

RESEARCH ON SURFACTANT-POLYMER
OIL RECOVERY SYSTEMS

Quarterly Report: September 1—December 31, 1978

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University of Florida
Gainesville, Florida



U. S. DEPARTMENT OF ENERGY

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Project Status Report
September 1—December 31, 1978

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In order to investigate the stability of polyacrylamides in different ionic concentrations, a flow through porous media study using silica gel (230-400 mesh) was carried out (30°C). The pressure drop values ($\Delta P/L$) along the length of the bed indicate that the system containing 500 ppm of CaCl_2 and 500 ppm of Calgon 815 or 835 in 1% NaCl behaves as Newtonian flow. On further increasing the concentration of CaCl_2 (1000-2000 ppm), the system exhibits a non-Newtonian flow behavior.

The effect of added surfactant (TRS 10-410) on the viscosity and screen factor behavior of unhydrolyzed (Calgon 800) and partially hydrolyzed polymers (Calgon 835) in aqueous solutions was studied. Also studied was the effect of surfactant on the Calgon 835 polymer in brine solutions. The intrinsic viscosity of Calgon 835 decreased with added surfactant and with added sodium chloride. But the effect of added TRS 10-410 to polymer solution in which sodium chloride was already present was very small. The decrease in the intrinsic viscosity suggests a shrinking of the polymer in the presence of surfactant (TRS 10-410). Aware that this surfactant contained both salt and oil, the intrinsic viscosity of Calgon 835 was also determined with Cities Service Surfactant (SDBS) and pure sodium lauryl sulfate. Both caused the viscosity to decrease.

The effect of added polymers (Calgon 835 and 800) on the interfacial tension of SDBS and TRS 10-80 equilibrated with dodecane and octane respectively was measured. The interfacial tensions were lower than those of the system without the polymer. The results also suggest that there may be an optimum polymer concentration from the point of view of low interfacial tension.

III. Thermodynamic Properties

Considerable progress has been made this quarter on a thermodynamic model of aqueous solubility. An accurate fit has been obtained for the solubility of noble gases and methane over a considerable temperature range, allowing determination of model parameters. Effort is ongoing on a model for solubility of linear aliphatic hydrocarbons. Completion of this effort will allow calculation of the major driving force for micellization, the excluded volume effect.

Investigations are continuing on the anisotropic-isotropic transitions in lyotropic liquid crystal and microemulsion system. Preliminary results confirm the existence of a small temperature range (~55° - 65°C) of co-existence of an isotropic and anisotropic phase for a potassium oleate system. Sketchy results indicate favoring of the anisotropic phase by the presence of methane but further work is required for thorough confirmation of this effect.

IV. Rock/Fluid Interactions

Surfactant Salting-Out By Indifferent Electrolytes

8-phenyl hexadecane sodium sulfonate (UT-1) was found to be salted-out of aqueous solutions by the addition of NaCl in amounts depending on the initial surfactant concentration. The fraction of surfactant salted-

out as a separate solid phase by the addition of one wt.% NaCl ranged from about 20 to 60% of that initially dissolved in distilled water when the initial surfactant concentration ranged from 0.001 to 0.1 wt.%.

The addition of n-dodecane (water/oil ratio = 2/1) either prevented salting-out or redissolved any surfactant which was salted-out; however, most of the surfactant partitioned to the oil phase, the fraction in the oil phase ranging from about 80 to more than 90%.

The partition coefficient (C_{oil}/C_{aq}) derived from these measurements was a strong function of the initial surfactant concentration, decreasing by about an order of magnitude as the initial surfactant concentration increased from 0.01 to 0.1 wt.%. The numerical value of the partition coefficient was considerably greater than unity for surfactant dissolved in one wt.% NaCl and considerably less than unity for solutions in distilled water.

Another series of salting-out experiments with the same surfactant (UT-1) in which the NaCl concentration was varied showed: 1) that salting-out begins at very low NaCl concentrations but that about 5 wt.% NaCl is required to make salting-out essentially complete, 2) that the addition of n-octane (w/o = 1/1) prevents salting-out, 3) that NaCl causes the surfactant to partition very strongly into the oil, and 4) that the partition coefficient is strongly NaCl concentration-dependent, ranging from much less than unity in distilled water to about 50 when the NaCl concentration exceeds one wt.%.

SUL-FON-ATE AA10 (or SDBS) behaves differently, but data on this surfactant are incomplete.

Surfactant Precipitation by Multivalent Cations

Precipitation-dissolution curves for SUL-FON-ATE AA10 (essentially sodium dodecylbenzene sulfonate) have been completed for several additional concentrations of calcium ions. These data show that surfactant precipitation increases as the calcium ion concentration increases but that inhibition of precipitation (or precipitate dissolution) begins at a surfactant/calcium ratio (Eq.S/Eq. Ca) near unity regardless of the actual calcium ion concentration. Complete inhibition of precipitation (or complete ppt. dissolution) is observed when $S/Ca > 3$. It appears that dissolution or inhibition occurs by calcium ion fixation in micelles because inhibition begins when the CMC has been exceeded.

CMC of Surfactants

It has been reported earlier that the addition of oil to aqueous surfactant solutions appeared to lead to a second CMC at lower surfactant concentrations than the normal CMC when the CMC was measured by surface tension. Experiments to check these observations by electrolytic conductivity measurements through the use of the Onsager Limiting Law

$$\Lambda = \Lambda_0 - b\sqrt{c}$$

were unsuccessful. The data appear normal for surfactant in distilled water and the CMC determined from the electrolytic conductivity measurements agreed well with the CMC from surface tension measurements. However, none of the conductivity data in the surfactant concentration range of the low concentration CMC appeared valid. Moreover, the addition of even a drop of oil to the aqueous solution appeared to affect the electrolytic conductivity measurements strongly.

Change Surfactant/Polymer Ods as Follows

Adsorption measurements have been postponed to a degree to make possible more complete studies of surfactant salting-out and multivalent cation precipitation. To an increasing degree it appears that these phenomena have been and still are affecting the adsorption isotherms which have been measured on most clay and Berea sandstone samples. The experimental results tend to scatter badly in some cases and they suggest incomplete cation exchange or the presence of calcium-bearing impurities such as gypsum which lead to surfactant precipitation. Two isotherms for the adsorption of $8-\phi C_{16}SO_3Na$ on Na-kaolin, with and without the addition of 0.5 vol. % n-dodecane suggest that oil may have an influence on the adsorption isotherm but the possibility of surfactant precipitation makes the conclusion very tenuous.

Polymer analysis has continued to be a problem and substantially no reliable data on polymer adsorption are yet available. Turbidimetric methods of polymer analysis have not proven satisfactory for adsorption measurements on kaolin which has been cation-exchanged. Rapid and nearly complete flocculation of kaolin which has not been cation-exchanged suggests that adsorption on raw clay is drastically different than on cation-exchanged clay.

State-of-the-Art-Survey of Surfactant Loss By Precipitation

A considerable number of papers have been located and are being analyzed. As noted in an earlier report, specific references to salting-out have so far been infrequent, but several discussions of the phenomenon have been located and are being studied. A card file for indexing information and a file for pertinent documents has been set up.

Two graduate students have been recruited to work on this task.

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I. INTERFACIAL PHENOMENA

Research Director: Professor D.O. Shah

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

1. Determine the Partition Coefficient of Synthetic Sulfonate (UT-1) Using C_8 and C_{12} as Oil

Investigator: Mr. J. Noronha

Materials and Methods:

The surfactant used was sodium 8-phenyl hexadecane benzene sulfonate (UT-1) synthesized at the University of Texas at Austin. It came in powder form and was used as received. The oils used were obtained from Chemical Samples Co., and were of 99% purity. Double distilled, deionized water was used in the preparation of all solutions.

Equilibration of two-phase oil-water systems was carried out in the following manner: After preparation of the solutions (WOR= 1/1 for the Octane systems and 1/2 for the Dodecane system), they were tumbled at 6 rpm for a period of two hours. The solutions were then set aside at room temperature for two weeks to allow for complete phase separation. Each phase was then removed and placed in a vial for the required measurements.

Interfacial tensions were measured with a spinning drop interfacial tensiometer maintained at room temperature. Surface tensions of the equilibrated aqueous phases were measured by the manual Wilhelmy plate technique and are accurate to ± 0.5 dynes/cm. Surfactant concentrations in either phase were measured by UV spectrophotometry (utilizing the benzene peak at 225 nm) and the 2-phase titration method (Octane system only). From these measurements, we obtained partition coefficients, defined as the ratio of the surfactant concentration (weight/unit volume) in the oil phase to that in the aqueous phase.

Results and Discussion:

All surfactant concentrations, unless otherwise specified, refer to the initial surfactant concentration in the aqueous phase before addition of the oil. Also note that all concentrations are on a % (w/v) basis.

Figures IA1 - IA4 illustrate the results for the system UT-1 + Water + Octane (WOR= 1/1), while Figures IA5 and IA6 show the results for the system UT-1 + Water + Dodecane (WOR = .2). We will first discuss the results for the Octane system.

Figure IA1 plots the surface tension of the equilibrated aqueous phase vs the initial surfactant concentration. Although there is some scatter among the points, it is possible to conclude there is a CMC near a surfactant concentration of 0.001%.

Figure IA2 plots the interfacial tensions for this UT-1 + Water + Octane system. Again there is some scatter among the points, but it is clear that there is a minimum in the interfacial tension at a surfactant concentration of 0.01%, a full order of magnitude larger than the measured cmc of 0.001%.

Figure IA3 plots the aqueous phase surfactant concentration (C_{aq}) for this system as measured by both the UV and 2-phase titration methods. Although there is some scatter in the points there is fair agreement between the concentrations measured by the two methods. In the low concentration region ($< 0.001\%$), C_{aq} does not increase rapidly with surfactant concentration. However, once beyond the CMC, there is a much greater rise in the value of C_{aq} .

Oil phase concentrations as measured by the UV spectrophotometry method were found to be unreliable and are not reported here. Partition coefficients (PC) were calculated from the measured aqueous phase concentration and an overall material balance. These results are shown in Figure IA4. There is an initial rise in the partition coefficient at low surfactant concentrations. It passes through a maximum close to the cmc and then decreases. Note that the partition coefficient has a value of 1.2 at 0.01% surfactant concentration, where the minimum in the interfacial tension was observed.

We now turn to the UT-1 + Dodecane system. Figure IA5 is a plot of the aqueous phase surface tension for this system. In agreement with previously reported results, this curve exhibits two CMC-type breaks-at 0.001% and 0.01% surfactant concentration.

Figure IA6 plots the interfacial tensions for this system. Once again there is a minimum in the curve which occurs at a surfactant concentration of 0.007%. This is very close to the "2nd CMC" observed in the surface tension plot.

Surfactant concentrations in the aqueous and oil phases and partition coefficient data are not reported because it was found that greater than 95% of the surfactant always remains in the aqueous phase. This is an important observation since it precludes the occurrence of a partition coefficient of unity. The partition coefficient always remains below 0.1.

Conclusions:

It is observed that a minimum in the interfacial tension occurs in both the octane and dodecane system. In the former case, it was correlated with a partition coefficient of unity, while in the latter case it was correlated with the occurrence of the "2nd CMC". In the former case, added surfactant partitions preferentially into the oil phase below the CMC but into the aqueous phase above the CMC. Since a minimum in the IFT for an isomerically pure surfactant has not been observed before, these results are to be repeated. It could be due to a homologous impurity and our repeat experiment will focus on this possibility.

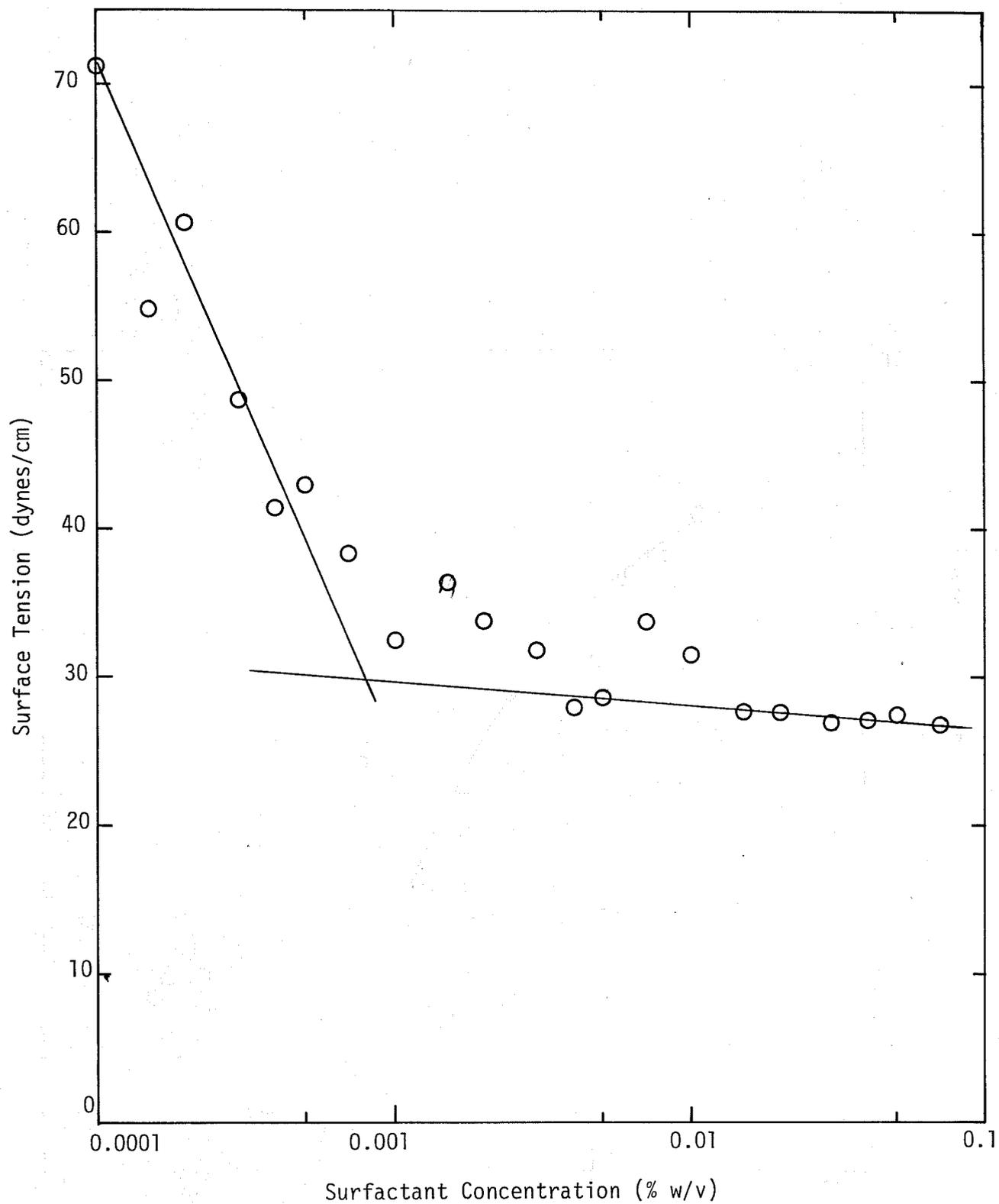


Figure IA1. Surface Tensions of The Equilibrated Aqueous Phases For the UT-1 + Water + Octane (WOR = 1.0) System

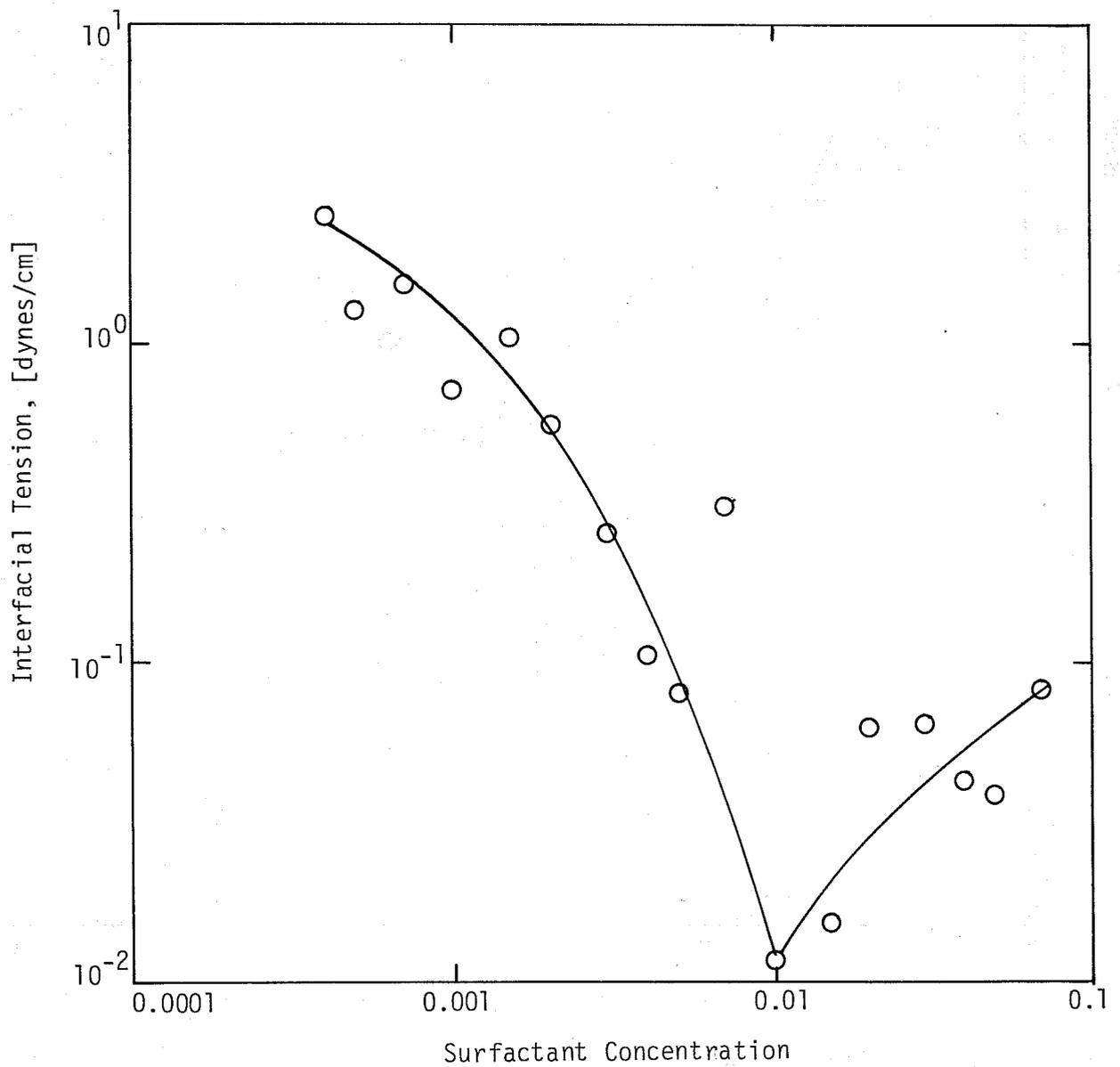


Figure IA2. Interfacial Tensions for The UT-1 + Water + Octane (WOR = 1.0) System

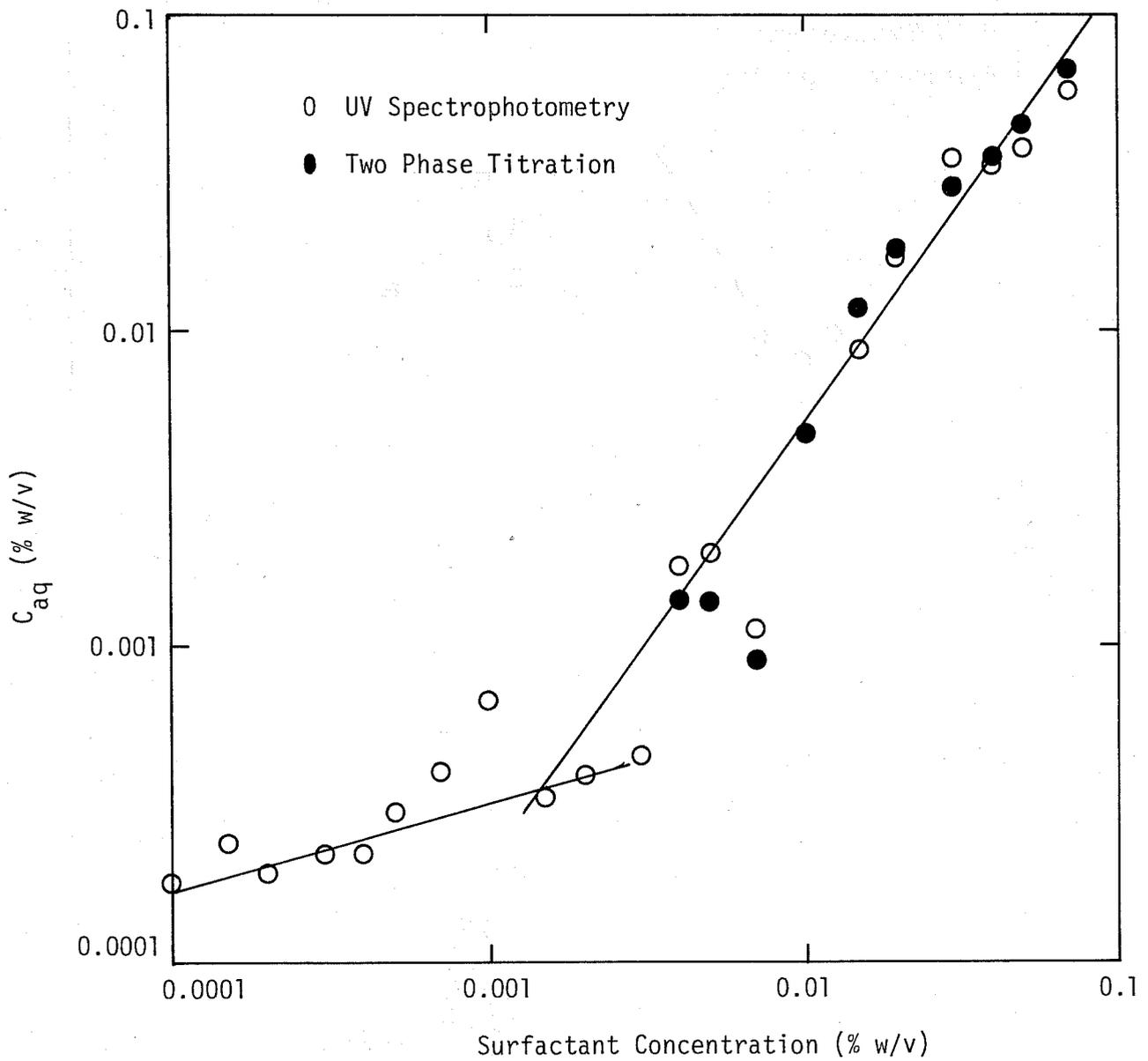


Figure IA3. Aqueous Phase Concentration (C_{aq}) For The UT-1 + Water + Octane (WOR = 1.0) System.

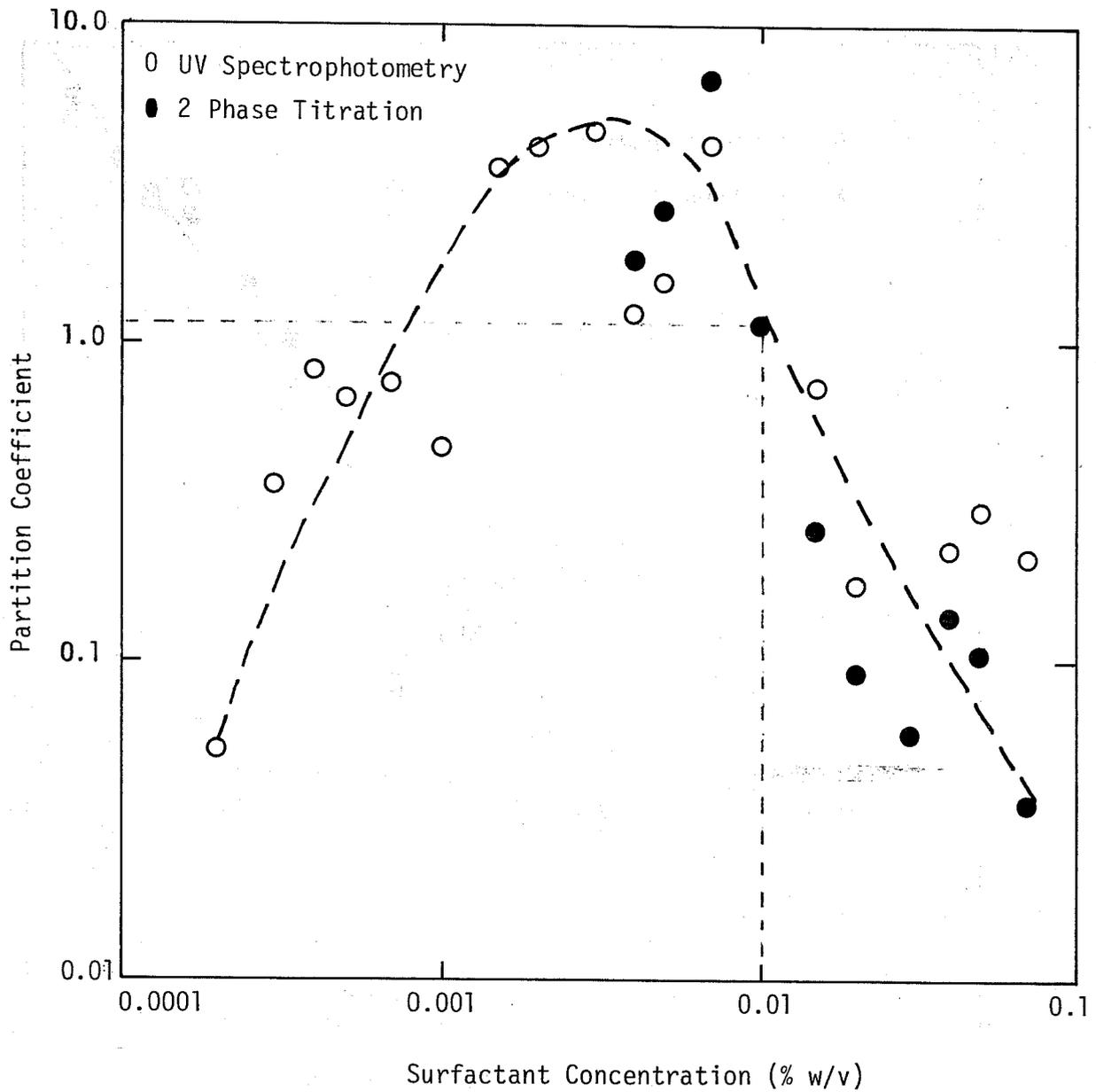


Figure IA4. Partition Coefficient (C_{oil}/C_{aq}) For the UT-1 + Water + Octane (WOR = 1.0) System

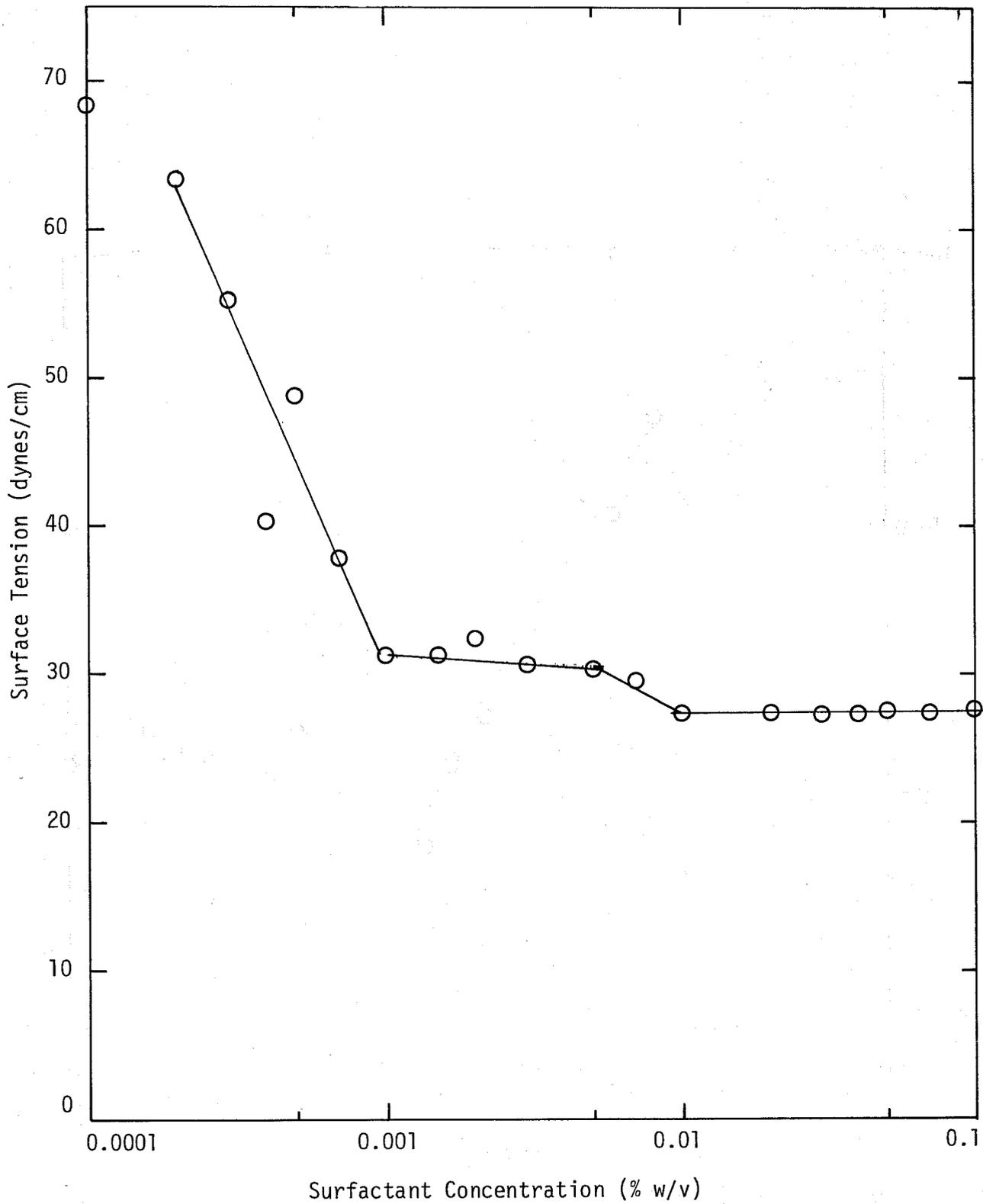


Figure IA5. Surface Tensions of The Equilibrated Aqueous Phases for The UT-1 + Water + Dodecane (WOR = 2.0) System

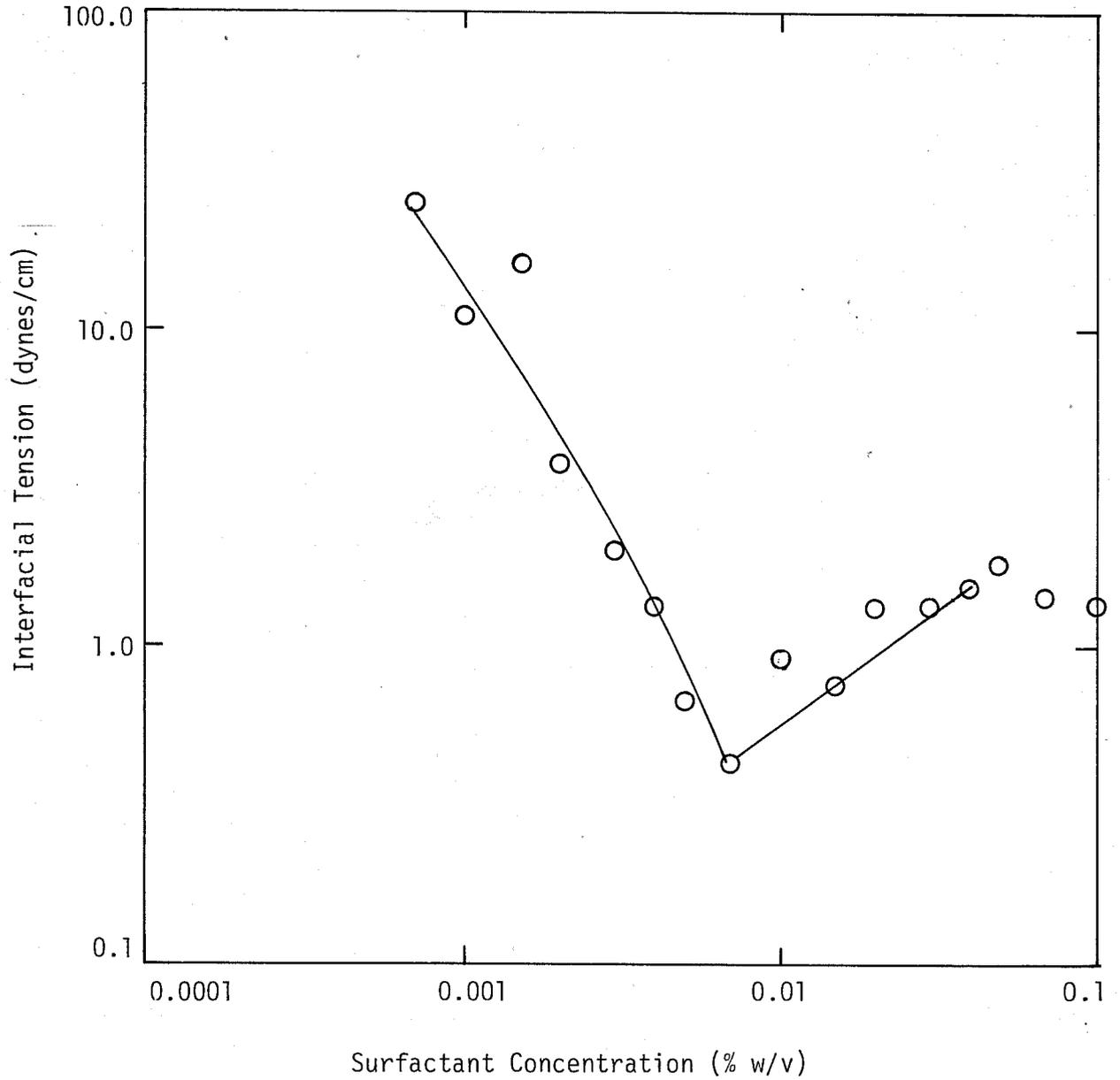


Figure IA6. Interfacial Tensions for The UT-1 + Water + Dodecane (WOR = 2.0) System

2. Determine the Effect of Oil/Brine Ratio on Partition Coefficient and Interfacial Tension Using TRS 10-80 in 1% NaCl and n-Octane as Oil.

Investigator: Mr. M. Chiang

One of the design criteria for chemical flooding process is the ability of the added chemicals to lower the oil/water interfacial tension (IFT). Chan (1978) had shown that there exist two IFT minima as the petroleum sulfonate concentration is increased in a water-oil system. Chan and Shah (Section A.2 Semi-Annual Report, December 1977) had shown that IFT minima in the low surfactant concentration region can be correlated with equal partitioning of surfactant into oil and brine phases and this occurs at the surfactant critical micelle concentration (CMC) of the aqueous phase. Thus, the minimum IFT was explained as a result of the maximum amount of surfactant monomers being at oil/brine interface when the partitioning is equal. Moreover, it was shown that for an oil-brine-surfactant system at a fixed temperature, its interfacial behavior and partition coefficient are determined by surfactant concentration, brine salinity, and oil type. If any of the two parameters are fixed, there is only one value of the third which yields "optimality" as exhibited by the partition coefficient and IFT.

The previous was done at a fixed water/oil ratio (WOR) of 1:2. However, in order to predict the surfactant flooding process with its constantly changing water/oil ratio (WOR) the effect of water/oil ratio on partition coefficient and IFT have been studied.

Materials and Methods:

Commercial petroleum sulfonate TRS 10-80 (80% active, Witco Co.) and Fisher A.C.S. certified grade NaCl crystals were dissolved in distilled, deionized water to make 0.5% TRS 10-80 in 1% NaCl stock solution by weight. Ninety-nine percent n-octane (Chemical Samples Co.) was used as oil to equilibrate with the surfactant solution.

Two sets of surfactant solutions were prepared by diluting the stock solution with 1% NaCl as follows:

Set A: 7 grams of stock solution is added to each of five 100 ml glass-stoppered graduate cylinders. Then, 1% NaCl is added to the mark of 15, 30, 50, 70, or 85 ml. Finally, n-octane is filled to the 100 ml mark in each cylinder.

Set B: The stock solution was diluted 10 times to become 0.05% TRS 10-80 in 1% NaCl. This was added to another set of five 100 ml graduate cylinders to the mark of 15, 30, 50, 70, or 85 ml. Again, n-octane is filled to the 100 ml mark in each cylinder.

These two sets of cylinders were then shaken vigorously by hand and left standing at $25^{\circ} \pm 1$. After 10 days of equilibration, the surfactant concentration in both the oleic and aqueous phases was measured by the

two-phase dye titration method of Reid et al, (1967) and the partition coefficient (surfactant (weight fraction in oil/surfactant weight fraction in brine) computed. For solutions of different WOR, the interfacial tension was also measured on a spinning drop tensiometer at 25°C.

Results and Discussion:

Two sets of surfactant solutions were prepared as described above. In Set A equal amounts of surfactant were deposited in each cylinder so that total surfactant concentration at each WOR was constant. In Set B the same aqueous surfactant solution was equilibrated with oil at various WOR or total surfactant concentration in the system decreases as WOR increases.

The surfactant concentration in both oil and brine were measured as the WOR varied. These are plotted in Figures IA7 and IA8 while their corresponding partition coefficients and IFT are shown in Figures IA9 and IA10 for sets A and B, respectively. In Figures IA9 and IA10, the partition coefficient decreases from greater than 1 to less than 1 as WOR decreases. It is in agreement with the result shown previously (Figure A.23, Semi-Annual Report, December 1977).

Figure IA10 shows that the IFT first decreases as the partition coefficient decreases from greater than 1 at high WOR, then IFT increases as partition coefficient further decreased to be much less than 1 at low WOR. The IFT minimum occurs as the partition coefficient is near unity, again, consistent with the previous result (Chan and Shah, 1977). However, the same correlation does not hold in Figure IA9. The IFT seems to be independent of the WOR and does not have a minimum as the partition coefficient passes through unity. Since IFT values are considerably higher in Figure IA9 than in Figure IA10 and those in the literature, the measured IFT values could be incorrect. Fresh solutions are being prepared to check these results.

It was proposed by Chan and Shah (1977) that when a surfactant solution composed of a mixture of petroleum sulfonates, e.g., TRS 10-80, equilibrated with an alkane, the high molecular weight sulfonate is considered more lipophilic, thus, partitioning into the oil phase; while the low molecular weight species is relatively hydrophilic, thus, staying in brine as illustrated by Figure IA11. The partitioning of the oil soluble species and the brine soluble species is determined by their activity coefficients, which are strong functions of the salinity and alkane carbon number but an unknown function of surfactant concentration of which here is varied with WOR.

If the partition coefficient is a weak function of surfactant, for the same total amount of surfactant, the same amount of lipophilic species must go into the oil phase regardless of the amount of oil or brine present. Table IA1 shows the fraction of initial surfactant partitioned in the oil phase for the solutions in Set A.

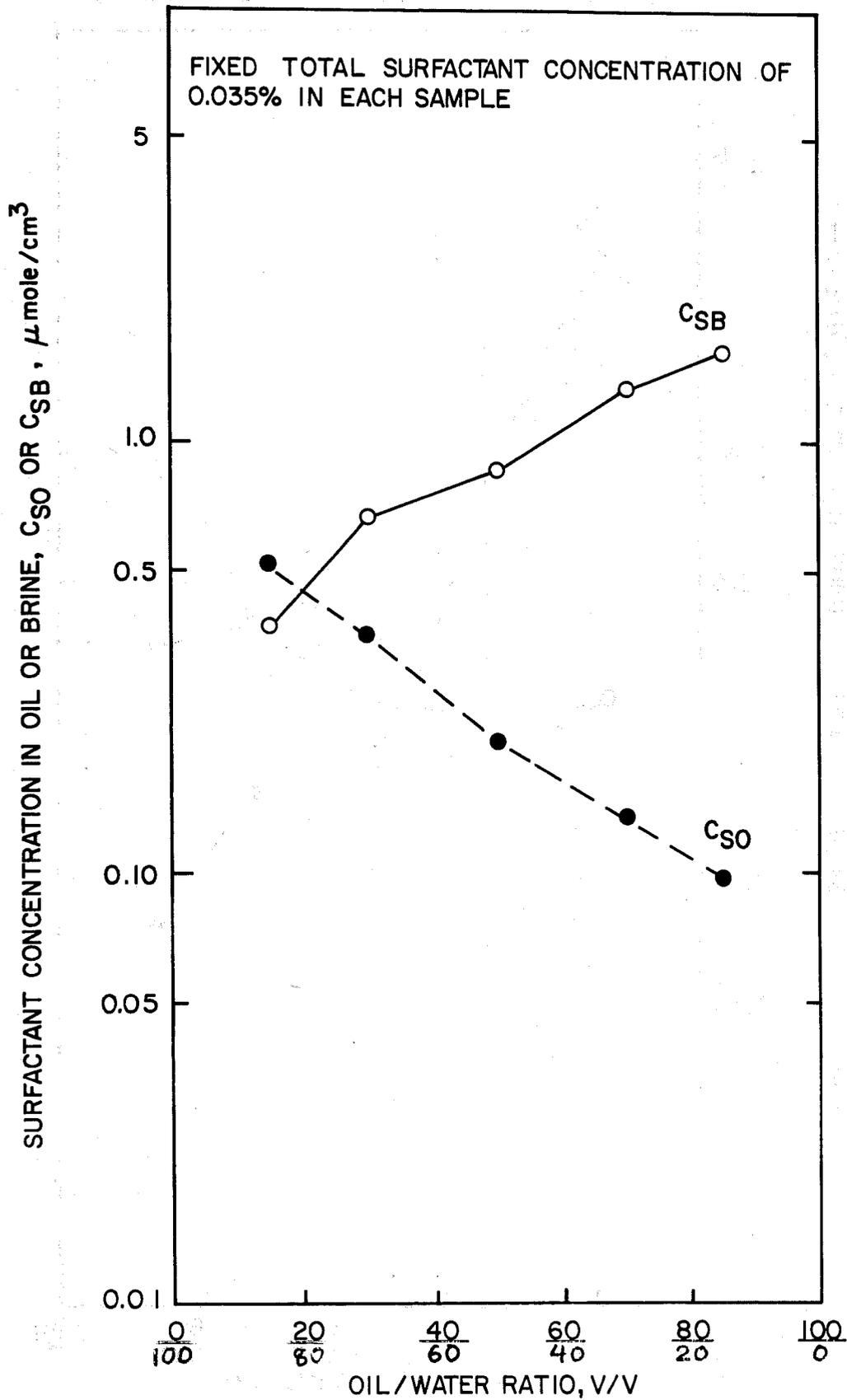
SURFACTANT PARTITIONING IN OIL AND BRINE
TRS 10-80 IN 1% NaCl EQUILIBRATED WITH n-OCTANE

Figure IA7

SURFACTANT PARTITIONING IN OIL AND BRINE 0.05%
 TRS 10-80 IN 1% NaCl EQUILIBRATED WITH n-OCTANE

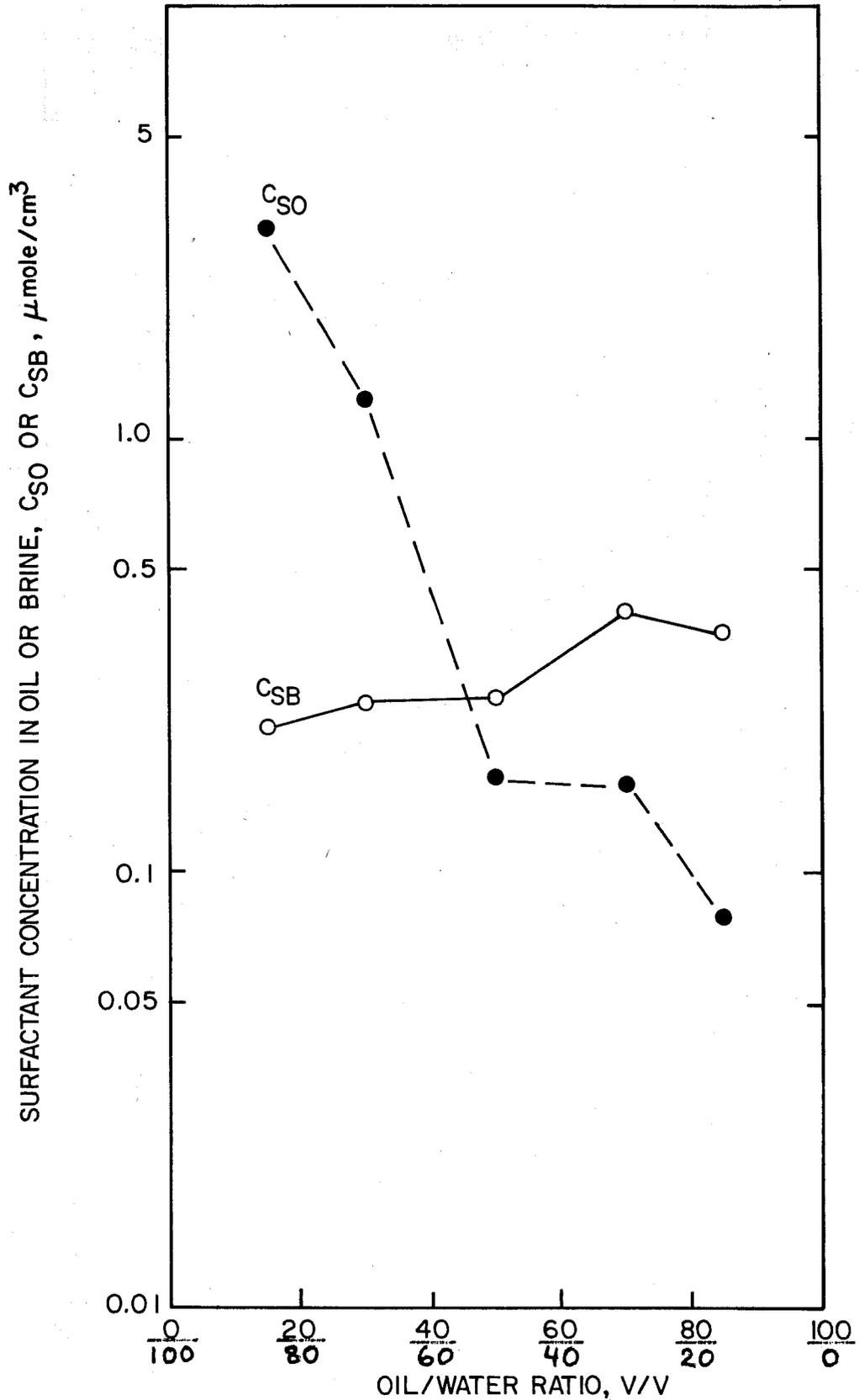


Figure IA8

EFFECT OF OIL/WATER RATIO ON INTERFACIAL TENSION AND
PARTITION COEFFICIENT OF TRS 10-80 IN 1% NaCl
EQUILIBRATED WITH *n*-OCTANE AT VARIOUS VOLUME RATIO

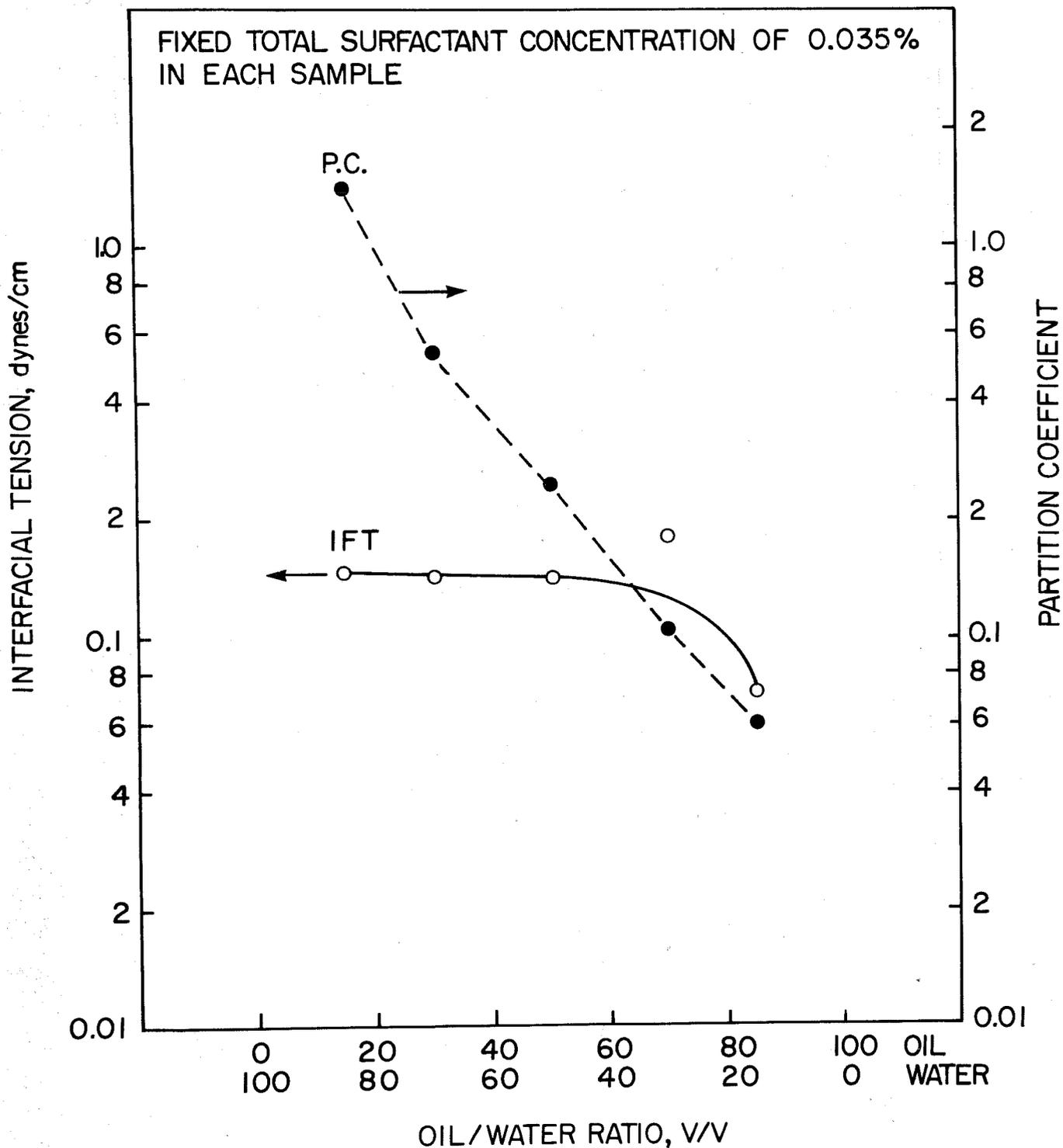


Figure IA9

EFFECT OF OIL/WATER RATIO ON INTERFACIAL TENSION AND PARTITION COEFFICIENT OF 0.05% TRS 10-80 IN 1% NaCl EQUILIBRATED WITH n-OCTANE AT VARIOUS VOLUME RATIO

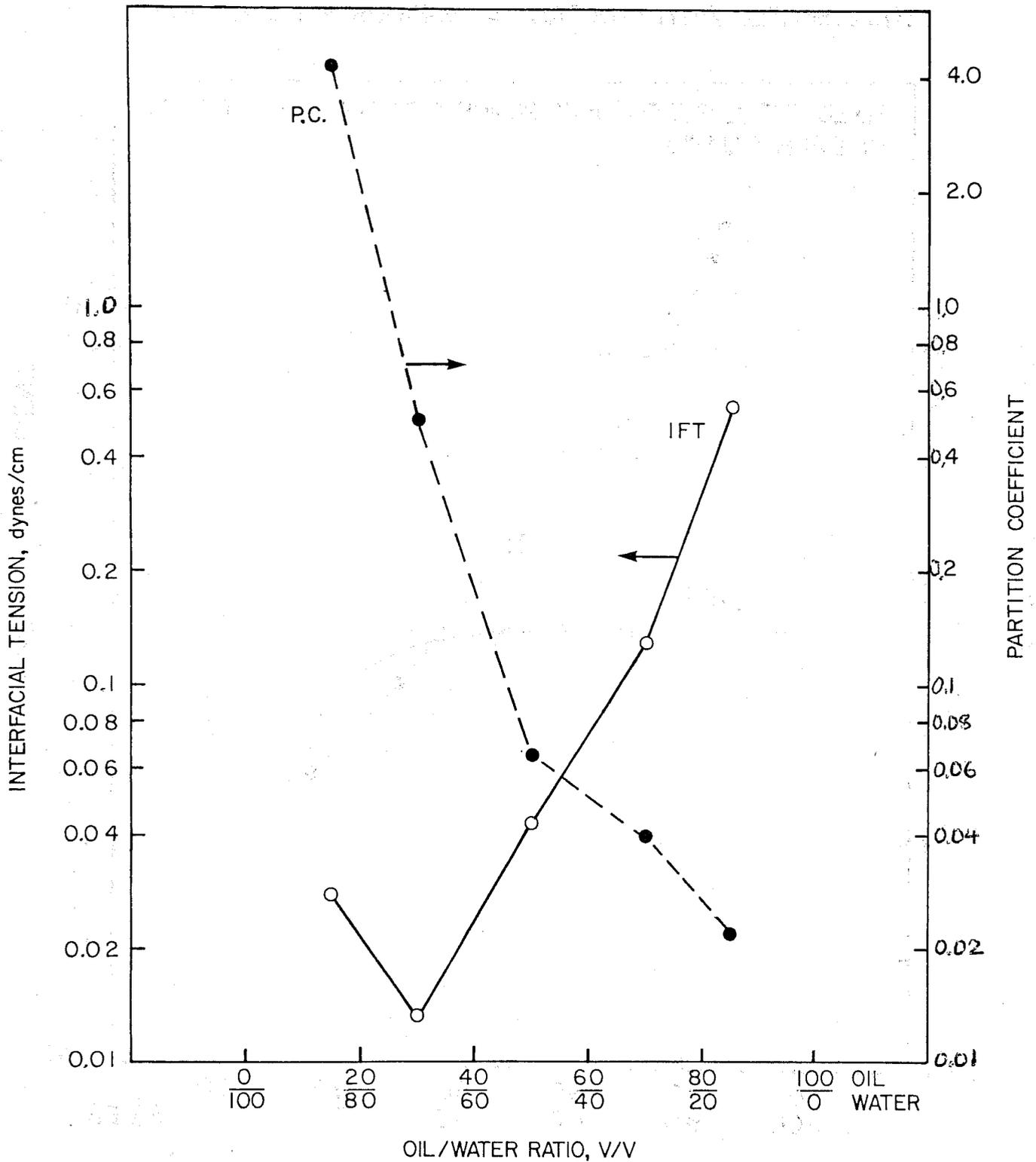


Figure IA10

RELATIVE CONCENTRATION OF EACH SPECIES

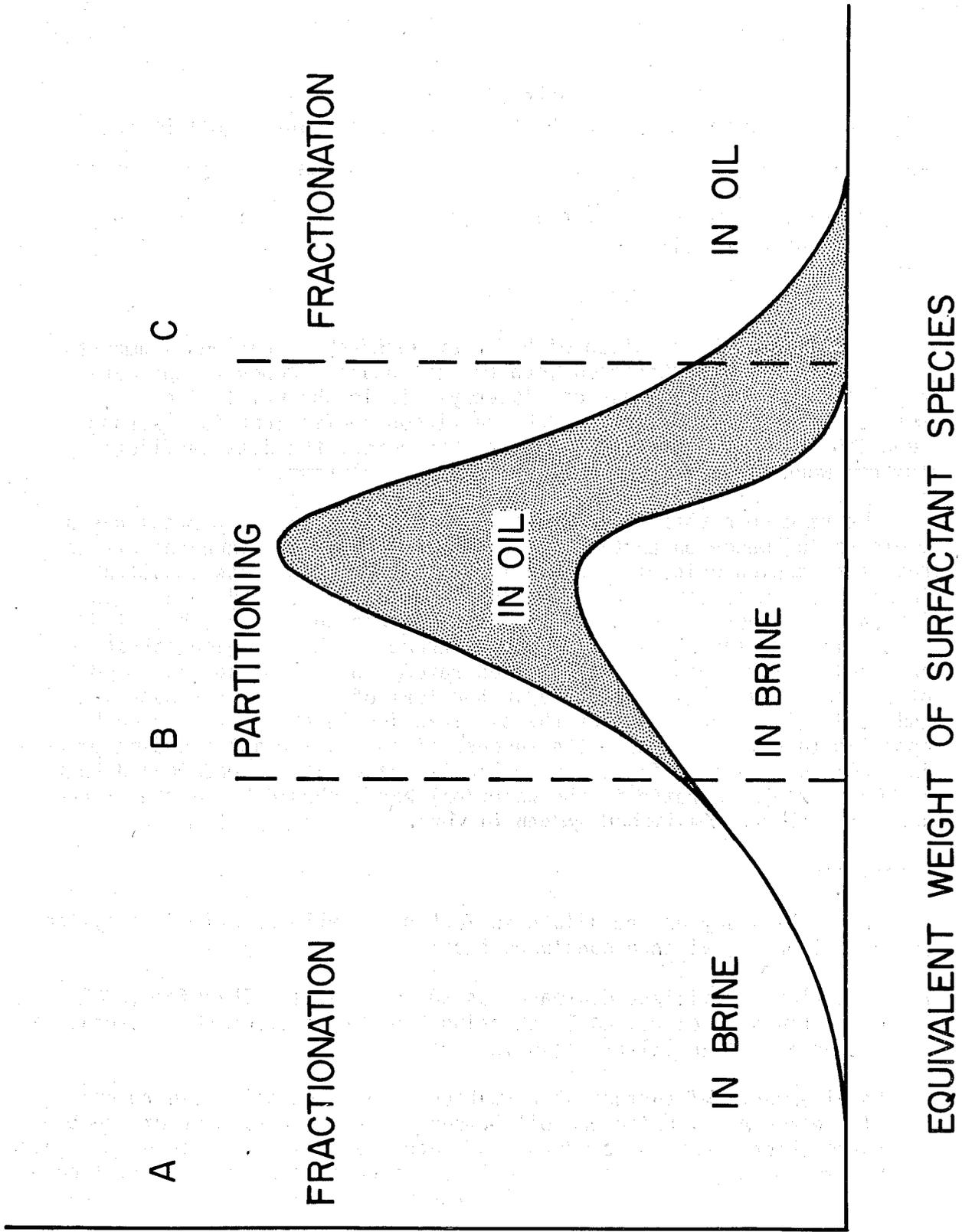


Figure IA11

Table IA1

Effect of Water/Oil Ratio on the Amount of Surfactant in Oil Phase

Water/Oil Ratio	15/85	30/70	50/50	70/30	85/15
% of Initial Surfactant Partitioned to the Oil Phase	25.4	19.5	19.6	18.4	18.7

All except the solution with WOR at **15/85** show that equal amounts of surfactant are partitioned into the oil phase. However, the data for Set B do not show this consistency. It is shown later for a pure component surfactant that the partition coefficient is a strong function of total concentration. At this point, the data conflict and further work is underway to bring about a resolution.

We have seen that the WOR used in the equilibration process has a profound influence on partition coefficient and IFT. Since one of the necessary design criteria for surfactant flooding process is ultra-low IFT, the question to be answered is "Which WOR should be used in laboratory screening of surfactants?" Because the whole range of WOR is possible during an oil displacement process, the question cannot be answered easily. However, in the laboratory core flooding tests, most of the tertiary oil is recovered in the form of an oil-water bank. Healy and Reed (1974) reported that the oil fraction in the oil/water bank is approximately 40%. Because the success of the surfactant flooding process is determined by the size of the oil/water bank, it is recommended that an WOR of **60/40** a ratio in the water/oil bank, should be adopted when screening **oil/brine/surfactant systems in vitro**.

Conclusion:

From the study on the dilute surfactant micelle solution/oil system, the experimental evidence concludes that:

1. Partition coefficient decreases as WOR decreases. Therefore, WOR care should be exercised in choosing the WOR to study the interfacial properties of an oil/brine/surfactant system.
2. Equal amounts of surfactant partitioned into the oil phase regardless of the amount of brine and oil present. It is in support of the proposed theory that for a mixture of petroleum sulfonates in equilibrated oil and brine, only a fixed amount of lipophilic surfactant will partition into the oleic phase while the hydrophilic portion will stay in the aqueous phase.

B. Determine Microstructure of Multicomponent Surfactant Formulations

1. Determine the Effect of Oil Chain Length on Solubilization of Water in Microemulsions Using Various Alcohols (C_4 to C_7)
2. Measure Dielectric Constants of Above Microemulsions

Investigator: Dr. V.K. Bansal

It has been reported recently by Hsieh and Shah, 1978 that the optimal salinity of a surfactant formulation depends upon the chain length of oil. It was also observed that the interfacial tension at the optimal salinity increases with increasing oil chain length. The mechanism by which oil chain length affects the properties of a microemulsion is being explored by measuring water solubilization capacity, dielectric constant and electrical resistance. Initially the microemulsions consist of fatty soap (sodium stearate) were studied to investigate the basic mechanism involved in the microemulsion formation. After completing the study on sodium stearate microemulsions the petroleum sulfonate systems will be investigated.

Materials and Methods:

Sodium stearate of 99% purity, supplied by Matheson-Coleman and Bell Inc., was used for preparing microemulsions. All the alcohols and the oils (octane-hexadecane) were purchased from Chemical Samples Co. and were of 99% purity or greater. Triple distilled water was used in making all the microemulsions.

Water Solubilization Limit: The microemulsions were prepared by mixing sodium stearate (1 gm), alcohol (4 ml or 8 ml), oil (10 ml), and water (1 ml) to get a clear solution. The water solubilization capacity was determined by adding water slowly from a graduated 1 ml pipette to the microemulsion, until turbidity was observed and two-phase formation occurred. In all the cases the end point was sharp (within ± 0.1 ml of added aqueous phase). At the end point the systems were initially turbid, but after a few minutes of standing the clear phases were formed.

Dielectric Constant: All the dielectric measurements reported here were made with a cylindrical dielectric cell with variable distance using an impedance meter, viz., R-X meter: type 250-B. The design of the dielectric cell and calculation procedure for dielectric constants have been reported elsewhere by Bansal et al. (1978).

Results and Discussions:

The water solubilization capacity of microemulsion formed with sodium stearate was studied as a function of alkyl chain length of oil (C_8 to C_{16}) and alcohol (C_4 to C_7) and is shown in Figures IB1 and IB2. In

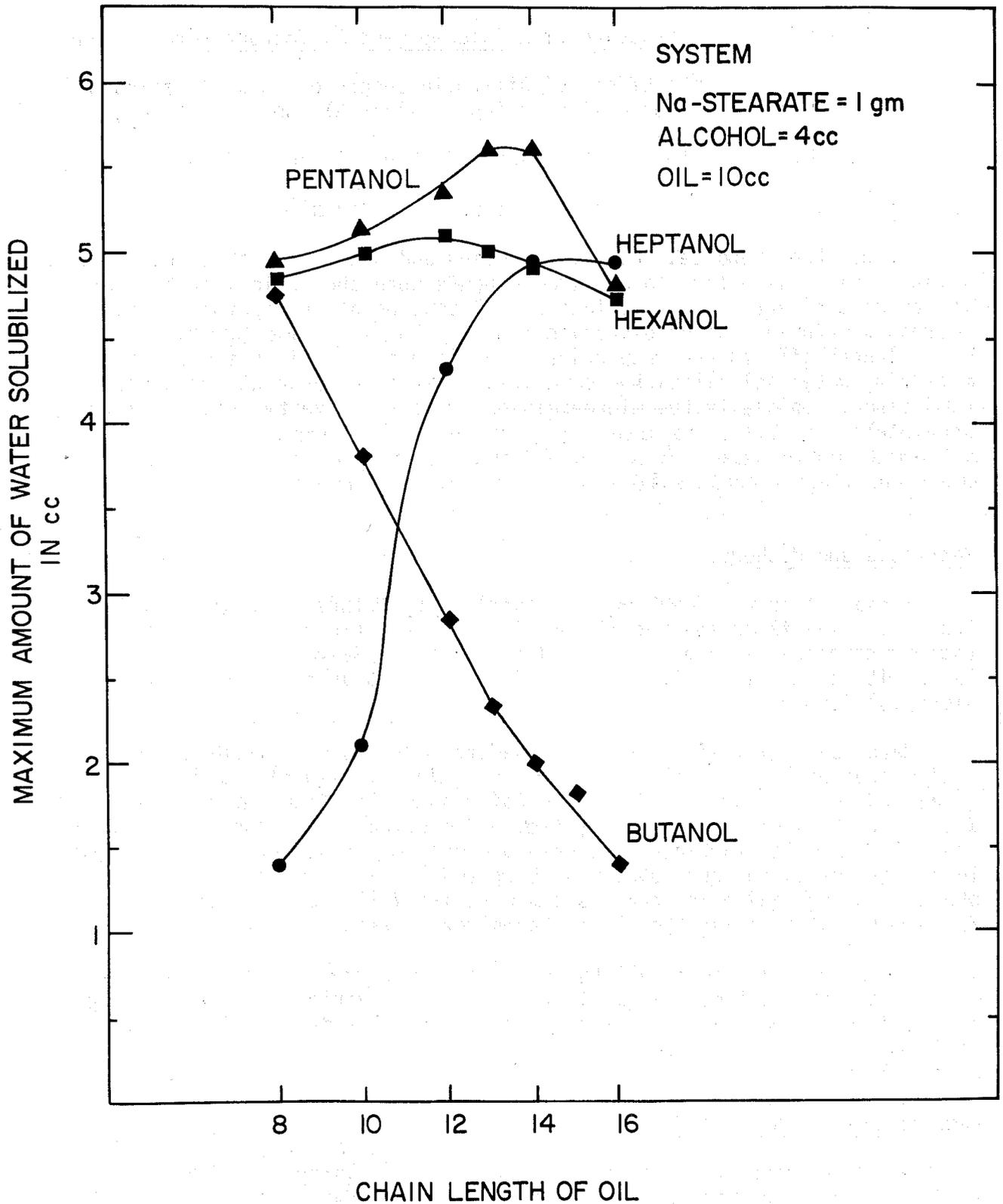
EFFECT OF OIL CHAIN LENGTH ON WATER SOLUBILIZATION
CAPACITY OF MICROEMULSION SYSTEM

Figure IB1

EFFECT OF OIL CHAIN LENGTH ON WATER SOLUBILIZING CAPACITY OF MICROEMULSIONS

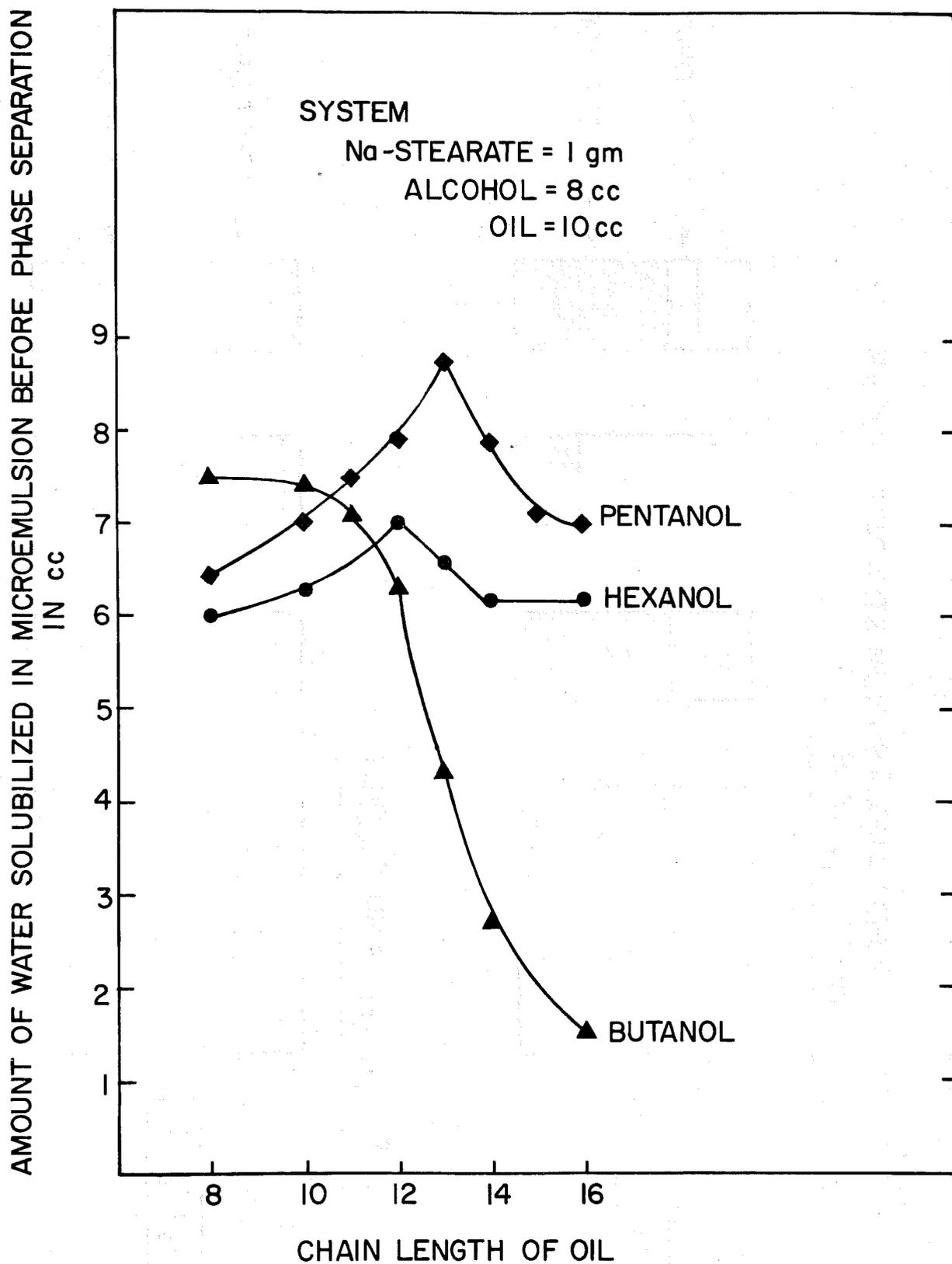
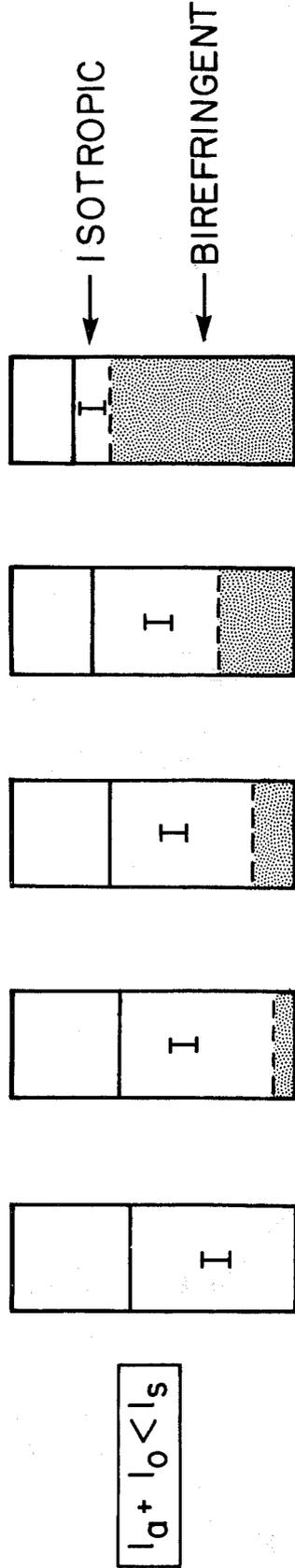


Figure IB2

PHASE BEHAVIOR OF MICROEMULSION SYSTEMS UPON INCREASING WATER/OIL RATIO

SYSTEM: OIL + PENTANOL + SODIUM STEARATE + WATER
FOR C₈, C₁₀ AND C₁₂ OILS



FOR C₁₃, C₁₄ AND C₁₆ OILS

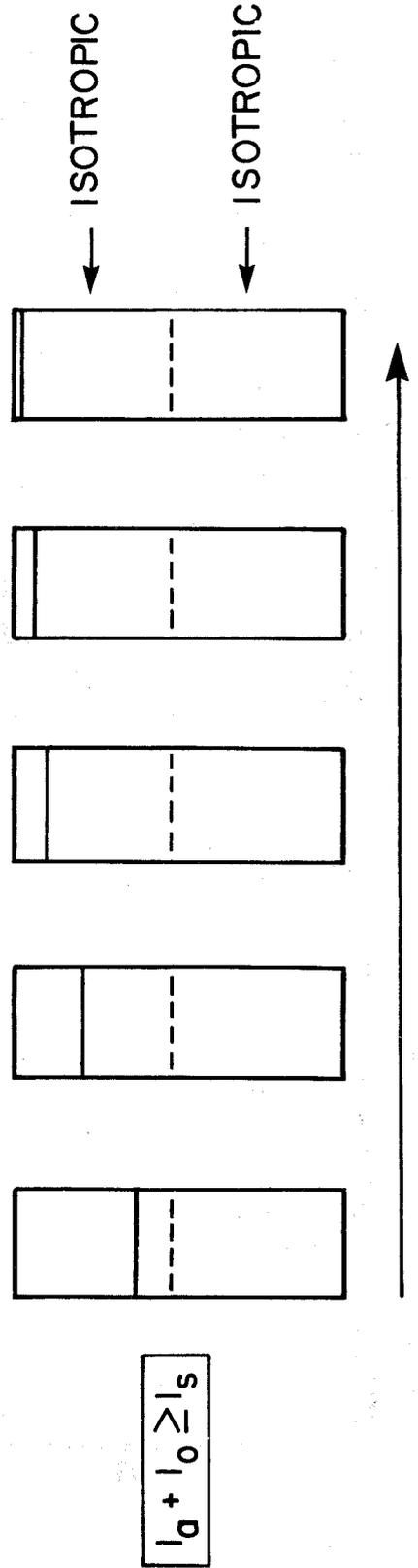


Figure IB3

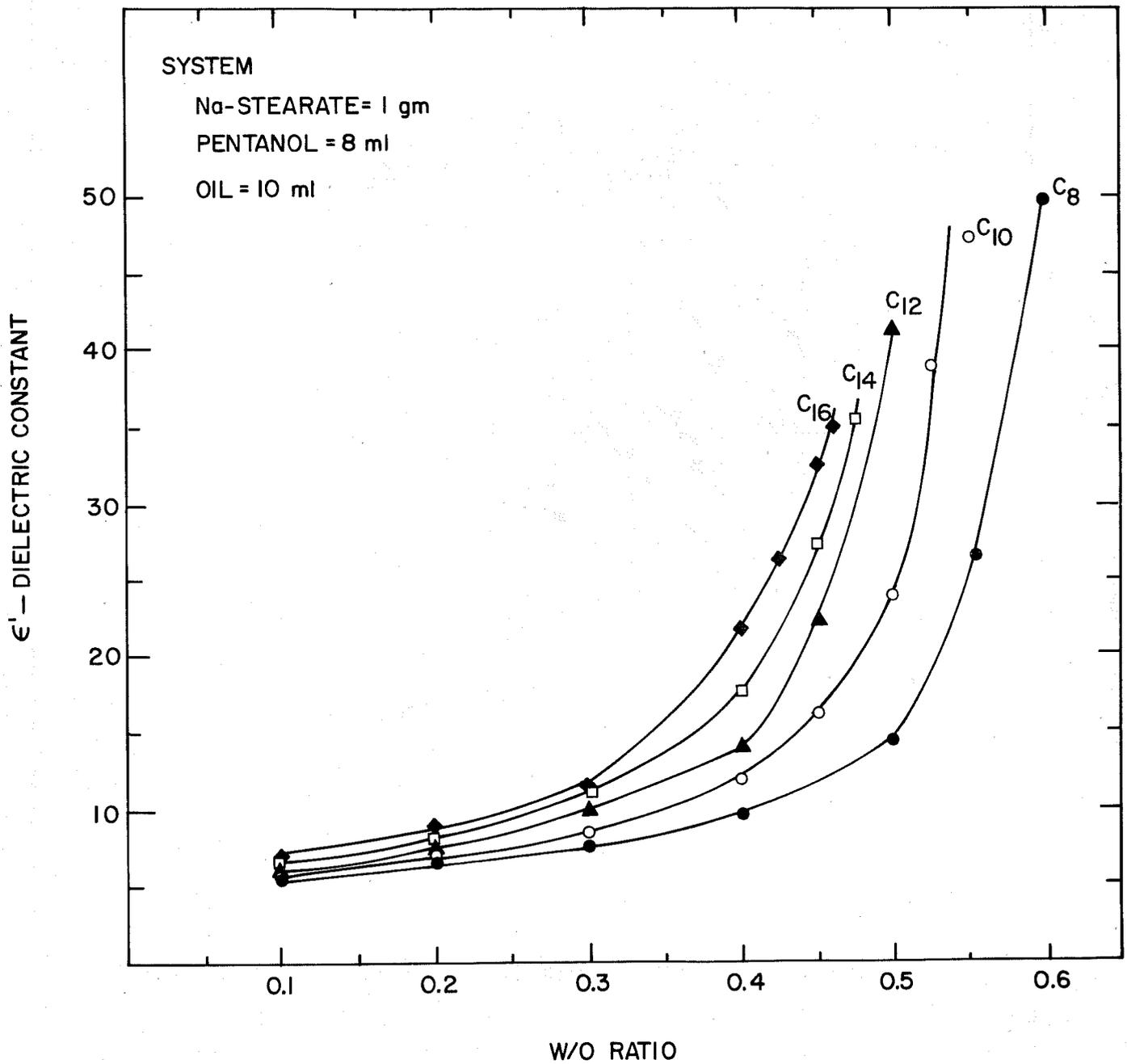
EFFECT OF OIL CHAIN LENGTH ON THE DIELECTRIC CONSTANT OF MICROEMULSION AT 1MH₂ FREQUENCY

Figure IB4

EFFECT OF OIL CHAIN LENGTH ON FORMATION OF MICROEMULSION

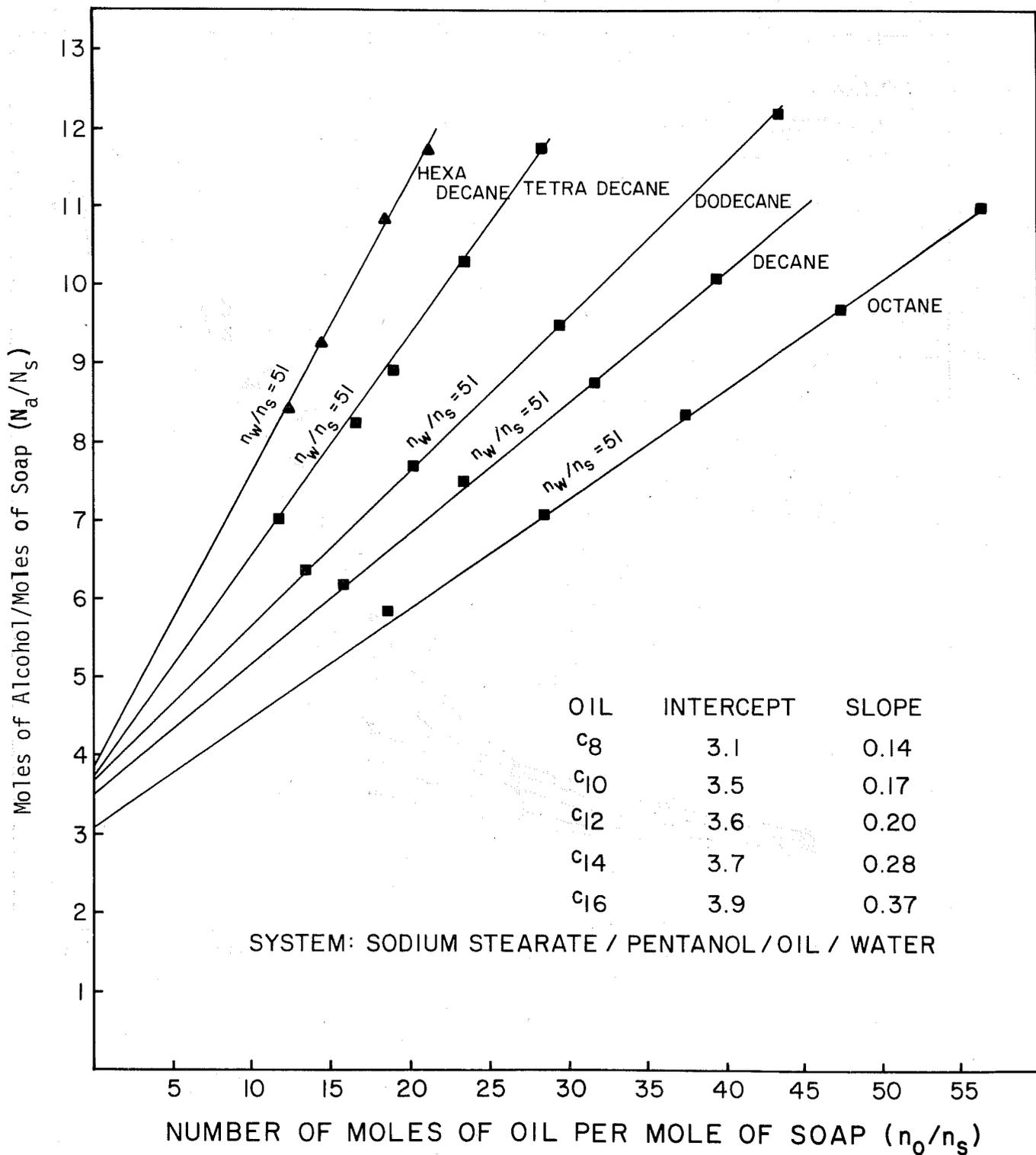


Figure IB5

the first case (Figure IB1) 4 ml of alcohol was used in preparing the microemulsion whereas in the second case (Figure IB2) 8 ml of alcohol was used. It was found that for n-butanol microemulsions the maximum amount of water solubilized in the microemulsion decreased continuously with increasing oil chain length whereas for n-heptanol it increased continuously. For n-pentanol and n-hexanol water solubilization reached a maximum when the oil chain length, ℓ_o , plus that of the alcohol, ℓ_a , was equal to that of the surfactant, ℓ_s . This effect was found to be more pronounced when 8 ml (Figure IB2) of alcohol was used in making microemulsion. It was interesting to note that for the n-pentanol system, when excess water was added to the microemulsion (above the water solubilization capacity), a birefringent aqueous phase separated out at the bottom when $\ell_a + \ell_o < \ell_s$ (Figure IB3). These observations indicate a chain length compatibility effect in microemulsion systems such as has been observed in monolayers, foams, emulsion and lubrication systems.

Electrical resistance and dielectric constant of the microemulsions as a function of water/oil ratio and alkyl chain length of oil (C_8 to C_{16}) have also been measured. It was found that at a given water/oil ratio the electrical resistance of the microemulsion increases with increasing oil chain length. The dielectric constant of the microemulsion at 1 MHz frequency as a function of water/oil ratio and alkyl chain length of oil is shown in Figure IB4. It is evident from this figure that the amount of water required to produce the same interfacial polarization (same value of dielectric constant) increases with decreasing oil chain length. It can also be concluded from Figure IB4 that at a given water/oil ratio the dielectric increment (due to interfacial polarization) increases with increasing oil chain length.

It was reported recently (Bansal et al.), 1979 that the value of the dielectric increment increases with the alcohol/surfactant ratio at the interface in the microemulsions. Figure IB5 shows the effect of alkyl chain length on the interfacial composition of the microemulsion at a given water/oil ratio; as expected, the oil chain length increases the alcohol/surfactant ratio (N_a/N_s) increases.

These phenomena are consistent with the concept that microemulsions form and vary their structure, only under particular circumstances of surfactant and alcohol partitioning between aqueous and oil phases with resultant interfacial activity of both species. In particular, the maximum solubilization of water probably occurs at a particular ratio of surfactant to alcohol in the interface; this, in turn, is primarily determined by species partition coefficients that here have been subtly varied by changing oil chain length.

C. Oil Displacement Efficiency of High Salinity Formulations

Investigator: Mr. M. Y. Chiang

Stable surfactant formulations consisting of commercial petroleum sulfonate, ethoxylated sulfonate, alcohol, and electrolyte solutions exhibiting ultra-low interfacial tension with alkane in presence of up to 20% NaCl and 1000 ppm Ca^{++} or Mg^{++} divalent cations were reported by Bansal and Shah (1978 a,b,c).

It was shown previously that a maximum of 76% tertiary oil was recovered in sand packs at 9% NaCl, the optimal salinity, when such a formulation was used. (Section B 1, Semi-Annual Report, December, 1977).

Here the same system is tested in Berea cores to find its oil displacement efficiency in consolidated porous media.

Materials and Methods:

The formulation tested consisted of 1.5% TRS 10-410, 2.5% EOR 200, 3% isobutanol and various amounts of NaCl mixed in deionized distilled water by weight on 100% active basis. The TRS 10-410 is 61.2% active petroleum sulfonate supplied by Witco Co. and the EOR 200 is 29.3% active ethoxylated sulfonate supplied by Ethyl Corp. Both sulfonates were used as received. Ninety-nine percent pure isobutanol and n-dodecane are obtained from Chemical Samples Co. Reagent grade sodium carbonate (Na_2CO_3) and Fisher grade sodium tripoly phosphate (STPP) were used as sacrificial agents in preflush, surfactant formulation, and polymer buffer solution. The mobility buffer used is composed of 2000 ppm Polymer 340 sent by Calgon Corp. dissolving in corresponding salt solutions.

Horizontally mounted Berea cores (1" x 1" x 12") casted in epoxy resin were used in the oil displacement experiments. The detailed flooding procedure is listed elsewhere. (See Section B 1.3.2, Semi-Annual Report, June, 1977).

Results and Discussion:

Figure ICl shows the effect of sacrificial agent on tertiary oil recovery of the surfactant formulation at its optimal salinity of 9% NaCl. About 45% tertiary oil was recovered at 0% sacrificial agents and no surfactant phase broke through the porous medium. However, the identical surfactant solution/oil system achieved 76% oil recovery in the sand pack and its effluent solution showed a surfactant rich middle phase. Therefore, it was conjectured that there was much surfactant loss to the Berea core resulting in a poor oil recovery. Hurd (1976) reported the use of STPP and Na_2CO_3 as effective chemical additives in preventing surfactant adsorption on rock mineral surface. We incorporated STPP and Na_2CO_3 at an arbitrary weight ratio of 1:1 as sacrificial agent in this system to attempt to improve oil recovery efficiency. Oil recovery was increased to 62% as sacrificial agents were increased to 0.3%. The decreasing in oil recovery efficiency at 0.5%

THE EFFECT OF SACRIFICIAL AGENT ON TERTIARY OIL RECOVERY IN BEREA CORES AT 25°C

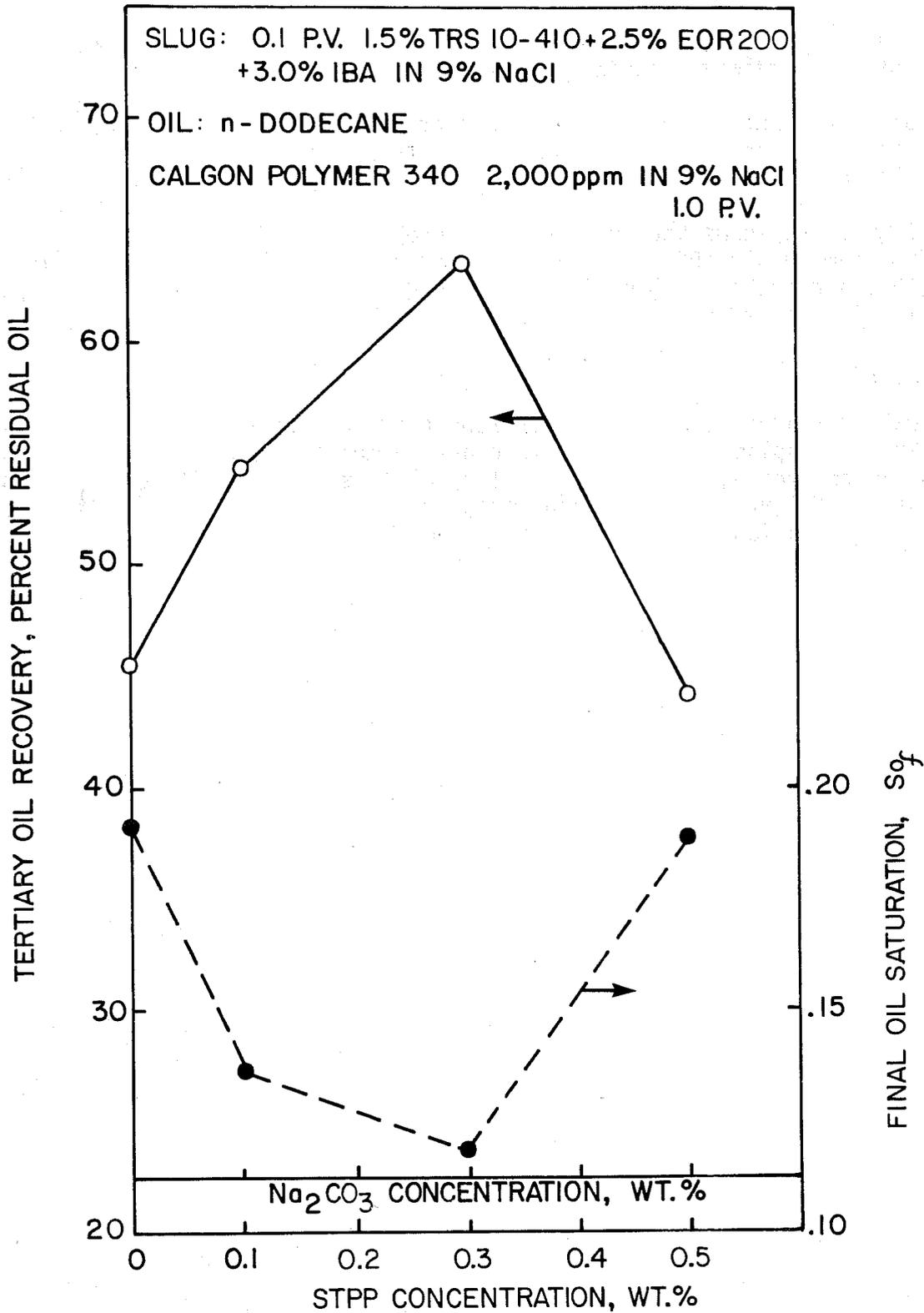


Figure IC1

STPP & 0.5% Na_2CO_3 can be partially explained by shifting of the optimal salinity due to increased ionic strength.

Studies on solubilization are in progress since the sacrificial agent probably affects liquid-liquid distribution as well.

Since 0.3% STPP & 0.3% Na_2CO_3 , appeared to improve the recovery the most, the same concentrations were added to other salinities to see its effect on oil recovery efficiency.

Figure IC2 shows that maximum oil recovery still occurs at 9% NaCl when the same 0.3% STPP & 0.3% Na_2CO_3 are included. Thus, it is possible that the same optimal salinity can be found for the surfactant solution/oil systems with and without sacrificial agents added.

Conclusions:

Oil displacement tests in both sand packs and Berea cores demonstrate that an oil-displacing-high-salt-tolerant formulation is possible by mixing petroleum sulfonate, cosolvent and electrolyte solutions with ethoxylated sulfonate. For the case of Berea cores, sacrificial agents are needed to overcome the surfactant loss in porous medium. The type and amount of sacrificial agent does affect the maximum amount of oil recovery.

TERTIARY OIL RECOVERY OF 1.5% TRS 10-410 + 2.5% EOR 200
+ 3.0% IBA IN X% NaCl + 0.3% STPP + 0.3% Na₂CO₃ IN
n-DODECANE IN BEREA CORES @ 25°C

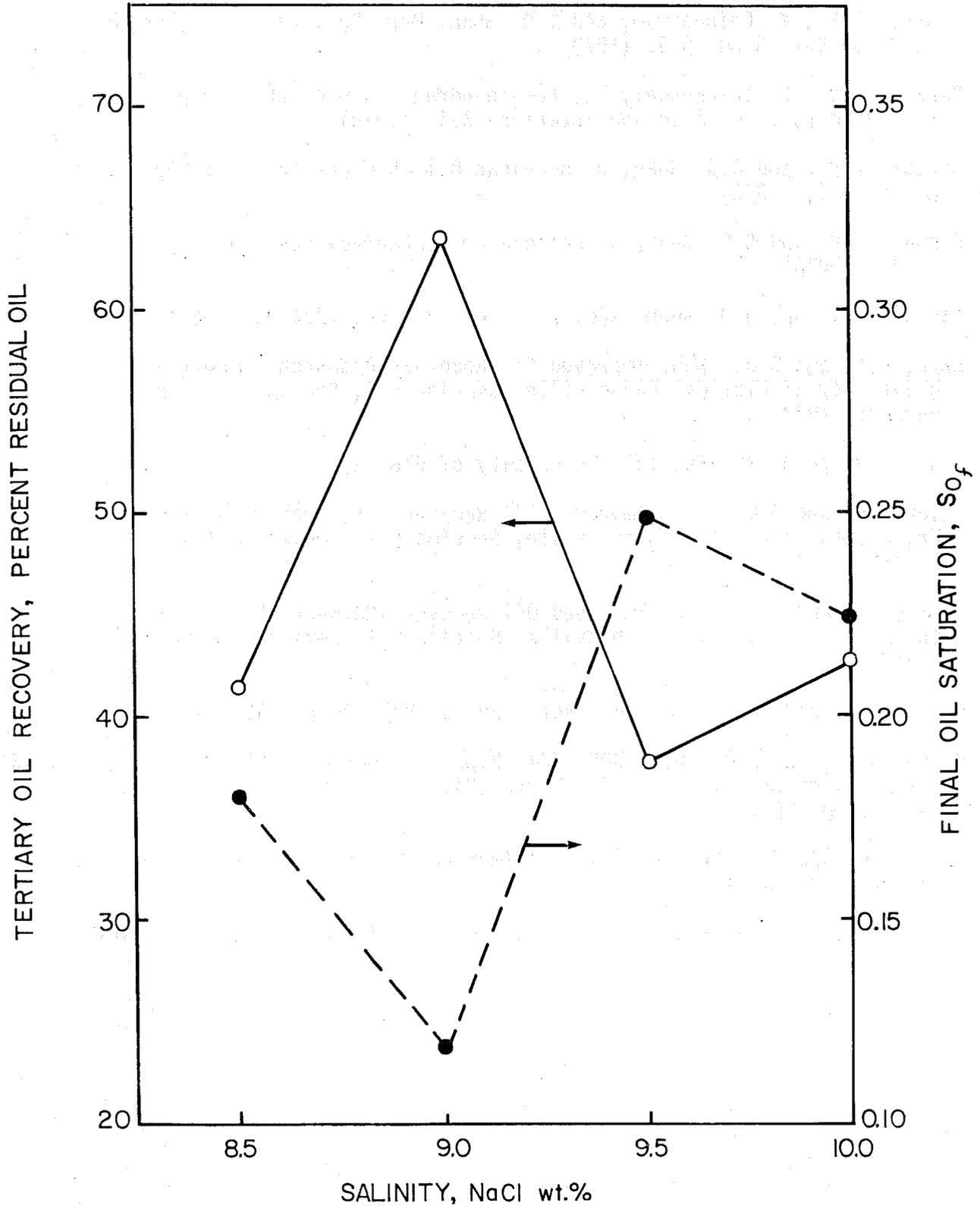


Figure IC2

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II. POLYMER RHEOLOGY AND FLUID MECHANICS

Research Director: Professor D.O. Shah

A. Molecular Characterization of Polymers

1. Determine the Effect of Na/Ca Ratio of Brine on Screen Factor and Intrinsic Viscosity of Polyacrylamide (Calgon 815 and Calgon 835) Solutions

Investigator: Dr. A.N. Sunder Ram

The addition of polymer solution to injection water can enhance oil recovery by improving the mobility control and by reducing the permeability of reservoir rock to water. When displacement efficiency is of primary importance, it is necessary to consider field conditions since mobility control must be maintained throughout the flooding. Mobility control characteristics can best be determined in the laboratory by measuring solution viscosity and screen factor. Here, the effect of Na/Ca ratio of brine for the two partially hydrolyzed polyacrylamides were investigated.

Materials and Methods:

The partially hydrolyzed polyacrylamides, Calgon 815 and Calgon 835 were obtained from Calgon Corporation. Sodium chloride and calcium chloride were of high grade purity. Double distilled water was used. Viscosity measurements were made on a Cannon-Fenske viscometer (#75). Readings were repeated until a constant viscosity was obtained. The screen factor was measured with an ordinary screen viscometer, Jennings, (1971).

For the preparation of the polymer solution, 500 ppm of solid polymer (C815 or C835) was added to a brine vortex and then agitated gently with a magnetic stirring bar for 6 hours. CaCl_2 (100-2000 ppm) was then mixed with the polymer solution. The sample solution was allowed to stand overnight at 30°C before measurement of viscosity and screen factor viscosity properties. To determine the intrinsic viscosity of the polymer, weighed amounts of polymer powder were added to a solution of NaCl (1%) and CaCl_2 (500 ppm) in water.

Results and Discussion:

The polymer solution data are summarized in Tables IIA1 - IIA3.

For the system containing 500 ppm of CaCl_2 in 1% NaCl solution and different concentrations of polymer, it was observed that the screen factor increased from about 3 units to 10 units for 50 to 500 ppm of polymer. The intrinsic viscosities of the polymers (C815 and C835) in this system were found to be 12.6 and 17.3 dl/gm (Figures IIA1 - IIA2).

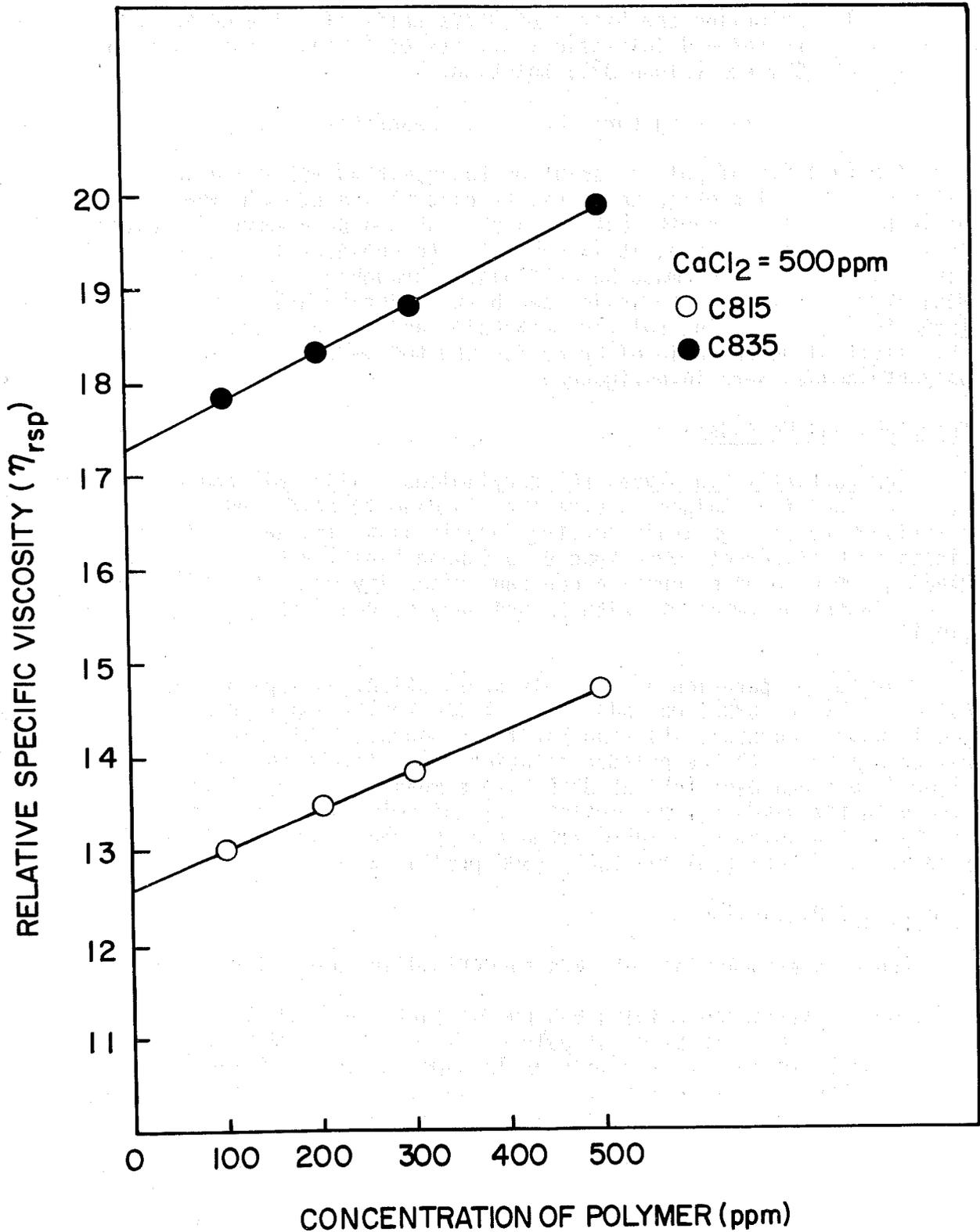
EFFECT OF Ca^{++} ION IN BRINE (1%) ON INTRINSIC VISCOSITY OF POLYMER SOLUTIONS

Figure IIA1

EFFECT OF Ca^{++} ION IN BRINE (1%) ON SCREEN FACTOR OF POLYMER SOLUTIONS

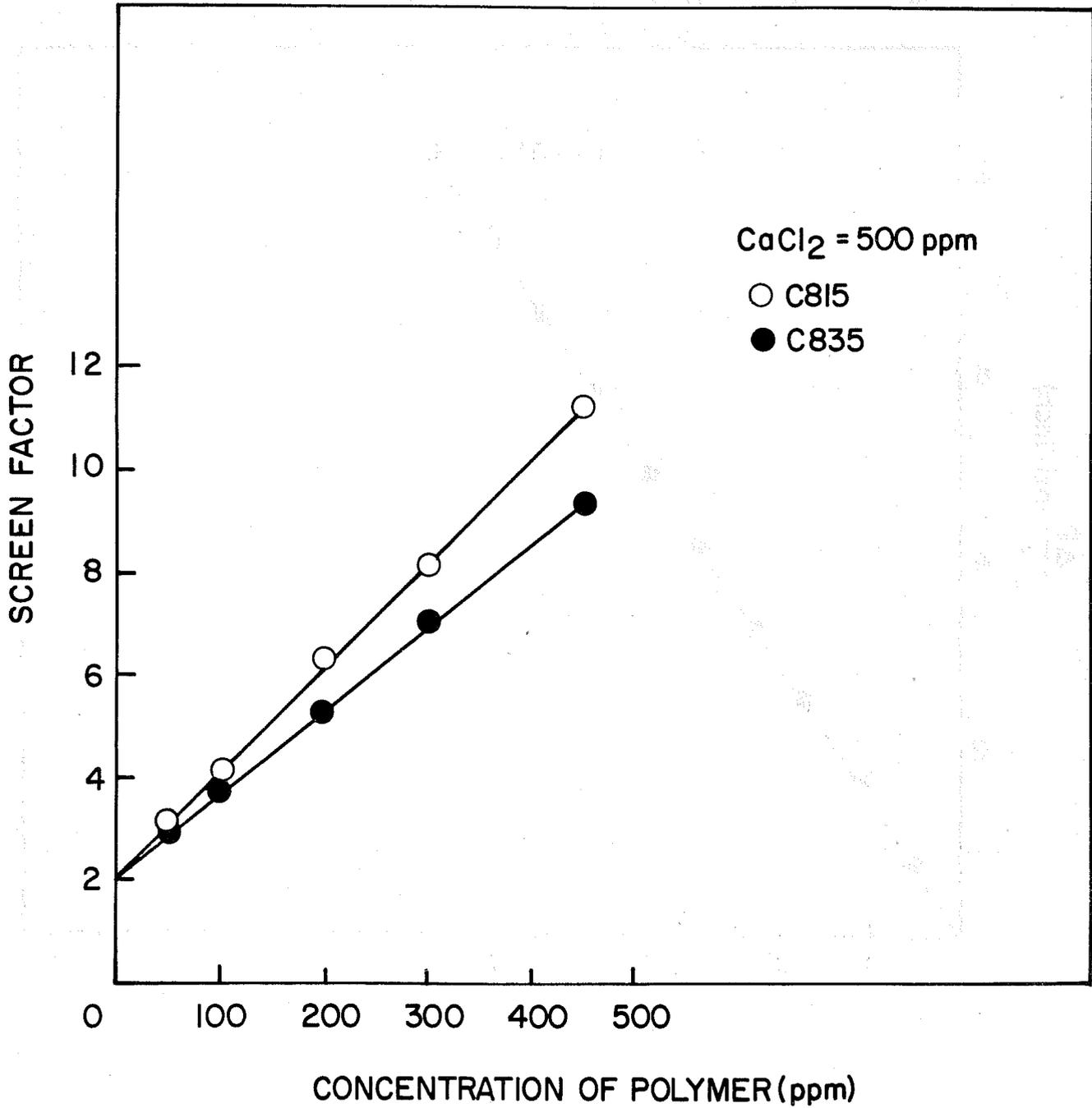


Figure IIA2

PRESSURE DROP OF WATER WITH FLOW RATE

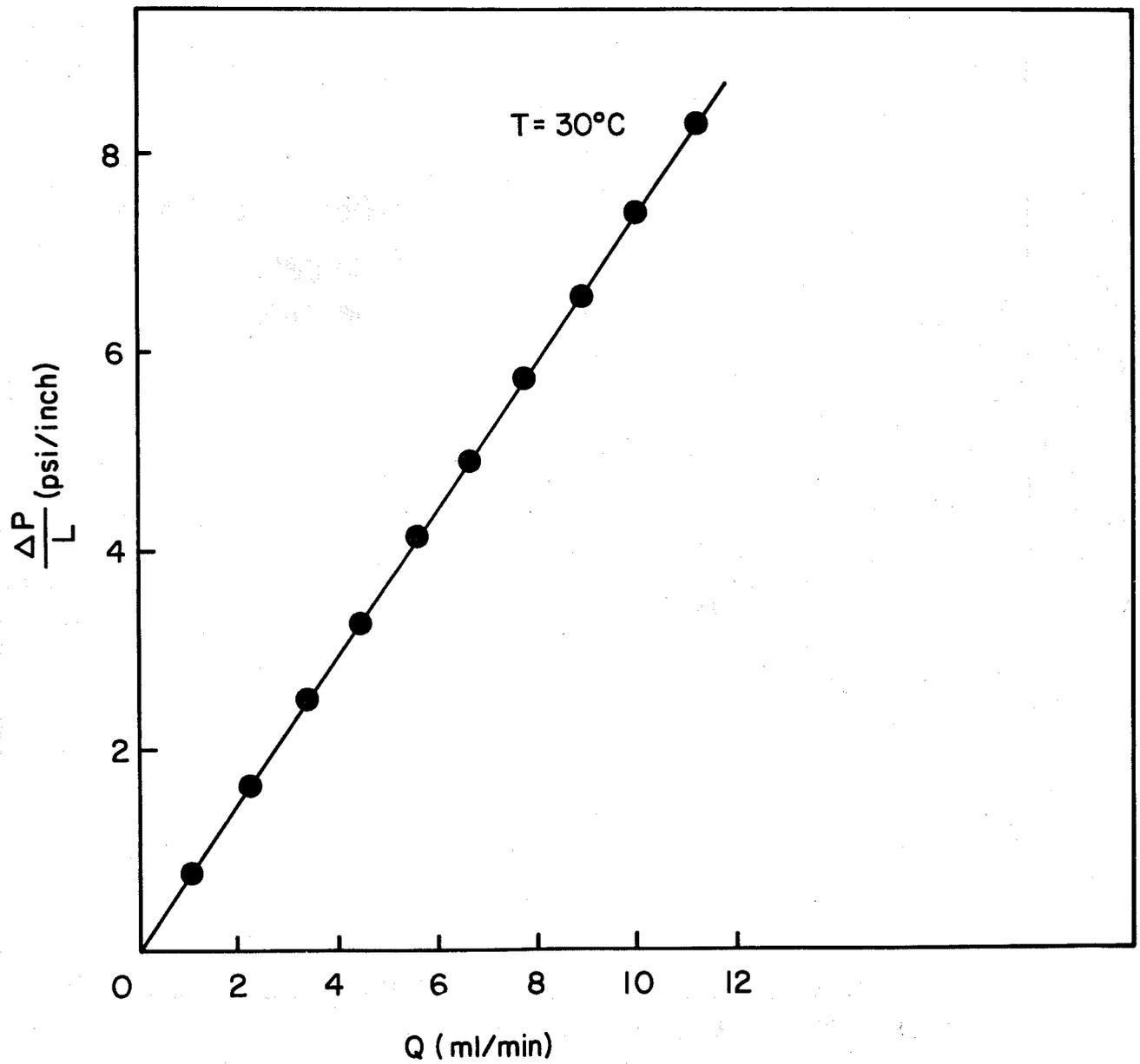


Figure IIA3

The screen factor for the polymer, C815 in 1% NaCl with varying concentrations of calcium chloride gradually dropped by 20% (100-2000 ppm) of its original value. In the case of C835 however, the reduction in the screen factor was initially more sharp, but finally decreased 20% in the same concentration region. Similarly, increases in the CaCl_2 concentration gradually reduced the viscosities of polymer solutions. For C815, it was up to 20% while C835 exhibited decreases up to 15%. These data, therefore, demonstrate that the greater the cation concentration, the greater is the reduction in their properties.

2. Determination of $\Delta P/L$ of the Polyacrylamide (C815 and C835) Solutions for Their Flow Through a Column Packed With Silica Gel

Investigator: Dr. A.N. Sunder Ram

The non-Newtonian flow effects, permeability reduction and polymer adsorption effects in oil displacement are a function of both the fluid and the rock material. The stability of polyacrylamides (C815 and C835) has been studied at different ionic concentrations: in flow through a silica gel.

Materials and Methods:

A stainless steel column 6 inches long (L) and 1/4 inch in diameter was used for the flow test. The column was packed with the silica gel [EM-Gel SI 200 \AA with particle size 0.040-0.063 mm (230-400 mesh ASTM)]. The mean pore diameter measured with a mercury pressure porosimeter gave a value of 210 \AA . The material was obtained from E. Merck.

The systems studied in the experiment are, C815/C835 (500 ppm) in 1% NaCl with 0, 100, 500, 1000, 1200, 1500 and 2000 ppm of CaCl_2 . The method of preparation of the polymer solution is similar to the procedure described in IIA1. Polymer solutions were taken in glass bottles with a capacity of 150 ml and placed in a concentric walled vessel through which water was circulated from a constant temperature bath (30°C). The polymer solution was pumped from the bottles by a Constametric I HPLC pump (Milton Roy Co., Serial No. 7804-03). The flow rate was accurately controlled by an built-in potentiometer setting. The pressure drop (against atmosphere) was measured using two pressure transducers, 0-100 and 0-500 psi range. For a particular polymer solution, pressure drop was measured as a function of flow rate. Fresh bed was dry packed to fill each column. Pressure drop for water at 30°C was measured as a function of flow rate (Figure IIA3). All the fresh bed strictly followed the standard pressure drop of water. Once a polymer solution for a given system is pumped through the bed, it was not recycled.

Results and Discussion:

The pressure drop, $\Delta P/L$ obtained for the polymer solutions (C815 and C835) are presented in Figures IIA4 and IIA5. The results for the systems, 0, 100 and 500 ppm of CaCl_2 show linear relations for $\Delta P/L$ vs Q plots. The remaining systems with higher concentration of CaCl_2 reveal a non-linear type of behavior. It was observed that C815 and C835 in 1000 ppm of CaCl_2 behave differently. The reason could be that C835 would not have formed a stable system when it was pumped through the porous medium. The system with 1200 ppm of CaCl_2 has the lowest $\Delta P/L$ values. In addition, it is at this concentration the transition from linear to non-linear behavior occurs.

PRESSURE DROP VARIATION WITH FLOW RATE AT DIFFERENT CaCl₂ CONCENTRATIONS

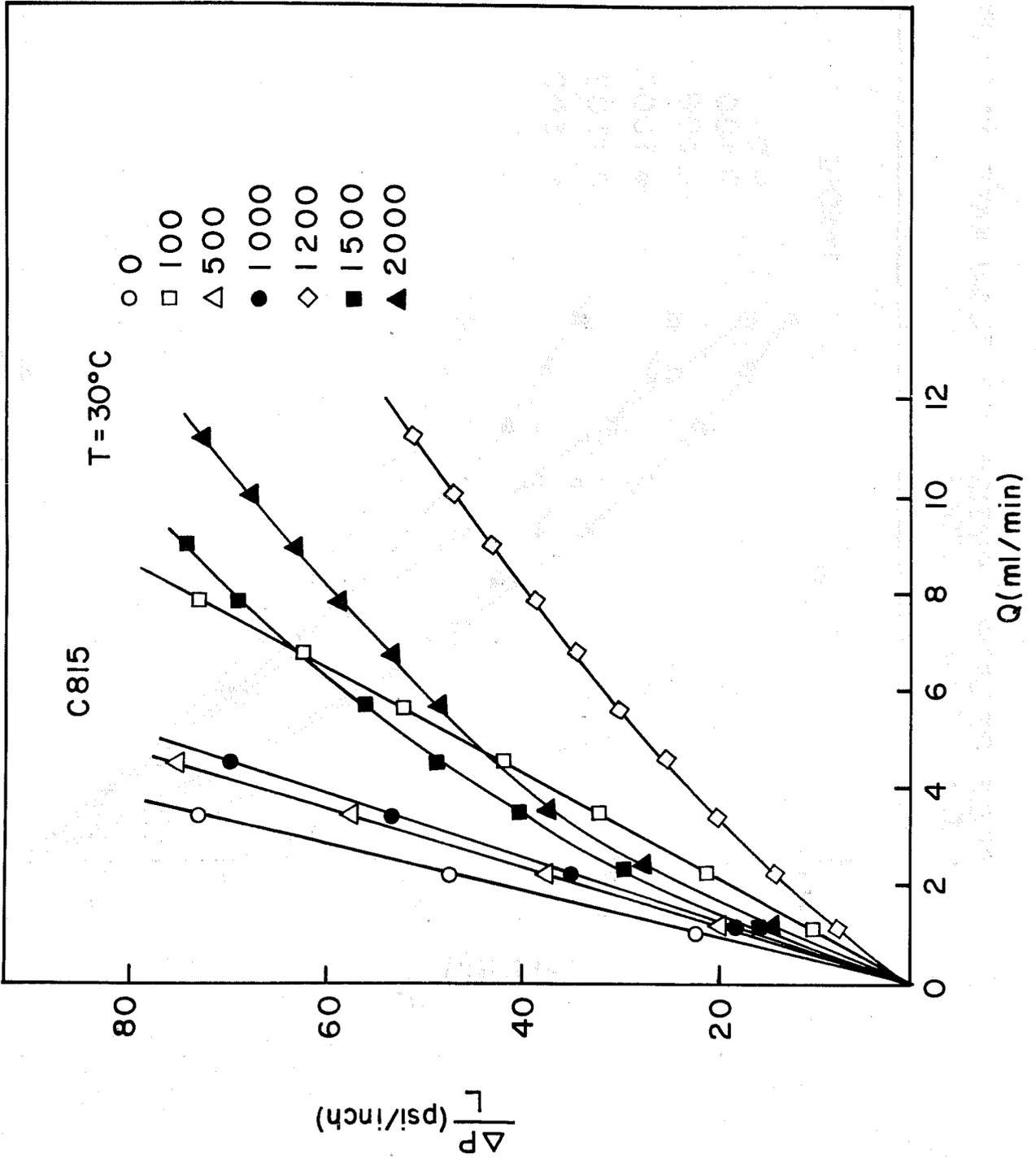


Figure IIA4

PRESSURE DROP VARIATION WITH FLOW RATE AT DIFFERENT
CaCl₂ CONCENTRATIONS

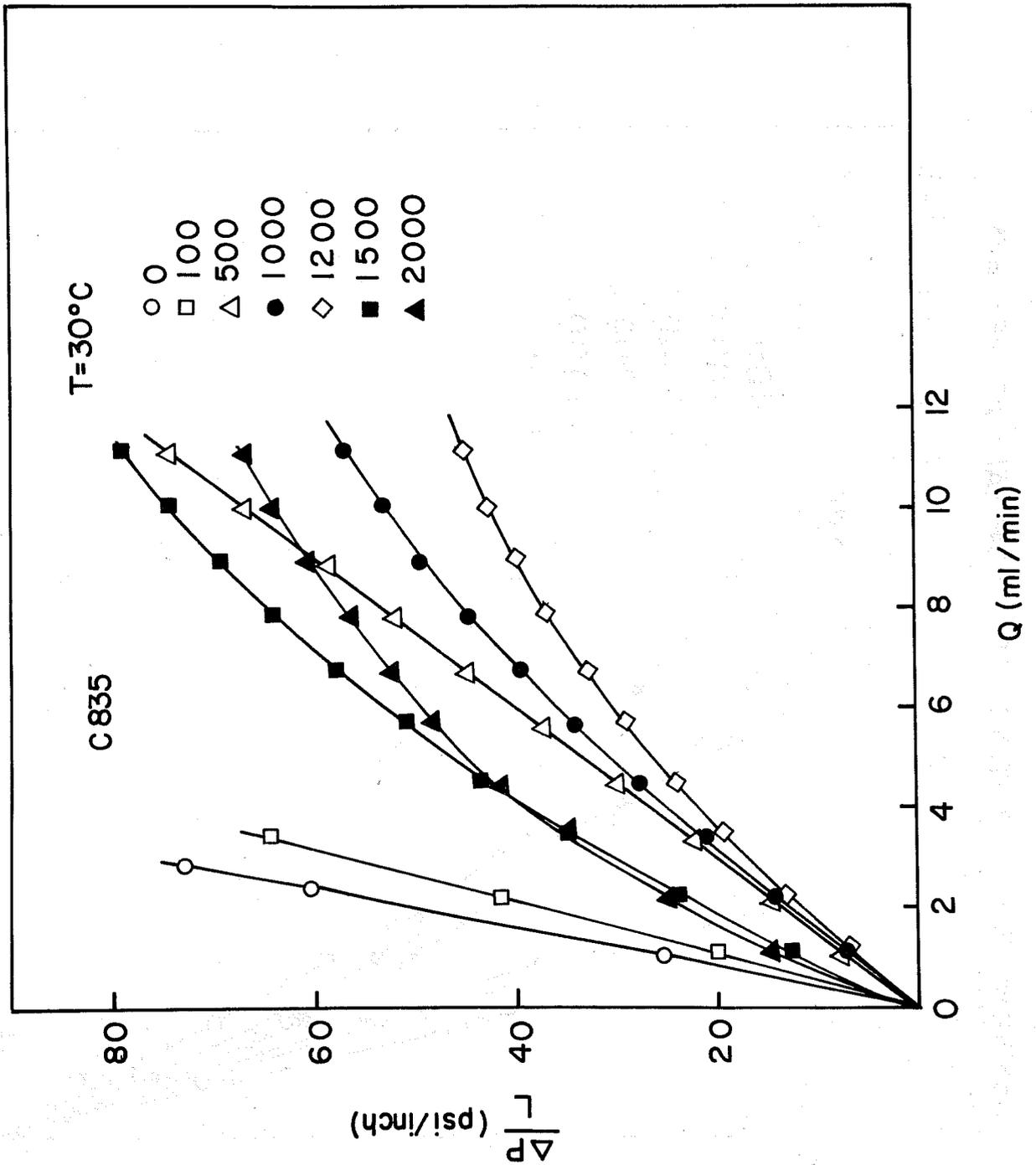


Figure IIA5

Table IIA1

Effect of 500 ppm Ca^{++} Ion in 1% NaCl Brine on Screen Factor of Polymer Solutions

Polymer Concentration (ppm)	T=30°C	
	Screen Factor C815	Screen Factor C835
50	3.09	2.90
100	4.11	3.78
200	6.23	5.10
300	8.13	7.04
500	11.20	9.32

Table IIA2

Effect of Ca^{++} Ion On Screen Factor for C815/C835 (500 ppm) In
1% NaCl Solution

CaCl ₂ (ppm)	T=30°C Screen Factor	
	C815	C835
0	11.53	10.46
100	10.87	8.95
500	10.70	9.04
1000	10.49	9.04
1200	10.52	8.90
1500	9.54	8.60
2000	9.24	8.47

Table IIA3

Effect of Ca^{++} Ion On Viscosity For C815/C835 (500 ppm)
Ion 1% NaCl Solution

CaCl ₂ (ppm)	T=30°C	
	Viscosity	
	C815	C835
0	1.49	1.68
100	1.43	1.62
500	1.40	1.58
1000	1.35	1.46
1200	1.33	1.46
1500	1.29	1.41
2000	1.27	1.35

Table IIA4

Effect of Ca^{++} Ion on Screen Factor for C815/C835 (500 ppm)

CaCl ₂ (ppm)	T=30°C Screen Factor			
	C815		C835	
	before flow	after flow	before flow	after flow
0	11.53	6.9	10.46	5.67
100	10.87	4.19	8.95	3.36
500	10.70	3.86	9.04	3.28
1000	10.49	3.59	9.04	3.17
1200	10.52	2.87	8.90	2.62
1500	9.54	2.37	8.60	2.27
2000	9.24	2.13	8.47	2.11

Table IIA5

Effect of Ca^{++} Ion on Viscosity for C815/C835 (500 ppm)

CaCl ₂ (ppm)	T=30°C Viscosity (cp)			
	C815		C835	
	before flow	after flow	before flow	after flow
0	1.49	1.41	1.68	1.63
100	1.43	1.36	1.62	1.52
500	1.40	1.31	1.52	1.44
1000	1.35	1.28	1.46	1.33
1200	1.33	1.23	1.46	1.27
1500	1.29	1.18	1.41	1.23
2000	1.27	1.17	1.35	1.20

Polymers appear to adsorb on the porous media as a monolayer with thickness approximately equal to the diameter of the molecular coil in that particular solvent, Dawson (1972), Smith (1970), Szabo (1975). Adsorption of polyelectrolytes such as partially hydrolyzed polyacrylamides is particularly sensitive to the nature of the dissolved salt and the solid surface, Willhite (1977). It has been reported that calcium ions were more effective in promoting adsorption of partially hydrolyzed polyacrylamides on negatively charged silica surfaces than sodium ions Smith (1970). To test the influence of this we measured the viscosity and screen factor of the polymer solution which flowed through the porous media (Tables IIA4 and IIA5). After flowing through the porous medium the screen factor in the CaCl_2 -free system was reduced by 40%. Addition of 100 ppm of CaCl_2 decreased the screen factor by 62% while at a concentration of 2000 ppm CaCl_2 , the value was further reduced by 77%. However, the viscosity of the polymer solutions, were only slightly affected by Ca^{++} ion (5-10%) (Figures IIA6 - IIA9).

Adsorption of polymer molecules appears to be irreversible on some surfaces, Silberg (1962), and Rowland (1966). Schamp and Huylebroeck (1973) found adsorption of polyacrylamide on montmorillonite kaolinite and illite to be irreversible. However, Szabo's work on one type of polyacrylamide on silica sand indicates substantial reversibility. We attempted to regenerate the silica gel column used for the flow through study. The silica gel was taken out from the steel column, washed several times with small amounts of water, finally with acetone and then dried at 150°C . It was observed that the regenerated bed strictly adhered to the pressure drop exhibited by fresh beds, indicating that the polymer can be desorbed.

EFFECT OF Ca^{++} ION CONCENTRATION ON SCREEN FACTOR

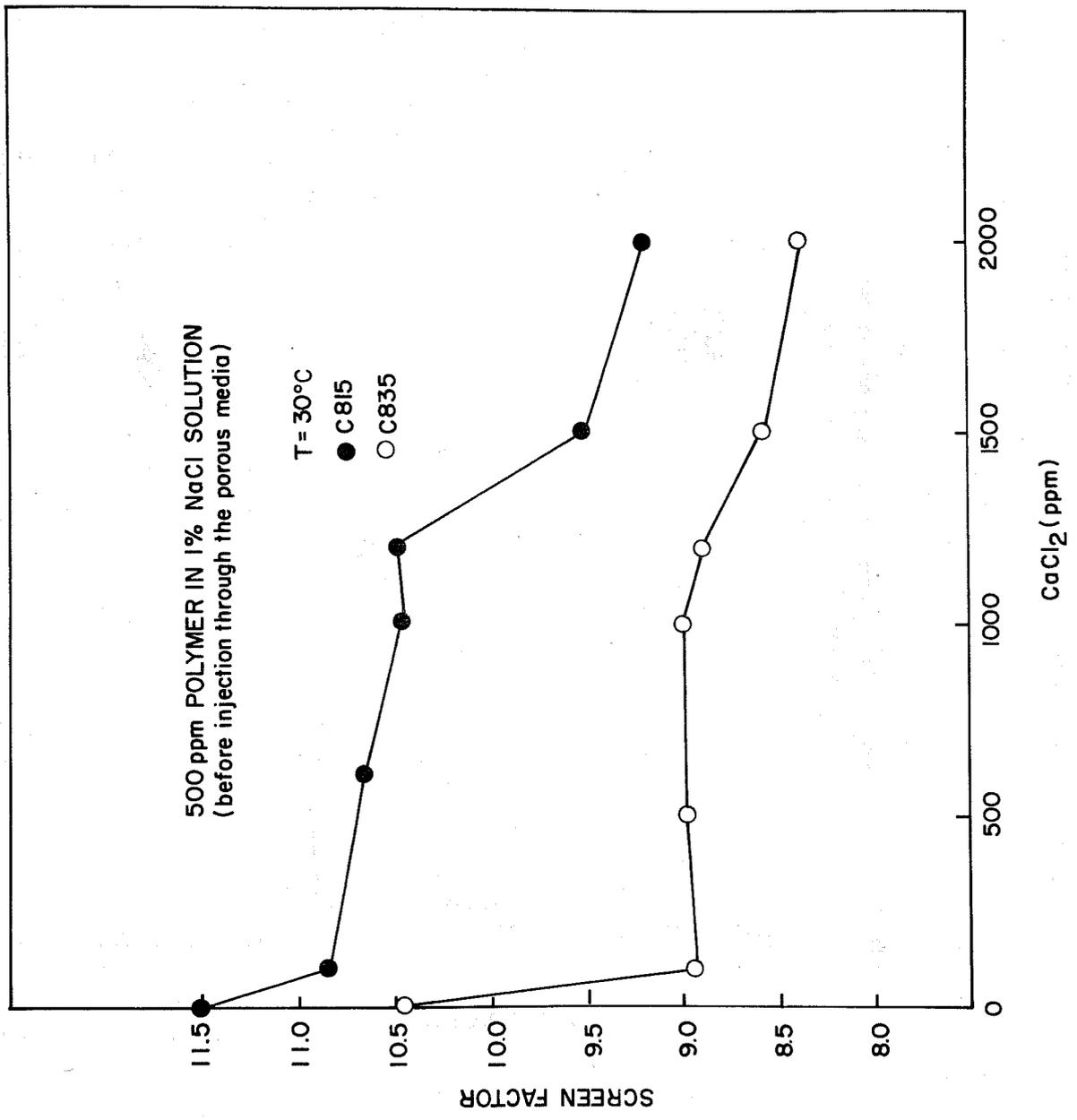


Figure IIA6

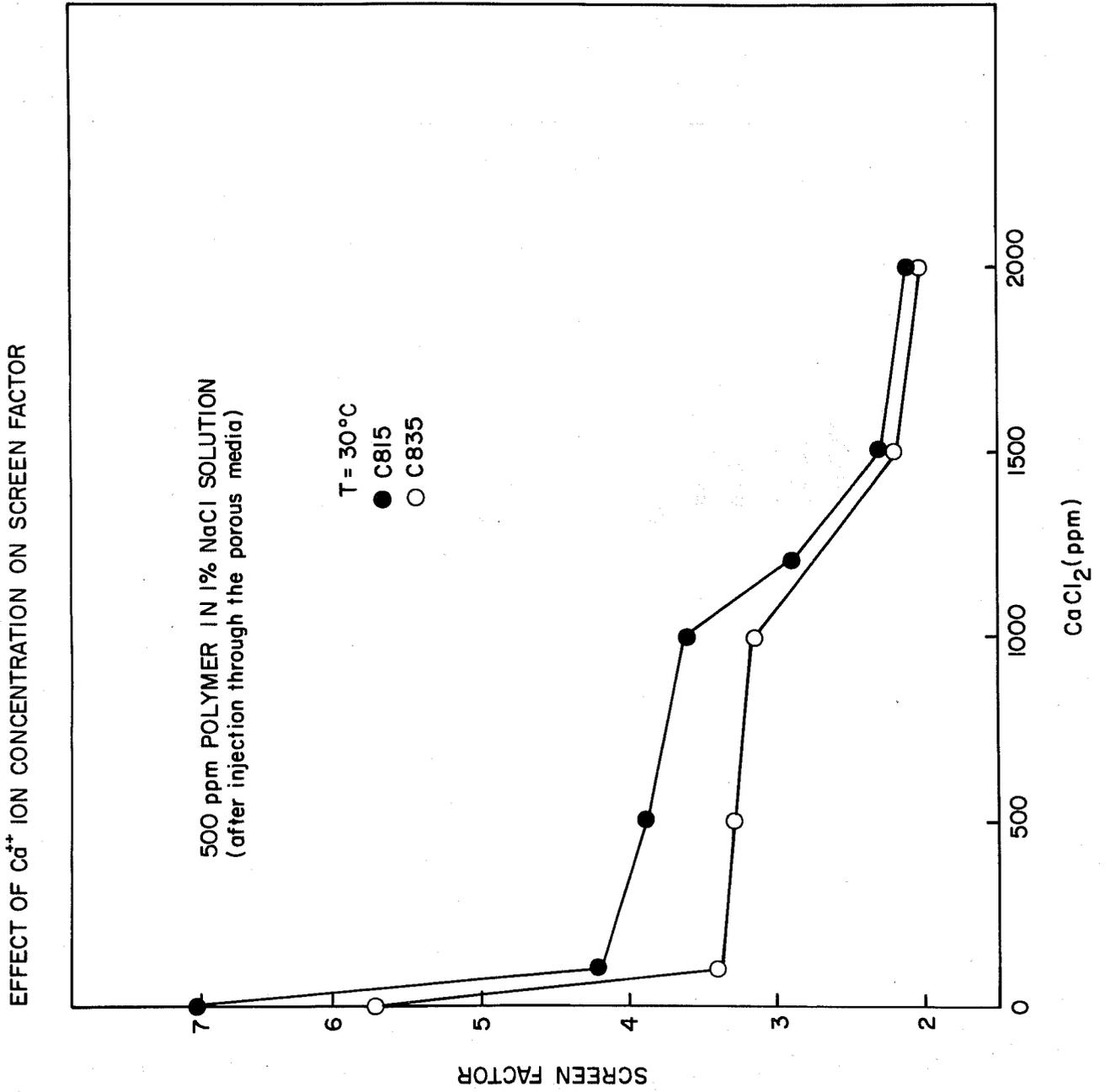


Figure IIA7

EFFECT OF Ca^{++} ION CONCENTRATION ON VISCOSITY

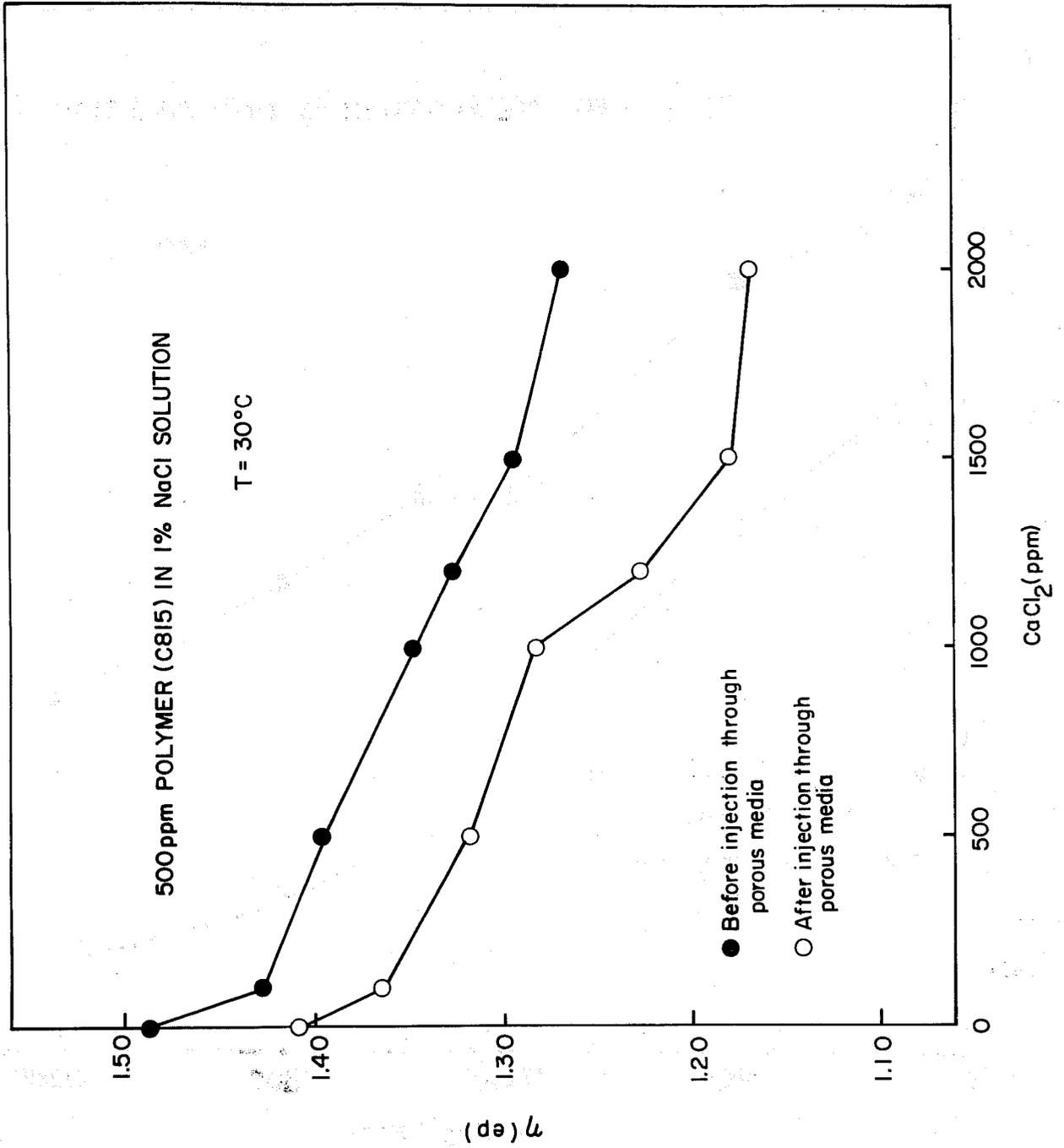


Figure IIA8

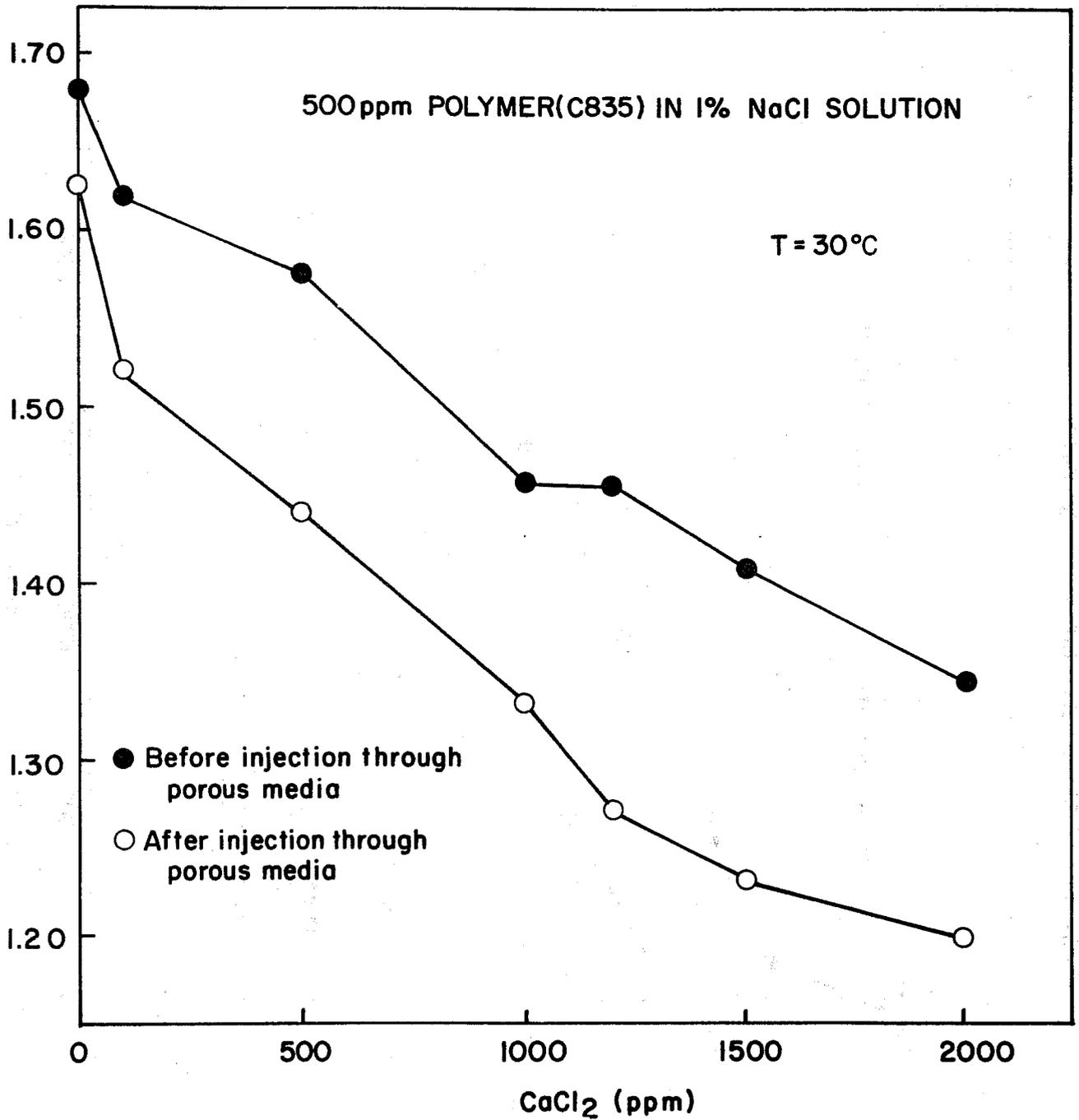
EFFECT OF Ca^{++} ION CONCENTRATION ON VISCOSITY

Figure IIA9

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B. Surfactant/Polymer Interaction

1. Determine the Effect of TRS 10-410 Surfactant on The Intrinsic Viscosity and Screen Factor of Calgon 835 and Calgon 800, in Aqueous Solution As a Function of Surfactant Concentration
2. Determine the Effect of Added TRS 10-410 (0.1, 1.0, 2.0%) On the Intrinsic Viscosity and Screen Factor of Polyacrylamide (C-835) in Various Brine Solutions

Investigator: Mr. N.N. Desai

Viscosity studies have been used to study the binding of small ions and surfactant molecules by macromolecules (Lewis and Robinson 1969, Reynolds and Tanford 1970). Changes in the intrinsic viscosity are indicative of the conformational transformation induced in the polymer by the binding of such ions (Lotan, 1973). In the following section, data are presented on the effect addition of anionic surfactants has on the viscosity of polyacrylamide in distilled water and in brine.

Materials and Methods:

The polymers studied were Calgon 835, a partially hydrolyzed polymer and Calgon 800, an unhydrolyzed polyacrylamide, both obtained from Calgon Corp. Surfactants used were TRS 10-410 from Witco Chemicals, sodium dodecyl benzene sulfonate from Cities Service Co. and sodium lauryl sulfate (99% pure) from BDH Chemicals. The solutions were made as follows:

A stock solution of 2000 ppm polymer was prepared in distilled water by gently stirring with a magnetic stirrer at a low speed (~ 100 rpm). In the light of the results presented in our Semi-Annual Report of June 1978 (Pages C-1 to C-21), this polymer solution was allowed to stay on the shelf for 10 days at room temperature before use. Individual samples were prepared by appropriate dilution of this stock solution, again by gently stirring. All contact with metals was avoided.

The viscosity was measured by a Cannon-Fenske capillary viscometer (flow time for distilled water 115.0 secs). All viscosity measurements were made at 30°C.

Figure IIB1 shows the viscosity (relative to water) of aqueous polymer solutions containing sodium chloride or surfactant or both, all as a function of the polymer concentration. It is seen that both the surfactant and the salt behave similarly in that they both cause a decrease in the polymer viscosity. At 500 ppm polymer, for instance, the addition of 1.0% TRS 10-410 causes a reduction of the polymer viscosity to about half. Figure IIB2 shows the reduced specific viscosity of the polymer in aqueous solution and the effect of added surfactant on it. The intrinsic viscosity $[\eta]$ was obtained by extrapolating the η_{sp}/c_p vs c_p plot to zero polymer concentration. $[\eta]$ shows a clear decrease with increased surfactant concentration, indicating a reduction in the hydro-

dynamic volume of the polymer, an effect also observed with sodium chloride (Table IIB1). Knowing that TRS 10-410 contains some sodium chloride and that the viscosity dependence on NaCl is sharp at low NaCl concentrations, the plots of Figure IIB3 were drawn. The polymer viscosity drops sharply with as little as 0.1% (or 1000 ppm) sodium chloride, and also shows the viscosity dependence on TRS 10-410 concentration. Since it is possible that the impurities in the TRS 10-410 surfactant may explain the viscosity behavior of the polymer-surfactant system described earlier, $[\eta]$ of Calgon 835 was measured in two surfactants of higher purity, SDBS and SLS. The intrinsic viscosity of Calgon 835 in aqueous solutions of 0.5 wt. % TRS 10-410, SDBS and SLS is 8.9, 4.4 and 6.25 l/gm, respectively. Hence, anionic surfactants cause a substantial decrease in the size of the polymer molecule. The intrinsic viscosity data for various salt and surfactant concentrations are summarized in Table IIB1. Note that though 0.02% NaCl or 1.0% TRS 10-410 decrease $[\eta]$ by comparable amounts the addition of 1.0% TRS 10-410 to Calgon 835 in 0.02% brine does not decrease $[\eta]$ any further.

The intrinsic viscosity of Calgon 800 showed dramatically different behavior. Figure IIB4 shows a plot of η_{sp}/c_p vs c_p for Calgon 800 in distilled H_2O and 1.0% TRS 10-410. ($[\eta]_{c-800}$ in distilled water is 0.65 l/gm.) However, Calgon 800 in 1.0% TRS 10-410 does not follow the same behavior. Instead, it shows a steep rise at low polymer concentration. Such behavior is typical of polyelectrolytes that show electrolytic chain expansion (Fuoss and Strauss, 1948). To obtain the intrinsic viscosity we use the Fuoss-Strauss plot shown in Figure IIB5. The value of $[\eta]_{c-800}$ in 1.0% TRS 10-410 is 125.0 dl/cm., indicative of a very large chain expansion, perhaps caused by the binding of the surfactant anions on the polymers. Figure IIB6 shows another aspect of the surfactant-polymer interactions. In distilled water, as the surfactant concentration is increased, the reduced viscosity decreases, but then increases. This needs to be investigated further and studies are underway on the effect of the surfactant concentration and added salt on this surfactant-polymer system.

Figure IIB7, shows the effect of added sodium chloride (curve 1) and/or TRS 10-410 (curve 2) on the screen factor of Calgon 835 in aqueous solutions. The effects are similar.

However, as Figure IIB8 shows Calgon 800 shows unusual behavior; there is a sharp decrease with addition of TRS 10-410, but on further addition of surfactant, the screen factor rises.

The effect on the 250 ppm polymer is significant but at 750 ppm polymer, the effect is dramatic.

The effect of addition of TRS 10-410 on the screen factor of Calgon 835 in 1.0% and 0.5% sodium chloride solutions is shown in Table IIB2. The sodium chloride completely masks any effect due to that TRS 10-410 may have.

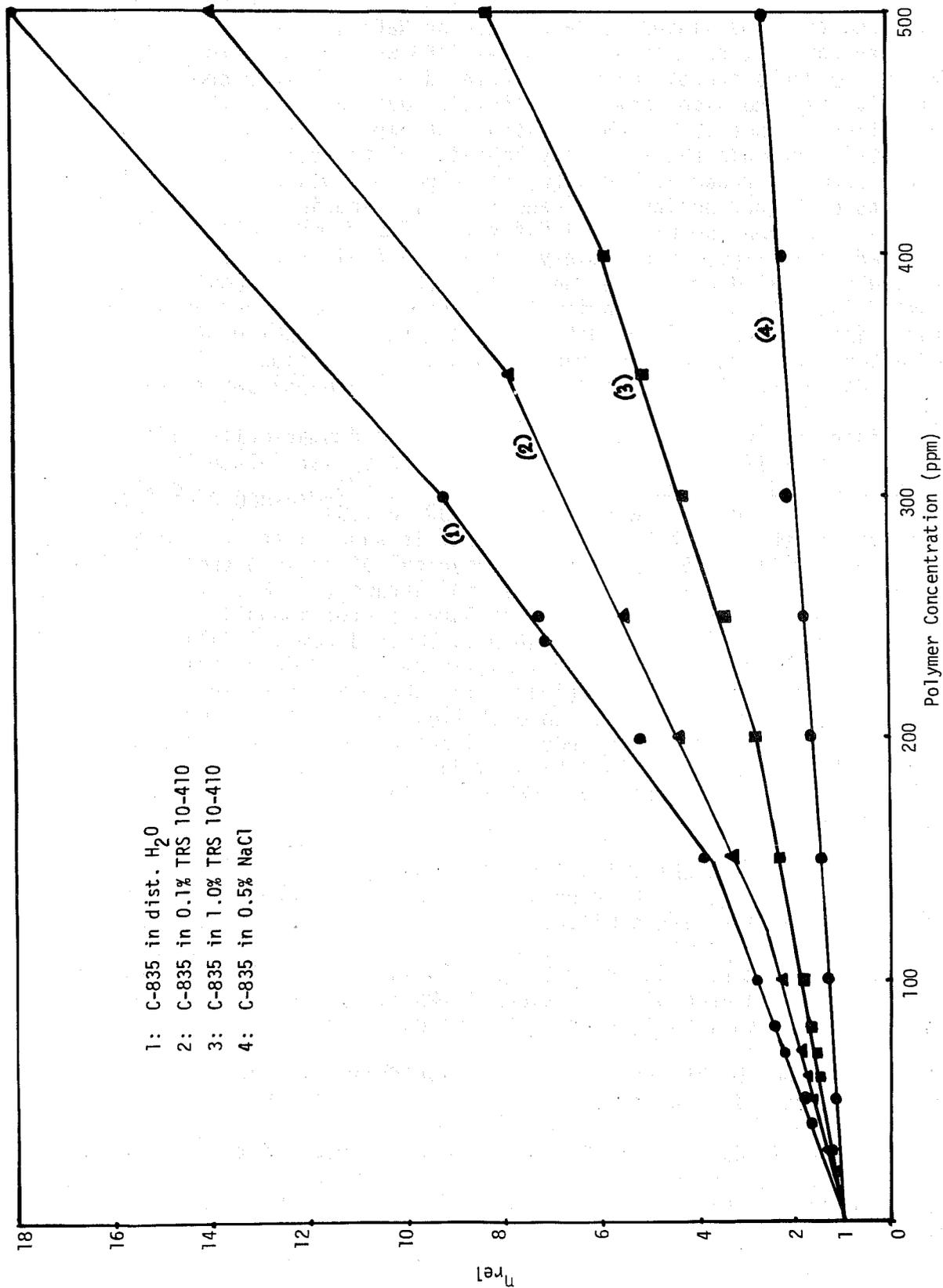


Figure IIB1. Effect of Salt (NaCl) and Surfactant (TRS 10-410) on The Relative Viscosity of Calgon 835 Polymer in Aqueous Solution

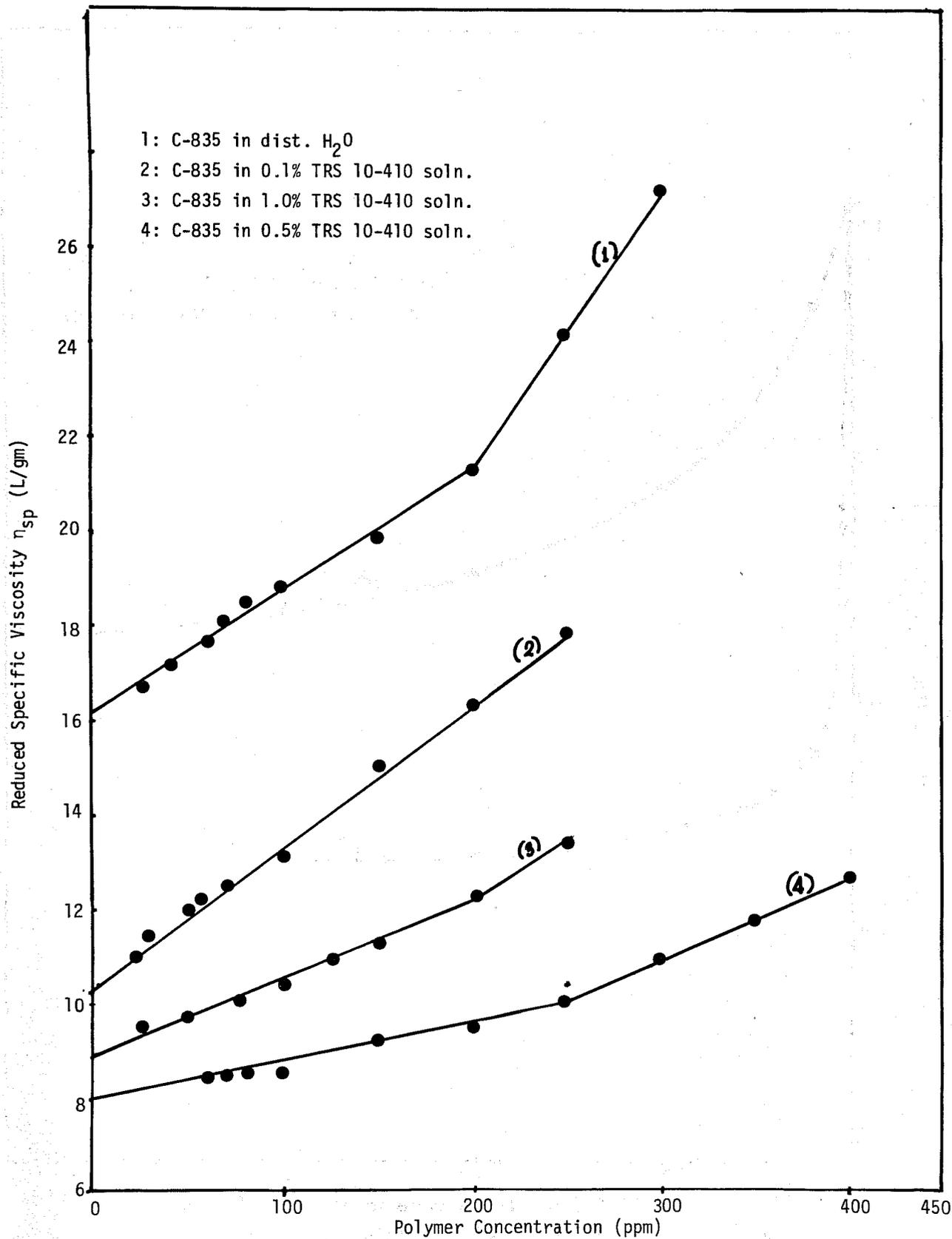


Figure IIB2. Effect of TRS 10-410 Surfactant on The Reduced Specific Viscosity of Calgon 835 Polymer

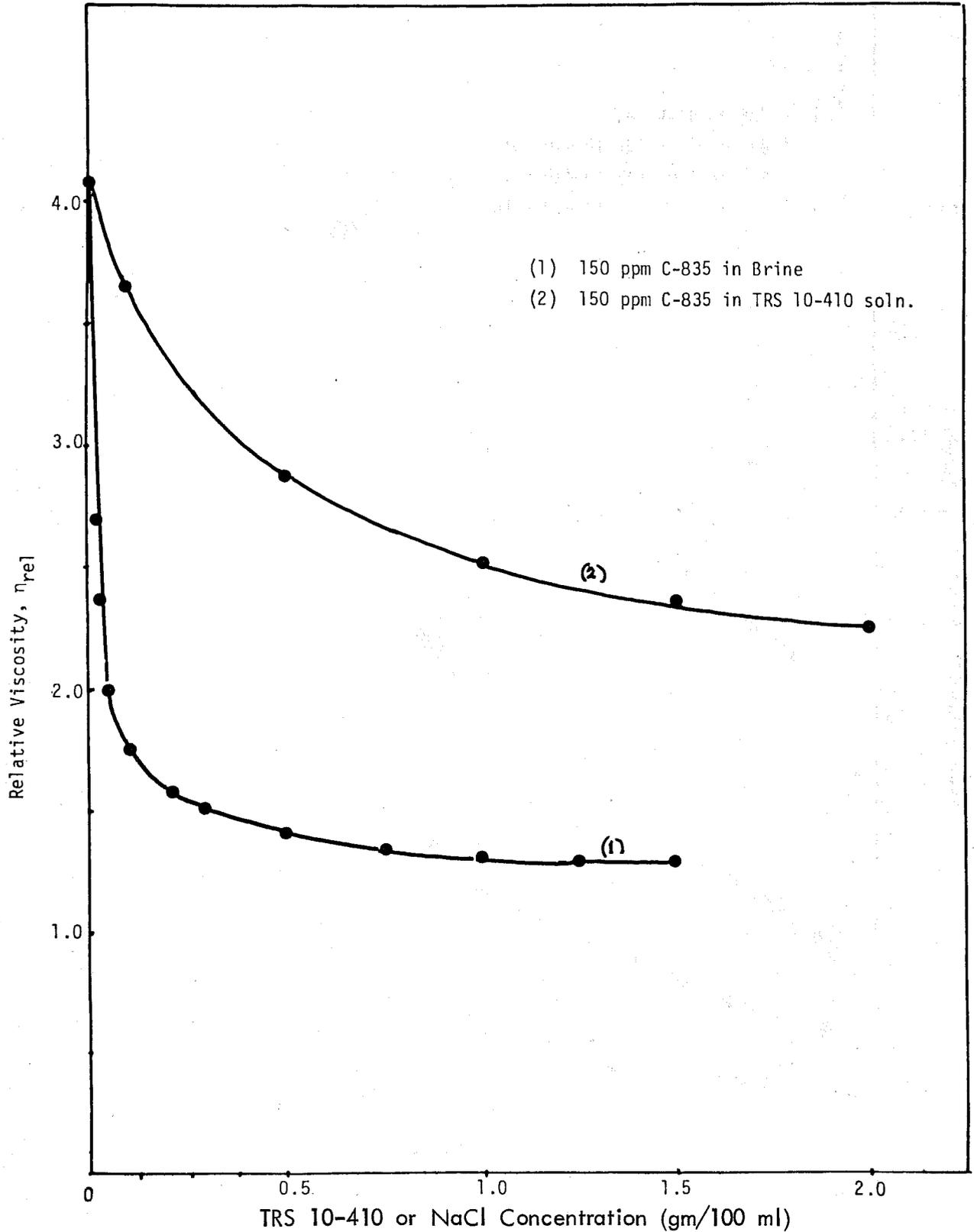


Figure IIB3. Relative Viscosity (to water) of Calgon 835 in Brine as a Function of The Sodium Chloride Concentration

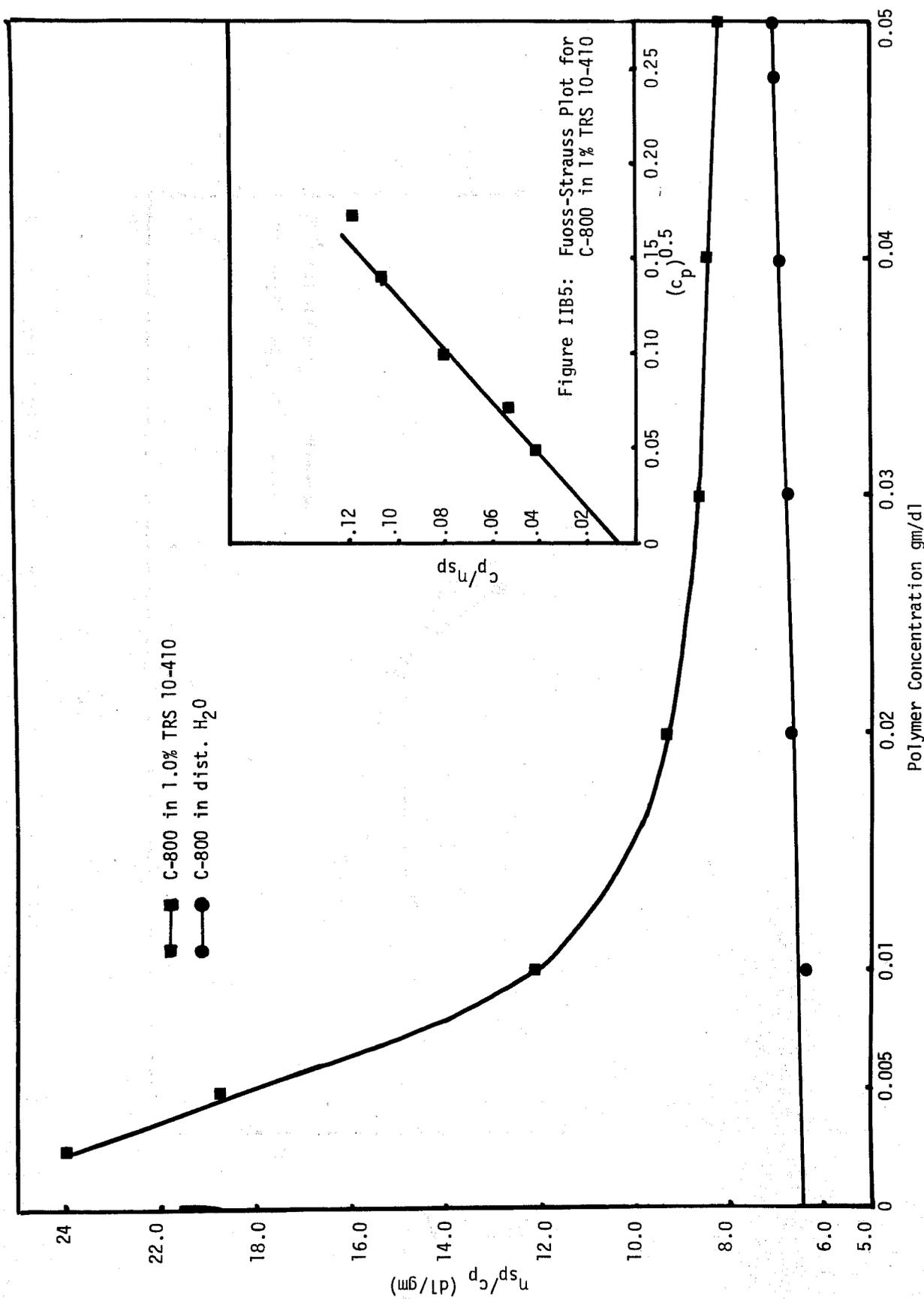


Figure IIB4. Reduced Specific Viscosity of Calgon-800 in Distilled Water and Aqueous Surfactant Solution

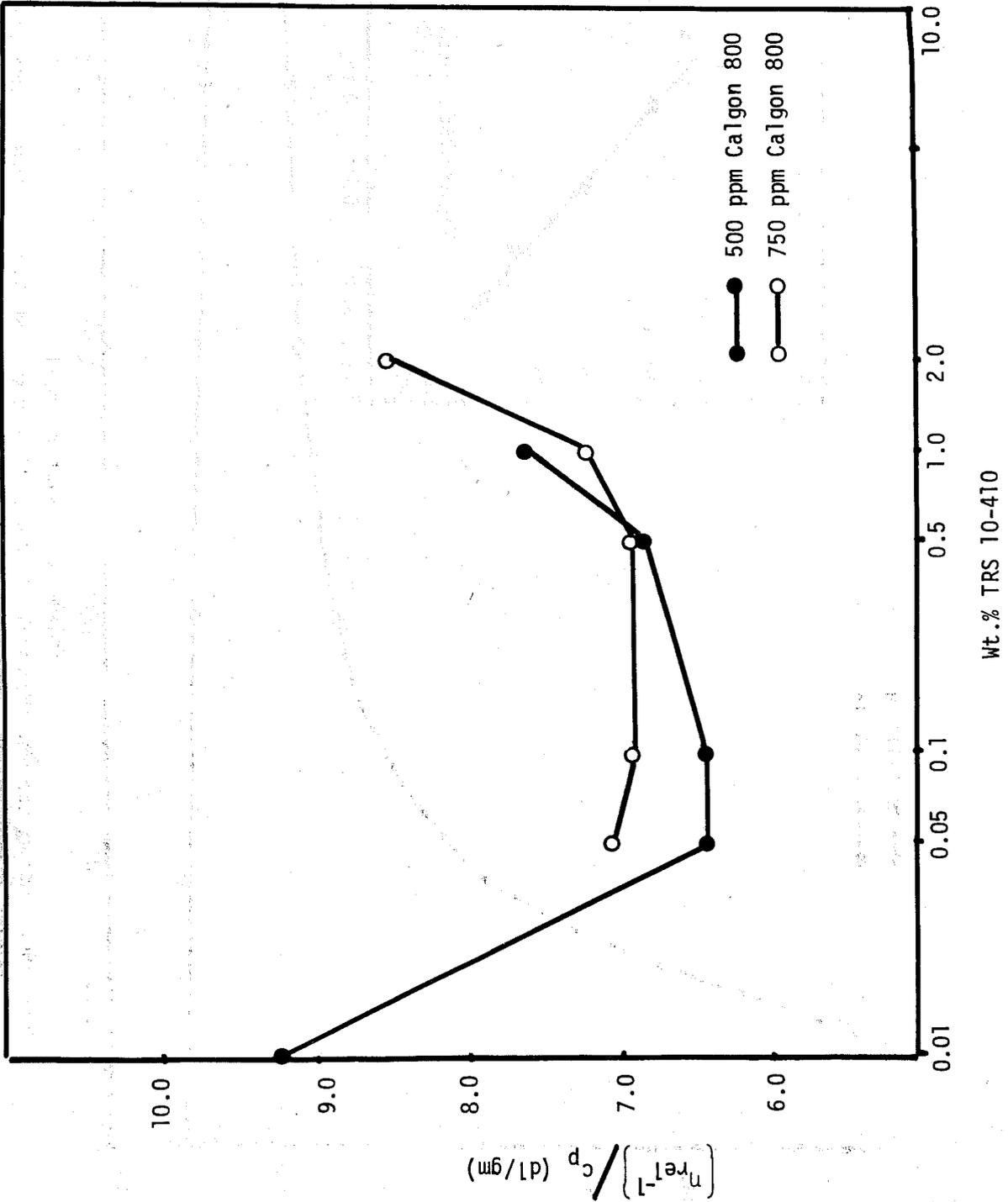


Figure IIB6. Reduced Specific Viscosity of CaIgon 800 + TRS 10-410 in Dist. H₂O

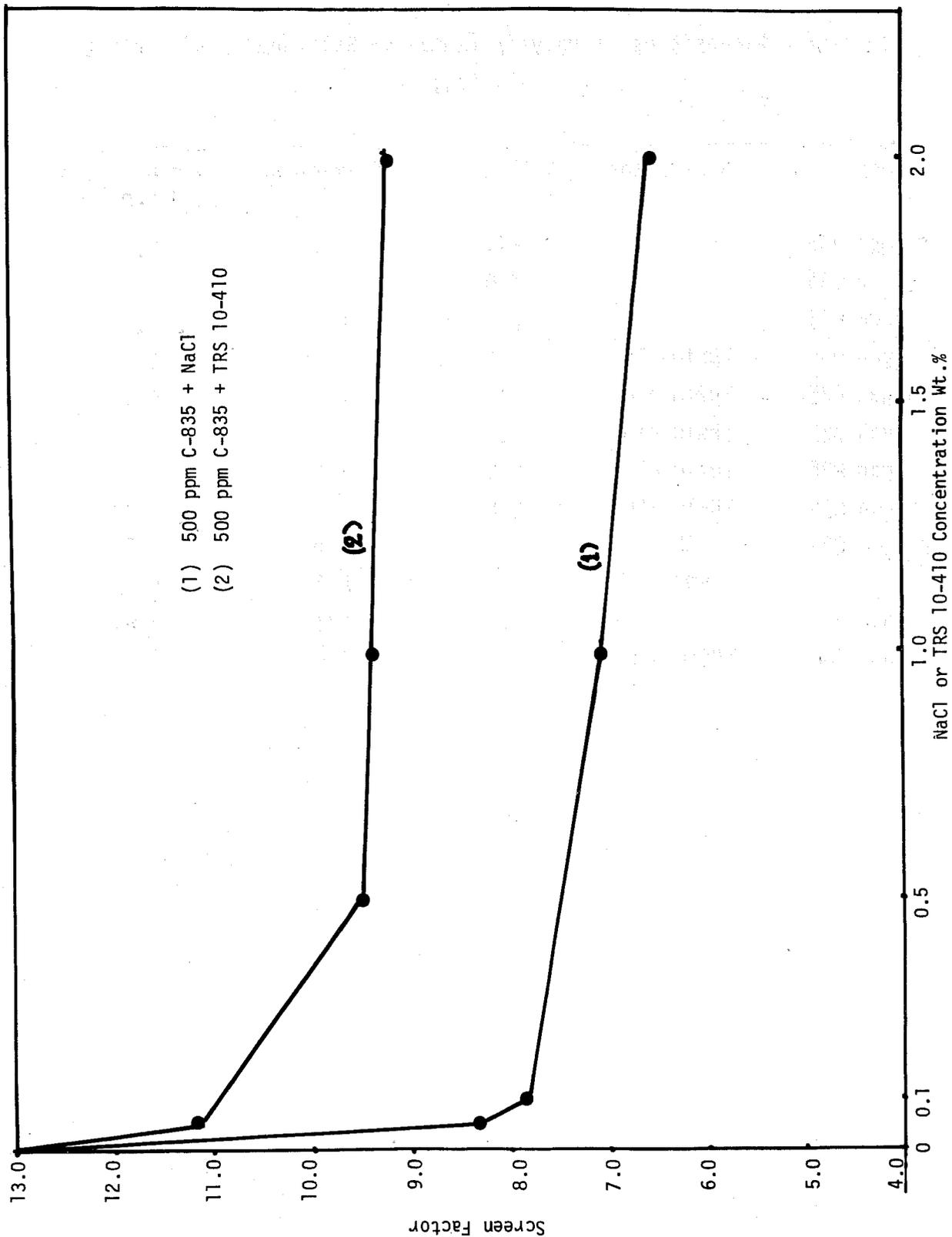


Figure II87. Screen Factor of Calgon Polyacrylamides

Table IIB1
 Intrinsic Viscosities of Polyacrylamide in Salt and/or Surfactant
 Solutions

Polymer Type	Surfactant	NaCl Conc. Wt.%	Surfactant	Intrinsic Vis. [η](ℓ /gm)
Calgon 835	-	nil	nil	16.2
Calgon 835	-	0.02	nil	7.0
Calgon 835	-	0.50	nil	2.23
Calgon 835	TRS10-410	nil	0.10	10.4
Calgon 835	TRS10-410	nil	0.50	8.9
Calgon 835	TRS10-410	nil	1.0	8.0
Calgon 835	TRS10-410	0.02	1.0	6.9
Calgon 835	TRS10-410	0.5	1.0	2.73
Calgon 835	SLS	nil	0.5	6.25
	SDBS	nil	0.5	4.40
Calgon 800	-	nil	nil	0.65
Calgon 800	TRS10-410	nil	1.0%	12.5

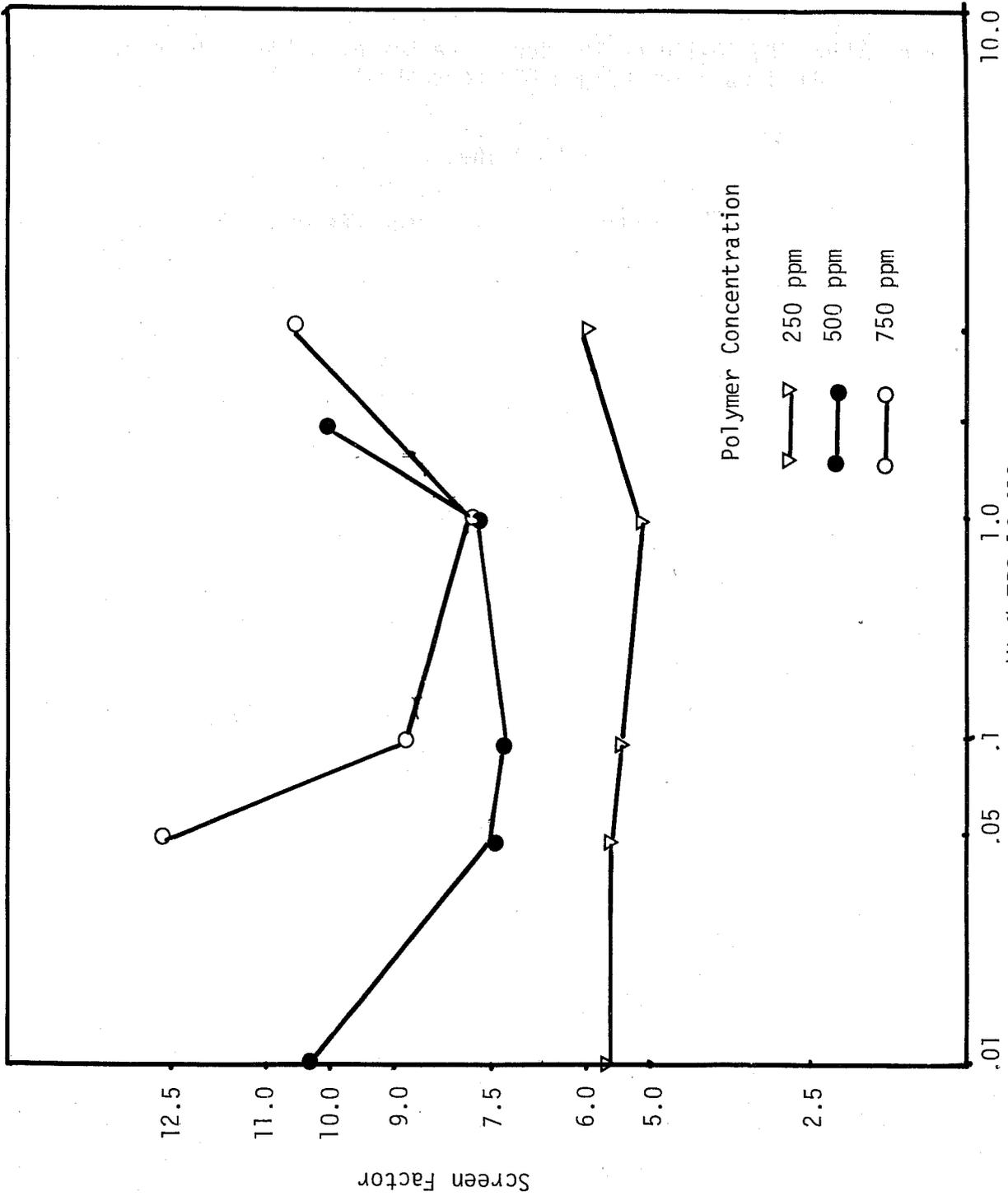


Figure IIB8. Effect of Added TRS 10-410 on The Screen Factor of C-800 in dist. H₂O

Table IIB2

Effect of Added TRS 10-410 on The Screen Factor of Calgon 835 in 0.5%
And 1.0% Brine. Calgon 835 Concentration: 500 ppm

In 1.0% Brine:

Wt. % TRS 10-410	Screen Factor
0.0	7.10
0.1	7.10
0.5	7.10
1.0	7.04

In 0.5% Brine:

Wt. % TRS 10-410	Screen Factor
0.0	7.5
0.05	7.6
0.1	7.8
0.5	8.2
1.0	8.0

3. Determine the Aging Effect of Added TRS 10-410 on the Viscosity and Screen Factor of Calgon 835 and 800 At Various Temperatures (30°C, 45°C, 65°C)

Investigator: Mr. N.N. Desai

In our Semi-Annual Report of June 1978, reported data on the effect of time and temperature of storage on the rheological properties of Calgon polyacrylamides in various brines. In general, the polymer underwent significant changes in the first 10 days or so, but thereafter the changes were minimal. Here, we report our findings of a similar study on a surfactant-polymer system. Calgon 800 and 835 were studied. The concentration of the surfactant was 2.0% wt. and the polymer concentration were 500 ppm. The results are reported in Table IIB3 and IIB4. All samples remained clear and homogeneous over the storage time reported. There was no evidence of precipitation or coacervation. Some general trends in the data are as follows:

The screen factor decreased with storage temperature and time for both Calgon 800 and 835.

The viscosity decreased with time and temperature for Calgon 835.

The viscosity increased with time and temperature for Calgon 800 system.

The first two are similar to observations reported in the 1978 report. The last observation is at present difficult to explain and needs to be further explored.

Table IIB3

Time and Storage Temperature Effect on The Screen Factor and Relative Viscosity of Calgon 800 in 1.0% TRS 10-410

Days	Temperature		
	30°C	45°C	65°C
2	9.26/1.39*	7.26/1.77	5.89/2.57
5	8.41/1.51	5.15/2.23	3.98/2.69
18	7.07/1.78	4.48/2.61	2.82/2.94
27	7.2/1.95	3.15/2.62	2.19/2.97

*Screen Factor/Relative Viscosity

At 0 days: Screen Factor - 9.21, Relative Viscosity - 1.39

Table IIB4

Time and Storage Temperature Effect on The Screen Factor and Relative Viscosity of Calgon 835 in 1.0% TRS 10-410

Days	Temperature of Storage		
	30°C	45°C	65°C
2	13.65/6.60	9.81/4.51	8.35/3.38
5	13.22/6.54	9.52/4.33	7.48/3.29
18	12.53/6.46	9.06/4.29	5.91/3.19
27	10.18/6.39	9.06/4.41	5.41/3.06

*Screen factor/relative viscosity

At 0 days: Screen factor -14.02, rel. vis. -6.71

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C. Interfacial Tension of Surfactant/Polymer Systems

Investigator: Mr. N.N. Desai

A major point of interest in tertiary oil recovery systems is the effect of polymer on the interfacial tension of surfactant formulations. This section presents some data on the interfacial tension effects of polyacrylamides on sodium dodecyl benzene sulfonate and TRS 10-80.

Materials and Methods:

The polymers used were Calgon 800 and 835. SDBS was supplied by the Cities Service Corp. Both dodecane and octane were 99% pure and supplied by the Chemical Samples Co.

Aqueous solutions containing the appropriate concentrations of the surfactant polymer and salt were prepared. In the case of TRS 10-80, 10 ml of n-octane were added to 10 ml of the aqueous solution. In the case of SDBS, 0.15 ml of n-hexanol was added to 10 ml of the aqueous solution and then topped with 10 ml of n-dodecane. The test tubes were then rotated end-over-end for 24 hours, then kept horizontally for 6 hours and centrifuged for 10 minutes. The interfacial tension was measured by the spinning drop tensiometer.

Results

The results are presented in Figure IIC1.

(1) The IFT of all samples containing polymers was lower than that of solution without the polymer. This was true for both Calgon 800 and Calgon 835.

(2) There is a minimum in the IFT. Initially the IFT decreases, but beyond a certain concentration which depends on the polymer but not the surfactant, the interfacial tension increases.

Since surfactant partitioning in the oil and brine phases and the interfacial surfactant concentration are the two major factors determining the interfacial tension, our next step is to study the effect of polymer on the partitioning of the surfactant.

TRS 10-80 System
 TRS 10-80 (Witco)[0.1%]
 n-Octane
 1.0% Wt.
 None

Surfactant
 Oil
 NaCl
 Alcohol

SDBS System
 SDBS (Cities Service Co.)
 [0.1%]
 n-Dodecane
 1.0% Wt.
 1.5 Vol.% n-hexanol

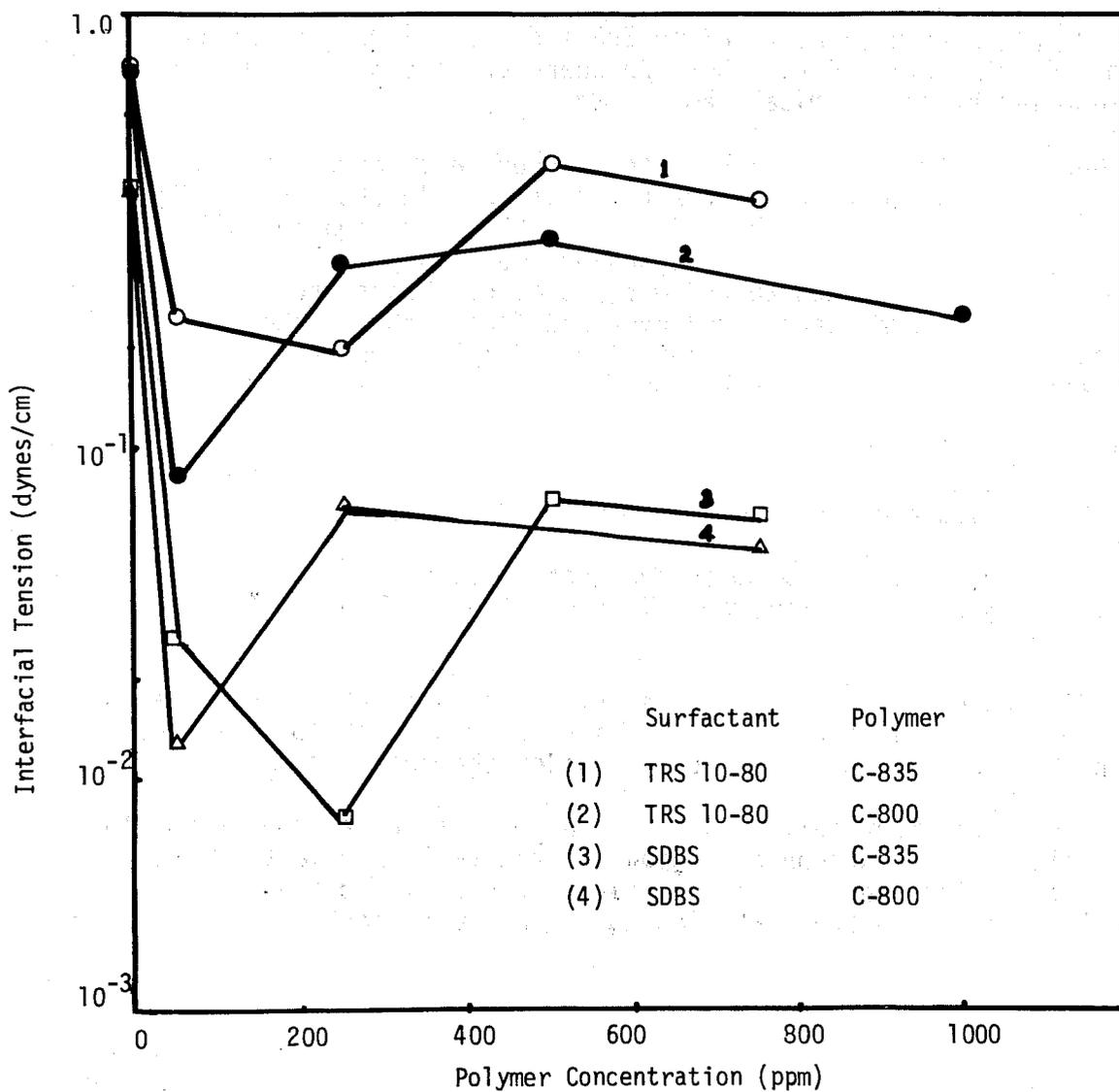


Figure IIC1. Effect of Added Polymer on the Interfacial Tension of SDBS and TRS 10-80 Systems

D. 1. Application of the Optimal Salinity Concept to Mobility Buffer Design-An Unique Graded-Salinity, Graded-Concentration Design

Investigator: Mr. S.I. Chou

In a recent manuscript (Chou and Shah, submitted to SPE) entitled, "The Importance of Salinity of Mobility Buffer Solution in Tertiary Oil Recovery" we have established the concept that the interactions at the micellar-polymer interface controls the oil-displacement efficiency and final oil saturation of tertiary oil recovery. This report describes part of our recent efforts of applying this concept, specifically to reducing the polymer requirement while maintaining adequate mobility control and high oil recovery efficiency.

Since the properties at the surfactant slug-polymer solution interface dominate, the concentration and salinity of the polymer solution can be designed in nearly any way as long as the fluids interface is maintained at or near optimal conditions. The graded-salinity, graded-concentration design of mobility buffer polymer solution design employs two or more banks of polymer solution in which the first bank of polymer solution is at the optimal salinity of the preceding surfactant formulation with succeeding polymer solutions at decreasing salinity and concentration but increasing viscosity. This is possible because the viscosity of polyacrylamide solution decreases with salinity and the decrease of viscosity due to the decrease of polymer concentration can be more than compensated by the decrease of the salinity of polymer solution.

Oil-displacement in sand packs by soluble oil formulations was used to demonstrate the performance of such a design. Some of our previous data are also presented here in order to form a basis of comparison. The results are shown in Table IID1 with the experimental details shown as footnotes. Test 1 is the standard experiment where only optimal salinity polymer solution was used, with which comparisons should be made. Tests 4 and 6 are typical examples of proper graded-salinity, graded-concentration design of polymer solutions where the above stated design criterion was satisfied. A comparison of Tests 1 and 6 shows that, with this design, tertiary oil recovery can be increased from 89% to 95% while the polymer consumption is reduced by nearly 40%. One mechanism for the increase of oil recovery is that the first polymer bank maintains ultra-low interfacial tension at the micellar-polymer interface but only enough viscosity to stably displace the micellar slug while the second polymer bank provides the viscous driving force to displace the oil ganglia left behind the micellar slug.

Conventional graded-concentration design of polymer solutions always results in unfavorable mobility ratios between successive polymer banks. When such unfavorable mobility ratios are employed, such as those shown in Tests 5, 7 and 8, oil recovery immediately drops from 89% (Test 1)

Table IID1 Graded-Salinity, Graded-Concentration Design of Mobility Buffer Polymer Solution for Soluble Oil Flooding^{a,b,c}

Test No.	Polymer Solution Design ^d	Tertiary Oil Recovery	S of	Surfactant Recovery at 1.3 PV
1	1000 ppm, 1.5% NaCl, 1PV	89%	3.2%	67%
2	250 ppm, 0% NaCl, 1PV	76%	6.7%	99%
3	250 ppm, 1.5% NaCl, 1PV	69%	10.2%	NA
4	1000 ppm, 1.5% NaCl, 0.2PV followed by 250 ppm, 0% NaCl, 0.8PV	88%	3.0%	84%
5	1000 ppm, 1.5% NaCl, 0.2PV followed by 0.8PV distilled water	78%	6.5%	NA
6	1000 ppm, 1.5% NaCl, 0.5PV followed by 250 ppm, 0% NaCl, 0.5PV	95%	2.3%	75%
7	1000 ppm, 1.5% NaCl, 0.5PV followed by distilled water 0.5PV	83%	5.0%	NA
8	1000 ppm, 1.5% NaCl, 0.2PV followed by 1.5% NaCl, 0.8PV	71%	8.1%	NA

a soluble oil = 10% TRS 10-410 + 4% IBA in dodecane, 5% PV slug

b connate water: 1.5% NaCl (optimal salinity)

c sand pack: 13" x 1", K ≈ 4.2 Darcy

d ppm refers to concentration of DOW PUSHER 700 in polymer solution

to 78%, 83% or 71% respectively. Although in this report we have only used two banks of polymer solutions, the idea can easily include more banks of polymer solutions where necessary to further improve the oil recovery. While the present surfactant formulation was soluble oil, it is anticipated that oil-displacement by aqueous surfactant formulations will give similar results.

Another advantage of this unique design to polymer solution is that surfactant loss can be reduced. For instance, analysis of the effluent surfactant concentration of Tests 1, 4 and 6 showed that the surfactant recovery at 1.3PV were 67, 84, & 75%, respectively. The reduction of surfactant loss can be attributed to two effects. One is on better mobility control minimizes surfactant dispersion. The second effect is that the dispersed surfactant can be subsequently partitioned or dissolved into the fresh polymer solution, decreasing the interfacial tension between the polymer solution and oil ganglia left behind the micellar slug. If the interfacial tension becomes sufficiently low, these oil ganglia may be mobilized and displaced with the help of the high viscosity of polymer solution. However, oil recovered by means of this low-tension mechanism is small in the present system, as the difference between tests 1 and 6 is only 6% in tertiary oil recovery. The surfactant recovery (@ 1.3PV) for Test 2, where fresh* polymer solution was used, was 99% while the oil recovery was only 76%. Thus it can be inferred that surfactant loss is not a detrimental factor in the present system. Such may not be the case for oil-displacement in Berea cores.

In summary, the graded-salinity, graded concentration design of polymer solution is capable of (1) reducing the polymer requirement, (2) providing higher viscous driving force and adequate mobility control between surfactant slug and successive polymer banks, (3) reducing surfactant loss, (4) producing low IFT at the surfactant slug-polymer solution interface. This design has been shown to be more beneficial than conventional graded-concentration design of polymer drives.

*Salt-free

2. Effect of CaCl_2 on Soluble Oil Flooding

Investigator: Mr. S.I. Chou

Reservoir clays and minerals are deleterious to surfactant-polymer flooding. By incorporating small amounts of clays and gypsum in sand packs, it was shown (Bernard 1975, Holm and Robertson, 1978) that the oil recovery by soluble oil flooding greatly diminishes. It should be noted that fresh polymer solution (polyacrylamide) was used in their studies. On the other hand, our results indicate that NaCl in connate water has negligibly small effects on oil recovery when the polymer solution is at the optimal salinity of the preceding surfactant formulation. However, the effect of calcium ions had not been determined in our system. Fresh polymer solution was also employed in this study; the results are shown in Table IID2.

As the connate water was changed from 1.5% NaCl (optimal salinity) to 3% NaCl + 1% CaCl_2 , and the polymer solution was at the optimal salinity, tertiary oil recovery decreased relatively little from 89% to 78%. However for fresh polymer solution, the same change of connate water composition caused a decrease of tertiary oil recovery from 76% to 49%. Therefore, for the system we have studied, the effect of CaCl_2 on soluble oil flooding is considerably less for polymer solution at the optimal salinity than for fresh polymer solution. Thus it may be that the drastic effect of calcium ions on oil recovery observed in literature is the consequence of fresh polymer solution being used.

In addition, we have observed without exception that the pressure drop was excessively high when fresh polymer solution was used. For example, in Test 6, a total apparent viscosity of nearly 1200 cp in porous media was developed during injection while it was always below 40 cp when polymer solution of optimal salinity was used.

Finally, the difference between fresh and optimal salinity polymer solution in oil recovery in Berea cores using hexadecane was studied using a soluble oil formulation.

The results are shown in Table IID3. Polymer solution of optimal salinity is superior to fresh polymer solution for oil-displacement in Berea cores, although the differences between them are smaller in this case compared to the sand pack results. Apparently, mobility control was not adequate when the viscosity of polymer solution (1000 ppm PUSHER 700 in 2.1% NaCl) was 6.6 cp. By increasing the viscosity from 6.6 cp to 15 cp by doubling the polymer concentration (Test 5), tertiary oil recovery increased from 75% to 82% for optimal salinity connate water. While it is possible that a comparable increase of oil recovery will be found for other connate water salinities by increasing the viscosity of polymer solution, Tests 1 through 4 reveal that connate water compositions are more important for oil recovery in Berea cores than in sand packs (see, for example, Table IID2). It is likely that preflush will be necessary to condition the porous media.

Table IID2 The Effect of CaCl_2 on Soluble Oil Flooding

<u>Test</u>	<u>Connate Water</u>	<u>Polymer Solution</u>	<u>Tertiary Oil Recovery^b</u>
1	1.5% NaCl	1000 ppm PUSHER 700	89%
2	3% NaCl + 0.5% CaCl_2	in 1.5% NaCl ($\mu=6.8\text{cp}$)	81%
3	3% NaCl + 1% CaCl_2		78%
4	1.5% NaCl	250 ppm PUSHER 700	76%
5	3% NaCl + 0.5% CaCl_2	in H_2O ($\mu = 31 \text{ cp}$)	57%
6	3% NaCl + 1% CaCl_2		49%

- a soluble oil = 10% TRS 10-410 + 4% IBA in dodecane, 5% PV slug
sand packs = 13" x 1", K = 4.2 Darcy
linear displacement velocity - 2.78 ft/day
- b oil recovery is complete within 1.2 PV total injection

Table IID3 Soluble Oil Flooding in Berea Cores^a

<u>Test</u>	<u>Connate Water</u>	<u>Polymer Solution</u>	<u>Tertiary Oil Recovery</u>	<u>Surfactant Recovery @ 1.3PV</u>
1	2.1% NaCl		75%	12%
2	5% NaCl	1000 ppm in 2.1% NaCl, $\mu = 6.6$ cp	63%	NA
3	10% NaCl		58%	3.2%
4	3% NaCl + 1% CaCl ₂		78% ^C	NA
5	2.1% NaCl	2000 ppm in 2.1% NaCl, $\mu = 15$ cp	82%	14%
6	2.1% NaCl	2000 ppm in 2.1% NaCl, 0.4PV followed by	90%	48%
7	2.1% NaCl	500 ppm in H ₂ O, 0.8PV	95%	40%
8	3% NaCl + 1% CaCl ₂		88%	48%
9	3% NaCl + 1% CaCl ₂		89%	20%
10	2.1% NaCl	500 ppm in H ₂ O	68%	44%
11	10% NaCl	$\mu = 57$ cp	50%	40%

a soluble oil = 10% TRS 10-410 + 4% IBA in hexadecane, 5% PV slug, optimal salinity = 2.1% NaCl

Berea cores = 12" x 1" x 1", permeability = 200 to 400 mD

linear displacement velocity = 3.1 ft/day

b ppm refers to concentration of PUSHER 700 in polymer solution

c 10% PV soluble oil slug

Table IID3 also shows that surfactant loss is quite significant for oil displacement in Berea cores. In Tests 1, 3 and 5 where optimal salinity polymer solution was used, cumulative surfactant recovery at 1.3PV effluent was less than 15%. When fresh polymer solution was used as in Tests 8 and 9, surfactant recovery was considerably higher (44% and 40%). This effect together with the higher viscosity of fresh polymer solution can explain the smaller differences in oil recovery between the two types of polymer solution in Berea cores as compared to sand pack results. However, these two advantages are not sufficient to overcome the unfavorable interfacial effects inherent to fresh polymer solutions in the present study.

The graded-salinity, graded-concentration design of polymer solution of Section IID1 has been applied here to Berea cores. Its superiority over either fresh or optimal salinity polymer solutions is even more significant than in sand packs. Tests 6 and 7 (identical experiments) illustrate such a design. The first bank polymer solution was maintained at the optimal salinity of the surfactant formulation thus capable of producing ultra-low interfacial tension at the slug-polymer solution interface. Its viscosity is also high enough to provide adequate mobility control. The second bank polymer solution with a higher viscosity and lower salinity (0% NaCl in this case) was capable of displacing the first polymer bank, and reducing surfactant loss by dissolving the dispersed surfactant. As a result, maximal oil recovery of 90% or 95% were obtained (See Table IID3). Furthermore, with this design, the effect of connate water salinity was nearly negligible. In Tests 8 and 9 (identical experiments), the connate water salinity was 3% NaCl + 1% CaCl₂, while the tertiary oil recovery were 88% or 89% respectively. As before, surfactant recovery in these two cases was comparable to those using fresh polymer solution.

3. Constant Salinity Design vs Contrast Salinity Design in Soluble Oil Flooding

For aqueous micellar-polymer flooding, some investigators (Paul and Froning, 1973; Gupta and Trushenski, 1978) have shown that a contrast salinity design of the preflush-micellar-polymer system may produce better oil recovery than that obtained from a constant salinity design. Their design basis is such that salinity profile should pass through the optimal salinity upon mixing of the injected fluids in porous media. We have shown that the salinity of polymer solution (adjacent to the surfactant slug) should be designed at or near the optimal salinity of the preceding surfactant formulation irrespective of connate water (or preflush water) salinities. The purpose of this study is to examine constant and contrast salinity designs in soluble oil flooding. It may also discern the fundamental differences between aqueous formulation and soluble oil in tertiary oil recovery. The results are shown in Table IID4.

Tests 1 and 2 are the so-called contrast salinity design where the average of connate water and polymer solution salinity is equal to the optimal salinity of surfactant formulation (1.5% NaCl). The other tests are from our previous studies which represent either constant connate water salinity or constant polymer solution salinity or both to form a basis of comparison. The data show that contrast salinity design of connate water-polymer solution gives **worse** oil recovery efficiency for soluble oil flooding. This result, in fact, is not surprising, since for good oil recovery we have found that slug integrity and adequate mobility control should be maintained, avoiding such mixing of connate water and polymer solution. Furthermore, before the salinity profile can actually pass through the optimal salinity in porous media, nearly 40% of the residual oil may have already been bypassed by the surfactant slug in a contrast salinity design process. Thus soluble oil tertiary oil recovery for contrast salinity design process (62% or 45%) was at a much lower than the 89% recovery obtained under optimal conditions (Test 3). It appears that for oil recovery by aqueous formulations, optimal salinity profile can exist in-situ simply by local mixing near the preflush-micellar or connate-micellar and micellar-polymer solution interfaces in a contrast salinity design process. Even so, the micellar-polymer interface was found to be predominantly more important (as compared to the connate water-micellar interface) according to Gupta and Trushenski (1978). This is, in fact, consistent with the above conclusions.

Table IID4 Constant Stability Design vs Contrast Salinity Design in Soluble Oil Flooding

<u>Test No.</u>	<u>Connate Water</u>	<u>Polymer Solution</u>	<u>Tertiary Oil Recovery</u>
1	0% NaCl	3% NaCl	45%
2	3% NaCl	0% NaCl	62%
3	1.5% NaCl	1.5% NaCl	89%
4	0% NaCl	1.5% NaCl	80%
5	3% NaCl	1.5% NaCl	80%
6	1.5% NaCl	0% NaCl	76%
7	1.5% NaCl	3% NaCl	58%

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III. THERMODYNAMIC PROPERTIES

Research Director: J.P. O'Connell

A. Theory General expressions will be adjusted to agree with data on solutions of spherical gases and chain molecules. Formulations will be established to make theory and data agree for chain length effects on all infinite dilution properties of surfactant over wide temperature ranges.

Investigator: Mr. R.J. Brugman

In the Semi-Annual Report of June, 1978, we presented equations for calculating the thermodynamic properties of gas solubilities of spherical gases in water using scaled particle theory as extended by Stillinger as a basis. At that time, agreement with data was good, but not enough to give us complete confidence about the quantitative form of the expressions.

Since that time, several developments have occurred which have temporarily set back our program, though we are now thoroughly convinced our revised methodology is sound. A question about our basic concept arose at the Gordon Conference on water and aqueous solutions after a presentation by J.P. O'Connell. While we asserted that micellization was entropy-driven by the excluded volume effect of the surfactant tail on the water, and this is essential to the thermodynamic process that our calculations follow, data indicate that at higher temperatures, micelle formation becomes an energy-driven process. An examination of our calculations for cavity formation in water confirm that this should be expected. The very large heat capacity change associated with cavity formation means that as temperature increases, the entropy effect of cavities decreases and the enthalpy effect increases dramatically. All other steps in our complete process for micellization are significantly less sensitive to temperature, demonstrating that it is still the excluded volume effect on the water which drives the process and must be accounted for in any basic theory.

These variations indicate that major changes occur in the water structure around a nonpolar solute as the temperature increases. Our modeling indicates that this seems to affect the contribution of curvature effects more than the planar surface tension or volume but this is still uncertain. None of this is inconsistent with the concept of a special cage of water molecules around a solute, nor with a structure which is fundamentally the same as at a water surface, if indeed, they are different. It is still unclear whether this distinction can be detected by our method.

One result of working with the solubility of the noble gases, methane, CF₄, SF₆ and neopentane for several months is to confirm the picture of Hildebrand that the nature of water-solute interactions is different for noble gases, fluorine compounds and hydrocarbons. We find that it cannot be accounted for in any way other than water structural rearrangements affecting the effective interfacial tension because we believe the fundamental relations

for all other effects correctly model the molecular interactions. While we had been skeptical that this was the case, it is the only explanation for the major discrepancies we find.

We have also made a major change in our quantitative expressions. Previously, we used the scaled-particle concept that the microscopic contact correlation function (related to the density of molecular centers about a cavity) could be accurately calculated from zero size up to the point where the cavity was just touched by three water molecular centers. Then a polynomial in inverse cavity size was assumed in the function up to macroscopic size. The fundamental assumption is that such a polynomial exists; this may not be the case. For example, the Gibbs-Tolman-Koenig equation (Koenig, 1950) cannot give the maximum in the contact correlation function without a singularity in the curvature dependence. Clearly, some functional relation must exist to take this function from microscopic to macroscopic scales, but it is uncertain whether the assumed polynomial form is correct.

To avoid this difficulty, we have shifted our method from the microscopic basis for all gases to a macroscopic basis to calculate the difference between a given solute and a reference solute. Thus, using Argon as the reference, we are determining the parameters for the Henry's constant of a spherical gas

$$\ln \left[H_k / H_{Ar} \right] = 4\pi\rho \int_{R_{Ar}}^{R_k} \mathcal{G}(R) R^2 dR + \left[\frac{G_k}{R_g T} - \frac{G_{Ar}}{R_g T} \right]_{\text{interaction}} + \left[\frac{G_k}{R_g T} - \frac{G_{Ar}}{R_g T} \right]_{\text{interface}}$$

The form of $\mathcal{G}(R)$ is

$$\mathcal{G}(R) = \frac{2\gamma_w^\infty \left[1 - \frac{\delta^\infty}{R} \right]}{R_g T R}$$

where, for the present, we have assumed γ_w^∞ is the pure-water surfactant tension and δ^∞ is fitted to temperature as $\delta^\infty = a + bT$. The form for $\mathcal{G}_{\text{interaction}}$ is the same as before, while that for $\mathcal{G}_{\text{interface}}$ is still uncertain. In general, these terms are weak functions of temperature and only the cavity heat capacities are quite large. Thus over the temperature range the enthalpy and entropy values change significantly, though their sum does not. This is consistent with our conjecture above about the temperature dependence of micelle formation. The term in the above correlation which causes this δ^∞ . At present, we are completing the correlation for the interfacial term and checking other minor aspects of the model.

Although the spherical terms are not completely determined, the variation of the various G quantities with nonspherical shape and chain conformation have been established in order to describe chain molecules. First the functional form and the integral over \mathcal{U} were modified to treat nonspherical shapes which are characterized by the Volume, V , Area, A and mean curvature J . Since we ignore volume effects, our form then becomes

$$G_{\text{cavity},k} - G_{\text{cavity},Ar} = \int_{Ar}^k \gamma_w^\infty (dA - \gamma_w^\infty \delta_w^\infty d(AJ)) = \gamma_w^\infty (A_k - A_{Ar}) \\ - \gamma_w^\infty \delta_w^\infty \left[\Sigma(AJ)_k - 2A_{Ar}/R_{Ar} \right]$$

where the summation for the nonspherical shape involves the product of area and mean curvature for all portions of the molecule. For a spherocylinder of radius R and length L (as used for ethane, etc.), $\Sigma AJ = \pi R + 2\pi L$ and $A = 4\pi R^2 + 2\pi RL$. Second, the interaction terms were modified to take into account cylindrical cavities. We assume the pair distribution function has the same form in a direction normal from the cylinder as from a sphere. Then,

$$G_{\text{interaction}} = \rho N \int_0^{L/2} \int_0^\infty \int_0^\pi \int_0^\pi d\phi \sin \theta d\theta r^2 \phi'(r) g(r, x, \theta) dx$$

where the potential is distributed along the axis of the cylindrical part of the spherocylinder, as

$$\phi(r) = \frac{\phi_{ws}(r)}{\frac{4\pi R^3}{3} + \pi R^2 L} \left\{ \left[\delta(X) + \delta(L-X) \right] \frac{2\pi R^3}{3} + \pi R^2 L \right\}$$

$$\text{and } g(r, x, \theta) = g_{ws}^{hs}(\tilde{r}')$$

with $\delta(X)$ being the Dirac delta function and \tilde{r}' being the (reduced) distance along the normal from the cavity to the point at r . The functions g_{ws}^{hs}

and $\phi_{ws}(\tilde{r})_{\rho}$ is the same as reported previously. The above relation assumes that the polarizability is distributed evenly throughout the volume of the molecules.

Because normal paraffins have internal rotation and vibrational degrees of freedom which are affected by the surrounding fluid, there are more contributions to the thermodynamic properties of solution, particularly from the ideal gas to aqueous solution (there will also be such effects upon micellization). The best way to account quantitatively for these is the Donohue-Prausnitz modification of the theory of Prigogine which is called the perturbed hard-chain theory (1978). We assume only the free volume effect on the molecule which gives an entropy change

$$\frac{\Delta S}{R} \text{ conformation} = (C-1) \left[\frac{3\tilde{\rho}^2 - 4\tilde{\rho}}{(1 - \tilde{\rho})^2} \right]$$

where $\tilde{\rho} = .7405 \rho v^* = 0.0905 \rho_w$ with ρ_w in mole/ml

and C is a parameter for each normal paraffin which has been obtained previously (Gmehling, et al., 1979).

While we have not yet reached the above milestone, we are close. Our investigation of the chain length effects in paraffin solubility and associated thermodynamic functions and in surfactants as reported by Desnoyers (1978) show the same quantitative behavior. While the properties of micellization are not precisely the same, our other effects of surfactant compression, on adsorption and conformational changes should account for the differences.

- B. Experiment The isotropic-anisotropic transition of the potassium oleate liquid crystal will be delineated as function of temperature and pressure up to 700 bar. Time dependence and hysteresis in the behavior will be delineated. Methane gas will be introduced into the cell.

Investigator: Mr. R.J. Brugman and Mr. Paul Coram

We have found the atmospheric transition from anisotropic to isotropic fluid covers a two-phase region of approximately 20°C starting at approximately 52°C. This is apparent not significantly affected by pressures up to 700 bar although it is possible that the transition is increased slightly with elevated pressure. Hysteresis does not seem a major problem with either increasing or decreasing temperature.

On an overall basis, 0.57 mole % of methane has been added to the cell. While temperature control problems make our conclusions tentative, we believe there is some increase in the transition temperature upon methane addition. Another sample is to be prepared and examined under more carefully controlled conditions.

C. Phase Behavior of Concentrated Surfactant Solutions

Investigators: Miss Charlotte Chen and Mr. Scott Singlevich

We have spent a little effort attempting to discern some of the features of the disappearance of the upper phase as a function of salt concentration by varying temperature in high salinity solutions. One interesting result is that as either a two-phase (water-external) or three phase solution is heated, oil is immediately ejected from the surfactant-rich phase. Even at 4% salinity of a 8% TRS 10-410, isobutanol, hexadecane system, three phases are immediately formed at temperatures as low as 50°C (and perhaps lower). When such solutions are cooled back to room temperature, the three phases remain. In fact, mechanical agitation and even sonication will not reform the original two-phase system. We speculate that the initial structures formed when brine is poured into the oil-surfactant mixture are nonequilibrium, perhaps with liquid crystals present, but increased temperature promotes formation of the equilibrium structure. We plan to study the influence of temperature cycling in the region near optimal salinity.

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IV. ROCK/FLUID INTERACTIONS

Research Director: Professor Robert D. Walker, Jr.

A. Surfactant/Polymer Precipitation

1. Surfactant Salting-Out: Extend measurements of influence of NaCl concentration and oil on salting-out of surfactants, and on the distribution between oil and aqueous phases.

Investigators: Dr. G. Rama Rao and Mr. J. Funk

It was shown in the previous Quarterly Progress Report that sodium dodecylbenzene sulfonate (SDBS = Cities Service SUL-FON-ATE AA10) was quite resistant to salting-out, and that it tended to remain in the aqueous phase when the solution was equilibrated with n-octane. In contrast, 8-phenyl hexadecyl sodium sulfonate (UT-1) was reported to salt-out very readily and to partition into n-octane in substantial amounts. These phenomena have been explored in greater depth for UT-1 and the earlier results generally confirmed. Similar experiments with SDBS were initiated but not completed owing to the academic problems of the student involved (no longer with the program).

Surfactant Salting-Out By Indifferent Electrolytes

Surfactant salting-out by the addition of so-called indifferent electrolytes such as NaCl has proved to be a problem in evaluating surfactant losses by adsorption for most of the alkylbenzene sulfonates with a hydrocarbon chain with more than 12 carbons. Qualitative and semi-quantitative results have been reported in earlier reports. In the following paragraphs we describe several quantitative experiments and discuss the results and some of their implications for micellar/polymer flooding.

Materials and Methods:

All of these studies were carried out with 8-phenyl hexadecyl sodium sulfonate (UT-1), which was used as received from the University of Texas at Austin. The desired amount of surfactant was weighed out and dissolved in water which had been distilled in an all-glass still after having been deionized previously. The required volume of surfactant stock solution was transferred to Pyrex screw-capped test tubes, and NaCl (ACS Reagent Grade) was either added to the surfactant solution as the dry salt or as a concentrated solution in water. If necessary, water was added to make the final desired volume, the mouth of each tube was covered with Saran Wrap, and the cap affixed. The tubes were mounted in an air bath maintained at 25°C and rotated for three days at one rpm. The tubes were removed and centrifuged to settle the salted-out surfactant, and a sample of the clear supernatant liquid was withdrawn for analysis. The concentration of surfactant in the equilibrium aqueous phase was determined by the two-phase double-dye method (dimidium bromide and disulfine blue) described by Reid et al. (1967).

Two series of salting-out experiments were run. In the first of these, the surfactant concentration was varied while the salt concentration was held constant at one wt.%. In the second series, the surfactant concentration was kept constant at 0.05 or 0.1 wt.%, and the salt concentration was varied.

Results and Discussion:

The results of the salting-out experiments in which the surfactant concentration was varied are shown in Figure IVA1, where the equilibrium surfactant concentration in the aqueous phase is shown on the ordinate and the initial surfactant concentration is shown on the abscissa. All of the points lie below the dotted diagonal indicating that salting-out of surfactant occurred at all surfactant concentrations studied (from 0.001 to 0.1 wt.%). This is not particularly surprising since UT-1 is not very soluble in water (about 0.15 wt.% at 25-30°C). However, the shape of the curve is interesting in that it indicates that the fraction of surfactant salted-out by one wt.% NaCl varies rather sharply in the surfactant concentration range of 0.02 to 0.05 wt.%. Also shown on Figure IVA1 for comparison is the aqueous-phase surfactant concentration in equilibrium with n-dodecane (W/O = 2/1) for the same initial surfactant concentration range. These data will be discussed more fully in a later paragraph in connection with another figure but we may note that no salting-out was observed in the presence of oil and that the surfactant partitioned into the oil at all surfactant concentrations when the NaCl concentration of the aqueous phase was one wt.%.

Returning to the salting-out of $\text{8}\phi\text{C}_{16}\text{SO}_3\text{Na}$ (UT-1) when no oil was present, the fraction of surfactant salted-out was calculated from a material balance and these data are plotted on Figure IVA2 as a function of the initial surfactant concentration in the aqueous phase. Although there is considerable scatter of the points at low surfactant concentrations, it appears that about one-third of the surfactant is salted-out by one wt.% NaCl at surfactant concentrations as small as 0.001 wt.%. When the surfactant concentration exceeds 0.01 wt.% the fraction salted-out increases to about one-half and then, rather surprisingly, begins to decline at about 0.05 wt.%. Considering the apparent sharpness of the down-turn of the fraction salted-out at the highest surfactant concentration tested, it may be found that little or no salting-out will be observed in one wt.% NaCl if the surfactant concentration is near saturation. It also seems clear that the increased sodium ion concentration deriving from the NaCl is depressing the ionization of the surfactant as well as decreasing the CMC. These effects will become more apparent as we examine the partition of surfactant between oil and NaCl solutions.

These observations of salting-out of UT-1 by one wt.% NaCl (and similar behavior which has been noted for desalted, deoiled SPBS and for Aerosol-OT) have clear implications for adsorption measurements. However, because of the inhibition of salting-out by oil and the promotion of surfactant partitioning to oil by NaCl, it seems appropriate to postpone discussion of the implications for surfactant adsorption until the influence of oil has been discussed.

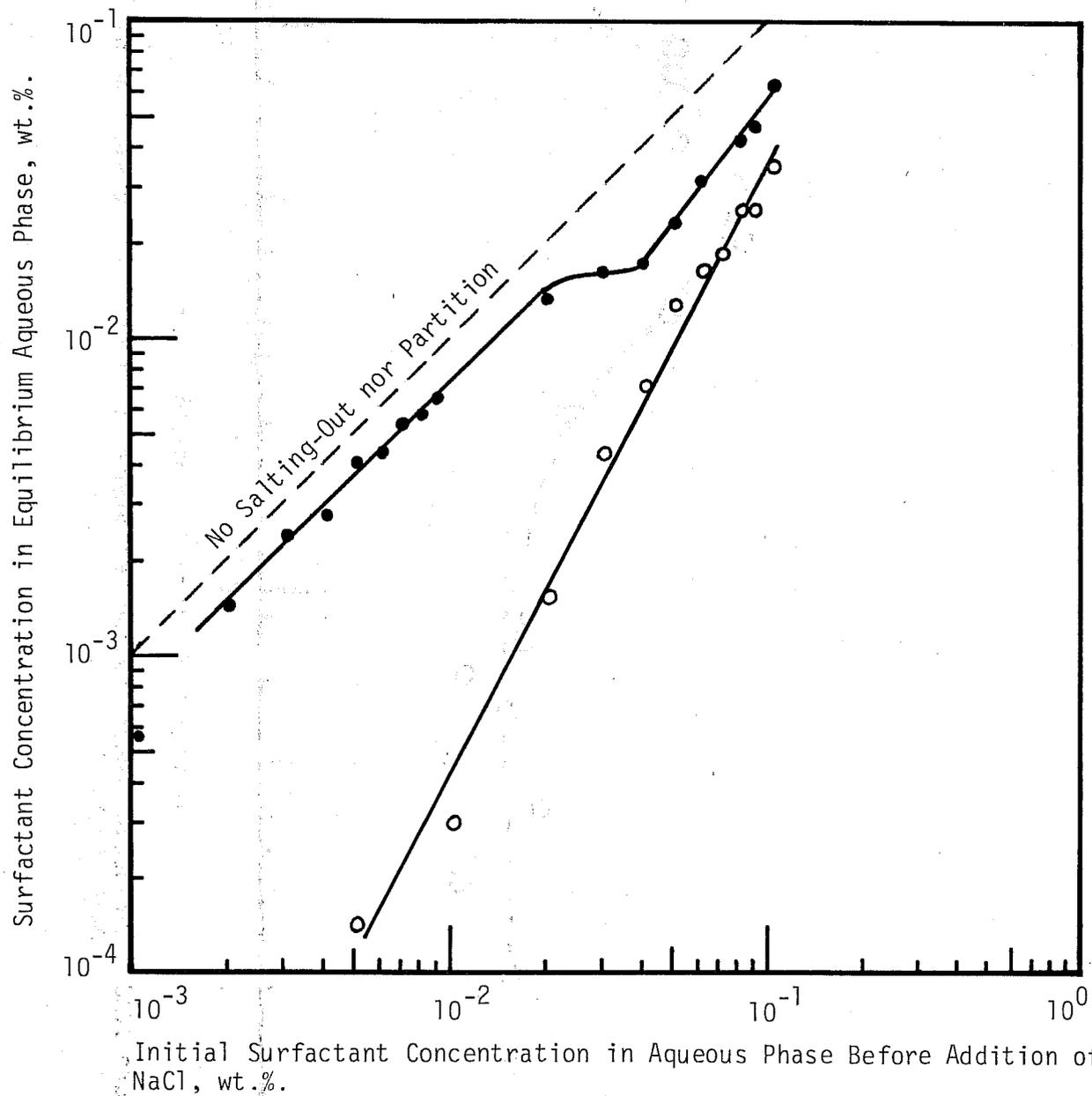


Figure IVA1. Surfactant Concentration Influence on Salting-Out.

● = 8-φC₁₆SO₃Na (UT-1) in 1 wt.% NaCl;

○ = 8-φC₁₆SO₃Na (UT-1) in 1 wt.% NaCl and 95% n-dodecane (W/O = 2/1) - partition into oil, no salting-out.

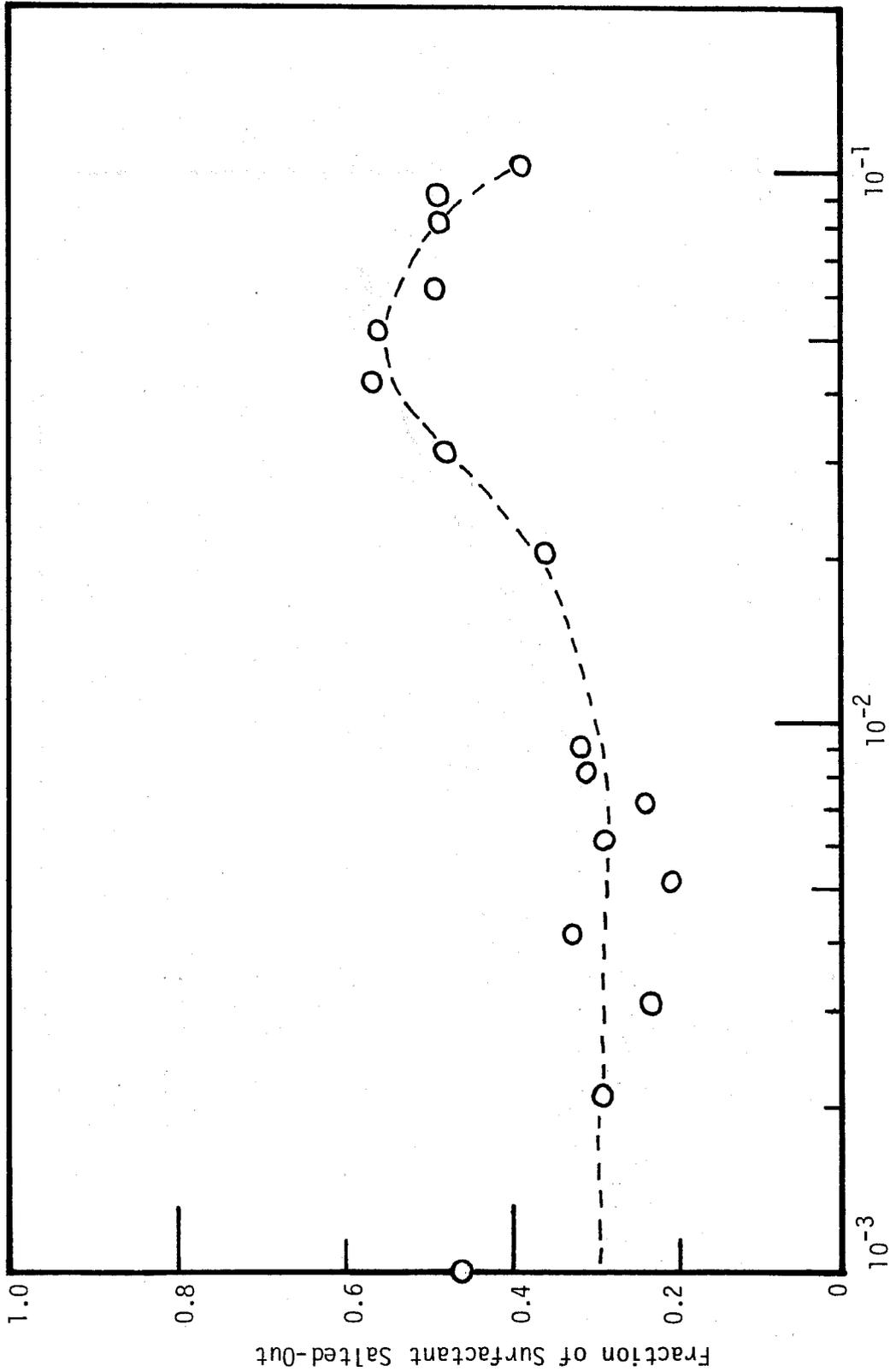


Figure IVA2. Surfactant Concentration Dependence of Salting-Out By NaCl (no oil).
 $8-\phi C_{16}SO_3Na(UT-1)$ in 1 wt. % NaCl

In the second series of salting-out experiments, the surfactant concentration was held constant (either 0.05 or 0.1 wt.%) and the NaCl concentration varied. The surfactant was UT-1. These results are summarized graphically in Figure IVA3, where the fraction of surfactant salted-out is shown as a function of the NaCl concentration. [It should be noted that the data points plotted at a NaCl concentration of 10^{-3} wt.% are really for distilled water and are so marked.] The data in this figure indicate that the fraction of surfactant salted-out increases slowly but steadily as the NaCl concentration increases. At a salt concentration of one wt.% roughly one-third of the surfactant was salted-out. When the NaCl concentration exceeded one wt.%, the fraction of surfactant salted-out increased sharply, becoming essentially complete when the NaCl concentration reached 5 wt.%.

Inhibition of Surfactant Salting-Out and Partitioning To Oil

There is fairly general agreement among the investigators that oil inhibits surfactant salting-out, at least for dilute surfactant solutions and for moderate salt concentrations. For adsorption measurements, however, it is necessary to assure that salting-out of surfactant is prevented and to know the surfactant concentration in the equilibrium aqueous phase since it is known that the addition of salt promotes partitioning of the surfactant into the oil phase. We, therefore, undertook to make these measurements.

Materials and Methods:

The surfactant, $8-\phi C_{16}SO_3Na$ (UT-1), water, and salt have been described earlier in this section. The oils used in these experiments were n-octane and n-dodecane (95% & 99% pure, Chemical Samples Co.). The procedure was also basically the same as that which has been described earlier except that oil was added after the surfactant-NaCl solution was prepared, and the oil was separated from the aqueous phase for analysis after equilibration and centrifugation. The volume of oil added was chosen to make the water/oil ratio either 2/1 or 1/1.

In a considerable number of the tests a stable macroemulsion was formed, and it posed several problems. In the first place, it was difficult though still possible to isolate clear, single-phase samples of the aqueous and oil phases for analysis. Secondly, it has not yet been possible to get precise estimates of the phase volumes. With care, however, it was possible in most cases to achieve adequate phase-separation and measurement of surfactant concentrations.

Results and Discussion:

The distribution of $8-\phi C_{16}SO_3Na$ (UT-1), between water and n-dodecane (95% and 99%) in the water/oil ratio of 2/1 is shown in Figure IVA4. The equilibrium concentration in the oil phase is plotted on the ordinate and the equilibrium concentration in the aqueous phase is plotted on the abscissa. Two aqueous solutions were tested: distilled water and one wt.% NaCl. The initial surfactant concentration in the aqueous phase ranged from 0.001 to 0.1 wt.%. The data in Figure IVA4 indicate that, while the distribution of surfactant between the water and oil phases is quite dependent on the surfactant concen-

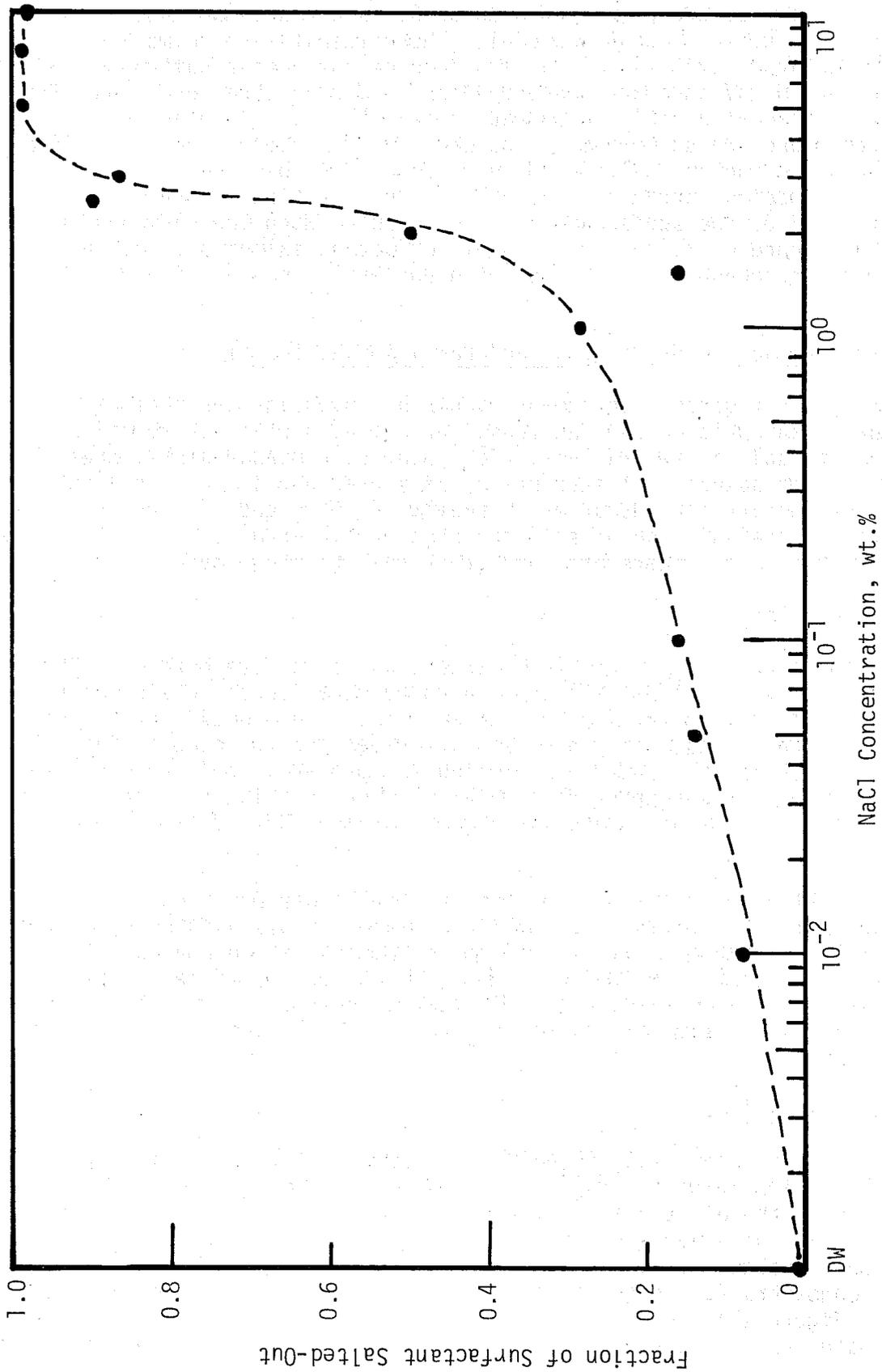


Figure IVA3. NaCl Concentration Dependence of Surfactant Salting-Out (no oil). $8-\phi C_{16}SO_3Na$ (UT-1) in Aqueous NaCl Solutions.

tration, the most striking effect is that due to the oil and salt. No salting-out was observed in any of these mixtures, so it is clear that salting-out was totally inhibited by the oil and that the surfactant distribution which was found was due to partitioning into the oil. Moreover, the effect of salt on the partitioning is pronounced: if the aqueous phase contains no salt, the surfactant tends to prefer the aqueous phase, whereas when the salt content of the aqueous phase is one wt.% NaCl, the surfactant tends to prefer very strongly to partition into the oil phase.

Partition coefficients, expressed as the ratio of the equilibrium oil-phase surfactant concentration to the equilibrium aqueous-phase concentration, were calculated from the data in Figure IVA4. These partition coefficients are plotted in Figure IVA5 as a function of the initial aqueous-phase concentration. The partition coefficient is seen from this figure to be strongly dependent on the surfactant concentration for both distilled water and one wt.% NaCl as the aqueous solvent. The higher the surfactant concentration the smaller the value of the partition coefficient; in both aqueous systems the partition coefficient decreases by an order of magnitude or more as the surfactant concentration increases from 0.01 to 0.1 wt.%.

The most significant difference between the behavior in distilled water and one wt.% NaCl is that the partition coefficients have a value less than unity for all surfactant concentrations when the aqueous solvent is distilled water while for one wt.% NaCl all of the partition coefficients have values well above unity. It is clear that variations in either surfactant concentration or salt concentration can lead to a system with a partition coefficient of unity. It may reasonably be expected that variation of the surfactant structure and that of the oil could also have a strong influence on the numerical value of the partition coefficient.

A second set of experiments with oil added was carried out with the surfactant concentration held constant while the salt concentration was varied. The oil used here was n-octane (99%) rather than n-dodecane, and the water/oil ratio was 1/1 rather than 2/1 as in the previous set; in other respects the experiments were identical. The results are shown in Figure IVA6, where the equilibrium surfactant concentration in either the oil or aqueous phase (expressed as a fraction of the initial aqueous phase concentration) is plotted as a function of the NaCl concentration.

The fraction of surfactant partitioning to the oil phase was essentially negligible until the salt concentration reached 0.1 wt.%. At a salt concentration in the general vicinity of 0.5 wt.% the partition coefficient passed through a value of unity and at salt concentration of one wt.% or higher the surfactant partitioned almost completely into the oil.

Closer examination of the fractions UT-1 in the equilibrium bulk phases reveals that a very substantial fraction of the surfactant is neither in the bulk oil nor the bulk aqueous phase. Since there was a stable macroemulsion layer but no precipitate, it is clear that this surfactant was in the emulsion. The fraction of the surfactant in the emulsion was calculated by a material balance and it is also plotted in Figure IVA6; it constitutes a surprisingly large fraction of the surfactant at salt concentrations less than about one wt.%. The surfactant fraction in the macroemulsion reaches a maximum at a salt concentration of about 0.1 wt.%. At this salt concentration substantially all of the surfactant is in the emulsion, but the

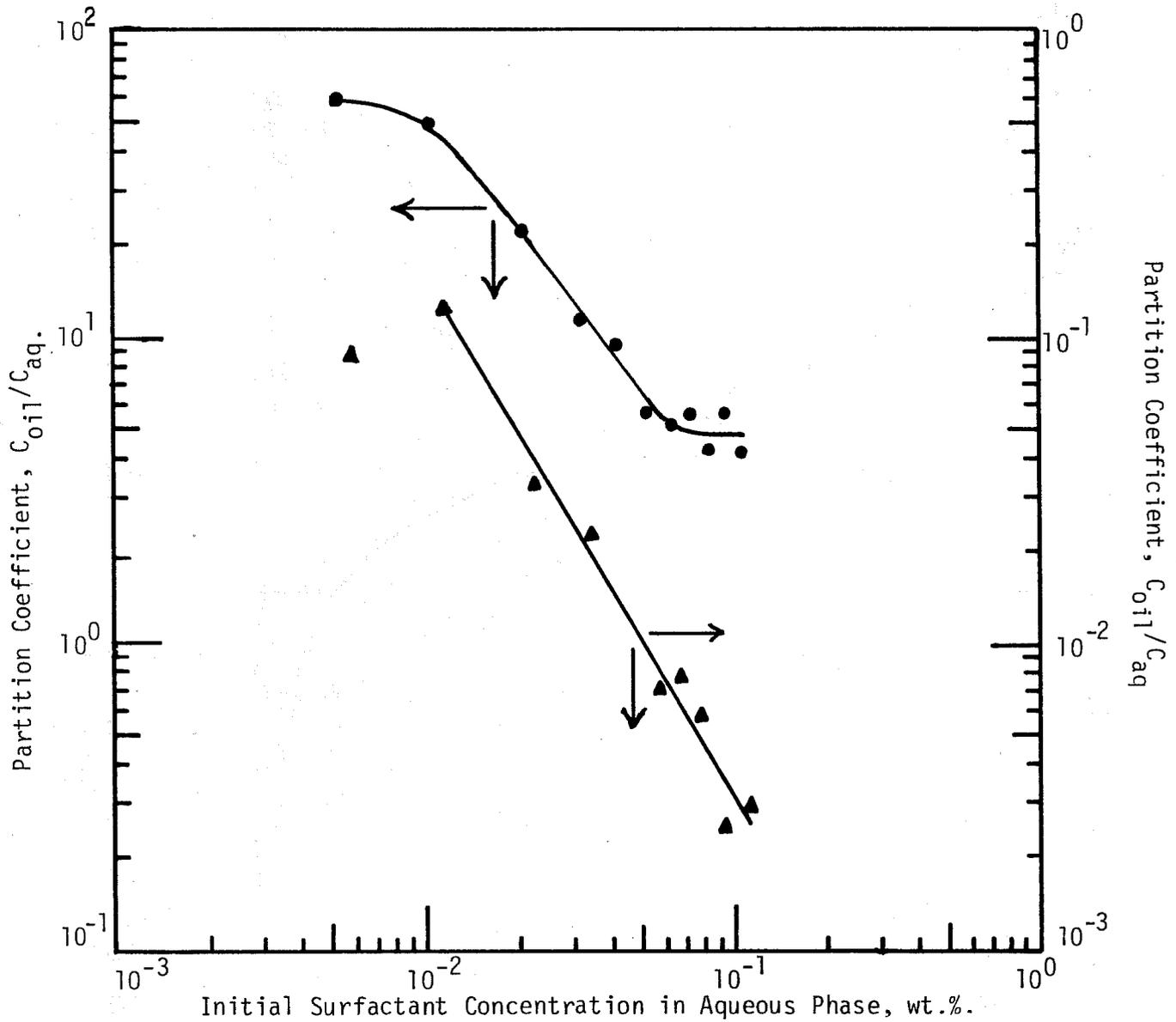


Figure IVA5. Surfactant Concentration Dependence of O/W Partition Coefficient.
 Surfactant = $8-\phi C_{16}SO_3Na(UT-1)$; oil = n-dodecane (99%).
 ▲ = distilled water; ● = 1 wt.% NaCl.

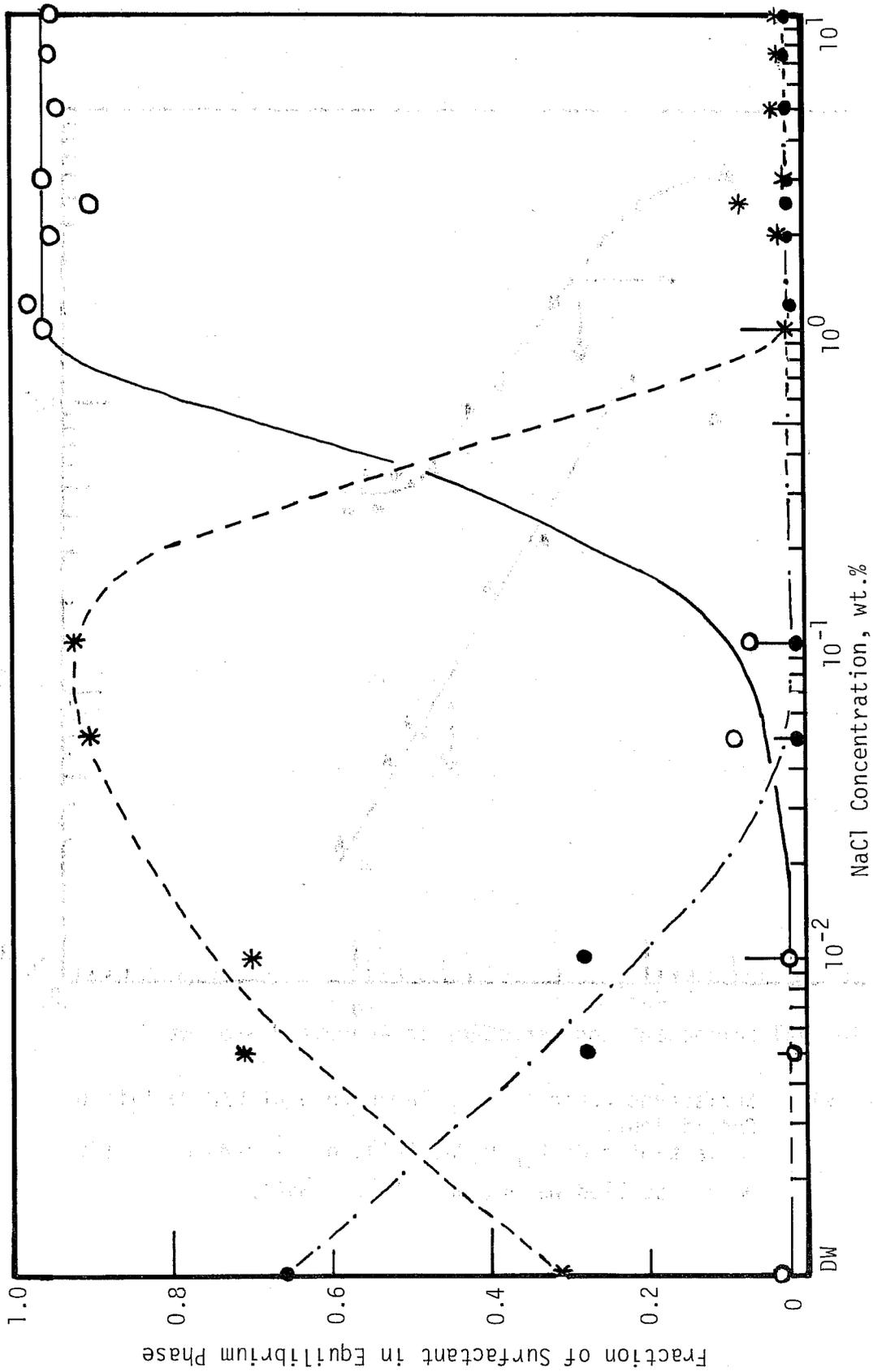


Figure IVA6. Influence of Salt Concentration on Surfactant Distribution Between Oil and Water.
 Surfactant = 8-φC₁₆SO₃Na(UT-1); oil = n-octane (99%).
 o = oil phase; ● = aqueous phase; * = emulsion.

volume of the emulsion is only 5 to 10% of the total volume of the system. In short, although the volumes of the equilibrium aqueous and oil phases are nearly as great as the volumes originally mixed, the bulk aqueous and oil phases are nearly devoid of surfactant. The emulsion is a very viscous, stable macroemulsion.

It is of some interest to inquire as to whether it is reasonable for essentially all of the surfactant to be concentrated in an interfacial layer surrounding oil droplets in a continuous aqueous medium. The rather crude calculations summarized below show that it is reasonable:

Assume that oil is emulsified in water and that all of the surfactant is concentrated in a layer at the surface of the oil droplets. If one assumes further that the interfacial area occupied by one surfactant molecule is 75 \AA^2 , then one can calculate the total interfacial area as follows:

Initial Surfactant Concentration = 0.1 wt.% = 1 mg/ml

Volume of initial aqueous solution = 10 ml = 10 cm^3

Area covered by surfactant = interfacial area

$$A_{\text{surf}} = \frac{(10 \text{ cm}^3)(1 \text{ mg/cm}^3)(6 \times 10^{23} \frac{\text{molecules}}{\text{mole}})(75 \text{ \AA}^2/\text{molecule})}{400 \times 10^3 \text{ mg/mole}}$$

$$= 4.5 \times 10^{20} \text{ \AA}^2$$

Assume oil droplets close-packed and vol. fr. oil = 0.67

$$V_{\text{emul}} \doteq 1 \text{ ml} = 1 \text{ cm}^3; \quad V_{\text{drop}} = (0.67)(1.0 \text{ cm}^3) \left(10^{24} \text{ \AA}^3/\text{cm}^3 \right)$$

$$= 6.7 \times 10^{23} \text{ \AA}^3$$

Now

$$\frac{V_{\text{drop}}}{A_{\text{surf.}}} = \frac{4\pi n r^3/3}{4\pi n r^2} = r; \quad r = \frac{3V_{\text{drop}}}{A_{\text{surf.}}}$$

where n = number of droplets/ cm^3 emulsion

r = radius of oil droplet

V_{drop} = volume of oil droplets/ cm^3 emulsion

$$r = \frac{(3)(6.7 \times 10^{23} A^3)}{4.5 \times 10^{20} A^2} \doteq 4.5 \times 10^3 A = 0.45 \mu\text{m}$$

A close-packed assembly of oil droplets having an average radius of about $0.45 \mu\text{m}$ would have sufficient interfacial area to accommodate the surfactant in an emulsion volume of one ml.

The number of droplets per ml emulsion would be

$$n \doteq \frac{V_{\text{drop}}}{4/3\pi r^3} = \frac{(3)(6.7 \times 10^{23} A^3)}{(4\pi)(4.5 \times 10^3 A)^3} \doteq 1.8 \times 10^{12}$$

Partition coefficients for the system $8-\phi\text{C}_{16}\text{SO}_3\text{Na}-\text{NaCl}_{\text{aq}}/\text{n-octane}$ were calculated from the equilibrium water and oil surfactant concentrations and there are shown in Figure IVA7. The strong influence of the salt concentration on the value of the partition coefficient is very evident, especially in the NaCl concentration range from 0.01 wt.% to about 0.5 wt.%. In this salt concentration range the partition coefficient changes by about three orders of magnitude, passing through unity at about 0.05 wt.% NaCl. For the salt concentrations of greatest interest in micellar/polymer flooding and in most surfactant adsorption studies the surfactant is strongly partitioned into the oil.

Implications for Adsorption and Surfactant Salting-Out and Partitioning Into Oil

It seems clear that adsorption measurements with alkylbenzene sulfonates are likely to be complicated by surfactant salting-out (either as a solid or possibly as liquid crystals) when the surfactant equivalent weight is greater than about 350 and when the salt concentration becomes appreciable, i.e., greater than about 0.01 wt.-%-provided no oil is present. For these conditions, surfactant salting-out would result in high levels of apparent surfactant adsorption, when in fact, most of the surfactant loss would be due to salting-out. Moreover, the surfactant concentration dependence of salting-out might lead to maxima (and possibly minima) in the apparent adsorption isotherm which derive from salting-out phenomena rather than adsorption (see, for example, Figure IVA2).

In addition to the influence on apparent adsorption of salted-out surfactant, the addition of salt to the surfactant solution results in a lowering of the CMC and a reduction in the effective concentration of the pre-micellar surfactant may be so small as to make true surfactant adsorption negligible, or nearly so.

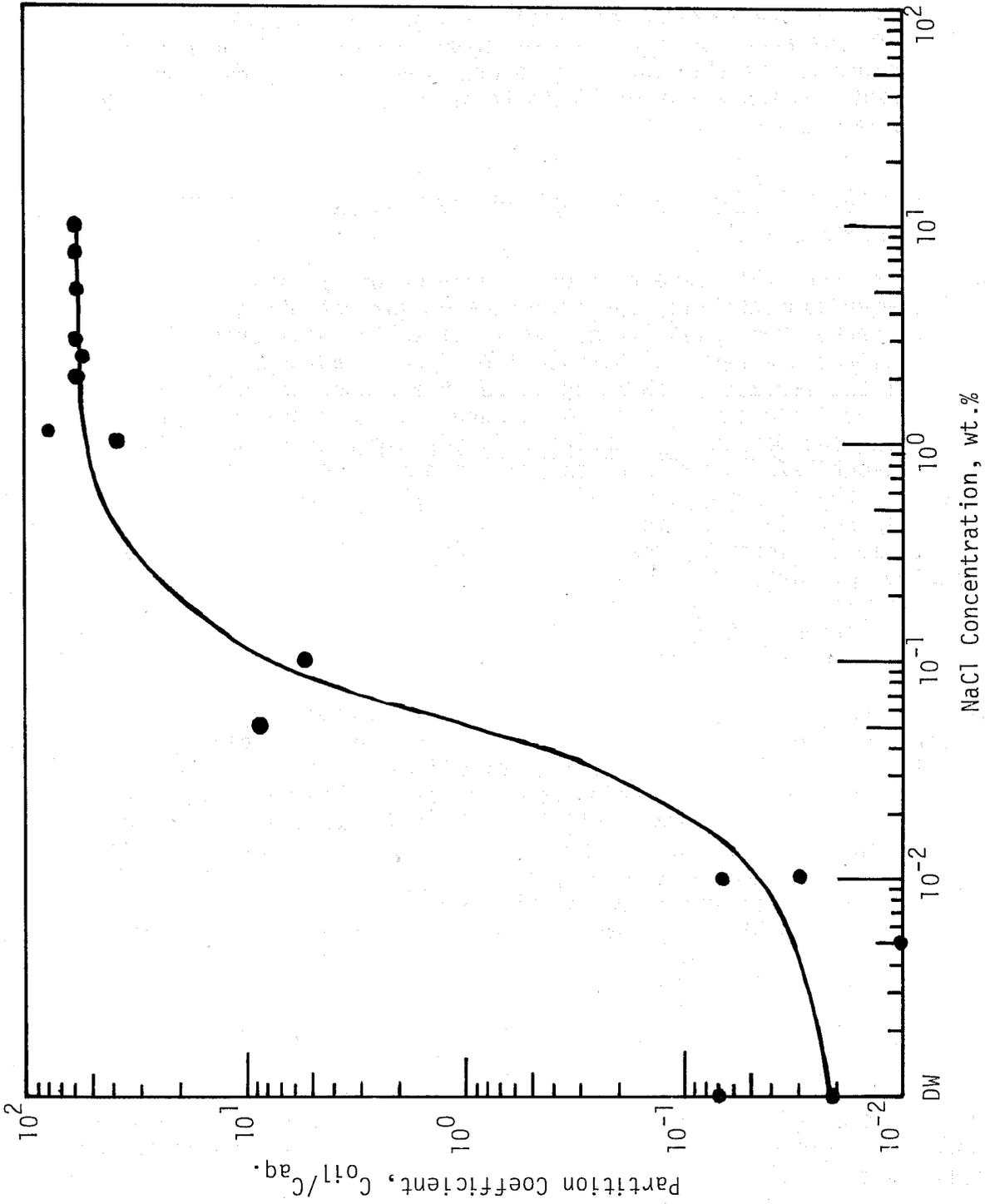


Figure IVA7. Salt Concentration Dependence of O/W Surfactant Partition Coefficient. Surfactant = $8-\phi C_{16}SO_3Na(UT-1)$; oil = n-octane (99%).

If both oil and salt are present, the situation becomes more complex. It appears that no salting-out of surfactant occurs but that partitioning of surfactant to the oil and its concentration in a macroemulsion may lead to very sharp reduction of the surfactant concentration in the aqueous phase. The strong surfactant and salt concentration dependence of the partition coefficient would be further complicating factors but these appear to become less important when the salt concentration is one wt.% or greater. However, at high salt concentrations the surfactant appears to partition so strongly into the oil that the equilibrium surfactant concentration in the aqueous phase becomes almost negligible; in addition there is the reduction of the CMC by the added salt, so the concentration of the surfactant species which appear to be involved in adsorption tends to become very small.

Significance of Salting-Out and Partitioning Surfactants for Dynamic Adsorption and Core Floods

The very strong salt-concentration dependence of salting-out of surfactants, when combined with the influence of surfactant equivalent weight on the phenomenon, clearly indicate that salting-out phenomena can severely affect the results obtained from dynamic adsorption experiments. If the surfactant solution to be injected contains a surfactant having an equivalent weight of 390 or greater and a salt concentration of about one per cent or greater, in our experience, surfactant will be salted-out before injection and may be more or less completely filtered out of the suspension depending on the structure of the bed. If the injected solution contains little or no salt, salting-out will tend to occur at the interface between the brine and the surfactant slug. Varying degrees of surfactant retention can be found in these circumstances, but it is obvious that they are not the results of adsorption and that the solution to the problem requires other measures than one would employ to minimize adsorption.

The influence of oil in preventing salting-out by acting as a solvent for surfactant has very important implications for any fixed bed experiments in which significant concentrations of oil are present. Moreover, comparison of the results of experiments without oil with those in the presence of oil would be extremely difficult because surfactant precipitation by salting-out would be a factor in the former case but not in the latter. Oil not displaced by a surfactant slug could, however, serve as a "sink" for retention of surfactant in the bed. On the other hand, this oil may be less accessible to the surfactant slug than that which is displaced and mass transfer of surfactant to retained oil may be less efficient than mass transfer to oil which is displaced.

To summarize, the results presented here seem to suggest that surfactant precipitation by salting-out, while very important for adsorption experiments, may not be as important for oil-displacement as the surfactant and salt concentration-dependence of partitioning to oil. Much more work is required to understand more fully the importance of these processes for micellar/polymer flooding.

2. Multivalent Cation Precipitation: Measure concentration dependence of multivalent cation precipitation of selected commercial and synthetic monoisomeric surfactants, determine the composition of the calcium salts, and evaluate the effect of oil on multivalent cation precipitation.

Investigator: Dr. G.Rama Rao and Mrs. Jean Meister

Surfactant Precipitation by Calcium Ions

Multivalent cation precipitation of anionic surfactants is well known, and we have shown in several earlier reports that more or less complete precipitation of surfactants can occur depending on the concentrations and ratios of surfactant and multivalent cation. On the other hand, for systems involving calcium ions as the multivalent cation, either no precipitation or dissolution of the precipitate has been observed to occur if the surfactant to calcium ratio is sufficiently large. Parenthetically, it may be noted that order of mixing is important: if one adds surfactant to an aqueous solution containing calcium ions, one observes precipitation of the calcium salt of the surfactant and then dissolution, whereas if one adds calcium ions to a surfactant solution, precipitation alone is observed. In the latter case, the early surfactant/calcium ratio being large, the system passes through the precipitate-dissolution stage and nothing significant is observed until precipitation is observed when the surfactant/calcium ratio becomes small.

These phenomena have been investigated more fully during the past quarter with a commercial surfactant, SUL-FON-ATE AA10 (Cities Service).

Materials and Methods:

As noted above, this study was carried out with Cities Service SUL-FON-ATE AA10. This is a commercial product which is 96% active, the remainder of the product consisting of about 2% water and 2% salt; it is designated by the manufacturer as sodium dodecylbenzene sulfonate. A limited number of comparative tests done in our laboratories indicate that the product is very comparable to commercial SDBS purchased from Pfaltz and Bauer (after drying and desalting). However, in a recent equipment demonstration of a Waters Associates Liquid Chromatograph the chromatogram for SDBS was found to differ slightly from that of SUL-FON-ATE AA10, primarily in the distribution of the component species.

The calcium chloride used in these experiments was ACS Reagent Grade.

Surfactant and calcium chloride stock solutions were prepared in the desired concentrations, and mixed in 15 ml screw-capped Pyrex tubes. The requisite amount of CaCl_2 solution was added from a burette, then distilled water to make the desired surfactant/calcium ratio was added. Finally, the required volume of surfactant stock solution was added from a burette. A sheet of Saran Wrap was stretched over the mouth of the tube and the cap affixed. The tubes were then placed in a rotator (one rpm) in an air bath at 25°C for 24 hours. The tubes were

removed from the air bath, centrifuged to settle the precipitate, and an aliquot of clear supernatant liquid withdrawn for analysis.

Results and Discussion:

The fraction of the surfactant precipitated was calculated from a material balance based on the amount of surfactant added and that found in the residual solution. [We believe that equilibrium is achieved in 24 hours because no changes in behavior have been observed after the first few moments following mixing; moreover, a few tests run as long as three days have given the same results as 24 hours. A more complete test of equilibrium will be done later].

These data are shown in Figures IVA8 for four concentrations of calcium ions: 20 ppm ($10^{-3}N$), 50 ppm ($2.5 \times 10^{-3}N$), 200 ppm ($10^{-2}N$), and 800 ppm ($4 \times 10^{-2}N$). The range of surfactant concentrations was chosen to yield a surfactant/calcium ratio (equivalent surfactant/equivalent calcium) of zero to 5. In this figure we have plotted fraction of surfactant precipitated $[(C_0 - C_e)/C_0]$ versus the surfactant/calcium ratio, S/Ca. In earlier reports we have presented data from similar experiments in the form of plots of the fraction of the surfactant remaining in solution, C_e/C_0 , versus the S/Ca ratio. We have chosen to make the change here because our **principal** concerns in these experiments were the surfactant precipitation and dissolution phenomena.

In Figure IVA8, we note, firstly, that a maximum is observed in the fraction of surfactant precipitated for each of the initial calcium ion concentrations (even for 20 ppm which is so small that it seems unlikely that many brines of such low calcium content will be encountered). Secondly, we note that the fraction of surfactant precipitated at the maximum increases as the calcium ion concentration increases, precipitation becoming essentially complete when the initial calcium ion concentration is 800 ppm (still a low concentration when compared to many reservoir brines). Thirdly, we observe dissolution of the precipitate (or inhibition of precipitation) for all calcium ion concentrations tested as the surfactant/calcium ion ratio increases. Clearly, calcium ions are being complexed or being fixed in micelles. A fourth observation which we can make from examination of Figure IVA8 is that the position of the maximum tends to move to smaller values of the S/Ca ratio as the initial calcium ion concentration increases. We also note that the maximum tends to sharpen somewhat as the calcium ion concentration increases. This may result from the surfactant being a mixture of species, whereas the other surfactants studied in this manner (Na lauryl sulfate and Aerosol-OT) are pure mono-isomeric compounds.

Comparison of the curves shown in Figure IVA8 with the figures from earlier reports for multivalent cation precipitation of the pure mono-isomeric surfactants referred to above reveals that all of the features of the graphs noted above can be found in the former figures, i.e., the phenomena represented are common to all of the anionic surfactants examined so far. Qualitatively also, the observations made concerning surfactant

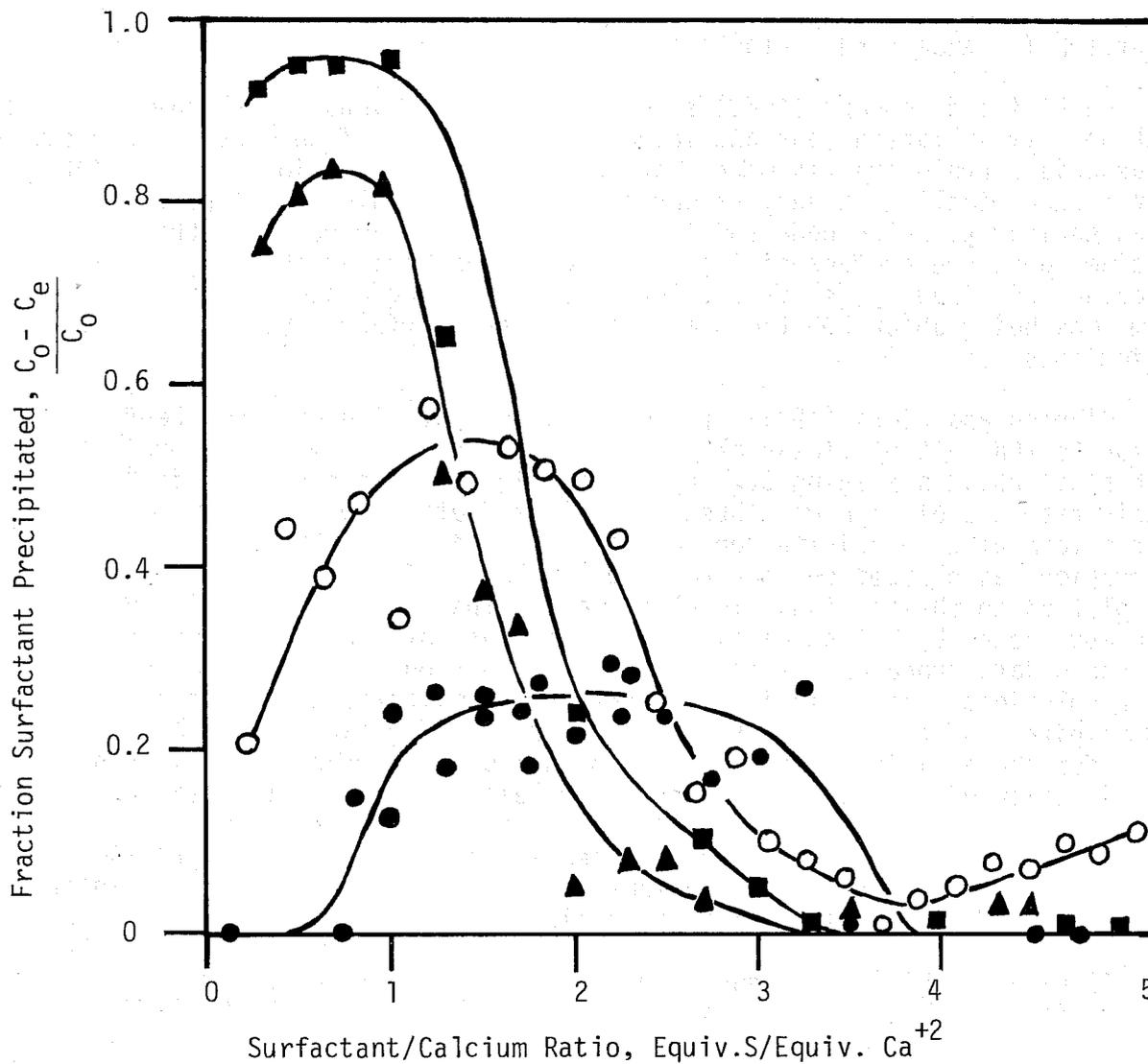


Figure IVA8. Surfactant Precipitation By Multivalent Cations.

Surfactant = SUL-FON-ATE AA10 (SDBS)

● = 20 ppm Ca^{+2} (0.001N); ○ = 50 ppm Ca^{+2} (0.0025N);

▲ = 200 ppm Ca^{+2} (0.01N); ■ = 800 ppm Ca^{+2} (0.04N).

precipitation in equilibrium adsorption experiments with desalted, de-oiled SPBS and TRS-10-410, and for $8-\phi C_{16}SO_3Na$ (UT-1) on clays are consistent with the phenomena noted above. It seems worth mentioning here that Matijevic and co-workers (1966 and 1971) found that precipitated calcium oleate did not redissolve in excess potassium oleate, and O'Brien and Wiers (1974) suggested that the multivalent cation precipitation behavior of carboxylate surfactants differs from that of the "surface active sulfonates". The authors suggested that in some fashion the precipitate formed by calcium and alkylbenzene sulfonate is more open to attack (by excess surfactant) than calcium oleate.

Corkill and Goodman (1962) studied the interactions of calcium ions with dodecyl sulfate anions and found that dodecyl sulfate micelles tended to associate predominantly with either calcium or sodium ions-but not both in the same micelle. A very strong preference for calcium was noted. In an earlier paper Shinoda and Ito (1961) had already reported that calcium ions were preferentially adsorbed over sodium at the air-solution interface of a dodecyl sulfate solution, the surface concentration of calcium ions being about 200 times as great as the surface concentration of sodium ions.

O'Brien and Wiers (1974) studied the precipitation of alkyl benzene sulfonate (Na salt of linear alkylbenzene sulfonate - commercial product with alkyl chain averaging C_{13}) by calcium ions. Both precipitation and precipitate dissolution were observed. These authors presented their data in the form of a "precipitation boundary" plot in which the calcium concentration was plotted on the ordinate and the surfactant concentration was plotted on the abscissa (log-log plot). The onset of precipitation, when approached by adding calcium to surfactant, or *vice versa*, was noted and these data produced a V-shaped plot. Points outside the V represent clear solutions; points inside the V represent mixtures which produce a precipitate of the calcium salt. Another way of viewing this plot-at least for the addition of increasing amounts of surfactant to a constant concentration of calcium ions-is that the left hand branch (low surfactant concentrations) of the V corresponds to the onset of precipitation, while the right hand branch corresponds to precipitate dissolution. Our findings are consistent with these observations, but our figures include more information, e.g. fraction of surfactant precipitated.

O'Brien and Wiers also suggested a reaction scheme to account for their observations which employed ordinary stoichiometry along with Sillen's (1954) "core-links" model of surfactant aggregation. These authors set forth a two-stage precipitation process



then

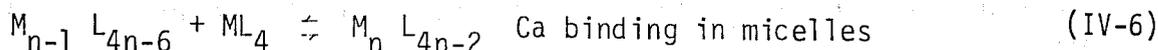
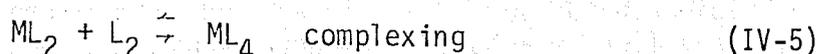
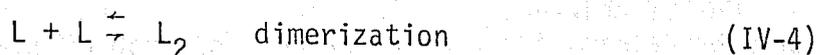


where M = calcium ions, and L = surfactant anion. The solubility product is then

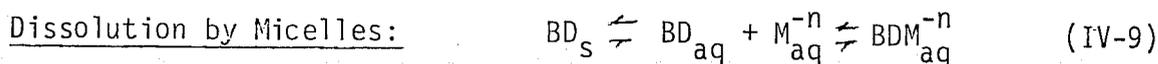
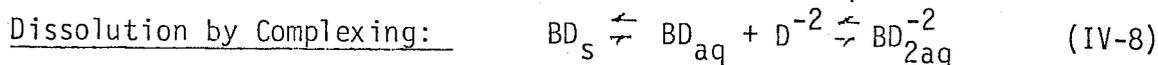
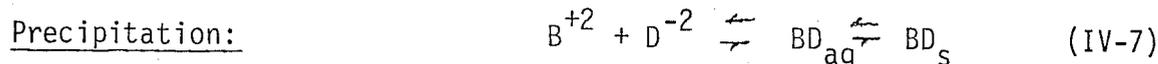
$$K_{SO} = [M][L]^2 \quad (IV-3)$$

and they deduced an approximate value of $K_{SO} \cong 1.15 \times 10^{-10}$ (or $pK_{SO} = 9.94$).

Dimerization, dissolution of the precipitate by complexing, and dissolution of the precipitate by fixation of the calcium ions in micelles were also considered as shown in the equations below



The presence of surfactant dimers in pre-micellar surfactant solutions has been discussed by several investigators and Berg (1977) showed by **calorimetric** measurements that dimers may be the most prevalent species below the CMC, at least for one surfactant. If we assume dimers to be a prevalent-pre-micellar species, Equations IV-1 through IV-6 can be simplified somewhat as shown below. Here we change nomenclature and let D = dimer, B = cation, and M = micelles; we also show the appropriate elective charge on ions.

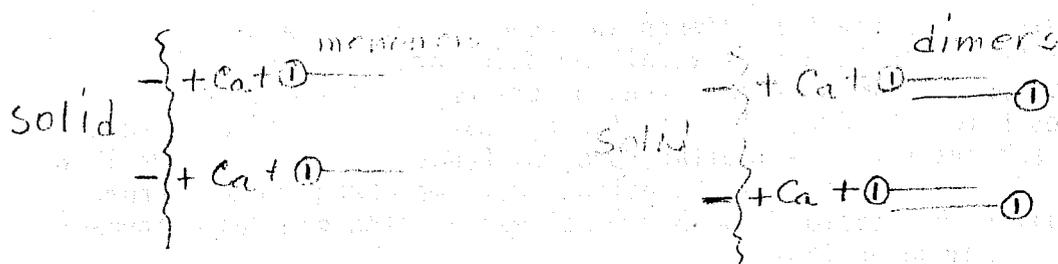


This reaction scheme, as does that of O'Brien and Wiers, accounts for surfactant precipitation by multivalent cations, and it suggests that precipitate dissolution can occur by either or both of two reactions: 1) complexing by dimers, or 2) calcium binding by micelles, depending on the surfactant concentration. Although Equations IV-7 through IV-9 have been written for **divalent** cations alone in the precipitate, the possibility of the precipitate containing both calcium and sodium ions is obvious, and this seems especially likely if precipitation occurs from micellar solutions. In this connection we may recall that Meister and co-workers (1978) showed that both sodium and calcium were lost from solution when alkylbenzene or petroleum sulfonates were precipitated by $CaCl_2$.

The precipitate dissolution reactions by complexing and micellar binding of calcium seem likely to be operative when the surfactant concentration is below and above the CMC. The surfactant concentration in the experiments with SUL-FON-ATE AA10 at a $CaCl_2$ concentration of 20 ppm appears to be below the CMC. Therefore this graph in Figure IVA8 may represent precipitate dissolution by complexing via excess pre-micellar surfactant (dimers). For the most part, however, precipitate dissolution occurs in micellar solutions, so most dissolution seems to be due to calcium binding in micelles.

Significance of Surfactant Precipitation For Adsorption

Since reservoir brines ordinarily contain significant to large concentrations of calcium, and clays and other minerals (such as gypsum) may contribute calcium ions to the brine, the probability of multivalent cation precipitation of surfactant in adsorption measurements is very large. In equilibrium adsorption measurements, a type of chemisorption of surfactant anions can occur at cation exchange sites which are occupied by calcium or other multivalent cations as depicted by the following schematic model



However, sodium ions from the surfactant or from added salts can replace the calcium ions in the cation exchange sites, and these displaced calcium ions cause surfactant precipitation. As the surfactant concentration is increased—particularly beyond the CMC—dissolution of the precipitate occurs.

When surfactant precipitation occurs, the apparent surfactant adsorption increases, and when the precipitate dissolves, the apparent adsorption decreases. Thus, an apparent adsorption isotherm having a maximum may be found, but the maximum has nothing to do with adsorption proper. Moreover, owing to the possible presence of slightly soluble calcium-bearing minerals like gypsum, surfactant precipitation and dissolution can play a much larger role in estimation of surfactant retention losses and apparent adsorption than might otherwise be the case. Although no criticism of the work of other investigators is intended, it seems worth noting here that the experimental conditions under which an appreciable number of the so-called static adsorption isotherms reported in the literature have been done, as well as the shape of the adsorption isotherms themselves, suggest that surfactant precipitation (by multivalent cations) and precipitate dissolution (by micellar surfactant at the higher concentrations) may have been significant factors in determining the shape of the adsorption isotherm.

In dynamic adsorption experiments and core floods surfactant precipitation and dissolution may have a significant influence on results, particularly on surfactant losses. Precipitation may occur in the leading edge of a surfactant slug when the brine contains appreciable concentration of calcium ions or when slightly soluble calcium-bearing minerals are present in significant amounts. The precipitate would redissolve, however, as the more concentrated surfactant of the main body of the surfactant slug contacts the precipitate. Reprecipitation may occur in the trailing edge of the surfactant slug as the surfactant concentration falls below the CMC, thus continuously reducing the inventory of surfactant in the slug.

The influence of oil on surfactant precipitation and dissolution, and the possible partition of the calcium sulfonates into the oil phase still remains to be studied. If the influence of oil on multivalent cation precipitation and dissolution is comparable to its influence on salting-out processes, an entirely different treatment of these phenomena will be required.

B. SURFACTANT/POLYMER ADSORPTION

1. Surfactant CMC: Measure CMC as necessary for interpretation of adsorption data.

Investigator: Dr. G. Rama Rao

It has been found quite generally that anionic surfactant micelles do not adsorb on clays, sand, and most other reservoir rock components in the most commonly encountered circumstances. The case for limestone or dolomite is less clear, although it would seem likely that micellar adsorption would occur on these minerals. For studies with clays, sandstones, and the like as adsorbents, it becomes necessary to know the CMC of the surfactant at the conditions of the experiment to assess the practical upper limit of surfactant concentration operative in the adsorption process. It is well-known, of course, that the CMC is depressed by electrolytes, and Shah and Chan (1978) showed that oil also affected the CMC of SDBS. In the previous quarterly report on this contract, we showed that two CMC's were observed when excess oil was present: one at about the same surfactant concentration as when no oil was present, and a second CMC at a surfactant concentration roughly an order of magnitude below the first.

Owing to the potential importance of these observations, further measurements of surfactant CMC were undertaken. Moreover, since different methods of measuring the CMC frequently give somewhat differing values, both surface tension (Wilhelmy plate) and electrolytic conductivity were measured.

Materials and Methods:

Two monoisomeric surfactants of high purity were chosen for these experiments: Aerosol-OT and $8-\phi C_{16}SO_3Na$ (UT-1). Since both appeared to be more than 95% pure (based on C, H, and S analyses), they were used without further treatment. Stock solutions were prepared by dissolving the surfactant in water which had been distilled in an all-glass still after deionization. Solutions of varying concentration were made by diluting the stock solution with the distilled water.

When the surfactant solution was to be equilibrated with oil, a known volume of surfactant solution (already diluted to the desired concentration) was transferred to a screw-capped tube, and enough n-dodecane was added to make the mixture 0.5 vol.% oil (generally 39ml surfactant solution and 1 ml oil). The tube was covered with Saran Wrap, and the cap affixed. Then the tube was placed on a rotator in an air bath maintained at $25 \pm 1^\circ C$ and rotated at one rpm for three days. The tube was removed and uncapped, the mixture centrifuged to separate the oil, and the oil layer carefully withdrawn. The remaining aqueous solution was then used for surface tension and electrolytic conductivity measurements.

It was determined in a separate experiment that the amount of surfactant partitioning to the oil was negligible. Therefore, no correction of surfactant concentration was made to account for partitioning into the oil phase.

Since both surface tension and electrolytic conductivity measurements were to be made, the surface tension was measured first with a Wilhelmy plate which was flamed between each solution. Then the electrolytic conductivity was measured on the same solution using an AC bridge.

Results and Discussion:

In Figure IVB1 we see the surface tension plotted as a function of the surfactant concentration. The features of the curves on this figure are consistent with those found for other surfactants, i.e., only one CMC is seen for the solutions in distilled water, while the solutions equilibrated with n-dodecane exhibited two CMC's, one corresponding to the distilled water CMC and another at a lower concentration. These two surfactants appear to differ somewhat in that a third CMC appears to be seen for Aerosol-OT. The evidence for the third CMC is tenuous, however, and more investigation is required to establish its authenticity. These results do confirm, though, our previous observation of a second CMC (when oil is present) at a surfactant concentration about an order of magnitude below the distilled water CMC.

The existence of a second CMC in certain circumstances has been reported by other investigators. Thus, Miura and co-workers (1972, 1973) presented evidence for a second CMC in sodium dodecyl sulfate when the CMC was measured by several techniques. These investigators found, however, that the second CMC occurred at a higher concentration than the CMC in distilled water. They did not measure the surface tension but they measured the electrolytic conductivity. When they plotted the specific conductivity versus the surfactant concentration, they found a fairly sharp decrease in the slope of the κ -c curve at the normal CMC; at considerably higher concentrations they found a second slight decrease in the slope of the curve. They suggested that the concentration at which the second change of slope occurred represented a second CMC. The observation was confirmed by other types of measurements, one of which was light-scattering.

Our surface tension measurements, although carried almost to the solubility limit; showed no evidence for such a high-concentration CMC in the case of $8-\phi C_{16}SO_3Na$ and only slight evidence in the case of Aerosol-OT. In any event Miura and co-workers did not report a low-concentration CMC which resulted from equilibration with oil.

Turning now to the electrolytic conductivity measurements, these are shown in Figures IVB2 through IVB5. In Figure IVB2, the concentration dependence of the specific conductivity of $8-\phi C_{16}SO_3Na$ is shown. The curves are normal in all respects in that the specific conductivity increases linearly with surfactant concentration and then breaks over at the CMC to give a straight line of smaller slope. Measurements were made on solutions equilibrated with two n-dodecane samples of different purities (95 and 99%). Up to the CMC neither the presence of oil nor its purity appeared to have any effect on the specific conductivity. At surfactant concentrations above the CMC, the specific conductivity was strongly affected by oil and oil purity made a significant difference. It seems clear from these results that oil has little effect on the specific conductivity of pre-micellar solutions, but a significant effect on the conductivity of micellar solutions.

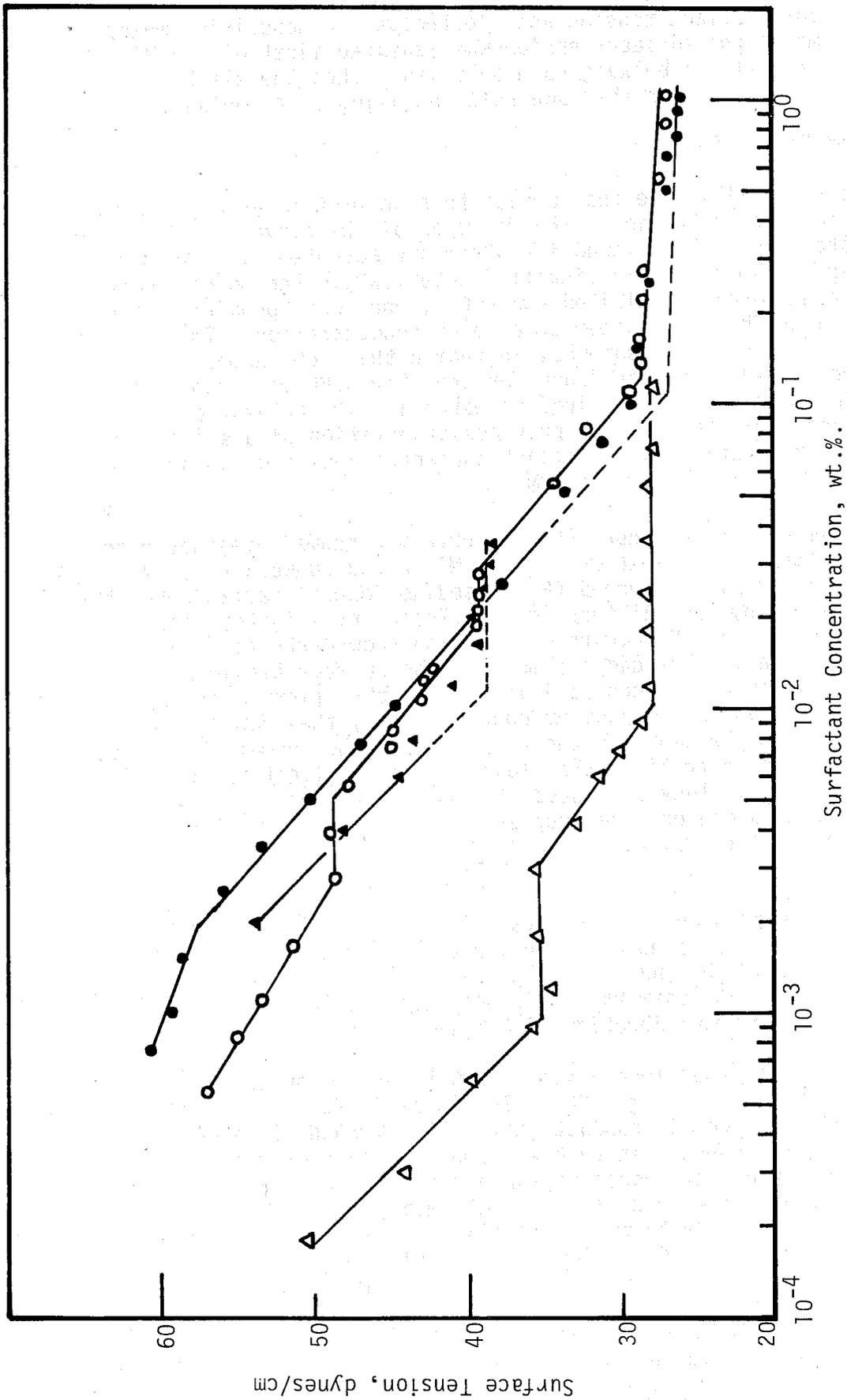


Figure IVB1. Surfactant Concentration Dependence of Surface Tension.

● = Aerosol-OT in distilled water. ○ = A-OT in DW equilibrated with 0.5 vol.% n-dodecane (95%). ▲ = 8- ϕ C₁₆SO₃Na in DW. △ = 8- ϕ C₁₆SO₃Na equilibrated with 0.5 vol.% n-dodecane (95%).

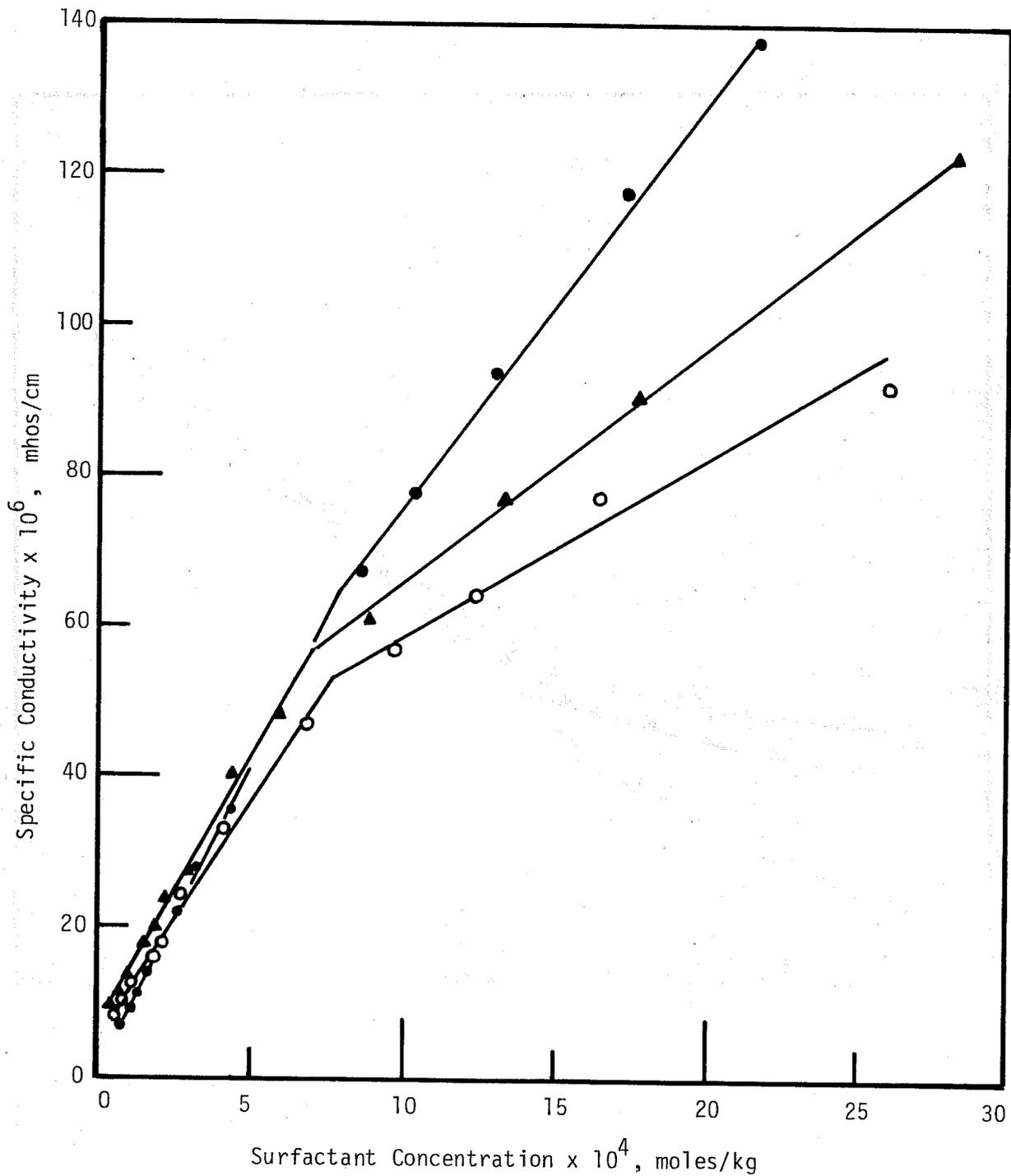


Figure IVB2. Surfactant Concentration Dependence on the Specific Electrolytic Conductivity.
Surfactant = $8-\phi C_{16}SO_3Na$ (UT-1)

● = distilled water; ▲ in DW equilibrated with 0.5 vol.% n-dodecane (95%), △ = in DW equilibrated with 0.5 vol.% n-dodecane (99%).

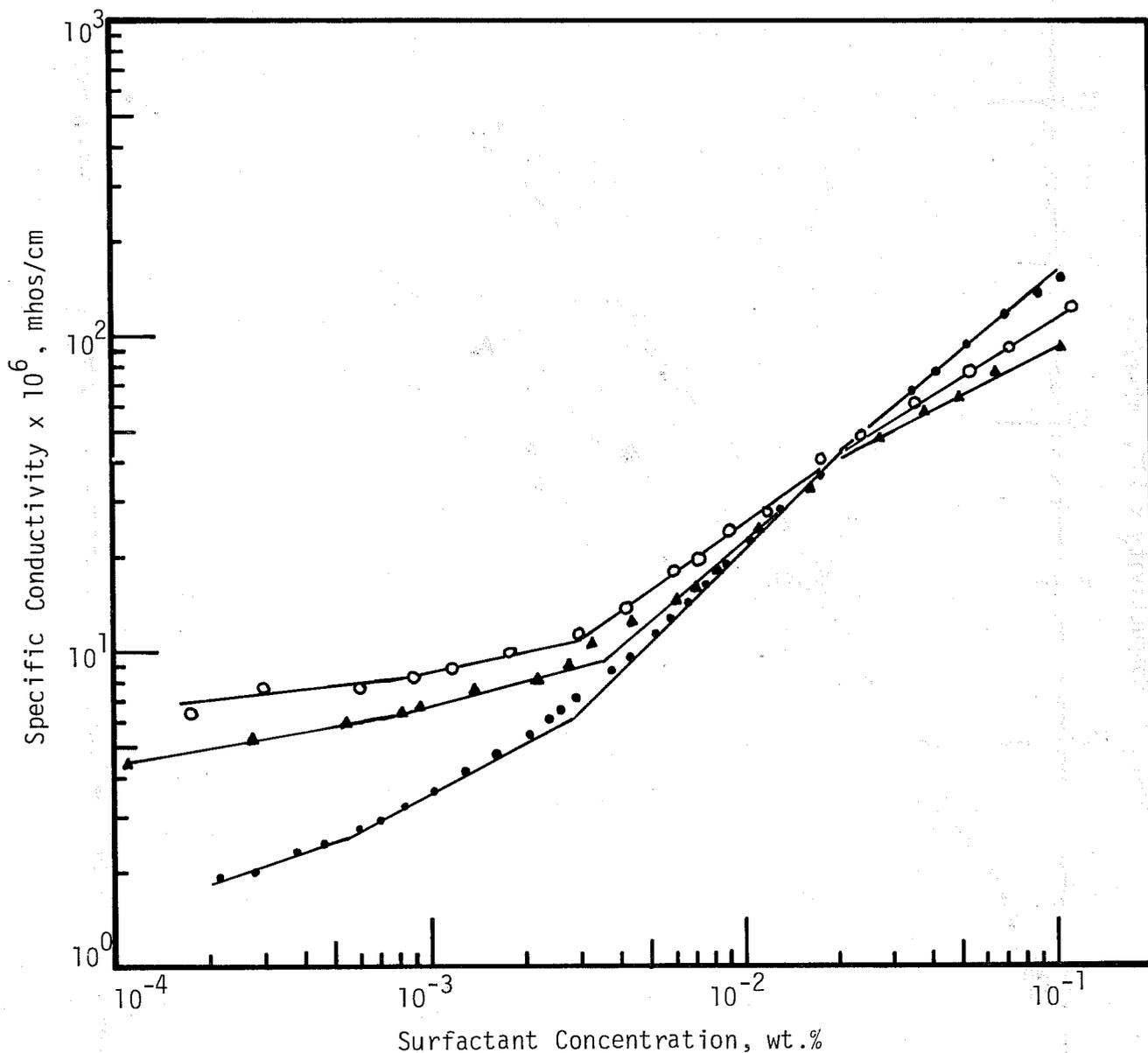
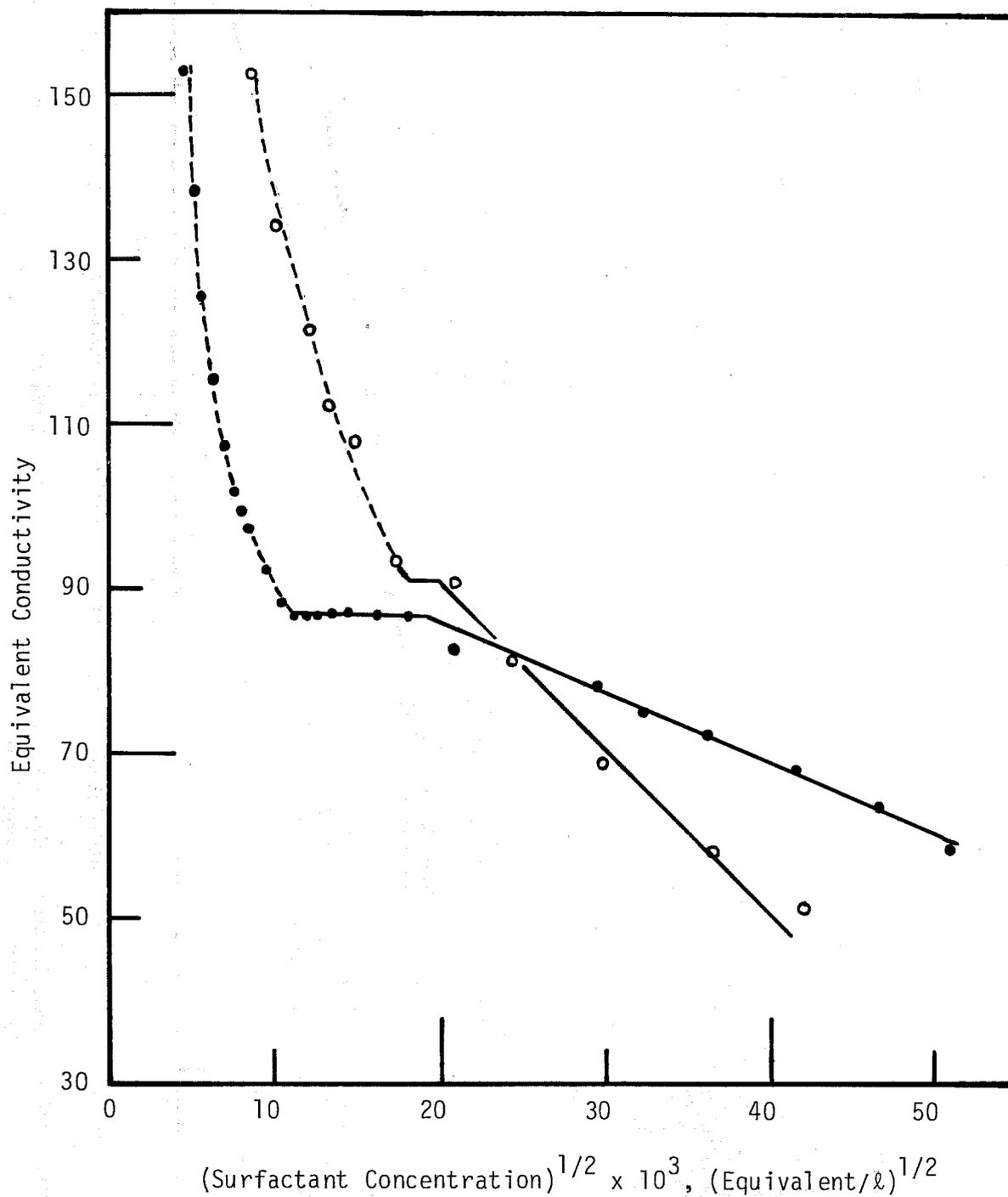


Figure IVB3. Surfactant Concentration Dependence of Specific Electrolytic Conductivity.

Surfactant = 8- ϕ C₁₆SO₃Na (UT-1)

● = in distilled water; o = in DW equilibrated with 0.5 vol.% n-dodecane (95%); ▲ in DW equilibrated with 0.5 vol.% n-dodecane (99%).



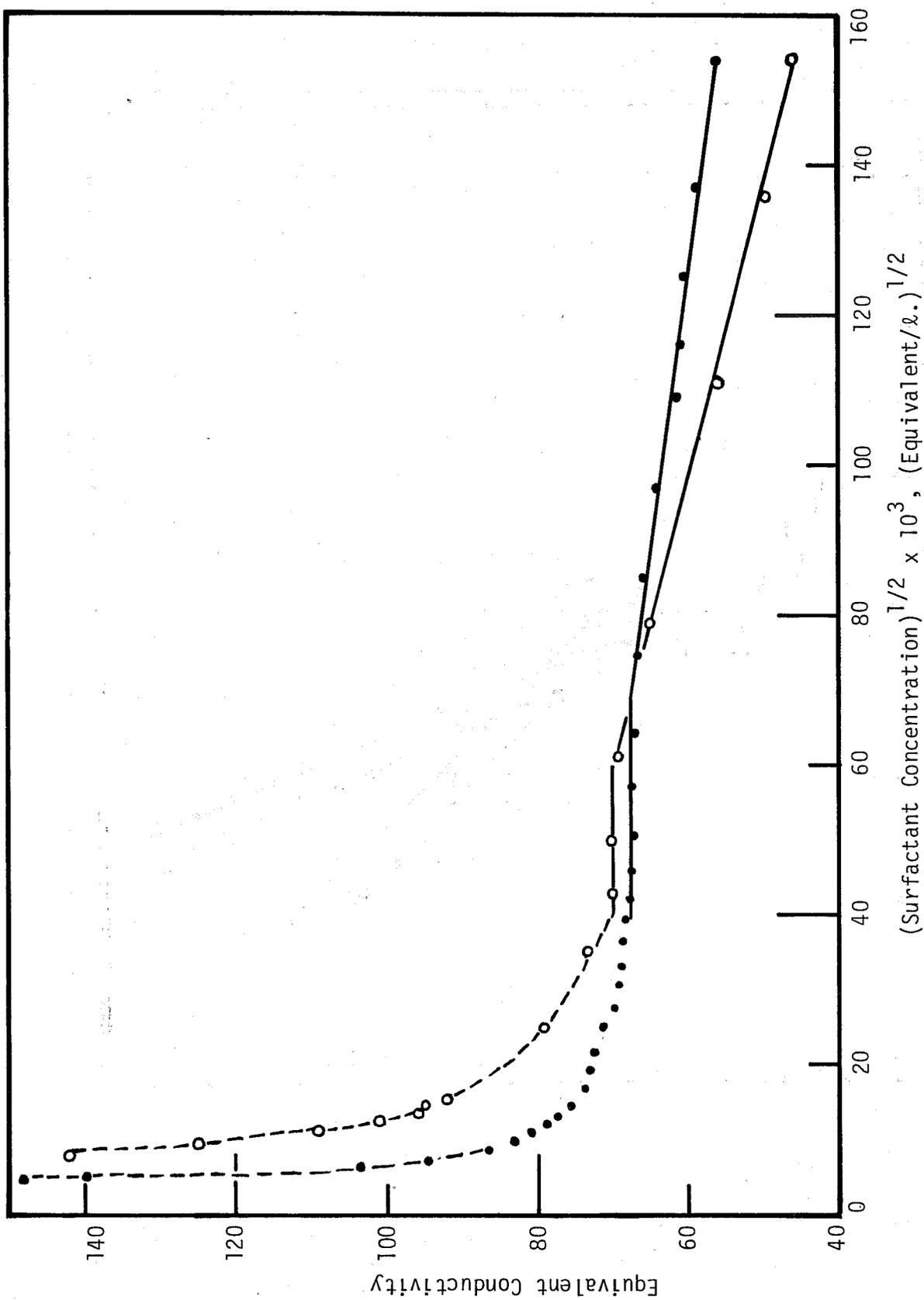


Figure IVB5. Concentration Dependence of Equivalent Conductivity.
 Surfactant = Aerosol-OT
 ● = in distilled water; ○ = in DW equilibrated with 0.5 vol.-% n-dodecane (95%).

If one plots the specific conductivity versus the surfactant concentration (wt.%) on log-log paper as shown in Figure IVB3, one does see several breaks in the curves, one of which corresponds approximately to the distilled water CMC. Two additional breaks in the curve are seen at low surfactant concentrations, but neither of these corresponds to the second (low concentration) CMC found in the surface tension-concentration plots. It seems questionable as to whether either of these discontinuities in the $\log \kappa$ vs $\log c$ plot should be attributed to a CMC - at least until further investigation is completed.

One of the best methods for establishing the presence of micelles from electrolytic conductivity measurements is a plot of the equivalent conductivity, Λ , versus the square root of the concentration. The Onsager limiting law takes the form

$$\Lambda = \Lambda_0 - bc^{1/2} \quad (\text{IV-10})$$

where Λ is the equivalent conductivity, Λ_0 is the equivalent conductivity at infinite dilution, b is a constant, and c is the concentration of surfactant. When Λ is plotted as a function of $c^{1/2}$, one obtains for simple electrolytes a slowly rising curve which extrapolates to Λ_0 . For surfactants, one normally sees a curve which rises at a moderate rate and which then flattens out at the CMC.

In view of theoretical basis and wide acceptance of the Λ vs $c^{1/2}$ plot, our conductivity data were converted to equivalent conductivities and plotted versus the square root of the surfactant concentration. These are plotted in Figure IVB4 for 8- ϕ C₁₆SO₃Na (UT-1) and in Figure IVB5 for Aerosol-OT. Two curves are shown for each surfactant: one in distilled water, and the second in distilled water and equilibrated with 0.5 vol.% n-dodecane (95%). At high concentrations the equivalent conductivity changes with surfactant concentration as expected. Although there is an effect due to the oil, the general trend of the curve is normal. In all of the curves on Figures IVB4 and 5, there is a significant change in slope at approximately the CMC found in distilled water by surface tension measurements. This discontinuity is followed by a plateau as expected.

For all of these solutions, however, the equivalent conductivity began to rise sharply at a surfactant concentration only slightly below the high-concentration (distilled water) CMC. In fact the equivalent conductivity for low concentrations increases to unreasonably large values, so that it is evident that conductivity measurements in this concentration range are invalid. These results indicate strongly that impurities in these oil samples and in the surfactant solutions so affected the electrolytic conductivity that the method cannot be used to locate low-concentration CMC's due to oil (at least not without much more elaborate purification procedures than we have been able to bring to bear).

Conclusions:

It appears that surface tension measurements do, indeed, indicate the presence of a second CMC at a concentration about an order of mag-

nitude below the distilled water CMC when the surfactant solution is equilibrated with n-dodecane. Electrolyte conductivity measurements confirm the high concentration CMC, and suggest a significant affect of oil on the conductivity of micellar solutions, but do not appear to be useful for low concentration CMC measurements. Electrolytic conductivity is not useful, of course, if the solution contains any appreciable concentration of other electrolytes.

2. Surfactant Adsorption: Measure Influence of NaCl and Oil on Equilibrium Adsorption of Selected Surfactants on Na-kaolin.

Investigators: Dr. G. Rama Rao and Mr. A.S. Wilder

The potential importance of surfactant adsorption on the usefulness of micellar/polymer flooding process for enhanced oil recovery is well understood, but the surfactant loss processes which can be operative in a reservoir-and particularly as they relate to apparent adsorption losses-are much less well understood. To illustrate, it has been pointed out earlier in this report how an apparent equilibrium adsorption isotherm with a maximum could be found which was due almost entirely to surfactant precipitation by multivalent cations at low surfactant concentrations and subsequent dissolution of the precipitate at higher surfactant concentrations. As has been noted in earlier reports, both surfactant salting-out by NaCl and precipitation by calcium have been shown to affect apparent adsorption measurements obtained in our laboratories, and this has been particularly true of surfactants of high purity and equivalent weight above about 350. For this reason surfactant adsorption studies have been slowed down to permit more complete evaluation of surfactant salting-out and precipitation processes-particularly as these are affected by the presence of oil.

One set of adsorption, experiments has been underway for some time, however, and these will be reported here. They related to the question of whether the presence of a small amount of oil influences the equilibrium adsorption isotherm in a significant way.

Materials and Methods:

The surfactant used in these experiments was 8- ϕ C₁₆SO₃Na (UT-1) which was used as received. The adsorbent was cation-exchanged kaolin (Na-kaolin) which had been desanded, extensively cation-exchanged with 1M NaCl, and then washed free of salt. The washed clay was dried, crushed and sieved through a 100-mesh sieve, and stored. Before use the cation-exchanged clay was dried again. It should be noted here that this particular clay sample was obtained just as dug from the clay deposit without any processing. Clays which have been processed by the normal techniques of dispersion in phosphate solutions, sedimentation, and filtration are irreversibly changed from the state of the raw clay.

For the adsorption measurements themselves, the dry clay was weighed out (generally in one gram portions) and transferred to a screw-capped test tube of about 15 ml capacity. To this clay 10 ml of surfactant solution of a selected concentration was added, the mouth of the tube was covered with Saran Wrap (which had been shown by earlier experiments to be inert to the surfactant solution), and the cap was attached. The clay

was mixed with the surfactant solution by slow inversion of the test tube several times. Finally the tube was placed on a rotator in an air bath kept at $25 \pm 1^\circ\text{C}$ and rotated at one rpm for three days. (It has been shown earlier that equilibrium appears to be achieved in these solutions in 24 hours or less.)

After three days, the tubes were removed from the rotator and the clay centrifuged out. An aliquot (usually 2 or 5 ml) of the clear supernatant liquid was withdrawn for analysis by the two-phase double-dye method of Reid et al. (1967). The amount of surfactant lost from the solution was calculated by a material balance, and the adsorption isotherm plotted as shown in Figure IVB6.

When the influence of oil on adsorption was to be studied, 0.5 ml of n-dodecane was added to the solution following mixing of the clay and the surfactant solution. Equilibration was carried out as described above, and then the mixture centrifuged. The small oil layer was withdrawn carefully and discarded (it contained only a negligible amount of surfactant), and then the aliquot of clear supernatant solution was withdrawn for analysis of the equilibrium surfactant concentration. The remainder of the procedure was the same as that described before. The adsorption isotherm for UT-1 adsorbed on Na-kaolin in the presence of 0.5 vol.% n-dodecane is shown in Figure IVB7.

Results and Discussion:

The adsorption isotherm of UT-1 on Na-kaolin in the absence of oil is shown in Figure IVB6 and that in the presence of oil in Figure IVB7. The CMC of $8-\phi\text{C}_{16}\text{SO}_3\text{Na}$ in distilled water is about 0.008 wt.% and it can be seen that a maximum of sorts occurs in both isotherms at about that surfactant concentration. It appears from the data that the adsorption is significantly greater at this maximum than is the adsorption in the absence of oil.

The first maximum is followed in both cases by a second maximum which occurs at a surfactant concentration well above the CMC. Although there is considerable scatter in the data for each of the isotherms, the presence of at least one maximum is difficult to refute. On the other hand, the general shape of the adsorption isotherms is suspiciously similar to the precipitation curves seen for other surfactants. The possibility that a small amount of calcium-bearing mineral might still be present in the clay cannot at this point be entirely ignored, for calcium concentrations as small as 2 to 10 ppm would almost certainly precipitate substantial fractions of UT-1. Interpretation of these isotherms should be held in abeyance until the solubility relationships of the calcium salt of UT-1 are more clearly understood. For those surfactants which would appear to have very insoluble calcium salts, analyses of the equilibrium solutions for calcium content seem necessary to ascertain whether what is observed in these adsorption isotherms is really adsorption or a combination of adsorption and precipitation.

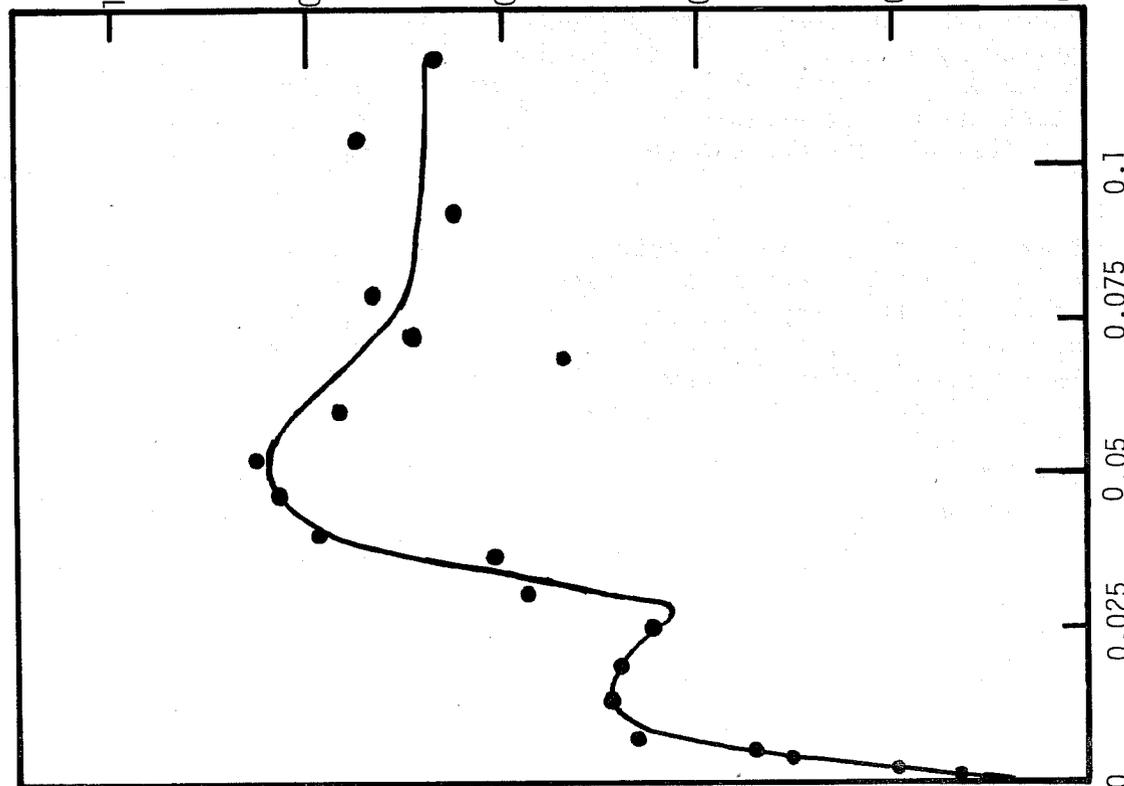


Figure IVB6. Equilibrium Adsorption of Surfactant on Cation-Exchanged Kaolin. $8-\phi C_{16}SO_3Na$ (UT-1) in distilled water.

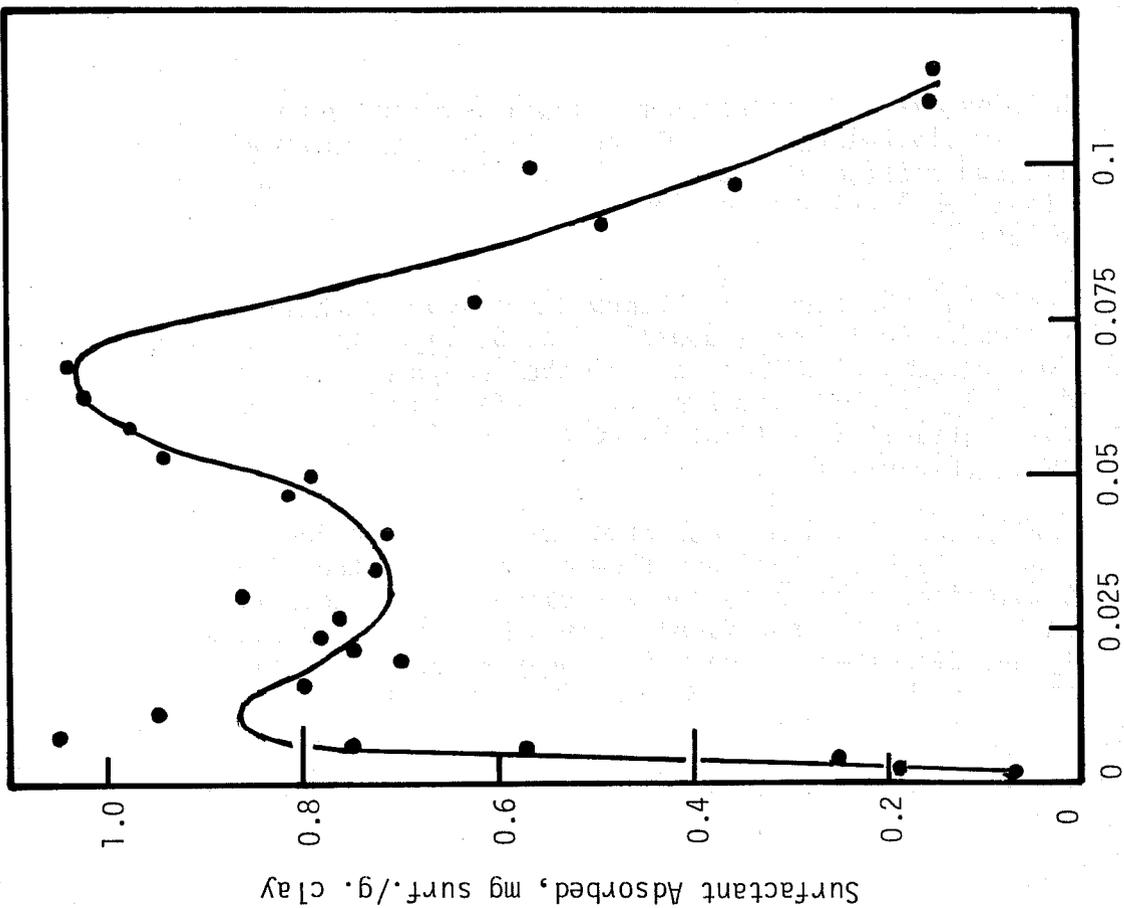


Figure IVB7. Equilibrium Adsorption of Surfactant on Cation-Exchanged Kaolin. $8-\phi C_{16}SO_3Na$ in DW equilibrated with 0.5 vol.% n-dodecane (95%).

3. Polymer Adsorption: Measure influence of NaCl concentration and oil on polyacrylamide adsorption on Na-kaolin and raw kaolin.

No reliable data on polymer adsorption are yet available owing to lack of suitable method of polymer analysis. Intensive efforts to make use of optical methods based on turbidity or spectrophotometry have not been successful, particularly when used with cation-exchanged clay. The principal problem with these methods has been that the cation-exchanged kaolin becomes so well dispersed in the polymer solutions and their viscosity is so large when the polymer concentration exceeds about 200 ppm, that the clay cannot be centrifuged from the solution completely. The result is that turbidity due to the polymer is masked by turbidity due to clay or that the turbidity due to the suspended clay masks absorption by colored materials. Two chemical methods (which are essentially iodometric analyses) are being explored. One of these is a slight modification of the iodometric method described by Foshee et al. (1976). The second method being explored is quite similar.

C. State-of-The-Art Survey of Surfactant Losses By Precipitation

1. Survey the Published Literature and Analyze Papers as to Pertinent Information.

Investigators: Professor R.D. Walker, Jr., Mr. M. Cospers, Mr. J. Funk, Mrs. J. Meister, Mr. G. Purcella

Two graduate students, Mr. Cospers and Mr. Purcella, have been recruited to work on this task, and they have been oriented as to the problem and the methods we plan to employ. A substantial number of apparently relevant papers have been collected and are being analyzed. An information indexing system has been put into operation.

As noted earlier, there is a voluminous literature in restricted areas, and a great paucity in other more relevant subject areas. For example there is a substantial body of published literature dealing with the influence of electrolytes on the CMC of surfactants. However, very few direct references to surfactant salting-out have been found, even in the papers which have as their principal subject the influence of electrolytes on the properties of surfactants. Insofar as the literature search has proceeded, very few quantitative studies of salting-out of surfactants appear to have been published.

On the other hand, the literature on surfactant precipitation by multivalent cations (such as soap precipitation by hard water) is so voluminous as to be impractical of analysis in the time available. In the area of surfactant precipitation by multivalent cations, it appears that a major problem will be the selection of the most pertinent literature and the analysis of related factors, such as the influence of oil on precipitation.

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