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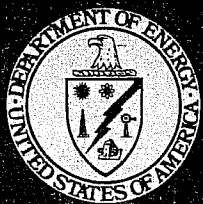
**RESEARCH ON SURFACTANT-POLYMER OIL RECOVERY SYSTEMS**

**Progress Status Report, April 1, 1979—June 30, 1979**

Date Published—December 1979

Work Performed for DOE  
Under Contract No. EW-78-S-19-0008

University of Florida  
Gainesville, Florida



**U. S. DEPARTMENT OF ENERGY**

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**RESEARCH ON SURFACTANT-POLYMER  
OIL RECOVERY SYSTEMS**

**Progress Status Report for the Period  
April 1, 1979—June 30, 1979**

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## Summary

Interfacial Phenomena: Research during the April-June, 1979 quarter was concerned with measurements of the CMC and partition coefficients of synthetic and petroleum sulfonates, and with evaluating the role of alcohols in dilute surfactant flooding processes.

The CMC of Petrostep-465 was found to occur in distilled water at about 0.01 wt.%. For NaCl solutions equilibrated with n-dodecane the CMC measured by surface tension decreased with increasing salt concentrations. However, when the NaCl concentration was 2.0 or 4.0 wt.% a sharp break in the surface tension vs. surfactant concentration was not observed - apparently owing to selective partitioning of the higher equivalent weight sulfonates to the oil phase.

The oil/water partition coefficient did not vary substantially as the oil chain length was varied from C<sub>6</sub> to C<sub>16</sub>, but it was affected by both surfactant and NaCl concentration. The partition coefficients were less than unity for NaCl concentrations of 0.1 wt.% or less and greater than unity for solutions containing one wt.% NaCl or more.

The effect of alcohol structure (one vol. % of the aqueous phase) on the O/W partition coefficient for the n-C<sub>12</sub>/water system was measured for surfactant concentrations of 0.01 and 0.1 wt.% P-465. It was found to decrease as the alcohol chain length increased, passing through a minimum with pentanol or hexanol. The effect was attributed to the relative oil/water solubility of the alcohol.

Oil displacement from sandpacks was found to be improved significantly when about 0.05 wt. % isobutanol was added to dilute solutions of commercial petroleum sulfonates. The increase in oil displacement was associated with a sharp reduction of the oil droplet coalescence time and is believed to be due to enhanced mass transfer of surfactant across the O/W interface.

Polymer Rheology and Fluid Mechanics: These experiments involved determination of the flow characteristics of selected polymers, and studies of surfactant/polymer interactions.

The relationship between pressure drop ( $\Delta P/L$ ) and flow rate (Q) through a silica gel column was found to be linear for a 500 ppm biopolymer solution when CaCl<sub>2</sub> was added to the solution in amounts up to 500 ppm. Higher CaCl<sub>2</sub> concentrations than 1000 ppm resulted in non-linear behavior. A maximum in the  $\Delta P/L$  value was noted with the biopolymer at 1200 ppm CaCl<sub>2</sub> concentration for a polyacrylamide.

An attempt to evaluate the influence of calcium ions on the adsorption of biopolymer on silica by measuring the change in viscosity of the polymer solution led to inconclusive results. An attempt to demonstrate the occurrence of a surfactant/polymer interaction by a dialysis technique also failed to produce definitive results.

The addition of partially hydrolyzed polyacrylamide to an oil/surfactant-brine system containing TRS 10-410, isobutanol, brine, and n-dodecane did not alter either the phase volumes or the interfacial tensions at equilibrium.

Thermodynamics: The molecular theory for aqueous solutions developed in a previous report has been extended to cover chain paraffin species with some success. However, inadequate agreement with experiment was obtained when it was applied to the micellization of alkyl sulfonates. A correlation of surface tension based on the corresponding states principle has met with some success and is being developed further.

The high pressure apparatus for observing isotropic-anisotropic transitions has finally been brought into service, and is being used for observations on systems of interest. Studies on systems containing potassium oleate and sodium stearate are yielding evidence of complex phenomena; they will be dealt with in later reports when more data are available.

Rock/Fluid Interactions: Research in this area during the April-June, 1979 period involved studies on the salting-out of surfactants by NaCl, the precipitation of surfactants by multivalent cations, the CMC of surfactants by the dye solubilization technique, on polymer analysis, and on the State-of-The-Art Survey of surfactant losses by precipitation.

The experiments involving the addition of short chain alcohols to inhibit or prevent salting out of surfactants are not yet complete, but it appears that several hundred moles of isopropanol are required to prevent the salting-out of one mole of SUL-FON-ATE AA10 by 2 wt.% NaCl.

A salting-out diagram for SUL-FON-ATE AA10 has been developed; it shows that this surfactant (even though it is very water-soluble) is strongly salted-out at NaCl concentrations greater than 2 wt.%. Pure, monoisomeric surfactants appear to be even more salt-sensitive, as do higher equivalent weight surfactants.

A surfactant precipitation diagram for use with multivalent cations has been developed, and the precipitation of SUL-FON-ATE AA10 by calcium ions depicted. The precipitation boundary, i.e., the calcium concentration at which precipitation of the calcium salt of the surfactant begins, has been delineated, and the concentration ranges in which precipitation and precipitate dissolution by excess surfactant identified. A mechanism for both precipitation and dissolution (or precipitation inhibition) by complex ion formation has been proposed, and it has been shown that solubility product constants and complex ion stability constants can be derived from experimental precipitation boundary curves.

The CMC of several surfactants was measured by the dye solubilization technique, using either Rhodamine 6G or Pinacyanol chloride. Fluorescence was observed in micellar solutions (especially with Rhodamine 6G), while scattered light was observed in pre-micellar solutions.



Over a period of several days a dye-surfactant precipitate settled out of pre-micellar solutions and the foaming ability of the solutions was diminished.

The method of polymer analysis described in an earlier report, based on our observation of quantitative precipitation of hydrolyzed polyacrylamides by cupric ions, has been tested further with good results. The copper content of the precipitate appears to be dependent on the degree of hydrolysis of the polyacrylamide; it can be determined by the cuproine method. Linear calibration curves are obtained for each polymer but the slope of the line is dependent on the degree of hydrolysis. The slope of the calibration curve appears to be directly proportional to the percentage hydrolysis of the polyacrylamide.

The State-of-The-Art Survey of surfactant losses by precipitation is continuing but the work is being hampered temporarily by personnel changes.



## I. INTERFACIAL PHENOMENA

Research Director: Professor D.O. Shah

### A. Measure CMC and Partition Coefficient of Synthetic and Petroleum Sulfonates

Investigator: Mr. Joseph Noronha

This is part of our continuing research into the partitioning of a surfactant between an aqueous and hydrocarbon phase. Here, we report on the partitioning of the surfactant Petrostep-465 (P-465). The surfactant was obtained from the Stepan Chemical Company and was used as received. The manufacturer's specifications for this surfactant are: 57.5% active sulfonate, 14.5% free oil, 24.9% water and 2.8% inorganic salt. All the oils and alcohols used were of 99% purity (Chemical Samples Company), NaCl was A.R. grade (Fisher Scientific), and water was deionized and distilled. Concentrations are in wt. % and refer to the initial concentration in the aqueous phase before addition of oil. The water-to-oil ratio was kept constant at 2.0 for all experiments. Samples were rotated (mixed) for 60 hours and then allowed to stand for two months before measurements were taken. Surface tensions were measured by the Wilhelmy Plate method and surfactant concentration by the two-phase mixed indicator titration method of Reid et al. (1967).

There were three parts in this investigation. In the first part, we studied the effect of oil chain length (of the hydrocarbon phase) on the partitioning of P-465 at various NaCl concentrations (aqueous phase). The cmc of P-465 had been previously determined to be 0.01 wt. % in distilled water. The oil chain length was varied from C<sub>6</sub> (hexane) to C<sub>16</sub> (hexadecane) for each of three surfactant concentrations (0.001%, 0.01%, 0.1%), and three salt concentrations (0.0%, 0.1%, 1.0% NaCl). For all the systems studied there was no appreciable effect of oil chain length on the O/W partition coefficient (oil phase concentration/aqueous phase concentration) of P-465. In addition, the partition coefficients were less than unity for 0.0% and 0.1% NaCl and greater than unity for 1.0% NaCl at all surfactant concentrations.

In the second part, we studied the effect of added alcohol (0.1 ml alcohol added to 10 ml aqueous + 5 ml oil) on the partitioning of P-465 between n-dodecane and water. The alcohols studied are listed in Table IA1 along with the partition coefficients at 0.01% and 0.1% P-465. Two things are immediately apparent from the table. Almost all the partition coefficients lay below a value of unity, and the partition coefficient decreases with increasing surfactant concentration. In addition, with increasing chain length of the alcohol, there appears to be a minimum in the partition coefficient near butanol or pentanol. This is approximately the transition region where alcohols change from being more water-soluble to being more oil-soluble. As expected, the more water-soluble the alcohol the larger is the partition coefficient.

Table IA1  
 Partition Coefficients of P-465 Between Water and  
 n-Dodecane in the Presence of Added Alcohol

Alcohol	O/W Partition Coefficient	
	0.01% P - 465	0.1% P - 465
Methanol	0.97	0.41
Isopropanol	0.94	0.37
n-butanol	0.79	0.35
i-butanol	0.69	0.37
t-butanol	0.52	0.27
n-pentanol	0.61	0.28
n-hexanol	0.77	0.26
n-heptanol	1.03	0.49

Finally, we studied the effect of added NaCl on the partitioning of P-465 between n-dodecane and brine. Four NaCl concentrations (0.1%, 1.0%, 2.0% and 4.0%) were investigated for a range of initial aqueous surfactant concentrations from 0.0001% to 0.1%. As before, the partition coefficients at all surfactant concentrations were below unity for 0.1% NaCl and above unity for 1.0%, 2.0% and 4.0% NaCl. The aqueous phase surface tension curves for these four NaCl concentrations are shown in Figure IA1. The curves for 0.1% and 1.0% NaCl show apparent cmc's near 0.02 and 0.004% P-465 respectively. No cmc can be detected in the curves for 2.0% and 4.0% NaCl in the concentration range studied. In addition, note that while the tensions for 1.0% NaCl are below those for 0.1% NaCl, the tensions for 2.0% and 4.0% are above those for 0.1% NaCl. This is because at these high salt concentrations virtually all the more surface active oil soluble surfactant is in the oil phase. With increasing salt concentration, the partition coefficient increases steeply and then levels off. Note that we should obtain a partition coefficient of unity between 0.1% and 1.0% NaCl.

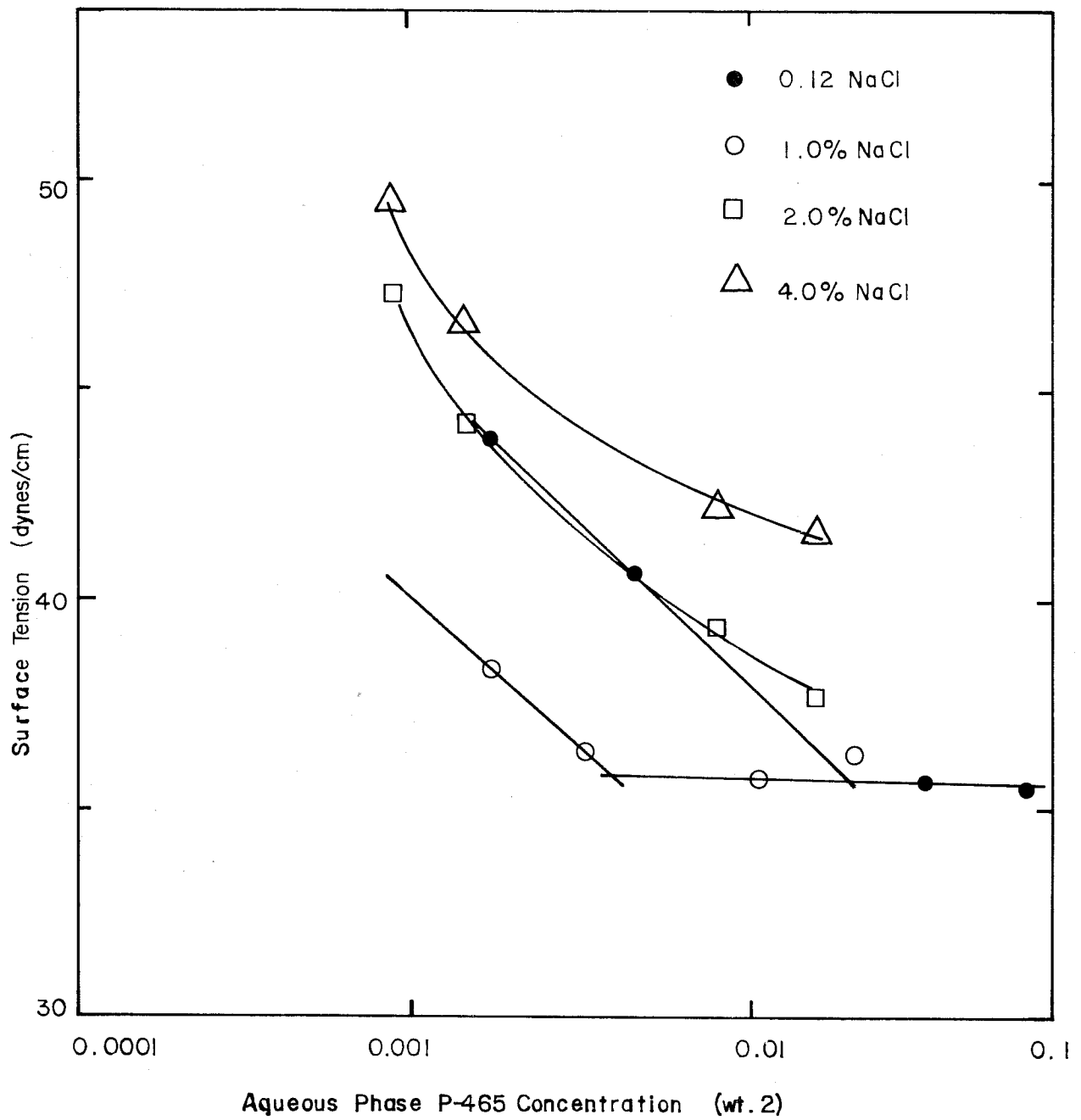


Figure IA| Aqueous Phase Surface Tension Curves for the System P-465/ Brine/Dodecane. WOR= 2.0

## B. Role of Alcohol in Dilute Surfactant Flooding Processes

Investigator: Mr. M. Chiang

Alcohol is one of the important constituents in the surfactant slug used in chemical flooding processes and the effect of alcohol on the physical-chemical properties of the surfactant solution has been studied extensively (Baviere, 1979; Hsieh, 1977; Jones, 1975; Puerto, 1977; Salter, 1977). However, all the systems investigated are in the high surfactant concentration range (1-10%). In the present study, the role of alcohol in oil displacement by dilute surfactant solutions (<0.1%) has been studied.

The following systems were examined: 0.1% TRS 10-410 with/without 0.06% IBA in 1.5% NaCl vs. n-dodecane, and 0.05% TRS 10-80 with/without 0.04% IBA in 1.0% NaCl vs. n-octane. Commercial petroleum sulfonates TRS 10-410 (61.2% active) and TRS 10-80 (90% active), as well as 99% pure IBA, n-dodecane, and n-octane, were used as received. Reagent grade NaCl and deionized, distilled water were used to make the brines. All percentages are calculated on a weight basis.

The interfacial tension (IFT) of the oils (n-dodecane, n-octane) after being equilibrated with surfactant solutions at an O/W volume ratio of 1:2, was measured using a Spinning Drop Interfacial Tensiometer, and the surfactant concentration in each phase was measured by means of the two-phase titration mixed-indicator method of Reid et al. (1967). The O/W partition coefficient, the ratio of surfactant concentration in oil to that in brine, was computed. The spreading time, i.e., the time for an oil droplet to spread out after being deposited on the underside of a polished quartz plate submerged in the aqueous surfactant solution, was measured. Interfacial viscosity (IFV) was measured using a viscous-traction interfacial viscometer constructed according to Wasan (1977). Oil displacement was conducted in a horizontally mounted sand pack, 1.06" diameter by 7.0" long, at a flooding velocity of 2.3 ft/day. For the TRS 10-80/n-octane system, surfactant solution flooding was preceded by 1% NaCl waterflooding; however, for the TRS 10-410/n-dodecane system, no waterflooding was undertaken. Except for IFT and partition coefficient measurements, all experiments were done with the non-equilibrated oils and surfactant solutions. The results are listed in Table IBI.

In Figure IBI the cumulative oil recovery profiles of the systems studied are shown. These curves show that the addition of 0.06% IBA to the TRS 10-410/n-dodecane system results in an improvement in the oil recovery by direct surfactant solution flooding (i.e. without waterflooding) from 84% to 98% after 3.5 PV surfactant solution injection. A much more dramatic difference is seen in the TRS 10-80/n-octane system, where the tertiary oil recovery increased from 0% without IBA to 77% with IBA (See Table IBI) after 2.7 PV surfactant solution injection.

Table IB1  
The Effect of IBA on Spreading Time, IFT, IFV, Partition Coefficient,  
and Oil Displacement Efficiency

<u>SYSTEM</u>	0.1% TRS 10-410 in 1.5% NaCl vs n-Dodecane	0.1% TRS 10-410 + 0.06% IBA in 1.5% NaCl vs. n-Dodecane	0.05% TRS 10-80 in 1% NaCl vs n-Octane	0.05% TRS 10-80 + 0.04% IBA in 1% NaCl vs. n- Octane
<u>Run</u>	S100-48	S100-43	S100-02	S100-44
<u>Spreading Time</u>	90 sec	1 sec	420 sec	1 sec
<u>IFT (dynes/cm)</u>	0.086	0.088	0.026	0.024
<u>Interfacial Viscosity (s.p.)</u>	0.096	0.08	0.023	0.01
<u>Partition Coefficient</u>	0.010	0.009	0.3	1.36
<u>Secondary Recovery</u>				
By Brine	-	-	61%	60%
By Surfac- tant soln.	.84	98%	-	-
<u>Tertiary Recovery</u>	-	-	0	76%
<u>Final Oil Saturation</u>	12%	1.3%	30%	5.4%

\*All displacement experiments are carried out with non-equilibrated systems in sand packs at 25°C.

Secondary and tertiary oil recovery values are percent of oil-in-place, whereas final oil saturation is percent of total pore volume.

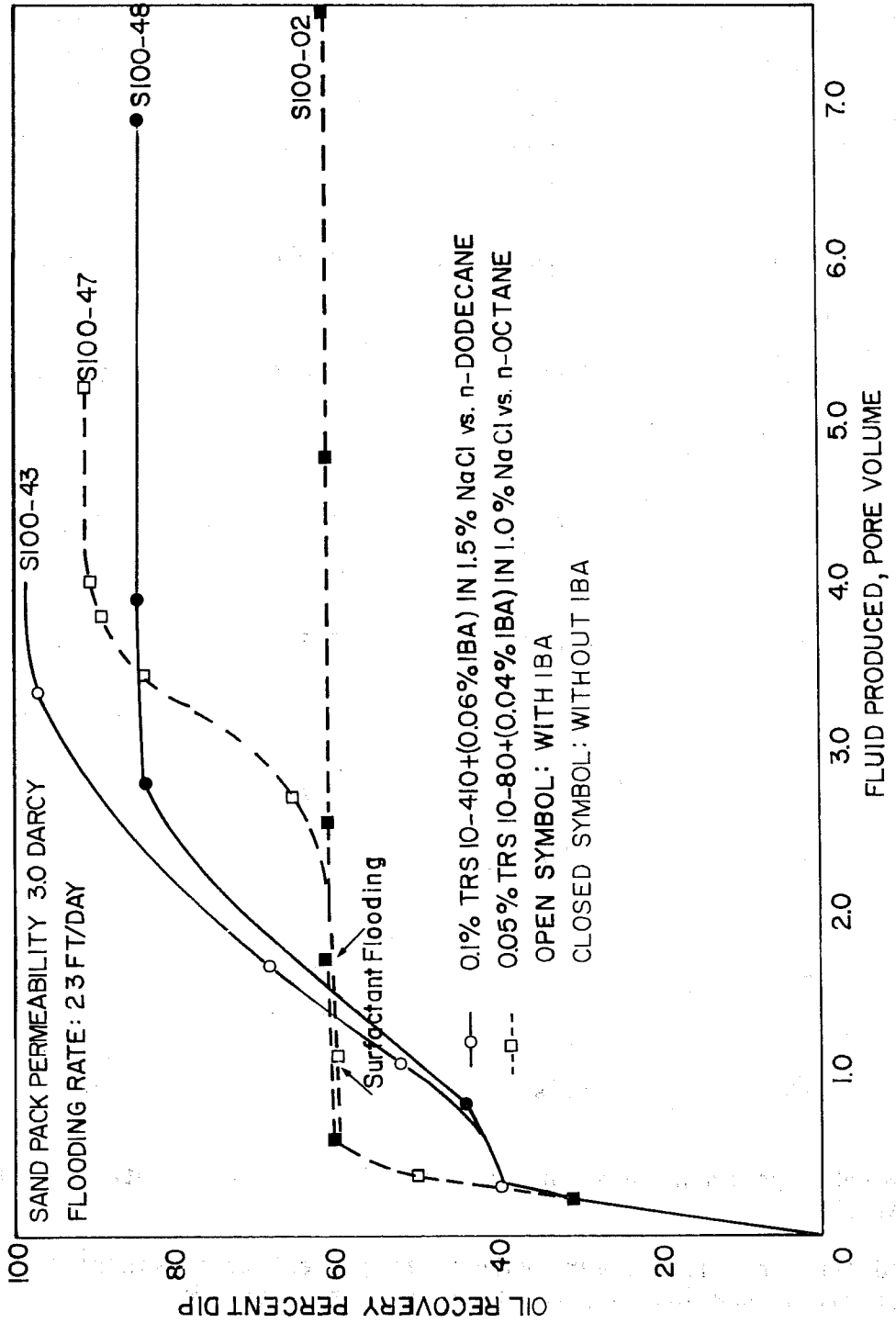


Figure IBI Cumulative Oil Recovery Profile by Dilute Surfactant Solution Flooding



Because the same IFT values were obtained for the systems with and without IBA, the observed differences in oil recovery cannot be explained in terms of the change in IFT. Also, the partition coefficients do not correlate with the oil displacement efficiency. However, the oil drop spreading time and the IFV do correlate with the oil recovery results. It has been suggested by Shah *et al.* (1972) that rigid potassium oleate films at a oil/water interface can be disordered and fluidized by the penetration of hexanol molecules. It has been shown by Wasan *et al.* (1977) that, for a commercial petroleum sulfonate-crude oil system, oil droplets in the presence of alcohol coalesce much faster than those without alcohol. Thus, for the systems studied here, IBA is believed to have penetrated the petroleum sulfonate film as evidenced by the reduction in IFV, and this facilitated coalescence of the oil droplets.

Furthermore, because the oil droplet spreading time is drastically reduced in the presence of alcohol, it is conjectured that surfactant mass transfer across the interface is enhanced by penetration of alcohol molecules into the surfactant film. As the surfactant solution contacts the oil ganglia, it is very likely that a rapid mass transfer occurs effecting a transient ultralow IFT and spontaneously the oil ganglia spread out and disintegrate into several microdroplets. A successful spreading and disintegration of the oil ganglia in the initial stage presumably leads to the formation of an oil-water bank which then successfully sweeps the oil ganglia along the porous medium by a coalescence process. Thus, it is proposed that not only the equilibrium properties such as IFT and IFV are important but the dynamic process of surfactant partitioning is involved in the mobilization of oil ganglia. The conditions that promote efficient mass transfer from the aqueous phase to the oil phase also deform the oil ganglia and produce a transient ultralow IFT. This would contribute to an early formation of oil water bank and a subsequent displacement of oil from the porous media.

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## II. POLYMER RHEOLOGY AND FLUID MECHANICS

Research Director: Professor D.O. Shah

### A. Molecular Characterization of Polymers

Investigator: Dr. A.N. SunderRam

1. Determine the  $\Delta P/L$  of Biopolymer Solutions Through a Silica Gel Column. Compare this Parameter with Screen Factor and Intrinsic Viscosity of the Same Polymers and with Polyacrylamides.

In this report a continuation of our work on flow through a column of silica gel with biopolymer is discussed.

#### Materials and Methods:

A similar setup to that used for the determination of  $\Delta P/L$  of polyacrylamide solutions was arranged for the biopolymer solutions (Project Status Report, December 1978). EM-GEL 200Å, obtained from the E. Merck, was used in this study.

A 500 ppm biopolymer solution, FLOCON Biopolymer 1035 (supplied by Pfizer) in 1% NaCl was sheared in a Waring Blender for 2 minutes. Different amounts of  $\text{CaCl}_2$  (100, 500, 1000, 1200, and 2000 ppm) were added to the polymer solution, and the pressure drop was measured as described in an earlier quarterly report (December 1978).

#### Results and Discussion:

The results indicate that the biopolymer with 0, 100 and 500 ppm of  $\text{CaCl}_2$  exhibits linear relations for  $\Delta P/L$  vs. flow rate (Q) plots (Figure IIA1). In the presence of higher concentrations of calcium chloride (1000-2000 ppm), however, the polymer solutions show a non-linear type of behavior. For the systems studied it was observed that there is an optimum  $\text{CaCl}_2$  concentration (1200 ppm) similar to the polyacrylamide systems, C815 and C835. In our earlier work, the polyacrylamide systems produced a minimum  $\Delta P/L$  value at the optimum  $\text{CaCl}_2$  concentration. However, the present study on biopolymer solutions shows a maximum  $\Delta P/L$  value under the same conditions. Further investigation is required to make a conclusion from these interesting observations.

To find the influence of calcium ions in promoting the adsorption of biopolymer on negatively charged silica surfaces we measured the viscosity and screen factor of the polymer solutions which flowed through the porous media. The results show that the rheological parameters are relatively insensitive to the calcium ion concentration.

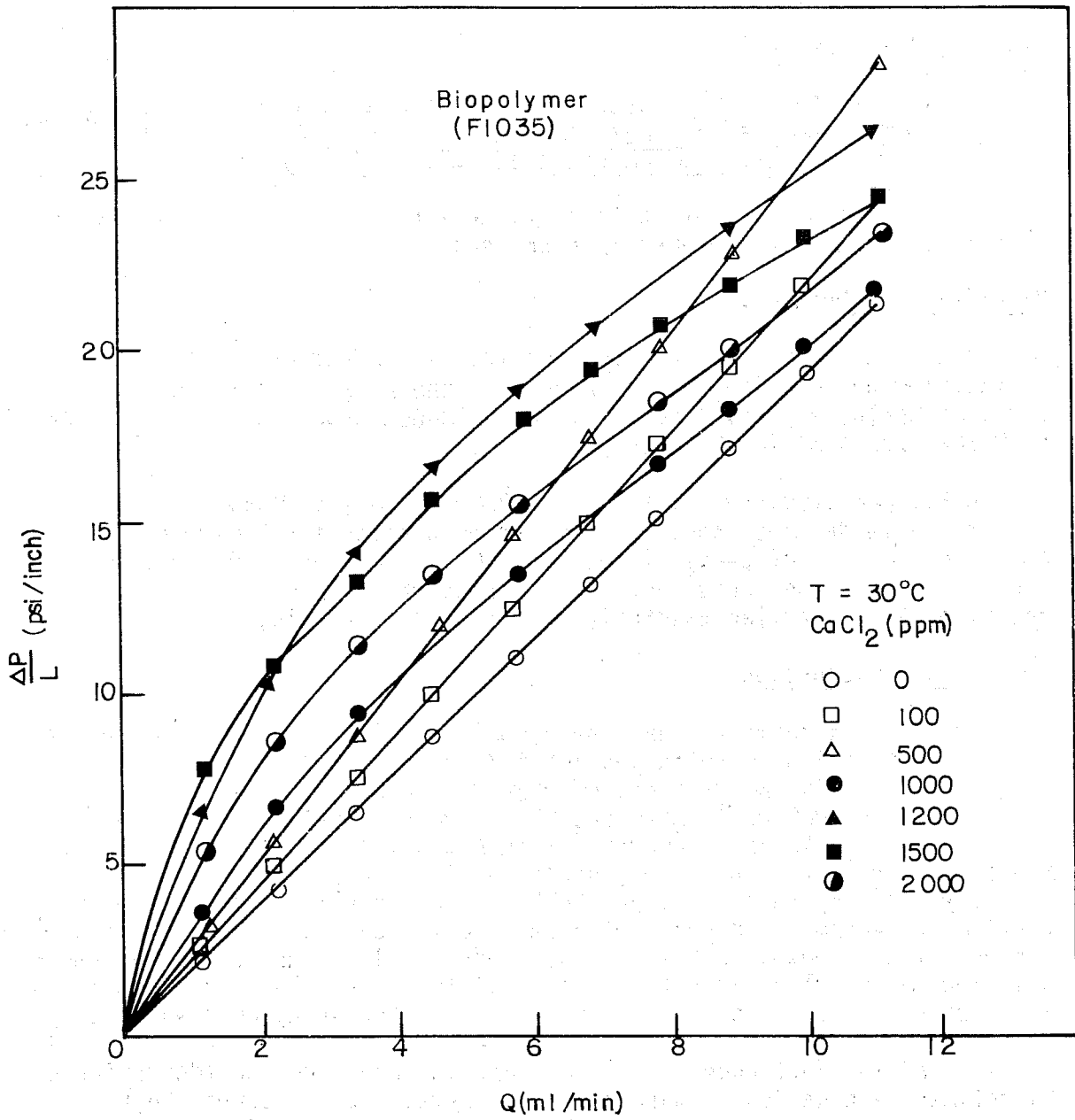


Figure IIA1 Pressure Drop Variation With Flow Rate at Different CaCl<sub>2</sub> Concentrations

## B. Surfactant/Polymer Interactions

Investigator: Mr. N.N. Desai

Interactions between surfactant and polymer may arise when they are mixed leading to binding of the surfactant to the polymer. It was decided to see if such binding does, in fact, occur in oil-recovery systems. Equilibrium dialysis was chosen as a direct method of measuring binding.

### Materials and Methods:

SUL-FON-ATE AA10 was supplied by the Cities Service Co. The polymers used were polyacrylamide, unhydrolyzed (C-800), and partially hydrolyzed (C-835); both were obtained from Calgon Corporation.

A sample containing known surfactant and polymer concentration in brine was confined in a cellulose tubing and equilibrated with brine of the same concentration at 30°C. Samples without the polymer were used as control. After equilibration, the surfactant concentrations in the external brine were measured using the two-phase mixed indicator method of Reid et al. (1967).

Prior to using this method for surfactant analyses of dialyzed samples, its validity in the presence of polyacrylamides was checked as follows: Samples containing fixed surfactant and various polymer concentrations were analyzed by titration. It was found that neither C-835 nor C-800 affected the results.

The dialysis experiments were conducted in two series:

- (i) fixed surfactant concentrations (.001, .005, .01 wt.%) and varying polymer concentrations (0 ppm to 1000 ppm);
- (ii) fixed polymer concentrations (550 ppm to 1000 ppm) and varying surfactant concentrations (.001 to .01%).

No difference was observed in the surfactant concentration of the dialysed samples in the presence or absence of polymer. Thus, these experiments provide no clear evidence for binding of the surfactant to the polymer.

Parallel studies in the presence of alcohol are underway.

## C. Phase Behavior of Surfactant Solutions in the Presence of Polymer

Investigator: Mr. N.N. Desai

Numerous studies have been done on the phase behavior of surfactant-cosurfactant-oil-brine systems. Here, we report some of our findings with an additional parameter, viz., polymer concentration.

The polymer used was Calgon 835 (partially hydrolysed polyacrylamide). The samples were prepared by mixing the various constituents in graduated cylinders and storing them at 30°C until the volumes of the various phases remained constant with time. The original compositions of the various samples were as follows:

Aqueous Phase:

Surfactant (TRS 10-410): 5% (g. as rec'd surfactant/100 ml soln.)  
 Cosurfactant (Isobutanol): 3 wt.%  
 Sodium Chloride: 1.0, 1.5, and 3.0 wt.%  
 Polymer: y ppm (y=50 to 1000 ppm)

50 ml of the aqueous phase were equilibrated with an equal volume of n-dodecane for 6 wks.

The equilibrium volumes of the various phases for two of the polymer concentrations studied are shown in Table IIC1. Evidently, the presence of the polyacrylamide does not alter the phase-volume relationships at any of the three salinities studied (below, at, and above optimal salinity).

The interfacial tensions of the three samples above optimal salinity are given in Table IIC2. Polymer concentration does not alter the interfacial tension. Note: At 1.0% salinity the phase-behavior appears to be a stronger function of the temperature and polymer concentration than at higher salinities, but the data in hand are too fragmentary to be conclusive. However, this behavior is being further explored and the findings will be dealt with in a later report.

Table IIC1  
 Effect of Polyacrylamide on the Phase Volumes of TRS 10-410  
 IBA/Brine/Dodecane System

NaCl Conc., Wt.%	Phase	No Polymer	250 ppm C835	750 ppm C835
1.0	Upper	43.0	43.0	43.0
	Middle	-	-	-
	Lower	57.0	57.0	57.0
1.5	Upper	32.5	32.5	33.0
	Middle	30.0	31.5	31.0
	Lower	37.5	36.0	36.0
3.0	Upper	54.0	55.0	55.0
	Middle	-	-	-
	Lower	46.0	45.0	45.0

Table IIC2  
Effect of Polyacrylamide on the Interfacial Tension Behavior  
of TRS 10-410/IBA/Brine/Dodecane System. Salinity: 3.0 wt.%

<u>Polymer Conc., ppm</u>	<u>Interfacial Tension dynes/cm</u>
0	0.5
250	0.033
750	0.065





### III. THERMODYNAMICS

Research Director: Professor J.P. O'Connell

#### Theory

Investigators: Dr. R. J. Brugman and Mr. Paul Coram

The molecular theory for aqueous solutions developed by Brugman and outlined in the previous report has been extended to chain paraffin species with some success. Table IIIA1 shows comparisons of calculations with data for the entropy of solution of hydrocarbons through n-hexane where the single parameter of the model was fitted to the solubility (free energy) at 25°C. Comparisons are made in Table IIIA2 for the chain length effect on the heat capacity of infinitely dilute alkylamine hydrobromides. In general, the agreement is considered good. However, when all the contributions to our model for micelle formation are brought together, they do not agree well with the thermodynamic functions of micellization for three of the sodium alkyl sulfonates. There are several places where we believe the model is deficient and are working to improve the agreement.

The investigation of a new basis for corresponding states correlation of surface tensions, which was begun two years ago but suspended, has been restarted. Initial results show that the basis in molecular theory is consistent with a highly successful solution theory for high pressure vapor-liquid equilibria (Mathias, 1978).

#### Experiment

Investigators: Mr. Paul Coram and Ms. Charlotte Chen

The high pressure apparatus for observing isotropic-anisotropic transitions has finally been thermostated to controlled uniformity of  $\pm 0.1^\circ\text{C}$ .

Investigation of the appropriate sample compositions of the potassium oleate system has turned up the usual myriad of behavior of concentrated surfactant systems. The atmospheric viscosity, isotropy, and phase behavior (including presence of solids) are highly sensitive to temperature, pH, and oil/water ratio. In particular, there are ranges of composition where the low-temperature phase is anisotropic and high temperature isotropic, and other where the opposite is true. In some cases, the "two-phase" region has a dispersed solid, in others not. In some cases, the formation of an interface between the phases takes a few hours to appear, in others several days. We plan to demonstrate a three dimensional-T-pH O/W phase behavior diagram when more data are obtained. In the meantime, a sample which transforms a fluid-isotropic phase to a viscous, anisotropic gel with only a small temperature change will be made with a sulfonate system displaying gelation.

Table IIIA1  
 Comparisons of Aqueous Solution Theory With  
 Experimental Thermodynamic Properties at 25°C

Substance	$\Delta G^\circ/RT$		$\Delta S^\circ/R$		$\Delta C_p^\circ/R$	
	Calc	Exp <sup>1</sup>	Calc	Exp	Calc <sup>p</sup>	Exp
CH <sub>4</sub>	10.60*	10.60	-16.8	-16.2 <sup>1</sup>	30.0	25.6 <sup>1</sup>
C <sub>2</sub> H <sub>6</sub>	10.31*	10.31	-18.0	-18.3 <sup>1</sup>	35.3	37.1 <sup>1</sup>
C <sub>3</sub> H <sub>8</sub>	10.52*	10.52	-19.4	-19.6 <sup>1</sup>	40.6	45.6 <sup>1</sup>
nC <sub>4</sub> H <sub>10</sub>	10.73*	10.73	-21.1	-21.2 <sup>1</sup>	51.9	46.1 <sup>1</sup>
nC <sub>5</sub> H <sub>12</sub>	11.15*	11.15	-22.9	-22.7 <sup>2</sup>	61.2	51.9 <sup>2</sup>
nC <sub>6</sub> H <sub>14</sub>	11.50*	11.51	-24.4	-24.2 <sup>2</sup>	69.2	59.2 <sup>2</sup>

\*Fitted

1. E. Wilhelm, R. Battino and R.J. Wilcock, Chem. Rev. 77, 219 (1977).
2. S.J. Gill, N.F. Nichols and I. Wadso, J. Chem. Thermo. 8, 445 (1976).

Table IIIA2  
 Comparisons of Chain Length Effects on Heat Capacities  
 of Infinitely Dilute Alkylamide Hydrobromides at 25°C

Segment	$C_p^{-\infty}/R$	
	Exp <sup>1</sup>	Calc
C <sub>1</sub> -C <sub>2</sub>	7.3	6.2
C <sub>2</sub> -C <sub>3</sub>	7.9	9.2
C <sub>3</sub> -C <sub>4</sub>	14.2	13.0
C <sub>4</sub> -C <sub>5</sub>	11.9	12.1
C <sub>5</sub> -C <sub>6</sub>	10.8	11.2
C <sub>6</sub> -C <sub>7</sub>	10.9	11.0
C <sub>7</sub> -C <sub>8</sub>	11.3	11.5

1. P.A. Leduc, J.L. Fortier and J.E. Desnoyers, J. Phys. Chem., 78, 1217 (1974).

Examination of a model brine-oil-surfactant-alcohol system showing three-phase behavior with rapid equilibration (sodium stearate) continues. We have found the ranges of surfactant-oil-water-alcohol conditions where the system can change from two-to three-to two-phases with salinity, the last transition involving disappearance of either the middle or the upper phase, depending on composition. Optimal salinities, defined by equal solubilized oil and water, have been found and the interfacial tensions are equal but about 1 dyne/cm. Measurements of the surfactant concentrations in the external phases are being made, as well as conductivity of the middle phase, to check on the structure. We have found that the appearance of external brine phase is highly temperature-sensitive. Also, some of the expected phase behavior is not found or is distorted because a white solid precipitate appears and settles at the interface. These particles are opaque and do not transmit in a polarizing microscope, indicating a crystal rather than a liquid crystal.

#### Reference

P.M. Mathias, Ph.D. Dissertation, University of Florida, (1978).



## IV. ROCK/FLUID INTERACTIONS

Research Director: Professor R.D. Walker, Jr.

Work in this area has been concerned with the following subjects: (1) additional studies on the salting-out of SUL-FON-ATE AA10, including the effect of adding short chain alcohols in varying quantities; (2) precipitation of SUL-FON-ATE AA10 by calcium ions; (3) measurements of the CMC of surfactants by the dye solubilization method; (4) further testing of the method of polymer analysis reported in the previous Project Status Report (Jan.-Mar., 1979); (5) limited progress on the State-of-The-Art-Survey of Surfactant Losses by Precipitation.

### A. Surfactant Salting-Out By Indifferent Electrolytes

Investigators: Dr. G. Rama Rao, Mr. James Funk, and Mr. Mark Stump

#### 1. Influence of Short Chain Alcohols on Surfactant Salting-Out

A limited number of experiments on the effect of short chain alcohols on the salting-out of SUL-FON-ATE AA10 have been undertaken; this work is still incomplete and will be described more fully in a later report. As is well-known, alcohols do inhibit surfactant salting-out, and in sufficient quantities can prevent it altogether within certain limits of salt concentration. It seems clear from the data in hand, however, that fairly large amounts of alcohol are required to prevent salting-out. For SUL-FON-ATE AA10, it appears that several hundred isopropanol molecules per surfactant anion are required to prevent salting-out even at relatively moderate salt concentrations, say 2 wt.% NaCl.

#### 2. The Salting-Out Diagram

Data on the salting-out of SUL-FON-ATE AA10 from water have been replotted on a 3-dimensional diagram, which we shall call the surfactant salting-out diagram, and they are shown in Figure IVA1. There are two horizontal axes, one representing the initial (total) concentration of surfactant and the other representing the concentration of salt; the vertical axis represents the fraction of surfactant remaining in solution at equilibrium i.e., the fraction of surfactant not salted-out. Curves for constant salt concentrations are plotted, and these define the surface which represents the boundary between salted-out (precipitated) surfactant and surfactant-saturated salt solution. The area to the left of and below the surface represents a one-phase system of surfactant dissolved in salt solution. The area above and to the right of the surface represents a two-phase system consisting of saturated solution and salted-out surfactant.

Examination of Figure IVA1 reveals that SUL-FON-ATE AA10 is not salted-out by one wt.% NaCl regardless of surfactant concentration, at least up to about 10 wt.% surfactant. However, at a slightly larger

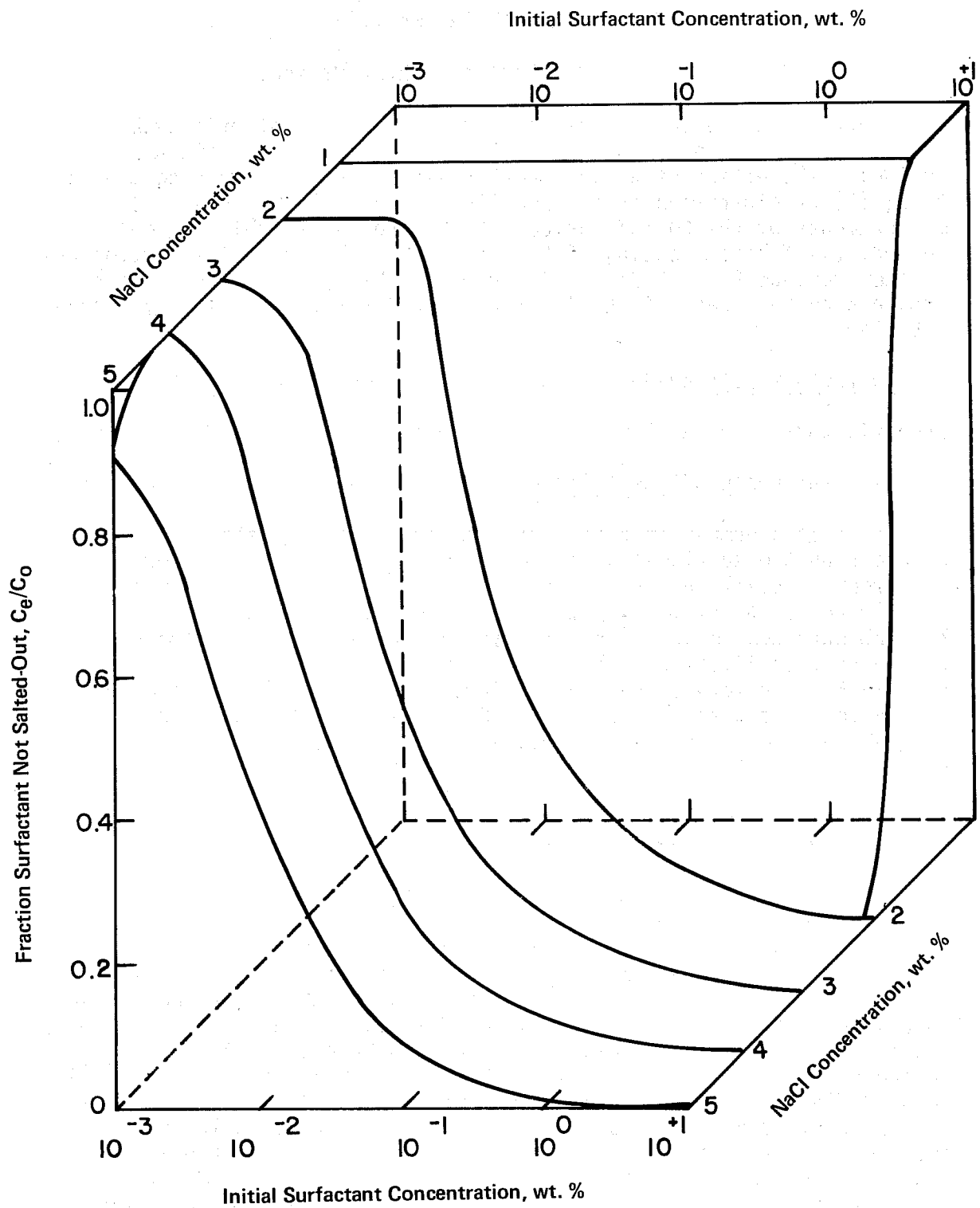


Figure IV(A) Salting-Out of SUL-FON-ATE AA10

salt concentration severe salting-out can be seen to occur for all surfactant concentrations appreciably larger than 0.005 wt.%. When the NaCl concentration exceeds 2 wt.% and the surfactant concentration exceeds about 0.01 wt.%, salting-out of SUL-FON-ATE AA10 approaches completion.

It seems likely that the salting-out diagram of other surfactants would be similar to that shown in Figure IVA1, but shifted as to both salt and surfactant concentrations according to the characteristics of the surfactant. For example, the salting-out curve for  $2\text{-}\phi\text{C}_{12}\text{SO}_3\text{Na}$  in one wt.% NaCl is quite similar to the salting-out curve for SUL-FON-ATE AA10 in 2 wt.% salt, but it is shifted nearly one decade towards lower surfactant concentrations. The few data available suggest that the salting-out surface shifts towards smaller surfactant and salt concentrations as the surfactant equivalent weight increases. Pure monoisomeric surfactants appear to be more sensitive to salting-out than are commercial mixtures having essentially equal average equivalent weights.

Even in its present elementary state, the surfactant salting-out diagram appears to be useful in developing a feel for the probable fate of a surfactant slug in contact with reservoir brine insofar as the influence of salt concentration is concerned. It is clear, however, that one must also consider the influence of multivalent cation precipitation, adsorption, and partitioning to oil. Ultimately, one would hope to be able to describe the total effect of all of these potential surfactant loss processes in a single set of equations or in a single surfactant loss diagram. Clearly, this goal is not yet in sight.

A factor which has not been studied but which has been noted is that salting-out is sometimes quite slow. The kinetics of the process may be very important for reservoir flooding owing to the extended time frame. This is an area which we propose to investigate at a later time.

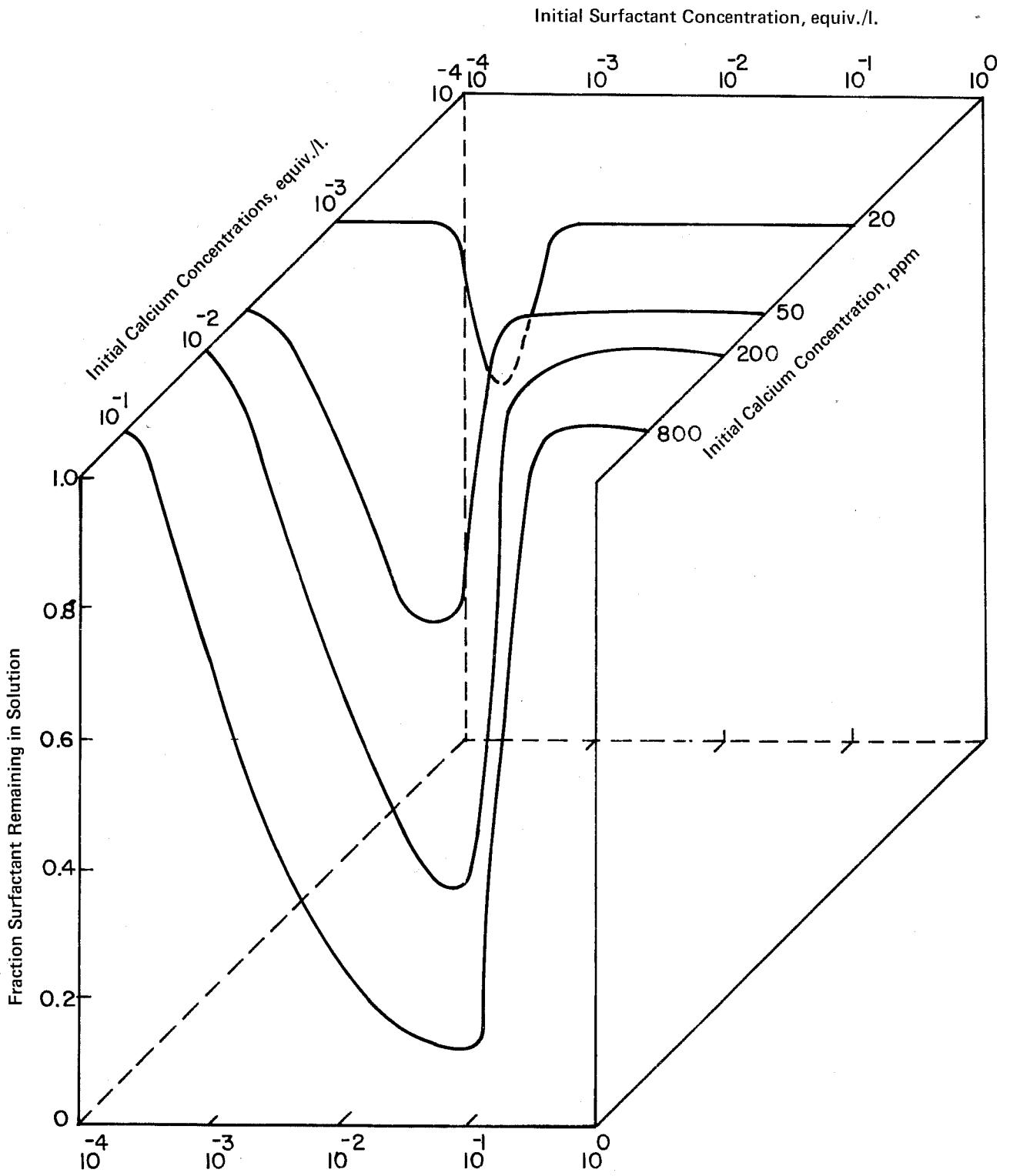
## B. Surfactant Precipitation by Multivalent Cations

Investigators: Dr. G. Rama Rao, Ms. Jean Meister, and Miss Jenny Saygers

### 1. Surfactant Precipitation Diagram

Data on the precipitation of SUL-FON-ATE AA10 by calcium ions have been recalculated and replotted in Figure IVA2, a 3-dimensional diagram which we shall refer to as the surfactant precipitation diagram. This diagram is similar to the surfactant salting-out diagram in that one of the horizontal axes represents the concentration of the species causing precipitation (calcium ions in this case), while the other horizontal axis and the vertical axis have the same significance as on the surfactant salting-out diagram.

The curves plotted on Figure IVA2 represent the precipitation curves for several constant concentrations of calcium ions. Together they define the surface separating a clear solution containing both calcium and surfactant and a two-phase region consisting of a saturated calcium-



Precipitation of SUL-FON-ATE AA10 by Calcium Ions

Figure IVA2

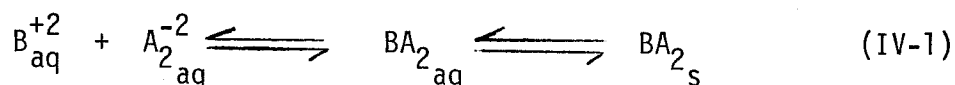


surfactant solution and a precipitate of the calcium salt of the surfactant. The left-hand wall of the valley thus defined represents a composition range where precipitation of the calcium surfactant predominates, while the right-hand wall represents the region where precipitation is inhibited or precipitate dissolved by excess surfactant. The floor of the valley represents the area of maximum surfactant precipitation. No valley exists where the solubility product is not exceeded and the bottom of the valley drops sharply as the calcium ion concentration increases. However, owing to our choice of expressing precipitation as a fraction of the surfactant added, it is clear that the bottom of the valley must approach zero asymptotically as the calcium concentration increases while at the same time the bottom of the valley broadens. Parenthetically, it may be desirable to convert the vertical axis to some function of surfactant remaining in solution, say  $\log C_e$ , rather than the ratio  $C_e/C_0$ .

It also seems worth noting that a curve joining the points defining the edge (beginning and ending) of the precipitation valley represents the "precipitation boundary" defined by other researchers.

## 2. The Mechanism of Multivalent Cation Precipitation and Dissolution

It seems clear that surfactant precipitation by multivalent cations is fairly straightforward and that it can be described a reaction such as



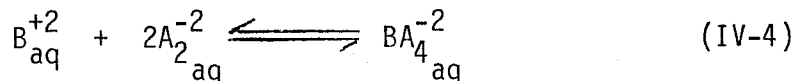
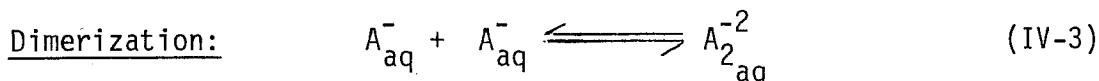
The solubility product is given by

$$K_{sp} = C_{B^{+2}} \times C_{A_2^{-2}} \quad \text{or} \quad C_{A_2^{-2}} = \frac{K}{C_{B^{+2}}} \quad (IV-2)$$

Limited solubility data in our laboratory indicate that for SUL-FON-ATE AA10 the solubility product constant at 30 C is between  $4 \times 10^{-10}$  and  $2 \times 10^{-9}$ ; the higher figure appears to be more nearly the correct one.

In the last Project Status Report (Jan.-Mar., 1979) we reported the probability that dissolution of calcium lauryl sulfate began before the CMC for lauryl sulfate was reached. We have tested this concept with a considerable number of samples of SUL-FON-ATE AA10 in which precipitate dissolution or inhibition of precipitation by excess surfactant was occurring by adding a few drops of Rhodamine 6G to the supernatant liquid and observing the color. These tests confirmed that much of the precipitate dissolution occurred before the CMC was reached. At low calcium concentrations it appears that the entire precipitation-dissolution region occurs before the CMC is reached. Thus, one is forced to the

conclusion that the onset of precipitate dissolution occurs at surfactant concentrations below the CMC and that the dissolution must begin by fixation of calcium in surfactant polyanions-not micelles. The reaction can be described by the following equations.



The dissolution reaction can be described by an equilibrium constant,  $K_{st}$ .

$$K_{st} = \frac{C_{BA_4}^{-2}}{C_{B^{+2}} \times C_{A_2}^{-2}}$$
 (IV-5)

If we consider precipitation alone, its onset is described by Equation IV-2, and a log-log plot of  $C_{B^{+2}}$  versus  $C_{A_2}^{-2}$  gives a straight line with slope of -1. The position of the line on the log  $C_{B^{+2}}$  vs. log  $C_{A_2}^{-2}$  graph depends on the value of  $K_{sp}$  (which we have seen to be about  $2 \times 10^{-9}$  for calcium SUL-FON-ATE AA10). If we consider the precipitate dissolution process described by Equation IV-5 and we combine Equation IV-5 with Equation IV-2, (also noting that at the completion of dissolution essentially all of the calcium is fixed in the surfactant polyanion, we obtain

$$C_{A_2}^{-2} = \frac{C_{BA_4}^{-2}}{C_{B^{+2}} K_{st}} = \frac{C_{B_0}^{+2}}{\frac{K_{sp}}{C_{A_2}^{-2}} \times K_{st}}$$

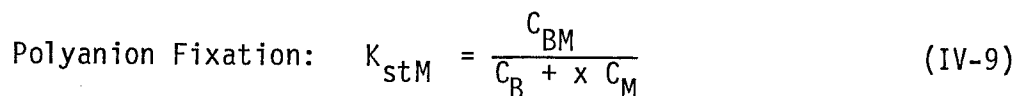
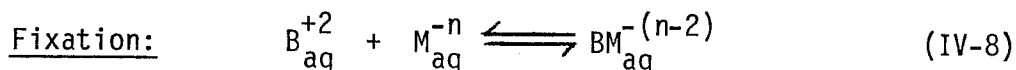
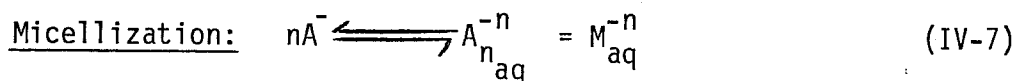
or

$$C_{A_2}^{-2} = \frac{C_{B_0}^{+2}}{K_{sp} K_{st}}$$
 (IV-6)

Equation IV-6 is the equation of a straight line with a slope of +1, and the position of the line on the graph is dependent on the product  $K_{sp} K_{st}$ . We have some preliminary indications that  $K_{st} \doteq 10^5$ , so  $K_{sp} K_{st} \doteq (2 \times 10^{-9})(10^5) \doteq (2 \times 10^{-4})$ . It should be borne in mind that the values of these constants are very tenuous but it

also seems clear that one can use this sort of analysis to locate the precipitation boundary for a given surfactant and that solubility product constants and complex ion stability constants can be derived from experimental measurements of precipitation boundaries.

At large calcium concentrations, precipitate dissolution by fixation of calcium in micelles must be a significant part of the dissolution process. The micellization and micellar fixation processes can be depicted as follows:



By analogy, one can develop a relationship between the initial concentration of calcium ions,  $C_{B_0}^{+2}$ , and the concentration of surfactant which must be added to just fix all of the calcium ions in the micelles, keeping in mind that the micellar concentration is zero below the CMC.

### 3. The Influence of Oil and Alcohol on Surfactant Precipitation

Oil: SUL-FON-ATE AA10 was mixed with calcium ions in various proportions and equilibrated with n-dodecane. The oil and water phases were separated and each was analyzed for surfactant. No partitioning of the surfactant to the oil phase was noted, except that at the point of maximum precipitation (one equivalent of surfactant per equivalent of calcium) a very slight amount of surfactant was found in the oil phase. It appears, then, that SUL-FON-ATE AA10 does not partition to oil regardless of the counterion with which it may be associated.

Alcohol: Isopropanol was added to mixtures of SUL-FON-ATE AA10 and calcium ions in amounts just sufficient to dissolve the precipitate. The entire precipitation-dissolution range was covered. The supernatant liquid was tested with Rhodamine 6G for micellization. This study is still incomplete and will be discussed more fully in a later report, but it is clear that there are sharp changes in the system near the sulfonate-calcium equivalence point. It appears that several hundred molecules of alcohol are required to solubilize each calcium ion.

### C. Surfactant CMC by Dye Solubilization

Investigators: Dr. G. Rama Rao, Mr. S.B. Balachandran and Miss Jane Sholine

Numerous researchers have used the dye solubilization method to evaluate the CMC of surfactants. Because of its simplicity and applicability to very limited volumes of solution, experiments were undertaken with two basic (cationic) dyes, Rhodamine 6G and Pinacyanol chloride.

Standard solutions of the dyes were made at concentrations of  $1 \times 10^{-4}$  moles/l and  $1 \times 10^{-3}$  moles/l. Constant volumes of these standard dye solutions of SUL-FON-ATE AA10 to make a range of surfactant concentrations with final dye concentrations of  $1 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $5 \times 10^{-5}$ , and  $1 \times 10^{-4}$  moles/l. These solutions were mixed carefully and the color observed.

With Rhodamine 6G a strong yellow-green fluorescence was observed in the micellar solutions. As the surfactant became more dilute, the fluorescence became somewhat less intense, and as the surfactant concentration approached the CMC, the solution became magenta colored with little or no fluorescence. As the surfactant was further diluted a cloudiness soon developed so that a strong Tyndall cone could be observed (white scattered light-not yellow-green fluorescence). For the more concentrated solutions of Rhodamine 6G and pre-micellar surfactant, a red precipitate (appearing to be an insoluble dye-surfactant complex) eventually settled to the bottom of the test tube leaving a less colored supernatant. Most, or all, of the foaming ability of the surfactant solution disappeared when the precipitate separated.

Spectral absorption curves were run on the dye-surfactant mixtures for each of the dyes at a final dye concentration of  $1 \times 10^{-5}$  moles/l with the following results:

Rhodamine 6G: A strong absorption band is observed at 535nm; the absorbance at 535nm remains constant so long as the surfactant concentration is above the CMC, At the CMC the absorbance at 535nm begins to decline and continues to do so as the surfactant becomes more dilute. At surfactant concentrations well below the CMC a second absorption band appears as a "shoulder" on the main absorption band; finally it becomes a major absorption band itself. One can estimate the CMC from a plot of the absorbance at 535nm versus surfactant concentration, but it appears to be nearly as precise and much simpler to make visual observations.

Pinacyanol Chloride: This dye possesses several significant absorption bands which change in their relative strength as the surfactant concentration changes. They occur at 455, 565, and 610nm, the 455nm band being most prominent in pre-micellar solutions. Micellar solutions appear blue while pre-micellar solutions appear slightly reddish owing to the strong blue to blue-green absorption band in these solutions. Again, visual observation appears to be a reasonably precise and simple way to determine the CMC.

The CMC of several surfactants was measured with each of the dyes. Although these tests, which are being carried out by Miss Jane Sholine-a high-school student who became available part-time for a short period this summer-and are still incomplete, it can be reported that good agreement with the CMC determined by other techniques has been achieved. The observation of greatest interest to date is that no second (low concentration) CMC has been observed by the dye solubilization technique when the surfactant solution was equilibrated with a slight excess of either n-octane or n-dodecane. This is, of course, in contrast to the results of our CMC determinations by surface tension measurements.

## D. Polymer Analysis and Polymer Adsorption

Investigator: Mr. S.B. Balachandran

### 1. Polymer Analysis By the Copper-Cuproine Method

This method, developed in our laboratories for analysis of hydrolyzed polyacrylamides in the presence of clays, was described in some detail in the last Project Status Report (Jan.-Mar., 1979). Briefly, it consists of precipitation of the polymer with  $\text{CuSO}_4$ , dissolution of the precipitate with hydroxylamine hydrochloride after washing, and colorimetric analysis of the copper in the precipitate by the cuproine method.

The method has been tested out with several other hydrolyzed polyacrylamides, and has been found to give linear calibration curves up to at least 1000 ppm polymer for every sample tested. A representative group of calibration curves are shown in Figure IVD1. No difficulties in analysis have been experienced but the slope of the calibration line is dependent on the degree of hydrolysis as is shown in Figure IVD2. Here, we see that the slope of the calibration curve is a linear function of the degree of hydrolysis. If we let  $m$  = the slope of the calibration curve, the percent hydrolysis for the materials tested is given by the equation

$$\% \text{ hydrolysis} = 60m - 8 \quad (\text{IV-10})$$

Since unhydrolyzed polyacrylamide is not precipitated by cupric ions, Equation IV-10 clearly breaks down when the hydrolysis falls to some value less than about 20%.

### 2. Polyacrylamide Adsorption on Kaolin

These experiments are still in progress and will be described in a later report.

## E. Other Work In Progress

The studies on surfactant adsorption and the work on the State-of-the-Art Survey of Surfactant Losses By Precipitation have been seriously disrupted by unfortunate and sudden personnel changes. Experiments and work in progress could not be completed and must be reported at a later time.

The most serious loss has been that of Dr. G. Rama Rao, whose visa expired and could not be extended in spite of all our efforts. His departure within one month of our first awareness of a problem has posed major difficulties because of his involvement in nearly every aspect of the work on Rock/Fluid Interactions. In addition, three graduate assistants experienced academic and financial problems and found it necessary to resign without completing their work.

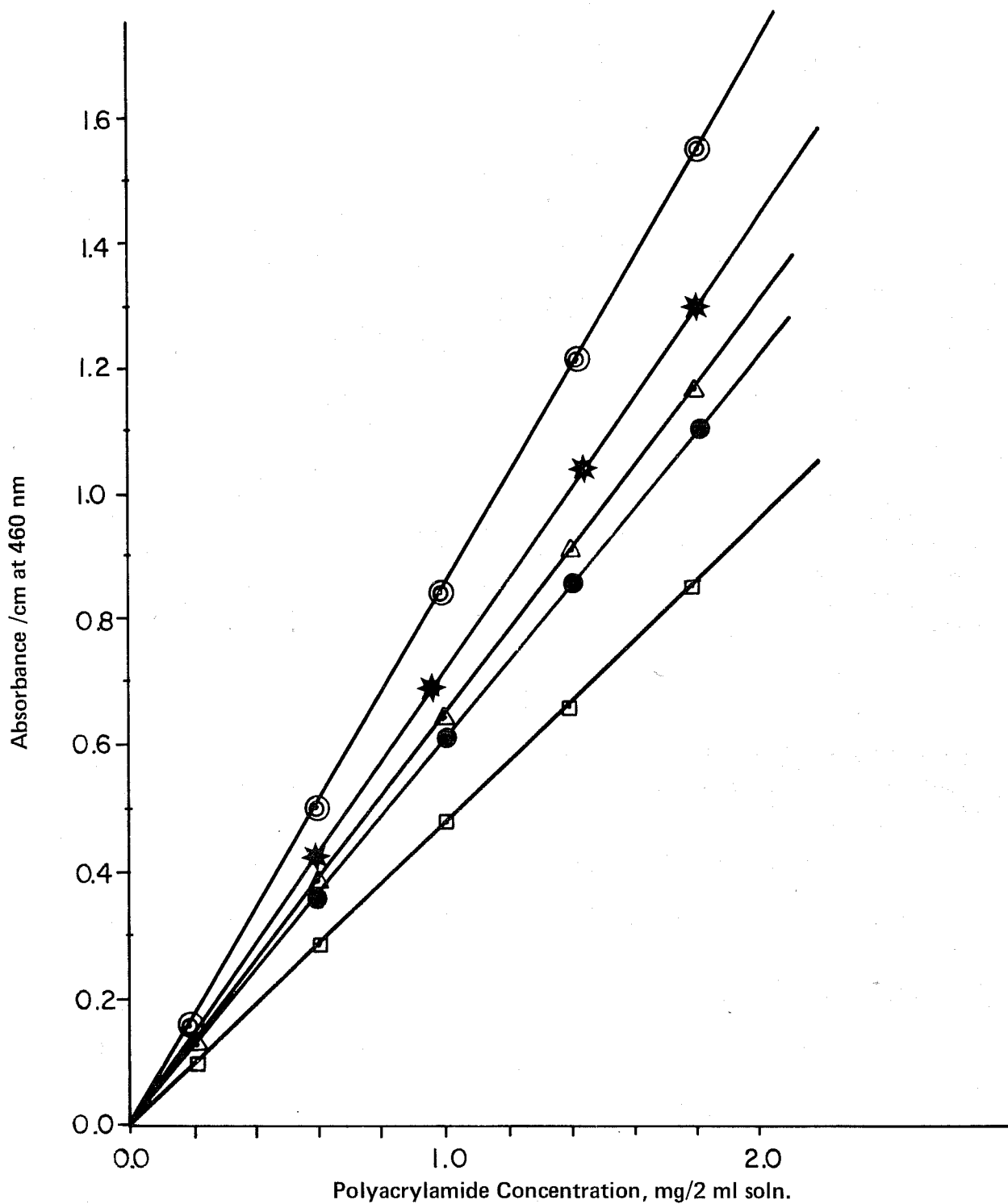


Figure IVD1

Calibration Plots for Partially Hydrolyzed Polyacrylamides

◎ = Calgon 835      △ = Calgon 825      □ = Calgon 815  
 ● = NHANCE      ★ = PUSHER 700

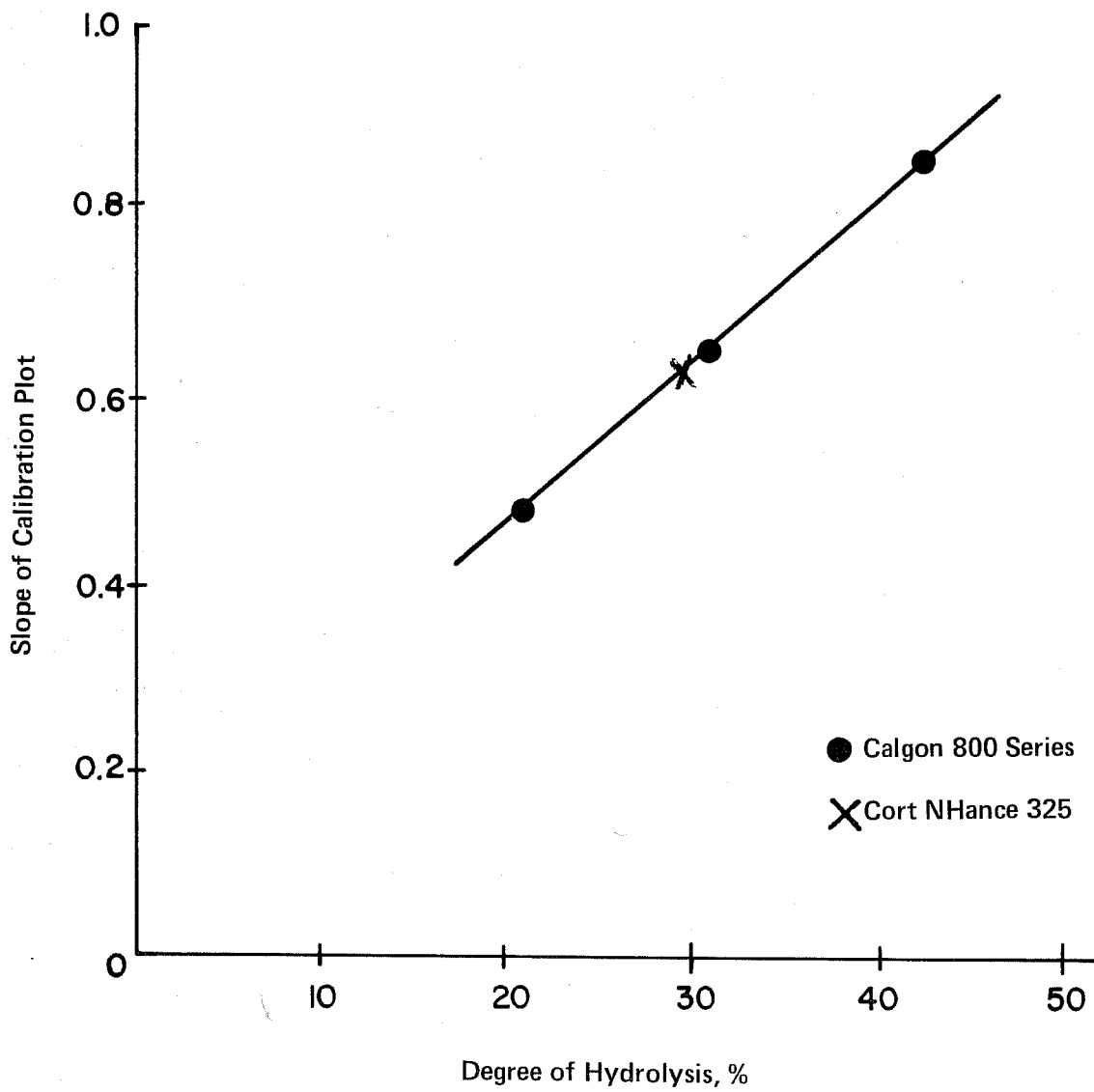


Figure IVD2      Dependence of Slope of Calibration Curve  
Hydrolysis of Polyacrylamide

We have been fortunate to be able to persuade Professor Rueben A. Keppel to come out of retirement to assist part-time on the State-of-the-Art Survey for the immediate future, and three outstanding high school seniors, who were on campus for a period of about eight weeks, were enlisted to assist part-time during the summer. So, in spite of the disruptions due to personnel changes, we hope to be able to make modest progress while searching for more permanent personnel.