The excess Gibbs free energy of adsorption of sodium dodecylbenzenesulfonate on polystyrene particles

Citation for published version (APA):

Tuin, G., & Stein, H. N. (1995). The excess Gibbs free energy of adsorption of sodium dodecylbenzenesulfonate on polystyrene particles. *Langmuir*, 11(4), 1284-1290. <https://doi.org/10.1021/la00004a040>

DOI:

[10.1021/la00004a040](https://doi.org/10.1021/la00004a040)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The Excess Gibbs Free Energy of Adsorption of Sodium Dodecylbenzenesulfonate on Polystyrene Particles

G. Tuin and H. N. Stein*

Laboratory of Colloid Chemistry and Thermodynamics, Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received July 15, 1994. In Final Form: December 28, 1994*

Adsorption of sodium dodecylbenzenesulfonate (SDBS) on polystyrene (PS) particles is described by the Langmuir equation only superficially: on closer look there are small but systematic differences with the experiments. This is expressed here as an excess G function (G^E) of the surfactant electrolyte on adsorption, which changes with increasing degree of occupation of adsorption sites (θ). At low θ values, G^E changes in positive direction with increasing θ ; at large θ values, this trend levels off and may even be in the opposite direction (depending on the value assumed for total saturation of the surface with surfactants). This is explained by changes in adsorption energy of the surfactant chain on the polystyrene surface: at very low θ values the chain is adsorbed in a flat configuration; at larger θ values this is no longer possible, but this is partially compensated by interaction between the hydrocarbon chains of surfactant ions adsorbed on neighboring sites. This explanation is confirmed by the effect of cosurfactant molecules on the adsorption.

Introduction

Adsorption of ionic surfactants has been investigated frequently; see, e.g., refs 1–17. Much attention has been paid to the case of adsorption of surfactants on mineral surfaces, in which ionic interaction between charged groups on the surface and on the surface active ions is important (see, e.g., refs 10–17). Quite different phenomena are expected with regard to the adsorption of ionic surfactants on the surface of a hydrophobic substance such as, e.g., polystyrene, especially when the charges on the surface and on the surface-active ions have the same sign such as to lead to repulsive rather than attractive forces between surface and surfactant. In such cases, nevertheless adsorption on a hydrophobic substance may occur, since the hydrophobic tails of the surfactant are attracted by hydrophobic groups on the polystyrene surface. This is the case discussed here.

Adsorption data of surfactants are, in some cases, interpreted by a Langmuir adsorption isotherm.^{8–10} However, on closer look there are, at least in the cases known to the present authors, small but systematic differences between the data and the linear relation between $1/\Gamma$ and $1/c$ predicted by the Langmuir equation (where Γ is the quantity adsorbed at concentration c in the surrounding liquid).

This has been remarked by Kronberg et al.^{18,19} These authors tried to connect the adsorption of nonionic surfactants with the interactions between surfactant molecules and solvent molecules, in solution and at the solid–liquid interface, expressed as two χ parameters (χ_{solution} and χ_{surface} , respectively). However, in order to obtain manageable equations, the assumption was introduced, that the configuration of the surfactant remains unchanged on adsorption and is independent of concentration in solution and of the degree of occupancy of the surface.

Böhmer et al.^{20–22} calculated the distribution of the adsorbed surfactant on the basis of the Scheutjes–Fleer self consistent field theory.^{23,24} Their treatment of the adsorption of ionic surfactants was restricted to cases in which the first layer of adsorbed surfactants was drawn to the surface primarily by electrostatic attraction (e.g., a cationic surfactant on a negatively charged surface), leading to a two-step adsorption.

However, the application of this theory requires the introduction of a number of interaction parameters, which are obtained as fitting parameters, which makes the application of their theory questionable.

In order to understand the effects observed on adsorption of surfactants, the deviations from the Langmuir equation are expressed here as an excess G -function (G^E) on adsorption. G^E comprises, in principle, all deviations from an idealized adsorption equation. When the idealized adsorption equation does not itself include interactions between the adsorbed molecules or ions (as is the case with the Langmuir equation), G^E includes all entropic and enthalpic effects of interaction between the ions both in the adsorbed state and in the surrounding liquid.

From experimental adsorption data, $(\Delta G^0 + G^E)/RT$ can be calculated, in which ΔG^0 is the change in standard Gibbs free energy on adsorption of the cations and anions of the surfactant. ΔG^0 is, by definition, independent of the degree of occupation of the adsorption sites and of the

* Abstract published in *Advance ACS Abstracts*, February 15, 1995.

(1) Maron, S. H.; Elder, M. E.; Ulevitch, I. N. *J. Colloid Interface Sci.* **1954**, *9*, 89.

(2) Vijayendran, B. R.; Bone, T.; Gajria, C. *J. Appl. Polym. Sci.* **1981**, *26*, 1351.

(3) Maurice, A. M. *J. Appl. Polym. Sci.* **1985**, *30*, 473.

(4) Vijayendran, B. R. *J. Appl. Polym. Sci.* **1979**, *23*, 733.

(5) Piirma, I.; Chen, S. R. *J. Colloid Interface Sci.* **1980**, *74*, 90.

(6) Urban, P. C. *J. Dispersion Sci. Technol.* **1981**, *2*, 233.

(7) Connor, P.; Ottewill, R. H. *J. Colloid Interface Sci.* **1971**, *37*, 642.

(8) Painter, D.; Hall, D. G.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans 1* **1988**, *84*, 773.

(9) Paxton, T. R. *J. Colloid Interface Sci.* **1969**, *31*, 19.

(10) Ali, S. I.; Steach, J. C.; Zollars, R. L. *Colloids Surf.* **1987**, *26*, 1.

(11) Bijsterbosch, B. H. *J. Colloid Interface Sci.* **1974**, *47* (1), 186.

(12) Fuerstenau, D. W. *J. Phys. Chem.* **1956**, *60*, 981.

(13) Gaudin, A. M.; Fuerstenau, D. W. *Trans. Metal Soc. AIME* **1964**, *202*, 958.

(14) Fuerstenau, D. W.; Healy, T. W.; Somasundaran, P. *Trans. Metal Soc. AIME* **1964**, *229*, 321.

(15) Fuerstenau, D. W. *Pure Appl. Chem.* **1970**, *24*, 135.

(16) Goodwin, J. W. *Trans. Br. Ceram. Soc.* **1971**, *70*, 65.

(17) Welzen, J. Th. A. M.; Stein, H. N.; Stevels, J. M.; Siskens, C. A. *M. J. Colloid Interface Sci.* **1981**, *81*, 455.

(18) Kronberg, B. *J. Colloid Interface Sci.* **1983**, *96* (1), 55.

(19) Kronberg, B.; Stenius, P.; Igeborn, G. *J. Colloid Interface Sci.* **1984**, *102* (2), 418.

(20) Böhmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 1594.

(21) Böhmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 2649.

(22) Böhmer, M. R.; Koopal, L. K. *Langmuir* **1992**, *8*, 2660.

(23) Scheutjes, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.

(24) Scheutjes, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 178.

concentration in the solution. The change in $(\Delta G^0 + G^E)/RT$ with θ reflects changes in G^E , expressing deviations from situations assumed as ideal both in solution and in the adsorbed state. In solution, the ideal state comprises absence of interaction between the dissolved ions. For adsorbed ionic surfactants, the most appropriate definition of an ideal state is localized adsorption for the surface-active ions and mobile adsorption for the counterion, again without interaction.

This attack leads us, according to our point of view, as far in analysis of adsorption data as one can get without other assumptions than the basic ones of statistical thermodynamics. The interpretation of the $(\Delta G^0 + G^E)/RT$ vs θ curves thus obtained must however make use of more detailed model assumptions.

In order to fully understand the meaning of the excess Gibbs free energy of adsorption G^E , we give in the theoretical section the derivation of the equations concerned. This appears to us to be especially useful since a combination of localized and mobile adsorption, as discussed here, is not frequently employed.

Theory

The two most simple idealized types of adsorption are localized adsorption and mobile adsorption.²⁵⁻²⁷

From the viewpoint of statistical thermodynamics, they are differentiated by the energy barrier which an adsorbed molecule or ion must pass when moving along the surface from one adsorption site to the next. When this is large compared to the thermal energy of a molecule, localized adsorption is the appropriate model, while the mobile adsorption should be regarded as the ideal for comparing experimental data when this energy barrier is small compared with kT (where k is Boltzmann's constant and T is the absolute temperature); it may even be nonexistent when there are no distinct adsorption sites as is the case, e.g., on a liquid/liquid interface or for an ion in the diffuse double layer. This difference leads to an essential difference in the partition function of a monolayer adsorbed in a localized or in a mobile way, respectively:

A. Localized Adsorption. The partition function of the adsorbed monolayer consisting of m molecules distributed over M sites, can be written as²⁵

$$Q = g(M, m) a(T)^m \quad (1)$$

where $a(T)$ is the partition function for internal degrees of freedom of an adsorbed molecule referred to the lowest internal state of a molecule in the surrounding solution and $g(M, m)$ is the number of distinguishable ways of distributing the adsorbed molecules over the sites. The partition function $a(T)$ can be written as:

$$a(T) = \exp\left(\frac{\chi}{kT}\right) j^s(T) \quad (2)$$

where χ is the minimum energy required to remove a molecule, adsorbed in its lowest energy state, from the surface to the bulk solution and $j^s(T)$ is the partition function for internal degrees of freedom of the molecule including vibrations relative to its mean position.

If the molecules are distributed over the sites at random, $g(M, m)$ is given by

$$g(M, m) = \frac{M!}{m!(M-m)!} \quad (3)$$

Therefore the contribution of the monolayer to the thermodynamic A function (Helmholtz free energy) is given by

$$A = -kT \ln Q = -kT [M \ln M - m \ln m - (M-m) \ln(M-m) + m \frac{\chi}{kT} + m \ln(j^s(T))] \quad (4)$$

and the chemical potential of an adsorbed molecule becomes

$$\mu = \left(\frac{\partial A}{\partial m}\right)_{T,V} = \mu^\square + kT \ln\left(\frac{\theta}{1-\theta}\right) \quad (5)$$

where $\chi + kT \ln j^s(T)$ have been replaced by $\mu^\square$ and θ is m/M , the degree of occupation of the adsorption sites.

When equilibrium is reached, the chemical potential of an adsorbed molecule must be equal to that of the molecule in solution. If there is no interaction between the molecules in solution, this chemical potential is given by $\mu^0 + kT \ln(c)$ (where c is the concentration of the ion). This leads, in the case of localized adsorption, to the Langmuir adsorption isotherm

$$\theta = \frac{c \exp\left(-\frac{\Delta G^0}{RT}\right)}{1 + c \exp\left(-\frac{\Delta G^0}{RT}\right)} \quad (6)$$

where $\Delta G^0 = \mu^0 - \mu^\square$ per mole of surfactant.

Thus, it is seen that the Langmuir adsorption isotherm can be derived without any assumptions with regard to the equality of size of solvent and solute molecules (as proposed by Kronberg¹⁸).

B. Mobile Adsorption. In this case, the formulas are quite similar to those given above, with the important difference that the number of distinguishable ways of distributing m identical adsorbed molecules over the surface is now given by $1/m!$. Thus, in this case the partition function of the adsorbed monolayer becomes

$$Q = \frac{1}{m!} \exp\left(\frac{\chi}{kT}\right) l(T) j^s(T) \quad (7)$$

in which $j^s(T)$ is now the partition function for the internal degrees of freedom of the adsorbed molecule including vibration normal to the surface. The motion of the molecule along the surface is included by $l(T)$, the partition function for translation in two dimensions in an area A , which is given by

$$l(T) = \frac{2\pi m' kTA}{h^2} \quad (8)$$

in which m' is the mass of the adsorbed molecule and h is Planck's constant. This leads to the following expression of the chemical potential of a molecule adsorbed on a surface in mobile adsorption

$$\mu = \mu^0 + kT \ln(\theta) \quad (9)$$

It should be borne in mind that in this case, the standard state for the surface referred to by μ^0 is $\theta = 1$, while in eq 5 it is $\theta = 0.5$. This does not, however, have any consequence on the final equation since the difference is

(25) Fowler, R.; Guggenheim, E. A. *Statistical Thermodynamics*, 2nd Impression; Cambridge University Press: Cambridge, 1956; pp 421-428.

(26) Jaycock, M. J.; Parfitt, G. D. *Chemistry at Interfaces*; J. Wiley and Sons: New York, 1981; p 183.

(27) Ross, S.; Olivier, J. P. *On Physical Adsorption*; Intersciences: New York, 1964; p 8.

a constant term (independent of concentration or degree of occupation of the surface).

On equalizing this to the chemical potential of a dissolved molecule, we obtain a "Henry" type of adsorption isotherm:

$$\theta = c \exp\left(-\frac{\Delta G^0}{kT}\right) \quad (10)$$

Adsorption of an Ionic Surfactant. Thus far, the theory relates to nonelectrolytes. In the present investigation, we are dealing with an ionic surfactant, with a surface active anion, adsorbed from an aqueous solution, on a hydrophobic surface which has, from its preparation, already some negative charges. The theory will be restricted to the case of univalent cations and anions. In this case, adsorbed anions will be fixed with their hydrophobic tails to adsorption sites, while the simultaneously adsorbed cations are present as counterions in the vicinity of the solid where there is nothing like a distinct site. The best model to compare experimental adsorption data with is, in such cases, mobile adsorption for adsorbed cations and localized adsorption for adsorbed anions.

When treating electrolytes such as an ionic surfactant (SDBS), the following changes have to be introduced in eqs 1–10: (a) In solution, the chemical potential of a surfactant molecule (cation + anion) is given by

$$\mu_{\text{cat+an}} = \mu_{\text{cat+an}}^\square + 2RT \ln(x) \quad (11)$$

(b) When we are dealing with an ionogenic surfactant with surface-active anion, the chemical potential of the anion in the adsorbed state can best be described by localized adsorption; in addition, the electrical work has to be taken into account which is necessary to bring an electrically charged group (of charge $-e_0$) to the potential ψ_δ , which is the average potential to which the adsorbed ionic head groups are subjected. Thus, the chemical potential of the adsorbed anion is taken to be described by

$$\mu_{\text{anion}} = \mu_{\text{anion}}^\square + RT \ln\left(\frac{\theta}{1-\theta}\right) - e_0 N_{\text{av}} \psi_\delta \quad (12)$$

where N_{av} is Avogadro's constant. (c) The adsorption of the cation is taken to be mobile. In addition, the adsorbed cation (electrical charge e_0) should be brought to the potential ψ_{average} , which is the average potential to which a counterion is subject in the electrical double layer. This leads to

$$\mu_{\text{cation}} = \mu_{\text{cation}}^\square + RT \ln(\theta) + e_0 N_{\text{av}} \psi_{\text{average}} \quad (13)$$

The chemical potential of the adsorbed electrolyte (cation + anion) becomes

$$\mu_{\text{cat+an,ads}} = \mu_{\text{cat+an,ads}}^\square + RT \ln\left(\frac{\theta^2}{1-\theta}\right) - e_0 N_{\text{av}} (\psi_\delta - \psi_{\text{average}}) \quad (14)$$

However, since the electrostatic terms are dependent upon the surface charge and therefore on the degree of occupation, θ , of the adsorption sites, it is more consequent to include them in G^E , the excess Gibbs free energy of adsorption. This takes into account all deviations from an adsorption determined by chemical potentials described by eq 11 for the dissolved electrolyte and by

$$\mu_{\text{cat+an,ads}} = \mu_{\text{cat+an,ads}}^\square + RT \ln\left(\frac{\theta^2}{1-\theta}\right) \quad (15)$$

for the adsorbed electrolyte.

The adsorption is thus determined thermodynamically by the equation

$$\mu_{\text{cat+an,dissolved}}^\square + 2RT \ln(x) = \mu_{\text{cat+an,ads}}^\square + RT \ln\left(\frac{\theta^2}{1-\theta}\right) + G^E \quad (16)$$

in which G^E takes into account interactions between the ions, both in the solution and in the adsorbed state, including the electrostatic interaction between the head groups of the surfactant mutually, between the counterions mutually, and between the counterions and the head groups.

By doing so, one can calculate the quantity

$$\frac{(\Delta G^0 + G^E)}{RT} = 2 \ln(x) - 2 \ln(\theta) + \ln(1-\theta) \quad (17)$$

from an experimentally known relationship between the concentration in the solution (x) and the degree of occupation of adsorption sites (θ). The concentration in the solution x is expressed here as the fraction of positions in the surrounding liquid, which is occupied by solute. ΔG^0 is, by definition, independent of the concentration in solution of the degree of occupation, θ , of the adsorption sites.

The question may be asked whether a Volmer type of adsorption isotherm²⁸ would not be more appropriate in the case at hand. This type of equation is employed in cases of mobile adsorption when the amount of adsorbate which can be accommodated at an interface is limited by the size of the entity to be adsorbed, corresponding with an expression for the partition function for translation in two dimensions in an area $A - mA_0$

$$l(T) = \frac{2\pi m' kT (A - mA_0)}{h^2} \quad (18)$$

instead of eq 8. A_0 is the minimum surface area which must be available for a molecule to be adsorbed.

However, in the case at hand, in which we apply a mobile adsorption equation to the cations of an anionic surfactant, the quantity of cations which can be adsorbed is indeed limited, but not by the size of the cations. The restriction is imposed by the electrostatic charge on the cations: no more cations can be adsorbed than the sum of the negative anionic groups on the surface and the adsorbed anions because this would violate electroneutrality. Such a restriction is imposed by electrostatic potential considerations and thus is included in G^E . Inclusion of the restriction by means of an area A_0 would correspond with an incorrect expression for the entropy of the adsorbed cations.

Recently, Oh and Shah²⁹ reported that the size of a counterion may limit the distance between adsorbed surface active ion, as shown by differences in area per adsorbed surfactant molecule at maximum surface coverage, between Li, Na, K, and Cs dodecyl sulfates. This should, however, not be taken as an argument for assuming localized adsorption for the counterions. In

(28) Aveyard, R.; Haydon, D. A. *An Introduction to the Principles of Surface Chemistry*; Cambridge Chemistry Texts: Cambridge, 1973; p 22.

(29) Oh, S. G.; Shah, D. O. *J. Phys. Chem.* **1993**, *97*, 284.

Table 1. Characterization of the PS Latex Used

latex	D_n (nm)	D_s (nm)	D_v (nm)	P_n	σ_0 ($\mu\text{C}/\text{cm}^2$) ^b
L-78 ^a	669	690	701	1.05	8.63

^a The particle size was determined by a Coulter LS-130.³² ^b The surface charge density was determined by conductometric titration.⁴⁰

solution, below the critical micelle concentration, the deviations from ideal behavior agree with reasonable accuracy with the predictions of the Debye-Hückel theory,³⁰ and even in micelles, where part of the counterions move (e.g., in electrophoresis) with the surface active ions,³¹ a considerable part of the counterions is not bound, which suggests that the shift of a bound counterion from one adsorption site to the next is a process of low activation energy compared with kT . The best way to combine this evidence with the findings of Oh and Shah²⁹ is to assume that at high degree of coverage groups of surface active ions adsorbed on adjacent sites create a pronounced local potential; additional surface active ions can then only be adsorbed on a neighboring site when the local potential is partially shielded by the nearby presence of counterions. Since this effect is typical of a matter of mutual influence between adsorbed ions, it is incorporated in the theory presented here in G^E . The findings of Oh and Shah²⁹ should be incorporated only by their influence on the surface area per adsorbed molecule at maximum surface coverage.

Experimental Section

Materials. Sodium dodecylbenzenesulfonate (SDBS), ex. Albright and Wilson (Nansa 1260, 25% (w/v) in water), was used without further purification. Surface tension (γ) measurements showed no minimum in the γ vs concentration curves, indicative for the absence of surface active impurities.

Water was twice distilled using an all-glass apparatus.

PS Latex. The preparation and characterization of the latex is described elsewhere.³² The diameter of the latex particles used (latex L-78) was measured shortly before use. In Table 1 the properties of this latex are given: number average diameter (D_n), surface average diameter (D_s), volume average diameter (D_v), degree of polydispersity ($P_n = D_v/D_n$), and the surface charge density (σ_0).

Determination of Solids Content. The solids percentage of the different PS latices were determined by drying a known amount of the latex in an oven at 105 °C, until constant weight was reached.

Procedure of the Surface Tension Measurement. Surface tension measurements were performed using a Krüss K10T automatic tensiometer (Krüss GmbH, Hamburg) equipped with a Du Nouy ring. Before the measurements the glass vessel (diameter 4 cm, height 2 cm, ground upper edges) was cleaned using chromic acid and washed with twice distilled water. The dry vessel was then heated in the gas flame of a Bunsen burner. During a measurements series the Du Nouy ring was also heated in a gas flame between measurements.

After addition of 20.0 g of PS latex to the glass vessel and a 10 min wait for thermal equilibrium, the surface tension was measured twice. Then 0.5 mL of 0.03 M SDBS solution in water was added and after 10 min the surface tension was measured. This procedure was repeated until the critical micelle concentration (cmc) was reached (the point where further addition of SDBS solution effects only a very slight surface tension decrease). All surface tension measurements were performed at 22 °C.

Supernatant Titration. For the supernatant titration the latex was centrifuged for 4 h at 20000 rpm in a Centrifon T-2060

Figure 1. Surface tension (γ) versus concentration SDBS in the water phase for two different supernatant titrations: ●, 3.6% solids; ■, 11.8% solids. The drawn lines are the Szyszkowski fits for the two different titrations.

centrifuge (Kontron Instruments, Italy). The supernatant titration was carried out as described for dispersions containing PS particles.

Results and Discussion

Adsorbed amounts of surfactant are calculated from surface tension measurements on addition of SDBS ("titration") to latices containing various amounts of PS. On adding SDBS to a latex the surface tension (γ) decreases as more SDBS solution is added (see ref 33, Figure 1). This decrease continues up to the point where further addition of SDBS solution results in a much smaller decrease in surface tension (the critical micelle concentration, cmc). In the presence of a larger solids percentage of PS particles, a larger amount of SDBS-solution has to be added to reach the cmc.

Similar titrations were performed on supernatant solutions obtained on centrifugation of latices. In Figure 1 two typical supernatant titration are shown. In this case the surface tension is plotted versus the concentration of SDBS in the water phase. The concentration of SDBS in the water phase was calculated from the added amount of SDBS solution to the sample cell. Because of the small surface area of the measuring vessel, the amount adsorbed at the water-air interface can safely be ignored.

Interpolation between the measured data is effected by adjusting the data to the Szyszkowski equation.³⁴ This equation relates the surface tension to the concentration of surfactant in the water phase:

$$\gamma - \gamma_0 = \sqrt{2RT} \Gamma^\infty \ln\left(\frac{c + a}{a}\right) \quad (19)$$

where γ is the surface tension at a certain concentration of SDBS in the water phase, γ_0 is the surface tension at concentration 0 of SDBS in the water phase, R is the gas constant, T is the temperature, c is the concentration of SDBS in the water phase, a is a constant, and Γ^∞ is the maximum surface excess of SDBS.

Szyszkowski made the assumption, based on empirical data, that the equation is only valid below the cmc for uncharged particles.

It appeared however, that the Szyszkowski equation has a broader validity. The equation is used by Rosen and Aronson³⁵ for alcohol and anionic surfactant, by

(30) Clayfield, E. J.; Matthews, J. B. *Proceedings of the 2nd International Congress of Surface Activity. Gas/liquid and liquid/liquid interface*; Butterworths Scientific Publications: London, 1957; p 172.

(31) Stigter, D.; Mysels, K. J. *J. Phys. Chem.* **1955**, *59*, 45.

(32) Tuin, G.; Peters, A. C. I. A.; Diemen, A. J. G. van; Stein, H. N. *J. Colloid Interface Sci.* **1993**, *158* (2), 508.

(33) Tuin, G.; Stein, H. N. *Langmuir* **1994**, *10* (4), 1054.

(34) Von Szyszkowski, B. *Z. Phys. Chem.* **1908**, *64*, 385.

(35) Rosen, M. J.; Aronson, S. *Colloids Surf.* **1981**, *3*, 201.

Figure 2. Adsorption isotherm for SDBS on latex L-78: ●, 3.6% solids; ○, 7.6% solids; ■, 11.8% solids.

Figure 3. Langmuir plot for the adsorption of SDBS on latex L-78: ●, 3.6% solids; ○, 7.6% solids; ■, 11.8% solids.

Müller³⁶ for cationic surfactants and Kegel et al.³⁷ for the system brine, anionic surfactant, alcohol, and cyclohexane. They all obtained good results in using the equation to describe their data. In the present investigation the fitting of the equation was performed using a least-squares method, in the same way as was done by Müller.³⁶

As can be seen from Figure 1 the Szyszkowski equation fits the data very well. There is, however, a small difference between the two supernatant titrations. Therefore supernatant titrations have been performed for the different solids percentages used.

Using the Szyszkowski equation, it is possible to calculate, on the basis of these data, the adsorption isotherm for adsorption of SDBS on PS. This is shown in Figure 2 for the different solids percentages used.

This isotherm is found, on closer look, not to conform to the Langmuir equation. This equation can be written as:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma^\infty} + \frac{1}{k_L \Gamma^\infty} \left(\frac{1}{c} \right) \quad (20)$$

where k_L is an adsorption/desorption constant (equal to $\exp(-\Delta G^0/RT)$ in eq 6). Equation 20 thus corresponds to a linear relation between $1/\Gamma$ and $1/c$.

As can be seen from Figure 3, this is certainly not the case. At low concentrations we observe a lower surface excess than expected from a best fit straight line through

Figure 4. Calculated $(\Delta G^0 + G^E)/RT$ as function of θ for $\Gamma^\infty = 1.5 \times 10^{-6}$ mol/m²: ●, 3.6% solids; ○, 7.6% solids; ■, 11.8% solids.

Figure 5. Calculated $(\Delta G^0 + G^E)/RT$ as function of θ for $\Gamma^\infty = 1.25 \times 10^{-6}$ mol/m²: ●, 3.6% solids; ○, 7.6% solids; ■, 11.8% solids.

the experimental data points, whereas at higher concentrations we observe a higher surface excess.

In order to understand this picture, the same data points were used to calculate $(\Delta G^0 + G^E)/RT$ of the adsorption of SDBS from solution on the basis of eq 17. In order to calculate θ , a value for the maximum surface excess has to be assumed. We used, in the first place, the value of 1.5×10^{-6} mol/m². This value was calculated on the basis of an adsorption area of a SDBS molecule of $55 \text{ \AA}^2$.³³ In Figure 4 the change in Gibbs free energy $((\Delta G^0 + G^E)/RT)$ as function of θ is shown for $\Gamma^\infty = 1.5 \times 10^{-6}$ mol/m².

It is found that $(\Delta G^0 + G^E)/RT$ is dependent on θ : at low θ values, it is decidedly larger in absolute value than at high θ values. The exact form of the curve in Figure 4 depends on the value assumed for the value of Γ^∞ used in the calculation. Thus, Figure 5 shows a similar graph based on $\Gamma^\infty = 1.25 \times 10^{-6}$ mol/m². The effect of $(\Delta G^0 + G^E)/RT$ being strongly negative at low θ values remains. A similar course of $(\Delta G^0 + G^E)/RT$ as a function of θ can be calculated from adsorption data of surfactants reported by, e.g., Kusters,³⁸ Ali et al.,¹⁰ and Böhmer et al.²⁰

Paxton⁹ found deviations in the Langmuir plot of adsorption of ionic surfactant (SDBS) on PS particles in absence of salt, similar to those reported here. At low concentrations of surfactant in the aqueous phase, Paxton observed a larger adsorption area than expected from the Langmuir plot. An explanation, however, was not given.

Painter⁸ reported the adsorption of sodium hexadecyl sulfate on PS particles in the presence of 10^{-4} mol/L NaBr. He divided the adsorption isotherm into two regions: at

(36) Müller, A. *Colloids Surf.* **1991**, *57*, 219.

(37) Kegel, W. K.; van Aken, G. A.; Bouts, M. N.; Lekkerkerker, H. N. W.; Overbeek, J. Th. G.; de Bruyn, P. L. *Langmuir* **1993**, *9*, 252.

(38) Kusters, J. H. M. Ph.D. Thesis, 1994, p 102.

low concentrations of surfactant (up to ca. 8×10^{-5} mol/L) the adsorption could well be described by a Langmuir adsorption isotherm, whereas at higher concentration a linear relationship between concentration of surfactant and surface excess was obtained. In the first part of the adsorption a large adsorption area for the surfactant was found. This value was comparable to the adsorption area of a surfactant molecule lying flat on the polymer surface.

Ali et al.¹⁰ reported the adsorption of a nonionic surfactant (octaphenoxyethoxylate, with 18 ethylene oxide units per molecule) on PS particles. Their Langmuir plot showed the same kind of deviations as reported here. This behavior was attributed to the driving force of adsorption, as was given by Kronberg¹⁸ and Kronberg et al.¹⁹ From thermodynamical analysis, they stated that a large part of the driving force of adsorption was due to replacement of a large number of surfactant–water interactions by surfactant–surfactant interactions. A minor part of the driving force was attributed to the replacement of surface–water contacts by surface–surfactant contacts.

However, Kronberg et al.^{18,19} supposed that the configuration of the adsorbed surfactant is independent of surface coverage and concentration. This can only be defended as a first-order approximation. Kronberg discusses the possibility that the surfactant is adsorbed in a flat configuration along the PS surface. This model is equal to the one proposed here at low θ values.

Our data clearly indicate that $(\Delta G^0 + G^E)/RT$ changes in the positive direction with increasing θ . This differs fundamentally from the phenomena reported by Fuerstenau et al.,^{12–15} in which a rapid increase of the adsorption above a certain surfactant concentration was found corresponding with hemimicelle formation. This would show up in a change of $(\Delta G^0 + G^E)/RT$ in the negative direction; this is found in the case discussed here only at large θ values.

Since ΔG^0 is, by definition, independent of θ , the variation of the quantity $\Delta G^0 + G^E$ with θ must be due to variations in G^E .

In G^E are included all effects due to interactions between the ions, both in solution and between adsorbed ions. The interactions between the ions in solution can, in the concentration range concerned, be described with reasonable precision by the Debye–Hückel equation which predicts that they are negligible (activity coefficients ranging between 1 and 0.95). The course of $(\Delta G^0 + G^E)/RT$ as a function of θ then should be ascribed to interaction between adsorbed ions.

There are two possible explanations, as far as we see: (a) The presence of negative ions on nearby sites effects an electrostatic repulsion on the ionic head groups of surfactant anions to be adsorbed; at high θ values, this is compensated by an attractive interaction between the hydrocarbon tails of adjacent surfactant ions. (b) At very low θ values, the hydrophobic tail of a surfactant ion is adsorbed onto the surface in a flat configuration, leading to a large (negative) adsorption energy which is equivalent to $\Delta G^0 + G^E$ being negative, but large in absolute sense. Adsorption in a flat configuration is no longer possible when many neighboring sites are already occupied by other surfactant ions. This leads to a decrease in absolute sense of $\Delta G^0 + G^E$ with increasing θ .

Of these, the electrostatic interactions between the adsorbed ions are accounted for by the term $-N_{ave_0}(\psi_\delta - \psi_{average})$ (eq 14). This term can be estimated on the basis of the Gouy–Chapman equation, assuming that the head groups of the chemisorbed anions form a kind of Stern plane while the counterions are in the diffuse part of the double layer. Thus, the potential ψ_δ is assumed to be that corresponding to a surface charge $-e_0\theta n_{sites}$, where n_{sites}

is the number of adsorption sites per unit surface area. This leads to³⁹

$$\sigma_0 = \epsilon_0 \epsilon_r \left(\frac{d\psi}{dx} \right)_{x=0} = \sqrt{2n_\infty kT \epsilon_0 \epsilon_r} \left(\exp\left(-\frac{ze_0\psi_\delta}{2kT}\right) - \exp\left(\frac{ze_0\psi_\delta}{2kT}\right) \right) \quad (21)$$

where ϵ_0 is the permittivity of the vacuum, ϵ_r is the relative permittivity, k is Boltzmann's constant, σ_0 is the surface charge density, and n_∞ is the concentrations of ions in mol/m³. From eq 21, ψ_δ can be explicitly formulated as

$$\psi_\delta = -\frac{2kT}{e_0} \ln(a + \sqrt{a^2 + 1}) \quad (22)$$

in which

$$a = \frac{\sigma_0}{2\sqrt{2n_\infty kT \epsilon_0 \epsilon_r}} \quad (23)$$

The average potential, to which the counterions are subject, is calculated from the Gouy–Chapman theory, by

$$\psi_{aver} = \frac{\int_{x=0}^{\infty} \psi dn}{\int_{x=0}^{\infty} dn} \quad (24)$$

where x is the distance from the plane of the head groups of the adsorbed anions and

$$n = n_\infty \exp\left(\frac{-ze_0\psi}{kT}\right) \quad (25)$$

Using formulas (24) and (25), this leads to

$$\psi_{aver} = \frac{kT}{ze_0} - \psi_\delta \frac{\exp\left(-\frac{ze_0\psi_\delta}{kT}\right)}{1 - \exp\left(-\frac{ze_0\psi_\delta}{kT}\right)} \quad (26)$$

In this expression, z is the valency of the counterion (sign included). Thus the argument of the exponential function is always >0 : if the negative ions are chemisorbed, then ψ_δ is <0 , while z is >0 ; with the minus sign before the quotient in the exponent, the argument as a whole becomes >0 . In the experimental conditions used in the present investigation, the absolute value of ψ_δ always is large enough to lead to

$$\psi_{aver} \approx \frac{kT}{ze_0} + \psi_\delta \quad (27)$$

in which again z is the valency (sign included) of the counterion.

It should be noted that the assumptions underlying the Gouy–Chapman theory are too strict for the case at hand. Especially the assumptions of the situation of the negative charges of the ionic headgroups of the adsorbed surfactant anions and of the sulfate groups on the PS surface, arising from the initiator, in one plane are not strictly applicable. However, even in the absence of surfactant, negative zeta-potentials larger (in absolute sense) than 60 mV have

(39) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*, 2nd ed.; Marcel Dekker, Inc.: New York, 1986; p 700.

been observed for the PS latex used here.⁴⁰ Thus, the absolute value $(\psi_\delta)^{1/2}$ will be ≥ 60 mV. If we introduce this in eq 26, we find that the value of $((ze_0(\psi_\delta - \psi_{\text{aver}}))/kT)$ can only vary between 1.10 and 1. Thus variations in this quantity can only account for a small part of the variation of $(\Delta G^0 + G^E)/RT$ with θ .

This means, that at the θ values found in this investigation, the electrostatic term can only partially be held responsible for the dependence of $\Delta G^0 + G^E$ on θ calculated from the experimental data. Thus, an important part of the change of $\Delta G^0 + G^E$ at θ values < 0.5 must be due to decrease in interaction energy of the surfactant anion to be adsorbed, with the polystyrene surface. This can be understood as arising from prevention of adsorption of surfactant molecules in a flat configuration along the PS surface with higher θ values.

The question may be raised why the attractive interaction between neighboring chains becomes predominant only at large θ values. This can be understood from the counteracting effect of freedom of movement of the adsorbed hydrocarbon chains when not bound directly to an adjacent hydrocarbon chain; only at large θ values are the chains so much limited in their movement that the attractive interaction prevails. This effect is analogous to the attractive interaction between dissolved surfactant molecules leading to micelle formation at large concentrations only. In the case of adsorbed surfactant ions, this effect will be strengthened, because at large θ values the surfactant chains will contact the polystyrene surface with their final CH_3- group only (if the explanation offered here for the dependence of $\Delta G^0 + G^E$ on θ is right); this leads to a large contact zone with an adjacent hydrocarbon chain.

The change of $(\Delta G^0 + G^E)/RT$ in the negative direction at large values of θ is analogous to the hemimicelle

formation observed by Fuerstenau et al. in the case of adsorption of ionic surfactants on mineral surfaces (refs 12–15).

Nevertheless, there is a net electrostatic repulsion between adsorbed surfactant ions, since $-e_0(\psi_\delta - \psi_{\text{average}})$ is > 0 . Thus, on simultaneous adsorption of a cosurfactant which has an attractive energy with the surfactant's hydrocarbon chain but no electrostatic repulsion with its head group, the adsorption of the surfactant itself is stimulated.³³

Thus, the increase of surfactant adsorption in the presence of a cosurfactant supports the explanation of the $(\Delta G^0 + G^E)/RT$ vs θ curve given here. In addition, this model agrees with calculations by Böhmer and Koopal^{20–22} on the distribution of surfactant segments in the vicinity of a solid surface, although the surfaces considered by these authors differ significantly from those investigated in the present study.

Conclusions

G^E , the excess change of the Gibbs free energy of adsorption of an ionic surfactant, is calculated here as comprising all effects of interaction between adsorbed ions and between ions in solution. As starting point, localized adsorption is assumed for the surface-active ion, while mobile adsorption is assumed for the counterion.

G^E is found to significantly depend on the degree of occupation, θ , of the adsorption sites. This dependence can be understood as indicating negative adsorption energy, large in absolute sense, at very low θ values, corresponding with adsorption of the surface-active ion on the surface in a flat configuration. At higher θ values, this is not longer possible and the absolute value of the adsorption energy decreases, corresponding to a change from a flat to a more dense configuration.

LA940560+

(40) Tuin, G.; Senders, J. H. J. E.; Stein, H. N. To be submitted for publication.