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INTERFACIAL TENSION BEHAVIOUR OF PETROLEUM SULFONATE-LIGNOSULFONATE SOLUTIONS

by

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A thesis submitted to the School of Graduate Studies
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ABSTRACT

The interfacial tension (IFT) behaviour of mixed surfactant solutions of Petrostep 420, Marasperse C-21 and NaCl were studied to examine the suitability of using these mixtures in potential enhanced oil recovery operations.

Mixtures of 2.5 wt.% Petrostep 420, 1.0 wt.% Marasperse C-21 and 1.5 wt.% NaCl yielded low IFT's but the data reproducibility was poor and the phase behaviour was a problem. The concentrations of both surfactants were reduced to get a dilute surfactant mixture of 0.2 wt.% Petrostep 420, 0.048 wt.% Marasperse C-21 and 1.5 wt.% NaCl which still exhibited low IFT's and which also showed better data reproducibility and better phase stability.

A universal IFT versus equivalent alkane carbon number (EACN) did not result but the concept of the EACN at which the minimum IFT occurs (n_{MIN}) being fixed for a given surfactant formulation is valid for these mixed surfactant solutions. Also investigated were the effect of aging, length of pre-equilibration time, order of mixing effects and some surfactant mixtures using Petrostep 450, Petrostep 465 and other petroleum sulfonates.

CHAPTER 1

INTRODUCTION

A major worldwide problem throughout the recent past has been the energy crisis. In the early 1970's energy consumption was not a pressing concern and as a result petroleum products were not efficiently used. Although it has always been realized that the supply of oil is finite and eventually will be depleted, it took the 1973 OPEC oil price hikes to focus attention on the fact that at 1972 rates of consumption the day of oil shortages was rapidly approaching. Added to this rapidly inflating price were the cutbacks in supply to the industrialized nations, for either political or economical reasons, and these nations were in and out of periods of oil shortages throughout the 1970's. Out of necessity these oil-importing countries had to find ways to increase the supply of oil until the technology was developed for the ultimate shift away from a petroleum-based energy supply.

The easiest way to extend the supply of oil to essential services was to adopt a policy of conservation. Since it takes time for people to change their ways it took a while, and continued price hikes, for conservation to take hold. Beyond this a route to increase the available oil was to discover new wells or make better use of existing ones. The escalated cost of oil meant that more remote areas could be explored

and also that less desirable deposits such as heavy oils and tar sands could be developed. As an alternative to finding new oil wells, existing wells may be more efficiently utilized to recover a greater percentage of the contained oil. This is known as enhanced oil recovery (EOR) and is the basis for this research.

One means of enhancing oil recoveries is to use a surfactant flood to displace additional oil. Research in this area using petroleum sulfonates is widespread. The unique feature about this work and previous ones at the University of Ottawa is that lignosulfonates are used as a cheaper substitute for part of the petroleum sulfonate and at the same time provide a synergistic interfacial tension (IFT) lowering effect.

In this research the primary areas of investigation involved the phase behaviour of these surfactant solutions, the variation in IFT upon reducing the concentrations of petroleum sulfonate and lignosulfonate and the applicability of empirical relations, published elsewhere, to these mixed surfactant solutions. Secondary factors which were examined in less detail were the effects of aging of the surfactant solutions, the effect of varying the concentrations of the components making up the solutions and the effects of using other types of petroleum sulfonates.

CHAPTER 2

LITERATURE REVIEW

2.1 Stages of Oil Production

2.1.1 Primary Recovery

Crude oils usually reside within the pores of a sedimentary rock rather than in underground pools as some representations depict. Therefore to recover oil from the ground involves displacing it from this porous network instead of simply pumping the oil up out of a pool.

The oil-containing rock reservoir is at a pressure greater than atmospheric due to the overburden on top of it. When a well is first drilled this excess pressure will cause some of the oil to flow naturally due to the release of dissolved gases in the crude and due to the slight liquid expansion caused by the release of the internal pressure. This is called primary recovery. The oil recovered in this stage may vary from a few percent to as high as 25% according to Doscher [16].

2.1.2 Secondary Recovery

As the demand for oil increased it became profitable to go back and recover additional oil from wells which had ceased to produce due to natural forces. This second stage of oil recovery was accomplished by means of a waterflood.

In this process, water is pumped down into a well where it will occupy some of the oil-containing capillaries thereby displacing this oil. In principle, if the entire rock formation could be waterflooded and if all of the capillaries could be swept then all of the oil would be recovered in this stage. However as Herbeck et al [20] point out neither of these idealizations occurs.

First of all the entire rock formation cannot be subjected to the waterflood. If the 5-spot pattern represented in Figure 2-1 is used then only a portion of the reservoir is contacted by the waterflood with the outside areas remaining untouched. Hence additional oil will only be recovered from the central region.

Secondly, in the region that is contacted by the waterflood not all of the oil-containing capillaries will be swept. This is depicted in Figure 2-2. In this figure two parallel capillaries are shown, each containing oil initially. One of these capillaries may offer less resistance to the oncoming waterflood and so the water will move through this capillary (upper one in Figure 2-2) faster than it moves through the lower capillary. This is known as fingering. Once the water reaches the point at which the two channels come together again recovery of oil from the lower capillary will cease and this slug of oil becomes trapped. These stranded oil-containing capillaries are often called oil ganglia. Doscher [16] reports that a further 15% of the

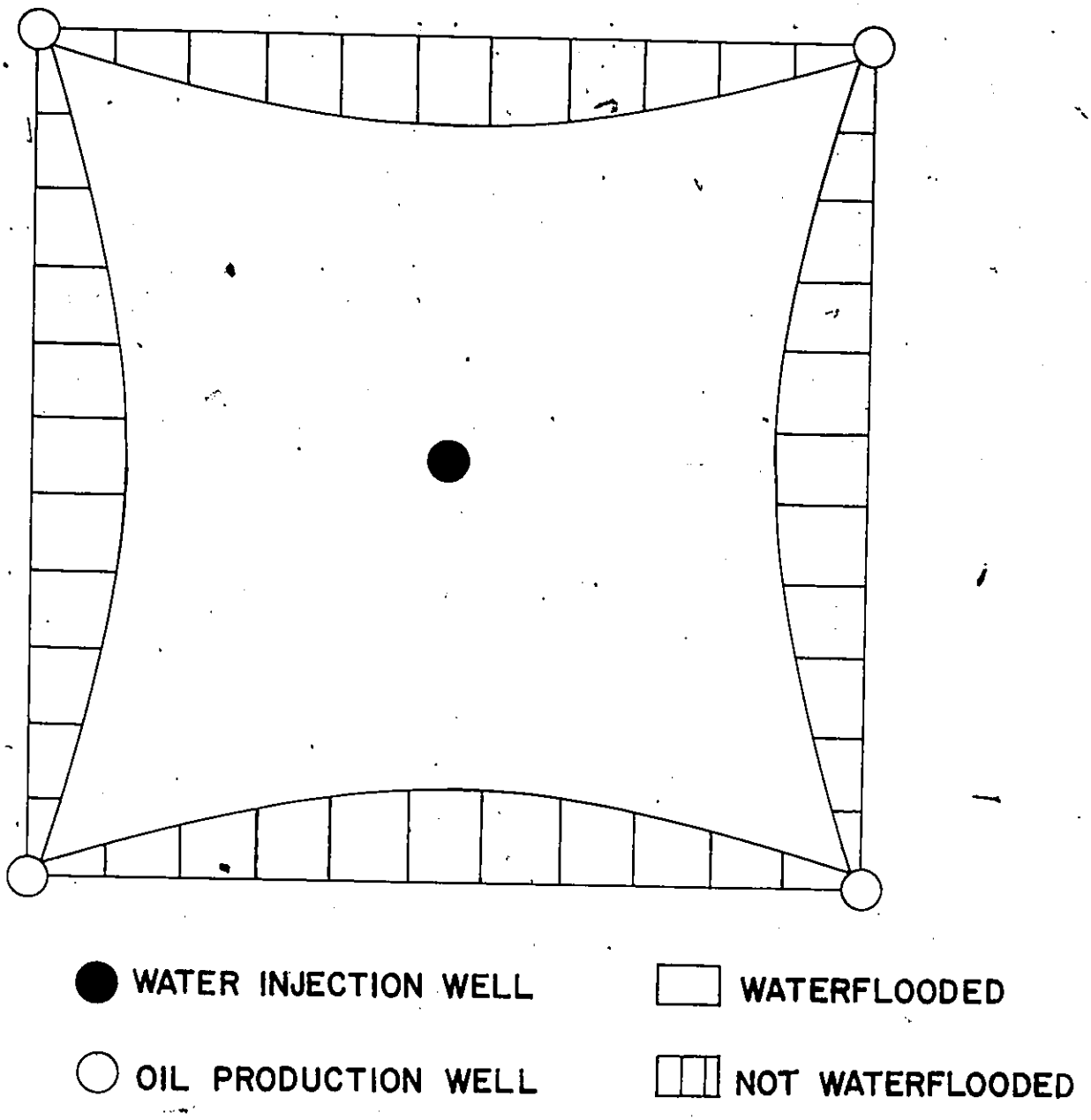

Figure 2-1: Overhead Representation of 5-Spot Waterflood Scheme [20].

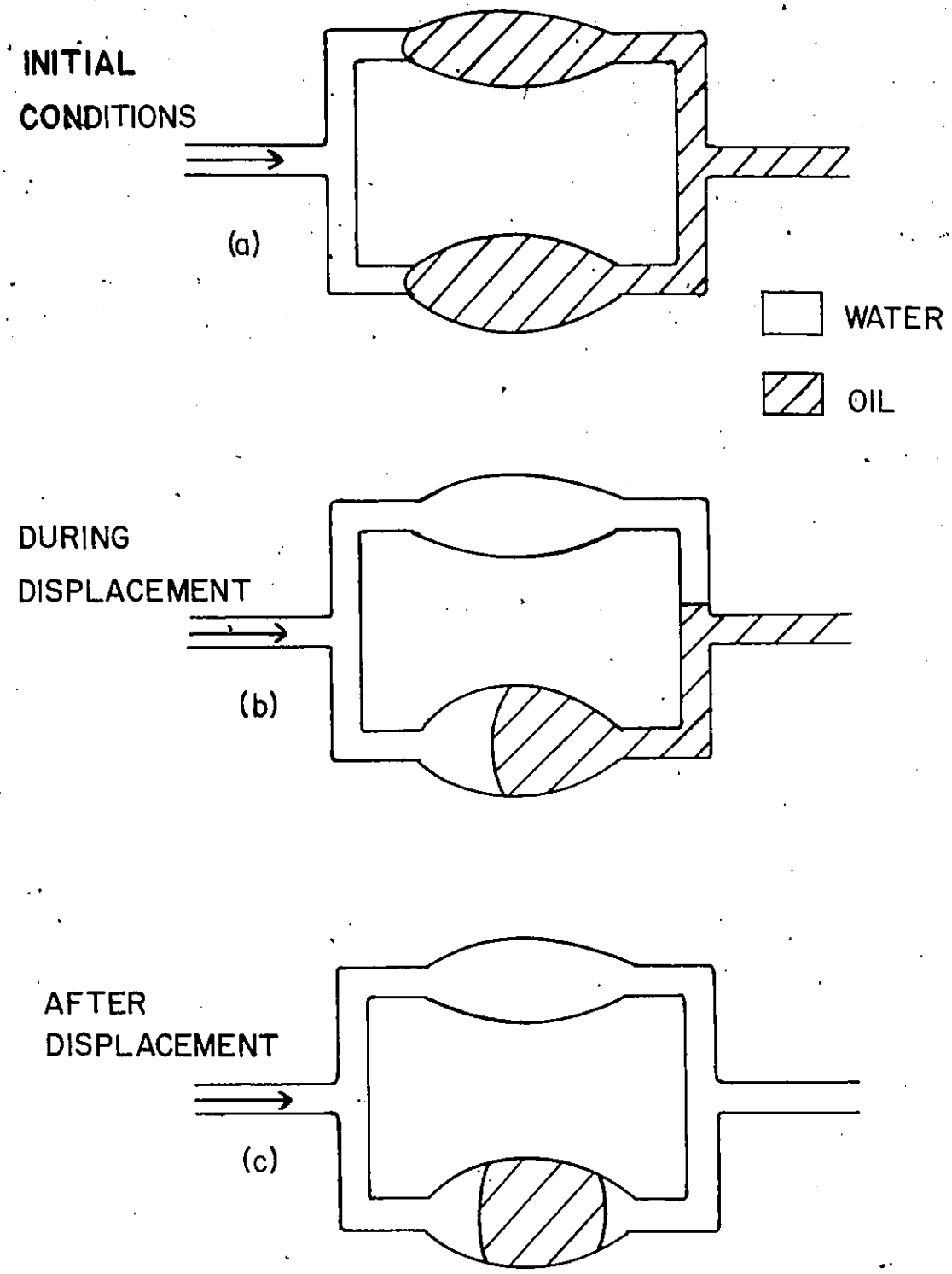

Figure 2-2: Mechanism of Stranding of an Oil-Containing Capillary [20].

total original oil is typically recovered during a waterflood.

2.1.3 Tertiary Recovery

Until recently it has not been economically attractive to go back and process these oil wells a third time. With the ever-rising cost of oil, however, such tertiary schemes are becoming viable. There is ample incentive to make these tertiary or enhanced oil recovery operations possible considering that 60% or more of the total original oil still remains in the ground after the primary and secondary stages of recovery. Even an increase in efficiency of a few percent becomes significant when one speaks in terms of the hundreds of billions of barrels that cannot be produced by conventional techniques. Morgan et al [27] estimate that a million barrels per day by 1990, or one-eighth of the present U.S. production, is quite possible using EOR processes.

Enhanced oil recovery can be achieved by several routes. One method is to increase the temperature of the oil by in situ combustion or steam injection to reduce the viscosity of the oil thereby making it easier to displace. A second approach is to use water-soluble polymers in the drive water. This thickened water will have a higher viscosity than water alone and will finger less, so that more of the oil-containing capillaries get swept. A third technique is to use water-soluble surfactants. The surfactant solution then leads to increased oil yields and this is the process upon which the

present research is based. Quite often some of these procedures are used in combination. For example, a surfactant solution is usually followed by a polymer solution to take advantage of both methods of producing additional oil.

2.2 Surfactant Flooding

This process is the tertiary scheme which is relevant to this work so it will be expanded upon. During a surfactant flood additional oil may be recovered through one of two mechanisms. The oil may be displaced from the rock capillary and remain as a separate phase, or the oil may be solubilized into the micelles of the surfactant leading to a single phase. This solubilization effect is likely responsible for considerably less oil recovery than the displacement mechanism.

Morgan et al [27] represent the displacement of the oil as in Figure 2-2(c) in which a stranded oil ganglion from a previous waterflood is shown. The pressure difference necessary to displace this oil is given by the equation

$$\Delta P = P_1 - P_2 = 2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \qquad (2\text{-}1)$$

where ΔP is the pressure difference, γ is the interfacial tension and R_1 and R_2 are the radii of curvature of the ends of the oil ganglion.

Starting with this equation and also taking into consideration the viscosity of the drive water, the flow rate of the water and the porosity of the rock formation Melrose and Brandner [24] have substituted typical values for these parameters to estimate that γ must be reduced from its usual value of 10 to 30 mN/m to around 10^{-3} mN/m to recover significant quantities of additional oil. The objective therefore is to find surfactants which are capable of exhibiting these ultralow interfacial tensions.

Once some of the oil has been displaced creating a mobile oil bank, this oil itself aids in additional recovery. When the mobile bank contacts further oil the IFT between the phases is zero and so it becomes easier for these subsequent ganglia to be displaced.

2.3 Surfactants which Lead to Ultralow Tensions

A wide range of commercial petroleum sulfonates have been used to generate the necessarily low IFT's [5,6,8,10,11,17,22,23,26,27,31,33,34]. These commercial petroleum sulfonates are made by sulfonation of a fraction from the petroleum refining process. They are made up of a range of different molecular weight species and usually contain some unconverted oil. These petroleum sulfonates are assigned average equivalent weights, often of the order of 400, but

the range of equivalent weights may be quite large. Cayias et al [10] report that a petroleum sulfonate of average equivalent weight 415, Witco 10-80, could be separated to give fractions with equivalent weights ranging from 321 to 511. As the equivalent weight increases the solubility in water decreases.

Low IFT's have also been reported for pure surfactant solutions [15,29,33,34]. In these papers isomerically pure surfactants were synthesized. The particular isomer structure was found to be important in determining the extent of IFT lowering [15].

2.4 Empirical Scaling Rules Relating IFT and Organic Composition

A group of researchers, mainly from the University of Texas at Austin, have published a series of papers [6,7,8,10, 15,26,27,31,33,34] which have presented trends noticed in the IFT behaviour of petroleum sulfonates.

2.4.1 Equivalent Alkane Carbon Number (EACN)

Similarities in the IFT curves of a surfactant versus homologous series of alkanes, alkylbenzenes and alkylcyclohexanes shown in Figure 2-3 led to the development of the concept of EACN by Cayias et al [8]. Some examples of organic compounds and their EACN's are shown in Table 2-1. For the

Table 2-1

EACN's of Various Organic Compounds [8]

Organic Compound	EACN
benzene	0
toluene	1
o-, m- or p-xylene	2
isopropylbenzene	3
cyclopentane	3
cyclopentylbenzene	3
cyclohexane	4
1,4-diethylbenzene	4
pentane	5
1-t-butyl-4-methylbenzene	5
cyclooctane	5
hexane	6
heptane	7
cyclopentylcyclohexane	7
octane	8
2-methylheptane	8
2,5-dimethylhexane	8
2,2,4-trimethylpentane	8
pentylcyclopentane	8
nonane	9
decane	10
undecane	11
dodecane	12
hexadecane	16

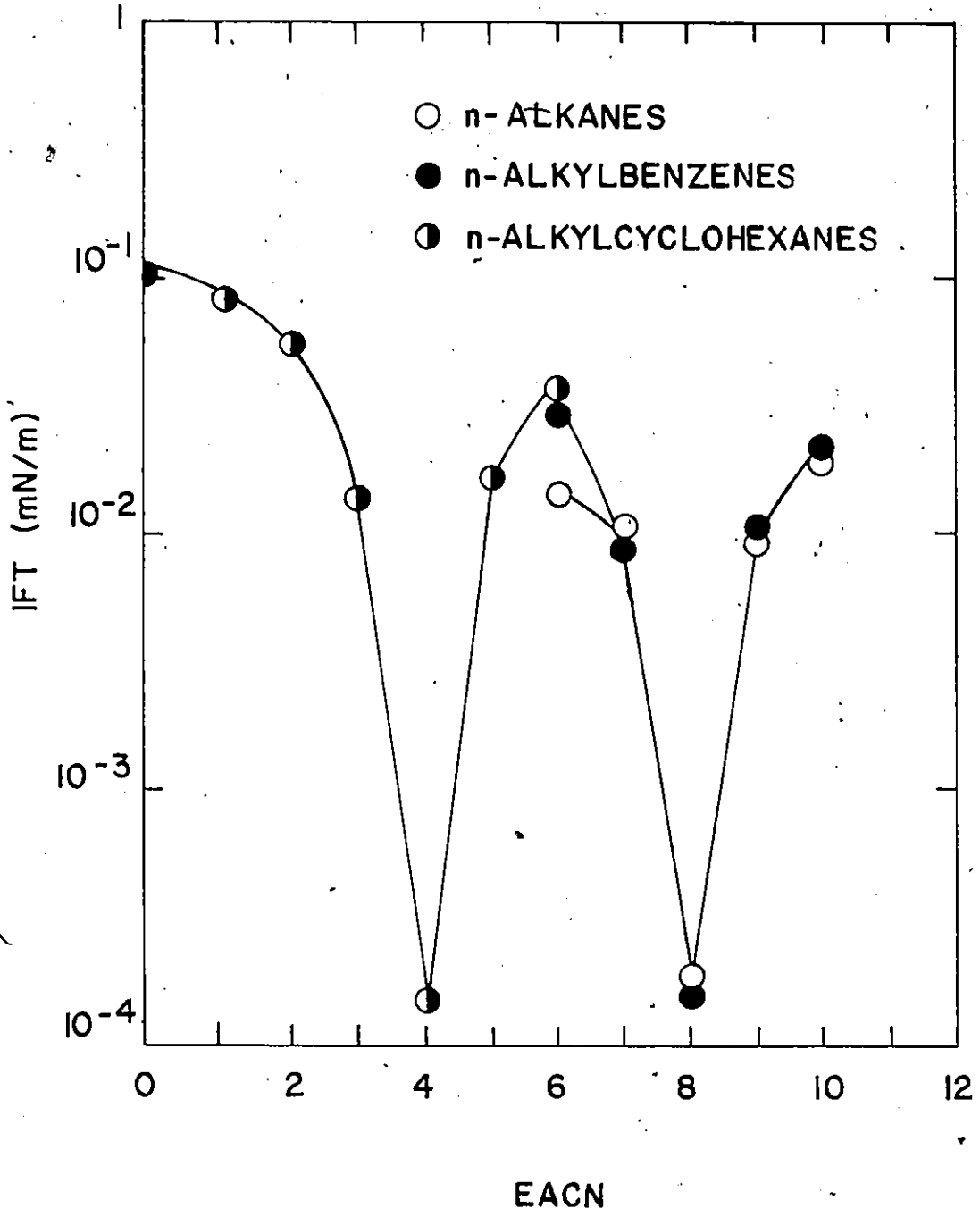

Figure 2-3: IFT's of Three Homologous Series of Hydrocarbons against 0.2% Witco 10-80 and 1.0% NaCl [10].

alkanes the EACN is defined as the number of carbon atoms in the molecule. The IFT's of the homologous series of alkylbenzenes were similar to those for the alkanes if the EACN of an alkylbenzene was taken to be the number of aliphatic carbon atoms. On this basis the EACN of benzene was defined to be 0 *. In order to get the curve for the alkylcyclohexanes to match the other two the EACN of cyclohexane was defined to be 4 **. The EACN of hexylcyclohexane would then be 10 and the IFT behaviour against hexylcyclohexane would be similar to that against decane or decylbenzene. Note that organic species of the same EACN are said to behave similarily, but they do not behave exactly the same. This means that the absolute magnitude of the IFT's may differ from one homologous series to another, but the minimum IFT would occur at the same EACN in each case. For example, heptane may exhibit a lower IFT against a particular surfactant than hexane or octane. Based on the EACN concept heptylbenzene and propylcyclohexane should also exhibit lower IFT's than their respective smaller and larger homologues.

The EACN of a binary or more complex mixture was found to obey the simple scaling equation

---

* the EACN of benzene has been assigned values of -1 and +1 as well to fit the empirical relations

** the EACN of cyclohexane has in some cases been taken to be 3

$$EACN = \Sigma x_i (EACN)_i \qquad (2\text{-}2)$$

where EACN is the overall value, x_i the mole fraction of the i^{th} component and $(EACN)_i$ its EACN [8]. Using this equation an equimolar mixture of hexane and heptane would have an EACN of 6.5.

All isomers of a particular organic molecule were found to have the same EACN, so that n-octane, iso-octane and all other octanes have EACN's of 8. Other special cases such as cyclopentane were assigned EACN's based on the validity of Equation (2-2) [8]. Values of EACN were assigned to complex crude oils again based on the validity of other empirical relations developed by Cayias et al [8]. This was done without knowing the entire composition of the oil and using Equation (2-2), since this is close to impossible. (Observe that Rossini [30] had isolated 175 components in a single crude oil with more to be found.)

2.4.2 EACN of Minimum Interfacial Tension - n_{MIN}

As mentioned, IFT's within one homologous series followed those in another based on the EACN concept. Likewise binary organic mixtures of the same EACN behaved similarily. The outcome of this was that although the absolute value of the minimum IFT might depend on the make-up of the organic the location of the minimum with respect to EACN was constant [6] for a particular surfactant formulation.

For example, if the minimum IFT was found to occur against heptane when using the alkanes, then the minimum IFT against binary mixtures of pentane and decane would occur for that mixture which had an EACN equivalent to heptane (ie. 7).

Just as organics were assigned EACN's, surfactants were assigned values of n_{MIN}, where n_{MIN} is defined as the EACN at which the minimum IFT results. Wade et al [33] developed a similar scaling equation to that for EACN. This equation can be used to calculate the n_{MIN} value for a mixture of surfactants.

$$n_{MIN} = \Sigma x_i (n_{MIN})_i \qquad (2\text{-}3)$$

where n_{MIN} represents the overall value, x_i the mole fraction and $(n_{MIN})_i$ the n_{MIN} of the i^{th} component.

As for the case of the EACN of organic species the n_{MIN} values for a range of surfactants were either experimentally determined or calculated on the basis of Equation (2-3) [33].

2.5 Dependence of n_{MIN} on System Parameters

On the basis of Equation (2-1) it is evident that the lower the IFT, the easier it will be to displace oil ganglia. In order to get the lowest possible IFT the n_{MIN} of the

surfactant should match the EACN of the oil. Therefore it is useful to know how n_{MIN} will change as the system parameters are altered.

Morgan et al [26] have summarized the effects of several variables with the results reproduced in Table 2-2. Based on the information in Table 2-2 it is noticed that there are several ways of shifting n_{MIN} to higher or lower values as the occasion warrants.

Shifting n_{MIN} and optimizing the low IFT's are two different things. For example, increasing the salt concentration may shift n_{MIN} to higher values, but it may also lead to an increase in the magnitude of the IFT. Given a crude oil of a determined EACN one would like the n_{MIN} of the surfactant to correspond to this EACN and at the same time have an optimized system to result in low IFT's. These may be opposing forces. The salt concentration, for one, has an optimum value so that concentrations higher and lower than this optimum value lead to higher IFT's, all else constant.

2.6 Low Interfacial Tensions using Lignosulfonates

Several researchers have reported the results of the initial studies at the University of Ottawa to use lignosulfonates as cheaper substitutes for petroleum sulfonates in EOR operations [3,4,13,14,28]. The use of lignosulfonates is attractive because they are cheaper and also because they

Table 2-2

Effect of System Parameters on n_{MIN} [26].

Variable Increased	Effect on n_{MIN}
surfactant molecular weight	increases
branching of surfactant alkyl structure	increases
electrolyte concentration	increases
concentration of pure surfactant	no change
concentration of surfactant mixture	decreases
temperature	decreases
age of pure surfactant	no change
age of surfactant mixture	decreases

are waste by-products of the sulfite pulp and paper process which must be economically used or else disposed of.

The use of petroleum sulfonate plus lignosulfonate was found to have a synergistic effect on the lowering of IFT. A phase stability limit between certain petroleum sulfonates and lignosulfonates was determined by Chiwetelu [13].

The only other discovered mention of using lignosulfonates for EOR operations was in a patent obtained by Kalfoglou [21]. In the patent Kalfoglou suggests the use of lignosulfonates to serve as sacrificial agents to be adsorbed onto the rock matrix thereby reducing the adsorption losses of the more expensive petroleum sulfonates. Kalfoglou does not discuss the usefulness of lignosulfonates for improving the IFT behaviour of these surfactant solutions.

2.7 Objectives of the Research

The objectives of this research were as follows:

(i) to test the mixed surfactant systems of petroleum sulfonate plus lignosulfonate to see if the empirical relations found by Cayias et al, which were developed for petroleum sulfonates alone, still apply.

(ii) to screen various surfactant types to see which show potential for producing low IFT's.

(iii) to study the phase behaviour accompanying the various surfactant formulations.

(iv) to take a first step towards optimizing a useful system from an economical point of view.

(v) to generally add to the basic knowledge of these mixed surfactant systems.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The petroleum sulfonate used in most of the experimental work was Petrostep 420 [R] (P420) manufactured by Stepan Chemical Company. Unless otherwise specified the general term petroleum sulfonate refers to this particular product. In physical terms Petrostep 420 is a viscous, tarry semi-solid material. It does not dissolve rapidly in water, but aqueous solutions can be made by successive leaching with hot water. The other petroleum sulfonates manufactured by Stepan which were used were Petrostep 450 and Petrostep 465. The provided analysis of each surfactant is shown in Table 3-1.

The other surfactants which were briefly used were sodium lauryl sulfate manufactured by Fisher; Alkanol 189-S [R], Petrowet R [R] and Petrowet RH manufactured by DuPont; and Petrosul 545 [R], Petrosul 742 and Petrosul 744CL manufactured by Penreco Inc.

The lignosulfonate used was Marasperse C-21 [R] (C-21) manufactured by American Can Company. It was received in the form of a dry, brown powder which dissolves quite readily in water. Its molecular weight is only broadly defined as

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a superscript R indicates a patented trademark

Table 3-1

Properties of Petroleum Sulfonates.

Property	Petrostep 420	Petrostep 450	Petrostep 465
equivalent weight	420	450	465
sulfonate	59.1% *	62.2%	57.5%
free oil	17.3%	15.2%	14.5%
water	19.5%	18.5%	24.9%
inorganic salt	4.1%	4.1%	2.8%

* all percentages are weight percent

Table 3-2

Chemical Properties of Marasperse C-21 (1).

Property	Value
pH (3% solution)	7.7
total sulfur as S	6.1% *
sulfate sulfur as S	0.4%
Ca	4.0%
Na	2.1%
reducing sugars	1.3%
methoxyl	8.8%

* all percentages are weight percent

Table 3-3

Manufacturer and Purity of Organic Compounds.

Hydrocarbon	Manufacturer	Grade
toluene	Fisher	99 mol%
p-xylene	J.T. Baker	"Baker"
cyclohexane	"	"Baker analyzed"
pentane	"	"Baker"
hexane	Phillips Petroleum	99 mol%
heptane	Eastman Chemicals	99%
octane	Matheson, Coleman, Bell	99 mol% +
nonane	"	"
decane	Eastman Chemicals	technical
undecane	Matheson, Coleman, Bell	99 mol% +
dodecane	Eastman Chemicals	99%
hexadecane	Matheson, Coleman, Bell	99 mol% +

being between 1000 and 50,000, and its structure is related to that of lignin. Some other properties are shown in Table 3-2. The structure of a section of a lignosulfonate molecule was reproduced by Bansal et al [4].

Whenever possible the organic component was of very high purity. These high purity liquids are usually designated as chromatoquality or 99%+ purity. The manufacturers and grades are shown in Table 3-3.

3.2 Preparation of Solutions

The first step was to make stock solutions of the petroleum sulfonate, lignosulfonate and salt. The desired mixed surfactant was made by mixing these concentrated stock solutions and diluting with water. For reasons to be mentioned later the NaCl was always added last. All dilutions were done on a weight basis so that throughout this work the units of concentration are weight percent. When a mixed organic solution was made it was also prepared on a weight basis keeping in mind that conversions to moles had to be done to calculate EACN's.

To prepare a sample for IFT measurement about 10 ml. of the mixed surfactant was poured into a test tube. About 2 ml. of the organic was then poured on top of the surfactant causing as little disturbance as possible. The test tube was capped and left to equilibrate, usually overnight.

3.3 Loading of Sample for IFT Measurement

The IFT measurements were performed on a Spinning Drop Interfacial Tensiometer. The design and mechanics of this apparatus are described elsewhere [9,13,19]. The difficult steps in the measurement were the filling of the capillary tube and the placement of the cap. The entire procedure will be described in a stepwise manner. There are some deviations from the procedure detailed in the Reference Manual [19] which are pointed out in the description. The procedure was as follows.

(i) The cap assembly was put together first so that the filling of the capillary tube was not interrupted. The O-ring and rubber septum were removed from the distilled water in which they were stored, dried, and placed in the cap. The septum was not pushed fully into the cap but only far enough to make it level with the O-ring. The final positioning would be accomplished when the capillary tube was inserted.

(ii) The capillary tube was flushed with some of the surfactant to be used. This pre-flush removed traces of water remaining from the previous washing and it would also have minimized any possible effects of surfactant adsorption on the glass by serving as a sacrificial agent. This means that some of the adsorption sites might become occupied during the pre-flush and not when the IFT measurement was being made.

(iii) The Scientific Glass Engineering microlitre syringe used for introduction of the organic droplet was flushed several times with the organic solution to be used to rid the syringe of traces of acetone from the previous washing.

(iv) A second sample of surfactant was withdrawn and the capillary tube filled by inserting the needle to the bottom and slowly removing it as the tube became filled with surfactant. A standard sized syringe and needle were sufficient for this operation. The tube was filled to within a few millimetres of the opening.

(v) A droplet of organic was discharged from the syringe just prior to the introduction into the capillary tube to rid the tip of air bubbles which could have formed due to evaporation. The tip was then dried to prevent "tailings" from being introduced and the needle was quickly inserted into the tube. A small droplet of organic was then expelled from the syringe near the centre of the capillary tube.

(vi) Sometimes an air bubble would be contained in the organic droplet even though the tip had been purged of air just prior to placing the needle into the capillary tube. This was most common with the highly volatile organic compounds. This air bubble was not desirable because it could have restricted the natural elongation of the organic droplet or distorted its shape. It was removed by withdrawing the needle, with the droplet still adhering to it, as far as the surfactant-air interface. The organic droplet could

then be removed without further exposing the tip to the air. The needle was then positioned in the centre of the tube again and another droplet expelled, this time usually air-free. This procedure was not mentioned in the manual.

(vii) The organic droplet usually adhered to the needle unless the drop was very large. It was detached by rapidly withdrawing the syringe.

(viii) Additional surfactant was added to the capillary tube to fill up the remaining few millimetres and to leave a pendant drop of excess surfactant.

(ix) Placing the cap on the tube was another stage which could cause problems. The capillary tube was held horizontally at this stage rather than vertically as suggested in the manual. With the tube held horizontally the organic droplet did not migrate toward the sealed end and equally important the tendency for air to enter would be diminished compared to holding the tube vertically. The capillary tube was then placed in the cap, making contact with the septum and pushing it into the end of the cap.

(x) Once the cap was properly in place the entire assembly was screwed into the rotating section of the spinning drop apparatus.

(xi) The spinning rate was adjusted and the sample left to spin.

(xii) The apparatus was levelled throughout the course of the

experiment to keep the organic droplet off of the tube ends.

(xiii) Measurements of the drop width were typically made every half hour. The experiments were continued until the drop width was constant to ±2% for 30 minutes or longer. The temperature was not controlled but was usually 26±1°C due to the heat generated by the apparatus.

(xiv) After an experiment the assembly was withdrawn from the rotating sleeve. The cap was removed and the O-ring and septum taken out. All three pieces were rinsed with distilled water and the O-ring and septum were placed in distilled water until the next experiment. (If a Teflon cap were being used it too could be stored in distilled water.)

(xv) The microsyringe was simply washed with acetone rather than hexane plus acetone as suggested in the manual. Hexane was not necessary because all of the hydrocarbons used were soluble in acetone. Only if a crude oil were used would a hexane wash be necessary.

(xvi) For the capillary tube and large syringe a water-acetone-water wash was sufficient. The capillary tube was periodically washed with hexane when air bubble problems became persistent. The capillary tube would not be visibly dirty but tiny air bubbles kept appearing in the surfactant solution. These problems were usually eliminated by a water-acetone-hexane-acetone-water wash.

3.4 Density Measurements

The densities of the organic and aqueous phases were measured on a Precision Density Meter model DMA 02C at 25.0±0.2°C. The procedure described in the instrument manual was followed using dry air and distilled water as the calibration standards.

After the initial set of experiments further density determinations were found to be unnecessary due to the following simplifications. Firstly, the time allowed for pre-equilibration did not alter the organic or surfactant densities so that the densities before and after pre-equilibration were the same. Secondly, the surfactant density was essentially equal to that of the corresponding brine solution. Since the surfactants added little to the overall density a constant surfactant density could be assumed throughout. Thirdly, for binary organics the combined density could be accurately calculated based on the assumption of ideal solutions. This is shown in Table 3-5. The other measured densities appear in Table 3-4.

3.5 Calculation of IFT

The IFT of any system can be calculated by placing a drop of one liquid into a second liquid and then spinning

Table 3-4

Densities of Organic Liquids and Surfactant Solutions at 25.0±0.2°C.

Component	Period, T	Density (g/cm^3)	Literature Density **
pentane	435419	0.6215	0.6262
hexane	439468	0.6555	0.6603
heptane	442573	0.6818	0.6838
octane	444575	0.6988†	0.7025
pure octane	444537	0.6985†	"
decane	447854	0.7269	0.7300
dodecane	449994	0.7453	0.7487
p-xylene	-	0.8571††	0.8611
cyclohexane	-	0.7746††	0.7786
surfactant *	480450	1.017	-
"	480170	1.015	-
"	480032	1.013	-
"	480032	1.013	-
dry air	353435	-	1.185×10^{-3}
water	478274	-	0.99707

* surfactant mixture- 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl

** source- Handbook of Chemistry and Physics

Note: literature densities of hydrocarbons at 20.0°C. If densities at 25.0°C could be found the agreement between literature and measured densities would be better.

† check to see effect of pre-equilibration on density

†† estimated

Table 3-5

Comparison of Densities Calculated Assuming Ideal Solutions and Measured Densities. *

EACN	Components	T	Density	Calculated Density
7.0	C_6-C_{12}	442437	0.6806	0.6795
8.0	"	444590	0.6989	0.6970
9.0	"	446443	0.7148	0.7126
10.0	"	447828	0.7266	0.7251
6.2	c-C_6-C_{10}	**	0.7467	0.7502

* sample calculation in Appendix A

** measured using density bottle

the whole assembly. The calculation of IFT depends on shapes and drop volumes and becomes very complicated. Details of this complex calculation were published by Cayias et al [9]. If, however, the droplet expands so that its length is 4 or more times its width then the so called Vonnegut infinite length equation can be used. In this equation the droplet is assumed to be cylindrical with hemispherical ends, and the only parameter to be measured is the drop width. The equation for calculating the IFT is

$$\gamma = \frac{1}{4}\Delta\rho\ \omega^2\ r^3 \qquad (3\text{-}1)$$

where γ is the IFT, $\Delta\rho$ is the density difference, ω is the angular velocity and r is the cylindrical radius.

Some substitutions can be made in Equation (3-1). The angular velocity can be represented in terms of ν the frequency as follows

$$\omega = 2\pi\ \nu \qquad (3\text{-}2)$$

The apparatus measures the period of revolution in msec/rev, T, therefore

$$\nu = \frac{10^3}{T} \qquad (3\text{-}3)$$

Combining Equations (3-2) and (3-3)

$$\omega = \frac{2\pi \times 10^3}{T} \qquad (3\text{-}4)$$

Using the spinning drop apparatus it is the cylindrical diameter that is measured so that

$$r = \frac{d}{2} \qquad (3\text{-}5)$$

Substituting Equations (3-4) and (3-5) into (3-1) yields

$$\gamma = \frac{1\Delta\rho}{4} \left(\frac{2\pi \times 10^3}{T}\right)^2 \left(\frac{d}{2}\right)^3 \qquad (3\text{-}6)$$

Some further revisions are still necessary. The glass in the capillary tube magnifies the drop width so to get the true IFT one must know the true width, not the measured one. The correction is

$$d(\text{true}) = \frac{d(\text{measured})}{1.332} \qquad (3\text{-}7)$$

Equation (3-6) then becomes

$$\gamma = 1.234 \times 10^6 \frac{\Delta\rho}{T^2} \left(\frac{d'}{1.332}\right)^3 \qquad (3\text{-}8)$$

where d' is the measured diameter. Finally the drop width is measured by an eyepiece and the units of measurement are 10^{-2} cm. In order to substitute the measured drop width directly into the IFT equation the following change is necessary

$$\gamma = 0.5222 \times 10^{6} \frac{\Delta\rho}{T^2} \left(\frac{d'}{10^2}\right)^3$$

or

$$\gamma = 0.5222 \frac{\Delta\rho \, d'^3}{T^2} \qquad (3\text{-}9)$$

where γ is in mN/m, $\Delta\rho$ is in g/cm^3, d' is in 10^{-2} cm (read directly off of the apparatus) and T is in msec/rev (read directly off of the apparatus).

For the higher IFT's the drop did not always elongate sufficiently for the infinite length approximation to become valid. In such cases the calculation of the IFT would be much more complicated. However the infinite length equation could still be used to give an estimate of the true IFT. The estimate obtained is always lower than the true value. The extent of elongation can be increased by rotating the drop faster or injecting a droplet of larger volume.

3.6 Density Difference Calculation

The density difference can be calculated from the following equation

$$\Delta\rho = \rho_1 - \rho_2 = \frac{T_1^2 - T_2^2}{A} \qquad (3\text{-}10)$$

where ρ_1 and ρ_2 are the densities of phases 1 and 2, T_1 and T_2 are the periods read directly off of the density meter for phases 1 and 2 and A is a constant obtained using calibration standards. Using dry air and distilled water as the references A was found to be 1.0426×10^{11}.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Phase Behaviour of Mixed Surfactant Solutions

The only literature found pertaining to the IFT's of mixed surfactant solutions of petroleum sulfonate-lignosulfonate were those which were the result of previous researchers at the University of Ottawa. Therefore much of the work to be reported is essentially novel and some of the work involves preliminary screening of potentially useful surfactant mixtures.

One of the problems which arose was the phase behaviour of these mixed surfactant solutions. The system was made up of four principal components: petroleum sulfonate, lignosulfonate, sodium chloride and water, but the surfactants themselves are composed of many fractions so the phase equilibria became quite complex. As seen in Tables 4-1 and 4-2, for a fixed petroleum sulfonate concentration the concentration of lignosulfonate largely determined the phase behaviour with the concentration of NaCl playing a lesser role.

When a mixture was unstable the same basic separation always occurred with only minor changes in the volume or colour of the sediment. The surfactant separated into two phases, a clear, brown upper phase and an opaque, brown

Table 4-1

Phase Behaviour of Surfactant Solutions of 3.0% Petrostep 420 and Varied Concentrations of Marasperse C-21 and NaCl (organic overtop, heptane).

Wt.% C-21	Wt.% NaCl	After 1 Day	3 Days	6 Days
0.0	0.0	no settling	no settling	no settling
"	1.0	"	"	"
"	2.0	"	"	"
1.0	0.0	"	"	"
"	1.0	"	"	streaking
"	2.0	some settling	some settling	separation
2.0	0.0	"	separation	"
"	1.0	"	"	"
"	2.0	"	"	"

Table 4-2

Phase Behaviour of Solutions of 2.5% Petrostep 420 with Marasperse C-21 and NaCl Concentrations Varied (organic overtop, heptane).

Wt.% C-21	Wt.% NaCl	After 1 Day	4 Days	7 Days
0.6	1.5	no settling	no settling	no settling
0.8	1.3	"	streaking	slight separation
"	1.5	"	"	streaking
"	1.7	"	"	"
1.0	1.1	"	separation	separation
"	1.3	"	"	"
"	1.5	"	"	"
"	1.7	"	"	"
"	1.9	"	"	"
1.2	1.3	separation	"	"
"	1.5	"	"	"
"	1.7	"	"	"
1.4	1.5	"	"	"

lower phase containing the settled surfactant. This clear phase in between the settled surfactant and the organic could be the microemulsion phase that many researchers talk about [11,27,29,31]. These third phase microemulsions are associated with concentrated surfactant mixtures and are in some cases thought to be essential for the appearance of low IFT's.

In the stable region the surfactant was uniformly brown and opaque. An indicator that a previously stable mixture was eventually going to separate was the appearance of dark streaks in the surfactant. The two situations of homogeneous and separated surfactant are shown schematically in Figure 4-1.

For a solution of 2.5% Petrostep 420 and 1.5% NaCl the critical concentration of Marasperse C-21 was 0.8 to 1.0%. Above this concentration the surfactant solution readily separated and below this concentration the solutions were homogeneous for a week or longer.

This phase instability could have been related to the calcium tolerance of Petrostep 420 mentioned by Meister et al [23]. Meister measured the concentrations of Ca^{2+} necessary to precipitate various petroleum sulfonates. For the case of Petrostep 420 a 5 wt.% solution was used with no salt added other than that already present in the surfactant as received. The results indicate that precipitation starts with a Ca^{2+} concentration of 0.01 moles/litre and at 0.02

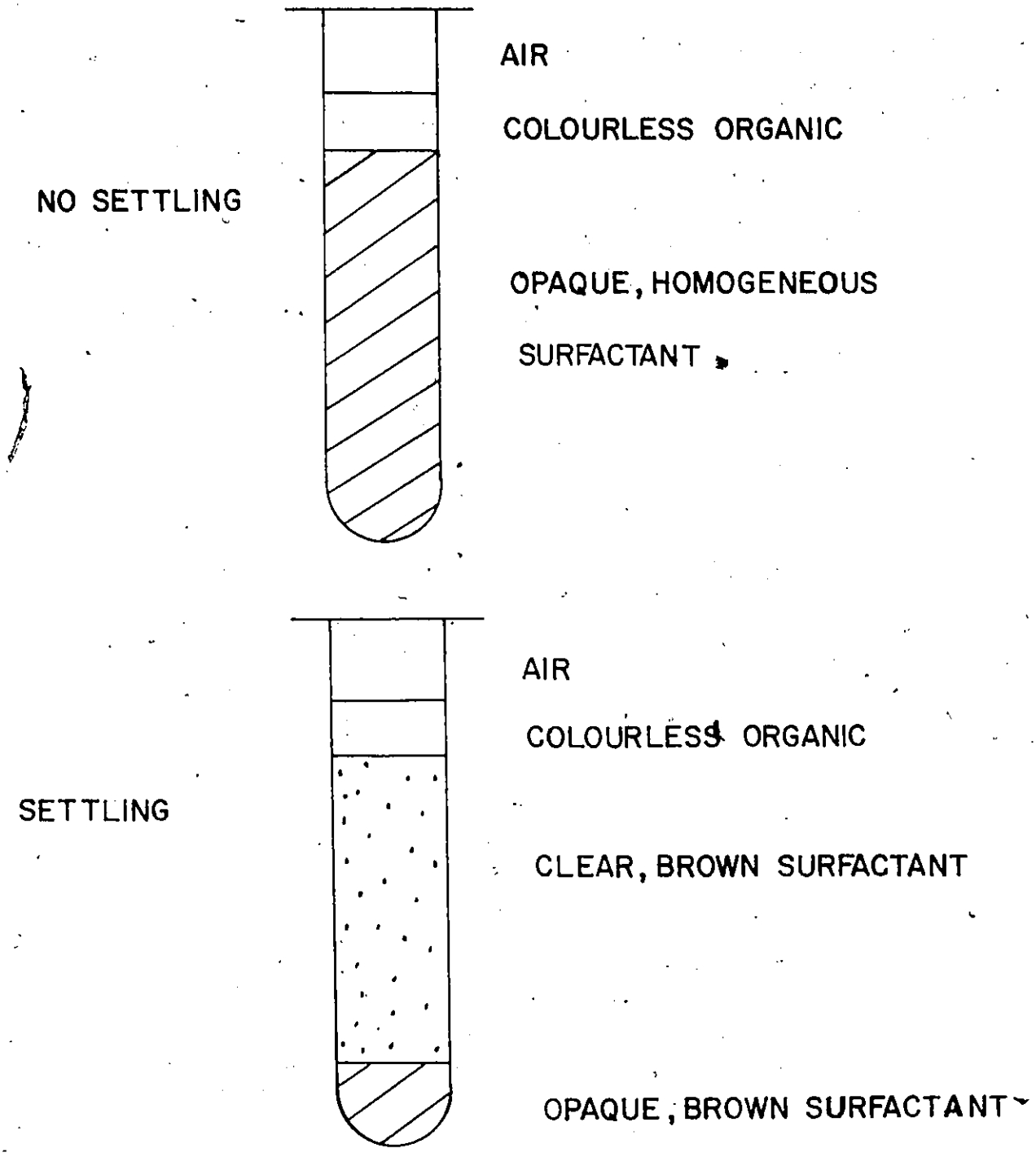

Figure 4-1: Representations of Homogeneous Surfactant and Separated Surfactant Solutions.

moles/litre the extent of precipitation is large. Referring to a 1.0% Marasperse C-21 solution the concentration of Ca^{2+} would be roughly 0.04% based on the information in Table 3-2. Converted this would be roughly 0.01 moles/litre. Therefore the calcium content of the lignosulfonate is sufficiently large that it might be necessary to consider the calcium tolerance of the Petrostep 420. It should be emphasized that the system used by Meister differs from the one used here in that no salt was added and the Petrostep 420 concentration was different. Nevertheless the Ca^{2+} content of the lignosulfonate is of the correct order of magnitude to present this type of stability problem.

4.2 Effect of Order of Mixing on Phase Behaviour and IFT

It is conceivable that the order of mixing of the surfactant solutions could alter their ultimate IFT lowering ability. For example, if the NaCl were added to the petroleum sulfonate it might create a different electrical double layer effect than if the NaCl were added to a mixture of petroleum sulfonate and lignosulfonate. Even if the true equilibrium IFT were not affected the time course of the non-equilibrium IFT's could be different.

The phase behaviour represented in Tables 4-1 and B-1 show that the order of mixing did not alter this behaviour except

for occasional minor variations in colour of precipitate. In Table B-1 the effect on IFT is shown. For each surfactant formulation the IFT's agree to within a factor of 4 which as will be discussed later is typical of the sort of experimental variation common with these concentrations of surfactant. Although the order of mixing may not affect the IFT, for the sake of consistency the salt was always added last. This procedure was also followed by Cayias et al [10].

Table B-1 also shows that adding 1% of NaCl or Marasperse C-21 separately results in a lower IFT than using the Petrostep 420 alone, by a factor of 10. Adding 1% of both further reduces the IFT by approximately another factor of 10. This table also shows evidence that there is an optimum salt concentration for these mixtures because the IFT's for 1.0% Marasperse C-21 and 1.0% NaCl are a factor of 10 or more lower than those for 1.0% Marasperse C-21 and 2.0% NaCl.

Lorentz et al [22] referred to the effects of order of mixing on a number of different petroleum sulfonates. They found that the order of mixing had greater effects on viscosity and conductance with lesser effects on IFT and phase stability. These differences were found to persist for weeks. A mixture of 7.2 wt.% Petrostep 420 and isobutyl alcohol with 0.9% NaCl was found to show no order of mixing effect. This, however, does not necessarily

mean that the solutions of Petrostep 420, Marasperse C-21 and NaCl would also show no order of mixing effects. Once again to be safe, NaCl was always added last.

4.3 Interaction between Organic and Surfactant Solutions

For the alkanes there was no visible interaction between the organic phase and the mixed surfactant solution. However, for the aromatic compounds and cyclohexane a white precipitate or emulsion formed in the interfacial region when concentrated surfactant mixtures were used. For dilute surfactant mixtures this white phase did not appear, but in both cases the organic clouded the surfactant in the spinning drop apparatus making the IFT measurement difficult. When the organics were poured over Petrostep 420 alone, the volume of emulsion was greater than when a mixed surfactant was used.

4.4 Concentrated Surfactant Mixture- 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl

This was the first surfactant formulation studied. It was arbitrarily selected because previous workers had found that it was capable of exhibiting the necessary low IFT's. However, it was later found that this mixture was on the borderline of phase stability as discussed previously. This

factor is thought to account in part for the large experimental fluctuations observed. Against heptane, which showed the lowest IFT's, variation in IFT by a factor of 10 can be seen in Table B-2.

As mentioned, the phase instability is thought to be partially responsible for this variation. Since the surfactant was in a state of sedimentation the actual concentration of each of the surfactants in the interfacial region would be a function of time.

This phase problem is not thought to be the only factor leading to the data scatter. In some cases the spinning drop would not elongate at all from its original spherical shape as if some sort of "skin" were restricting its expansion. Sometimes the organic droplet would surge and then start its elongation, but in other cases no elongation occurred at all.

A third factor that may have been responsible for the data scatter was the length of time allowed for the spinning drop to equilibrate. The spinning was continued until the drop width had stabilized, but in some cases it was possible that this plateau was just an intermediate one and that further spinning would have led to a lower IFT.

When the concentrated surfactant solutions were spun in the interfacial tensiometer the organic droplet often became surrounded by a brown film after some time. This film may have been due to adsorption of surfactant aggregates.

Frances et al [18] report similar behaviour and suggest that this adsorption is necessary for the appearance of low IFT's. Lack of this sort of adsorption may explain the observation that some droplets did not expand at all.

Due to the experimental variations the data in Table B-2 was thought to be best represented in one of two ways. One was to plot the average IFT obtained against each organic and the second was to plot the minimum IFT obtained against each organic. The justification behind this second plot being that most of the factors which can lead to experimental errors in the measurement will result in higher IFT's. Therefore the absolute minimum IFT might be a better estimation of the actual IFT than the average value. These two plots are shown in Figure 4-2. The two plotting methods yield different curves obviously, but they do show some similarities. One is that the minima of the two curves occur at the same EACN or in other words n_{MIN} of the surfactant is the same in both cases. Secondly, these curves show a broad, rounded minimum in contrast to the curves in Figure 2-3 which exhibit sharp, spiked minima. This broader minimum is potentially beneficial because then it is not so critical that the EACN of the oil match the n_{MIN} of the surfactant to get low IFT's. If the two are fairly closely matched then the IFT will be very near the lowest possible value.

It was intended to extend this work to binary mixtures

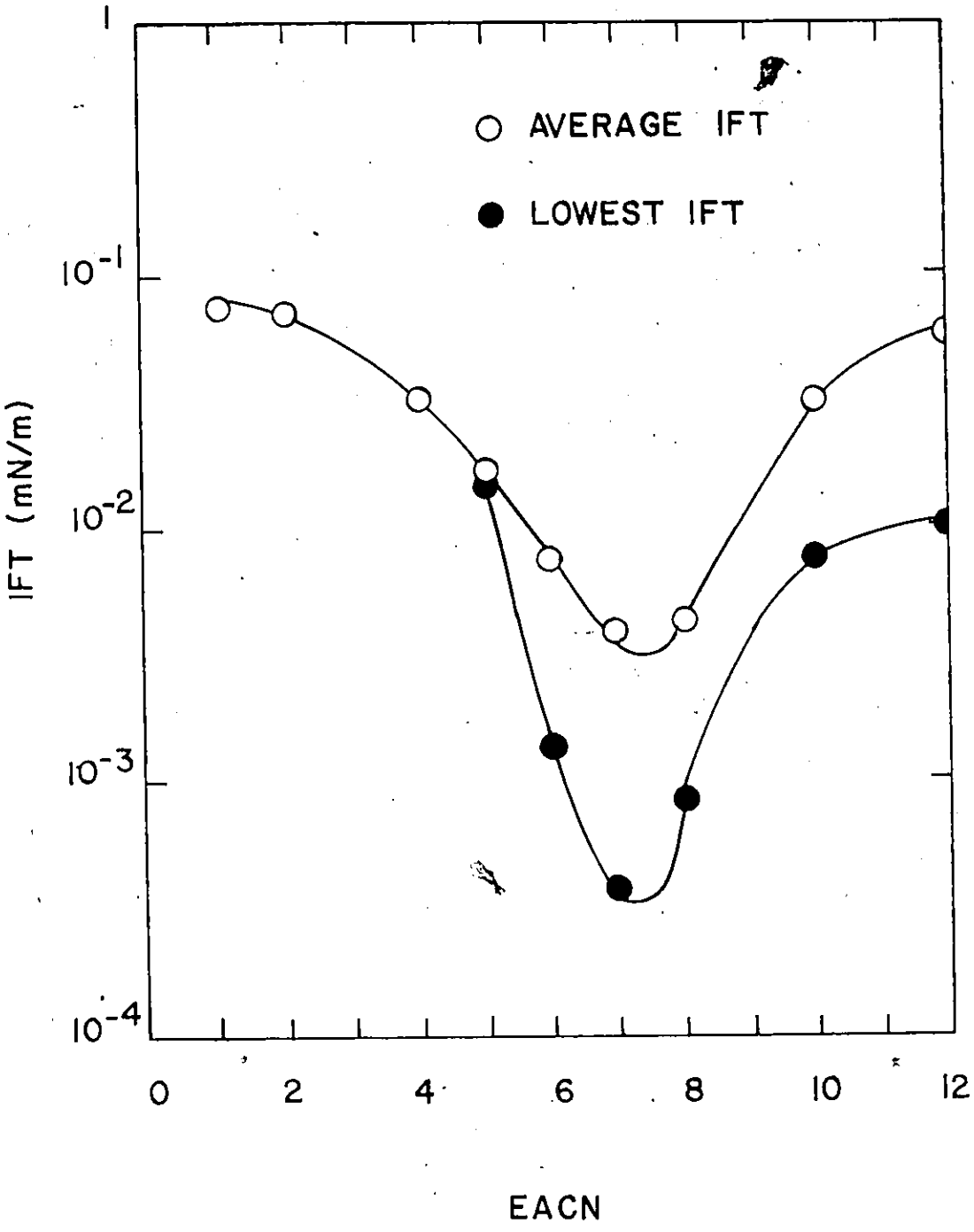

Figure 4-2: IFT's of One-Component Organics against 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl.

but the data in Table B-3 shows variations of 2 orders of magnitude. With the large experimental variations no significant trend could be plotted.

4.5 Effect of Variations in Surfactant Solution Compositions

4.5.1 Petrostep 420

The data in Table B-4 represents the experiments in which the concentration of Petrostep 420 was increased from 2.5% to 4.0%. For the same concentrations of lignosulfonate and salt the IFT does not change indicating that a plateau in IFT had been reached with respect to increased concentrations of petroleum sulfonate.

4.5.2 Marasperse C-21

Table B-1 indicates that adding 1% of Marasperse C-21 to a 3% solution of Petrostep 420 decreases the IFT by a factor of 10 even without the addition of salt. If 1% of NaCl is added also then the IFT is further decreased by about a factor of 10. Referring to Table B-4 it can be seen that for fixed concentrations of petroleum sulfonate and NaCl an increase in lignosulfonate concentration reduces the IFT.

4.5.3 NaCl

As for lignosulfonate, Table B-1 shows that the addition

of NaCl to a solution of petroleum sulfonate reduces the IFT by a factor of 10. At fixed petroleum sulfonate and lignosulfonate concentrations the concentration of salt could have a significant effect on the IFT. For example, for 3% Petrostep 420 and 1% Marasperse C-21 changing the salt concentration from 0 to 1% lowered the IFT by a factor of 10 and then changing it from 1 to 2% raised it back to its original value again. This is in keeping with the concept that for a particular surfactant mixture there is an optimum salt concentration.

4.5.4 Alcohol

Some researchers use alcohols in their surfactant mixtures as an additional component. The use of an alcohol co-surfactant is usually for the purpose of increasing the solubility of the surfactant in the aqueous phase. A couple of tests were done using 1% of 2-propanol with the surfactant solutions of 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5 and 2.0% NaCl. The results in Table B-5 may indicate that the use of 2-propanol shifts the optimum salt concentration. With no alcohol the IFT is lower for 2% NaCl but with the alcohol the 1.5% NaCl solution yields a lower IFT. The use of 2-propanol was not continued because it tended to make the surfactant solution cloudier.

4.6 Surfactant Mixture- 3.0% Petrostep 420 and 1.5% NaCl

Some experiments were done without any lignosulfonate so that there would be something to compare the mixed surfactant results to and also to see if the petroleum sulfonate alone followed the same IFT versus EACN behaviour.

For one-component organic phases, Table B-6 shows that the IFT's are remarkably constant over the entire range of EACN. The ultralow IFT's obtained using heptane are not thought to be significant because the organic droplets in the spinning drop apparatus were what are referred to as oscillating drops in the operating manual [19]. This means that they expanded and contracted periodically so that the drop width was a function of time. The slightly lower IFT's against hexane are likely due to the fact that these samples were spun considerably longer than the rest. Table B-7 shows that for binary mixtures the IFT's are once again very consistent. Therefore the Petrostep 420 alone does not exhibit a minimum IFT in this EACN region and the IFT's are as much as 2 orders of magnitude higher than when 1% Marasperse C-21 is added to the solution. Wade et al [33] have empirically determined that the n_{MIN} value for 0.2% Petrostep 420 and 1.0% NaCl is 1.8. This would account for the absence of a minimum in the EACN range studied and would also explain the constant IFT's. Since the EACN's studied were more than 3 units from this proposed n_{MIN} value, the

IFT versus EACN curve would be in a plateau region between EACN's 5 and 12.

4.7 Petrostep 465

4.7.1 Surfactant Mixture- 3.0% Petrostep 465 and 1.5% NaCl

This petroleum sulfonate is a higher molecular weight analogue to Petrostep 420. Compared to an n_{MIN} value of 1.8 for Petrostep 420, Wade et al suggest that Petrostep 465 has an n_{MIN} value of 10.0. Whereas the n_{MIN} value of Petrostep 420 could not be experimentally verified it should be possible in the case of Petrostep 465. Some experiments of this nature were done with the results shown in Table B-8. The problem encountered was that the surfactant solutions were very cloudy. By cloudy it is meant that there was considerable suspended material in the rotating capillary tube which tended to adhere to the organic droplet eventually obstructing it and making the IFT measurement difficult. The three results obtained may indicate lower IFT's in the EACN range 11-12 than against hexane. In comparison with Table B-6 the IFT's of the petroleum sulfonate alone are 2 orders of magnitude lower for the Petrostep 465 than for Petrostep 420.

4.7.2 Surfactant Mixture- 2.5% Petrostep 465, 1.0% Marasperse C-21 and 1.5% NaCl

With this surfactant mixture there was a different sort

of phase problem than with the Petrostep 420. In this case an oily precipitate settled out which was difficult to redissolve. As indicated in Table B-9 when the precipitate was not redissolved the IFT's tended to be higher than when it was redissolved.

In Table B-9 the IFT's are relatively constant with no definite minimum IFT. There may be a slight lowering in IFT at the high EACN end indicating that n_{MIN} may be off-scale at a yet higher EACN. The IFT's for some binary mixtures shown in Table B-10 are similar to those for the one-component organic phases.

4.8 Further IFT Dependence on Concentrations of Marasperse C-21 and NaCl

To try to reduce the data scatter which was previously seen it was thought that a surfactant mixture which settled rapidly might be better because it would reach its equilibrium conditions faster. In Table B-11 the results of some experiments in which the lignosulfonate concentration was increased and the salt concentration was varied are shown. The salt variation once again points out the concept that there is an optimum salt concentration. Increasing the lignosulfonate concentration to these high values has no large effect on IFT. A Marasperse C-21 concentration of 1.4% was selected for the next set of experiments because it gave a low IFT and

settled quickly.

The hoped for better reproducibility did not materialize as shown in Tables B-12 and B-13. Against heptane IFT's varying by as much as 2 orders of magnitude resulted. The minimum in the IFT versus EACN curve still occurs in the range heptane-octane so this data was not plotted.

4.9 Other Types of Surfactants

Some other surfactants were tried by themselves, with salt and with both salt and lignosulfonate. The surfactants used were sodium lauryl sulfate, Alkanol 189-S, Petrowet RH, Petrowet R, Petrosul 545, Petrosul 742 and Petrosul 744CL. The results are shown in Table B-14. The IFT's using the surfactants alone are all greater than 1 mN/m. Using salt and lignosulfonate the IFT's can be reduced 1 or 2 orders of magnitude. No IFT's of the order of 10^{-3} mN/m were observed. With some of the Petrosul 742 solutions very low IFT's seemed to result but the solutions were so dirty that an IFT measurement could not be made. Some of the Petrosuls might have potential for EOR studies if the concentrations were optimized.

4.10 Reduction in Surfactant Concentrations

4.10.1 Reduced Marasperse C-21 Concentrations

As a result of the problems associated with the concentrated surfactant mixtures it was decided to obtain a more dilute surfactant mixture which would first of all be homogeneous and secondly which still exhibited the necessary low IFT's.

The first step in this direction was to hold the concentrations of Petrostep 420 and NaCl fixed at the values of 2.5% and 1.5% respectively and to decrease the Marasperse C-21 concentration. These results are shown in Figure 4-3 and Table B-15. Below 0.8% Marasperse C-21 all of these surfactant mixtures are stable for a week or longer. This was sufficient for this research because all that was necessary was to have the surfactant homogeneous over the time frame in which the IFT measurement was made.

Referring to Figure 4-3 it is noted that reducing the lignosulfonate concentration to 0.5% has no significant effect on the IFT, but if the concentration is further reduced then the IFT's start to rise rapidly. To avoid the sort of borderline problems which affected the concentrated surfactant solutions, a lignosulfonate concentration of 0.6% was selected. This particular formulation could have been used but it was desirable to try to further reduce the total surfactant concentration. This would further improve

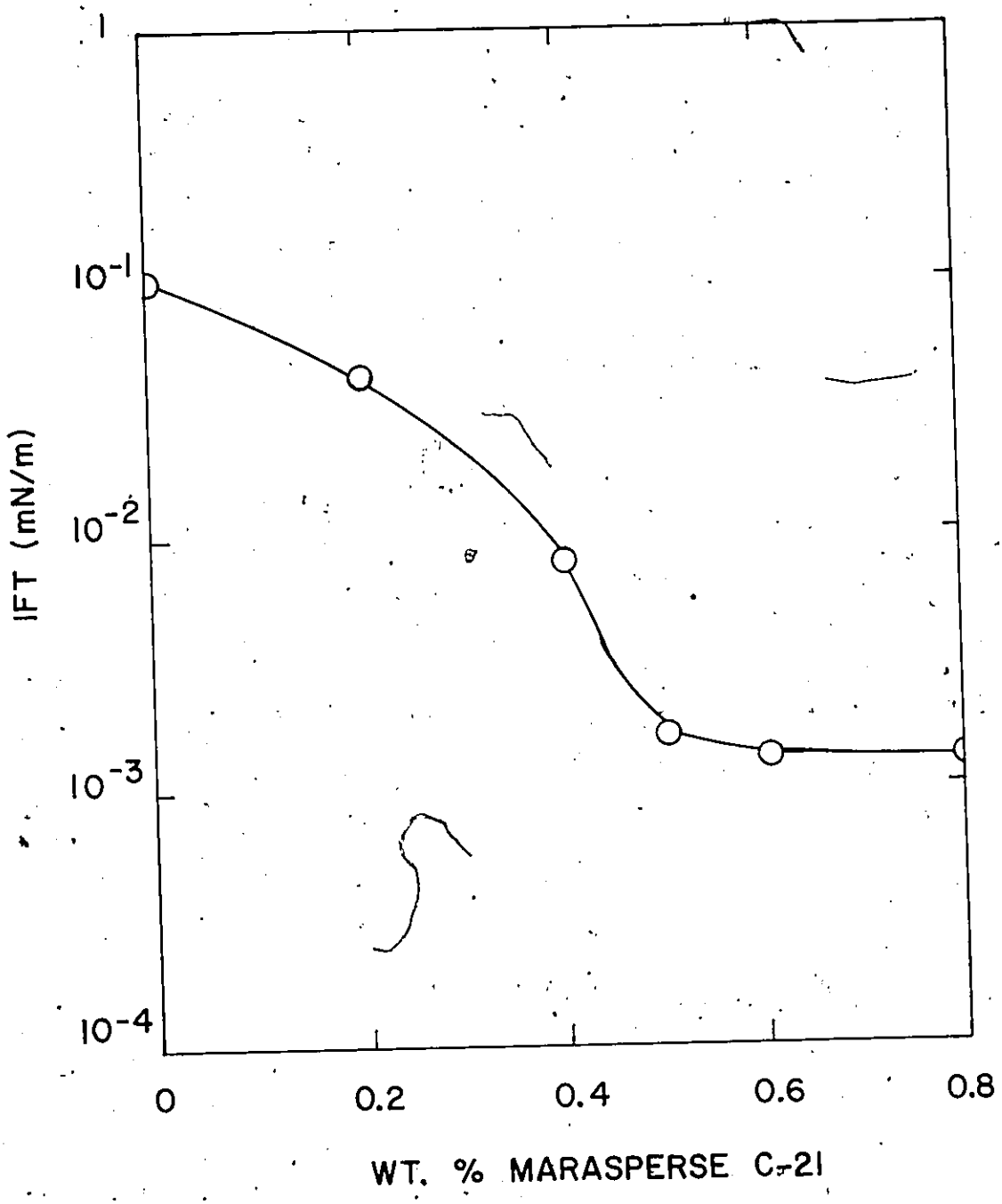

Figure 4-3: Dependence of IFT on Concentration of Marasperse C-21 for Fixed Concentrations of 2.5% Petrostep 420 and 1.5% NaCl.

the phase stability and from an economical viewpoint the lower the surfactant concentration the better.

4.10.2 Reduced Total Surfactant Concentration

In the next set of experiments the ratio of Petrostep 420 to Marasperse C-21 was fixed at 2.5 to 0.6 on the basis of the previous results, and the concentration of petroleum sulfonate was lowered with the lignosulfonate concentration lowered proportionally. Figure 4-4 and Table B-16 show these results.

Figure 4-4 also shows a set of blank experiments using no lignosulfonate. Above 0.1% Petrostep 420 where both of these curves are essentially constant the synergistic effect of the petroleum sulfonate and lignosulfonate is once again noticed, with the IFT's for the mixed surfactant being an order of magnitude lower than the corresponding solutions of petroleum sulfonate alone.

From the curve plotted for the mixed surfactant it can be seen that the concentration of petroleum sulfonate can be reduced to 0.1% without significantly altering the IFT. Further reduction causes the IFT to rise rapidly. This sort of abrupt change in IFT behaviour may be related to the critical micelle concentration of this surfactant. Once again to move away from the limiting concentration a value of 0.2% Petrostep 420 was selected, and the corresponding Marasperse C-21 concentration was 0.048%.

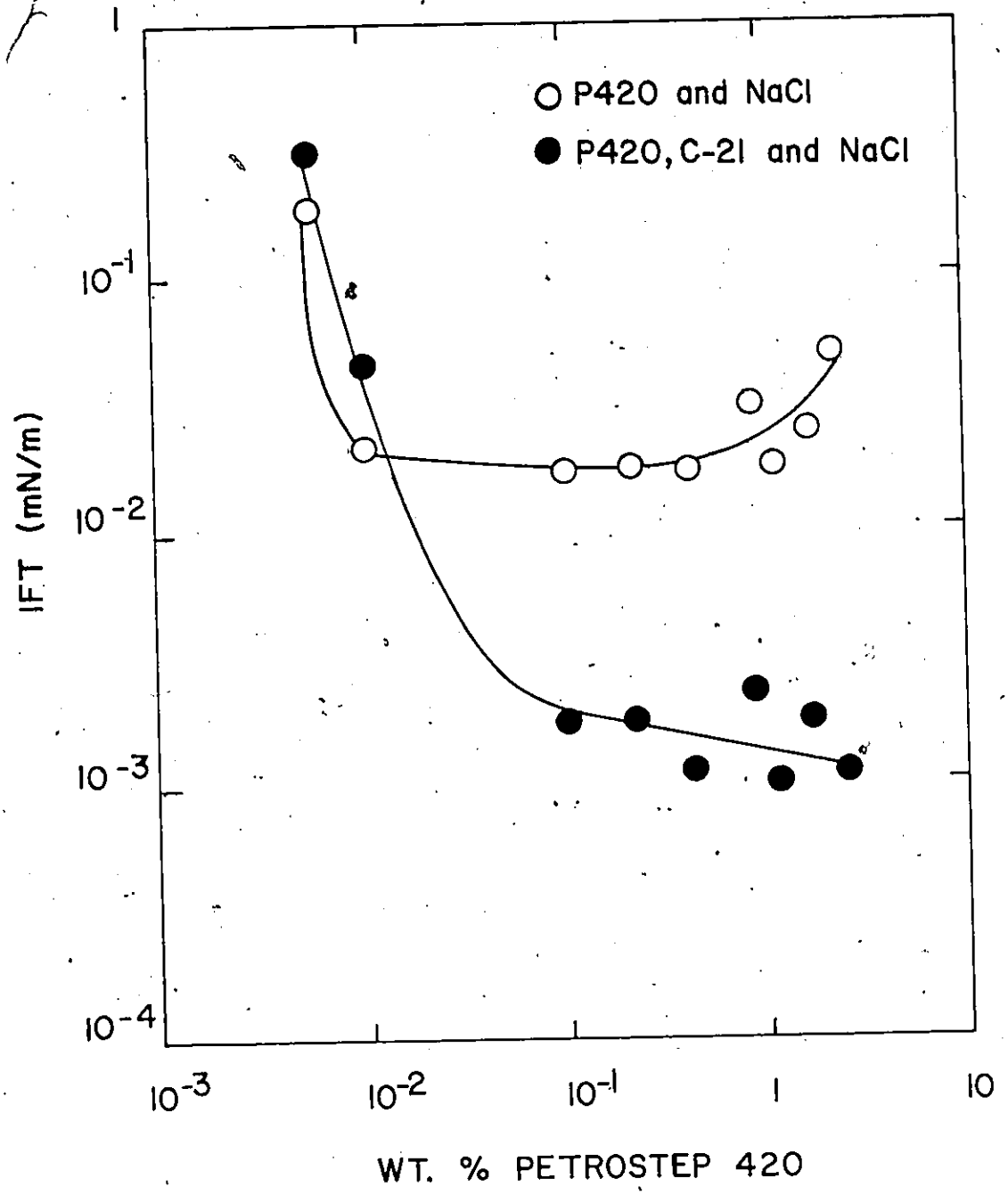

Figure 4-4: Dependence of IFT on Total Surfactant Concentration of Fixed 1.5% NaCl Solutions (ratio of P420 to C-21 fixed at 2.5 to 0.6 for mixed surfactant solutions).

4.11 Dilute Surfactant Solution- 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl

Using this dilute surfactant mixture the experiments which were attempted with the concentrated surfactant were to be repeated. That is, the IFT versus EACN curve was to be obtained for single organics and then binary mixtures to see if the two types of curves were similar.

This dilute surfactant was obviously much clearer than the concentrated mixture which made the IFT measurement easier and more accurate. These solutions were also stable for long periods of time, but after a month or so they too started to show signs of sedimentation.

The experimental data in Table B-17 shows that the range of experimental error is no more than a factor of 3 and in most cases considerably better. This is a marked improvement over the situation with the concentrated surfactant solutions where variations of an order of magnitude or more were seen.

The IFT versus EACN curve for the single, one-component organics is shown in Figure 4-5. The curve is of similar shape to those for the concentrated surfactant, and n_{MIN} has shifted only slightly to give a value of about 6.4.

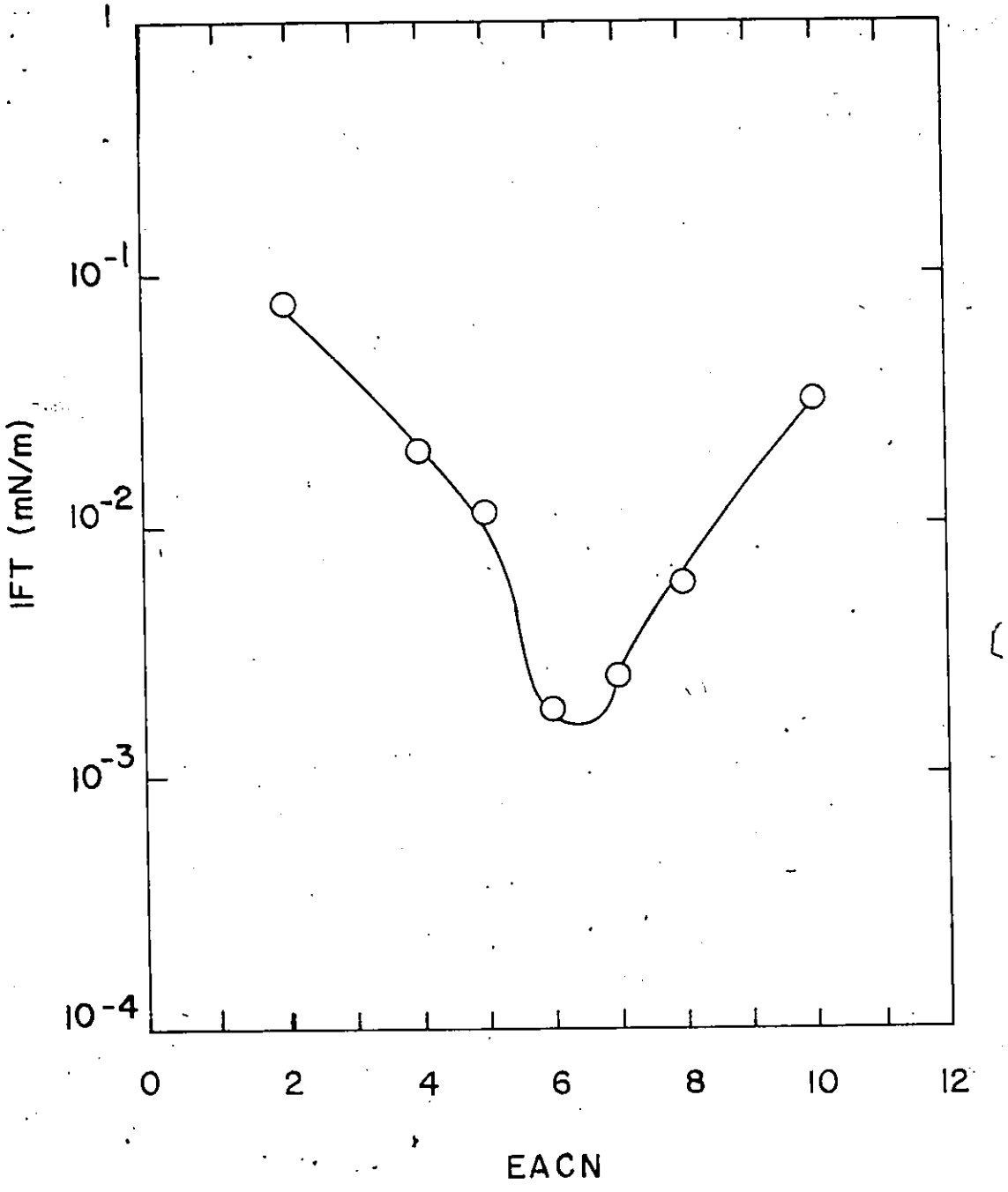

Figure 4-5: IFT of One-Component Organics against 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl.

4.11.1 Binary Mixtures

The next step was to prepare binary mixtures and again obtain IFT versus EACN curves. These curves are shown in Figures 4-6 and 4-7 for pentane-octane, pentane-decane, hexane-decane and cyclohexane-decane with the data in Table B-18.

In comparing the results for the single and binary organics the concept of a universal curve appears not to be valid because it is possible to get greatly different IFT's at the same EACN depending on the make-up of the organic phase. However, the idea that n_{MIN} is a constant for a given surfactant mixture appears to be relatively valid. The minimum IFT's for all of the curves occur at the same EACN (±0.5 EACN unit). As briefly mentioned before a minor variation in n_{MIN} of this size is not critical because of the rounded nature of these curves, in contrast to the sharp minima curves in which a variation of this order could significantly alter the IFT.

The cyclohexane-decane curve is notable in that it shows a deeper minimum than the single organic curve. This was different since all the previous IFT's of binary mixtures had been equal to or greater than the corresponding one-component IFT. This cyclohexane-decane mixture also clearly demonstrates the EACN concept. Both components separately show IFT's of the order of 5×10^{-2} mN/m, but in the proper combination mixtures of these two can lead to IFT's of

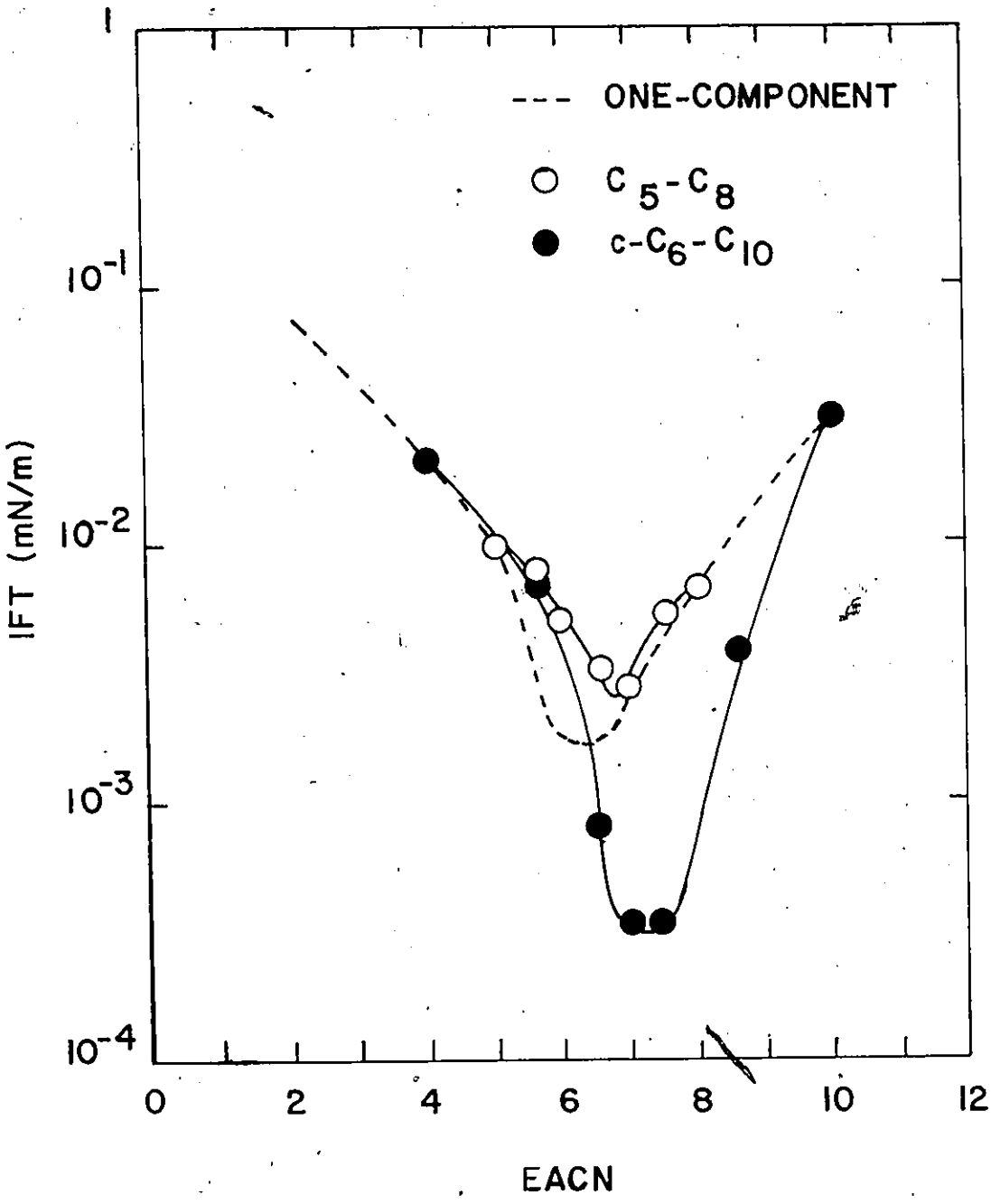

Figure 4-6: IFT of Binary Organic Mixtures against 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl.

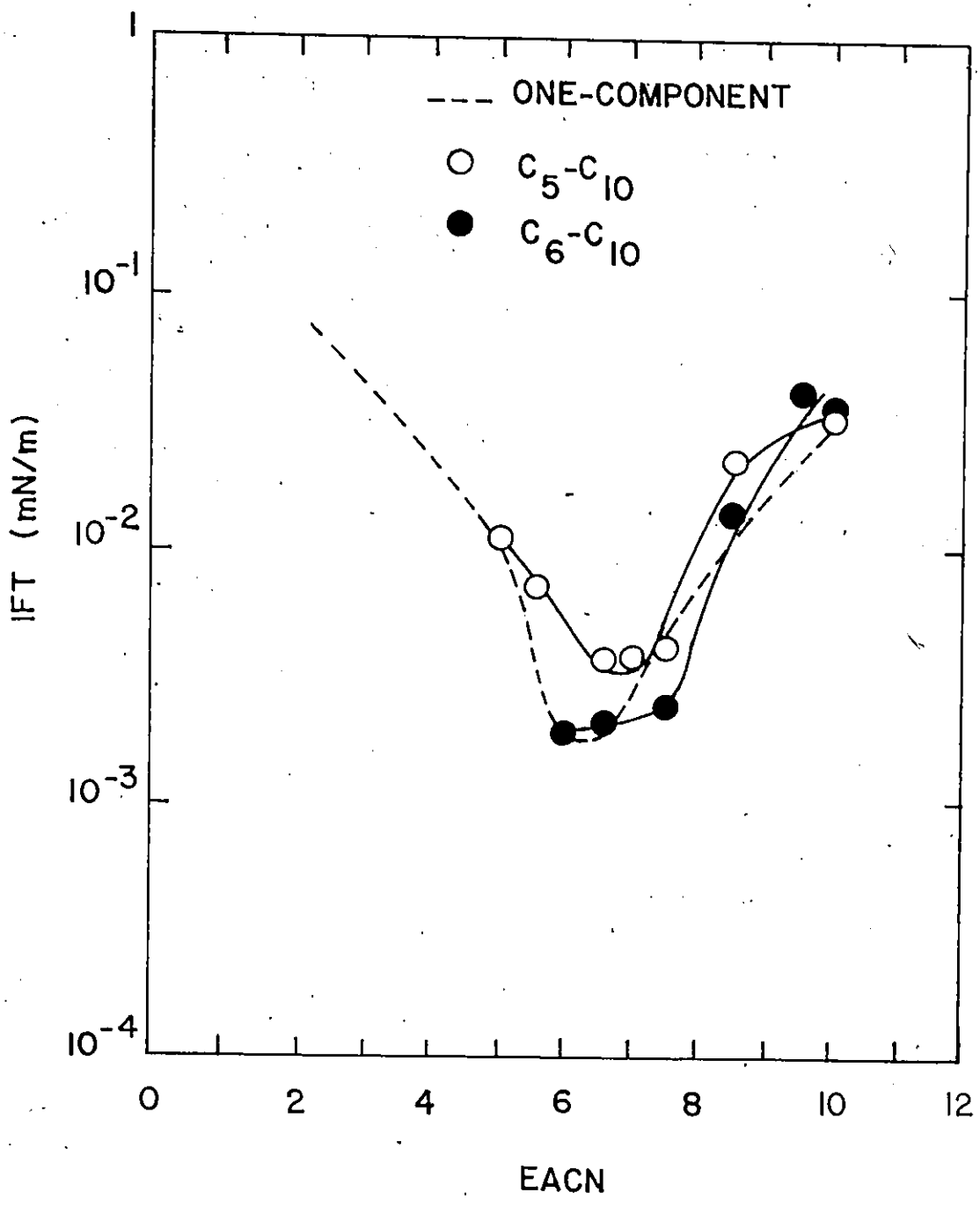

Figure 4-7: IFT of More Binary Organic Mixtures against 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl.

5×10^{-4} mN/m or 2 orders of magnitude lower.

4.11.2 Ternary Mixtures

The initial objective was to extend this work to ternary mixtures to see if similar IFT versus EACN curves resulted. In referring to Figures 4-6 and 4-7, however, it becomes evident that a truly random ternary mixture will not yield a smooth curve like the one- and two-component solutions, but rather oscillations would occur. This idea can be qualitatively explained as follows. Say, for example, the three components were pentane, cyclohexane and decane. One particular mixture of these three might contain very little pentane, then the IFT of the ternary mixture would be close to the IFT of the binary mixture of cyclohexane and decane with the same EACN. At the next EACN the ternary mixture might contain very little cyclohexane and so the IFT would be close to that of the corresponding pentane-decane binary mixture. For this reason a smooth curve would not result, but rather jumping up and down would occur leading to a rough curve or possibly obscuring any trend at all.

This concept can likewise be extended to crude oils. A range of oils of differing EACN's might not lead to a smooth curve either. However, this effect could be damped in the case of oils since the relative amount of any one component is quite small.

It was thought that the only way to get a smooth curve

was to apply a restriction. The three components were cyclohexane, hexane and decane and the restriction was that the amounts of cyclohexane and hexane were fixed and the amount of decane was varied to obtain the desired EACN. Since two components were fixed and one was varied this system really modelled something more like a binary system than a true ternary solution. The data is represented in Table B-19 and the same sort of curve is seen to result in Figure 4-8, with its minimum at the same EACN as the one- and two-component curves.

Using the same three components two different mixtures of EACN 6.5 were made up, as listed in Table B-19, to show that significantly different IFT's can result depending upon the make-up of the organic. This is demonstrated in Figure 4-8 in which the IFT's for the two solutions differ by a factor of 5.

In summary the important result is that n_{MIN} is essentially constant for a given surfactant. Given an oil with an EACN equal to the n_{MIN} of the surfactant a minimum IFT, with respect to other EACN's and n_{MIN}'s, can be predicted but the absolute value of the IFT may have to be measured.

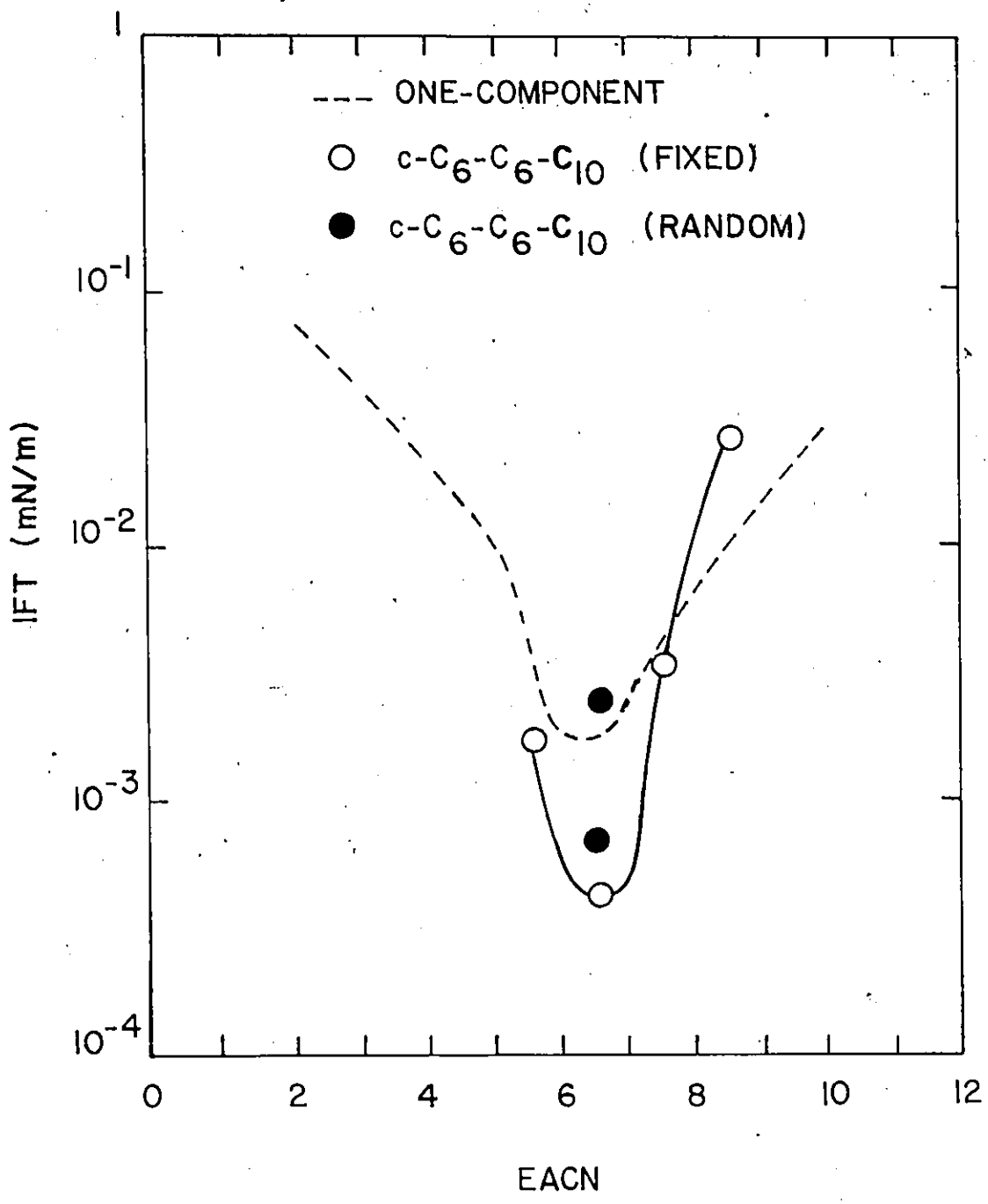

Figure 4-8: IFT of Ternary Organic Mixtures against 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl.

4.12 Effect of Aging and Length of Pre-equilibration Time

A problem that is often mentioned in the literature is the effect of aging on a surfactant (eg. Cayias et al [7]). The premise is that as a surfactant ages it loses some of its activity and the IFT's then start to increase.

Some evidence of aging has been seen, the most notable example being the case of a dilute mixed surfactant solution of 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl. This solution was made up from stock solutions of each of the surfactants which were 4 months old and a series of IFT measurements were made in the first month. The mixed surfactant was put away and used again four months later. At that time the IFT's were 2 to 3 times higher than before. In an attempt to restore the lower IFT's a fresh mixed surfactant solution was made from the same stock solutions which were then 8 months old, and in fact the previous low IFT's were again observed. The consequence of this seems to be that the mixed surfactant solution, including salt, is more prone to aging effects than are the individual stock solutions on their own.

The stock solution of Petrostep 420 underwent sedimentation, but the mixture could be made homogeneous again by shaking. The stock solution of Marasperse C-21 developed a surface film after some time. This film was clear and

pliable but could not be redissolved by shaking. It may have resulted from a polymerization reaction or from bacterial action on residual wood sugars in the lignosulfonate.

One other set of time dependent studies was done to test to see if the time allowed for pre-equilibration altered the IFT. The results in Tables B-20 and B-21 indicate that up to 3 days of pre-equilibration led to the same IFT's providing the surfactant solution phase structure did not change. The low value for no pre-equilibration in Table B-20 is thought to be due to the fact that the surfactant mixture was homogeneous for this measurement, but the mixture had settled for all of the rest. With the mixed surfactant solutions, as the time of pre-equilibration got longer the IFT's started to increase. For a surfactant solution without any lignosulfonate the results in Table B-22 indicate that the IFT's seemingly decrease with time. However, this results because the organic phase is eventually solubilized by the surfactant.

Provided the surfactant phase behaviour is stable it does not matter whether the time of pre-equilibration is 0 to 3 days, so samples were usually left overnight. This certainly does not allow for mutual saturation, but it just provides for initial contact between the phases.

4.13 Petrostep 450

4.13.1 Surfactant Mixture- 0.2% Petrostep 450 and 1.5% NaCl

Some experiments were performed using Petrostep 450 in place of Petrostep 420. According to Morgan et al [26] the use of a higher molecular weight surfactant should shift n_{MIN} to higher values. The value of n_{MIN} reported by Wade et al [33] for Petrostep 450 is 4.5. The data in Table B-23, without any lignosulfonate, show essentially constant IFT's in the EACN range 4 to 7. If n_{MIN} for this surfactant is 4.5 a noticeable lowering of IFT should have occurred against cyclohexane and pentane.

4.13.2 Surfactant Mixture- 0.2% Petrostep 450, 0.048% Marasperse C-21 and 1.5% NaCl

If this surfactant mixture was found to yield an n_{MIN} value larger than when Petrostep 420 was used then on the basis of the scaling equation

$$n_{MIN} = \Sigma x_i (n_{MIN})_i \qquad (2\text{-}3)$$

one could develop two equations (one for Petrostep 420 plus Marasperse C-21 and one for Petrostep 450 plus Marasperse C-21) in which the unknowns would be the molecular weight and n_{MIN} value of the Marasperse C-21. Assuming the scaling equation to be valid these parameters

could be calculated. The calculated molecular weight could be compared with the literature value to see if the two were of the same order of magnitude, and thus give some indication of the applicability of Equation (2-3) to these mixed surfactant systems.

However, the results in Table B-23 and Figure 4-9 show that the n_{MIN} value for this formulation is the same as for Petrostep 420. In other words the use of Petrostep 450 does not shift n_{MIN} significantly. The curve in Figure 4-9 is essentially the same as the one for the corresponding solution of Petrostep 420 in Figure 4-5.

Since the n_{MIN} values of the two mixed surfactants are the same even though the n_{MIN} values for Petrostep 450 and Petrostep 420 are reportedly different, means that the scaling rule must not be valid. That this scaling equation breaks down for lignosulfonates is not too surprising. First of all lignosulfonates have a very high molecular weight and to expect linear behaviour over this wide range is being overly optimistic. Secondly, lignosulfonates are not true surfactants in the same sense that petroleum sulfonates are. They are simply large molecules which exhibit some surface active properties.

Although the linear scaling rule does not seem to apply it is still possible that lignosulfonate can be assigned an n_{MIN} value and some sort of non-linear equation used. If this were the case it could be used to explain the

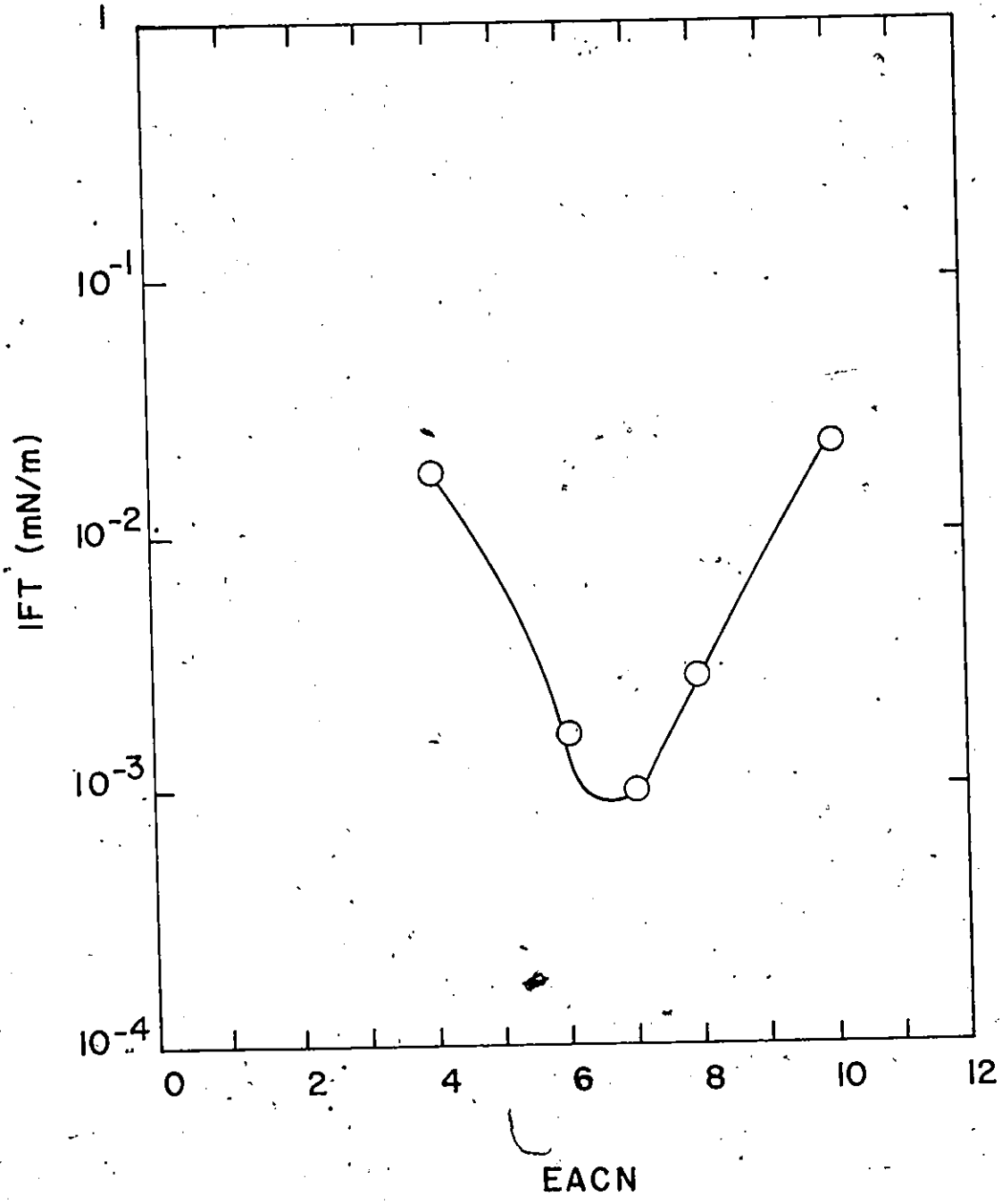

Figure 4-9: IFT of One-Component Organics against 0.2% Petrostep 450, 0.048% Marasperse C-21 and 1.5% NaCl.

synergistic effect that lignosulfonate and petroleum sulfonate produce in the EACN range studied. Petrostep 420 and Petrostep 450 on their own have low n_{MIN} values and if the n_{MIN} value of Marasperse C-21 was high then in the proper combination a surfactant mixture could be made which would exhibit an n_{MIN} around heptane. This could account for the high IFT's using lignosulfonate and petroleum sulfonate separately and the much lower IFT when using them together.

It was hoped that a dilute surfactant solution of Petrostep 465 could have been tested as well, but it did not dissolve as well as the other two and in the IFT measurement these solubility problems clouded up the capillary tube. Therefore these experiments were not continued.

CHAPTER 5

MECHANISMS TO EXPLAIN THE LOW IFT BEHAVIOUR

This section is a qualitative account of possible reasons for the existence of low IFT's and also for the existence of the minima in the IFT versus EACN curves. The ideas are unsubstantiated at this point but they may be of some assistance to future workers trying to develop a quantitative explanation for these phenomena.

5.1 Suggested Explanations in the Literature

In the literature there have been several attempts to explain this low IFT behaviour. Frances et al [18] and Chiu [12] suggest that the low IFT's are related to the size of the surfactant aggregates. There is some discussion as to whether these aggregates are in the form of micelles or if they are liquid crystalline. For the present purposes such a distinction is not necessary and it is sufficient just to refer to aggregates in general. Chiu relates the oil recovery ability of the surfactant (which is in turn related to IFT) to the aggregate size and its dependence on the salt concentration or the presence of alcohol, by looking only at the aqueous phase without any oil phase present. If the aggregate size is larger or smaller than a determined optimum size the recovery

efficiency becomes decreased.

Similarly, Frances et al relate the low IFT's to the formation of surfactant aggregates. In their opinion the dissolved surfactant concentration is not responsible for the low IFT's. They also suggest that these dispersed aggregates are responsible for experimental variations due to time effects, order of mixing effects, droplet shapes and surfactant phase turbidity.

Whereas the previous papers relate the low IFT to the surfactant aggregates, Antoniewicz and Rodriguez [2] and Chan [11] correlate this phenomenon with the concentration of surfactant molecules at the oil-surfactant solution interface. Chan relates the IFT with the surface charge density and finds the minimum IFT results when the interfacial charge is a maximum. Maximum interfacial charge is found to occur when the critical micelle concentration of the surfactant solution, including equilibrated oil, is reached. Another indicator of minimum IFT is that the surfactant partition coefficient between the oil and the aqueous phase is equal to one.

5.2 Additional Suggestions about this Mechanism

There are two observations which must be explained. One is the reason for the production of ultralow tensions by the surfactant solutions and the other is the reason

for a minimum IFT against a particular EACN organic phase.

5.2.1 Ultralow Tensions

The papers referred to in the previous section present different viewpoints. The low IFT's are thought to be due to the surfactant aggregates on one hand and due to the free surfactant concentration at the interface on the other. These views can be reconciled if the entire equilibrium is examined. When the concentration of a surfactant exceeds its critical micelle concentration an equilibrium will be set up between the free surfactant molecules and the aggregates as follows

free surfactant ⇌ surfactant aggregates

Now instead of looking at half of the equilibrium the factors affecting the entire equilibrium can be considered. For example, even though the low IFT's may be found to correlate with the size of the aggregates it is possible that the aggregate size itself is just an indicator of the free surfactant concentration. In such a case the aggregate size is measured but really it is the free surfactant concentration which is microscopically responsible for the low IFT's.

This equilibrium will be influenced by several variables.

The salt concentration will alter the double layer characteristics of the surfactant and will affect the critical micelle concentration and the size of the micelles. The concentration of surfactant may also shift the equilibrium. As far as this research is concerned the presence of lignosulfonates may shift the equilibrium, or they may actually be incorporated into the aggregate structure thereby altering its size.

In any case when suitable conditions are reached low IFT's may result due to the presence of the surfactant aggregates and free surfactant. The aggregates may solubilize some of the oil thereby increasing the compatibility between the phases and decreasing the IFT. The free surfactant will align at the interface exerting a spreading pressure which decreases the IFT.

5.2.2 Minimum in IFT versus EACN Curves

Once it has been determined that a particular surfactant formulation results in low IFT's it is still necessary to explain why a minimum IFT results against an organic phase having a particular EACN. The concept of EACN has been successfully used to correlate the observed data but it has no physical significance in terms of explaining what is happening at the molecular level. Therefore there may be another parameter which runs parallel to the EACN which can help to physically explain the existence of these minima.

If another measureable parameter could be found to characterize the make-up of the organic phase this would be beneficial when it comes to predicting the IFT of a crude oil. The EACN of a crude oil cannot be calculated nor measured without relying upon the validity of certain empirical relations. However, if a predetermined physical property could be measured then it might be possible to get some indication of its IFT behaviour on this basis.

Once again assuming that the overall equilibrium must be considered, this physical property could play a part in determining the equilibrium conditions. If such is the case then it becomes realistic that certain organic compounds may result in optimum equilibrium conditions and hence a lower IFT than larger or smaller homologues.

The EACN could be replaced as a method of defining the organic phase if some other function of the following type could be developed..

$$EACN = f(a_1, a_2, a_3, \ldots)$$

In this equation the a_i's are measurable properties which can be combined in some functional way to generate the EACN.

There would be a large number of such measurable properties which could be tested if the objective were to correlate EACN with these properties for one-component organics. The following properties are some of those which

could be considered: molecular size, solubility in surfactant, density, viscosity, surface tension, molecular structure and conductivity. If, however, binary or more complex solutions were to be similarily modelled then the number of possible parameters for study decreases. For example, one can speak of the solubility of a binary mixture in a surfactant solution but the meaning of this is not so well-defined as for the one-component organics. The properties out of the previous list which would still be well-defined when speaking of a homogeneous multi-component organic solution are: density, viscosity, surface tension and conductivity.

In summary it has been suggested that by looking at the free surfactant-aggregate equilibrium and the factors which shift the equilibrium position, one can explain the occurrence of low IFT's and the appearance of a minimum IFT against certain organic mixtures. It has also been mentioned that it might be possible, and would definitely be desirable, to establish some functional relationship between readily measureable parameters as an alternate means of designating the make-up of the organic phase instead of using the EACN.

CHAPTER 6

CONCLUSIONS

1. A concentrated surfactant solution of 2.5 wt.% Petrostep 420, 1.0 wt.% Marasperse C-21 and 1.5 wt.% NaCl yields ultralow IFT's but the data reproducibility is poor and the phase behaviour rather complex.

2. A dilute surfactant mixture of 0.2 wt.% Petrostep 420, 0.048 wt.% Marasperse C-21 and 1.5 wt.% NaCl also yields ultralow IFT's. The reproducibility is much better and there are no phase stability problems over short time intervals. The minimum in the IFT curve occurs at approximately the same EACN (6.5) for both of the above-mentioned surfactant formulations.

3. A surfactant mixture containing Petrostep 420, Marasperse C-21 and NaCl is more prone to aging effects than are each of the components when stored separately.

4. The order of mixing did not play a large role in determining the IFT or phase behaviour.

5. NaCl or another electrolyte must be present to achieve ultralow IFT's.

6. Petrostep 420 and Marasperse C-21 exhibit a synergistic IFT lowering effect in the EACN range studied.

7. Petrostep 450 could be used in experimental work but the use of Petrostep 465 resulted in a very cloudy surfactant mixture which made the IFT measurements difficult.

8. The ratio of Petrostep 420 to Marasperse C-21 and the total concentration of surfactant can be reduced to determined levels without any appreciable increase in IFT.

9. The concept of a fixed n_{MIN} value for any given surfactant is confirmed using different binary mixtures of organics. The concept cannot be easily extended to a completely random ternary or more complex mixture.

10. The time allowed for pre-equilibration before an IFT measurement need not be accurately controlled, but if the time allowed is very long the IFT will start to increase.

11. A surfactant mixture of 0.2 wt.% Petrostep 450, 0.048 wt.% Marasperse C-21 and 1.5 wt.% NaCl exhibits a minimum IFT at roughly the same EACN as the corresponding mixture involving Petrostep 420.

CHAPTER 7

RECOMMENDATIONS

1. The effects of varying surfactant concentrations have been studied insofar as they influence IFT so studies could be performed to determine how the concentrated and dilute surfactant mixtures perform in actual displacement studies.

2. If the IFT behaviour of these systems were to be better defined, one could test the effect of $CaCl_2$ along with and instead of NaCl. The concentrations of Petrostep 420, Marasperse C-21 and NaCl could also be optimized from an economical standpoint using an actual crude oil as the organic phase against which low IFT's should be maintained.

3. Some work could be done to determine a physical property or properties which run "parallel" to the EACN to be used as an alternate means of characterizing the organic phase.

4. The mechanistic behaviour at the molecular level could be studied and surfactant aggregates could be examined to see if the lignosulfonate incorporates into the structure. The effect of different organics on aggregate swelling and/or free surfactant concentration might also be studied.

NOMENCLATURE

A	calibration constant of density meter
C_5	pentane
C_6	hexane
$c\text{-}C_6$	cyclohexane
C_8	octane
C_{10}	decane
C_{12}	dodecane
C-21	Marasperse C-21 (lignosulfonate)
d	actual drop diameter
d'	measured drop diameter
EACN	equivalent alkane carbon number
EOR	enhanced oil recovery
IFT	interfacial tension
n_{MIN}	EACN at which minimum IFT occurs
ΔP	pressure difference
P420	Petrostep 420 (petroleum sulfonate)
r	drop radius
R_1, R_2	radii of curvature of ends of oil capillary
T	period of revolution on spinning drop tensiometer
T_1, T_2	periods read off of density meter
x_i	mole fraction of i^{th} component
γ	interfacial tension
ν	frequency of revolution
ρ	density

$\Delta\rho$ density difference

ω angular velocity of rotation

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APPENDIX A

Sample Calculation of Density of Binary Organic Solution Assuming Ideality

Example, binary mixture of 3.0g of C_6 and 2.94g of C_{12}.

Component	Molecular Weight	Density, g/cm^3
hexane	86	0.6555
dodecane	170	0.7453

no. of moles of hexane = $\frac{3.0}{86} = 0.0349$

no. of moles of dodecane = $\frac{2.94}{170} = 0.0173$

mole fraction of hexane = $\frac{0.0349}{0.0349+0.0173} = 0.669$

mole fraction of dodecane = $\frac{0.0173}{0.0349+0.0173} = 0.331$

EACN = (6x0.669) + (12x0.331) = 8.0

volume of hexane = $\frac{3.0}{0.6555} = 4.577\ cm^3$

volume of dodecane = $\frac{2.94}{0.7453} = 3.945\ cm^3$

ideal density = $\frac{3.0+2.94}{4.577+3.945} = 0.6970\ g/cm^3$ as in Table 3-5

Compare the calculated density of 0.6970 g/cm^3 with the measured value of 0.6989 g/cm^3.

APPENDIX B

TABLES OF DATA

Table B-1

Order of Mixing Effects on the IFT of Heptane against 3.0% Petrostep 420 and Variable Concentrations of Marasperse C-21 and NaCl.

Wt.% C-21	Wt.% NaCl	Added last	Time* (sec)	Width (10^{-2}cm)	Period (msec/rev)	IFT (mN/m)
0.0	0.0	-	9550	6.471	11.40	3.63×10^{-1}
"	1.0	-	4820	3.120	11.92	3.72×10^{-2}
"	2.0	-	6290	4.629	12.65	1.08×10^{-1}
1.0	0.0	-	19310	2.220	12.08	1.30×10^{-2}
"	1.0	NaCl	1790	1.582	19.81	1.76×10^{-3}
"	"	C-21	890	2.170	20.39	4.28×10^{-3}
"	"	P420	6320	1.236	19.59	8.56×10^{-4}
"	2.0	NaCl	11920	3.134	13.05	3.14×10^{-2}
"	"	C-21	9270	5.628	15.71	1.26×10^{-1}
"	"	P420	9200	5.248	15.10	1.10×10^{-1}
2.0	0.0	-	7140	3.978	18.96	2.95×10^{-2}
"	1.0	NaCl	9270	1.648	20.12	1.92×10^{-3}
"	"	C-21	9660	1.594	18.25	2.16×10^{-3}
"	"	P420	8820	1.470	18.01	1.70×10^{-3}
"	2.0	NaCl	6600	2.014	18.48	4.16×10^{-3}
"	"	C-21	2620	1.971	19.59	3.47×10^{-3}
"	"	P420	8270	1.672	22.70	1.58×10^{-3}

* this time is the elapsed time of the spinning of the capillary tube when the equilibrium drop width was measured

Table B-2

IFT Data for 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl against One-Component Organics.

Organic	Time	Width	Period	IFT
toluene	5500	4.993	11.05	8.04×10^{-2}
xylene	6800	4.966	11.78	7.27×10^{-2}
cyclohexane	5400	4.004	15.96	3.16×10^{-2}
pentane	2930	2.672	17.26	1.32×10^{-2}
"	8730	3.000	16.17	2.13×10^{-2}
"	3900	2.808	18.79	1.28×10^{-2}
hexane	4900	1.382	19.25	1.34×10^{-3}
"	8830	1.681	16.92	3.12×10^{-3}
"	8530	1.501	18.36	1.87×10^{-3}
"	16300	2.031	11.10	1.22×10^{-2}
"	17520	1.814	12.11	7.91×10^{-3}
"	7500	2.499	14.72	1.34×10^{-2}
heptane	3600	1.483	18.70	1.62×10^{-3}
"	3440	1.736	17.58	2.94×10^{-3}
"	3620	1.073	19.77	5.47×10^{-4}
"	8600	1.016	21.75	3.85×10^{-4}
"	4400	1.617	18.97	2.03×10^{-3}
"	5450	1.200	21.01	6.80×10^{-4}
"	5400	1.949	12.66	8.00×10^{-3}
"	1 day	1.870	12.52	7.20×10^{-3}
"	7450	2.496	19.33	7.23×10^{-3}
"	3550	2.253	17.94	6.17×10^{-3}
"	5800	1.871	14.61	5.33×10^{-3}
octane	5100	1.291	21.79	7.50×10^{-4}
"	4520	1.346	18.47	1.20×10^{-3}
"	6900	1.396	19.79	1.15×10^{-3}

Table B-2 (cont.)

Organic	Time	Width	Period	IFT
octane	4400	1.312	19.44	9.81×10^{-4}
"	8100	2.800	15.80	1.46×10^{-2}
"	10200	2.048	14.46	6.80×10^{-3}
decane	15600	2.121	14.24	7.09×10^{-3}
"	13400	2.965	13.02	2.31×10^{-2}
"	7500	4.050	13.43	5.55×10^{-2}
undecane	8500	3.576	11.44	5.01×10^{-2}
dodecane	5770	4.028	13.71	4.91×10^{-2}
"	3250	3.178	21.78	9.56×10^{-3}
"	3220	3.475	14.36	2.87×10^{-2}
"	6600	4.373	10.27	1.12×10^{-1}

Table B-3

IFT Data for 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl against Binary Organic Mixtures.

EACN	Components	Time	Width	Period	IFT
6.0	C_5-C_{12}	15800	5.010	16.72	8.45×10^{-2}
7.0	C_6-C_{12}	6250	4.511	8.99	1.97×10^{-1}
"	"	5010	2.826	17.80	1.24×10^{-2}
"	"	8780	1.434	11.20	4.08×10^{-3}
"	"	6650	2.214	17.93	5.86×10^{-3}
"	"	8800	1.920	17.81	3.87×10^{-3}
8.0	"	8970	1.250	14.63	1.50×10^{-3}
"	"	7620	2.880	17.64	1.26×10^{-2}
"	"	8000	5.830	13.47	1.79×10^{-1}
"	"	6280	5.551	12.55	1.78×10^{-1}
"	"	5250	2.718	13.06	1.93×10^{-3}
"	"	8030	2.312	13.22	1.16×10^{-2}
"	"	7850	3.293	13.76	3.10×10^{-2}
"	"	16400	5.082	13.37	1.12×10^{-1}
"	"	15800	4.853	15.84	7.48×10^{-2}
9.0	"	6230	2.244	17.83	5.54×10^{-3}
"	"	3250	2.850	15.90	1.43×10^{-2}
"	"	6100	4.089	15.83	4.25×10^{-2}
"	"	16300	2.707	18.17	9.36×10^{-3}
10.0	"	9000	2.394	16.99	7.12×10^{-3}
"	"	22300	2.570	17.75	8.06×10^{-3}
"	"	5830	3.081	15.90	1.72×10^{-2}
"	"	7600	4.811	16.21	6.34×10^{-2}
"	"	7450	5.873	15.13	1.32×10^{-1}

Table B-4

IFT Data of Hexane against Surfactant Solutions with Variable Concentrations of Petrostep 420, Marasperse C-21 and NaCl.

Wt.% P420	Wt.% C-21	Wt.% NaCl	Time	Width	Period	IFT
2.5	0.5	0.5	10800	2.693	17.65	1.15×10^{-2}
"	"	"	16050	1.988	18.25	4.33×10^{-3}
"	"	1.5	9250	3.195	18.06	1.87×10^{-2}
"	"	"	10800	2.957	18.06	1.48×10^{-2}
"	1.5	0.5	6000	1.578	24.94	1.17×10^{-3}
"	"	"	5530	1.548	20.63	1.61×10^{-3}
"	"	1.5	14910	1.295	19.88	1.04×10^{-3}
"	"	"	16340	1.368	20.10	1.19×10^{-3}
4.0	0.5	0.5		drop solubilized		
"	"	"			"	
"	"	1.5	15700	3.590	17.10	2.98×10^{-2}
"	"	"	15550	2.065	11.37	1.28×10^{-2}
"	1.5	0.5	3000	1.497	20.98	1.42×10^{-3}
"	"	"	7590	1.395	20.93	1.16×10^{-3}
"	"	1.5	5400	1.290	23.41	7.46×10^{-4}
"	"	"	6090	1.428	19.63	1.44×10^{-3}

Table B-5

Effect of 1% of 2-Propanol on IFT of Octane against Surfactant Solutions of 2.5% Petrostep 420 and 1.0% Marasperse C-21 at Two NaCl Concentrations.

Wt.% NaCl	Alcohol	Time	Width	Period	IFT
1.5	no	3900	2.096	16.92	5.12×10^{-3}
"	yes	3100	1.656	26.82	1.05×10^{-3}
2.0	no	9700	1.260	13.11	1.93×10^{-3}
"	yes	7000	3.248	15.94	2.23×10^{-2}

Table B-6

IFT Data for 3.0% Petrostep 420 and 1.5% NaCl against One-Component Organics.

Organic	Time	Width	Period	IFT	
pentane	3800	4.240	12.10	1.06×10^{-1}	
"	2900	4.377	12.72	1.06×10^{-1}	
hexane	18100	3.227	9.90	6.39×10^{-2}	
"	15400	3.275	10.13	6.38×10^{-2}	
heptane	6300	1.557	21.44	1.42×10^{-3}	*
"	10150	1.370	28.21	5.57×10^{-4}	*
"	8350	5.193	13.13	1.04×10^{-1}	
"	6500	5.100	14.40	1.10×10^{-1}	
octane	3800	4.733	10.98	1.44×10^{-1}	
"	6300	4.777	10.91	1.50×10^{-1}	
decane	6100	4.987	10.52	1.67×10^{-1}	
"	6700	4.988	10.48	1.69×10^{-1}	
dodecane	9550	5.273	9.97	2.05×10^{-1}	
"	9300	5.160	9.70	2.03×10^{-1}	

* oscillating drop

Table B-7

IFT Data for 3.0% Petrostep 420 and 1.5% NaCl against Binary Organic Mixtures.

EACN	Components	Time	Width	Period	IFT
5.5	C_5-C_{12}	15000	4.171	10.51	1.28×10^{-1}
"	"	10800	4.280	10.40	1.42×10^{-1}
6.0	"	8300	4.283	10.08	1.45×10^{-1}
"	"	13600	4.458	10.60	1.48×10^{-1}
7.0	C_6-C_{12}	13800	4.336	10.12	1.38×10^{-1}
"	"	16300	4.657	11.80	1.26×10^{-1}
8.0	"	6850	5.198	11.79	1.64×10^{-1}
"	"	6000	4.410	9.93	1.43×10^{-1}
9.0	"	5700	5.073	11.19	1.62×10^{-1}
"	"	7600	5.549	12.04	1.82×10^{-1}
10.0	"	6600	5.868	12.33	1.98×10^{-1}
"	"	10400	5.900	12.53	1.95×10^{-1}

Table B-8

IFT Data for 3.0% Petrostep 465 and 1.5% NaCl.

Organic	Time	Width	Period	IFT
hexane	1750	2.357	16.85	8.62×10^{-3}
undecane	4200	1.748	30.88	8.07×10^{-4}
dodecane	5750	2.474	36.66	1.57×10^{-3}

Table B-9

IFT Data for 3.0% Petrostep 465, 1.0% Marasperse C-21 and 1.5% NaCl against One-Component Organics (Petrostep 465 contains re-suspended precipitate unless otherwise noted).

Organic	Time	Width	Period	IFT
pentane	6330	3.820	17.78	3.64×10^{-2}
"	8250	3.438	14.75	3.86×10^{-2}
"	7900	3.461	17.33	2.82×10^{-2}
hexane	7450	3.646	15.91	3.60×10^{-2}
"	3100	3.310	15.12	3.19×10^{-2} *
"	6000	3.573	16.04	3.31×10^{-2}
"	4300	3.337	14.71	3.20×10^{-2}
heptane	11000	3.166	9.73	5.82×10^{-2} *
"	5400	3.918	16.40	3.87×10^{-2}
"	3900	3.471	15.18	3.15×10^{-2}
octane	23100	3.383	9.51	7.08×10^{-2} *
"	2500	3.458	15.80	2.71×10^{-2}
"	1300	3.322	13.01	3.55×10^{-2}
decane	23200	3.817	8.99	1.03×10^{-1} *
"	11500	4.237	21.69	2.42×10^{-2}
undecane	25400	3.937	9.50	9.70×10^{-2} *
"	4400	3.442	15.91	2.32×10^{-2}
dodecane	10300	3.248	16.39	1.79×10^{-2}
hexadecane	10850	2.984	16.43	1.26×10^{-2}

* precipitate not re-suspended

Table B-10

IFT Data for 2.5% Petrostep 465, 1.0% Marasperse C-21 and 1.5% NaCl against Binary Mixtures of Hexane and Dodecane (precipitate re-suspended in each case).

EACN	Time	Width	Period	IFT
7.0	4750	3.833	16.47	3.62×10^{-2}
8.0	1200	4.025	18.90	3.01×10^{-2}
9.0	1200	3.624	16.56	2.70×10^{-2}
10.0	3000	3.619	16.93	2.47×10^{-2}

Table B-11

IFT Data for 2.5% Petrostep 420 and Varied Marasperse C-21 and NaCl Concentrations against Heptane.

Wt.% C-21	Wt.% NaCl	Time	Width	Period	IFT
0.6	1.5	13300	1.889	21.65	2.50×10^{-3}
0.8	1.3	8000	1.644	22.17	1.57×10^{-3}
"	1.5	8500	1.421	21.68	1.06×10^{-3}
"	1.7	5130	1.372	20.72	1.05×10^{-3}
1.0	1.1	8360	2.271	17.53	6.63×10^{-3}
"	1.3	19120	5.617	11.14	2.49×10^{-1}
"	1.5	11970	6.545	11.46	3.72×10^{-1}
"	1.7	12970	3.450	10.77	6.16×10^{-2}
"	1.9	10120	2.610	12.35	2.03×10^{-2}
1.2	1.3	8500	1.868	14.47	5.42×10^{-3}
"	1.5	25800	1.554	16.97	2.27×10^{-3}
"	1.7	17930	3.266	16.54	2.22×10^{-2}
1.4	1.5	7430	1.578	20.10	1.69×10^{-3}
1.7	"	8660	1.763	21.21	2.12×10^{-3}
2.0	"	8340	2.027	22.37	2.90×10^{-3}
2.5	"	6860	3.140	18.95	1.62×10^{-2}

Table B-12

IFT Data for 2.5% Petrostep 420, 1.4% Marasperse C-21 and 1.5% NaCl against One-Component Organics.

Organic	Time	Width	Period	IFT
p-xylene	3280	6.432	16.09	8.48×10^{-2}
pentane	5690	2.570	13.53	1.91×10^{-2}
"	1600	3.218	18.23	2.06×10^{-2}
hexane	9110	2.209	16.26	7.65×10^{-3}
heptane	13540	4.340	17.28	4.76×10^{-2}
"	11770	1.708	24.98	1.39×10^{-3}
"	11920	2.180	17.65	5.79×10^{-3}
"	5990	1.400	22.84	9.15×10^{-4}
"	12410	2.257	23.68	3.57×10^{-3}
"	7530	1.705	20.16	2.12×10^{-3}
"	16770	4.402	14.27	7.29×10^{-2}
"	6080	2.382	14.78	1.08×10^{-2}
"	6210	3.934	19.58	2.76×10^{-2}
octane	900	1.572	26.38	9.21×10^{-4}
"	11290	1.471	16.08	2.03×10^{-3}
nonane	12470	2.727	21.19	6.78×10^{-3}
"	13880	2.497	18.28	8.11×10^{-3}
decane	12230	5.284	16.42	8.82×10^{-2}
dodecane	8570	3.747	14.03	3.76×10^{-2}

Table B-13

IFT Data for 2.5% Petrostep 420, 1.4% Marasperse C-21 and 1.5% NaCl against Binary Mixtures of Hexane and Decane.

EACN	Time	Width	Period	IFT
6.5	7980	1.508	19.83	1.58×10^{-3}
"	13820	2.308	13.77	1.17×10^{-2}
7.5	10200	4.060	13.76	6.01×10^{-2}
"	13670	6.249	17.05	1.42×10^{-1}
8.5	11520	4.706	13.91	8.68×10^{-2}
"	7810	4.191	18.84	3.34×10^{-2}
9.5	10090	4.015	15.81	3.98×10^{-2}
"	7410	3.720	20.70	1.85×10^{-2}

Table B-14

IFT's of Other Surfactants: Alone, with 1% NaCl and with 1% NaCl and 1% Marasperse C-21 against Hexane.

Surfactant	IFT Alone	IFT 1% NaCl	IFT 1% Nacl and 1% C-21
1.5% sodium lauryl sulfate	4.10	3.42	1.53
2% Alkanol 189-S	3.76	0.670	0.115
2% Petrowet RH	2.28	1.95	0.601
2% Petrowet R	2.58	2.25	0.924
3% Petrosul 545	6.16	0.372	0.632
3% Petrosul 742	4.39	*	*
3% Petrosul 744CL	5.01	0.057	0.367

* very cloudy, difficult to measure

Table B-15

IFT Data for 2.5% Petrostep 420, 1.5% NaCl and Varied Concentrations of Marasperse C-21 against Heptane.

Wt.% C-21	Time	Width	Period	IFT
0.0	5750	3.926	9.97	1.06×10^{-1}
0.2	10510	3.084	10.91	4.29×10^{-2}
0.4	15850	2.236	15.22	8.40×10^{-3}
0.5	16280	1.563	20.55	1.57×10^{-3}
0.6	12120	1.525	21.69	1.31×10^{-3}
0.8	4590	1.283	19.00	1.02×10^{-3}

Table B-16

IFT Data for Varied Petrostep 420 Concentrations, with and without Marasperse C-21, and 1.5% NaCl against Heptane.

Wt.% P420	Wt.% C-21	Time	Width	Period	IFT
0.0	0.0	5240	11.790	10.37	2.53
0.005	"	17990	5.690	12.77	1.97×10^{-1}
0.01	"	9200	2.677	13.19	1.92×10^{-2}
0.1	"	25350	2.791	14.49	1.80×10^{-2}
0.2	"	17190	2.785	13.71	2.00×10^{-2}
0.4	"	16910	2.405	11.00	2.00×10^{-2}
0.8	"	8220	2.987	11.25	3.66×10^{-2}
1.2	"	18990	2.956	14.38	2.17×10^{-2}
1.6	"	11130	3.812	13.32	5.43×10^{-2}
2.4	"	7480	4.647	18.05	5.38×10^{-2}
0.005	0.0012	17740	7.009	13.18	3.45×10^{-2}
0.01	0.0024	10820	4.288	16.24	5.20×10^{-2}
0.1	0.024	15310	1.465	17.68	1.75×10^{-3}
0.2	0.048	15760	1.358	16.20	1.66×10^{-3}
0.4	0.096	16480	1.222	16.54	1.16×10^{-3}
0.8	0.19	12050	1.676	18.59	2.37×10^{-3}
1.2	0.29	11290	1.433	22.69	9.95×10^{-4}
1.6	0.38	9470	1.544	18.67	1.84×10^{-3}
2.0	0.48	7720	1.559	22.67	1.28×10^{-3}

Table B-17

IFT Data for 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl against One-Component Organics.

Organic	Time	Width	Period	IFT
p-xylene	6280	6.868	19.02	7.38×10^{-2}
cyclohexane	2700	3.726	17.81	2.05×10^{-2}
pentane	7270	2.815	19.44	1.21×10^{-2}
"	14080	3.024	21.74	1.20×10^{-2}
hexane	16300	1.632	21.46	1.77×10^{-3}
"	16640	1.469	18.62	1.72×10^{-3}
"	12540	1.559	17.61	2.29×10^{-3}
"	16410	1.747	20.08	2.48×10^{-3}
heptane	17430	2.070	19.76	3.95×10^{-3}
"	12780	1.222	17.46	1.04×10^{-3}
"	18760	1.521	23.27	1.13×10^{-3}
octane	22450	2.254	19.33	5.06×10^{-3}
"	19420	2.721	20.09	8.24×10^{-3}
decane	19650	3.987	16.57	3.39×10^{-2}

Table B-18

IFT Data for 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl against Binary Organic Mixtures.

EACN	Components	Time	Width	Period	IFT
5.5	C_5-C_{10}	24000	2.354	17.93	7.97×10^{-3}
"	"	22040	2.183	17.72	6.51×10^{-3}
6.5	"	22810	2.202	19.57	5.05×10^{-3}
"	"	23105	2.013	20.32	3.58×10^{-3}
7.0	"	23510	2.076	18.82	4.41×10^{-3}
"	"	14160	2.568	18.95	8.25×10^{-3}
7.5	"	22620	2.311	20.31	5.05×10^{-3}
"	"	21005	2.167	19.75	4.40×10^{-3}
8.5	"	19000	3.779	18.26	2.57×10^{-2}
"	"	19270	3.563	18.45	2.11×10^{-2}
6.5	C_6-C_{10}	20350	1.690	21.64	1.87×10^{-3}
"	"	17840	1.793	20.12	2.57×10^{-3}
7.5	"	38930	1.711	20.38	2.05×10^{-3}
"	"	38680	2.029	22.32	2.85×10^{-3}
8.5	"	24190	3.107	19.04	1.33×10^{-2}
"	"	23950	3.210	18.81	1.48×10^{-2}
9.5	"	36060	4.096	16.99	3.58×10^{-2}
"	"	36300	4.497	15.85	5.44×10^{-2}
5.5	C_5-C_8	11660	2.480	18.64	8.62×10^{-3}
"	"	11530	2.459	19.29	7.85×10^{-3}
6.0	"	14300	2.139	19.27	4.98×10^{-3}
"	"	18640	2.533	18.24	9.23×10^{-3}
6.5	"	14430	1.952	20.45	3.23×10^{-3}
"	"	11000	2.032	19.59	3.96×10^{-3}
7.0	"	22950	1.841	19.62	2.84×10^{-3}
"	"	20770	2.428	17.36	8.33×10^{-3}

Table B-18 (cont.)

EACN	Components	Time	Width	Period	IFT
7.5	C_5-C_8	13390	2.409	21.39	5.20×10^{-3}
"	"	17080	2.538	22.48	5.51×10^{-3}
5.5	c-C_6-C_{10}	13660	3.230	21.28	9.95×10^{-3}
"	"	13560	2.657	22.48	4.96×10^{-3}
6.5	"	18990	1.279	21.42	6.26×10^{-4}
"	"	8460	1.447	21.74	8.80×10^{-4}
"	"	6660	1.573	22.80	1.03×10^{-3}
7.0	"	16440	0.903	19.91	2.59×10^{-4}
7.5	"	10560	0.920	21.41	2.39×10^{-4}
"	"	7950	1.068	20.29	4.17×10^{-4}
8.5	"	23400	2.174	21.08	3.32×10^{-3}
"	"	23430	2.340	20.68	4.30×10^{-3}

Table B-19

IFT Data for 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl against Ternary Mixtures.

EACN	Wt. c-C_6	Wt. C_6	Wt. C_{10}	Time	Width	Period	IFT
5.5	0.50	0.50	0.19	18630	1.594	19.26	1.72×10^{-3}
6.5	"	"	0.73	10060	1.001	19.57	4.05×10^{-4}
7.5	"	"	1.71	9140	2.093	20.17	3.37×10^{-3}
8.5	"	"	4.00	11420	3.721	18.21	2.32×10^{-2}
6.5	1.00	1.02	1.47	8170	1.292	20.60	7.86×10^{-4}
"	0.50	2.22	1.14	16690	1.755	19.96	2.30×10^{-3}

Table B-20

Effect of Time of Pre-equilibration on IFT of 2.5% Petrostep 420, 1.0% Marasperse C-21 and 1.5% NaCl against Hexane.

Pre-equil. Time, days	Time	Width	Period	IFT
0	11100	1.560	23.01	1.34×10^{-3}
1	10100	2.127	12.92	1.08×10^{-2}
2	19300	2.757	13.78	2.06×10^{-2}
3	14900	2.453	12.61	1.73×10^{-2}
7	7200	2.094	13.84	8.97×10^{-3}
15	18400	3.755	11.42	7.58×10^{-2}
28	1 day	6.142	15.70	1.76×10^{-1}
35		no elongation		

Table B-21

Effect of Time of Pre-equilibration on IFT of 0.2% Petrostep 420, 0.048% Marasperse C-21 and 1.5% NaCl against Heptane.

Pre-equil. Time, days	Time	Width	Period	IFT
0	22590	1.480	19.28	1.52×10^{-3}
1	19970	1.246	18.30	1.01×10^{-3}
3	16650	1.260	20.26	8.49×10^{-4}
9	22940	1.881	19.19	3.14×10^{-3}

Table B-22

Effect of Time of Pre-equilibration on IFT of 3.0% Petrostep 420 and 1.5% NaCl against Hexane.

Pre-equil. Time, days	Time	Width	Period	IFT
0	20000	3.471	12.07	7.76×10^{-2}
1	21900	3.378	11.56	5.75×10^{-2}
3	21950	3.249	11.94	4.47×10^{-2}
6	17700	4.078	12.13	8.57×10^{-2}
8	21150	2.008	12.00	1.05×10^{-2}
9	5100	4.274	12.76	8.92×10^{-2}
14	20500	1.413	15.15	2.23×10^{-3}
23	3250	1.438	16.22	2.10×10^{-3}

Table B-23

IFT Data for 0.2% Petrostep 450, with and without 0.048% Marasperse C-21 and 1.5% NaCl against One-Component Organics.

Organic	Wt.% C-21	Time	Width	Period	IFT
cyclohexane	0.0	7280	2.797	19.78	7.02×10^{-3}
pentane	"	9190	2.805	19.83	1.15×10^{-2}
hexane	"	11790	2.523	19.60	7.85×10^{-3}
heptane	"	14170	2.734	19.24	9.61×10^{-3}
cyclohexane	0.048	10120	3.569	18.16	1.73×10^{-2}
hexane	"	17190	1.518	19.28	1.77×10^{-3}
heptane	"	19780	1.394	20.55	1.12×10^{-3}
octane	"	16990	1.933	20.48	2.84×10^{-3}
decane	"	11950	3.580	18.20	2.04×10^{-2}