-cresolphthalein complexone in 28 mL ammonia buffer and 72 mL water) were also added to the 100 mL flask. The flask was then filled with demineralized water. The titrant is an EDTA solution of \(1.37*10^{-3}\) mol/L (40 mg EDTA in 100 mL water). In the presence of calcium and the o-cresolphthalein complexone indicator the solutions had a magenta color, which turned to colorless during the EDTA titration.

#### 7.2.2 UV measurements of phenanthrene

The concentration of phenanthrene in the surfactant solutions was measured using UV-vis (Uvikon XL from Bio-Tek Instruments, Inc.). In the UV spectrum of phenanthrene four peaks can be observed, i.e. at wavelengths of 325 nm, 332 nm, 340 nm, and 348 nm. The maximum
UV absorption takes place at 332 nm, and therefore this wavelength was chosen to determine the concentration of phenanthrene. The influence of the surfactant concentration on the UV absorption of a fixed amount of phenanthrene was investigated and the influence was negligible. The path length in the quartz cell was 10 mm and the temperature was 50 °C.

### 7.2.3 Membrane equipment
All UF experiments were performed using a UF membrane set-up, as shown in Figure 7.2. The cross flow membrane modules were equipped with flat sheet membranes. The regenerated cellulose acetate (Operating range: 1<pH<11, T<55 °C) and polyether sulfone membranes (Operating range: 0<pH<14, T<95 °C) used in the experiments were supplied by Microdyn-Nadir GmbH, Wiesbaden, Germany. Both membranes have a molecular weight cut-off of about 3 kD and were mounted in parallel support plates. For both membranes the total surface area was equal to 63.25 cm². The pump had a flow rate between 50 L/h and 300 L/h, with a maximum counter pressure of 35 psi (with 1 psi equal to 6900 Pa). The total volume of the system was about 1.5 L. Temperatures were maintained at constant level by a Lauda Ecoline RE 306 cooling thermostat. In all experiments, the permeate was collected and weighted on a mass balance. The retentate stream was recycled back into the feed vessel. All fouling matter was removed from the membranes by pumping a 0.5 wt% Dowfax 8390 solution through the system for some hours.

![Figure 7.2: Schematic view of the UF membrane installation used.](image)
7.2.4 Hysteresis experiments

Resistance measurements were carried out in order to determine the fouling rate of different surfactants. For these experiments a pressure hysteresis approach was chosen. The procedure consisted of a stepwise increase in the applied pressure, followed by a stepwise decrease of the pressure. For one hysteresis cycle the pressure was changed in the following order: 5 psi, 10 psi, 20 psi, 30 psi, 20 psi, 10 psi, and 5 psi. Each pressure value was maintained for 30 minutes to equilibrate the system and to obtain a constant flux. Before and after each hysteresis cycle demineralized water was pumped through the system for 30 minutes at 5 psi as a reference for the clean membrane resistance and the irreversible flow resistance. In all hysteresis experiments a surfactant concentration of 0.25 wt% of CAE-85 or Pluronics P85 was used. The clean membrane resistance was also determined by performing a hysteresis experiment with pure water. The obtained flux was used to calculate this resistance.

7.2.5 Smoothing method

The permeate flux was measured using a mass balance. In the case of high fouling rates the flux decreases significantly. Within the time interval (3 minutes) where the permeate mass was monitored only a few drops were collected. The mass of the drops of the permeate determined the accuracy, and the experimental error could rise up to 50%. This resulted in relative high fluctuations in the flux and resistance values. To overcome this problem a smoothing technique was applied within each pressure interval \[26\]. An average value for the water flux, \( J_{w,n} \), was obtained by calculating a moving average of the flux values. The average ‘smoothed’ water flux, \( \overline{J}_{w,n} \), consisted of five flux values, ranging from \( J_{w,n-2} \) to \( J_{w,n+2} \):

\[
\overline{J}_{w,n} = \frac{\sum_{i=-2}^{2} J_{w,n+i}}{5}
\]

(7.1)

where \( n \) is the running index. It has to be noted that the first data points and the last data points of each pressure interval were calculated using less than five fluxes, because the smoothing technique cannot be used beyond the boundaries of the pressure interval, i.e. where the system parameters change.
7.2.6 Reversibility experiments
To study the reversibility of counterion binding in the CAE-85 surfactant system the following ultrafiltration experiments were carried out. An aqueous solution of 1.2 L of 0.5 wt% CAE-85 (concentration carboxylate groups equal to $2.65 \times 10^{-3}$ mol/L) and $1.12 \times 10^{-3}$ mol/L CaCl$_2$ was pumped through the membrane installation, shown in Figure 7.2. The pH of this solution was equal to 6.3. In this series of experiments only the cellulose acetate membrane module was used. The applied trans-membrane pressure and the flow rate were kept constant during the experiments, and were equal to 20 psi and 150 L/h, respectively. Next a temperature cycle was applied where the solution temperature was switched successively between a temperature below and above the CMT. The temperature was changed as follows, from 20 °C to 50 °C, back to 20 °C and again up to 50 °C. The temperatures were kept constant for 1.5 h. At each temperature, the concentration of calcium in the permeate stream was measured once. The concentration of calcium in the feed was also determined before and after the experiment. As a reference, an experiment with a solution of CaCl$_2$ without CAE-85 surfactant was performed. No retention of calcium was observed and it was concluded that calcium could move freely through the CA membrane.

7.2.7 Solubilization experiments
For the solubilization experiments, different solutions were prepared by adding phenanthrene to the CAE-85 surfactant or Pluronic surfactant solution at a temperature of 25 °C (below the CMT) and of 50 °C (above the CMT). The solutions were stirred at 50 °C for 24 h to reach equilibrium conditions. Solid particles that were not dissolved after 24 h, were left to precipitate and only the clear solution was used in the experiments. At 25 °C no detectable amount of phenanthrene was dissolved in a CAE surfactant solution after 24 h of stirring.

7.2.8 MEUF experiment
To study the influence of phenanthrene on the calcium binding of CAE-85 the following ultrafiltration experiment was carried out. A surfactant solution of 1.2 L of 0.5 wt% CAE-85 (concentration carboxylate groups is $2.60 \times 10^{-3}$ mol/L) and $1.23 \times 10^{-3}$ mol/L CaCl$_2$. The pH of this solution was equal to 6.5. The feed solution was pumped through the membrane set-up, as shown in Figure 7.2. Again, only the cellulose acetate membrane was used. A trans-membrane pressure of 20 psi, a flow rate of 150 L/h, and a temperature of 50 °C were
applied. After an equilibration time of 1.5 h the calcium concentration in the permeate was measured. Next, 450 mg phenanthrene was added to the feed solution, and the solution was stirred at 50 °C for 24 h. After the equilibration period of 24 h the membrane experiment was continued. The concentration of calcium in the permeate was measured again, after 1.5 h, and in addition the phenanthrene concentration in the feed and in the permeate stream was measured after the experiment.

7.3 Theoretical background

7.3.1 Membrane permeation

Ultrafiltration membranes are porous membranes where the rejection of components is mainly determined by the size and shape of the solutes relative to the pore size of the membrane. Ultrafiltration is a pressure driven membrane process. The water flux, $J_w$, through the membrane is given by Darcy’s law:

$$J_w = \frac{\Delta P}{\eta R_T}$$  \hspace{1cm} (7.2)

where $\Delta P$ is the effective transmembrane pressure [Pa], $\eta$ the viscosity of the permeate [Pa s] and, $R_T$ the total resistance towards solvent flow [1/m].

The permeate flux is given by:

$$J_w = \frac{G}{A_m \rho}$$  \hspace{1cm} (7.3)

where $G$ is the permeate mass flow [kg/s], $A_m$ the membrane area of one cross flow module [$m^2$], and $\rho$ the density of the solution [kg/m$^3$].

The total resistance is corrected for the pressure and temperature through the viscosity, according to Eq. (7.2). As a result, the total resistance depends only on the membrane and solute properties. The total resistance, $R_T$, is calculated from experimental data using Eqs. (7.2), (7.3) and (7.4) and can be split into two contributions, i.e. the clean membrane resistance, $R_m$, and the fouling resistance, $R_c$, according to:
\[ R_t = R_m + R_c \]  

(7.4)

The clean membrane resistance, \( R_m \), is the intrinsic resistance of the clean membrane, and depends only on the membrane properties. The fouling resistance, \( R_c \), can be divided into a resistance contribution of reversible fouling and a contribution of irreversible fouling. Fouling will mainly be caused by components in the water stream that have strong affinity for the membrane surface material. The nature of the interaction can be electrostatic, or can be the result of adsorption or complexation, and is often affected by concentration polarization. Concentration polarization is the accumulation of rejected solutes near the membrane surface and depends on the water permeation. As a result there will be a concentration gradient of the solute near the membrane surface. In the case that the solute concentration near the surface increases to a concentration above the saturation concentration, deposition of the solute, i.e. called scaling for anorganic materials, will occur and may result in a decrease in the flux across the membrane.

Maintaining a constant cross flow and constant temperature will provide information about the reversibility of the fouling. In general, the fouling rate will be higher at higher pressures. In the case of reversible fouling, the total membrane resistance, \( R_f \), observed for the increasing pressure path should be the same as observed for the decreasing pressure path. In the case of irreversible fouling the resistance values will stay at a higher level during the decreasing pressure path and the flux will not return to its original value.

The rejection of a solute in a continuous membrane process, \( \Omega \), can be defined by:

\[
\Omega = 1 - \frac{C_{sol,p}}{C_{sol,f}}
\]  

(7.5)

where \( C_{sol,p} \) is the concentration of the solute in the permeate stream and \( C_{sol,f} \) is the concentration of the solute in the feed stream. When the mixing in the feed is poor and the bulk concentration of solutes is different as compared to the concentration at the membrane surface, Eq. (7.5) becomes the definition for the ‘observed rejection’. The ‘true’ rejection is calculated by replacing the concentration of solute in the feed, \( C_{sol,f} \), with the solute concentration at the membrane surface.
7.3.2 Solubilization of phenanthrene

Pluronic micelles are capable of solubilizing a relatively large amount of hydrophobic components in the core. The size of the Pluronic micelles is large (about 10 to 20 nm) and a large micelle core is formed during micellization. The solubility of polycyclic aromatic hydrocarbons, like naphthalene and phenanthrene, are known to increase significantly in Pluronic surfactant solutions [21, 27]. Furthermore, it is known that the solubilization behavior is thermo-reversible. Above the CMT solubilization takes place and below the CMT the surfactant molecules do not form micelles. As a result hydrophobic components become insoluble and will precipitate. In this way aqueous extraction processes for hydrocarbons can be developed in which the surfactant can be reused in the process. The solubilization ratio of a component, $\beta$, at a certain temperature and surfactant concentration is defined as:

$$\beta = \frac{S_{mic}}{S_w}$$

(7.6)

where $S_{mic}$ is the solubility of a component in the surfactant solution and $S_w$ the solubility of a component in pure water.

7.4 Results and discussion

7.4.1 Resistance experiments

To study the fouling behavior of P85 and CAE-85 surfactants on the CA and the PES membranes a number of hysteresis experiments have been performed. Experiments have been performed at three different flow rates, i.e. 100, 150, and 200 L/h, and at two different temperatures, i.e. 20 °C (below the CMT) and 50 °C (above the CMT). Also, the influence of the pH on the fouling behavior has been studied. Most experiments have been performed at a pH value between 6 and 7, however, two experiments were performed at a pH of 2.2. As a reference, the clean membrane resistances, $R_m$, has been measured for the CA and the PES membrane. The results for the clean membrane resistance are given in Table 7.1.
Table 7.1: The clean membrane resistance, $R_m$, for the CA and the PES membrane at 20 °C and 50 °C.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Clean membrane resistance $R_m$ [1/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CA</td>
</tr>
<tr>
<td>20</td>
<td>$2.1 \times 10^{13}$</td>
</tr>
<tr>
<td>50</td>
<td>$2.4 \times 10^{13}$</td>
</tr>
</tbody>
</table>

In the experiments with the CA membrane and for 0.25 wt% solutions of P85 or CAE-85 surfactant the total resistance does not increase, and the value of the total resistance is close to the value of the clean membrane resistance, for all the different experiments. From this it can be concluded that no fouling occurs with the P85 or the CAE-85 surfactant on the CA membranes. Adsorption of the relatively hydrophobic surfactant molecules is prevented by the hydrophilic nature of the CA membrane. Therefore, CA membranes are an attractive option in combination with P85 or CAE-85 surfactants. All resistance values plotted in Figure 7.3 and Figure 7.4 have been obtained from experiments with PES membranes. The results for the hysteresis experiments for P85 and for CAE-85 surfactant solutions at a flow rate of 150 L/h are shown in Figure 7.3. In all the experiments, during the first and the last 30 minutes pure water is used instead of the surfactant solution. The solid line describes the stepwise pressure change during the experiment.

![Figure 7.3 (a): Resistance results for the hysteresis experiments of 0.25 wt% P85 and CAE-85 solutions with a pH value of about 6.5, performed at a flow rate of 150 L/h at 20 °C and 50 °C, using PES membranes.](image)
In Figure 7.3a it can be seen that the total resistance at 20 °C is lower for both P85 and CAE-85 surfactants, as compared to the total resistance at 50 °C. This can be explained by a decrease in solubility of the Pluronic-based surfactants at higher temperatures. Ethylene oxide groups and propylene oxide groups become less polar at higher temperatures, which makes the surfactant more hydrophobic and hence more susceptible for adsorption on hydrophobic membranes. Figure 7.3a also shows that the total membrane resistance is higher for P85 as compared to CAE-85 surfactant.

The largest difference in the resistance between the two surfactants is observed at 50 °C. Below the CMT, at 20 °C, the Pluronic-based surfactant molecules do not aggregate, and the hydrophobic PPO blocks are free to interact with the membrane surface. The ionic charge of CAE-85 can be the reason that a slightly lower resistance is observed for CAE-85, because the ionic charge will reduce the attraction to the hydrophobic membrane surface. Above the CMT, at 50 °C, the surfactants are aggregated in micelles. The charged surface of the CAE-85 micelles reduces the adsorption of the hydrophobic parts of the micelle on the membrane. Therefore, the adsorption of the P85 surfactants on the membrane is higher because the micelles are more hydrophobic, as compared to CAE-85 micelles.

It should be noted that the fouling is practically irreversible, because the resistance value does not decrease significantly in the last 30 minutes of the experiment, i.e. when pure water is used. The resistance values are levelling off directly after the pure water flow is changed to
the surfactant solution. From this it can be concluded that the cake resistance, $R_c$, is independent of the applied pressure. Finally, it can be said that despite the use of a smoothing method some scattering in the resistance data can be observed at 210 minutes. The high fouling rate and low pressure result in a large error in the resistance values at the end of the experiments.

In Figure 7.3b, it can be seen that the total resistance values increase significantly when the pH is lowered to a value of 2.2. The pH of the solution is below the iso-electric point of the PES membrane, which is around pH of 3, giving the membrane a positive charge. Also, the free electron-pairs of the ether oxygen groups of the CAE-85 surfactant make the surfactant act like it has a small negative charge, that partly will be screened by the $H^+$-ions. As a result the interaction between the CAE-surfactant and the PES membrane will increase, and a higher fouling resistance is obtained. In Figure 7.4 results for the resistance experiments for a flow rate of 100 L/h and 200 L/h are presented. For a flow rate of 100 L/h only experiments with P85 have been performed. It follows from Figure 7.4a that the total resistance for the P85 solution at 50 °C is almost equal to the resistance obtained for a flow rate of 150 L/h. However, the values for 20 °C are significantly higher as compared to the results for a flow rate of 150 L/h, most likely due to the fact that the membrane was not completely clean at the start of the experiment.

**Figure 7.4 (a): Resistance results for the hysteresis experiments of 0.25 wt% P85 solutions with a pH value of about 6.5, performed at a flow rate of 100 L/h at 20 °C and 50 °C, using PES membranes.**
During the first 30 minutes of the experiment pure water is pumped through the system, and the total resistance, $R_T$, should match the clean membrane values for PES membranes as tabulated in Table 7.1. It can be seen that the total resistance is higher than the clean membrane resistance, $R_m$. When the total resistance for the experiment at 20 °C in Figure 7.4a is corrected for this difference then the values are similar to the values obtained for the experiments at 150 L/h. From this it can be concluded that when using an already ‘fouled’ membrane, the cake resistance, $R_c$, resulting from the fouling caused by the surfactant during the experiment, seems to be cumulative with the resistance from the pre-fouled membrane. The total resistance at a flow rate of 200 L/h, as shown in Figure 7.4b, is similar to the resistance at 150 L/h.

From a comparison of the resistance values of P85 at 50 °C for a flow rate of 100 L/h, 150 L/h, and 200 L/h it can be concluded that the total resistance decreases slightly with an increase in flow rate. This can be explained by the higher shear forces of the liquid near the membrane surface area for a higher flow rate, which will reduce the formation of a surfactant layer on the membrane.

### 7.4.2 Reversibility of calcium binding

The CAE-85 surfactant is able to bind divalent cations above the critical micellization temperature (CMT). For the CAE-85 surfactant the CMT is equal to about 33 °C.
Ultrafiltration is used to determine the ability of the CAE-85 surfactant to bind divalent cations reversibly in order to use the CAE-85 surfactant in a separation process. In this respect, the binding capacity of the CAE-85 micelles and the reversibility of the binding are important issues.

To evaluate the binding reversibility, a CAE-85 solution with calcium chloride has been used as the feed stream. The temperature is alternated between 20 °C (below CMT) and 50 °C (above the CMT), and the CA membrane has been used to retain the CAE-85 aggregates. The concentration of calcium in the feed at the start of the experiment is equal to 1.12*10^-3 mol/L. According to the binding isotherm for calcium (as determined in Chapter 4), at a temperature of 50 °C and at a molar ratio, r, of 0.42 the free concentration of calcium is 6.47*10^-4 mol/L, and this is 58% of the added amount.

In Figure 7.5 results for the concentration of calcium in the permeate are given. The permeate concentration of calcium is clearly lower at 50 °C than at 20 °C. At 20 °C the rejection of calcium, Ω_{ca}, is 29.6 % and the permeate concentration is much lower than the feed concentration of 1.12*10^-3 mol/L. This can be explained by the Donnan equilibrium effect [28-30], which is observed in membrane systems with charged colloids. Except for the anionic CAE-85 surfactant molecules all cations and anions are able to permeate freely through the CA membrane, which is known from literature [31, 32]. However, because the negatively charged CAE-85 unimers are retained by the membrane the flux of the chloride co-ions through the membrane is enhanced. As a result of electro-neutrality a cationic species, Ca^{2+} or Na^{+}, has to accompany the chloride anions. The sodium cations have a higher flux through the membrane because of the higher diffusivity per unit charge for sodium. As a result, there will be some retention of the calcium ions at 20 °C. At 50 °C the rejection of calcium is equal to 41.2%, and this value is close to the value expected from the isotherm (42.2 %, see Chapter 4). It has to be noted that the rejection is not solely the membrane rejection, but it also includes the rejection caused by the micellar system.
At 50 °C the Donnan equilibrium effect is less pronounced, because the anionic charged end groups of the CAE-85 surfactants are covered by calcium ions. The remaining free charges (sodium, calcium and chloride ions) are no longer “forced” by the charged surfactant molecules to go through the membrane, and will therefore be distributed equally over both sides of the membrane. Furthermore, it should be noted that by decreasing the temperature from 50 °C to 20 °C the concentration of calcium in the permeate returns to a value close to the original value at 20 °C. This indicates that the binding of calcium to CAE-85 aggregates is reversible. The small increase in permeate concentration, which was observed for the two right bars in Figure 7.5 as compared with the two bars on the left, is most likely the result of the sampling procedure in which the feed stream becomes more concentrated in calcium cations when samples (10 mL) are taken from the permeate stream with a lower calcium concentration than the feed stream.

7.4.3 Solubilization of phenanthrene
In order to study the simultaneous removal of metal ions and organic compounds and the effect of the surfactant modification on the solubilization behavior, phenanthrene has been used as the solute. The solubility of phenanthrene in water, $S_w$, is about $1.0 \times 10^{-3}$ g/L (UV absorption $<< 0.01$ A.U.)$^{33,34}$. 

![Figure 7.5: Permeate calcium concentrations during a temperature cycle of 20 °C, 50 °C, 20 °C and 50 °C, using a CA membrane and a 0.5 wt% CAE-85 solution with CaCl$_2$ as the feed.](image-url)
In Figure 7.6 the results are shown for the maximum solubility of phenanthrene in 1.0 wt% P85 and CAE-85 surfactant solutions, which have been determined by UV absorption measurements.

For the P85 solution it can be observed that the UV absorption levels off at a phenanthrene concentration of about 0.95 g/L. This means that the maximum solubility of phenanthrene, \( S_{\text{mic}} \), is equal to 0.95 g/L, which corresponds according to Eq. (7.6) to a solubility ratio, \( \beta \), of 950. In the presence of calcium no significant difference in UV absorption for P85 is noticed, see Figure 7.6a. For the 1.0 wt% CAE-85 solution the UV absorption levels off at a
phenanthrene concentration of about 0.90 g/L, which corresponds to a solubility ratio, $\beta$, equal to 900, a value slightly lower than for the P85 solution. There can be two explanations for the slightly lower $\beta$ observed for the CAE-85 surfactant solution. First, in a 1.0 wt% P85 solution there are more surfactant molecules present than in a 1.0 wt% CAE-85 solution, caused by the slightly lower molecular weight for P85 (4568 g/mol) as compared to CAE-85 (4768 g/mol).

![Figure 7.7](a): UV absorption results (325 nm) for phenanthrene in a 1.0 wt% CAE-85 solution at 50 °C as function of the solution pH.

![Figure 7.7](b): UV absorption results (332 nm) for phenanthrene in a 1.0 wt% CAE-85 solution at 50 °C with the addition of calcium chloride at two different pH values.

Second, the formation of micelles is energetically less favored when the surfactant has charged end groups. Overall, better-defined micelles with a higher solubilization capacity
will be formed in P85 surfactant solutions. From Figure 7.6b it is difficult to determine if there is an influence of the pH and the calcium concentration on the maximum solubility of phenanthrene. In Figure 7.7a the effect of the pH of a 1.0 wt% CAE-85 solution on the UV absorption of phenanthrene is shown. It has to be noted that the data of Figure 7.7a and the data of Figure 7.7b are measured at different wavelengths (see caption Figure 7.7) and can therefore not be linked directly. It can be observed that there is a quite strong decrease in UV absorption when the pH of the solution is increased, which indicates a decrease in solubilization capacity for phenanthrene\textsuperscript{[34]}. Again, it can be concluded that the charged end groups of the CAE-85 surfactant form less structured micellar aggregates than the P85 surfactants. However, when the charged end groups are shielded or covered by cations, like calcium, the micelles become more structured and the solubilization capacity of the micelles will increase. This is shown in Figure 7.7b where an increasing UV absorption is observed with increasing calcium chloride concentration.

It can be concluded that the charge density of the micelle is an important factor in the solubilization capacity for phenanthrene. Highly charged micelles form less structured aggregates with a higher energy, because of the electrostatic head group repulsion. The shielding of the charged end groups or the binding of cations will decrease this electrostatic repulsion and increase the capacity to solubilize phenanthrene.

### 7.4.4 Simultaneous removal of calcium and phenanthrene with MEUF

To study the simultaneous removal of phenanthrene and calcium by the CAE-85 surfactant and to determine the influence of phenanthrene on the binding capacity of the CAE-85 surfactant a MEUF experiment has been performed. The results of the experiment are given in Table 7.2. In Figure 7.8 a schematic representation is given for the simultaneous removal of calcium and phenanthrene by surfactants.

<table>
<thead>
<tr>
<th>Concentration in:</th>
<th>Calcium [mol/L]</th>
<th>Phenanthrene [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>$1.23 \times 10^{-3}$</td>
<td>375</td>
</tr>
<tr>
<td>Permeate before phenanthrene addition</td>
<td>$7.3 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>Permeate after phenanthrene addition</td>
<td>$7.4 \times 10^{-3}$</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>
From Table 7.2 it follows that there is almost no difference in the permeate calcium concentration before and after the addition of phenanthrene to the CAE-85 surfactant solution. Phenanthrene does not seem to have a large effect on the calcium binding. Additionally, it can be seen that the rejection of phenanthrene in this experiment is almost 100%, because no phenanthrene was detected in the permeate stream. From this it can be concluded that it is possible to remove calcium and phenanthrene simultaneously with high retention for phenanthrene at 50 °C by using a CAE-85 surfactant solution. Added to the fact that at 25 °C no calcium binding occurs and no phenanthrene can be solved, this can lead to new separation processes for removing metal ions and small organics with a surfactant that easily can be regenerated.

![Schematic picture](image)

Figure 7.8: Schematic picture of the simultaneous removal of calcium ions and phenanthrene by surfactant self-assembly.

### 7.5 Conclusions

The main conclusion of the hysteresis experiments is that both P85 and CAE-85 surfactant solutions will induce fouling on the PES membranes. As a result of the ionic charge of the CAE-85 surfactant less fouling of the PES membrane will occur. Especially at 50 °C, the degree of fouling observed for the CAE-85 micelles is lower than for P85 micelles. At pH values below the iso-electric point of the membrane the fouling increases significantly by the attracting electrostatic forces between membrane and surfactants. In all cases, the fouling is
almost irreversible and independent of the applied pressure. On the other hand, there is no fouling observed for the CA membranes. Both the P85 and CAE-85 surfactant do not have any noticeable interaction with the CA membrane.

Furthermore, a temperature cycle between 20 °C and 50 °C in ultrafiltration experiments showed that the binding of calcium to CAE-85 is reversible. However, there is a substantial retention of calcium at temperatures below the CMT, which can be explained by the Donnan effect.

The solubilization of phenanthrene in CAE-85 micelles is slightly lower for CAE-85 as compared to P85, which can be explained by the charged end groups of CAE-85. Additionally, the solubilization capacity of CAE-85 is favored by lowering the pH or increasing the calcium concentration, because then the charge of the end groups is counterbalanced by the added cations. However, the solubilization of phenanthrene has almost no influence on the degree of calcium binding to the CAE-85 surfactant, and therefore it can be used to remove simultaneously organics and metal ions from a water stream above the critical micellization temperature.

The results in this work show that thermo-reversible CAE surfactants can be used successfully in membrane processes, which opens the way to new separation processes that have a substantial lower waste production as compared to conventional membrane processes.

7.6 References

Chapter 8

Implementation of CAE surfactants in RO membrane processes for antiscalant purposes: a process evaluation

Abstract

Scale formation on membranes is the main bottleneck to enhance the water recovery in membrane water purification processes. Carboxylic acid end standing (CAE) surfactants seem to be a promising alternative for conventional antiscalants, because of the thermo-reversible regeneration behavior. In this Chapter an economical evaluation is given for the implementation of CAE surfactants as an antiscalant or as an ion exchanger in an industrial scale reverse osmosis membrane process. Various process configurations have been compared with reference base cases to minimize the influence of estimation errors. It can be concluded that the use of CAE-85 as an antiscalant seems to be the most feasible option, while it has lower treatment costs and a higher water recovery as compared to the base case. The degree of heat integration and the binding capacity of the CAE surfactant are the key factors for obtaining a feasible process.
8.1 Introduction

8.1.1 Scaling and antiscalning
In water purification processes clean water is produced from surface water, ground water, brackish water or seawater using reverse osmosis or nanofiltration membranes \[1-3\]. Depending on the source, the feed water contains different amounts and types of organic solutes and dissolved ions. During water production the concentration of ions in the retentate stream of subsequent membrane modules will increase, and at a certain point the concentration of the low solubility salts, like BaSO\(_4\) and CaSO\(_4\), will exceed the solubility limit. Salt particles will be formed and will precipitate on the membrane surface, decreasing the water permeation flux, see Figure 8.1. The process of deposition of the formed salts on the membrane surface is called scaling \[4-8\].

![Figure 8.1: Schematic representation of scale formation in reverse osmosis membrane modules.](image)

Two scaling mechanisms can be distinguished. In the mechanism of bulk precipitation the particles are formed in the solution at supersaturated conditions and will deposit on the membrane surface. With the surface precipitation mechanism, supersaturated conditions are obtained near the membrane surface by concentration polarization, resulting in the formation of small solid particles on the membrane surface.

The current technology to remove divalent cations commonly involves the use of ion exchange resins \[9-11\] or chemical antiscalants \[12, 13\]. The regeneration of ion exchange resins typically involves consecutive washing steps with acid and caustic, thus leading to the production of substantial amounts of waste salt. Alternatively, to prevent scaling, antiscalants are added to the (feed) water stream before the ‘scaling-sensitive’ stage of the membrane process. Antiscalants are additives that act like crystallization inhibitors and therefore will delay the formation of salt particles \[14\]. In this way the induction time for salt precipitation is extended. The interaction between the antiscalants and the salt ions is
irreversible, and in general antiscalants have to be disposed after single use, thus creating a substantial environmental burden seen the scale of the process involved\textsuperscript{[15]}. This means that for the development of benign water purification processes, a new type of regenerable water softener is indispensable. In this respect, thermo-reversible carboxylic end standing (CAE) surfactants might be a promising alternative for the use of antiscalants.

Similar to standard Pluronics\textsuperscript{[16]}, the CAE surfactants have a critical micellization temperature (CMT). Reversible binding of the ions to the CAE surfactant aggregates is realized by means of a temperature shift\textsuperscript{[17]}. Above the CMT the CAE surfactants form anionic micelles with a high affinity for multivalent cations, while below the CMT the micellar structure will breakup resulting in the release of the cations. As a result of the good solubility of the CAE surfactants, these are the first high molecular weight anionic surfactants that are highly soluble in the presence of hardness ions, like calcium or barium.

In this Chapter, the use of CAE surfactants as an antiscalant or an ion exchanger in RO membrane water purification processes will be evaluated and the economical aspects\textsuperscript{[18]} are studied. Different process configurations of a membrane purification process are considered with implementation of the CAE surfactants as an antiscalant or an ion exchanger. Using a scaling model and an economical model the feasibility of the different process configurations are discussed and compared with a reference base case.

8.2 Theory

8.2.1 Scaling model and assumptions

Scaling mechanisms are difficult to model because of the complex crystallization and precipitation kinetics involved\textsuperscript{[19-23]}. The formation of salt particles is subject to many influences and is sensitive to changes in the process conditions. In this work a simplified model is used to describe the scaling mechanism, because detailed information about the membrane process is not available and is not needed to come to a preliminary cost evaluation. Industrial water supply companies often make use of empirical models to predict scaling, because of the better workability and better performance of these models\textsuperscript{[24, 25]}. The Matlab model used in this work consists of four process unit operations, i.e. reverse osmosis (RO) spiral wound membrane modules, heat exchangers, pumps and an ion exchange (or antiscalant) unit. The final process configuration of the membrane modules, i.e. a
‘Christmas tree’ configuration \([3]\) is modeled by combining individual modules connected in series or in parallel, see Figure 8.2. The equations of the model are given in Appendix A. In the following the model assumptions are discussed for the different units.

The composition of the feed stream and the applied process conditions are given in Table 8.1. The values are based on data for a typical industrial process (KIWA Water research) for a plant that processes 22.5 million \(\text{m}^3\) water. However, in this work the composition of the feed stream is simplified in the calculations by only using the following ions: \(\text{Ba}^{2+}\), \(\text{Ca}^{2+}\), \(\text{Na}^{+}\), \(\text{Cl}^{-}\), and \(\text{SO}_4^{2-}\).

**Table 8.1: Inlet stream data used in model calculations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet flow</td>
<td>0.78 (\text{m}^3/\text{s})</td>
</tr>
<tr>
<td>Barium concentration</td>
<td>(5.8 \times 10^{-7}) (\text{mol/L})</td>
</tr>
<tr>
<td>Calcium concentration</td>
<td>(1.58 \times 10^{-3}) (\text{mol/L})</td>
</tr>
<tr>
<td>Sodium concentration</td>
<td>(6.2 \times 10^{-4}) (\text{mol/L})</td>
</tr>
<tr>
<td>Sulfate concentration</td>
<td>(5.9 \times 10^{-4}) (\text{mol/L})</td>
</tr>
<tr>
<td>Chloride concentration</td>
<td>(2.6 \times 10^{-3}) (\text{mol/L})</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>(5.95 \times 10^{-3}) (\text{mol/L})</td>
</tr>
<tr>
<td>Temperature</td>
<td>15 °C</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>15 bar</td>
</tr>
<tr>
<td>Annual working hours</td>
<td>8000 (\text{h/yr})</td>
</tr>
</tbody>
</table>

In the model for the scaling in a reverse osmosis spiral wound membrane unit no distinction between surface precipitation and bulk precipitation is assumed. With the permeation of water the concentration of salts near the membrane will increase until supersaturated conditions. The increase in the concentration close to the membrane surface is known as concentration polarization. In the model it is assumed that only \(\text{BaSO}_4\) will cause scaling, because it has the lowest solubility in water. An empirical relation for the induction time for \(\text{BaSO}_4\) scaling is used to determine the moment when particle formation starts. Without taking any further precipitation kinetics into account this can directly be related to an increase in cake resistance. The increase in cake resistance leads to a decrease of the permeation flux. The relations for the permeate flux and the cake resistance will be solved as function of time using a Runge Kutta method, and as a function of the module length using a forward finite differences method \([26]\). Furthermore, it is assumed that there is no permeation of ions and salt.
particles through the membrane. The solute fluxes to the membrane surface were calculated using a Newton method taking into account osmotic pressure. The mass transfer coefficient in spiral wound modules for turbulent flow can be described by the Deissler equation \(^{27}\) and to model the behavior of individual ions the Bromley equation \(^{28}\) was used to determine the activity coefficient. In the model the individual spiral wound module has a length of 1 meter and a membrane area of 37 m\(^2\). Additionally, the feed water has a temperature of 15 °C and in all cases where the CAE-85 surfactant is active to bind cations, the temperature is increased to 35 °C, which is above the CMT of the surfactant. The effect of the temperature was mainly included in the model by the viscosity change. The pressure losses are calculated in the spiral wound modules according to Rautenbach \(^{27}\), and in the heat exchangers according to Bird \(^{29}\). A typical equation for weak cationic ion exchangers is used to describe the pressure loss in the CAE-85 ion exchanger.

For the design of the ion exchange unit it is assumed that the CAE-85 surfactant can be used in a fixed bed mode or in beads where the core consists of the surfactant solution and the shell is a polymeric layer that easily can retain the surfactants inside and provides free transport for water and ions. The capacity of the ion exchanger is based on binding data obtained from the isotherms as described in Chapters 3 and 4 (a typical strong cation exchanger will have a capacity in the order of 1 Eq/L). The capacity is important to determine the volume and size of the ion exchanger, which is used in the cost equation to calculate the ion exchange costs. However, in practice the ion exchanger costs mostly will be determined by the costs for the ion exchange resin. The costs for the CAE-85 ion exchange resin will be higher as compared to conventional resins, because of the additional development costs. The ion exchanger can be regenerated by purging with an aqueous monovalent cation-containing stream. For the design of the antiscalant unit it is assumed that the CAE-85 has the ability to act like an antiscalant. The dependence of the costs on the surfactant concentration is also described in this Chapter.

It has to be noted that the configuration of the membrane modules and the values for the unknown parameters or constants, e.g. the characteristic parameter for membrane fouling, are chosen such that in the reference case (base case) there is 85% recovery after the final RO module. A recovery of 85% is a typical value for a process without the implementation of any scaling precautions \(^{30}\).
8.2.2 Economical model for process evaluation

In the economical model the treatment costs per m$^3$ of produced water is calculated based on the process costs of one year $^{[31]}$. The treatment costs in the model are based on six components, i.e. the capital amortization costs, the labor costs, the operating costs, the membrane module replacement costs, the intrinsic costs and the disposal costs. This description for the treatment costs is an extension of the equation given by Lipski and Côté $^{[32]}$.

The capital costs consist of the investment in the membrane modules, heat exchangers, ion exchangers and pumps. A bare module factor compensates for piping and instrumentation costs. It is assumed that the labor and the amortization costs are fractions of the capital costs. The operating costs consist of the utilities consumption, i.e. steam, electricity, and water to regenerate the ion exchanger. The intrinsic costs in the model are determined by the costs for the feed water that has been pretreated before it enters the RO process modules. The disposal costs consist of the disposal of the concentrated retentate stream, which contains a very high content of salts and organic matter. The membrane replacement costs are based on the description from Lipski and Côté $^{[32]}$, where it is assumed that membranes have a lifetime of about 5 years.

The equations to estimate the investment costs for the heat exchanger, the ion exchanger and the antiscalant unit are taken from Turton and Bailie $^{[33]}$. In these equations the Maxwell & Swift values for the year 2003 are used in the calculations. Furthermore, a CAE-85 ion exchange resin price of 4500 €/m$^3$ was estimated and in the case CAE-85 is used as an antiscalant a price of 8400 €/ton was estimated.

All equations regarding the scaling model and the economical model are given in Appendices A, B and C.

8.3 Results and discussion

8.3.1 Base case for CAE surfactants implemented as an ion exchanger

In practice it is difficult to make an accurate economical evaluation of a process design, because very detailed in house information is needed in order to include all aspects of the process. In order to make a sensible comparison between different process configurations and to minimize errors as a result of the estimations a reference base case is used. This base case
is devised out of water purification membrane process data from industry (Witteveen + Bos). By using the base case as a reference process a qualitative and (semi-) quantitative analysis can be made for the feasibility of the alternative process configurations. The base case consists of a ‘Christmas tree’ configuration with three sections. The number of modules is calculated by assuming an 85 % recovery after section 3 (just before scaling will occur) and a distribution of the modules over the different sections according to the ratios 4:2:1 (section 1: section 2: section 3). The base case is given in Figure 8.2 and Table 8.2.

![Figure 8.2: Base case for the situation where CAE surfactants are implemented as an ion exchanger.](image)

**Table 8.2: Overview for the process values of the base case.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow</td>
<td>0.78 m³/s</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>15 ºC</td>
</tr>
<tr>
<td>Number of modules</td>
<td>2912</td>
</tr>
<tr>
<td>Membrane area per module</td>
<td>37 m²</td>
</tr>
<tr>
<td>Recovery</td>
<td>85 %</td>
</tr>
<tr>
<td>Total RO area</td>
<td>107744 m²</td>
</tr>
<tr>
<td>Treatment costs</td>
<td>0.431 €/m³ of water produced</td>
</tr>
</tbody>
</table>

**8.3.2 Case A: Ion exchanger after third RO section**

For case A a CAE surfactant ion exchanger with 99% efficiency (99% removal of the divalent ions) is included in the process after section three, followed by an additional RO section according to Figure 8.3. CAE surfactants will only bind divalent cations above the CMT. As a consequence, a heat integration unit (HI) and a heat exchanger (HE) have to be added in order to heat up the stream before it enters the ion exchanger. The heated permeate
outlet stream can be used to preheat the inlet stream and steam is used in the heat exchanger to come to the desired inlet temperature of the ion exchanger, i.e. 35 °C for CAE-85. The process values of case A are given in Table 8.3.

From Table 8.3 it can be concluded that the treatment costs are higher for case A as compared to the base case, despite the fact that the recovery has increased to 98.2 %. Three important aspects have to be quoted here. First, the capacity of the ion exchanger turns out to be one of the critical points of case A. When the capacity of the ion exchanger increases the treatment costs of the produced water will decrease sharply until the break even capacity of 1 Eq/L, at which the treatment costs are equal to the treatment costs for the base case.

![Diagram](image)

**Figure 8.3: Case A, additional ion exchanger and a RO section after the base case.**

**Table 8.3: Overview for the process values of case A.**

<table>
<thead>
<tr>
<th></th>
<th>Case A values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery</td>
<td>98.2 %</td>
</tr>
<tr>
<td>Total RO area</td>
<td>122676 m²</td>
</tr>
<tr>
<td>Ion exchanger capacity</td>
<td>0.05 Eq/L</td>
</tr>
<tr>
<td>Heat integration area</td>
<td>1102 m²</td>
</tr>
<tr>
<td>Heat exchanger area</td>
<td>9.16 m²</td>
</tr>
<tr>
<td>Treatment costs</td>
<td>0.537 €/m³ of water produced</td>
</tr>
</tbody>
</table>

Second, the costs for a smaller ion exchanger that has to be regenerated more frequently are lower than the costs for a larger ion exchanger with less regeneration cycles. Third, it is always more beneficial to heat the inlet stream before the ion exchanger using the heat integrator (provided sufficient temperature difference) than using a heat exchanger that uses steam.
8.3.3 Case B: Ion exchanger before third section

For case B the heat exchanger is placed before the third RO section. Also in this case a heat integration unit and a heat exchanger are placed before the ion exchanger to heat the inlet stream. The inlet stream of the ion exchanger in case B is larger than the inlet stream in case A. Therefore, a larger amount of heat is needed to raise the temperature to 35 °C as compared to case A. On the other hand, in case B the permeate stream of section 3 will be used for heat integration and therefore more heat is delivered by the heat integration unit. In table 8.4 the process values for case B are given.

From Table 8.4 it can be concluded that the treatment costs for case B are even higher than the costs obtained for case A. Despite the reduction in membrane area in case B a larger stream has to be heated in case B, which apparently has a larger influence on the treatment costs than the reduction in membrane area. Finally, for case B an increase in the ion exchange capacity will lead to a sharp decrease of the treatment costs.

![Figure 8.4: Case B, additional ion exchanger before the third RO section of the base case.](image)

Table 8.4: Overview for the process values of case B.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery</td>
<td>98.34 %</td>
</tr>
<tr>
<td>Total RO area</td>
<td>116956 m²</td>
</tr>
<tr>
<td>Ion exchanger capacity</td>
<td>0.05 Eq/L</td>
</tr>
<tr>
<td>Heat integration area</td>
<td>2302 m²</td>
</tr>
<tr>
<td>Heat exchanger area</td>
<td>13.2 m²</td>
</tr>
<tr>
<td>Treatment costs</td>
<td>0.565 €/m³ of water produced</td>
</tr>
</tbody>
</table>
8.3.4 Base case for CAE surfactants implemented as an antiscalant

For the antiscalant case a different base case is chosen, in which a commercial antiscalant is added to the process before the third RO section in a typical concentration of 3 mg/L \[8\]. In Figure 8.5 the base case for a process with antiscalant addition is shown. In Table 8.5 the process values of the antiscalant base case are given. All other process conditions remain the same as in the ion exchange base case.

![Figure 8.5: Base case for the situation where CAE surfactants are implemented as an antiscalant.](image)

<table>
<thead>
<tr>
<th>Recovery</th>
<th>90.03%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antiscalant concentration</td>
<td>3 mg/L</td>
</tr>
<tr>
<td>Total RO area</td>
<td>114182 m²</td>
</tr>
<tr>
<td>Treatment costs</td>
<td>0.452 €/m³ of water produced</td>
</tr>
</tbody>
</table>

From Figure 8.5 it can be concluded that the recovery increases by about 5% as a result of the addition of the conventional antiscalant. However, the treatment costs per m³ produced water are slightly higher as compared to the ion exchange base case. This is remarkable, because the antiscalant base case usually is widely applied in water remediation industry. Probably an overestimation is made regarding the price of the antiscalant (equal to 8400 €/ton) or the antiscalant disposal costs.
8.3.5 Case C: Addition of CAE surfactant as an antiscalant before the third RO section

In case C a CAE surfactant is implemented as an antiscalant to replace the conventional antiscalant of the base case. To regenerate the CAE surfactant, a recycle loop is built in the process, together with a heat integration unit and a heat exchanger to bring the water stream to the temperature (35 °C) that is required for the formation of the active CAE micelles.

In this situation the water stream has to be cooled after the final RO section in order to separate the CAE surfactants from the sorbed contaminants. Consequently, an additional heat exchanger and a decanter for the separation are added to the process after the third RO section.

![Figure 8.6: Case C, CAE surfactant implementation in the base case using a recycle loop.](image)

| Table 8.6: Overview for the process values of case C. |
|---------------------------------|---------------------------------|
| Recovery | 98.23 % |
| Total RO area | 116990 m² |
| Heat integration area | 2273 m² |
| Heat exchanger area | 13.4 m² |
| Heat exchanger regeneration area | 77 m² |
| Treatment costs | 0.447 €/m³ of water produced |

From Table 8.6 it can be concluded that the recovery will increase substantially to 98%, and the costs to produce water will be somewhat lower as compared to the antiscalant base case. This is mainly due to the recycling of the surfactant.

In general, three aspects are relevant in order to reduce the treatment costs of the water. First, when a lower concentration of surfactant is sufficient this will lead to a further reduction of
the treatment costs. Second, in the current calculations it is assumed that the steam for the heat exchangers has to be purchased. When heat integration can be achieved by using rest heat from other processes, the treatment costs will decrease significantly. Third, other CAE surfactants can be synthesized with different critical micellization temperatures. In the case that a CAE surfactant is used that is active at the ambient inlet water temperature, no heat exchangers are needed before the final RO section. Consequently, a small retentate stream has to be cooled after the final membrane separation unit, which is a cost effective process operation. In the calculation for case C this can make a difference of about 5% in the treatment costs.

**8.3.6 Cost comparison**

**Base case treatment costs**

- Intrinsic costs: 27%
- Disposal costs: 4%
- Maintenance costs: 20%
- Pump op. costs: 13%
- Amortization costs: 31%
- Membrane replacement costs: 5%

**Case A treatment costs**

- Intrinsic costs: 19%
- Maintenance costs: 18%
- Membrane replacement costs: 4%
- Pump op. costs: 14%
- Amortization costs: 27%
- HE op. costs: 3%
- Regeneration water costs: 1%
- Resin/Surf loss costs: 14%

**Case B treatment costs**

- Intrinsic costs: 18%
- Maintenance costs: 17%
- Membrane replacement costs: 4%
- Pump op. costs: 17%
- HE op. costs: 4%
- Regeneration water costs: 1%
- Resin/Surf loss costs: 13%

**Figure 8.7 (a): Classification of the relative treatment costs for ion exchange cases.**
In Figure 8.7a and 8.7b the relative treatment costs are analyzed for all cases and it can be seen which cost entries are most important in the breakdown of the total treatment costs. The feasibility of the ion exchange case will be dependent on the capacity of the ion exchanger and from Figure 8.7a it can be concluded that the heat integration costs and the heat supply costs, i.e. the price for steam, are important for an economical process operation. Resin losses are taken as 4% of the total amount of resin needed in one year, which can be classified as a conservative percentage.

From Figure 8.7b it can be concluded that the heat operation costs in case C will replace the costs for surfactant loss in the base case. Consequently, heat integration will be a key issue in the feasibility of the use of CAE surfactants for antiscalant purposes.

In Figure 8.8 a cost comparison is given for the treatment costs, the operating costs and the capital costs for all cases. It can be observed that for cases A and B, where an ion exchanger has been implemented, that a sharp increase in operating costs occurs, mainly as a result of the additional heat and pump costs, which is only a relatively small part of treatment costs. Furthermore, it can be concluded that total recycling of an antiscalant without extra chemical treatment steps will lead to a lowering of the treatment costs for the production of water. Overall, case C seems to be the most feasible option for the implementation of CAE surfactants membrane water purification processes.
In Figure 8.8 a cost comparison is given for the treatment costs, the operating costs and the capital costs for all cases. It can be observed that for cases A and B, where an ion exchanger has been implemented, a sharp increase in operating costs occurs, mainly as a result of the additional heat and pump costs, which is only a relatively small part of treatment costs. Furthermore, it can be concluded that total recycling of an antiscalant without extra chemical treatment steps will lead to a lowering of the treatment costs for the production of water. Overall, case C seems to be the most feasible option for the implementation of CAE surfactants membrane water purification processes.

8.4 Conclusions

In this Chapter an economical evaluation is given for a RO membrane process in order to evaluate the implementation of the CAE-85 surfactant as an antiscalant or ion exchanger. Using the CAE-85 surfactant as an ion exchanger results in all cases in a higher water recovery but also in higher treatment costs per m$^3$ of produced water. For the different cases studied, the use of the CAE surfactants as an antiscalant turns out to be the most feasible option and results in a higher recovery and in lower treatment costs per m$^3$ of produced water. In general, there seems to be three main issues that determine the feasibility of the process. First, the binding capacity of the CAE-85 micelles for divalent ions and the corresponding
design of the ion exchanger/antiscalant unit. Second, when using CAE surfactants, a temperature shift is needed in order to perform a regeneration cycle and consequently the degree of heat integration and the method of heat supply have a high impact on the final treatment costs. Finally, the performance and the design of the regeneration units will determine the loss of surfactant or resin deactivation, hence determining the environmental load and disposal costs.

8.5 References

Appendix A: Scaling model

The model has been developed using Matlab 6.1. The operating units of the process consist of reverse osmosis units, heat exchangers, pumps and an ion exchanger or antiscalant unit, depending on the case. It is assumed that the feed stream contains $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Na}^+$, $\text{SO}_4^{2-}$ and $\text{Cl}^-$ ions as a model system and that $\text{BaSO}_4$ is the scaling salt.

A.1 Reverse osmosis unit design

A.1.1 Water flux and cake resistance

The equations for the volume of the solvent through the membrane, Eq. (A.1), and the cake resistance, Eq. (A.2), are calculated in time with a Runge Kutta method and in distance with a forward finite differences method. The equation for the cake resistance was obtained from Okazaki and Kimura.

\[ \frac{dV}{dt} = A J \]  
\[ \frac{dR_c}{dt} = K (C_{sw} - C_s)^2 \]

where $V$ is the collected volume of permeate [m$^3$], $A$ is the superficial membrane area [m$^2$], $J$ is the permeate flux through the membrane [m/s], $R_c$ is the cake resistance [1/m], $C_{sw}$ is the
solute concentration near the membrane surface [kg/m$^3$], $C_s$ is the saturation concentration of BaSO$_4$ at 15 °C [0.00211 kg/m$^3$] and $K$ is a characteristic parameter for membrane fouling [$1.4 \times 10^9$ 1/m]. The parameter $K$ can be interpreted as a combination of the resistance factor per unit weight of scaled mass and the growth rate constant of scaled mass per unit membrane surface area.

The equations for the water flux, $J_w$, and solute flux, $J_s$, through the membrane, Eqs. (A.3) and (A.4), are solved simultaneously using the Newton method to obtain the values of $J$ and $C_{sw}$ for each component.

\[
J_w = \frac{(\Delta P - \Delta \pi)}{\eta (R_m + R_c)}
\]  
(A.3)

where $\Delta P$ is the pressure gradient over the membrane [$1.5 \times 10^6$ Pa], $\Delta \pi$ is the osmotic pressure [Pa], $\eta$ = the fluid viscosity [Ns/m$^2$], and $R_m$ is the clean membrane resistance [$2.15 \times 10^{14}$ 1/m].

\[
J_s = k_s \ln \frac{(C_{sw} - C_{sp})}{(C_{sb} - C_{sp})}
\]  
(A.4)

where $J_s$ is the solute flux through the membrane [m/s], $k_s$ is the mass transfer coefficient [m/s], $C_{sp}$ is the solute concentration in the permeate [0 kg/m$^3$], and $C_{sb}$ is the solute concentration in the bulk [0.0004 kg/m$^3$].

The osmotic pressure, $\Delta \pi$, is defined as:

\[
\Delta \pi = \frac{RT}{V_wC_t} (C_{sw} - C_{sp})
\]  
(A.5)

where $R$ is the ideal gas law constant [8.31451 Pa m$^3$/mol K], $T$ is the absolute temperature [K], $V_w$ is the molar volume of water [$18 \times 10^{-6}$ m$^3$/mol], and $C_t$ is the total concentration of the fluid [kg/m$^3$].
A.1.2 Mass transfer in spiral wound membranes

To describe the mass transfer in spiral wound membranes for turbulent flow, the Deissler equation\(^{[27]}\) was used:

\[
Sh = \frac{k_s d_h}{D} = 0.023 \frac{Re^{0.875} Sc^{0.25}}{D} = 0.023 \left( \frac{d_h \nu \rho}{\eta} \right)^{0.875} \left( \frac{\eta}{\rho D} \right)^{0.25} \tag{A.6}
\]

Where \(Sh\) is the Sherwood number, \(Re\) is the Reynolds number, \(Sc\) is the Schmidt number, \(k_s\) is the mass transfer coefficient [m/s], \(d_h\) is the hydraulic diameter, which is equal to the feed spacer distance [m], \(D\) is the ion diffusivity [m\(^2\)/s], \(\nu\) is the linear velocity [m/s], \(\rho\) is the bulk density [kg/m\(^3\)] and \(\eta\) is the fluid viscosity [Ns/m\(^2\)].

A.1.3 Diffusivity

The salt diffusivity is calculated as an average of the diffusivity of the ions\(^{[35]}\) according to Eq. (A.7).

\[
D = \frac{(z^+ + z^-)(D^+ D^-)}{(z^+D^- + z^-D^+)} \tag{A.7}
\]

Where \(z^+\) and \(z^-\) are the cation and anion charge, respectively, and \(D^+\) and \(D^-\) are the cation and anion diffusivity.

A.1.4 Induction time

To calculate the induction time for precipitation of BaSO\(_4\) an empirical equation was included in the model\(^{[8]}\).

\[
\frac{1}{\log t_w} = 0.182 + 0.114 \left[ \ln \left( \frac{1}{(\log C_{so}^2)^2} \right) \right]^2 \tag{A.8}
\]

Where \(C_{so}\) is the initial saturation concentration of BaSO\(_4\) and \(t_w\) the induction time for BaSO\(_4\).
A.1.5 Activity coefficient
The Bromley equation \(^{[28]}\) was used to calculate the activity coefficient. It assumes that the influence of individual ions can be calculated considering them as a single salt by calculating an average Bromley coefficient. This can be applied, when the ionic strength is lower than 6 mol/L.

\[
\log \gamma_{\pm}^{1/z} = \frac{-0.511\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)I}{\left(1+\frac{1.5}{z^+z^-}I\right)^{1/2}} + \frac{BI}{z^+z^-} \tag{A.9}
\]

where \(I\) is the ionic strength, and \(B\) is the average Bromley coefficient.

A.2 Heat exchanger design

A.2.1 Heat balance
In the model a heat integration unit, i.e. a heat exchanger was implemented to have a more efficient process.

\[
Q_c = F\rho C_H (T_{out} - T_{in}) \tag{A.10}
\]

where \(Q_c\) is the heat flow [W], \(F\) is the inlet flow \([\text{m}^3/\text{s}]\), \(C_H\) is the heat capacity \([4.185 \text{ kJ/kg K}]\), \(T_{in}\) is the inlet temperature of the retentate \([\text{K}]\), and \(T_{out}\) is the outlet temperature of the retentate \([\text{K}]\).

The transfer area \(A\) is given by:

\[
A = \frac{Q_c}{U\Delta T_{in}} \tag{A.11}
\]

Where \(U\) is the overall mass transfer coefficient \((1.7 \text{ kW/m}^2\text{K} \text{ for water and 2.27 kW/m}^2\text{K for steam at 150°C})\), and \(\Delta T_{in}\) is the logarithmic temperature difference.
A.3 Ion exchanger unit design

A.3.1 Resin volume
The ion exchange unit consists of a resin that will bind the divalent cations when the temperature is above the CMT. This resin can be regenerated by lowering the temperature to below the CMT, where the divalent ions will be liberated. The amount of resin needed for the operation and the efficiency of the process are calculated with the following equations. The resin volume is defined by:

$$ V_{res} = \frac{n_{COOH,tot}}{R_{cap}} \quad (A.12) $$

Where, $n_{COOH,tot}$ is the total amount of binding sites [mol] and $R_{cap}$ is the capacity of the resin [Eq/L]. The bound amount of divalent ions can then be defined as:

$$ n_{bound} = 0.5 \theta n_{COOH,tot} \quad (A.13) $$

Where, $n_{bound}$ is equal to the amount divalent ions bound to ion exchanger [mol] and $\theta$ the surface occupancy or fractional binding.

A.3.2 Vessel diameter
For the diameter of the ion exchanger the following equation can be used.

$$ d_{ie} = \left( \frac{4V_{res}}{\pi R_{HD}} \right) \quad (A.14) $$

where $R_{HD}$ is the height to diameter ratio [2 m/m].
A.4 Antiscalant concentration

When the CAE surfactant is used as an antiscalant, the amount of antiscalant that will be needed per year can be calculated as follows.

\[ n_{\text{surf}} = C_{\text{surf}} F (3600 t_{\text{avh}}) 10^{-6} \]  \hspace{1cm} (A.15)

Where \( n_{\text{surf}} \) is the number of tons of surfactant needed per year [mol/yr], \( C_{\text{surf}} \) is the surfactant concentration [3 mg/L used in calculations, as taken from Boerlage \cite{8}], \( F \) is the volumetric flow [m\(^3\)/s] and \( t_{\text{avh}} \) is the number of annual working hours per year [8000 h/yr].

Appendix B: Costs calculations

B.1 Definition of treatment, capital and operating costs

The treatment costs, \( C_{\text{treat}} \), are estimated based on six components: capital amortization, labor requirements, module replacement, \( C_{\text{mr}} \), utilities consumption (operating costs, \( C_{\text{op}} \)), intrinsic costs, \( C_{\text{int}} \), and disposal costs, \( C_{\text{dis}} \). The definition of the treatment costs presented here is an extension of the equation presented by Lipski and Cote \cite{32}.

The intrinsic costs consist of the water pretreatment costs [10 €/m\(^3\)]. The disposal costs, \( C_{\text{dis}} \) [10 €/m\(^3\)], consist of the taxes paid for the water disposal into the environment [10 €/m\(^3\)]. Amortization costs, \( C_{\text{am}} \) [€/yr], are a fraction of the investment paid in one year and is defined in Eq. (B.1) and the maintenance costs, \( C_{\text{main}} \), which are equal to the labor costs is defined in Eq. (B.2).

\[ C_{\text{am}} = f_{\text{am}} C_{\text{cap}} = 0.15 C_{\text{cap}} \]  \hspace{1cm} (B.1)
\[ C_{\text{main}} = f_{\text{lab}} C_{\text{cap}} = 0.10 C_{\text{cap}} \]  \hspace{1cm} (B.2)
Where \( f_{am} \) is the fraction for amortization [1/yr] and \( f_{lab} \) is the fraction for labor [1/yr]. With Eqs. (B.1) and (B.2) the treatment costs are defined as follows.

\[
C_{\text{treat}} = 0.25 C_{\text{cap}} + C_{\text{mr}} + C_{\text{op}} + C_{\text{int}} + C_{\text{dis}} \tag{B.3}
\]
\[
C_{\text{cap}} = BM (C_{\text{mem}} + C_{\text{mod}}) + C_{\text{he}} + C_{\text{ie}} + C_{\text{pump}} \tag{B.4}
\]
\[
C_{\text{op}} = (W_{\text{he}} + W_{\text{ie}} + W_{\text{pump}}) I_{\text{avr}} \tag{B.5}
\]

Where, \( C_{\text{mem}} \) are the total membrane costs [70 €/m\(^2\) * total membrane area, \( A_{\text{mem}} \) [m\(^2\)], \( BM \) is the bare module factor that includes all instruments, piping per bare module [3.5], \( C_{\text{mod}} \) are the total module costs [100 €/m\(^2\) * \( A_{\text{mem}} \) [m\(^2\)], \( C_{\text{he}} \) are the heat exchanger costs, \( C_{\text{ie}} \) are the ion exchanger costs (this term will be replaced by \( C_{\text{su}} \) when dealing with an antiscalant case), \( C_{\text{pump}} \) are the capital costs of the pump, \( W_{\text{he}} \) are the heat exchanger operating costs (water/steam) [€/yr], \( W_{\text{ie}} \) are the ion exchanger operating costs (regeneration water) [€/yr], and \( W_{\text{pump}} \) are the operating costs of the pumps (electricity) [€/yr].

### B.2 Heat exchanger costs

The equations to calculate the heat exchanger costs are from Turton and Bailie\(^{[33]}\). The costs for the heat exchanger are given by Eq. (B.6).

\[
C_{\text{he}} = C_{\text{P,he}} F_{\text{bm,he}} rt \frac{MS_{03}}{MS_{96}} \tag{B.6}
\]

Where, \( C_{\text{P,he}} \) are the equipment costs [$], \( F_{\text{bm,he}} \) is the heat exchanger bare module factor, \( rt \) is the €/$ ratio, which is equal to 1.216, \( MS_{03} \) is the Maxwell & Swift value for 2003, which is equal to 1116 and \( MS_{96} \) is the Maxwell & Swift value for 1996, which is equal to 1039. The heat exchanger equipment costs, \( C_{\text{P,he}} \), are given by Eqs. (B.7) to (B.9)

\[
\log C_{\text{P,he}} = K_1 + K_2 \log(A_{\text{he}}) + K_3 (\log(A_{\text{he}}))^2 \tag{B.7}
\]
\[
F_{\text{bm,he}} = B_1 + B_2 F_{\text{w}} F_{\text{p}} \tag{B.8}
\]
\[
\log F_P = C_1 + C_2 \log(P) + C_3 (\log(P))^2 \quad \text{(B.9)}
\]

Where, \( A_{he} \) is the heat exchanger area [m\(^2\)], \( F_P \) is the pressure factor and \( P \) is the pressure [Bar]. The constants \( K_1, K_2, K_3, B_1, B_2, C_1, C_2, C_3 \) and \( F_m \) are available in literature \([33]\) for different types of heat exchangers and different materials of construction.

### B.3 Ion exchanger costs

The equations to calculate the ion exchanger (ion exchange cases) costs are from Turton and Bailie \([33]\).

\[
C_{ie} = C_{vessel} + C_{resin} \quad \text{(B.10)}
\]

\[
C_{vessel} = C_{P,ie} + F_{bm,ie} \frac{MS_{93}}{MS_{96}} \quad \text{(B.11)}
\]

Where, \( C_{vessel} \) are the vessel costs, \( C_{resin} \) are the resin costs, \( C_{P,ie} \) are the ion exchanger equipment costs, and \( F_{bm,ie} \) is the ion exchanger bare module factor.

\[
\log C_{P,ie} = K_1 + K_2 \log(h_e) + K_3 (\log(h_e))^2 \quad \text{(B.12)}
\]

\[
F_{bm,ie} = B_1 + B_2 F_m F_P \quad \text{(B.13)}
\]

where \( F_P \) is equal to 1 (for operating pressure lower than 2.7 bar), and \( h_e \) is the vessel height [m]. The constants \( K_1, K_2, K_3, B_1, B_2 \) and \( F_m \) are available in literature \([33]\) for different types of heat exchangers and materials of construction. The total resin costs can be calculated by Eq. (B.14).

\[
C_{resin} = V_{res} y_{resin} \quad \text{(B.14)}
\]

Where, \( y_{resin} \) are the volumetric resin costs [4500 €/m\(^3\)].
B.4 Surfactant unit costs

The equation to calculate the costs of the surfactant unit (antiscalant case) is given by Eq. (B.15).

\[ C_{su} = C_{vessel} + M_{surf} y_{surf} \]  \hspace{1cm} (B.15)

Where, \( C_{su} \) are the costs of the surfactant unit and \( M_{surf} \) is the amount of surfactant and \( y_{surf} \) is the surfactant price [8400 €/ton]

B.5 Membrane replacement costs

Equation. (B.16) to calculate the membrane replacement costs is from Lipski and Coté \cite{32}.

\[ C_{mr} = \frac{1}{t_{mem}} C_{mem} \] \hspace{1cm} (B.16)

Where, \( t_{mem} \) is the lifetime of the membrane [5 yr].

Appendix C: Calculation of pressure losses

C.1 Spiral wound membranes

The following approximation is recommended by Rautenbach \cite{27} for spiral wound modules.

\[ \Delta P = 10^5 P_c F^2 (N - 0.8(N - 1) E) \] \hspace{1cm} (C.1)

Where, \( \Delta P \) is the pressure loss [Pa], \( P_c \) is the pressure constant [1.342*10^-5 bar s^2/m^6], \( F \) is the inlet volumetric flow per module [m^3/s], \( N \) is the number of modules in series, which is equal to 8 and \( E \) is the total water recovery.
C.2 Heat exchangers

The pressure losses are calculated with equations from Bird \(^{[29]}\) for a shell and tube heat exchanger that has 100 tubes of 2.5 m each.

\[
\Delta P = \frac{4L}{d} \frac{1}{2} \rho \nu^2 f
\]  \hspace{1cm} (C.2)

Where, \(L\) is the tube length [m], \(d\) is the tube diameter [1 in =2.54 cm], \(\rho\) is the fluid density [kg/m\(^3\)], \(\nu\) is the linear velocity [m/s], \(f\) is the Fanning factor, which can be calculated from Blasius formula \((0.0791 \times \text{Re}^{-1/4})\).

C.3 Ion Exchangers

The following equation is specific for the pressure losses in beds of weak cation resins.

\[
\Delta P = 10^3 (0.02 \nu - 0.0347) l
\]  \hspace{1cm} (C.3)

Where, \(l\) is the bed depth [m].
Chapter 9

Carboxylic acid end standing Pluronic surfactants: Overview and future outlook

Abstract

In the final Chapter a summary and future outlook is given regarding CAE surfactants. First, a mechanistic picture is presented to describe the results of the experiments for the cation binding to CAE micelles. Next, some general advantages and disadvantages are given regarding the use of CAE surfactants in practical processes. The subject of toxicity is addressed and also a comparison with conventional ionic surfactants is given. Additionally, some synthetic opportunities are presented in order to develop thermo-reversible surfactants that have higher binding capacities, stronger binding affinities or cationic end groups. Finally, an outlook on future applications for CAE surfactants that can benefit from the thermo-reversible ion exchange principle will be given.
9.1 Introduction

In this thesis the thermo-reversible CAE surfactant system has been described, starting with the synthesis procedure, followed by the metal binding characteristics and concluded with a preliminary process design. Considering future applications a critical evaluation regarding the potential of the CAE surfactants is presented. First, a mechanistic picture is given for the behavior of counterions in the CAE-85 system. The results obtained in the previous Chapters are combined, which provides a qualitative description for the distribution of the counterions in the CAE-85 system. Second, the advantages and disadvantages of the use of CAE surfactants in process applications are discussed with regard to the thermo-reversible behavior. Additionally, eco- and human toxicology topics of CAE surfactants will be conferred as this is important when CAE surfactants will be implemented in aqueous membrane processes for drinking water production. Furthermore, a comparison with conventional anionic surfactants is made [1]. Third, to enlarge the number of opportunities for thermo-reversible self-assembly applications, suggestions are made for the development of thermo-reversible surfactants with a higher binding capacity for multivalent cations, i.e. the so-called randomized carboxylated surfactants, CAE surfactants with different CMTs and thermo-reversible surfactants with positively charged end groups, e.g. amine terminated Pluronic surfactants. Finally, some ideas are given for further process applications for thermo-reversible surfactants, especially CAE surfactants, within different areas.

9.2 Mechanistic picture

In the previous Chapters the behavior of cations in a CAE-85 micellar system has been studied using several techniques. In this paragraph an overview is given of these Chapters, which leads to a mechanistic picture for the distribution of monovalent and divalent counterions in the CAE-85 micellar system. The CAE-85 surfactant is a high molecular weight surfactant (MW = 4748 g/mol) that has large polar parts, which consist of an ethylene oxide block and a small anionic carboxylic end group [2]. The CAE-85 micelle has a micelle size and an aggregation number that is almost equal to the value for the unmodified Pluronic P85. For CAE-85 a CMT and a sphere-to-rod
transition have been observed that is comparable with the values found for the unmodified P85\textsuperscript{[3]} and despite the anionic nature of CAE-85 a cloud point was observed by adding simple salts like NaCl.

The large polar part of the CAE-85 surfactant makes the corona of the micelle relatively large as compared to conventional surfactant systems, like SDS, with as a consequence that the carboxylic end group of the CAE-85 surfactant can be located throughout the entire corona area and does not form a ‘well-defined’ charged surface. The low mass ratio between the carboxylic end group and the polymer chain combined with a large corona area will result in a low overall charge density for the micellar surface, which is illustrated in Figure 9.1.

Figure 9.1: Schematic representation of a spherical CAE-85 micelle with sodium and calcium cations. The circles determine the core and corona boundaries of the micelle.

The low charge density results in a negligible counterion ion condensation effect for monovalent ions above the CMT as confirmed by the Eisenberg plot and the base titration plot in Chapter 5. Below the CMT almost complete dissociation of the monovalent cations has been observed as can be concluded by the data from the Eisenberg plot, the data from the
∆K plot and the use of Walden’s rule in Chapter 5. Furthermore, it can be seen that the mobility of monovalent cations is strongly influenced by the micelle density in the solution. In a 0.5 wt% CAE-85 solution below the CMT, i.e. when only CAE-85 unimers are present, there is restriction of the mobility of the sodium cations as compared to the situation above the CMT where micelles are present. However, in a 1.0 wt% solution there is a fairly high restriction in mobility (33%) as a result of the presence of CAE-85 micelles. This large difference in behavior is remarkable seen the small difference in surfactant concentration between both situations.

Different experimental results obtained with ITC and conductometry combined with experimental results using ion selective electrodes \(^4\), and modelling results \(^4\) show a clear affinity of multivalent cations for CAE-85 micelles. Binding isotherms are obtained for calcium to CAE-85 with ITC and conductometry, which can be observed in Figure 9.2.

From Figure 9.2 it can be concluded that both techniques result in similar binding isotherms, which confirms the applicability and accuracy of both techniques. Additionally, it can be said that the solubilization of phenanthrene has no large influence on the binding capacity of the CAE-85 micelles, which follows from the UV measurements described in Chapter 7. On the contrary, it is clear that the dissociation degree of the CAE surfactants has a large influence on the binding capacity, because it determines the availability of anionic carboxylic groups.

![Figure 9.2: Comparison of isotherms for the binding of calcium in a 1.0 wt% CAE-85 solution at 50 °C measured with ITC and conductometry.](image-url)
The binding of counterions in the CAE-85 is mainly electrostatic, which can be concluded from the ITC plots of Chapter 4. However, despite the absence of monovalent cation condensation that is caused by the low surface charge density, this surface charge density is high enough for the attraction of multivalent cations. In addition, it is seen that the ability for divalent cations to obtain full coverage of the micelle is difficult, which is mainly because the divalent cation needs two carboxylic end groups to coordinate, i.e. specific binding. This specific binding is not the formation of a strong bidentate, like in polyacrylic acid systems, but a loose ion pair. With an increase in calcium concentration the probability to find two carboxylic end groups close together will decrease and this will reduce the specific binding of the divalent cation. On the other hand, the calcium cation still reduces the effective charge of the micelle, i.e. electrostatic screening.

Furthermore, the effect of salt additives on the behavior of the CMT and the cloud point of surfactants should follow the effects expected from the Hofmeister series. However, for the effect of salt additives on the CMT of CAE-85 surfactant a deviated behavior has been found that can only be explained when there is an interaction between the cations and the ether groups of the surfactant chain. This interaction is larger for multivalent ions as compared to monovalent ions and is not detectable with ITC measurements.

9.3 (Dis)advantages of the use of thermo-reversible surfactants in applications

9.3.1 Dependence of CAE surfactant properties on solution parameters

The properties of a particular surfactant in solution depend strongly on the number, shape and size of the micelles formed in these solutions \[^5\]. The micelles are highly dynamic structures and their behavior is determined by the interactions between surfactants, the interactions of the surfactant with the solvent and the interactions of the surfactant and the solvent with the additives \[^6, 7\]. Therefore, properties like the (pseudo)-phase behavior and sorption capacity for ions and organics are strongly dependent on the solution parameters, like pH, temperature, ionic strength and additive species, as shown in Chapter 4 and 6. Also the physico-chemical parameters, like viscosity and surface tension can change drastically with a change in solution parameters. This dependence on the solution properties of micelles has certain consequences for a possible implementation in a process.
The dynamic nature of the micelle has advantages and disadvantages. An advantage of micellar systems is the flexibility. A wide range of applications can be attained because the micellar system is easy to fine-tune to the desired properties by choosing the right process conditions [8]. At the same time this flexibility is a disadvantage, because when some solution parameters are changing during a process this can have a strong influence on the efficiency of the micellar system regarding its purpose. For thermo-reversible surfactant systems most important will be the influence of the solution properties on the value of the CMT and cloud point and the influence on the binding of counterions.

9.3.2 CAE surfactants versus conventional anionic surfactants
Apart from their thermo-reversible behavior CAE surfactants will behave different in a number of ways as compared to conventional anionic surfactants, like sodium dodecyl sulfate (SDS) [1, 9]. First, the size of the polymeric CAE surfactants and micelles is larger as compared to conventional anionic surfactants, which makes them easier to separate, e.g. using membrane technology. On the other hand, the large size of the CAE surfactant, especially that of the head group, results in a more complicated structure of the micelle and is therefore more difficult to describe and to model. Second, the low CMC (above the CMT) of the CAE surfactants assures a sorption activity at low surfactant concentrations and an increased retention of the surfactant in membrane systems. Third, a very high solubility in water can be obtained in spite of the presence of a high concentration of multivalent (cat)ions. Fourth, as an anionic surfactant with a high polymeric content, CAE surfactants can relatively easy obtain the cloud temperature, above which a phase separation occurs. However, in certain applications this clouding behavior will be an undesired phenomenon. Finally, the polydispersity of the CAE surfactants results in broad (pseudo)-phase transitions and the unknown exact composition of the surfactant makes experimental techniques for quantitative measurements of the concentration difficult.

9.3.3 Ecotoxicity and human toxicology
Surfactants are widely used on a global scale [1, 8]. In Table 9.1 a survey of the global surfactant market is shown. From Table 9.1 it can be concluded that the major part of the surfactants is used in household applications. Consequently, the environmental strain regarding surfactants is mainly caused by household wastewater streams.
In general, the aquatic toxicity of surfactants strongly depends on the nature of the surfactant \cite{10, 11}. Concerning most surfactants a high surfactant concentration in natural waters can lead to fish mortality or can seriously damage the diversity of plant cultures. In case of phosphate containing surfactants biodegradation can lead to eutrophication \cite{10}. However, all surfactants will lower the surface tension of the water, which is disastrous for all living organisms in aqueous environments. The biodegradability of surfactants also depends on the nature of the surfactant \cite{12}. For Pluronic surfactants, and probably for CAE surfactants as well, the biodegradation is slow, which emphasizes the need for regeneration cycles for this type of surfactants.

Table 9.1: Global surfactant market 1999 (Source: I.C.I. Surfactants (Belgium))

<table>
<thead>
<tr>
<th>(*1000) volume metric tons</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Household detergents</td>
<td>4000</td>
</tr>
<tr>
<td>Industrial and institutional cleaning</td>
<td>530</td>
</tr>
<tr>
<td>Personal care</td>
<td>860</td>
</tr>
<tr>
<td>Crop protection</td>
<td>200</td>
</tr>
<tr>
<td>Oilfield</td>
<td>440</td>
</tr>
<tr>
<td>Paints and coatings</td>
<td>160</td>
</tr>
<tr>
<td>Textile spin finish</td>
<td>160</td>
</tr>
<tr>
<td>Textile auxiliaries</td>
<td>500</td>
</tr>
<tr>
<td>Construction</td>
<td>470</td>
</tr>
<tr>
<td>Emulsion polymerization</td>
<td>290</td>
</tr>
<tr>
<td>Food</td>
<td>200</td>
</tr>
<tr>
<td>Leather</td>
<td>60</td>
</tr>
<tr>
<td>Ore/mineral</td>
<td>150</td>
</tr>
<tr>
<td>Plastic additives</td>
<td>40</td>
</tr>
<tr>
<td>Pulp and Paper</td>
<td>120</td>
</tr>
<tr>
<td>Explosives</td>
<td>10</td>
</tr>
<tr>
<td>Other</td>
<td>380</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>8570</strong></td>
</tr>
</tbody>
</table>

Pluronics and CAE surfactants are stable chemicals that are known to have a very low toxicity \cite{13}. However, when humans or animals have frequent contact with these surfactants dissolved in water, it can lead to allergies, skin infections or defatting of the skin \cite{14}. Usually, ionic surfactants tend to be more aggressive in this behavior as compared to nonionic surfactants. Therefore, CAE surfactants probably will be slightly more aggressive as compared to Pluronic surfactants as a result of the anionic end groups.
In some biomedical applications Pluronics are used as a polymer drug carrier for drug delivery devices\textsuperscript{[14, 15]}. The disadvantage of using Pluronic surfactants in these applications is the decrease in time of the surfactant concentration, as a result of the dissolution of the surfactants in the blood circulation stream. Smaller Pluronic surfactants have a higher solubility and are therefore more susceptible for dissolving in the blood than larger Pluronic surfactants. When the surfactant concentration drops below the CMC then suddenly the drug inside the micelles will be released. Additionally, the dissolved Pluronic surfactants in the blood are able to accumulate in the liver and spleen. Overall, a high concentration of Pluronic surfactants in the body is not considered healthy\textsuperscript{[14, 15]}. 

9.4 Synthetic prospects in the future

9.4.1 Modification of Pluronics

In this thesis the modification of three different Pluronic surfactants is reported, i.e. L81, P85 and L64. The synthesis procedure described in Chapter 2 is a general procedure for the modification of a Pluronic surfactant into a CAE surfactant. This provides the opportunity to synthesize CAE surfactants using all surfactants from the Pluronic grid (BASF)\textsuperscript{[5]}, each with different physical and chemical properties.

The critical micellization temperature can be chosen, because it is mainly determined by the length of the PPO block of the Pluronic surfactant, which will not change during the modification reaction\textsuperscript{[2]}. Furthermore, a choice can be made regarding the mass, micellar size, and the balance between hydrophobicity and hydrophilicity. When physico-chemical aspects are more important Pluronics can be chosen with a different behavior in solution viscosity, in surface tension or foaming capacity. In terms of functionality the capacity for cation binding or solubilization of organics will be influenced by choosing the right Pluronic surfactant. Finally, Pluronics are available in three aggregation states, i.e. a liquid, a paste and a solid state, which will not be changed by the modification\textsuperscript{[5]}. The possibilities can be extended by forming mixed micelles using different CAE surfactants, where the properties of both CAE surfactants can be combined in order to provide the desired functionality.
9.4.2 Synthesis of carboxylic acid randomized (CAR) surfactants

The large CAE-85 micelle has a low surface charge density because it has only two carboxylic groups per molecule, while the molecular mass is 4748 g/mol. In theory, more carboxylic groups along the PEO chain could probably increase the surface charge density with as a result that the binding capacity for cations will increase. However, when too many carboxylic groups are present along the chain of the Pluronic surfactant divalent cations will bind irreversibly to the chain and no thermo-reversible binding behavior will be observed. Additionally, higher repulsion forces between the head groups of the surfactant will increase the size of the micelle and, therefore, results in a less compact structure.

During the development of a synthesis procedure for CAE-85, an off-spec batch of CAE-85 has been synthesized that turns out to have a larger affinity for binding cations than a good batch of CAE-85. In the off-spec batch the CAE-85 molecules show a slightly increased content of carboxylic acid groups along the chain, which can be explained as follows.

During the modification the reaction mixture should be absolutely free of peroxides. Two major sources for peroxides can be distinguished in this synthesis procedure. First, the diethyl ether used in the purification step for the Pluronics may contain peroxides after long-term storage. Second, it is known that Pluronic surfactants, which are classified as polyethers, can react with atmospheric oxygen after long-term storage to form peroxide side chains on the secondary and tertiary carbon atoms. Regardless of the origin, the Pluronic surfactants with peroxide side chains (1) can be synthesized to form the so-called carboxylic acid randomized (CAR) surfactants (4), as depicted in Figure 9.3. When compound (1) is heated to a temperature of 90 – 110 °C the peroxide group will decompose to form a radical, i.e. a reactive centre on the carbon atom (2). Addition of maleic anhydride leads to compound (3), where the shifted reactive center will be deactivated by the solvent. When the final product will be dissolved in water the anhydride group will form a CAR surfactant (4). The two carboxylic groups will have a difference in acidity.
In order to obtain carboxylic groups along the Pluronic chains to form compound (1) the addition of a small amount of hydrogen peroxide to the reaction mixture could be an option in the synthesis of CAR surfactants.

9.4.3 Modification of Pluronic surfactants with amine-terminated or sulfonated end groups

The CAE-85 surfactant is the first surfactant that shows thermo-reversible cation binding behavior\(^1\). However, this does not mean that there is no room for improvement in terms of increasing the binding capacity, the binding affinity or exploration of new types of thermo-reversible surfactant systems.

Carboxylic end groups, like the end groups of CAE-85, are known to have a lower affinity for cations than e.g. sulfonate groups. The sulfonate group is more polar than the carboxylic group and it is therefore expected that when a Pluronic surfactant can be modified with sulfonate end groups the binding affinity for cations can be increased. From literature\(^{16}\) a synthesis route is known to obtain a sulfonated Pluronic surfactant like in Figure 9.4. The synthesis procedure for the sulfonated Pluronic consists of more steps as compared to that for CAE-85. The CAE-85 surfactant is an anionic surfactant that can bind cationic counterions. It is a logical step to modify a Pluronic surfactant with cationic end groups to bind anionic counterions. In general, a cationic Pluronic surfactant can be obtained by introducing an amine or amino group into the polymer.
A \[
\begin{align*}
&\text{HO}_2\text{S} \quad \text{EO}_p \quad \text{PO}_q \quad \text{EO}_p \quad (\text{CH}_2)_2 \quad \text{SO}_3\text{H} \\
&\text{B} \\
&\text{H}_2\text{N} \quad \text{EO}_p \quad \text{PO}_q \quad \text{EO}_p \quad (\text{CH}_2)_2 \quad \text{NH}_2 \\
&\text{C} \quad \text{Br(CH}_3)_3\text{N} \quad \text{EO}_p \quad \text{PO}_q \quad \text{EO}_p \quad (\text{CH}_2)_2 \quad \text{N(CH}_3)_3\text{Br}
\end{align*}
\]

Figure 9.4: Chemical structure of (A) a Pluronic surfactant with sulfonated end groups, (B) a Pluronic with amino end groups and (C) a Pluronic with trimethyl amine end groups.

In literature \cite{16} a synthesis procedure is described for the synthesis of an amino terminated Pluronic surfactant (B) and a quaternary amine terminated Pluronic surfactant (C), see Figure 9.4. The quaternary amine end group will bind anions stronger than the amino end group. However, from the described synthesis procedures it follow that the synthesis of the amino terminated Pluronic surfactant involves toxic chemicals like azides, which is clearly a disadvantage when considering scaling up.

9.5 Future applications for CAE surfactants

In recent years more research is focused on the development of ‘intelligent’ thermo-responsive systems in order to obtain a better control of chemical species on a molecular scale \cite{17, 18}. A few examples can be mentioned, like thermo-responsive catalysts \cite{19} that have an enhanced catalytic activity above a certain temperature, providing a strong on/off mechanism for reaction rates, or thermo-sensitive membranes \cite{20} that have a strong temperature dependent retention behavior for specific components. In the following paragraphs some ideas of possible applications for CAE surfactant self-assembly, besides the antiscalant application, will be given to illustrate the potential of the principle.

9.5.1 Thermo-reversible ion exchangers

Ion exchangers are used in a wide range of aqueous applications \cite{21, 22} and it is obvious that CAE surfactants can play a role in the development of future ion exchangers because of the
regeneration by a temperature switch. The only missing part in the development would be the implementation of the CAE surfactant into an ion exchanger unit. The thermo-reversibility of the CAE surfactants functions when the surfactants are dissolved in water and this means that a configuration has to be developed in which a compartment of an aqueous solution of CAE surfactants is ‘immobilized’ in order to retain the surfactant molecules in the ion exchange unit, while the contaminated feed stream should be able to make contact with the CAE micelles in order to exchange ions.

The immobilization of CAE surfactants in beads consisting of a polymeric shell and a core of a CAE surfactant solution can be a way to deal with this problem. The bead should have the property to retain the CAE surfactants within the bead and on the other hand the divalent cations should be able to pass freely through the polymeric shell to bind to the CAE micelles within the bead. The nature of the shell is comparable to an ultrafiltration membrane with a molecular weight cut off in the range of 1000–5000 Dalton. The ‘bead’-concept is schematically depicted in Figure 9.5a.

A second way to develop an ion exchanger based on CAE surfactants is the complete immobilization of the CAE surfactant molecules on a flexible backbone, e.g. on a dendrimer, in such a way that the freedom of the surfactant chain below the CMT is large enough too prevent the binding of divalent cations, while above the CMT the large polymeric chains will cluster in order to form a charged surface that can bind divalent cations. The hydrophobic parts will have the tendency to cluster at temperatures above the CMT and therefore increase the charge density of the region near the surface. In this case a fixed bed configuration can be chosen in which the surfactant loss will be minimized and the pressure drop will be comparable with the pressure drop of conventional ion exchangers. The principle of immobilized CAE diblock surfactants (end group-PEO-PPO) is shown in figure 9.5b. The key success factor for this system is the development of a system that has a low divalent cation binding below the CMT.
9.5.2 Ion exchange in industrial and household applications

Ion exchangers are used in industry to remove ions from aqueous streams for desalination purposes, treatment of waste streams coming from chemical plants and for heavy metal removal. On the household level we can think of using CAE surfactant ion exchangers for softening purposes. Household appliances, like washing machines and dishwashers suffer on the long term from scaling problems due to the hardness of the water. Combining a small ion exchanger within the apparatus can prolong the lifetime of the apparatus significantly. An advantage here is the fact that washing machines and dishwashers already need warm water to operate effectively, just like CAE surfactant ion exchangers. In this case regeneration can be achieved by flushing the ion exchanger with cold tap water.

9.5.3 Simultaneous removal of metal ions and organics by MEUF

Many polluted waste streams not only contain metal ions that have to be removed but also contain organic materials that often are classified as contaminants. Micellar-enhanced ultra
filtration (MEUF) is used to remove either metal ions or organics from aqueous streams. A disadvantage of this way of processing is that a relatively high amount of surfactant is needed, i.e. almost stoichiometric, to obtain an effective removal of the contaminants. Combined with the fact that the binding is irreversible, the process can become expensive. However, in Chapter 7 it is shown that CAE surfactants are able to remove metal ions and organics simultaneously and it is shown that the surfactants can be regenerated by a temperature treatment. Additional advantages of CAE surfactants when applied in MEUF processes are the high molecular weight and the low CMC (at temperatures above the CMT), which decreases the amount of surfactant loss by permeation, even in UF membrane processes.

9.5.4 Drug delivery devices
The interest for drug delivery devices with an external trigger has increased in the past few years. Polymeric micellar systems, including Pluronic surfactants, are also being used as drug carriers for drug delivery systems. In these systems low-frequency ultrasound is used to release the drug from the gel phase that is formed at the specific body temperature and concentration of the Pluronic surfactant. With the development of CAE surfactants that can bind cations and solubilize organics as a function of temperature, one can think of new opportunities for the CAE surfactants in the biomedical field. Especially the temperature dependent bind- and release behavior of ionic components can be useful.

9.5.5 Thermo-responsive membranes
Membrane technology is a separation technology that is based on the separation of molecules by size. In the production of pharmaceutical products an increase in complex syntheses with multiple steps is seen, and consequently the need for tools allowing a separation of molecules with excellent performance in a qualitative and quantitative way will increase too. Examples of membrane technology are known from literature where the charge density of an ionic membrane can be influenced by a change in temperature in order to control the permeation of calcium. The principle of thermo-reversible cation binding can also be used for this purpose. When CAE surfactants are chemically bound to the membrane surface material, e.g. in the way depicted in Figure 9.5b, then the permeation of cations will be influenced strongly by the temperature. Above the CMT the hydrophobic PPO parts will form a layer on the membrane.
surface and the charged end groups of the PEO will be brought closer together, which increases the charge density near the membrane surface. Both aspects will lead to higher calcium retention as compared to the situation below the CMT. Another feature of the immobilized CAE surfactant configuration is the potential to selectively separate hydrophilic molecules from molecules that are more hydrophobic as a function of temperature. When using CAE surfactants with relatively short PEO parts, above the CMT a hydrophobic layer will be created on the membrane surface. This is caused by the PPO part clustering and the layer could retain the more hydrophilic solutes, where the more hydrophobic solutes will permeate more easily through the membrane. Below the CMT this separation between hydrophilic and hydrophobic molecules will be less effective. These applications probably need rather specific membrane designs for each system.

9.6 Conclusions

In this Chapter an overview is given for the results presented in this thesis together with some recommendations for possible applications, opportunities, and potential bottlenecks. First, it can be concluded that CAE surfactants are high molecular weight anionic surfactants that form large, low charged micelles above the critical micellization temperature. This low surface charge density, partly caused by the large and flexible polar parts of the surfactant, is the reason that no stabilization layer of monovalent cations is formed, i.e. no substantial condensation effect is observed. On the contrary, multivalent cations show an electrostatic and (semi) specific interaction with the CAE micelles. The specific interaction is not a strong bidentate complexation but can be classified as a loose ion pair. For studying the behavior of cations in the CAE surfactant system ITC and conductometry were found to be both suitably and complementary.

Second, as any surfactant system the behavior of the CAE surfactant is sensitive to the solution properties or the process parameters. However, the relatively large size of the polymeric CAE micelles makes the surfactants more suitable for the implementation in processes, because of the decreased chance of surfactant loss and increased ease of surfactant regeneration. Additionally, its low toxicity will be an advantage in process applications, but the low biodegradation is a potential drawback.
Third, the variety of thermo-reversible surfactants can be increased e.g. by synthesizing surfactants with a higher binding capacity, with end groups that bind cations stronger or with cationic terminated end groups. The development of synthesis routes for these surfactants has already partly been described in literature.

Finally, the principle of thermo-reversible ion binding and thermo-reversible solubilization provides numerous opportunities for utilization. Ion exchange applications on industrial scale as well as on a household level have the largest potential in the near future. Considering the versatile features of thermo-reversible self-assembly the long-term perspectives of end group modified Pluronic surfactants seem promising.

9.7 References

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About the author

Johan Custers was born on the 1st of December 1976 in Roermond, which is located in the south of the Netherlands. In 1995 he graduated from the Scholengemeenschap Sint Ursula Horn and he continued his career with a study in Chemical Engineering at the Eindhoven University of Technology. His graduation project that is called ‘The optimalization of the synthesis of (S)(+)-propane-1,2-diol’ was performed at two research groups, i.e. at the Applied Organic Chemistry Group and at the Process Technology Group under supervision of prof.dr. L.A. Hulshof and dr. J. Meuldijk, respectively. After he graduated in 2001 he started as a PhD-student in the Process Development Group of prof.dr.ir. J.T.F. Keurentjes on the project called ‘The development of ion selective thermo-reversible polymers’. From the 1st of April 2006 he is employed by Afira Water Technologies in Eindhoven.