Electric field enhanced coalescence for intensified entrainment reduction
Barega, E.W.

DOI:
10.6100/IR759336

Published: 01/01/2013

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 author's 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

Citation for published version (APA):

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.

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Electric field enhanced coalescence for intensified entrainment reduction

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven,
op gezag van de rector magnificus prof.dr.ir. C.J. van Duijn,
voor een commissie aangewezen door het College voor Promoties, in het
openbaar te verdedigen op woensdag 16 oktober 2013 om 16:00 uur

door

Esayas Wolde Barega

geboren te Addis Ababa, Ethiopië
This was an ISPT (Institute for Sustainable Process Technology) project

Electric field enhanced coalescence for intensified entrainment reduction
Barega, Esayas W.
ISBN: 978-90-386-3450-0

A catalogue record is available from the Eindhoven University of Technology Library

Copyright © Esayas W. Barega, The Netherlands, 2013
All rights reserved
Printed by Gildeprint, Enschede, The Netherlands
Summary

Intensification of industrial extraction processes is a challenging task because of the interaction between the mass transfer and phase separation steps. Small droplets are required to increase the mass transfer and are obtained by increasing the energy input during mixing. However, small droplets are difficult to separate and can be easily entrained by the continuous phase. Entrainment results in a loss of valuable chemicals, a decrease in product purity and capacity, and accumulation of unwanted impurities in the product stream. Thus, the optimal condition for liquid-liquid extraction is a tradeoff between good mass transfer and good separation. Nevertheless, this challenge can be overcome by increasing the size of droplets before the separation step.

The main goal of this research is to intensify the separation of the dispersed phase and decrease entrainment for two industrial liquid-liquid extraction systems, i.e., caprolactam-toluene-water and ethyl benzene (EB)-α-methyl benzyl alcohol (MBA)-water by electric field enhanced coalescence.

The thesis starts with an overview of entrainment, entrainment reduction technologies, and bulk extraction processes (Chapter 1). As the next step (Chapter 2), a static-mixer settler setup was developed and constructed for entrainment quantification. Later an electric field was incorporated in a static-mixer pipe to increase the size of droplets by coalescence and to reduce entrainment. Moreover, different drop size measurement techniques have been investigated to measure the drop size created in a static-mixer with and without the application of electric field. The photography method was selected based on its accuracy, simplicity of applicability in the setup, and cost.

With the experimental setup in place, entrainment was determined for the two systems, i.e., caprolactam-toluene-water and EB-MBA-water with and without electric field. In both systems, the aqueous phase was dispersed in the organic phase. Therefore, the dispersed phase entrainment was determined by measuring the total water content and subtracting the physical solubility.

**MBA-EB-water system**

This ternary system represents part of the industrial propylene oxide styrene monomer (POSM) process. The key process step of interest to this work is the caustic wash step, which involves the removal of phenols from the major EB-MBA organic stream. The caustic wash is carried out in a static-mixer and this is followed by phase separation in a separation drum. The main issues are the long...
residence time in a separation drum, which results in the loss of propylene oxide (PO) and the mutual entrainment of phases due to incomplete separation, i.e., salty water effluent in the organic phase and parts of the EB-MBA stream in the aqueous phase.

As the first step, physical properties (density, viscosity, interfacial tension and water solubility) were determined for the ternary MBA-EB-water system (Chapter 3). This is done to identify the component in the ternary system that governs the mass transfer and phase separation. It was found from these measurements that the concentration of MBA is the major factor influencing all the properties measured. The water solubility, the density, and the viscosity increased notably at higher concentrations of MBA; while, the interfacial tension decreased strongly.

In the next step, the entrainment was quantified for the ternary system in a static-mixer settler setup (Chapter 4). The role of MBA concentration (20% v/v versus 33% v/v MBA in EB), flow rate of the organic continuous phase (54-96) L/hr, phase ratio (5,10,20 % v/v), and temperature (20,30,40)°C on entrainment was investigated. All process variables were found to have a considerable influence on the amount of entrainment. The drop size decreased and the entrainment increased from 600 ppm to 2785 ppm as the MBA concentration changed from 20% v/v to 33% v/v. For the MBA-EB-water system, the major part of the total entrainment (including water solubility) resulted from the physical solubility, which changed from 4600 ppm at 20% v/v to 9300 ppm at 33% v/v MBA concentration. At higher temperatures, the drop size increased and consequently entrainment decreased. Moreover, the entrainment was found to increase at higher phase ratios.

Subsequently, an electric field was incorporated to reduce entrainment (Chapter 5). The influence of electric field strength (0.4 versus 1) kV/cm and type (DC/AC square wave), frequency of the square wave (0-100) Hz, flow, temperature (20,30,40)°C, and phase ratio (5,10,20 % v/v) was investigated. By applying a DC field of 0.4 kV/cm, the entrainment could be reduced from 2785 ppm to 1025 ppm. The entrainment decreased further to 628 ppm by increasing the field strength to 1 kV/cm. The AC field was more efficient than DC field and the entrainment reduction was frequency dependent with lower frequencies of 3-10 Hz being the optimum. The entrainment decreased at higher temperature while better entrainment reduction efficiencies were obtained at lower phase ratios of 5% v/v and 10% v/v compared to 20% v/v.
Caprolactam-toluene-water system

The caprolactam-toluene-water ternary system is part of the industrial caprolactam production process. Various synthesis routes have been developed for caprolactam production with cyclohexanone oxime as the main intermediate. The cyclohexanone oxime is first formed by the reaction of cyclohexanone and hydroxylamine. This is followed by the Beckmann rearrangement of cyclohexanone oxime to caprolactam. Afterwards, caprolactam is recovered from the neutralized Beckmann rearrangement mixture by phase separation followed by extraction of the resulting crude caprolactam phase using an organic solvent (forward extraction) and back extraction with water.

In the extraction step, a rotating disc contactor (RDC) column is usually employed. Drop size is a key variable influencing both mass transfer and hydrodynamics of this column. Small drop sizes provide large interfacial area and higher mass transfer rates resulting in a smaller column size. However, the capacity of the column depends on to what extent these small drop sizes are present and specifically their entrainment by the continuous phase. During the extraction step, while extracting the aqueous-caprolactam phase with toluene in an RDC column, entrainment of the aqueous phase into the organic solvent phase occurs as a result of using a high agitation speed, a high flux of the dispersed and continuous phases, and the reduction of interfacial tension of the two phases at a higher caprolactam concentration.

As a first step, entrainment was quantified in a static-mixer settler setup to identify process conditions which lead to high entrainment and to have reference for entrainment reduction using electric field (Chapter 4). The influence of caprolactam concentration (5.35% w/w versus 28.5% w/w), flow rate of the organic continuous phase (54-96) L/hr, phase ratio (5,10,20 % v/v), and temperature (20,30,40)°C on entrainment was investigated. By increasing the caprolactam concentration from 5.35% w/w to 28.5% w/w, the drop size decreased and the entrainment increased from less than 200 ppm to 1373 ppm. In contrast to the MBA-EB-water system, the entrainment increased at higher temperatures. Additionally, the entrainment for the caprolactam-toluene-water system increases between a phase ratio of 5% v/v and 10% v/v phase ratio and then decreases again at a phase ratio 20% v/v.

In the next step, the electric field was applied to reduce entrainment (Chapter 5). The effect of electric field strength (0.4 versus 1) kV/cm and type (DC/AC square wave), frequency of the square wave (0-100) Hz, flow, temperature (20,30,40)°C,
and phase ratio (5,10,20)% v/v on entrainment reduction was studied. Improved entrainment reduction was obtained by increasing the electric field strength. By applying a DC field of 1 kV/cm the entrainment was reduced from 1373 ppm to 275 ppm. The AC field was found to be more efficient than DC field. For an AC field, the entrainment reduction was frequency dependent with the optimal values of 3-10 Hz. In contrast to the MBA-EB-water system, better entrainment reduction was obtained at 20°C. The entrainment reduction efficiency increased between a phase ratio of 5% v/v and 10% v/v, and decreased again at a phase ratio of 20% v/v.

Since the industrial extraction process of caprolactam is carried out using a rotating disc contactor (RDC), a technical feasibility study was performed in a pilot scale rotating disc contactor (RDC) column (Chapter 6). The electric field is incorporated in the RDC by integrating the electro-coalescer at the outlet of the organic continuous phase. The electro-coalescer consists of a glass tube with electrodes, and a small settler to remove the coalesced drops by electric field. Reference experiments were performed to investigate the influence of process variables such as caprolactam concentration in the aqueous phase (5.35% w/w versus 28.5% w/w), total flux, and solvent to feed ratio (S/F) on entrainment. All studied process variables resulted in a small amount of entrainment less than 600 ppm. Thus entrainment was increased to 2425 ppm by lowering the column top settler outlet and by increasing the caprolactam concentration to 39.2% w/w. The difference in entrainment downstream of the electro-coalescer with and without the application of the electric field was small (187 ppm without electric field compared to 62 ppm with the application of electric field) due to droplet deposition in the electro-coalescer tube. However, the entrained drops increase size in the presence of electric field which indicated the potential of the technology to be successful in an RDC column.

Finally, a model to determine the influence of frequency was developed combining the electrostatics based on the lossy capacitor model and the population balance model (Chapter 7). This model takes into account the electrical and as well as physical properties of the dispersion and insulation material. The developed model was validated by the measured drop sizes with and without electric field for the caprolactam-toluene-water system for two different flowrates. The model adequately describes the measured drop sizes for the two flowrates within 10%. Thus, the developed model can be used as a useful tool during scale-up and design of an electro-coalescer to predict the optimal operating settings when either the design or the electrical properties of the dispersion and insulation change.
General conclusion and outlook

It can be concluded from this research that electric-field enhanced coalescence is an interesting technology to intensify entrainment reduction. The potential of the technology was demonstrated in a laboratory scale static-mixer settler setup for two extraction systems. Efforts to the successful implementation of the technology at an industrial scale was illustrated by performing a technical feasibility study on a pilot scale rotating disc contactor (RDC). Although promising results were obtained with regard to the observation of drop size increase by integrating electro-coalescer at the outlet of the continuous phase, further research is needed to demonstrate this improvement in terms of considerable entrainment reduction.
# Table of contents

Summary........................................................................................................................................... i  

Chapter 1  
Introduction..................................................................................................................................... 1  
 1.1 Background.................................................................................................................................... 1  
    1.1.1 Entrainment .......................................................................................................................... 1  
    1.1.2 Entrainment reduction technologies ...................................................................................... 3  
 1.2 Bulk processes .............................................................................................................................. 9  
    1.2.1 Caprolactam Process ............................................................................................................. 9  
    1.2.2 Propylene Oxide and Styrene Monomer (POSM) Process .................................................... 11  
 1.3 Problem statement ...................................................................................................................... 12  
 1.4 Scope and Outline of the thesis .................................................................................................... 14  
  Reference List................................................................................................................................. 17  

Chapter 2  
Development of an experimental setup and drop size measurement technique for entrainment quantification................................................................. 21  
  2.1 Introduction ................................................................................................................................. 22  
  2.2 Development of experimental setup ............................................................................................ 22  
  2.3 Drop size measurement .............................................................................................................. 26  
    2.3.1 Overview of different techniques .......................................................................................... 26  
    2.3.2 Selection of measuring technique ......................................................................................... 28  
    2.3.3 Drop size measurement in the setup ...................................................................................... 29  
  2.4 Conclusions ............................................................................................................................... 31  
  Nomenclature ................................................................................................................................... 33  
  Appendix 2.A: Dimensioning of the static mixer ......................................................................... 34  
  Appendix 2.B: Checking drop size change during microscopy .................................................... 36  
  Reference List.................................................................................................................................... 37  

Chapter 3  
Experimental density, viscosity, interfacial tension and water solubility of ethyl benzene-\(\alpha\)-methyl benzyl alcohol-water system .......................... 39  
  3.1 Introduction................................................................................................................................... 40  
  3.2 Experimental............................................................................................................................... 41  
    3.2.1 Materials ............................................................................................................................. 41  
    3.2.2 Measurement techniques ..................................................................................................... 41  
  3.3 Results and discussion ............................................................................................................... 43
## Contents

3.3.1 Water solubility .................................................................................................................. 43  
3.3.2 Density .................................................................................................................................. 44  
3.3.3 Viscosity .................................................................................................................................. 45  
3.3.4 Interfacial tension ................................................................................................................. 48  
3.3.5 Effect of NaOH (0.01 mol.kg\(^{-1}\)) solution .................................................................... 49  

3.4 Conclusions .............................................................................................................................. 50

Nomenclature .............................................................................................................................. 52

Appendix 3.A: Physical properties of ethyl benzene (EB)-\(\alpha\)-methyl benzyl alcohol (MBA)-water system ........................................................................................................... 53

Reference List .............................................................................................................................. 55

## Chapter 4

**Influence of physical properties and process conditions on entrainment behaviour in a static mixer settler setup**

4.1 Introduction ............................................................................................................................. 58

4.2 Materials & Methods .............................................................................................................. 60

4.2.1 Materials ............................................................................................................................. 60

4.2.2 Experimental setup and procedure .................................................................................... 60

4.3 Results and Discussion .......................................................................................................... 62

4.3.1 Effect of caprolactam concentration (the role of interfacial tension) ............................. 62

4.3.2 Effect of MBA concentration (the role of viscosity of the continuous phase and density difference) ........................................................................................................... 64

4.3.3 Effect of NaOH (pH=12) as dispersed phase ..................................................................... 66

4.3.4 Effect of phase ratio ........................................................................................................... 68

4.3.5 Effect of temperature ......................................................................................................... 72

4.4 Conclusions ............................................................................................................................. 75

Reference List .............................................................................................................................. 77

## Chapter 5

**Entrainment reduction in a static-mixer settler setup by electric field enhanced coalescence**

5.1 Introduction ............................................................................................................................. 80

5.2 Materials & Methods .............................................................................................................. 83

5.2.1 Materials ............................................................................................................................. 83

5.2.2 Experimental set-up and procedure .................................................................................... 83

5.3 Results and Discussion .......................................................................................................... 84

5.3.1 Coalescence with DC field of 1kV/cm ............................................................................ 84

5.3.2 Effect of field strength ....................................................................................................... 86
5.3.3 Effect of frequency ................................................................. 87
5.3.4 Effect of phase ratio ............................................................... 89
5.3.5 Effect of temperature ............................................................. 91
5.4 Conclusions ........................................................................... 93
Reference List ............................................................................. 95

Chapter 6
Entrainment reduction by electric field enhanced coalescence in a pilot scale rotating disc contactor (RDC) ......................................... 97

6.1 Introduction ............................................................................. 98
6.2 Experimental section ............................................................... 99
  6.2.1 Materials ............................................................................. 99
  6.2.2 Experimental setup ............................................................... 99
  6.2.3 Methods ............................................................................. 101
6.3 Results and discussion .............................................................. 103
  6.3.1 Effect of caprolactam concentration on entrainment .............. 103
  6.3.2 Effect of solvent to feed ratio on entrainment without electric field ... 104
  6.3.3 Entrainment profile column settler ....................................... 106
  6.3.4 Effect of electric field with a new column settler .................. 108
6.4 Conclusions ........................................................................... 110
  Appendix 6.A: Method for determining dispersed phase entrainment in the column top settler ............................................................. 112
  Reference List ........................................................................... 113

Chapter 7
A combined lossy capacitor population balance model (LCPBM) for calculating the influence of frequency on electric field enhanced coalescence in a static-mixer settler setup ................................................. 115

7.1 Introduction ............................................................................. 116
  7.1.1 Zhang trajectory analysis ..................................................... 117
  7.1.2 Sadek and Hendricks model ................................................. 118
  7.1.3 Modeling approach of this work .......................................... 119
7.2 Model development ................................................................. 121
  7.2.1 Population balance model (PBM) ......................................... 123
  7.2.2 Hydrodynamic model ......................................................... 124
  7.2.3 Electrical circuit model ....................................................... 125
7.3 Materials and procedure .......................................................... 130
  7.3.1 Materials ........................................................................... 130
To my mother and father
Introduction

Intensification of industrial liquid-liquid extraction processes is a challenging task due to the interaction between the mass transfer and phase separation steps involved in the process. Additionally, the entrainment resulting from mass transfer intensification has remained one of the major operational issues of solvent extraction processes. This work aims at addressing the entrainment issue in industrial bulk extraction processes (Propylene Oxide Styrene Monomer (POSM) and caprolactam production), so that the full process capacity can be utilized. This chapter starts with a background on entrainment and currently used entrainment reduction technologies. After that, the investigated industrial separation processes and the entrainment problem in these processes are discussed. Finally, the problem statement, scope and outline of the thesis are presented.

1.1 Background

1.1.1 Entrainment

Liquid-liquid extraction is a process used to separate two compounds based on their solubility difference in a solvent.\textsuperscript{1,2} The method was first applied industrially in the petrochemical industries and later for the recovery and purification of penicillin. Afterwards, during the rise of the nuclear industry in the 1940’s, the process was applied to refine radioactive materials. From the 1960’s onwards, it has become an established technique to purify non-radioactive metals such as copper.\textsuperscript{2}

Liquid-liquid extraction involves two important steps; the creation of dispersion by mixing to induce mass transfer between the phases, and the phase separation step.\textsuperscript{3} Good mass transfer requires a large interfacial area and small droplets; this is realized by a high energy input during mixing. However, this leads to the production of micro size droplets, which make the phase separation difficult and consequently entrainment occurs. Entrainment is the presence of the dispersed organic or aqueous phase at the outlet of the continuous phase due to incomplete separation of micro-size droplets and physical solubility.
Illustrations of entrainment problems can be found in almost every application where solvent extraction is used; such as, biochemical, metallurgical, petrochemical and chemical processes. Examples include: (1) in the recovery of penicillin from an aqueous solution using butyl acetate where mutual entrainment of the phases can occur due to the presence of surfactant proteins, and this causes the loss of both the valuable product and solvent\textsuperscript{4,5}, (2) in metal extraction by an organic solvent where mutual entrainment of the phases occurs, resulting in solvent loss and carryover of unwanted metals in the extract, which interfere with downstream processes\textsuperscript{6}, (3) loss of expensive solvent by entrainment in uranium extraction from wet-phosphoric acid\textsuperscript{7}, and (4) as will be described later, the bulk chemical processes investigated in this work.

Entrainment is a key operational problem with several consequences for the operation and economics of the process.\textsuperscript{7-11} First, it causes the loss of expensive solvent.\textsuperscript{12} Second, it affects the product quality\textsuperscript{13}, decreases the production capacity, and leads to the fouling and corrosion of downstream process equipment. This calls for additional separations to remove entrainment. Third, when impurities of the process are soluble in the feed stream, entrainment of the raffinate into the solvent stream leads to the progression of these unwanted species into the downstream processes. Therefore, extra separation is needed for the removal of these impurities. Moreover, this can be critical in certain cases; for example, in the solvent extraction process of metals, the presence of entrained impurities directly influences the subsequent downstream electrowinning (electrolysis) process for pure metal production.\textsuperscript{6}

The economic penalty of entrainment stems from the loss of expensive solvent, decrease of product quality and capacity, and the separation cost of the entrainment.\textsuperscript{11,14} In the absence of a solvent recovery method, solvent loss is a critical economical factor especially for the case of expensive reagents used in most solvent extraction processes.\textsuperscript{11} As an example, Bishop and Gray\textsuperscript{15} made some calculations to estimate the change of operating cost from an increase of 5 ppm solvent loss by entrainment for a 720 m\textsuperscript{3}/hr capacity plant. The increase in the yearly operating cost due to entrainment was estimated to be 90,000 US dollars, while it was only 7000 US dollars due to solvent loss by evaporation. The cost of entrainment loss can rise to millions for actual entrainment (few hundred to even thousands ppm) encountered in real processes. The entrainment of the aqueous phase in the organic solvent can also have a significant economic penalty. This is a cumulative cost resulting from product loss, fouling and corrosion of equipments,
decrease of process capacity and product quality, entrainment of unwanted impurities, and separation cost associated with the removal of entrainment.

Therefore, the control and reduction of entrainment in solvent extraction processes is an absolute requirement to maintain good operating conditions, efficiencies, economic production, and utilization of full capacity. 8

1.1.2 Entrainment reduction technologies

Different technologies have been developed in the past decades by the oil and gas industry for increasing coalescence and reduction of entrainment. These include inclined and corrugated plates, packed and fibrous bed coalescers, membrane coalescers, ultrasonic irradiation, chemical demulsifiers, hydrocyclones, electric field, temperature increase, and salt addition. 16 As shown schematically in Figure 1.1, the technologies involve the application of external fields, new equipment, and change in operating conditions. Especially, as reported by Stankiewicz and Moulijn 17, external fields can intensify both steps of extraction; i.e., improvement of mass transfer and dispersed phase coalescence.

Inclined plates

In inclined plate separators, the incoming dispersion is divided into multiple inclined channels as depicted in Figure 1.2.a. As a result, the droplets of the
dispersed phase travel a short distance before being collected at the surface. Moreover, the collection plates are inclined thus the droplets can move along the surface, meet other drops along the way, and coalesce to form larger drops before they leave the surface.\textsuperscript{1} The limitation of this kind of separator is that very fine drops move very slowly under the action of gravity, which makes the separator impractical below a size of 50 microns.\textsuperscript{1} Another technology from HAT international is capable of removing fine drops as small as 5-20 microns. In this case, the plates are arranged as a matrix pack (see Figure 1.2.b). While the drops pass through the pack they encounter a frequent direction change, collide with each other and the metal surfaces, and easily coalesce into large droplets.\textsuperscript{18} The limitation is that the flow through the matrix pack should be laminar to avoid further breakup of the drops.

![Figure 1.2: (a) Inclined horizontal gravity settler (b) Matrix plate coalescers](image)

**Fiber bed coalescers**

Fiber beds work on the principle that, when the dispersion flows through the bed, the droplets are captured by the fibrous material due to wetting.\textsuperscript{1,19-21} The succeeding drops coalesce with these drops and the size of the drops increases until the liquid flow pulls them out from the bed. The mechanism of coalescence as shown in Figure 1.3 includes four steps\textsuperscript{19}; (1) drops captured on filaments due to their affinity with the surface, (2) droplets coalescence, (3) formation of large droplets, and (4) movement out of the bed by drag force. The flow velocity and fiber diameter affect the performance of this type of coalescer. Higher velocity and large fiber diameter lower the separation efficiency. The main drawback of fiber bed coalescers is the possibility of clogging by solids. Furthermore, the presence of surfactant molecules decreases the separation efficiency.\textsuperscript{19-21} For instance, the commonly used glass fiber has both hydrophilic (silane group) and hydrophobic parts. The water drops enlarge at the hydrophilic site but surfactants also adsorb at the interface which interfere with the coalescence process.
Membrane coalescers

This method is used to separate fine droplets of sizes down to 1 micron. The mechanism of demulsification of a water in oil emulsion into hydrophilic glass membranes is illustrated in Figure 1.4.\textsuperscript{22} The demulsification mainly takes place because of the pore size of the membrane. Accordingly, a decrease in the pore size of the membrane increases the demulsification efficiency.\textsuperscript{1,22-24} By using pore diameters less than the diameter of dispersed phase drops, the droplets deform and consequently rupture while trying to pass through the membrane. In contrast, the flux through the membrane decreases while using small size pores. This means both demulsification efficiency and permeation flux should be considered when choosing a specific pore size.\textsuperscript{22-24} The drawback of this technology is the capacity limitation by a high pressure drop encountered in turbulent flows, and the possibility of clogging.

Ultrasound demulsification

Ultrasonic coalescence is caused by the interaction of the acoustic force resulting from ultrasonic irradiation with the drop.\textsuperscript{25-27} Depending on their acoustic property, the drops gather either at pressure nodes or antinodes, and this causes the coalescence of drops. Once the drops are gathered at the nodes/anti-nodes, the scattering of the ultrasonic irradiation from neighboring drops produces a secondary acoustic force, which causes further coalescence of the drops. Figure 1.5 shows the coalescence of drops by ultrasound irradiation at 2MHz with an irradiation power of 2W. The drops increased in size from 2-6µm to 0.11-0.18mm.\textsuperscript{25} Despite some use in oil-in-water emulsions coalescence\textsuperscript{27}, and great
potential for coalescence of drops with the bulk interface\textsuperscript{28}, ultrasound coalescence is still under development for large scale applications.

![Diagram of membrane coalescence mechanism](image)

**Figure 1.4:** Membrane coalescence mechanism. (a) droplets in the emulsion are adsorbed on the surface of the porous glass membrane (b) drops entering the pore must deform (drops amplified) (c) droplets in the pore are broken are adsorbed on the pore wall (drops amplified)\textsuperscript{22}

![Images of droplets before and after irradiation](image)

**Figure 1.5:** Droplets flocculation caused by ultrasonic irradiation\textsuperscript{25}

**Chemical demulsification**

The basis of this technology is the fact that the fine droplets are stable with respect to coalescence due to the presence of the surface active impurities adsorbed on the surface of droplets that prevents film drainage.\textsuperscript{13,29} As shown in Figure 1.6, the mechanism of demulsification is the result of displacement of the emulsifier from the surface.\textsuperscript{13} As a result, the interfacial viscosity decreases and this enhances the drainage rate. A number of chemical demulsifiers exist in literature.\textsuperscript{29} Most chemical agents used for demulsification of water are high molecular weight polymers such as copolymers of polyethylene and ethylene oxide together with glycerol, phenol formaldehyde resins, siloxanes, melamine formaldehyde resins, polyamides and polyols. The downside of using this technique is the introduction
of additional chemicals to the system which requires extra separation downstream of the process.

Figure 1.6: Mechanism of demulsification by chemical demulsifiers. (a) Approach of demulsifier to surface of drop covered by stabilizer (b) replacement of the stabilizer by demulsifier (c) facilitated drainage

Centrifuges

In centrifuges the separation between the two liquid phases is effected by a high gravity force. This makes the separation of emulsified systems possible, which are difficult to separate under normal gravity force. The heavy phase moves out to the periphery of the centrifuge while the light concentrates at the center. Higher rotational speed of the centrifuge provides higher driving force while there is at the same time a possibility for further emulsification as a result of increase in shear force imparted on the liquid-liquid system. Therefore, an optimum rotor speed should be selected to avoid emulsification and at the same time get good separation. The negative aspect of using this technology are the high operational and capital costs.

Hydrocyclones

The principle behind hydrocyclone operation has its roots in gas-solid separations by cyclone. The energy of the fluid is used to generate a vortex that induces a centrifugal acceleration much larger (can be up to 100x) than the gravitational acceleration. The swirling flow reduces the residence time and separates the micro-droplets in the range of 10-300 microns. Hydrocyclones are interesting options for separation because of easy design, installation, maintenance and operation. However, a number of challenges can be encountered when hydrocyclone is used for liquid-liquid separation. In liquid-liquid dispersions, the density difference is small, which makes the separation difficult. Moreover, due to the sensitive nature of the dispersed phase, the high flow rate used for inducing swirling flow causes further break-up of the drops. Furthermore, the efficiency is influenced by split ratio (ratio of underflow to overflow), which is mainly dependent on phase continuity (organic or aqueous continuous). For instance, for
aqueous dispersed phase, this may result in a significant loss of the organic to the aqueous phase. Therefore, the dependence on process variables makes operational flexibility, control and scale up difficult.

**Electro-coalescence**

Different mechanisms are responsible for coalescence by electric field. These include enhancement of the collision of droplets, chain formation by the droplets, dipole coalescence, electrophoresis, and dielectrophoresis as depicted in Figure 1.7.\textsuperscript{35-43} In the three stage mechanism of coalescence (i.e., approach of drops, film thinning, film rupture, and coalescence of drops), the application of electric field increases the motion of drops and thereby creates an increased chance of contact between the drops. Hence, it improves the coalescence rate by increasing the collision rate of drops.\textsuperscript{38,41} Moreover, under electric field, the aqueous drops become polarized; hence, they acquire induced charges, which create a dipole-dipole attraction force between them.\textsuperscript{38} The magnitude of this attraction force depends on the magnitude of the applied electric field, the size of droplets, and the separation distance between them. Furthermore, if the drops acquire charge by touching electrodes and from free charges present in the dispersion, they will move under the action of electrostatic attraction of charged electrodes (electrophoretic and dielectrophoretic forces), which leads to extra coalescence of drops.\textsuperscript{36,37}

![Figure 1.7: Different coalescence mechanisms under an electric field\textsuperscript{43}](image)

**Magnetic separation**

Patents by Dvorchik et al.\textsuperscript{44} and recently by Zahn et al.\textsuperscript{45} describe a magnetic separation process for treating spilled oil on large water surfaces. In these processes, magnetic property is first imparted to the oil phase. This is achieved by adding nano-size magnetic particles coated with suitable surfactants, which are added to prevent the agglomeration of magnetic particles. Subsequently, the magnetized dispersed phase is separated from the non-magnetized phase using
magnetic traps. The magnetic particles are then recovered from the separated magnetized dispersed phase by existing magnetic separation techniques and reused again in the process.\textsuperscript{44,45} Additionally, large scale applications of magnetic separation can be found in water treatment for the removal of pollutants and color from water.\textsuperscript{46,47} However, magnetic separation of oil and water for onshore applications are not known.

1.2 Bulk processes

1.2.1 Caprolactam Process

Caprolactam, also known as 2-oxohexamethyleneimine, is one of the most widely used chemical intermediates. The yearly production of caprolactam is expected to be 5 million ton by year 2015 and 90% the produced amount of caprolactam is used for the production of nylon fibers. Various synthesis routes have been developed for caprolactam with cyclohexanone oxime as the main intermediate. As shown in reaction scheme presented below, the cyclohexanone oxime is first formed by the reaction of cyclohexanone and hydroxylamine. This is followed by the Beckmann rearrangement of cyclohexanone oxime to caprolactam. A molar ratio of 1 to 1.5 of cyclohexanone oxime to sulphuric acid is used. After the rearrangement reaction, 1.8 ton of ammonium sulphate is produced per ton of caprolactam.\textsuperscript{48,49}

\begin{align*}
2 \text{C}_6\text{H}_{10}\text{O} + (\text{NH}_2\text{OH})_2\text{SO}_4 + 2 \text{NH}_2\text{OH} & \rightarrow 2 \text{C}_6\text{H}_{11}\text{NO} + (\text{NH}_2\text{OH})\text{SO}_4 + 4 \text{H}_2\text{O} \\
\end{align*}

Reaction between cyclohexanone and hydroxylamine to from oxime

\begin{align*}
\text{C}_6\text{H}_8\text{NO} + \text{Oleum} & \rightarrow \text{C}_6\text{H}_{11}\text{NOH} + \frac{1}{2} \text{H}_2\text{SO}_4 \\
\text{C}_6\text{H}_{11}\text{NOH} + \text{NH}_3 & \rightarrow \text{C}_6\text{H}_{11}\text{NH}_2 + \frac{1}{2} (\text{NH}_2\text{OH})_2\text{SO}_4
\end{align*}

Beckmann rearrangement of cyclohexanone oxime to caprolactam

The main reactions for caprolactam production end up with the Beckmann rearrangement as a final step. The caprolactam from this final step is bound to sulphuric acid. The DSM recovery process for caprolactam is shown in Figure 1.8. In this process, the bound caprolactam is first recovered from the reaction mixture
by neutralization with gaseous or aqueous ammonia, resulting in the formation of two liquid phases.\textsuperscript{48,49} The top phase contains 65-70 % w/w caprolactam, 1-1.5% w/w ammonium sulfate, and the rest water, in equilibrium with a nearly saturated 40% w/w aqueous ammonium sulfate bottom phase containing 1-1.5% w/w residual caprolactam. The crude caprolactam is recovered by solvent extraction followed by back extraction with water and solvent distillation.\textsuperscript{48} The advantage of back extraction is the possibility to remove impurities and a more concentrated product, while the disadvantage is the energy requirement for evaporation of water compared to solvent distillation.

The main process of interest in this work is the crude caprolactam extraction with organic solvent shown as process step 5 in Figure 1.8. The process is carried out in rotating disc contactor (RDC) extraction column. The challenge encountered in this process is the extraction column capacity limitation by flooding and excessive entrainment of the aqueous phase in the organic solvent, which is caused by the surface active nature of caprolactam.

![Diagram of DSM caprolactam recovery process](image)


The high caprolactam concentration (65-70 % w/w) fed to the extraction column lowers the interfacial tension of the system to less than 5mN/m.\textsuperscript{51} Consequently, micro sized aqueous droplets are produced; which are difficult to separate and easily entrained with the solvent. This results in less concentrated product from the
extraction column; hence, reduces the product quality and capacity of the column. Especially, the loss of quality due to water entrainment is a critical factor since commercial production of nylon requires 99.9% w/w pure caprolactam and the presence of water influences molecular weight growth during polymerization. The integration of entrainment reduction technologies therefore enables the reduction of entrainment, creates the possibility to increase the process capacity by operating the column close to the flooding point, and allows meeting stringent product quality specifications.

1.2.2 Propylene Oxide and Styrene Monomer (POSM) Process

Propylene oxide, also known as 1,2-epoxypropane, is a valuable organic compound primarily used as a reaction intermediate for the production of polyether polyols, propylene glycol, and glycols. Propylene oxide is manufactured by two main processes; the chlorohydrins process and the hydroperoxide process, where styrene is a co-product. The total yearly production of propylene oxide was estimated to be 5.78 million ton/yr in 1999, with half came from each of the above processes.

The production route relevant to this work is the hydroperoxide process. The process is depicted in Figure 1.9. In this process, first, ethyl benzene (EB) is oxidized by air and is converted to ethylbenzenehydroperoxide (EBHP). The conversion of the process is 10-15%; therefore, the unconverted EB is recycled back to the reactor after concentration of EBHP to 35-40% by distillation. The EBHP is sent to the epoxidation reactor, where it reacts with propylene in the presence of a homogenous molybdenum catalyst. The epoxidation forms propylene oxide as a product and α-methyl benzyl alcohol (MBA) as a co-product. After epoxidation, propylene oxide and the excess of propylene are distilled overhead. The propylene oxide is further purified by a series of distillations. The bottom product of distillation mainly contains MBA, EB, acidic components, and catalyst. The acidic components and the molybdenum catalyst are removed by neutralization with caustic solution (pH=12-13). This is done by mixing the organic phase with caustic solution in a static mixer, followed by phase separation. After removal of acids, the organic stream is treated by a series of distillation to purify MBA. MBA after dehydration gives the styrene monomer.

The main process step of interest to this research is the caustic wash step. The focus is on the caustic wash in a static mixer followed by phase separation. The main issues of the caustic wash process are:

- Long residence time in a separation drum, which causes propylene oxide loss by caustic catalyzed reactions
Incomplete phase separation that results in mutual entrainment of the phases, i.e. the water phase containing MBA and ethyl benzene, while the organic phase contains a salty water effluent.

In this case, the coalescence technologies should reduce the residence time required for separation, and avoid or minimize mutual entrainment of the phases.

Figure 1.9: The Ethyl benzene (EB) hydroperoxide process to propylene oxide (PO) and styrene:\textsuperscript{53}; Major steps are: 1. EB oxidation with air to form EBHP 2. Epoxidation reaction between propylene and EBHP to propylene oxide and MBA 4. Caustic wash to remove acidity 5. PO purification by distillation 6. MBA distillation 7. MBA dehydration into styrene

1.3 Problem statement

Despite the prevalent use of the entrainment removal technologies presented in section 1.1 in the oil and gas industries, their application in bulk extraction processes has received little attention.\textsuperscript{39} In the off-shore oil treatment, the need for small gravity settlers because of space limitations demands alternative separation.\textsuperscript{16} Moreover, the severe corrosion problem in the pipeline due to the presence of free emulsified water\textsuperscript{54} requires efficient separation, which cannot be achieved only by gravity separation.

Although it is possible to use the same separation principles in bulk extraction processes, direct application of the technologies is not straightforward. Applying new equipment and chemicals is not an option in bulk processes. The addition of
new equipment requires space and modification of the existing infrastructure. The use of new chemicals is also not viable as it introduces new components to the process, which eventually need separation in downstream process.

The other possibilities are external fields, i.e., centrifuges, ultrasound, magnetic field, and electric field. The use of centrifuge separators is hampered by the operational and investment costs, while ultrasound and magnetic field are still under development and application at industrial scale has not been established yet. The use of an electric field is an attractive option for a number of reasons. First, it is a proven technology in the petrochemical industry, hence, can easily be adapted to bulk processes. Second, it does not require much space and change of the existing infrastructure, therefore, it can easily be incorporated in the existing process. Third, it has low power requirements due to the very low electrical current across the dispersion. Finally, the maintenance cost is very low as no mechanical moving parts are involved.

Despite these promising aspects of using an electric field, the direct application in solvent extraction processes is not easy. As reported by Bailes, the challenge in using an electric field for this process results from the phase ratio employed. The high phase ratio in the region of 1:1 used in solvent extraction will result in many conducting drops. The subsequent bridging of the electrodes and the accompanied loss of coalescence force and efficiency make the implementation of electrical field difficult. Therefore they used insulated electrodes and pulsed DC as a means of energisation to solve the problem. However, the systems used have a relatively high interfacial tension. Thus, the application of an electric field resulted in higher separation efficiency.

Nevertheless, the application of an electric field creates an additional challenge in extraction systems with low interfacial tension and in the presence of surface active components. Firstly, the low interfacial tension causes reduction of the drop size. Thus, the electrical attractive force responsible for coalescence decreases since the electrophoretic, dielectrophoretic, and dipole-dipole attraction, forces are proportional to drop size to the power 2, 3, and 6, respectively. Secondly, the presence of surface active components hinders the coalescence process. The surface active compound adsorbs at the interface between the drops, and this prevents direct contact and coalescence of drops by the electric field. Therefore, the coalescence of this kind of solvent extraction systems by an electric field is difficult and was rarely investigated with the only exception being emulsion liquid membrane processes.
Chapter 1

The bulk extraction processes investigated in this thesis are typical for this kind of systems characterized by lower interfacial tension, and one of their components is surface active. In caprolactam-toluene-water system, the interfacial tension decreases to less than 5 mN/m depending on caprolactam concentration. On top of that, caprolactam acts as a surface active component. For the POSM caustic wash process, Ethyl benzene (EB)-α-methyl benzyl alcohol (MBA)-water can be taken as a model system. The interfacial tension of this system can be as low as 10 mN/m depending on MBA concentration. Additionally, MBA acts as a surface active component.

The state of art gravity separation for these kind of extraction systems is therefore not sufficient and suffers from several drawbacks; such as, large size of settlers, high solvent inventory, long residence time, less product purity, product loss, decrease of process capacity, and high entrainment levels. A new separation principle is therefore required that avoids the aforementioned drawbacks of the traditional process.

This research focuses on the application of electric field enhanced coalescence technology to intensify the phase separation and reduce entrainment in bulk industrial extraction processes. The use of an electric field is a breakthrough from the state of art separation technology with significant operational and economic advantages. By integrating an electric field before state of art gravity separation, the coalescence between drops can be enhanced and bigger size droplets are produced. Consequently, the residence time required for separation is considerably reduced. Therefore, a more compact settler is sufficient compared to the traditional separation process, which results in a lower solvent inventory. Additionally, entrainment is massively reduced because of larger size droplets produced by coalescence. Accordingly, entrainment related problems such as product loss, less product purity and decrease of production capacity are eliminated.

1.4 Scope and Outline of the thesis

The goal of this research work can be stated as the intensification of dispersed phase separation in bulk industrial extraction processes by enhancing coalescence of small size drops. The main objectives are full utilization and increase of the process capacity, and specifically, the reduction of entrainment problem in the bulk processes. Many factors such as equipment design, physical properties (e.g. low interfacial tension, high viscosity, low density difference, and physical solubility), flow rate, energy input during mixing and the presence of interfacial active impurities can play a role in the generation of high entrainment levels. The
underlying reasons for entrainment presence should therefore be identified to select the appropriate entrainment reduction strategy. Moreover, bench mark experiments are needed to determine the amount of entrainment without the application of an electric field. Hence, five milestones are distinguished in achieving the project objective; (1) development of an experimental setup for entrainment characterization (2) execution of experiments to identify the role of physical properties and process conditions (3) incorporation of entrainment reduction technology in the setup, (4) proof of the entrainment reduction concept at pilot scale in rotating disc contactor (RDC), and (5) development of a model to understand and predict electro-coalescence.

Therefore, first, a set-up for entrainment characterization and reduction is designed and constructed. The static-mixer settler setup was used to keep the industrial relevance in particular for the POSM process. Additionally, static-mixers are relatively new mixing devices with some advantages over traditional stirred vessels such as a strongly reduced solvent inventory and the possibility to achieve a nearly plug flow condition. Despite these advantages their entrainment behavior has not been investigated. Entrainment however can limit the capacity of this type of mixers. Thus, their separation characteristics should be evaluated together with the aforementioned advantages. In conjunction with measuring the entrainment, ways for drop size characterization are evaluated. These are discussed in chapter two.

Physical properties play an important role in the observed change of entrainment behavior and can be the main reason for high entrainment. Therefore, they should be known beforehand to understand which property change is responsible for the observed change in entrainment. The physical properties of caprolactam system are measured before. However, for EB-MBA-Water system, physical property data is missing. Therefore, the physical properties are measured for this system and are presented in chapter three, while in chapter four the results of bench mark experiments and the effect of physical properties and process conditions on the entrainment are discussed for both industrial processes. Chapter five discusses entrainment reduction using electric field enhanced coalescence in a static-mixer settler setup for the two selected systems. The proof of concept for application of electric field in a pilot scale was carried out using a rotating disc contactor (RDC) extraction column. The experimental results of the pilot scale experiment are thus discussed in chapter six. Ultimately, a model is developed to determine the influence of frequency on electric field enhanced coalescence (mean sauter diameters). This model is presented and validated with the experimental data in
chapter seven. Finally, in chapter eight, the conclusions of this work are presented together with recommendations for future work.
Reference List


(49) Van Delden, M. L., Caprolactam Extraction in a Pulsed Disc and Doughnut Column With a Benign Mixed Solvent. University of Twente, Enschede, 2005.


Development of an experimental setup and drop size measurement technique for entrainment quantification

Abstract

To realize the project objective, first an experimental setup is developed to quantify and reduce entrainment. With the constructed setup in place, base experiments can be carried out to quantify entrainment and its dependence on the physical properties (interfacial tension, viscosity of the continuous and dispersed phase, density), and process conditions. Afterwards, modifications are made in the setup by incorporating electric field to reduce entrainment. Additionally, since entrainment depends on the drop sizes created by mixing, a method is developed to measure the drop sizes. In such a way, it is possible to relate the measured drop sizes with entrainment. In this chapter, the developed experimental setup and the drop size measurement technique are described.
2.1 Introduction

The mixer-settler is commonly used for carrying out mass transfer processes in the chemical, metallurgical and pharmaceutical industries. This operation consists of two steps; a mixing step where mass transfer occurs between the solvent and the feed phase in a mixer and a separation step where the dispersed phase is separated from the continuous phase in a settler. The aim of the mixing step is to increase the interfacial area of mass transfer by droplet formation. Nevertheless, the drawback is entrainment of the small droplets created during mixing which decreases the process capacity.

To quantify the role of physical properties and process conditions on entrainment and later on to investigate the possibilities for increasing the process capacity by decreasing entrainment, an experimental setup should be developed. Additionally, a drop size measurement technique needs to be selected to determine the drop sizes created by mixing. This chapter presents the experimental setup for entrainment quantification and drop size measurement technique.

2.2 Development of experimental setup

Figure 2.1 depicts a schematic drawing of the experimental setup developed for entrainment quantification and reduction. As shown, the setup consists of two gear pumps for the organic and aqueous phases, variable area flow meters to measure the flows, a static-mixer to mix the phases, an electric field to coalesce the droplets created by the static-mixer, a settler for separation of the phases, a coalescer to enlarge entrained droplets of one phase on the other, and buffer tanks (secondary settlers) to remove the enlarged droplets. Each of these apparatuses (units) is described in more detail below.

Storage tanks and pumps

The stock tanks of the experimental setup are used to store the organic and aqueous phases. As shown in Figure 2.2 (a), the stock tanks are made of glass and have a capacity of 10.5 liters. The temperature inside the tanks is controlled by a glass spiral heat exchanger, which is connected to a water bath. The tanks are equipped with a flexible thermocouple to read the temperature. The dimensions of the stock tanks and the spiral heat exchangers are given in Table 2.1.

Two gear pumps (Verdergear Van Wijk and Borema B.V.) are used to pump the organic and aqueous phases through the experimental setup. The organic phase pump has a maximum capacity of 2 l/min, while the aqueous phase has a capacity of 1 l/min. The flow can be adjusted from the panel on the pumps which can be set
as percentage of the maximum flow. The storage tanks are connected to gear pumps and a recycle from the buffer tanks, which enabled continuous operation of the process.

Table 2.1 Technical details of the stock tanks and their spiral heat exchangers

<table>
<thead>
<tr>
<th>Stock tanks</th>
<th>Heat Exchangers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness</td>
<td>Wall thickness heat exchanger</td>
</tr>
<tr>
<td>0.005 m</td>
<td>0.0015 m</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>Diameter pipe heat exchanger</td>
</tr>
<tr>
<td>0.19 m</td>
<td>0.012 m</td>
</tr>
<tr>
<td>External</td>
<td>Diameter of spiral</td>
</tr>
<tr>
<td>0.2 m</td>
<td>0.13 m</td>
</tr>
<tr>
<td>Height tank</td>
<td>Number of spirals</td>
</tr>
<tr>
<td>0.4 m</td>
<td>18</td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
</tr>
<tr>
<td>1 bar</td>
<td></td>
</tr>
</tbody>
</table>

**Static mixer**

The mixing of the organic and aqueous phases was carried out using the static mixer shown in Figure 2.2 (b). This static mixer is of the Kenics type KMD05 and has an inner diameter of 14.6 mm and a length of 400 mm. The static mixer is placed in a glass tube of an inner diameter 14.6 mm and length 500 mm. The extended section of the glass from the end of the static-mixer to the settler is 100 mm long. This enabled drop size measurement and later incorporation of the electric field. The dimensioning of the static mixer was carried out by scaling down from the relevant industrial process to achieve comparable process conditions (drop size and entrainment). The dimensioning was done using the scale down rule of static mixers for turbulent flow\(^1\), i.e., keeping the specific energy dissipation and the residence time constant. The scale down approach is described in Appendix 2.A.

**Settler**

The separation of the dispersed phase is achieved using a gravity settler depicted in Figure 2.3. The settler has a volume of 0.009 m\(^3\) (length=0.3 m, width=0.2 m, height=0.15 m). The settler has glass windows at both sides to have a visual observation of what is happening inside the settler. The interface level in the settler is maintained at 0.05 m from the bottom of the settler. The settler inlet with a 0.017 m inner diameter is in the organic phase, at 0.12 m level from the bottom of the settler. This was done to minimize the turbulence effect from the incoming dispersion which could lead to the entrainment of droplets at the interface. At the end of the settler, outlets are made for the continuous light phase and heavy dispersed phase, at the top and bottom of the settler, respectively.
Figure 2.1. Schematic representation of the experimental set-up: 1, 2. Stock tanks, 3. Static mixer, 4. electrodes, 5. Settler, 6, 7. fiber coalescers, 8,9. waste tanks, 10,11. Secondary settlers

Figure 2.2. Stock tanks (a) and Kenics static mixer (b) in the experimental setup
Fiber coalescers and secondary settlers

The entrained droplets from the settler are coalesced by fibers. For aqueous entrainment in the organic phase, glass wool is used while Teflon fiber is used for organic entrainment in aqueous phase. Once enlarged, the drops are removed in buffer tanks (secondary settlers).

Electric field

For entrainment reduction with an electric field, an electro-coalescer is integrated into the extended section of the static mixer as shown in Figure 2.5. The electro-coalescer is connected to a voltage generator. The electrodes are made of stainless steel and have dimensions of length 70 mm, width 10 mm, and thickness 1mm. The distance between electrodes is 10mm. The electrodes are insulated with a Kynar® material, which is resistant to toluene. In addition, the material of insulation is non-wetting to water, which prevents the formation of spark. The electrodes are connected to the voltage generator which can deliver a maximum voltage of 1kV, and a square wave of frequency between 3-100 Hz. The voltage and frequency are measured with a Fluke 175 multimeter.
2.3 Drop size measurement

2.3.1 Overview of different techniques

Numerous ways of drop size measurement techniques are reported in literature. In this chapter, the methods will only be described briefly to evaluate their applicability for the developed setup. In general, two different methods can be distinguished for drop size measurement in liquid-liquid dispersions; in-line measuring techniques, and the external sampling techniques as shown schematically in Figure 2.6. In-line measurement technique is preferred over the external sampling because of possible drop size change during sampling, especially, for fast coalescing systems. The in-line measurement is typically based on four techniques; sound, laser, image (photography), and tomography methods.

The sound method employs the interaction between an acoustic wave and the dispersion. Two methods are available; the acoustic spectroscopy, and the electro-acoustic spectroscopy. The dispersion is subjected to acoustic waves in a frequency range of 1-100 MHz. After passing through the dispersion, the acoustic waves change both intensity and direction. The acoustic instrument measures the attenuation at each wave length, which depends on the drop sizes and their concentration.

The laser techniques are based on light diffraction and scattering and are classified into Fraunhofer diffraction, Phase Doppler Anemometry, In-line particle size probe, and 3 Dimensional optical reflectance measurements (3D ORM). The Fraunhofer diffraction is based on light scattering. A laser beam is sent through a single or multiple slit, where the droplets are passing. The droplets scatter light while passing and this is detected by concentric annular detectors placed on the focal point of the lens. The intensity of the scattered light depends on the drop size and its concentration, which renders the possibility to measure the size distribution.
Figure 2.6. Overview of the different drop size measurement techniques

Figure 2.7a shows the Phase Doppler Anemometry. The technique is based on light scattering by two laser beams. The two laser beams focus the light at one measurement volume, where the droplets are passing through. The droplets scatter light and this is detected by the sensor.\textsuperscript{11,12} This technique is limited to dispersion of 1%.\textsuperscript{2} The In-line particle size probe measurement technique is based on laser, light reflection and diffraction. In-line particle size probe detects shadow of particles and measures the velocity and drop size when it passes a small channel in which the laser beam is focused. The in-line particle size probe method is able to detect dispersions of 20%.\textsuperscript{13} The 3D ORM drop size measurement technique is shown in Figure 2.7b. This method is also based on light scattering. A sapphire window rotates at high speed and scatters back light from the laser beam. Particles cause a disturbance in the chord length of the laser beam and this is detected by the probe.\textsuperscript{2,14,15} With the laser and sound methods, drop size measurement is automated.

Imaging techniques are the most commonly used methods. They are also the least expensive methods compared to the sound and laser techniques. Three different image based drop size measurement can be distinguished; photo/video technique, endoscope with CCD camera, and microscope.\textsuperscript{2}

In the photo technique, a digital camera is used to take image of the dispersion from outside through a glass wall. The images can be processed and analyzed by software or by manual counting and measuring. The disadvantage of the method is manual counting of the drops and “near-to-wall problem”\textsuperscript{17} encountered with concentrated dispersion. One way to avoid this problem is using endoscopy with the camera. The endoscope is a tube with an optical lens and optical fiber placed in
it. By placing the endoscope at different positions, the drop size can be measured at every position.

Tomography is based on differences of electrical conductivity or permeability of two phases. This method is commonly used for flow pattern detection and hold up characteristics. A source sends electrical pulses by electrodes which are located around the reactor, and detects these pulses and produces a 3D image of the flow patterns.

![Schematic picture of (a) Phase Doppler Anemometry (PDA) and (b) 3D-ORM drop size measurement](image)

**Figure 2.7.** Schematic picture of (a) Phase Doppler Anemometry (PDA) and (b) 3D-ORM drop size measurement

### 2.3.2 Selection of measuring technique

Drop size formed by the static mixer dictates the entrainment behavior. Therefore, a suitable drop size measuring technique needs to selected and validated. Since there are a number of possible measurement techniques, the following criteria were set for the selection of the technique. First, the method should provide accurate and reproducible measurements. Additionally, the method needs to be easily applicable in the developed setup. Furthermore, the method should be inexpensive, and preferably automated. Comparison of the drop size measurement techniques according to the set criteria is given below.

1. **Cost:** the sound and laser techniques are an order of magnitude more expensive than the image technique.
2. **Accuracy:** the laser and sound methods rely on diffraction correlations developed to relate the drop size with intensity of the diffracted wave and they are based on certain assumptions. The accuracy of the measurements
thus depends on whether the assumptions are valid. Additionally, the diffraction methods measure the chord size rather than drop diameter.\textsuperscript{2,19} The photo methods on the other hand give accurate drop size measurement. They are the only methods which are able to analyze high dispersion rates and validation of the drop sizes by predictive models is possible.\textsuperscript{2}

3. Simplicity of the applicability in the setup: the static mixer pipe should be modified to allow measurement by the sound and laser techniques while with the photo technique the measurement can be done from outside, thus no modification is required.

4. Drop size measurement automation: The sound and laser based tools are equipped with software packages that enable automatic measurement. The photo method requires external manual data treatment such as drop size recognition, counting, and manual measurement of the drop sizes, which is time consuming. Softwares are in development for automatic recognition and measurement of drop sizes. Edge detection algorithms such as Hough transform\textsuperscript{17,20,21} are implemented in these softwares to recognize drops as circles. However, the methods do not recognize some drops and in some cases adjacent drops are detected as a single drop. Therefore, although the methods are promising, they need further improvement before used as automatic drop size measurement technique.

Considering factors such as cost, accuracy, simplicity, and applicability of the technique in the setup, the photo method was found to be the most suitable drop size measurement technique to apply it in the setup. To measure the drop size of entrained droplets, microscopy integrated with a digital camera was used.

2.3.3 \textit{Drop size measurement in the setup}

As shown schematically in Figure 2.8a\&b, the drop sizes were determined by taking pictures of the drops in the glass pipe extension of the static mixer using a Canon 50D camera. To do this, the end section of the static mixer is illuminated by reflection of light from the mirror. To prevent any light passing through the extended section of static mixer pipe, two black cardboards are installed. Additionally, white artistic paper is used to uniformly diffuse the light over the section of pipe. Adhesive paper of 20 mm length was posted in the pipe to have a reference length in drop size measurements. The images containing the droplets are taken through the glass tube of the static mixer multiple times and then analyzed by the Adobe Photoshop software CS5. Drop sizes from multiple millimeters down to 100 microns can be measured with this technique.
To determine the size of entrained droplets less than 100 micron external sampling was needed. The samples are examined with a Bressers type microscope with 50 times magnification. Droplets down to a size of 10 microns can be detected by the microscope. The microscope is connected to the digital camera using an adapter. As described before, there is a possibility of change in drop size during sampling. Thus, this was checked by taking the image of entrained drops at different times. As depicted in Figure 2B.1 (Appendix 2.B), no change of drop sizes was observed for 6 minutes. Extensive measurement of the entrained droplets for every process condition was not made. The analysis of entrained droplets showed that most droplets have a diameter between 20-40 microns and the percentage that lie in this range increased with an increase of the continuous phase flowrate. Additionally, the total concentration of these entrained droplets (entrainment) was determined for every change in process condition as will be described in Chapter 4.

Furthermore, the image of drops in the static mixer pipe was taken for every change in process condition, with and without electric field. This drop size measurement technique causes error due to the curvature of a pipe. As emphasized by different authors\textsuperscript{22-28}, drop size measurement by photography in a curved pipe might lead to image distortion due to the cylindrical shape of the pipe and the difference in refractive indices of the glass pipe and used fluids. To avoid the distortion, usually the viewing section of the curved pipe is covered with a transparent rectangular box filled with the same fluid as in the pipe.\textsuperscript{27,28} Nevertheless, applying this method to solve the distortion problem was not possible since the same section of pipe was used to incorporate electric field. Additionally, as pointed out by some authors such as Tavoularis\textsuperscript{28}, this method does not guarantee the image will not be distorted due to the sensitivity of the refractive index of the dispersion. For the method to be successful, the refractive index of the fluid inside the pipe and inside the rectangular box must be kept the same. Thus, the error of the measurement due to curvature was determined by placing spheres of metal with 3.9672 mm diameter at different locations from the center of the pipe as shown in Figure 2.9. The error was 0.2\% when the measurement was done close to the center of the static mixer pipe. It increased to 3.2\% when the measurement was done close to the wall of the static mixer pipe.
2.4 Conclusions

A static-mixer settler experimental setup has been developed for entrainment characterization and reduction. The setup consists of two gear pumps for the organic and aqueous phases, a static mixer to mix the phases, an electric field to coalesce the droplets created by the static mixer, a settler for separation of the phases, a coalescer to enlarge entrained droplets, and secondary settlers to remove the enlarged droplets. Additionally, different techniques for drop size measurement have been investigated. Considering factors such as cost, accuracy, simplicity, and applicability of the technique in the setup, the photo method was found to be a suitable drop size measurement technique for application in the setup. The accuracy of the selected technique, specifically the error due to curved pipe of the static mixer was determined by placing metal spheres with known diameter. The
maximum error due to the curvature was found to be 3.2%. Additionally, the measurement of the entrained drop size showed that most entrained drops have sizes between 20-40 microns. In addition to size measurement, the total concentration of these entrained will be made.
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Diameter of static-mixer, m</td>
</tr>
<tr>
<td>$E_{\text{disp}}$</td>
<td>Specific energy dissipation rate, m$^2$/s$^3$</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational acceleration, m/s$^2$</td>
</tr>
<tr>
<td>L</td>
<td>Length of static mixer, m</td>
</tr>
<tr>
<td>P</td>
<td>Pressure, Pa</td>
</tr>
<tr>
<td>Q</td>
<td>Volumetric flow, m$^3$/s</td>
</tr>
<tr>
<td>V</td>
<td>Superficial velocity, m/s</td>
</tr>
</tbody>
</table>

#### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>Density of continuous phase, kg/m$^3$</td>
</tr>
<tr>
<td>$\triangle$</td>
<td>Difference</td>
</tr>
</tbody>
</table>

#### Sub/superscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>disp</td>
<td>Dissipation</td>
</tr>
<tr>
<td>lb</td>
<td>Laboratory scale</td>
</tr>
<tr>
<td>up</td>
<td>Upscale existing process</td>
</tr>
</tbody>
</table>
Appendix 2.A: Dimensioning of the static mixer

The dimension of the static mixer was determined by scale down of the existing process keeping the specific energy dissipation (energy dissipation rate per unit mass) and the residence time constant. The energy dissipation for turbulent flow is given as a product of volumetric flowrate and pressure drop. The specific energy dissipation is obtained by dividing the energy dissipation with the mass of the continuous phase enclosed in a static-mixer:

\[ E_{\text{disp}} = \frac{\Delta P_{db} Q_{db}}{\rho \pi D_{up}^2 L_{up}} = \frac{\Delta P_{lb} Q_{lb}}{\rho \pi D_{lb}^2 L_{lb}} \quad (2\text{A}.1) \]

\[ \Delta P = \frac{LV^2}{2Dg} \quad (2\text{A}.2) \]

\[ \Delta P_{up} = \frac{L_{up}V_{up}^2}{2D_{up}g} \quad (2\text{A}.2.1) \]

\[ \Delta P_{lb} = \frac{L_{lb}V_{lb}^2}{2D_{lb}g} \quad (2\text{A}.2.2) \]

\[ Q = \frac{\pi D^3 V}{4} \quad (2\text{A}.3) \]

\[ Q_{up} = \frac{\pi D_{up}^3 V_{up}}{4} \quad (2\text{A}.3.1) \]

\[ Q_{lb} = \frac{\pi D_{lb}^3 V_{lb}}{4} \quad (2\text{A}.3.2) \]

The equation that keeps the residence time constant can be written as:

\[ \frac{L_{up}}{V_{up}} = \frac{L_{up}}{V_{up}} \quad (2\text{A}.4) \]

Using the expressions for the volumetric flow from equations (2A.3.1) and (2A.3.2) and the equation for the pressure drop from equation (2A.2.1) and (2A.2.2) in equation (2A.1), the following final expression is obtained:

\[ \frac{V_{up}^3}{D_{up}} = \frac{V_{lb}^3}{D_{lb}} \quad (2\text{A}.5) \]
The flowrate and static-mixer diameter of the existing process are known. For the laboratory scale setup, the flow rate through the static-mixer is known. Hence, the only unknown in equation (2A.5) is the diameter of the laboratory scale static-mixer.
Appendix 2.B: Checking drop size change during microscopy

Figure 2B.1. Image of entrained drops from a microscope (a) 1 min after sampling (b) 6 min after sampling
Reference List


Chapter 2


Experimental density, viscosity, interfacial tension and water solubility of ethyl benzene-α-methyl benzyl alcohol-water system

This chapter has been published as: Esayas W. Barega, Edwin Zondervan, André B. de Haan, (2013). Experimental density, viscosity, interfacial tension and water solubility of ethyl benzene-α-methyl benzyl alcohol-water system, Journal of Chemical Thermodynamics, 63, 31-37.

Abstract

In this chapter, physical properties density, viscosity, interfacial tension, and water solubility are measured for the α-methyl benzyl alcohol (MBA)-Ethyl benzene (EB) system at different concentrations of MBA in contact with water and sodium hydroxide solution (0.01 mol.kg⁻¹) as aqueous phases. The properties are measured to identify the component which plays the governing role in changing the physical properties relevant to mass transfer and phase separation (entrainment behavior) of the ternary system. The measurements revealed that concentration of MBA is the major factor influencing all the properties. The water solubility, the density, and the viscosity increased strongly at higher concentrations of MBA; while, the interfacial tension decreased notably. The use of 0.01 mol.kg⁻¹ NaOH as an aqueous phase resulted in a decrease of the interfacial tension and a minor decrease in the water solubility. The density data are correlated using a quadratic mixing rule to describe the influence of concentration at any temperature. The viscosity data are correlated using the Nissan and Grunberg and Katti-Chaudhri equations. The Szyzkowski’s equation is used to correlate the interfacial tension data. The water solubility data is described using exponential function. All the used correlations described the experimental physical property data well.
3.1 Introduction

Physical properties play a significant role in several separation processes. This includes liquid-liquid extraction that involves mass transfer and phase separation steps. The physical properties in this regard control the drop size and its distribution\(^1-3\), which are important for both the mass transfer and phase separation steps. Several studies have shown that physical properties determine the drop size by influencing the relative breakage and coalescence rates\(^1,4-7\) and the interfacial and viscous forces that resist the droplet breakup.\(^8,9\) Moreover, once the drops are formed, the coalescence between the droplets and their separation depend on the physical properties.\(^2,3,10-14\)

The physical properties depend on the composition of the liquid-liquid system and the temperature and mostly the concentration of one component in the system may be critical for much of the observed change in physical properties. Therefore, the measurement of physical properties is an important step before entrainment quantification. This enables to identify the physical property change and the component responsible for an increase in entrainment. As mentioned in Chapter 1, the entrainment is quantified for two extraction systems, i.e., caprolactam-toluene-water and \(\alpha\)-methyl benzyl alcohol (MBA)-ethyl benzene (EB)-water systems. Therefore, their physical properties need to be known. The physical properties of the caprolactam-toluene-water system are known and measured before.\(^15\) However, the physical properties are not known for the MBA-EB-water system.

This chapter presents the density, viscosity, interfacial tension and water solubility of the ternary MBA-EB-Water system. Additionally, interfacial tension and water solubility data are measured for MBA-EB-NaOH (0.01 mol.kg\(^{-1}\)) system. We examine the influence of \(\alpha\)-methyl benzyl alcohol (MBA) concentration and temperature on the physical properties of the ternary systems 1) \(\alpha\)-methyl benzyl alcohol (MBA)-Ethyl benzene (EB)-water and 2) MBA-EB-NaOH (0.01 mol/kg). Some data exists on pure component viscosity, density\(^16-20\) and interfacial tension\(^21,22\) for the EB system. Therefore, the ternary data are measured at different concentrations of MBA and at different temperatures. Subsequently, the measured data are described by correlations from literature. The density data are described based on a quadratic mixing rule\(^23\), the viscosity data using the Nissan and Grunberg equation\(^23,24\) and Katti-Chaudhri equation\(^25\), the interfacial tension data by Szyzkowski’s equation\(^26\), and an exponential function to describe the water solubility data.


3.2 Experimental

3.2.1 Materials

Ethyl benzene (purity > 99%) was supplied by Merck (Germany), anhydrous sodium hydroxide (NaOH, purity > 99.9%) and alpha-methyl benzyl alcohol (purity > 99%) were supplied by Sigma-Aldrich (USA). Milli-Q super distilled water was used for all the measurements.

3.2.2 Measurement techniques

Water solubility

The equilibrium water solubility in the MBA-EB organic phase was determined at 298.15 K and 313.15 K temperatures and at different concentrations between (0-80%) mole basis of MBA in EB. 25 ml organic solution of MBA-EB at the required concentration of MBA and 25 ml of water were introduced in a jacketed equilibrium glass vessel, which had an inner chamber of 70 ml. The temperature in the double walled glass vessel was controlled using a thermostatic bath (Julabo F25) with uncertainty of 0.1 K. The organic and aqueous phases were agitated for half an hour at 500 rpm and subsequently allowed to settle for half an hour until clear phases were observed. To check whether the used duration of time was sufficient to reach equilibrium, the mixing time was increased to an hour and the water solubility was determined again. No change in the water solubility was observed, which ensured that equilibrium was reached. A 2.5 ml sample was taken from organic top phase and the water content was determined by using a Coulometric Karl-Fischer titration with a Metrohm 652 KF Coulometer (Applikon, The Netherlands). The same procedure was repeated three times and the water content was determined with a maximum uncertainty of 0.0005 in mass fraction.

Interfacial tension

Interfacial tensions were determined for the ternary systems MBA-EB-Water and MBA-EB-NaOH solution (0.01mol.kg⁻¹) at different concentrations of MBA (0-65) % mole basis and at 298.15 K and 313.15 K using Kruss 11 automatic tensiometer with a thermostated vessel (Wilten Physica, Belgium) temperature control. The thermostat vessel was connected to a Julabo F25 heating/cooling bath (Julabo Labortechnik, Germany), and the temperature was controlled with uncertainty of 0.1 K. Interfacial tensions were determined by the Du Nouy ring method using a standard ring and corrected by the Harkins&Jordan²⁷ method. The different concentrations of MBA in EB were prepared and agitated together with Milli-Q water until equilibrium was reached between the phases. This was done in the same
manner as for the determination of the water solubility. After the phases settled, 10 ml samples of organic and aqueous phases were taken from the top and bottom phases, respectively. The aqueous heavy phase was then placed in the thermostated vessel of the tensiometer. The ring was placed above the surface of the heavy phase, and the surface of the heavy phase was detected at a speed of 10 mm/min. After detection, the ring was immersed to 3 mm in the heavy phase at a speed of 0.2 mm/min. The heavy phase was then covered with the light phase and the interfacial tension was measured at a speed of 0.2 mm/min and with a relaxation of 10%. The measurement was continued until a standard deviation of the three consecutive measurements ≤ 0.3 mN/m was obtained.

Density

The density of the MBA-EB-water system at different concentrations of MBA (0-100% mole basis) in the organic phase and temperatures of 298.15 K, 303.15 K, 308.15 K and 313.15 K was determined by an automatic density meter DMA 5000 (Anton Paar, Austria). Solutions of MBA-EB at the desired concentration of MBA were prepared and injected into a density meter. The measuring cell in the densitometer was heated to the required temperature of the sample and then the measurement was started. After the density measurement was completed, the measuring cell was rinsed three times with acetone and water to clean it from the remaining chemicals from the used sample. The measurement was repeated three times and the densities were measured with an accuracy of 0.5 kg/m³.

Viscosity

The viscosity of the MBA-EB-water system at the above concentrations of MBA and temperatures of 298.15 K, 303.15 K, 308.15 K and 313.15 K was determined by capillary ubbelohde viscometer 50103/0c, with a capillary constant of 0.003244 mm²/s² ±0.65% (Schott, Germany). After samples of different concentrations of MBA in EB were prepared at the desired temperature, the samples were poured into the viscometers. The capillaries filled with the sample were immersed in a Lauda water bath equipped with thermostat, which controls the temperature with an uncertainty of 0.1 K. To measure the viscosity, the sample was sucked up in a capillary until it passes a top marker. Then the time required for the meniscus of the sample to descend from the top to the bottom marker was measured using a digital stopwatch with a resolution of 0.01s. The procedure was repeated three times. The kinematic viscosity was determined by multiplying the time with the capillary constant. Afterwards, the dynamic viscosity was calculated by
multiplying the kinematic viscosity with the density. The dynamic viscosity was determined with the relative standard uncertainty of 0.003 mPa.s.

3.3 Results and discussion

3.3.1 Water solubility

The effect of MBA concentration in the organic phase on water solubility is shown in Figure 3.1. The values are listed in Table 3A.1 (Appendix 3.A). Generally, it can be observed that the water solubility increases considerably with an increase in MBA concentration in the organic phase. This can be attributed to the increased availability of MBA molecules for hydrogen bonding with water molecules as a result of their high concentration in the organic phase, which moves the water to the organic phase. The water solubility also increased at elevated temperatures. However, compared to the MBA concentration, the effect of temperature on the water solubility was found to be small.

The influence of MBA concentration on the water solubility can be correlated by the exponential function shown in equation (3.1) where \( x_w \) is the solubility of water in the organic MBA-EB phase in mass fraction, and \( x_1 \) is the concentration of MBA in the organic phase in mole fraction (water free basis).

\[
x_w = c_1 \exp \left( \frac{x_1}{c_2} \right) + c_3
\]

The determined parameters are given table 3.1. As can be observed from Figure 3.1 and table 3.1, a good agreement was obtained between the experimental and calculated values.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>AARE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values, Water T = 298.15 K</td>
<td>0.00691</td>
<td>0.39314</td>
<td>-0.00685</td>
<td>1.48</td>
</tr>
<tr>
<td>Values, Water T = 313.15 K</td>
<td>0.00898</td>
<td>0.43166</td>
<td>-0.00896</td>
<td>0.79</td>
</tr>
<tr>
<td>Values, 0.01 mol.kg(^{-1}) NaOH T = 298.15 K</td>
<td>0.00568</td>
<td>0.37034</td>
<td>-0.00546</td>
<td>1.87</td>
</tr>
</tbody>
</table>
Figure 3.1: Water solubility in mass fraction, $x_{w}$, versus MBA mole fraction in the organic phase, $x_1$ (water free basis). ■, $T=298.15$ K and water aqueous phase; ●, $T=313.15$ K and water aqueous phase; ▲, $T=298.15$ K and 0.01 mol kg$^{-1}$ NaOH aqueous phase; —, fitted values according to Eq. (3.1)

3.3.2 Density

The variation in the density of the MBA-EB-water system with an increase in the concentration of MBA in the organic phase and temperature is depicted in Figure 3.2 and the values are listed in Table 3A.2 (Appendix 3.A). It can be observed that the density of the organic MBA-EB-Water ternary system increases strongly at high MBA concentrations. This implies for a given density of the aqueous phase (Milli-Q water) that the density difference between the phases becomes smaller at higher concentrations of MBA. Additionally, an increase in temperature from 298.15 K to 313.15 K resulted in a decrease in the density of the mixture.

The composition dependence of binary and ternary densities is usually correlated by a Redlich-Kister polynomial expansion\textsuperscript{28} at one temperature using excess molar volume data. In this work, the measured ternary system densities $\rho_m$ are correlated using equation (3.3) based on simple quadratic rule\textsuperscript{23} at any temperature.

$$\rho_m = \sum_i x_i \rho_i + \sum_i x_i \sum_j x_j K_{ij} (\rho_i \rho_j)^{0.5}$$  \hspace{1cm} (3.3)

In the equation, $\rho_m$ is the density of the ternary EB-MBA-Water system at any temperature, $\rho_i$ and $\rho_j$ are the densities of pure components MBA,EB, and water, $x_i$ and $x_j$ are the liquid mole fractions, and $K_{ij}=K_{ji}$ ($K_{ii}=K_{jj}=0$) is the binary fitting parameter that accounts for deviation from ideality. The liquid mole fractions of
MBA, EB, and water in equation (3.3) are calculated from concentrations of MBA and EB before water saturation and from the water solubility. The parameters $K_{ij}$ are determined by minimizing the average absolute relative error (AARE). The parameters $K_{ij}$ and AARE are given in Table 3.2. As can be seen from Figure 3.2, a good agreement was obtained between the experimental and calculated density values.

### 3.3.3 Viscosity

The results of viscosity measurements are presented in Table 3A.3 (Appendix 3.A). The mixture viscosity increases considerably as the MBA concentration in the organic phase increases and it decreases at higher temperatures. As in the case of water solubility and density, the concentration of MBA was found to be the main factor influencing the measured viscosity values. Therefore, it can be expected that the MBA concentration plays a key role in the dispersion and separation behavior of the ternary system. Additionally, the temperature is also expected to play an important role as the density and viscosity values were notably influenced.

The ternary system dynamic viscosities are correlated using the compositional models the Nissan and Grunberg equation$^{23,24}$ and Katti-Chaudhri equation$^{25}$ as shown in equations (3.4) and (3.5), respectively.

$$\ln(\eta_m) = \sum x_i \ln(\eta_i) + \sum_i \sum_j x_ix_j G_{ij}$$  \hspace{1cm} (3.4)

$$\ln(\eta_m v_m) = \sum x_i \ln(\eta_i v_i) + \sum_i \sum_j \frac{x_ix_j W_{ij}}{RT}$$  \hspace{1cm} (3.5)

In these equations, $\eta_m$ represents the dynamic viscosity of the ternary system at a given temperature, $x_i$ and $x_j$ the liquid mole fractions, $v_m$ the mixture molar volume, $v_i$ and $\eta_i$ the pure component molar volumes and viscosities, respectively. The mole fractions in equations (3.4) and (3.5) are calculated in the same way as in density equation.

<table>
<thead>
<tr>
<th>Table 3.2: Parameters and AARE of equation (3.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBA (1) + EB (2) + Water (3)</td>
</tr>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>MBA+EB (12)</td>
</tr>
<tr>
<td>MBA+Water (13)</td>
</tr>
<tr>
<td>EB+Water (23)</td>
</tr>
<tr>
<td>AARE/%</td>
</tr>
</tbody>
</table>
The binary parameters $G_{ij}$ and $W_{ij}$ are adjustable quantities accounting for intermolecular interactions. For the Nissan and Grunberg equation, the interaction parameter $G_{ij}$ can be calculated by the group contribution method. However, in this paper, a linear temperature dependent equation is used where $H_{ij}/K^1$ is the temperature dependent coefficient and $M_{ij}/$- is the temperature independent coefficient. In the Katti-Chaudhri equation, the temperature dependence is included in the equation; therefore, one parameter $W_{ij}/J.mol^{-1}$ is sufficient to describe the interaction.

$$G_{ij} = H_{ij}T + M_{ij}$$  \hspace{1cm} (3.6)

The parameters are determined by minimizing the absolute value of the relative error (AARE) and are shown in Table 3.3. The deviation between the experimental and calculated dynamic viscosities using equations (3.4) and (3.5) are presented in Figure 3.3. It can be observed that the deviation between the experimental and calculated dynamic viscosity values and the AARE are comparable. However, using Katti-Chaudhri equation has an advantage since only three parameters are optimized to describe the experimental data at all temperatures and concentrations, while in the Nissan and Grunberg equation six parameters should be determined. The obtained binary interaction parameters from both equations are negative for MBA-EB, implying a repulsive interaction between these molecules. In contrast, positive interaction parameters are obtained for MBA-Water, implying attractive interactions.
interaction between the molecules. The interaction parameter between EB-Water is positive but less than that of MBA-Water implying a weaker attraction between the molecules compared to MBA-Water. The experimental dynamic viscosities and the calculated values from the Katti-Chaudhri are depicted in Figure 3.4. It can be seen that the experimental data agree well with the calculated values.

![Figure 3.3: Relative deviations between the experimental measured viscosities and calculated by: □, Katti-Chaudhri equation; ■, Nissan and Grunberg equation at T=298.15 K (top left), T=303.15 K (top right), T=308.15 K (bottom left), and T=313.15 K (bottom right)
Figure 3.4: Dynamic viscosity, $\eta$, versus mole fraction of MBA in the organic phase, $x_1$ (water free basis), at different temperatures: ■, $T=298.15$ K; □, $T=303.15$ K; ▲, $T=308.15$ K and; ▄, $T=313.15$ K;—, calculated values using Katti-Chaudhri equation

![Graph showing dynamic viscosity vs. mole fraction of MBA](image)

Table 3.3: Parameters and AARE of equation (3.4) & (3.5)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$H_{ij}$/J.mol$^{-1}$</th>
<th>$M_{ij}$/J.mol$^{-1}$</th>
<th>$W_{ij}$/J.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBA+EB (12)</td>
<td>-0.0046</td>
<td>-0.0074</td>
<td></td>
</tr>
<tr>
<td>MBA+Water (13)</td>
<td>0.0071</td>
<td>-0.0022</td>
<td></td>
</tr>
<tr>
<td>EB+Water (23)</td>
<td>9.7E-5</td>
<td>-0.0016</td>
<td></td>
</tr>
<tr>
<td>AARE /%</td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBA+EB (12)</td>
<td></td>
<td></td>
<td>-3537</td>
</tr>
<tr>
<td>MBA+Water (13)</td>
<td></td>
<td></td>
<td>9151</td>
</tr>
<tr>
<td>EB+Water (23)</td>
<td></td>
<td></td>
<td>1743</td>
</tr>
<tr>
<td>AARE /%</td>
<td></td>
<td></td>
<td>1.91</td>
</tr>
</tbody>
</table>

3.3.4 Interfacial tension

The influence of MBA concentration in the organic phase and temperature on the interfacial tension of the two phase system is depicted in Figure 3.5. The values are shown in Table 3A.4 (Appendix 3.A). As can be seen from the figure, the interfacial tension decreased sharply at first and then levels off at higher concentrations of MBA. The influence of temperature on the interfacial tension is also shown in Figure 3.5. Generally, a slightly lower interfacial tension was
observed at higher temperature; however, the effect of MBA concentration was more pronounced.

Therefore, from the obtained results it can be inferred that the presence of MBA assists in the formation of a dispersion (small drop sizes), as the interfacial tension of the system decreased notably at higher concentration of MBA. Nevertheless, this decrease of interfacial tension might worsen the phase separation due to the formation of small droplets.

The effect of the MBA concentration on the interfacial tension is correlated using the Szyzkowski correlation as depicted in equation (3.7) where $A_{sz}/N.m.K^{-1}$ and $B_{sz}/mol.L^{-1}$ are the Szyzkowski adsorption coefficients, and $\gamma_{i,T}$, $\gamma_{o,T}$ representing the interfacial tension with MBA concentration $C_i/mol.L^{-1}$ and without MBA at temperature $T/K$, respectively.

$$\gamma_{i,T} = \gamma_{o,T} (1 - A_{sz} (\ln\left(\frac{C_i}{B_{sz}}\right) + 1))$$

The Szyzkowski coefficients were determined at 298.15 K and 313.15 K based on the measured change of interfacial tension with MBA concentration and are given in table 3.4. The interfacial tension data was correlated well with Szyzkowski equation. As can be observed in Figure 3.5, a good agreement was obtained between the experimental and calculated values.

3.3.5 Effect of NaOH (0.01 mol.kg$^{-1}$) solution

In addition to using water as an aqueous phase, the effect of 0.01 mol.kg$^{-1}$ NaOH solution as an aqueous phase was studied. The influence on water solubility is shown in Table 3A.1 (Appendix 3.A). A slightly lower water content in the organic phase was observed by using 0.01 mol.kg$^{-1}$ NaOH solution instead of water. This minor decrease in water content can be attributed to the fact that ions bind water in their shell$^{29,30}$, which reduces the water activity and therefore its tendency to solubilize in the organic phase.

The influence of 0.01 mol.kg$^{-1}$ NaOH solution on interfacial tension was also measured. It can be observed from Figure 3.5 and Table 3A.4 (Appendix 3.A) that lower interfacial tension values were obtained when using 0.01 mol.kg$^{-1}$ NaOH. The decrease can be attributed to the deprotonation of MBA by NaOH creating an ionic surfactant in similar manner to the lowering of interfacial tension of acidic crude oil systems by Alkali injection.$^{31}$ The observed change was more significant at lower concentrations of MBA and decreased at higher concentrations. The water
solubility and the interfacial tension data are correlated using equation (3.1) and (3.7), respectively. The determined parameters and AARE are given in Tables 3.1 and 3.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aqueous phase water T=298.15 K</th>
<th>Aqueous phase water T=303.15 K</th>
<th>Aqueous phase 0.01 mol.kg⁻¹ NaOH T=298.15 K</th>
<th>Aqueous phase 0.01 mol.kg⁻¹ NaOH T=313.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{SZ}/N\cdot m^{-1}\cdot K^{-1}$</td>
<td>0.1575</td>
<td>0.1484</td>
<td>0.1305</td>
<td>0.1299</td>
</tr>
<tr>
<td>$B_{SZ}/mol\cdot L^{-1}$</td>
<td>0.0459</td>
<td>0.0437</td>
<td>0.0261</td>
<td>0.0480</td>
</tr>
<tr>
<td>AARE</td>
<td>3.13</td>
<td>1.11</td>
<td>2.40</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Using 0.01 mol.kg⁻¹ NaOH solution as an aqueous phase can also influence the density and dynamic viscosity values. However, this influence was considered to be not significant in view of the fact that the water solubility values showed a minor change when using 0.01 mol.kg⁻¹ NaOH solution. Since the density and dynamic viscosities of the ternary system MBA-EB-water are dependent on the water solubility, a minor change in the water solubility means a minor change in those properties. Hence, measurement of these properties was not performed.

### 3.4 Conclusions

The water solubility, density, viscosity, and the interfacial tension of EB-MBA-water system were measured to identify the component that plays a major role in changing the measured properties. The measured data gave an insight that the concentration of MBA is a main factor influencing all the measured properties relevant to dispersion and phase separation. All the measured physical properties were found to change strongly with the concentration of MBA. The water solubility, the density and the viscosity of the mixture EB-MBA were found to increase considerably at higher concentrations of MBA. Additionally, the interfacial tension of the system decreased notably at higher concentration. By using 0.01 mol.kg⁻¹ NaOH as an aqueous phase, the interfacial tension decreased and slightly lower water solubility was obtained. Moreover, the properties were correlated and described adequately using correlations from literature for density, viscosity and interfacial tension.
Figure 3.5: Interfacial tension, $\gamma$, versus molar concentration of MBA, C, at different temperatures and aqueous phases: ■, $T=298.15$ K and aqueous phase water; □, $T=313.15$ K and aqueous phase water; ▲, $T=298.15$ K and aqueous phase 0.01 mol.kg$^{-1}$ NaOH; △, $T=313.15$ K and aqueous phase 0.01 mol.kg$^{-1}$ NaOH; —, calculated from Eq. (3.7)
Chapter 3

Nomenclature

AARE  Absolute average relative error, %
A_{sz}  Szyzkowski adsorption coefficient, mol.L^{-1}
B_{sz}  Szyzkowski adsorption coefficient, mol.L^{-1}
c      Constant in water solubility correlation Eq. (1), -
C_i    Concentration of MBA, mol.L^{-1}
G_{ij}  Binary interaction parameter in Nissan Grunberg equation, -
H_{ij}  Temperature dependent coefficient in expression for G_{ij}, K^{-1}
K_{ij}  Binary interaction parameter in density correlation Eq. (3), -
M_{ij}  Temperature independent coefficient in expression for G_{ij}, -
P      Pressure, MPa
R      Gas constant = 8.314 J.mol^{-1}.K^{-1}
T      Temperature, K
W_{ij}  Binary interaction parameter in Katti-Chaudhri equation, J.mol^{-1}
x_1    Mole fraction of MBA in the organic MBA-EB phase, -
x_i    Mole fraction of component i, -
X_w    Solubility of water in the organic MBA-EB phase in mass

Greek letters

\gamma_{i,T}  Interfacial tension at temperature T and molar concentration C_i
\gamma_{i,o}  Interfacial tension at 293 K, N.m^{-1}
\eta_i        Pure component dynamic viscosity, mPa.s
\eta_m        Mixture dynamic viscosity, mPa.s
\nu_i         Pure component molar volume, m^3.mol^{-1}
\nu_m         Mixture molar volume, m^3.mol^{-1}
\rho_i        Pure component density, kg.m^{-3}
\rho_m        Mixture density, kg.m^{-3}

Abbreviations

EB            Ethyl benzene
MBA           \alpha-methyl benzyl alcohol
rpm           Rotations per minute
Appendix 3.A: Physical properties of ethyl benzene (EB)-α-methyl benzyl alcohol (MBA)-water system

Table 3A.1: Water solubility, \(x_w\) (mass fraction), at different mole fractions of MBA in the organic phase \((x_1, \text{water free concentrations})\) at different temperatures, and water / 0.01kg.mol\(^{-1}\) NaOH aqueous phases and pressure \(P= 0.1\) MPaf

<table>
<thead>
<tr>
<th>(x_1)</th>
<th>(x_w) at (T = 298.15 \text{ K}) water</th>
<th>(x_w) at (T = 313.15 \text{ K}) water</th>
<th>(x_w) at (T = 298.15 \text{ K}) 0.01 mol.kg(^{-1})NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1014</td>
<td>0.0021</td>
<td>0.0024</td>
<td>0.0020</td>
</tr>
<tr>
<td>0.2025</td>
<td>0.0047</td>
<td>0.0054</td>
<td>0.0043</td>
</tr>
<tr>
<td>0.3334</td>
<td>0.0093</td>
<td>0.0103</td>
<td>0.0085</td>
</tr>
<tr>
<td>0.4037</td>
<td>0.0125</td>
<td>0.0140</td>
<td>0.0119</td>
</tr>
<tr>
<td>0.5039</td>
<td>0.0189</td>
<td>0.0199</td>
<td>0.0175</td>
</tr>
<tr>
<td>0.6535</td>
<td>0.0284</td>
<td>0.0309</td>
<td>0.0268</td>
</tr>
<tr>
<td>0.8025</td>
<td>0.0464</td>
<td>0.0487</td>
<td>0.0441</td>
</tr>
</tbody>
</table>

Standard uncertainties are \(u(T) = 0.1\) K, \(u(x_1) = 5E-5\), \(u(x_w) = 5E-3\)

Note that the compositions presented in table B.1 are not tie lines. What the table shows is how the water solubility in the organic phase \((x_w)\), when a binary (MBA+EB) organic phase initially without water (as given by different concentrations of MBA in EB ,\(X_1\)) is contacted by either water or 0.01 mol/kg NaOH solution.

Table 3A.2: Experimental density \(\rho/\text{kg.m}^{-3}\) of the ternary \{MBA (1) + EB (2) + Water (3)\} system (organic phase) at different mole fractions of MBA, \(P = 0.1\) MPa and \(T = (298.15,303.15,308.15,\) and 313.15 \(\text{K}\) g

<table>
<thead>
<tr>
<th>(x_1)</th>
<th>(x_2)</th>
<th>(x_3)</th>
<th>(T/\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>298.15</td>
</tr>
<tr>
<td>0.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>862.5</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.9967</td>
<td>0.0033</td>
<td>863.3</td>
</tr>
<tr>
<td>0.1001</td>
<td>0.8874</td>
<td>0.0124</td>
<td>875.8</td>
</tr>
<tr>
<td>0.1969</td>
<td>0.7755</td>
<td>0.0276</td>
<td>890.4</td>
</tr>
<tr>
<td>0.3151</td>
<td>0.6299</td>
<td>0.0550</td>
<td>910.4</td>
</tr>
<tr>
<td>0.3742</td>
<td>0.5527</td>
<td>0.0731</td>
<td>919.9</td>
</tr>
<tr>
<td>0.4399</td>
<td>0.4513</td>
<td>0.1088</td>
<td>936.7</td>
</tr>
<tr>
<td>0.5496</td>
<td>0.2914</td>
<td>0.1591</td>
<td>958.1</td>
</tr>
<tr>
<td>0.6072</td>
<td>0.1495</td>
<td>0.2434</td>
<td>981.0</td>
</tr>
<tr>
<td>0.6557</td>
<td>0.0000</td>
<td>0.3443</td>
<td>1009.5</td>
</tr>
<tr>
<td>1.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1009.0</td>
</tr>
</tbody>
</table>

gStandard uncertainties are \(u(T) = 0.1\) K, \(u(x_1) = 5E-5\), \(u(\rho) = 0.5\) kg.m\(^{-3}\)

In the table, the data in italics represent the water saturated EB and MBA densities. However, pure component values are used in the correlation of density.
Table 3A.3: Experimental dynamic viscosity $\eta$/mPa.s of the ternary \{MBA (1) + EB (2) + Water (3)\} system (organic phase) at different mole fractions of MBA, $P = 0.1$ MPa, and $T = (298.15,303.15,308.15,\text{ and } 313.15)$ K.$^h$

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>$T/K$</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>298.15</td>
<td>303.15</td>
<td>308.15</td>
<td>313.15</td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>1.0000</td>
<td>0.0000</td>
<td>0.638</td>
<td>0.609</td>
<td>0.568</td>
<td>0.541</td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.9967</td>
<td>0.0033</td>
<td>0.614</td>
<td>0.581</td>
<td>0.549</td>
<td>0.521</td>
<td></td>
</tr>
<tr>
<td>0.1001</td>
<td>0.8874</td>
<td>0.0124</td>
<td>0.723</td>
<td>0.678</td>
<td>0.636</td>
<td>0.598</td>
<td></td>
</tr>
<tr>
<td>0.1969</td>
<td>0.7755</td>
<td>0.0276</td>
<td>0.847</td>
<td>0.782</td>
<td>0.727</td>
<td>0.678</td>
<td></td>
</tr>
<tr>
<td>0.3151</td>
<td>0.6299</td>
<td>0.0550</td>
<td>1.195</td>
<td>1.088</td>
<td>0.998</td>
<td>0.919</td>
<td></td>
</tr>
<tr>
<td>0.3742</td>
<td>0.5527</td>
<td>0.0731</td>
<td>1.335</td>
<td>1.213</td>
<td>1.099</td>
<td>1.013</td>
<td></td>
</tr>
<tr>
<td>0.4399</td>
<td>0.4513</td>
<td>0.1088</td>
<td>1.726</td>
<td>1.544</td>
<td>1.396</td>
<td>1.260</td>
<td></td>
</tr>
<tr>
<td>0.5496</td>
<td>0.2914</td>
<td>0.1591</td>
<td>2.565</td>
<td>2.246</td>
<td>1.976</td>
<td>1.752</td>
<td></td>
</tr>
<tr>
<td>0.6072</td>
<td>0.1495</td>
<td>0.2434</td>
<td>4.073</td>
<td>3.462</td>
<td>2.970</td>
<td>2.580</td>
<td></td>
</tr>
<tr>
<td>0.6557</td>
<td>0.0000</td>
<td>0.3443</td>
<td>7.561</td>
<td>6.122</td>
<td>5.052</td>
<td>4.228</td>
<td></td>
</tr>
<tr>
<td>1.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>8.703</td>
<td>6.981</td>
<td>5.714</td>
<td>4.748</td>
<td></td>
</tr>
</tbody>
</table>

$^h$ Standard uncertainties are $u(T) = 0.1$ K, $u(x) = 5E-5$, and relative standard uncertainty $u(\eta) = 0.003$ mPa.s. In the table, the data in italics represent the water saturated EB and MBA dynamic viscosities. However, only pure component dynamic viscosities are used in viscosity correlations.

Table 3A.4: Experimental interfacial tension $\gamma$/N.m$^{-1}$ for the ternary \{MBA (1) + EB (2) + Water (3)\} organic system contacted with water / NaOH 0.01 mol.kg$^{-1}$ solution aqueous phase, at different mole fractions of MBA in the organic phase, at $P = 0.1$ MPa and $T = (298.15, \text{ and } 313.15)$ K.$^i$

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>$\gamma$/N.m$^{-1}$</th>
<th>$\gamma$/N.m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T = 298.15$ K</td>
<td>$T = 313.15$ K</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.9967</td>
<td>0.0033</td>
<td>0.0346</td>
<td>0.0307</td>
</tr>
<tr>
<td>0.0503</td>
<td>0.9426</td>
<td>0.0071</td>
<td>0.0224</td>
<td>0.0197</td>
</tr>
<tr>
<td>0.1001</td>
<td>0.8874</td>
<td>0.0124</td>
<td>0.0167</td>
<td>0.0161</td>
</tr>
<tr>
<td>0.1969</td>
<td>0.7755</td>
<td>0.0276</td>
<td>0.0138</td>
<td>0.0134</td>
</tr>
<tr>
<td>0.3151</td>
<td>0.6299</td>
<td>0.0550</td>
<td>0.0117</td>
<td>0.0114</td>
</tr>
<tr>
<td>0.3742</td>
<td>0.5527</td>
<td>0.0731</td>
<td>0.0106</td>
<td>0.0104</td>
</tr>
<tr>
<td>0.4399</td>
<td>0.4513</td>
<td>0.1088</td>
<td>0.0098</td>
<td>0.0092</td>
</tr>
</tbody>
</table>

$^i$ Standard uncertainties are $u(T) = 0.1$ K, $u(x) = 5E-5$, $u(\gamma) = 0.2$ mN/m

54
Reference List


Influence of physical properties and process conditions on entrainment behaviour in a static mixer settler setup

This chapter has been published as: Esayas W. Barega, Edwin Zondervan, André B. de Haan, (2013). Influence of physical properties and process conditions on entrainment behaviour in a static mixer settler setup, Industrial Engineering and Chemistry Research, 52, 2958-2968

Abstract

In this chapter, we investigate the entrainment behavior of caprolactam-toluene-water and ethylbenzene (EB)-α-methyl benzyl alcohol (MBA)-water/NaOH (pH=12) systems in a static-mixer settler setup. The role of physical properties (interfacial tension, the viscosity of the dispersed and continuous phase, density difference, and physical solubility), and process conditions (flow rate, phase ratio, and temperature) on the entrainment is examined. Drop sizes and dispersed phase entrainment were measured for both systems. For the caprolactam-toluene-water system, increasing the caprolactam concentration from 5.35% w/w to 28.5% w/w decreased the drop size and increased the entrainment from 200 ppm to 1373 ppm. For the EB-MBA-water system, increasing the MBA concentration from 20% v/v to 33% v/v decreased the drop size and increased the entrainment sharply from 600 ppm to 2785 ppm. Different entrainment trends were observed for the two systems with temperature and phase ratio. The phase ratio effect resulted from on one hand turbulent attenuation and increased coalescence, and on the other hand increased shear and hindered settling at high phase ratios. The temperature influence was determined by its counteracting effects on the interfacial tension and the viscosities of continuous and dispersed phases.
Chapter 4

4.1 Introduction

As described in Chapter 1, entrainment is one of the major operational problems of solvent extraction processes that can cause loss of the expensive solvent, impurity accumulation in the final product, and a decrease in product quality and capacity, which in turn translate into large operating cost.\textsuperscript{1-4} These include the solvent extraction processes of chemical, biochemical and metallurgical industries.\textsuperscript{1-5}

In this Chapter, we study entrainment for two extraction systems: 1) caprolactam-water-toluene and 2) Ethyl benzene (EB)-\(\alpha\)-methyl benzyl alcohol (MBA)-Water. Commercial fiber-grade caprolactam requires high purity (> 99.9% w/w).\textsuperscript{6} During the extraction step, while extracting the aqueous-caprolactam phase with toluene, entrainment of the aqueous phase into the organic solvent phase can occur as a result of the reduction of interfacial tension of the two phases due to a high caprolactam concentration. The high concentration of caprolactam (60-70% w/w) in the feed reduces the interfacial tension to values less than 5mN/m.\textsuperscript{7} This leads to the formation of micro droplets and eventually to their entrainment in the organic phase, having a number of consequences: 1) product dilution, which means that product specifications are no longer met and the production capacity decreases 2) the downstream separation cost increases in meeting the product specifications 3) an associated increase in the impurities occurs as more entrainment of the aqueous phase leads to an increase in aqueous-phase soluble unwanted components in the organic phase.\textsuperscript{6}

In EB-MBA-Water system, due to long settling time and incomplete phase separation, a number of entrainment related problems occur. This system is part of the industrial propylene oxide-styrene monomer process.\textsuperscript{8} The process step of interest is the caustic (NaOH) wash step and its function is to remove acidic and phenol components from major EB-MBA stream. Acidic components are first extracted by caustic solution (pH=12) in a static mixer. This is followed by phase separation, which requires a long residence time. The long residence time causes fouling and product loss due to caustic catalyzed side reactions. Moreover, the salty water phase entrainment to the organic phase results in the fouling of the equipments downstream, product loss due to side reactions, and increased downstream separation cost.

To investigate the possibility of intensifying dispersed phase separation, first the role of process conditions and physical properties on entrainment needs to be determined. This characterization (quantification) of entrainment yields information about conditions, which result in a high amount of entrainment.
Additionally, the quantification provides a reference in which the reduction of entrainment to be aimed for.

Thus in this chapter, we investigate entrainment for the aforementioned extraction systems using the static mixer settler setup described in Chapter 1. The static mixer was chosen as a mixing device to maintain the industrial relevance in particular for the EB-MBA-water system. Static mixers are a relatively new class of mixers with distinctive advantages over stirred tanks; namely, first, the turbulent energy is distributed more uniformly resulting in narrow droplet size distributions\(^9\),\(^{12,24}\), second, they provide very efficient mixing without back-mixing and less energy input\(^9\),\(^{12,13,25,26}\), and third, in contrast to stirred tanks, they avoid large solvent inventory that leads to a huge equipment intensification.\(^{12}\)

Although in the past most research work was directed towards entrainment generated by stirred vessels, to best of our knowledge, no experimental entrainment data is available regarding processes with static-mixers. The available research on static mixers mainly focuses on drop size measurement and correlations to describe the experimental results.\(^{24,27-30}\) Only a few studies can be found concerning their phase separation behavior. For example, (Merchuk et al., 1980)\(^{12,31}\) compared stirred tank, static mixer, and packed tubes on the basis of batch separation time and the thickness of the dispersion band formed in a settler. They found the same thickness of the dispersion for both static mixers and stirred tanks. (Godfery et al., 1980)\(^{12,32}\) compared the stirred vessel with a Sulzer static mixer based on phase separation and observed comparable settler performance. However, in all the works, the separation performance was compared based on the thickness of dispersion and in a batch process.

The role of physical properties on entrainment behavior was also not studied. Thus, in this chapter we investigate the influence of interfacial tension, viscosity, density and solubility on the entrainment behavior for the selected systems. Furthermore, the role of flow condition, phase ratio, and temperature on the entrainment behavior is examined. In the caprolactam–toluene-water system, the concentration of caprolactam is varied, which changed mainly the interfacial tension. In a similar manner, for the EB-MBA-water system, the concentration of MBA is varied, which changed mostly the density difference and the viscosity of the continuous phase as well as the water solubility. In addition, for the second system (EB-MBA-Water), NaOH (pH=12) is used as an aqueous phase to study the influence of dispersed phase viscosity. For both systems, the influence of temperature and phase ratio on the entrainment behavior is studied. Drop sizes
created by static mixer are also measured to relate them with the entrainment measured.

4.2 Materials & Methods

4.2.1 Materials

Toluene (purity > 99%) and ethyl benzene (EB) (purity > 99%) were supplied by Merck Germany. \(\varepsilon\)-caprolactam (purity > 99%), anhydrous sodium hydroxide (purity > 99%), and \(\alpha\)-methyl benzyl alcohol (MBA) (purity > 99%) were supplied by Sigma-Aldrich (USA). Milli-Q super distilled water was used for all the experiments.

4.2.2 Experimental setup and procedure

Procedure

The experimental setup developed in Chapter 2 was used for entrainment quantification. Before starting the experiments, for the caprolactam-toluene-water system, an equilibrated amount of caprolactam in the toluene and Milli-Q water was prepared to avoid mass transfer effects. Two different concentrations of 5.35% w/w and 28.51% w/w caprolactam in the aqueous phase were used. Corresponding to these concentrations in the aqueous phase, the equilibrium caprolactam concentrations in the organic phase and the physical properties are given in Table 4.1. For the EB-MBA-water system, 20% v/v and 33% v/v of MBA in EB were used as organic phase. In addition, Milli-Q water and sodium hydroxide solution (0.0004g NaOH/ml of H\(_2\)O) were used as an aqueous phase. The corresponding equilibrium solubility of water in the organic phase and the physical properties are given in Table 4.2.

Once the organic and aqueous phases are prepared for each system, the organic and aqueous tanks, the settler, and the secondary settlers were filled with equilibrated organic and aqueous phases. The static mixer was primed with the organic phase in order to pre-wet the internals with the continuous phase. Once the other part of the system was filled with each phase, the organic pump flow was adjusted from 30 l/hr to 96 l/hr and the aqueous flow was adjusted to 10% of the organic flow. For each flow, the experiment is run three times the residence time to ensure equilibrium. The recycle phases were checked for equilibrium by measuring the concentrations at the outlet of the organic continuous phase and taking sample of the recycled stream from the storage tanks. Additionally, a visual check concludes that the recycled phases are non-hazy, and the coalescers operate adequately.
Table 4.1. Equilibrium concentrations in the organic phase and the respective physical properties of the caprolactam-toluene-water system\(^7\) at 20\(^\circ\)C

<table>
<thead>
<tr>
<th>Caprolactam concentration in the aqueous phase (w/w %)/T(C)</th>
<th>Equilibrium caprolactam concentration in the organic phase/water solubility (w/w %)</th>
<th>Interfacial tension (mN/m)</th>
<th>Density Organic continuous phase (kg/m(^3))</th>
<th>Viscosity Organic Continuous phase (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.35/20</td>
<td>0.37/0.06</td>
<td>18</td>
<td>868</td>
<td>0.594</td>
</tr>
<tr>
<td>28.51/20</td>
<td>3.39/0.16</td>
<td>7.3</td>
<td>877</td>
<td>0.635</td>
</tr>
<tr>
<td>5.35/40</td>
<td>0.64/0.13</td>
<td>17</td>
<td>848</td>
<td>0.467</td>
</tr>
<tr>
<td>28.31/40</td>
<td>4.96/0.28</td>
<td>5.3</td>
<td>857</td>
<td>0.513</td>
</tr>
</tbody>
</table>

Table 4.2. Equilibrium concentrations in the organic phase and the respective physical properties of the EB-MBA-water system (Chapter 3) at 20\(^\circ\)C

<table>
<thead>
<tr>
<th>MBA concentration in the EB organic Phase (v/v %)/T(C)</th>
<th>Equilibrium water solubility in the organic phase (w/w%)</th>
<th>Interfacial tension (mN/m)</th>
<th>Density Organic Continuous phase (kg/m(^3))</th>
<th>Viscosity Organic Continuous phase (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/20</td>
<td>0.465</td>
<td>13.8</td>
<td>890</td>
<td>0.847</td>
</tr>
<tr>
<td>33/20</td>
<td>0.93</td>
<td>11.7</td>
<td>910</td>
<td>1.195</td>
</tr>
<tr>
<td>20/30</td>
<td>0.50</td>
<td>13.6</td>
<td>886</td>
<td>0.782</td>
</tr>
<tr>
<td>33/30</td>
<td>0.98</td>
<td>11.5</td>
<td>906</td>
<td>1.088</td>
</tr>
<tr>
<td>20/40</td>
<td>0.55</td>
<td>13.4</td>
<td>877</td>
<td>0.678</td>
</tr>
<tr>
<td>33/40</td>
<td>1.02</td>
<td>11.4</td>
<td>897</td>
<td>0.919</td>
</tr>
</tbody>
</table>

**Entrainment quantification and drop size measurement**

For the systems used in this work, the aqueous phase was dispersed in the organic phase, which is similar to the industrial processes to keep the industrial relevance. The dispersed aqueous phase entrainment to the organic stream can then be determined by water content measurement. Under equilibrium conditions, some water is present in the organic phase due to the physical solubility. This was determined by circulating the two phases at a low flowrate (therefore no droplet entrainment) until equilibrium was established. Once this was determined, the droplet entrainment was measured by subtracting the solubility from the total water content. Therefore, to determine the amount of entrainment, 30 ml of the organic stream was taken by opening the organic outlet valve from the settler. From this, 1 ml of organic sample was analysed six times for water content. The mass fraction of water in the organic phase was measured by a coulometric Karl Fischer titration.
with a 652 KF Coulometer (Applikon, The Netherlands) with a precision of 
±0.005% (w/w).

The drop sizes were determined by taking pictures of the drops in the glass pipe 
extension of the static mixer using a Canon 50D camera as described in Chapter 2. 
Using this method only droplet sizes greater than 100 microns could be measured. 
The images containing the droplets are taken multiple times and then analyzed by 
the Adobe photoshop software CS5.

4.3 Results and Discussion

4.3.1 Effect of caprolactam concentration (the role of interfacial tension)

As shown in Table 4.1, the interfacial tension of the caprolactam-water-toluene 
system decreased from 18 mN/m to 6 mN/m with an increase of caprolactam 
concentration. Accordingly, as depicted in Figure 4.1, smaller mean diameters 
were observed for high caprolactam concentration and at high shear rates. This is 
the expected behavior as equilibrium drop sizes are determined by the balance of 
the break-up forces and the interfacial tension and viscous forces that resist drop break-up. At a low caprolactam concentration, the interfacial tension is 
sufficiently high; hence, there will be more resistance to drop break-up, which 
results in bigger drops. In contrast, at a high caprolactam concentration, the low 
interfacial tension makes the drop break-up easier; therefore, smaller drop sizes are 
observed. The cumulative droplet size distribution obtained for the two different 
caprolactam concentrations are also depicted in Figure 4.1. As can be seen from the 
figure, for both interfacial tensions, the droplet size distribution shifts to smaller 
drop sizes at high flow rates (high shear rate). This is due to increased shear at 
higher flowrates. Additionally, the drop size distribution further moves to smaller 
drop sizes at a high concentration. This is expected due to the lowering of the 
interfacial tension of the system.

In Figure 4.2, the water entrainment is depicted for different flows (shear rates) and 
concentrations of caprolactam. The superficial shear rates corresponding to each 
flowrate of the continuous phase are calculated according to equation (4.1) and are 
presented in Table 4.3. In equation (4.1), \( V \) and \( D \) stand for the superficial velocity 
of the continuous phase, and the internal diameter of the static mixer pipe, 
respectively.

\[
\text{Shear rate} = \frac{8V}{D} \tag{4.1}
\]
Table 4.3. Continuous phase flowrates used in the experiments and the corresponding shear rates

<table>
<thead>
<tr>
<th>Continuous phase flowrate* (L/hr)</th>
<th>Superficial velocity continuous phase (m/s)</th>
<th>Superficial shear rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>0.06</td>
<td>33</td>
</tr>
<tr>
<td>48</td>
<td>0.08</td>
<td>44</td>
</tr>
<tr>
<td>54</td>
<td>0.09</td>
<td>49</td>
</tr>
<tr>
<td>60</td>
<td>0.10</td>
<td>55</td>
</tr>
<tr>
<td>72</td>
<td>0.12</td>
<td>65</td>
</tr>
<tr>
<td>84</td>
<td>0.14</td>
<td>76</td>
</tr>
<tr>
<td>96</td>
<td>0.16</td>
<td>87</td>
</tr>
</tbody>
</table>

*The dispersed phase flow was adjusted to 10% of the continuous phase flow rate

Figure 4.2 reveals that for both concentrations of caprolactam, no entrainment is observed at flowrates of the continuous phase below 54 l/hr (shear rate 49 s⁻¹). Additionally, it can be observed that both flow and caprolactam concentration affect the entrainment values. The effect of flow is more pronounced at higher caprolactam concentration due to interfacial tension reduction, which resulted in smaller droplet sizes. It can be seen from Figure 4.2 that water entrainment is relatively low (less than 200 ppm) at 5.35% w/w caprolactam concentration even at the maximum shear rate used. This is because of the large drop sizes that are created when using this caprolactam concentration. These drops can settle fast and they barely reach the end of the settler; hence, small or no entrainment occurs. However, when the caprolactam concentration is increased to 28.5% w/w, more small drops are produced as shown in Figure 4.1. These are entrained to the end of the settler before they have the time to settle; hence, a significant increase of water entrainment is observed. The water entrainment now increased to an average of 1373 ppm. Moreover, for 28.5% w/w caprolactam concentration, a sharp increase in entrainment can be observed as the shear rate changed from 65 s⁻¹ to 76 s⁻¹. This indicates that the flooding condition in the settler that causes massive entrainment of the dispersed aqueous phase is approached. In general, it can be concluded from Figures 4.1 and 4.2 that the amount of entrainment increases with a decrease in droplet sizes (mean sauter diameters). As discussed, this decrease in droplet sizes was resulted from the increase in flow rate (shear rate) and an increase in the caprolactam concentration.
Figure 4.1: Influence of caprolactam concentration in the aqueous phase and shear rate on (a) mean sauter diameters: □, 28.51% (w/w); ■, 5.35% (w/w) caprolactam and (b) size distributions: □, 5.35% (w/w) caprolactam, 55 s\(^{-1}\) shear rate; ■, 5.35% (w/w) caprolactam, 87 s\(^{-1}\) shear rate; ▽, 28.5% (w/w) caprolactam, 55 s\(^{-1}\) shear rate; ▼, 28.5% (w/w) caprolactam, 87 s\(^{-1}\) shear rate

Figure 4.2: Influence of caprolactam concentration and shear rate on aqueous phase entrainment into the organic phase: ■, 5.35% (w/w); ●, 28.5% (w/w) caprolactam in the aqueous phase. The error bars are based on duplicate experiments performed at each flowrate. In some of the data points, the error bars are small, therefore they are not visible. The same holds for other graphs below

4.3.2 Effect of MBA concentration (the role of viscosity of the continuous phase and density difference)

The change of physical properties with MBA concentration is shown in Table 4.2. Here, it can be observed that the interfacial tension of the EB-MBA-Water system does not change much for the used concentrations of 20% v/v and 33% v/v MBA.
However, the continuous phase viscosity and density increased notably at 33% v/v MBA compared to 20% v/v MBA. As can be seen from Figure 4.3, and in similar manner to the caprolactam case, the mean sauter diameters decreased at high shear rates. Besides, for the same shear rate, smaller mean sauter diameters were obtained at 33% v/v MBA concentration. This is expected because of the viscosity increase of the continuous phase at higher MBA concentration that increases the shear on the droplets. It can also be observed from Figure 4.3 that the drop size distribution shifts to smaller sizes at high shear rates and high concentration of MBA. For a given concentration of MBA, the interfacial force remains the same while the shear force increases at higher flows (shear rates). Thus, for a given concentration of MBA, smaller drops are produced at high shear rates; therefore, the distribution shifts to smaller size drops.

Figure 4.3: Influence of MBA concentration in the organic phase and shear rate on (a) mean sauter diameters: □, 33% (v/v) MBA; ■, 20% (v/v) MBA and (b) size distributions: ■, 20% vol. MBA, 55 s⁻¹ shear rate; ●, 20% (v/v) MBA, 87 s⁻¹ shear rate; ▲, 33% (v/v) MBA, 55 s⁻¹ shear rate; ▼, 33% (v/v) MBA, 87 s⁻¹ shear rate

Figure 4.4 depicts the entrainment behavior obtained for the two concentrations of MBA and for different shear rates. It can be observed that for both concentrations of MBA the entrainment increases at higher shear rates. At lower shear rates, no considerable difference in droplet entrainment was observed for the two concentrations. This is because at low shear rates, the amount of small size droplets produced is small; therefore, little or no entrainment occurs. However, when the flowrate is increased, more small size drops are produced at 33% v/v than at 20% v/v MBA concentration, hence, more entrainment (2785 ppm in comparison to 600 ppm) was observed for this concentration. An additional reason for the observed increase of the entrainment is the increase of the continuous phase viscosity and the decrease in density difference at higher concentration, which reduces the separation rate.
Moreover, it can be seen from Figure 4.4 that the droplet entrainment is small (<600 ppm) in comparison to the 4650 ppm physical water solubility (Table 4.2) for 20% v/v MBA concentration. Similarly, at 33% v/v MBA concentration, the obtained droplet entrainment of 2785 ppm represents the small part of the overall entrainment considering the physical solubility value of 9300 ppm. Furthermore, it can be noticed that the entrainment due to the physical solubility increased considerably with the increase in MBA concentration. Thus, the critical component that dictates the droplet entrainment behavior as well as solubility for this system is MBA concentration. Therefore, physical solubility here has an important contribution to the overall entrainment, in contrast to previously reported findings in mixer settler processes of uranium extraction.\textsuperscript{15,22} Finally, in similar manner to the caprolactam-toluene-water system, the amount of entrainment increases with a decrease in mean sauter diameters.

4.3.3 Effect of NaOH (pH=12) as dispersed phase

The effect of using sodium hydroxide (pH=12) as a dispersed phase instead of water is presented in Figure 4.5. As can be seen from the figure, the drop size increased and the distribution shifted to larger drop sizes when the sodium hydroxide is used. This is due to the viscosity increase of the aqueous phase due to the added sodium hydroxide. This increase in the viscosity of the dispersed phase results in more resistance to the drop break-up, and therefore, the drop sizes become larger. Additionally, it can be observed from Figure 4.5 that the increase in
the mean sauter diameter as well as the change in size distribution is significant at low shear rates as compared to high shear rates. This may be because at high shear rates the drop break-up force will be stronger than the viscous force that leads to the production of more fine droplets; therefore, the influence of dispersed phase viscosity becomes less. On the other hand, at low shear rates, the viscous forces become more significant than the break-up force; hence, the viscosity change will affect the mean sauter diameters and the drop size distributions.

Figure 4.5: Effect of dispersed phase viscosity on (a) mean sauter diameters: ○, water dispersed phase; ●, NaOH (pH=12) dispersed phase and (b) drop size distributions: ■, water dispersed phase, 44 s⁻¹ shear rate; ▲, water dispersed phase, 55 s⁻¹ shear rate; ●, NaOH (pH=12) dispersed phase, 44 s⁻¹ shear rate; ▼, NaOH (pH=12) dispersed phase, 55 s⁻¹ shear rate, and MBA concentration is 33% (v/v)

Figure 4.6: Effect of dispersed phase viscosity on entrainment at 33% (v/v) MBA concentration: ■, water dispersed phase; ●, NaOH (pH=12) dispersed phase

The influence on entrainment by using sodium hydroxide (pH=12) as a dispersed phase is shown in Figure 4.6. As can be observed, the entrainment is very low
when using sodium hydroxide (pH=12) solution compared to using water. This is the expected behavior considering the larger mean sauter diameters obtained at higher viscosity of the dispersed phase shown in Figure 4.5. In addition to the larger drop diameters produced, the addition of sodium hydroxide (pH=12) increases the density of dispersed phase, therefore, density difference between the dispersed and continuous phases increases. This improves the separation rate of the drops in the settler, hence, the observed lower entrainment at higher dispersed phase viscosity.

4.3.4 Effect of phase ratio

Effect on the drop size

The influence of phase ratio on the drop size has been studied by different authors. Different mechanisms have been identified to describe this influence, and they depend on the type of drop breakup that occurs in the mixer. For turbulent flow in a static mixer, in addition to the shear breakage which occurs for viscosity ratios ($\mu_d/\mu_c$) less than 3, the drop breakup can also result from the interaction between the eddy of the continuous phase and the drop. In this regard, the presence of the dispersed phase has an effect of turbulent attenuation. This implies increased drop sizes at a higher phase ratio. However, the increase of the volume fraction of the dispersed phase at higher phase ratios increases the effective continuous phase viscosity and this increases the shear on the droplets. An additional consideration for coalescing systems is the possibility of increased coalescence at high phase ratios, which mostly occurs for low flow rates. Hence, the drop sizes can increase or decrease with phase ratio depending on the relative change of the aforementioned effects. At low phase ratios, the holdup in the static-mixer is not yet large enough to cause turbulent dampening. Nevertheless the viscosity changes appreciably enough even in the presence of a small amount of the dispersed phase. Therefore, the latter effect dominates at low phase ratios, while the effect of turbulent attenuation becomes significant at high phase ratios. The holdup in a static-mixer is also dependent on the drop size of the dispersed phase in addition to phase ratio. For systems with lower interfacial tension, the holdup increases dramatically with the consequence of turbulence appearing at lower phase ratios. The relationship between the drop size and phase ratio can be described using dimensionless numbers. This is reported in literature by many authors and the general expression is shown in equation (4.2):

$$\frac{d_{32}}{D} = \left( \frac{\rho V^2 D}{\sigma} \right)^{\alpha(\phi)} \left( \frac{\rho V D}{\mu_c} \right)^{\beta(\phi)} \left( \frac{\mu_d}{\mu_c} \right)^{\gamma(\phi)} (1 + c\phi)$$

(4.2)
where \( d_{32} \) is the mean sauter diameter, \( D \) is the static-mixer inner diameter, \( V \) is the superficial velocity, \( \sigma \) is the interfacial tension, \( \rho \) is the density of the continuous phase, \( \mu_d \) is the viscosity of the dispersed phase, \( \mu_c \) is the viscosity of the continuous phase, and \( \phi \) is the phase ratio. \( A, \beta, \gamma, \alpha \) and \( c \) are coefficients of the different dimensionless numbers. In this equation, the first term on the right represents the Weber number, the second term Reynolds number, the third term the viscosity ratio, and the last term the increased coalescence rate at high phase ratio. Thus, all the aforementioned effects of phase ratio can be interpreted using equation (2). For instance, the turbulent attenuation at higher phase ratio can be incorporated by using the coefficient of the Weber number. This can be described by allowing the coefficient to decrease with the phase ratio.\(^{36}\) Similarly, the increase of viscosity at high phase ratios can be incorporated by including the dispersed phase volume fraction.

Figures 4.7 (a) and (b) show the influence of phase ratio on the drop size and distribution for the EB-MBA-water system for two shear rates. For both shear rates, the drop size decreased at higher phase ratios. Moreover, the distribution shifted to smaller droplet sizes with an increase in phase ratio. In the light of the argument given before, this is attributed to the increase in the effective viscosity of the continuous phase, which in turn, increases the shear applied on the droplets. Figures 4.7 (c) and (d) depict that the drop sizes for the caprolactam-toluene-water system go through a minimum at a phase ratio of 10%. This is different as compared to the previous system. This is explained by the lower interfacial tension of the caprolactam system which results in smaller drop sizes. This causes a steep increase in the holdup in static-mixer therefore the effect on turbulent dampening becomes significant. Therefore, the drop size decreases with phase ratio until a minimum is reached and later on increases with phase ratio as the turbulence attenuation effect becomes dominant.
Figure 4.7: Effect of phase ratio on mean sauter diameters and drop size distribution (a,b) for MBA-EB-water (c,d) caprolactam-toluene-water systems; for mean sauter diameters (a,c): ■,76s\(^{-1}\) shear rate; ●,87s\(^{-1}\) shear rate, and for the distributions (b,d): ■, 5% (v/v) phase ratio; ●, 10% (v/v) phase ratio; ▲, 20% (v/v) phase ratio at 87s\(^{-1}\) shear rate

**Effect on entrainment**

The influence of phase ratio on entrainment is caused by two major factors: namely, the influence on the drop size formed in the static-mixer as described in the previous section, and the influence on phase separation in the settler. The decrease of drop size leads to a more difficult separation; hence, depending on the change of drop size with phase ratio in the static-mixer, the entrainment can increase or decrease. In a settler, the effect of phase ratio stems from its effect on density difference, viscosity of the continuous phase and the hindered settling. With an increase in phase ratio, the viscosity increases and the density difference decreases (when the dispersed phase has the higher density). As a result, the entrainment tends to increase with phase ratio. The hindered settling also decreases the separation rate at higher phase ratios which means a further increase of entrainment.
Figure 4.8: Effect of phase ratio on entrainment for (a) MBA-EB-water and (b) caprolactam-toluene-water system: in both cases; ■, 76 s⁻¹ shear rate; □, 87 s⁻¹ shear rate. The error bars are based on duplicate experiments performed at each flowrate. In some of the data points, the error bars are small, therefore they are not visible.

Figure 4.8 (a) depicts the influence of phase ratio for MBA-EB-water system. As can be seen, the entrainment increases with phase ratio. This behavior can be expected as the drop sizes decreased with increasing phase ratio, which is shown in Figure 4.7 (a). Additionally, the influence of hindered settling and increased viscosity increases the entrainment further. In contrast, for the caprolactam-toluene-water system, the entrainment goes through maximum as shown in Figure 4.8 (b). This is concurrent with the trend obtained for the variation of the drop size with phase ratio presented in Figure 4.7 (c). As evident from figures 4.7 (c) and (d),
the smallest droplet size and the highest percentage of the small size drops were obtained at phase ratio of 10%. Therefore, the highest amount of entrainment was found at 10% phase ratio in accordance with the drop size trend. Nevertheless, especially at 20% a contrast occurs regarding the two effects mentioned before. Although, the drop size increases at 20% which led to less entrainment, it can also be expected that the increase of viscosity and hindered settling to increase entrainment. However, in this scenario, it may be considered the former effect to surmount the later.

4.3.5 Effect of temperature

Effect on the drop size

Two important changes may be distinguished; a decrease in interfacial tension and a decrease in viscosity of both the dispersed and continuous phases as a result of an increase in temperature. A decrease in the interfacial tension facilitates the break-up of droplets while a decrease in the viscosity promotes the coalescence of droplets. On one hand, as shown by Berkman et. al.24, the drop size is proportional to square root of the ratio of the dispersed to continuous phase viscosity when the viscosity ratio is greater than one. On the other hand, as illustrated by the work of Hinze27, the drop size is proportional to the interfacial tension to the power 0.6. Therefore, the extent of these counteracting changes in the properties determines whether the mean drop size formed in the static-mixer increases or decreases at higher temperature. The influence of temperature on the mean droplet size and distribution for the MBA-EB-Water system at 33% MBA concentration is shown in Figures 4.9 (a) and (b). It can be observed that the size distribution shifts to larger droplet sizes at higher temperatures. Consequently, the mean droplet sizes increased at higher temperatures when compared to 20°C. This can be explained by a decrease of the viscosity of the EB-MBA continuous phase with temperature, which is depicted in Table 4.2. Additionally, it can be observed from this table that the change of interfacial tension of the system with temperature is minimal. Therefore, on the basis of the argument given before, the mean diameter should increase at higher temperatures, as the effect of viscosity is more pronounced than the interfacial tension.

Interestingly, in contrast to the EB-MBA-water system, a reverse behavior was observed for the change of mean droplet size with temperature for the caprolactam-toluene-water system. As can be observed from Figures 4.9 (c) and (d), the mean sauter diameters decreased and the size distributions shifted to smaller droplet sizes at higher temperature. Here, both the viscosity ratio and the interfacial tension
act together to decrease the mean droplet size. As can be seen from Table 4.1, both the interfacial tension and viscosities considerably decrease with temperature. The decrease of interfacial tension leads to a decrease of mean drop sizes. For the caprolactam-toluene-water system, the dispersed phase has a higher viscosity than the continuous phase and this leads to viscosity ratio greater than one. With an increase of temperature, this viscosity ratio decreases, and therefore, smaller droplet sizes are produced as shown by Grace.39

Effect on entrainment

Considering the settler, the influence of temperature on entrainment can be inferred from its effect on the viscosity of the continuous phase. As the temperature increase results in a decrease in the viscosity of the continuous phase, the separation rate is expected to increase with temperature. However, this is not sufficient to predict the influence of temperature on entrainment as the mean drop sizes produced in a static-mixer are also influenced by temperature. When the mean droplet size increases with temperature, this will act in conjunction with the accompanied viscosity decrease to increase the separation rate. Nevertheless, when the drop size decreases with temperature, the separation behavior in the settler depends on the influence of the drop size and viscosity decrease with the dependence on the former being relatively strong.

Figure 4.10 (a) shows the influence of temperature on the entrainment behavior for the MBA-EB-water system. As can be seen from the figure, the entrainment decreases with an increase in temperature. This is expected considering the increase of droplet sizes at higher temperature as given in Figure 4.10 (a) on top of the viscosity decrease with temperature. Figure 4.10 (b) shows the entrainment behavior for the caprolactam-toluene-water system at different temperatures. As can be observed from the figure, in contrast to the MBA-EB-water system, the entrainment increased at higher temperatures. This is consistent with the decrease of the drop size with temperature depicted in Figure 4.9 (c).
Figure 4.9: Effect of temperature on mean sauter diameters and size distributions (a,b) for MBA-EB-water (c,d) for caprolactam-toluene-water systems; for the distributions: ▲, temperature=20°C; ●, temperature=30°C; ■, temperature=40°C

<table>
<thead>
<tr>
<th>Mean sauter diameter [mm]</th>
<th>Temperature [°C]</th>
<th>Cumulative size distribution [%]</th>
<th>Drop size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>20</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>0.30</td>
<td>25</td>
<td>80</td>
<td>0.4</td>
</tr>
<tr>
<td>0.28</td>
<td>30</td>
<td>60</td>
<td>0.3</td>
</tr>
<tr>
<td>0.26</td>
<td>35</td>
<td>40</td>
<td>0.2</td>
</tr>
<tr>
<td>0.24</td>
<td>40</td>
<td>20</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean sauter diameter [mm]</th>
<th>Temperature [°C]</th>
<th>Cumulative size distribution [%]</th>
<th>Drop size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>20</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>0.18</td>
<td>25</td>
<td>80</td>
<td>0.4</td>
</tr>
<tr>
<td>0.17</td>
<td>30</td>
<td>60</td>
<td>0.3</td>
</tr>
<tr>
<td>0.16</td>
<td>35</td>
<td>40</td>
<td>0.2</td>
</tr>
<tr>
<td>0.15</td>
<td>40</td>
<td>20</td>
<td>0.1</td>
</tr>
</tbody>
</table>
4.4 Conclusions

This chapter demonstrated the influence of physical properties and process conditions on the drop sizes formed in a static mixer and on the entrainment from settler for two extraction systems, i.e., toluene-caprolactam-water and MBA-EB-Water. For the caprolactam-toluene-water system, the decrease of interfacial tension by increasing caprolactam concentration decreased the drop size and increased the entrainment from less than 200 ppm to 1373 ppm. For the EB-MBA-water system, the viscosity of the continuous phase increases and the density
difference decreases at high MBA concentration. Consequently, the drop size decreased and the entrainment increased sharply from 600 ppm to 2785 ppm. Furthermore, the solubility was found to considerably influence the overall entrainment. Especially, for the EB-MBA-water system, the water solubility doubled as the MBA concentration increased. Different entrainment behavior was observed for the two systems with variation of temperature and phase ratio. For the MBA-EB-water system, the entrainment decreased at high temperatures. For the caprolactam-toluene-water system the entrainment increased at high temperature. The entrainment increased for MBA-EB-water system at high phase ratio, whilst, it goes through a maximum for the caprolactam-toluene-water system. The phase ratio effect resulted from on one hand turbulent attenuation and increased coalescence, and on the other hand increased shear and hindered settling at high phase ratios. The temperature influence was determined by its counteracting effects on the interfacial tension and the viscosities of continuous and dispersed phases.
Reference List

(3) Gergensen, G. V. Copper Leaching, Solvent extraction and Electrowinning Technology.Wiley, Newyork,1999.
Chapter 4


Entrainment reduction in a static-mixer settler setup by electric field enhanced coalescence

This chapter has been accepted as: Esayas W. Barega, Edwin Zondervan, André B. de Haan, (2013). Entrainment reduction in a static-mixer settler setup by electric field enhanced coalescence, Journal of Separation Science and Technology, in Press.

Abstract

In this chapter, we investigate the application of electric field enhanced coalescence for entrainment reduction in the static-mixer settler setup for the caprolactam-toluene-water and ethyl benzene (EB)-α-methyl benzyl alcohol (MBA)-water systems. The mixing of the organic and aqueous phases was carried out in a static mixer and an AC/DC electric field was applied at the end of the static mixer pipe. In this way, the drop sizes from the static mixer are increased to intensify their subsequent separation in the settler. The drop size and entrainment were measured at different flow conditions, with and without electric field, and at a field strength of 0.4 kV/cm and 1 kV/cm, at frequencies ranging from 3 to 100 Hz. Significant coalescence of the dispersed phase was observed, which resulted in 4-5 times less entrainment compared to one without electric field reported in Chapter 4. The AC field was more efficient than the DC field and an optimum frequency of 3-10 Hz was obtained for both systems. Additionally, the role of phase ratio and temperature was examined. For the caprolactam system, the entrainment reduction efficiency increased up to a phase ratio of 10% v/v and decreased again at 20% v/v. For the MBA-EB-water system, the efficiency did not change much between a phase ratio of 5% v/v and 10% v/v but decreased at a phase ratio of 20% v/v. Furthermore, an opposite effect of temperature on entrainment reduction was found for the two systems. For the MBA-EB-water system, entrainment decreased at high temperature, while it increased for the caprolactam-toluene-water system.
5.1 Introduction

It was demonstrated in Chapter 4 that there is considerable entrainment for the two investigated systems especially at the higher flowrates and higher concentrations of caprolactam and \( \alpha \)-methyl benzyl alcohol (MBA). As described in the preceding chapters this increased entrainment has negative consequences on the process. There will be a limitation on the process capacity. Moreover, the operational costs increase further in removing entrainment and the solvent added to maintain the same capacity.\(^1\),\(^2\) Therefore, a new separation principle that avoids the disadvantages of the gravity separation is desired to intensify and improve the phase separation.

As described in Chapter 1, different technologies have been developed in the oil and gas industry to enhance coalescence and separation of the dispersed phase\(^3\)\(-\)\(^5\), which eventually reduce entrainment. Among the different techniques, the application of an electric field is an attractive option for a number of reasons. First, the application of electric field does not require much space and need for modification of the existing process infrastructure. Therefore it can easily be incorporated in the process. Second, it has low power requirements due to the very low electrical current across the dispersion. Third, it does not require intensive maintenance; as no moving mechanical parts are involved.\(^6\),\(^7\) And finally, it has been used frequently for crude oil dehydration\(^4\),\(^8\)\(-\)\(^10\) with proven and significant enhancement of phase separation; hence, it should be easily adaptable to bulk extraction processes.

The use of electric field enhanced separation dates back to the early work of Cottrell in 1911\(^4\),\(^11\), where an electrostatic precipitator was used to remove dust particles from an air stream. Afterwards, the electric field was extensively used in the petrochemical industry for the separation of emulsified water droplets from crude oil. Many mechanisms such as chain formation, dipole coalescence, electrophoresis, dielectrophoresis, and random collision were reported to account for the electric field coalescence effect.\(^12\) In the electric field, the aqueous drops acquire induced charges, which create a dipole-dipole attraction force between them, and this eventually causes their coalescence. Moreover, once the drops acquire charge, they move under the action of electrostatic attraction of the charged electrodes, which leads to collisions and coalescence enhancement of drops.

A plethora of literature exists on electric field coalescence with applications generally directed to the separation of water-in-crude oil emulsions. In these applications, pulsed DC and AC fields were used more frequently. In addition,
different designs of electro-coalescers were employed including rectangular duct, circular vessels and columns. Some new designs, for example, spinning type electro-coalescers were also recently investigated to combine the action of electric and centrifugal fields. The electro-coalescer was mostly placed between the stirred vessel and the settler, albeit in some applications, the electrodes were directly integrated into the settler. Different studies have also been made focusing on the effect of different electrical and process parameters on the efficiency of the electric field. Authors such as Bailes, Drelich et.al., Eow et.al., and Kim et.al. investigated the influence of electric field frequency. Different optimum frequencies were found depending on the electrical properties of the systems used, and the type and thickness of insulation used. Bailes and Drelich et. al. found an optimum frequency below 10Hz, while others found the efficiency to increase at higher frequencies. Additionally, field strength, hold-up fraction of the dispersed phase, and operational conditions such as temperature, and physical properties, e.g. viscosity, and interfacial tension were found to have influence on the separation.

Despite the abundant literature on the use of an electric field in the petrochemical industries, only few studies focus on the application to solvent extraction processes. As pointed out by Bailes, the application of an electric field to solvent extraction systems is hampered by two factors; 1) the high water content of solvent extraction systems causing electrode bridging due to the large number of conducting drops, and 2) the loss of electro-coalescence force between the electrodes due to modification of the conductivity of the continuous phase by the conducting drops, which lowers the efficiency and consequently results in high power consumption. Therefore they used insulated electrodes and pulsed DC as means of energizing to solve the short-circuiting problem.

However, an additional challenge is encountered when the electric field is used for solvent extraction systems with low interfacial tension and in the presence of surface active components. First, the low interfacial tension reduces the drop size; accordingly, the electrical attractive force responsible for the coalescence decreases. Second, the surface active compound adsorbs at the interface between the drops and the continuous phase. This hinders the coalescence process by acting as a physical barrier in preventing direct coalescence of drops by electric field. To our knowledge, the coalescence of this kind of extraction systems by electric field in a continuous process was not investigated except for the application in emulsion liquid membranes and in the work of Bailes and Larkai for sulphuric acid-20% LIX64N in Escaid system.
The solvent extraction systems investigated in this work, i.e., caprolactam-toluene-water, and ethyl benzene-α-methyl benzyl alcohol (MBA)-water, are characterized by low interfacial tensions, with one of their components being surface active. In the caprolactam-toluene-water system, the interfacial tension decreases to less than 5 mN/m\(^1\) depending on the concentration of the surface active component caprolactam. For the ethyl benzene (EB)-α-methyl benzyl alcohol (MBA)-water system, the interfacial tension can be as low as 10 mN/m as shown in Chapter 3\(^2\), where MBA acts as a surface active component.

This chapter describes a novel way of entrainment reduction by applying electric field enhanced coalescence to a static-mixer settler combination and is shown in Figure 5.1. All experimental research on electric field coalescence was based on dispersions created by stirred vessels since these are the most widely used mixing devices in extraction processes. The use of static-mixers offers a unique opportunity since the electric-field can directly be incorporated in the same pipe as the static-mixer without the need for a separate electro-coalescer. Thus, intensification of both the mixing and the separation step can be achieved without introducing extra equipment. This is not the case in stirred tanks due to their large size; consequently, the electro-coalescer is either placed separately between the mixer and settler or integrated into the settler. Furthermore, since the diameter of the static-mixer is small compared to the dimension of the settler, placing the electric field in the static- mixer pipe enables maintaining high field strength with relatively small potential difference (voltage).

Therefore, in this chapter we examine the potential application of the technology for the two bulk solvent extraction systems. Moreover, we examine the influence of field strength, type of field (AC or DC), frequency of the electric field, temperature, and phase ratio on the entrainment reduction. For both systems, the drop sizes are measured to determine the extent of coalescence by the electric field.
5.2 Materials & Methods

5.2.1 Materials

Toluene (purity > 99.9%) was supplied by Merck Germany. ε-caprolactam (purity > 99%), ethyl benzene (EB) (purity > 99%), and α-methyl benzyl alcohol (MBA) (purity > 99%) were supplied by Sigma-Aldrich (USA). Milli-Q super distilled water was used for all the experiments.

5.2.2 Experimental set-up and procedure

The experimental set-up developed and described in Chapter 2 (Figure 2.1) was used to perform the experiments. The electric-field is now incorporated and used for entrainment reduction. To quantify the entrainment reduction, the same procedure was followed as in Chapter 4. For the caprolactam-toluene-water system, first an equilibrated amount of caprolactam in toluene and Milli-Q water was prepared to avoid mass transfer effects. A concentration of 28.51% w/w caprolactam in the aqueous phase was used. This concentration was chosen since it gives considerable entrainment from previous experiment without electric field shown in Chapter 4. Corresponding to this concentration in the aqueous phase, the equilibrium caprolactam concentration in the organic phase and the physical properties are given in Table 4.1 (Chapter 4). Similarly, for the EB-MBA-water system, 33% v/v of MBA in EB was prepared and used as organic phase. This concentration was chosen for the same reason as for the caprolactam system. For
this system, Milli-Q water was used as an aqueous phase. The corresponding equilibrium solubility of water in the organic phase and the physical properties are given in Table 4.2 (Chapter 4).

Once the organic and aqueous phases were prepared for each system, the organic and aqueous tanks, the settler, and the secondary settlers were filled with equilibrated organic and aqueous phases. The static mixer was primed with the organic phase to pre-wet the internals with the continuous phase. Once the other part of the system was filled with each phase, the organic pump flow was varied between 54 l/hr to 96 l/hr in 5 levels, and the aqueous flow was adjusted to 10% of the organic flow. The shear rates corresponding to these flows are given in Table 4.3 (Chapter 4). To study the phase ratio effect, the aqueous flow was also adjusted to 5% and 20% of the organic flow.

After the flowrate was set to the required value, the voltage source was switched on. For each flow, the experiment is run for three times the residence time in the settler to ensure equilibrium. The equilibrium was checked by measuring the water content of the continuous phase at the outlet of the settler at different residence times until no change in the water content was observed. For both systems, first the effect of the DC field strength of 1 kV/cm was evaluated at each flow. Subsequently, at the maximum flow, experiments were performed with a DC field of 0.4 kV/cm and a square wave of the same strength at different frequencies; 3, 5, 10, 25, 50, and 100 Hz. It was not possible to evaluate the influence of frequencies below 3Hz and above 100 Hz with the source used. The entrainment was quantified in the same manner as described in Chapter 4 (section 4.2.3).

5.3 Results and Discussion

5.3.1 Coalescence with DC field of 1kV/cm

The influence of a 1kV/cm DC field on the entrainment reduction for the caprolactam-toluene-water and MBA-EB-water systems at a temperature of 20°C and phase ratio of 10% (v/v) is presented in Figures 5.2 (a) and (b), respectively. It can be observed that a considerable amount of entrainment is present especially at high shear rates (flowrates) for both systems when no electric field was applied. However, by applying an electric field most of this entrainment was removed. For instance, at the maximum flow rate (shear rate) used in the experiment, the entrainment decreased from 1373 ppm to 275 ppm for the caprolactam-toluene-water in the presence of electric field, while it decreased from 2785 ppm to 628 ppm for the MBA-EB-water system. Additionally, for both systems, the entrainment tends to increase with an increase in flow rate (shear rate) in the
presence and absence of electric field. The figures reveal that without electric field the entrainment increases steeply as the flow rate approaches the flooding limit. Nevertheless, this increase of entrainment was dampened in the presence of electric field. This indicates that the settler capacity has increased significantly in the presence of electric field. The increase of settler capacity and decrease of entrainment is attributed to drop coalescence in the presence of the electric field, which increases the size of droplets fed to the settler. As a result, their settling velocity increases; hence, the droplets can be removed before they reach the end of the settler. The influence of electric field on the droplet size for the two systems is depicted in Figures 5.2 (c) and (d). For all the shear rates used, it can be seen that the drop sizes were considerably increased by applying electric field, which consequently resulted in the observed intensified reduction of entrainment in both systems.

Figure 5.2: Effect of 1 kV/cm DC electric field on entrainment reduction and mean sauter diameters for caprolactam-toluene-water (a,c) and for MBA-EB-water (b,d) systems as function of shear rate. Experimental conditions are: temperature 20°C and a phase ratio of 10% (v/v). The error bars are based on experiments performed in duplicate for all flowrates. The error bars for some data points are not visible because they are small.
5.3.2 Effect of field strength

Generally, the efficiency of electro-coalescence can be increased by using a higher field strength. This is because both the droplet-droplet electrical attraction force and drop mobility increase at high field strength, which enhances coalescence between the drops. However, increased electric field strength also means more power requirement, which increases the operating cost. In addition it might lead to further breakup and dispersion of drops instead of coalescence, when the electrostatic force exceeds the interfacial restoring forces. Therefore, a lower field strength was used to evaluate the separation efficiency at lower power consumption.

In Figures 5.3 (a) and 5.3 (b), the entrainment reduction achieved with DC fields of 0.4 kV/cm and 1 kV/cm is compared for the caprolactam-toluene-water and MBA-EB-water systems, at a temperature of 20°C, a phase ratio of 10% v/v, and at the maximum shear rate. It can be observed that by using electric field strength of 0.4 kV/cm, the entrainment decreased from 1373 ppm to 425 ppm for the caprolactam-toluene-water system, and from 2785 ppm to 1025 ppm for the MBA-EB-water system. At field strength of 1 kV/cm, these entrainment values decreased further down to 275 ppm and 628 ppm for the caprolactam-toluene-water and MBA-EB-water systems, respectively. This is expected since a higher field strength results in enhancement of the electrostatic attraction force responsible for coalescence of drops. In addition, the higher field strength increases the magnitude of induced charges on the drops, which further increases the attraction force between the drops. Furthermore, it can be concluded from Figures 5.3 (a) and (b) that while extra reduction of entrainment was obtained at a field strength of 1 kV/cm, the decrease flattened with the change of field strength from 0.4 kV/cm to 1 kV/cm. Other studies also reported a similar dependence of separation efficiency on the field strength, and the saturation of separation efficiencies at high field strength. A possible explanation is that at low field strength, the induced dipole and droplet elongation cause increased separation. However, at higher field strength the performance flattens due to charge saturation and possibility of breakup of elongated drops.
Figure 5.3: Effect of DC electric field strength on entrainment reduction (a) for caprolactam-toluene-water, and (b) for MBA-EB-water. Experimental conditions are: temperature 20°C, phase ratio 10% (v/v), and at the maximum shear rate. The error bars are based on experiments performed in duplicate. The error bars for some data points are not visible because they are small.

5.3.3 Effect of frequency

According to past studies by Bailes$^{13,14}$, Drelich$^8$, Eow$^{15}$, the influence of frequency on electro-coalescence results from two effects. First, once the electric field is applied, the build-up of interfacial charge on the drops will not occur instantaneously, but takes some time. There is a lag between the application of electric field and build up of charge. This depends on the relaxation time of the various dielectrics (the dispersion and insulation), electrical properties of the continuous phase and the electrode coating material, and its thickness. This overall time constant governs the electric field in the system and the build-up of interfacial charge. Additionally, the frequency dependence results from the way the applied voltage distributes across the insulation and dispersion with time.$^{13,14,25}$ Initially, upon the application of the electric field, the potential difference distributes itself based on the ratios of capacitances of the dispersion and the insulation. This means most of the applied potential (field) will initially distribute itself across the dispersion because the insulation has a higher capacitance. However, with time the ultimate distribution of the potential difference depends on the ratio of the resistances$^{14,25}$ and most of the potential difference distributes itself across the insulation. Therefore, the frequency should be high enough to maintain high field in the dispersion, but at the same time should allow for the field and interfacial charge to fully develop. This determines the optimum frequency that should be used to obtain maximum coalescence.

The effect of electric field frequency on entrainment reduction for the caprolactam-toluene-water and MBA-EB-water systems is shown in Figures 5.4 (a) and (b) at a
field strength of 0.4 kV/cm, a temperature of 20°C, a phase ratio of 10% v/v, and at the maximum shear rate. The figures reveal similar dependence of entrainment reduction on the frequency of the electric field for both systems. It can be concluded that all frequencies of the AC field have lower entrainment than a DC field (frequency of 0 Hz). This is expected since using DC field fields results in a situation where most of the field will be across the insulation for a significant period of the cycle. Additionally, frequencies lower than 10 Hz were found to be more effective in the reduction of entrainment compared to higher frequencies. For the caprolactam-toluene-water system the lowest entrainment was observed at 3 Hz and the entrainment was found to increase gradually as the frequency was increased. Similarly, for the MBA-EB-water system, lower entrainment values were found at frequencies less than 10 Hz. The entrainment, however, increased sharply for frequencies greater than 10 Hz. This can be explained by the fact that less time is available for the charge to fully develop when the frequency of the AC field is increased to higher values. As a result less charge will be induced on the drops, which decreases the attraction force responsible for coalescence. Therefore, the electro-coalescence efficiency decreases and results in an increase of entrainment at higher frequencies as depicted in Figures 5.4 (a) and (b). Despite these general observations regarding the frequency effect, it can be observed from Figures 5.4 (a) and (b) that a measurement uncertainty of within ± 150 ppm has more influence on the observed trend for the caprolactam-toluene-water system than the MBA-EB-water system. This is attributed to lower average entrainment values obtained with electric field in the range of 200 ppm for the caprolactam system, which are close to the uncertainty value (error bars).

Figure 5.4: Effect of AC field frequency on entrainment reduction (a) for caprolactam-toluene-water (b) for MBA-EB-water. Experimental conditions are: field strength 0.4 kV/cm, temperature 20°C, phase ratio 10% (v/v), and at the maximum shear rate. The error bars are based on experiments performed in duplicate for all frequencies.
5.3.4 Effect of phase ratio

The effect of phase ratio on entrainment reduction by electric field results from two opposing trends associated with the increase of holdup at high phase ratios. On one hand, the distance between drops in the dispersion decreases as the phase ratio increases due to the increased number of droplets at high phase ratio. This increases the dipole-dipole attraction force, since this force is inversely proportional to the fourth power of the inter-droplet distance:

$$F = \frac{24\pi \varepsilon_o \varepsilon_1 r^6 E^2}{(d+2r)^4}$$

(5.1)

where $\varepsilon_o$ is the permittivity of vacuum, $\varepsilon_1$ the dielectric constant of the continuous phase, $d$ the distance between the near surfaces of the two drops, $E$ the electric field strength and $r$ the drop radius.

The electro-coalescence efficiency is expected to increase dramatically at increased phase ratio considering only this effect. On the other hand, a high phase ratio will also result in dispersion with a large water holdup, which is described by Sun et.al. as creating a “sponge phase” containing an abundant water phase at the interface of the water and continuous organic phase. This considerably decreases the electro-coalescence efficiency by creating a conductive path. Therefore, it can be expected that the electro-coalescence efficiency increases with increased phase ratio up to a certain value due to increased attraction force resulting from a reduced distance between the drops. However, a further increase of the phase ratio will reduce the efficiency again as a result of the conduction effect induced by the large number of droplets.

The influence of phase ratio on entrainment reduction by an electric field for the caprolactam-toluene-water system and MBA-EB-water is presented in Figures 5.5 (a) and (b), at a field strength of 0.4 kV/cm and a temperature of 20°C. As can be observed for both systems the entrainment values increase at high phase ratios. This can be explained by the relative increase of dispersed phase flow (more drops into electro-coalescer) at higher phase ratios. Nevertheless, this is not equivalent to the electro-coalescence efficiency; since, the entrainment without the application of an electric field is different for the different phase ratios. The efficiency of electric field is determined by comparing the entrainment reduction obtained to that of the entrainment without applying an electric field, as presented in Equation 5.2. The entrainment values without electric field for the different phase ratios are given in Table 5.1 for the two systems.
Figures 5.5 (c) and (d) depict the entrainment removal efficiencies calculated using Equation 5.2 and Table 5.1 for the two systems at a field strength of 0.4 kV/cm, and a temperature of 20°C. For the caprolactam-toluene-water system, the electro-coalescer efficiency increased first as the phase ratio is changed from 5% v/v to 10% v/v phase ratio. However, the efficiency decreased again at a phase ratio of 20% v/v. As described before, the increase of efficiency from 5% v/v to 10% v/v phase ratio results from the reduction of the inter-droplet distance between the drops, which increases the electro-coalescence attraction force. The decrease of efficiency at the phase ratio of 20% v/v can be attributed to the conductive loss created by the presence of abundant water phase. In contrast, for the MBA-EB-water system, the efficiency did not change much when a phase ratio was changed from 5% v/v to 10% v/v. However, at a phase ratio of 20% v/v, the efficiency of the separation declined sharply, particularly, when using a DC field and higher frequencies of 50 Hz and 100 Hz. This indicates that for the MBA-EB-water system, the decrease of coalescence efficiency due to conduction effects happens already at a lower phase ratio of 10% v/v. This can be expected since in the MBA-EB-water system, the dispersed phase consists only of water in contrast to the former system, where the dispersed phase also contains caprolactam. This results in a higher conductivity of the dispersed phase for the MBA-EB-water system, which decreases the coalescence efficiency. Additionally, it can be observed from Figure 5.5 that for all phase ratios the AC field is more efficient in entrainment reduction compared to the DC field (frequency of 0 Hz).

Table 5.1. Entrainment values without electric field at different phase ratios at a temperature of 20°C and at the maximum shear rate.

<table>
<thead>
<tr>
<th>Phase ratio (v/v %)</th>
<th>Entrainment (ppm)</th>
<th>Phase ratio (v/v %)</th>
<th>Entrainment (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprolactam-toluene-water system</td>
<td>EB-MBA-Water system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>280</td>
<td>5</td>
<td>1530</td>
</tr>
<tr>
<td>10</td>
<td>1373</td>
<td>10</td>
<td>2785</td>
</tr>
<tr>
<td>20</td>
<td>1258</td>
<td>20</td>
<td>4678</td>
</tr>
</tbody>
</table>
Figure 5.5: Effect of AC field frequency and phase ratio on entrainment reduction and separation efficiency (a,c) for caprolactam-toluene-water (b,d) for MBA-EB- systems. Experimental conditions are: field strength 0.4 kV/cm, temperature 20°C, and at the maximum shear rate.

5.3.5 Effect of temperature

The influence of temperature on entrainment reduction by the electric field depends on two factors; (1) whether the drop size increases or decreases with temperature, and (2) the decrease in the viscosity of the continuous phase, which increases the separation rate in the settler. The first factor (drop size) has two effects. First, the drop size created by the static-mixer governs the effectiveness of the electric field by influencing different electrical forces responsible for electro-coalescence. The electrophoretic, dielectrophoretic, and dipole-dipole attraction, forces are proportional to drop size to the power 2, 3, and 6, respectively. And second, the drop size affects the settling velocity, according to Stokes’ law. Thus, as the drop size created by the static-mixer decreases, the electric field effectiveness decreases, and the accompanied decrease of settling velocity leads to more entrainment.
In Figure 5.6 (a), the influence of temperature on entrainment reduction by the electric field is shown for the caprolactam-toluene-water system at a field strength of 0.4 kV/cm, a phase ratio of 10% v/v, and at the maximum shear rate. As can be observed, higher entrainment values were obtained at 30°C and 40°C compared to 20°C. This increase of entrainment at high temperatures was explained by measuring the drop sizes. As can be observed from the experimentally measured drop sizes depicted in Figure 5.6 (c), the mean sauter diameters were found to decrease with an increase in temperature. This is due to the decrease in interfacial tension and viscosity ratio of the dispersed to continuous phase ($\frac{\mu_d}{\mu_c}$). The decrease in interfacial tension facilitates drop breakup. Additionally, as shown by Grace27, the decrease in viscosity ratio further increases the drop breakup when the viscosity ratio is larger than 1. Thus, the smaller drop sizes created by static-mixer for the caprolactam-toluene-water system at higher temperature, and the accompanied decrease of electrical forces responsible for electro-coalescence explain the increase of entrainment at high temperature.

In Figure 5.6 (b), the influence of temperature on entrainment reduction is presented for the MBA-EB-water system at a field strength of 0.4 kV/cm, a phase ratio of 10% v/v, and at the maximum shear rate. In contrast to the caprolactam system, it can be observed that lower entrainment values were obtained at higher temperatures. This is a result of the way the drop size changes with temperature for the two systems. In contrast to the caprolactam system, it can be seen from Figure 5.6 (d) that the mean sauter diameters increase with an increase of temperature for the MBA-EB-water system. As can be seen from Table 4.1, for MBA-EB-water system, the change of interfacial tension is not significant, while the viscosities considerably decrease at temperatures of 30°C and 40°C. The influence of temperature on drop size thus comes from its effect on the viscosities. The increase of temperature decreases the viscosity ratio and according to Grace27 favors coalescence since the viscosity ratio is less than 1. Hence, the drop sizes increase at higher temperatures resulting in the decrease of entrainment for the MBA-EB-water system.

In addition, it can be concluded from Figure 5.6 that the influence of frequency on the entrainment remained unchanged at higher temperatures. The DC field was found to be less efficient than the AC field. Moreover, the efficiency of the electric field was found to decrease at higher frequencies.
Figure 5.6: Effect of AC field frequency and temperature on entrainment reduction and mean sauter diameters for caprolactam-toluene-water (a,c) and for MBA-EB-water (b,d) systems. Experimental conditions are: field strength 0.4 kV/cm, phase ratio 10% (v/v), and at the maximum shear rate. The error bars for the water entrainment are based on experiments performed in duplicate for all frequencies and temperatures. The error bars for some data points are not visible because they are small.

5.4 Conclusions

In this chapter, electric-field enhanced coalescence was successfully applied in a static-mixer to intensify entrainment reduction for the caprolactam-toluene-water and MBA-EB-water systems. By applying a DC field of 1kV/cm, the entrainment was considerably reduced from 1373 ppm to 275 ppm for the caprolactam-toluene-water, and from 2785 ppm to 628 ppm for the MBA-EB-water system. The AC field was more efficient in entrainment reduction compared to the DC field since similar entrainment reduction efficiency could be obtained at field strength of 0.4 kV/cm. The entrainment reduction was found to be frequency dependent with lower frequencies of 3-10 Hz being the optimum for both systems. Moreover, the entrainment reduction was influenced by phase ratio and temperature. Higher temperatures led to less entrainment for the MBA-EB-water system, while more
entrainment was found for the caprolactam-toluene-water system. This was explained by the way the drop sizes changed with temperature for the two systems. The effect of phase ratio on entrainment reduction was expressed in terms of efficiency to account for the change in the dispersed phase flow and entrainment with phase ratio. For the caprolactam system, the entrainment reduction efficiency increased up to a phase ratio of 10% v/v and decreased afterward at phase ratio of 20% v/v. For the MBA-EB-water system, the efficiency did not change much between a phase ratio of 5% v/v and 10% v/v; however, in a similar way as the caprolactam system, the efficiency decreased again at a phase ratio of 20% v/v.
Reference List


(22) Nogueira, J. M. F. Continuous Extraction of Crude Tall Oil. *Separation Science and Technology* 1997, 32, 2807.


Entrainment reduction by electric field enhanced coalescence in a pilot scale rotating disc contactor (RDC)

Abstract

This chapter presents a technical feasibility study on entrainment reduction using electric field coalescence for a caprolactam-toluene-water system in a pilot scale rotating disc contactor (RDC) column. The electric field is incorporated in the RDC by integrating the electro-coalescer at the outlet of the organic continuous phase. Reference experiments were carried out to determine the amount of entrainment without the electric field. The influence of caprolactam concentration, total flux, and solvent to feed ratio (S/F) on entrainment was investigated. All studied process variables resulted in a small amount of entrainment. A maximum entrainment of 600 ppm was obtained at a column outlet when using a 28.5% w/w caprolactam concentration. These entrainment values further decreased to less than 100 ppm downstream of the continuous phase outlet due to the deposition of droplets on the electro-coalescer pipe. Thus, to increase the amount of entrainment at the column outlet two approaches were used: 1) increasing the caprolactam concentration to 39.2% w/w, and 2) the outlet of organic continuous phase is lowered in the column top settler. The first approach decreased the flooding capacity but did not increase the entrainment. With the second approach, an entrainment value of 2425 ppm was obtained at the column outlet. Due to droplet deposition, the entrainment value decreased from 187 ppm downstream of the electro-coalescer to 62 ppm when a DC field of 1kV/cm was applied. The drop sizes were also observed to increase in the presence of the electric field.
6.1 Introduction

Industrially caprolactam is recovered from the neutralized Beckmann rearrangement mixture by phase separation followed by extraction of the resulting crude caprolactam phase using an organic solvent (forward extraction) and back extraction with water.\(^1\) In these processes a rotating disc contactor (RDC) column is usually employed. Drop size is a key variable influencing both mass transfer and hydrodynamics of this column.\(^2\) Small drop sizes provide large interfacial area and higher mass transfer rates resulting in a smaller column size. However, the capacity of the column depend on to what extent these small drop sizes are present and specifically their entrainment by the continuous phase.\(^2\)

Commercial fiber-grade caprolactam requires high purity (\(>99.9\%\ w/w\)).\(^3\) During the extraction step, while extracting the aqueous-caprolactam phase with toluene in an RDC column, entrainment of the aqueous phase into the organic solvent phase occurs as a result of using a high agitation speed or/and a high flux of the dispersed and continuous phases. This is exacerbated by the reduction of interfacial tension of the two phases at a high caprolactam concentration.\(^4\) As a result, micro droplets are formed and eventually entrained in the organic phase. Entrainment has negative consequences on the process such as a decrease in product quality and process capacity as well as accumulation of impurities in the organic continuous phase. Therefore, the agitation speed and flux in the column should be limited to avoid excessive entrainment and flooding. However, a higher agitation speed and flux are required to increase the mass transfer and throughput of the column, respectively. Hence, ways should be developed to coalesce and separate the entrained droplets from the organic stream to maximize the column capacity.

It has been demonstrated in chapter 5 that electric-field enhanced coalescence can intensify the entrainment reduction for the caprolactam-toluene-water and ethyl benzene (EB)-methyl benzyl alcohol (MBA)-water systems in a static-mixer settler setup. This presents an opportunity to use the same principle for entrainment reduction in a rotating disc contactor (RDC).

Some applications of electric-field for intensification of mass transfer in liquid-liquid extraction are reported in literature.\(^5\) An electric field is mainly applied to induce high degree of circulation around and within the drop to increase diffusion and the mass transfer coefficient. Moreover, Yamaguchi et al.\(^6,7\) and Bailes and Stitt\(^8\) applied electric field in laboratory scale columns to study the holdup behavior. Yamaguchi et al.\(^6,7\) used equally spaced electrodes inside a spray column and found that the holdup after applying the electric field depends on the flowrate.
of the dispersed phase. At low flowrate of the dispersed phase (i.e. less coalescence of the dispersed phase due to a low holdup), the holdup was found to increase with an increase in the applied voltage. At higher flowrate of the dispersed phase, the holdup first decreased with an increase in the applied voltage and later starts to decrease.\textsuperscript{6,7} Bailes and Stitt\textsuperscript{8} however controlled the holdup and the coalescence-re-dispersion process by using impellers for high shear mixing and applying the electrodes in the settling zone of the dispersed to promote coalescence.\textsuperscript{8}

Despite the aforementioned research, to our knowledge the application of an electric field for coalescence in liquid-extraction columns was not reported before. In this chapter, we investigate the application of electric-field coalescence for entrainment reduction in a pilot-scale rotating disc contactor for the caprolactam-toluene-water system. We investigate first the role of caprolactam concentration, total flux, and solvent to feed ratio on the amount of entrainment without an electric field. Afterwards, the effect of the electric field is evaluated at the operational conditions that resulted in a maximum amount of entrainment.

6.2 Experimental section

6.2.1 Materials

Toluene (purity > 99\%) was purchased from Merck (Germany). \(\varepsilon\)-caprolactam (purity > 99\%) was supplied by Sigma Aldric (USA). Milli-Q super distilled water was used in all experiments.

6.2.2 Experimental setup

The rotating disc contactor (RDC) shown schematically in Figure 6.1 has a total length of 4.5 m and was used to perform the experiments. The column contains of a top and a bottom settler with a nominal length of 0.5 m and an inner diameter of 0.09 m. The effective settler length is 0.28 m, measured between the point of widening and the organic continuous phase outlet. Between the two settlers, there are nine glass segments that contain the column internals and are presented schematically in Figure 6.2. Each segment has a length of 0.36 m and a diameter of 0.06 m. Per segment there are eight stirred compartments, with alternating discs and stators. The discs are 0.04 m in diameter (Dr) and have a thickness of 0.0015 m. The stators have the same thickness as the discs, an inside (Ds) diameter of 0.022 m, and an outside diameter of (Dc) 0.06 m. The distance between the two discs (Hc) is 0.032 m. All column internals are made of stainless steel (SS 316). The shaft has a diameter of 0.01 m and is attached to the engine, which is mounted at the top of the column. The engine supplies the rotational energy with a speed of 120-800 rotations per minute.
Since the experiments were carried out at equilibrium condition, the column is only connected to two storage tanks, each with a volume of 0.20 m$^3$. The storage tanks were kept under nitrogen purge in order to avoid a build-up of organic vapor. The heavy aqueous phase tank contains water and caprolactam at the desired concentration, which is pumped to the heavy phase inlet at the top of the column. Another pump is used to recycle separated aqueous phase from the column bottom settler back to the heavy aqueous phase storage tank. The light organic phase storage tank contains toluene and caprolactam at a concentration which is in equilibrium with the aqueous phase. The light organic phase is fed to column by the light phase inlet at the bottom of the column and leaves the column at the top.

All the experiments are performed at a temperature of 20°C. Although high temperatures were not used, constant temperature in the column can be maintained by means of water bath (Julabo F32-MW) and is controlled by a PT100 temperature control using water as a heating fluid.

To evaluate the effect of the electric field on entrainment reduction, first, an electro-coalescer is integrated at the outlet of the organic continuous phase at the top of the column, which is shown in Figures 6.1 and 6.3. The electro-coalescer consists of a glass tube that contains electrodes, with a length of 0.17 m and a diameter of 0.0146 m. The tube is U-bent as depicted in Figure 6.3 to ensure that liquid is always maintained between the electrodes to prevent spark ignition. The parallel placed plate electrodes have a length 0.07 m and a width of 0.01 m. The electrodes are made of stainless steel and insulated with a 0.00025 m thick Kynar® layer. To obtain a homogenous electric field, the electrodes are placed parallel at a distance of 0.01 m from each other. For safety precautions, a continuously purged nitrogen box is placed around the glass tubing containing the electrodes.

After the electric field tube, a mini settler is installed to remove coalesced droplets. The mini-settler is made of glass and has a diameter of 0.085 m and a length of 0.105 m. All glass parts are connected by Rotolex clamps and Viton® rings as sealings. Entrainment samples are taken from two sample ports as depicted in Figure 6.1. One sample port was placed between the column outlet and the electro-coalescer containing the electrodes, whereas the other sample port is placed after the mini-settler.
6.2.3 Methods

The entrainment is quantified by taking samples of the continuous phase at the outlet of the column settler (Port 1 in Figure 6.3). Since the dispersed phase is the aqueous phase, entrainment was determined by measuring the water content in the organic continuous phase. Under equilibrium condition, when no dispersed phase droplets are present, the organic phase contains some physically dissolved water.
This quantity was measured by running experiments at the lowest rotational speed of 120 rpm for 2 hours until equilibrium between the phases was reached. Additionally, the effect of rotor speed on the water solubilities was determined. The same water concentrations as the physical solubility were measured at higher rotational speeds except at rotational speed of 800 rpm. When using rotational speed of 800 rpm, the water concentration increased due to entrainment. The determined water solubilities at different caprolactam concentrations and at a temperature of 20°C are given in Table 6.1. These water data was validated by batch equilibrium data measured by Van Delden et al. The droplets entrainment was calculated by subtracting the physical solubility from the total water content.

To quantify entrainment, samples of the organic toluene phase were taken from the outlet of the column settler and after the mini-settler. After removing the dead volume for 5 seconds, a 25 ml sample of the continuous phase was collected and the water content was analyzed by 795 KFT Titrino Metrohm Karl Fisher titration apparatus. To measure the water content, a 1 ml sample was injected into the
apparatus three times and the value was averaged. The water contents were determined with an accuracy of 0.005% w/w water.

6.3 Results and discussion

6.3.1 Effect of caprolactam concentration on entrainment

The effect of caprolactam concentration on entrainment without electric field was evaluated at concentrations of 5.35% w/w and 28.5% w/w caprolactam in the aqueous phase at a fixed solvent to feed ratio of 5 (mass basis) and a rotational speed of 800 rpm. These concentrations are the same as those used in our entrainment experiment using static-mixer. In particular, using the caprolactam concentration of 28.5% w/w resulted in significant entrainment as shown in Chapter 4. Therefore, the same concentrations as in the static-mixer experiment are chosen to quantify and reduce entrainment by electric field enhanced coalescence in a rotating disc contactor (RDC). The solvent to feed ratio was chosen in similar manner to the industrial process.¹

For the 5.35% w/w caprolactam concentration, the continuous phase flux was changed from 6.2-20.8 m/hr, while it was changed from 6.1-17.3 m/hr for the 28.5% w/w caprolactam concentration. For the latter concentration, the continuous phase fluxes higher than 17.3 m/hr resulted the flooding of the column. This column flooding at a lower flux for the 28.5% w/w concentration can be attributed to the decrease in drop size that results from the decrease of the interfacial tension at higher caprolactam concentrations.¹ This decrease in the drop size in turn reduces the relative velocity between the phases which eventually decreases the flooding flux.

The influence of caprolactam concentration on entrainment is depicted in Figure 6.4. Firstly, the figure reveals that for both concentrations the entrainment was not significant and not affected by the total flux. Secondly, a slightly higher entrainment was found at 28.5% w/w concentration compared to 5.35% w/w. The average entrainment at 28.5% w/w caprolactam concentration is about 600 ppm and decreased to less than 200 ppm at 5.35% w/w concentration. Thirdly, Figure 6.4 shows that the entrainment measured at the outlet of the organic continuous phase was found to reduce after flooding occurred. This can be attributed to a dense swarm of entrained droplets in the top settler, which form a liquid layer of the dispersed phase.⁹ Therefore, the droplets entrained from the column will coalesce in this dispersed phase layer resulting in a continuous phase with less dispersed phase droplets.
Since a relatively higher entrainment value was obtained at 28.5% w/w caprolactam concentration compared to 5.35% w/w, the concentration of caprolactam was further increased to 39.2% w/w. The entrainment obtained at 39.2% w/w caprolactam concentration is also shown in Figure 6.4. It can be observed that entrainment was not increased as expected at this concentration. While the entrainment by solubility increased from 1600 ppm to 2700 ppm by changing the caprolactam concentration from 28.5% w/w to 39.2% w/w, the entrainment by dispersed phase droplets was found to be only 200 ppm. The main effect of the change in caprolactam concentration was that flooding condition was already achieved at a flux greater than 5 m/hr, which is considerably lower than the flooding flux of 17.3 m/hr obtained for the 28.5% (w/w) caprolactam concentration. Therefore, the main influence of increasing caprolactam concentration from 28.5% w/w to 39.2% w/w was found to be a decrease in the flooding capacity, not an increase of entrainment.

Figure 6.4: Influence of caprolactam concentration in the aqueous phase on water entrainment at the outlet of the continuous organic phase at different flux ($V_d + V_c$) at a fixed solvent to feed phase ratio (mass basis) of 5, at a temperature of 20°C, and at a rotational speed of 800 rpm. The error bars at lower fluxes less than 10 m³/m².hr for a caprolactam concentration of 5.35% w/w are not visible because no entrainment was found for these fluxes during repeated experiments.

6.3.2 Effect of solvent to feed ratio on entrainment without electric field

Figure 6.5 shows the effect of solvent to feed ratio (organic continuous phase to aqueous dispersed phase) on entrainment for 5.35% w/w and 28.5% w/w caprolactam concentrations at a temperature of 20°C and rotational speed of 800
rpm. The solvent feed ratio was adjusted by changing the dispersed phase flow while keeping the solvent flow constant.

Figure 6.5 reveals that for the 28.5% w/w caprolactam concentration, the entrainment increases with a decrease in the solvent to feed ratio (S/F) from 7.5 to 3.75. However, the entrainment decreases as the solvent to feed ratio further decreased to 2.5. This can be explained in terms of coalescence and breakage phenomena occurring inside the column. At high S/F of 7.5, there is more solvent and less dispersed phase flow (few drops). Hence, drop coalescence can be considered to be minimal at this S/F due to few drops present. Decreasing the S/F ratio from 7.5 to 3.75 thus increases the dispersed phase flow and leads to the formation of more drops by breakage. Consequently, the holdup increases and decreases the relative velocity between the phases, which in turn increases the entrainment. However, once a considerable amount of drops are formed at intermediate S/F ratio value of 3.75, a further decrease of S/F ratio to 2.5 leads to the coalescence between the drops and decreases the holdup. Therefore, the entrainment decreases due to the increase in the relative velocity between the phases as a result of decrease in the holdup.

Figure 6.5 shows the same kind of relationship between the S/F ratio and entrainment for 5.35% w/w caprolactam concentration. It can be observed that the entrainment increases when the S/F is changed from 10 to 3.3. Nevertheless, it decreases again when the S/F is further decreased to 2.5.

![Figure 6.5: Influence of solvent to feed ratio on water entrainment at different total fluxes (Vd+Vc) at a rotational speed of 800 rpm. In the figure, for the 28.5% (w/w) caprolactam concentration, flooding did not occur at the used fluxes and solvent to feed ratios (the](image-url)
flooding for this concentration of caprolactam occurs at a higher flux of 20 m³/m².hr as shown in Figure 6.4)

6.3.3 Entrainment profile column settler

The obtained entrainment values at all used caprolactam concentrations are relatively very low (less than 600 ppm). Therefore, it was not possible to use them for comparison of entrainment reduction with the application of an electric field. Apart from the already investigated means of increasing entrainment by increasing the caprolactam concentration, another possible way to get high entrainment is by adjusting the outlet position of the organic continuous phase at the column top settler. This is because more entrained droplets are present at lower positions of the settler compared to the exit. Before making the adjustments, the entrainment profile of the column settler was determined. Samples were collected by introducing a hose in the top settler as shown in Appendix 6.A. Some of the dimensionless heights where the samples were taken are depicted in Figure 6.6.

Figure 6.7 presents the entrainment profile of the whole section of the column settler including lower positions and entrance into the top settler. This was done for 39.2% w/w caprolactam concentration at S/F ratio of 5 and a rotational speed of 800 rpm. This caprolactam concentration was chosen since stable and small size drops can be formed at 39.2% w/w concentration compared to the 28.5% w/w concentration. The stability of the droplets was determined from batch separation experiment, where it was found that the stability increases with an increase in caprolactam concentration. More stable droplets are required to avoid their deposition in the electro-coalescer pipe.

It can be observed from Figure 6.7 that the entrainment decreased sharply from around 5100 ppm at the entrance of the column top settler to 300 ppm at the exit of the continuous phase (settler outlet). This confirmed that more entrainment can be obtained by placing the organic phase outlet at lower position in the column top settler. A new column settler was therefore made with the outlet at the height of 12 cm from the base of the column top settler, which represents a dimensionless height of 0.43. The dimensionless height for the outlet is expected to result in an entrainment of 1500 ppm on the basis of Figure 6.7. The new settler and old settler are presented in Figure 6.8.
Figure 6.6: Dimensionless height in the top column settler

Figure 6.7: Entrainment as a function of dimensionless settler height at a flux of 3.6 m/hr, a caprolactam concentration of 39.2% (w/w), S/F ratio of 5 and at a rotational speed of 800 rpm

Figure 6.8: Old column settler (left) and new column settler (right) with new outlet position for the continuous phase
6.3.4 Effect of electric field with a new column settler

With the new settler in place, entrainment quantification was done by taking samples at the new outlet port of the continuous phase for a caprolactam concentration of 39.2% (w/w) at S/F of 5 and rotational speed of 800 rpm. The measurement was made at the flux of 3.6 m/hr since all higher fluxes resulted in flooding of the column for this caprolactam concentration. Figure 6.9 shows that an entrainment of 1600± 200 ppm was obtained with the new settler, which is in good agreement with an expected value of 1500 ppm. This value of entrainment is sufficiently high to be used for evaluating the effect of the electric field. Therefore, the entrainment values at the outlet of the column top settler, after the electro-coalescer (entrance to the mini-settler), and after the mini-settler should be measured to compare the entrainment values with and without electric field. In principle, the entrainment values at the outlet of the column settler should be the same as at the outlet of electro-coalescer, since drops are only coalescing to form larger droplets in the electro-coalescer. After the mini-settler, the entrainment will decrease because some entrainment is removed. Therefore, the purpose of the electro-coalescer will be to reduce the entrainment as much as possible by enlarging the droplets fed to the mini-settler.

Accordingly, entrainment was measured before the mini-settler (downstream the electro-coalescer) without and with an electric field. It can be observed from Figure 6.9 that the entrainment measured directly after the electro-coalescer (before the mini-settler) without applying electric field was found to be 200 ppm. This was a rather small value which was not expected because it was assumed that the droplets remain in the continuous phase, and are not separated in the electric-field tube. A visual check was therefore made to evaluate if this is the cause for the decrease in the entrainment value. From the observation during experiment, it was found that indeed droplets are accumulating in the U-bend of electric field. This shape was chosen for safety reasons as it can maintain always a liquid between electrodes to prevent a spark ignition. However, the droplets are accumulating in the U-bend of the electric-field. Therefore, only 200 ppm of entrainment was entering the mini-settler. Therefore, the design of electro-coalescer was revamped to mitigate this problem. The U-shape was avoided and now a liquid layer was maintained by inclining the electro-coalescer as shown in Figure 6.10. Additionally, the mini-settler was reduced in size (diameter 0.045 m and length 0.05 m) as shown in Figure 6.10.
Figure 6.9: Comparison of entrainment at the outlets of the new and old column settlers and directly after the electro-coalescer (sample port 2)

After these modifications, an entrainment of 2425 ppm was obtained at the outlet of the organic continuous phase. However, still lower values were obtained downstream the electro-coalescer since droplets deposited on the electro-coalescer tube, which is shown in Figure 6.11. The entrainment downstream the electro-coalescer was found to be 187 ppm without electric field and 62 ppm when a DC field of 1kV/cm was applied. Inspite of this small difference, the effect of the electric field was checked by taking pictures of the drops with and without electric field. This is shown in Figure 6.12. The scale of the distance between the electrodes (1 cm) is also shown to enable the comparison of the drops size. Without
electric field, it can be seen that the drops stand only few mm above the electrode surface, while with electric field the size of considerable amount of drops is increased and almost touching the electrode surface. This shows clearly the effect of electric field on the drops in the electro-coalescer tube. Therefore, further investigation should be made to utilize this potential at the same time avoiding the drops deposition problem to quantify the entrainment reduction.

6.4 Conclusions

The electro-coalescer was integrated into a pilot scale rotating disc contactor (RDC) to reduce entrainment for the caprolactam-toluene-water system. The effect of caprolactam concentration, solvent to feed ratio, and fluxes on entrainment was studied. All studied process variables resulted in a small amount of entrainment. A maximum entrainment of 600 ppm was obtained at 28.5% w/w caprolactam concentration and the entrainment decreased to less than 200 ppm at 5.35% w/w concentration. To increase the amount of entrainment, the caprolactam concentration was increased to 39.2% w/w, and the outlet of the continuous phase in the column settler was lowered. The first approach decreased the flooding capacity, however, did not result in increased entrainment at the outlet of the continuous phase. With the second approach, an entrainment value of 2425 ppm was obtained. This entrainment value decreased to 187 ppm upstream of the electro-coalescer without electric field and to 62 ppm when a DC field of 1 kV/cm was applied. Additionally, the effect of electric field was verified by taking pictures of drops with and without electric field. The drop sizes were observed to increase considerably when electric field was applied. However, the deposition of droplets on the electro-coalescer pipe still occurs which lowered the entrainment values both in the presence and absence of electric field.
Figure 6.11: Droplets deposited on the electro-coalescer tube (left) and segregation of the droplets at outlet of the column (right)

Figure 6.12: Droplets without electric field deposited on the glass pipe (top) and droplets growth in the presence of electric field (bottom)
Appendix 6.A: Method for determining dispersed phase entrainment in the column top settler

A hose was introduced into the column settler, between point 1 and 3, entering the column settler via a metal t-piece in the piping of the safety valve. The hose had an inner diameter of 1mm. The hose was pin-holed through the sealing-rubber of a 25 ml sample bottle (point 1). The air in the sample bottle was removed by a syringe with a needle through the sealing-rubber (point 2). This will create an under pressure in the sample bottle, allowing liquid from the column settler (point 3) to flow against gravity into the sample bottle (point 1).
Reference List

(1) Van Delden, M. L., Caprolactam Extraction in a Pulsed Disc and Doughnut Column With a Benign Mixed Solvent. University of Twente, Enschede, 2005.


A combined lossy capacitor population balance model (LCPBM) for calculating the influence of frequency on electric field enhanced coalescence in a static-mixer settler setup

This chapter has been Submitted as: Esayas W. Barega, Edwin Zondervan, André B. de Haan, (2013). A combined lossy capacitor population balance model (LCPBM) for calculating the influence of frequency on electric field enhanced coalescence in a static-mixer settler setup, Journal of Chemical Engineering Science.

Abstract

In this chapter a combined lossy capacitor population balance model (LCPBM) is developed to predict the effect of a square wave frequency on electric-field coalescence (drop size) in a static mixer settler setup for the caprolactam-toluene-water system. The electrical-circuit model is based on the lossy capacitor model where the insulation and the dispersion are considered as a leaky dielectric. The charge and the electric field are determined from the circuit model and coupled in the hydrodynamic equation to calculate the velocities of drops. The velocities are in turn used in the population balance model (PBM) to determine the mean sauter diameters. Three approaches are used to calculate the electrical force and the charge on the drops: 1) the Bailes’ charge hypothesis where the drops pick charge from the free dispersion-insulation interfacial charge, and the force calculated based on electrophoretic contribution, 2) the force determined from the Taylor-Melcher leaky dielectric model considering the force due to the free charge and the difference in dielectric permittivity’s of the dispersion and insulation, and 3) by accounting for the free charge convection by the fluid motion which results in equal redistribution of the polarization charge between the dispersion and the insulation. The (LCPBM) model was validated by measuring drop sizes using a square wave of 0.4 kV/cm and frequencies between 3-100 Hz for two flowrates. The mean sauter diameters were calculated within 10% at lower frequencies for both flowrates. At higher frequencies of 50 Hz and 100 Hz, a 20% error was obtained for the first approach, while a better prediction with 10% error was found for the second and third approaches with the later model being the best.
Chapter 7

7.1 Introduction

The use of an electric field to intensify the separation of emulsified water in oil is a mature technology in oil and gas industry.\textsuperscript{1,2} By subjecting the oil stream containing micro droplets of water to an AC or DC electric field, the droplet size can be increased, and consequently the separation process can be improved significantly. Many mechanisms were reported to account for the electric field coalescence effect. These include chain formation, dipole coalescence, electrophoresis, dielectrophoresis, and random collision.\textsuperscript{1} In the electric field, the aqueous drops acquire induced charges, which create a dipole-dipole attraction force between them, and this eventually causes their coalescence. Moreover, once the drops acquire charge, they move under the action of electrostatic attraction of charged electrodes, which leads to the collision and coalescence enhancement of drops.

While significant progress was made on understanding the electro-coalescence effect, the implementation of the technology at industrial scale requires an optimal design and optimal operational values of an electro-coalescer. The main drivers for determining these optimal design and operational values are a requirement for a compact electro-coalescer, and a high separation efficiency with less energy consumption.\textsuperscript{3,4} This necessitates knowing the optimal operating parameters such as frequency of an AC field, temperature, and phase ratio which yield the best separation efficiency. In this regard, rough indication of optimal operational parameters can be obtained from a laboratory experiment. Yet, due to differences in dispersion, electrode and insulation material dimension change, and other non-linearities, a correct prediction of the optimal operational parameters based only on laboratory experiments cannot be made. Therefore, an experimental approach of establishing the optimum will not be sufficient as it requires a laborious task of experimenting for every change in the electrical properties of the dispersion. Nevertheless, an approach unifying the experiments with fundamental physical model describing the particles attraction and the electric field in the dispersion is a significant step in predicting the optimum operational parameters.\textsuperscript{4}

In this chapter, a model that predicts the influence of an AC field (square wave) frequency on the drop size and distribution in a static mixer-settler setup is developed. The population balance model coupled with a model for an electrical force is commonly used to predict the evolution of the drop size due to electro-coalescence specifically for DC field. In this regard, the work of Zhang et.al.\textsuperscript{5} and Sadek and Hendricks\textsuperscript{6} can be emphasized and in both approaches a DC field was applied. The two approaches differ in the way the coalescence rate of the
population balance model is calculated. However, the two approaches are not sufficient to describe the influence of frequency as described below.

7.1.1 Zhang trajectory analysis

Zhang et.al.\textsuperscript{5} used a trajectory analysis to track a relative motion between two drops to predict pairwise collision and coalescence between the drops. The trajectories of the droplets are determined from equation of motion while they are subjected to gravitational, drag, and electrical forces. The authors introduced a coalescence efficiency term in the coalescence rate equation of Zhang and Davis\textsuperscript{7} (see equation (7.5)), which was defined as the ratio of the actual collision rate including electric field to that one without electric field. The electrical force between the drops is calculated using equations of Davis\textsuperscript{8} which are derived for two spherical conducting drops in a uniform field. The forces decomposed into radial and tangential components are given by equation (7.1a) and (7.1b), respectively: \textsuperscript{5,8}

\begin{align*}
F_{e,ij}^r &= 4\pi\varepsilon d_j^2 E_o^2 (F_1 \cos^2 \psi + F_2 \sin^2 \psi) \quad (7.1a) \\
F_{e,ij}^\theta &= 4\pi\varepsilon d_j^2 E_o^2 (F_3 \sin(2\psi)) \quad (7.1b)
\end{align*}

Where, $E_o$ is the magnitude of the externally applied electric field, $\psi$ the angle the electric field makes with the line connecting the centers of the two drops, and $d_j$ the drop diameter. The force coefficients $F_i$ in equations (7.1a) and (7.1b) are a complicated series of expressions that depend on the distance between the colliding drops and the size ratio between the drops. The coefficients are given by Davis\textsuperscript{8}, and a large number of terms in the series need to be calculated to get convergence. The coalescence efficiency term is determined from a trajectory analysis by a trial and error where one of the drops is fixed in space while the other drop is allowed to graze over the fixed drop.\textsuperscript{9} An initial drop separation is assumed and this distance is successively increased until the drop misses the other drop. This determines the limiting trajectory from which the coalescence efficiency is determined.

This procedure is repeated for every possible combination in drop size classes which makes the approach computationally intensive. Additionally, the approach is valid for dilute dispersions and for low Reynolds number flows\textsuperscript{5} where the drops trajectories do not cross each other.\textsuperscript{9} Furthermore, the electric field force between the drops is calculated using equations of Davis which are valid for two spherical conducting drops in a uniform field. The electric field as described before depends on the distance between the drops. The field increases strongly as the distance...
between the drops decreases and is influenced by the presence of drops in the vicinity.\textsuperscript{10} Even for a low strength field, the forces between adjacent droplets from induced polarization can become large. The equations are thus valid for a two droplet system and for a dispersed phase content less than 5\%.\textsuperscript{10,11} These equations can be modified to account for a multi-droplet system.\textsuperscript{11} Nevertheless, the distance between the drops is still required to calculate the electric field force. As our work deals with higher dispersed fractions (10% v/v), it is not possible to accurately determine the distance between the drops.

On top of the above factors, the equations are derived for a uniform and steady DC field. It is not possible to maintain a steady and uniform field in our case even when a DC field is applied due to the insulation on the electrodes. When the electrodes are insulated, the difference in electrical properties (permittivity and conductivity) between the insulation and dispersion results in a time varying field (dynamic field). Thus, the trajectory analysis of Zhang approach was not found suitable to calculate drop sizes because: (1) in addition to being computationally intensive, determining the trajectories is accurate only when they do not cross each other for example in dilute dispersions and the two droplet system, (2) the electric field force is calculated based on Davis equations which are valid under specific conditions (uniform and steady field as well as two droplet system), and (3) the distance between drops is required to calculate the electric field in Davis equations which is difficult to determine for higher dispersed fractions and when the drop motion is random.

### 7.1.2 Sadek and Hendricks model

In the work of Sadek and Hendricks\textsuperscript{6}, the coalescence rate of the population balance model was obtained from velocities calculated from the momentum balance including the electric field. This avoids the trial and error procedure associated with the trajectory analysis. In this case, the electrical force was determined from the electrophoretic force, which includes the charge on the drop, and the electric field across the dispersion. The charge on the drops was calculated from an equation of Cho\textsuperscript{12} shown in equation (7.2a), and was used to calculate the electrophoretic force (equation (7.2b)):

\[
q = \frac{6.6\pi\varepsilon d_i^2 E}{4} \quad (7.2a)
\]

\[
F_e = qE \quad (7.2b)
\]

where , $E$ is the magnitude of the electric field, $q$ the charge on the drop, $\varepsilon$ the permittivity of the continuous phase, and $d_i$ the diameter of the drop. The equation
of Cho is derived for a drop contacting a bare charging electrode. As in the case of the previous approach, equation (7.2a) is applicable when the electric field \( E \) is uniform and steady (not changing with time), and bare electrodes are used. The equation is not valid for insulated electrodes as the interfacial charge develops at the electrode insulation-dispersion interface which changes with time. Moreover, the equation is not valid for an AC field (square wave) since both the interfacial charge and the field across the dispersion depend on the frequency of the square wave. The approach of Sadek and Hendricks is thus also not sufficient to model the drop sizes at different frequencies of an AC field (square wave). Hence, an approach to incorporate the frequency dependence and the field modification due to the difference in the electrical properties of the dispersion and the insulation is required to predict the drop sizes at different frequencies of an AC field.

7.1.3 Modeling approach of this work

In this work a two-layer lossy capacitor model of Joos and Snaddon\textsuperscript{13} is proposed as a possible method to incorporate the non-steady field, and the interfacial charge at the electrode-dispersion interface to predict the effect of frequency effect on the drop sizes. In the two-layer lossy capacitor model, the insulation and the dispersion are considered as leaky dielectrics with capacitive and resistive components connected in parallel. In this case, the resistor accounts for the conductive losses by the dielectric whereas the capacitive component accounts for dielectric polarization. The resulting electrical circuit of the two-layer capacitor model can be treated in the same manner as other electrical circuits. Therefore, it can be analyzed using the standard electrical-circuit equations from which the dynamic behavior of the electric field across the dispersion and the charge at the electrode-insulation interface can be determined. Nevertheless, still the question remains on how to determine the electric field and the charge on the drops afterwards which are required in determining the electrical force on the drops.

Three approaches are followed and compared in this work to calculate the electrical force. The first approach is based on the charge hypothesis of Bailes\textsuperscript{4,14} where the drops are considered to pick the free dispersion-insulation interfacial charge. The free interfacial charge is obtained from Gauss law\textsuperscript{4} applied at the dispersion-insulation interface. The dynamic behavior of the fields across the dispersion and the insulation in this case are obtained from the lossy capacitor model. The electrical force is calculated from the free interfacial charge and from the field across the dispersion based on electrophoretic force.
In the second approach, the model of Taylor and Melcher for leaky dielectrics is used to determine the electrical force. The electrical force in this case includes the contribution of both free charges and dielectric polarization. The electric field force for the case of one dielectric is determined from equation (7.3). As can be seen from equation (7.3), this includes the electric field force due to the free charge (first term), the electric field force due to spatial gradient of permittivity hence polarization (second term) and the force due to the change in permittivity with density (third term which is zero for an incompressible medium).

\[ f_v = q_v E - \frac{1}{2} E^2 \nabla \varepsilon + \frac{1}{2} \rho_m \left( \frac{d\varepsilon}{d\rho_m} \right) T E^2 \]  

In equation (7.3), \( f_v \) represents the electrical force per unit volume of dielectric, \( q_v \) is the free charge per unit volume of dielectric, \( \varepsilon \) is the permittivity of the dielectric fluid, \( \varepsilon_0 \) is the permittivity of free space, \( \rho_m \) is the density, and \( E \) is the electric field. A similar expression as Equation (7.3) is derived for two dielectrics by Zaghdoudi and Lallemand. In our case, the dispersion and insulation are considered as the two dielectric. The derivation will be illustrated later.

In the third approach, we consider the possibility of free charge transport by the fluid motion. This results in the polarization charge equally redistributing itself between the two electrode insulations and the dispersion. The polarization charge on the insulation and the dispersion is different when a free interfacial charge is present. However, once the free charge is transported by the fluid motion, the polarization charge on the insulation and the dispersion redistributes itself resulting in equal charges on the insulations and the dispersion. The drops are then considered to pick this redistributed charge. The electric force is obtained from the electrophoretic contribution calculated based on this charge and the field across the dispersion.

It is noted that in all the approaches the root mean square values of the free interfacial charge and electric field are used since both are dynamic. Once the electric field force is calculated based on the three approaches, it is incorporated in the hydrodynamic equation which is based on a momentum balance to calculate the velocities of drops. The velocities in turn are used to calculate the coalescence kernel term of the population balance model which is used to predict the drop size evolution with time.

We therefore present a novel combined lossy capacitor population balance model (LCPBM) to predict the influence of square wave frequency on drop size and
distribution in a static-mixer settler setup for a caprolactam-toluene-water system. The electrical circuit model of the system is built based on the two-layer lossy capacitor model of Joos and Snaddon. This enabled us to determine a time dependent (non-steady) field experienced by the dispersion and the dispersion-insulation interfacial charge. The proposed model is validated by measuring drop sizes for a caprolactam-toluene-water system at various frequencies of a square wave between 3-100 Hz and for two different flowrates. First, the modeling approach used this work is described in detail. This is followed by discussion of the results of model validation using the experimental data. Finally, the sensitivity analysis was done to study the influences of insulation thickness and dispersion resistance.

### 7.2 Model development

An input-output diagram of the combined lossy capacitor population balance model (LCPBM) is presented in Figure 7.1. The inputs to this model are the physical properties (viscosity of the continuous phase, densities of the continuous and dispersed phase), electric field strength and frequency, insulation material properties (dimensions, resistivity, and dielectric constant), and size distribution without electric field. These inputs are used in the model to predict the final size distributions and mean sauter diameters. As shown in Figure 7.2, the model consists of three major models, namely; a population balance model, an electrical circuit model, and a hydrodynamics model. The focal point of these equations is the coalescence kernel, which is an input to the population balance model (PBM). The coalescence kernel has a velocity term (see equation (7.5)), which is calculated from the hydrodynamic model (see equation (7.7)) based on the balance of different forces (drag, electric field and gravitational forces) acting on a droplet. The electric field force in equation (7.7) calculated from the electrical circuit model and based on the three approaches of charge and electrical force described in the introduction section. This links the electrical circuit model to the equation of hydrodynamics. After velocities are calculated using the hydrodynamic equation that includes electrical force, they are used in the PBM to calculate the coalescence rate and drop size evolution with time. Additionally, the different inputs to the models are illustrated in Figure 7.2. The flowrate determines the residence time in the electric field; thus, specifies the time duration over which the population balance model is solved. Physical properties, specifically the viscosity and density of the continuous phase, are used to determine a drag force in the hydrodynamic equation. The electrical properties of the dispersion and insulation, and the source voltage and frequency are inputs to model the dynamic behavior of an electric field.
and charge in the electrical circuit model. An initial size distribution without electric field is required to solve the population balance model and was obtained from measured experimental data. Based on these inputs, the final size distribution and mean sauter diameter with electric field are determined. Further details of the population balance model, the hydrodynamic model and the electrical circuit model are discussed in the next sections.

Figure 7.1: Input Output diagram of the lossy capacitor population balance model (LCPBM)

Figure 7.2: Behavioral diagram showing the relationship between variables
7.2.1 Population balance model (PBM)

The population balance model (PBM) predicts the evolution of drop size distribution with time. Starting with an initial size distribution and taking into account droplet breakage and coalescence phenomena. To model electric field enhanced coalescence, only the coalescence term is sufficient. As proposed by Zhang and Davis\(^7\) the resulting PBM that describes the change of size distribution with time is given by equation (7.4).

\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} J_{i,j,j} - \sum_{j=1}^{N} J_{i,j,j} \tag{7.4}
\]

In the equation, \( n_i \) represents the number of drops of size \( d_i \) per unit volume of dispersion. \( J_{i,j} \) is the rate of coalescence per unit volume of dispersion of drops of size \( d_i \) with size \( d_j \) and \( N \) is the number of classes in which a distribution of drops is discretized. The first term in equation (7.4) represents the birth rate of drops of size \( d_i \) by the coalescence of smaller size drops, while the second term stands for the loss of drops of size \( d_i \) by coalescence with other drops.

The collision rate \( J_{i,j} \) can be expressed by Zhang and Davis equation (7.5)\(^7\) as:

\[
J_{i,j} = \beta n_i n_j \pi / v_i - v_j / (d_i + d_j)^2 \tag{7.5}
\]

In this equation, \( v_i \) and \( v_j \) stand for the velocity of drops of size \( d_i \) and \( d_j \) relative to the continuous phase, and \( \beta \) is a constant that depends only the geometry. The velocity terms in equation (7.5) are determined by a hydrodynamic model which is described in the following section.

The population balance equation is solved using the fixed pivot technique of Kumar and Ramakrishna.\(^18\) In this approach, the population of particles is distributed only on the selected fixed grid points with volumes \( x_1, x_2, \ldots, x_N \). Thus, due to the coalescence and breakup process, if a drop is formed with a volume \( V \) which does not lie on the grid points, such a particle is distributed into the neighboring grid points in such a way that two required properties are conserved. The population balance model that conserves mass and number of particles is used as given in equation (7.6) by Kumar and Ramakrishna\(^18\):

\[
\frac{dN_i}{dt} = \frac{1}{2} \sum_{j,k}^{j \geq k} (1 - \frac{1}{2} \delta_{j,k}) \eta J_{j,k} N_j(t) N_k(t) - N_i(t) \sum_{k=1}^{N} J_{i,k} N_k(t) \tag{7.6}
\]

where,
\[ \eta = \frac{x_{i+1} - V}{x_{i+1} - x_i}, \text{ if } x_i \leq V \leq x_{i+1} \]
\[ \eta = \frac{V - x_{i-1}}{x_i - x_{i-1}}, \text{ if } x_{i-1} \leq V \leq x_i \] (7.6a)

\( V \) in this case is obtained from \( V_j + V_k \) based on \( j \) and \( k \) values satisfying the constraint \( x_{i-1} \leq x_{j+k} \leq x_{i+1} \). \( \delta \) is the Kronecker delta operator which assumes a value of 1 if \( j=k \) and 0 if \( j \neq k \).

### 7.2.2 Hydrodynamic model

The velocity of drops in the collision rate equation (7.5) is obtained from a momentum balance on a discrete particle shown in equation (7.7):

\[ m_i \frac{dv_i}{dt} = F_{\text{drag}} + F_g + F_e \] (7.7)

where \( m_i \) represents the mass of drop size \( d_i \), \( F_{\text{drag}} \) a drag force, \( F_g \) a gravitational force, and \( F_e \) an electrical force. The time independent form of equation (7.6) is used, which results in an electric field and a gravitational force balanced by a drag force. The drag force is described by equation (7.8) as follows.

\[ F_{\text{drag}} = \frac{1}{2} \rho_c C_d \pi d_i^2 v_i^2 \] (7.8)

The correlation proposed by Schiller and Naumann\(^{19}\) is used to describe the drag coefficient \( C_{do} \) as:

\[ C_{do} = \frac{24}{\text{Re}_p} (1 + 0.15 \text{Re}_p^{0.687}) \] (7.8a)

The above drag correlation is applicable only for a dilute dispersion. At higher volume fraction the velocity of the drop is reduced as a result of interaction with the other drops. The increase of drag coefficient in a droplet swarm can be expressed by Richardson and Zaki\(^{20}\) equation (7.8b):

\[ C_d = C_{do} (1 - \phi)^{-4.65} \] (7.8b)

where \( \phi \) represents the volume fraction of the dispersed phase.
The gravitational force is obtained from equation (7.9).

\[ F_g = mg = \frac{\pi d_i^3 \rho g}{6} \]  
(7.9)

### 7.2.3 Electrical circuit model

The electrical force \( F_e \) in equation (7.7) can result from the contribution of a dipole-dipole interaction, dielectrophoretic and an electrophoretic force due to the interaction of the charged drops with the field. In this work, the electric field force is calculated using equation (7.10a), when the first approach described in the introduction section, i.e., based on the dispersion-insulation interfacial charge and electrophoretic force is used to calculate the electrical force.

\[ F_e = Q_{ei} E_e = q_{ei} E_e A \]  
(7.10a)

In equation (7.10a), \( E \) stands for the field strength across the dispersion, \( q_{ei} \) is the dispersion-insulation interfacial charge per unit area, \( Q_{ei} \) the dispersion-insulation interfacial charge, and \( A \) is the cross-sectional area of the electrodes perpendicular to the field. As stated in the introduction, the main premise in calculating the charges is the Bailes’ hypothesis that drops peak the free charges\textsuperscript{4,14} from the dispersion-insulation interfacial charge. Once charged the drops move under the action of the electric field (electrophoretic force) as described by equation (7.10a), which results in their collision and coalescence. The electrical force for the second approach, i.e., Maxwell electric stress (as described by equation (7.3) in the introduction section) is calculated using equation (7.10b):

\[ F_e = f_s A \]  
(7.10b)

where \( f_s \) is the electrical stress. In the third approach, the electrical force is calculated based on the redistributed polarization charge and the electric field across the dispersion using equation (7.10c):

\[ F_e = Q_p E_e \]  
(7.10c)

where \( Q_p \) is the redistributed polarization charge and will be described later. Thus, the electric field force calculated using equations (7.10a)-(7.10c) are coupled inside the hydrodynamic equation (7.7) to calculate the velocities required in the coalescence rate (equation (7.5)). In the equation, the insulation-dispersion interfacial charge and the field across the dispersion are changing with time. Hence, the root mean square values are used. The unknowns in equations (7.10a)-(7.10c) (the dispersion insulation interfacial charge, the redistributed polarization
charge, field across dispersion, and the Maxwell electric stress) are obtained from
the circuit analysis of the system consisting of the dispersion and the electrodes
insulation. Each of the above quantities is described below.

**Electrical force calculated based on the free insulation-dispersion interfacial
charge (Model 1)**

In conformity with the two-layer capacitor model of an electro-coalescer developed
by Joos and Snaddon\textsuperscript{13} and Midtgård\textsuperscript{4}, a three parallel resistor capacitor circuit
model is used (See Figure 7.3). As both electrodes are insulated in our case, an
extra resistor-capacitor is added to represent the additional insulated electrode
compared to the two layer model.

The electrical circuit model is derived from the Kirchhoff’s current and voltage
laws. Kirchhoff’s current law as shown in equation (7.11) requires that the total
current \( I \) passing through the external circuit will also flow through all the three
resistor-capacitor circuits. And, from the voltage law given in equation (7.12), the
sum of all the potential differences across the circuit should sum up to zero.

\[
I = I_R + I_c = \frac{V_i}{R_i} + C_i \frac{dV_i}{dt} = \frac{V_e}{R_c} + C_e \frac{dV_e}{dt}
\]  
(7.11)

\[-V_{dc} + V_i + V_i + V_e = 0
\]  
(7.12)

In equations (7.11) and (7.12) \( I, I_R \) and \( I_C \) represent the total current, current
through the resistor and capacitor, respectively. \( R, C, \) and \( V \) represent the
resistance, capacitance, and voltage, respectively. The subscripts \( e \) and \( i \) stands for
the dispersion and the insulation respectively. Combining equations (7.11) and
(7.12) and rearranging gives a differential equation for the voltage across the
emulsion:

\[
(C_e + \frac{C_i}{2R_i}) \frac{dV_e}{dt} + (\frac{1}{R_c} + \frac{1}{R_i})V_e = \frac{V_{dc}}{2R_i}
\]  
(7.13)

SimElectronics in Matlab R2010b was used to solve the electrical circuit model of
the system shown in equation (7.12). By dividing the resulting voltages of the
dispersion and insulation by the thickness, the fields across each layer are obtained.
These provide the dispersion field \( E_e \) in electric field force equations (7.10a)-(7.10c).

Moreover, once the voltages are known, the dispersion-insulation interfacial charge
is calculated by applying Gauss law (equation (7.14)) on the Gauss surface
indicated in Figure 7.3. The detailed derivation can be found in the work of Mitgärd.\footnote{4}

\[ \oint_S D \cdot dS = Q_{ei} \]  

(7.14)

where \( D \) is the electric displacement and \( Q_{ei} \) is the free charge enclosed by surface \( S \). The electric displacement is related to the electric field through a constitutive equation (7.15):

\[ D = \varepsilon E \]  

(7.15)

where \( \varepsilon \) represents the permittivity of the material and \( E \) is the electric field strength.

Using equation (7.15) and Gauss law as shown in equation (7.14), the following expression for the dispersion-insulation interfacial charge is obtained.

\[ Q_{ei} = q_{ei} A = C_e V_e - C_i V_i \]  

(7.16)

Thus, the interfacial free charge calculated from equation (7.16) is used in equation (7.10a) to calculate the electric field force.
Electrical force calculated according to the leaky dielectric model of Taylor and Melcher (Model 2)

Another approach to include the effect of electrical force on the hydrodynamics is through the leaky dielectric model of Taylor and Melcher\(^\text{15}\) which is described by equation (7.3). In addition to the electrical force due to free charge, this model allows to incorporate the electrical force due to polarization difference between the dispersion and insulation. A net electrical force will act on the dispersion which in turn transmits to the drops. Taking out the term that represents the change of dielectric constant with density, equation (7.3) can be rewritten for a single dielectric as follows.

\[
f_v = q_v E - \frac{1}{2} E^2 \nabla \epsilon \tag{7.17}
\]

In equation (7.17), \(f_v\) is the electrical force per unit volume of the dielectric which results from the free charges present with in the dielectric (first term) and from the spatial gradient of permittivity with in the dielectric (second term). Equation (7.17) applies to one dielectric, \(f_v\) can be expressed as an electrical stress (Maxwell stress) by using Gauss’ law\(^\text{15,16}\):

\[
f_{sj} = \epsilon_j (u_j E_j) - \frac{1}{2} \epsilon_j E_j^2 u_j \tag{7.18}
\]

where \(j\) represents either the dispersion or the insulation and \(u_j\) is the unit normal vector in each dielectric. The net resultant stress for two dielectrics which resides at their interface is given as:

\[
f_s = f_{se} + f_{si} \tag{7.19}
\]

where \(f_s\) is the resultant stress), \(f_{si}\) is stress due to insulation and \(f_{se}\) is due to the dispersion.

Inserting equation (7.18) into equation (7.19) one obtains:

\[
f_s = \epsilon_e (n_e E_e) - \epsilon_l (n_l E_l) - \frac{1}{2} \epsilon_e E_e^2 n_e - \frac{1}{2} \epsilon_l E_l^2 n_l \tag{7.20}
\]

Taking the unit normal vector pointing in the direction from the dispersion to the insulation, equation (20) can be rewritten as:

\[
f_s = \epsilon_e E_e E_e - \epsilon_l E_l E_l - \frac{1}{2} \epsilon_e E_e^2 + \frac{1}{2} \epsilon_l E_l^2 = \frac{1}{2} \epsilon_e E_e^2 - \frac{1}{2} \epsilon_l E_l^2 \tag{7.21}
\]
The force $F_e$ can be written in terms of the stress $f_x$ as in equation (7.10b) using the cross-sectional area $A$ normal to the electric field:

$$F_e = f_x A = \frac{1}{2} \varepsilon_x E_x^2 A - \frac{1}{2} \varepsilon_i E_i^2 A$$  \hspace{1cm} (7.22)

Using the expression for capacitance, equation (7.22) can be rearranged as:

$$F_e = \frac{1}{2} C_e V_e E_e - \frac{1}{2} C_i V_i E_i = \frac{1}{2} E_e (C_e V_e - \frac{E_i}{E_e} C_i V_i)$$  \hspace{1cm} (7.23)

The final expression including the dispersion-insulation free interfacial charge (equation (7.16) can be obtained from equation (7.23).

$$F_e = \frac{1}{2} E_e (C_e V_e - C_i V_i + C_i V_i \frac{E_i}{E_e} C_i V_i) = \frac{1}{2} E_e (Q_{ei} + C_i V_i (1 - \frac{E_i}{E_e}))$$  \hspace{1cm} (7.24)

The first and second terms in equation (7.24) show respectively the contributions of the electrical force due to the free charge and the force due the difference in the polarization of the dispersion and insulation.

**Electrical force calculated based on charge redistribution (Model 3)**

Equation (7.16) for the free interfacial charge does not consider free charge transport by fluid motion. In the situation where there is free charge convection, it can be considered that the polarization charge on the dispersion and insulation redistributes itself equally to maintain continuity of the displacement field. As can be seen from equations (7.14) and (7.16), the displacement field jumps by an amount equal to the free interfacial charge. When the free charge is transported away by fluid motion, equation (7.16) can be equated to 0 and this results in equal polarization charge ($C_i V_i = C_e V_e$). After an initial period of voltage distribution governed by the capacitances of the insulation and the dispersion, the voltage distribution at a later time is governed by their resistances. This results in a larger potential difference across the insulations and a reduced potential difference across the dispersion and results in some dispersion-insulation interfacial charge to develop. This momentarily increases the charge in the insulation and decreases the charge in the dispersion due to the voltage distribution. Nevertheless, without free interfacial charge (based on the above premise of free interfacial charge transport), it can be considered that the charge between the positive and negative terminals of the circuit redistributes itself in such a way that the total charge between the positive and the negative terminals remains the same. The polarization charge
redistributed among the three capacitors (also equal to the charge between the positive and negative terminals of the circuit) is thus calculated using equation (7.25):

\[ Q_p = \frac{1}{3} (C_e V_e + C_i V_i + C_i V_i) \] (7.25)

where \( Q_p \) is the polarization charge. In similar manner to equation (7.16), the charge is calculated from equation (7.25) and implemented in equation (7.10c) to calculate the electric field force.

7.3 Materials and procedure

7.3.1 Materials

Toluene (purity > 99%) was supplied by Merck Germany. \( \varepsilon \)-caprolactam (purity > 99%) was supplied by Sigma-Aldrich (USA). Milli-Q water was used for all the experiments.

7.3.2 Experimental setup, drop size measurement and procedure

Experimental setup, drop size measurement, and procedure

A static mixer settler setup shown in Figure 1.1 in Chapter 1 was used to perform the electric-field coalescence experiment and acquire drop size data. The drop sizes were determined by taking pictures of drops in a static-mixer pipe in area covered by the electrodes using a canon 50D camera as described in Chapter 1 and 4. The model validation here was done for experiments carried out for a caprolactam-toluene-water system. A 28.51% w/w concentration of caprolactam in water was used as an aqueous dispersed phase. In equilibrium with this concentration in an aqueous phase, a toluene with 3.39% w/w caprolactam was used as an organic continuous phase. The results from flowrates of 60 l/hr and 96 l/hr of the continuous phase were used. A 10% v/v dispersed phase was used an aqueous phase.

Capacitance measurement

The capacitance of the dispersion was measured using a capacitance meter made by Glass and electrical workshop (GTD) at Eindhoven University of Technology. The instrument works by measuring the “RC” time constant of the unknown capacitor and a known fixed resistor in series. A microcontroller charges the capacitor by applying a known voltage across the RC circuit. Simultaneously, it measures the voltage across the capacitor. The voltage rises at a certain rate which is proportional to the capacitance. The microcontroller then determines the time it
Chapter 7

7.4 Results and discussion

7.4.1 Mean sauter diameter and size distribution

The fields across the dispersion and insulation, and the free dispersion-insulation interfacial charge required in equations (7.10a)-(7.10c), (7.24), and (7.25) are obtained from the Matlab simulation output based on the electrical circuit model of the system presented in section 7.2.3. These constitute the electrical force used in hydrodynamic model. The electrical circuit model given in equation (7.12) is initially solved for a simulation time of 0.44 seconds. This residence time corresponds to a continuous phase flowrate of 96 l/hr. Later, a simulation time of 0.70 seconds is used, when a continuous phase flowrate is changed to 60 l/hr. The electrical circuit was solved based on the electrical properties of the dispersion and insulation as given in Table 7.1. In this regard, the insulation and dispersion capacitance and resistance were obtained using standard equations (7.26) and (7.27), respectively, and were used as inputs in the electrical-circuit model.

\[
C = \frac{\varepsilon_r \varepsilon_o A}{t_h} \tag{7.26}
\]

\[
R = \frac{\rho t_h}{A} \tag{7.27}
\]

In equations (7.26) and (7.27), \(\varepsilon_r\) stands for the relative permittivity (dielectric constant) of the material, \(\varepsilon_o\) the permittivity of free space, \(\rho\) the electrical resistivity of the material, \(t_h\) the thickness, and \(A\) the cross section of the material perpendicular to the field.
Table 7.1: Physical and electrical properties of the dispersion and the insulation

<table>
<thead>
<tr>
<th>Insulation properties</th>
<th>Dispersion properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant 6.5</td>
<td>Resistance 250 M</td>
</tr>
<tr>
<td>thickness 0.25 mm</td>
<td>Capacitance 10 pF</td>
</tr>
<tr>
<td>length 70 mm</td>
<td>Density continuous phase 877 kg/m³</td>
</tr>
<tr>
<td>width 10 mm</td>
<td>Viscosity continuous phase 0.635 mPa.s</td>
</tr>
<tr>
<td>Resistivity 1E14 ohm.cm</td>
<td></td>
</tr>
<tr>
<td>Material Kynar®</td>
<td></td>
</tr>
</tbody>
</table>

*The capacitance of the dispersion was directly measured as described in section 2.2.*

The voltages across the dispersion and the dispersion-insulation free interfacial charge are calculated at different frequencies of the AC field (square wave) and are given in Appendix 7.A. These are the inputs to calculate the electric field force according to equations (7.10a)-(7.10c). It is noted that both the dispersion-insulation interfacial charge and the fields across the dispersion and insulation are the same for model 1 and model 2. For model 3, the voltages across the dispersion and insulation remain unchanged. Nevertheless, the electrical force is calculated based on the polarization charge redistributed according to equation (7.25). The difference between the three models lies in what constitutes the electrical force. In the first model, only the electrophoretic force acting on the free charge is considered as given by equation (7.10a). In the second model (equation (7.10b), in addition to the electrophoretic force on the free charge, the force due to the change in the permittivity between the dispersion and insulation is included (equation (7.24)). In the third model, the electrical force is calculated based on redistributed charge (equation (7.25)), and is calculated from equation (7.10c).

As can be seen from the simulation outputs shown in Figures 7A.1 and 7A.2 (Appendix 7.A), both the dispersion-insulation interfacial charge and the voltages are dynamic (change with time). Therefore, the root mean square (rms) values of the voltage and charge are used in calculating the electrical force. With the electrical force calculated, the parameter $\beta$ in equation (7.5) was first optimized to describe the experimental Sauter diameter obtained for a DC field at a flowrate of 96 l/hr. The DC field is modeled as 1 Hz since the Simulink electrical circuit model requires frequency as an input for the source voltage. This is the right frequency to use because square wave is used and the half-cycle time corresponding to this frequency (0.5 s) is greater than the residence time (0.44 s) of the fluid in the electro-coalescer. Once the value for $\beta$ was determined for the DC field and 96 l/hr, the same value was used to predict the Sauter diameters at other frequencies of the square wave at the same flowrate. Moreover, the same $\beta$ value was used later to predict the Sauter diameters for the different frequencies at a flowrate of 60 l/hr. $\beta$
values of $1.278 \times 10^{-3}, 2.945 \times 10^{-4}, 1.578 \times 10^{-3}$ were found to describe the experimental mean sauter diameter when using equation (7.10a), (7.10b), and (7.10c) to calculate the electrical force, respectively.

Furthermore, the influence of the number of drop size classes on the predicted mean sauter diameters and distribution by the population balance model was studied. These are presented in Figures (7.4a) and (7.4b). Figure 7.4a shows that the predicted sauter diameter changes considerably when the number of classes is less than 40. However, the mean sauter diameter value was found to converge when using more than 40 classes. As shown in Figure 7.4b, a similar trend can be observed for the change of size distribution with a number of classes. Thus, the population balance model was solved using 106 classes. In addition, the population balance model was solved for drop classes between minimum and maximum sizes of 0.05 mm and 0.85 mm, respectively, when using a flowrate of 96 l/hr. The maximum diameter was readjusted to 1.15 mm at a flowrate of 60 l/hr. These minimum and maximum values were chosen in accordance with the measured experimental drop size data.

Figure 7.4: Effect of number of drop classes on predicted sauter diameter (a) and number fraction (b)

Figure 7.5 presents the predicted and experimental mean sauter diameters at different frequencies for a continuous phase flowrate of 96 l/hr and the electrical force calculated according to equation (7.10a) (model 1), equation (7.10b) (model 2), and equation (7.10c) (model 3). It can be observed that the change of the experimental mean sauter diameters with frequency was adequately predicted by the developed lossy capacitor population balance model (LCPBM). All the three models predict the experimental sauter diameter values within 10% at lower frequencies. However, the deviation increased to 20% at frequencies of 50 and 100.
Hz for model 1 when the electrical force is calculated using equation (7.10a). Additionally, it can be observed that with model 1 the sauter mean diameters keep on decreasing at higher frequencies in contrast to the experimentally observed mean sauter diameters which flattened at higher frequencies. Furthermore, for model 1, it can be observed that a larger mean sauter diameter was predicted for the DC field compared to 50 Hz and 100 Hz. These drawbacks of model 1 are remediated in models 2 and 3. All the experimental mean sauter diameters are predicted within 10% absolute relative error. Moreover, the sauter diameters start to flatten at higher frequencies. The improvement of model 2 is attributed to the fact that in addition to the electrical force due to free charge, the additional electrical force resulting from the difference in dielectric polarization of the dispersion and insulation is considered as shown in equation (7.24). Model 3 was found to give the best description of the experimental data. The model accounts for free charge transport due to fluid motion which results in the redistribution of polarization charge to maintain continuity of the displacement field.

Figure 7.6a&b show the influence of frequency on the predicted number fraction and cumulative size distribution, respectively, at a continuous phase flowrate of 96 l/hr using model 3. It can be observed from Figure 7.6a that the number fraction of large size drops is higher at lower frequencies of 3-5 Hz compared to a higher
frequency such as 25 Hz. In contrast, the proportion of small size drops decreases at lower frequencies of 3-5 Hz compared to 25 Hz. Similarly, Figure 7.6b shows that the size distribution shifts to larger size drops at lower frequencies of 3 and 5 Hz and shifts to smaller drop sizes at higher frequencies.

In Figure 7.7, the developed lossy capacitor population balance model (LCPBM) was used to predict the sauter mean diameters at various frequencies for a continuous phase flowrate of 60 l/hr. The same value of $\beta$ optimized previously for a flowrate of 96 l/hr was used. The experimentally determined size distribution without electric field at a flowrate of 60 l/hr was used as an initial condition in the population balance model. Additionally, the time of simulation (residence time in the electric field) is now increased to 0.70 seconds, which corresponds with a flowrate of 60 l/hr. Figure 7.7 clearly shows that the proposed model could also adequately predict the experimental mean sauter diameters at a flowrate of 60 l/hr and uses the same value of $\beta$ from 96 l/hr. All the sauter mean diameters are predicted within 10%. Thus, the developed model can be extrapolated for drop size prediction at various flowrates.

7.4.2 Influence of dispersion resistance and insulation thickness

This section presents a sensitivity analysis study on the effect of dispersion resistance and insulation thickness. The electrical force is calculated based on model 3 (Equation (7.10c)). This is an important factor to consider since the industrial dispersion may have components which modify its resistance. Additionally, a different insulation thickness may be required which alters its capacitance. Thus, it will be important to know how these changes affect the optimum frequency.
Chapter 7

Figure 7.6: Cumulative size distribution (a) and number fraction (b) at different frequencies of the AC field (square wave) calculated according to model 3 (equation (7.10c)) for the continuous phase flow of 96 l/hr.

Figure 7.7: Comparison of the experimental mean Sauter diameters with calculated values from the different models at different frequencies of the AC field (square wave) and at a continuous phase flowrate of 60 l/hr. The values for 96 l/hr are also depicted in the figure to show that the same value of $\beta$ was used in the model to predict all the mean Sauter diameters at a continuous phase flowrate of 60 l/hr. Model 1 is based on electrophoretic force acting on the dispersion insulation free interfacial charge (equation (7.10a)), Model 2) is based on Maxwell electrical stress obtained from Taylor-Melcher leaky dielectric model (equations (7.10b)& (7.24)), and Model 3) is based on the charge redistribution as given in equation (7.24) and the electrical force calculated according to equation (7.10c).

Figure 7.8a presents the influence of dispersion resistance on the voltage developed across the dispersion at a frequency of 5 Hz. This frequency value was chosen since it was the optimum value in the base case. The figure reveals that the time required for the voltage to decay (time constant) increases with an increase in the dispersion resistance. It can be noticed that for a more conductive (less resistance)
dispersion, less time will be required for the voltage across the dispersion to decay to zero. To get the optimum performance, a switch in polarity should be made at a frequency corresponding to the time constant of the system since this enables sufficient interfacial charge to develop. That means for larger values of dispersion resistance, a longer time will be required to make the polarity switch. This shifts the optimum frequency to lower values. In contrast, for a more conductive (less resistance) dispersion, the polarity switch should be made fast, and this shifts the optimum frequency to higher values.

The effect of dispersion resistance on the mean sauter diameters predicted by the population balance model at different frequencies is depicted in Figure 7.9a. In line with the previous argument, the maximum mean sauter diameter was obtained at a frequency of 3 Hz as the dispersion resistance was increased to 1000 $\text{M} \Omega$ from the base case of 250 $\text{M} \Omega$. On the contrary, by decreasing the dispersion resistance to 67 $\text{M} \Omega$, the maximum mean sauter diameter was found at a frequency of 25 Hz. It can be further noted from Figure 7.9a that higher frequencies will result in large mean sauter diameters for a less resistance dispersion. However, for high resistance dispersion, larger mean sauter diameters are found at lower frequencies.

To study the influence of insulation capacitance, the insulation thickness was increased. This will decrease the capacitance of the insulation. From the base case of insulation thickness 0.25 mm which corresponds to a capacitance of 167 $\text{pF}$, the insulation thickness was increased to 0.52 mm and 1.04 mm. This decreases the insulation capacitance to 80 $\text{pF}$ and 40 $\text{pF}$, respectively. The influence of insulation capacitance on the dispersion voltage is presented in Figure 7.8b. Firstly, it can be observed that the time required for the dispersion voltage to decay (time constant) of the system decreases with a decrease in the insulation capacitance. This shifts the optimum frequency to higher frequency values. Secondly, it can be noticed that a decrease in the insulation capacitance resulted in a decrease of the maximum dispersion voltage at the beginning of each of the half cycles. This is as expected since the potential at first distributes itself based on the ratio of capacitances. Therefore, the decrease in the capacitance of the insulation means a considerable portion of the potential will now also be across the insulation.

In Figure 7.9b, the effect of insulation capacitance on the mean sauter diameters is shown for various frequencies. The figure demonstrates that at all frequencies the mean sauter diameters were found to decrease at lower insulation capacitances. This indicates that for a thicker insulation, more source voltage will be required to have the same coalescence efficiency. Moreover, the optimum frequency value
shifted to a higher frequency as the insulation capacitance decreases. This is expected considering the decrease in the time constant at lower insulation capacitances as can be observed in Figure 7.8b.

Figure 7.8: Effect of dispersion resistance (a) and capacitance of insulation (b) on the dispersion voltage at a frequency of 5 Hz and a continuous phase flowrate of 96 l/hr. The voltages are calculated based on the electrical circuit model equation (7.13). These profiles of voltages across the dispersion and the insulation are calculated based on electrical circuit equation (Equation (7.13)) and holds true for all the three models

Figure 7.9: Effect of dispersion resistance (a), and capacitance of insulation (b) on predicted mean sauter diameters at different frequencies of an AC field and a continuous phase flowrate of 96 l/hr calculated according to equation model 3 (Equation 7.10c)

### 7.5 Conclusions

A combined lossy capacitor population balance model (LCPBM) was developed to predict the influence of square wave frequency on electric field coalescence (drop size and distribution) for the caprolactam-toluene-water system in a static-mixer settler setup. The charge and field in the dispersion were obtained from the lossy
dielectric model of Joos and Snaddon. These in turn are used in the coalescence kernel of the population balance model to predict the mean sauter diameters obtained experimentally. Three approaches were used to calculate the electrical force: 1) electrophoretic force acting on the dispersion-insulation free charge picked by the drops, 2) force calculated based on the Taylor-Melcher leaky dielectric model considering both the free and polarization charges, and 3) the electrical force calculated based on equal redistribution of the polarization charge. The proposed model could adequately describe the experimental mean sauter diameters at different frequencies and flowrates. The mean sauter diameters were predicted within 10% at frequencies below 25 Hz. At higher frequencies of 50 and 100 Hz, a relative error of 20% was found when using the first approach to calculate the electrical force. However, a better prediction with less than 10% relative error was found with a second and a third approach. Additionally, a sensitivity analysis was made to study the influence of dispersion resistance and insulation thickness on the optimum frequency and mean sauter diameters. Both parameters affected the optimum frequency and mean sauter diameters strongly. An increase in the dispersion resistance shifted the optimum frequency to lower frequencies and an increase in insulation thickness to higher frequencies. Additionally, smaller mean sauter diameters (less coalescence effect) were observed at all frequencies when using a thicker insulation. It is thus possible to predict the optimal operating settings when the design or the electrical properties of the dispersion and insulation change. Hence, the developed model can be used as a useful tool during scale-up and design of an electro-coalescer.
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross-sectional area of the material, m²</td>
</tr>
<tr>
<td>C_d</td>
<td>Drag coefficient, -</td>
</tr>
<tr>
<td>C_e</td>
<td>Capacitance of dispersion, pF</td>
</tr>
<tr>
<td>C_i</td>
<td>Capacitance of insulation, pF</td>
</tr>
<tr>
<td>d_i</td>
<td>Drop size of drop class i, mm</td>
</tr>
<tr>
<td>E_e</td>
<td>Electric field strength, V/m</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational acceleration, m/s²</td>
</tr>
<tr>
<td>F_d</td>
<td>Drag force, N</td>
</tr>
<tr>
<td>F_e</td>
<td>Electrical force, N</td>
</tr>
<tr>
<td>F_g</td>
<td>Gravitational force, N</td>
</tr>
<tr>
<td>F_c,ij</td>
<td>Electric field force tangent to the center of two drops (Eq. 7.1a), N</td>
</tr>
<tr>
<td>F_r,ij</td>
<td>Electric field force along the radial direction of two drops (Eq. 7.1b), N</td>
</tr>
<tr>
<td>f_s</td>
<td>Maxwell electrical stress due to dispersion and insulation, N/m²</td>
</tr>
<tr>
<td>f_se</td>
<td>Maxwell electrical stress due to dispersion, N/m²</td>
</tr>
<tr>
<td>f_si</td>
<td>Maxwell electrical stress due to insulation, N/m²</td>
</tr>
<tr>
<td>f_v</td>
<td>Electrical force per unit volume of the dielectric, equation (3)</td>
</tr>
<tr>
<td>I</td>
<td>Total current passing through the circuit, Ampere (C/s)</td>
</tr>
<tr>
<td>I_C</td>
<td>Current passing through the capacitor, Ampere (C/s)</td>
</tr>
<tr>
<td>I_R</td>
<td>Current passing through the resistor, Ampere (C/s)</td>
</tr>
<tr>
<td>J_ij</td>
<td>Coalescence (collision) rate of drops of size d_i and d_j per unit time and volume of the dispersion, 1/m³.s</td>
</tr>
<tr>
<td>m_i</td>
<td>Mass of drop class i, kg</td>
</tr>
<tr>
<td>n_i</td>
<td>Number of drops of size d_i per unit volume of dispersion, 1/m³</td>
</tr>
<tr>
<td>N_i</td>
<td>Number of drops of size d_i, -</td>
</tr>
<tr>
<td>q</td>
<td>Charge on the drop according to Cho equation (1), C</td>
</tr>
<tr>
<td>q_s</td>
<td>Charge per unit area of the insulation, C/m²</td>
</tr>
<tr>
<td>q_v</td>
<td>Free charge per unit volume of a leaky dielectric, C/m³</td>
</tr>
<tr>
<td>Q_e-i</td>
<td>Dispersion-insulation free interfacial charge, C</td>
</tr>
<tr>
<td>Q_p</td>
<td>Polarization charge, C</td>
</tr>
<tr>
<td>R_e</td>
<td>Resistance of dispersion, Ohm</td>
</tr>
<tr>
<td>R_i</td>
<td>Resistance of insulation, Ohm</td>
</tr>
<tr>
<td>R_e_p</td>
<td>Reynolds number of the drop, [-], Re_p=ρv_cd_i/μ</td>
</tr>
<tr>
<td>x_i</td>
<td>Volume at fixed class i, m³</td>
</tr>
<tr>
<td>u_j</td>
<td>Unit normal vector</td>
</tr>
<tr>
<td>V</td>
<td>Volume, m³</td>
</tr>
<tr>
<td>v_i</td>
<td>Velocity of a drop of size d_i relative to the continuous phase, m/s</td>
</tr>
<tr>
<td>V_DC</td>
<td>Potential difference supplied by a source, V</td>
</tr>
<tr>
<td>V_d</td>
<td>Potential difference across the dispersion, V</td>
</tr>
<tr>
<td>V_i</td>
<td>Potential difference across the insulation, V</td>
</tr>
<tr>
<td>t</td>
<td>Time, s</td>
</tr>
<tr>
<td>t_e</td>
<td>Thickness of dispersion, m</td>
</tr>
<tr>
<td>t_i</td>
<td>Thickness of insulation, m</td>
</tr>
</tbody>
</table>
### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_h$</td>
<td>Thickness, m</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Geometric constant in PBM</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Kronecker delta</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Permittivity of the material, C/V.m</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space (≈8.854e-12 C/V.m)</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity (dielectric constant)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Parameter described in equation (5a)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity, ohm/cm</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Density of the continuous phase, kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>Density of the dielectric material, kg/m$^3$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Volume fraction of the dispersed phase, -</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of the continuous phase, kg.m$^{-1}$.s$^{-1}$</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>An angle the electric field makes with the line connecting the center of two drops, degree</td>
</tr>
</tbody>
</table>

### Super/subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>Insulation</td>
</tr>
<tr>
<td>$j$</td>
<td>either of the dispersion or insulation</td>
</tr>
<tr>
<td>$e$</td>
<td>Dispersion</td>
</tr>
<tr>
<td>$dc$</td>
<td>Direct current</td>
</tr>
<tr>
<td>$e$-$i$</td>
<td>Dispersion-Insulation</td>
</tr>
</tbody>
</table>
Appendix 7.A: Dynamic behavior of voltage across the dispersion/insulation and dispersion insulation interfacial charge

Figure 7A.1. Effect of AC field (square wave) frequency on the voltage across dispersion at a continuous phase flowrate of 96 l/hr. The voltage applied across the positive and negative electrodes is 400 V and the DC field is modeled as 1 Hz and equation (13) is used as an electrical circuit model.
Figure 7A.2. Effect of AC field (square wave) frequency on the insulation voltage at a continuous phase flowrate of 96 l/hr. The voltage applied across the positive and negative electrodes is 400 V and the DC field is modeled as 1 Hz and equation (13) is used as an electrical circuit model.
Figure 7A.3. Effect of AC field (square wave) frequency (a) on the mean square dispersion voltage, and, (b) charge calculated based on equation (16), ■; and, charge calculated according to equation (25), ▲. The residence time is based on a continuous phase flowrate of 96 l/hr equation (13) is used as electrical circuit model.
Figure 7A.4. Effect of AC field (square wave) frequency on the dispersion-insulation interfacial charge per unit area at a continuous phase flowrate of 96 l/hr calculated from equation (16) based on an electrical circuit model given by equation (13).
Reference List


(14) Bailes, P. J. An Electrical Model for Coalescers that employ Pulsed DC Fields. Transactions of Institute of Chemical Engineers 1995, 73, 559.


Conclusions and outlook

As stated in Chapter 1, the state of the art in separation of the dispersed phase in bulk industrial extraction processes has several drawbacks, such as large size of settlers, high solvent inventory, long residence time, less product purity, product loss, decrease of process capacity, and high entrainment levels. The main objective of this thesis was to intensify the reduction of entrainment using the electric field enhanced coalescence technology. Despite the prominent use in the oil and gas industry, the application of this technology received limited attention for bulk extraction processes. In this work, the potential of this technology was evaluated for entrainment reduction in two industrial extraction processes, i.e. caprolactam-toluene-water and ethyl benzene (EB)-α-methyl benzene alcohol (MBA)-water systems. The main conclusions from these research are described in the following section.

8.1 Conclusions

Entrainment quantification to determine the influence of physical properties and process conditions

The influence of concentration, flowrate (shear rate), phase ratio, and temperature on entrainment was investigated. The results showed that all the process variables influence entrainment considerably in both studied systems. For the caprolactam-toluene-water system, the entrainment increased at higher flowrates (shear rates) and higher caprolactam concentration. For the EB-MBA-water system, the entrainment increased at higher MBA concentration and higher flowrates. An increase in flowrate resulted in more shear on the droplets whereas an increase in a caprolactam and an MBA concentration decreased the interfacial tension and increased the viscosity of the continuous organic phase, respectively. Thus, entrainment increased under these conditions. For the EB-MBA-water system, it can be concluded from the comparison of the physical solubility and droplets entrainment that the water solubility is the major part of the overall entrainment and this was mainly determined by the concentration of MBA.
The phase ratio effect on entrainment was found to be extraction system dependent. Mechanisms such as hindered settling, turbulent dampening, and enhanced coalescence at higher phase ratios could explain this difference. For the caprolactam-toluene-water system, the maximum amount of entrainment was observed at a phase ratio of 10% v/v compared to phase ratios of 5% v/v and 20% v/v. In contrast, for the EB-MBA-water system, the entrainment increased with an increase in the phase ratio from 5% v/v to 20% v/v.

The influence of temperature on entrainment was also found to be extraction system dependent. In this case, the counteracting effects of temperature on the interfacial tension and the dispersed and continuous phase viscosities were considered to determine the observed mean sauter diameters and entrainment. The drop sizes decreased and entrainment increased with an increase of temperature from 20°C to 40°C for the caprolactam-toluene-water system whilst a reverse entrainment trend with temperature was found for the EB-MBA-water system.

**Entrainment reduction by electric field enhanced coalescence**

In the next step, the electric field was integrated at the end of the static mixer pipe to reduce entrainment. It can be concluded from the obtained results that electric field enhanced coalescence is a superior means to reduce entrainment for both investigated systems. A 4-5 times reduction of entrainment was obtained by employing the electric field. The AC field was more efficient in entrainment reduction compared to the DC field. The entrainment reduction was found to be frequency dependent with lower frequencies of 3-10 Hz being the optimum for both systems. As pointed out in literature, the frequency effect was determined by the time required to have sufficient dispersion-insulation interfacial charge and the dynamic behavior of the voltage (electric field) distribution between the dispersion and the insulation with time. In this regard, the DC field was less efficient since it maintained a low field across the dispersion for a significant period in a cycle. Higher frequencies resulted in less dispersion-insulation interfacial charge and therefore in less coalescence and more entrainment.

Additionally, the entrainment reduction was influenced by the phase ratio and temperature. Higher temperatures resulted in a better entrainment reduction for the MBA-EB-water system and in less entrainment reduction for the caprolactam-toluene-water system. This was found to be in line with the drop sizes and entrainment values obtained without electric field. The influence of phase ratio on electro-coalescence was considered to be the result of its effect on the distance
between droplets which determines the dipole-dipole force and on the conductivity of the dispersion which increases with phase ratio. For the caprolactam-toluene-water system, the entrainment reduction efficiency increased up to a phase ratio of 10% v/v and decreased afterwards at phase ratio of 20% v/v. For the MBA-EB-water system, the efficiency did not change much between a phase ratio of 5% v/v and 10% v/v; however, in a similar way as for the caprolactam system, the efficiency decreased again at a phase ratio of 20% v/v.

Electric field enhanced coalescence for intensified entrainment reduction a pilot scale rotating disc contactor (RDC) column

On the basis of the demonstrated capability of the electric-field enhanced coalescence to reduce entrainment in a static mixer settler setup (Chapter 5), a technical feasibility study was performed in a pilot scale rotating disc contactor (RDC) column in particular for the caprolactam-toluene-water system. Due to droplet deposition in the electro-coalescer, there was little difference in entrainment with and without electric field. Entrainment values of 187 ppm and 62 ppm were observed downstream of the electro-coalescer without and with electric field, respectively. Therefore, although it was not possible to demonstrate the effect of electric field in a sufficiently quantitative manner in the pilot scale RDC column, there is a potential for this technology to be successful in an RDC column.

Model for frequency effect on electric field enhanced coalescence

A combined lossy capacitor population balance model (LCPBM) was developed (Chapter 7) to determine the effect of AC square wave frequency on the experimentally observed mean sauter diameters. The model was used to calculate the mean sauter diameters at various frequencies between 0-100 Hz and at two flowrates. The experimental mean sauter diameter data were adequately predicted by the model within 10%. Thus, the developed model can be used to determine the optimal frequency settling when the electrical properties of the dispersion and/or insulation change.

8.2 Outlook

It was shown that electric field enhanced coalescence is a superior means to intensify entrainment reduction. Additionally, this work investigated a way to successfully implement the technology in a pilot scale RDC column by integrating the electro-coalescer at the outlet of the continuous organic phase. Challenges were encountered due to droplets deposition on the electro-coalescer tube which decreased the difference in entrainment with and without electric field. Therefore
future research should define an operating window for the column, where there is a reasonable amount of entrainment with a flowrate that avoids droplets deposition to verify the technology at a larger scale. This could be achieved for example by using a different column internal. For example, the experimental results of Onink\(^3\) show that severe entrainment can be operational limiting regime when using a Kuhni internal column for aromatic extraction with ionic liquid.

Although the current approach of integrating the electro-coalescer at the column outlet has its own advantage, it is not possible to control the drop size inside the column and the capacity of the column. Future research can consider employing the field inside the column to increase the flooding capacity. In conjunction with this, the application of the technology for both dispersion and coalescence in extraction columns can be assessed. This entails investigating the optimal design of the electro-coalescer with respect to geometry and evaluation of the best configuration to incorporate it inside the column. Finally, for the electric field to be applied at an industrial scale, a proper assessment of safety is needed. More technology demonstration projects can be considered at a larger scale to address the technical challenges associated with scale-up and to gain more acceptance by the industry.

**Reference List**


Acknowledgements

This work would not be possible without the support of many individuals. I would like here to register my acknowledgement to some of them. First and foremost, I would like to express my sincere thanks to Prof. André de Haan my promotor. Dear André, thank you for giving me the opportunity to work in this project. Although I did not have that much practical experience when I started the project, you gave me a chance and allowed me to develop and learn through it. I owe you gratitude for your guidance, support, motivation, and for challenging me to achieve the highest possible in my work throughout the project. I would like to thank you also for the valuable suggestions and remarks in improving the quality of papers, this thesis, and conference presentations.

Special thanks to Dr. Edwin Zondervan my co-promotor and daily supervisor. Dear Edwin, thank you for all the academic and non-academic discussions we had during the project. I would like to thank you also for your suggestions and help in the development of Matlab model, as well as in the preparation of papers, this thesis, and conference presentations. Your positive attitude helped me to get going when things seemed difficult. Thank you for that.

I would like to thank members of the doctoral committee, Prof.dr.ir. A.I.Stankiewicz, Prof.dr.ir. R.M.Boom, Prof.dr.ir. M. van Sint Annaland, Dr. T.van Gerven, and Dr. M. Plantenga for their willingness to participate in my promotion and suggestions on the improvement of my thesis.

I acknowledge the Insitute for Sustainable Process Technology (ISPT) and the industrial partners DSM and Lyondell Chemie B.V. I sincerely thank Wouter Hoek, Dr. Katarina Babic and Karla Danen for providing valuable information regarding their industrial processes as well as the lively discussion during the project progress meetings.

I am greatly obliged to the technical support of Dolf Liempt, Wouter Gerritsen, and Anton Bombeck who helped in building the setup. I would like to thank Wilko Weggemans in facilitating the procurement of chemicals. My deep appreciation to Erik Wittebol from GTD for his help in incorporating electric field in the setup and his great willingness in answering my questions.

My deep gratitude to all my master students Luuk Smulders, Ab Iterson, Paul Luijcks, and Aurélien Legerand for all the energy, effort, motivation, and dedication they put on the project.
I also would like to thank my colleagues Miran, Martijn, Esteban, Juan Pablo, Jeroen, Mark, Ferdy, Miguel, Lesly, Caecilia, Ana, Agnieszka, and Marjette. I thank you all for your support and making my stay in the group enjoyable. Our group activities and the trip to south america holds special memory to me. Special thanks to Miran for being a good conference companion, and lately Martijn and Miguel for discussions during coffee and lunch breaks.

I would like to thank my family for their support and encouragement throughout my PhD. I especially thank my beloved wife, “my enate”, for her love and immense support. Thank you for being with me in the difficult and good moments of my life. Last but not least, I would like to thank all friends I met during my stay in Netherlands for their companionship and the nice time we spent together.
List of Publications

Journal Publications


Conference proceedings


Oral Presentation

1. E.W. Barega, E. Zondervan, A.B. de Haan, A combined lossy capacitor population balance model for predicting the influence of frequency on electric field enhanced coalescence, 9th European Conference of Chemical Engineering (ECCE), Den Haag, The Netherlands, 2013.


Poster Presentation

Curriculum Vitae

The Author of this thesis finished his high school education in 1999, at Black Lion secondary school at Addis Ababa, Ethiopia. He later joined and studied at the Technology Faculty of Addis Ababa University, where he graduated in July 2004 with a Bachelor of Science degree in Chemical Engineering. Starting August 2004, he worked as a graduate assistant and assistant lecturer at the Department of Chemical Engineering at Addis Ababa University for two years. In September 2006, he joined Eindhoven University of Technology in the Netherlands to pursue a Master program. In August 2008, he graduated within the Chemical Reactor Engineering group as a Master of Science in Process Engineering. His thesis written under the supervision of Dr.ir. Krzysztof Ptasinski and Dr. Ana Sues entitled “Modeling and Simulation of synthetic natural gas (SNG) production technology by direct gasification of biowaste streams”. In November 2008, he started working as a PhD Student in the Process Systems Engineering group of Prof. dr.ir. André de Haan at Eindhoven University of Technology. His work on electric field enhanced coalescence led to this thesis.