



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* *Voire référence*

*Our file* *Notre référence*

## NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

## AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

**Comparison of Transient Interfacial Tension Behaviours of  
Oil/Alkaline Systems as Measured by the Drop Volume  
and Spinning Drop Tensiometers**

**Sheila D. Ball**

A thesis submitted to the School of Graduate Studies and Research  
in partial fulfillment of the requirements for the  
degree of  
**Master of Applied Science**  
in the Department of Chemical Engineering  
University of Ottawa

April 1995



Sheila D. Ball, Ottawa, Canada, 1995



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 0-612-07787-X

Canada



UNIVERSITÉ D'OTTAWA  
UNIVERSITY OF OTTAWA

## ABSTRACT

The measurement of interfacial tension (IFT) as a function of time is useful for the study of reactions occurring at an interface. Reactions of particular importance occur in enhanced oil recovery (EOR) processes using alkaline flooding agents, in which injected alkaline solutions react with acidic oil trapped in the reservoir. The *in situ* surfactants produced by the reaction lower the interfacial tension and thus increase the amount of oil recovered by decreasing the capillary forces that trap the oil in the reservoir. The formation of the surfactants, their accumulation at the interface and subsequent desorption to the bulk oil and aqueous phases are all influenced by the age of the interface. Therefore, the reactive system requires a study of the transient IFT in order to better understand the interaction of the acid with the caustic reagents. In order to select the most effective alkaline agents available, an accurate method of measuring transient IFT is required.

There are several methods available for measuring IFT values although relatively few are able to easily monitor the IFT as a function of time. In this study, two methods of measuring the transient IFT have been examined. A relatively new method which uses an instrument called the drop volume tensiometer (DVT) has been studied. This instrument accurately measures the time elapsed for a known number of liquid droplets, formed under a constant flow rate, to detach from a submerged capillary orifice with the size of the droplet being directly proportional to the liquid-liquid IFT. The results from this

instrument have been compared to those obtained by the spinning drop tensiometer (SDT), which is the instrument most frequently used for studying transient IFT values. The SDT obtains the IFT by measuring the dimensions of a droplet of liquid suspended in a more dense liquid contained in a rotating horizontal tube. Because the two instruments employ fundamentally different techniques the limitations of each will be explored.

Interfacial tensions between oil and alkaline solutions were measured using the drop volume tensiometer and compared to those measured using the spinning drop tensiometer. The trend observed for the IFT as time progressed was surprisingly similar in both cases. However, the SDT values exhibited an increase in IFT after a minimum was reached whereas the DVT values did not generally exhibit this increase. The IFT values between four different 25 mM alkaline solutions and a 10 mM synthetic oil were compared and the IFT values obtained, before the minimum was reached, were: KOH, NaOH, Na<sub>2</sub>SiO<sub>3</sub> and LiOH in descending order. The transient IFT values between a representative crude oil and one of the alkaline solutions were also compared and the IFT values obtained, before the minimum was reached, were: LiOH, NaOH, Na<sub>2</sub>SiO<sub>3</sub> and KOH in descending order.

Transient IFT values between different concentrations of acidified oil and alkaline solutions were also compared. The crude oil had lower minimum IFT values than the synthetic oil due to its greater concentration of acidic components.

The SDT appears to still be the preferred method for monitoring ultralow IFT values (< 0.1 mN/m) as a function of time. However, it cannot be used to measure the IFT at the moment the oil droplet is created nor in the first 30 seconds once the two

phases come into contact. In contrast, the DVT can only detect IFT at one discrete time, but measurements at different flow rates may be conducted, corresponding to different drop formation times, which results in a dynamic IFT trend.

In addition, the DVT appeared to be able to measure IFT values below the manufacturer's stated lower limit of 0.2 mN/m, when employing highly viscous solutions, but was imprecise below this threshold level for solutions of lower viscosity. The minimum IFT values obtained with the two different instruments were identical for lower concentrations of the alkaline solutions but not for the higher concentrations. The DVT appeared to possess greater reproducibility and a value of the error was given for an average of the IFT values for several droplets. In contrast, the SDT required oil droplets of the same volume which were difficult to achieve experimentally. Even with identical droplet volumes, the shapes of the transient IFT curves were not generally reproducible after the minimum IFT value was obtained.

Despite the differences in the methods of measuring IFT values using the DVT and SDT, it appears that the trends and many of the values were similar. Therefore, both instruments can be used for reliably measuring transient IFT values between oil and aqueous solutions.

## ACKNOWLEDGMENTS

This work would not have been possible without my supervisors Drs. V. Hornof and G. H. Neale who provided guidance and support throughout this work. I would also like to thank the technical staff of the chemical engineering department for their aid. My appreciation for the unlimited support I received from my husband, Keith Bowes, and my family is boundless. A special thank you to my parents and in-laws for editing, listening and providing aid in many ways.

## NOMENCLATURE

$A^-$	anionic moiety of a surfactant
D	density ratio of acid to alkali
DVT	drop volume tensiometer
$d_{\text{tube}}$	diameter of the capillary tube for the SDT, m
EOR	enhanced oil recovery
$F_x$	external forces acting on system (oil droplet) in the x-direction, N
g	gravitational constant, $m/s^2$
HA	acidic hydrocarbon component of the crude oil
IFT	interfacial tension, $mN/m$
$M_{\text{alk}}$	molarity of the alkaline solution, $mol/L$
$M_{\text{in}}$	rate at which x-momentum flows into the system (droplet) at the tube tip
$M_{\text{oil}}$	molarity of the oil solution, $mol/L$
$M_{\text{out}}$	rate at which x-momentum flows out of the system (oil droplet)
MP	micellar polymer
MR	molar ratio of acid to alkali
$M_R$	ratio of the molarity of acid to alkali
$M_{\text{sys}}$	total x-momentum of system (oil droplet)
P	period of rotation, $ms/rev$
Q	volumetric flow rate, $m^3/s$
Re	Reynolds number

$r_m$	radius of the spinning drop, m
RSD	relative standard deviation, %
$R_{tube}$	radius of the tube, m
SDT	spinning drop tensiometer
t	time, s
V	volume ratio of acid to alkali

Greek letters:

$\gamma$	interfacial tension, mN/m
$\mu$	viscosity of a liquid, kg.m/s
$\omega$	angular rotation, rev/s
$\pi$	pi
$\rho_a, \rho_b$	density of the dense and light phases respectively, kg/m <sup>3</sup>

Subscripts:

aq	values pertaining to the aqueous alkaline solution
oil	values pertaining to the acidified oil solution
R	ratio of acid to alkali

Terminology:

dynamic	mass of droplet changes with time during the experiment measuring IFT
transient	mass of droplet remains constant during the experiment measuring IFT

# TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGMENTS	iv
NOMENCLATURE	v
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xix
<b>1. Introduction</b>	<b>1</b>
<b>2. Theoretical Aspects and Background</b>	<b>6</b>
2.1 Interfacial Reaction	6
2.2 Theory of Alkaline Flooding in EOR	9
2.3 Instruments for Measuring IFT	13
2.3.1 Summary of available instruments	13
2.3.2 Spinning drop tensiometer	15
2.3.3 Drop volume tensiometer	16
2.4 Development of SDT Method	18
2.5 Comparison of the DVT and SDT Instruments	20
<b>3. Methodology</b>	<b>22</b>
3.1 Materials	22
3.2 Experimental Apparatus	23
3.2.1 Spinning Drop Tensiometer (SDT)	23

3.2.2 Drop volume tensiometer (DVT)	24
3.3 Measurement Procedures	29
3.3.1 SDT experimental procedure	29
3.3.2 DVT experimental procedure	30
3.4 Experimental Aspects	32
<b>4. Experimental Results and Discussion</b>	<b>34</b>
4.1 IFT Results Measured with the SDT and DVT	34
4.1.1 Reproducibility with the SDT	34
4.1.2 Reproducibility with the DVT	42
4.1.3 Effects of acid and alkali concentrations	45
4.1.4 Comparison of alkali tested on SDT and DVT	49
4.1.5 Effects of linoleic acid concentration	55
4.1.6 Crude oil tested on the SDT	61
4.1.7 Crude oil tested on the DVT	64
4.2 Momentum Balance Applied to the DVT	69
<b>5. Comparison of the SDT and DVT</b>	<b>71</b>
5.1 Trends of the Transient IFT	71
<b>6. Modeling</b>	<b>74</b>
6.1 Modeling of Transient IFT via Linear Regression	74
6.2 Modeling Difficulties and Considerations	76
<b>7. Conclusions</b>	<b>77</b>
<b>8. Recommendations</b>	<b>78</b>

<b>9. References</b>	79
<b>10. Appendices</b>	84
Appendix A: Experimental Data for the SDT	85
Appendix B: Experimental Data for the DVT	130
Appendix C: Calculations for the Momentum Balance	144
Appendix D: Linear Regression using SAS	145

## LIST OF TABLES

Table 1: Estimated water usage for EOR process and estimated percent recovery of residual oil-in-place	2
Table 2: Comparison of the spinning drop and drop volume tensiometers	20
Table 3: Experimental materials and their properties	22
Table 4: Comparison of the minimum IFT values of oil/aqueous solutions tested on the SDT and DVT	73
Table 5: Values of R-squared and the constants from linear regression	74
Table A1 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 1	89
Table A2 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 2	89
Table A3 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 3	90
Table A4 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 4	90
Table A5 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 5	91
Table A6 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 6	91

Table A7 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 7	92
Table A8 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 1	93
Table A9 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 2	93
Table A10 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 3	94
Table A11 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 4	94
Table A12 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 5	95
Table A13 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 6	95
Table A14 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 7	96
Table A15 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 1	97
Table A16 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 2	97
Table A17 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 3	98

Table A18 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 4	98
Table A19 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 5	99
Table A20 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 6	99
Table A21 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT; Trial 7	100
Table A22 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 1	101
Table A23 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 2	101
Table A24 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 3	102
Table A25 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 4	102
Table A26 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 5	103
Table A27 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 6	103
Table A28 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT; Trial 7	104

Table A29 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.1 $\mu$ L	105
Table A30 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.3 $\mu$ L	105
Table A31 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.5 $\mu$ L	106
Table A32 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 1.4 $\mu$ L	106
Table A33 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 1.5 $\mu$ L	107
Table A34 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 1.7 $\mu$ L	107
Table A35 : IFT between 10 mM synthetic oil and 2.5 mM NaOH tested on the SDT, 2.8 $\mu$ L	108
Table A36 : IFT between 1 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.5 $\mu$ L	108
Table A37 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, 1.5 $\mu$ L	109
Table A38 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT, 1.5 $\mu$ L	109
Table A39 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4 $\mu$ L	110

Table A40 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4 $\mu$ L	110
Table A41 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.9 $\mu$ L	111
Table A42 : IFT between 30 mM synthetic oil and 25 mM LiOH tested on the SDT, 1.2 $\mu$ L	111
Table A43 : IFT between 30 mM synthetic oil and 25 mM KOH tested on the SDT, 1.4 $\mu$ L	112
Table A44 : IFT between 30 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 1.7 $\mu$ L	112
Table A45 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.2 $\mu$ L	113
Table A46 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.3 $\mu$ L	113
Table A47 : IFT between 20 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.2 $\mu$ L	114
Table A48 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.8 $\mu$ L	114
Table A49 : IFT between 340 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.8 $\mu$ L	115
Table A50 : IFT between 50 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.6 $\mu$ L	115

Table A51 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.9 $\mu$ L	116
Table A52 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.3 $\mu$ L	116
Table A53 : IFT between 20 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.3 $\mu$ L	117
Table A54 : IFT between 30 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.45 $\mu$ L	117
Table A55 : IFT between 40 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.5 $\mu$ L	118
Table A56 : IFT between 50 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.45 $\mu$ L	118
Table A57 : IFT between 60 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.3 $\mu$ L	119
Table A58 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5 $\mu$ L	119
Table A59 : IFT between 20 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5 $\mu$ L	120
Table A60 : IFT between 30 mM synthetic oil and 25 mM KOH tested on the SDT, 0.6 $\mu$ L	120
Table A61 : IFT between 40 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5 $\mu$ L	121

Table A62 : IFT between 50 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5 $\mu$ L	121
Table A63 : IFT between 60 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5 $\mu$ L	122
Table A64 : IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 1.4 $\mu$ L	122
Table A65 : IFT between 20 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 0.8 $\mu$ L	123
Table A66 : IFT between 30 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 0.5 $\mu$ L	123
Table A67 : IFT between 40 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 0.5 $\mu$ L	124
Table A68 : IFT between 50 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 0.4 $\mu$ L	124
Table A69 : IFT between 60 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT, 0.3 $\mu$ L	125
Table A70 : IFT between Lloydminster crude oil and 2.5 mM NaOH tested on the SDT	125
Table A71 : IFT between Lloydminster crude oil and 25 mM NaOH tested on the SDT	126
Table A72 : IFT between Lloydminster crude oil and 25 mM NaOH tested on the SDT	126

Table A73 : IFT between Lloydminster crude oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT	127
Table A74 : IFT between Lloydminster crude oil and 25 mM LiOH tested on the SDT	127
Table A75 : IFT between Lloydminster crude oil and 25 mM KOH tested on the SDT	128
Table A76 : IFT between 20 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.5 µL	128
Table A77 : IFT between 40 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4 µL	129
Table A78 : IFT between 50 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.5 µL	129
Table B1 : Dynamic IFT between 10 mM synthetic oil with 25 mM NaOH tested on the DVT	134
Table B2 : Dynamic IFT between 10 mM synthetic oil with 25 mM NaOH tested on the DVT	134
Table B3 : Dynamic IFT between 10 mM synthetic oil with 25 mM LiOH tested on the DVT	135
Table B4 : Dynamic IFT between 10 mM synthetic oil with 25 mM LiOH tested on the DVT	135
Table B5 : Dynamic IFT between 10 mM synthetic oil with 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the DVT	136

Table B6 : Dynamic IFT between 10 mM synthetic oil with 25 mM KOH tested on the DVT	137
Table B7 : Dynamic IFT between 10 mM synthetic oil with 2.5 mM NaOH tested on the DVT	138
Table B8 : Dynamic IFT between 1 mM synthetic oil with 25 mM NaOH tested on the DVT	139
Table B9 : Dynamic IFT between Lloydminster crude oil with 25 mM LiOH tested on the DVT	140
Table B10 : Dynamic IFT between Lloydminster crude oil with 25 mM NaOH tested on the DVT	140
Table B11 : Dynamic IFT between Lloydminster crude oil with 2.5 mM NaOH tested on the DVT	141
Table B12 : Dynamic IFT between Lloydminster crude oil with 25 mM LiOH tested on the DVT (leak)	142
Table B13 : Dynamic IFT between Lloydminster crude oil with 2.5 mM NaOH tested on the DVT (leak)	143

## LIST OF FIGURES

Figure 1: A geometrical model of the chemical reactions at the interface	6
Figure 2: Schematic diagram of chemical flooding (alkaline)	9
Figure 3: Drop volume tensiometer DVT-10 tip at drop separation	16
Figure 4: Sequence of drop detachment	16
Figure 5: Droplet in rotating capillary in the SDT	24
Figure 6: Sample tube and detector of DVT-10 apparatus	25
Figure 7: Drop volume method: balance of forces	26
Figure 8: Dynamic IFT between Lloydminster crude oil and 25 mM LiOH and NaOH tested on the DVT	27
Figure 9: Dynamic IFT between 10 mM synthetic and Lloydminster crude oil with 2.5 mM NaOH tested on the DVT	28
Figure 10: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT	35
Figure 11: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT	36
Figure 12: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT	37
Figure 13: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM $\text{Na}_2\text{SiO}_3$ tested on the SDT	38

Figure 14: Transient IFT between 10 mM synthetic oil and 25 mM NaOH solution tested on the SDT	40
Figure 15: Transient IFT between 10 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> solutions tested on the SDT	41
Figure 16: Representation of uneven elongation of a droplet rotating in the SDT	42
Figure 17: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT	43
Figure 18: Dynamic IFT of 10 and 1 mM synthetic oil against 25 and 2.5 mM NaOH tested on the DVT	46
Figure 19: Transient IFT of 1 and 10 mM synthetic oil against 25 and 2.5 mM NaOH tested on the SDT	47
Figure 20: Transient IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	49
Figure 21: Transient IFT between 30 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	50
Figure 22: Transient IFT between 60 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	51
Figure 23: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT	53
Figure 24: Transient IFT between 10, 30 and 60 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	55

Figure 25: Transient IFT between 10 - 60 mM synthetic oil and 25 mM NaOH tested on the SDT	57
Figure 26: Transient IFT between 10 - 60 mM synthetic oil and 25 mM LiOH tested on the SDT	58
Figure 27: Transient IFT between 10 - 60 mM synthetic oil and 25 mM KOH tested on the SDT	59
Figure 28: Transient IFT between 10 - 60 mM synthetic oil and 25 mM Na <sub>2</sub> SiO <sub>3</sub> tested on the SDT	60
Figure 29: Transient IFT of Lloydminster crude oil and 10 mM synthetic oil against 25 and 2.5 mM NaOH tested on the SDT	62
Figure 30: Transient IFT of Lloydminster crude & 10 mM synthetic oil with 25 mM aqueous alkali tested on the SDT	64
Figure 31: Dynamic IFT between Lloydminster crude oil and 25 mM LiOH and NaOH tested on the DVT	66
Figure 32: Dynamic IFT between Lloydminster crude oil and 10 mM synthetic oil against 2.5 mM NaOH tested on the DVT	67
Figure A1: Transient IFT between 20 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	86
Figure A2: Transient IFT between 40 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	87
Figure A3: Transient IFT between 50 mM synthetic oil and 25 mM aqueous alkali tested on the SDT	88

Figure B1: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT	131
Figure B2: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT	132
Figure B3: Dynamic IFT between 1 and 10 mM synthetic oil with 25 mM NaOH tested on the DVT	133

# 1. INTRODUCTION

Interfacial tension is an important property in a variety of fields such as oil recovery, solvent extraction, food processing and pharmaceuticals. It occurs whenever two immiscible liquids come into contact and it is a key factor influencing the shape of fluid interfaces and their deformability. Thus, in porous media, such as oil reservoirs, the tension determines if the fluid droplets can deform sufficiently to pass through the pore structure when a pressure gradient is applied. The composition at the interface can differ dramatically from that of either bulk phase which is especially noticeable when surface-active materials (surfactants) are present. Surfactants can significantly decrease the interfacial tensions, which is desirable in an oil reservoir to improve the oil mobility. Any combination of two liquids acts to minimize its interfacial area because they both need to minimize their surface energy thereby enabling surfactants to increase the contact between the two liquids (Miller and Neogi, 1985).

Enhanced oil recovery (EOR) has become very important as the consumption of oil is now surpassing the primary production of oil reservoirs in Canada. The objective of EOR technologies, called tertiary recovery when agents are injected into the reservoir to improve oil production, is to recover as much additional oil as possible not recovered by primary and/or secondary recovery operations. Primary is the oil production resulting from the natural pressures in the reservoir while secondary involves pumping water into the reservoir. A major problem in oil recovery is overcoming the interfacial tension forces between the oil, water and the rock. Oil becomes increasingly more difficult to recover

from a reservoir as water saturation increases and as oil saturation decreases, primarily due to two main phenomena. If the rock is water-wet, the interfacial tension forces tend to create droplets of oil which block pore openings, while if it is oil-wet these forces tend to cause the oil to bind to the rock. Therefore, reduction of these interfacial tension forces is a major objective of EOR (Donaldson et al., 1985).

Alkaline (caustic) flooding is used to decrease these interfacial tensions. Sodium hydroxide is the most common chemical used in caustic flooding but sodium orthosilicate and sodium carbonate are also used. Other chemicals, such as sodium silicate and potassium hydroxide, have been used. Alkaline solutions are relatively inexpensive compared to conventional surfactants (Chiwetelu et al., 1990c). Caustic slugs can be depleted by the precipitation of hydroxides in the presence of divalent cations such as calcium and magnesium in the connate water, which is the water naturally present in oil reservoirs. This is why it is suitable for sandstone reservoirs but not for carbonate rock reservoirs. Also, when anhydrite or gypsum are present in the rock, calcium will react with the alkali slug to precipitate calcium hydroxide, and clays having high ion exchange capacity will exchange hydrogen for sodium producing water, which makes the slug ineffective by tying up the sodium. Silica and carbonates will not react with caustic agents to cause deleterious effects. The amount of water required to produce a barrel of oil with caustic flooding ranges from 22 to 33 barrels as seen in Table 1. The alkaline or other chemical solution is usually injected after the reservoir conditioning preflush, while polymers are usually added later to further improve the oil recovery (Donaldson et al., 1985).

**Table 1: Estimated water usage for EOR processes and estimated percent recovery of residual oil-in-place (Donaldson et al., 1985)**

Process	Water usage, <sup>a</sup> bbl water/bbl oil	Percent recovery of residual oil-in-place
Surfactant-polymer	10-15	30-43
Polymer	16-50	4
Alkaline (caustic)	22-33	6-13
Carbon dioxide (CO <sub>2</sub> )	1-3	15-19
In-situ combustion, wet	0.5-1	28-38
Steam	2-5	25-45

<sup>a</sup> Department of Energy (DOE), 1981.

Choosing the best alkaline solutions to inject will result in lower costs and improved performance. Measurement of the lowering of the interfacial tension is one of the easiest ways to quantify the performance of any particular alkaline solution with any particular oil. Therefore, accurate methods for measuring the interfacial tension between any two immiscible liquids are of vital importance. It is also necessary to measure the IFT as a function of time, since the alkaline solution is in contact with the oil for a lengthy period of time, and therefore knowledge of the transient IFT is needed to identify the best solution. Since tests in the field are very costly, it is important to have a reliable method to measure transient IFT. Therefore the method of lowering IFT needs to be better understood and the best solutions selected before the field trials are commenced.

Since the IFT needs to be measured as a function of time, it is important to define the meaning of two particular terms that will be used throughout this thesis. Any interfacial measurement that detects changes over time due to changes in interfacial area and not to changes in total mass can be considered to be *transient* in nature. Such a situation exists in the SDT. The description *dynamic* IFT is reserved for systems in which the interface is deliberately forced to be away from equilibrium by adding mass as a function of time resulting in the presence of mass transfer and chemical reaction at the

interface. This is the situation which is encountered in the DVT. These two terms have been chosen here to clarify the difference between the methods studied.

Several currently available methods for measuring IFT have been characterized and their limitations explored by Chiwetelu et al. (1988). However, there is a relatively new technique which has not been thoroughly studied but is showing promise as an easy to use and reliable instrument. The drop volume tensiometer (DVT) was reviewed by Hool and Schuchardt (1992), who found that new tip geometries allowed for calculations of IFT without the use of traditional correction factors and within a range of 0.1-100 mN/m, with 1-2% relative standard deviation (RSD). A new tip geometry was required so that a spherical droplet would form without wetting the outside of the tip. Without the new tip the volume of a drop formed under flowing conditions depends, not only on the interfacial tension, but also on the drop formation rate.

Under dynamic conditions the drop volume depends on the interfacial tension and on the drop formation rate as the flowing liquid increases the drop mass at higher drop formation rates. However, the circulation current created at the same time in the surrounding medium tends to make the drop volume smaller at higher rates, because of premature drop detachment (Jho and Burks, 1983). These findings, and limitations of each method, were tested in this study with the specific goal of studying the IFT, in systems involving alkaline solutions in contact with acidified oil, so that the results could be used to determine the best reagents required for EOR.

Comparisons were made against the IFT data obtained using the spinning drop tensiometer (SDT) since it is one of the most common and easy-to-use methods at this

time. The spinning drop method was first proposed by Vonnegut (1942), but it was Princen et al. (1967) who provided a complete theoretical basis, and Cayias et al. (1975) who clearly demonstrated the precision and simplicity of the method. However, there are several drawbacks to the particular tensiometer, developed by the University of Texas, that was used in this study. In particular: (i) the temperature control is poor as the high rotation speeds generate heat resulting in an increase in temperature during the course of the experiment; (ii) there is imprecision in the determination of the interfacial age since a finite time is needed to measure the width of an infinite drop; (iii) when both the length and diameter need to be read then there is considerable error in the measurement; and (iv) when the rotating droplet contracts and expands very rapidly, even the width measurements are subject to considerable error (Chiwetelu et al., 1988).

The results presented in this report reveal the simplicity of the DVT and the precision of its results in comparison with the SDT, along with its limitations. However, each method is valuable for specific needs and therefore it is anticipated that the comparison will lead to a greater understanding of the different phenomena occurring at the interface as oil and alkaline solutions come into contact and surfactants are formed.

The objective of this work was to compare the performance of lowering the IFT between oil and aqueous alkali by testing different alkaline solutions against different oils and at various concentrations. The comparison of two different methods, namely the SDT and the DVT, for measuring the IFT was also included.

## 2. THEORETICAL ASPECTS AND BACKGROUND

### 2.1 Interfacial Reaction

The geometrical model of the interface depicted in Figure 1 below was introduced by Chiwetelu et al. (1990a). It shows the transient nature of the chemical reactions at the interface. Sodium hydroxide reacts chemically with the naturally occurring acidic (carboxylic and phenolic) components in the crude oil, thereby generating IFT-reducing surfactants in situ at the oil/aqueous interface. Later on, the reactants are depleted by the reaction and the surfactants diffuse away from the interface which cause the IFT to increase.

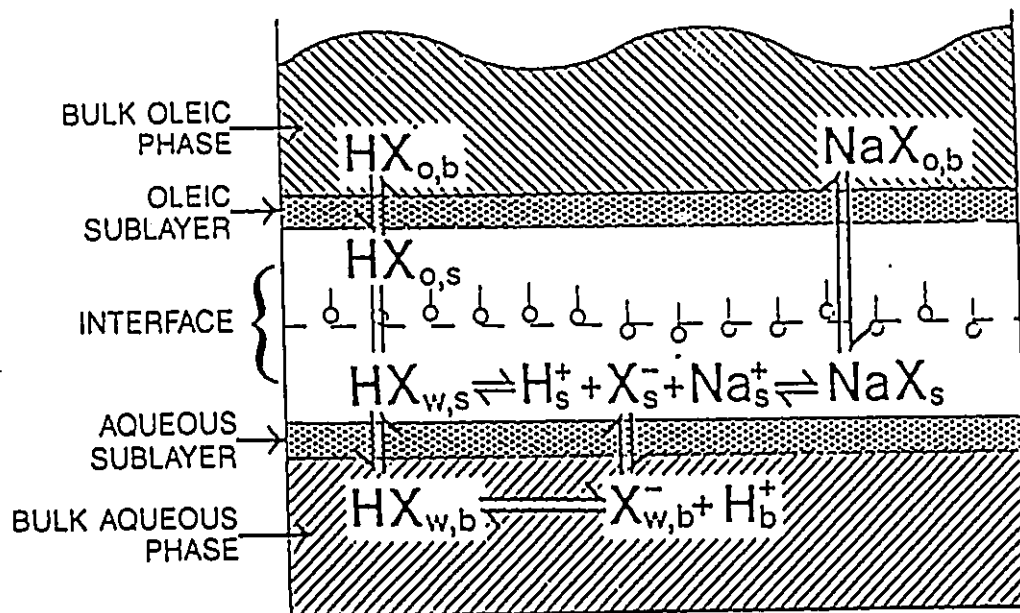


Figure 1: A geometrical model of the interface (Chiwetelu et al., 1990a)

The ratio of viscous to capillary (interfacial) forces in a reservoir needs to be high for significant oil recovery and elevating the ratio, called the capillary number, can be done

by reducing the oil/aqueous IFT (Babu et al., 1986). Lower capillary forces enable the oil to be swept out of the reservoir more easily. Heavy oils, in particular, are well suited to this recovery method on account of their higher than average acid content. Since the IFT behaviour of a reacting system is a very complicated transient phenomenon (involving chemical reactions, diffusion, and convective mass transfer effects), the IFT measurements must be made on a continuous basis over an extended period of time (Neale et al., 1987).

Any interfacial measurement that detects changes over time can be considered to be transient. For dynamic IFT, the interface is deliberately forced to be away from equilibrium by adding mass as a function of time. The rate at which a new interface is formed can be controlled and changed to study its effect on IFT. Surfactants in solution require time to diffuse to an interface. Once at the interface, the molecules orientate themselves to allow that portion of the molecule most compatible with the other phase to be beside or in that phase. The molecules align themselves with adjacent molecules until minimum surface free energy is reached. For many surfactants, the rate of orientation seems to be slower than the rate of diffusion.

The acid species, initially present in the oil, is transported to the interface where it is partitioned and ionized at the aqueous sublayer. The surface-active soap anion is thus formed, and is adsorbed at the oil/aqueous interface, giving rise to an electrical double layer. The surface concentration of this soap anion is reduced by desorption to the aqueous phase, particularly by the formation of the inactive soap complex in the presence of excess sodium ions. Chiwetelu et al. (1990b) developed a physicochemical model to

account for the dynamic IFT behaviour in multicomponent acidified oleic systems contacted by a spectrum of aqueous caustic concentrations.

Rubin and Radke (1980) attempted to explain qualitatively the observed minimum in dynamic IFT by postulating an adsorption/desorption of surfactant species at the crude oil/aqueous interface. They attributed the occurrence of a dynamic minimum to the presence of "desorption barriers" (Babu et al., 1984). The concentration of both the alkaline phase and the acid in the oil phase affect the IFT.

Decreasing the concentration of NaOH caused the IFT to increase sharply at any given time for the transient IFT as determined by Khulbe et al. (1985). It would be expected, in a dilute alkali solution, that, as the  $\text{Na}^+$  ions react with the active phase to make surfactant, the free  $\text{Na}^+$  concentration would decrease sharply near the oil/aqueous interface. No free  $\text{Na}^+$  ions would be available immediately and thus the IFT would increase sharply and the oil drops would split into smaller droplets.

At low acid concentrations, the addition of an alkali to the added surfactant solution causes the IFT to increase. At medium to high acid concentrations, addition of an alkali can produce ultralow IFT. This was explained by Rudin and Wasan (1992) as a synergistic effect between the acid and its generated soap. In other words, the acid behaves like an impurity which greatly lowers the IFT.

Below a caustic level of 250 mM, the rate of ionization and subsequent adsorption of the carboxylate anions far exceeds that of their desorption into the respective bulk phases. Under this scenario, tensions show a decreasing trend as the surface active anions accumulate at the oil/aqueous interface. However, beyond this caustic level, the

desorption rate to the bulk exceeds that of adsorption . Consequently, tensions show only an increasing trend in this region as determined by Chiwetelu et al. (1990c).

## 2.2 Theory of Alkaline Flooding in EOR

A typical alkaline flooding process is shown in Figure 2.

### CHEMICAL FLOODING (Alkaline)

The method shown requires a preflush to condition the reservoir and injection of an alkaline or alkaline/polymer solution that forms surfactants in situ for releasing oil. This is followed by a polymer solution for mobility control and a driving fluid (water) to move the chemicals and resulting oil bank to production wells.

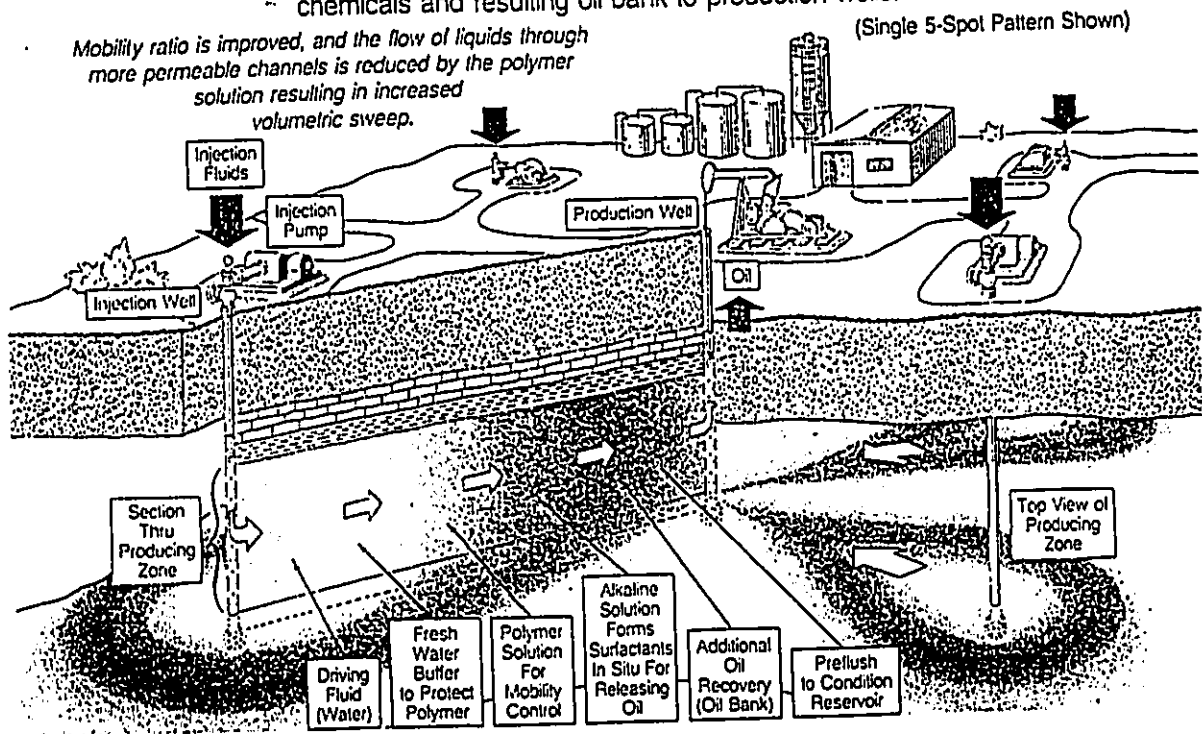
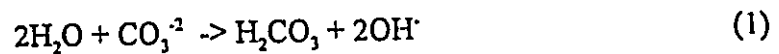


Figure 2: Schematic diagram of chemical flooding (alkaline). (Lake, 1989)

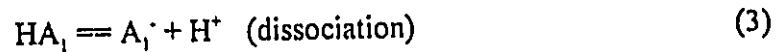
The figure depicts the usual method of alkaline flooding in a reservoir. There is usually a brine preflush to precondition the reservoir, an oil-displacing chemical, a mobility buffer driving agent, and the process is usually driven by chase water. This is a similar

process to that used in polymer and micellar polymer (MP) flooding. The alkaline process is called high-pH flooding because of the excess of hydroxide anions, and can be achieved by (i) dissociation of hydroxides; or (ii) addition of chemicals that preferentially bind hydrogen ions since the concentrations are related through the dissociation of water. The most commonly used alkalis are sodium hydroxide, sodium orthosilicate, and sodium carbonate. The hydroxide produces high pH via the former mechanism whereas the following two do so through the latter mechanism, as follows:



High pH chemicals are usually less costly than chemicals used in the micellar polymer process so that they are often used in field applications.

The hydroxyl ion is not a surfactant itself but the crude oil usually contains an acidic hydrocarbon component  $\text{HA}_2$ , some of which can partition into the aqueous phase where it reacts with the  $\text{OH}^-$ , as follows:



The nature of  $\text{HA}_2$  is dependent on the crude oil type. The acid number indicates the amount of  $\text{HA}_2$  originally present in the crude and is defined as the milligrams of potassium hydroxide required to neutralize one gram of crude oil. A good alkaline flooding crude candidate will have an acid number of 0.5 mg/g or greater although oils with smaller numbers have been used. The anionic species  $\text{A}_1^-$  is a surfactant which can lower the interfacial tension (IFT) at oil/aqueous interfaces (Lake, 1989).

The interfacial region consists mainly of long-chain carboxylic acids with a wide range of molecular weights (about 300-400) and chemical structures. Although most of the long-chain acids found were saturated aliphatics, some unsaturated, substituted, and aromatic acids and diacids were also identified. Substances containing nitrogen and sulfur heteroatoms were also found to be concentrated at the interface. The interfacial films were stabilized by resins, porphyrins, porphyrin ring oxidation products and protein/metal salts (Sharma et al., 1989).

The three main mechanisms by which high-pH flooding displaces the oil are: IFT lowering, wettability reversal and emulsion formation. The IFTs are sensitive to both caustic concentration and salinity. The decrease in IFT is limited by the spontaneous emulsification of the oil-water mixture when the IFT reaches a minimum. A cosurfactant can increase the optimal salinity in a system by changing the hydrophilic or lipophilic character of the system, its solubilization of water or oil, and thus the IFT because the material on both sides of the interface become more similar in nature (Rosen, 1989).

A change in wettability often increases the oil recovery since in the original wetting state of the medium, the non-wetting phase occupies large pores, and the wetting phase occupies small pores. When the wettability of a medium is reversed, non-wetting fluid will exist in small pores, and wetting fluid in large pores. The resulting fluid redistribution, as the phases attempt to attain their natural state, would make both phases amenable to recovery through application of viscous forces.

Alkaline chemicals can cause improved oil recovery through the formation of emulsions. Emulsification results in the lowering of the mobility ratio since most

emulsions have a substantially increased viscosity and a lower ratio increases the amount of oil recovered by increasing the area of the reservoir swept by the flood. Furthermore, solubilization and entrainment of oil in a flowing aqueous stream has a positive effect on recovery. The first mechanism improves displacement and volumetric sweep. Interactions of the alkaline chemicals and the minerals present in the reservoir rock can cause excessive retardation in the propagation of these chemicals through the medium. Attention must be paid to the salinity, type of clay and other liquids present in the reservoir in order for alkaline flooding to be successful (Lake, 1989).

Mehdizadeh and Handy (1989) performed alkaline floods at high temperatures which showed that an increase in dynamic IFT occurs with increasing temperature. Recovery of the residual oil takes place at IFTs as high as 1 mN/m. A model was developed by Ramakrishnan and Wasan (1990) which includes the adsorption of alkali on the solid surface as the alkali interacts with the minerals in the core. This model shows that the choice of a faster front competes with that of higher oil recovery.

Studies have also shown that application of surfactant and polymer enhanced alkaline flooding have been very successful (Hawkins et al., 1991). There was synergism of alkali and polymer resulting from a combination of improved sweep and mobilization of residual oil due to reduced IFT. The alkali/surfactant/polymer slugs were used to recover waterflood residual oil and, because of lower IFT, these slugs recovered significantly more residual oil than did the slugs without added surfactants (Hawkins et al., 1991).

Other investigators (Rudin and Wasan, 1990) varied the molar ratios of two or more alkalis that span the appropriate pH range, i.e. the desired pH for ultimate

spontaneous emulsification, and the desired pH for ultralow IFT. The addition of a surfactant will also increase the duration of ultralow IFTs. A kinetic model was developed that treats the process of convective diffusion of an acid species from the oil phase into the water phase while undergoing an interfacial reaction (Sharma et al., 1989).

## **2.3 Instruments for Measuring IFT**

### **2.3.1 Summary of available instruments**

Several techniques have been developed for the measurement of interfacial tensions. This project compares two commonly used techniques of measuring IFT, namely the spinning drop tensiometer and the drop volume tensiometer. Both methods were originally proposed to measure an interface at equilibrium where the area between the phases remains static. However, even with constant liquid volumes the interfacial area may change as the interfacial tension adjusts due to reactions occurring at the interface. It is important to recognize this difficulty before considering dynamic interfacial tension in detail. Surface active agents lower the IFT to a greater degree than diffusion of one phase into the other.

Other methods include the du Nouy ring method, which involves measuring the vertical force required to drag a horizontal circular platinum ring through the liquid-liquid interface, and is suitable for interfacial tensions as low as 1 mN/m. The Wilhelmy plate method is similar but it uses a vertical plate as the sensing element. The maximum force is measured during withdrawal and a dimensional analysis neglecting viscous effects is

employed. These two methods can only measure the IFT at one condition for each experiment, causing transient studies to be extremely time consuming and tedious.

The pendant drop method can be used for interfacial tensions as low as about  $10^{-4}$  mN/m. It involves a drop of one fluid being suspended in another fluid from a capillary tube. Gravity elongates the drop while the interfacial tension opposes elongation because of the accompanying increase in interfacial area. The liquid surrounding the drop must be transparent so that changes in drop shape can be monitored to determine time dependent effects on interfacial tension. Pendant drops of the less dense phase can also be tested by turning the fluid cell upside down. Transient measurements can easily be made with the pendant drop method.

The drop volume technique can accurately measure IFT as low as 0.2 mN/m. It involves slowly increasing the size of a pendant drop until the drop can no longer be prevented from rising, then it breaks off and the time of droplet formation is measured and the total volume of a known number of drops is calculated. This method is unsuitable when diffusion or adsorption effects require considerable time for the equilibrium value of the interfacial tension to be reached (Miller and Neogi, 1985). The drop volume tensiometer is similar to the drop weight method used to measure the surface tensions of surfactant solutions, consequently the drop breakaway process was studied extensively with this process (Pierson and Whitaker, 1976).

The surfactant adsorption process that takes place during drop formation has been analyzed mathematically and, for the type of drops used in the drop weight method, convective transport is generally unimportant and the surface concentration is controlled

by the diffusion and adsorption processes (Pierson and Whitaker, 1976). The drop volume method was used to measure surface tensions by Tornberg (1978) and, although the area of the drop increases as the surface tension decreases with time, the drop volume remains constant. The drop volume and maximum bubble pressure methods were also used to investigate the kinetics of adsorption for solutions that slowly attain their equilibrium surface tension (Joos and Rillaerts, 1981).

### 2.3.2 Spinning drop tensiometer (SDT)

The spinning drop method works well from around 10 mN/m to as low as  $10^{-5}$  mN/m. It involves the injection of a drop of the less dense fluid into a circular capillary tube containing the denser fluid and the whole system is then rotated. Then the drop elongates along the axis of rotation in the centrifugal field with the interfacial tension opposing the elongation because of the increase in area. Eventually a configuration which minimizes the free energy of the system is reached. Assuming that the drop length is much greater than the radius,  $r_m$  (length/diameter  $> 4$ ), the following expression holds (Miller and Neogi, 1985):

$$\gamma = ((\rho_{aq} - \rho_{oil}) \omega^2 r_m^3)/4 \quad (5)$$

The spinning drop tensiometer is useful because no contact between the fluid interface and a solid surface is required; and, both the drop and the surrounding fluid layer can also be made rather thin, so that results can be obtained even when the surrounding fluid is somewhat turbid, as frequently found in practical systems. Also, the interfacial tension can be monitored as a function of time (Miller and Neogi, 1985). As the droplet

changes in shape, transient velocity profiles will become established both inside the droplet and within a boundary layer region in the exterior phase, and these will necessarily have a direct effect on mass transfer rates of various reactant and product species to, and away from, the surface (Neale et al., 1987).

### **2.3.3 Drop volume tensiometer (DVT)**

The DVT works by injecting a lighter phase into a denser phase with a syringe pump through a narrow capillary. An infrared light emitting diode (IR LED) and photodiode then detect the droplets that detach from the capillary tip. The time between subsequent drops is then measured, which is converted to the volume of the drops by using the flow rate. When the droplet forms, a balance of forces exists at the orifice until the drop grows large enough to detach. At this instant, the volume of the drop is directly proportional to the IFT between the two phases (DVT manual, 1992).

The flow rate determines the rate at which droplets, and thus the new interface, are produced. Since fresh liquid is being added constantly, the effect of mutual diffusion of the liquids into each other is minimized. The variation in IFT with the flow rate is then due to the effects of diffusion and orientation of any surface active molecules present. Rheological properties of the interface populated by surfactants also contribute to this variation (DVT manual, 1992). The special orifice tip design of the DVT-10 has an orifice with the wall thickness at the tip being only a few micrometers. This ensures valid results because a spherical drop will cleanly detach from the tip. An orifice with a blunt tip would cause an error in diameter of the drop that detaches, depicted in Figures 3 and 4.

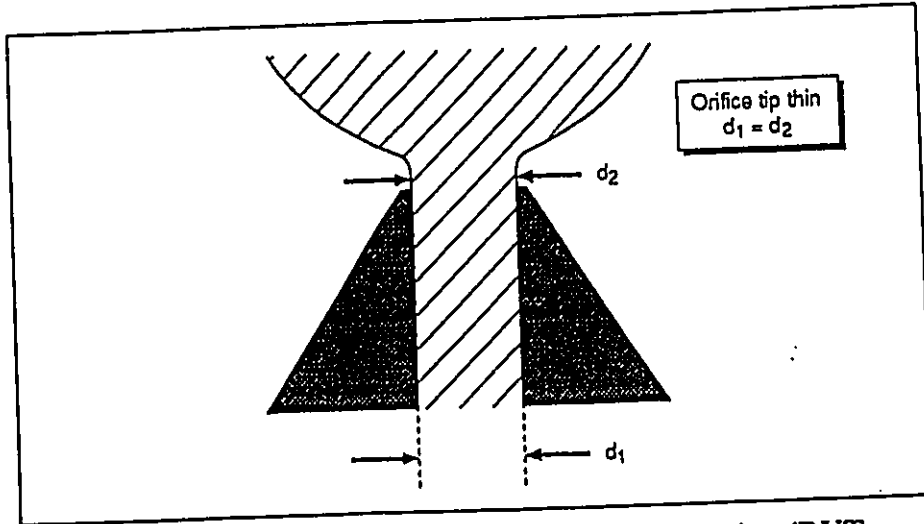


Figure 3: Drop volume tensiometer tip at drop separation (DVT manual, 1992)

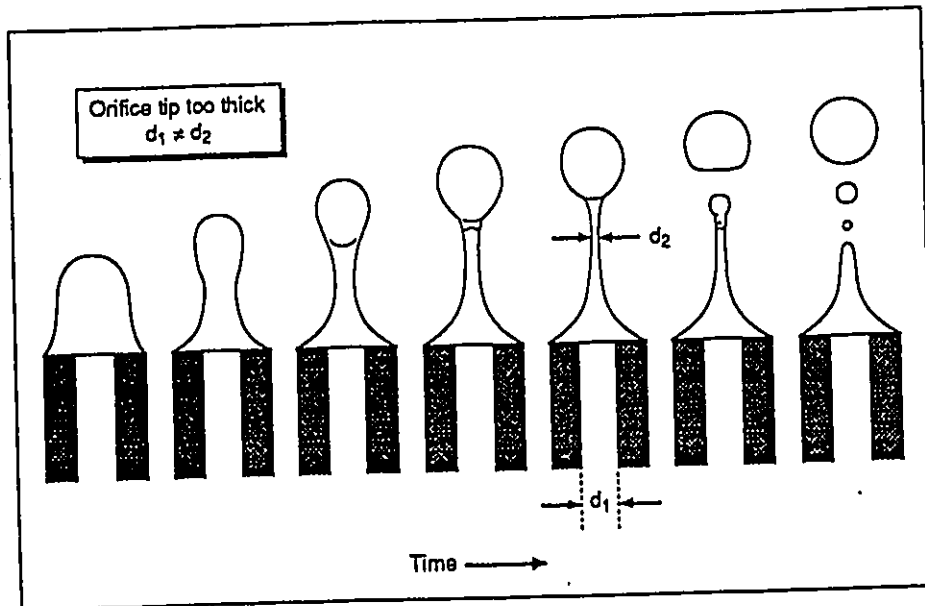


Figure 4: Sequence of drop detachment (DVT manual, 1992)

In general, at flow rates above 2.0 mL/h, acceleration of low viscosity fluid begins to contribute more than 1% of the detachment force and the data then need to be corrected. As liquid viscosity increases, the flow rate must be decreased to obtain results otherwise there is a steady stream of liquid out of the tip so that no droplets are formed. A smaller volume syringe has a smaller diameter piston, requiring a longer piston stroke

per unit volume delivered. This means the syringe pump stepper motor must produce more counts per unit time to deliver an equivalent volume from a smaller syringe than from a larger one, resulting in a higher accuracy.

It is very easy to deplete the surfactant from the aqueous solution, when measuring dynamic IFT for surfactant solutions, after even a few drops of oil have been studied. The vast majority of the surfactant monomer molecules are at the oil/aqueous interface at the top of the glass sample tube, therefore a fresh solution is needed. Adsorption of surfactant at the oil/aqueous interface can change the surfactant concentration in the bulk phase enough that the observed dynamic IFT will increase with each succeeding drop.

## 2.4 Development of SDT Method

Princen et al. (1967) developed the theoretical basis for the spinning drop method and conducted experiments on several systems and compared these with results obtained with other methods. This technique worked on the assumptions that (1) the angular velocity of rotation,  $\omega$ , of the drop is sufficiently large that buoyancy effects due to gravity are negligible; (2) the axis of the drop is aligned on the horizontal axis of rotation; (3) the surface of the drop is described by a surface of revolution; and (4) the surface or interfacial tension,  $\gamma$ , is not a function of curvature. Cayias et al. (1975) determined that both the diameter and length need to be measured if the injected volume cannot be accurately determined. With the SDT, the accurate drop volume may not be known because when the syringe needle is withdrawn from the capillary tube, smaller droplets may be left behind, and, once rotation is started, these small drops may coalesce, thus

changing the volume of the large drop being measured. Also, when there are multiple drops the experiment would have to be terminated because several drops may interfere with the IFT values. Also, the volume would have to be estimated, thereby the precision is limited.

The buoyancy effects could be neglected in this study because the rotational speed of the SDT was above 5000 rpm, as determined by Currie and van Nieuwkoop (1982). It was also noted that in some cases, the interface is unstable as the composition shifts due to flow or gravitational effects resulting in an interfacial layer of constantly changing composition. This results in a change of density difference and the drop volume, and consequently to a change in the drop diameter and length (Capelle, 1981).

The SDT is useful for measuring low and ultralow IFTs between fluids such as those encountered in oil recovery. It is particularly suited since it can monitor the transient changes in IFT that occur when a chemical reaction is taking place at the interface, such as that between acidic oil and alkaline solutions. As the reaction progresses, surfactants are generated at the interface, where they adsorb, causing a reduction in IFT that causes the droplet to elongate and the diameter to decrease. Later, the IFT begins to increase as the reactants are used up and as the generated surfactants diffuse away from the interface, resulting in the droplet contracting and the diameter increasing (Touhami et al., 1994). As the droplet changes shape, transient velocity profiles will become established within the two fluids, which will have a direct effect on the mass transfer rates of the various reactant and product species to, and away from, the interface, and thus on the computed IFT (Touhami et al., 1994).

## 2.5 Comparison of the DVT and SDT Instruments

In principle, the IFT between two pure liquids should be independent of the rate of interface formation (neglecting diffusion of the phases into each other). With the spinning drop method, the drop shape is analyzed, however this method does not allow good control of the speed of the interface area change as a function of time. It is suitable for an interface age greater than a few minutes. This technique is less precise than the drop volume method and is more laborious to perform. Table 2 lists the major differences between the two methods.

Table 2: Comparison of the spinning drop and drop volume tensiometers

	Spinning Drop Tensiometer	Drop Volume Tensiometer
Mass	Constant.	Steadily increasing.
Time	Infinite time for one drop.	One time for one drop.
	$t > t_0 + t_i$ as drop created in time, $t_0$ .	$t = t_0$ as drop created in time, $t_0$ .
	Drop studied after placed in unit.	Studied only once after created.
	Shape & surface area changes.	Mass increase; shape changes.
	Can measure equilibrium.	No equilibrium measurements.
	Molecules have identical age.	Molecules have different ages.
Injection	Manual.	Automatic.
Contact	No contact with solid surfaces.	Droplet in contact with tip (solid).

As seen in the above table, the SDT measures the *transient* IFT because the mass of the system is constant, whereas the DVT measures the *dynamic* IFT because mass is constantly being added to the droplet. The meaning of time for the two tensiometers can be seen to be quite different and needs to be further examined. Time, with the SDT, is defined as the time during which one droplet deforms as the reactions take place at the interface and therefore the drop can be studied for very long periods of time. In contrast, time for the DVT is equal to the reciprocal flow multiplied by the volume of the drop

created. Timing variations are obtained by studying different drops at different flow rates and obtaining an IFT measurement at the moment when the droplet breaks away from the tip.

Thus, the SDT can be used to study the same droplet over a period of time only after it has been created in time  $t_0$  (here  $t_0$  is the time for droplet injection) and after a period of time,  $t_1$  (here  $t_1$  is the time after the droplet was created, until measurements can be taken after the capillary is placed in the instrument). The DVT can be used to study the IFT only at the moment of  $t_0$  when the droplet has been created and breaks away.

Since different droplet interfaces are being studied in the dynamic experiments, IFT comparisons are only possible if care is taken to appreciate the different meaning of time for each of the two different tensiometers. The DVT measures dynamic IFTs because the mass is constantly being added whereas the SDT measures transient IFTs because the mass is constant throughout the experiment.

### 3. METHODOLOGY

#### 3.1 Materials

Table 3 contains details of the materials used in the experiments and their properties. All of the chemicals, except the light paraffin oil which came from BDH Chemicals Ltd., were obtained from Fisher Scientific Ltd. The synthetic oil consisted of linoleic acid dissolved in light paraffin oil in a series of concentrations. Thus, 10, 20, 30, 40, 50 and 60 mM solutions of linoleic acid in light paraffin oil (density of 840 kg/m<sup>3</sup>), were prepared in volumetric flasks. The 60 mM was the highest concentration that could reasonably be obtained due to the limited solubility of linoleic acid in light paraffin oil.

Table 3: Experimental materials and their properties.

Identification	Density at 25 C (g/mL)	Supplier
NaOH	0.9982	Fisher
LiOH	0.9979	Fisher
KOH	0.9985	Fisher
Na <sub>2</sub> SiO <sub>3</sub>	0.9985	Fisher
light paraffin oil	0.8400	BDH
linoleic acid	0.9000	Fisher
10 mM synthetic oil	0.8420 *	prepared
20 mM synthetic oil	0.8495	prepared
30 mM synthetic oil	0.8496	prepared
40 mM synthetic oil	0.8498	prepared
50 mM synthetic oil	0.8500	prepared
60 mM synthetic oil	0.8501	prepared
1 mM synthetic oil	0.8492	prepared
crude oil diluted	0.9393	prepared
crude oil	0.9702	Lloydminster
toluene	0.8700	Fisher

\* This solution was made with a different batch of paraffin oil

Paraffin oil doped with linoleic acid was chosen for testing because this solution has been found to simulate acidic oil (Hornof et al., 1994). Also several investigators

found that saturated alkanolic as well as mono and di-unsaturated C18 alkanolic acids were all present in the oils they examined (Chiwetelu et al., 1990c).

The alkaline solutions were all prepared using weighed pellets dissolved in distilled water in volumetric flasks. The diluted crude oil was prepared by dissolving a given volume of untreated crude oil (from Lloydminster oil fields) into a known volume of toluene in the volume ratio of 2:1. The crude oil had to be diluted because the oil itself was too viscous and plugged the syringes, even when heated. The solution was then covered with parafilm to prevent the toluene from evaporating. A fairly low dilution of crude oil with toluene had to be chosen because it was determined that there was a decrease in the value of the IFT as the proportion of toluene increases (Neale and Ding, 1992). All components in contact with the crude oil were rinsed with toluene, then with acetone, then with distilled water.

### **3.2 Experimental Apparatus**

The SDT and DVT apparatus are described in this subsection.

#### **3.2.1 Spinning drop tensiometer (SDT)**

The solutions were tested on the Texas Model 300 spinning drop tensiometer using a reciprocal speed of 7.5 ms/rev at a temperature of 25°C. A glass capillary, of internal diameter 2 mm and length 10 cm, was filled with the alkaline solution using a 1 mL syringe, and then a droplet of oil was injected using a 10 µL Hamilton syringe. The timer was started as soon as the droplet of oil was injected and the capillary was placed in the tensiometer. Measurements were started after about 40-50 seconds, and taken at 50

or 100 second intervals for about 1500 seconds or until a constant value of IFT was reached. If the droplet length became less than four times the width, then both the length and width had to be measured, however the precision decreased due to the time required for these measurements. Figure 5 shows the droplet in the rotating capillary.

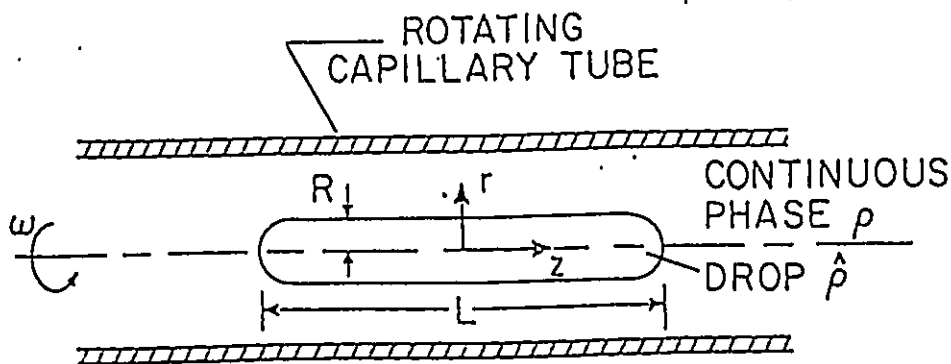
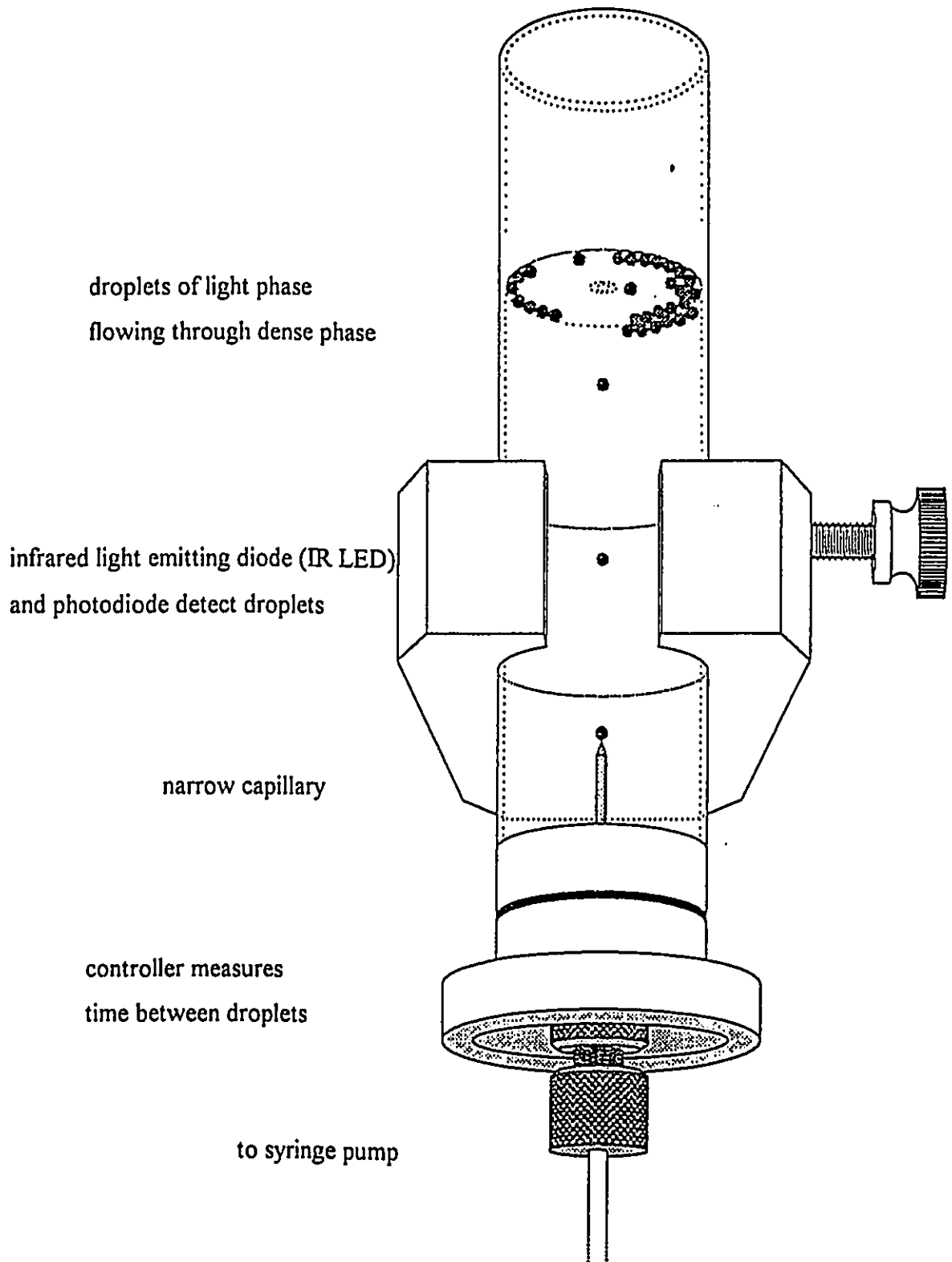


Figure 5: Droplet in rotating capillary in the SDT

### 3.2.2 Drop volume tensiometer (DVT)

The oil/aqueous systems were also tested using the DVT-10 drop volume tensiometer. This instrument consists of a control and data reduction module, a sample cell, a capillary, a photocell assembly and a syringe pump. The controller is menu driven, requiring the operator to input the sample density, flow rate of the syringe pump, and the number of drops to be counted. The syringe and capillary orifice sizes must also be entered.

The interfacial tension is calculated as each drop detaches, along with statistics for the experiment. Results were predicted by the manufacturer to be reproducible to 1% relative standard deviation (RSD). Figure 6 shows the sample tube with the detector.



**Figure 6: DVT-10 sample tube with detector (DVT manual, 1992)**

Figure 7, taken from the DVT manual (1992), illustrates the method that the DVT uses to calculate the IFT based on the balance of forces at the capillary tip. The separation force balances the adhesion force for values of IFT above 0.2 mN/m. IFTs below this threshold value cannot be accurately determined by the instrument due to the large relative standard deviation (RSD) involved when the IFTs of several drops are averaged. The orifice of the capillary has a diameter of 254  $\mu\text{m}$ , which works well for a wide range of flow rates and liquid viscosities. The thickness of the orifice wall at the tip is only a few  $\mu\text{m}$  which ensures valid results which require no corrections because as seen in Figure 3, the thin tip allows the vertical forces to be used due to the sphere not being in contact with the tip. Tips with thicker walls would cause errors in calculating the diameter of the droplet.

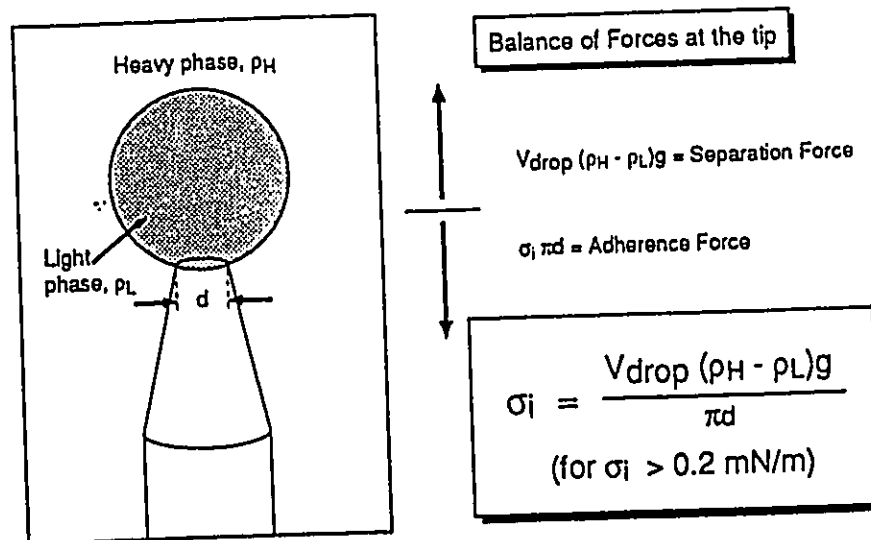


Figure 7: Drop volume method (DVT manual, 1992)

Figures 8 and 9 reveal the importance of ensuring that there is no leakage at the place where the tube from the syringe pump meets the capillary. The figures show that

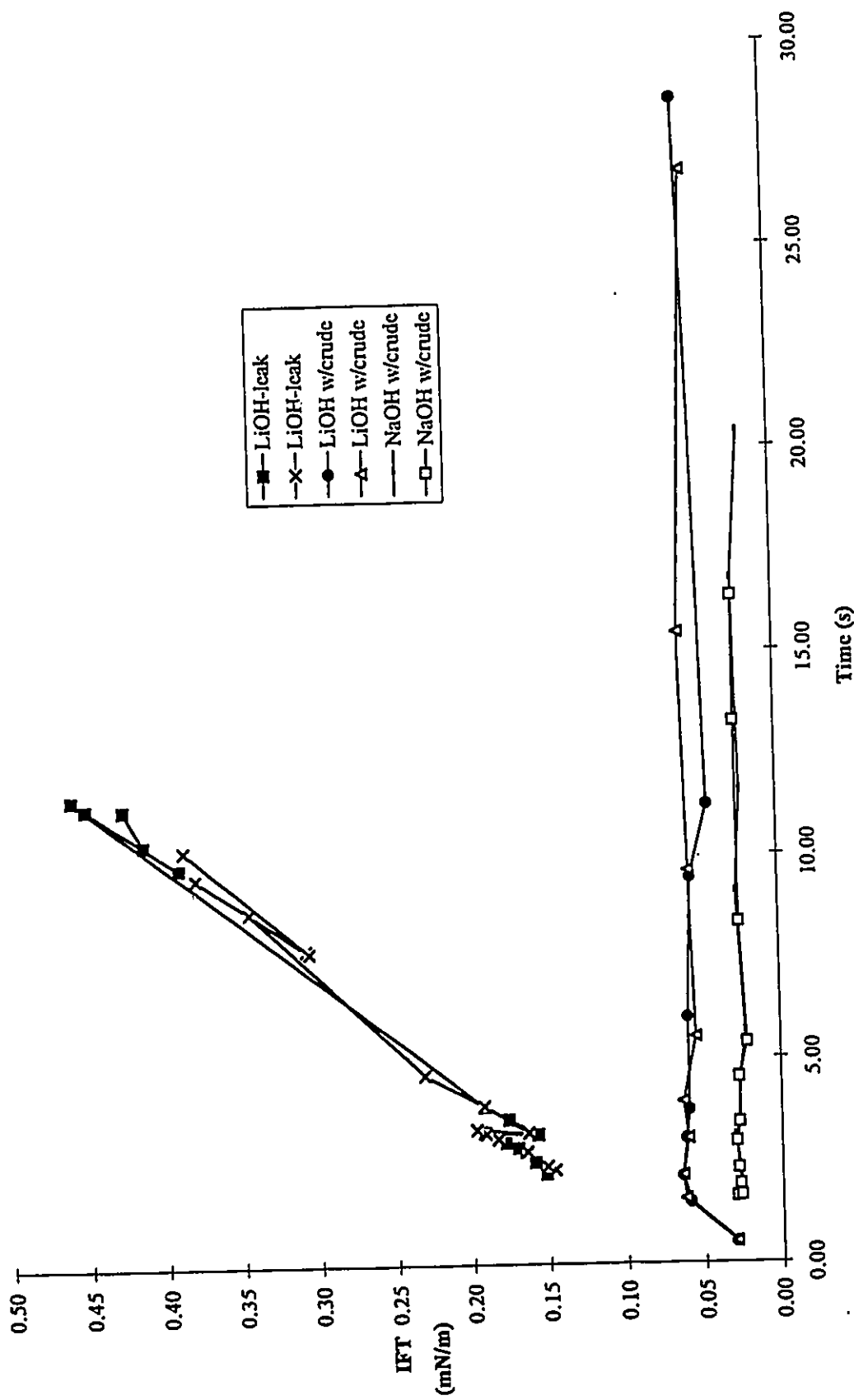


Figure 8: Dynamic IFT between Lloydminster crude oil and 25 mM LiOH and NaOH tested on the DVT

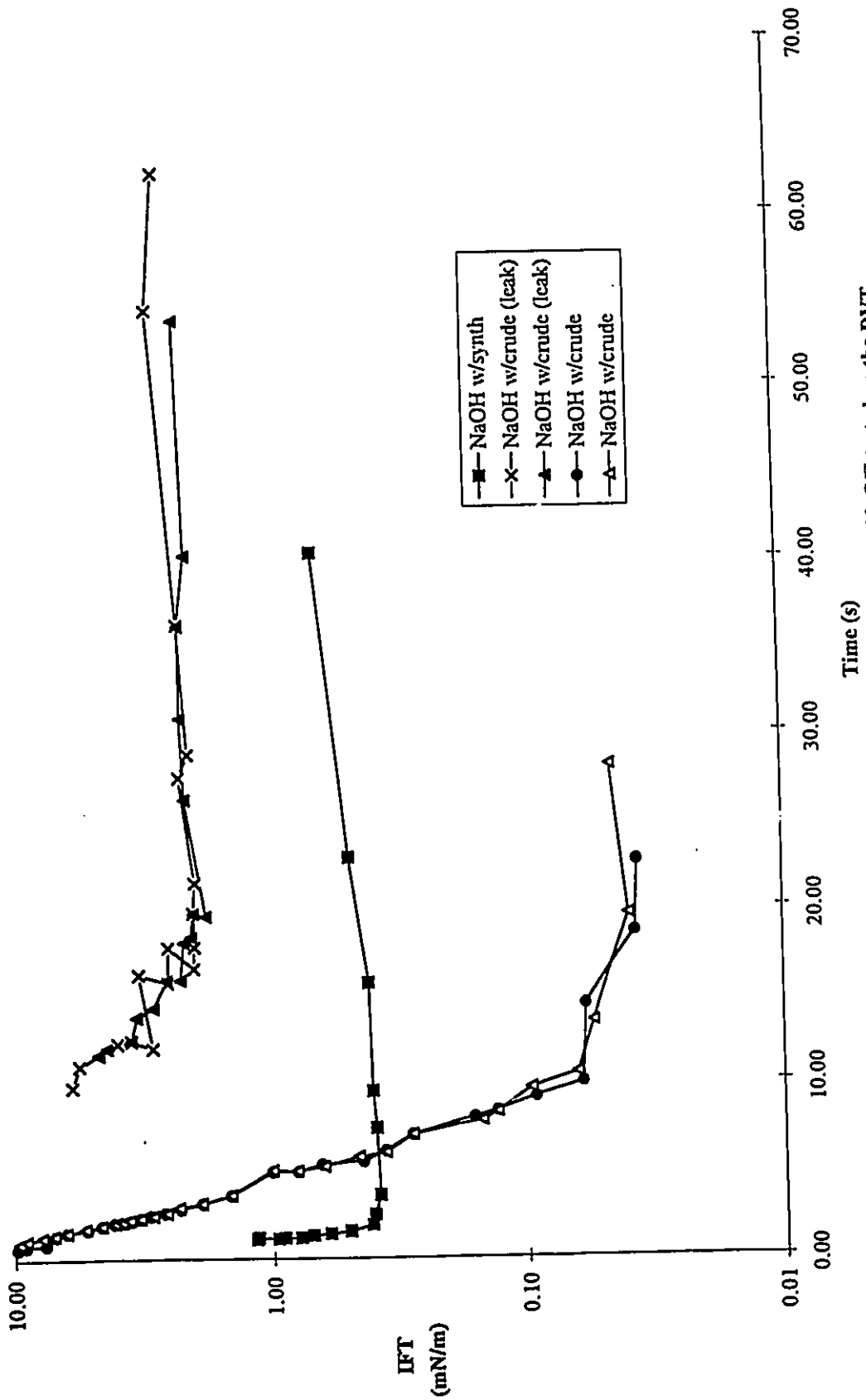


Figure 9: Dynamic IFT between 10 mM synthetic and Lloydminster crude oil with 2.5 mM NaOH tested on the DVT

when leakage occurred higher apparent IFT values were obtained compared to the values shown without leaks occurring. Higher IFT values were obtained due to the volume of the droplet being smaller than the flow indicates because all of the liquid is not being passed through the capillary. Figure 8 shows that the value of IFT increases with time since this involves lower flow rates and probably a higher percentage of liquid leaks out of the total flow because the pressure is not enough to force it through the capillary tip.

Leakage was prevented from happening further by placing the tube into the plastic end before tightening the plastic end into the assembly supporting the capillary. The plastic then pinches the tubing once it is screwed in tightly. Correct operation of the instrument is vital for accurate results to be obtained.

### **3.3 Measurement Procedures**

The procedures used for each of the two equipments are described in two separate subsections.

#### **3.3.1 SDT experimental procedure**

The SDT experiments were performed as follows:

1. A 10  $\mu\text{L}$  syringe was filled to 6  $\mu\text{L}$  with the lighter oleic phase, 10 mM linoleic acid in paraffin oil, and the 1 mL syringe was half filled with the denser aqueous phase, the alkaline solution. (The larger 1 mL syringe had to be used for the crude oil because it was too viscous to handle with the smaller syringe.)
2. The capillary was filled with the alkaline phase and then a drop of the oil phase was injected into the alkaline phase, noting the volume, and the timer was started.

3. The cap, with a rubber seal, was placed onto the capillary, tightened into the tensiometer, and the rotation was started. The reciprocal speed of rotation was adjusted to read 7.51 ms/rev and the temperature was maintained between 25 and 27°C.
4. The strobe was turned on and the level of the instrument adjusted so that the droplet remained centered in the capillary. A measurement was taken as soon as the droplet became stable.
5. Measurements were taken by moving the cross-hairs to each end of the droplet and taking the difference to obtain the diameter. If the length/diameter was less than 4, then the length of the droplet was also taken (by rotating the cross-hairs).
6. Measurements were recorded every 50 or 100 seconds depending on how quickly the droplet was elongating or contracting. The measurements were stopped when the droplet no longer appeared to elongate or contract significantly.
7. The capillary was removed once the rotation was turned off and the tube was cleaned with distilled water and rinsed with the next solution.

### **3.3.2 DVT experimental procedure**

The DVT experiments were performed as follows:

1. A 1.0 mL syringe was filled with the lighter phase, synthetic oil or crude oil, and all bubbles were removed. The syringe was then directly attached to the switching valve by using the Luer lock tip. The syringe was then filled using the refill option of the syringe pump with the line attached to the sample solution. The valve was then switched to fill the line leading to the sample cell.

2. The capillary tip was attached to the bottom of the cell and the glass tube was attached to the rubber bottom. The cell was slid onto the photocell assembly and positioned so that the bottom edge of the photocell was about 1-2 mm above the capillary tip. The sample cell was mounted in a clamp to hold it vertical. It was found to be essential that the cell be maintained in a vertical position and free of vibrations, or the IFT was affected.
3. The glass tube was filled with the denser liquid phase, such as one of the alkali solutions, until the liquid surface was about 10 mm above the top of the photocell.
4. A cover was placed over the cell and all tubing and fittings were checked.
5. The pump was started at about 1.0 mL/h, which allowed the air bubbles to escape the tip. After 30-60 seconds, a drop of the light phase formed. This droplet was checked to confirm that it was symmetrical around the capillary tip and that the capillary was not clogged or damaged. After 2-3 droplets had been formed, the pump was turned off.
6. The main menu was selected and the parameters were entered, including the capillary diameter of 254  $\mu\text{m}$ . A droplet limit of three was normally chosen.
7. The flow rate was set on the pump and controller. The pump was re-started. The sensitivity was adjusted ensuring that the drops were being detected properly; i.e. that there was one beep per drop that detached.
8. Using the menu the gathering of data was started.
9. Once the data had been collected, the pump was turned off. The flow rate was changed. The dense phase solution was also changed because surfactant accumulates at any available interface and most of the surfactant may form at the air/liquid interface rather than the liquid/liquid interface where the IFT measurements are being made.

10. Steps 3-9 were continued until all of the desired flow rates had been tested.
11. When the experiment was finished, the tubing and syringe were cleaned with acetone and the solvent was ejected from the tubing and capillary using compressed nitrogen or a syringe.

### 3.4 Experimental Aspects

The spinning drop tensiometer and the drop volume tensiometer were used to test synthetic oil and Lloydminster crude oil with four different alkalis, i.e. sodium, potassium, and lithium hydroxides and sodium orthosilicate. Sodium hydroxide had been used in a field study in the Lloydminster area of Western Canada and the recovery over waterflooding was improved (Babu et al., 1984). Under certain circumstances, Chiwetelu et al. (1994) found that sodium hydroxide was the best. The optimum concentration of alkali was found to be close to 25 mM for all temperatures that Chiwetelu et al. (1992) studied. Concentrations of alkali above 25 mM could not be measured by the DVT to obtain IFT values since the initial interfacial tension may drop to values below 0.1 mN/m (Chiwetelu et al., 1988). According to the DVT manual (1992) the lower limit of IFT that the DVT can measure is 0.2 mN/m.

The time and width measurements from the Texas Model 300 spinning drop tensiometer, were entered into a spreadsheet software program (EXCEL) and the interfacial tension was calculated using the simplified equation [5]. The DVT-10 tensiometer was also used and the time, volume of a drop, IFT and error were recorded and entered into the spreadsheet. The IFT was then plotted versus time. The log of the

interfacial tension was used in some cases in order to view the trend of the curves more easily. The densities of the solutions were tested using a PAAR DMA 48 density meter, manufactured in Austria. Accurate density values were required in order to calculate the IFT by both methods.

The figures of IFT as a function of time were compared for the two instruments used. In addition, the four alkali trends were compared depending on the concentrations of acidified oil and the alkaline solutions. All of the measurement data for the SDT is available in Appendix A while that for the DVT is in Appendix B.

## **4. EXPERIMENTAL RESULTS AND DISCUSSION**

### **4.1 IFT Results Measured with the SDT and DVT**

#### **4.1.1 Reproducibility with the SDT**

Four different alkalis were tested on the SDT to determine the transient IFT against acidic oil. Multiple runs were performed for each alkali to check the reproducibility of the measurements. Figures 10-13 contain replicate runs for the sodium hydroxide, lithium hydroxide, potassium hydroxide and sodium orthosilicate solutions, respectively. They reveal that although the trends of the transient IFT curves were the same, the slope of the increasing IFT and the time of onset of the IFT rise, after the minimum was reached, varied to a large degree. This confirms the results found by Chouinard (1992).

Therefore, the transient curves were hard to duplicate using the SDT. However, it became evident that the volume of the drop played a significant role in controlling the shape of the transient IFT curve. The smaller the drop, the sooner the minimum was reached and the steeper was the IFT increase following the minimum. It has been previously found that, usually, the smaller the drop volume the lower the tension (Franses et al., 1980). The minimum may be lower because the interface is smaller so the acidic molecules can orientate and react faster. The steeper slope can be explained by noting that a smaller drop has less volume and thus there should be less acidic molecules in the oil to diffuse to the interface; therefore the minimum should be reached quickly and the IFT increase swiftly as the components for the reaction are depleted due to diffusion into the two phases.

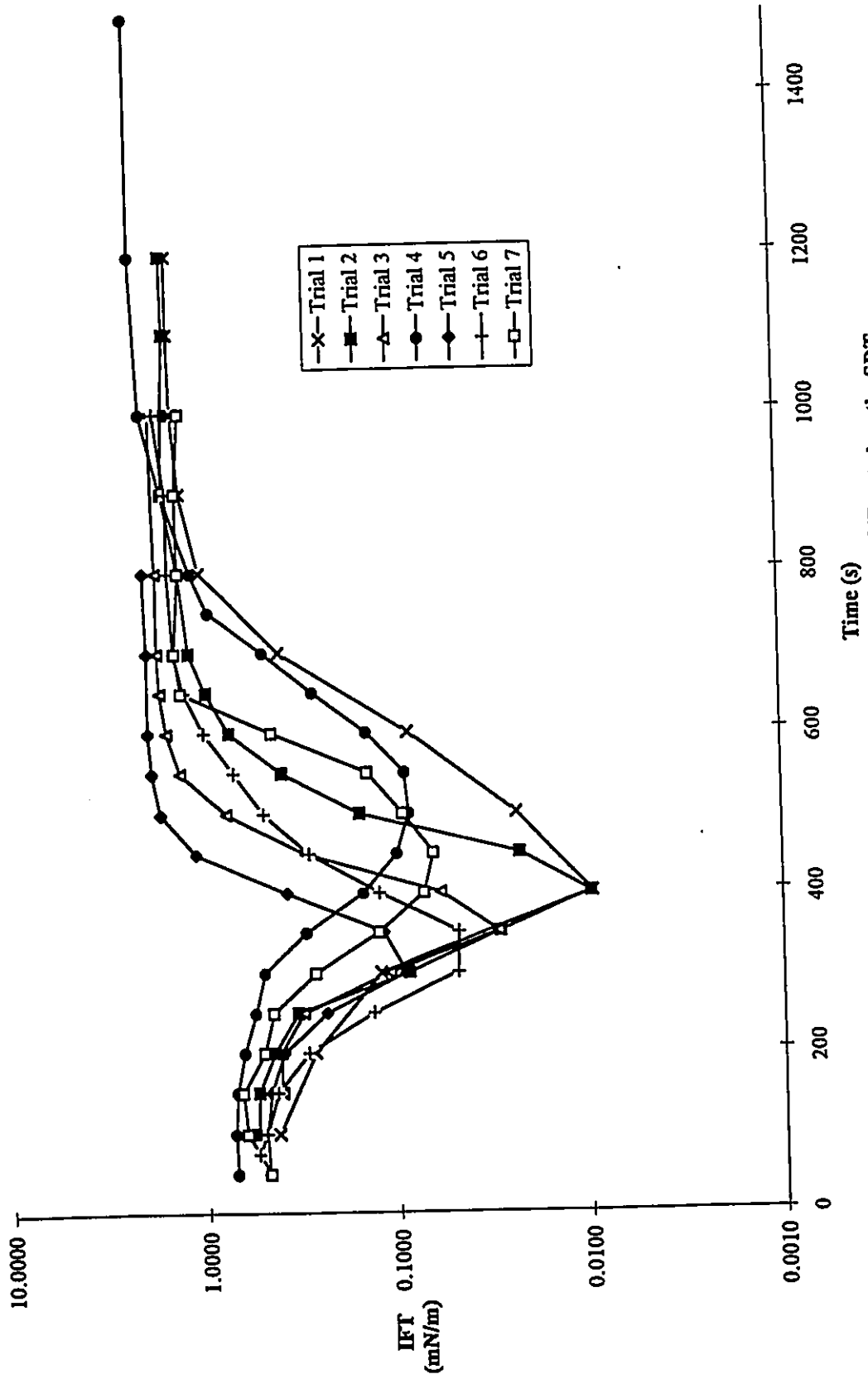


Figure 10: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT

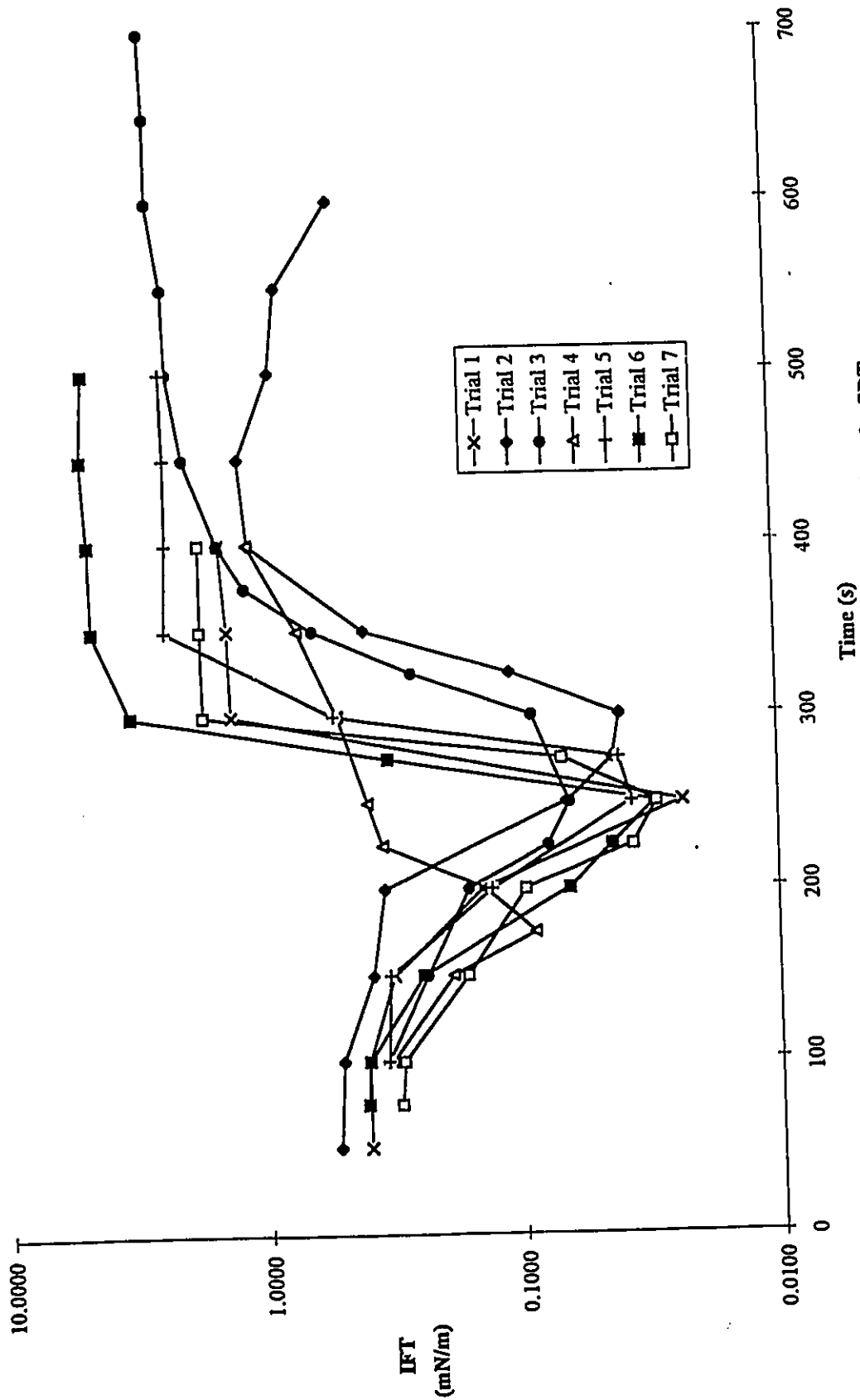


Figure 11: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT

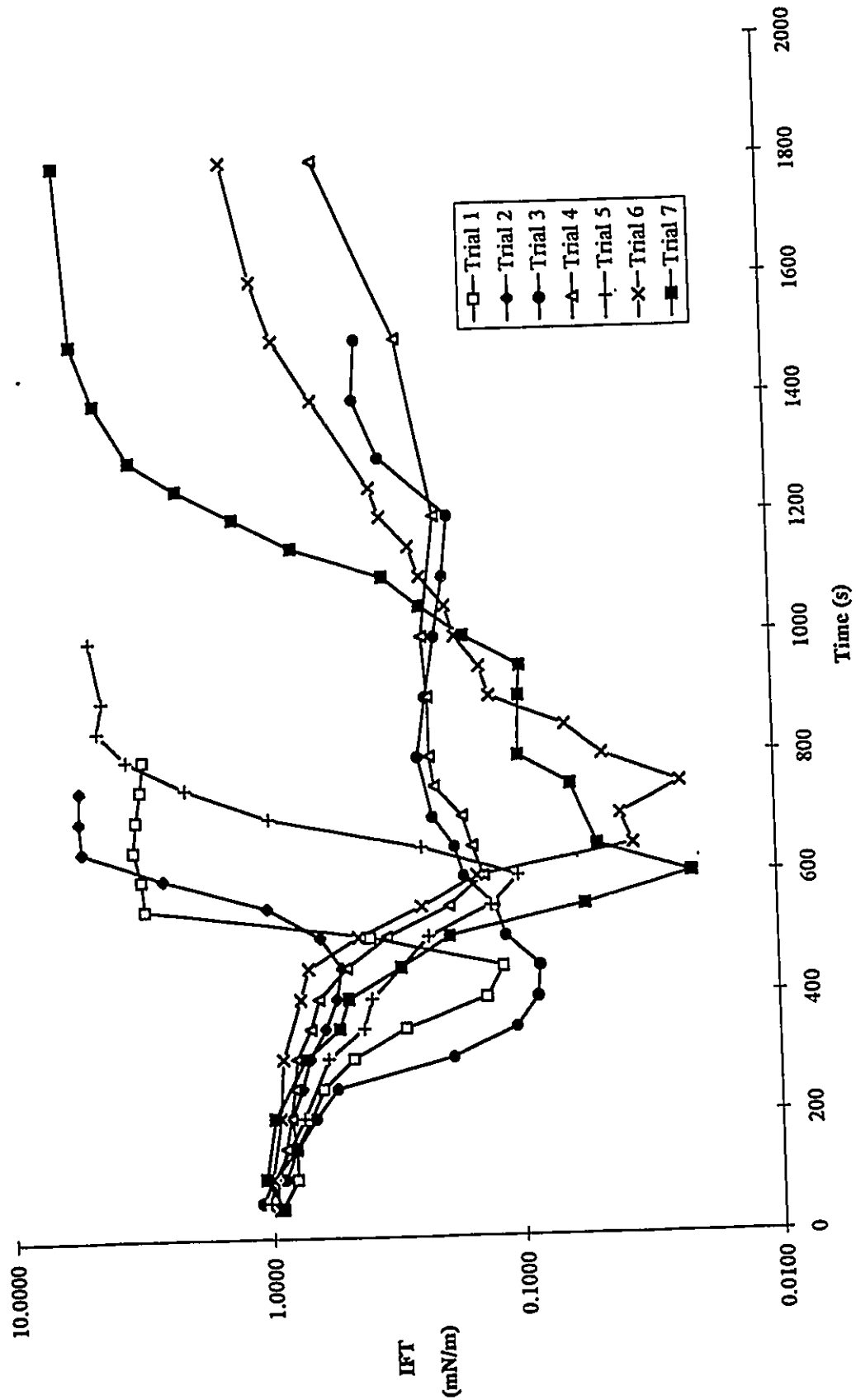


Figure 12: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT

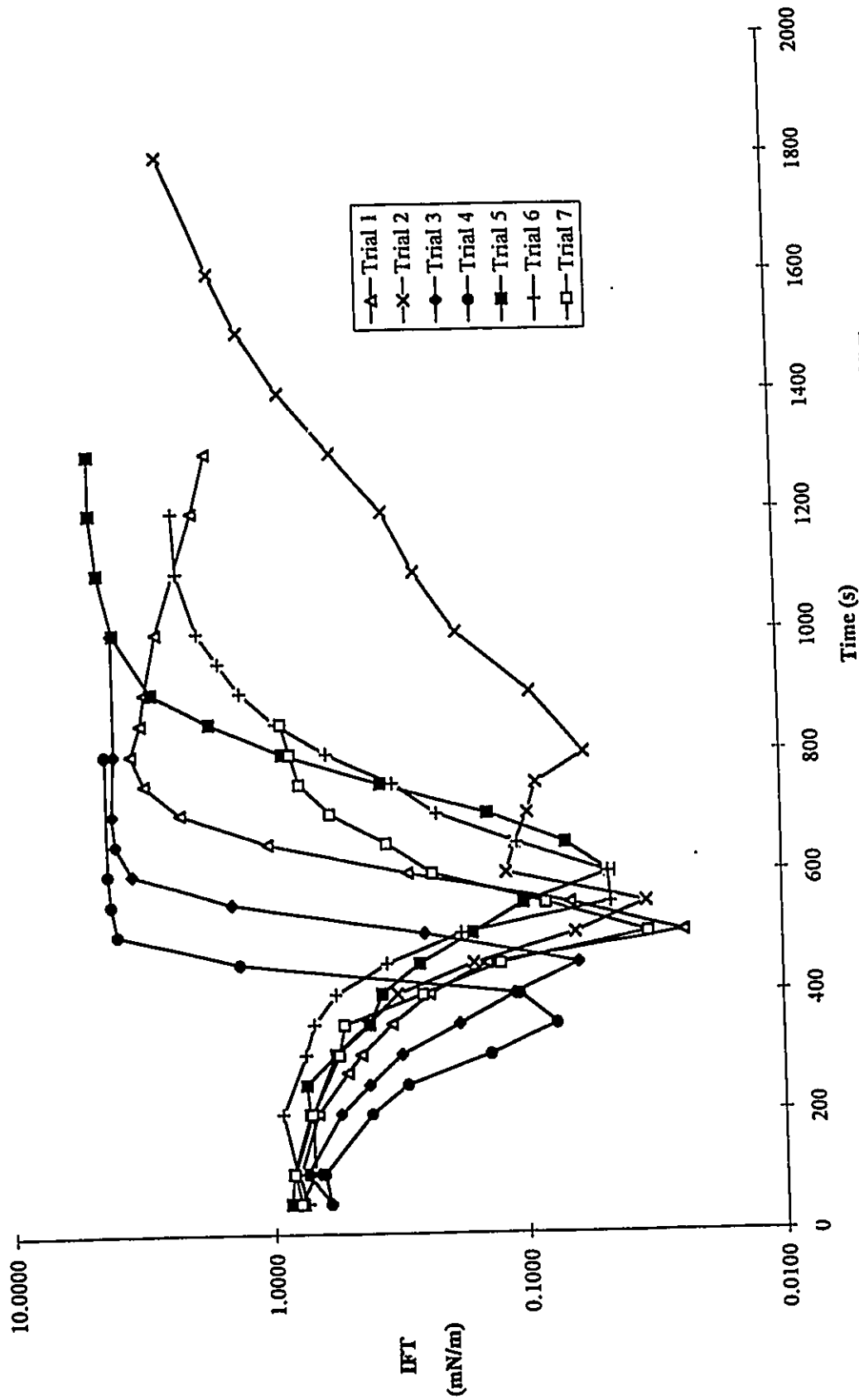


Figure 13: Multiple trials of transient IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT

It was observed that when the drops were all of the same size, the reproducibility was better but the increasing slope still varied somewhat. This can be seen in Figures 14 and 15 which show IFT values for 10 mM linoleic acid in paraffin oil and 25 mM NaOH and Na<sub>2</sub>SiO<sub>3</sub>, respectively. The numerical value in the legend represents the molar ratio of acid to alkali, which is calculated by dividing the number of moles of the acid in the oil phase by the number of moles of alkali in the aqueous solution, as follows:

$$MR = \text{moles}_{\text{acid}} / \text{moles}_{\text{alk}} \quad (6)$$

The SDT instrument would be more usable if a method of injecting a constant and exactly repeatable amount of liquid into the capillary were developed, since it is difficult to achieve exactly the same volume in a series of experiments. Another problem with the SDT is, that, even if the same amount is injected from the syringe, the droplet often breaks into smaller droplets once the rotation is started. Babu et al. (1984) found that with crude oil droplet volumes varying between 0.5 and 2.5 μL, the minimum interfacial tension values varied marginally although the time at which the minimum occurred remained essentially unchanged. Khulbe et al. (1985) used droplets in the range of 2-3 μL in volume without significant variation in IFT values, which works well for crude oil but for linoleic acid solutions, stable drops of this volume were almost impossible to form. Therefore, the experiments were selected to compare systems with similar droplet volumes which can be distinguished by the molar ratio of acid to alkali, MR, as determined by equation [6] as well as enabling different concentrations of acid to be compared.

One possible qualitative explanation for the transient IFT trend results observed considers what is occurring at the interface. The relatively high caustic concentration

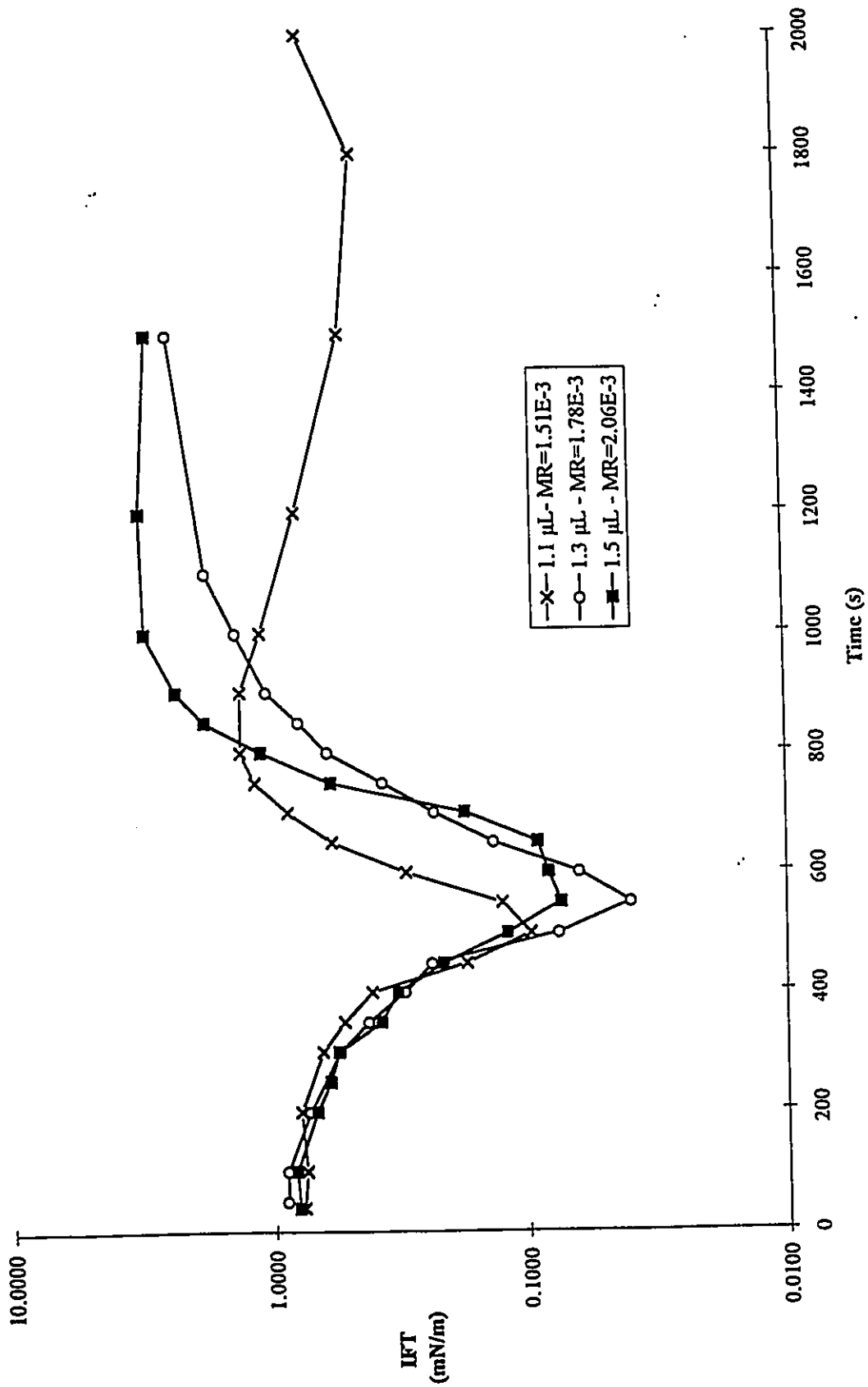


Figure 14: Transient IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT

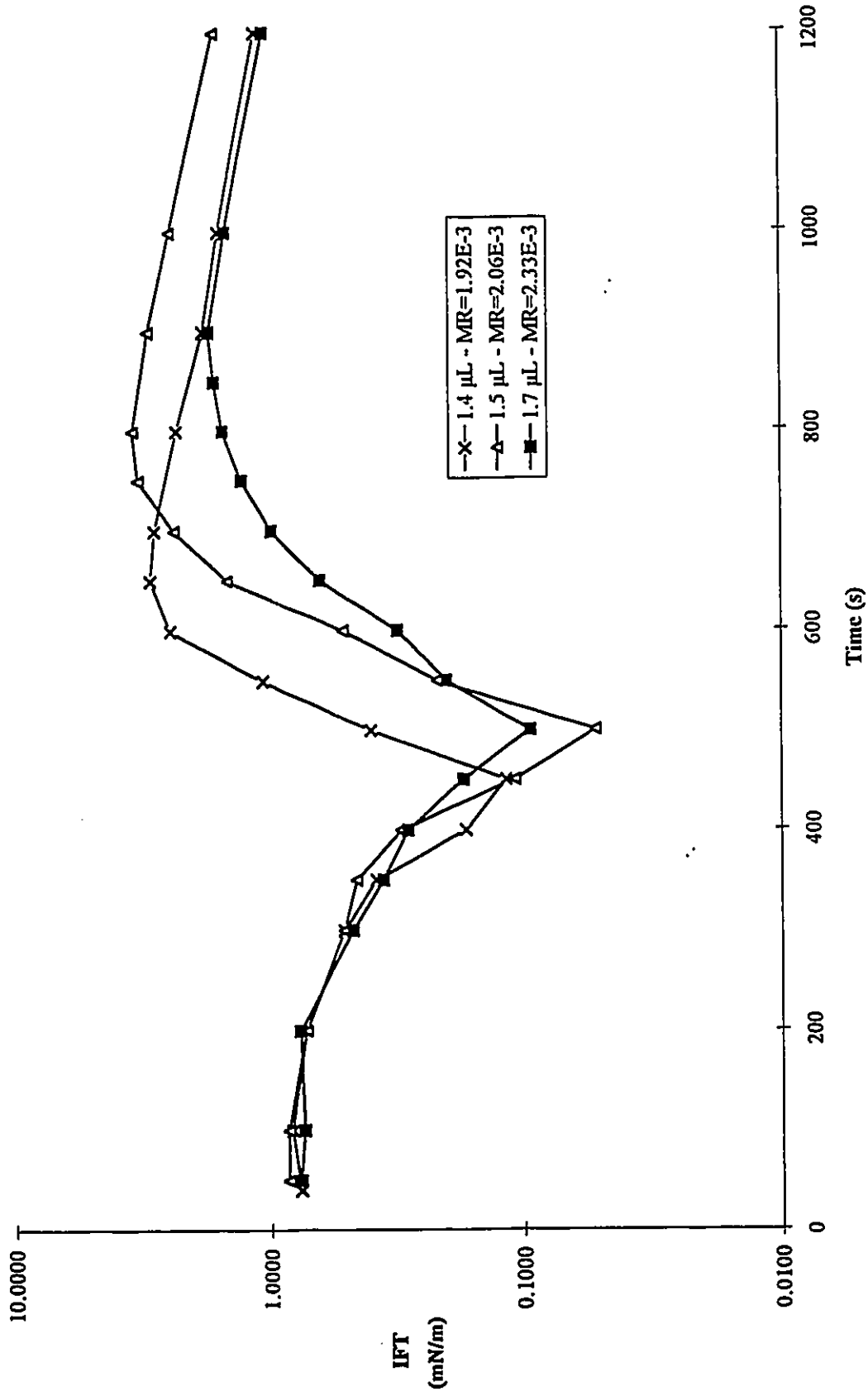


Figure 15: Transient IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT

means that more surfactant soaps are produced by reaction with the acid in the oil phase. Accumulation of the relatively high initial soap concentration at the interface causes the IFT to drop significantly. The IFT increases after the minimum is reached due to a combination of large mass transfer driving forces and electrostatic repulsion, resulting in much reduced interfacial surfactant concentration (Chiwetelu et al., 1988). These forces appeared to cause uneven elongation and contraction in some instances, as shown in Figure 16. This behaviour was also observed by Chouinard (1992).

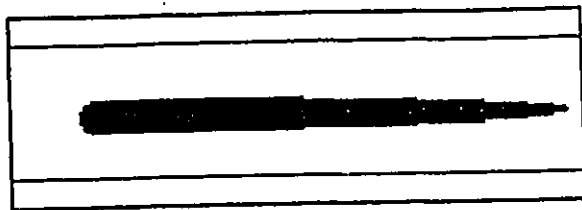


Figure 16: Representation of uneven elongation of a droplet rotating in the SDT

#### 4.1.2 Reproducibility with the DVT

Figure 17 shows the dynamic interfacial tension measured with the drop volume tensiometer between the 25 mM NaOH and LiOH solutions and 10 mM synthetic oil with four trials for each hydroxide represented by a number in the legend. The results for the other two alkaline solutions can be seen in the figures provided in Appendix B. The figures show that the trends are fairly reproducible although there is some variability from run to run. This is most likely due to the IFT values being close to the manufacturer's recommended lower limit of 0.2 mN/m for this instrument. The greatest variability is observed in the case of LiOH which gave rise to the lowest IFT values (about 0.2 mN/m).

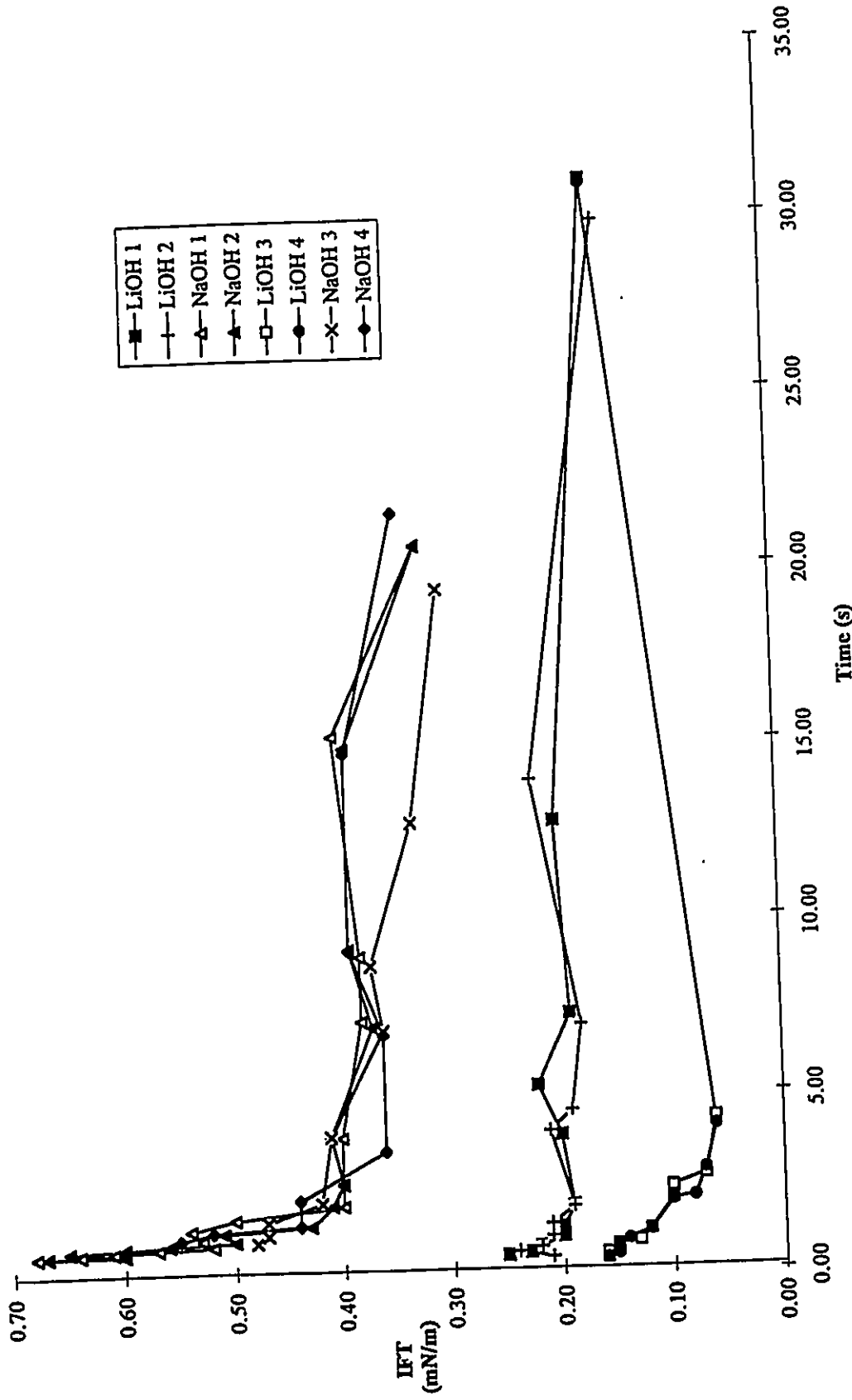


Figure 17: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT

Time, as defined for these experiments, is the time necessary for one drop to form and detach, taken as an average of three consecutive drops. It was confirmed that using fresh solution of alkali in the measurement tube between each change in the flow rate did not seem to significantly alter the measured IFT. Thus, the surfactant is not forming at the air/liquid interface in any significant amounts. This is likely due to the acid being the limiting factor since the alkali is in excess at these concentrations and few drops are being averaged. The erratic values obtained at high flow rates may be explained by the fact that the droplets are following each other so closely that the detector has difficulty in differentiating two separate drops from each side of a single drop as they pass the detector.

Each point, on every curve for all of the eight runs, represents an average of 3 drops which gave a relative standard deviation (RSD) between 1-4%. The RSD value is higher for longer times because the flow rate becomes quite small. The flow rate and time are inversely related since low flow rates mean a longer time for the interface to form before it detaches. The trend of IFT versus flow rate can be seen in the Appendix B data. The smaller flow rate may result in larger errors due to any vibrations having a larger effect. Also, the syringe pump output may be subject to fluctuations or pulsations. A syringe with a smaller internal diameter should be used for smaller flow rates since the pump stepper motor would then produce more counts (higher accuracy) per unit time to deliver an equivalent volume from a smaller syringe than from a larger one (DVT manual, 1992). However, there is a danger that some systems would then operate at a flow rate that is lower than the rate of diffusion. This means that the apparent IFT measured would

not include any surfactants at the interface and the effect of the surfactants on the IFT would not be determined.

The minimum IFT value obtained for the NaOH solution was about ten times the value as measured by the SDT. This could be due to two possibilities: (i) the two instruments do not read the same values; or (ii) the DVT was not able to measure the minimum IFT due to the flow rate not being small enough with the values so close to the lower limit of the instrument. These possibilities were checked by testing lower concentrations of oil and aqueous solutions because then the IFT values were larger and a comparison could be made between the two instruments once again, as seen below.

#### **4.1.3 Effects of acid and alkali concentrations**

Figure 18 shows the dynamic IFT between 25 and 2.5 mM NaOH and 10 mM synthetic oil as well as that between 25 mM NaOH and 1 mM synthetic oil. Appendix B contains the figures which show IFT as a function of flow rather than time for the same systems as above. Measurements at lower alkali and acid concentration were conducted on the DVT because the IFT values were near the level of detectability at the higher concentrations of the oil and aqueous solutions. As can be seen, the lower concentration IFT values are higher and a smooth curve is obtained with excellent reproducibility, validating the explanation that the poor results obtained for the 25 mM alkali were due to the IFT values being too close to the precise detectable level of 0.2 mN/m for the DVT.

In addition, lowering the acid concentration by a factor of ten increased the IFT by a factor of ten, resulting in the minimum being increased to 2.4 mN/m from about 0.3

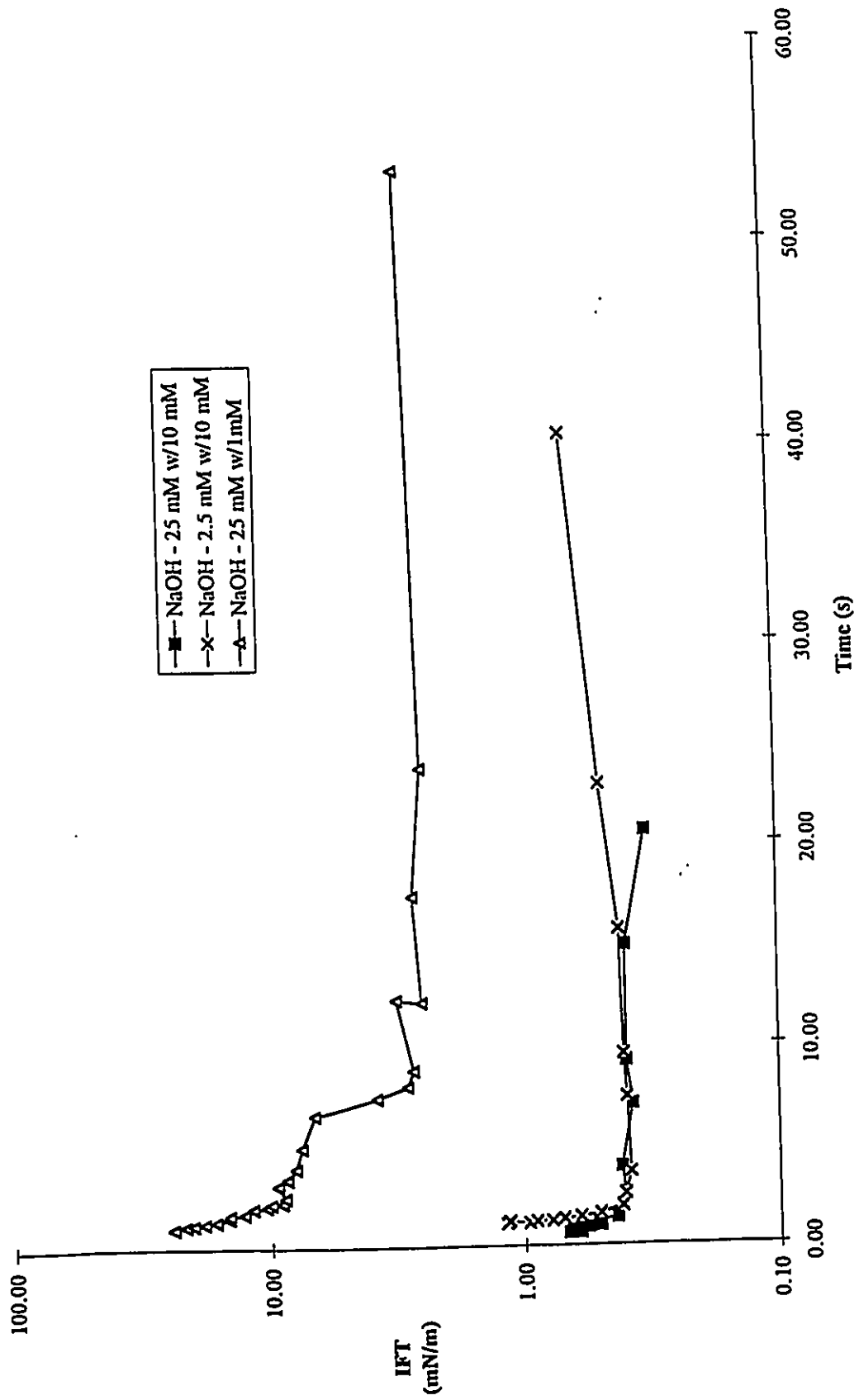


Figure 18: Dynamic IFT of 10 and 1 mM synthetic oil against 25 and 2.5 mM NaOH tested on the DVT

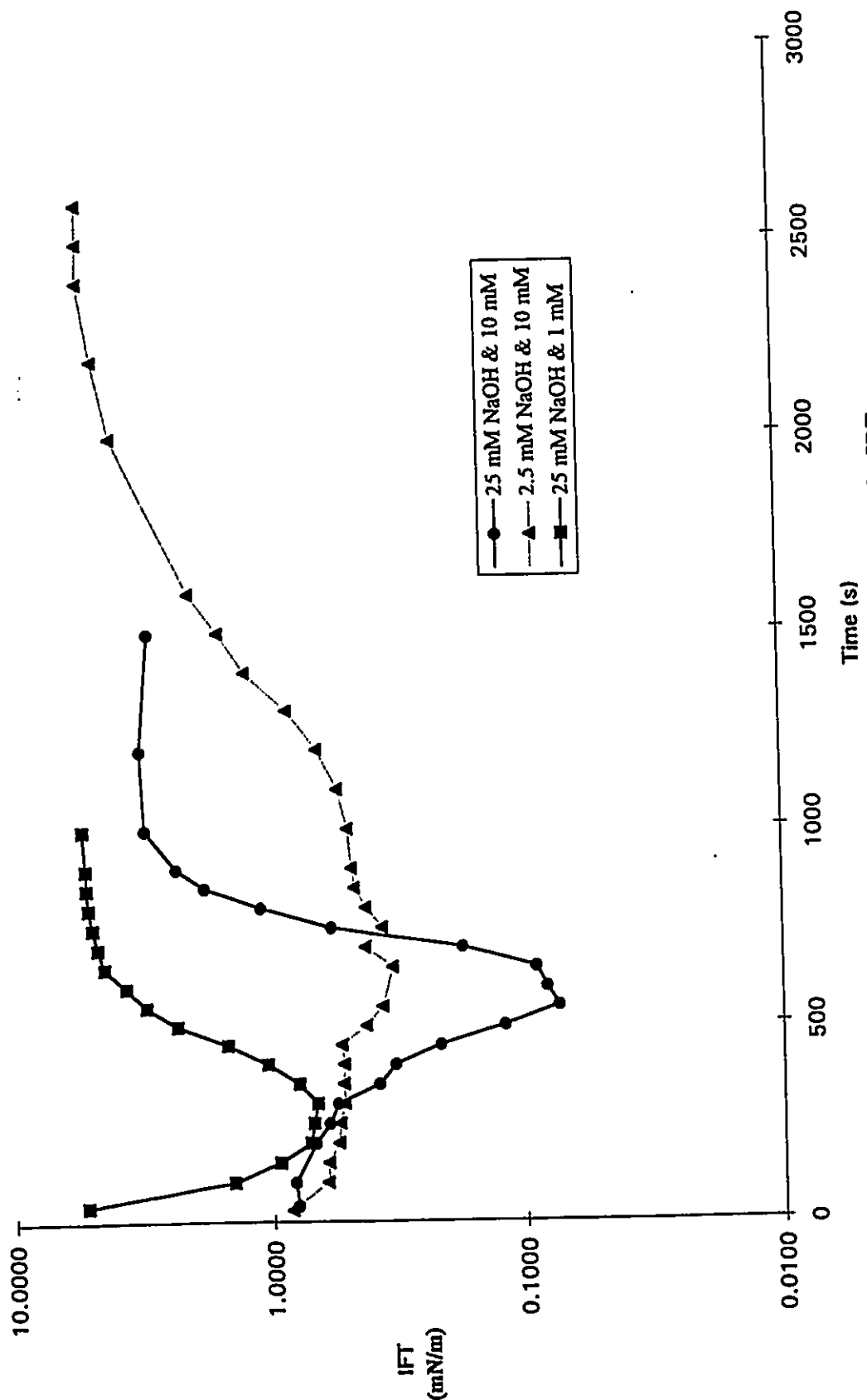


Figure 19: Transient IFT of 1 and 10 mM synthetic oil against 25 and 2.5 mM NaOH tested on the SDT

mN/m (for 25 mM NaOH). Figure 18 reveals that when the alkali concentration was lowered by a factor of ten, the IFT increased somewhat at the beginning and end of the curve although the minimum IFT was not much different (0.37 mN/m compared to about 0.3 mN/m for 25 mM NaOH). The higher acid concentration has a much greater effect than higher alkaline concentrations which suggests that the acid is the limiting factor in the creation of the surfactant. Again two possible explanations exist: (i) it may be that the alkali is in excess so its concentration is not significant; or (ii) the DVT did not measure the minimum IFT value accurately for the 25 mM solution due to the lower limit of limiting time factor. Measurements on the SDT helped evaluate these possibilities.

Figure 19 reveals the transient IFT values tested on the SDT for 2.5 mM and 25 mM NaOH with 10 mM synthetic oil and 25 mM NaOH with 1 mM synthetic oil. The curves indicate that the minimum IFT value for the 2.5 mM NaOH and 10 mM synthetic oil is about the same whereas the 1 mM oil with 25 mM NaOH has a higher value for the DVT measurement than the SDT measurement. The lack of similarity between the 25 mM NaOH IFT values may be due to the DVT being unable to accurately measure the IFT minimum values either, because the minimum had not yet been reached with the flows measured, or the values became unreliable due to being near the threshold limit of the instrument. A more likely explanation is that the DVT method does not show any significant difference in IFT values for a change in the alkaline concentration in this range of 2.5 to 25 mM since there is less time for reaction at the interface when compared to the SDT.

#### 4.1.4 Comparison of alkali tested on the SDT and DVT

Figures 20 to 22 show the transient IFT between 25 mM alkaline solutions and each of the acid concentrations (10, 30 and 60 mM, respectively) using the SDT. The initial IFT measured varies with the type of alkali. The same trend is observed in all of the cases with the order of highest initial IFT to lowest as follows: KOH, NaOH,  $\text{Na}_2\text{SiO}_3$ , and LiOH. The concentration of the acid does not affect the initial IFT but may play a role in the trend of the transient IFT. The minimum IFTs and the IFT values obtained at the end of the measurement seemed to vary in their order for the different alkali. This could be an effect of the droplet volume variations which were difficult to control. Babu et al. (1984) also found that the minimum value varied somewhat from run to run with a variation in droplet volume.

The minimum values are all very close to one another and vary with multiple trials so that there is not a definite trend that can be established. The acid concentration may affect the minimum value order. It was previously determined by Chiwetelu et al. (1992) that there was an optimum concentration for NaOH and there is likely optimum concentrations for the other hydroxides as well. Lithium hydroxide appeared to give the lowest IFT for the lower acid values while sodium orthosilicate had IFT values just above lithium for all concentrations. These two alkalis had the highest IFT values for the acid concentration of 60 mM. Potassium hydroxide had the highest IFT value at the lower acid concentration with the lowest at 60 mM while sodium hydroxide was just below potassium at 10 mM synthetic oil and just above potassium for 60 mM. The trend may also vary due to the difference in droplet volume since the droplets generally became

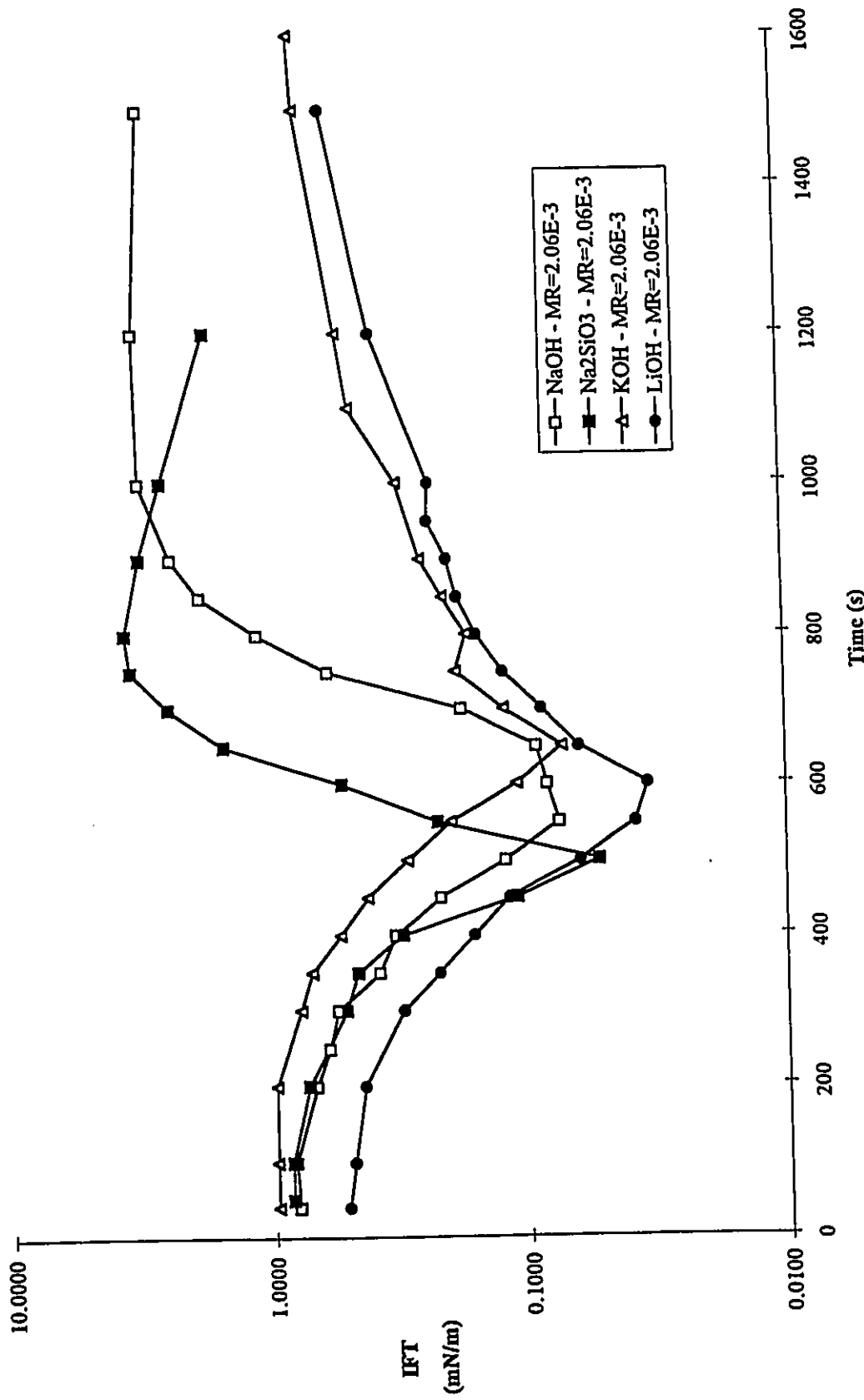


Figure 20: Transient IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

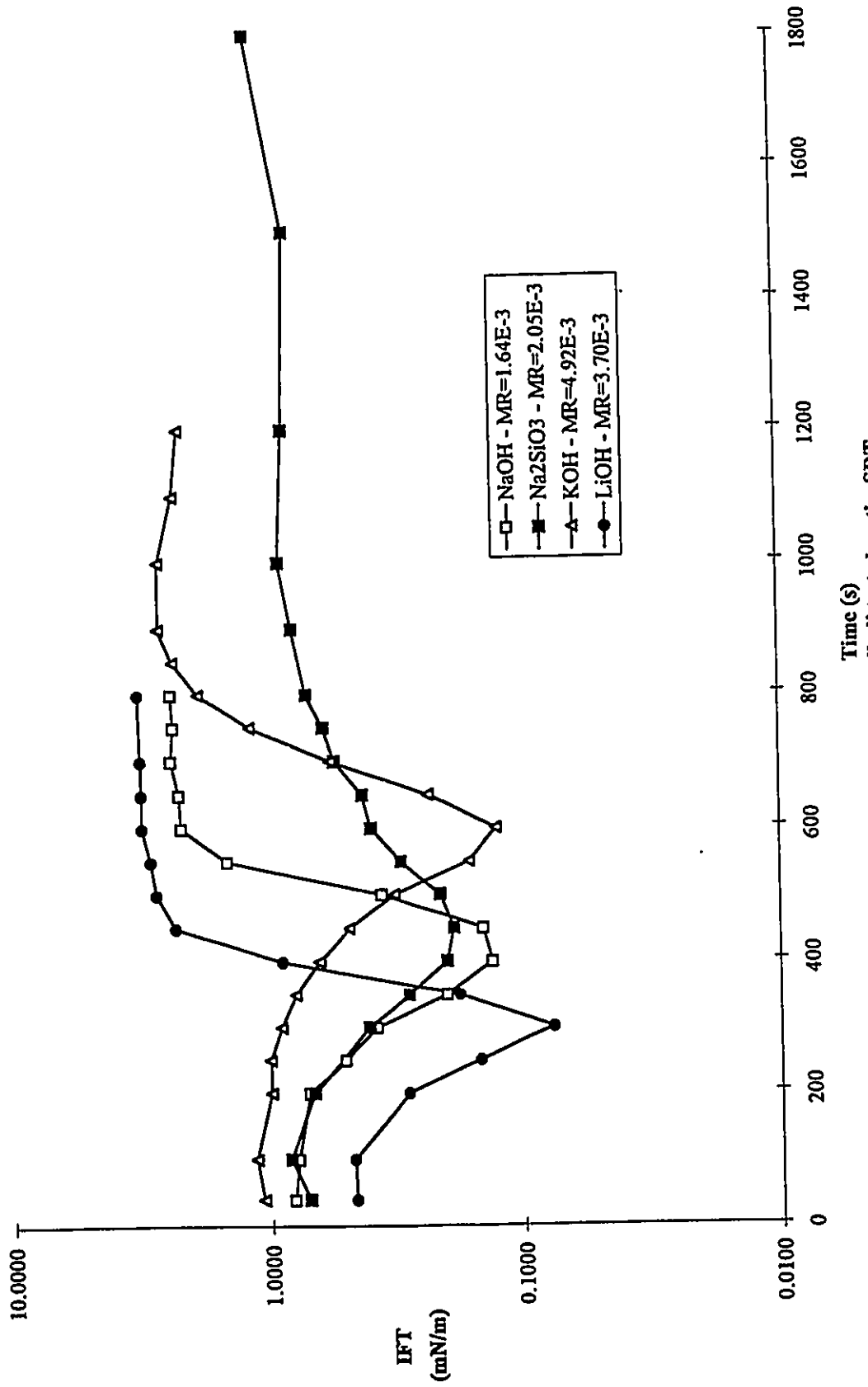


Figure 21: Transient IFT between 30 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

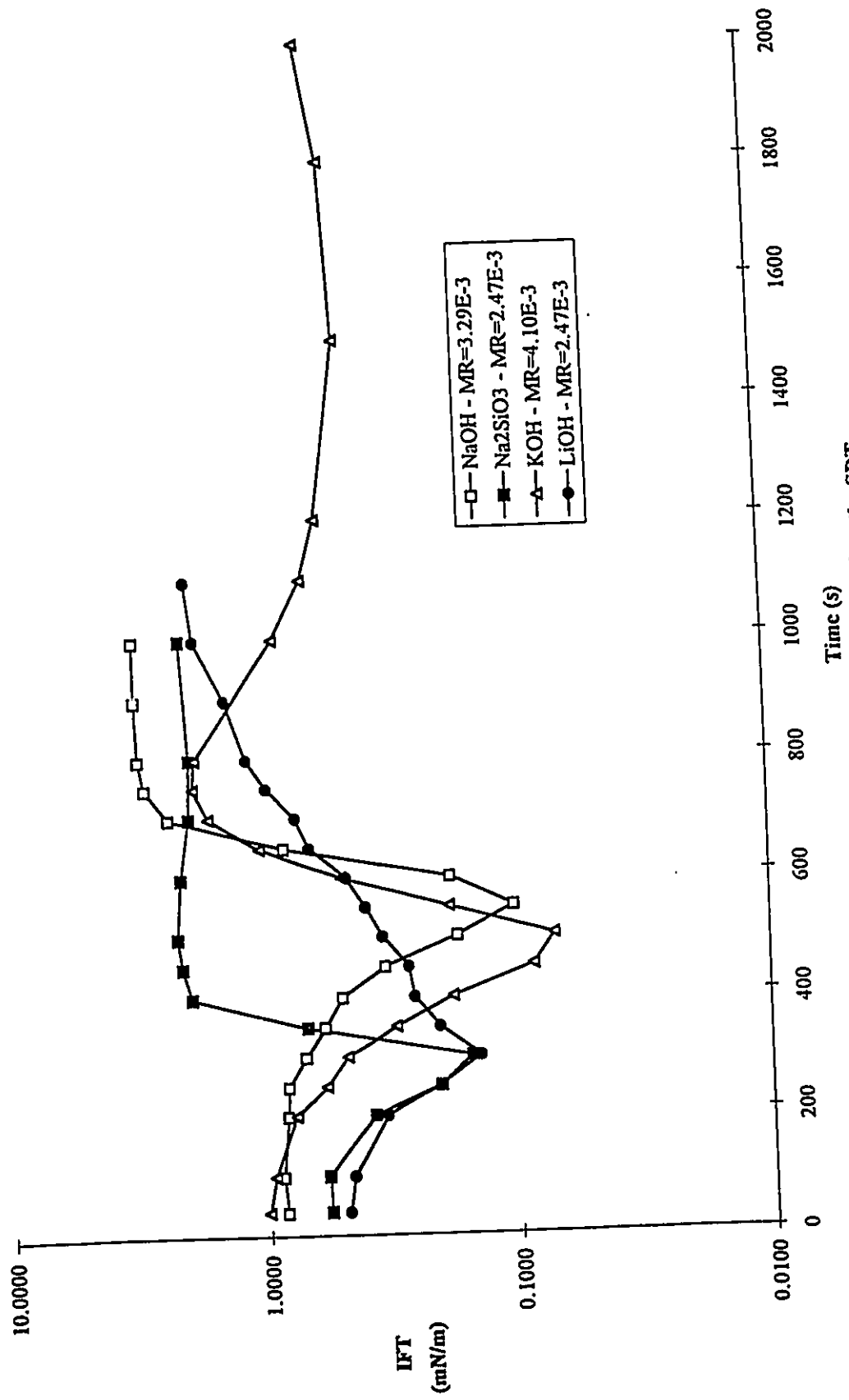


Figure 22: Transient IFT between 60 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

smaller as the acid concentration increased, revealed by the MR value. This occurred because it became very difficult to obtain a large stable droplet.

Figure 23 shows the order of alkali observed on the DVT. The trend observed seems to indicate values of IFT in decreasing order: KOH, NaOH,  $\text{Na}_2\text{SiO}_3$  and LiOH. This conforms with the same order as obtained by the SDT for the initial IFT values. Higher concentrations of acid were not tested on the DVT because the minimum expected IFT values would be so close to the lower working limit of the instrument and therefore produce unreliable results. The consistently lower IFT value for lithium hydroxide observed may be caused by lithium's tendency to form covalent bonds compared to the other alkali metals, and the fact that its salts are generally less soluble in water (Khulbe et al., 1987).

The effect of the alkali is dependent on several factors. In ionic surfactants, such as the ones produced by the interaction between caustic and heavy oil, those with more tightly bound counterions (ions with small hydrated radii (e.g.,  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ )), appear to be more effectively adsorbed than those with less tightly bound ones ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{F}^-$ ), although the effect is predicted to be rather small (Rosen, 1989). The counterions with greater polarizability tend to decrease the critical micelle concentration (CMC), although once again the effect is small. The degree of hydration and the number of hydration layers around the polar region of the surfactant increase with the increasing atomic weight of the cation; thus potassium salt would be expected to have a lower rate of diffusion from the interface than salts of lighter cations, resulting in a more prolonged period of low IFT. These effects are concentration dependent as any free alkali metal hydroxide, being a

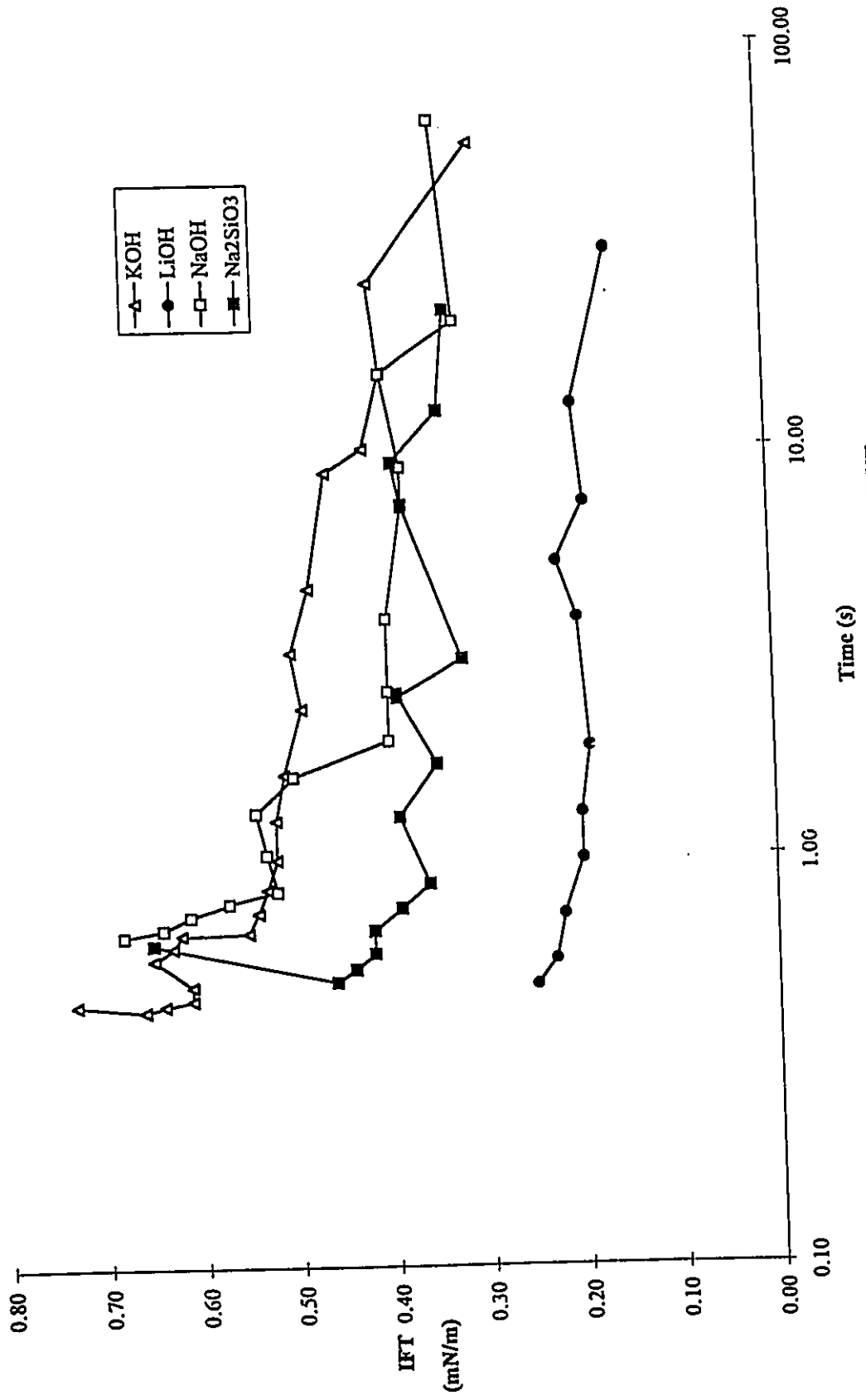


Figure 23: Dynamic IFT between 25 mM aqueous alkali and 10 mM synthetic oil tested on the DVT

strong electrolyte, would affect the solution behaviour of the surfactants formed (Khulbe et al., 1987).

#### 4.1.5 Effects of linoleic acid concentration

In Figure 24, it is observed that as the acid concentration increases, the IFT values increase. This was unexpected since there is more acidic material in the oil to react with the alkali to produce surfactant. The slope of the increase in IFT, after the minimum was reached appeared to be less steep and started later in time for the higher acidic oil concentrations. This could be due to the acidic components taking longer to reach the interface and react at the surface, so a more prolonged minimum was maintained. The diffusion into the bulk phases was slower, due to the gradual production of surfactant which is then depleted from the interface. However, this trend had to be confirmed, since it was found that as the acid concentration in the oil was increased, the size of the stable droplet decreased, which as previously observed, can affect the IFT measured by the SDT.

Figures 25, 26, 27 and 28 show the interfacial tension versus time for 25 mM alkali and 10-60 mM linoleic acid for sodium, lithium and potassium hydroxides and sodium orthosilicate, respectively. In general, the minimum was lower for the higher acid concentrations than for the lower values in contrast to the earlier results supporting the fact that the droplet volume did affect the IFT trend. Especially the values for 10 mM synthetic oil in most of the figures show the effect of the smaller droplets and may also be a result of the lower density of this particular solution. The minimum IFT was lower for oils containing more acid because the time was long enough for some of the surfactant to

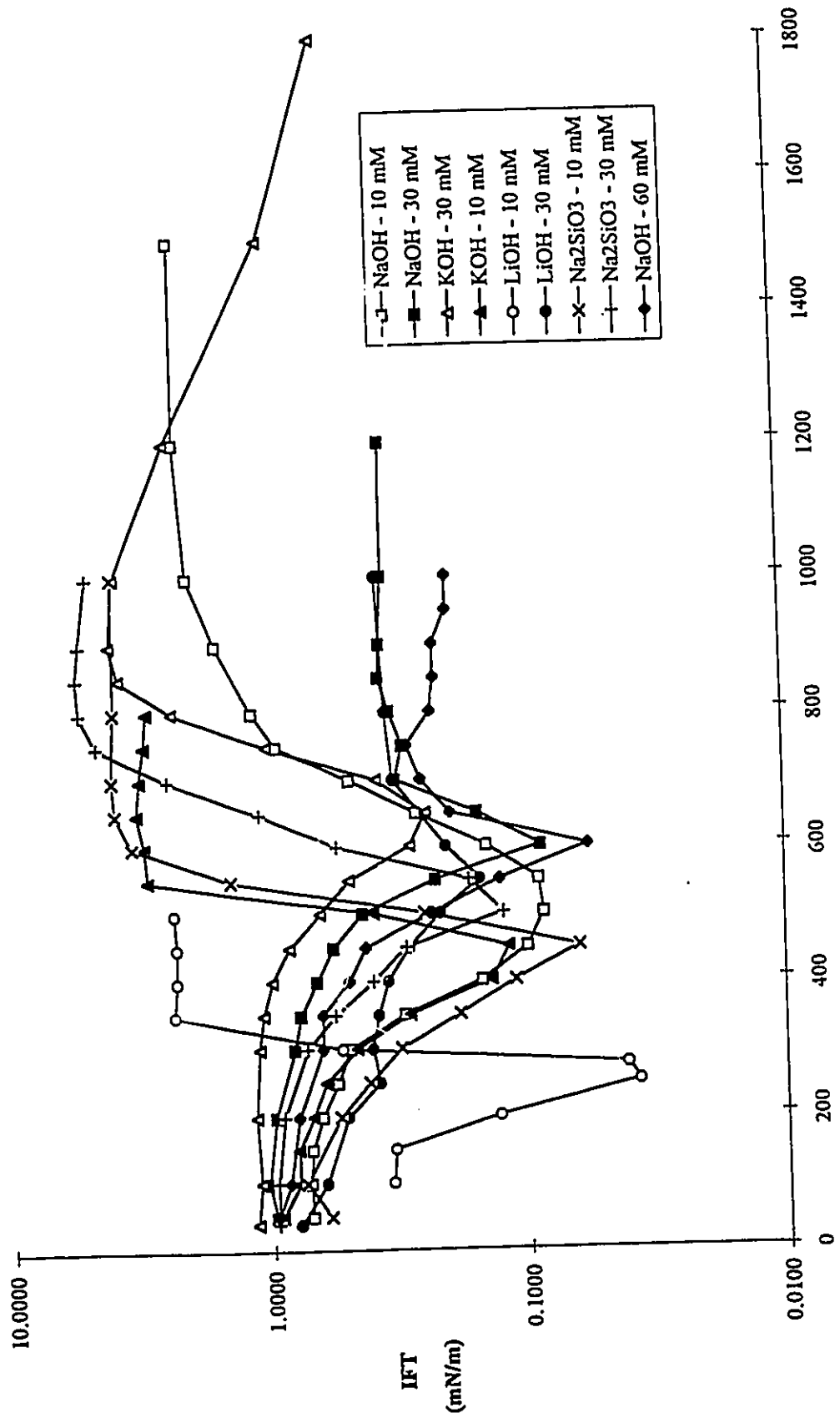


Figure 24: Transient IFT between 10, 30 and 60 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

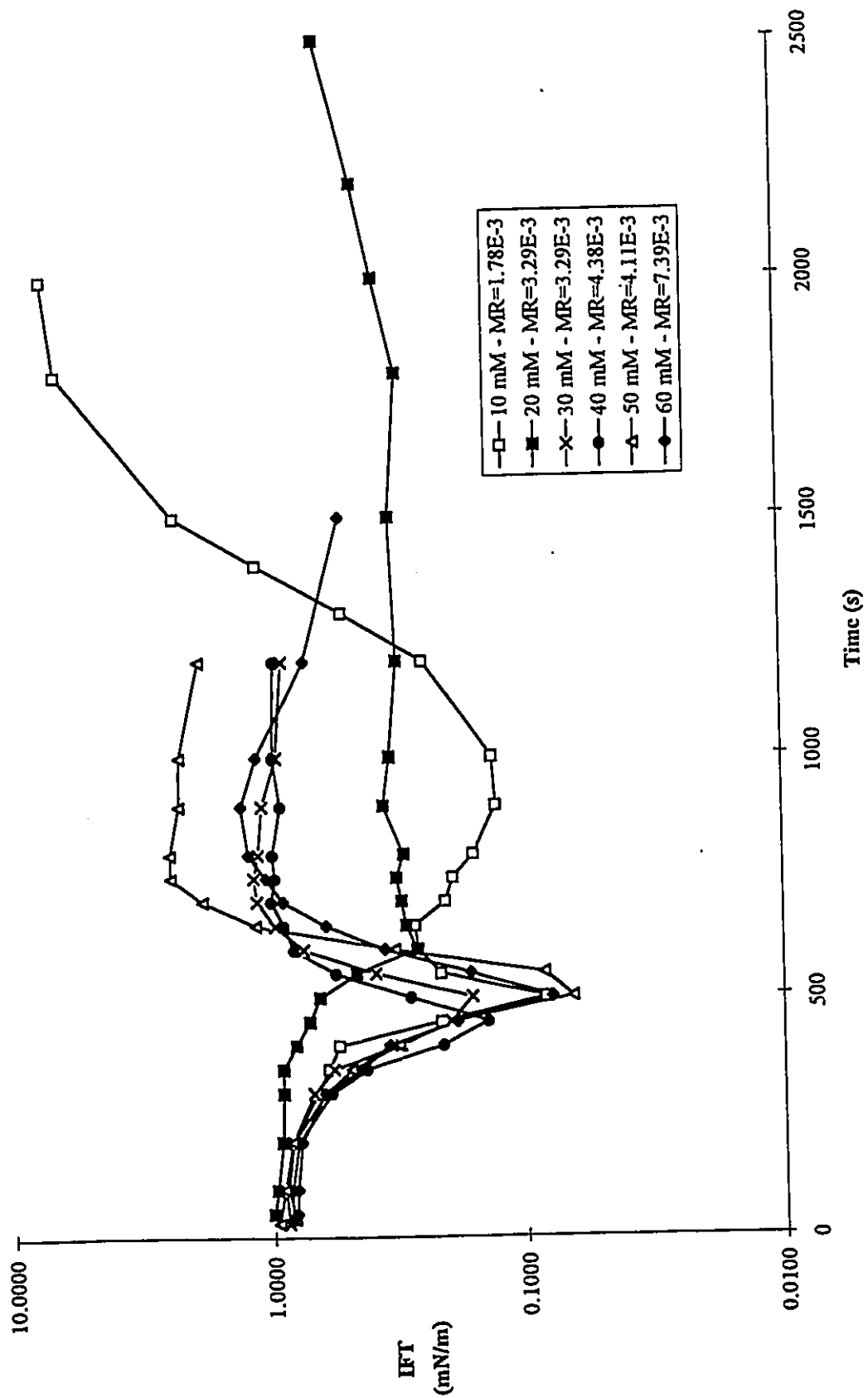


Figure 25: Transient IFT between 10 - 60 mM synthetic oil and 25 mM NaOH tested on the SDT

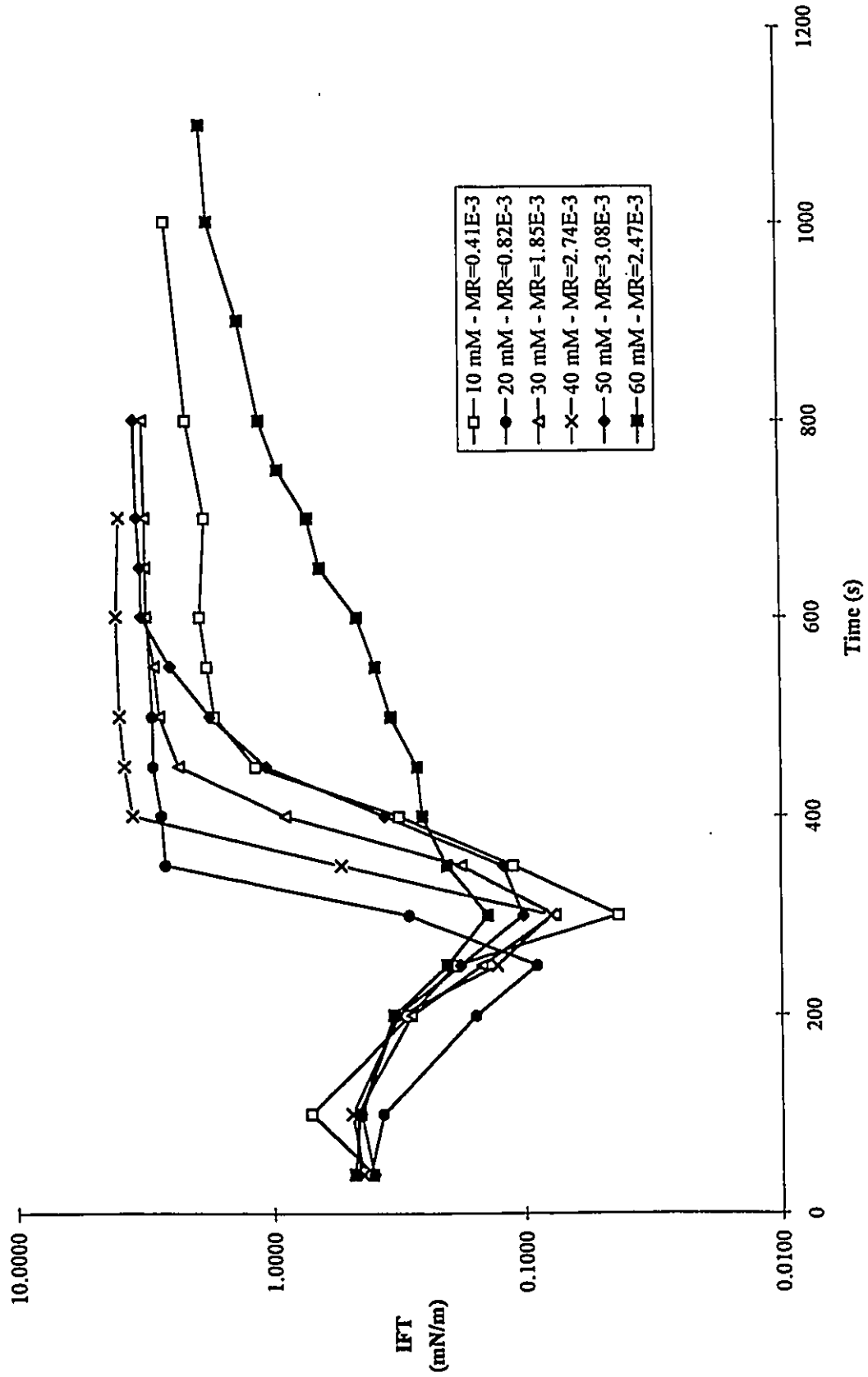


Figure 26: Transient IFT between 10 - 60 mM synthetic oil and 25 mM LiOH tested on the SDT

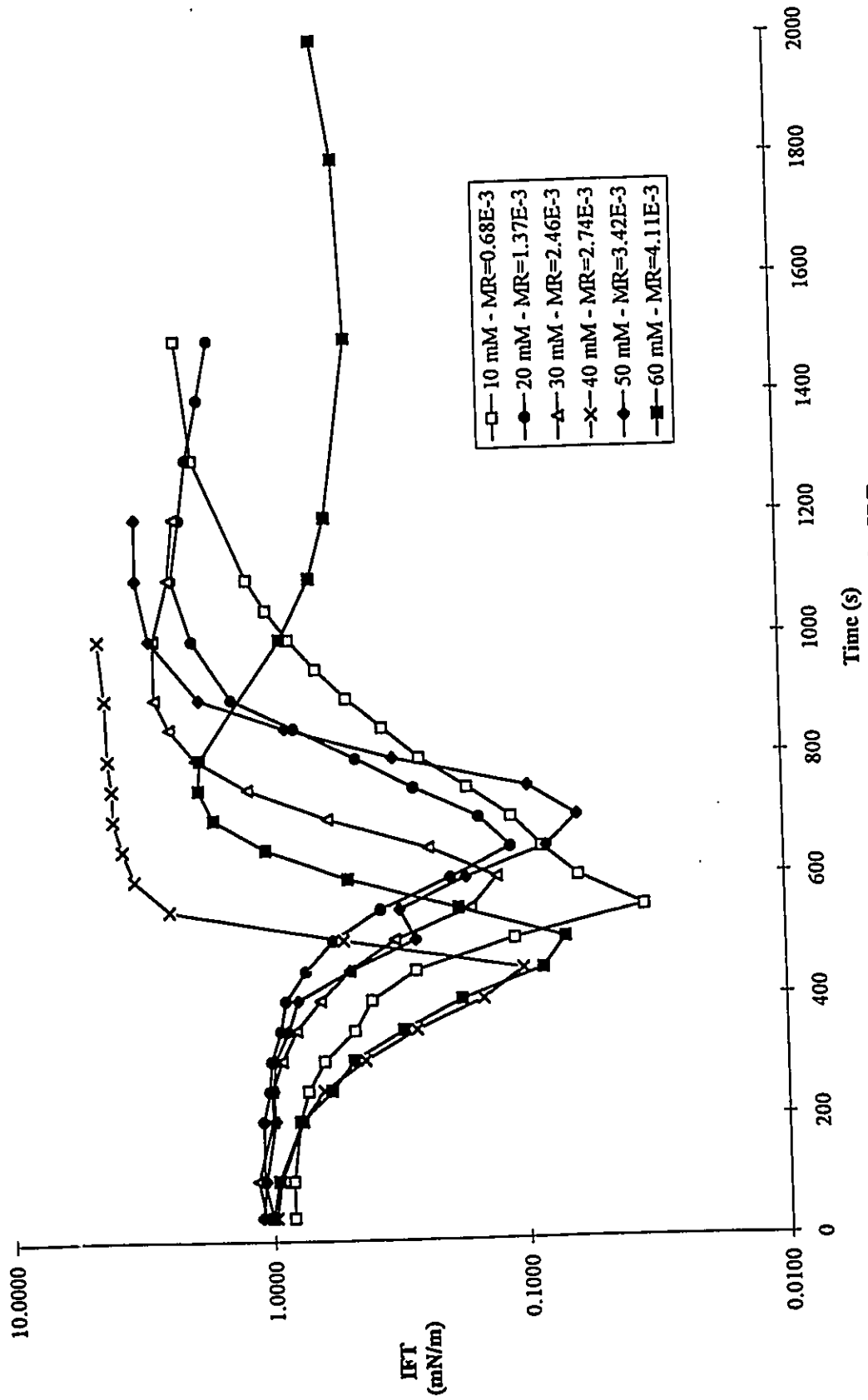


Figure 27: Transient IFT between 10 - 60 mM synthetic oil and 25 mM KOH tested on the SDT

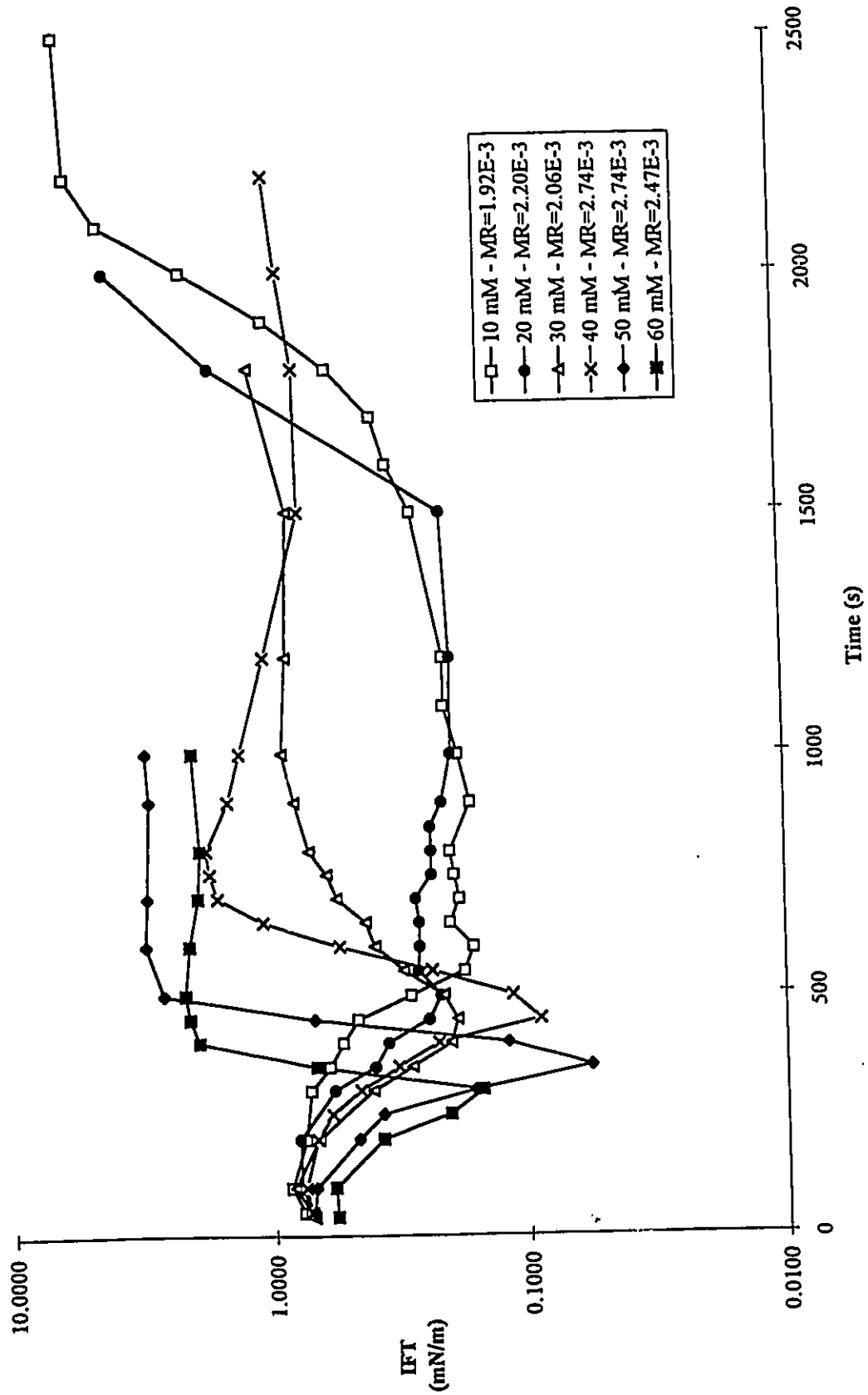


Figure 28: Transient IFT between 10 - 60 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT

be produced at the interface and there was more acid available to react when concentrations of acid were higher.

The trend generally shows that as the acid concentration in the oil increases, the IFT reaches the minimum more quickly and the subsequent increase in slope is faster afterwards with exceptions when the MR value was very low such for the 10 mM curve in Figures 25, 26 and 27. Again it is likely that the different trends for the different alkalis correspond to an optimum ratio of acid to alkali which was dependent on the type of alkali. Lithium, seen in Figure 26, in particular, showed a trend with lower IFT values for the lower acid concentrations, compared to the higher concentrations.

The greatest difficulty in comparing the four alkaline solutions with the different acid concentrations was due to the dissimilar volumes of the oil droplets. The MR values, from the legends of the figures, reveal that although potassium had droplets of similar size for the comparison, the other three alkaline solutions had generally smaller droplets for the higher concentration of acidic oil. Stable droplets of larger size could not be obtained by the manual injection. Thus, the steeper slope of increase and quick rise may likely be due to the small droplet size.

#### **4.1.6 Crude oil tested on the SDT**

Figure 29 compares the transient IFT behaviour for 2.5 mM NaOH against crude oil and 10 mM synthetic oil. The general trend is the same for the crude oil and the synthetic oil, except that the crude oil exhibits much lower values of IFT (at least five times lower). The crude oil and hydroxide solutions were expected to yield lower IFT

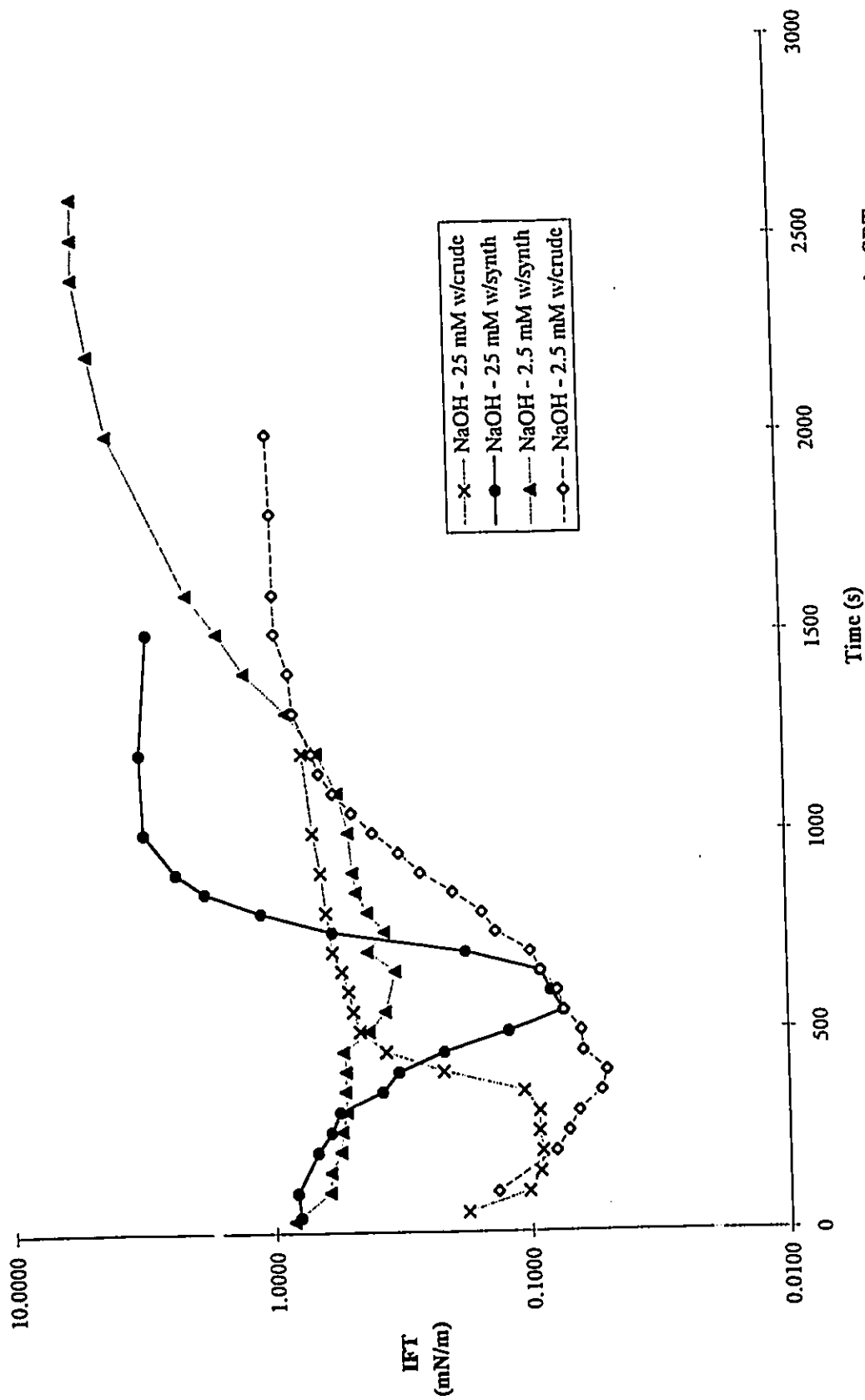


Figure 29: Transient IFT of Lloydminster crude oil and 10 mM synthetic oil and 2.5 mM NaOH tested on the SDT

because there were acidic components in the crude oil with an overall concentration about 60 times higher than in the synthetic oil. For the 25 mM alkali, the minimum was reached faster and maintained longer and the end IFT was lower than the synthetic oil although the minimum IFTs were about the same suggesting a slower diffusion away from the interface for the crude oil so the IFT lowering was maintained longer.

The minimum and steady state IFT were reached faster in the case of the crude oil. The minimum IFT appeared to be reached over 250 seconds faster for the 2.5 mM NaOH and it appears that a minimum was reached nearly 400 seconds faster in the case of the 25 mM NaOH. The minimum was reached faster for the crude oil due to the larger concentration of acidic components at the interface, whereas for the synthetic oil there may be a time lag for the acidic components to diffuse to the interface.

The rise appeared sharper for the 25 mM NaOH when compared with the 2.5 mM NaOH for both types of oil. The lower concentration, 2.5 mM NaOH solution, may have taken longer for the alkaline components to diffuse to the interface, react and then be depleted from the interface, which would explain the gradual decrease and increase in the IFT values. In contrast, the 25 mM NaOH had a large amount of alkaline components at the interface from the beginning due to its higher concentration, but the acidic components would quickly be depleted by the reaction, resulting in the observed sharp rise.

The droplet volume should not have affected the measured IFT values because the volume was well above the 3  $\mu\text{L}$  limit, observed by Khulbe et al. (1985). This larger volume resulted from the use of a larger syringe, used to prevent clogging, by the 20 times more viscous crude oil, as mentioned earlier.

Figure 30 shows the transient interfacial tension between diluted Lloydminster crude oil and the four 25 mM alkaline solutions. The trend shows that the initial IFT values appeared to be in the following decreasing order: KOH, LiOH, NaOH and  $\text{Na}_2\text{SiO}_3$ , with the order of the minimum IFT in decreasing order LiOH, NaOH, KOH and  $\text{Na}_2\text{SiO}_3$ . In Figure 30, it is again seen that the minimum IFT values are reached much quicker for the crude oil than for the synthetic oil and a lower IFT is maintained longer.

The values can also be compared to the values obtained by Khulbe et al. (1987). These workers obtained a similar trend with undiluted Lloydminster crude oil as was observed here, that is, in decreasing order: LiOH, NaOH,  $\text{Na}_2\text{SiO}_3$  and KOH, although their values were somewhat different. The sodium orthosilicate did not perform as well as in this study, which may be due to the dilution with toluene. The difference in values is not significant when the error bounds caused by the poor reproducibility of the SDT is considered.

#### 4.1.7 Crude oil tested on the DVT

Figure 31 shows the dynamic IFT between the diluted Lloydminster crude oil and 25 mM LiOH and NaOH. The values reveal that the crude oil has lower IFT as expected due to its greater amount of acidic components. Rosen (1989) determined that the efficiency of adsorption of the surfactant at the interface appears to increase steadily with an increase in the length of the hydrophobic group up to at least 20 carbon atoms, as well as in the presence of phenyl groups. This indicates that the larger number and

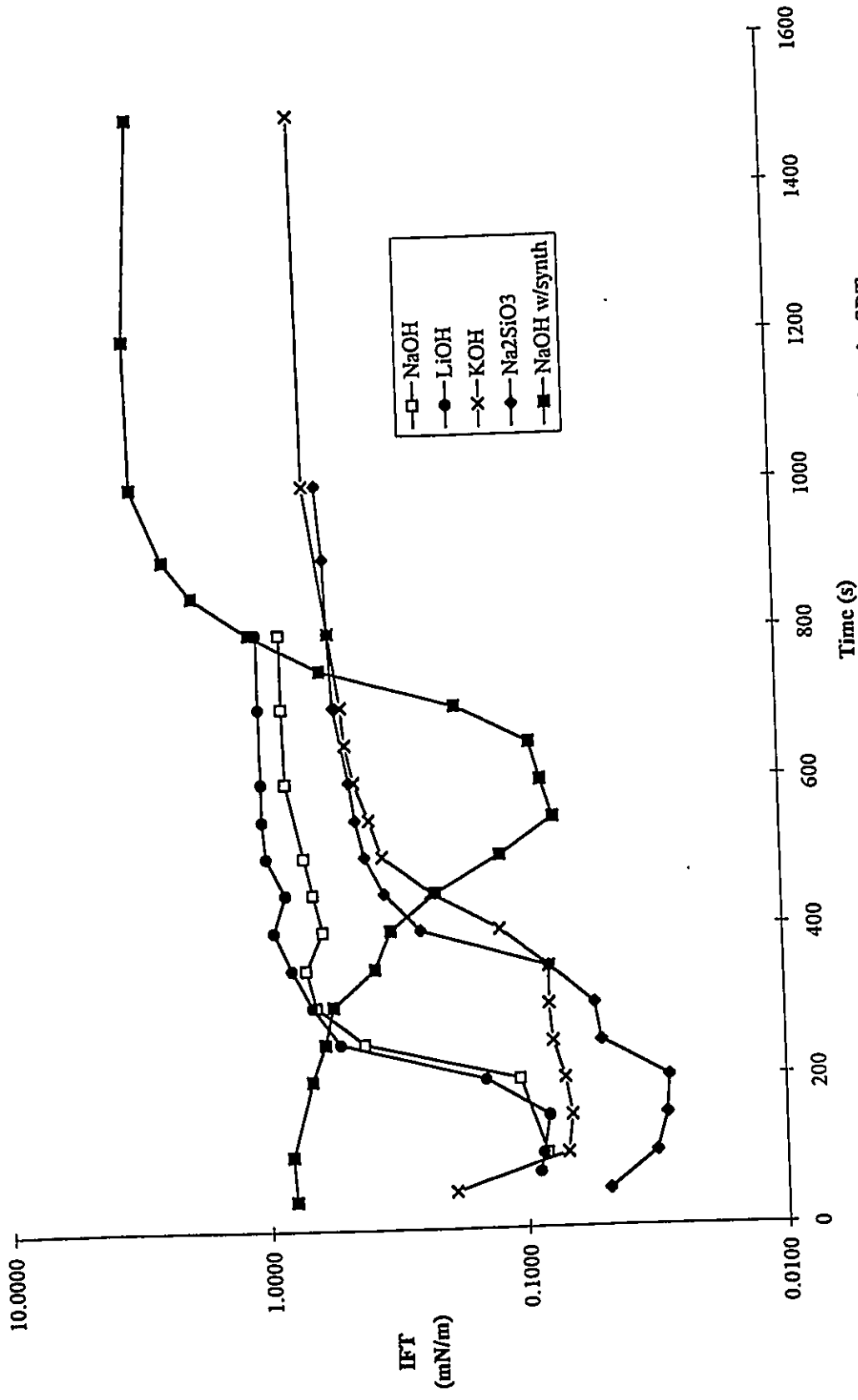


Figure 30: Transient IFT of Lloydminster crude & 10 mM synthetic oil with 25 mM aqueous alkali tested on the SDT

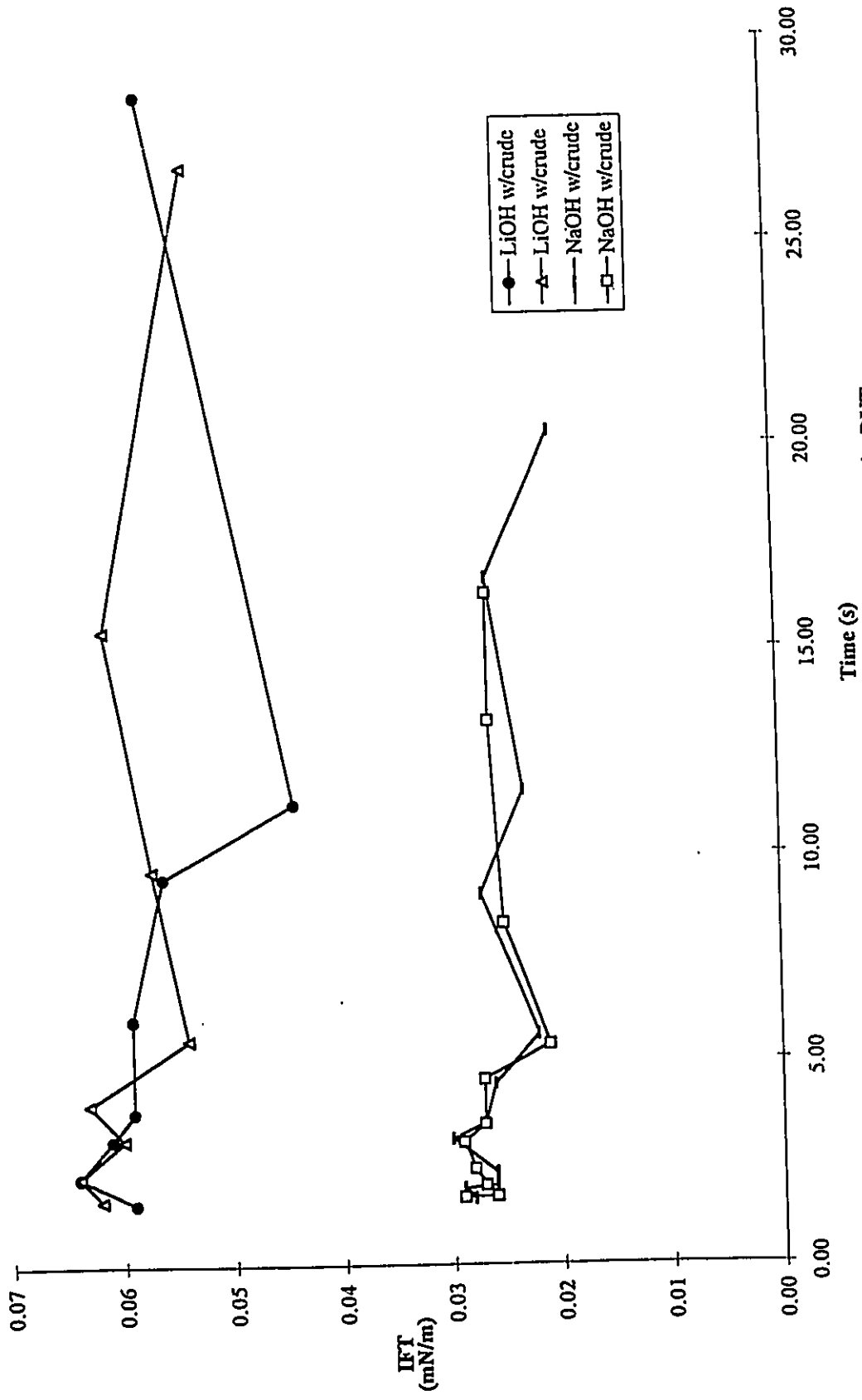


Figure 31: Dynamic IFT between Lloydminster crude oil and 25 mM LiOH and NaOH tested on the DVT

molecular weight of the acid components would cause a larger decrease in the IFT for the crude oil.

The NaOH solution generates lower IFT values than LiOH solution, which is in agreement with the SDT data obtained for the crude oil. The ultralow values obtained by the DVT for the 25 mM alkaline solution were somewhat reproducible but there was very little decrease of IFT with time, which again may be due to the swift reaction of acid with alkali at these high concentrations. The smaller times could not be accurately measured because at high flow rates the crude oil flowed continually without forming any definite droplets. The values for the 25 mM alkali are low, often below the limit of 0.2 mN/m, which may explain why the values of IFT were lower than those obtained by the SDT. However, the values were not too far off compared to the value obtained by the SDT, especially considering its limited reproducibility.

Figure 32 shows the dynamic IFT of the diluted Lloydminster crude oil and the synthetic oil against the 2.5 mM NaOH. The IFT curve starts higher and the minimum is reached later than with the synthetic oil. It was also observed that at higher flow rates (i.e. at shorter times) the drop forms a sphere plus a smaller appendage beneath the sphere as it detaches so the values may not be as reliable. At low flow rates (longer contact times) IFT values drop below 0.2 mN/m and the experimental error becomes larger. However, the values in this region appear surprisingly reproducible which may be due to the less viscous nature of the crude oil. Other solutions of lower viscosity would have to be tested to see if the lower limit of the instrument can be extended for less viscous solutions.

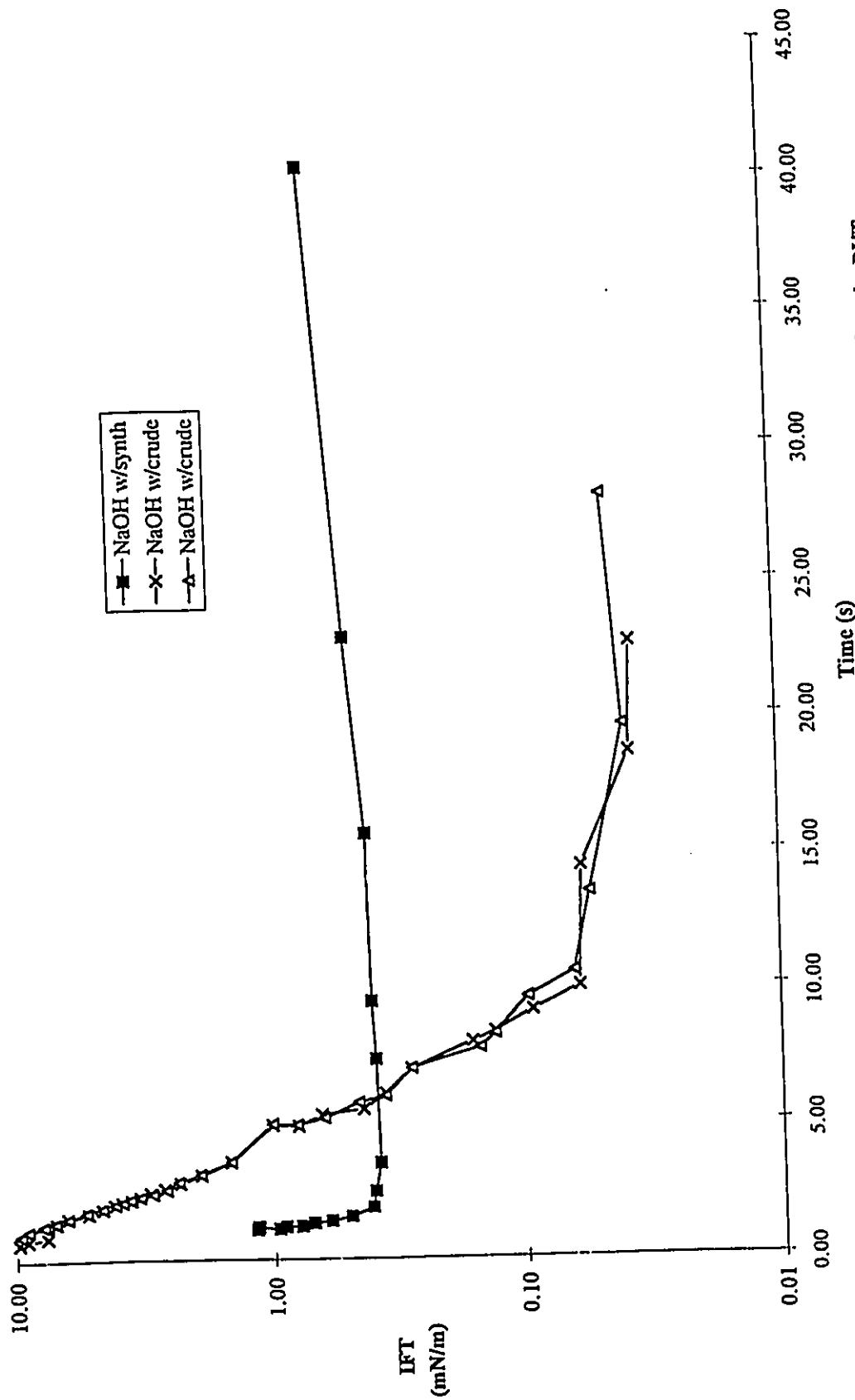


Figure 32: Dynamic IFT between Lloydminster crude oil and 10 mM synthetic oil against 2.5 mM NaOH tested on the DVT

## 4.2 Momentum Balance Applied to the DVT

The motion of the oil in the tube of the DVT was neglected in the IFT calculation performed by the DVT, as follows:

$$IFT = V_{drop} (\rho_{alk} - \rho_{oil}) g / (\pi d_{tube}) \quad (7)$$

where the volume of the drop can be calculated from  $\pi d_{drop}^3/6$ . This equation represents the balance of forces at the capillary tip, that is the buoyancy, gravity and the capillary forces as seen in Figure 7. The full force balance can be determined by applying the Unsteady State Macroscopic Momentum Balance, a vector equation, in the vertical x-direction to the fluid inside the oil droplet at an arbitrary time, t. The equation is as follows:

$$dM_{sys}/dt = M_{in} - M_{out} + \text{sum}(F_x) \quad (8)$$

where,

$M_{sys}$  = total x-momentum of system (oil droplet)

$M_{in}$  = rate at which x-momentum flows into the system (droplet) at the tube tip

$M_{out}$  = rate at which x-momentum flows out of the system (oil droplet)

$\text{sum}(F_x)$  = sum of all external forces acting on system (oil droplet) in the x-direction

The momentum flowing out of the system is zero as long as the droplet remains attached at any given time. The momentum entering is the mass flow rate times the mean velocity and can be derived to be equal to  $8 \rho_{oil} Q^2 / \pi d_{tube}^2$ , (see Appendix C). The IFT is then:

$$IFT = V_{drop} (\rho_{alk} - \rho_{oil}) g / (\pi d_{tube}) + 8 \rho_{oil} Q^2 / (\pi^2 d_{tube}^3) \quad (9)$$

Since  $M_{sys}$  remains fairly constant throughout the process,  $dM_{sys}/dt = 0$ .

The second term in Equation [9] has been neglected in the equation that the DVT uses to calculate the IFT. Thus, the value of this term needs to be calculated to see if it can reasonably be assumed to be negligible under the conditions used here and under what conditions it may become important. The DVT manual (1992) suggests that at flow rates above 2 mL/h, acceleration of low viscosity fluid begins to contribute more than 1% of the detachment force and the data then needs to be corrected. Calculations were performed as shown in the example provided in Appendix E. Results indicated that for values at 2 mL/h all of the IFT values for 25 mM aqueous alkali were accurate but at higher flow rates the correction factor should be applied, depending on the precision required. None of the flow rates used here had a deviation in the IFT value of over 1 % due to the kinetic energy. For 2.5 mM NaOH, flow rates of 50 mL/h and below had IFT values with less than 1 % deviation due to the kinetic energy. Therefore, each fluid tested here was not significantly affected by the kinetic energy at any of the flow rates for which measurements were taken.

## **5. COMPARISON OF THE SDT AND DVT INSTRUMENTS**

### **5.1 Trends of the Transient IFT**

The manufacturer stated that the DVT cannot accurately measure IFT values below 0.2 mN/m which makes it unable to reliably measure the transient IFT values between 25 mM alkali and acids, for the synthetic oil. Even for 2.5 mM NaOH and crude oil the minimum IFT becomes suspect as it drops so low. However, the crude oil values appeared to be reproducible for IFT values as low as 0.03 mN/m. This may be due to the high viscosity of the crude oil, over 400 mPa.s compared to about 20 mPa.s for the synthetic oil. The higher viscosity may enable the droplets to form and breakaway more cleanly than for the lower viscosity droplets. Further studies would have to be performed on other highly viscous liquids to validate this postulate. Also, the DVT controller should supply more than two decimal places of precision for the average IFT values, if values below 0.2 mN/m are to be usable, otherwise the relative standard deviation becomes too large.

In contrast, no difficulty is encountered when the SDT is employed for measuring the transient IFT. However, the SDT trends are less reliable since greater variability was observed when the experiment was repeated. In addition, it is not possible to obtain transient IFT values within the first 40 seconds with the SDT and it is very difficult to obtain droplets of reproducible volumes for the SDT measurements.

The DVT can only give one value of the IFT right after the formation of the interface, and cannot reflect the changes nor deformations of the droplet with time, once it

was formed. The maximum age of the interface considered here was less than 1.5 minutes, and was usually less than 1 minute up to the time at which the droplet broke away from the tip. The DVT can give measurements for longer interface age if lower flow rates are used. For the SDT, the maximum time measured was about 50 minutes although the instrument can continue to measure for an indefinite amount of time (for any one experiment).

The minimum IFT obtained appears to be of the same order for both the DVT and the SDT: for example, crude oil gives a minimum of 0.05 mN/m for both, although the DVT is in an unreliable range. The trends of the curves are different due to the different significance of "time" in the two types of measurements. The maximum IFT is in the first few seconds when measured by the DVT (about 10 mN/m) whereas the SDT can only measure the IFT after about 40 seconds. Thus, the IFT may already have dropped from its maximum value. The DVT does not show an increase in IFT afterwards because the oil is the limiting reagent in the reaction, and since it is continually being added, the surfactant is not depleted from the interface. This difference is due to the age of the interface not being identical between the two instruments and making a direct comparison impossible. Table 4 compares the minimum IFT values from the SDT and the DVT for both the synthetic and crude oils.

Table 4 shows that the minimum values are the same for both instruments when measuring lower concentrations of oil and alkaline solutions. At higher concentrations, the IFT drops too low for the DVT to precisely measure the values. The similarity in the minimum values and the general decreasing trend of the IFT as a function of time when

measured by the two instruments suggests that, even though the methods of measurements are completely different, the IFT measured is similar both in the absolute value and the trends observed.

Table 4: Comparison of the minimum IFT values of oil/aqueous solutions tested on the SDT and DVT.

	IFT (SDT) (mN/m)	IFT (DVT) (mN/m)
NaOH & synthetic oil		
2.5 mM NaOH	0.30	0.30
25 mM NaOH	0.03	0.30
NaOH & crude oil		
2.5 mM NaOH	0.05	0.05
25 mM NaOH	0.09	0.03

## 6. MODELING

### 6.1 Modeling of Transient IFT via Linear Regression

An attempt was made to find a model that would explain the trend of the transient IFT obtained by the SDT. Only the minimum IFT was modeled. The known dependent variables for IFT were grouped into dimensionless numbers as follows:

$$\text{IFT} = f\{\rho_{\text{oil}}, \rho_{\text{alk}}, M_{\text{oil}}, M_{\text{alk}}, V_{\text{oil}}, V_{\text{alk}}, \omega, t\} \quad (10)$$

$$\text{IFT} = f\{\rho_{\text{oil}}/\rho_{\text{alk}} = \rho_R, M_{\text{oil}}/M_{\text{alk}} = M_R, V_{\text{oil}}/V_{\text{alk}} = V_R, \rho_{\text{alk}} \cdot R_{\text{tube}} \cdot \omega / \mu_{\text{alk}} = \text{Re}\} \quad (11)$$

$$\text{IFT} = (\rho_R)^a * (M_R)^b * (V_R)^c * (\text{Re})^d \quad (12)$$

However, since the rotational speed was kept very close to constant,  $\omega = 7.51 \pm 0.02$  ms/rev, there was no statistical difference between the runs and the Re term was dropped. Also, Babu et al. (1984) found that the effect of rotating speed on interfacial tension is insignificant for ultralow interfacial tension systems within the 5000-7500 RPM range. The viscosity ratio was excluded because it was found that the oil viscosity appeared to have very little effect on the absolute value of the IFT in the vicinity of the minimum IFT so it would not make a significant difference confirmed by Neale et al. (1987). The density ratio was included for synthetic oil because different concentrations were used and the density differences were found to be significant. The logarithm was taken on both sides to give a linear expression for the IFT dependence on each of the independent variables.

$$\log \text{IFT} = a \log(\rho_R) + b \log(M_R) + c \log(V_R) \quad (13)$$

The measured data were included for each of the four alkalis and for all of the data together. The data set included values for 10-60 mM and multiples of 10 mM linoleic acid. Two trials were included for NaOH and Na<sub>2</sub>SiO<sub>3</sub>, 10-60 mM, while only one trial was included for LiOH and KOH. The multiple trial values could not be included because the volume was not known. The data set was entered into a linear regression program in a statistical package, provided by SAS (SAS<sup>R</sup> User's Guide, 1985). Appendix D contains the computer program, an example of the output and a copy of the complete data set.

Table 5, below contains the linear regression results from SAS.

Table 5: Values of R-squared and the constants obtained from linear regression

Trial	R <sup>2</sup>	Intercept	Error (+/-)	Volume ratio	Error (+/-)	Molarity ratio	Error (+/-)	Density ratio	Error (+/-)
All	0.06	-0.6	0.4	0.2	0.2	0.2	0.1		
All w/D	0.31	12	3	0.01	0.1	-0.9	0.3	182	40
NaOH	0.54	14	4	0.01	0.2	-1.2	0.3	210	56
NaSiO	0.34	9.5	5	-0.3	0.3	-0.7	0.6	159	80
KOH	0.84	12	4	0.9	0.2	-0.6	0.4	145	52
LiOH	0.77	6.6	5	0.7	0.2	0.02	0.4	80	66

As can be seen in Table 5, the R<sup>2</sup> term was far below the value of one which represents a good representation of the linear model to correspond to the experimental results. Thus, there was not an acceptable linear model as described by the previous equations for any of the four alkalis. It is therefore concluded that other unknown factors must be important in determining the minimum IFT value.

## 6.2 Modeling Difficulties and Considerations

Since the value of  $R^2$  was unacceptably low (i.e. well below 1.0), it is reasonable to assume that there are other factors which should be included in the model. Thus, the model proposed here is not viable. Perhaps the time at which the minimum was reached, and the length of time it was maintained, need to be included in the model. Unfortunately, these terms are difficult to accurately determine since IFT values were only measured at 50 second intervals, due to the time required for each measurement. This makes it mathematically difficult to model the IFT as a function of time. A detailed quantitative analysis of the effect of various variables on the IFT evaluation could be useful.

The  $R^2$  term was particularly low for NaOH and  $\text{Na}_2\text{SiO}_3$ , which were the alkalis which contained multiple trials. The difficulty in obtaining reproducible minimum IFT values becomes important. Perhaps if droplets of larger volumes, or else identical volumes, could be injected then the model may be more accurate. Also, the viscosities of all of the solutions might be measured and included in the model in the event that they do affect the minimum value. Drifting or uneven elongation of the droplet could cause measurement errors, which might be detected by increasing the number of experiments performed.

## 7. CONCLUSIONS

1. Although the DVT and SDT use different methods to measure the IFT, similar results were obtained.
2. The DVT measured the dynamic IFT whereas the SDT measured the transient IFT after the instrument was loaded.
3. The DVT results were more reproducible with statistical error values provided, as an average of several droplets which makes it better for measuring higher IFT values.
4. The DVT was able to measure IFT values below the lower limit of 0.2 mN/m for the crude oil but for higher viscosities it was not reproducible below this value. The SDT measured the entire range of IFT values required which makes it the better choice when measuring lower IFT values.
5. The general trend of decreasing IFT to a minimum was similar for both instruments. However, the SDT showed an increase in IFT thereafter whereas the DVT did not. This is concluded to be due to the continuous addition of the limiting reagent for surfactant formation in the latter method and the improved conditions for mass transfer.
4. The DVT and SDT detected similar minimum IFT values for 2.5 mM NaOH, however the values for 25 mM NaOH were different.
5. The crude oil had lower IFT values against alkaline solutions than the synthetic acidified oil as well as reaching the minimum IFT quicker.

## 8. RECOMMENDATIONS FOR FURTHER WORK

Further tests on the DVT and SDT should be performed for acidified oils and alkaline solutions with minimum IFT values well above 0.2 mN/m for precise comparison of the DVT and SDT responses. Further experiments with liquids of low viscosity and concentrations should also be performed to confirm that liquids of lower viscosity can be tested on the DVT to yield accurate apparent IFT values.

A method to inject a specific volume of light phase into the capillary containing the denser phase should be developed to improve the precision of the IFTs measured by the SDT. In addition, higher concentrations of acidified oil need to be stabilized so that the injected droplets do not break into smaller droplets once rotation is underway. Uneven elongation may also be prevented if the droplets could be injected in the same position along the capillary every time, further away from the closed end. If the previous recommendations could be achieved then the poor reproducibility of the SDT may be improved. However, the possibility exists that the system itself is not reproducible due to unknown factors which could be investigated if the other possibilities are eliminated.

Modeling of the minimum IFT obtained could be performed if either the reproducibility of the results could be improved or if the unknown factors could be determined. Modeling based on results obtained by the DVT could also be performed since, due to the good reproducibility of this instrument, valid results may be obtained.

## 9. REFERENCES

- Babu, D. R., V. Hornof and G. Neale, "Effects of Temperature and Time on Interfacial Tension Behavior Between Heavy Oils and Alkaline Solutions", *Can. J. Chem. Eng.* **62**, 156-159 (1984).
- Babu, D. R., V. Hornof and G. Neale, "Evaluation of Aqueous Chemical Systems for Heavy Oil Recovery Processes", *Fuel* **65**, 4-8 (1986).
- Capelle, A., "Measurement of Low Interfacial Tension Between Crude Oil and Formation Water with Dissolved Surfactants by the Spinning Drop Technique: Fact or Fiction?" in "Surface Phenomena in Enhanced Oil Recovery", D. O. Shah (ed.), Plenum Press, New York, 229-236 (1981).
- Cayias, J. L., R. S. Schechter and W. H. Wade, "The Measurement of Low Interfacial Tension *via* the Spinning Drop Technique", *ACS Symposium Series* (8), 234-247 (1975).
- Chiwetelu, C. I., V. Hornof and G. H. Neale, "The Measurement of Dynamic Interfacial Tension by Photo-micropendography", *J. Colloid Interface Sci.* **125** (2), 586-601 (1988).
- Chiwetelu, C. I., V. Hornof and G. H. Neale, "Mechanisms for the Interfacial Reaction Between Acidic Oils and Alkaline Reagents", *Chem. Eng. Sci.* **45** (3), 627-638 (1990a).

- Chiwetelu, C. I., V. Hornof and G. Neale, "A Dynamic Model for the Interaction of Caustic Reagents with Acidic Oils", *AIChE* 36 (2), 233-241 (1990b).
- Chiwetelu, C. I., G. H. Neale and V. Hornof, "Interfacial Activity of Linoleic Acid/Caustic Systems", *J. Surface Sci. Technol.* 6 (4), 305-315 (1990c).
- Chiwetelu, C. I., G. H. Neale, H. Hornof and A. E. George, "Effects of Temperature and Alkali Concentration on the Dynamic Interfacial Tension Between Heavy Oil and Alkaline Solutions", *In Situ*, 16 (3), 251-268 (1992).
- Chiwetelu, C. I., G. H. Neale, V. Hornof and A. E. George, "Recovery of a Saskatchewan Heavy Oil Using Alkaline Solutions", *J. Can. Petrol. Technol.* 33 (4), 37-42 (1994).
- Chouinard, S. "Effects of the Orientation of the Phases and the Aqueous Phase Viscosity on Intefacial Tension as Measured by the Spinning Drop Tensiometer", CO-OP Work Term Report, Department of Chemical Engineering, University of Ottawa, 38 pp. (1992).
- Currie, P. K. and J. Van Nieuwkoop, "Buoyancy Effects in the Spinning-Drop Interfacial Tensiometer", *J. Colloid Interface Sci.* 87 (2), 301-316 (1982).
- Donaldson, E. C., G. V. Chilingarian and T. F. Yen (eds), "Enhanced Oil Recovery, I: fundamentals and analyses", Elsevier Science Publishers B.V., Amsterdam (1985).
- Franses, E. I., J. E. Pulg, Y. Talmon, W. G. Miller, L. E. Scriven and H. T. Davis, "Roles of Liquid Crystals and Micelles in Lowering Interfacial Tension", *J. Phys. Chem.* 84, 1547-1556 (1980).

- Hawkins, B., K. Taylor and H. Nasr-El-Din, "Mechanisms of Surfactant and Polymer Enhanced Alkaline Flooding: Application to David Lloydminster and Wainwright Sparky Fields", Paper presented at CIM/AOSTRA Technical Conference, Banff, AB, April 21-24 (1991).
- Hool, K. and B. Schuchardt, "A New Instrument for the Measurement of Liquid-Liquid Interfacial Tension and the Dynamics of Interfacial Tension Reduction", *Meas. Sci. Technol.* 3 (5), 451-457 (1992).
- Hornof, V., G. H. Neale and A. Yu, "Effect of Flooding Sequence on the Displacement of Acidic Oil by Alkaline Solutions", *J. Petrol. Sci. Eng.* 10, 291-297 (1994).
- Jho, C. and R. Burke, "Drop Weight Technique for the Measurement of Dynamic Surface Tension", *J. Colloid Interface Sci.* 95 (1), 61-71 (1983).
- Joos, P. and E. Rillaerts, "Theory on the Determination of the Dynamic Surface Tension with the Drop Volume and Maximum Bubble Pressure Methods", *J. Colloid Interface Sci.* 79 (1), 96-100 (1981).
- Khulbe, K. C., V. Hornof and G. Neale, "Interfacial Activity of Heavy Oil and its Maltene Constituents Against Caustic Solutions", *AOSTRA J. Res.* 2, 95-101 (1985).
- Khulbe, K. C., G. Neale and V. Hornof, "Effects of Cations on the Interaction of Alkaline Agents with Heavy Oil", *J. Colloid Interface Sci.* 117 (2), 578-581 (1987).
- Lake, L. W. "Enhanced Oil Recovery", Prentice-Hall, Inc., New Jersey (1989).
- Mehdizadeh, A. and L. L. Handy, "Further Investigation of High-Temperature Alkaline Floods", *SPE Res. Eng.* 5, 171-177 (1989).

- Miller, C. A. and P. Neogi, "Interfacial Phenomena: Equilibrium and Dynamic Effects", Marcel Dekker, Inc., New York (1985).
- Neale, G. H., K. C. Khulbe and V. Hornof, "Effects of Oil Phase Viscosity on Interfacial Tension Behaviour of Oil/Alkaline Systems as Measured by the Spinning Drop Tensiometer", *Can. J. Chem. Eng.* 65, 700-703 (1987).
- Neale, G. H. and Z. M. Ding, "Effects of Oil Acidity and Clay Particles on the Interfacial Tension Behaviour of Crude Oil Systems", *J. Surface Sci. Technol.* 8 (3), 271-281 (1992).
- Pierson, F. W. and S. Whitaker, "Studies of the Drop-Weight Method For Surfactant Solutions I", *J. Colloid Interface Sci.* 54 (2), 203-218 (1976).
- Princen, H. M., I. Y. Z. Zia and S. G. Mason, "Measurement of Interfacial Tension from the Shape of a Rotating Drop", *J. Colloid Interface Sci.* 23, 99-107 (1967).
- Ramakrishnan, T. S. and D. T. Wasan, "Effect of Adsorption on the Optimal Displacement of Acidic Crude Oil by Alkali", *AIChE J.* 36 (5), 725-737 (1990).
- Rosen, M. J. "Surfactants and Interfacial Phenomena", 2nd edition, John Wiley and Sons, Inc., New York (1989).
- Rudin, J. and D. T. Wasan, "Surfactant-Enhanced Alkaline Flooding at Intermediate pH", *AIChE J.* 87 (280), 89-97 (1990).
- Rudin, J. and D. T. Wasan, "Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: Effect of Added Surfactant", *Ind. Eng. Chem. Res.* 31 (8), 1899-1906 (1992).
- SAS<sup>R</sup> User's Guide: Basics, Version 5 Edition, SAS Institute Inc., Cary, NC (1985).

- Sharma, M. M., L. K. Jang and T. F. Yen, "Transient Interfacial Tension Behavior of Crude-Oil/Caustic Interfaces", SPE Res. Eng. 5, 228-236 (1989).
- Touhami, Y., G. H. Neale and V. Hornof, "Effects of Water-Soluble Polymers and Aqueous-Phase Viscosity on the Interfacial Tension Behavior of Reacting Oil-Alkaline Systems", J. Appl. Polymer Sci. 53, 309-316 (1994).
- Tornberg, E., "The Application of the Drop Volume Technique to Measurements of the Adsorption of Proteins at Interfaces", J. Colloid Interface Sci. 64 (3), 391-402 (1978).
- Vonnegut, B., "Rotating Bubble Method for the Determination of Surface and Interfacial Tensions", Rev. Sci. Instrum. 13, 6-9 (1942).

# APPENDICES

## APPENDIX A

Figures A1 to A3 contain the IFT as a function of time for the three other concentrations of synthetic oil tested; 20, 40 and 50 mM, respectively. Tables A1 to A78 contain the measurement data and the calculated IFT values for all of the tests performed on the SDT. The following list reveals the tables which contain the required values for each of the figures:

Tables A1-7	Figures 10 & 24	Tables A8-14	Figures 11 & 24
Tables A15-21	Figures 12 & 24	Tables A22-28	Figures 13 & 24
Tables A29-31	Figures 14, 19, 20, 29 & 30	Tables A32-34	Figures 15 & 20
Tables A35-36	Figures 19 & 29	Tables A37-38	Figure 20
Table A39	Figure 21	Table A40	Figure 22
Tables A41-45	Figure 24	Tables A46-51	Figure 25
Tables A52-57	Figures 21, 22, 26, & A1-3	Tables A58-63	Figures 21, 22, 27 & A1-3
Tables A64-69	Figures 21, 22, 28 & A1-3	Tables A70-71	Figure 29
Tables A71-75	Figure 30	Table A76	Figure A1
Table A77	Figure A2	Table A78	Figure A2

The IFT value was calculated as follows:

$$\gamma = (\rho_{aq} - \rho_{oil}) \omega^2 r_m^3 / 4$$

where  $r_m$  is the droplet radius calculated by the width of the drop divided by two.

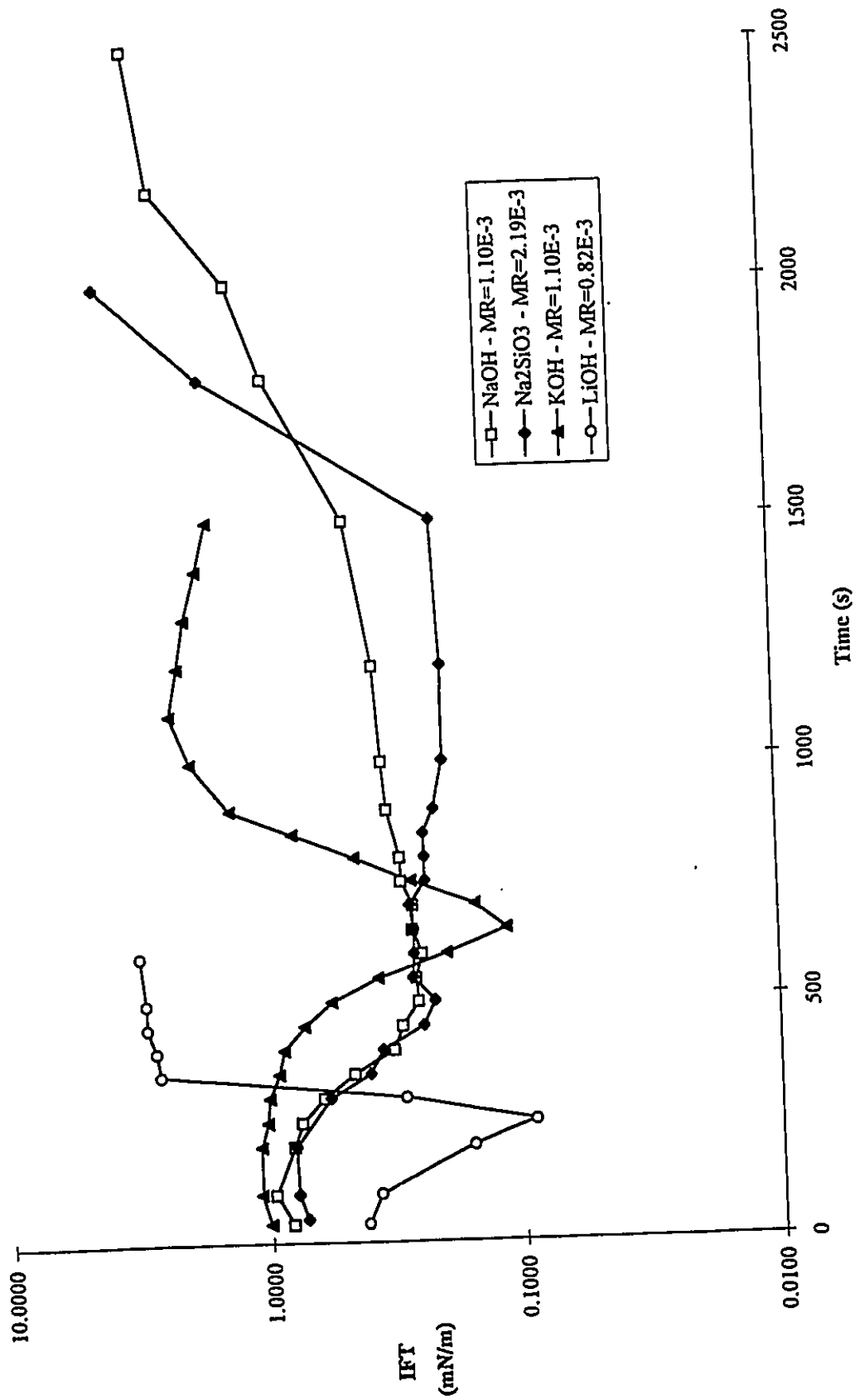


Figure A1: Transient IFT between 20 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

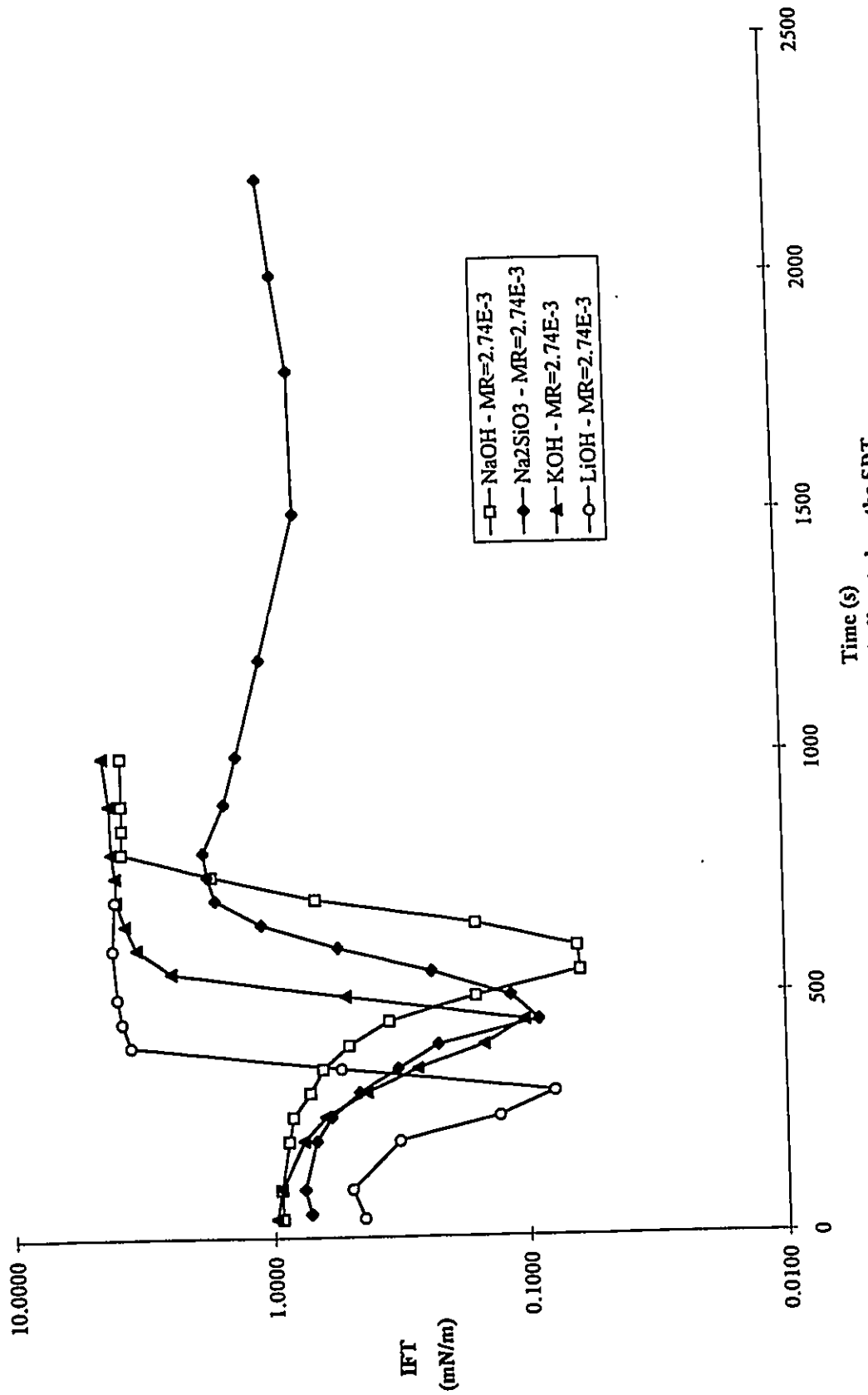


Figure A2: Transient IFT between 40 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

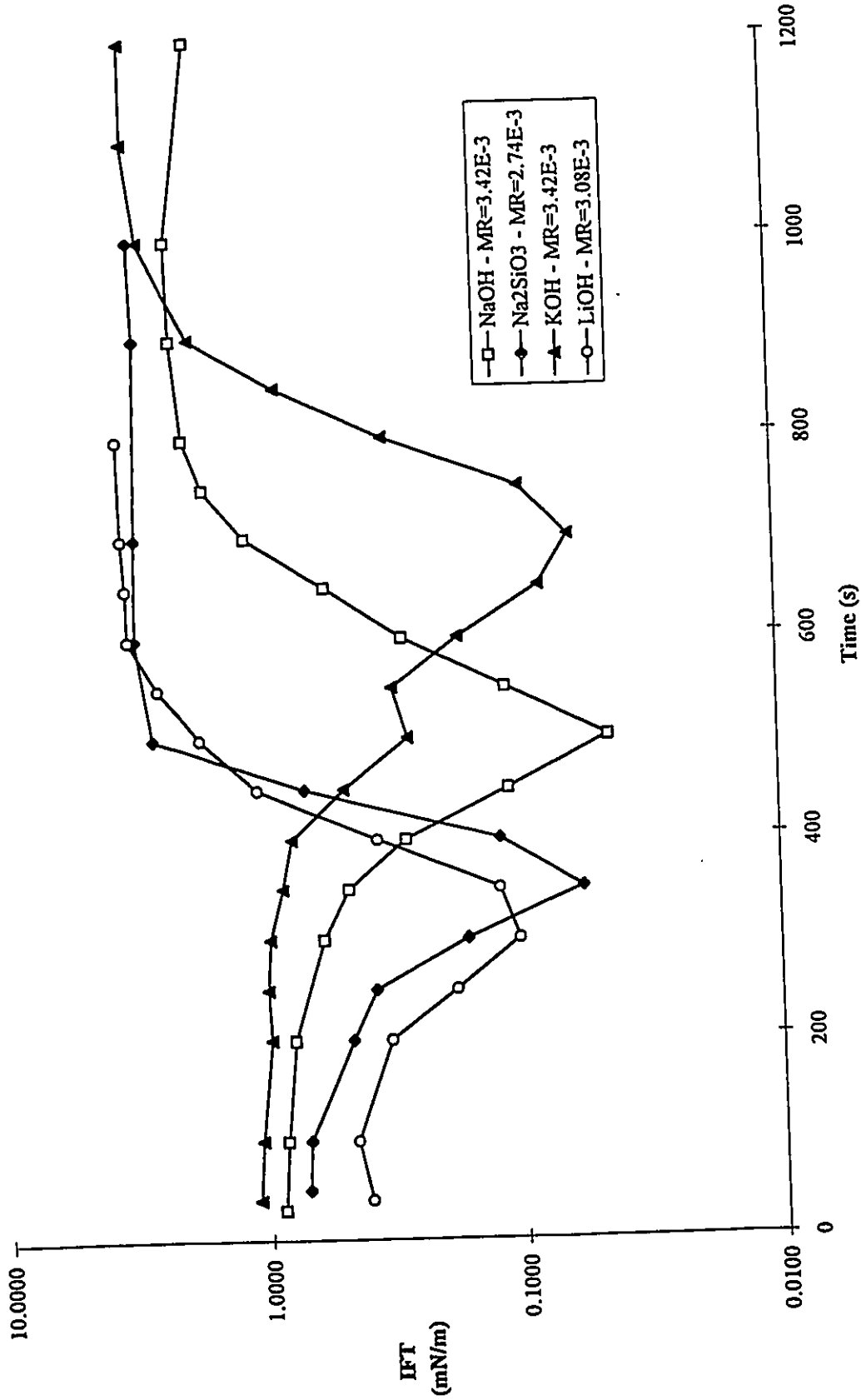


Figure A3: Transient IFT between 50 mM synthetic oil and 25 mM aqueous alkali tested on the SDT

Table A1 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 1

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	29.45	24.45	0.0500	0.4238
200	29.05	24.74	0.0431	0.2714
300	28.49	25.20	0.0329	0.1207
400	27.70	26.29	0.0141	0.0095
500	27.84	25.94	0.0190	0.0233
600	28.36	25.44	0.0292	0.0844
700	29.32	24.46	0.0486	0.3892
800	30.10	23.44	0.0666	1.0015
900	30.47	23.29	0.0718	1.2548
1000	30.45	23.08	0.0737	1.3571
1100	30.54	23.10	0.0744	1.3961
1200	30.55	23.11	0.0744	1.3961

Table A2 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 2

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	30.01	24.57	0.0544	0.5458
150	30.18	24.76	0.0542	0.5398
200	29.77	24.70	0.0507	0.4418
250	29.60	24.99	0.0461	0.3321
300	28.60	25.66	0.0294	0.0861
350	28.27	26.23	0.0204	0.0288
400	27.86	26.44	0.0142	0.0097
450	28.05	26.17	0.0188	0.0225
500	29.10	25.54	0.0356	0.1530
550	29.52	24.68	0.0484	0.3844
600	30.22	24.24	0.0598	0.7250
650	30.47	23.93	0.0654	0.9483
700	30.74	23.75	0.0699	1.1578
800	30.81	23.56	0.0725	1.2919
900	31.02	23.33	0.0769	1.5417
1000	31.08	23.44	0.0764	1.5118
1100	30.94	23.40	0.0754	1.4532
1200	30.97	23.37	0.0760	1.4882

Table A3 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 3

Time, s	Top	Bottom	Width, cm	IFT, mN/m
150	29.48	24.56	0.0492	0.4037
200	29.53	24.59	0.0494	0.4087
250	29.27	24.76	0.0451	0.3110
300	28.68	25.50	0.0318	0.1090
350	28.16	26.11	0.0205	0.0292
400	28.32	25.74	0.0258	0.0582
450	29.36	24.94	0.0442	0.2927
500	30.08	24.01	0.0607	0.7582
550	30.80	23.52	0.0728	1.3080
600	30.83	23.16	0.0767	1.5297
650	30.92	23.07	0.0785	1.6399
700	30.92	23.01	0.0791	1.6778
800	30.94	23.01	0.0793	1.6906
1000	31.16	23.11	0.0805	1.7685

Table A4 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 4

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.99	24.06	0.0593	0.7069
100	30.02	24.06	0.0596	0.7177
150	30.07	24.15	0.0592	0.7034
200	29.95	24.22	0.0573	0.6378
250	29.86	24.40	0.0546	0.5518
300	29.64	24.39	0.0525	0.4906
350	29.38	24.94	0.0444	0.2967
400	28.80	25.28	0.0352	0.1479
450	28.70	25.63	0.0307	0.0981
500	28.49	25.57	0.0292	0.0844
550	28.55	25.59	0.0296	0.0879
600	28.81	25.36	0.0345	0.1392
650	29.16	24.90	0.0426	0.2621
700	29.68	24.49	0.0519	0.4739
750	30.27	23.83	0.0644	0.9055
800	30.66	23.36	0.0691	1.1185
900	31.14	22.96	0.0770	1.5477
1000	31.24	22.79	0.0835	1.9737
1200	31.25	22.63	0.0861	2.1638
1500	31.42	22.62	0.0863	2.1789

Table A5 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 5

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.72	24.51	0.0521	0.4794
100	29.72	24.47	0.0525	0.4906
150	29.75	24.60	0.0515	0.4631
200	29.59	24.71	0.0488	0.3940
250	29.32	25.21	0.0411	0.2354
300	28.70	25.72	0.0298	0.0897
350	28.83	25.58	0.0325	0.1164
400	29.74	24.97	0.0477	0.3679
450	30.63	23.76	0.0687	1.0992
500	31.23	23.34	0.0789	1.6651
550	31.27	23.13	0.0814	1.8285
600	31.38	23.15	0.0823	1.8898
700	31.37	23.13	0.0824	1.8967
800	31.35	23.02	0.0833	1.9595

Table A6 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 6

Time, s	Top	Bottom	Width, cm	IFT, mN/m
75	29.92	24.49	0.0543	0.5428
100	29.77	24.51	0.0526	0.4934
150	29.71	24.69	0.0502	0.4289
200	29.37	24.94	0.0443	0.2947
250	28.96	25.56	0.0340	0.1332
300	28.45	26.03	0.0242	0.0480
350	28.45	26.04	0.0241	0.0475
400	28.97	25.67	0.0330	0.1218
450	29.34	24.98	0.0436	0.2810
500	29.88	24.66	0.0522	0.4822
550	30.08	24.20	0.0588	0.6892
600	30.59	23.98	0.0661	0.9791
650	30.74	23.59	0.0715	1.2392
700	30.94	23.52	0.0742	1.3849
800	30.99	23.42	0.0757	1.4706
900	31.19	23.41	0.0758	1.4765
1000	31.08	23.29	0.0790	1.6715

Table A7 : iFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT; Trial 7

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.74	24.55	0.0519	0.4739
100	30.00	24.32	0.0568	0.6212
150	29.93	24.15	0.0578	0.6546
200	29.76	24.48	0.0528	0.4990
250	29.72	24.64	0.0508	0.4444
300	29.28	25.00	0.0428	0.2658
350	28.77	25.46	0.0331	0.1229
400	28.50	25.74	0.0276	0.0713
450	28.46	25.81	0.0265	0.0631
500	28.55	25.56	0.0299	0.0906
550	28.83	25.39	0.0344	0.1380
600	29.42	24.39	0.0503	0.4314
650	30.77	23.55	0.0722	1.2759
700	30.84	23.45	0.0739	1.3682
800	30.80	23.55	0.0725	1.2919
900	30.70	23.50	0.0730	1.3188
1000	30.72	23.55	0.0715	1.2392

Table A8 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 1

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.52	24.59	0.0493	0.4062
100	29.57	24.64	0.0493	0.4062
150	29.32	24.77	0.0455	0.3193
200	28.82	25.36	0.0346	0.1404
250	27.90	26.00	0.0190	0.0233
300	30.75	23.45	0.0730	1.3188
350	30.76	23.41	0.0735	1.3461
400	30.85	23.35	0.0750	1.4302

Table A9: IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 2

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.80	24.40	0.0540	0.5338
100	29.75	24.42	0.0533	0.5133
150	29.64	24.80	0.0484	0.3844
200	29.60	24.94	0.0466	0.3431
250	28.54	25.86	0.0268	0.0653
275	28.10	25.77	0.0233	0.0429
300	28.26	25.98	0.0228	0.0402
325	28.75	25.60	0.0315	0.1060
350	29.52	24.64	0.0488	0.3940
400	30.94	24.07	0.0687	1.0992
450	31.07	24.04	0.0703	1.1778
500	31.17	24.80	0.0637	0.8763
550	31.15	24.94	0.0621	0.8119
600	31.14	25.86	0.0528	0.4990

Table A10 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 3

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	29.64	24.98	0.0466	0.3431
150	29.27	25.16	0.0411	0.2354
200	29.16	25.55	0.0361	0.1595
225	28.59	25.76	0.0283	0.0768
250	28.55	25.89	0.0266	0.0638
300	28.66	25.70	0.0296	0.0879
325	29.35	25.11	0.0424	0.2584
350	30.25	24.56	0.0569	0.6245
375	30.59	23.64	0.0695	1.1381
400	31.00	23.47	0.0753	1.4474
450	31.34	23.04	0.0830	1.9384
500	31.50	22.84	0.0866	2.2017
550	31.60	22.87	0.0873	2.2556
600	31.80	22.71	0.0909	2.5463
650	31.80	22.71	0.0909	2.5463
700	31.84	22.67	0.0917	2.6141

Table A11 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 4

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	29.58	24.98	0.0460	0.3300
150	28.96	25.16	0.0380	0.1860
175	28.51	25.55	0.0296	0.0879
200	29.19	25.76	0.0343	0.1368
225	30.56	25.89	0.0467	0.3453
250	30.57	25.70	0.0487	0.3916
300	30.42	25.11	0.0531	0.5076
350	30.52	24.56	0.0596	0.7177
400	30.53	23.64	0.0689	1.1088

Table A12: IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 5

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	29.92	25.27	0.0465	0.3409
150	30.06	25.45	0.0461	0.3321
200	29.14	25.78	0.0336	0.1286
250	28.83	26.62	0.0221	0.0366
275	28.77	26.48	0.0229	0.0407
300	30.52	25.15	0.0537	0.5250
350	31.92	23.05	0.0887	2.3658
400	32.04	23.23	0.0881	2.3181
450	32.02	23.23	0.0879	2.3024
500	32.04	23.19	0.0885	2.3499

Table A13: IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 6

Time, s	Top	Bottom	Width, cm	IFT, mN/m
75	30.11	25.15	0.0496	0.4137
100	30.41	25.48	0.0493	0.4062
150	29.66	25.50	0.0416	0.2441
200	29.08	26.41	0.0267	0.0645
225	28.87	26.53	0.0234	0.0434
250	28.65	26.59	0.0206	0.0296
275	30.07	25.49	0.0458	0.3257
300	32.30	22.44	0.0986	3.2497
350	33.17	22.16	0.1101	4.5245
400	33.23	22.15	0.1108	4.6114
450	33.35	22.09	0.1126	4.8398
500	33.25	22.12	0.1113	4.6741

Table A14 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT; Trial 7

Time, s	Top	Bottom	Width, cm	IFT, mN/m
75	30.02	25.54	0.0448	0.3048
100	30.23	25.79	0.0444	0.2967
150	29.45	25.82	0.0363	0.1622
200	29.34	26.30	0.0304	0.0952
225	28.68	26.48	0.0220	0.0361
250	28.84	26.79	0.0205	0.0292
275	29.12	26.41	0.0271	0.0675
300	31.68	23.74	0.0794	1.6970
350	31.69	23.71	0.0798	1.7227
400	31.68	23.72	0.0796	1.7098

Table A15: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 1

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.40	23.92	0.0648	0.9224
100	30.30	24.14	0.0616	0.7924
150	30.25	24.08	0.0617	0.7963
200	30.14	24.25	0.0589	0.6927
250	30.16	24.50	0.0566	0.6147
300	29.88	24.73	0.0515	0.4631
350	29.42	25.04	0.0438	0.2849
400	28.90	25.48	0.0342	0.1356
450	28.82	25.57	0.0325	0.1164
500	29.55	24.69	0.0486	0.3892
550	31.95	22.40	0.0955	2.9527
600	31.93	22.30	0.0963	3.0276
650	32.06	22.23	0.0983	3.2201
700	32.13	22.39	0.0974	3.1325
750	31.91	22.32	0.0959	2.9900
800	31.95	22.44	0.0951	2.9158

Table A16: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 2

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	30.59	24.21	0.0638	0.8804
150	30.52	24.35	0.0617	0.7963
200	30.62	24.37	0.0625	0.8277
250	30.46	24.42	0.0604	0.7470
300	30.34	24.45	0.0589	0.6927
350	30.17	24.57	0.0560	0.5954
400	30.00	24.60	0.0540	0.5338
450	30.02	24.71	0.0531	0.5076
500	30.28	24.63	0.0565	0.6114
550	30.74	24.13	0.0661	0.9791
600	32.12	23.09	0.0903	2.4962
650	33.12	21.66	0.1146	5.1023
700	33.13	21.59	0.1154	5.2099
750	33.14	21.64	0.1150	5.1559

Table A17: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 3

Time, s	Top	Bottom	Width, cm	IFT, mN/m
60	31.14	24.29	0.0685	1.0896
100	30.92	24.28	0.0664	0.9925
150	30.75	24.59	0.0616	0.7924
200	30.64	24.83	0.0581	0.6649
250	30.44	25.01	0.0543	0.5428
300	29.62	25.82	0.0380	0.1860
350	29.33	26.20	0.0313	0.1040
400	29.18	26.25	0.0293	0.0853
450	29.14	26.23	0.0291	0.0835
500	29.32	26.10	0.0322	0.1132
550	29.33	26.01	0.0332	0.1241
600	29.52	25.89	0.0363	0.1622
650	29.64	25.91	0.0373	0.1759
700	29.72	25.74	0.0398	0.2137
800	29.79	25.65	0.0414	0.2406
900	29.65	25.62	0.0403	0.2219
1000	29.70	25.79	0.0391	0.2026
1100	29.50	25.71	0.0379	0.1846
1200	29.50	25.79	0.0371	0.1731
1300	29.80	25.25	0.0455	0.3193
1400	29.94	25.05	0.0489	0.3964
1500	29.81	24.98	0.0483	0.3820

Table A18: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 4

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.92	24.34	0.0658	0.9658
100	30.75	24.22	0.0653	0.9440
150	30.68	24.31	0.0637	0.8763
200	30.70	24.44	0.0626	0.8316
250	30.64	24.46	0.0618	0.8002
300	30.76	24.64	0.0612	0.7771
350	30.47	24.61	0.0586	0.6822
400	30.44	24.73	0.0571	0.6311
450	30.17	24.94	0.0523	0.4850
500	30.06	25.44	0.0462	0.3343
550	29.64	25.83	0.0381	0.1875
600	29.34	25.92	0.0342	0.1356
650	29.47	25.94	0.0353	0.1491
700	29.59	25.96	0.0363	0.1622
750	29.65	25.70	0.0395	0.2089
800	29.66	25.66	0.0400	0.2170
900	29.73	25.72	0.0401	0.2186
1000	29.70	25.64	0.0406	0.2269
1200	29.55	25.68	0.0387	0.1965
1500	29.78	25.49	0.0429	0.2677
1800	29.83	24.40	0.0543	0.5428

Table A19: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 5

Time, s	Top	Bottom	Width, cm	IFT, mN/m
60	30.89	24.19	0.0670	1.0196
100	30.53	23.92	0.0661	0.9791
200	30.37	24.36	0.0601	0.7359
300	30.14	24.57	0.0557	0.5858
350	29.83	24.85	0.0498	0.4187
400	29.78	24.92	0.0486	0.3892
450	29.53	25.10	0.0443	0.2947
500	29.38	25.31	0.0407	0.2286
550	29.16	25.80	0.0336	0.1286
600	28.86	25.78	0.0308	0.0991
650	29.44	25.31	0.0413	0.2388
700	30.80	24.27	0.0653	0.9440
750	31.43	23.04	0.0839	2.0022
800	32.41	22.42	0.0999	3.3799
850	32.79	21.93	0.1086	4.3421
900	32.54	21.85	0.1069	4.1414
1000	32.84	21.77	0.1107	4.5989

Table A20: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 6

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.99	24.47	0.0652	0.9396
100	30.83	24.18	0.0665	0.9970
200	30.77	24.31	0.0646	0.9139
300	30.72	24.33	0.0639	0.8845
400	30.52	24.49	0.0603	0.7433
450	30.37	24.50	0.0587	0.6857
500	29.92	24.88	0.0504	0.4340
550	29.63	25.48	0.0415	0.2423
600	29.31	25.82	0.0349	0.1441
650	28.68	26.50	0.0218	0.0351
700	28.72	26.46	0.0226	0.0391
750	28.52	26.63	0.0189	0.0229
800	28.67	26.29	0.0238	0.0457
850	28.83	26.18	0.0265	0.0631
900	29.19	25.87	0.0332	0.1241
950	29.24	25.83	0.0341	0.1344
1000	29.31	25.64	0.0367	0.1676
1050	29.43	25.66	0.0377	0.1817
1100	29.45	25.39	0.0406	0.2269
1150	29.55	25.36	0.0419	0.2494
1200	29.78	25.22	0.0456	0.3214
1250	29.86	25.17	0.0469	0.3497
1400	30.23	24.68	0.0555	0.5796
1500	30.58	24.37	0.0621	0.8119
1600	30.78	24.18	0.0660	0.9746
1800	31.02	23.85	0.0717	1.2496

Table A21: IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, Trial 7

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.85	24.40	0.0645	0.9097
100	31.05	24.28	0.0677	1.0519
200	30.95	24.38	0.0657	0.9614
300	30.71	24.75	0.0596	0.7177
350	30.38	25.01	0.0537	0.5250
400	30.35	25.14	0.0521	0.4794
450	30.02	25.58	0.0444	0.2967
500	29.78	25.96	0.0382	0.1890
550	29.11	26.58	0.0253	0.0549
600	28.70	26.86	0.0184	0.0211
650	28.98	26.55	0.0243	0.0486
750	29.34	26.72	0.0262	0.0610
800	29.09	26.03	0.0306	0.0971
900	29.18	26.14	0.0304	0.0952
950	29.18	26.16	0.0302	0.0934
1000	29.52	25.95	0.0357	0.1542
1050	29.78	25.71	0.0407	0.2286
1100	30.07	25.52	0.0455	0.3193
1150	30.71	24.74	0.0597	0.7213
1200	31.46	24.34	0.0712	1.2236
1250	31.86	23.44	0.0842	2.0237
1300	32.67	22.99	0.0968	3.0750
1400	33.09	22.38	0.1071	4.1647
1500	33.64	22.21	0.1143	5.0623
1800	33.73	21.87	0.1186	5.6554

Table A22: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 1

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.74	24.66	0.0608	0.7619
100	30.65	24.50	0.0615	0.7886
200	30.58	24.76	0.0582	0.6683
270	30.32	25.02	0.0530	0.5047
300	30.23	25.14	0.0509	0.4471
350	29.98	25.35	0.0463	0.3365
400	29.78	25.66	0.0412	0.2371
450	29.47	26.01	0.0346	0.1404
500	28.74	26.82	0.0192	0.0240
550	29.12	26.43	0.0269	0.0660
600	30.03	25.66	0.0437	0.2829
650	30.98	24.34	0.0664	0.9925
700	32.16	23.52	0.0864	2.1865
750	32.54	22.96	0.0958	2.9806
800	32.74	22.79	0.0995	3.3395
850	32.57	22.91	0.0966	3.0559
900	32.44	22.92	0.0952	2.9250
1000	32.34	23.17	0.0917	2.6141
1200	31.78	23.60	0.0818	1.8556
1300	31.61	23.79	0.0782	1.6212

Table A23: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 2

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.98	24.82	0.0616	0.7924
100	30.75	24.86	0.0589	0.6927
200	30.82	24.91	0.0591	0.6998
300	30.60	25.10	0.0550	0.5640
350	30.43	25.44	0.0499	0.4212
400	30.29	25.75	0.0454	0.3172
450	29.72	26.12	0.0360	0.1582
500	29.37	26.72	0.0265	0.0631
550	29.06	26.92	0.0214	0.0332
600	29.54	26.29	0.0325	0.1164
650	29.40	26.24	0.0316	0.1070
700	29.49	26.45	0.0304	0.0952
750	29.26	26.30	0.0296	0.0879
800	29.14	26.58	0.0256	0.0569
900	29.28	26.29	0.0299	0.0906
1000	29.51	25.80	0.0371	0.1731
1100	29.85	25.65	0.0420	0.2512
1200	29.99	25.38	0.0461	0.3321
1300	30.44	25.09	0.0535	0.5191
1400	30.78	24.55	0.0623	0.8197
1500	31.26	24.23	0.0703	1.1778
1600	31.47	23.82	0.0765	1.5177
1800	32.06	23.22	0.0884	2.3419

Table A24: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 3

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.55	24.94	0.0561	0.5986
100	30.72	24.69	0.0603	0.7433
200	30.40	24.98	0.0542	0.5398
250	30.18	25.21	0.0497	0.4162
300	29.94	25.44	0.0450	0.3089
350	29.66	25.89	0.0377	0.1817
400	29.31	26.12	0.0319	0.1100
450	29.15	26.52	0.0263	0.0617
500	29.85	25.68	0.0417	0.2458
550	31.28	23.84	0.0744	1.3961
600	32.68	22.71	0.0997	3.3597
650	32.92	22.45	0.1047	3.8909
700	33.06	22.50	0.1056	3.9921
800	33.01	22.53	0.1048	3.9021
1000	32.98	22.52	0.1046	3.8798

Table A25: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 4

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.33	24.71	0.0562	0.6018
100	30.50	24.78	0.0572	0.6345
200	30.12	25.18	0.0494	0.4087
250	29.82	25.40	0.0442	0.2927
300	29.40	25.96	0.0344	0.1380
350	29.14	26.32	0.0282	0.0760
400	29.22	26.08	0.0314	0.1050
450	31.48	24.20	0.0728	1.3080
500	32.90	22.45	0.1045	3.8687
550	33.06	22.43	0.1063	4.0720
600	33.09	22.37	0.1072	4.1764
800	33.12	22.37	0.1075	4.2115

Table A26: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 5

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.03	24.70	0.0633	0.8599
100	30.98	24.70	0.0628	0.8396
200	30.85	24.90	0.0595	0.7141
250	30.88	24.87	0.0601	0.7359
300	30.67	25.18	0.0549	0.5610
350	30.44	25.48	0.0496	0.4137
400	30.31	25.55	0.0476	0.3656
450	30.10	25.86	0.0424	0.2584
500	29.81	26.20	0.0361	0.1595
550	29.56	26.47	0.0309	0.1000
600	29.18	26.79	0.0239	0.0463
650	29.52	26.80	0.0272	0.0682
700	29.79	26.36	0.0343	0.1368
750	30.51	25.79	0.0472	0.3565
800	31.16	24.83	0.0633	0.8599
850	31.94	24.06	0.0788	1.6588
900	32.65	23.32	0.0933	2.7533
1000	33.32	22.92	0.1040	3.8134
1100	33.45	22.60	0.1085	4.3301
1200	33.60	22.53	0.1107	4.5989
1300	33.54	22.48	0.1106	4.5865

Table A27: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 6

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.62	24.60	0.0602	0.7396
100	30.60	24.39	0.0621	0.8119
200	30.71	24.25	0.0646	0.9139
300	30.50	24.49	0.0601	0.7359
350	30.40	24.55	0.0585	0.6787
400	30.26	24.80	0.0546	0.5518
450	29.80	25.12	0.0468	0.3475
500	29.30	25.57	0.0373	0.1759
550	28.78	26.40	0.0238	0.0457
600	28.68	26.28	0.0240	0.0469
650	29.04	25.90	0.0314	0.1050
700	29.51	25.52	0.0399	0.2153
750	29.75	25.20	0.0455	0.3193
800	30.38	24.84	0.0554	0.5764
850	30.69	24.25	0.0644	0.9055
900	31.14	23.98	0.0716	1.2444
950	31.27	23.65	0.0762	1.5000
1000	31.57	23.46	0.0811	1.8083
1100	31.70	23.12	0.0858	2.1413
1200	31.80	23.14	0.0866	2.2017

Table A.28: IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, Trial 7

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.18	25.04	0.0614	0.7847
100	31.24	24.98	0.0626	0.8316
200	30.94	25.02	0.0592	0.7034
300	30.85	25.42	0.0543	0.5428
350	30.77	25.43	0.0534	0.5162
400	30.05	25.85	0.0420	0.2512
450	29.74	26.42	0.0332	0.1241
500	29.24	27.11	0.0213	0.0328
550	29.69	26.80	0.0289	0.0818
600	30.23	26.18	0.0405	0.2252
650	30.60	25.95	0.0465	0.3409
700	30.95	25.45	0.0550	0.5640
750	31.11	25.09	0.0602	0.7396
800	31.17	24.99	0.0618	0.8002
850	31.28	24.94	0.0634	0.8639

Table A29 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.1  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.75	24.65	0.0610	0.7678
100	30.79	24.74	0.0605	0.7491
200	30.82	24.68	0.0614	0.7830
300	30.60	24.86	0.0574	0.6397
350	30.38	25.01	0.0537	0.5238
400	30.17	25.22	0.0495	0.4103
450	29.82	26.11	0.0371	0.1727
500	29.64	26.59	0.0305	0.0960
550	29.55	26.22	0.0333	0.1249
600	30.10	25.65	0.0445	0.2981
650	30.54	25.00	0.0554	0.5751
700	31.03	24.71	0.0632	0.8539
750	31.24	24.26	0.0698	1.1503
800	31.42	24.14	0.0728	1.3051
900	31.46	24.19	0.0727	1.2997
1000	31.17	24.34	0.0683	1.0777
1200	30.80	24.68	0.0612	0.7754
1500	30.47	25.15	0.0532	0.5093
1800	30.18	25.10	0.0508	0.4434
2000	30.72	24.80	0.0592	0.7018

Table A30 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.3  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.27	24.85	0.0642	0.8951
100	31.20	24.79	0.0641	0.8909
200	30.91	24.94	0.0597	0.7197
300	30.76	25.31	0.0545	0.5476
350	30.53	25.52	0.0501	0.4254
400	30.24	25.76	0.0448	0.3041
450	30.10	25.97	0.0413	0.2383
500	29.62	26.81	0.0281	0.0751
550	29.26	26.99	0.0227	0.0396
600	29.34	26.70	0.0264	0.0622
650	29.82	26.41	0.0341	0.1341
700	30.15	26.07	0.0408	0.2297
750	30.56	25.80	0.0476	0.3648
800	30.87	25.27	0.0560	0.5940
850	31.14	25.04	0.0610	0.7678
900	31.52	24.80	0.0672	1.0265
1000	31.81	24.45	0.0736	1.3486
1100	32.12	24.09	0.0803	1.7514
1500	32.60	23.70	0.0890	2.3846

Table A32 : IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 1.4 μL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.50	24.42	0.0608	0.7602
100	30.58	24.35	0.0623	0.8179
200	30.41	24.42	0.0599	0.7270
300	30.15	24.82	0.0533	0.5122
350	29.91	25.06	0.0485	0.3859
400	29.40	25.72	0.0368	0.1686
450	29.01	25.76	0.0325	0.1161
500	29.83	24.91	0.0492	0.4028
550	30.97	24.15	0.0682	1.0730
600	31.94	22.89	0.0905	2.5072
650	32.27	22.66	0.0961	3.0020
700	32.23	22.73	0.0950	2.9001
800	31.95	23.08	0.0887	2.3606
900	31.58	23.41	0.0817	1.8446
1000	31.37	23.57	0.0780	1.6052
1200	30.88	23.95	0.0693	1.1258

Table A31 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.5 μL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.97	24.78	0.0619	0.8023
100	31.00	24.76	0.0624	0.8219
200	30.89	25.03	0.0586	0.6807
250	30.68	25.06	0.0562	0.6004
300	30.71	25.24	0.0547	0.5536
350	30.44	25.62	0.0482	0.3788
400	30.40	25.82	0.0458	0.3250
450	30.07	26.08	0.0399	0.2149
500	29.70	26.42	0.0328	0.1194
550	29.54	26.75	0.0279	0.0735
600	29.65	26.76	0.0289	0.0816
650	29.56	26.58	0.0298	0.0895
700	29.88	26.16	0.0372	0.1741
750	30.85	25.30	0.0555	0.5783
800	31.48	24.63	0.0685	1.0872
850	32.13	24.04	0.0809	1.7910
900	32.46	23.65	0.0881	2.3130
1000	32.94	23.29	0.0965	3.0397
1200	32.95	23.20	0.0975	3.1352
1500	32.77	23.29	0.0948	2.8818

Table A33 : IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 1.5 μL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.91	24.61	0.0630	0.8458
100	30.78	24.48	0.0630	0.8458
200	30.73	24.74	0.0599	0.7270
300	30.45	25.12	0.0533	0.5122
350	30.32	25.18	0.0514	0.4593
400	29.92	25.43	0.0449	0.3062
450	29.52	26.35	0.0317	0.1078
500	29.03	26.54	0.0249	0.0522
550	29.72	25.70	0.0402	0.2197
600	30.55	25.20	0.0535	0.5180
650	31.48	23.89	0.0759	1.4790
700	32.23	23.30	0.0893	2.4088
750	32.68	22.71	0.0997	3.3522
800	32.82	22.70	0.1012	3.5058
900	32.54	22.87	0.0967	3.0586
1000	32.28	23.23	0.0905	2.5072
1200	31.62	23.73	0.0789	1.6614

Table A34 : IFT between 10 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 1.7 μL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.25	25.16	0.0609	0.7640
100	30.92	24.90	0.0602	0.7380
200	30.94	24.85	0.0609	0.7640
300	30.57	25.37	0.0520	0.4756
350	30.36	25.62	0.0474	0.3602
400	30.11	25.71	0.0440	0.2881
450	29.85	26.14	0.0371	0.1727
500	29.51	26.48	0.0303	0.0941
550	29.98	26.08	0.0390	0.2006
600	30.23	25.69	0.0454	0.3165
650	30.84	25.10	0.0574	0.6397
700	31.25	24.61	0.0664	0.9903
750	31.60	24.34	0.0726	1.2944
800	31.81	24.11	0.0770	1.5442
850	31.94	24.03	0.0791	1.6741
900	31.98	23.95	0.0803	1.7514
1000	31.77	24.14	0.0763	1.5025
1200	31.30	24.53	0.0677	1.0496

Table A35 : IFT between 10 mM synthetic oil and 2.5 mM NaOH tested on the SDT (cont'd)

Time, s	Top	Bottom	Width, cm	IFT, mN/m
2700	33.42	21.82	0.1160	5.2798
2800	33.40	21.82	0.1158	5.2526
3000	33.41	21.80	0.1161	5.2935

Table A36 : IFT between 1 mM synthetic oil and 2.5 mM NaOH tested on the SDT, 1.5 µL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	33.48	21.70	0.1178	5.2719
100	31.62	24.00	0.0762	1.4269
150	31.11	24.47	0.0664	0.9441
200	30.89	24.84	0.0605	0.7142
250	30.75	24.77	0.0598	0.6897
300	30.85	24.93	0.0592	0.6691
350	30.93	24.68	0.0625	0.7874
400	31.22	24.36	0.0686	1.0411
450	31.68	23.94	0.0774	1.4954
500	32.23	23.25	0.0898	2.3354
550	32.73	22.89	0.0984	3.0727
600	33.00	22.56	0.1044	3.6697
650	33.43	22.30	0.1113	4.4465
700	33.51	22.16	0.1135	4.7154
750	33.52	22.02	0.1150	4.9049
800	33.62	21.99	0.1163	5.0731
850	33.65	21.96	0.1169	5.1520
900	33.65	21.95	0.1170	5.1652
1000	33.70	21.90	0.1180	5.2988

Table A35 : IFT between 10 mM synthetic oil and 2.5 mM NaOH tested on the SDT, 2.8 µL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
30	30.57	24.26	0.0631	0.8498
100	30.36	24.70	0.0566	0.6133
150	30.33	24.69	0.0564	0.6069
200	30.32	24.85	0.0547	0.5536
250	30.34	24.90	0.0544	0.5446
300	30.28	24.91	0.0537	0.5238
350	30.31	24.93	0.0538	0.5267
400	30.35	24.98	0.0537	0.5238
450	30.34	24.94	0.0540	0.5326
500	30.15	25.15	0.0500	0.4228
550	29.98	25.22	0.0476	0.3648
650	29.97	25.36	0.0461	0.3314
700	30.18	25.18	0.0500	0.4228
750	29.98	25.23	0.0475	0.3625
800	30.20	25.21	0.0499	0.4203
850	30.13	24.97	0.0516	0.4647
900	30.22	25.02	0.0520	0.4756
1000	30.22	24.96	0.0526	0.4923
1100	30.32	24.90	0.0542	0.5386
1200	30.52	24.77	0.0575	0.6431
1300	30.82	24.53	0.0629	0.8418
1400	31.24	24.12	0.0712	1.2209
1500	31.51	23.81	0.0770	1.5442
1600	31.82	23.42	0.0840	2.0049
2000	32.94	22.42	0.1052	3.9381
2200	33.22	22.15	0.1107	4.5887
2400	33.46	21.96	0.1150	5.1444
2500	33.44	21.95	0.1149	5.1310
2600	33.37	21.89	0.1148	5.1176

Table A37 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, 1.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.98	24.38	0.0660	0.9725
100	30.90	24.29	0.0661	0.9769
200	30.94	24.34	0.0660	0.9725
300	30.67	24.56	0.0611	0.7716
350	30.55	24.65	0.0590	0.6947
400	30.33	24.92	0.0541	0.5356
450	30.12	25.14	0.0498	0.4178
500	29.89	25.48	0.0441	0.2901
550	29.67	25.81	0.0386	0.1945
600	29.35	26.19	0.0316	0.1067
650	29.06	26.30	0.0276	0.0711
700	29.29	26.01	0.0328	0.1194
750	29.57	25.79	0.0378	0.1827
800	29.47	25.81	0.0366	0.1658
850	29.67	25.75	0.0392	0.2038
900	29.78	25.59	0.0419	0.2488
1000	29.89	25.41	0.0448	0.3041
1100	30.35	25.21	0.0514	0.4593
1200	30.38	25.05	0.0533	0.5122
1500	30.62	24.66	0.0596	0.7161
1600	30.71	24.68	0.0603	0.7416

Table A38 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT, 1.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.32	24.98	0.0534	0.5151
100	30.13	24.89	0.0524	0.4867
200	30.18	25.12	0.0506	0.4382
300	29.81	25.32	0.0449	0.3062
350	29.63	25.61	0.0402	0.2197
400	29.37	25.75	0.0362	0.1605
450	29.22	25.98	0.0324	0.1150
500	28.90	26.27	0.0263	0.0615
550	28.72	26.49	0.0223	0.0375
600	28.59	26.44	0.0215	0.0336
650	28.83	26.20	0.0263	0.0615
700	29.03	26.10	0.0293	0.0851
750	29.17	25.89	0.0328	0.1194
800	29.27	25.72	0.0355	0.1513
850	29.46	25.71	0.0375	0.1784
900	29.54	25.68	0.0386	0.1945
950	29.71	25.62	0.0409	0.2314
1000	29.58	25.51	0.0407	0.2280
1200	29.91	25.09	0.0482	0.3788
1500	30.31	24.79	0.0552	0.5689

Table A39 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.95	24.64	0.0631	0.8081
100	30.94	24.70	0.0624	0.7815
200	30.80	24.78	0.0602	0.7017
250	30.54	25.14	0.0540	0.5064
300	30.19	25.28	0.0491	0.3807
350	29.80	25.84	0.0396	0.1997
400	29.52	26.07	0.0345	0.1321
450	29.55	26.01	0.0354	0.1427
500	30.30	25.48	0.0482	0.3602
550	31.60	23.93	0.0767	1.4512
600	32.23	23.43	0.0880	2.1918
650	32.28	23.43	0.0885	2.2294
700	32.37	23.31	0.0906	2.3919
750	32.36	23.37	0.0899	2.3369
800	32.38	23.34	0.0904	2.3761

Table A40 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.00	24.58	0.0642	0.8482
100	31.02	24.54	0.0648	0.8722
200	30.88	24.52	0.0636	0.8246
250	30.91	24.58	0.0633	0.8130
300	30.69	24.70	0.0599	0.6889
350	30.52	24.86	0.0566	0.5812
400	30.41	25.06	0.0535	0.4908
450	30.11	25.42	0.0469	0.3307
500	29.67	25.93	0.0374	0.1677
550	29.27	26.12	0.0315	0.1002
600	29.72	25.91	0.0381	0.1773
650	30.85	24.55	0.0630	0.8015
700	32.26	23.30	0.0896	2.3057
750	32.58	22.98	0.0960	2.8359
800	32.68	22.92	0.0976	2.9800
900	32.70	22.88	0.0982	3.0353
1000	32.72	22.89	0.0983	3.0446

Table A41 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.9  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.40	24.69	0.0671	0.9717
100	31.45	24.59	0.0686	1.0383
200	31.36	24.67	0.0669	0.9630
300	31.19	24.89	0.0630	0.8042
350	31.13	24.94	0.0619	0.7628
400	31.00	25.11	0.0589	0.6572
450	30.85	25.26	0.0559	0.5618
500	30.73	25.61	0.0512	0.4317
550	30.20	26.10	0.0410	0.2217
600	29.67	26.68	0.0299	0.0860
650	29.94	26.33	0.0361	0.1513
700	30.47	25.87	0.0460	0.3131
750	30.33	25.84	0.0449	0.2911
800	30.48	25.82	0.0466	0.3255
850	30.50	25.69	0.0481	0.3579
900	30.44	25.71	0.0479	0.3535
1000	30.48	25.70	0.0474	0.3425
1200	30.48	25.75	0.0473	0.3404

Table A42 : IFT between 30 mM synthetic oil and 25 mM LiOH tested on the SDT, 1.2  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.95	24.69	0.0626	0.7890
100	30.37	24.59	0.0578	0.6211
200	30.07	24.67	0.0540	0.5064
250	29.79	24.89	0.0490	0.3784
300	29.94	24.94	0.0500	0.4020
350	30.01	25.11	0.0490	0.3784
400	30.01	25.26	0.0475	0.3447
450	30.06	25.61	0.0445	0.2834
500	30.15	26.10	0.0405	0.2137
550	30.27	26.68	0.0359	0.1488
600	30.30	26.33	0.0397	0.2012
700	30.50	25.87	0.0463	0.3192
800	30.57	25.84	0.0473	0.3404
1000	30.65	25.82	0.0483	0.3624

Table A44 : IFT between 30 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 1.7  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.23	24.56	0.0667	0.9544
100	31.25	24.58	0.0667	0.9544
200	31.14	24.61	0.0653	0.8956
300	30.92	24.84	0.0608	0.7229
350	30.72	25.15	0.0557	0.5558
400	30.42	25.45	0.0497	0.3948
450	30.20	25.71	0.0449	0.2911
500	29.69	26.34	0.0335	0.1209
550	29.79	26.08	0.0371	0.1642
600	30.74	25.24	0.0550	0.5351
650	31.40	24.48	0.0692	1.0658
700	32.81	23.68	0.0913	2.4477
750	33.56	22.34	0.1122	4.5429
800	33.97	22.18	0.1179	5.2710
850	33.96	22.10	0.1186	5.3655
900	33.95	22.21	0.1175	5.2175
1000	33.46	22.50	0.1145	4.8280

Table A43 : IFT between 30 mM synthetic oil and 25 mM KOH tested on the SDT, 1.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.28	24.17	0.0711	1.1560
100	31.20	24.18	0.0702	1.1127
200	31.25	24.15	0.0710	1.1511
300	31.22	24.21	0.0701	1.1079
350	31.18	24.27	0.0691	1.0612
400	31.05	24.33	0.0672	0.9760
450	30.92	24.55	0.0637	0.8313
500	30.62	24.81	0.0581	0.6308
550	30.35	25.03	0.0532	0.4843
600	30.00	25.58	0.0442	0.2777
650	29.90	25.69	0.0421	0.2400
700	30.16	25.28	0.0488	0.3738
750	31.23	24.48	0.0675	0.9892
800	32.32	23.35	0.0897	2.3213
850	33.05	22.59	0.1046	3.6808
900	33.22	22.31	0.1074	3.9844
1000	32.96	22.65	0.1057	3.7982
1200	31.59	23.91	0.0905	2.3840
1500	30.59	24.88	0.0671	0.9717
1800	30.43	24.96	0.0563	0.5740
5000	33.61	22.92	0.0751	1.3623

Table A45 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.2  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.64	24.95	0.0669	0.9597
100	30.84	24.40	0.0644	0.8561
200	30.75	24.49	0.0626	0.7863
300	30.45	24.64	0.0581	0.6286
350	30.59	24.79	0.0580	0.6254
400	30.36	25.01	0.0535	0.4908
450	30.24	25.15	0.0509	0.4227
500	29.84	25.69	0.0415	0.2291
550	29.29	25.90	0.0339	0.1249
600	29.04	26.44	0.0260	0.0563
650	29.61	25.70	0.0391	0.1916
700	29.87	25.60	0.0427	0.2495
750	29.94	25.50	0.0444	0.2806
800	29.68	25.55	0.0413	0.2258
850	29.71	25.63	0.0408	0.2177
900	29.71	25.62	0.0409	0.2193
950	29.54	25.79	0.0375	0.1690
1000	29.43	25.63	0.0380	0.1759

Table A46 : IFT between 10 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.3  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.20	24.95	0.0625	0.8258
100	31.11	24.73	0.0638	0.8784
200	31.11	24.83	0.0628	0.8378
300	31.02	25.21	0.0581	0.6634
350	30.83	25.22	0.0561	0.5972
400	30.72	25.29	0.0543	0.5416
450	30.10	26.13	0.0397	0.2116
500	29.55	26.65	0.0290	0.0825
550	30.02	26.05	0.0397	0.2116
600	30.12	25.87	0.0425	0.2597
650	30.06	25.77	0.0429	0.2671
700	29.86	25.95	0.0391	0.2022
750	29.83	26.01	0.0382	0.1886
800	29.78	26.19	0.0359	0.1565
900	29.60	26.25	0.0335	0.1272
1000	29.55	26.17	0.0338	0.1306
1200	30.02	25.86	0.0416	0.2435
1300	30.44	25.14	0.0530	0.5036
1400	31.27	24.42	0.0685	1.0872
1500	32.11	23.38	0.0873	2.2505
1800	33.97	21.63	0.1234	6.3561
2000	34.18	21.33	0.1285	7.1772

Table A47 : IFT between 20 mM synthetic oil and 25 mM NaOH tested on the SDT, 1.2  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.25	24.48	0.0677	0.9987
100	31.22	24.52	0.0670	0.9680
200	31.19	24.61	0.0658	0.9169
300	31.17	24.62	0.0655	0.9044
350	31.16	24.61	0.0655	0.9044
400	30.98	24.69	0.0629	0.8009
450	30.86	24.83	0.0603	0.7057
500	30.79	24.94	0.0585	0.6443
550	30.46	25.24	0.0522	0.4578
600	30.09	25.75	0.0434	0.2631
650	30.17	25.69	0.0448	0.2894
700	30.19	25.65	0.0454	0.3012
750	30.26	25.65	0.0461	0.3153
800	30.14	25.63	0.0451	0.2952
900	30.39	25.61	0.0478	0.3515
1000	30.26	25.57	0.0469	0.3320
1200	30.17	25.60	0.0457	0.3072
1500	30.25	25.60	0.0465	0.3236
1800	30.12	25.60	0.0452	0.2972
2000	30.23	25.40	0.0483	0.3627
2200	30.30	25.17	0.0513	0.4345
2500	30.65	24.94	0.0571	0.5992

Table A48 : IFT between 30 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.8  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
30	31.05	24.57	0.0648	0.8751
100	31.07	24.53	0.0654	0.8997
200	30.97	24.59	0.0638	0.8352
300	30.84	24.86	0.0598	0.6878
350	30.59	24.97	0.0562	0.5709
400	30.12	25.54	0.0458	0.3090
450	29.80	25.87	0.0393	0.1952
500	29.64	25.96	0.0368	0.1603
550	30.33	25.41	0.0492	0.3830
600	30.89	24.76	0.0613	0.7409
650	31.18	24.51	0.0667	0.9544
700	31.39	24.36	0.0703	1.1174
750	31.40	24.30	0.0710	1.1511
800	31.36	24.36	0.0700	1.1032
900	31.26	24.35	0.0691	1.0612
1000	31.12	24.50	0.0662	0.9331
1200	31.05	24.57	0.0648	0.8751

Table A49 : IFT between 40 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.8  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.27	24.85	0.0642	0.8499
100	31.26	24.84	0.0642	0.8499
200	31.15	24.87	0.0628	0.7955
300	30.85	25.18	0.0567	0.5855
350	30.63	25.55	0.0508	0.4211
400	30.15	26.13	0.0402	0.2087
450	29.94	26.43	0.0351	0.1389
500	30.28	25.85	0.0443	0.2792
550	30.85	25.29	0.0556	0.5521
600	31.33	25.01	0.0632	0.8108
650	31.33	24.82	0.0651	0.8861
700	31.47	24.72	0.0675	0.9878
750	31.45	24.78	0.0667	0.9531
800	31.46	24.75	0.0671	0.9704
900	31.37	24.82	0.0655	0.9026
1000	31.37	24.69	0.0668	0.9574
1200	31.40	24.76	0.0664	0.9403

Table A50 : IFT between 50 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.6  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
30	31.33	24.64	0.0669	0.9604
100	31.27	24.70	0.0657	0.9096
200	31.12	24.72	0.0640	0.8408
300	30.92	25.16	0.0576	0.6130
350	30.62	25.29	0.0533	0.4857
400	30.29	25.68	0.0461	0.3142
450	29.98	26.08	0.0390	0.1903
500	29.41	26.68	0.0273	0.0653
550	29.61	26.64	0.0297	0.0840
600	30.29	25.64	0.0465	0.3225
650	31.72	24.65	0.0707	1.1335
700	32.19	23.91	0.0828	1.8208
750	32.75	23.65	0.0910	2.4171
800	32.83	23.71	0.0912	2.4331
900	32.50	23.63	0.0887	2.2384
1000	32.60	23.77	0.0883	2.2083
1200	32.23	23.92	0.0831	1.8407

Table A52 : IFT between 10 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.3  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	29.62	24.68	0.0494	0.4078
100	30.63	24.69	0.0594	0.7089
200	29.40	24.98	0.0442	0.2921
250	29.21	25.39	0.0382	0.1886
300	28.73	26.40	0.0233	0.0428
350	29.20	26.01	0.0319	0.1098
400	29.97	25.44	0.0453	0.3144
450	31.07	24.08	0.0699	1.1553
500	31.66	23.75	0.0791	1.6741
550	31.75	23.67	0.0808	1.7843
600	31.74	23.48	0.0826	1.9063
700	31.71	23.58	0.0813	1.8177
800	31.90	23.31	0.0859	2.1440
1000	32.22	23.10	0.0912	2.5658

Table A51 : IFT between 60 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.9  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.59	25.26	0.0633	0.8130
100	31.50	25.19	0.0631	0.8053
200	31.43	25.21	0.0622	0.7713
300	31.26	25.47	0.0579	0.6222
350	30.91	25.73	0.0518	0.4455
400	30.72	25.98	0.0474	0.3414
450	30.31	26.46	0.0385	0.1829
500	29.90	27.00	0.0290	0.0782
550	30.31	26.61	0.0370	0.1624
600	30.83	26.04	0.0479	0.3523
650	31.24	25.51	0.0573	0.6030
700	31.64	25.12	0.0652	0.8884
750	31.90	25.04	0.0686	1.0348
800	32.07	24.85	0.0722	1.2064
900	32.07	24.70	0.0737	1.2831
1000	31.91	24.88	0.0703	1.1136
1200	31.43	25.36	0.0607	0.7169
1500	30.94	25.52	0.0542	0.5104

Table A53 : IFT between 20 mM synthetic oil and  
25 mM LiOH tested on the SDT, 0.3  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.40	25.34	0.0506	0.4170
100	30.38	25.52	0.0486	0.3695
200	29.70	26.05	0.0365	0.1565
250	29.42	26.39	0.0303	0.0895
300	29.99	25.51	0.0448	0.2894
350	32.66	23.32	0.0934	2.6223
400	32.68	23.23	0.0945	2.7161
450	32.76	23.08	0.0968	2.9193
500	32.76	23.06	0.0970	2.9374
600	32.65	22.79	0.0986	3.0852

Table A54 : IFT between 30 mM synthetic oil and  
25 mM LiOH tested on the SDT, 0.45  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.04	24.80	0.0524	0.4628
100	30.03	24.76	0.0527	0.4707
200	29.62	25.16	0.0446	0.2853
250	29.08	25.50	0.0358	0.1476
300	28.78	25.91	0.0287	0.0760
350	29.45	25.64	0.0381	0.1779
400	30.62	24.12	0.0650	0.8833
450	32.01	23.03	0.0898	2.3291
500	32.25	22.75	0.0950	2.7576
550	32.21	22.56	0.0965	2.8902
600	32.41	22.52	0.0989	3.1113
650	32.36	22.45	0.0991	3.1302
700	32.39	22.47	0.0992	3.1397
800	32.41	22.43	0.0998	3.1970

Table A55 : IFT between 40 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	29.84	24.66	0.0518	0.4464
100	29.92	24.56	0.0536	0.4946
200	29.54	24.90	0.0464	0.3209
250	28.90	25.48	0.0342	0.1285
300	28.75	25.85	0.0290	0.0783
350	29.85	24.35	0.0550	0.5344
400	32.52	22.21	0.1031	3.5200
450	32.62	22.05	0.1057	3.7930
500	32.70	21.99	0.1071	3.9458
600	32.75	21.93	0.1082	4.0686
700	32.86	22.14	0.1072	3.9568

Table A56 : IFT between 50 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.45  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.33	25.32	0.0501	0.4034
100	30.47	25.26	0.0521	0.4536
200	30.07	25.39	0.0468	0.3288
250	29.65	25.82	0.0383	0.1802
300	29.49	26.33	0.0316	0.1012
350	29.56	26.21	0.0335	0.1206
400	30.28	25.46	0.0482	0.3592
450	31.28	24.40	0.0688	1.0446
500	31.83	23.67	0.0816	1.7428
550	32.25	23.04	0.0921	2.5058
600	32.68	22.65	0.1003	3.2365
650	32.82	22.76	0.1006	3.2656
700	32.94	22.78	0.1016	3.3640
800	32.99	22.75	0.1024	3.4440

Table A57 : IFT between 60 mM synthetic oil and 25 mM LiOH tested on the SDT, 0.3  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	29.90	24.58	0.0532	0.4826
100	29.91	24.68	0.0523	0.4585
200	29.64	24.93	0.0471	0.3349
250	29.24	25.25	0.0399	0.2036
300	29.02	25.50	0.0352	0.1398
350	28.96	24.98	0.0398	0.2021
400	29.11	24.82	0.0429	0.2531
450	29.15	24.79	0.0436	0.2657
500	29.30	24.58	0.0472	0.3371
550	29.47	24.52	0.0495	0.3888
600	29.54	24.30	0.0524	0.4612
650	29.86	24.02	0.0584	0.6384
700	29.95	23.88	0.0607	0.7169
750	30.30	23.68	0.0662	0.9299
800	30.42	23.41	0.0701	1.1041
900	30.89	22.96	0.0746	1.3307
1000	31.01	22.72	0.0817	1.7480
1100	31.17	22.66	0.0835	1.8661

Table A58 : IFT between 10 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.07	24.82	0.0625	0.8258
100	31.05	24.80	0.0625	0.8258
200	30.96	24.84	0.0612	0.7754
250	30.91	24.95	0.0596	0.7161
300	30.76	25.09	0.0567	0.6166
350	30.50	25.33	0.0517	0.4674
400	30.44	25.54	0.0490	0.3980
450	30.08	25.79	0.0429	0.2671
500	29.57	26.39	0.0318	0.1088
550	29.20	27.04	0.0216	0.0341
600	29.39	26.77	0.0262	0.0608
650	29.53	26.61	0.0292	0.0842
700	29.63	26.44	0.0319	0.1098
750	29.87	26.23	0.0364	0.1631
800	30.18	25.99	0.0419	0.2488
850	30.41	25.74	0.0467	0.3445
900	30.66	25.48	0.0518	0.4701
950	30.88	25.21	0.0567	0.6166
1000	31.15	25.01	0.0614	0.7830
1050	31.35	24.79	0.0656	0.9549
1100	31.57	24.63	0.0694	1.1306
1300	32.15	24.03	0.0812	1.8110
1500	32.35	23.86	0.0849	2.0700

Table A60 : IFT between 30 mM synthetic oil and 25 mM KOH tested on the SDT, 0.6  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.69	23.75	0.0694	1.0751
100	30.75	23.67	0.0708	1.1414
200	30.62	23.86	0.0676	0.9936
250	30.59	23.82	0.0677	0.9980
300	30.52	23.97	0.0655	0.9038
350	30.36	24.10	0.0626	0.7890
400	30.19	24.37	0.0582	0.6340
450	29.91	24.59	0.0532	0.4843
500	29.65	25.01	0.0464	0.3213
550	29.21	25.52	0.0369	0.1616
600	28.99	25.59	0.0340	0.1264
650	29.59	25.42	0.0417	0.2332
700	30.10	24.48	0.0562	0.5709
750	31.04	23.91	0.0713	1.1658
800	31.50	23.17	0.0833	1.8590
850	31.91	22.92	0.0899	2.3369
900	32.08	22.70	0.0938	2.6544
1000	32.04	22.67	0.0937	2.6459
1100	31.84	22.89	0.0895	2.3058
1200	31.74	22.96	0.0878	2.1769

Table A59 : IFT between 20 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.13	24.34	0.0679	1.0075
100	31.13	24.17	0.0696	1.0851
200	31.03	24.08	0.0695	1.0804
250	31.01	24.20	0.0681	1.0165
300	30.96	24.20	0.0676	0.9942
350	30.95	24.39	0.0656	0.9086
400	30.85	24.40	0.0645	0.8636
450	30.63	24.57	0.0606	0.7163
500	30.41	24.83	0.0558	0.5592
550	29.99	25.16	0.0483	0.3627
600	29.58	25.67	0.0391	0.1924
650	29.29	26.03	0.0326	0.1115
700	29.42	25.84	0.0358	0.1477
750	29.85	25.51	0.0434	0.2631
800	30.20	25.05	0.0515	0.4396
850	30.66	24.48	0.0618	0.7596
900	31.40	23.96	0.0744	1.3255
1000	31.79	23.44	0.0835	1.8737
1100	32.16	23.31	0.0885	2.2309
1200	32.01	23.40	0.0861	2.0543
1300	31.92	23.50	0.0842	1.9213
1400	31.69	23.60	0.0809	1.7041
1500	31.59	23.79	0.0780	1.5273

Table A61 : IFT between 40 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.12	24.40	0.0672	0.9747
100	30.28	23.66	0.0662	0.9318
200	30.02	23.84	0.0618	0.7581
250	29.82	24.03	0.0579	0.6234
300	29.54	24.43	0.0511	0.4286
350	29.28	24.90	0.0438	0.2699
400	28.78	25.21	0.0357	0.1461
450	28.62	25.46	0.0316	0.1013
500	29.82	24.41	0.0541	0.5086
550	31.54	22.44	0.0910	2.4204
600	32.22	22.14	0.1008	3.2896
650	32.33	21.92	0.1041	3.6234
700	32.53	21.85	0.1068	3.9127
750	32.47	21.78	0.1069	3.9237
800	32.55	21.75	0.1080	4.0461
900	32.55	21.70	0.1085	4.1025
1000	32.67	21.63	0.1104	4.3218

Table A62 : IFT between 50 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.58	24.57	0.0701	1.1049
100	31.57	24.64	0.0693	1.0675
200	30.25	23.54	0.0671	0.9690
250	30.23	23.48	0.0675	0.9865
300	30.25	23.56	0.0669	0.9604
350	30.03	23.61	0.0642	0.8487
400	29.99	23.76	0.0623	0.7756
450	29.73	24.41	0.0532	0.4830
500	29.56	25.19	0.0437	0.2677
550	29.19	24.62	0.0457	0.3061
600	28.73	24.99	0.0374	0.1678
650	28.36	25.43	0.0293	0.0807
700	28.30	25.63	0.0267	0.0611
750	28.46	25.37	0.0309	0.0946
800	29.42	24.80	0.0462	0.3163
850	30.11	23.75	0.0636	0.8252
900	31.15	22.93	0.0822	1.7815
1000	31.77	22.27	0.0950	2.7500
1100	31.95	22.09	0.0986	3.0747
1200	31.99	22.14	0.0985	3.0653

Table A63 : IFT between 60 mM synthetic oil and 25 mM KOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.36	24.56	0.0680	1.0079
100	31.24	24.58	0.0666	0.9469
200	31.03	24.83	0.0620	0.7639
250	30.77	25.11	0.0566	0.5812
300	30.57	25.28	0.0529	0.4745
350	30.25	25.70	0.0455	0.3019
400	29.93	26.12	0.0381	0.1773
450	29.54	26.56	0.0298	0.0848
500	29.50	26.71	0.0279	0.0696
550	29.94	26.11	0.0383	0.1801
600	30.70	25.38	0.0532	0.4826
650	31.44	24.65	0.0679	1.0034
700	32.07	24.14	0.0793	1.5984
750	32.17	23.89	0.0828	1.8195
800	32.21	23.98	0.0823	1.7868
1000	31.23	24.81	0.0642	0.8482
1100	30.95	25.10	0.0585	0.6417
1200	30.78	25.21	0.0557	0.5539
1500	30.59	25.42	0.0517	0.4429
1800	30.62	25.32	0.0530	0.4772
2000	30.75	25.14	0.0561	0.5659

Table A64 : IFT between 10 mM synthetic oil and 25 mM Na2SiO3 tested on the SDT, 1.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.13	25.03	0.0610	0.7678
100	31.33	25.00	0.0633	0.8579
200	31.14	25.09	0.0605	0.7491
300	31.14	25.19	0.0595	0.7125
350	30.92	25.30	0.0562	0.6004
400	30.92	25.53	0.0539	0.5297
450	30.67	25.53	0.0514	0.4593
500	30.39	26.01	0.0438	0.2842
550	30.15	26.43	0.0372	0.1741
600	30.09	26.47	0.0362	0.1605
650	30.12	26.24	0.0388	0.1976
700	30.00	26.23	0.0377	0.1812
750	30.12	26.29	0.0383	0.1900
800	30.07	26.20	0.0387	0.1961
900	29.94	26.31	0.0363	0.1618
1000	30.01	26.25	0.0376	0.1798
1100	30.07	26.15	0.0392	0.2038
1200	30.17	26.26	0.0391	0.2022
1500	30.22	25.95	0.0427	0.2633
1600	30.39	25.80	0.0459	0.3271
1700	30.48	25.69	0.0479	0.3718
1800	30.81	25.34	0.0547	0.5536
1900	31.33	24.73	0.0660	0.9725
2000	32.29	23.87	0.0842	2.0192
2100	33.40	22.68	0.1072	4.1671
2200	33.98	22.22	0.1176	5.5013
2500	34.06	22.02	0.1204	5.9037
3000	34.31	21.88	0.1243	6.4962

Table A66 : IFT between 30 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.71	24.68	0.0603	0.7052
100	30.88	24.50	0.0638	0.8352
200	30.61	24.67	0.0594	0.6741
300	30.13	25.11	0.0502	0.4069
350	29.82	25.37	0.0445	0.2834
400	29.50	25.54	0.0396	0.1997
450	29.60	25.72	0.0388	0.1879
500	29.69	25.65	0.0404	0.2121
550	29.95	25.40	0.0455	0.3030
600	30.11	25.15	0.0496	0.3925
650	30.13	25.04	0.0509	0.4241
700	30.48	24.93	0.0555	0.5498
750	30.57	24.85	0.0572	0.6019
800	30.72	24.71	0.0601	0.6982
900	30.87	24.60	0.0627	0.7928
1000	30.94	24.44	0.0650	0.8833
1200	30.98	24.58	0.0640	0.8431
1500	30.77	24.45	0.0632	0.8119
1800	31.15	24.11	0.0704	1.1222

Table A65 : IFT between 20 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 0.8  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.49	24.4	0.0609	0.7269
100	30.61	24.37	0.0624	0.7820
200	30.53	24.26	0.0627	0.7933
300	30.30	24.66	0.0564	0.5774
350	29.98	25.00	0.0498	0.3975
400	29.95	25.17	0.0478	0.3515
450	29.55	25.33	0.0422	0.2419
500	29.61	25.54	0.0407	0.2170
550	29.66	25.31	0.0435	0.2649
600	29.68	25.35	0.0433	0.2613
650	29.71	25.38	0.0433	0.2613
700	29.69	25.32	0.0437	0.2686
750	29.67	25.51	0.0416	0.2317
800	29.64	25.48	0.0416	0.2317
850	29.58	25.41	0.0417	0.2334
900	29.61	25.58	0.0403	0.2107
1000	29.52	25.61	0.0391	0.1924
1200	29.52	25.62	0.0390	0.1909
1500	29.47	25.49	0.0398	0.2029
1800	31.44	23.54	0.0790	1.5868
2000	32.88	22.16	0.1072	3.9649

Table A67 : IFT between 40 mM synthetic oil and  
25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.12	25.05	0.0607	0.7183
100	31.15	24.97	0.0618	0.7581
200	31.07	25.11	0.0596	0.6800
250	30.91	25.22	0.0569	0.5917
300	30.62	25.40	0.0522	0.4568
350	30.42	25.77	0.0465	0.3229
400	30.09	25.98	0.0411	0.2230
450	29.59	26.56	0.0303	0.0893
500	29.73	26.44	0.0329	0.1144
550	30.21	26.03	0.0418	0.2346
600	30.93	25.41	0.0552	0.5402
650	31.52	24.59	0.0693	1.0690
700	32.08	24.14	0.0794	1.6078
750	32.13	24.01	0.0812	1.7196
800	32.23	24.03	0.0820	1.7709
900	31.85	24.17	0.0768	1.4549
1000	31.64	24.25	0.0739	1.2963
1200	31.38	24.54	0.0684	1.0278
1500	31.05	24.95	0.0610	0.7290
1800	30.94	24.79	0.0615	0.7471
2000	31.11	24.69	0.0642	0.8499
2200	31.19	24.54	0.0665	0.9446

Table A68 : IFT between 50 mM synthetic oil and  
25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 0.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.72	24.68	0.0604	0.7068
100	30.65	24.65	0.0600	0.6928
200	30.22	24.97	0.0525	0.4641
250	30.01	25.13	0.0488	0.3728
300	29.41	25.72	0.0369	0.1612
350	28.89	26.28	0.0261	0.0570
400	29.23	25.89	0.0334	0.1195
450	30.78	24.81	0.0597	0.6825
500	32.35	22.99	0.0936	2.6302
600	32.57	22.74	0.0983	3.0467
700	32.63	22.85	0.0978	3.0004
900	31.89	22.21	0.0968	2.9093
1000	31.93	22.16	0.0977	2.9913

Table A69 : IFT between 60 mM synthetic oil and 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the SDT, 0.3 µL

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.46	24.83	0.0563	0.5720
100	30.58	24.92	0.0566	0.5812
200	30.24	25.35	0.0489	0.3748
250	29.77	25.79	0.0398	0.2021
300	29.48	25.87	0.0361	0.1508
350	30.81	24.86	0.0595	0.6752
400	32.01	23.56	0.0845	1.9339
450	32.20	23.52	0.0868	2.0962
500	32.19	23.40	0.0879	2.1769
600	32.11	23.44	0.0867	2.0890
700	32.01	23.59	0.0842	1.9134
800	31.96	23.60	0.0836	1.8728
1000	32.04	23.51	0.0853	1.9894

Table A70 : IFT between Lloydminster crude oil and 2.5 mM NaOH tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	30.19	24.04	0.0615	0.1344
200	29.55	24.39	0.0516	0.0794
250	29.43	24.46	0.0497	0.0709
300	29.36	24.54	0.0482	0.0647
350	29.14	24.64	0.0450	0.0526
400	29.12	24.69	0.0443	0.0502
450	29.31	24.56	0.0475	0.0619
500	29.36	24.59	0.0477	0.0627
550	29.61	24.59	0.0502	0.0731
600	29.68	24.57	0.0511	0.0771
650	29.79	24.42	0.0537	0.0894
700	29.89	24.36	0.0553	0.0977
750	30.08	23.96	0.0612	0.1324
800	30.27	23.90	0.0637	0.1493
850	30.52	23.57	0.0695	0.1939
900	30.95	23.29	0.0766	0.2596
950	31.07	22.90	0.0817	0.3150
1000	31.47	22.65	0.0882	0.3963
1050	31.71	22.34	0.0937	0.4752
1100	32.01	22.11	0.0990	0.5605
1150	32.14	21.82	0.1032	0.6349
1200	32.32	21.79	0.1053	0.6744
1300	32.58	21.47	0.1111	0.7921
1400	32.62	21.40	0.1122	0.8159
1500	32.83	21.16	0.1167	0.9180
1600	32.87	21.18	0.1169	0.9227
1800	32.81	21.10	0.1171	0.9275
2000	32.89	21.08	0.1181	0.9515

Table A72 : IFT between Lloydminster crude oil and 25 mM NaOH tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	30.88	24.14	0.0674	0.1769
100	30.43	24.82	0.0561	0.1020
150	30.36	24.94	0.0542	0.0920
200	30.29	24.91	0.0538	0.0899
250	30.42	24.99	0.0543	0.0925
300	30.40	24.98	0.0542	0.0920
350	30.56	24.89	0.0567	0.1053
400	31.33	24.11	0.0722	0.2174
450	31.89	23.31	0.0858	0.3648
500	32.18	22.92	0.0926	0.4586
550	32.37	22.94	0.0943	0.4844
600	32.41	22.85	0.0956	0.5047
650	32.46	22.72	0.0974	0.5337
700	32.65	22.65	0.1000	0.5776
800	32.75	22.58	0.1017	0.6076
900	32.91	22.59	0.1032	0.6349
1000	32.82	22.27	0.1055	0.6783
1200	32.96	22.12	0.1084	0.7357

Table A71 : IFT between Lloydminster crude oil and 25 mM NaOH tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
100	29.93	24.69	0.0524	0.0831
200	30.31	24.65	0.0566	0.1047
250	31.88	22.88	0.0900	0.4211
300	32.55	22.18	0.1037	0.6441
350	32.65	21.99	0.1066	0.6997
400	32.35	22.24	0.1011	0.5969
450	32.56	22.18	0.1038	0.6460
500	32.74	22.10	0.1064	0.6958
600	32.85	21.67	0.1118	0.8072
700	32.85	21.62	0.1123	0.8180
800	32.85	21.61	0.1124	0.8202

Table A73 : IFT between Lloydminster crude oil and  
25 mM Na2SiO3 tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	29.86	25.50	0.0436	0.0479
100	29.75	25.96	0.0379	0.0314
150	29.61	25.94	0.0367	0.0286
200	29.69	26.05	0.0364	0.0279
250	29.48	25.05	0.0443	0.0502
300	29.62	25.11	0.0451	0.0530
350	29.97	24.82	0.0515	0.0789
400	31.12	23.57	0.0755	0.2486
450	31.60	23.21	0.0839	0.3411
500	31.80	22.93	0.0887	0.4031
550	31.95	22.85	0.0910	0.4353
600	32.02	22.77	0.0925	0.4572
700	32.23	22.60	0.0963	0.5158
800	32.25	22.51	0.0974	0.5337
900	32.29	22.47	0.0982	0.5470
1000	32.44	22.44	0.1000	0.5776

Table A74 : IFT between Lloydminster crude oil and  
25 mM LiOH tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
75	30.23	24.87	0.0536	0.0889
100	30.18	24.88	0.0530	0.0860
150	30.10	24.90	0.0520	0.0812
200	30.75	24.48	0.0627	0.1424
250	32.44	22.76	0.0968	0.5239
300	32.86	22.37	0.1049	0.6668
350	33.12	22.00	0.1112	0.7942
400	33.47	21.79	0.1168	0.9204
450	33.20	21.94	0.1126	0.8246
500	33.58	21.69	0.1189	0.9709
550	33.63	21.64	0.1199	0.9956
600	33.61	21.61	0.1200	0.9981
700	33.69	21.66	0.1203	1.0056
800	33.70	21.65	0.1205	1.0106

Table A75 : IFT between Lloydminster crude oil and 25 mM KOH tested on the SDT

Time, s	Top	Bottom	Width, cm	IFT, mN/m
50	31.12	24.21	0.0691	0.1906
100	30.39	25.46	0.0493	0.0692
150	30.39	25.53	0.0486	0.0663
200	30.39	25.44	0.0495	0.0701
250	30.46	25.34	0.0512	0.0775
300	30.50	25.33	0.0517	0.0798
350	30.45	25.30	0.0515	0.0789
400	30.81	24.86	0.0595	0.1217
450	31.61	24.32	0.0729	0.2238
500	32.18	23.76	0.0842	0.3448
550	32.34	23.60	0.0874	0.3856
600	32.45	23.33	0.0912	0.4382
650	32.65	23.31	0.0934	0.4706
700	32.60	23.18	0.0942	0.4828
800	32.74	23.02	0.0972	0.5304
1000	33.10	22.71	0.1039	0.6479
1500	33.18	22.67	0.1051	0.6706

Table A76 : IFT between 20 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	30.96	24.61	0.0635	0.8241
100	31.05	24.37	0.0668	0.9594
200	30.91	24.61	0.0630	0.8048
250	30.84	24.70	0.0614	0.7450
300	30.65	24.91	0.0574	0.6087
350	30.40	25.17	0.0523	0.4604
400	30.09	25.47	0.0462	0.3174
450	29.96	25.46	0.0450	0.2933
500	29.95	25.67	0.0428	0.2523
550	29.92	25.61	0.0431	0.2577
600	29.94	25.72	0.0422	0.2419
650	29.99	25.65	0.0434	0.2631
700	30.01	25.68	0.0433	0.2613
750	30.05	25.58	0.0447	0.2875
800	30.10	25.62	0.0448	0.2894
900	30.10	25.46	0.0464	0.3215
1000	30.16	25.46	0.0470	0.3342
1200	30.13	25.33	0.0480	0.3559
1500	30.36	25.18	0.0518	0.4473
1800	31.31	24.79	0.0652	0.8921
2000	31.42	24.20	0.0722	1.2113
2200	32.31	23.29	0.0902	2.3619
2500	32.63	22.97	0.0966	2.9012

Table A77 : IFT between 40 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.4  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
40	31.18	24.58	0.0660	0.9234
100	31.16	24.54	0.0662	0.9318
200	30.98	24.52	0.0646	0.8659
250	30.95	24.58	0.0637	0.8302
300	30.75	24.70	0.0605	0.7113
350	30.67	24.86	0.0581	0.6299
400	30.43	25.06	0.0537	0.4974
450	30.18	25.42	0.0476	0.3464
500	29.58	25.93	0.0365	0.1562
550	29.24	26.57	0.0267	0.0611
600	29.23	26.54	0.0269	0.0625
650	29.64	26.00	0.0364	0.1549
700	30.98	25.10	0.0588	0.6530
750	31.87	23.86	0.0801	1.6507
800	33.17	22.70	0.1047	3.6864
850	33.19	22.74	0.1045	3.6653
900	33.17	22.72	0.1045	3.6653
1000	33.16	22.71	0.1045	3.6653

Table A78 : Transient IFT between 50 mM synthetic oil and 25 mM NaOH tested on the SDT, 0.5  $\mu$ L

Time, s	Top	Bottom	Width, cm	IFT, mN/m
30	30.88	24.37	0.0651	0.8849
100	30.88	24.45	0.0643	0.8527
200	30.69	24.45	0.0624	0.7793
300	30.49	24.80	0.0569	0.5909
350	30.17	24.90	0.0527	0.4695
400	29.74	25.32	0.0442	0.2770
450	29.22	25.98	0.0324	0.1091
500	28.84	26.44	0.0240	0.0443
550	29.15	25.89	0.0326	0.1111
600	29.87	25.45	0.0442	0.2770
650	30.08	24.52	0.0556	0.5513
700	30.99	23.96	0.0703	1.1144
750	31.45	23.50	0.0795	1.6116
800	31.68	23.25	0.0843	1.9216
900	31.86	23.19	0.0867	2.0904
1000	31.89	23.15	0.0874	2.1414
1200	31.56	23.44	0.0812	1.7173

## APPENDIX B

Figures B1 to B3 contain the IFT values versus time for the aqueous alkali, IFT versus flow for the same system and IFT versus flow for the lower concentrations of acidified oil and NaOH solutions, respectively. Tables B1 to B13 contain the measurement data and calculated IFT values for the tests performed on the DVT. The following list gives the figures which were plotted using the values from the given table:

Table B1	Figures 17 & B1	Table B2	Figures 17, 18, 23 & B1-B3
Table B3	Figures 17, 23 & B1-B2	Table B4	Figure 17
Table B5	Figures 17, 23 & B1-B2	Table B6	Figures 17, 23 & B1-B2
Table B7	Figures 9, 18 & B3	Table B8	Figures 18 & B3
Table B9	Figures 8 & 31	Table B10	Figures 8 & 31
Table B11	Figures 9 & 32	Table B12	Figure 8
Table B13	Figure 9		

The DVT values were calculated by the DVT controller using the following equation:

$$\gamma = V_{\text{drop}} (\rho_{\text{aq}} - \rho_{\text{oil}}) g / \pi d_{\text{capillary}}$$

where  $V_{\text{drop}}$  is calculated by the time, detected by the diodes, divided by the flow rate. The time detected is divided by the average number of drops tested to give the time for each drop which is in the end columns in each table.

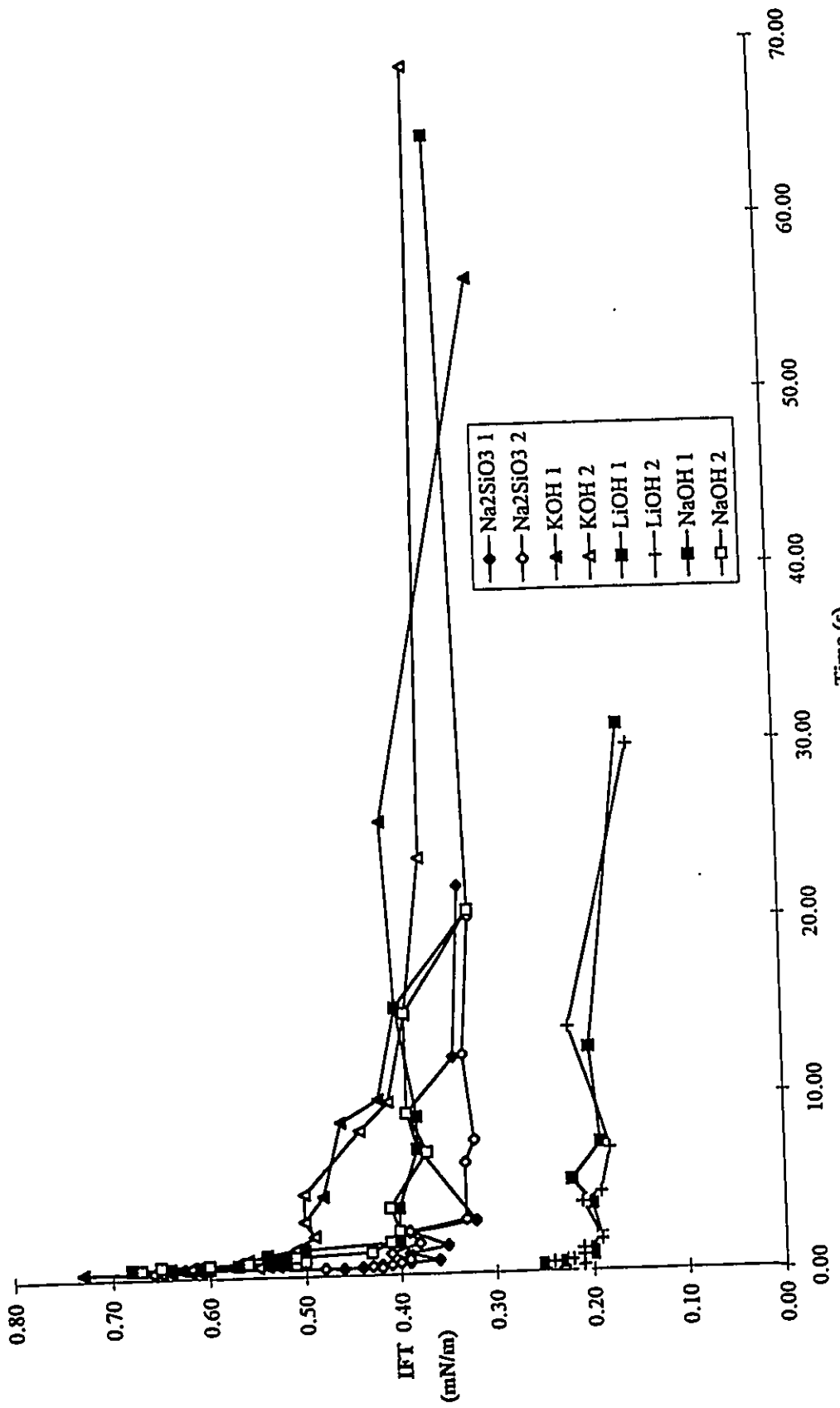


Figure B1: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT

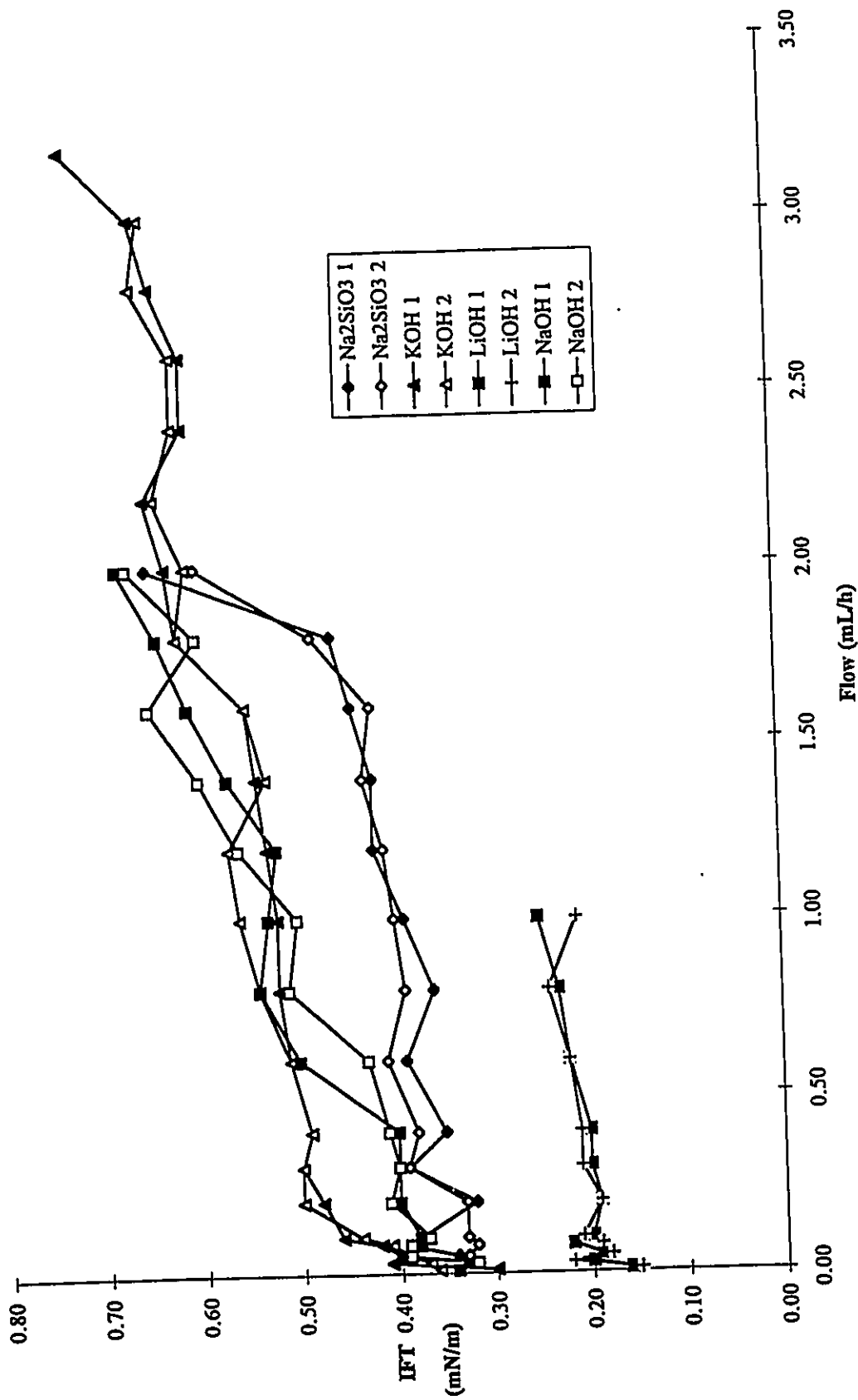


Figure B2: Dynamic IFT between 10 mM synthetic oil and 25 mM aqueous alkali tested on the DVT

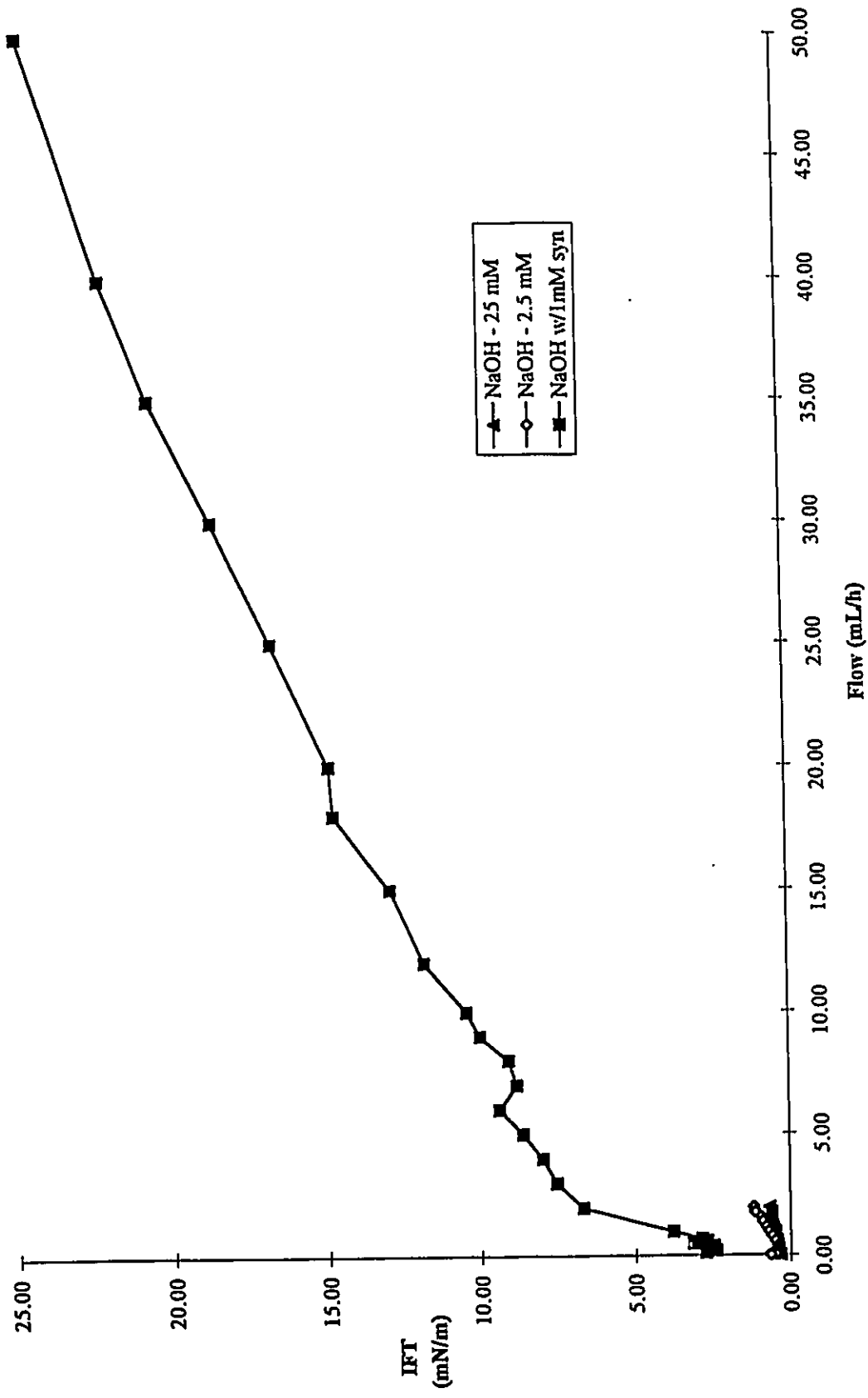


Figure B3: Dynamic IFT between 1 and 10 mM synthetic oil with 25 mM NaOH tested on the DVT

*Handwritten signature*

Table B1: Dynamic IFT between 10 mM synthetic oil with 25 mM NaOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
1.00	2.81	0.26	0.48	2.65	3.13	0.28	0.55	3.39	0.94
0.80	3.39	0.25	0.47	0.89	3.70	0.27	0.52	3.78	1.13
0.60	4.50	0.25	0.47	1.21	4.17	0.22	0.44	8.36	1.50
0.40	6.07	0.22	0.42	2.48	6.32	0.25	0.44	6.31	2.02
0.20	11.70	0.21	0.41	2.50	10.36	0.18	0.36	3.69	3.90
0.10	20.75	0.19	0.36	0.74	20.41	0.19	0.36	2.33	6.92
0.08	26.22	0.20	0.37	2.08	27.52	0.20	0.39	2.45	8.74
0.05	38.31	0.18	0.33	0.62	44.29	0.19	0.39	5.33	12.77
0.03	58.10	0.16	0.30	5.64	64.67	0.16	0.34	9.83	19.37

Table B2: Dynamic IFT between 10 mM synthetic oil with 25 mM NaOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
2.00	1.95	0.35	0.68	1.35	1.93	0.35	0.67	2.83	0.65
1.80	2.03	0.34	0.64	1.14	1.92	0.31	0.60	1.37	0.68
1.60	2.18	0.32	0.61	1.06	2.32	0.33	0.65	2.46	0.73
1.40	2.34	0.30	0.57	0.98	2.46	0.31	0.60	3.75	0.78
1.20	2.50	0.27	0.52	1.60	2.68	0.29	0.56	1.72	0.83
1.00	3.07	0.28	0.53	1.14	2.89	0.26	0.50	1.57	1.02
0.80	3.88	0.29	0.54	0.90	3.62	0.26	0.51	1.66	1.29
0.60	4.75	0.26	0.50	0.55	4.11	0.22	0.43	2.38	1.58
0.40	5.79	0.21	0.40	0.68	5.83	0.21	0.41	0.97	1.93
0.30	7.62	0.21	0.40	1.34	7.70	0.22	0.40	1.85	2.54
0.20	11.55	0.21	0.40	1.94	11.63	0.21	0.41	3.28	3.85
0.10	21.56	0.19	0.38	4.84	21.08	0.20	0.37	5.46	7.19
0.08	26.98	0.20	0.38	1.49	27.60	0.21	0.39	3.49	8.99
0.05	45.78	0.22	0.40	3.77	44.76	0.20	0.39	3.82	15.26
0.03	61.89	0.18	0.32	3.82	61.78	0.17	0.32	4.71	20.63
0.01	194.09	0.16	0.34	16.60					64.70

Table B3: Dynamic IFT between 10 mM synthetic oil with 25 mM LiOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
1.00	1.46	0.13	0.25	4.93	1.25	0.11	0.21	3.53	0.49
0.80	1.69	0.12	0.23	1.56	1.77	0.13	0.24	2.28	0.56
0.60	2.18	0.12	0.22	3.67	2.14	0.12	0.22	4.91	0.73
0.40	2.97	0.11	0.20	1.83	3.00	0.11	0.21	0.76	0.99
0.30	3.85	0.11	0.20	2.99	4.04	0.11	0.21	2.80	1.28
0.20	5.57	0.10	0.19	2.76	5.51	0.10	0.19	3.98	1.86
0.10	11.56	0.11	0.20	1.70	11.90	0.11	0.21	2.50	3.85
0.08	15.82	0.12	0.22	3.72	13.65	0.10	0.19	3.81	5.27
0.05	22.02	0.11	0.19	7.37	21.07	0.09	0.18	5.88	7.34
0.03	38.29	0.11	0.20	2.23	41.83	0.11	0.22	5.04	12.76
0.01	92.93	0.09	0.16	22.50	89.42	0.11	0.15	27.97	30.98

Table B4: Dynamic IFT between 10 mM synthetic oil with 25 mM LiOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
0.80	1.21	0.09	0.16	3.63	1.18	0.08	0.16	5.66	0.40
0.60	1.58	0.09	0.16	2.42	1.49	0.08	0.15	1.76	0.53
0.40	2.24	0.08	0.15	2.34	2.16	0.08	0.15	3.23	0.75
0.30	2.59	0.07	0.13	2.10	2.70	0.08	0.14	1.61	0.86
0.20	3.54	0.06	0.12	1.13	3.48	0.06	0.12	1.32	1.18
0.10	6.13	0.06	0.10	2.34	6.01	0.05	0.10	2.79	2.04
0.08	7.14	0.05	0.10	2.10	6.29	0.05	0.08	1.82	2.38
0.05	8.14	0.04	0.07	3.92	8.56	0.04	0.07	3.14	2.71
0.03	12.88	0.04	0.06	5.86	12.23	0.03	0.06	5.44	4.29
0.01	123.01	0.11	0.21	4.91	92.61	0.07	0.16	18.46	41.00

Table B5: Dynamic IFT between 10 mM synthetic oil with 25 mM Na<sub>2</sub>SiO<sub>3</sub> tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Time, s
2.00	1.86	0.34	0.65	6.55	1.72	0.31	0.60	2.23	0.62	0.57
1.80	1.49	0.26	0.46	6.81	1.54	0.26	0.48	1.71	0.50	0.51
1.60	1.60	0.25	0.44	6.24	1.52	0.22	0.42	1.53	0.53	0.51
1.40	1.75	0.23	0.42	3.47	1.77	0.23	0.43	3.44	0.58	0.59
1.20	2.00	0.22	0.42	2.32	1.99	0.22	0.41	2.20	0.67	0.66
1.00	2.26	0.21	0.39	0.77	2.29	0.21	0.40	0.38	0.75	0.76
0.80	2.59	0.19	0.36	2.35	2.80	0.21	0.39	1.08	0.86	0.93
0.60	3.76	0.21	0.39	4.25	3.87	0.22	0.41	1.75	1.25	1.29
0.40	5.08	0.18	0.35	4.04	5.47	0.20	0.38	1.51	1.69	1.82
0.30	7.51	0.21	0.39	1.97	7.50	0.21	0.39	1.59	2.50	2.50
0.30	7.35	0.21	0.39	4.18	7.49	0.21	0.39	2.16	2.45	2.50
0.20	9.15	0.16	0.32	4.17	9.39	0.18	0.33	2.08	3.05	3.13
0.10	21.80	0.22	0.38	7.25	19.03	0.18	0.33	1.00	7.27	6.34
0.08	27.68	0.20	0.39	3.53	22.82	0.18	0.32	4.45	9.23	7.61
0.05	37.00	0.18	0.34		37.37	0.17	0.33	4.84	12.33	12.46
0.03	65.97	0.17	0.33	8.61	60.71	0.18	0.32	5.41	21.99	20.24
0.01	172.76	0.58	0.92	20.69					57.59	0.00

Table B6: Dynamic IFT between 10 mM synthetic oil with 25 mM KOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
3.20	1.32	0.40	0.73	3.48	1.25	0.34	0.65	0.70	0.44
3.00	1.27	0.33	0.66	3.69	1.36	0.35	0.66	1.12	0.42
2.80	1.31	0.33	0.64	1.34	1.39	0.33	0.62	2.29	0.44
2.60	1.35	0.33	0.61	2.35	1.50	0.32	0.62	1.76	0.45
2.40	1.46	0.31	0.61	3.37	1.66	0.33	0.64	0.91	0.49
2.20	1.70	0.35	0.65	2.06	1.75	0.32	0.61	1.33	0.57
2.00	1.82	0.34	0.63	1.73	1.98	0.33	0.62	1.53	0.61
1.80	1.96	0.33	0.62	2.36	1.97	0.30	0.55	2.70	0.65
1.60	1.98	0.28	0.55	3.10	2.18	0.27	0.53	1.60	0.66
1.40	2.21	0.28	0.54	3.09	2.70	0.30	0.57	1.16	0.74
1.20	2.52	0.28	0.53	2.42	3.17	0.29	0.56	0.47	0.84
1.00	2.98	0.28	0.52	2.50	3.89	0.29	0.54	1.79	0.99
0.80	3.71	0.28	0.52	1.92	4.86	0.27	0.51	0.64	1.24
0.60	4.81	0.27	0.51	1.91	6.92	0.26	0.49	0.87	1.60
0.40	6.94	0.26	0.49	1.50	9.52	0.26	0.50	2.61	2.31
0.30	9.53	0.26	0.50	2.93	14.19	0.27	0.50	0.78	3.17
0.20	13.70	0.25	0.48	0.94	24.76	0.26	0.50	1.77	4.57
0.10	26.22	0.25	0.46	2.24	29.51	0.22	0.44	0.24	8.74
0.08	30.02	0.23	0.42	1.63	44.48	0.22	0.41	1.81	10.01
0.05	45.87	0.21	0.40	2.39	70.83	0.20	0.39	1.68	15.29
0.03	77.16	0.21	0.41	1.92	206.16	0.20	0.37	1.68	23.61
0.01	169.42	0.17	0.30	7.32		0.18	0.36	7.76	56.47

Table B7: Dynamic IFT between 10 mM synthetic oil with 2.5 mM NaOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
2.00	3.33	0.61	1.17	1.14	3.34	0.61	1.17	0.69	1.11
1.80	3.35	0.55	1.06	1.37	3.62	0.60	1.15	0.41	1.12
1.60	3.41	0.51	0.96	1.11	3.42	0.51	0.96	1.01	1.14
1.40	3.53	0.45	0.87	0.85	3.66	0.47	0.90	0.63	1.18
1.20	3.83	0.42	0.81	0.99	3.69	0.40	0.78	1.08	1.28
1.00	4.04	0.37	0.71	0.93	4.02	0.37	0.70	0.57	1.35
0.80	4.51	0.34	0.63	2.00	4.28	0.32	0.60	0.53	1.50
0.60	4.76	0.26	0.50	0.79	4.76	0.26	0.50	0.18	1.59
0.40	5.95	0.22	0.42	1.72	5.81	0.22	0.41	2.23	1.98
0.30	7.61	0.21	0.40	1.12	7.60	0.21	0.40	0.57	2.54
0.20	10.47	0.19	0.37	1.03	10.81	0.20	0.38	0.56	3.49
0.10	21.82	0.20	0.38	0.60	22.24	0.21	0.39	0.30	7.27
0.08	29.33	0.22	0.41	1.92	28.60	0.21	0.40	1.21	9.78
0.05	47.16	0.23	0.41	3.74	47.16	0.23	0.41	3.74	15.72
0.04	68.83	0.27	0.48	6.79	68.83	0.27	0.48	6.79	22.94
0.03	121.15	0.32	0.64	6.07	121.15	0.32	0.64	6.07	40.38

Table B8: Dynamic IFT between 1 mM synthetic oil with 25 mM NaOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
50.00	2.93	13.26	24.61	1.29	2.93	13.26	24.61	1.29	0.98
40.00	3.29	11.83	22.09	1.85	3.29	11.83	22.09	1.85	1.10
35.00	3.49	11.52	20.57	2.21	3.49	11.52	20.57	2.21	1.16
30.00	3.68	10.42	18.57	3.18	3.68	10.42	18.57	3.18	1.23
25.00	3.97	9.27	16.68	1.44	3.97	9.27	16.68	1.44	1.32
20.00	4.40	8.08	14.82	2.40	4.40	8.08	14.82	2.40	1.47
18.00	4.85	8.05	14.71	2.64	4.85	8.05	14.71	2.64	1.62
15.00	4.99	7.08	12.61	2.39	5.10	7.04	12.89	1.62	1.70
12.00	5.83	6.38	11.80	1.57	5.83	6.38	11.80	1.57	1.94
10.00	6.19	5.67	10.43	0.61	6.19	5.67	10.43	0.61	2.06
9.00	6.60	5.43	10.03	2.04	6.58	5.51	9.99	1.04	2.19
8.00	7.00	5.13	9.45	0.93	6.72	4.91	9.06	0.89	2.24
7.00	7.52	4.81	8.89	0.91	7.46	4.81	8.81	0.70	2.49
6.00	8.88	4.89	9.00	0.68	9.26	5.16	9.38	0.65	3.09
5.00	9.93	4.63	8.39	1.15	10.21	4.73	8.62	1.06	3.40
4.00	11.55	4.26	7.80	0.47	11.80	4.37	7.98	0.22	3.93
3.00	14.27	4.01	7.23	1.17	14.86	4.16	7.53	0.91	4.95
2.00	19.96	3.62	6.75	3.08	19.75	3.73	6.68	1.89	6.58
1.00	22.72	2.11	3.84	0.74	22.30	2.08	3.77	0.67	7.43
0.70	24.19	1.55	2.86	2.10	24.03	1.59	2.84	1.82	8.01
0.60	27.22	1.53	2.76	1.54	26.39	1.49	2.68	1.39	8.80
0.50	38.46	1.78	3.25	1.34	36.88	1.72	3.12	0.75	12.29
0.40	40.96	1.49	2.77	1.96	36.48	1.36	2.47	0.87	12.16
0.30	58.32	1.63	2.96	0.94	52.27	1.47	2.65	1.26	17.42
0.20	73.05	1.33	2.47	1.65	71.39	1.29	2.41	2.10	23.80
0.10	155.76	1.39	2.63	3.34	160.69	1.48	2.72	4.06	53.56

Table B9: Dynamic IFT between Lloydminster crude oil with 25 mM LiOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
0.30	1.53	0.06	0.03	33.45	1.54	0.03	0.03	45.88	0.51
0.20	4.49	0.09	0.06	5.20	4.71	0.09	0.06	3.02	1.50
0.15	6.44	0.09	0.06	2.38	6.48	0.09	0.06	2.64	2.15
0.10	9.23	0.09	0.06	1.63	9.16	0.09	0.06	5.50	3.08
0.08	11.25	0.08	0.06	0.81	11.85	0.09	0.06	2.24	3.75
0.05	18.00	0.08	0.06	2.39	16.53	0.08	0.05	7.48	6.00
0.03	28.30	0.07	0.06	6.75	28.83	0.08	0.06	1.09	9.43
0.02	33.77	0.06	0.04	1.72	46.31	0.08	0.06	4.71	11.26
0.01	85.73	0.08	0.06	6.92	80.44	0.06	0.05	14.63	28.58

Table B10: Dynamic IFT between Lloydminster crude oil with 25 mM NaOH tested on the DVT

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
0.09	4.84	0.04	0.03	3.43	4.92	0.04	0.03	8.05	1.61
0.08	5.53	0.04	0.03	6.00	5.00	0.04	0.03	3.49	1.84
0.07	5.78	0.04	0.03	5.12	5.80	0.04	0.03	7.42	1.93
0.06	6.71	0.04	0.03	3.75	7.00	0.04	0.03	4.10	2.24
0.05	9.22	0.04	0.03	6.13	8.98	0.04	0.03	5.12	3.07
0.04	10.36	0.03	0.03	8.04	10.35	0.04	0.03	5.82	3.45
0.03	13.32	0.04	0.03	11.91	13.63	0.04	0.03	15.29	4.44
0.02	16.88	0.03	0.02	2.55	16.16	0.03	0.02	4.30	5.63
0.02	27.08	0.03	0.03	9.80	24.99	0.03	0.03	8.77	9.03
0.01	34.72	0.03	0.02	17.36	39.77	0.03	0.03	28.16	11.57
0.01	50.06	0.04	0.03	10.32	48.98	0.03	0.03	11.71	16.69
0.01	60.86	0.03	0.02	23.11	-	0.03	0.03	-	20.29



Table B12: Dynamic IFT between Lloydminster crude oil with 25 mM LiOH tested on the DVT (leak)

Flow, mL/h	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ L	IFT, mN/m	Error, %	Time, s
0.35	2.21	0.21	0.15	0.00	2.31	0.20	0.15	0.00	0.74
0.35	2.51	0.22	0.16	0.00	2.40	0.21	0.15	0.00	0.84
0.30	2.78	0.23	0.17	0.00	3.08	0.26	0.18	0.00	0.93
0.30	3.00	0.25	0.18	0.00	2.77	0.23	0.16	0.00	1.00
0.30	2.86	0.24	0.17	0.00	3.22	0.27	0.19	0.00	0.95
0.30	3.24	0.27	0.19	0.00	3.32	0.27	0.20	0.00	1.08
0.25	3.18	0.22	0.16	0.00	3.23	0.23	0.16	0.00	1.06
0.25	3.55	0.25	0.18	0.00	3.89	0.27	0.19	0.00	1.18
0.25	3.86	0.27	0.19	0.00	4.65	0.32	0.23	0.00	1.29
0.20	11.51	0.64	0.46	0.00	8.65	0.48	0.34	0.00	3.84
0.20	9.78	0.54	0.39	0.00	7.72	0.43	0.31	0.00	3.26
0.20	11.30	0.63	0.45	0.00	9.51	0.53	0.38	0.00	3.77
0.20	10.38	0.58	0.41	0.00	7.66	0.42	0.31	0.00	3.46
0.19	11.25	0.59	0.43	0.00	10.23	0.54	0.39	0.00	3.75

Table B13: Dynamic IFT between Lloydminster crude oil with 2.5 mM NaOH tested on the DVT (leak)

Flow, mL/h	Time, s	Vol, $\mu$ l	IFT, mN/m	Error, %	Time, s	Vol, $\mu$ l	IFT, mN/m	Error, %	Time, s
3.00	9.85	8.19	5.89	0.00	-	-	-	0.00	3.28
2.50	11.06	7.66	5.52	2.00	11.66	6.46	4.65	0.00	3.69
1.60	12.32	5.46	3.93	1.80	12.04	6.01	4.32	0.00	4.11
1.40	12.46	4.84	3.48	0.00	12.49	4.85	3.49	0.00	4.15
1.20	12.05	4.01	2.88	0.00	13.80	4.59	3.30	0.00	4.02
1.00	16.22	4.50	3.24	0.00	14.31	3.97	2.86	0.00	5.41
0.80	15.74	3.49	2.51	0.00	15.86	3.52	2.53	0.00	5.25
0.70	17.78	3.45	2.48	0.00	15.90	3.10	2.23	0.00	5.93
0.60	16.58	2.76	1.99	0.00	18.04	3.00	2.16	0.00	5.53
0.55	17.81	2.72	1.96	0.00	18.39	2.81	2.02	0.00	5.94
0.50	19.79	2.74	1.98	0.00	19.77	2.74	1.97	0.00	6.60
0.45	21.53	2.69	1.94	0.00	19.60	2.45	1.76	0.00	7.18
0.40	27.51	3.05	2.20	0.00	26.27	2.92	2.10	0.00	9.17
0.35	28.85	2.80	2.02	0.00	30.90	3.00	2.16	0.00	9.62
0.30	36.30	3.02	2.18	0.00	36.22	3.02	2.17	0.00	12.10
0.25	54.37	3.77	2.72	0.00	40.24	2.79	2.01	0.00	18.12
0.20	62.31	3.46	2.49	0.00	53.73	2.98	2.15	0.00	20.77

## Appendix C

The momentum balance was performed to ensure that the kinetic energy due to the flow rate of the liquid was negligible in the energy balance of the liquid balanced at the capillary tip in the DVT method. The momentum balance was performed in the text and the sample calculations are included here for the equation determined as follows:

$$\text{IFT} = V_{\text{drop}} (\rho_{\text{alk}} - \rho_{\text{oil}}) g / (\pi d_{\text{tube}}) + 8 \rho_{\text{oil}} Q^2 / (\pi^2 d_{\text{tube}}^3) \quad (9)$$

where flow rate = F mL/h,  $d_{\text{tube}} = 2.54\text{E-}4$  m,  $g = 9.81$  m/s<sup>2</sup>,  $\rho_{\text{oil}} = 842$  kg/m<sup>3</sup>,  $\rho_{\text{NaOH}} = 998.2$  kg/m<sup>3</sup>.

$V_{\text{drop}} = \pi d_{\text{drop}}^3 / 6$  and  $Q = 2.778\text{E-}10$  F m<sup>3</sup>/s.

Thus, for 2 mL/h a volume of 0.352  $\mu\text{L}$  was obtained and the IFT was 0.68 mN/m according to the DVT instrument. According to the above equation:

$$\text{IFT} = 0.676 \text{ mN/m} + 0.0128 \text{ mN/m} = 0.689 \text{ mN/m}$$

which establishes that at this flow rate for this system of fluids the kinetic energy is negligible.

The DVT manual (1992) suggests that at flow rates over 1.5 mL/h, the kinetic energy may start playing a significant role but for the 25 mM aqueous alkali with flow rates 2 mL/h and below the kinetic energy was found to be negligible. For the lower concentration of NaOH (i.e. 2.5 mM) the flow rates as high as 50 mL/h had a kinetic energy effect of less than 1 %. Obviously the values should be checked for each systems of fluid used however, it appeared that for all of the measurements taken in this study, none of the flow rates used gave an IFT value which was significantly affected by the kinetic energy effect (i.e. never more than 1% difference).

## APPENDIX D

### Program in SAS to Perform Linear Regression

TITLE 'MINIMUM IFT PARAMETERS FOR DIMENSIONLESS VARIABLES';

DATA IFTFN; /\* V = Volume ratio, M = Molar ratio, D = Density ratio, G = IFT \*/

INPUT V M D G;

CARDS; /\* 30 mM NaOH, Na<sub>2</sub>SiO<sub>3</sub>, KOH, LiOH, 60 mM NaOH, all 2 Trials \*/

-2.21042	0.0791812	-0.06931	-1.0915	
-2.18642	0.0791812	-0.06931	-1.0655	
-2.56384	0.0791812	-0.06931	-0.7293	
-2.23508	0.0791812	-0.06931	-0.9176	
-2.31966	0.0791812	-0.06931	-0.6198	
-2.31966	0.0791812	-0.06931	-0.6269	
-2.35164	0.0791812	-0.06931	-0.4798	
-2.38616	0.0791812	-0.06931	-0.8274	
-2.35164	0.3802112	-0.06905	-1.2495	
-2.56225	0.3802112	-0.06905	-1.3354	
-2.42399	-0.397940	-0.07321	-1.0177	/* 10-60 mM NaOH, 2 Trials */
-2.35144	-0.397940	-0.07321	-1.0835	
-2.18663	-0.096910	-0.06936	-0.8416	
-2.38620	-0.096910	-0.06936	-0.5799	
-2.56229	0.0791812	-0.06931	-0.7951	
-2.86332	0.0791812	-0.06931	-0.8791	

-2.56229	0.2041200	-0.06920	-0.8573	
-2.56229	0.2041200	-0.06920	-1.2041	
-2.76641	0.3010300	-0.06910	-1.3536	
-2.68723	0.3010300	-0.06910	-1.1851	
-2.51114	0.3802112	-0.06905	-1.1068	
-2.62028	0.3802112	-0.06905	-1.1481	
-2.31925	-0.397940	-0.07321	-0.7945	/* 10-50 mM Na <sub>2</sub> SiO <sub>3</sub> , 1 Trial */
-2.28929	-0.096910	-0.06936	-0.6227	
-2.76641	0.0791812	-0.06931	-0.7261	
-2.76641	0.2041200	-0.06920	-0.6805	
-3.06744	0.3010300	-0.06910	-0.2580	
-2.56229	-0.397940	-0.07321	-1.0526	/* 10-60 mM Na <sub>2</sub> SiO <sub>3</sub> , 1 Trial */
-2.56229	-0.096910	-0.06936	-0.7158	
-2.98826	0.0791812	-0.06931	-0.2930	
-2.76641	0.2041200	-0.06920	-1.0491	
-2.86332	0.3010300	-0.06910	-1.2441	
-2.98826	0.3802112	-0.06905	-0.8216	
-2.86332	-0.397940	-0.07321	-1.0526	/* 10-20 mM Na <sub>2</sub> SiO <sub>3</sub> , 1 Trial */
-2.86332	-0.096910	-0.06936	-0.7158	
-2.98817	-0.397940	-0.07321	-1.3696	/* 10-60 mM LiOH, 1 Trial */
-2.98817	-0.096910	-0.06936	-1.0482	
-2.81217	0.0791812	-0.06931	-1.1192	

-2.98826	0.2041200	-0.06920	-1.1062	
-2.81217	0.3010300	-0.06910	-0.9948	
-2.76641	0.3802112	-0.06905	-0.8545	
-2.76641	-0.397940	-0.07321	-1.4672	/* 10-60 mM KOH, 1 Trial */
-2.76641	-0.096910	-0.06936	-0.9527	
-2.68723	0.0791812	-0.06931	-0.8982	
-2.76641	0.2041200	-0.06920	-0.9944	
-2.76641	0.3010300	-0.06910	-1.2140	
-2.76641	0.3802112	-0.06905	-1.1574	
-2.74938	-0.397940	-0.07321	-1.0353	/* 10 mM NaOH, 3 Trials */
-2.74938	-0.397940	-0.07321	-1.5229	
-2.74938	-0.397940	-0.07321	-1.2823	
-2.74938	-0.397940	-0.07321	-1.1818	/* 10 mM LiOH, 3 Trials */
-2.68723	-0.397940	-0.07321	-1.4737	
-2.52090	-0.397940	-0.07321	-0.9842	
-2.68723	-0.397940	-0.07321	-1.2823	/* 10 mM Na <sub>2</sub> SiO <sub>3</sub> , 3 Trials */
-2.63287	-0.397940	-0.07321	-1.0264	
-2.71719	-0.397940	-0.07321	-0.9352	
-2.68723	-0.397940	-0.07321	-1.1481	/* 10 mM KOH, 3 Trials */
-2.63287	-0.397940	-0.07321	-0.9884	
-2.50160	-0.397940	-0.07321	-1.1481 ;	

PROC REG DATA = IFTFN;      MODEL G = V M D;

# MINIMUM IFT PARAMETERS FOR DIMENSIONLESS VARIABLES

11:15 Monday, April 10, 1995

1 Model: MODEL1

Dependent Variable: G

## Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	3	1.32648	0.44216	8.285	0.0001
Error	55	2.93531	0.05337		
C Total	58	4.26179			
Root MSE		0.23102	R-square	0.3113	
Dep Mean		-0.98654	Adj R-sq	0.2737	
C.V.		-23.41689			

## Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob >  T
INTERCEP	1	11.834608	2.78517958	4.249	0.0001
V	1	0.013210	0.13841665	0.095	0.9243
M	1	-0.879144	0.26207989	-3.354	0.0014
D	1	181.648411	40.51709422	4.483	0.0001