**MECHANISMS FOR THE INTERACTIONS BETWEEN
ACIDIC OILS AND SURFACTANT ENHANCED
ALKALINE SOLUTIONS**

by

Youssef Touhami

**A thesis submitted to the School of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY**

in the

**Department of Chemical Engineering
University of Ottawa
Ottawa, Canada**

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-16469-1

Canada

UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

Abstract

The reduction of interfacial tension between acidic oils and floodwater is one of the most important mechanisms of improved oil recovery. It is well known that a low transient interfacial tension is necessary for oil mobilization and that a low equilibrium interfacial tension is needed for its displacement. The predominant improved oil recovery techniques for achieving low interfacial tension are micellar and alkaline flooding. In such processes, surfactant is adsorbed at the oil-water interface and thus reduces the interfacial tension. In the micellar process, commercial surfactants are injected along with the aqueous phase, while in the alkaline process surfactants are produced in situ by a reaction between acids in the oil and the injected alkaline reagents. In the alkaline process, interfacial tension is transient in nature reflecting the formation of surfactants in situ, their accumulation at the oil/water interface and their subsequent desorption to the bulk oil and aqueous phases. All of these processes are influenced by the age of the interface. The use of an externally added surfactant to augment the activity of an in-situ produced surfactant can lead to an improvement in interfacial activity of the alkaline reagent. That is, addition of a small quantity of surfactant to the alkaline solution may cause interfacial tension to become lower than with either surfactant or alkali alone.

A precise and accurate method for monitoring and measuring both equilibrium and transient interfacial tension is required to help to develop an understanding of the mechanisms that govern the interactions of acidic oils with alkaline reagents. For this purpose, an apparatus has been set up based upon the drop shape method for the determination of surface and interfacial tension. The system, built around a commercial pendant drop instrument, incorporates computer based video image analysis. A user interface is designed and built around the core subprograms. A

filter routine using a global threshold is used along with an edge-tracing algorithm for the extraction of the drop profile. The tension is calculated using the Jennings and Pallas algorithm. The time needed to digitize a single frame and to extract the drop profile coordinates is about 0.5 s. This instrument is capable of determining the surface tension of water of 72.00 ± 0.07 mN/m. The method is suitable for measuring transient as well as dynamic interfacial tensions. Furthermore, the relaxation of surfactant adsorption layers at the oil/water interfaces can also be inferred from the data obtained.

An interfacial activity model has been proposed to predict the equilibrium interfacial tension behavior of acidic oil/surfactant enhanced alkaline systems. The model accounts for a mixed interfacial layer and mixed micelle formation by the un-ionized acid, ionized acid and added surfactant. A mass action model is adopted for the formation of micelles in conjunction with an empirical relationship for the change in the critical micelle concentration. The agreement between model predictions and experiments is satisfactory and confirms the mechanisms proposed. For the acidic oil/alkali system, it has been found that un-ionized acid adsorbs onto the interface along with ionized acid resulting in lower interfacial tension, but fails to produce ultralow values because the ionic strength is not constant as the pH varies. Also it has been found that the acid lowers the interfacial tension of the oil/added surfactant systems by simultaneously adsorbing onto the interface, and reducing the critical micelle concentration of the added surfactant.

A mechanistic interpretation of the transient interfacial tension behavior arising from the interactions between acidic oil and surfactant-alkaline systems is developed. A physico-chemical model based on Nernstian theory of convective diffusion, Langmuirian theory of interfacial sorption kinetics, and electrical interfacial phenomena has been invoked to account for the transient nature of the interfacial tension. The results show that the interfacial tension arising from the interaction of these chemical combinations with model acidic oil exhibits a marked transient behavior. The magnitude of interfacial tension variations changes not only with alkali concentration but also with surfactant concentration. The pertinent sorptive rate constants that characterize transient behavior are precisely estimated by correlating experimental

interfacial tension data with the proposed model. A very good overall agreement is obtained between the experimental values and those predicted by the model.

A better model of the interactions between acidic oil and alkaline solutions has been developed. The improvement is mainly related to an enhanced measurement technique, modification of the adsorption isotherms as well as the kinetic equations. These changes allow for the co-adsorption of the un-ionized acid along with the ionized acid at the interface. The extension of the acidic oil/alkaline model to incorporate an additional pre-formed surfactant is also accomplished by a modification of the adsorption isotherms, of the micellar relationship and of the resulting equilibria.

Acknowledgments

I would like to express my sincere gratitude to my supervisors, Dr. V. Hornof and Dr. G.H. Neale, for their generous financial support, their expert guidance and their patient prodding throughout the course of this work.

Mr. Habib Khalfallah of the Department of Electrical Engineering, University of Ottawa is deserving of special thanks for his help in setting up the digitization system and the TRACER program. I would like to thank Dr. N.R. Pallas of BP Research, Cleveland, Ohio, for his useful help concerning the drop shape analysis. I am grateful to the Government of the Republic of Tunisia for providing me with a graduate scholarship.

Finally I wish to thank my wife Lamia and our two daughters, Ikram and Serine, for their invaluable support and encouragement throughout the program.

Claims to Original Research

Claims to Original Research

This thesis contains both experimental and theoretical studies on the interfacial behavior of acidic oil/surfactant-enhanced alkaline systems. During these studies model oil has been used. Following is a brief summary of the claims to original research.

1- Development of a new instrument:

The classic pendant drop tensiometer has been automated for precise and accurate measurement of surface and interfacial tensions. The modified instrument is capable of accurately measuring tensions in the range from 0.2 mN/m to 72 mN/m. The instrument is suitable for monitoring transient interfacial tension, dynamic interfacial tension as well as relaxation phenomena at oil/water interface.

2- Acquisition of new experimental data:

Experimental equilibrium and transient interfacial tension data have been measured for acidified oil/surfactant-enhanced alkaline systems. It has been found that an optimum concentration exists, with respect to both alkali and added surfactant, at which the interfacial tension is the lowest. The optimum concentration has been found to be dependent on acid concentration. The effects of micellization on transient interfacial tension behavior have been investigated and discussed.

3- Development of new interfacial activity models:

Equilibrium and transient interfacial activity models for the interactions between acidified oil and surfactant-enhanced alkaline systems have been formulated theoretically. An approach based on the concept of a mixed interfacial layer has been used in conjunction with the extended Langmuir adsorption isotherm to account for simultaneous adsorption of un-ionized acid, ionized acid and added surfactant. Furthermore, mixed micelle formation involving these three components has been taken into account using regular solution theory.

4- Validation of the interfacial activity models:

It has been found that the lowering of the interfacial tension of the acidic oil/caustic systems is a result of the simultaneous adsorption of un-ionized and ionized acid at the interface. It has also been found that the lowering of interfacial tension of the acidified oil/surfactant-enhanced alkaline systems is a result of the simultaneous adsorption of un-ionized acid, ionized acid, and added surfactant at the interface. The un-ionized and ionized acids have been found to reduce the critical micelle concentration of the added surfactant and the interrelationship of their effects has been expressed quantitatively.

Publications and Presentations

The work presented in this thesis has been published, or is in the process of being published as described below:

Full Refereed Journal Papers:

- 1- Touhami, Y., Hornof, V., and Neale, G.H.: *Interfacial Tension Behavior of an Acidified Oil/Surfactant System*, Journal of Colloid and Interface Science, **166**, 506 (1994).
- 2- Touhami, Y., Hornof, V., and Neale, G.H.: *Mechanisms for the interactions between acidic oils and surfactant enhanced alkaline solutions*, Journal of Colloid and Interface Science, **177**, 446 (1995).
- 3- Mollet, C., Touhami, Y., and Hornof, V.: *A comparative study of the effect of ready-made and in-situ formed surfactant on interfacial tension measured by drop volume tensiometry*, Journal of Colloid and Interface Science, **178**, 523 (1996).
- 4- Mollet, C., Touhami, Y., and Hornof, V.: *Influence du dodecyl sulfate de sodium sur la tension interfaciale du système biphasé butanol-eau*, Canadian Journal of Chemical Engineering, **74**, (April 1996).
- 5- Touhami, Y., Hornof, V., and Neale, G.H.: *A modified pendant drop method for interfacial tension measurement*, Colloids and Surfaces A-Physicochemical and Engineering Aspects, **112**(1), 31 (1996).
- 6- Touhami, Y., Hornof, V., and Neale, G.H.: *Transient Interfacial Tension in Acidic Oil/Surfactant Enhanced Alkaline Systems, Part 1: Experimental Studies*, in preparation.
- 7- Touhami, Y., Hornof, V., and Neale, G.H.: *Transient Interfacial Tension in Acidic Oil/Surfactant Enhanced Alkaline Systems, Part 2: Theoretical Studies*, in preparation.

Conference Presentations:

- 1- Touhami, Y.: *Tension interfaciale dynamique entre les huiles lourdes et les solutions alcalines*, ACFAS Conference, Sherbrooke, Quebec, May 21-24, 1991.
- 2- Touhami, Y., Hornof, V. and Neale, G.H.: *Surfactant enhanced alkaline process: Mechanisms of the acidic oil-alkaline interactions*, 42nd Canadian Chemical Engineering Conference, Toronto, Ontario, October 18-21, 1992.
- 3- Hornof, V., Mollet, C., and Touhami, Y.: *Effect of ready-made and in situ-formed surfactant on oil/water interfacial tension measured by drop volume tensiometry*, 79th Canadian Society for Chemistry Conference and Exhibition, St. John's, Newfoundland, June 23-26, 1996.
- 4- Touhami, Y., Hornof, V. and Neale, G.H.: *Adsorption of binary surfactant at the oil/water interface*, 46th Canadian Chemical Engineering Conference, Kingston, Ontario, September 29-October 2, 1996.

Contents

Abstract	i
Acknowledgments	iv
Claims to Original Research	v
Table of Contents	ix
List of Tables	xv
List of Figures	xvi
Nomenclature	xxv
1 Introduction	1
1.1 Motivation	1
1.2 Objectives of this Study	3
I Literature Survey	5
2 Enhanced Oil Recovery Practice	6
2.1 Oil Recovery Processes	6
2.2 Alkaline Oil Recovery	7

CONTENTS	x
2.2.1 Mechanisms of Alkaline Oil Recovery	7
2.2.2 Interfacial Tension Reduction	8
2.2.3 Wettability Reversal	9
2.2.4 Emulsion Formation	10
2.3 Oil Chemistry	11
3 Mechanisms for Acidic Oil/Alkaline Interactions	13
3.1 Interfacial Tension Phenomena	13
3.2 Models of Acidic Oils/Alkaline Interactions	15
3.2.1 Equilibrium Considerations	15
3.2.2 Non-equilibrium Considerations	18
3.3 Surfactant-Enhanced Alkaline Systems	20
II Experimental Aspects	22
4 Design of the Automated Pendant Drop	23
4.1 Introduction	23
4.2 Automated Pendant Drop Tensiometry	27
4.2.1 Experimental Set-up	27
4.2.2 Temperature Control	31
4.2.3 Density, Viscosity and pH Measurements	31
4.3 Drop Shape Analysis	33
4.3.1 Image Segmentation by Thresholding	33
4.3.2 Edge Detection by Contour Tracing	34
4.4 Determination of Interfacial Tension from Drop Profiles	38
4.4.1 Description of the Drop Profile	38
4.4.2 Determination of the Interfacial Tension	41
4.5 Other Methods for Interfacial Tension Measurement	49
4.5.1 Spinning Drop Tensiometer	49
4.5.2 Drop Volume Tensiometer	51
5 Experimental Procedures	52

CONTENTS

xi

5.1	Experimental Design	52
5.1.1	Materials	52
5.1.2	Experimental Strategies	53
5.2	Computer Program for Instrument Control	54
5.3	Calibration of the Pendant Drop Apparatus	54
5.3.1	Instrument Parameters	54
5.3.2	Surface and Interfacial Tension Results	59
5.3.3	Features of the Modified Pendant Drop Tensiometer	62
III	Models for Acidic Oil/Alkaline Interactions	69
6	Development of the Equilibrium Model	70
6.1	Model Formulation	70
6.2	Interfacial Reactions and Equilibria	71
6.3	Model Equations	75
6.3.1	Relating Anion Concentrations to the Equilibrium Parameters	75
6.3.2	Micellar Relationships	77
6.3.3	Relating Anion Concentration to Interfacial Tension	78
6.4	Solution of the Equilibrium Model Equations	81
6.4.1	Specification of the Model Parameters	81
6.4.2	Model Constant Evaluation	81
6.4.3	Solution Methodology	82
7	Development of the Transient Model	84
7.1	Model Formulation	84
7.2	Interfacial Reactions and Related Equilibria	88
7.3	Sorption Kinetic Rate Equations	88
7.4	Species Bulk Transport	90
7.5	Differential Equations of the Transient Model	91
8	Solution of the Transient Model Equations	94
8.1	Specification of the Model Parameters	94

8.1.1	Calculation of the Equilibrium Sorptive Constants	95
8.1.2	Calculation of the Boundary Layer Thicknesses	96
8.1.3	Calculation of the Diffusion Coefficients	97
8.2	Solution Methodology	98
8.2.1	Diffusion Kinetics of the Acidified Oil/Water System	99
8.2.2	Diffusion Kinetics of the Acidified Oil/Caustic System	100
8.2.3	Diffusion Kinetics of the Oil/Surfactant System	101
8.2.4	Diffusion Kinetics of the Acidified Oil/Surfactant System	102
IV	Results and Discussion	103
9	Equilibrium Model Analysis	104
9.1	Acidified Oil/Alkaline Systems	105
9.2	Acidified Oil/Surfactant Systems	111
9.3	Acidified Oil / Surfactant and Alkaline Systems	121
10	Transient Model Analysis: Data	125
10.1	Generality	125
10.2	Interfacial Tension Data for Acidified Oil / Alkaline Systems	126
10.2.1	Acidified Oil/Water Systems	126
10.2.2	Acidified Oil/Alkaline Systems	132
10.2.3	Interfacial Tension Data Measured by the Drop Volume and Spinning Drop Tensiometers	146
10.3	Interfacial Tension Data for Acidified Oil / Surfactant Systems	152
10.4	Interfacial Tension Data for Acidified Oil / Caustic and Surfactant Systems	161
10.4.1	Effects of Added Surfactant Concentration	163
10.4.2	Effects of Caustic Concentration	174
11	Transient Model Analysis: Predictions	181
11.1	Evaluation of the Model Constants	181
11.1.1	Sorptive Equilibrium Constants	181

CONTENTS

xiii

11.1.2	Diffusion Coefficients	184
11.1.3	Boundary Layer Thicknesses	186
11.2	Estimates of the Kinetic Rate Parameters	187
11.2.1	Kinetic Rate Constants of Linoleic Acid	187
11.2.2	Kinetic Rate Constant of Sodium Dodecyl Sulfate	196
11.3	Model Predictions	201
11.3.1	Model Predictions for the Acidified Oil/Sodium Dodecyl Sulfate System	201
11.3.2	Model Predictions for the Acidified Oil/Sodium Dodecyl Sulfate and Caustic Mixture Systems	205
12	Conclusions and Recommendations	212
12.1	Conclusions	212
12.2	Recommendations	215
	Bibliography	216
V	Appendices	227
A	Micellar Relationships	228
A.1	Expression for the Micellization Constant	228
A.2	Critical Micellar Concentration Relationships	230
B	Fractional Surface Coverage	232
C	Physical Properties of Solutions	235
C.1	Properties of Aqueous Solutions	235
C.2	Properties of Oil Solutions	237
D	Transient Interfacial Tension Data	238
D.1	0.1 mol/m ³ Acidified Oil / Surfactant- Alkaline Systems	238
D.1.1	Effects of Added Surfactant Concentration	238

CONTENTS

xiv

D.1.2 Effects of Caustic Concentration	243
--	-----

List of Tables

5.1	Results for the surface tension of pure water at 25 °C	60
5.2	Averaged results for the surface tension of pure water at 25 °C	61
5.3	Interfacial tension of hydrocarbons against pure water at 25 °C and per cent deviation from reported literature values [71,72,110].	61
9.1	Adsorption parameters for un-ionized acid.	110
9.2	Adsorption parameters for ionized acid.	110
9.3	Adsorption and micellization parameters for sodium dodecyl sulfate.	120
9.4	Effects of acid concentration on adsorption and micellization parameters for sodium dodecyl sulfate.	120
9.5	Effects of NaOH concentration on adsorption and micellization parameters for sodium dodecyl sulfate.	120
11.1	Sorptive equilibrium constants of un-ionized and ionized acid at different initial acid concentrations.	183
11.2	Sorptive equilibrium constant of sodium dodecyl sulfate at the oil/water interface.	184
11.3	Diffusion coefficients of the solutes	185
11.4	Kinetic rate constants of un-ionized acid.	191
11.5	Kinetic rate constants of ionized acid.	191
11.6	Kinetic rate constants of sodium dodecyl sulfate	197
C.1	Densities of the caustic/sodium dodecyl sulfate solutions at 25°C (g/cm ³)	236
C.2	pH of the caustic/sodium dodecyl sulfate solutions at 25°C	236
C.3	Physical Properties of Oleic Solutions at 25° C	237

List of Figures

4.1	Schematic diagram of the pendant drop tensiometer and the video image digitization system.	29
4.2	Details of the cell	30
4.3	Gray level histogram.	34
4.4	Chain codes.	36
4.5	Flowchart for the TRACER edge detection.	37
4.6	Representation of the drop profile coordinate system	40
4.7	Illustration of the computation of residuals.	44
5.1	Calibration plot.	57
5.2	(a) Typical experimental versus calculated drop profile and (b) the corresponding residual plot.	58
5.3	Surface tension of pure water versus time at 25°C.	60
5.4	Transient interfacial tension for acidified paraffin oil (1 mol/m ³) against sodium dodecyl sulfate solution (7 mol/m ³).	64
5.5	Transient interfacial tension for acidified paraffin oil (1 mol/m ³) against sodium dodecyl sulfate (2 mol/m ³) and NaOH (2.5 mol/m ³) solution.	64
5.6	Transient interfacial tension for acidified paraffin oil (10 mol/m ³) against NaOH (25 mol/m ³) solution.	65
5.7	Dynamic experiment: volume, surface area and interfacial tension change as functions of time for a drop of paraffin oil expanding in sodium dodecyl sulfate solution (7 mol/m ³).	67

5.8	Transient relaxation experiment: Volume, surface area and interfacial tension change as functions of time for a drop of paraffin oil expanding in sodium dodecyl sulfate solution (7 mol/m^3).	68
6.1	Schematic of the acidic oil/alkali interactions	72
7.1	Geometrical model of the interface: transient model	87
9.1	Experimental and predicted interfacial tension of acidified paraffin oil against distilled water.	108
9.2	Residual plot.	108
9.3	Experimental and predicted interfacial tension of acidified oil/caustic solutions at different acid concentrations.	109
9.4	Residual plot.	109
9.5	Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system.	114
9.6	Residual plot.	114
9.7	Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for decane/water system.	115
9.8	Residual plot.	115
9.9	Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system at different acid concentrations.	116
9.10	Residual plot.	116
9.11	Effect of acid concentration in the aqueous phase on the normalized critical micelle concentration of sodium dodecyl sulfate.	117
9.12	Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system at different NaOH concentrations.	118
9.13	Residual plot.	118
9.14	Effect of NaOH concentration on the critical micelle concentration of sodium dodecyl sulfate.	119

9.15	Effect of NaOH concentration on interfacial tension for 0.1 mol/m ³ acid concentration at different sodium dodecyl sulfate concentrations.	123
9.16	Effect of NaOH concentration on interfacial tension for 1.0 mol/m ³ acid concentration at different sodium dodecyl sulfate concentrations.	124
10.1	Transient interfacial tension behavior of paraffin oil against water. . .	127
10.2	Equilibrium interfacial tension of paraffin oil against aqueous NaOH solutions.	127
10.3	Transient interfacial tension behavior of paraffin oil acidified with 0.1 mol/m ³ linoleic acid against water.	129
10.4	Transient interfacial tension behavior of paraffin oil acidified with 1 mol/m ³ linoleic acid against water.	129
10.5	Transient interfacial tension behavior of paraffin oil acidified with 10 mol/m ³ linoleic acid against water.	130
10.6	Transient interfacial tension behavior of paraffin oil acidified with 100 mol/m ³ linoleic acid against water.	130
10.7	Transient interfacial tension behavior of acidified paraffin oil against water at different acid concentrations.	131
10.8	Comparison between transient interfacial tension of acidified paraffin oil against water obtained by the pendant drop (●,■) and the drop volume (○,□) tensiometer.	131
10.9	Transient interfacial tension behavior of 0.1 mol/m ³ acid	136
10.10	Transient interfacial tension behavior of 0.1 mol/m ³ acid in paraffin oil against 2.5 mol/m ³ NaOH solution.	136
10.11	Transient interfacial tension behavior of 0.1 mol/m ³ acid in paraffin oil against 12.5 mol/m ³ NaOH solution.	137
10.12	Transient interfacial tension behavior of 0.1 mol/m ³ acid in paraffin oil against 25 mol/m ³ NaOH solution.	137
10.13	Transient interfacial tension behavior of 0.1 mol/m ³ acid in paraffin oil against 125 mol/m ³ NaOH solution.	138

10.14	Transient interfacial tension behavior of 0.1 mol/m ³ acid in paraffin oil against 250 mol/m ³ NaOH solution.	138
10.15	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 0.25 mol/m ³ NaOH solution.	139
10.16	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 1.25 mol/m ³ NaOH solution.	139
10.17	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 2.5 mol/m ³ NaOH solution.	140
10.18	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 5 mol/m ³ NaOH solution.	140
10.19	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 12.5 mol/m ³ NaOH solution.	141
10.20	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 25 mol/m ³ NaOH solution.	141
10.21	Transient interfacial tension behavior of 1 mol/m ³ acid in paraffin oil against 125 mol/m ³ NaOH solution.	142
10.22	Transient interfacial tension behavior of 10 mol/m ³ acid in paraffin oil against 0.25 mol/m ³ NaOH solution.	143
10.23	Transient interfacial tension behavior of 10 mol/m ³ acid in paraffin oil against 1.25 mol/m ³ NaOH solution.	143
10.24	Transient interfacial tension behavior of 10 mol/m ³ acid in paraffin oil against 2.5 mol/m ³ NaOH solution.	144
10.25	Transient interfacial tension behavior of 10 mol/m ³ acid in paraffin oil against 12.5 mol/m ³ NaOH solution.	144
10.26	Transient interfacial tension behavior of 10 mol/m ³ acid in paraffin oil against 25 mol/m ³ NaOH solution.	145
10.27	Dynamic interfacial tension behavior of acidified paraffin oil against aqueous NaOH solutions as measured by the drop volume tensiometer. Acid concentration: (a): 0.1, (b): 1.0 and (c): 10 mol/m ³	149

10.28	Comparison between transient interfacial tension of acidified paraffin oil against caustic solutions obtained by the pendant drop (●, ■, ♦) and the drop volume (○, □, ◇) tensiometer. (a) 0.1 mol/m ³ acid / 12.5 mol/m ³ NaOH, (b) 1 mol/m ³ acid / 2.5 mol/m ³ NaOH, and (c) 10 mol/m ³ acid / 1.25 mol/m ³ NaOH.	150
10.29	Comparison between transient interfacial tension of acidified paraffin oil against caustic solutions obtained by the spinning drop (●), the pendant drop (■), and the drop volume (♦) tensiometer. (a) 1 mol/m ³ acid / 25 mol/m ³ NaOH and (b) 10 mol/m ³ acid / 25 mol/m ³ NaOH.	151
10.30	Transient interfacial tension behavior of paraffin oil against sodium dodecyl sulfate solutions.	155
10.31	Transient interfacial tension behavior of 0.1 mol/m ³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.	156
10.32	Transient interfacial tension behavior of 1 mol/m ³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.	157
10.33	Transient interfacial tension behavior of 10 mol/m ³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.	158
10.34	Transient interfacial tension behavior of 100 mol/m ³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.	159
10.35	Effect of linoleic acid concentrations on transient interfacial tension behavior of paraffin oil against 6 mol/m ³ sodium dodecyl sulfate solution.	160
10.36	Effect of linoleic acid concentrations on transient interfacial tension behavior of paraffin oil against 7 mol/m ³ sodium dodecyl sulfate solution.	160
10.37	Phase diagram for micellization.	162
10.38	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 1 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	167
10.39	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 2 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	168
10.40	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 3 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	169

10.41	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 4 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	170
10.42	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 5 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	171
10.43	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 6 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	172
10.44	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against 7 mol/m ³ sodium dodecyl sulfate and NaOH solutions.	173
10.45	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 0.25 mol/m ³ NaOH solution.	175
10.46	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 1.25 mol/m ³ NaOH solution.	176
10.47	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 2.5 mol/m ³ NaOH solution.	177
10.48	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 12.5 mol/m ³ NaOH solution.	178
10.49	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 25 mol/m ³ NaOH solution.	179
10.50	Transient interfacial tension behavior for 1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 125 mol/m ³ NaOH solution.	180
11.1	Experimental and predicted transient interfacial tension of acidified paraffin oil against distilled water. (a) 1 mol/m ³ and (b) 10 mol/m ³ .	192
11.2	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 0.25 mol/m ³ NaOH solution.	193
11.3	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 1.25 mol/m ³ NaOH solution.	193
11.4	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 2.5 mol/m ³ NaOH solution.	194
11.5	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 5.0 mol/m ³ NaOH solution.	194

11.6	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 12.5 mol/m ³ NaOH solution.	195
11.7	Experimental and predicted transient interfacial tension of 1 mol/m ³ acidified paraffin oil against 25 mol/m ³ NaOH solution.	195
11.8	Experimental and predicted transient interfacial tension of paraffin oil against 1 mol/m ³ sodium dodecyl sulfate solution.	198
11.9	Experimental and predicted transient interfacial tension of paraffin oil against 4 mol/m ³ sodium dodecyl sulfate solution.	198
11.10	Experimental and predicted transient interfacial tension of paraffin oil against 5 mol/m ³ sodium dodecyl sulfate solution.	199
11.11	Experimental and predicted transient interfacial tension of paraffin oil against 6 mol/m ³ sodium dodecyl sulfate solution.	199
11.12	Experimental and predicted transient interfacial tension of paraffin oil against 7 mol/m ³ sodium dodecyl sulfate solution.	200
11.13	Experimental and predicted transient interfacial tension of paraffin oil against 8 mol/m ³ sodium dodecyl sulfate solution.	200
11.14	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 1 mol/m ³ sodium dodecyl sulfate solution.	202
11.15	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 3 mol/m ³ sodium dodecyl sulfate solution.	202
11.16	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 4 mol/m ³ sodium dodecyl sulfate solution.	203
11.17	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 5 mol/m ³ sodium dodecyl sulfate solution.	203
11.18	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 6 mol/m ³ sodium dodecyl sulfate solution.	204

11.19	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 7 mol/m ³ sodium dodecyl sulfate solution.	204
11.20	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 1 mol/m ³ sodium dodecyl sulfate and (a) 1.25 mol/m ³ (b) 2.5 mol/m ³ NaOH solutions.	207
11.21	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 2 mol/m ³ sodium dodecyl sulfate and (a) 0.25 mol/m ³ , (b) 1.25 mol/m ³ and (c) 2.5 NaOH solutions. .	208
11.22	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 3 mol/m ³ sodium dodecyl sulfate and (a) 0.25 mol/m ³ , (b) 1.25 mol/m ³ and (c) 2.5 NaOH solutions. .	209
11.23	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 4 mol/m ³ sodium dodecyl sulfate and (a) 0.25 mol/m ³ and (b) 2.5 mol/m ³ NaOH solutions.	210
11.24	Experimental and predicted transient interfacial tension behavior of 1 mol/m ³ acidified paraffin oil against 5 mol/m ³ sodium dodecyl sulfate and (a) 0.25 mol/m ³ and (b) 1.25 mol/m ³ NaOH solutions.	211
D.1	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against 1 mol/m ³ sodium dodecyl sulfate and NaOH solutions. . .	239
D.2	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against 4 mol/m ³ sodium dodecyl sulfate and NaOH solutions. . .	240
D.3	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against 5 mol/m ³ sodium dodecyl sulfate and NaOH solutions. . .	241
D.4	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against 7 mol/m ³ sodium dodecyl sulfate and NaOH solutions. . .	242
D.5	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 0.25 mol/m ³ NaOH solution. .	244
D.6	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 1.25 mol/m ³ NaOH solution. .	245

D.7	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 2.5 mol/m ³ NaOH solution. . .	246
D.8	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 12.5 mol/m ³ NaOH solution. .	247
D.9	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 25 mol/m ³ NaOH solution. . .	248
D.10	Transient interfacial tension behavior for 0.1 mol/m ³ acid in paraffin oil against sodium dodecyl sulfate and 125 mol/m ³ NaOH solution. .	249

Nomenclature

Symbols

a	aspect ratio, (M_x/M_z)
A	surface area per molecule, $\text{\AA}^2$
A_0	minimum surface area per molecule, $\text{\AA}^2$
A_p	numerical aperture
A_s	surface area, m^2
B_1	rate constant for adsorption, m/s
B_2	rate constant for desorption, $1/\text{s}$
C_i	molar concentration, mol/m^3
CMC, CMC'	critical micelle concentration, mol/m^3
d	resolution of digitization, m
d_c	capillary diameter, m
D_c	dielectric constant of water
D_i	diffusion coefficients, m^2/s
$F_{1-\varphi}$	F test statistic for a confidence interval of $1 - \varphi$
$F_m(\epsilon)$	premicellization constant (Eq. 6.28)
g	gravitational acceleration (9.80662 m/s^2)
k	Boltzman constant ($1.38 \times 10^{-6} \text{ erg/}^\circ\text{C}$)
k_a	rate constant for adsorption, m/s
k_d	rate constant for desorption, $1/\text{s}$
k_i	sorptive rate constants, $\text{m}^3/\text{mol.s}$
$K_{D,X}$	salt distribution coefficient
K_d	dimerization constant, m^3/mol

$K_i, K_{L,i}$	sorptive equilibrium constants, m^3/mol
K'_{NaX}	salt equilibrium constants, mol/m^3
$K_{o,HX}$	acid partition coefficient defined by Eq. A.21
$K_{o,X}$	ionized acid partition coefficient defined by Eq. A.22
K_{HX}^D	acid ionization constant, mol/m^3
K_{NaX}^D, K_{NaS}^D	salt equilibrium dissociation constants, mol/m^3
K_m	micellization equilibrium constant
K_p	acid distribution ratio oil/water
K_w	ionic product of water, mol^2/m^6
m'	number of carbon atoms in the acid
M_i	molecular weight
M_c	concentration of charges in the micelle
M_{Na}	concentration of Na bound to the micelle
M_S	concentration of micelle
M_x	X magnification, pixel/m
M_z	Z magnification, pixel/m
n	aggregation number
N	Avogadro number (6.02×10^{23})
N_{Ca}	capillary number
ΔP	pressure difference across the interface, N/m^2
Q	objective function
r_i	residual, m
R	gas constant ($1.986 \text{ cal}/\text{mol} \cdot ^\circ\text{C}$ or $8.314 \times 10^7 \text{ erg}/\text{mol} \cdot ^\circ\text{C}$)
R_d	radius of the spinning drop, m
R_o	radius of curvature at the origin, m
R_1, R_2	radii of curvature, m
$R_{(a,i)}$	net rate of adsorption/desorption of species i , $\text{mol}/\text{m}^2 \cdot \text{s}$
s	dimensionless arc length
S	arc length, pointer in the tracer algorithm
SSR	sum of squares of the residuals
t	time, s

T	temperature, °K
$\mathbf{T}$	$n \times n$ orthogonal matrix
$\mathbf{U}$	vector defined by Eq. 4.14
v	Darcy velocity, m/s
V_A	molar volume of solute m^3/mol
V_c	critical volume, m^3
V_i	phase volume, m^3
$\mathbf{V}$	transformed $\mathbf{U}$ matrix
V_d	volume of the droplet, m^3
w_i	free energy per methylene group, cal/mol
W_i	total energy of desorption per mole, cal/mol
x	mole fraction of un-ionized acid in the mixed micelle
y	mole fraction of ionized acid in the mixed micelle
(x, z)	dimensionless drop profile coordinates
(X, Z)	drop profile coordinates, m
(X_0, Z_0)	apex coordinates, m
z_i	ionic valency

Subscripts

ads	adsorbed
cal	calculated
e	electrolyte
exp	experimental
HA, HX	acid species
m	micellar, mixture
max	maximum
NaX, NaS	inactive soap species or salts
S^-	added surfactant
X^-	in-situ generated surfactant
i	phase identity

j	number of phases
o	oil phase
obs	observed coordinates
s	sublayer
w	aqueous phase, water

Greek letters

α	association parameter defined by Eq. 7.17
α	fraction of unbound sites on the micelles
α	U parameter ($=1/\gamma$)
β	drop shape
δ_i	Nernstian film thickness, m
e	electronic charge (4.774×10^{-10} e.s.u.)
$\epsilon_D, \epsilon_Q, \epsilon_R, \epsilon_V$	convergence criteria for JP optimization algorithm
γ	interfacial tension, mN/m
γ_0	initial interfacial tension, mN/m
Γ	overall surface concentration, mol/m ²
Γ_i	surface concentration of adsorbed species, mol/m ²
$\Gamma_{i,max}$	saturation adsorption, mol/m ²
λ	wavelength of the illumination light, m
ν	kinematic viscosity, cS
μ	viscosity, mPa.s
ω_d	association parameter in the Wilke-Chang correlation
ω_i	constant scale factors
Ω	speed of rotation, rpm
∂	partial derivative
ϕ	turning angle, degrees
φ	confidence limit
π	mathematic constant, 3.1415927...
Π	surface pressure, mN/m

ψ_G	Gouy-Chapman interfacial potential, mV
ψ_o, ψ'_o	interfacial potential, mV
ρ	density, g/cm ³
σ	surface charge density, standard deviation
σ_r	variance of the residuals at the minimum
θ	total fractional surface coverage
θ_i	fractional surface coverage for adsorbed specie <i>i</i>
Θ	contact angle, <i>degrees</i>
ϵ	fraction of the surfactant in the micelle form

Chapter 1

Introduction

1.1 Motivation

The study of the properties of liquid-fluid interfaces has far reaching practical implications in many areas of modern science and technology. Engineering applications of surface science range from the study of interfacial interaction in biological cell membranes to crude oil recovery and include areas such as catalysis, coating, dispersion, flotation of minerals, lubrication, as well as biomedical and pharmaceutical applications. Interfacial tension is the single most accessible experimental parameter that describes the thermodynamic state and structure of an interface.

The principal field of interest in this laboratory is improved oil recovery. The mechanism of improved oil recovery depends to a great extent on the properties of the crude oil/water/rock interfaces. Understanding the physics of these interfaces including capillary forces, contact angle, wettability, viscous forces and interfacial tension is a necessary prerequisite towards understanding the mobilization of the oil trapped in a porous rock and improving the oil recovery. The above variables can be combined in a dimensionless parameter called the capillary number, N_{Ca} , defined by:

$$N_{Ca} = \frac{\mu v}{\gamma \cos \Theta} \quad (1.1)$$

where μ is the aqueous phase viscosity, v is the Darcy velocity, Θ is the contact angle and γ is the oil-water interfacial tension. In oil recovery processes, capillary forces cause large quantities of oil to be left behind in well-swept zones of water flooded oil reservoirs. Capillary forces are the consequence of interfacial tension between the oil and aqueous phase and they resist externally applied viscous forces. Lowering of the interfacial tension helps recover additional oil by reducing these capillary forces. Several processes based on this principle have been designed, the most important ones being micellar [1] and alkaline [2] flooding. In both processes, surfactants are adsorbed at the oil/water interface and thus reduce the interfacial tension. In the micellar process, ready-made surfactants are injected with the aqueous phase, while in the alkaline process, surfactants are produced in-situ by the reaction between the naturally occurring acidic components in the oil and the alkaline reagents. In order to achieve a significant oil recovery, ultra-low to low interfacial tension (10^{-2} -1 mN/m) is required [3-5].

Transient (i.e. time dependent) interfacial tension has been observed repeatedly in crude oil/alkaline systems [3,5-9]. In some cases interfacial tension increased dramatically as the oil/water interface aged. This was attributed to the migration of soap products away from the interface after their initial formation. The effect of transient interfacial tension behavior on oil recovery is of great significance. The interest in transient interfacial tension in such systems has resulted in several attempts to model this behavior, either physically or chemically [10-21]. Despite successful laboratory tests, field performance of alkaline flooding technology has often failed badly owing to unfavorable mobility ratio, excessive alkali consumption and a failure to reduce interfacial tension in the actual reservoir. The use of a synthetic surfactant

to augment the effect of the in-situ produced surfactant gave an improvement in the interfacial activity of the alkaline reagents in the reservoir. Surfactant-enhanced alkaline augmented polymer flooding has now become the state-of-the-art methodology in chemical flooding [22-26]. Recent laboratory studies have shown that the interfacial tension arising from the interaction of these chemical combinations with acidic oil displayed a marked transient behavior [19,27-32]. The magnitude of this transient interfacial tension was found to vary with the nature and origin of the oil, alkali concentration and salinity, and also with the surfactant concentration. Therefore, in order to facilitate the design of effective surfactant-alkaline-polymer systems, more fundamental and applied research must be carried out in order to elucidate further the phenomena of transient interfacial tension.

A major drawback in the study of thermodynamic interfacial properties has been the experimental difficulties associated with measurement of the dependence of interfacial tension on time. Recent advances in video image acquisition and processing and the availability of microcomputers have created the possibility of fast and accurate measurements. The major advantage of the image processing technique is the feasibility of routine automation of absolute interfacial tension measurements and the study of transient interfacial effects.

1.2 Objectives of this Study

The principal objective of this investigation is to seek a fundamental understanding of the mechanisms that govern the interaction of acidified oil with surfactant-enhanced alkaline reagents at the oil-water interface, and the attendant transient interfacial tension phenomena. The work consists of the following main components:

- (i) Improvement of the micropendographic measurement system using a computer based video image analysis,
- (ii) Development of a chemical equilibrium model for acidified oil in contact with surfactant-enhanced alkaline solutions,
- (iii) Development of a mechanistic model which accounts quantitatively for the transient interfacial tension behavior in systems comprising acidified oil in contact with surfactant-enhanced alkaline solutions.

In part I of the thesis, current theories and models of acidic oil/alkaline interactions are summarized. In Part II, the design of the automated pendant drop tensiometer and its further applications are discussed in detail. Part III deals with the proposed equilibrium and transient models for the mechanisms for the interactions between acidic oils and surfactant-enhanced alkaline solutions. Part IV discusses the experimental interfacial tension data and model predictions.

Part I
Literature Survey

Chapter 2

Enhanced Oil Recovery Practice

2.1 Oil Recovery Processes

Over a period of many millions of years, water, oil, and gas have accumulated in certain underground porous rock formations and have separated into fairly distinct layers according to their densities. Crude oil is trapped in the pores of the rock by natural forces resulting from viscosity, interfacial tension, and capillarity. Oil recovery from underground reservoirs involves the displacement of the oil from the interstices of the porous rock and its subsequent transport into the well-bore of production wells. This process requires energy which may be available in the reservoir in the form of dissolved gas coming out of solution, or water encroaching from an adjoining aquifer. Upon drilling a well, the natural driving forces ensure a continuous oil production for a certain period of time ranging from months to years. This process is referred to as "primary recovery". The oil recovery achieved is quite low, usually 20 to 40% of the original oil in place [33,34]. As the oil is being produced, the natural reservoir energy is gradually depleted to the point where there is insufficient force to drive the oil to the surface. At that point, a fluid such as gas or water is injected into the reservoir to displace the oil; this process is referred to as "secondary recovery".

The oil recovery achieved by this secondary flooding is low, only an additional 5 to 10% recovery of the original oil in place [35], owing to the chemical and physical properties of water, and particularly to the large capillary forces trapping the oil in the reservoir matrix. A part of the remaining 60 to 70% oil can often be produced by various other methods, collectively known as "tertiary" or "improved oil recovery" techniques [35,36]. Improved oil recovery processes include chemical processes, solvent processes and thermal recovery. Chemical flooding processes include three different types of flooding: polymer flooding, micellar-polymer injection and alkaline flooding.

2.2 Alkaline Oil Recovery

2.2.1 Mechanisms of Alkaline Oil Recovery

Much work has been done to elucidate the mechanisms postulated for improved oil recovery by alkaline waterflooding. Nutting [37,38] believed that alkaline solutions released residual oil from adherence to the reservoir rock matrix. He also stated that the caustic inhibited the formation of semi-solid, oil/water interfacial films. Atkinson [39] reported that caustic solutions had the ability to overcome the capillary forces, viscous resistances to flow, and adhesion of the oil to the sand, thereby releasing the oil. Subkow [40] reported that the formation of an oil-water emulsion in the pore spaces was an important step for improving oil recovery. The disparate behavior of alkaline flooding processes is related to the wide variation of alkali-oil and alkali-rock interactions. In a review by Johnson [41], a summary of various proposed mechanisms for alkaline waterflooding has been given. They include interfacial tension reduction, emulsification and entrainment [40], emulsification and entrapment [4], wettability reversal (oil-wet to water-wet) [42], wettability reversal (water-wet to oil-wet) [3], and

emulsification and coalescence [5].

In addition to interfacial tension reduction, wettability reversal and emulsion formation appear to be the dominant concepts for all these proposed mechanisms.

2.2.2 Interfacial Tension Reduction

The use of alkalis in waterflooding has been extensively investigated. Nutting [38] described the use of alkali salts such as sodium carbonate and sodium silicate. Strong bases, such as sodium hydroxide, were dismissed because of their excessive reactivity with crude oil. Campbell [43,44] stated that sodium silicate, sodium hydroxide, sodium carbonate, and sodium phosphate are the most widely used reagents for alkaline water flooding. These reagents, in the majority of cases, are added to the flood water to increase oil recovery. This improvement is achieved by in-situ generation of surfactant soaps by an interaction of the alkali with carboxylic acids present in crude oil. It was observed that the formation of soap molecules is mainly responsible for the lowering of interfacial tension that is necessary for improved oil recovery. Cooke et al. [3] suggested that interfacial tension values below 2.0 mN/m are required for additional oil to be recovered by caustic flooding. Several researchers [3,5-9] found that the accumulation of surface-active soap at the oil-water interface is time dependent, and thus the interfacial tension is also transient. This transient behavior fuelled a controversy among researchers concerning which interfacial tension value would be operative in an actual field situation. Some researchers [5,6] argued that equilibrium interfacial tension values are representative in the actual field, while others [10,13,45] stated that the minimum interfacial tension obtained in transient measurements is the most applicable value. McCaffery [6] believed that the minimum interfacial tension

would not be characteristic for the reservoir situation because it is attained a short time after the initial oil-caustic contact. Rubin and Radke [10] stated that the minimum interfacial tension observed using the spinning drop tensiometer is indicative of the lowest achievable reservoir equilibrium value. Later, deZabala and Radke [45] confirmed Rubin and Radke's point of view. They obtained interfacial tension data from multiple contacting of a fixed alkaline solution with fresh acidic oil and observed that the minima were close to those for single contacts.

2.2.3 Wettability Reversal

It was shown by Owen and Archer [46] that increasing the degree of water wetness of the reservoir rock increases the ultimate oil recovery. The wettability was reported to decrease the water/oil contact angle. Wagner and Leach [42] confirmed this hypothesis by using high-pH chemicals. Johnson [41] believed that increased oil recovery is the result of two mechanisms: (i) a relative permeability effect, that causes the mobility ratio of a displacement front to decrease, and (ii) shifting of the capillary desaturation curve. On the other hand, Cooke et al. [3] have reported improved oil recovery with increased oil wetness. However, Ehrlich et al. [47] showed that oil recovery is at a maximum when the wettability of a permeable medium is neither strongly water-wet nor strongly oil-wet. Therefore, a change in wettability, rather than the final wettability of the medium, appears to be the important factor. This change causes the trapped residual oil, originally discontinuous in the porous medium, to be converted into a continuous wetting phase. In addition to the low interfacial tension present, an emulsion of water droplets is formed and they become trapped in the porous medium. The resulting phase redistribution then makes both phases vulnerable to

recovery through viscous forces.

2.2.4 Emulsion Formation

Alkaline chemicals can cause improved oil recovery through the formation of emulsions [4]. The in-situ emulsification of residual oil is a consequence of the reduction in interfacial tension. The emulsification increases oil recovery in at least three ways: entrainment, entrapment and coalescence. The in-situ emulsification of the crude oil, and entrainment into a continuous flowing caustic water, have been suggested by Subkow [40]. The caustic has the ability to prevent adherence of the oil to the sand surface. The condition necessary for continuous entrainment appears to be maintaining the interfacial tension at a low level while moving the mixture through the reservoir.

For the emulsification and entrapment mechanism, many studies have shown that the residual oil in a water-wet porous media could be emulsified and moved downstream, to be entrapped again by pore throats too small for the oil emulsion droplets to penetrate. This mechanism results in a reduced water mobility that improves both vertical and areal sweep efficiency. This mobility ratio improvement is particularly important in water flooding viscous oils where sweep efficiency is poor. The improvement in sweep efficiency in this type of reservoir caused by a more favorable mobility ratio would be more important economically than the recovery of residual oil left behind after a water flood. As proposed by Castor et al. [5] the entrained oil droplets must coalesce to form a stable oil bank, depending on the stability of the in-situ emulsification.

2.3 Oil Chemistry

Crude oil is known to contain naturally occurring acidic components. These acids have to be identified with certainty and especially those responsible for the formation of surface active soap molecules by the interaction with alkali in flood water. Lochte [48] stated that both phenols, and fatty acids of small and long chain aliphatic components, were present. Early work by Seifert and Howells [49] working with Midway Sunset oil from California, suggested that the polar constituents of the oil were responsible for its high interfacial activity. Further, they isolated these polar components into carboxylic and phenolic fractions. The carboxylic acids were the most dominant interfacially active component and consisted of saturated aliphatics with molecular weight in the 300–400 range. Seifert and Teeter [50,51] and Seifert et al. [52] identified also mono-cyclic and poly-cyclic naphthenic acids as well as aromatic components.

Jang et al. [53] separated a Long Beach crude oil into various fractions and showed that the interfacial activity against alkali was due to an asphalt-like solid. A further analysis by gas chromatography and mass spectroscopy identified various long chain carboxylic acids, confirming the views of Seifert and Howells [49], and demonstrating that more than one species is involved in the diffusion and reaction process that occurs at the crude oil-caustic interface. Sharma et al. [15] proposed that the lowering in interfacial tension is probably caused by two different components: one being an acid with a low molecular weight and the other having a significantly higher molecular weight. Dunning et al. [54] positively correlated crude oil interfacial activity with the Ni-porphyrin complex associated with asphaltenes. Khulbe et al. [55] separated, in a conventional manner, Lloydminster crude oil into two main fractions, namely asphaltene and maltene components. The maltene constituents were then

separated by column chromatography into five fractions, each of which was tested for its effect on interfacial tension against alkaline solutions. They found significant interfacial activity even with the maltene fractions and concluded that asphaltenes by themselves were not responsible for the interfacial activity associated with untreated heavy oil against caustic solutions.

Chapter 3

Mechanisms for Acidic Oil/Alkaline Interactions

3.1 Interfacial Tension Phenomena

Transient interfacial tension is a phenomenon which is normally associated with the transfer of surface active materials between two immiscible liquid phases which are in contact. The surface active material is originally present in one of the liquid phases, but when the two phases are brought into contact, there is a tendency for some of the surfactant molecules to diffuse to the other liquid phase in which it was originally absent. Ordinarily, this diffusion of surfactant molecules would be expected to be governed by the law of unsteady-state mass transfer until an equilibrium is established in the respective bulk fluids. However, surfactants by their very nature tend to adsorb and accumulate at the interface separating the two bulk phases. The rate of adsorption is governed by the amount of surfactant already adsorbed and by the presence of any barriers to the removal of adsorbed species from the interface. Thus, the entire adsorption process is time-dependent. Consequently, the prevailing (apparent) interfacial tension remains strongly time-dependent until an equilibrium condition is attained. This so-called transient interfacial tension plays a considerable

role in a number of processes including liquid-liquid extraction and chemical improved oil recovery. In the latter case, reacting species in the form of carboxylic acids are originally present in the crude oil. The injection of an alkaline floodwater into the reservoir enables water-borne bases to contact and to react with the acids present in the oil phase. The result is the in-situ formation of surface-active soaps which are responsible for the dramatic reduction in oil-water interfacial tension as well as for its transient nature. Sherwood and Wei [56] have shown that the transfer of solutes between immiscible solvents is strongly influenced by the presence of adsorption barriers, particularly when surface reactions are involved.

Ward and Tordai [57] were the first to describe quantitatively the role of diffusion in the time-dependent interfacial tension behavior of solutions. However, it was left to England and Berg [58] and later Rubin and Radke [10] to relate the effect of these interfacial barriers on the rate of accumulation and hence on the magnitude of transient interfacial tension. The analytical solution of England and Berg [58] for the transfer of surfactant takes into account the effects of molecular diffusion in both bulk phases, the adsorptive accumulation at the interface, and energies of adsorption and/or desorption. Their analysis, for non-reacting systems, showed that interfacial resistances signified by sorptive barriers were largely responsible for the phenomena of transient interfacial tension. As demonstrated by Sherwood and Wei [56], the Fickian diffusion model adopted by England and Berg is inadequate because the problem is essentially a convective diffusion case. The convective diffusion has been used whenever convection currents were involved. In a reacting system, interfacial turbulence is generated by the gradient in chemical potential. This phenomenon is known as Marangoni disturbances or interfacial tension-driven interfacial disturbances [58-61]. In consequence,

convective diffusion in the immediate vicinity of the interface is spontaneously set up. The conditions under which interfacial turbulence is particularly intense have been outlined clearly by Hornof and Baig [62] and Sternling and Scriven [63].

3.2 Models of Acidic Oils/Alkaline Interactions

3.2.1 Equilibrium Considerations

The mechanisms for lowering of interfacial tension in acidic oil/alkali systems related to improved oil recovery have been studied for many years. The proposed mechanisms are based on the interfacial reactions between acidic components in the oil and alkali in the injected aqueous phase. Such reactions produce an ionized form of the acid. The adsorption of these soaps at the interface lowers the interfacial tension significantly. The interfacial tension reduction is transient in nature as observed by a number of investigators. Among others factors, the interfacial tension behavior of acidic oil/alkaline solutions is also a function of alkali concentration, often with a minimum occurring at an optimum alkali concentration. This minimum depends principally on the acid number of the oil, alkali type and ionic strength.

Several mechanisms have been proposed to explain the lowering of interfacial tension [11,12,13,16,64] and to explain the existence of the interfacial tension minimum. Early theories considered that the existence of a minimum is accounted for by the formation, at high NaOH concentrations, of undissociated salts which in turn may [12] or may not [11] partition into the oleic phase. Therefore, the formation of the salt will cause a decrease in the concentration of the ionized acid and consequently the interfacial tension increases. Ionic strength change is believed to be the main factor in explaining the minimum in interfacial tension observed when alkali concentration

is increased.

Cratin [64] studied the effect of pH on the interfacial tension of crude oil asphaltenes and resins against acidic and alkaline aqueous media. He noted a significant interfacial tension reduction which occurred both at low and high pH. He then postulated the existence of a zwitterion species which could be hydrolyzed to yield surface active species.

Several research works failed to explain the exact interfacial behavior of acidic oil/alkaline systems. This was mainly owing to the complex chemistry of the acidic oil. Crude oils contain a vast range of naturally occurring acidic compounds with widely different interfacial properties. This makes the modelling of interactions between acid and alkali very difficult. Chan and Yen [11] were the first to use a hypothetical representative acid species, namely HA . Their model considered only the adsorption of ionized acid at the interface while the minimum in interfacial tension resulted from the precipitation of the ionized acid in the aqueous phase.

The model proposed by Ramakrishnan and Wasan [12] follows the same reasoning as that of Chan and Yen [11]. However, instead of precipitation of the ionized acid into the aqueous phase, it is believed to partition preferentially into the oil phase. Ramakrishnan and Wasan [12] were the first to consider the electrical properties of the interface in the formulation of their model. Once again, the interfacial tension minimum is found to be controlled by ionic strength when alkali concentration in the aqueous phase is varied.

In the work published by Chiwetelu et al. [16], a model acidic oil phase was used. Their system, composed of hexadecane as a solvent, in which a single well defined long chain fatty acid (oleic acid) was dissolved in a concentration range of 0.1 to 1

mol/m³, mimics a real crude oil system well. In related work [65,66], paraffin oil containing linoleic acid gave similar results. The use of a simple model system helped to control the design of experiments and thus enhanced the understanding of the known and unknown mechanisms that govern the interactions in acidic oil/alkaline systems. The model proposed by Chiwetelu et al. [16] incorporated the electrical properties of the interface. They found that the ionization constant of the acid and the equilibrium constant governing the formation of the inactive and non-dissociated soap, and its subsequent partitioning into the oil phase, determined the magnitude of the interfacial tension. The pK_a values obtained for oleic acid were of the order of 6.2 and 6.9 and varied with the initial acid concentrations, but were independent of caustic concentration. Conversely, pK_a values for lauric acid were found to be dependent on aqueous caustic concentrations. The results noted above were in agreement with the work done by Patil et al. [67].

Despite the development mentioned above, the fundamental problem of the mechanisms of the interactions between acidic oil and alkaline solution was not solved. For instance, theories that have been developed to date do not consider dimerization of the acid in the oil, micelle formation, and particularly adsorption of the un-ionized acid onto the interface. Consequently, the effect of pH and ionic strength on equilibrium interfacial tension was not adequately described. It was not until recently, that Mingzhe et al. [68] extended the model proposed by Borwankar and Wasan [14] to include the effects of micelle formation on the interfacial tension behavior. However, they ignored the adsorption of the un-ionized acid. They suggested that the decrease in the concentration of ionized acid at the interface at high NaOH concentration is due to micelle formation and also to the suppression of the electric double layer at

high ionic strength. This in turn decreases the amount of surfactant adsorbed and the interfacial tension increases. More recently, Rudin and Wasan [20,21] improved the above model to account for a mixed interfacial layer and a mixed micelle formation by the ionized acid and the un-ionized acid. The simultaneous adsorption of these two species results in an ultralow interfacial tension and the incorporation of the acid into the micelle results in the reduction of the critical micelle concentration of the ionized acid.

3.2.2 Non-equilibrium Considerations

Rubin and Radke [10] extended the analysis of England and Berg [58] to the case of phases of finite extent using the Nernst film theory to account for the rate of convective diffusion of the solute. This treatment considers that interphase transport is governed by concentration gradients in a diffusion boundary layer of thickness δ . Their experimental data obtained by spinning drop tensiometry did not allow any quantification of sorption kinetic parameters because the interfacial area was not conserved and because of hydrodynamic end effects in the spinning capillaries. Later Brown and Radke [69] allowed for area variations of the oil droplet spinning in the capillary tube of the tensiometer. Their theoretical and experimental analysis showed that transient tension minima for acidic oils in contact with alkali are caused by significant sorption barriers at the oil/water interface. The concepts of Rubin and Radke [10] are not directly applicable to an alkaline displacement. Later deZabala [13,45] and Chiwetelu et al. [17,18] applied the modelling of Rubin and Radke to reactive systems encountered in the flooding of acidic oil with alkali. Rubin and Radke [10] and Sharma et al. [15] stated that the interfacial tension minimum must occur concurrently with a

maximum in surface-active species adsorption in order to properly satisfy the Gibbs adsorption equation. Therefore, the origin of transient tension minima is a result of the net accumulation of surface-active species at the interface. This tension minimum should be observed when either the net rate of adsorption is significantly higher than the net rate of desorption, or when the convective diffusion resistance of the aqueous phase exceeds that of the oil phase.

Other transient models have since been proposed by Trujillo [7], Sharma et al. [15], Borwankar and Wasan [14] and Chiwetelu et al. [17,18]. Trujillo [7] applied the analysis of England and Berg [58] to study the transient interfacial tension of crude oil/caustic systems. The interfacial tension results reported are for contact times in excess of 1000 seconds. The author argued that data for times shorter than one hour could not be used for the most transient part since the system had not reached thermal or hydrostatic equilibrium. Others researchers [10,17] believe, however, that this view is incorrect and that thermal and mechanical equilibrium is generally reached much sooner, at about 15 minutes of spinning in the tensiometer. The desorption rate constants predicted by Trujillo [7] were dependent on the pH of the aqueous phase.

Sharma et al. [15] presented a transient model for the acidic oil/caustic systems which took into account all of the chemical effects. Their considerations appear to be incorrect in that several ionic reactions, which should by nature be instantaneous, are considered as rate processes. Despite this, they incorporated electrical interfacial effects into the model. Their use of electrophoretic mobility instead of double layer potential is also incorrect according to Davies and Rideal [71].

Borwankar and Wasan [14] improved the model of Trujillo [7] and found that

the interfacial reaction rate constants, representing adsorption/desorption barriers, are independent of the composition of the aqueous phase. This was a significant improvement over Trujillo's model. The authors cited above employed a system chemistry in which crude oil acids were represented by one hypothetical single species, HA . Borwankar and Wasan [14] took into consideration the electrical nature of the adsorbed surfactant layer and used the penetration theory to model convective diffusion at short times.

Chiwetelu et al. [17,18] recently reported a physico-chemical model based on convective diffusion, sorption kinetics and interfacial phenomena to account for the transient interaction between single as well as binary carboxylic acids dissolved in a defined oil phase, and caustic reagents. The model took into account the equilibrium relationships among the various interacting species. Model predictions compared favorably with experimental data over a wide range of acid and caustic concentrations.

3.3 Surfactant-Enhanced Alkaline Systems

Experimental studies [19,27-32] have shown that the interfacial tension behavior arising from an interaction between surfactant-enhanced alkaline mixtures and acidic oil exhibited a marked synergistic effect. This effect is found to be a function of the concentration and type of the added surfactant. Rudin and Wasan [19-21] have shown that the free acid, when present in the aqueous phase, contributes to the synergistic interactions taking place between the added surfactant and the ionized acid species. Touhami et al. [70] confirmed the conclusion made by Rudin and Wasan that the free acid contributes to the lowering of interfacial tension in acidic oil/surfactant systems. An explanation for this is still lacking, indicating an incomplete understanding of the

mechanisms that govern the interactions between the active species in the oil and the surfactant enhanced alkaline reagents.

Based on the theories that have been developed to date, the mechanisms for the interfacial behavior of the surfactant-enhanced alkaline systems can be supported by theoretical modeling. To accomplish this, a theoretical model for surfactant-enhanced alkali/acidic oil system must be developed. The inclusion of a surfactant species into the model can be accomplished by the modification of the adsorption isotherms, of the micellar relationship and of the resulting equilibria.

Part II

Experimental Aspects

Chapter 4

Design of the Automated Pendant Drop Tensiometer

4.1 Introduction

The concept of interfacial tension presupposes the existence of a thermodynamic equilibrium between the two fluid phases. Several standard texts and reviews in surface science [71-74] discuss the various methods which are in use for surface and interfacial tension measurements. Techniques such as the du Nouy ring and Wilhelmy plate methods are commonly used to measure static tensions. Owing to new technology, the main virtue of these two methods is the ability to follow ageing effects with solutions of surface active agents. As the platinum ring or the plate is never detached from the liquid surface, the surface tension may be followed for periods of hours without disturbing any part of the surface. For interfacial tension measurements, it is evident that these techniques are only possible if the affinity of one phase to platinum is greater than that of the second phase. Such properties are almost impossible to control in practice as observed by Chivetelu et al. [75,76]. With regard to transient interfacial tension measurements, the most widely used technique is the spinning drop tensiometer [77-79]. Other well recognized methods are those which

make use of static pendant and sessile drops [80-83]. The pendant and sessile drop methods offer several advantages in the determination of surface or interfacial tension. These two methods are independent of any contact angle between the liquid and a solid support unlike the du Nouy ring and Wilhelmy plate methods. In particular the pendant drop method is a true equilibrium method and is best suited for transient surface and interfacial tension measurements [82].

Recent interest in surface science and particularly in adsorption kinetics has led to the improvement of the existing tensiometers and to the development of new tensiometers capable of measuring surface and interfacial tension changes with time [75,76,84-86], as well as relaxation phenomena in the adsorbed layer [87,88]. Most techniques which have been developed involve the determination and analysis of axisymmetric pendant or sessile fluid drop profiles. The drop shape methods have gained renewed attention recently owing to new technological developments in digital image acquisition and processing. Image processing has found a significant use in a broad range of scientific disciplines and technologies. A digital image processor consists generally of a video source, such as a camera, which produces an analog video signal containing image data. The signal is thereafter transmitted to the image processor and converted to a digital signal containing the image data in the form of digital picture elements, called *pixels*. The image is stored in the frame memory and can be accessed for display or subsequent computer processing.

Several works describing a computerized instrument for drop shape measurement have been published [89-95]. McCracken et al. [89] were the first to describe an automated drop shape apparatus. They employed an image digitizer capable of processing an image of 256×256 picture elements (pixels), with 64 gray levels to estimate

the light intensity. Much credit for image digitization and processing with an online connection of a video camera to a computer is due to Girault et al. [90,91]. They developed a technique to measure interfacial tension from pendant drop data using a video image profile digitizer. The image of a liquid drop was digitized into 128×128 pixels with 256 gray levels. The digitized image was then transferred to a microcomputer and a global thresholding technique was used to obtain the drop shape. Global thresholding assumes an object background image and picks a threshold that divides the image pixels into either object or background. The pixel with gray level value equal to or higher than the threshold value is given the value of 1; below the threshold, it is given the value of 0. Girault et al. [90,91] used a histogram of frequency of occurrence of individual gray levels against gray level to determine the appropriate threshold value. The edge of the image is then extracted by nearest neighbor analysis of each pixel. Global thresholding is useful in simple situations, but is found to be inadequate in many applications. Experimentally, this means that global thresholding is too sensitive to the lighting conditions. Following the work of Girault et al., several improved methods have been developed and tested adequately [85,86,92-95].

Anastasiadis et al. [92] presented a design which used a more sophisticated digitization hardware and a solid state CCD video camera. Determination of the interfacial tension used a novel technique for robust shape comparison. This technique included rotational resistance smoothing of the drop profile. They reported a precision of 0.5 % in the determination of the surface tension of glycerin.

A fully computerized pendant drop system was also designed by Carlà et al. [94]. They claimed a very good overall data reproducibility of 0.06% with an acquisition time of about 45 seconds for each experimental data point. Drop profile coordinates

were extracted on line and the information in each frame was compressed into a 1500 byte buffer without loss. The digitization algorithm used only an 11 pixel wide band centered on the profile. In this way, the time needed to digitize and process a single frame was only about 0.7 seconds. Cheng et al. [93] extracted the drop profile coordinates with a sub-pixel resolution, thus improving the accuracy in determining the drop profile coordinates compared to the more common closest pixel method. Also, Cheng et al. [93] employed a mathematical routine to correct for the optical distortion of the image. In addition, Cheng et al. [93] and Anastasiadis et al. [92] smoothed the profile coordinate data before analysis to obtain the tension. This method produced an apparent reduction in the confidence limits of the calculated tension. However, it is the opinion of Pallas and Harrison [85] that the confidence limits resulting from such treatment may not correctly represent the variance in the unsmoothed data set.

Hansen and Rødsrud [95] used the local threshold and interpolation technique, combined with an edge-tracing algorithm for the determination of the drop profile coordinates. These workers calculated the interfacial tension by two different methods, viz. the inflection of the drop profile method and the fitting of the theoretical Young-Laplace profile. Values determined by the first method were used as first estimates for the second optimization problem. With the use of their simple filter routine, the reproducibility was good and was typically in the range of 0.01-0.03 mN/m for a wide range of known liquids. The routine required 2 to 3 seconds to extract a typical drop profile of 400 to 700 data points.

4.2 Automated Pendant Drop Tensiometry

The micropendographic system designed in this laboratory by Chiwetelu et al. [75] used a manual digitization technique. This technique was found to be time consuming and tedious when a large data is being collected, including processing the photographic film, manual digitization of the drop profile, and analyzing the data set obtained. Interfacial tension in reactive systems, such as those involving acidic oils and alkaline solutions, exhibits a very dramatic decrease in the first few seconds which the spinning drop and the micropendographic methods are unable to monitor. This feature can be achieved when a pendant drop tensiometer is coupled with video image processing and a simple edge-detection algorithm. In the next section, detail of the design of an automated pendant drop tensiometer and the implementation of the edge-detection routine for the determination of the drop profile is discussed.

4.2.1 Experimental Set-up

A block diagram of the experimental set-up using digital image processing is shown in Fig. 4.1. The main components of the pendant drop tensiometer are a Ramé-Hart contact angle goniometer equipped with an environmental chamber for temperature control, an Olympus lighting system, and an Olympus optical system. The optical system consists of a Sony Model XC-77 monochrome video camera equipped with a 570×485 pixels charge coupled device (CCD). This type of camera has the advantage over tube cameras in that it provides the geometric linearity required and thereby eliminates optical distortion which is typically present. The CCD cameras were tested and found to be sufficiently sensitive and accurate for use in liquid-fluid systems. The camera, fitted with a C-mount, is mounted onto a microscope. The microscope is

equipped with a variety of objective lenses to allow a wide variation of magnification and focal length. The microscope is also provided with a focusing telescope and a light measuring port.

The cell and its associated housing unit are designed to be accommodated within the environmental chamber. The cell is made of quartz and has a path length of 10 mm. As shown in Fig. 4.2, the cell has open ends and when assembled has a maximum volume of 1.0 ml. The bottom and top covers are made of Teflon and are sealed to the cell. The bottom cover holds the capillary tube for dispensing the oil droplet. This design allows the use of different capillary types with different diameters. The top cover is also sealed to the cell and supports the necessary Teflon tubing for filling and flushing the cell. The cell is fixed to a support specially designed to fit into the environmental chamber. This simple design makes removal of the cell, changing of the capillary, and especially the cleaning procedure much easier. The optical rail is seated upon a vibration-isolation table (Vibradamp Support from Fisher) to damp out vibrations.

For liquid-liquid interfacial tension measurements, a pendant drop of the lighter liquid is formed at the tip of the capillary tube immersed in the other liquid. For this purpose a Harvard Apparatus Model 44 syringe pump capable of very precise flow rate control is used to deliver the oil droplet of any required size in exactly 1 second. Simultaneously, the timer is started and the profiles of the drop are recorded according to a preset timing mode. It is possible to invert the cell so that the surface tension could also be measured. The video signal of the pendant drop is transmitted to a Matrox PIP-512B digital video processor (Matrox Electronic Systems Ltd.) which performed the frame grabbing and image digitization. In the high resolution mode,

Figure 4.1: Schematic diagram of the pendant drop and the video image digitization system.

Figure 4.2: Details of the cell

the image is comprised of a 512 by 512 pixels array with 256 gray levels each, where zero represents black and 255 represents white. The image analysis software routines are coded in C language and are executed using a microcomputer.

The video camera can easily be replaced by a 35 mm automatic camera for manual digitization. For this purpose a special Kodak Technical Pan film (TK 135-36) is used. Drop profile coordinates are acquired by projecting the 35 mm negative onto the optical comparator (Scherr-Tumico Model 20-4200) comprising a translucent manual digitization screen capable of measuring (X, Z) coordinates to an accuracy of 0.01 mm.

4.2.2 Temperature Control

The environmental chamber within which the experiments are conducted is kept at a temperature of $25 \pm 0.1^\circ\text{C}$, by the continuous circulation of cooling water from a Haake F3 precision temperature bath. The actual temperature of the measurement cell is monitored with a type K thermocouple and displayed on a Thermo-electric digital read-out.

4.2.3 Density, Viscosity and pH Measurements

Density Measurement

The densities of all working solutions were measured using an Anton Parr Precision densitometer model DMA 48 at a temperature of $25 \pm 0.01^\circ\text{C}$.

Viscosity Measurement

A pre-calibrated Cannon-Fenske viscometer was used, for both the oil phase and alkaline solutions, with an oil bath for temperature control. Viscosity measurements

were made after 15 minutes equilibration at 25°C.

pH Measurement

The pH of the aqueous solutions was measured with an Orion Research digital ionanalyzer model 501 using a Fisher Scientific high pH glass electrode. Calibration of the pH meter was carried out using pH 7 and pH 12 buffers prior to each measurement. Room temperature of 23 to 25° C prevailed during most of the measurements.

4.3 Drop Shape Analysis

Several edge detection methods were summarized and discussed by Pallas and Harrison [85]. There are three principal factors concerning the choice of an edge detection method, namely: (i) the appearance of the edge as compared to the full image, (ii) the error range in tension resulting from fitting of the edge data, and (iii) the speed with which the data analysis could be implemented. The feature based shape processing of the pendant drop consists of the following steps:

- (a) image segmentation by thresholding the original image using the gray level histogram [96],
- (b) boundary detection by contour tracing [97,98].

4.3.1 Image Segmentation by Thresholding

Thresholding is the main industrial image processing technique used to separate the objects from their background. One of the practical problems encountered is related to the changes in lighting conditions. It is generally possible to compensate for effects such as shadows and reflectance using one of the following methods: image enhancement followed by a global thresholding [96]; or local thresholding (adaptive thresholding) [99]. The major disadvantage of both methods is that long processing time prohibits their use when only a PC type computer with a simple image acquisition board is used. For these reasons global thresholding [96] is employed for image segmentation with a robust processing algorithm to compensate for any inaccuracies. The images dealt with here are composed of light objects on a dark background. One way to extract objects from their background is to select a threshold which separates the two intensity modes. Therefore, the threshold will be the gray level value

Figure 4.3: Gray level histogram.

corresponding to the local minimum that separates the two intensity modes on the gray-level image histogram as shown in Fig. 4.3. After thresholding a binary image is obtained consisting of a set of black and white pixels. Each concentration of white pixels, assuming that the background of the image is darker than the objects, corresponds to a region in the scene. At this stage the problem is to separate and locate each region. In our case, this is accomplished using contour tracing.

4.3.2 Edge Detection by Contour Tracing

The contour tracing routine [97,100] traces boundaries by ordering successive edge points. For each traversed pixel the coordinates are memorized and the pixel's gray

level on the threshold image is set to 2. This operation, called contour marking, avoids tracing the same contour twice. The procedure terminates when the current pixel reaches the initial one. The boundary tracing involves two steps: (1) locating each region in the image and (2) boundary tracing each region that has been found.

Locating regions (step 1) is accomplished by scanning the thresholded image from left to right and top to bottom. Every time a new region is encountered, the tracer routine is called (step 2). Such situations, where a new region is encountered, are characterized by the pattern "black pixel followed by white pixel". The white pixel in this case constitutes the initial boundary pixel. From the initial boundary point, the contour is followed in such a manner that the region within the boundary is always kept to the left of the path being followed [97]. The search scheme consists of finding, for the current boundary pixel, the rightmost white pixel with respect to the current boundary orientation. This is accomplished through the concept of chain coding (Fig. 4.4).

Let S be the search direction in terms of the code of Fig 4.4. S , then, indicates which of the neighbors of the preceding boundary cell correspond to the cell currently considered. For the starting boundary point, S is equal to 6. The neighbors of the current cell (I,J) are now checked, as indicated by the flowchart shown in Fig. 4.5. In this situation, the neighbors are tested in an order of decreasing likelihood. The most likely next boundary neighbor is the one that has the same chain-code value as the current one. This is related to the fact that most of the contours in this case are piecewise linear, and consequently, most of the chain-code values are constant. In this way, the algorithm is performed quickly. The loop is executed three times at the most in order to avoid circling around a set that only has one pixel.

$(I-1, J-1)$ 3	$(I, J-1)$ 2	$(I+1, J-1)$ 1
$(I-1, J)$ 4	(I, J)	$(I+1, J)$ 0
$(I-1, J+1)$ 5	$(I, J+1)$ 6	$(I+1, J+1)$ 7

Figure 4.4: Chain codes.

Figure 4.5: Flowchart for the TRACER edge detection.

This procedure produces a closed path and follows external contours in a counter-clockwise manner. Memorization of the boundary points is done as follows: first the coordinates of the initial boundary point are memorized; then, for each boundary pixel traced, the chain-code value indicating the direction to the next neighbor on the contour is memorized in a stack. It should be noted that storing the chain-code value instead of the pixel coordinates saves a great deal of memory space. Also, by knowing the coordinates of the initial edge point and the chain-code values between the different pixels on the boundary, we can recover the coordinates of any boundary pixel whenever necessary.

4.4 Determination of Interfacial Tension from Drop Profiles

4.4.1 Description of the Drop Profile

The classical form of the Young and Laplace equation [72] relates the pressure drop, ΔP , across an interface at a given point to the two principal radii of curvature, R_1 and R_2 , at that point, and to the interfacial tension, γ , i.e.,

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (4.1)$$

For a pendant or sessile drop of a known fluid in mechanical equilibrium with a surrounding fluid, the balance between capillary and buoyancy forces is given by:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R_o} + \Delta\rho gZ \quad (4.2)$$

where R_o is the radius of curvature at the origin in the X - Z coordinate system, $\Delta\rho$ is the difference in the density of the two bulk phases, and g is the gravitational acceleration.

Following the development of Rotenberg et al. [101] the equation of Young and Laplace may be expressed as a set of three first-order differential equations, namely

$$\begin{aligned}\frac{dx}{ds} &= \cos \phi \\ \frac{dz}{ds} &= \sin \phi \\ \frac{d\phi}{ds} &= 2 + \beta z - \frac{\sin \phi}{x}\end{aligned}\tag{4.3}$$

where x and z are the X and Z coordinates of a point on a drop profile reduced to dimensionless variables by dividing them by R_o . Similarly, s is the dimensionless arc length from the apex to the point (x,z) , ϕ is the turning angle at that point (Fig. 4.6) and β , the drop shape, is defined by:

$$\beta = \frac{\Delta \rho g R_o^2}{\gamma}\tag{4.4}$$

The complete shape of the curve defined by the functions $x(s)$ and $z(s)$ may be obtained by simultaneous integration of Eqs. 4.3 subject to the initial conditions:

$$x(o) = z(o) = \phi(o) = 0\tag{4.5}$$

The functions x, z , and ϕ depend upon the parameter β . The first derivatives of the functions x, z , and ϕ with respect to β are generally required for the optimization problem to obtain the interfacial tension. Differentiating Eqs. 4.3 with respect to β gives;

$$\begin{aligned}\frac{dx'}{ds} &= -\phi' \sin \phi \\ \frac{dz'}{ds} &= \phi' \cos \phi \\ \frac{d\phi'}{ds} &= z + \beta z' - \frac{\phi' \cos \phi}{x} + \frac{x' \sin \phi}{x^2}\end{aligned}\tag{4.6}$$

Figure 4.6: Representation of the drop profile coordinate system

with the initial conditions (' denotes prime)

$$x'(o) = z'(o) = \phi'(o) = 0 \quad (4.7)$$

Similarly, the expression for the second derivatives are obtained by differentiating Eq. 4.6 with respect to β

$$\begin{aligned} \frac{dx''}{ds} &= -(\phi')^2 \cos \phi - \phi'' \sin \phi \\ \frac{dz''}{ds} &= -(\phi')^2 \sin \phi + \phi'' \cos \phi \\ \frac{d\phi''}{ds} &= -2 \frac{\sin \phi}{x^3} (x')^2 + 2 \frac{\cos \phi}{x^2} x' \phi' + \frac{\sin \phi}{x^2} x'' \\ &\quad + 2z' + \beta z'' + \frac{\sin \phi}{x} (\phi')^2 - \frac{\cos \phi}{x} \phi'' \end{aligned} \quad (4.8)$$

with the initial conditions

$$x''(o) = z''(o) = \phi''(o) = 0 \quad (4.9)$$

For a given β , Eqs. 4.3, 4.6 and 4.8 form a system of nine, first-order, ordinary

differential equations that, together with the initial conditions, can be solved numerically to yield a set of values, $x_j, z_j, x'_j, z'_j, x''_j$, and z''_j which approximate the functions $x(s), z(s), x'(s), z'(s), x''(s)$, and $z''(s)$ at the point s_j .

4.4.2 Determination of the Interfacial Tension

In the original work of Bashforth and Adams [80], and then Andreas et al. [82] only two physical dimensions taken from photographs of hanging drops, d_s and d_e , were required for interfacial tension determination. The solution scheme consisted of integrating the differential equation up to a specified point and correlating the coordinates measured with the interfacial tension through the shape parameter β . Andreas et al. [82] reported an accuracy of 0.5% for interfacial tensions calculated using this method. A better approach is to measure more than one set of coordinates and fit these to the solution of the differential equation describing the profile using a computational technique. Vos and Los [102] used as many as 100 coordinate measurements obtained by a laser striascopic imaging technique. These authors were able to achieve an accuracy of 0.05%. Girault et al. [91] used the Laplace equation at the inflexion plane of the drop located by a polynomial fitting technique. Anastasiadis et al. [92] proposed a novel technique for the determination of interfacial tension by analysis of the axisymmetric fluid drop profile. The technique coupled recent developments in digital image processing with modern methods for robust shape comparison.

Several related numerical techniques have been reported [90-93,101,103]. The most commonly used method for interfacial tension determination relies on an optimization procedure. This procedure is based on a non-linear fitting of one set of

experimental drop profiles to a numerically generated drop profile, based on the solution of the Laplace equation of capillarity. The procedure employed was to construct an objective function which is the measure of the discrepancy between the calculated Laplacian curve and the measured curve. This function is the sum of the squares of the normal distances between the measured and calculated points. The objective function is then minimized numerically. The two powerful numerical methods for determination of interfacial tension have been reported and are described below.

RBN Algorithm

The algorithm of Rotenberg et al. [101] was developed to determine the liquid-fluid interfacial tension and contact angle as well as the volume and the surface area from sessile and pendant drops. It used the incrementally loaded Newton-Raphson method. The required data were limited to (X, Z) coordinates of the drop profile, densities of the liquid and fluid phases and the local gravity. This algorithm terminated due to the computational change from the configuration of a pendant drop to the configuration of a sessile drop. The failure of the program is found to be due to the computation of an inadequate initial value of the drop parameters. Recently, Cheng et al. [93] developed two related techniques, namely the axisymmetric drop shape analysis-profile (ADSA-P) for interfacial tension pendant drops and the axisymmetric drop shape analysis-contact diameter (ADSA-CD) for interfacial tension and contact angle from sessile drops, to overcome the problem associated with the original program. Rather than relying on all the measured coordinates, the ADSA-P used a few arbitrary points selected from the drop profiles.

Jennings and Pallas Algorithm (JP)

Jennings and Pallas [103] used a more sophisticated method, rotational discrimination, which is essentially a modified form of the Gauss-Newton technique in the optimisation procedure. The algorithm of Jennings and Pallas [103] was adopted in this work because it was found to be superior to that of Rotenberg et al. [101] in terms of computer processing time and of the integrated error analysis. Following the procedure of Jennings and Pallas [103] the computer processing time for one drop profile of water was evaluated. It was found that the routine of Jennings and Pallas requires much less CPU time than the routine of Rotenberg and co-workers. Also, with the method of Jennings and Pallas, two additional experimental parameters, namely the aspect ratio and the rotational angle of the system, were determined. In addition, this algorithm was designed to handle a large data set of profile coordinates, which is the case of data generated using computer-based drop image processor. It is believed that use of this algorithm enhances the precision of the pendant drop technique. From a practical point of view, it is obvious that improvement in the numerical technique is of great importance for studying the transient interfacial tension. A brief description of the JP Algorithm is presented in the next section.

Objective Function

Consider a set of m data points of the experimental drop profile, (X_i^{obs}, Z_i^{obs}) ; $i = 1, 2, \dots, m$. The observed coordinates are magnified and must be scaled to real physical dimensions by use of an experimentally determined magnification factor. In the case when the observed coordinates are obtained by the use of an image processing and a television camera, the vertical and horizontal magnifications may not be the same.

Figure 4.7: Illustration of the computation of residuals.

The ratio of the two magnifications defines the aspect ratio, $a = M_x/M_z$, which is a fixed constant of the apparatus. Since the exact location of the apex (X_0, Z_0) is not known, the coordinates must be translated and even rotated by an angle of rotation θ to correct for any misalignment of the optical system. More explicitly, the coordinates are given by:

$$\begin{aligned} X_i &= (X_i^{obs}/M_x - X_0) \cos \theta + (aZ_i^{obs}/M_x - Z_0) \sin \theta \\ Z_i &= (aZ_i^{obs}/M_x - Z_0) \cos \theta - (X_i^{obs}/M_x - X_0) \sin \theta \end{aligned} \quad (4.10)$$

Suppose that the calculated Laplace curve, $(X(s_i), Z(s_i))$, differs from the transformed experimental points (X_i, Z_i) by the distance, r_i , then the objective function is defined as the sum of the squared residuals r_i and is given by:

$$Q = \sum_{i=1}^m r_i^2 \quad (4.11)$$

where

$$r_i = \pm [(X(s_i) - X_i)^2 + (Z(s_i) - Z_i)^2]^{\frac{1}{2}} \quad (4.12)$$

The values of $(X(s_i), Z(s_i))$ are related to the dimensionless coordinates $(x(s_i), z(s_i))$ by the factor R_0 . As the coordinates of the calculated drop profile, (x_j, z_j) are obtained at discrete dimensionless arc length intervals, Δs , it is unlikely that there will be a point $(x_j, z_j) = (x(s_i), z(s_i))$. Therefore, the point $(x(s_i), z(s_i))$ must be computed by interpolation between the existing points (x_j, z_j) . This is done for each transformed data pair (X_i, Z_i) by first locating the two nearest computed points (X_j, Z_j) and (X_{j+1}, Z_{j+1}) . The three pairs (X_i, Z_i) , (X_j, Z_j) and (X_{j+1}, Z_{j+1}) form a triangle as shown in Fig. 4.7. The distance, r_i , may then be computed:

$$r_i \simeq \frac{(Z_j - Z_i)(X_j - X_{j+1}) - (X_j - X_i)(Z_j - Z_{j+1})}{[(X_j - X_{j+1})^2 + (Z_j - Z_{j+1})^2]^{\frac{1}{2}}} \quad (4.13)$$

Minimization of the Objective Function

The problem now is to find the set of parameters that gives the best fit between the calculated and observed drop shape using nonlinear least-squares minimization. Consider the vector, $\mathbf{U}$, defined by:

$$\mathbf{U} = [\theta/\omega_\theta, a/\omega_a, X_0/\omega_{X_0}, Z_0/\omega_{Z_0}, R_0/\omega_{R_0}, \alpha/\omega_\alpha] \quad (4.14)$$

where the ω are constant scale factors which will be chosen in order to optimize the performance of the minimization algorithm and $\alpha = 1/\gamma$. In terms of $\mathbf{U}$, Q becomes:

$$Q(\mathbf{U}) = \sum_{i=1}^m r_i^2(\mathbf{U}) \quad (4.15)$$

The objective function is then minimized using rotational discrimination, which is essentially a modified form of Gauss-Newton technique. These two techniques assume that the residuals can be approximated at each iteration by planes in the n -dimensional parameter space, and recognize that the minimum of Q occurs at a point U^* such that $Q'(U^*) = 0$, where U^* is the solution to the minimization problem. Q' may be approximated as a truncated Taylor series about a base point U^0 :

$$Q'(U) \simeq Q'(U^0) + Q''(U^0)(U - U^0) \quad (4.16)$$

An estimate of the solution for U^* may be given by:

$$U^* \simeq U^0 - [Q''(U^0)]^{-1} Q'(U^0) \quad (4.17)$$

This suggests the iterative procedure

$$U^{k+1} = U^k + \Delta U^k \quad ; k = 0, 1, 2, \dots \quad (4.18)$$

where ΔU^k is the solution of

$$Q''(U^k) \Delta U^k = -Q'(U^k) \quad (4.19)$$

The elements of Q' may found by differentiation of the objective function with respect to each of the n elements of U .

$$Q'_p(U) = \frac{\partial Q(U)}{\partial U_p} = 2 \sum_{i=1}^m r_i \frac{\partial r_i}{\partial U_p}; \quad p = 1 \dots n \quad (4.20)$$

and similarly

$$Q''_{pq}(U) = \frac{\partial^2 Q(U)}{\partial U_p \partial U_q} = 2 \sum_{i=1}^m \frac{\partial r_i}{\partial U_p} \frac{\partial r_i}{\partial U_q} + 2 \sum_{i=1}^m r_i \frac{\partial^2 r_i}{\partial U_p \partial U_q} \quad (4.21)$$

A good approximation of Q'' may be obtained by omitting the term containing the second derivatives in Eq. 4.21 and therefore only first-order derivatives of r_i need to be computed. Eq. 4.21 can now be written as:

$$Q''_{pq}(U) \simeq 2 \sum_{i=1}^m \frac{\partial r_i}{\partial U_p} \frac{\partial r_i}{\partial U_q}; \quad p, q = 1 \dots n \quad (4.22)$$

Jennings and Pallas [103] preferred the rotational discrimination over the Gauss-Newton method for solving Eq. 4.19 in order to avoid certain computational problems associated with Gauss-Newton such as large oscillations and large moves in null-effect directions toward the minimum.

Rotational discrimination performs the decomposition of $Q''(U^k)$ as follows:

$$T^T(U^k)Q''(U^k)T(U^k) = E(U^k) \quad (4.23)$$

where $E(U^k)$ is an $n \times n$ diagonal matrix whose elements are the eigenvalues of $Q''(U^k)$ and $T(U^k)$ is an orthogonal $n \times n$ matrix whose columns are the corresponding eigenvectors of $Q''(U^k)$.

Also, rotational discrimination uses a change of coordinate system from $(U_1, U_2, \dots, U_n)$ to $(V_1, V_2, \dots, V_n)$ where the $T^T(U^k)$ is the transformation matrix.

$$V(U) = T^T(U^k)(U - U^k) \quad (4.24)$$

The solution of the Eq. 4.19 through the use of the rotational discrimination can now be computed by:

$$\Delta U^k = T^T(U^k)V(U^k) \quad (4.25)$$

Computation of the Confidence Intervals

The confidence Intervals on the parameters are computed by using the formula for the approximate joint confidence region:

$$(\mathbf{U}^c - \mathbf{U}^*)^T \mathbf{Q}''(\mathbf{U}^*) (\mathbf{U}^c - \mathbf{U}^*) = 2\sigma_r^2 n F_{1-\varphi}(n, m - n) \quad (4.26)$$

where $\mathbf{U}^*$ is the solution to the minimization problem, $F_{1-\varphi}(n, m - n)$ is the F test statistic for a confidence level of $1 - \varphi$ and $(n, m - n)$ degree of freedom, and σ_r^2 is the sample variance of the residuals at the minimum:

$$\sigma_r^2 = \frac{\mathbf{Q}(\mathbf{U}^*)}{m - n} \quad (4.27)$$

The approximate joint confidence region is valid only when the following assumptions are valid: (1) The residuals are a random function of their position on the drop. (2) The residuals are normally distributed with a mean of zero. (3) $\mathbf{U}^*$ is a minimum of the objective function. (4) $\Delta \mathbf{U}$ is sufficiently small that the approximation of $\mathbf{Q}$ given by Eq. 4.22 is valid.

Data input and Convergence Criteria

Initial guesses for the parameters, θ , a and α , are supplied to the program. The other guesses will be made by the program if none are supplied. The initial guess for X_0 is obtained by taking the average of the largest and smallest X value found in the data. The initial guess for Z_0 is obtained by scanning the data for the point with the largest or smallest Z , depending upon the orientation of the drop. The initial guess for R_0 is taken to be half the drop width or the vertical distance between the apex and the widest place on the drop, whichever is larger. Four convergence criteria were chosen for the minimization problem. Convergence is assumed when any of the

following criteria are satisfied: (i) The largest element in V is smaller than ϵ_V (10^{-7}). (ii) The largest relative change in the physical parameters (θ , α , X_0 , Z_0 , R_0 , γ) is smaller than ϵ_R (10^{-7}). (iii) The relative change in the objective function is smaller than ϵ_Q (10^{-7}). (iv) The directional derivative with respect to V of the objective function in the direction of steepest descent is smaller than ϵ_D (10^{-7}). The ϵ data are supplied along with the input data.

4.5 Other Methods for Interfacial Tension Measurement

4.5.1 Spinning Drop Tensiometer

Low interfacial tension measurements were performed using the University of Texas Model 500 Spinning Drop Tensiometer (SDT). This apparatus is the most popular and convenient means of measuring low to very low transient interfacial tension. Apart from the buoyancy effects noted earlier [104], interfacial tension measurements using this technique are affected also by circulatory flows [105,106] as well as by imprecise temperature control [75]. However, recent studies [75,76] have confirmed that the method is fairly accurate and reliable for low interfacial tension measurements.

Details of the general measurement procedure have been outlined by Gardner [107]. For transient tension measurements, Reive [108] has described in detail the procedure for loading the capillary assembly. Briefly, the procedure which was used in this study consisted of introducing a small droplet of oil into a glass capillary tube, approximately 2 mm in diameter and 100 mm in length, which had been previously filled with the aqueous solution. A Hamilton micro-syringe was used for the injection of the oil droplet. The tube was then quickly inserted into the cap

assembly and screwed into the rotating sleeve of the SDT. When spun, the droplet elongates due to rotational forces until a balance is struck between these forces and the interfacial forces.

From a purely experimental point of view, the classical spinning drop tensiometer has a number of drawbacks which make the instrument inconvenient for dynamic tension measurement. The University of Texas tensiometer is designed for air cooling of the rotor housing which makes temperature control difficult to realize, especially when operating at high speeds and extended times. In fact, heat is usually generated in the motor and bearings, and this in turn heats up the capillary tube housing. This temperature gradient within the spinning capillary tube can produce undesirable circulatory flows [104]. Also, the determination of interfacial age is imprecise, because measurement of the linear dimensions of the oil droplet are made during the course of the experiments. It is quite difficult and unreliable to make any measurement for contact time less than one minute. Often drifting of the spinning droplet towards one end occurs, which makes measurement of the dimensions difficult to achieve, especially when the droplet length has to be measured simultaneously.

For more accurate and precise dynamic interfacial tension measurements in the low and moderate tension regimes, Chiwetelu et al. [65] have successfully modified the basic configuration of the University of Texas tensiometer. At gyrostatic equilibrium, the interfacial tension is related to the drop radius R_d , the speed of rotation Ω , and the density difference between the two phases $\Delta\rho$ by the equation [77]

$$\gamma = \frac{R_d^3 \Omega^2 \Delta\rho}{4} \quad (4.28)$$

If the length of the drop is greater than four times its diameter, a cylinder with hemispherical ends approximation is adequate. When this criterion is not satisfied, the

drop has an ellipsoidal shape and several authors [77-79] have developed a procedures for determining interfacial tension.

4.5.2 Drop Volume Tensiometer

The drop volume tensiometer recently developed by Hool and Schuchard [109] was also used to measure the interfacial tension. The drop volume tensiometer model DVT-10 from Krüss (Germany) is equipped with a processing unit, a photocell assembly for detecting the droplets, and a Harvard Apparatus Model 44 syringe pump capable of very precise flow rate control. The instrument accurately measures the time elapsed to form a known number of liquid droplets under a constant flow rate. The size of the droplet at detachment is directly proportional to the liquid-liquid interfacial tension. With the newly designed capillary tube [109], interfacial tension can be calculated without the use of the traditional correction factor and within the range of 0.2-100 mN/m with 1-2% relative standard deviation. The drop volume tensiometer is intended to measure interfacial tension at one discrete drop formation time, but measurements at different flow rates may be conducted corresponding to different drop formation times to obtain dynamic profiles.

The interfacial tension is calculated based on the balance between the adhesion force holding the drop down at the orifice and to the gravity force pulling it away. Explicitly, interfacial tension is given by the following equation [72]:

$$\gamma = \frac{V_d \Delta \rho g}{\pi d_c} \quad (4.29)$$

where V_d is the volume of the drop, $\Delta \rho$ is the density difference between the two phases, g the gravity factor, and d_c is the capillary diameter.

Chapter 5

Experimental Procedures

5.1 Experimental Design

5.1.1 Materials

The oil phase employed in this work was light paraffin oil obtained from BDH Chemicals Ltd. Fisher purified grade linoleic acid was dissolved in the light paraffin oil solvent to simulate an acidic crude oil and to achieve the desired working acid concentrations of 0.1, 1.0, 10.0 and 100 mol/m³. The density of the paraffin oil was 0.8423 g/cm³ and its viscosity was 19.25 mPa.s at 25°C. The caustic reagent employed in the study was sodium hydroxide ACS grade supplied by BDH Chemicals Ltd. Sodium dodecyl sulfate (SDS) of a high purity grade (Analar biochemical) was also obtained from BDH Chemicals Ltd. Sodium dodecyl sulfate was selected over other possible candidates that could generate even lower interfacial tensions (e.g. sodium oleate) because of the inherent limitation of the pendant drop technique, which is not suitable for measuring interfacial tensions lower than about 0.1 mN/m. Double distilled, deionized and deaerated water was used in the preparation of the aqueous solutions. A rigorous cleaning procedure for all vessels, glassware and syringes was used. The

procedure consisted of initial washing with water, then followed by ethanol and finally acetone. All glassware was further cleaned with hot chromic acid solution and thoroughly rinsed with water. Drying of the cell, syringes and glassware was effected with air followed by nitrogen.

5.1.2 Experimental Strategies

The investigative strategy was to obtain accurate and reliable transient interfacial tension data. Such data would be used for the determination of the model parameters which would be developed at later stages of the work.

Strategy I: System calibration:

- to study the effect of the experimental parameters on the precision and the accuracy of the apparatus,
- to perform preliminary runs in order to determine suitable experimental conditions, mainly the working concentrations, oil droplet volume, size of the needle, exposure time, timing mode for lapse time between drop profiles and number of drop profiles per run.

These results were used as a basis for Strategy II.

Strategy II: Equilibrium and transient interfacial tension measurements:

- to perform blank runs with single components, namely caustic and surfactant solutions contacting the oil system,
- to carry out interfacial tension measurement for the surfactant-caustic mixtures,
- to analyze the data and develop the equilibrium and transient models.

5.2 Computer Program for Instrument Control

A computer program for control of the experiment was designed and built around the core subprograms, to allow the operator maximum control over the system. The program, a user interface, was used interactively in a menu format to: (i) perform the calibration, (ii) create and edit the parameter file for subsequent analysis of the profile coordinate data, and (iii) choose the timing mode for the time between profiles. The instrument control program designed here enabled us in an interactive mode to choose an edge detection threshold technique other than the tracer method described earlier. It also allowed us to choose whether to record just the profile coordinates or to save the entire image of $512 \times 512 \times 8$ bit (256 level) gray scale for later examination, and to examine the live image or a previously stored image.

5.3 Calibration of the Pendant Drop Apparatus

5.3.1 Instrument Parameters

A thorough analysis of the effect of error in the determination of the various instrumental parameters on the interfacial tension is necessary. There are four instrumental parameters which determine the precision and accuracy of the apparatus: resolution, aspect ratio, calibration, and edge detection method.

Resolution

The resolution of the instrument is its ability to resolve small distances. It is a direct function of the resolution of the camera used, the numerical aperture of the microscope and the wavelength of the light source. For any microscope, the resolution

power is given by:

$$d = 0.61 \frac{\lambda}{A_p} \quad (5.1)$$

where d is the smallest resolvable distance, λ is the wavelength of the illuminating light, and A_p is the numerical aperture. A typical average resolvable distance value is about 8.010^{-4} cm . This value is very sensitive to the wavelength of the light source, therefore a judicious choice of light source is absolutely necessary. Using a CCD sensor, it was possible to read an edge directly to about one pixel or better. Such results can not be obtained by means of a photographic film.

Aspect Ratio

The aspect ratio (AR) is defined as the ratio of the X to Z magnification. Its value is generally affected by a number of factors, including horizontal blanking signals and timing signals. The overall AR for the PIP-512B system, including the camera, is found to be 0.8508 ± 0.0002 or about 0.024 % error. This value is comparable to that reported for the RS170 compatible equipment of 0.83. Pallas and Harrison [85] reported from simulations that the percent error in interfacial tension due to error in AR is equal to about half the percent error in the AR. Therefore, only about 0.012 % error in interfacial tension due to the aspect ratio error is expected.

Calibration

Calibration is considered to be the greatest potential source of error [85]. This is due in part to the fact that the interfacial tension measured by drop shape analysis is proportional to the square of the magnification. Thus, the percent error in the tension is twice that in the calibration. The error in the calibration is not only a function

of the error in the calibration object, but also a function of the percent of the video lines used for the calibration. For the calibration procedure, one needs to observe an object whose dimensions are well known, and to compare the known dimensions to those observed. This results in two magnifications M_x and M_z in pixels per cm. Generally, stainless-steel spheres or rods are used for this purpose. A more accurate way of selecting the calibration object is the use of a cross-scale reticle (Gaertner Scientific Corp.). This method was originally adopted by Pallas and Harrison [85]. An intensity curve is generated as a function of the (X,Z) coordinates, from which the magnification is extracted. Fig. 5.1 shows the plot of the extracted minima for the M226 (80 mm) lens. An average value was found of 1874.675 *pixel/cm* as M_x with an associated error of 0.0265 %. On that basis, a 0.053 % error in interfacial tension due to calibration is expected. A similar analysis for other lenses was carried out. Fig. 5.2 shows a comparison between the experimental and the calculated drop profiles using Eq. 4.3. The calculated residuals, r_i , are also presented for each value of Z .

Figure 5.1: Calibration plot.

Figure 5.2: (a) Typical experimental versus calculated drop profile and (b) the corresponding residual plot.

5.3.2 Surface and Interfacial Tension Results

The instrument was then tested in order to assess its accuracy and reproducibility by measuring the surface and the interfacial tensions of several pure substances. Pure water and commercially available high-purity hydrocarbons were used to demonstrate the use of high speed recording to produce a significant improvement in the precision of surface and interfacial tension measurements. Surface tension data of water at 25°C are presented in Table 5.1. Each experiment was performed on one drop, recording the profiles as functions of time. Each experiment thus resulted in hundreds of profile data sets of approximately one thousand (X,Z) coordinates. The resulting surface tension versus time curve is shown in Fig. 5.3. It can be seen that over the time period of this run no trends with respect to time are detectable. The data were analyzed using the statistical procedure outlined by Pallas and Harrison [85]. The data for each run were combined as the sum of the weighted variance of the means and a 99.9 % confidence interval was calculated. The total estimated error in the surface tension was estimated by taking the square root of the sum of each contribution, namely, the error in the calculated tension and the error due to the calibration. These results are presented in Table 5.2. The surface tension of water at 25°C was found to be 72.00 ± 0.07 mN/m. This value is considered to be in excellent agreement with the literature value of 71.99 ± 0.05 mN/m [85]. Table 5.3 gives the interfacial tension of several hydrocarbons against water at 25 °C. The standard deviation is calculated from 20 consecutive measurements on the same drop. The measurements were performed on pre-equilibrated solutions containing equal volumes of both phases. Also given are literature data for these systems [71,72,110]. The measured values compared well with the literature data in the range of the deviations shown in the table.

Figure 5.3: Surface tension of pure water versus time at 25°C.

Table 5.1: Results for the surface tension of pure water at 25 °C

Number of profiles	Mean surface tension (mN/m)	Standard deviation of the mean
110	72.023	0.0302
110	71.982	0.0271
110	71.992	0.0660

Table 5.2: Averaged results for the surface tension of pure water at 25 °C

Mean surface tension, γ (mN/m)	Standard deviation, σ	Confidence interval 99.9% (mN/m)	Estimated total error (mN/m)
72.000	0.019	0.062	72.000 $\pm$ 0.073

Table 5.3: Interfacial tension of hydrocarbons against pure water at 25 °C and per cent deviation from reported literature values [71,72,110].

System	Measured (mN/m)	Standard Deviation (mN/m)	Literature (mN/m)	Deviation (%)
n-Hexane	50.62	0.05	50.41	0.415
n-Heptane	50.73	0.04	50.77	0.079
n-Octane	51.32	0.05	51.22	0.195
n-Decane	51.75	0.07	51.70	0.096
n-Dodecane	52.37	0.04	52.46	0.172
Benzene	34.54	0.07	34.71	1.274
Toluene	35.61	0.05	35.70	0.252
n-Butanol	1.84	0.09	1.8	2.220
n-Pentanol	4.38	0.07	4.4	0.456

5.3.3 Features of the Modified Pendant Drop Tensiometer

Once the modified pendant drop apparatus had been tested for accuracy and speed, its utility was investigated in some practical situations related to surface science. Three different tests were performed, namely transient, dynamic and relaxation measurements. The system studied consisted of an acidified oil (i.e paraffin oil containing linoleic acid) as the oil phase and an aqueous solution of sodium dodecyl sulfate and caustic as the water phase. This system was chosen to reflect an enhanced oil recovery process involving caustic and surfactant reagents. Other systems, including acidic crude oils, are under investigation. In our opinion, there has been some ambiguity in the literature concerning the definition of "transient" and "dynamic" interfacial tension, as previously observed in the publications of Chiwetelu et al. [18], Sharma et al. [15], Rubin and Radke [10] and Nagarajan and Wasan [87]. An attempt at a clear unambiguous definition followed by an experimental example is given in the following section.

The first test, referred to as transient measurement, consisted of measuring the interfacial tension of a static drop of constant mass and changing interfacial area until equilibrium was attained. In this case an oil droplet of constant volume was formed in exactly one second using a programmable syringe pump, and immediately the drop profiles were taken according to a chosen timing mode. Generally, frames were taken every second at the beginning and, thereafter, the time interval was increased. Fig. 5.4 shows the transient interfacial tension for two separate runs on the same system for a period of one hour contact time. Each run contained 120 data points. Another example is the transient interfacial tension data of a reactive system of interest to surfactant enhanced alkaline oil recovery. Fig. 5.5 shows the transient interfacial

tension behavior of acidified oil (1 mol/m^3) against 2 mol/m^3 sodium dodecyl sulfate and 2.5 mol/m^3 caustic solution. A very marked drop in interfacial tension is obtained for this system in a short period of time. As can be seen also, approximately 1 hour is required to reach equilibrium from the time of first contact. Interfacial tension as low as 0.2 mN/m can be measured by the modified pendant drop tensiometer. Data on acidic oil (10 mol/m^3) against 25 mol/m^3 caustic are shown in Fig. 5.6. It is noted in this case that as the interfacial reaction continues, the drop becomes elongated and unstable and subsequently detaches from the capillary tip. This can be improved by judicious choice of a capillary tip diameter to obtain stable drops but having the geometry required for interfacial tension calculation. Satherley et al. [111] successfully measured ultralow interfacial tensions for drops with a shape factor, β , more negative than -1.3.

The second test dealt with dynamic interfacial tension measurements. Dynamic interfacial tension measures changes in a liquid/liquid interface while new interfacial area is being created for the case of a droplet of *increasing* mass. The rate at which new interface is formed can be controlled and changed to study its effect on interfacial tension. The dynamic interfacial tension in this case is comprised of two parts, i.e. a compositional contribution which is a function of the instantaneous interfacial excess of surfactant species, and a rheological stress contribution which arises from the resistance to the deformation process by the interface [87]. The measurement can be performed on a growing drop or on a drop that has reached the equilibrium state. For the former case, a drop of oil is formed at a constant expansion rate while the interfacial tension is monitored automatically by the pendant drop tensiometer. This proceeds until the drop is detached from the capillary tip.

Figure 5.4: Transient interfacial tension for acidified paraffin oil (1 mol/m^3) against sodium dodecyl sulfate solution (7 mol/m^3).

Figure 5.5: Transient interfacial tension for acidified paraffin oil (1 mol/m^3) against sodium dodecyl sulfate (2 mol/m^3) and NaOH (2.5 mol/m^3) solution.

Figure 5.6: Transient interfacial tension for acidified paraffin oil (10 mol/m^3) against NaOH (25 mol/m^3) solution.

For the latter case, a drop of oil is injected into the aqueous phase and the interfacial tension is allowed to attain its equilibrium value. The drop is then expanded to a given final size depending on the expansion rate applied. Fig. 5.7 shows the change of volume, surface area and interfacial tension as a function of time at an expansion rate of $5.20 \times 10^{-5} \text{ cm}^3/\text{s}$. This mode of operation is similar to the technique described recently by Nagarajan and Wasan [87] who developed a novel method called expanding drop tensiometry.

The phenomenon of relaxation of the surfactant adsorption layer at the oil/water interface is receiving increasing interest [87,88,112]. Most of the experimental set-ups have been developed to study the relaxation behavior at liquid-gas interfaces and therefore a new method should be developed to study this effect at liquid-liquid interfaces. The modified pendant drop apparatus described in this work is suitable for this purpose. In this case, an oil drop is injected into the aqueous surfactant solution and the interfacial tension is monitored with time until a constant value is obtained. Then, the drop is subjected to some perturbation by increasing or decreasing its volume and consequently its interfacial area. Different modes of perturbation of the interfacial area can be applied to the drop by means of a programmable syringe pump, for example step, first-order and second-order. For a step perturbation, the volume is changed suddenly by ΔV and consequently the interfacial area by ΔA_s . This operation can be repeated as many times as required. A typical relaxation experiment is shown in Fig. 5.8 for the same system used in the previous section.

Figure 5.7: Dynamic experiment: volume, surface area and interfacial tension change as functions of time for a drop of paraffin oil expanding in sodium dodecyl sulfate solution (7 mol/m^3).

Figure 5.8: Transient relaxation experiment: Volume, surface area and interfacial tension change as functions of time for a drop of paraffin oil expanding in sodium dodecyl sulfate solution (7 mol/m^3).

Part III

**Models for Acidic Oil/Alkaline
Interactions**

Chapter 6

Development of the Equilibrium Model

In this chapter, an equilibrium model for the surfactant-enhanced alkali/acidic oil systems is presented. The proposed model represents an extension of the model describing the acidic oil/alkali systems [12]. The validity of the proposed model was examined experimentally using a system consisting of a simulated acidic oil, a surfactant and an alkali reagent.

6.1 Model Formulation

Figure 6.1 shows the proposed system chemistry for the contacting of an acidic oil with a solution containing an alkaline reagent and a surfactant. The proposed equilibrium model takes into account the dimerization of the acid in the oil and its partitioning between the oil and aqueous phases. The acid ionizes at the aqueous side of the interface forming a surface active anion (i.e. ionized acid). At a high sodium ion concentration, the ionized acid forms an undissociated sodium salt, which, according to Ramakrishnan and Wasan [12], partitions preferentially to the oil phase. It also takes into account the adsorption of the un-ionized acid along with the ionized acid

in a mixed interfacial layer [20,21].

The added surfactant is considered firstly to simultaneously adsorb at the interface with the ionized and un-ionized acid, and secondly to partition to the oil phase depending on its relative solubility in the oil. Thirdly, there is a possibility for it to form micelles in the aqueous phase depending on the ionic strength. When the un-ionized acid and the ionized acid are present, mixed micelles are formed. The micellization is modelled using either the phase separation model or the mass action model. In the phase separation model the micelle (which includes the counterions) is treated as a separate phase. The micelle and the unassociated surfactant ions are assumed to be in an association-dissociation equilibrium and the mass action model is applied.

6.2 Interfacial Reactions and Equilibria

Aspects of the system chemistry outlined by Chan and Yen [11] as well as by Ramakrishnan and Wasan [12] are incorporated in the present analysis. The un-ionized acid is represented as HX and the subscripts o and w refer to the oil phase and aqueous phase respectively. The reaction mechanism involves the following steps:

1. Dimerization of the acid in the oil phase;

with a dimerization constant, K_d , defined as:

$$K_d = \frac{C_{(HX_o)_2}}{C_{HX_o}^2} \quad (6.2)$$

where C_i is the concentration of species i at equilibrium.

Figure 6.1: Schematic of the acidic oil/alkali interactions.

2. Partitioning of the acid, HX , to the aqueous sublayer;

with a partition coefficient, K_p , defined as;

$$K_p = \frac{C_{HX_o}}{C_{HX_w}} \quad (6.4)$$

3. Dissociation of the acid at the aqueous side of the interface according to the reaction;

Reaction (6.5) is governed by an ionization constant, K_{HX}^D , given by the following;

$$K_{HX}^D = \frac{C_{H^+} C_{X^-}}{C_{HX_w}} \quad (6.6)$$

The equilibrium ionic concentrations are influenced by the ionic product of water according to the following equation;

$$K_w = C_{H^+} C_{OH^-} \quad (6.7)$$

4. Formation of the surface inactive soap complex at the aqueous side of the interface in accordance with the reaction;

with an associated equilibrium constant, K'_{NaX} , defined as;

$$K'_{NaX} = \frac{C_{Na^+} C_{X^-}}{C_{NaX_w}} \quad (6.9)$$

5. Preferential partition of the inactive soap complex to the oil phase with a distribution ratio, $K_{D,X}$, defined as;

$$K_{D,X} = \frac{C_{NaX_w}}{C_{NaX_o}} \quad (6.10)$$

By combining Eqs. (6.9) and (6.10), we can define a global equilibrium parameter governing the formation of NaX and its subsequent removal to the oil phase as follows;

$$\begin{aligned} K_{NaX}^D &= K'_{NaX} K_{D,X} \\ &= \frac{C_{Na^+} C_{X^-}}{C_{NaX_o}} \end{aligned} \quad (6.11)$$

6. Partition of the added surfactant to the oil phase in accordance with the following equilibrium;

with an associated constant, K_{NaS}^D , defined as;

$$K_{NaS}^D = \frac{C_{Na^+} C_{S^-}}{C_{NaS_o}} \quad (6.13)$$

7. Micelle formation by considering the following equilibria;

with a micellization constant, K_m , defined as;

$$K_m = \frac{C'_m}{(C'_{S^-})^n (C'_{Na^+})^{n(1-\alpha)}} \quad (6.15)$$

where C'_m is the concentration of micelles, n is the aggregation number for the added surfactant, and α is the fraction of unbound sites on the micelles.

6.3 Model Equations

6.3.1 Relating Anion Concentrations to the Equilibrium Parameters

If V_w and V_o are the volumes of the aqueous and oil phases respectively, and $C_{(HX_o)_i}$, $C_{(NaOH)_i}$ and $C_{(NaS_w)_i}$ are the initial concentrations of the acid in the oil, of the caustic in the aqueous phase, and of the added surfactant in the aqueous phase respectively, the conservation equations for the surface active species are written as follows:

1. Molal balance for X^- ;

$$V_w C_{HX_w} + V_w C_{X^-} + V_o C_{HX_o} + V_o C_{NaX_o} + 2V_o C_{(HX_o)_2} = V_o (C_{HX_o})_i \quad (6.16)$$

Rearrangement of Eq. (6.16) with use of the equilibrium relationships yields the following equation:

$$\left(\frac{V_w}{V_o} + \frac{V_w}{V_o} \frac{K_w}{K_{HX}^D C_{OH^-}} + \frac{K_w K_p}{K_{HX}^D C_{OH^-}} + \frac{C_{Na^+}}{K_{NaX}^D} \right) C_{X^-} + 2K_d \left(\frac{K_p K_w}{K_{HX}^D C_{OH^-}} \right)^2 C_{X^-}^2 = (C_{HX_o})_i \quad (6.17)$$

2. Molal balance for S^- ;

$$V_w C_{S^-} + V_o C_{NaS_o} + V_w M_S = V_w (C_{NaS_w})_i \quad (6.18)$$

where M_S is the concentration of the micelles. Rearrangement of Eq. (6.18) yields:

$$M_S = (C_{NaS_w})_i - \left(1 + \frac{V_o}{V_w} \frac{C_{Na^+}}{K_{NaS}^D} \right) C_{S^-} \quad (6.19)$$

3. Molal balance for Na^+ ;

$$V_w C_{Na^+} + V_o C_{NaX_o} + V_o C_{NaS_o} + V_w M_{Na} = V_w [(C_{NaOH})_i + (C_{NaS_w})_i] \quad (6.20)$$

$$M_{Na} = (1 - \alpha)M_S \quad (6.21)$$

where M_{Na} is the concentration of Na bound to the micelle. Rearrangement of Eq. (6.20) with the use of Eq. (6.21), yields:

$$C_{Na^+} = \frac{(C_{NaOH})_i + \alpha (C_{NaS_w})_i + (1 - \alpha)C_{S^-}}{\left(1 + \frac{V_o}{V_w} \frac{C_{X^-}}{K_{NaX}^D} + \alpha \frac{V_o}{V_w} \frac{C_{S^-}}{K_{NaS}^D}\right)} \quad (6.22)$$

4. Charge balance in the aqueous phase;

$$C_{Na^+} + C_{H^+} = C_{X^-} + C_{S^-} + C_{OH^-} + M_C \quad (6.23)$$

where

$$M_C = \alpha M_S \quad (6.24)$$

where M_C is the concentration of charges in the micelles. Rearrangement of Eq. (6.23) gives:

$$C_{Na^+} = \frac{C_{OH^-} + C_{X^-} + (1 - \alpha)C_{S^-} + \alpha (C_{NaS_w})_i}{\left(1 + \alpha \frac{V_o}{V_w} \frac{C_{S^-}}{K_{NaS}^D}\right)} \quad (6.25)$$

5. Combining Eq. (6.22) and Eq. (6.25) yields the OH^- balance:

$$\begin{aligned} C_{OH^-} &= (C_{NaOH})_i - \frac{V_o}{V_w} (C_{HX_o})_i \\ &+ \frac{V_o}{V_w} \left[\left(\frac{V_w}{V_o} \frac{K_w}{K_{HX}^D C_{OH^-}} + \frac{K_w K_p}{K_{HX}^D C_{OH^-}} \right) C_{X^-} + 2K_d \left(\frac{K_p K_w}{K_{HX}^D C_{OH^-}} \right)^2 C_{X^-}^2 \right] \end{aligned} \quad (6.26)$$

The system of equations obtained so far provides three equations and four unknowns. To completely describe the system chemistry, one needs another equation to be specified, which comes from the formation of micelles.

6.3.2 Micellar Relationships

Considering the equilibrium equation (6.14) and assuming monodispersed micelles, the mass action model gives the following expression for C'_m :

$$C'_m = K_m (C'_{S-})^n (C'_{Na+})^{n(1-\alpha)} \quad (6.27)$$

The exact expression for the micellization constant, K_m , at the critical micelle concentration is given by (see Appendix A):

$$\begin{aligned} K_m &= \left[\frac{\varepsilon}{n(1-\varepsilon)^n(1-\varepsilon+\alpha\varepsilon)^{n(1-\alpha)}} \right] \left(\frac{1}{CMC} \right)^{n(2-\alpha)-1} \\ &= F_m(\varepsilon) \left(\frac{1}{CMC} \right)^{n(2-\alpha)-1} \end{aligned} \quad (6.28)$$

where ε is the fraction of the surfactant in the micellar form.

A simplified form, where the factor $F_m(\varepsilon)$ is approaching unity, has been used by Fainerman [113] with a relatively low error. This error becomes essentially insignificant when evaluating the logarithm of K_m . Therefore, by expressing the micellization constant through the CMC, the expression for the monomer concentration can be obtained:

$$C_{S-} = \frac{(C_{NaS_w})_o - nC'_m}{\left(1 + \frac{V_o}{V_w} \frac{C_{Na+}}{K_{NaS}^D} \right)} \quad (6.29)$$

$$C_{S-} = \frac{(C_{NaS_w})_o - nF_m(\varepsilon) \left(\frac{C'_{S-}}{CMC} \right)^n \left(\frac{C'_{Na+}}{CMC} \right)^{n(1-\alpha)} CMC}{\left(1 + \frac{V_o}{V_w} \frac{C_{Na+}}{K_{NaS}^D} \right)} \quad (6.30)$$

The critical micelle concentration of the mixture system also needs to be known to complete the system of equations. It is a function of the ionic strength as well as of the acid concentration. This relationship is obtained experimentally from interfacial

tension data. The effect of the un-ionized and ionized acid concentrations on the CMC of the mixture is expressed by the following relationship as developed in Appendix A.

$$\frac{CMC}{CMC'} = 1 - K_{o,HX}C_{HX_w} - K_{o,X}C_{X^-} \quad (6.31)$$

The expression for CMC is substituted into Eq. (6.30) to give the final expression for C_{S^-} .

Eqs. (6.17), (6.26) and (6.30) are solved together with either Eq. (6.22) or Eq. (6.25) to obtain the concentrations C_{X^-} , C_{S^-} , C_{Na^+} , and C_{OH^-} . The surface concentrations are subsequently related to the interfacial tension through the adsorption isotherms as indicated below.

6.3.3 Relating Anion Concentration to Interfacial Tension

1. The adsorption isotherm derived by Davies [114] is used to relate the bulk concentrations of the anions, X^- and S^- , to the surface concentrations, Γ :

$$C_{X^-} = \left(\frac{B_2}{B_1}\right)_X \frac{\Gamma_{X^-}}{1-\theta} \exp\left(-\frac{W_X + N\epsilon\psi_o}{RT}\right) \quad (6.32)$$

$$C_{S^-} = \left(\frac{B_2}{B_1}\right)_S \frac{\Gamma_{S^-}}{1-\theta} \exp\left(-\frac{W_S + N\epsilon\psi_o}{RT}\right) \quad (6.33)$$

where W_j is the energy barrier for desorption of anion j per mole, B_1 is the adsorption rate constant, and B_2 is the desorption rate constant. According to Davies and Rideal [71], the ratio B_1/B_2 is independent of the hydrodynamics of the adsorption process and hence remains constant. We consider the adsorption of the un-ionized acid onto the interface to occur mainly from the oil-side of the interface. Adsorption from the water-side will be negligible compared to the oil-side adsorption, because C_{HX_w} is too low to affect the interfacial tension.

The adsorption isotherm for HX_o is given by:

$$C_{HX_o} = \left(\frac{B_2}{B_1} \right)_{HX_o} \frac{\Gamma_{HX_o}}{1 - \theta} \exp \left(-\frac{W_{HX}}{RT} \right) \quad (6.34)$$

where θ is the fractional surface covered by adsorption and is related to the surface species by [21]:

$$\theta = \frac{\Gamma_{X^-}}{\Gamma_{X^-,max}} + \frac{\Gamma_{HX_o}}{\Gamma_{HX_o,max}} + \frac{\Gamma_{S^-}}{\Gamma_{S^-,max}} \quad (6.35)$$

where $\Gamma_{j,max}$ is the maximum number of molecules per unit surface area for species j . It is assumed that the interface behaves ideally. This assumption is reasonable for a single ionic surfactant [115], but may not hold for a mixed interfacial layer.

2. The Gouy-Chapman model is used for the determination of the interfacial double layer potential:

$$\psi_o = -\frac{2kT}{\epsilon} \sinh^{-1} \left(\frac{\sigma}{\sqrt{C_{N_s^+}}} \sqrt{\left(\frac{500\pi}{D_c RT} \right)} \right) \quad (6.36)$$

where σ is the surface charge density and D_c is the dielectric constant of water.

Substitution of the values of the known quantities at 25°C yields:

$$\psi_o = -51.4 \sinh^{-1} \left(\frac{136.9}{A \sqrt{C_{N_s^+}}} \right) \quad (6.37)$$

3. The Frumkin-Volmer-Davies-Hachisu (FVDH) equation of state, previously adopted by Chiwetelu et al. [16], is used to relate the surface pressure Π , and thereby the interfacial tension γ , to the surface concentration of adsorbed species, Γ :

$$\Pi = \gamma_o - \gamma = \frac{kT}{A_o} \ln \left(\frac{A}{A - A_o} \right) + \sqrt{\frac{8D_c N C_{N_s^+} (kT)^3}{10^3 \epsilon^2 \pi}} \left(\cosh \left(\frac{\epsilon \psi_o}{2kT} \right) - 1 \right) \quad (6.38)$$

The areas A and A_o are evaluated in $\text{\AA}^2$ per ion as follows:

$$A = \frac{1}{\Gamma N 10^{-20}} \quad (6.39)$$

$$A_o = \frac{1}{\Gamma_{\max, m} N 10^{-20}} \quad (6.40)$$

where

$$\Gamma = \Gamma_{X^-} + \Gamma_{HX_o} + \Gamma_{S^-} \quad (6.41)$$

and

$$\begin{aligned} \frac{1}{\Gamma_{\max, m}} &= \frac{\Gamma_{X^-}}{\Gamma_{X^-} + \Gamma_{HX_o} + \Gamma_{S^-}} \frac{1}{\Gamma_{X^-, \max}} \\ &+ \frac{\Gamma_{HX}}{\Gamma_{X^-} + \Gamma_{HX_o} + \Gamma_{S^-}} \frac{1}{\Gamma_{HX_o, \max}} \\ &+ \frac{\Gamma_{S^-}}{\Gamma_{X^-} + \Gamma_{HX_o} + \Gamma_{S^-}} \frac{1}{\Gamma_{S^-, \max}} \end{aligned} \quad (6.42)$$

6.4 Solution of the Equilibrium Model Equations

6.4.1 Specification of the Model Parameters

The equilibrium model equations represent a system of coupled, non-linear algebraic relationships which must be solved simultaneously. The model parameters to be estimated are the equilibrium dissociation constants K_{HX}^D , K_{NaX}^D and K_{NaS}^D with the dependent variable being the surface pressure, Π . The independent variables which are determined experimentally are $(C_{HX_0})_i$, $(C_{NaOH})_i$, $(C_{NaS_w})_i$; and the phase volume ratio V_w/V_o . The remaining variables, namely K_p , K_d , W_i , B_2/B_1 and $\Gamma_{i,max}$ are considered as model constants and are evaluated on the basis of information available from the literature.

6.4.2 Model Constant Evaluation

B_1/B_2 Ratio

Based on the consideration of the thickness of the adsorbed film, Davies and Rideal [71] assigned a value of $20\text{\AA}$ for the ratio B_1/B_2 . This ratio was found to be independent of the hydrodynamics of the adsorption process, and consequently has a constant value.

Partition Coefficient, K_p

Tanford [116] proposed a relationship for the estimation of the partition coefficient of saturated fatty acid to be a linear function of the chain length. However, data reported for oleic as well as linoleic acid indicated that such an equation would not be quite appropriate for unsaturated acids. The use of Traube's Rule [72] does not improve the poor agreement with the reported data.

Adsorption Saturation, Γ_{max}

The adsorption saturation or maximum surface concentration, Γ_{max} , or alternatively A_o , values are generally obtained from the Π - A experimental data. The wide difference in the value of Γ_{max} reported in the literature resulted from the different techniques used for measuring the surface pressure, Π . Generally, Γ_{max} values obtained from surface or interfacial tension measurement were found to be lower than those obtained by direct measurement.

In this study, it was decided to determine these parameters by fitting experimental interfacial tension data for each interfacial active species independently, and comparing them with available literature values.

6.4.3 Solution Methodology

There are wide differences in the literature for the values of Γ_{max} , the distribution coefficient, K_p , the dimerization constant, K_d , and the adsorption energy, W_i . Since information available from the literature is often rather general in nature, the accuracy of the reported values is questionable. Therefore, the constants should be estimated together with the designed model parameters. However, this would lead to multiparameterization, which reduces the accuracy of parameter estimates [117]. This problem can be avoided when parameters from individual interfacial tension data are determined separately.

The objective function for the minimization problem is defined as the sum of squares of the residuals between the experimental and calculated interfacial tension. Explicitly, it can be written as:

$$SSR = \sum_{i=1}^m (\gamma_{exp} - \gamma_{cal})^2 \quad (6.43)$$

In this regression problem, the dependent variable, γ , is not explicitly related to one or more functions of the independent variables together with the model parameters.

The nonlinear parameter estimation routine of Levenberg-Marquardt [118,119] was employed. This routine, DUNLSF, is available from the IMSL packages [120] at the University of Ottawa. This routine is particularly suitable because it does not require analytical derivatives which are very difficult to evaluate due to the complexity of the problem. As in all parameter estimation problems, good initial guesses are important. In the present work, the initial guesses are obtained from literature values and then checked using the grid search method [121]. Input data include the pertinent initial acid concentration in the oil phase, caustic concentration and added surfactant concentration in the aqueous phase, and the experimental equilibrium interfacial tension data. For each data point, the routine DUNLSF is called by the main program. Then, the residuals are evaluated as well as the sum of squares of the residuals (SSR). The routine, DUNLSF, continuously seeks to minimize the SSR by an automatic adjustment of the values of the parameters until convergence is achieved. The convergence criteria are 10^{-5} between successive sums of squares of residuals, and an agreement in successive parameters estimates up to the fifth significant digit. The main program includes an integrated statistical analysis for the estimates and provides the 95% confidence intervals for the parameter estimates.

Chapter 7

Development of the Transient Model

7.1 Model Formulation

In this chapter, a diffusive-kinetic analysis of the interactions between acidic oil and aqueous surfactant-enhanced alkaline solutions is presented. The model is an extension of the acidic oil/alkaline interactions modelling [14,17], but includes the effects of the adsorption of an added surfactant on the interfacial tension behavior of the system under consideration. This analysis is not limited to applications in enhanced oil recovery, but also applies to processes such as liquid-liquid extraction, foaming and interfacial reactions in biological membranes.

For the system under investigation, the acid adsorbs at the interface and partitions itself from the oil phase to the aqueous sublayers from where it then undergoes ionization depending on its ionization constant as well as on the pH prevailing at the interface. The ionized acid (i.e. the soap anion) produced and the added surfactant adsorb at the interface in a mixed interfacial layer. As the active anions adsorb at the interface, an electrical double layer is set up with an interfacial potential which

depends on the total surface excess concentration. The model also features the formation of the inactive soap complex and its subsequent desorption to the bulk oil phase as well as the partition of the added surfactant to the bulk oil phase depending on its relative solubility in the oil.

In order to distinguish the diffusive steps from the sorptive-kinetic ones, the model allows for the existence of sublayers adjacent to the interface and having boundary layer thicknesses δ . The species transport from the bulk to the interface is modelled by the Nernst film theory which provides a simplified description of convective diffusion and has two advantages. Firstly, the effect of convection can be examined by altering the film thickness. Secondly, phases of arbitrary geometry can be considered as long as the film thickness is small in comparison to the local mean radius of curvature.

The transfer of the surface active species across the oil/water interface consists of the following steps:

- (i) Transfer of the reacting species from the bulk phases to the interface by convective diffusion;
- (ii) Interfacial reactions and associated equilibria leading to the formation of the surface active soap species;
- (iii) Transfer of reaction products from the interface to the bulk phases by convective diffusion;
- (iv) Surfactant adsorption and desorption resulting in variable surface excess concentration and consequently in variable transient interfacial tension phenomena.

A geometrical model of the interface has been constructed in accordance with the different steps outlined above (Figure 7.1). The principal assumptions used in the development of the transient model are listed below:

- (a) Single molecular transport is considered as surface active species are below their critical micellization concentrations,
- (b) Surface coverage is limited to a monolayer,
- (c) Ideal solution behavior of all interacting species in the bulk phases and at the interface,
- (d) Formation of a mixed interfacial layer with a diffusion boundary layer thickness, δ , on each side of the interface.

Figure 7.1: Geometrical model of the interface: transient model.

7.2 Interfacial Reactions and Related Equilibria

The process involves the following steps:

1. Adsorptive dissociation of acid,

2. Desorption of X^- to the aqueous sublayer,

3. Removal of X^- to the oil sublayer as the inactive complex NaX ,

4. Desorption of X^- to the aqueous sublayer as HX_w ,

5. Adsorption of S^-

6. Desorption of S^- to the oil sublayer as the complex NaS ,

7.3 Sorption Kinetic Rate Equations

Langmuirian sorption kinetics are employed to describe the adsorption and desorption of the surface active species, HX_o , X^- and S^- , to and from the interface according to the reactions outlined above.

- (i) Net rate of adsorption of X^- from the aqueous sublayer in accordance with Eq. 7.2,

$$R_{(a,X)} = k_a C_{X^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - k_d \Gamma_X \quad (7.7)$$

Using the notation introduced by Borwankar and Wasan [14], a new sorptive rate constant are defined as follows:

$$k_X = \frac{k_a}{\Gamma_{X,max}} \quad (7.8)$$

and equilibrium sorptive rate constant as follows:

$$K_X = \frac{k_a}{k_d \Gamma_{X,max}} \quad (7.9)$$

Eq. 7.7 is then expressed in terms of these new constants as follows;

$$R_{(a,X)} = k_X \Gamma_{X,max} \left[C_{X_{w,s}^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_X}{K_X} \right] \quad (7.10)$$

- (ii) Net rate of adsorption of HX_o from the oil sublayer in accordance with Eq. 7.1,

$$R_{(a,HX_o)} = k_{HX_o} \Gamma_{HX,max} \left[C_{HX_{o,s}} (1 - \theta) - \frac{\theta_{HX}}{K'_{HX}} - \frac{\theta_X}{K''_{HX}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.11)$$

- (iii) Adsorption of HX_w from the aqueous sublayer in accordance with Eq. 7.4,

$$R_{(a,HX_w)} = k_{HX_w} \Gamma_{HX,max} \left[C_{HX_{w,s}} (1 - \theta) - \frac{\theta_X}{K_{HX_w}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.12)$$

- (iv) Adsorption of NaX_o from the oil sublayer according to Eq. 7.3,

$$R_{(a,NaX_o)} = k_{NaX_o} \Gamma_{X,max} \left[C_{NaX_{o,s}} (1 - \theta) - \frac{\theta_X}{K_{NaX_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.13)$$

- (v) Adsorption of S^- from the aqueous sublayer in accordance with Eq. 7.5,

$$R_{(a,S_w)} = k_{S_w} \Gamma_{S,max} \left[C_{S_{w,s}^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_S}{K_{S_w}} \right] \quad (7.14)$$

(vi) Adsorption of NaS_o from the oil sublayer according to Eq. 7.6,

$$R_{(a,NaS_o)} = k_{NaS_o} \Gamma_{S,max} \left[C_{NaS_o,s} (1 - \theta) - \frac{\theta_S}{K_{NaS_o}} C_{Na+} \exp \left(-\frac{\epsilon\psi_o}{kT} \right) \right] \quad (7.15)$$

Following the scheme proposed by Borwankar and Wasan [14], the rate expressions for X^- and HX_w are combined through an association parameter, α , as follows:

$$\begin{aligned} R_{(a,X+HX_w)} &= R_{(a,X)} \exp \left(\frac{-\epsilon\psi_o}{kT} \right) \alpha \\ &= k_X \alpha \Gamma_{X,max} \left[C_{X_w,s} (1 - \theta) - \frac{\theta_X}{K_{X_w}} \exp \left(\frac{-\epsilon\psi_o}{kT} \right) \right] \end{aligned} \quad (7.16)$$

where the association parameter is given by the following expression;

$$\alpha = 1 + \frac{C_{H+}}{K_{HX}^D} \quad (7.17)$$

and with the assumption that:

$$D_{X_w} = D_{HX_w} \quad (7.18)$$

7.4 Species Bulk Transport

The Nernstian convective diffusion theory as outlined by Levich [122] and first adopted for this type of problem by Rubin and Radke [10], is employed to describe the transport of any given species from the bulk phase to the sublayer. The general expression may be written as follows;

$$V_j \frac{dC_i}{dt} = -\frac{A_s D_i}{\delta_j} (C_i - C_{i,s}) \quad (7.19)$$

and then can be expanded for all the relevant interfacial species of the transient system.

1. Transport of HX_o ,

$$V_o \frac{dC_{HX_o}}{dt} = -\frac{A_s D_{HX_o}}{\delta_o} (C_{HX_o} - C_{HX_o,s}) \quad (7.20)$$

2. Transport of $X_w^- + HX_w$,

$$V_w \alpha \frac{dC_{X^-}}{dt} = -\frac{A_s \alpha D_{X^-}}{\delta_w} (C_{X^-} - C_{X^-,s}) \quad (7.21)$$

3. Transport of NaX_o ,

$$V_o \frac{dC_{NaX_o}}{dt} = -\frac{A_s D_{NaX_o}}{\delta_o} (C_{NaX_o} - C_{NaX_o,s}) \quad (7.22)$$

4. Transport of S_w^- ,

$$V_w \frac{dC_{S^-}}{dt} = -\frac{A_s D_{S^-}}{\delta_w} (C_{S^-} - C_{S^-,s}) \quad (7.23)$$

5. Transport of NaS_o ,

$$V_o \frac{dC_{NaS_o}}{dt} = -\frac{A_s D_{NaS_o}}{\delta_o} (C_{NaS_o} - C_{NaS_o,s}) \quad (7.24)$$

7.5 Differential Equations of the Transient Model

Since the resistances due to the sorption kinetics and convective diffusion are in series and there is no net species accumulation in the sublayers, it is necessary that:

$$R(a, i) = \frac{D_i}{\delta_j} (C_i - C_{i,s}) \quad (7.25)$$

Equation 7.25 is used together with each of the sorptive kinetic rate expressions to solve for the sublayer concentrations, namely $C_{HX_{o,s}}$, $C_{NaX_{o,s}}$, $C_{X,s}$, $C_{NaS_{o,s}}$ and $C_{S,s}$. Thereafter, the expressions for the sublayer concentrations are substituted into the bulk transport equations. The resulting set of ordinary differential equations is as follows;

- (i) Diffusive kinetic equation for HX_o ;

$$V_o \frac{dC_{HX_o}}{dt} = - \frac{D_{HX_o} A_s k_{HX_o} \Gamma_{HX,max}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta) + D_{HX_o}]}$$

$$\left[C_{HX_o}(1-\theta) - \frac{\theta_{HX}}{K'_{HX}} - \frac{\theta_X}{K''_{HX}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.26)$$

(ii) Diffusive kinetic equation for NaX_o ;

$$V_o \frac{dC_{NaX_o}}{dt} = - \frac{D_{NaX_o} A_s k_{NaX_o} \Gamma_{X,max}}{[k_{NaX_o} \delta_o \Gamma_{NaX,max} (1-\theta) + D_{NaX_o}]} \left[C_{NaX_o}(1-\theta) - \frac{\theta_X}{K_{NaX_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.27)$$

(iii) Diffusive kinetic equation for $(X^- + HX_w)$;

$$V_w \frac{dC_{X_w^-}}{dt} = - \frac{D_{X_w^-} A_s k_{X_w^-} \Gamma_{X,max}}{[k_{X_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{X,max} (1-\theta) + D_{X_w^-}]} \left[C_{X_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1-\theta) - \frac{\theta_X}{K_{X_w^-}} \right] \quad (7.28)$$

(iv) Diffusive kinetic equation for S^- ;

$$V_w \frac{dC_{S_w^-}}{dt} = - \frac{D_{S_w^-} A_s k_{S_w^-} \Gamma_{S,max}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{S,max} (1-\theta) + D_{S_w^-}]} \left[C_{S_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1-\theta) - \frac{\theta_S}{K_{S_w^-}} \right] \quad (7.29)$$

(v) Diffusive kinetic equation for NaS_o ;

$$V_o \frac{dC_{NaS_o}}{dt} = - \frac{D_{NaS_o} A_s k_{NaS_o} \Gamma_{S,max}}{[k_{NaS_o} \delta_o \Gamma_{NaS,max} (1-\theta) + D_{NaS_o}]} \left[C_{NaS_o}(1-\theta) - \frac{\theta_S}{K_{NaS_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.30)$$

(vi) Diffusive kinetic equation governing acid accumulation at the interface, θ_{HX} :

$$\frac{d\theta_{HX_o}}{dt} = \frac{D_{HX_o} k_{HX_o}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1-\theta) + D_{HX_o}]} \left[C_{HX_o}(1-\theta) - \frac{\theta_{HX}}{K'_{HX}} - \frac{\theta_X}{K''_{HX}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.31)$$

(vii) Diffusive kinetic equation governing in-situ surfactant accumulation at the interface, θ_X :

$$\begin{aligned}
\frac{d\theta_X}{dt} = & \frac{D_{NaX_o} k_{NaX_o}}{[k_{NaX_o} \delta_o \Gamma_{X,max} (1 - \theta) + D_{NaX_o}]} \\
& \left[C_{NaX_o} (1 - \theta) - \frac{\theta_X}{K_{NaX_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \\
& + \frac{D_{X_w^-} \alpha k_{X_w^-}}{[k_{X_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{X,max} (1 - \theta) + D_{X_w^-}]} \\
& \left[C_{X_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_X}{K_{X_w^-}} \right] \quad (7.32)
\end{aligned}$$

- (viii) Diffusive kinetic equation governing added surfactant accumulation at the interface, θ_S :

$$\begin{aligned}
\frac{d\theta_S}{dt} = & \frac{D_{S_w^-} k_{S_w^-}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{S,max} (1 - \theta) + D_{S_w^-}]} \\
& \left[C_{S_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_S}{K_{S_w^-}} \right] \\
& + \frac{D_{NaS_o} k_{NaS_o}}{[k_{NaS_o} \delta_o \Gamma_{S,max} (1 - \theta) + D_{NaS_o}]} \\
& \left[C_{NaS_o} (1 - \theta) - \frac{\theta_S}{K_{NaS_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (7.33)
\end{aligned}$$

The above ordinary differential equations together with the global algebraic relationships presented in Chapter 6 characterize the overall interfacial behavior of the system.

Chapter 8

Solution of the Transient Model Equations

8.1 Specification of the Model Parameters

The system consists of seven coupled non-linear ordinary differential equations, which must be solved simultaneously along with the algebraic equations. The parameters of the regression problem are the kinetic rate constants k_{HX_o} , k_{NaX_o} , k_{X_w} , k_{NaS_o} and k_{S_w} . With the understanding that adsorption barriers and desorption barriers refer to the net effect produced by the reversible kinetic steps, k_{HX_o} and k_{S_w} characterize the adsorption barriers, and k_{X_w} , k_{NaX_o} and k_{NaS_o} are measures of the desorption barriers. The specification of the model constant is as follows;

- (a) Independent variables :

$$V_w, V_o, A_s, C_{OH^-} \text{ and } C_{Na^+}.$$

- (b) Model constants Type 1: equilibrium parameters;

$$K'_{HX_o}, K''_{HX_o}, K_{NaX_o}, K_{X_w}, K_{NaS_o}, K_{S_w} \text{ and } \Gamma_{i,max}.$$

- (c) Model constants Type 2: boundary layer thickness;

$$\delta_o \text{ and } \delta_w.$$

(d) Model constants Type 3: Fickian diffusion coefficients;

$$D_{HX_o}, D_{NaX_o}, D_{X_w}, D_{NaS_o} \text{ and } D_{S_w}.$$

8.1.1 Calculation of the Equilibrium Sorptive Constants

The Langmuir model equation can be written in the well known form as follows:

$$K_{L,i}C_i = \frac{\theta_i}{1 - \sum_j \theta_j} \exp\left(\frac{\epsilon\phi_0}{kT}\right) \quad (8.1)$$

where the equilibrium constants, $K_{L,i}$, in $m^3/mole$ are defined as:

$$K_{L,i} = \left(\frac{B_1}{B_2}\right) \frac{\exp\left(\frac{W_i}{RT}\right)}{\Gamma_{i,max}} \quad (8.2)$$

The desorption energy, W_i , and the saturation adsorption, $\Gamma_{i,max}$, are obtained from the equilibrium study developed in Chapter 6. Eq. 8.2 is used for the determination of the equilibrium sorptive constants K'_{HX_o} , K_{X_w} , and K_{S_w} .

Other equilibrium constants

K''_{HX_o} :

In accordance with Eq. 7.1, K''_{HX_o} is given by the following relationship

$$K''_{HX_o} = \frac{[X_{ads}^-][H^+]}{[HX_o]} \quad (8.3)$$

By definition, K^D_{HX} is given by

$$K^D_{HX} = \frac{[X_w^-][H^+]}{[HX_w]} \quad (8.4)$$

and the partition coefficient, K_p , is as follows

$$K_p = \frac{[HX_o]}{[HX_w]} \quad (8.5)$$

The combination of Eqs. 8.3, 8.4 and 8.5, gives

$$K''_{HX_o} = \frac{K_{X_w} K_{HX}^D}{K_p} \quad (8.6)$$

K_{NaX_o} :

Using Eq. 7.3, the expression for K_{NaX_o} may be written as follows

$$K_{NaX_o} = \frac{[X_{ads}^-][Na^+]}{[NaX_o]} \quad (8.7)$$

By definition, K_{NaX}^D is written as follows

$$K_{NaX}^D = \frac{[X_w^-][Na^+]}{[NaX_o]} \quad (8.8)$$

then the combination of Eqs. 8.7 and 8.8 leads to the following relationship

$$K_{NaX_o} = K_{X_w} K_{NaX}^D \quad (8.9)$$

K_{NaS_o} :

Similarly, the expression for K_{NaS_o} is given by

$$K_{NaS_o} = K_{S_w} K_{NaS}^D \quad (8.10)$$

8.1.2 Calculation of the Boundary Layer Thicknesses

The boundary layer thickness, δ , characterizes the magnitude of the convection currents in the vicinity of the interface. For a typical situation, δ can vary from 1000 μm or more when there is just natural convection and no stirring, to about 10 μm when there is significant forced convection [122]. Based on the approximate solution to the convective diffusion equation derived by Levich [122], Chiwetelu [17] derived an expression to estimate the boundary layer thickness:

$$\delta \propto D^{\frac{1}{3}} \nu^{\frac{1}{6}} \quad (8.11)$$

This relationship can be used to calculate δ for any given system, provided that the value for a reference system is available. The analysis leading to the evaluation of the pertinent variable is developed on the basis of the work done by deZabala [13] as well as by Rubin and Radke [10]. For the sake of simplicity, the same procedure is used in this work.

8.1.3 Calculation of the Diffusion Coefficients

The generalized Wilke-Chang correlation [123] is used for estimation of the diffusion coefficients in paraffinic solvent as well as in water with different association parameters, ω_d . The association parameter assumes a value of 1 for the oil solvent and a value of 2.6 for water. The generalized correlation is given by:

$$D_{AB}^o = \frac{7.4 \times 10^{-8} \sqrt{\omega_d M_B T}}{\eta V_A^{0.6}} \quad (8.12)$$

where

T	absolute temperature
η	viscosity of solution
V_A	molar volume of solute
ω_d	association parameter for solvent
M_B	molecular weight of solvent

The molar volume of solute is estimated by the correlation of Tyn and Calus [124]

which is given by:

$$V_A = 0.285 V_c^{1.048} \quad (8.13)$$

where V_c is the critical volume. The critical volumes are obtained by Vetere's method [125].

The applicable relationship is as follows:

$$V_c = 33.04 + \left(\sum \Delta V_i M_i \right)^{1.029} \quad (8.14)$$

8.2 Solution Methodology

The solution methodology adopted to solve this regression problem consists of estimating the kinetic parameters and solving the differential equations simultaneously. This analysis is referred to as parameters estimation in differential equations. The best estimates of these parameters are taken as those that minimize the sum of squares of deviations between the observed and predicted response variable, i.e. the interfacial tension. After conversion of the estimation algorithm, the model adequacy is confirmed by checking for discrepancies between observed and predicted values of the response, and analyzing the residual plots. Non-random plots of residuals versus predicted values of the response indicates lack of fit. Plots of the observed values of the response versus the predicted values offer an easy way to detect inadequacies.

The non-linear iterative method of Levenberg-Marquardt [119] that produces least squares estimates of the parameters is applied to solve this problem. The IMSL [120] routine DUNLSF is found appropriate for this task and the IMSL [120] routine DIVPAG is used for the solution of the differential equations. However, in view of the stiffness of the equations, the analytical Jacobian matrix of partial derivations is required as input to the algorithm. Transient interfacial tension data including the interfacial area and the volume of the drop are supplied to the main program. Also supplied are the various model parameters calculated in the previous section. The grid search method is used to obtain good initial guesses for the regression problem. The procedure first evaluates the residual sum of squares at each combination of starting values. The starting values with the lowest sum of squares then serve as the initial estimates of the parameters.

In order to obtain a better understanding of the mechanisms for the interactions between acidic oil and the aqueous surfactant-alkaline mixture, the procedure used in the analysis of the equilibrium model is adopted here. The procedure consists of modelling the interfacial activity of each surface active species. Interfacial tension data for these systems, namely, carboxylic acid, surfactant, carboxylic acid-alkaline, and carboxylic acid-surfactant are available. Interfacial activity of the binary and tertiary systems is then checked using results from the individual analysis. The diffusion kinetic equations for each of the models are presented in the next section.

8.2.1 Diffusion Kinetics of the Acidified Oil/Water System

$$V_o \frac{dC_{HX_o}}{dt} = - \frac{D_{HX_o} A_s k_{HX_o} \Gamma_{HX,max}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta_{HX}) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta_{HX}) - \frac{\theta_{HX}}{K_{HX}} \right] \quad (8.16)$$

$$V_w \frac{dC_{HX_w}}{dt} = - \frac{D_{HX_w} A_s k_{HX_w} \Gamma_{HX,max}}{[k_{HX_w} \delta_w \Gamma_{HX,max} (1 - \theta_{HX}) + D_{HX_w}]} \left[C_{HX_w} (1 - \theta_{HX}) - \frac{\theta_{HX}}{K_{HX}} \right] \quad (8.17)$$

$$\begin{aligned} \frac{d\theta_{HX}}{dt} = & \frac{D_{HX_o} k_{HX_o}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta_{HX}) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta_{HX}) - \frac{\theta_{HX}}{K_{HX}} \right] \\ & + \frac{D_{HX_w} k_{HX_w}}{[k_{HX_w} \delta_w \Gamma_{HX,max} (1 - \theta_{HX}) + D_{HX_w}]} \left[C_{HX_w} (1 - \theta_{HX}) - \frac{\theta_{HX}}{K_{HX}} \right] \end{aligned} \quad (8.18)$$

8.2.2 Diffusion Kinetics of the Acidified Oil/Caustic System

$$V_o \frac{dC_{HX_o}}{dt} = - \frac{D_{HX_o} A_s k_{HX_o} \Gamma_{HX,max}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta) - \frac{\theta_{HX}}{K'_{HX}} - \frac{\theta_X}{K''_{HX}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (8.23)$$

$$V_o \frac{dC_{NaX_o}}{dt} = - \frac{D_{NaX_o} A_s k_{NaX_o} \Gamma_{X,max}}{[k_{NaX_o} \delta_o \Gamma_{X,max} (1 - \theta) + D_{NaX_o}]} \left[C_{NaX_o} (1 - \theta) - \frac{\theta_X}{K_{NaX_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (8.24)$$

$$V_w \frac{dC_{X_w^-}}{dt} = - \frac{D_{X_w^-} A_s k_{X_w^-} \Gamma_{X,max}}{[k_{X_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{X,max} (1 - \theta) + D_{X_w^-}]} \left[C_{X_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_X}{K_{X_w^-}} \right] \quad (8.25)$$

$$\frac{d\theta_{HX_o}}{dt} = \frac{D_{HX_o} k_{HX_o}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta) - \frac{\theta_{HX}}{K'_{HX}} - \frac{\theta_X}{K''_{HX}} C_{H^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \quad (8.26)$$

$$\begin{aligned} \frac{d\theta_X}{dt} = & \frac{D_{NaX_o} k_{NaX_o}}{[k_{NaX_o} \delta_o \Gamma_{X,max} (1 - \theta) + D_{NaX_o}]} \left[C_{NaX_o} (1 - \theta) - \frac{\theta_X}{K_{NaX_o}} C_{Na^+} \exp\left(-\frac{\epsilon\psi_o}{kT}\right) \right] \\ & + \frac{D_{X_w^-} k_{X_w^-}}{[k_{X_w^-} \delta_w \exp\left(\frac{\epsilon\psi_o}{kT}\right) \Gamma_{X,max} (1 - \theta) + D_{X_w^-}]} \left[C_{X_w^-} \exp\left(\frac{\epsilon\psi_o}{kT}\right) (1 - \theta) - \frac{\theta_X}{K_{X_w^-}} \right] \end{aligned} \quad (8.27)$$

8.2.3 Diffusion Kinetics of the Oil/Surfactant System

$$S_{w,s}^- \stackrel{K_s}{\rightleftharpoons} S_{ads}^- \quad (8.28)$$

$$S_{ads}^- + Na^+ \stackrel{K_{NaS}}{\rightleftharpoons} NaS_{o,s} \quad (8.29)$$

$$V_w \frac{dC_{S_w^-}}{dt} = - \frac{D_{S_w^-} A_s k_{S_w^-} \Gamma_{S,max}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon \psi_o}{kT}\right) \Gamma_{S,max} (1 - \theta_S) + D_{S_w^-}] \left[C_{S_w^-} \exp\left(\frac{\epsilon \psi_o}{kT}\right) (1 - \theta_S) - \frac{\theta_S}{K_{S_w^-}} \right]} \quad (8.30)$$

$$V_o \frac{dC_{NaS_o}}{dt} = - \frac{D_{NaS_o} A_s k_{NaS_o} \Gamma_{S,max}}{[k_{NaS_o} \delta_o \Gamma_{S,max} (1 - \theta_S) + D_{NaS_o}] \left[C_{NaS_o} (1 - \theta_S) - \frac{\theta_S}{K_{NaS_o}} C_{Na^+} \exp\left(-\frac{\epsilon \psi_o}{kT}\right) \right]} \quad (8.31)$$

$$\begin{aligned} \frac{d\theta_S}{dt} = & \frac{D_{S_w^-} k_{S_w^-}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon \psi_o}{kT}\right) \Gamma_{S,max} (1 - \theta_S) + D_{S_w^-}] \left[C_{S_w^-} \exp\left(\frac{\epsilon \psi_o}{kT}\right) (1 - \theta_S) - \frac{\theta_S}{K_{S_w^-}} \right]} \\ & + \frac{D_{NaS_o} k_{NaS_o}}{[k_{NaS_o} \delta_o \Gamma_{S,max} (1 - \theta_S) + D_{NaS_o}] \left[C_{NaS_o} (1 - \theta_S) - \frac{\theta_S}{K_{NaS}} C_{Na^+} \exp\left(-\frac{\epsilon \psi_o}{kT}\right) \right]} \end{aligned} \quad (8.32)$$

8.2.4 Diffusion Kinetics of the Acidified Oil/Surfactant System

$$V_o \frac{dC_{HX_o}}{dt} = - \frac{D_{HX_o} A_s k_{HX_o} \Gamma_{HX,max}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta) - \frac{\theta_{HX}}{K_{HX}} \right] \quad (8.36)$$

$$V_w \frac{dC_{HX_w}}{dt} = - \frac{D_{HX_w} A_s k_{HX_w} \Gamma_{HX,max}}{[k_{HX_w} \delta_w \Gamma_{HX,max} (1 - \theta) + D_{HX_w}]} \left[C_{HX_w} (1 - \theta) - \frac{\theta_{HX}}{K_{HX}} \right] \quad (8.37)$$

$$V_w \frac{dC_{S_w^-}}{dt} = - \frac{D_{S_w^-} A_s k_{S_w^-} \Gamma_{S,max}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon \psi_o}{kT}\right) \Gamma_{S,max} (1 - \theta) + D_{S_w^-}]} \left[C_{S_w^-} \exp\left(\frac{\epsilon \psi_o}{kT}\right) (1 - \theta) - \frac{\theta_S}{K_{S_w^-}} \right] \quad (8.38)$$

$$V_o \frac{dC_{NaS_o}}{dt} = - \frac{D_{NaS_o} A_s k_{NaS_o} \Gamma_{S,max}}{[k_{NaS_o} \delta_o \Gamma_{S,max} (1 - \theta) + D_{NaS_o}]} \left[C_{NaS_o} (1 - \theta) - \frac{\theta_S}{K_{NaS_o}} C_{Na^+} \exp\left(-\frac{\epsilon \psi_o}{kT}\right) \right] \quad (8.39)$$

$$\begin{aligned} \frac{d\theta_{HX}}{dt} &= \frac{D_{HX_o} k_{HX_o}}{[k_{HX_o} \delta_o \Gamma_{HX,max} (1 - \theta) + D_{HX_o}]} \left[C_{HX_o} (1 - \theta) - \frac{\theta_{HX}}{K_{HX}} \right] \\ &+ \frac{D_{HX_w} k_{HX_w}}{[k_{HX_w} \delta_w \Gamma_{HX,max} (1 - \theta) + D_{HX_w}]} \left[C_{HX_w} (1 - \theta) - \frac{\theta_{HX}}{K_{HX}} \right] \end{aligned} \quad (8.40)$$

$$\begin{aligned} \frac{d\theta_{S_w^-}}{dt} &= \frac{D_{S_w^-} k_{S_w^-}}{[k_{S_w^-} \delta_w \exp\left(\frac{\epsilon \psi_o}{kT}\right) \Gamma_{S,max} (1 - \theta) + D_{S_w^-}]} \left[C_{S_w^-} \exp\left(\frac{\epsilon \psi_o}{kT}\right) (1 - \theta) - \frac{\theta_S}{K_{S_w^-}} \right] \\ &+ \frac{D_{NaS_o} k_{NaS_o}}{[k_{NaS_o} \delta_o \Gamma_{S,max} (1 - \theta) + D_{NaS_o}]} \left[C_{NaS_o} (1 - \theta) - \frac{\theta_S}{K_{NaS}} C_{Na^+} \exp\left(-\frac{\epsilon \psi_o}{kT}\right) \right] \end{aligned} \quad (8.41)$$

Part IV

Results and Discussion

Chapter 9

Equilibrium Model Analysis

Equilibrium interfacial tension data for acidic oil/surfactant and caustic mixtures are presented in this chapter. Equilibrium interfacial tension measurements are carried out with preequilibrated samples. These samples are made by periodically shaking equal volumes of aqueous and oil phases for one month at a constant temperature of 25 °C. The physical properties of the oil and aqueous solutions are listed in Appendix C tables C1-C3.

Pertinent parameter estimates are obtained for single and binary mixtures. Using these parameters, the model for the interaction between acidic oil/ surfactant-enhanced caustic systems is validated. The effects of initial acid concentration in the oil phase as well as the effects of the caustic concentration in the aqueous phase on the micellization and the adsorption parameters of the added surfactant, sodium dodecyl sulfate, are investigated and semi-empirical relationships are developed between them.

9.1 Acidified Oil/Alkaline Systems

In the absence of added alkali, the interfacial tension of the acidic oil/water system can be calculated using Eq. (6.16), Eq. (6.33) and Eq. (6.37) while omitting the electrical term in the proposed model. In Eq. (6.16), the terms for ionized acid and undissociated salt will be negligible when no alkali is added. The acid parameters, namely $A_{o,HX}$, W_{HX} , K_p and K_d , can therefore be determined from the fitting of experimental interfacial tension data. The parameter estimates for linoleic acid dissolved in paraffin oil are listed in Table 9.1. The reference interfacial tension, γ_o , corresponds to the interfacial tension of pure paraffin oil against water and is measured to be 51.7 mN/m. This value is within the expected range of hydrocarbon interfacial tensions against water. For comparison, the interfacial tension for decane/water is measured to be 50 mN/m, which is in good agreement with literature values [72]. Fig. 9.1 shows a comparison between the experimental and predicted interfacial tension as a function of initial acid concentration. The agreement is very good in the limit of no added alkali. Fig. 9.1 also shows that the interfacial tension decreases steadily with increasing acid concentration up to 100 mol/m³ indicating not only that the acid is surface active, but also that the interfacial tension is dependent upon the concentration of acid in the oil phase, not in the water phase. Shown in Fig 9.2 is a plot of the residuals versus the measured and predicted response. This plot indicates the adequacy of the proposed model for the interfacial activity of the acid.

For the acidic oil/alkali system, three initial acid concentrations are used, namely 0.1, 1 and 10 mol/m³. The NaOH concentration is varied from 0.25 to 250 mol/m³. The model equations for acidic oil/alkali system are applicable at low acid concentrations. When the acid concentration is high, the concentration of the ionized acid in the

aqueous phase will be sufficient to form micelles and the model developed by Rudin and Wasan [21] is more appropriate. Under such conditions, the model Eqs. 6.17 and 6.26 are solved together with either Eq. 6.22 or 6.25, excluding the terms for added surfactant, to yield C_{X-} , C_{OH-} and C_{Na+} . Using the adsorption isotherms, Eqs. 6.31 and 6.33, the interfacial tension can be then obtained using Eq. 6.37.

Equilibrium interfacial tension data for the acidic oil/alkali solutions as a function of acid concentration are shown in Fig 9.3. This figure indicates that the interfacial tension depends on the alkali concentration as well as on the acid concentrations. The very marked drop of the interfacial tension is an indication of the high effectiveness of the ionized acid as a surfactant even at such a low concentration.

Fig. 9.3 shows a comparison between the experimental and predicted interfacial tensions. As mentioned before, a good agreement is obtained for the low acid concentrations of 0.1 and 1 mol/m³ respectively. As seen in Fig. 9.3, the agreement for 10 mol/m³ acid concentration is satisfactory in the limiting case when the micellization is not accounted for. In this case it is believed that the micellization, in addition to the partition of the undissociated salt into the oil phase, reduces the concentration of the ionized acid and hence the interfacial tension increases, resulting in a minimum near the critical micelle concentration. The residual plot is shown in Fig 9.4 and indicates no particular trends for the predicted interfacial tension.

The parameters for the ionized acid obtained by non-linear regression are shown in Table 9.2. The desorption energy, W_X , is lower than what would be expected from the Davies and Rideal [72] equation, which uses 3385 J per CH_2 group and the number of carbons evaluated by Traube's Rule. The ionization constant as shown in Table 9.2, decreases as the initial acid concentration is increased from 0.1 to 10

mol/m³. This marked dependence of the ionization constant on acid concentration was also observed by Chiwetelu et al. [16] for solutions of oil acid in hexadecane. Patil et al. [67] observed the same trend for C₁₄-C₁₈ fatty acids. They reported that the apparent ionization constants varied not only with acid concentration, but also with the electrical field strength of the aqueous phase as well as the applicable surface pressure. The equilibrium constant, K_{NaX}^D , showed only a marginal change with the acid concentration increase. The high values of K_{NaX}^D indicate that the ionized acid is preferentially partitioning into the oil phase.

Figure 9.1: Experimental and predicted interfacial tension of acidified paraffin oil against distilled water.

Figure 9.2: Residual plot.

Figure 9.3: Experimental and predicted interfacial tension of acidified oil/caustic solutions at different acid concentrations.

Figure 9.4: Residual plot.

Table 9.1: Adsorption parameters for un-ionized acid.

Parameters	Measured	Literature
$A_{0,HX} (\text{\AA}^2)$	28.07 ± 1.45	20–35 [126]
$W_{HX} (J/mol)$	22945 ± 670	20000–23000 [71]
K_p	$(4.500 \pm 0.254) \times 10^5$	
$K_d (l/mol)$	$(3.026 \pm 0.107) \times 10^3$	

Table 9.2: Adsorption parameters for ionized acid.

Parameters	Acid concentration (mol/m^3)		
	0.1	1.0	10.0
$A_{0,X} (\text{\AA}^2)$		41.50 ± 1.67	
$W_X (J/mol)$		51481 ± 1233	
$K_{HX}^D (mol/l)$	6.982×10^{-6}	$(4.438 \pm 0.234) \times 10^{-6}$	1.124×10^{-6}
$K_{NaX}^D (mol/l)$	2.624×10^{-3}	$(1.133 \pm 0.108) \times 10^{-3}$	1.643×10^{-4}

9.2 Acidified Oil/Surfactant Systems

It is well known that the interfacial or surface tension of a surfactant solution remains constant when the surfactant concentration exceeds the critical micelle concentration. To be able to predict the interfacial tension, one needs to calculate the monomer and counter-ion concentrations as a function of the total surfactant concentration. In this case the mass action model is adopted. Moroi [127] reported that the mass action model is applicable for the micelle formation of sodium dodecyl sulfate. The model equations 6.22, 6.25 and 6.30 are solved for the monomer and counter-ion concentrations in the absence of any added acid and alkali. The interfacial tension is then obtained using the adsorption isotherm and the equation of state. The micellization parameters, namely α and n , are taken from the literature [127] and subsequently checked against the calculated values. The critical micelle concentration of sodium dodecyl sulfate is obtained from the interfacial tension data and is found to be 8 mol/m^3 for the paraffin oil/water interface compared to 8.5 mol/m^3 for the decane/water interface. The estimated value for $\log K_m$ using Eq. 6.28 is 232, a value which is close to the value of 230 obtained by Moroi [127].

Figs. 9.5 and 9.7 show the comparison between the experimental and predicted interfacial tensions as a function of the surfactant concentration for paraffin oil/water and decane/water systems respectively. The good agreement reflects the applicability of the mass action model to micelle formation. The parameter estimates for sodium dodecyl sulfate at the paraffin oil/water interface as well at the decane/water interface are shown in Table 9.3. The calculated parameters for sodium dodecyl sulfate at the decane/water interface compared very well with the literature values as shown in Table 9.3.

Fig. 9.9 shows the effect of acid concentration on interfacial tension behavior of sodium dodecyl sulfate solutions. It is evident that the acid has the effect of reducing the interfacial tension obtainable with sodium dodecyl sulfate alone. An increase in initial acid concentration causes the interfacial tension to be lower at all surfactant concentrations. The acid is seen to reduce the critical micelle concentration of the added surfactant in a systematic way and especially at high acid concentrations. Similar behavior has been reported by Shinoda [128,129] and Nishikido [130], for the case of alcohol/surfactant mixtures, and they explained this behavior by the formation of mixed micelles. Recently, Rudin and Wasan [19-20] showed that oleic acid in the aqueous phase behaved in a way similar to that of an alcohol in forming a mixed micelle with its soap. Therefore, acid appears to be adsorbing onto the interface, resulting in an interfacial tension lower than that of the added surfactant alone, and in the formation of mixed micelles. The present finding is similar to that reported by Rudin and Wasan [19] except that the added surfactant used in the present study is highly water soluble, and the acid is unable to partition it out of the aqueous phase. This explains the absence of any minimum in interfacial tension as acid concentration is increased.

The adsorption parameters and the critical micelle concentrations as a function of acid concentration are shown in Table 9.4. Although there is no significant variation in the adsorption parameters, the critical micelle concentration is found to be dependent on the concentration of the acid. The following relationship expresses the variation of the normalized critical micelle concentration as a function of acid concentration in the aqueous phase, C_{HX_w} , as obtained from the measured interfacial tension.

$$\frac{CMC'}{CMC} = 1 - K_{o,HX} C_{HX_w} \quad (9.1)$$

where CMC' is the critical micelle concentration of the mixture. This equation is equivalent to Eq. 21 developed by Rudin and Wasan [21]. Their equation is applied at and above the critical micelle concentration using the phase separation model. Fig. 9.11 shows a plot of the normalized critical micelle concentration as a function of the acid concentration in the aqueous phase. The plot is linear with a slope of $7.024 \times 10^4 \text{ m}^3/\text{mol}$ and an intercept of 0.995.

As mentioned before, it is necessary to investigate the effect of the concentration of NaOH on the critical micelle concentration as well as on the adsorption parameters. Fig. 9.12 shows the effect of NaOH concentration on the interfacial tension of sodium dodecyl sulfate, from which the critical micelle concentration values were obtained. The corresponding residual plot is shown in Fig. 9.13. Table 9.5 lists the adsorption parameters and the critical micelle concentration at different NaOH concentrations. When the NaOH concentration increases, the maximum adsorption of the surfactant increases owing to the change in the electrical potential at the oil/water interface. The desorption energy in turn changes from 45000 J/mol for neutral water to 40000 J/mol when NaOH is added. A very significant decrease of the critical micelle concentration accompanying the increase of the NaOH concentration is obtained. A log-log plot of the critical micelle concentration as a function of NaOH concentration is as expected, a straight line (Fig. 9.14). The regression analysis gives the following empirical relationship between the critical micelle concentration and NaOH concentrations in mol/l:

$$\log CMC = -3.232 - 0.537 \log(C_{NaOH}) \quad (9.2)$$

Figure 9.5: Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system.

Figure 9.6: Residual plot.

Figure 9.7: Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for decane/water system.

Figure 9.8: Residual plot.

Figure 9.9: Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system at different acid concentrations.

Figure 9.10: Residual plot.

Figure 9.11: Effect of acid concentration in the aqueous phase on the normalized critical micelle concentration of sodium dodecyl sulfate.

Figure 9.12: Experimental and predicted interfacial tension as a function of sodium dodecyl sulfate concentration for paraffin oil/water system at different NaOH concentrations.

Figure 9.13: Residual plot.

Figure 9.14: Effect of NaOH concentration on the critical micelle concentration of sodium dodecyl sulfate.

Table 9.3: Adsorption and micellization parameters for sodium dodecyl sulfate.

Parameters	Paraffin oil	Decane	
		Measured	Literature
$A_{0,S} (\text{\AA}^2)$	80.00 ± 3.00	44.93 ± 2.20	45.00 [131]
$W_S (\text{J/mol})$	45000 ± 630	40205 ± 420	41600 [131]
CMC (mol/m^3)	8.0	8.5	8.5 [131]
n	64	64	64 [129]
α	0.33	0.30	0.27 [129]

Table 9.4: Effects of acid concentration on adsorption and micellization parameters for sodium dodecyl sulfate.

Parameters	Acid concentration (mol/m^3)			
	0.1	1.0	10.0	100.0
$A_{0,S} (\text{\AA}^2)$	80.0	80.0	79.0	86.0
$W_S (\text{J/mol})$	50000	52000	49000	51000
CMC (mol/m^3)	8.0	7.6	7.4	6.0

Table 9.5: Effects of NaOH concentration on adsorption and micellization parameters for sodium dodecyl sulfate.

Parameters	NaOH concentration (mol/m^3)		
	0	30	125
$A_{0,S} (\text{\AA}^2)$	80.0	50.0	46.0
$W_S (\text{J/mol})$	45000	40000	40000
CMC (mol/m^3)	8.0	3.8	1.8

9.3 Acidified Oil / Surfactant and Alkaline Systems

In the previous two sections, all of the relevant parameters affecting the interfacial activity in acidic oil/alkali and acidic oil/surfactant systems have been determined. These parameters are used for the validation of the proposed model (Eqs. 6.17, 6.22, 6.25, 6.26 and 6.30-6.41) in conjunction with the empirical Eqs. 6.42 and 6.43. It was assumed that the interface behaves ideally and therefore any deviation of the predicted interfacial tension from the experimental data will be an indication of a synergistic effect. To demonstrate the validity of the model, measurements of equilibrium interfacial tension for binary mixtures of added surfactant and alkali contacting acidic oil were carried out. Figs. 9.15 and 9.16 show the effect of added surfactant on interfacial tension as a function of NaOH concentrations for 0.1 and 1 mol/m³ acid respectively. For 0.1 mol/m³ acid, the interfacial tension values are lower than when no surfactant was added (Fig. 9.3). The lowering of interfacial tension is found to be strongly dependent on the concentration of added surfactant. At 1 mol/m³ of added surfactant, the critical micelle concentration will never be reached in the range of the NaOH concentration used (0.25–125 mol/m³) and therefore the interfacial tension decreases continuously as the concentration of NaOH is increased. When the concentration of the added surfactant is increased to 3 mol/m³, the critical micelle concentration is reached just before 50 mol/m³ NaOH and the interfacial tension remains constant beyond that concentration. The same trend is observed for the other added surfactant concentrations.

When the acid concentration is increased to 1 mol/m³, two different behaviors are observed. When the critical micelle concentration is not reached, the interfacial

tension behavior is similar to that in which no surfactant is added. Increasing the surfactant concentration from 2 to 7 mol/m³ shifts the interfacial tension curve to lower values. The interfacial tension goes through a minimum as the NaOH concentration is increased. The minimum shifts to lower NaOH concentrations as the concentration of the added surfactant is increased, and it occurs at the critical micelle concentration. The critical micelle concentration values are slightly lower than those calculated from Eq. (6.43). This decrease in the critical micelle concentration may be explained by the formation of mixed micelles. The lowering in interfacial tension for these systems is a result of the simultaneous adsorption of un-ionized acid, ionized acid and added surfactant at the interface.

The above model was found to predict the equilibrium interfacial tension fairly well at low NaOH concentrations and up to 25 mol/m³. Beyond that concentration, the model predicts interfacial tension values lower than those found experimentally. In view of the limitations imposed by the assumptions made in formulating the model equations (i.e. ideal behavior at the interface), this discrepancy between theory and experiment can be best explained by the existence of a synergistic effect when surfactant and alkali are combined. The existence of a such a synergistic effect has been previously reported to be beneficial [25,29-31] to enhanced oil recovery.

Figure 9.15: Effect of NaOH concentration on interfacial tension for 0.1 mol/m³ acid concentration at different sodium dodecyl sulfate concentrations.

Figure 9.16: Effect of NaOH concentration on interfacial tension for 1.0 mol/m³ acid concentration at different sodium dodecyl sulfate concentrations.

Chapter 10

Transient Model Analysis: Interfacial Tension Data

10.1 Generality

The data points presented in all of the following figures are the average from at least two replicate experiments. For all the graphs, symbols are used for experimental data points, whereas lines are used for calculated tensions. The interfacial variables of interest are the interfacial tension, the interfacial area and the droplet volume. These three sets of data were obtained simultaneously by the modified pendant drop measurement system. The interfacial tensions have been plotted as a function of interfacial age. The zero time for all experiments refers to the time when the drop has completely formed at the capillary tip. This corresponds to about 1 second after the droplet has begun to be injected. The interfacial tension data were collected according to a pre-set timing mode within the data acquisition system. Generally, the time interval is set at 1 second for the first 20 seconds, and then increases to 5, 30 and 60 seconds, giving a data set of 120 to 150 data points per run of 1 hour. The final time can be extended whenever a long term effect is observed. The extended (i.e. steady state) interfacial tension data were compared with the interfacial tension

data obtained from equilibrium measurements.

10.2 Interfacial Tension Data for Acidified Oil / Alkaline Systems

10.2.1 Acidified Oil/Water Systems

The interfacial tension of the reference system paraffin oil/water was measured as a function of time. Fig. 10.1 shows that the interfacial tension decreases slowly over a period of several minutes and attains a steady state value of 50 mN/m. This value is somewhat lower than the corresponding value of 51.7 mN/m measured for preequilibrated solutions using the pendant drop method and the 51.4 mN/m using the drop volume method. In order to check the purity of the paraffin oil, a series of control experiments was carried out in which the interfacial tension of paraffin oil was measured against aqueous solutions of NaOH in the concentration range of 0-250 mol/m³. As shown in Fig. 10.2, a small decrease in interfacial tension was observed in comparison to that found against pure water. This decrease, which is probably owing to the presence of a small amount of impurities in the oil, amounted to about 5 mN/m at the highest NaOH concentration used; it is not considered to have any significant effect on the data presented subsequently in this work.

The transient interfacial tension behavior of the acidified paraffin oil against water at different acid concentrations ranging from 0.1 mol/m³ to 100 mol/m³ is shown in Fig. 10.3 through Fig. 10.6. Carboxylic acids are known to act as weak surfactants [19,70,132,133] and as such are capable of reducing the interfacial tension at the oil/water interface. Generally, for the acidified paraffin oil/water system, the interfacial tension exhibits a similar trend as the acid concentration is increased from

Figure 10.1: Transient interfacial tension behavior of paraffin oil against water.

Figure 10.2: Equilibrium interfacial tension of paraffin oil against aqueous NaOH solutions.

0.1 mol/m³ to 100 mol/m³. During the first few minutes, the interfacial tension first drops rapidly, and then more gradually, until equilibrium is attained. As can be seen from Fig. 10.3, for an acid concentration as low as 0.1 mol/m³, there is an apparent decrease in interfacial tension with respect to time in comparison to the reference system. As shown in Fig. 10.4, the transient interfacial tension is also transient when 1 mol/m³ acid solution is contacted with water. The interfacial tension at an interfacial age of 5 seconds is about 42 mN/m, but with extended contact time the interfacial tension dropped monotonically to a steady state value of 35 mN/m after about 15 minutes. When the acid concentration is increased to 10 and 100 mol/m³, the same behavior is obtained and steady state interfacial tension values of 20 mN/m and 12 mN/m are obtained, respectively. The transient interfacial tension behavior of acidified paraffin oil against distilled water at different acid concentrations is compared in Fig. 10.7. Similar behavior was observed by Hunsel et al. [132] for cholesterol as well as by Bleys and Joos [133] for lauric acid and palmitic acid dissolved in hexane and contacted with water. Bleys and Joos [133] concluded that the observed long-term effects are due to some relaxation mechanisms, including reorientation or solvation, in the interface itself, rather than to diffusional or adsorption barrier effects. The steady state values obtained from the transient measurements are quite comparable to those obtained from equilibrium measurements. The small difference between the two is probably due to the different oil-to-water volume ratios used in the two experiments. Fig. 10.8 shows the comparison between interfacial tension obtained by the pendant drop and that obtained by the novel drop volume tensiometer.

Figure 10.3: Transient interfacial tension behavior of paraffin oil acidified with 0.1 mol/m³ linoleic acid against water.

Figure 10.4: Transient interfacial tension behavior of paraffin oil acidified with 1 mol/m³ linoleic acid against water.

Figure 10.5: Transient interfacial tension behavior of paraffin oil acidified with 10 mol/m³ linoleic acid against water.

Figure 10.6: Transient interfacial tension behavior of paraffin oil acidified with 100 mol/m³ linoleic acid against water.

Figure 10.7: Transient interfacial tension behavior of acidified paraffin oil against water at different acid concentrations.

Figure 10.8: Comparison between transient interfacial tension of acidified paraffin oil against water obtained by the pendant drop (●, ■) and the drop volume (○, □) tensiometer.

10.2.2 Acidified Oil/Alkaline Systems

Interfacial tension behavior against caustic solutions was investigated at three acid concentrations, namely 0.1, 1 and 10 mol/m³. The caustic concentration ranged from as low as 0.25 mol/m³ to a maximum of 250 mol/m³. For neutral water, the interfacial tension behavior for the acidified oil at different acid concentrations is shown in Fig. 10.7. This figure serves as a reference when analyzing the effect of caustic additive on the interfacial tension behavior of the acidified oil/caustic systems. In the presence of caustic, the interfacial tension behavior of the system changes dramatically. Figures 10.9-10.20 depict the behaviors observed using the pendant drop tensiometer for 0.1, 1 and 10 mol/m³ of linoleic acid in paraffin oil against caustic solutions. Data for the same fluid systems, obtained using the drop volume and the spinning drop tensiometers, were compared with the pendant drop tensiometer results.

It is seen that even when the acid concentration is as low as 0.1 mol/m³ (Figs. 10.9-10.14), the interfacial tension drops to as low as 8 mN/m provided the concentration of NaOH is sufficiently high. In Fig. 10.9, the interfacial tension at an interfacial age of 1 second is about 44 mN/m, but with extended contact time the interfacial tension drops monotonically to an equilibrium value of 24 mN/m. At a caustic concentration of 2.5 mol/m³, a similar decreasing trend in interfacial tension is observed until an equilibrium value of 20 mN/m is attained as shown in Fig. 10.10. In the case when 12.5 and 25 mol/m³ NaOH are employed (Figs. 10.11 and 10.12), there is an apparent minimum in interfacial tension at contact times of approximately 900 and 600 seconds, respectively. In Fig. 10.13, the working NaOH concentration is 125 mol/m³. The interfacial tension goes through a characteristic minimum after 200 seconds of phase

contact. Thereafter, the tension slowly increases to about 12 mN/m at an extended time. When caustic concentration is increased further to 250 mol/m³, as shown in Fig. 10.14, the interfacial tension minimum drops to 6 mN/m and is reached at an interfacial age of 120 seconds. Beyond the minimum, the interfacial tension increases to a value of 8 mN/m after one hour.

For the 1.0 mol/m³ acid concentration, the transient interfacial tension versus time curves are depicted in Figs. 10.15-10.21. A general feature one can observe from these figures is a rapid decrease in interfacial tension as a function of time until a minimum is attained, followed by an increase at a rate characteristic of the NaOH concentration. As the concentration of caustic is increased from 0.25 mol/m³ up to 125 mol/m³, the interfacial tension minimum decreases systematically and the time at which the minimum occurs shifts to a lower value. Compared with the equilibrium interfacial tension data independently obtained and presented in the previous chapter, the steady-state tension is generally lower in magnitude. This is an indication that equilibrium is not reached within the run time of one hour. Therefore, based on the equilibrium data, it is expected that the transient interfacial tension will continue to rise until the attainment of its equilibrium value.

When the concentration of acid is 10 mol/m³, interfacial tensions less than 1 mN/m are obtained even when the concentration of the caustic is as low as 2.5 mol/m³. In view of the inherent limitations of the pendant drop tensiometer when measuring ultralow tensions, interfacial tension data for this system were generated using the spinning drop tensiometer and/or the drop volume tensiometer instead. In particular, when the interfacial tension is low, the drop elongates excessively and its shape is no longer suitable for boundary tension calculations. Moreover, the drop

detaches very rapidly and the total contact time does not cover the whole process taking place at the oil/water interface. The interfacial tension data obtained using the pendant drop tensiometer for the 10 mol/m³ acidified oil and caustic at a concentration ranging from 0.25 mol/m³ to 25 mol/m³ are presented in Figs. 10.22-10.26. The data presented here are the best data that can be obtained using the pendant drop tensiometer, even though their reproducibility is rather poor.

Transient interfacial tension behavior at a caustic concentration of 0.25 mol/m³ is shown in Fig. 10.22. The tension drops continuously with time and there is no apparent minimum in interfacial tension. In Fig. 10.23, the working NaOH concentration is 1.25 mol/m³. A shallow drop in tension to a minimum value of 2 mN/m at an interfacial age of 2 minutes is observed. Beyond this contact time, the interfacial tension rises gradually. A similar behavior is exhibited when the caustic concentration is increased to 2.5 mol/m³, as shown in Fig. 10.24. When the caustic concentration is increased further to 12.5 and 25 mol/m³ (Figs 10.25 and 10.26), the tension at 1 second is only about 1 mN/m and drops almost by one order of magnitude in 100 seconds contact time. At this level of interfacial tension, the droplet detaches and no additional data can be recorded. For higher caustic concentration, it was impossible to measure the interfacial tension of this system because of the problem associated with the pendant drop method, as mentioned earlier.

The effects of caustic concentration on transient interfacial tension of acidified oil/caustic systems have been studied by various researchers [11,12,16,17]. It has been shown that very low interfacial tensions are obtained only over a narrow range of caustic concentration (typically 2.5 to 25 mol/m³). Chan and Yen [11] suggested that this behavior is influenced by the effective caustic concentration at which the

interfacial pH approached the pK_a of the acid present in the oil.

At caustic concentrations below the optimum concentration, the acid species present at the interface are almost completely ionized, resulting in a high initial accumulation of the surface-active soap anions. As these surface-active anions are charged, an electrical double layer is formed at the interface and this tends to stabilize the adsorbed ions. The result is a relatively large barrier to desorption of the anions into the aqueous phase, which explains the decrease in interfacial tension at extended contact times.

At NaOH concentrations above the optimum, surface inactive soap complexes are formed as a result of a chemical reaction between the active anions and excess sodium ions [12,16]. This results in a gradual loss of the adsorbed anions and a subsequent decrease in the resistance to desorption. Consequently, the IFT increases at extended times. In the case of linoleic acid systems, 25 mol/m³ is the critical caustic concentration at which significant desorption of the soap anions begins to occur.

Figure 10.9: Transient interfacial tension behavior of 0.1 mol/m^3 acid in paraffin oil against 0.25 mol/m^3 NaOH solution.

Figure 10.10: Transient interfacial tension behavior of 0.1 mol/m^3 acid in paraffin oil against 2.5 mol/m^3 NaOH solution.

Figure 10.11: Transient interfacial tension behavior of 0.1 mol/m³ acid in paraffin oil against 12.5 mol/m³ NaOH solution.

Figure 10.12: Transient interfacial tension behavior of 0.1 mol/m³ acid in paraffin oil against 25 mol/m³ NaOH solution.

Figure 10.13: Transient interfacial tension behavior of 0.1 mol/m^3 acid in paraffin oil against 125 mol/m^3 NaOH solution.

Figure 10.14: Transient interfacial tension behavior of 0.1 mol/m^3 acid in paraffin oil against 250 mol/m^3 NaOH solution.

Figure 10.15: Transient interfacial tension behavior of 1 mol/m^3 acid in paraffin oil against 0.25 mol/m^3 NaOH solution.

Figure 10.16: Transient interfacial tension behavior of 1 mol/m^3 acid in paraffin oil against 1.25 mol/m^3 NaOH solution.

Figure 10.17: Transient interfacial tension behavior of 1 mol/m³ acid in paraffin oil against 2.5 mol/m³ NaOH solution.

Figure 10.18: Transient interfacial tension behavior of 1 mol/m³ acid in paraffin oil against 5 mol/m³ NaOH solution.

Figure 10.19: Transient interfacial tension behavior of 1 mol/m^3 acid in paraffin oil against 12.5 mol/m^3 NaOH solution.

Figure 10.20: Transient interfacial tension behavior of 1 mol/m^3 acid in paraffin oil against 25 mol/m^3 NaOH solution.

Figure 10.21: Transient interfacial tension behavior of 1 mol/m³ acid in paraffin oil against 125 mol/m³ NaOH solution.

Figure 10.22: Transient interfacial tension behavior of 10 mol/m³ acid in paraffin oil against 0.25 mol/m³ NaOH solution.

Figure 10.23: Transient interfacial tension behavior of 10 mol/m³ acid in paraffin oil against 1.25 mol/m³ NaOH solution.

Figure 10.24: Transient interfacial tension behavior of 10 mol/m³ acid in paraffin oil against 2.5 mol/m³ NaOH solution.

Figure 10.25: Transient interfacial tension behavior of 10 mol/m³ acid in paraffin oil against 12.5 mol/m³ NaOH solution.

Figure 10.26: Transient interfacial tension behavior of 10 mol/m³ acid in paraffin oil against 25 mol/m³ NaOH solution.

10.2.3 Interfacial Tension Data Measured by the Drop Volume and Spinning Drop Tensiometers

Transient interfacial tension measurements were carried out for the acidified paraffin oil/caustic systems using two different yet somewhat related methods, namely the drop volume and the spinning drop tensiometry. The first aim of these measurements was to check the accuracy of the transient data obtained by the pendant drop tensiometer and of the trends exhibited by the interfacial tension versus time curves. In equilibrium measurements, it has been shown that the interfacial tension of pure hydrocarbons against water, as measured by the pendant drop tensiometer, agreed very well with the literature values. The second aim of this supplementary study was to obtain additional data out of the measurement range of the pendant drop technique, i.e. at very low values of interfacial tension. The dynamic interfacial tension curves for the acidified paraffin oil/caustic systems obtained by the drop volume tensiometer is shown in Fig. 10.27 at three different acid concentrations. In this case the time on the x-axis represents the time at which the droplet detaches from the capillary tip, or specifically the drop-formation time. Joos and Rillaerts [134] found that the surface age (t_a) of the droplet equals three-sevenths of the dropping time (t_d), and, as a consequence, care must be taken when analyzing interfacial tension data from the drop volume tensiometer. The surface age, t_a , is equivalent to the time of measurement for both the pendant drop tensiometer and the spinning drop tensiometer.

It will be noted that the duration of the experiment as shown in Fig. 10.27 does not exceed 500 seconds. This is due to the difficulties associated with the drop volume method in recording tensions at longer times of drop formation, which necessitate very slow flowrate. Within this time period, the curves shown in Fig. 10.28

for reactive acidified oil/caustic systems, are similar both in their shape and in the absolute magnitude of the interfacial tension to those measured with the pendant drop technique. Although both methods give approximately the same values of the interfacial tension minimum, the data corresponding to the drop volume tensiometer show only a decreasing trend with time. For the same system, data obtained using the pendant drop method often show an increase in interfacial tension after the minimum has been attained. This is probably owing to the continuous addition of the surface active reagent to the droplet in the drop volume technique. The data shown in Fig. 10.27(c) for 10 mol/m³ acid concentration indicate that the drop volume tensiometer is also incapable of accurately determining tensions of less than 0.8 mN/m. At caustic concentrations higher than 2.5 mol/m³ the interfacial tension curves are very difficult to reproduce and the error in the calculated tension may exceed 20 %.

At lower interfacial tension values, the deviation between tensions obtained by the pendant drop and the drop volume methods becomes more apparent. As shown in Figs. 10.27(b) and (c), the interfacial tension no longer exhibits the same trend. The interfacial tension drops more sharply for the drop volume than for the pendant drop tensiometer. For lower interfacial tensions, such as those generated at higher acid concentrations against caustic solutions, a comparison was made between the three methods as shown in Fig. 10.29. Fig. 10.29(a) shows the interfacial tension behavior for 1 mol/m³ acid concentration against 25 mol/m³ NaOH. As can be seen from this figure, tension measurements by the spinning drop tensiometer cannot be monitored and recorded at least during the first 40 seconds due to the time required for loading the instrument. The interfacial tensions obtained by the spinning drop technique differ markedly from those obtained by the two other techniques. The

interfacial tension values observed are lower in magnitude, and the minimum occurs at a longer time. After an extended contact time, however, the tension values are comparable for the three methods. When the acid concentration is 10 mol/m^3 , interfacial tensions below 1 mN/m are obtained by all three instruments. However, the drop volume technique is not capable of following the change in interfacial tension with time and the tension is almost constant at 0.4 mN/m . On the other hand, the interfacial tensions obtained by the pendant drop and the spinning drop methods are in fair agreement with respect to the magnitude of the minimum value and the time at which the minimum occurs.

From these comparisons, it can be concluded that within the moderate to high tension range (i.e. $5\text{--}72 \text{ mN/m}$), the drop volume tensiometer and the pendant drop tensiometer yield comparable tension data for both non-reactive and reactive systems. The spinning drop tensiometer and the pendant drop tensiometer yield similar data in the low tension range (i.e. $0.01\text{--}5 \text{ mN/m}$), although tensions measured by the pendant drop tensiometer could be inaccurate since reproducibility is poor. The spinning drop technique is the only one among these three techniques employed that can be used for measuring low to ultralow interfacial tensions (i.e. for tensions less than 1 mN/m).

Figure 10.27: Dynamic interfacial tension behavior of acidified paraffin oil against aqueous NaOH solutions as measured by the drop volume tensiometer. Acid concentration: (a): 0.1, (b): 1.0 and (c): 10 mol/m³.

Figure 10.28: Comparison between transient interfacial tension of acidified paraffin oil against caustic solutions obtained by the pendant drop ($\bullet, \blacksquare, \blacklozenge$) and the drop volume ($\circ, \square, \diamond$) tensiometer. (a) 0.1 mol/m³ acid / 12.5 mol/m³ NaOH, (b) 1 mol/m³ acid / 2.5 mol/m³ NaOH, and (c) 10 mol/m³ acid / 1.25 mol/m³ NaOH.

Figure 10.29: Comparison between transient interfacial tension of acidified paraffin oil against caustic solutions obtained by the spinning drop ($\bullet$), the pendant drop ($\blacksquare$), and the drop volume ($\blacklozenge$) tensiometer. (a) 1 mol/m³ acid / 25 mol/m³ NaOH and (b) 10 mol/m³ acid / 25 mol/m³ NaOH.

10.3 Interfacial Tension Data for Acidified Oil / Surfactant Systems

Transient interfacial tension data for fluid pairs composed of acidified paraffin oil and sodium dodecyl sulfate solutions were measured and are presented in Figs. 10.30-10.34. Fig. 10.30 shows the transient interfacial tension behavior of pure paraffin oil against sodium dodecyl sulfate solutions at concentrations ranging from 1 to 10 mol/m³. As expected, the sodium dodecyl sulfate solution is found to exhibit an interfacial activity significantly higher than that of distilled water. For a 1 mol/m³ solution, the interfacial tension decreases gradually from its initial value of 40 mN/m to about 26 mN/m after one hour contact time. When the concentration of sodium dodecyl sulfate is increased to 2 mol/m³, the initial rate of decrease of interfacial tension versus time is greater than that exhibited by the 1 mol/m³ solution. The interfacial tension decreases rapidly from 1 to 200 seconds and then slowly beyond 200 seconds. At longer contact times, the interfacial tension stabilizes near a constant and steady-state value. Thus, the interfacial tension measured is a transient one reflecting an unsteady-state interface. Curves corresponding to surfactant concentrations ranging from 3 to 10 mol/m³ generally show behavior similar to that for the 2 mol/m³ concentration.

There is no particular change in interfacial tension values when sodium dodecyl sulfate concentrations of 8, 9 and 10 mol/m³ are used. This indicates that a limiting sodium dodecyl sulfate concentration is reached, corresponding to the critical micellar concentration, which is about 8 mol/m³. This confirms the results obtained from the equilibrium measurements. In Fig. 10.30 the lowest achievable interfacial tension

occurs at about 10 mN/m, i.e. at the critical micellar concentration. Another important observation from Fig. 10.30 is that the interfacial tension does not go through a minimum. This is an indication that sodium dodecyl sulfate remains at the interface and does not partition into the oil phase.

The effect of acid concentration in the oil phase on the interfacial activity of sodium dodecyl sulfate at the oil/water interface is shown in Figs. 10.31-10.34 for acid concentrations of 0.1, 1, 10 and 100 mol/m³ respectively. The results obtained from the equilibrium model analysis for this particular system indicate that the acid in the oil phase and the sodium dodecyl sulfate in the aqueous phase adsorb simultaneously at the interface. As a consequence, the interfacial tension of the combined system is lower than that for the surfactant or the acid alone. Generally, the data presented in Figs. 10.30-10.34 are in agreement with the equilibrium results presented in Chapter 9.

The presence of acid in the oil phase at a concentration as low as 0.1 mol/m³ brings about a small apparent decrease in interfacial tension as a function of time for all surfactant concentrations employed. For a surfactant concentration of 1 mol/m³, the decrease in interfacial tension with time is more pronounced and a steady-state value of 20 mN/m is obtained, which is lower than that obtained in the absence of the acid in the oil. For the same acid concentration, the curves obtained with higher surfactant concentrations show a similar behavior, as shown in Fig. 10.31. When a higher acid concentration of 1 mol/m³ is used, a similar decreasing trend in interfacial tension is observed as shown in Fig. 10.32. A further decrease in interfacial tension compared to the 0.1 mol/m³ acid concentration is obtained with a correspondingly lower steady-state value. The limiting surfactant concentration in the case of these two acid concentrations changes only marginally and is situated between about 7 and

8 mol/m³, which is somewhat lower than for the surfactant system alone. It is only when the acid concentration is increased to 10 and 100 mol/m³ that a significant change in interfacial tension is observed. The corresponding interfacial tension versus time plots are shown in Figs. 10.33 and 10.34 respectively.

The effect of linoleic acid concentration on transient interfacial tension behavior of paraffin oil against 6 mol/m³ and 7 mol/m³ sodium dodecyl sulfate solutions is clearly shown in Figs. 10.35 and 10.36. Similar effects are observed for other sodium dodecyl sulfate concentrations. The analysis of the equilibrium interfacial tension data for these system, as described in the previous chapter, revealed the existence of a relationship between the initial acid concentration and the critical micelle concentration of the surfactant. This relationship is represented by Eq. 9.1, and states that the acid reduces the critical micelle concentration of the surfactant. No ultralow minimum is observed in the interfacial tension behavior either as a function of time or as a function of acid concentration. This is primarily due to the fact that sodium dodecyl sulfate is very soluble in water and the acid is unable to partition it out of the aqueous phase. More quantitatively, the desorption barriers are negligible compared to the adsorption barriers and hence the interfacial tension shows only a continuous decrease with time.

Figure 10.30: Transient interfacial tension behavior of paraffin oil against sodium dodecyl sulfate solutions.

Figure 10.31: Transient interfacial tension behavior of 0.1 mol/m³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.

Figure 10.32: Transient interfacial tension behavior of 1 mol/m³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.

Figure 10.33: Transient interfacial tension behavior of 10 mol/m³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.

Figure 10.34: Transient interfacial tension behavior of 100 mol/m³ linoleic acid in paraffin oil against sodium dodecyl sulfate solutions.

Figure 10.35: Effect of linoleic acid concentrations on transient interfacial tension behavior of paraffin oil against 6 mol/m³ sodium dodecyl sulfate solution.

Figure 10.36: Effect of linoleic acid concentrations on transient interfacial tension behavior of paraffin oil against 7 mol/m³ sodium dodecyl sulfate solution.

10.4 Interfacial Tension Data for Acidified Oil / Caustic and Surfactant Systems

Experimental studies were conducted in order to determine the mechanisms responsible for the lowering of transient interfacial tension in acidic oil/surfactant-enhanced alkali systems. It was proved from the equilibrium data analysis that the un-ionized acid as well as the ionized acid, and the added surfactant, all contribute to the lowering of the interfacial tension of such a mixed system. The un-ionized acid was found to simultaneously adsorb onto the interface with either the ionized acid and/or the added surfactant and this resulted in a lowering of the interfacial tension. Synergism was also observed and quantified between the various surface active species present. For acidified oil/surfactant systems, the un-ionized acid reduces the critical micelle concentration of the system in a systematic way. The critical micelle concentration of the system was also reduced by the un-ionized acid and the ionized acid when alkali was added.

The critical micelle concentration of the system is mainly a function of the NaOH concentration and the un-ionized and the ionized acid concentrations are of relatively minor importance. The un-ionized and the ionized concentrations are in turn dependent on the prevailing pH of the aqueous solution. At a pH less than the effective pK_a of the system, un-ionized and ionized acid are both present and a mixed micelle of the three species is formed. When the pH is greater than the effective pK_a , the acid is completely ionized and a mixed micelle of the ionized acid and the added surfactant is formed. The effective pK_a of the system results from the ability of the acid to become distributed between the oil and the aqueous phases. For a common acid, a pK_a from ionization of 6, plus a pK_p from the partition coefficient between oil and water of 5.6,

Figure 10.37: Phase diagram for micellization.

gives a value of 11.6 for the pK_a of the system. In either case, one can observe two regions in the interfacial tension behavior. In the first region, the total surface active species concentration is less than the effective critical micelle concentration of the system, and the diffusion process is governed by monomeric transport. In the second region, the total concentration of surface active species exceeds the effective critical micelle concentration of the system, and combined monomeric and micellar transport phenomena govern the diffusion process.

It was found useful to construct a phase diagram for micellization as an aid in the analysis of the interfacial tension behavior of the mixed systems. This diagram is shown in Fig. 10.37 and shows the monomeric and the micellar boundary as a function of the NaOH and the sodium dodecyl sulfate concentrations. This diagram

is based on the effect of NaOH concentration on the critical micelle concentration of the added surfactant. It is expected that the micellization boundary (solid line) will be affected by the coexistence of un-ionized and ionized acid species and shift to lower added surfactant concentration (dotted line), as shown in Fig. 10.37.

10.4.1 Effects of Added Surfactant Concentration

The experimental interfacial tension data are plotted as a function of time in Figs. 10.38-10.44, which feature the effects of both the caustic concentration and the added surfactant concentration. Two levels of acid concentration were employed. The interfacial tension versus time behavior for the surfactant and caustic mixtures against acidified paraffin oil exhibits similar trends when either the caustic or surfactant concentrations are varied. Only data for the acid concentration of 1 mol/m^3 will be discussed here, while data for the 0.1 mol/m^3 acid may be found in Figs. D.1-D.4 (Appendix D). At low surfactant concentration (1 mol/m^3), the critical micelle concentration of the system is not reached even when a high NaOH concentration is used. The interfacial tension versus time curves are similar to those obtained when no surfactant is added except that the absolute values of the tensions are lower. At low NaOH concentrations, the lowering of the interfacial tension is caused by competitive adsorption of the un-ionized acid (because the effective pK_a is not reached), the ionized acid, and the added surfactant.

When the sodium dodecyl sulfate concentration is increased to 2 mol/m^3 , interfacial tensions at low NaOH concentrations are lower than those for the NaOH system alone, and interfacial tension minima occur at earlier contact times. At NaOH concentrations of 12.5 mol/m^3 and higher, the interfacial tensions drop very quickly to

values less than 1 mN/m. As can be seen from Fig. 10.39, tensions for 12.5 and 25 mol/m³ NaOH are lower than those for 125 mol/m³. This indicates that the optimum NaOH concentration is located between 12.5 and 25 mol/m³. At optimum NaOH concentration, the effective pK_a of the acid is reached and the ionized acid concentration is maximum. Also, since the effective critical micelle concentration of the system is not reached at 25 mol/m³ NaOH, it is expected that the interfacial activity of the system will be at its maximum. This explains the marked drop in interfacial tension. At NaOH concentrations higher than 25 mol/m³, the interfacial tension will be affected, for two reasons. First, a surface inactive soap complex is formed because of excess sodium ions in the aqueous phase and is removed to the oil phase; this results in decreasing the ionized acid concentration. Second, formation of mixed micelles, which occurs at about 70 to 80 mol/m³ NaOH concentration, reduces the amount of free sodium dodecyl sulfate and ionized acid available for adsorption. This explains the increase in interfacial tension at NaOH concentrations higher than 25 mol/m³.

The same pattern is repeated when a sodium dodecyl sulfate concentration of 3 mol/m³ is used (Fig. 10.40). In this case, the effective critical micelle concentration of the system is also reached at NaOH concentrations higher than 25 mol/m³. As can be noted from Fig. 10.40, the optimum NaOH concentration is at 12.5 mol/m³ NaOH, and tension values for 125 mol/m³ NaOH are higher than those obtained for the 2 mol/m³ sodium dodecyl sulfate solutions. At 125 mol/m³ NaOH, however, the interfacial tension stabilizes very quickly and a constant value is reached after only 30 seconds.

As shown in Figs. 10.41-10.44, there is a clear transition in the interfacial tension

behavior when the sodium dodecyl sulfate concentration is increased to 4 mol/m^3 and higher (i.e. 5, 6 and 7 mol/m^3). When the NaOH concentration is lower than 12.5 mol/m^3 , the observed behavior is similar to that seen in the two earlier systems. The interfacial tensions are once again lower than those for caustic solutions alone contacting 1 mol/m^3 acidified oil, with a correspondingly lower interfacial tension minimum. For example, at NaOH concentrations as low as 0.25 mol/m^3 , the initial interfacial tension is about 27 mN/m , and it drops to 15 mN/m after one hour of contact time. With the presence of 4 mol/m^3 added surfactant, the initial interfacial tension of about 12 mN/m and 4.5 mN/m at extended time is recorded. At NaOH concentration of 2.5 mol/m^3 , an interfacial tension minimum of 4 mN/m is attained after 2000 seconds, whereas for the mixture, the minimum in interfacial tension decreases to 1 mN/m and lasts only 300 seconds. When the NaOH concentration is increased to 12.5, 25 and 125 mol/m^3 , the interfacial tension is not only lower, but the minima are attained much earlier, namely at about 50, 40 and 20 seconds respectively. After the minimum the interfacial tension does not increase as for the case of NaOH solutions alone, but it stabilizes at a nearly constant value, equal to the interfacial tension minimum. It is also noted that the steady-state interfacial tension increases with increasing NaOH concentration from 12.5 mol/m^3 to 125 mol/m^3 . This is in good agreement with the equilibrium interfacial tension data given in Chapter 9.

From the data presented in Figs. 10.38-10.44, there exists an optimum concentration with respect to both NaOH and sodium dodecyl sulfate, at which the interfacial tension of the mixture systems is the lowest. These concentrations are, respectively, between 2 and 3 mol/m^3 sodium dodecyl sulfate and 12.5 and 25 mol/m^3 NaOH. According to the interfacial tension data for the 0.1 mol/m^3 acid system shown in

Figs. D.1-D.4, the optimum region is shifting to higher sodium dodecyl sulfate concentrations, namely 3 and 4 mol/m³. Because the effective concentration of the ionized acid in the aqueous phase is less than that corresponding to the 1 mol/m³ acid system, a higher sodium dodecyl sulfate concentration is required to attain the optimum interfacial tension. It is expected that the optimum region for the 10 mol/m³ acid system will shift to a lower surfactant concentration. In conclusion, the interfacial activity of the acidified oil/caustic solutions has been found to be markedly improved by the addition of a ready-made surfactant, such as sodium dodecyl sulfate. The fact that the transient interfacial tension is stabilized at a nearly constant and low value is of great importance to the chemical improved oil recovery process, where low interfacial tension conditions should be sustained for prolonged periods of time.

Figure 10.38: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 1 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure 10.39: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 2 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure 10.40: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 3 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure 10.41: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 4 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure 10.42: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 5 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure 10.43: Transient interfacial tension behavior for 1 mol/m^3 acid in paraffin oil against 6 mol/m^3 sodium dodecyl sulfate and NaOH solutions.

Figure 10.44: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against 7 mol/m³ sodium dodecyl sulfate and NaOH solutions.

10.4.2 Effects of Caustic Concentration

Figs. 10.45-10.50 shown in this section represent the inversion of Figs. 10.38-10.44, in that the effects of NaOH concentration on the transient interfacial tension of acidified oil/surfactant systems may be investigated at different acid concentrations. In general, the transient interfacial tensions presented in Figs. 10.45-10.50 are lower than those obtained for the single systems. The decrease in interfacial tension versus time is much faster than that of the acidified oil/caustic systems shown in Figs. 10.15-10.21.

A clear transition in the interfacial tension behavior is observed when NaOH concentration is increased from 2.5 mol/m^3 to 12.5 mol/m^3 and higher, at all sodium dodecyl sulfate concentrations employed. At low NaOH concentration, the concentration of the ionized acid is not high enough for the mixed micelles to be formed, and the interfacial tension behavior shown in Figs. 10.45-10.47 results from the simultaneous adsorption of the various surface active species at the oil/water interface. At an NaOH concentration of 12.5 mol/m^3 and higher, the ionized acid concentration is sufficient for the mixed micelles to be formed, and the interfacial tension behavior shown in Figs. 10.48-10.50 reflects this phenomenon.

Figure 10.45: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 0.25 mol/m³ NaOH solution.

Figure 10.46: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 1.25 mol/m³ NaOH solution.

Figure 10.47: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 2.5 mol/m³ NaOH solution.

Figure 10.48: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 12.5 mol/m³ NaOH solution.

Figure 10.49: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 25 mol/m³ NaOH solution.

Figure 10.50: Transient interfacial tension behavior for 1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 125 mol/m³ NaOH solution.

Chapter 11

Transient Model Analysis: Model Predictions

11.1 Evaluation of the Model Constants

The model constants are evaluated according to the procedure outlined in Chapter 8 and they are listed in Tables 11.1-11.3. The model constants include three types of constants: the model constants type 1 (i.e. the sorptive equilibrium constants), the model constants type 2 (i.e. the Nernstian film thicknesses), and the model constants type 3 (i.e. the diffusion coefficients).

11.1.1 Sorptive Equilibrium Constants

The sorptive equilibrium constants for the un-ionized acid and the ionized acid are listed in Table 11.1 for different acid concentrations. The sorptive equilibrium constants, K'_{HX_0} and $K_{X_{\infty}}$, are independent of the initial acid concentration. The order of magnitude of these constants indicates that the un-ionized acid has a weak interfacial activity and the ionized acid has a very high interfacial activity. On the other hand, as values of the acid ionization constant, K_{HX}^D , as well as the equilibrium constant K_{NaX}^D , vary with the initial acid concentration, it follows that the sorptive

equilibrium constants, K''_{HX_0} and K_{NaX_0} , evaluated therefrom, will also differ.

The calculated and literature values for the sorptive equilibrium constant of sodium dodecyl sulfate are listed in Table 11.2. At the paraffin oil/water interface a value of 7.447×10^4 m³/mol is found. At the decane/water interface, sodium dodecyl sulfate has a higher adsorption capacity of 3.695×10^{-6} mol/m² and a lower desorption energy, W_S , of 40 205 J/mol compared to those at the paraffin oil/water interface. The resulting K_{S_w} value of 6.038×10^3 m³/mol is consequently smaller. The calculated K_{S_w} value of sodium dodecyl sulfate at the decane/water interface is in good agreement with the values reported by Borwankar [135] for the decane/water and heptane/water systems, as shown in Table 11.2. The small difference is due to a different method of calculation. When the paraffin oil is acidified, the K_{S_w} constant is found to be higher than that for the pure paraffin oil. Although the adsorption saturation is the same for both systems, the energy of desorption, W_S , increases from 45 000 J/mol to 50 000 J/mol and this results in a higher K_{S_w} value. The increase in the energy of desorption of sodium dodecyl sulfate at the paraffin oil/water interface results from the adsorbed acid at the interface which inhibits the desorption of sodium dodecyl sulfate. This requires more energy for sodium dodecyl sulfate to desorb from the interface. The reported value of K_{S_w} at the air/water interface is much smaller than that at the oil/water interface, which explains the different adsorption behavior of the surfactant at the air/water and the oil/water interfaces. From the sorptive equilibrium constants quoted in Tables 11.1 and 11.2, the ionized acid is found to be more interfacially active than the sodium dodecyl sulfate.

Table 11.1: Sorptive equilibrium constants of un-ionized and ionized acid at different initial acid concentrations.

Parameters	Acid concentration (mol/m ³)		
	0.1	1.0	10.0
$\Gamma_{max,HX}$ (mol/m ²)	5.915×10^{-6}		
K_p	4.500×10^5		
K_d (m ³ /mol)	3.026		
$\Gamma_{max,X}$ (mol/m ²)	4.000×10^{-6}		
K_{HX}^D (mol/m ³)	6.982×10^{-3}	4.438×10^{-3}	1.124×10^{-3}
K_{NaX}^D (mol/m ³)	2.624	1.133	1.643×10^{-1}
K'_{HX_0} (m ³ /mol)	3.557	3.557	3.557
K''_{HX_0}	8.200×10^{-3}	5.212×10^{-3}	1.320×10^{-3}
K_{X_w} (m ³ /mol)	5.285×10^5	5.285×10^5	5.285×10^5
K_{NaX_0}	1.387×10^6	5.988×10^5	8.683×10^4

Table 11.2: Sorptive equilibrium constant of sodium dodecyl sulfate at the oil/water interface.

System	Adsorption saturation, $\Gamma_{\max,S}$ (mol/m ²)	Sorptive equilibrium constant, K_{S_w} (m ³ /mol)
paraffin oil/water	2.075×10^{-6}	7.447×10^4
decane/water	3.695×10^{-6}	6.038×10^3
acidified paraffin oil/water	2.075×10^{-6}	5.603×10^5
paraffin oil/water (NaOH)	3.321×10^{-6}	6.186×10^3
decane/water (NaCl) [135]	3.670×10^{-6}	1.078×10^4
heptane/water (NaCl) [135]	4.450×10^{-6}	3.200×10^3
air/water [135]	10.000×10^{-6}	6.040×10^2

11.1.2 Diffusion Coefficients

The correlation used for the calculation of the diffusion coefficients in the oil and in the water phase has already been presented as Eq. 8.12. The calculated diffusivities of linoleic acid are 4.150×10^{-7} cm²/s in paraffin oil and 4.495×10^{-6} cm²/s in water. An estimated molar volume of linoleic acid of 421.5 cm³/mol is used. The diffusion coefficient in water is higher than that in the oil because the latter has a viscosity 20 times that of the aqueous solution. The calculated diffusivity for sodium dodecyl sulfate in water is 5.345×10^{-6} cm²/s which is in agreement with the published value

of $5.70 \times 10^{-6} \text{ cm}^2/\text{s}$, reported by Kamenka et al. [136]. The diffusivity of sodium dodecyl sulfate is concentration dependent as found by Weinheimer et al. [137], who reported that the diffusion coefficient increases with increase in sodium dodecyl sulfate concentration above the critical micelle concentration. It is also found that the diffusion coefficient of sodium dodecyl sulfate varies with salt concentration. Fainerman [138] reported a value of $3.80 \times 10^{-6} \text{ cm}^2/\text{s}$ in 100 mol/m^3 NaCl solution and $4.60 \times 10^{-6} \text{ cm}^2/\text{s}$ in 500 mol/m^3 NaCl solution. It should be noted that the value reported by Kamenka et al. [136] corresponds to the diffusivity of the monomer. In the same manner, the micelle diffusion coefficient has been estimated to be $8.00 \times 10^{-8} \text{ cm}^2/\text{s}$ by Stigter et al. [139].

Table 11.3: Diffusion coefficients of the solutes

Solute	Diffusion Coefficient (cm^2/s)
HX_o	4.150×10^{-7}
NaX_o	4.150×10^{-7}
HX_w	4.495×10^{-6}
X_w	4.495×10^{-6}
S_w	5.345×10^{-6}
	5.700×10^{-6} [136]
	3.800×10^{-6} [138]
	4.600×10^{-6} [138]

11.1.3 Boundary Layer Thicknesses

The Nernstian film thicknesses, δ_o and δ_w , were estimated for linoleic acid and are 0.186 and 2.850 μm respectively. The Nernstian film thickness for the oil side is much smaller than the corresponding value for the water side. According to Rubin and Radke [10], this results from to higher convection currents in the oil phase. The characteristic length of adsorption is defined as $\Gamma_{\text{max}}K$. For the oil side, its value is $2.1 \times 10^{-5} \text{ m}$ (21 μm), while for the water side it is $2.14 \times 10^{-3} \text{ m}$ (2140 μm). It is clear that the estimated Nernstian film thicknesses are far smaller than the characteristic lengths of adsorption for both sides of the interface. This is a requirement for the applicability of Nernstian film theory to model the convective diffusion transport of the surface active solutes.

11.2 Estimates of the Kinetic Rate Parameters

In certain industrial processes, transient interfacial tensions are as important as the equilibrium interfacial tensions. While the equilibrium adsorption is characterized by a sorptive equilibrium constant, the transient adsorption is characterized by kinetic rate constants reflecting the case of a kinetic adsorption. The proposed transient model relies heavily on the equilibrium model and the associated mechanisms for the interactions of the carboxylic acid with the aqueous solutions. Once the model constants are evaluated, the solution methodology, as outlined in Section 8.2, is then applied for the estimation of the kinetic rate constants.

11.2.1 Kinetic Rate Constants of Linoleic Acid

The best correlation of the experimental data for the acidified oil/water system is obtained with the corresponding kinetic rate constants $k_{HX_o} = 0.254 \text{ m}^3/\text{mol.s}$ and $k_{HX_w} = 0.075 \text{ m}^3/\text{mol.s}$ for an acid concentration of 1 mol/m^3 , as shown in Table 11.4. For the acid concentration of 10 mol/m^3 a small increase in the rate constants is obtained. The kinetic rate constants of the acid can be considered independent of the acid concentration with an associated error of less than 11 %, which is considered to be acceptable. The kinetic rate constant, k_{HX_o} , is in the range of the rate constant values reported in the literature. For example, Chiwetelu et al. [17] found an estimated value of $0.226 \text{ m}^3/\text{mol.s}$ for oleic acid at a concentration of 0.3125 mol/m^3 . The k_{HX_o} value reported by Borwankar and Wasan [14] for crude oil with acid concentration of 14.3 mol/m^3 was estimated at $0.46 \text{ m}^3/\text{mol.s}$. The comparison between the model predictions using these values and the experimental data is shown in Fig. 11.1. As can be seen from Fig. 11.1, the agreement is very good.

For the reactive acidified oil/caustic system, two additional rate constants have to be estimated, namely k_{NaX_o} and k_{X_w} . The rate constant k_{HX_w} , estimated above, is then used during the computation. It is noted that the global kinetic rate constant, k_{X_w} , comprises the kinetic rate constant k_{HX_w} as mentioned in the formulation of the transient model, reflecting the existence of an equilibrium between X_w and HX_w in the aqueous phase. In the case where 1 mol/m³ acid concentration is used, the final parameter estimates of the kinetic rate constants are listed in Table 11.5. It is particularly important to note that these rate constants, estimated from the large set of experimental data, are independent of the aqueous phase composition within an estimated error of less than 10 %. The parameter estimates listed in Table 11.5 are in agreement with the rate constant values reported by Chiwetelu et al. [17] for hexadecane acidified with oleic acid, and by Borwankar and Wasan [14] for a crude oil.

The procedure used in this study for the estimation of the rate constant differs from the procedure used by Chiwetelu et al. [17] and Borwankar and Wasan [14]. In their analyses, the desorption rate constant, k_{X_w} , was fixed at a given and arbitrary value which allowed them to estimate simultaneously the rate constants k_{HX_o} and k_{NaX_o} . In the present analysis, k_{X_w} is estimated separately from the acidified oil/water set of data, taking into account the adsorption of the acid at the oil/water interface. This in turn makes the estimation of k_{NaX_o} and k_{X_w} from the acidified oil/caustic set of data much easier and more precise. Figs. 11.2-11.7 show the comparison between the predicted and the experimental transient interfacial tension for the 1 mol/m³ acid concentration in contact with different caustic concentrations. As can be seen from Figs. 11.2-11.7, a good agreement is obtained between the model predictions using the

parameter estimates of Table 11.5 and the experimental transient interfacial tension data. In comparison with the model fitting of Chiwetelu et al. [17] and Borwankar and Wasan [14], there is a remarkable improvement in the modelling of the interactions between the acidic oil and the caustic reagent. This is mainly due to the incorporation of un-ionized acid as being adsorbed at the interface along with the ionized acid in the model formulation, as opposed to considering only ionized acid being adsorbed at the oil/water interface.

The relative importance of convective diffusion on transient interfacial tension was checked by altering the boundary layer thicknesses, δ . As a result, it was found that the convective diffusion, as modelled by the Nernstian film theory, does not affect the transient tensions to any appreciable extent. On the other hand, it was found that the predicted transient interfacial tension is significantly influenced by the equilibrium parameters and, more particularly, by the kinetic rate constants. However, the parameters that are associated with sorption kinetics influence the predicted interfacial tension more than the diffusive ones. The interfacial potential associated with the adsorption of active anions at the interface also plays an important role in controlling the transient interfacial tension. Its role is as important as the sorption kinetics. Thus, high interfacial potential, as encountered in the acidified oil/caustic systems, can prevent further adsorption of the surface active anion at the interface. In terms of sorption kinetics, a large acid adsorption rate constant is necessary in order to accumulate a sufficient amount of active species at the interface subject to the prevailing interfacial potential. The interfacial potential, in turn, is determined by the effective caustic concentration in the bulk as well as by the total surface excess concentration. If the desorption rate constants, k_{NaX_o} and k_{X_w} , are also high,

then the surface concentration of the ionized acid is quickly reduced, resulting in an increase in the interfacial tension at extended times. The interplay of adsorption and desorption barriers is in fact a function of the caustic concentration. Therefore, at low NaOH concentrations, the rate of ionization and subsequent adsorption of the un-ionized acid and the ionized acid exceeds that of their desorption into the respective phases. Thus, tensions show only a decreasing trend as the surface active species continue to accumulate at the oil/water interface, as seen in Figs 11.2-11.4. At high caustic levels, the desorption rate to the bulk phases exceeds that of adsorption. Consequently tensions show an increasing trend after reaching a minimum. However, at intermediate NaOH concentrations, the adsorption barriers are just as important as the desorption barriers, and the interfacial tension passes through a minimum and then increases with time, as shown in Figs. 11.5-11.7.

Table 11.4: Kinetic rate constants of un-ionized acid.

System specifications	Kinetic rate constants ($\text{m}^3/\text{mol.s}$)	
	k_{HX_o}	k_{HX_w}
Acid concentration (mol/m^3)		
1	0.254 ± 0.010	0.075 ± 0.005
10	0.286 ± 0.012	0.084 ± 0.005

Table 11.5: Kinetic rate constants of ionized acid.

System specifications	Kinetic rate constants ($\text{m}^3/\text{mol.s}$)		
	k_{HX_o}	k_{NaX_o}	k_{X_w}
1 mol/m^3 linoleic acid at paraffin oil/water interface for all NaOH concentrations	0.254 ± 0.010	0.351 ± 0.022	0.562 ± 0.035

Figure 11.1: Experimental and predicted transient interfacial tension of acidified paraffin oil against distilled water. (a) 1 mol/m^3 and (b) 10 mol/m^3 .

Figure 11.2: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 0.25 mol/m^3 NaOH solution.

Figure 11.3: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 1.25 mol/m^3 NaOH solution.

Figure 11.4: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 2.5 mol/m^3 NaOH solution.

Figure 11.5: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 5.0 mol/m^3 NaOH solution.

Figure 11.6: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 12.5 mol/m^3 NaOH solution.

Figure 11.7: Experimental and predicted transient interfacial tension of 1 mol/m^3 acidified paraffin oil against 25 mol/m^3 NaOH solution.

11.2.2 Kinetic Rate Constant of Sodium Dodecyl Sulfate

For sodium dodecyl sulfate adsorbing at the oil/water interface, the comparisons of the model calculations with the experimental data are shown in Figs. 11.8-11.13. The values of k_{S_w} which best fit the data are listed in Table 11.6. As shown in this table, the adsorption rate constants are not independent of concentration, with k_{S_w} increasing with increasing sodium dodecyl sulfate concentration. This result suggests that electrostatic effects slow down the adsorption.

The adsorption rate constant values of sodium dodecyl sulfate at the oil/water interface were compared with available literature values at the air/water interface [135,140,141]. Borwankar [135] applied his model to the data of Fainerman [138] for sodium dodecyl sulfate at a concentration of 0.2 mol/m³ and in the presence of 100 mol/m³ and 500 mol/m³ NaCl salt. He found that a value of 67 m³/mol.s for k_{S_w} gave an adequate fit for both sets of data. The same data have been used by Chang and Franses [141] with their modified model based on Langmuir kinetics. The values reported by them, however, were far greater than those reported by Borwankar [135] and they varied with the NaCl concentration. Chang and Franses [141] also used the surface tension data of Koulbek [142] for different concentrations of sodium dodecyl sulfate and in the absence of NaCl. The adsorption rate constant that fitted those data varied with the sodium dodecyl sulfate concentration. For sodium dodecyl sulfate concentration of 1.7 mol/m³, k_{S_w} was estimated to be 55 m³/mol.s, increasing to 90 m³/mol.s for concentration of 3.3 mol/m³.

While the adsorption rate constant of sodium dodecyl sulfate at the oil/water interface is less than that at the air/water interface, the estimated values in this study are in agreement with the values of Chang and Franses [141], at least for

sodium dodecyl sulfate concentrations less than 5.9 mol/m^3 . It is thus demonstrated that the use of the simplified version of the Nernstian film theory as employed by Rubin and Radke for the diffusion process [10], is valid for the case of sodium dodecyl sulfate.

Table 11.6: Kinetic rate constants of sodium dodecyl sulfate.

System Specifications	Kinetic rate constant ($\text{m}^3/\text{mol.s}$) k_{S_w}
sodium dodecyl sulfate concentration (mol/m^3)	
1	19.5
3	22.3
5	28.0
8	42.0

Figure 11.8: Experimental and predicted transient interfacial tension of paraffin oil against 1 mol/m³ sodium dodecyl sulfate solution.

Figure 11.9: Experimental and predicted transient interfacial tension of paraffin oil against 4 mol/m³ sodium dodecyl sulfate solution.

Figure 11.10: Experimental and predicted transient interfacial tension of paraffin oil against 5 mol/m³ sodium dodecyl sulfate solution.

Figure 11.11: Experimental and predicted transient interfacial tension of paraffin oil against 6 mol/m³ sodium dodecyl sulfate solution.

Figure 11.12: Experimental and predicted transient interfacial tension of paraffin oil against 7 mol/m³ sodium dodecyl sulfate solution.

Figure 11.13: Experimental and predicted transient interfacial tension of paraffin oil against 8 mol/m³ sodium dodecyl sulfate solution.

11.3 Model Predictions

The fundamental objective of this section is to solve the model equations using parameter values which would have been determined from single component analysis of the constituent un-ionized acid, ionized acid and sodium dodecyl sulfate. The resulting transient interfacial tensions determined from the model were then compared with the respective experimental values. In the formulation of the transient model, micellar adsorption was not considered and, therefore, only tension data for which the total concentration of surface active species was less than the effective critical micelle concentration were considered in the following analysis. Micellar effects on adsorption may complicate the interpretation of transient tension data, requiring a more elaborate model as well as data concerning micellization kinetics.

11.3.1 Model Predictions for the Acidified Oil/Sodium Dodecyl Sulfate System

Comparative plots for the acidified oil at an acid concentration of 1 mol/m^3 against aqueous sodium dodecyl sulfate solutions are given as Fig. 11.14-11.19. The agreement between experimental tension values and those predicted by the model is good. The good agreement shown in Figs. 11.14-11.19 for this simple system indicates that the proposed model for the binary adsorption of the un-ionized acid and the added surfactant is valid. This also indicates that there are no interactions between the adsorbed acid and the surfactant at the oil/water interface and therefore the assumption of ideal behavior is valid.

Figure 11.14: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 1 mol/m³ sodium dodecyl sulfate solution.

Figure 11.15: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 3 mol/m³ sodium dodecyl sulfate solution.

Figure 11.16: Experimental and predicted transient interfacial tension behavior of 1 mol/m^3 acidified paraffin oil against 4 mol/m^3 sodium dodecyl sulfate solution.

Figure 11.17: Experimental and predicted transient interfacial tension behavior of 1 mol/m^3 acidified paraffin oil against 5 mol/m^3 sodium dodecyl sulfate solution.

Figure 11.18: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 6 mol/m³ sodium dodecyl sulfate solution.

Figure 11.19: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 7 mol/m³ sodium dodecyl sulfate solution.

11.3.2 Model Predictions for the Acidified Oil/Sodium Dodecyl Sulfate and Caustic Mixture Systems

The model represents the global mechanisms for the interactions that can exist between the un-ionized acid, the ionized acid and the added surfactant. It was found that some difficulties arose during the solution of the governing differential equations. The nonlinearity of the differential equations and their large number made the analysis difficult, especially as regards the numerical integration where the integration time steps were small, in order to predict the desired changes in the surface concentrations and, subsequently, the transient interfacial tension. The resulting transient interfacial tensions predicted by the model are compared with the experimental values. Such comparative plots for the systems, constituted by an acid concentration of 1 mol/m^3 , and NaOH and sodium dodecyl sulfate at a concentration ranging from 1 mol/m^3 to 7 mol/m^3 , are shown in Figs. 11.20-11.24. The NaOH concentrations were chosen in order to avoid the formation of micelles.

At caustic concentrations below 12.5 mol/m^3 , the agreement between the experimental tension values and those predicted is good for all sodium dodecyl sulfate concentrations used. Although a good agreement is obtained, a close inspection of the transient interfacial tension curves indicates that the model does not yield exact predictions of tension values at very short times. Experimental data exhibit a plateau lasting about 10 seconds. This plateau is mainly due to the interfacial potential prevailing at the interface. A high interfacial potential, which is the case here, will prevent further adsorption of surface active anions until their concentration in the vicinity of the interface is large enough to overcome the potential barriers. When that happens, the adsorption starts to take place again and subsequently the interfacial

tension continues to decrease subject to the adsorption/desorption barriers. At extended times, the small apparent deviations between the experimental and predicted interfacial tension values are generally within the limits of experimental error of the measurement system. It is expected that discrepancies between the experimental and predicted tension values will be evident at high NaOH concentrations. First, micelle formation affects the measured interfacial tension in a fashion that the model does not account for. Second, hydrodynamic instabilities related to small pendant droplet size during the measurement contribute in part to uncertainty in the experimental data.

Concluding Remarks

Within the range of caustic concentrations used, it is reasonable to claim that the proposed mechanisms and models for the interactions of carboxylic acid with the aqueous solutions of caustic and the added surfactant, i.e. sodium dodecyl sulfate, are valid. Diffusion kinetics considerations, as demonstrated in this study, are found to be appropriate for modelling the transient interfacial tension of such systems. The transient interfacial tension behavior observed is a consequence of the co-existence of adsorption/desorption barriers as well as of interfacial potential barriers, rather than being of purely diffusive origin. The key assumption made in this analysis for the single and for the extended mixture models is that ideal behavior prevails both at the interface and within the bulk phases. An extension of the present models to real systems such as crude oils, which are not ideal solutions, would have to account for the non-ideality by modifying the fractional surface coverage relationship.

Figure 11.20: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 1 mol/m³ sodium dodecyl sulfate and (a) 1.25 mol/m³ (b) 2.5 mol/m³ NaOH solutions.

Figure 11.21: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 2 mol/m³ sodium dodecyl sulfate and (a) 0.25 mol/m³, (b) 1.25 mol/m³ and (c) 2.5 NaOH solutions.

Figure 11.22: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 3 mol/m³ sodium dodecyl sulfate and (a) 0.25 mol/m³, (b) 1.25 mol/m³ and (c) 2.5 NaOH solutions.

Figure 11.23: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 4 mol/m³ sodium dodecyl sulfate and (a) 0.25 mol/m³ and (b) 2.5 mol/m³ NaOH solutions.

Figure 11.24: Experimental and predicted transient interfacial tension behavior of 1 mol/m³ acidified paraffin oil against 5 mol/m³ sodium dodecyl sulfate and (a) 0.25 mol/m³ and (b) 1.25 mol/m³ NaOH solutions.

Chapter 12

Conclusions and Recommendations

12.1 Conclusions

- 1- A modified pendant drop tensiometer suitable for the measurement of equilibrium, transient and dynamic interfacial tensions has been successfully designed and tested.
- 2- The accuracy of this instrument is better than 0.1% in the determination of the surface tension of water as well as in the determination of interfacial tensions in a wide range of hydrocarbon/water systems.
- 3- Data on transient interfacial tension behavior for interfacially-reactive systems, such as encountered in alkaline oil recovery processes, have been obtained.
- 4- Interfacial tension values that could be measured and monitored ranged from as low as 0.2 mN/m to as high as 72 mN/m and interfacial ages extended from 1 s to several hours depending on the specific aqueous phase composition.

- 5- Interfacial tension data determined by the modified pendant drop tensiometer are comparable with those measured with other commercially available instruments such as the spinning drop and the drop volume tensiometers for the same systems.
- 6- An interfacial activity model has been proposed to account for the interactions between acidic oil and alkali in the presence of added surfactant. The model predicts the equilibrium interfacial tension well.
- 7- In acidic oil/alkali systems, the interfacial tension is determined by two parameters, namely, the ionization constant and the equilibrium constant governing the formation of inactive and undissociated soap species. The two parameters have been found to be dependent on acid concentration.
- 8- When the added surfactant is water soluble, the lowering in interfacial tension for the acidic oil/surfactant systems is a result of the simultaneous adsorption of the acid onto the interface.
- 9- The lowering in interfacial tension for acidic oil/alkali systems in the presence of added surfactant results from the simultaneous adsorption of the un-ionized acid, the ionized acid and the added surfactant onto the interface. A synergistic effect appears to exist between the added surfactant and alkali.
- 10- Transient tension experimental studies reveal the existence of a characteristic behavior exhibited by the acidified oil against aqueous solutions. The transient interfacial behavior is a function of acid concentration in the oil phase, caustic concentration, and added surfactant concentration in the aqueous phase.

- 11- There exists an optimum concentration with respect to both caustic and sodium dodecyl sulfate , at which the interfacial tension is the lowest. The optimum concentration has been found to be dependent on acid concentration.
- 12- A physico-chemical model based on convective diffusion, Langmuir sorption kinetics and electrical phenomena has been proposed to account for transient interactions between acidified oil and surfactant-enhanced alkaline systems.
- 13- The transient interfacial tension predicted by the model compares well with experimental data for acidified oil/caustic systems as well as for the oil/added surfactant solutions.
- 14- The pertinent sorptive rate constants have been estimated for the un-ionized acid, the ionized acid and the added surfactant by means of a nonlinear least squares method. The adsorption rate constant of the un-ionized acid is independent of its concentration. The sorptive rate constants associated with the ionized acid and its salt have been found to be independent of the aqueous caustic concentrations. The adsorption rate constant of sodium dodecyl sulfate has also been found to be a function of its concentration.
- 15- The validity of the extended transient model for the interactions between acidified oil and caustic solutions in the presence of added surfactant is confirmed by the close agreement between the predicted interfacial tensions and the experimental data.

12.2 Recommendations

- 1- The measurement of interfacial tension, using the modified pendant drop tensiometer, should be extended to the very low tension range. This would depend on the choice of drop geometry. The drop shape could be better controlled by the choice of capillary tip.
- 2- The interactions between un-ionized acid, ionized acid and added surfactant have been assumed to be ideal in the model. However, mixed interfacial species, both nonionic and ionic, may interact non-ideally at the oil/water interface. Such interactions should be accounted for by incorporating non-ideality into the adsorption isotherms.
- 3- The transient interfacial activity model developed for the acidified oil/alkaline plus added surfactant systems has been formulated for total surface active species concentration below the effective critical micelle concentration of the system. The transient model should be extended to account for the micellar effects by obtaining data on micellization kinetics.

Bibliography

- [1] Gogarty, W.B.: *Status of Surfactant or Micellar Methods*, J. Pet. Tech., 93-102 (Jan 1976).
- [2] Mayer, E.H., Berg, R.L., Carmichael, J.D, and Weinbrandt, R.M.: *Alkaline Injection for Enhanced Oil Recovery-A Status Report*, J. Pet. Tech., 209-221 (Jan 1983).
- [3] Cooke, C.E. Jr, Williams, R.E., and Kolodzie, P.A.: *Oil Recovery by Alkaline Waterflooding*, J. Pet. Tech., 1365-1374 (Dec 1974).
- [4] Jennings, H.Y., Johnson, C.E. Jr, and McAuliffe, C.D.: *A Caustic Waterflooding Process for Heavy Oils*, J. Pet. Tech., 1344-1352 (Dec 1974).
- [5] Castor, T.P., Somerton, W.H., and Kelly, J.F.: *Recovery Mechanisms of Alkaline Flooding in Surface Phenomena in Enhanced Oil Recovery*, Shah, D.O.(Editor), Plenum Press, New York, 249-291 (1981).
- [6] McCaffery, F.G.: *Interfacial Tensions and Aging Behaviour of Some Crude Oils against Caustic Solutions*, J. Can. Pet. Tech., 71-74 (July-Sept. 1972).
- [7] Trujillo, E.M.: *The Static and Dynamic Interfacial Tension between Crude Oil and Caustic Solutions*, Soc. Pet. Eng. J., 23, 645-656 (1983).
- [8] Babu, D.R., Hornof, V., and Neale, G.H: *Evaluation of Aqueous Chemical Systems for Heavy Oil Recovery Processes*, Fuel, 65, 4-7 (1986).
- [9] Pasquarelli, C.H. and Wasan, D.T.: *The effect of Film-Forming Materials on the Dynamic Interfacial Properties in Crude Oil/Aqueous Systems*, in *Surface Phenomena in Enhanced Oil Recovery*, Shah, D.O. (Editor), Plenum Press, New York, 237-238 (1981).
- [10] Rubin, E. and Radke, C.J.: *Dynamic Interfacial Tension Minima in Finite Systems*, Chem. Eng. Sci., 35, 1129-1138 (1980).
- [11] Chan, M. and Yen, T.F.: *A Chemical Equilibrium Model for Interfacial Activity of Crude Oil in Aqueous Alkaline Solution: The Effect of pH, Alkali and Salt*, Can. J. Chem. Eng., 60, 305-308 (1982).

- [12] Ramakrishnan, T.S. and Wasan, D.T.: *A Model for Interfacial Activity of Acidic Crude Oil/Caustic Systems for Alkaline Flooding*, Soc. Pet. Eng. J., **23**, 602-612 (1983).
- [13] deZabala, E.F.: *Tertiary Recovery of Acidic Crude Oils from Oilsands: Mechanisms and Modelling*, Ph.D. Thesis, University of California, Berkeley (1984).
- [14] Borwankar, R.P. and Wasan, D.T.: *Dynamic Interfacial Tension in Acidic Crude Oil/Caustic Systems, Part I: A Chemical Diffusion-Kinetic Model*, AIChE J., **32**(3), 455-466 (1986).
- [15] Sharma, M.M., Jang, L.K., and Yen, T.F.: *Transient Interfacial Tension Behavior of Crude Oil/Caustic Interfaces*, SPE Reservoir Eng., **4**(2), 228-236 (1989).
- [16] Chiwetelu, C. I., Hornof, V., and Neale, G. H.: *Interaction of Aqueous Caustic with Acidic Oils*, J. Can. Pet. Tech., **28**(4), 71-78 (1988).
- [17] Chiwetelu, C.I., Hornof, V., and Neale, G.H.: *Mechanisms for The Interfacial Reaction Between Acidic Oils and Alkaline Reagents*, Chem. Eng. Sci., **45**(3), 627-638 (1990).
- [18] Chiwetelu, C.I., Hornof, V., and Neale, G.H.: *A Dynamic Model for the Interaction of Caustic Reagents with Acidic Oils*, AIChE J., **36**(2), 233-241 (1990).
- [19] Rudin, J. and Wasan, D.T.: *Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: Effect of Added Surfactant*, Ind. Eng. Chem. Res., **31**, 1899-1906 (1992).
- [20] Rudin, J. and Wasan, D.T.: *Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: 1. Experimental Studies*, Colloids and Surfaces, **68**, 67-79 (1992).
- [21] Rudin, J. and Wasan, D.T.: *Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: 2. Theoretical Studies*, Colloids and Surfaces, **68**, 81-94 (1992).
- [22] Nelson, R.C., Lawson, J.B., Thigpen, D.R., and Stegemeier, G.L.: *Cosurfactant Enhanced Alkaline Flooding*, SPE/DOE 12672, presented at the SPE/DOE Fourth Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 15-18, 1984.
- [23] Saleem, S.M. and Hernandez, A.: *Enhanced Oil Recovery of Acidic Crudes by Caustic Cosurfactant-Polymer Flooding*, J. Surf. Sci. Tech., **3**(1), 1-10 (1987).
- [24] Potts, D.E. and Kuehne, D.L.: *Strategy for Alkaline/Polymer Flood Design with Berea and Reservoir-Rock Corefloods*, SPE Reservoir Eng., **3**(4), 1143-1152 (1988).

- [25] Shuler, P.J., Kuehne, D.L., and Lerner, R.M.: *Improving Chemical Flood Efficiency with Micellar/Alkaline/Polymer Processes*, J. Pet. Tech., 41(1), 80-88 (1989).
- [26] Nelson, R.C.: *Chemically Enhanced Oil Recovery: The State of the Art*, Chem. Eng. Prog., 85, 50-57 (1989).
- [27] Huang, Y.D., Yang, P.H., and Qin, T.L.: *A Study on the Dynamic Interfacial Tension of Crude Oil/Alkali (Alkali-Polymer) Systems, In Situ*, 13(4), 259-274 (1989).
- [28] Surkalo, H.: *Enhanced Alkaline Flooding*, J. Pet. Tech, 42(1), 6-7 (1990).
- [29] Peru, D.A. and Lorenz, P.B.: *Surfactant-Enhanced Low-pH Alkaline Flooding*, SPE Reservoir Eng., 5(3), 327-332 (1990).
- [30] Taylor, K.C., Hawkins, B.F., and Islam, M.R.: *Dynamic Interfacial Tension in Surfactant-Enhanced Alkaline Flooding*, J. Can. Pet. Tech., 29, 50-55 (1990).
- [31] Hawkins, B., Taylor, K., and Nasr-El-Din, H.: *Mechanisms of Surfactant and Polymer Enhanced Alkaline Flooding: Application to David Lloydminster and Wainwright Sparky Fields*, J. Can. Pet. Tech., 33(4), 52-63 (1994).
- [32] Chiwetelu C.I., Hornof, V., Neale, G.H., and George, A.E.: *Use of Mixed Surfactants to Improve the Transient Interfacial Tension Behavior of Heavy Oil/Alkaline Systems*, Can. J. Chem. Eng., 72, 534-540 (1994).
- [33] Taber, J.J. and Martin, F.D.: *Technical Screening Guides for the Enhanced Recovery of Oil*, SPE 12069, presented at the 58th Annual Conference and Exhibition of the Society of Petroleum Engineers, San Francisco, California, 1983.
- [34] Taber, J.J.: *Research on Enhanced Oil Recovery: Past, Present, and Future*, Pure App. Chem., 52, 1323-1347 (1980).
- [35] Jha, K.N.: *Enhanced Oil Recovery: An Introduction*, Chemistry in Canada, 34, 19-26 (1982).
- [36] Prince, J.P.: *Enhanced Oil Recovery Potential in Canada - A Methodological Review*, Canadian Energy Research Institute, Calgary (1978).
- [37] Nutting, P.G.: *Soda Process for Petroleum Recovery*, Oil and Gas J. , 25(45), 76, 150 (1927).
- [38] Nutting, P.G.: *Principles Underlying Soda Process*, Oil and Gas J. , 25(50), 32, 106 (1927).

- [39] Atkinson, H.: *Recovery of Petroleum from Oil Bearing Sands*, U.S. Patent No 1,651,311 (1927).
- [40] Subkow, P.: *Process for the Removal of Bitumen from Bituminous Deposits*, U.S. Patent No 2,288,857 (1942).
- [41] Johnson, C.E.: *Status Of Caustic and Emulsion Methods*, J. Pet. Tech., 85-92 (Jan 1976).
- [42] Wagner, O.R. and Leach, R.O.: *Improving Oil Displacement Efficiency by Wettability Adjustment*, AIME Pet. Trans., 216 63-72 (1956).
- [43] Campbell, T.C.: *The Role of Alkaline Chemicals in Oil Displacement Mechanisms in Surface Phenomena in Enhanced Oil Recovery*, Shah D.O. (Editor), Plenum Press, New York, 293-306 (1981).
- [44] Campbell, T.C.: *The Role of Alkaline Chemicals in the Recovery of Low-Gravity Crude Oils*, J. Pet. Tech., 2510-2516 (Nov 1982).
- [45] deZabala, E.F. and Radke, C.J.: *The Role of Interfacial Resistances in Alkaline Waterflooding of Acid Oils*, SPE 11213, presented at the 57th Annual Fall Technical Conference of AIME, New Orleans, LA, Sept 26-29, 1982.
- [46] Owens, W.W. and Archer, D.L.: *The Effect of Rock Wettability on Oil/Water Relative Permeability Relationships*, J. Pet. Tech., 873-878 (July 1971).
- [47] Ehrlich, R., Hasiba, H.H., and Raimond, P.: *Alkaline Waterflooding for Wettability Alteration - Evaluation of Potential Field Application*, J. Pet. Tech., 1335-1343 (Dec. 1974).
- [48] Lochte, H.L.: *Petroleum Acids and Basis*, Ind. Eng. Chem., 44(11), 2597-2601 (1952).
- [49] Seifert, W.K. and Howells, W.G.: *Interfacially Active Acids in a California Crude Oil*, Anal. Chem., 41(12), 1638-1647 (1969).
- [50] Seifert, W.K. and Teeter, R.M.: *Preperative Thin Layer Chromatography and High Resolution Mass Spectrometry of Crude Oil Carboxylic Acids*, Anal. Chem., 41(6), 786-795 (1969).
- [51] Seifert, W.K. and Teeter, R.M.: *Identification of Polycyclic Aromatic and Heterocyclic Crude Oil Carboxylic Acids*, Anal. Chem., 42(7), 750-758 (1970).
- [52] Seifert, W.K., Gallegos, E.G., and Teeter, R.M.: *Proof of Structure of Steroid Carboxylic Acids in a California Petroleum by Deuterium Labelling, Synthesis and Mass Spectrometry*, J. Am. Chem. Soc., 94(16), 5880-5887 (1972).

- [53] Jang, L.K., Sharma, M.M., Chang, Y.I., Chan, M., and Yen, T.F.: *Correlation of Petroleum Component Properties for Caustic Flooding*, AIChE Symposium Series, 78(212), 97-104 (1982).
- [54] Dunning, H.N., Moore, J.W., and Denekas, M.D.: *Interfacial Activities and Porphyrin Contents of Petroleum Extracts*, Ind. Eng. Chem., 45(8), 1759-1765 (1953).
- [55] Khulbe, K.C., Neale, G.H., and Hornof, V.: *Interfacial Activity of Heavy Oil and Its Maltene Constituents Against Caustic Solution*, AOSTRA J. Research, 2(2), 95-101 (1985).
- [56] Sherwood, T.K. and Wei, J.C.: *Interfacial Phenomena in Liquid-Liquid Extraction*, Ind. Eng. Chem., 49(6), 1030-1034 (1957).
- [57] Ward, A.F.H. and Tordai, L.: *Time Dependence of Boundary Tension of Solution - I. The Role of Diffusion in Time Effects*, J. Chem. Phys., 14, 453-461 (1946).
- [58] England, D.C. and Berg, J.C.: *Transfer of Surface-Active Agents Across a Liquid-Liquid Interface*, AIChE J., 17(2), 313-322 (1971).
- [59] Clift, R. and Weber, M.E.: *Bubbles, Drops and Particles*, Academic Press, New York (1978).
- [60] Sawistowski, H.: *Recent Advances in Liquid-Liquid Extraction*, (C. Hansen, Ed.), Pergamon, Oxford (1971).
- [61] Ostrovsky, M.V. and Good, R.J.: *Mass Transfer and Dynamic Liquid-Liquid Interfacial Tension*, J. Colloid Interface Sci, 106(1), 131-139 (1985).
- [62] Hornof, V. and Baig, F.U.: *Influence of Interfacial Reaction and Mobility Ratio on the Displacement of Oil in a Hele-Shaw Cell*, Exp. Fluids, 18, 448-453 (1995).
- [63] Sternling, C.V. and Scriven, L.E.: *Interfacial Turbulence: Hydrodynamic Instability and Marangoni Effect*, AIChE J., 5(4), 514-523 (1959).
- [64] Cratin, P.D.: *A Quantitative Characterization of pH-Dependent Systems*, Ind. Eng. Chem., 61(2), 35-45 (1969).
- [65] Chiwetelu, C.I., Neale, G.H., and Hornof, V.: *Interfacial Activity of Linoleic Acid/Caustic Systems*, J. Surface Sci. Tech., 6(4), 305-315 (1990).
- [66] Nasr-El-Din, H.A., Khulbe, K.C., Hornof, V., and Neale, G.H.: *Effects of Interfacial Reaction on the Radial Displacement of Oil by Alkaline Solutions*, Rev. Inst. Francais du Pétrole, 45(2), 231-244 (1990).

- [67] Patil, G.S., Mathews, R.H., and Cornwall, D.G.: *Estimation of Ionization in Unstable Fatty Acid Monolayers from Desorption Kinetics*, in *Monolayers-Advances in Chemistry Series 144*, ACS, (Goddard, E.D., Editor), Washington DC, 44-66 (1975).
- [68] Mingzhe, T., Pu, L., Lufang, Z., and Yajie, Z.: *An Improved Model For Interfacial Activity of Acidic Oil/Caustic System for Alkaline Flooding*, SPE 14855, presented at the SPE International Meeting on Petroleum Engineering, Beijing, China, 189-199 (Mars 17-20, 1986).
- [69] Brown, J.B. and Radke, J.C.: *Area Effects in Spinning Drop Dynamic Interfacial Tensions*, Chem. Eng. Sci., **35**, 1458-1460 (1980).
- [70] Touhami, Y., Hornof, V., and Neale, G.H.: *Interfacial Tension Behavior of an Acidified Oil/Surfactant System*, J. Colloid Interface Sci., **166**, 506-508 (1994).
- [71] Davies, J.T. and Rideal, E.K.: *Interfacial Phenomena*, 2nd Edition, Academic Press, New York (1963).
- [72] Adamson, A.W.: *Physical Chemistry of Surfaces*, 3rd Edition, John Wiley and Sons, New York (1976).
- [73] Harkins, W.D. in A. Weissberger (Ed.): *Physical Methods of Organic Chemistry*, **1**, Interscience, New York (1959).
- [74] Padday, J.F. in Matijević, E. (Ed.): *Surface and Colloid Science*, **1**, Wiley-Interscience, New York (1969).
- [75] Chiwetelu, C.I., Hornof, V., and Neale, G.H.: *The Measurement of Dynamic Interfacial Tension by Photo-Micropendography*, J. Colloid Interface Sci., **125**, 586-601 (1988).
- [76] Chiwetelu, C.I., Neale, G.H., and Hornof, V.: *Dynamic Tension in Finite Oil Droplets*, Chem. Eng. Comm., **84**, 13-20 (1989).
- [77] Princen, H.M., Zia, I.Y.Z., and Mason, S.G.: *Measurement of Interfacial Tension from the Shape of a Rotating Drop*, J. Colloid Interface Sci., **23**, 99-107 (1967).
- [78] Cayias, J.L., Schechter, R.S., and Wade, W.H.: *the Measurement of Low Interfacial Tension via the Spinning Drop Technique in Adsorption at Interfaces*, ACS Symposium Series (8), (Mittal, K.L., Editor), Washington D.C., 234-247 (1975).
- [79] Slattery, J.C. and Chen, J.D.: *Alternative Solution for Spinning Drop Interfacial Tensiometer*, J. Colloid Interface Sci., **64**, 371-373 (1978).

- [80] Bashforth, F. and Adams, J.C.: *An Attempt to Test the Theories of Capillary Action*, Cambridge Univ. Press, Cambridge (1883).
- [81] Ambwani, D.S and Tomlinson, F. in Good, R.J., and Stromberg, R.R. (Eds.): *Surface and Colloid Science*, 11, Plenum, New York, 93-119 (1979).
- [82] Andreas, J.M., Hauser, E.A., and Tucher, W.B.: *Boundary Tensions by Pendant Drops*, J. Phys. Chem., 42 1001-1017 (1938).
- [83] Stauffer, C.E.: *the Measurement of Surface Tension by the Pendant Drop Technique*, J. Phys. Chem., 69, 1933-1938 (1965).
- [84] Taylor, K.C. and Schramm, L.L: *Measurement of Short-Term Low Dynamic Interfacial Tensions: Application to Surfactant Enhanced Alkaline Flooding in Enhanced Oil Recovery*, Colloids Surfaces, 47, 245-253 (1990).
- [85] Pallas, N.R. and Harrison, Y.: *An Automated Drop Shape Apparatus and Surface Tension of Pure Water*, Colloids Surfaces, 43, 169-194 (1990).
- [86] Lin, S.Y., McKeigue, K., and Maldarelli, C.: *Diffusion-limited Interpretation of the Induced Period in the Relaxation in Surface Tension Due to the Adsorption of Straight Chain, Small Polar Group Surfactant: Theory and Experiment*, Langmuir, 7, 1055-1062 (1991).
- [87] Nagarajan, R. and Wasan, D.T.: *Measurement of Dynamic Interfacial Tension by an Expanding Drop Tensiometer*, J. Colloid Interface Sci., 159, 164-173 (1993).
- [88] Miller, R., Sedev, R., Schano, K., and Neumann, A.W.: *Relaxation of Adsorption Layers at Solution/Air Interfaces Using Axisymmetric Drop-Shape Analysis*, Colloids Surfaces, 69, 209-216 (1993).
- [89] McCracken, M.S., Severance, W.F., and Jones, T.: *Video Digidizer*, Anal. Chem., 54, 2394-2397 (1982).
- [90] Girault, H.H.J., Schiffrin, D.J., and Smith, B.D.V.: *Drop Image Processing for Surface and Interfacial Tension Measurements*, J. Electroanal. Chem., 137, 207-217 (1982).
- [91] Girault, H.H.J., Schiffrin, D.J., and Smith, B.D.V.: *The Measurement of Interfacial Tension of Pendant Drops Using a Video Image Profile Digitizer*, J. Colloid Interface Sci., 101, 257-266 (1984).
- [92] Anastasiadis, S.H., Chen, J.K, Koberstein, J.T., Siegel, A.F., Sohn, J.E., and Emerson, J.A.: *The Determination of Interfacial Tension by Video Image Processing of Pendant Fluid Drops*, J. Colloid Interface Sci., 119(1), 55-66 (1987).

- [93] Cheng, P., Rotenberg, Y., Boruvka, L., and Newmann, A. W.: *Automation of Axisymmetric Drop Shape Analysis for Measurements of Interfacial Tensions and Contact Angles*, Colloids Surfaces, 43, 151-167 (1990).
- [94] Carlà, M., Cecchini, R., and Bordi, S.: *An Automated Apparatus for Interfacial Tension Measurements by the Sessile Drop Technique*, Rev. Sci. Instrum., 62(4), 1088-1092 (1991).
- [95] Hansen, F.K. and Rødsrud, G.: *Surface Tension by Pendant Drop: 1. A Fast Standard Instrument Using Computer Image Analysis*, J. Colloid Interface Sci., 141(1), 1-9 (1991).
- [96] Weszak, J.S.: *Syrvey: A Survey of Threshold Selection Techniques*, Computer Graphics and Image Processing, 7, 259-265 (1978).
- [97] Pavlidis, T.: *Algorithms for Graphics and Image Processing*, Computer Science Press, Rockville (1982).
- [98] Pavlidis, T.: *Structural Pattern Recognition*, Springer Verlag, New York (1982).
- [99] Fu, K.S., Gonzalez, R.C., and Lee, C.S.G.: *Robotics: Control, Sensing, Vision and Intelligence*, Mc Graw-Hill, New York (1987).
- [100] Khalfallah, H.: *Visual Position Recovery for an Automated Guided Vehicle Using Pseudo-Random Encoding*, M.A.Sc. Thesis, University of Ottawa, Ottawa (1991).
- [101] Rotenberg, Y., Boruvka, L., and Newmann, A.W.: *Determination of Surface Tension and Contact Angle from the Shapes of Axisymmetric Fluid Interfaces*, J. Colloid Interface Sci., 93, 169-183 (1983).
- [102] Vos, H. and Los, J.M.: *Interfacial Tensions from Sessile-Drop Profiles. The Interface Hg/0.116 KCl at 25° C*, J. Colloid Interface Sci., 74, 360-369 (1980).
- [103] Jennings, J.W. and Pallas, N.R.: *An Efficient Method for the Determination of Interfacial Tensions from Drop Profiles*, Langmuir, 4, 959-967 (1988).
- [104] Currie, P.K. and van Nieuwkoop, J.: *Buoyancy Effects in the Spinning-Drop Interfacial Tensiometer*, J. Colloid Interface Sci., 87, 301-316 (1982).
- [105] Manning, C.D. and Scriven, L.E.: *Interfacial Tension Measurement with a Spinning Drop in Gyrostatic Equilibrium*, Rev. Sci. Instrum., 48, 1699-1705 (1977).
- [106] Chatenay, D., Langevin, D., and Meunier, J.: *Measurement of Low Interfacial Tension, Comparison Between a Light Scattering Technique and the Spinning Drop Technique*, J. Dispersion Sci., 3(3), 245-260 (1982).

- [107] Gardner, J.E. and Hayes, M.E.: *The Spinning-Drop Interfacial Tensiometer Model 500: Instruction Manual*, Department of Chemistry, University of Texas at Austin, Texas (1975).
- [108] Reive, D.M.: *Interfacial Tension Behaviour of a Canadian Heavy Oil against Caustic Solutions*, M.A.Sc. Thesis, University of Ottawa, Ottawa (1985).
- [109] Hool, K. and Schuchardt, B.: *A New Instrument for the Measurement of Liquid-Liquid Interfacial Tension and the Dynamics of Interfacial Tension Reduction*, Meas. Sci. Tech., **3**, 451-457 (1992).
- [110] Donahue, D.J. and Bartell, F.E.: *The Boundary Tension at Water-organic liquid Interfaces*, J. Phys. Chem., **56**, 480-487 (1952).
- [111] Satherley, J, Girault, H.H.J., and Schiffrin, D.J.: *The Measurement of Ultralow Interfacial Tension by Video Digital Techniques*, J. Colloid Interface Sci., **136**, 574-580 (1990).
- [112] Miller, R., Loglio, G., Tesei, U., and Schano, K.-H., *Surface Relaxations as a Tool for Studying Dynamic Interfacial Behaviour*, Advances in Colloid and Interface Sci., **37**, 73-96 (1991).
- [113] Fainerman, V.B.: *Adsorption Kinetics from Concentrated Micellar Solutions of Ionic Surfactants at the Water-Air Interface*, Colloids Surfaces, **62**, 333-347 (1992).
- [114] Davies, J.T.: *The application of Gibbs Equation to Charged Monolayers and Their Desorption from Oil/Water Interface*, Trans. Faraday Soc., **48**, 1052-1061 (1952).
- [115] Lucassen-Reynders, E.H.: *Surface Equation of State for Ionized Surfactants*, J. Phys. Chem., **70**, 1777-1785 (1966).
- [116] Tanford, C.: *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, John Wiley and Sons, New York (1980).
- [117] Bard, Y.: *Nonlinear Parameter Estimation*, Academic Press, New York (1974).
- [118] Marquardt, D.W.: *Solution of Nonlinear Chemical Engineering Models*, Chem. Eng. Progress, **55**(6), 65-70 (1959).
- [119] Marquardt, D.W.: *An Algorithm for Least Squares Estimation of Nonlinear Parameters*, J. Soc. Ind. Appl. Math., **11**(3), 431-441 (1963).
- [120] IMSL Corporation: *The IMSL Libraries: Problem-Solving Software Systems for Numerical Fortran Programming*, 1-4, Houston, TX (1982).

- [121] Kittrell, J.R., Mezaki, R., and Watson, C.C.: *Estimation of Parameters for Nonlinear Least Squares Analysis*, Ind. Eng. Chem., 57(12), 19-27 (1965).
- [122] Levich, V.G.: *Physico-Chemical Hydrodynamics*, Prentice Hall, New Jersey (1962).
- [123] Wilke, C.R. and Chang, P.: *Correlation of Diffusion Coefficients in Dilute Solutions*, AIChE J., 1, 264-270 (1955).
- [124] Tyn, M.T. and Calus, W.F.: *Diffusion Coefficients in Dilute Binary Mixtures*, J. Chem. Eng. Data, 20(1), 106-109 (1975).
- [125] Reid, R.C., Prausnitz, J.M., and Sherwood, T.K.: *The Properties of Gases and Liquids*, 3rd Edition, McGraw-Hill, New York (1977).
- [126] van Voorst Vader, F.: *Adsorption of Detergents at the Liquid-Liquid Interface*, Trans. Faraday Soc., 56, 1067-1079 (1960).
- [127] Moroi, Y.: *Mass Action Model of Micelle Formation: Its Application to Sodium Dodecyl Sulfate Solution*, J. Colloid Interface Sci., 122, 308-314 (1988).
- [128] Shinoda, K.: *The Effect of Chain Length, Salt and Alcohols on the Critical Micelle Concentration*, Bull. Chem. Soc. Japan, 26, 101-105 (1953).
- [129] Shinoda, K.: *The Effect of Alcohols on the Critical Micelle Concentrations of Fatty Acid Soaps and the Critical Micelle Concentration of Soap Mixtures*, J. Phys. Chem., 58, 1136-1141 (1954).
- [130] Nishikido, N., Moroi, Y., Uehara, H., and Matuura, R.: *Effect of Alcohols on the Micelle Formation of Nonionic Surfactants in Aqueous Solutions*, Bull. Chem. Soc. Japan, 47, 2634-2638 (1974).
- [131] Rehfeld, S.J.: *Adsorption of Sodium Dodecyl Sulfate at Various Hydrocarbon/Water Interfaces*, J. Phys. Chem., 71, 738-745 (1967).
- [132] van Hunsel, J., Bleys, G., and Joos, P.: *Adsorption Kinetics at the Oil/Water Interface*, J. Colloid Interface Sci., 114, 432-441 (1986).
- [133] Bleys, G. and Joos, P.: *Adsorption Kinetics of Bolaform Surfactants at the Air/Water Interface*, J. Phys. Chem., 89, 1027-1032 (1985).
- [134] Joos, P. and Rillaerts, E.: *Theory on the Determination of the Dynamic Surface Tension with the Drop Volume and Maximum Bubble Pressure Methods*, J. Colloid Interface Sci., 79, 96-100 (1981).
- [135] Borwankar, R.P.: *Surfactant Adsorption at Fluid-Fluid Interfaces with Application to Alkaline Flooding*, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Illinois (1984).

- [136] Kamenka, N., Lindman, B., and Brun, B.: *Colloid Polym. Sci.*, **252**, 144 (1972).
- [137] Weinheimer, R.M., Evans, D.F., and Cussler, E.L.: *Diffusion in Surfactant Solutions*, *J. Colloid Interface Sci.*, **80**, 357-368 (1981).
- [138] Fainerman, V.B.: *Kinetics of Adsorption of Sodium Dodecyl Sulfate from Aqueous Solutions in the Presence of NaCl*, *Colloid J. USSR*, **40**, 769-776 (1978).
- [139] Stigter, D., Williams, R.J., and Mysels, K.J.: *J. Phys. Chem.*, **59**, 330 (1955).
- [140] Chang, C.H., Wang, N.-H.L., and Franses, E.I.: *Adsorption Dynamics of Single and Binary Surfactants at the Air/Water Interface*, *Colloids and Surfaces*, **62**, 321-332 (1992).
- [141] Chang, C.H. and Franses, E.I.: *Modified Langmuir-Hinshelwood Kinetics for Dynamic Adsorption of Surfactants at the Air/Water Interface*, *Colloids and Surfaces*, **69**, 189-201 (1992).
- [142] Koulbek, J.: *J. Colloid Interface Sci.*, **41**, 17 (1972).
- [143] Yang, R.T.: *Gas Separation by Adsorption Processes*, Butterworths, Boston (1987).

Part V

Appendices

Appendix A

Micellar Relationships

A.1 Expression for the Micellization Constant

Considering the equilibrium equation (6.14) and assuming monodispersed micelles, the mass action model gives the following expression for the micelle concentration, C_m :

$$C_m = K_m (C_{S^-})^n (C_{Na^+})^{n(1-\alpha)} \quad (\text{A.1})$$

The material balance equations of surfactant ions, S^- , and counterions, Na^+ , in a micellar solution have the following form:

$$C = C_{S^-} + nC_m \quad (\text{A.2})$$

$$C = C_{Na^+} + n(1-\alpha)C_m \quad (\text{A.3})$$

From Eqs. A.2 and A.3, and excluding C_m , we derive:

$$C_{Na^+} = (1-\alpha)C_{S^-} + \alpha C \quad (\text{A.4})$$

Introducing a value for the degree of micellization, ε_i , which represents the fraction of the ions of the i th sort which are associated.

$$\varepsilon_i = \frac{C - C_i}{C} \quad (\text{A.5})$$

Expanding Eq. A.5 for each component, we get:

$$C_{S^-} = C(1 - \varepsilon_1) \quad (\text{A.6})$$

$$C_{Na^+} = C(1 - \varepsilon_2) \quad (\text{A.7})$$

Combining Eqs. A.2 and A.6 and Eqs. A.3 and A.7 we get:

$$C_m = \varepsilon_1 \frac{C}{n} \quad (\text{A.8})$$

$$C_m = \varepsilon_2 \frac{C}{n(1 - \alpha)} \quad (\text{A.9})$$

Taking the logarithm of K_m ,

$$\ln K_m = \ln C_m - n \ln C_{S^-} - n(1 - \alpha) \ln C_{Na^+} \quad (\text{A.10})$$

Taking into account Eqs. A.8 and A.9, Eq. A.10 becomes:

$$\ln K_m = \ln\left(\frac{\varepsilon_1}{n}\right) + [1 - n(2 - \alpha)] \ln C - n \ln(1 - \varepsilon_1) - n(1 - \alpha) \ln(1 - \varepsilon_2) \quad (\text{A.11})$$

$$K_m = \left[\frac{\varepsilon_1}{n(1 - \varepsilon_1)^n(1 - \varepsilon_2)^{n(1 - \alpha)}} \right] \left(\frac{1}{C} \right)^{n(2 - \alpha) - 1} \quad (\text{A.12})$$

From Eqs. A.9 and A.10 it is clear that:

$$\varepsilon_2 = (1 - \alpha)\varepsilon_1 \quad \text{or} \quad 1 - \varepsilon_2 = 1 - \varepsilon_1 + \alpha\varepsilon_1 \quad (\text{A.13})$$

The final expression for the micellization constant is given by;

$$K_m = \left[\frac{\varepsilon_1}{n(1 - \varepsilon_1)^n(1 - \varepsilon_1 + \alpha\varepsilon_1)^{n(1 - \alpha)}} \right] \left(\frac{1}{C} \right)^{n(2 - \alpha) - 1} = F_m(\varepsilon) \left(\frac{1}{CMC} \right)^{n(2 - \alpha) - 1} \quad (\text{A.14})$$

At a surfactant concentration equal to the CMC, $\epsilon_1 \ll 1$, and, therefore, the last two terms in Eq. A.12 may be negligible. Because of the small value of ϵ_1 and the large value of n , the first term of Eq. A.12 becomes small compared with the second term. Thus, provided that ϵ_1 is small, i.e. $C = \text{CMC}$, Eq. A.12 becomes:

$$\ln K_m = (1 - n(2 - \alpha)) \ln \text{CMC} \quad (\text{A.15})$$

$$K_m = \left(\frac{1}{\text{CMC}} \right)^{n(2-\alpha)-1} \quad (\text{A.16})$$

A.2 Critical Micellar Concentration Relationships

In the case when a mixed micelle is formed, it is assumed that the surfactant ion, the acid and the ionized acid dissolve each other in a state of regular solution and the following relation is obtained:

$$\frac{C_{S-}}{C'_{S-}} = (1 - x - y) \quad (\text{A.17})$$

where C'_{S-} is the concentration of surfactant ion in solution equilibrium with the surfactant ion micelle, C_{S-} is the concentration of surfactant ion in solution equilibrium with the mixed micelle, and x and y are the mole fractions of the acid and ionized acid in the mixed micelle, respectively.

The acid and the ionized acid are considered to undergo partitioning between the micellar state and the solution as follows:

$$\frac{C_{HX_w}}{x} = K'_{o,HX} \exp \left(-\frac{m'w_{HX}}{kT} \right) \quad (\text{A.18})$$

and

$$\frac{C_{X-}}{y} = K'_{o,X} \exp \left(-\frac{m'w_{X-} + \epsilon\psi'_o}{kT} \right) \quad (\text{A.19})$$

Combining Eq. A.17, Eq. A.18 and Eq. A.19,

$$\frac{C_{S^-}}{C'_{S^-}} = 1 - K_{o,HX} C_{HXw} - K_{o,X} C_{X^-} \quad (A.20)$$

Where

$$K_{o,HX} = \frac{\exp\left(\frac{m'w_{HX}}{kT}\right)}{K'_{o,HX}} \quad (A.21)$$

and

$$K_{o,X} = \frac{\exp\left(\frac{m'w_{X^-} + e\psi'_o}{kT}\right)}{K'_{o,X}} \quad (A.22)$$

Making appropriate substitutions into Eq. A.20 results in:

$$\frac{C_{S^-}}{C'_{S^-}} = 1 - \left(K_{o,X} + \frac{K_{o,HX} K_w}{K'_{HX} C_{OH^-}} \right) C_{X^-} \quad (A.23)$$

In the case when a single micelle is formed (i.e. no interaction between the surfactant and the remaining active species) Eq. A.23 becomes:

$$C'_{S^-} = C_{S^-} \quad (A.24)$$

Appendix B

Fractional Surface Coverage in a Multicomponent System

For an n-component mixture adsorbing at an interface, the fractional surface coverage corresponding to a component i is given by the extended Langmuir Model:

$$\theta_i = \frac{K_{L,i}C_i}{1 + \sum K_{L,j}C_j} \quad (\text{B.1})$$

The total fractional surface coverage, θ_t , is:

$$\theta_t = \sum \theta_i = \frac{\sum K_{L,i}C_i}{1 + \sum K_{L,j}C_j} \quad (\text{B.2})$$

If, however, each species maintains its own molecular area (i.e. the area covered by one molecule that is not influenced by the presence of other species on the surface) then the amount of i adsorbed in the mixture is:

$$\Gamma_i = \frac{\Gamma_{i,max}K_{L,i}C_i}{1 + \sum K_{L,j}C_j} \quad (\text{B.3})$$

where $\Gamma_{i,max}$ is the monolayer amount for i when the pure component adsorption is considered.

The thermodynamic consistency of Eq. B.3 has been discussed by Yang [143]. Following a reversible isothermal cycle in a system undergoing adsorption-desorption,

it is shown that the monolayer adsorption must be equal for all species, or $\Gamma_{i,\max} = \Gamma_{j,\max}$. For binary mixtures, the following averaged $\Gamma_{\max,m}$ value has been used for both species for a gas binary mixture [143] and for liquid binary mixtures [72,21]. The averaged $\Gamma_{\max,m}$ is then given by:

$$\frac{1}{\Gamma_{\max,m}} = \frac{X_1}{\Gamma_{1,\max}} + \frac{X_2}{\Gamma_{2,\max}} \quad (\text{B.4})$$

where

$$X_i = \Gamma_i / \sum_{i=1}^2 \Gamma_i \quad \text{and} \quad \sum_{i=1}^2 X_i = 1 \quad (\text{B.5})$$

This postulation is based on the additivity of surface areas per molecule of each species rather than on the additivity of the number of moles per unit area at the interface. Assuming that this relation holds for an n-component mixture one can write:

$$\frac{1}{\Gamma_{\max,m}} = \sum_{i=1}^n \frac{X_i}{\Gamma_{i,\max}} \quad (\text{B.6})$$

For a single adsorbing species, the fractional surface coverage, θ , is given by:

$$\theta = \frac{\Gamma}{\Gamma_{\max}} \quad (\text{B.7})$$

The following proof shows that the total fractional surface coverage, θ , is the summation of the individual fractional surface coverages, θ_i . By definition, we have;

$$\theta = \frac{\Gamma}{\Gamma_{\max,m}} = \frac{\sum_{i=1}^n \Gamma_i}{\Gamma_{\max,m}} \quad (\text{B.8})$$

$$= \left(\sum_{i=1}^n \Gamma_i \right) \left(\sum_{i=1}^n \frac{X_i}{\Gamma_{i,\max}} \right) \quad (\text{B.9})$$

$$= \left(\sum_{i=1}^n \Gamma_i \right) \left(\sum_{i=1}^n \frac{\Gamma_i}{\sum_{j=1}^n \Gamma_j} \frac{1}{\Gamma_{i,\max}} \right) \quad (\text{B.10})$$

$$= \left(\sum_{i=1}^n \Gamma_i \right) \frac{1}{\left(\sum_{j=1}^n \Gamma_j \right)} \left(\sum_{i=1}^n \frac{\Gamma_i}{\Gamma_{i,max}} \right) \quad (B.11)$$

$$= \sum_{i=1}^n \frac{\Gamma_i}{\Gamma_{i,max}} \quad (B.12)$$

In the case of a three component system, we obtain;

$$\theta = \frac{\Gamma_{X-}}{\Gamma_{X-,max}} + \frac{\Gamma_{HX_o}}{\Gamma_{HX_o,max}} + \frac{\Gamma_{S-}}{\Gamma_{S-,max}} \quad (B.13)$$

The adsorption maximum for the mixture is then given by:

$$\begin{aligned} \frac{1}{\Gamma_{max,m}} &= \frac{\Gamma_{X-}}{\Gamma_{X-} + \Gamma_{HX_o} + \Gamma_{S-}} \frac{1}{\Gamma_{X-,max}} \\ &+ \frac{\Gamma_{HX}}{\Gamma_{X-} + \Gamma_{HX_o} + \Gamma_{S-}} \frac{1}{\Gamma_{HX_o,max}} \\ &+ \frac{\Gamma_{S-}}{\Gamma_{X-} + \Gamma_{HX_o} + \Gamma_{S-}} \frac{1}{\Gamma_{S-,max}} \end{aligned} \quad (B.14)$$

Appendix C

Physical Properties of Solutions

C.1 Properties of Aqueous Solutions

The physical properties required in this study (such as density and pH) have been measured for all of the aqueous solutions. Table C.1 lists the density values for the solutions at different sodium dodecyl sulfate and NaOH concentrations. The density of distilled water is 0.99704 g/cm^3 at 25°C . As shown in Table C.1, the density of the aqueous solutions increases with both increasing NaOH and sodium dodecyl sulfate concentrations. Table C.2 lists the pH of the aqueous mixture solutions of NaOH and sodium dodecyl sulfate at various working concentrations. The pH of the sodium dodecyl sulfate solutions in the absence of NaOH is about 10.0 at 25°C . The pH of the aqueous NaOH solutions decreases marginally with addition of increasing amounts of sodium dodecyl sulfate .

Table C.1: Densities of the caustic/sodium dodecyl sulfate solutions at 25°C (g/cm³)

NaOH (mol/m ³)	sodium dodecyl sulfate (mol/m ³)							
	0	1	2	3	4	5	6	7
0.00	0.9970	0.9971	0.9972	0.9973	0.9973	0.9974	0.9974	0.9975
0.25	0.9971	0.9971	0.9972	0.9973	0.9973	0.9974	0.9974	0.9975
1.25	0.9971	0.9972	0.9973	0.9974	0.9974	0.9975	0.9975	0.9976
2.50	0.9972	0.9972	0.9973	0.9974	0.9975	0.9975	0.9976	0.9977
12.50	0.9976	0.9976	0.9977	0.9978	0.9978	0.9979	0.9978	0.9980
25.00	0.9981	0.9981	0.9982	0.9983	0.9985	0.9987	0.9988	0.9989
125.00	1.0022	1.0023	1.0023	1.0024	1.0025	1.0026	1.0026	1.0027
250.00	1.0074	1.0075	1.0077	1.0077	1.0078	1.0079	1.0080	1.0081

Table C.2: pH of the caustic/sodium dodecyl sulfate solutions at 25°C

NaOH (mol/m ³)	sodium dodecyl sulfate (mol/m ³)			
	0	1	4	7
0.00	7.01	10.0	10.0	10.0
0.25	10.35	10.08	10.08	10.04
1.25	11.09	10.81	10.80	10.74
2.50	11.40	11.06	11.11	11.05
12.50	12.06	11.89	11.83	11.75
25.00	12.39	12.24	12.13	12.05
125.00	13.03	12.82	12.85	12.76
250.00	13.29	13.20	13.16	13.06

C.2 Properties of Oil Solutions

The physical properties of the oil solutions are listed in Table C.3. The light paraffin oil doped with linoleic acid at different concentrations constitutes the oil solutions. The paraffin oil has a density of 0.8423 g/cm^3 and a viscosity of 19.260 mPa.s . The addition of increasing quantities of linoleic acid to the paraffin oil does not change the density appreciably, but the viscosity increases marginally at higher acid concentrations.

Table C.3: Physical Properties of Oleic Solutions at 25°C

Identification	Density (g/cm^3)	Viscosity (mPa.s)
Light paraffin oil	0.8423	19.25
Light paraffin oil doped with linoleic acid (mol/m^3)		
0.1	0.8423	19.29
1	0.8423	19.45
10	0.8425	19.77
20	0.8431	19.79
100	0.8444	19.82

Appendix D

Transient Interfacial Tension Data

D.1 0.1 mol/m³ Acidified Oil / Surfactant- Alkaline Systems

D.1.1 Effects of Added Surfactant Concentration

Figure D.1: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against 1 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure D.2: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against 4 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure D.3: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against 5 mol/m³ sodium dodecyl sulfate and NaOH solutions.

Figure D.4: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against 7 mol/m³ sodium dodecyl sulfate and NaOH solutions.

D.1.2 Effects of Caustic Concentration

Figure D.5: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 0.25 mol/m³ NaOH solution.

Figure D.6: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 1.25 mol/m³ NaOH solution.

Figure D.7: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 2.5 mol/m³ NaOH solution.

Figure D.8: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 12.5 mol/m³ NaOH solution.

Figure D.9: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 25 mol/m³ NaOH solution.

Figure D.10: Transient interfacial tension behavior for 0.1 mol/m³ acid in paraffin oil against sodium dodecyl sulfate and 125 mol/m³ NaOH solution.