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RESEARCH ON SURFACTANT-POLYMER OIL RECOVERY SYSTEMS

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University of Florida
Gainesville, Florida

U. S. DEPARTMENT OF ENERGY

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Project Status Report for January 1—March 31, 1979

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Union Oil Company
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Witco Chemical Corporation

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graduate student fellowship for the oil
recovery research program.

Summary

I. Interfacial Phenomena

The apparatus for studying ultrafiltration microemulsions through Nuclepore filters has been set up. The permeability of these filters to water-and oil-external microemulsions with different solubilized water contents was measured with filter pore diameters ranging from 150Å to 1000Å. It was expected that when the microemulsion droplet size was larger than the pore diameter, extra resistance to flow would be developed because the droplet would have to be deformed in order to pass through the smaller pore constrictions. The results showed that, however, as the solubilized water content (and hence the microemulsion droplet size) increased, the relative permeability of a 150Å Nuclepore filter to microemulsions remained more or less constant. Therefore, contrary to our expectations, the extra resistance to flow due to deformation of the microemulsion droplets was quite small. Currently, we are using the Nuclepore filter to study the diffusion of water soluble and oil-soluble tracers in microemulsions to ascertain whether this technique can be used to determine the external phase as well as the size of microemulsions.

The difference between H₂O and D₂O systems in solubilization, coacervation of aqueous surfactant solution and surfactant partitioning between oil and brine has been investigated. H₂O system was found to be more hydrophilic than the D₂O system which is the consequence of stronger hydration of surfactant and counterions in the H₂O system. Interfacial alcohol concentration as measured by the titration method was higher for the H₂O system. The results are consistent with the electrical resistance and dielectric relaxation measurements where it was shown that the interfacial polarization or surface potential was also higher in the H₂O system. From studies of counterion specificity, a semi-quantitative measure of the effect of hydration on solubilization in microemulsions is reported.

The effect of mixed electrolyte (NaCl and CaCl₂, NaCl and AlCl₃) on solubilization, interfacial tension and optimal salinity were reported. As CaCl₂ content is increased, the optimal NaCl concentration linearly decreases. This linear dependency seems to be independent of oil chain length of the systems as one mole of CaCl₂ was found to be equivalent to about 16 moles of NaCl for solubilization in middle-phase microemulsions for both dodecane and hexadecane systems. The addition of CaCl₂ did not change the interfacial tension appreciably as long as the NaCl concentration was reduced accordingly. Similar effects were observed for the NaCl/AlCl₃ system except that one mole of AlCl₃ was found to be equivalent to about 22 moles of NaCl in this study.

II. Polymer Rheology and Fluid Mechanics

This section is deleted from this report pending completion of work.

III. Thermodynamics

Theory

A method for predicting all thermodynamic properties of aqueous solutions of spherical and chain nonpolar substances has been essentially completed and gives very good agreement with experiment. Except for two effects, the complete expression for the thermodynamic properties associated with micellization have been written for a pure ionic surfactant and tests of the theoretical results have been initiated with mixed success.

Group contribution estimates of chain length effects on surfactant distribution coefficients at very low concentrations support the dramatic chain length effects observed between C_{12} and C_{16} sulfonates.

Experiment

Experimental observation of temperature, pressure and dissolved gas effects on the isotropic-anisotropic transitions of lyotropic liquid crystals apparently show that promotion of the anisotropic phase under pressure or with methane is a transient effect.

Phase behavior studies using temperature cycling show that surfactants behave differently with regard to stabilizing two or three phases as a function of increased salt and temperature. The difference in phase behavior of petroleum sulfonates and sodium stearate may indicate that the middle phase of petroleum sulfonates has a different structure.

Studies of phase behavior with raising and lowering temperatures through planned cycles also show differences. Apparently, many studies of phase behavior at room temperature have not reached equilibrium although temperature cycling would accelerate the approach to the ultimate state.

IV. Rock/Fluid Interactions

The salting-out behavior of SUL-FON-ATE AA10 (a commercial product having approximately the composition $C_{12}\phi SO_3Na$) and $2-\phi C_{12}SO_3Na$ (a synthetic monoisomeric surfactant) have been measured. SUL-FON-ATE AA10 can tolerate one wt.% NaCl but higher salt concentrations cause salting-out. Even one wt. % NaCl causes salting-out of $2-\phi C_{12}SO_3Na$. Neither surfactant partitions to oil in measurable amounts, regardless of either surfactant or salt concentrations.

A mechanism for surfactant salting-out by indifferent electrolytes is suggested. It is based on depression of surfactant ionization and of the CMC by added indifferent electrolyte leading to a condition in which the solubility of the sodium salt of the surfactant is exceeded and precipitation occurs.

Elementary analyses of calcium salts of several anionic surfactants confirmed that these materials can be represented by the formula CaA_2 , where A is the surfactant anion. No appreciable amount of sodium was found in the precipitate even though some of the precipitates were formed from micellar solutions. The precipitation behavior of calcium lauryl sulfate has been studied for four constant concentrations of calcium. Precipitation was first observed; this was followed by precipitate dissolution when excess surfactant was added. On the basis of estimates of the CMC of the surfactant at the electrolyte concentrations noted, it appeared that precipitate dissolution began for each calcium concentration before the CMC was reached.

Mechanisms have been postulated for both surfactant precipitation and precipitate dissolution. These emphasize surfactant dimerization and complex ion formation.

It was found that distilled water extracted no appreciable amount of calcium or magnesium from cation exchanged kaolin, but that one wt.% NaCl did. Moreover, earlier work with other clays suggested that brine can continue to extract multivalent cations from apparently well cation exchanged materials. The amounts of multivalent cations extracted by one wt.% NaCl are sufficient to cause significant surfactant precipitation.

On the basis of these and related observations two adsorption mechanisms have been proposed. A third mechanism, which is based on surfactant precipitation by multivalent cations and subsequent precipitate dissolution by excess surfactant, results in apparent adsorption with a maximum but actually involves no adsorption. The first adsorption mechanism results in a Langmuir-like adsorption isotherm modified by hemimicelle formation. It is believed to be due primarily to electrostatic attraction of surfactant anions to positively charged crystal sites. This mechanism, of course, leads to a well-defined adsorption plateau with the "shoulder" at an equilibrium surfactant concentration near the CMC.

The second adsorption mechanism is based on the attraction of surfactant anions to multivalent cations in the exchange sites. Multivalent cations are postulated as "bridges" between the adsorbent surface and the adsorbed surfactant.

Owing to the solubility of calcium surfactants in excess surfactant, this mechanism results in an adsorption isotherm with a maximum.

A third mechanism for apparent adsorption but actually based on precipitation involves either cation exchange with brine or extraction of multivalent cations from the adsorbent to result in surfactant precipitation and subsequent precipitate dissolution by excess surfactant. This mechanism would lead to an apparent adsorption isotherm with a maximum.

A reliable method of analysis for hydrolyzed polyacrylamides has been found which can be used when cation exchanged clay is being used as the adsorbent. It is based upon precipitation of the polymer by cupric ions, and analysis of the copper in the precipitate by the neocuproine method. Polymer adsorption experiments are in progress and the results available indicate that polymer adsorption on cation exchanged kaolin is small to negligible, while adsorption on raw kaolin (Ca and Mg in the exchange sites) is appreciable.

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I. INTERFACIAL PHENOMENA

Research Director: Professor D. O. Shah

Determine Microstructure of Multicomponent Surfactant Formulations

A. Set Up Instrumentation for Ultrafiltration

Investigator: Mr. S. I. Chou

Introduction:

The objective of this study was to develop a new technique to investigate the microstructure of microemulsions using Nuclepore filters (Nuclepore Corp., Pleasanton, CA) with pore diameter of 150Å to 1000Å and a thickness of 10μ. The concept assumes that when microemulsion droplet size is larger than the pore diameter, extra resistance to flow will be developed because the droplet has to be deformed in order to pass through. It was anticipated that the permeability of microemulsions would show a sudden decrease when the droplet size was greater than some critical value. The following experiments were designed to test this idea.

Materials and Methods:

The filter paper (polycarbonate) was mounted in a millipore in-line filtration apparatus. A CMP-2V pump (Laboratory Data Control) was used to provide constant flow rate of the solution. The pressure drop across the filter was measured by a pressure transducer and continuously recorded. Before each experiment, the system was thoroughly cleansed and dried to removed trace contaminants which might have caused phase separation of the microemulsion. The permeability of the microemulsion was determined from the pressure drop at several flow rates. The filter paper is apparently consistent judging from the permeability of water as shown in Table IA1.

Oil external microemulsions were prepared by adding brine (1.5% NaCl) to surfactant and alcohol solution in dodecane (10.75% TRS 10-410 and 2.23% IBA, w/w). Assuming uniform droplet size and constant interfacial area per surfactant molecule, the microemulsion droplet size increases with increasing solubilized water, here varied from 1.0 to 4.5 ml/gm surfactant. The relative permeability of these microemulsions through Nuclepore filters of 150Å pore diameter was measured and is shown in Table IA2. The calculated droplet diameters, also shown in Table IA2 were based on surface areas of 65Å² and 30Å² for surfactant and alcohol molecules as suggested by Hsieh (1977). The data scatter somewhat, but there is no evidence of sudden decrease of permeabilities. In fact, there is a trend, the permeabilities appear to increase slightly as the solubilized water amount is increased. Note that the largest calculated droplet diameter was 240Å which is much larger than the pore diameter (150Å). It seems that the interfacial resistance due to the deformation of microemulsion droplets is quite small.

Table IA1 Water Permeability Through Nuclepore Filters

Pore Diameter (Å)	150	300	500	800	1000
Q/P (ml/hr psi) Run (1)	0.611	0.79	2.52	13.7	38.4
(2)	0.604	0.732	2.60	13.6	38.4
(3)	0.634	0.553			
Average Permeability (10^{-7} Darcy)	2.6 ± 0.1	2.9 ± 0.6	10.7 ± 0.2	56.9 ± 0.4	164

Table IA2 Ultrafiltration of Oil-External Microemulsions^{a,b}

Solubilized Brine (ml/gm surfactant)	1	2	3	3.5	4	4.5
Viscosity (cp)	5.6	8.9	10.2	11.0	10.5	10.4
Droplet Diameter, Calc. (Å)	87	131	175	197	219	240
Relative Permeability, k_r^c Run (1)	1.15	1.46	1.15	1.5	1.32	1.7
(2)	1.24	1.3	1.67	1.3	1.66	1.47
(3)				2.2	1.67	2.0

I-3

a 1 gm TRS 10-419, 8 gm dodecane and 0.305 gm IBA add 1.5% NaCl brine as shown

b prefilter at 1000Å, filter at 150Å

c $k_r \equiv (Q \cdot \mu / \Delta P)_{\text{microemulsion}} / (Q \cdot \mu / \Delta P)_{H_2O}$

Currently, we are using the Nuclepore filter as the membrane for equilibrium diffusion of oil-soluble and water-soluble tracers in microemulsions. This technique may be able to detect the external phase as well as the size of microemulsions.

B. Determine the Effect of D_2O Substitution for H_2O on Middle Phase Formation and Solubilization Parameters

Investigator: Mr. S.I. Chou

Introduction:

Petroleum sulfonates used in tertiary oil recovery often form a surfactant-rich phase upon mixing with alcohol, oil and brine which may be in equilibrium with one or more phases. Theories for the thermodynamic stability of microemulsions such as that of Ruckenstein and Chi (1975) show the importance of electrostatic effects on size and stability. A significant factor may be the hydration of the counter ions similar to that on micelles (Mukerjee, et al., 1967). Although H_2O and D_2O are chemically similar and their dielectric constants are almost identical, there may be differences in hydrogen (deuterium) bonding between H_2O and D_2O with the surfactant head groups and counterions as has been postulated for their interactions with phospholipids (Walter and Hayes, 1971) and proteins (Weber and Teale, 1965). Therefore, the effects of H_2O and D_2O on microemulsion stability have been studied. The following phenomena are reported: (1) solubilization in middle-phase microemulsions, (2) coacervation of aqueous surfactants solutions, (3) maximum solubilization of brine in oil external microemulsions, (4) alcohol/surfactant ratio at the micellar interface of oil-external microemulsion, (5) partitioning of surfactant between oil and brine at low surfactant concentrations, (6) electrical resistance and (7) dielectric relaxation of oil-external microemulsions, and (8) counter-ion specificity in the solubilization in middle-phase microemulsions.

Materials and Methods:

Petroleum sulfonate TRS 10-410 (Witco Chemical Co.) was used as received. This surfactant has an average equivalent weight of 418 and is 62% active. Isobutanol (IBA) of 99.9% purity and dodecane of 99% purity were obtained from Chemical Samples Co. The D_2O was > 99.8% deuterium (Stohler Isotope Chemicals). Deionized, distilled H_2O was used. Samples were prepared by first making solutions of surfactant and alcohol in oil of desired compositions and subsequently mixed with H_2O or D_2O brine. In the study of solubilization in microemulsion and surfactant partitioning, the samples were allowed to equilibrate in a constant temperature bath ($25 \pm 0.1^\circ C$) for about one and a half months. Other experiments were performed at room temperature ($23 \pm 1^\circ C$). Electrical resistance was measured by a Beckman model RC16B2 AC bridge and a conductivity cell of cell constant 1 cm^{-1} (Beckman G1) at 1000 Hz. Dielectric measurements were made by a Hewlett-Packard 250B RX meter. The dielectric cell was described elsewhere (Bansal, et al, 1978). The details of calculation of dielectric parameters were according to Sachs, et al. (1970).

Results and Discussion:

Within suitable range of compositions, the surfactant-alcohol-oil-brine system forms three phases with practically all the surfactant in the middle-phase. The amount of oil and water solubilized in the middle-phase microemulsion is shown in Figure IB1. As salinity (%NaCl) increases, the amount of oil solubilized (V_o) increases while the amount of water solubilized (V_w) decreases. The salinity at which equal solubilization of oil and water occurs is defined as the optimal salinity of the system (Healy and Reed, 1974). It is smaller for D_2O systems than H_2O systems. The two systems are identical if the D_2O system is ~0.27% NaCl higher in salinity. The H_2O system requires a higher salinity to achieve the hydrophilic-lipophilic balance for optimal salinity.

Coacervation of the aqueous surfactant solution supports this hypothesis. Upon increasing salinity of the surfactant solution, phase separation occurs with practically all the surfactant in the coacervate phase. Figure IB2 shows the volume fraction of coacervate phase as a function of salinity. The salinity required to form a given volume fraction of coacervate phase is higher for the H_2O system. If the H_2O system is considered as more hydrophilic, a higher concentration of counter ions (Na^+) is required to compress the electrical double layer around the dispersed phase to the point needed to cause phase separation. The difference between H_2O and D_2O system in coacervation salinity is about 0.3% NaCl, approximately the same as the 0.27% NaCl difference in solubilization in middle-phase microemulsion (Figure IB1).

Surfactant partition coefficients (defined as surfactant concentration in oil divided by that in water) are also different in the two systems. As shown in Figure IB3, the partition coefficients are always higher in the D_2O systems. This is consistent with the concept that the surfactant is more hydrophilic in H_2O systems.

Figure IB4 shows the maximal solubilization of brine (1.5% NaCl) in oil-external microemulsions as a function of alcohol/surfactant ratio. Since isobutanol (IBA) is preferentially soluble in oil, increasing the alcohol/surfactant ratio has the same effect as increasing salinity. As shown in Figure IB4, the difference between H_2O and D_2O system is quite significant. Each system has an alcohol/surfactant ratio for maximal solubilization which is lower for D_2O . The effect of alcohol concentration on the solubilization of microemulsion is a complicated one. Qualitatively, alcohol influences the following: (1) distribution of alcohol between interfacial phase and bulk phases, (2) surface potential of micelle, (3) distribution of surfactant between interfacial phase and bulk

SOLUBILIZATION IN MIDDLE-PHASE MICROEMULSION OF
H₂O AND D₂O SYSTEMS AS A FUNCTION OF SALINITY.

Figure IB1

COACERVATION OF SURFACTANT SOLUTION IN H_2O OR D_2O
BRINE VS SALINITY

Figure IB2

PARTITION COEFFICIENT OF H_2O AND D_2O SYSTEMS AS
A FUNCTION OF SURFACTANT CONCENTRATION.

Figure IB3

MAXIMAL SOLUBILIZATION OF BRINE IN W/O MICROEMULSION
IN H_2O AND D_2O SYSTEMS AS A FUNCTION OF
ALCOHOL/SURFACTANT RATIO.

Figure IB4

phase, (4) specific free energy of the interfacial film and (5) curvature and packing condition of interfacial film. While we will not elucidate all these effects in this study, it will be shown that the interfacial alcohol concentration and surface potential of (water-swollen) micelles are higher in the H_2O system.

The amount of alcohol in an interfacial film can be approximately determined by the titration method (Bowcott and Schulman, 1955). At constant brine/surfactant ratio, the amount of alcohol required to form a microemulsion is measured as a function of oil/surfactant ratio, as shown in Figure IB5. In the present system, the amount of alcohol required linearly increases with the oil/surfactant ratio. The intercept is regarded as the alcohol/surfactant ratio at the micellar interface, assuming negligible partition of alcohol into brine. Figure IB5 shows that the interfacial alcohol concentration is higher in the H_2O system. If the degree of ionization of interfacial surfactant molecules is higher in the H_2O system, more alcohol molecules would be adsorbed in the interfacial film. Electrical resistance of the two systems supports this view. As shown in Figure IB6, the specific electrical resistance (at 1KHz) of the D_2O microemulsion is more than one order of magnitude higher than that of the H_2O system for all compositions studied.

Dielectric measurements on D_2O and H_2O containing systems showed significant differences in their behavior. Preliminary results on dielectric parameters in the frequency range of 1 to 100 MHz are shown in Figures IB7 and IB8 for H_2O and D_2O microemulsions. A detailed study on these systems has just been completed and the results will be reported at a later date.

The free energy of solvation of ions (with few exceptions) is lower (more negative) in H_2O than D_2O (Arnett and McKelvey, 1969). The difference between free energies of solvation in the two solvents is the free energy of transfer, which depends on the ionic species. The following experiment is designed to give a semi-quantitative measure of the importance of hydration effects on solubilization in microemulsions. A surfactant and alcohol solution (6.25% TRS 10-410 + 3.75% IBA in dodecane, w/w) is equilibrated with equal volumes of brine of different salts ($LiCl$, $NaCl$, KCl and NH_4Cl). The salinity of each salt is at the optimal salinity of the H_2O system. At this point the difference between H_2O and D_2O systems will be maximal because the variation of the amount of solubilized brine and oil is greatest in the neighborhood of optimal salinity. The ratio of solubilized oil (or water) in D_2O systems over that in H_2O systems is shown in Figure IB9 as a function of free energy of transfer of the counter-ion from H_2O to D_2O . The values of free energy of transfer were taken from the review paper by Arnett and McKelvey (1969).

MINIMUM ALCOHOL REQUIRED TO FORM W/O MICROEMULSIONS
IN H_2O AND D_2O SYSTEMS AS A FUNCTION OF OIL/SURFACTANT
RATIO.

Figure IB5

ELECTRICAL RESISTANCE (1 KHz) OF MICROEMULSIONS FORMED BY H₂O OR D₂O BRINE AS A FUNCTION OF WATER CONTENT.

Figure IB6

DIELECTRIC CONSTANT OF OIL-EXTERNAL MICROEMULSIONS FORMED BY H₂O OR D₂O BRINE

Figure IB7

GLOBAL LOSS FACTOR OF OIL-EXTERNAL MICROEMULSIONS FORMED BY
H₂O OR D₂O BRINE.

Figure IB8

The ratio of solubilization between D_2O and H_2O is largest when the free energy of transfer of counter ion is largest. Extrapolating to zero free energy of transfer, the ratio of solubilized oil is 1.3 and the ratio of solubilized water is 0.5. These values are probably related to the hydration of surfactant ions.

Conclusions:

The difference between H_2O and D_2O systems in relation to solubilization and interfacial phenomena has been reported. The H_2O systems are significantly more hydrophilic in terms of solubilization, coacervation and surfactant partitioning than are D_2O systems. The results can be interpreted as stronger hydration of surfactant and counterions in H_2O . From studies of counter ion specificity, the effect of hydration of surfactant and counter ion on the solubilization in micro-emulsion has been determined.

CORRELATION OF WATER ISOTOPE EFFECTS ON SOLUBILIZATION
IN MIDDLE-PHASE MICROEMULSION WITH FREE ENERGY OF
TRANSFER OF COUNTER IONS

Figure IB9

C. Determine the Effect of Mono-, Di-, and Tri-valent Ions on Optimal Salinity of TRS10-410 + IBA + Oil + Brine Systems

Investigator: Mr. S.I. Chou

Introduction:

The importance of the effect of counterions on the stability of colloidal systems is well-known. Some of the earliest studies were due to Schulze (1882) and Hardy (1900^{a,b}). They found that the effectiveness of electrolytes to induce instability of lyophobic colloids is critically dependent on the valency of counterions (ions opposite in charge to that of the colloidal particles). One mole of divalent ion can be as effective as 40-80 moles of monovalent ion. Theoretical calculations based on the DLVO theory (Derjagin and Landau, 1941; Verwey and Overbeek, 1948) also showed that, for large particles with high surface potential, the critical electrolyte concentration for the onset of instability was proportional to the inverse 6th power of the valency of counterions. The calculations are qualitatively consistent with the Schulze-Hardy rule.

In this study the effect of mixed electrolytes (NaCl and CaCl_2 , NaCl and AlCl_3) on solubilization and interfacial tension in middle-phase microemulsion systems will be reported.

Materials and Methods

Petroleum sulfonates, TRS 10-410 (Witco Chemical Company) was used as received. The surfactant has an average molecular weight 418 and is 62% active. Isobutanol (99.9% pure) and dodecane (99% pure) were obtained from Chemical Samples Company. The samples were put on a rotating tumbler for 24 hours and then allowed to equilibrate in a constant temperature bath maintained at $25 \pm 0.1^\circ\text{C}$ for about one and a half months. Interfacial tension was measured by a spinning drop tensiometer.

Results and Discussion:

The surfactant solution of 6.25% TRS 10-410 and 3.75% IBA in dodecane or hexadecane was equilibrated with equal volume of brine at $25 \pm 0.1^\circ\text{C}$. At equilibrium, the solubilization parameters were measured and are shown in Figures IC1 and IC2. As CaCl_2 content increases, the optimal NaCl concentration (at which equal solubilization of oil and water occurs) decreases. The solubilization parameter, interfacial tension and optimal salinity of the system containing CaCl_2 alone were also measured as shown in Figures IC3 and IC4. From these data, one can correlate the optimal NaCl concentration with the CaCl_2 content of the system. This is shown in Figure IC5. It was found that the optimal NaCl concentration linearly decreases with the CaCl_2 content.

THE EFFECT OF SALINITY ON THE SOLUBILIZATION PARAMETER OF 6.25% TRSIO-410+3.75% IBA IN DODECANE EQUILIBRATED WITH EQUAL VOLUMES OF BRINE CONTAINING CaCl_2

Figure ICL

THE EFFECT OF SALINITY ON THE SOLUBILIZATION PARAMETER OF 6.25% TRS10-410+3.75% IBA
IN HEXADECANE EQUILIBRATED WITH EQUAL VOLUMES OF BRINE CONTAINING CaCl_2

Figure IC2

THE EFFECT OF CaCl_2 CONCENTRATION ON THE SOLUBILIZATION PARAMETERS AND INTERFACIAL TENSIONS OF 6.25% TRSIO-410 + 3.75% IBA IN DODECANE EQUILIBRATED WITH BRINE.

Figure IC3

THE EFFECT OF CaCl_2 CONCENTRATION ON THE SOLUBILIZATION
PARAMETERS OF 6.25% TRSIO-410 AND 3.75% IBA IN HEXADECANE
EQUILIBRATED WITH BRINE

Figure IC4

CORRELATION OF THE OPTIMAL SALINITY OF NaCl/CaCl₂ BRINE;
THE DATA REPRESENTS CONJUGATE NaCl & CaCl₂ CONCENTRATIONS
GIVING EQUAL SOLUBILIZATION OF WATER AND OIL IN MIDDLE-
PHASE MICROEMULSION

Figure IC5

Furthermore, the linear dependency is independent of oil chain length, (dodecane and hexadecane). From the slope of the lines, it was found that one mole of CaCl_2 is equivalent to about 16 moles of NaCl for solubilization in middle-phase microemulsion. This correlation allows prediction of the optimal salinity of CaCl_2 systems from optimal NaCl salinities of the same system.

Interfacial tensions for dodecane systems were measured. Figure IC6 shows that the addition of CaCl_2 does not change the interfacial tension appreciably, if the NaCl concentration is reduced accordingly. When the systems were at their corresponding optimal salinities, the interfacial tension of CaCl_2 systems was slightly lower, consistent with the solubilization data shown in Figure IC1.

The effect on solubilization and interfacial tension by adding AlCl_3 to NaCl systems was quite similar to that for NaCl/ CaCl_2 systems. Therefore, this system was not studied extensively. Some preliminary results are shown in Figures IC7 and IC8 and it is found that one mole of AlCl_3 is equivalent to approximately 22 moles of NaCl in the present system.

We have also studied the effect of mixed electrolytes on coacervation of aqueous surfactant solution and solubilization of water in w/o microemulsion (Chou and Shah, 1979). The complete results, which will be presented in future reports, indicate that the effect of counterion valency is the same for coacervation and solubilization in middle-phase microemulsions but it is distinctly different for solubilization in w/o microemulsions.

THE EFFECT OF SALINITY ON THE INTERFACIAL TENSIONS OF 625% TRSIO-410+3.75% IBA
IN DODECANE EQUILIBRATED WITH EQUAL VOLUMES OF BRINE CONTAINING CaCl_2

Figure IC6

THE EFFECT OF SALINITY ON THE SOLUBILIZATION PARAMETERS OF 6.25% TRSIO-410
+ 3.75% IBA IN DODECANE EQUILIBRATED WITH EQUAL VOLUMES OF BRINE CONTAINING AlCl_3

Figure IC7

THE EFFECT OF SALINITY ON THE INTERFACIAL TENSION OF 6.25% TRSIO-410 + 3.75% IBA
IN DODECANE EQUILIBRATED WITH EQUAL VOLUMES OF BRINE CONTAINING AlCl_3

Figure 1C8

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II. POLYMER RHEOLOGY AND FLUID MECHANICS

(This section is deleted from this report pending completion of work).

III. THERMODYNAMIC PROPERTIES

Research Director: Professor J.P. O'Connell

A. Theory

1. Complete expressions will be written relating the CMC, mean aggregate size and size distribution to the above quantities and functional relations associated with surfactant interactions (head group repulsion, chain attraction and conformation) in pure component micelles. Appropriate functions for the interactions will be proposed and testing of their validity will begin for pure ionic and nonionic surfactants.

Investigator: Mr. R.J. Brugman

A method for predicting all thermodynamic properties of aqueous solution of spherical and chain nonpolar substances has been essentially completed and gives very good agreement with experiment. The expressions are substantially the same as reported for the second quarter 1978-79 except that the curvature dependence of the surface tension is fitted for the function

$$\delta = - 8.3195 + 2.6052 \times 10^3/T - 1.8993 \times 10^5/T^2$$

Results for the free energy (solubility), entropy, enthalpy and heat capacity for several gases are shown in Table IIIA1 reproduced from the Ph.D. Dissertation of Robert Brugman (1979). In general the agreement is considerably better than ever obtained previously (such as Pierotti, 1965) but not within experimental error. However, we feel this is adequate to proceed to modelling hydrocarbon chains.

For these species, the relations are the same as given in the above report. The four interaction integrals are complex functions of chain length and temperature. After analyzing the solubility data for paraffins from methane to decane the length of chain segment has been fitted to a quadratic in inverse temperature. Some results are given in Table IIIA2. The agreement is less satisfying than above probably because the interaction terms are less well described by the first order terms. One surprising result is that the large negative entropy of solution arises not from the cavity term as in the spherical gases, but from the interaction term, especially at higher temperatures. However, the cavity term still contributes most to the heat capacity. Whether this is to be expected is not known, and is being checked. While comparisons of all properties of long chain paraffins in water is not possible, the chain length effects on paraffinic surfactants at infinite

Table IIIA1
Thermodynamic Properties of Aqueous Solution of Spherical Gases

Solute	T(°K)	$\frac{\Delta \bar{G}^{\circ}_{cal}}{RT}$	$\frac{\Delta \bar{G}^{\circ}_{exp}}{RT}$	$\frac{\Delta \bar{H}^{\circ}_{cal}}{RT}$	$\frac{\Delta \bar{H}^{\circ}_{exp}}{RT}$	$\frac{\Delta \bar{S}^{\circ}_{cal}}{R}$	$\frac{\Delta \bar{S}^{\circ}_{exp}}{R}$	$\frac{\Delta C_p^{\circ}_{cal}}{R}$	$\frac{\Delta C_p^{\circ}_{exp}}{R}$
He	277.15	11.79	11.802±.001	-1.51	-1.399±.152	-13.30	-13.20±.08	17.33	14.69±2.1
	298.15	11.86	11.863±.001	-0.23	-0.290±.020	-12.08	-12.15±.02	16.30	14.18±0.6
	323.15	11.82	11.841±.002	1.05	0.818±.091	-10.77	-11.02±.09	16.55	13.85±2.2
	358.15	11.63	11.691±.005	2.65	2.074±.387	-8.99	-9.62±.41	18.35	13.32±3.5
Ne	277.15	11.55	11.543±.001	-2.95	-3.050±.111	-14.50	-14.59±.11	18.60	18.82±2.9
	298.15	11.71	11.710±.002	-1.44	-1.539±.026	-13.15	-13.25±.03	18.63	18.13±0.9
	323.15	11.76	11.773±.035	0.15	-0.037±.133	-11.61	-11.81±.13	19.58	17.70±3.0
	358.15	11.64	11.689±.003	2.15	1.678±.533	-9.49	-10.01±.57	21.81	17.13±4.6
Ar	277.15	10.16	10.159±.002	-6.93	-6.969±.077	-17.09	-17.13±.08	21.92	23.91±3.0
	298.15	10.59	10.588±.009	-4.82	-4.825±.034	-15.41	-15.42±.30	24.14	23.48±2.0
	323.15	10.88	10.883±.068	-2.48	-2.644±.288	-13.37	-13.53±.04	26.52	23.11±4.8
	358.15	10.99	11.031±	0.50	-0.138±.893	-10.49	-11.17±.96	29.52	22.53±7.0
Kr	277.15	9.42	9.457±	-9.19	-8.727±.099	-18.61	-18.18±.10	25.69	26.44±3.4
	298.15	10.00	10.004±	-6.64	-6.283±.035	-16.64	-16.29±.04	28.45	25.60±0.9
	323.15	10.42	10.410±	-3.81	-3.840±.171	-14.23	-14.25±.18	31.21	25.08±4.0
	358.15	10.63	10.657±	-0.23	-1.031±.734	-10.86	-11.69±.79	34.33	24.66±7.1

Table IIIA1 (Continued)

Solute	T (°K)	$\frac{\Delta \bar{G}_{cal}^{\circ}}{RT}$	$\frac{\Delta \bar{G}_{exp}^{\circ}}{RT}$	$\frac{\Delta \bar{H}_{cal}^{\circ}}{RT}$	$\frac{\Delta \bar{H}_{exp}^{\circ}}{RT}$	$\frac{\Delta \bar{S}_{cal}^{\circ}}{R}$	$\frac{\Delta \bar{S}_{exp}^{\circ}}{R}$	$\frac{\Delta \bar{C}_p^{\circ}}{R}$	$\frac{\Delta \bar{C}_p^{\circ}}{R}$
Xe	277.15	8.69	8.775±.001	-11.96	-10.696±.125	-20.65	-19.47±.12	31.72	31.41±4.2
	298.15	9.45	9.448±.001	-8.75	-7.769±.040	-18.19	-17.22±.04	35.36	30.56±1.3
	323.15	10.01	9.953±.006	-5.20	-4.829±.231	-15.21	-14.78±.24	38.58	29.98±5.1
	358.15	10.31	10.272±.062	-0.76	-1.444±.926	-11.07	-11.72±.99	41.72	29.42±8.6
CH ₄	277.15	10.04	10.104±.005	-8.87	-7.954±.30	-18.91	-18.06±.30	27.42	26.71±5.7
	298.15	10.59	10.596±.004	-6.21	-5.549±.05	-16.81	-16.14±.04	30.17	25.55±2.5
	323.15	10.98	10.946±.003	-3.29	-3.188±.07	-14.27	-14.14±.07	32.86	24.48±1.5
	358.15	11.13	11.333±.008	0.39	-0.526±.28	-10.73	-11.66±.29	35.84	23.85±5.1
CF ₄	277.15	11.90	11.891±.003	-9.65	-10.103±.271	-21.55	-21.99±.29	39.06	48.44±7.3
	298.15	12.48	12.478±.002	-6.10	-6.052±.059	-18.58	-18.53±.06	42.25	46.55±1.7
	323.15	12.81	12.801±.005	-2.25	-2.032±.300	-15.06	-14.84±.30	44.89	45.44±7.2
	358.15	12.80	12.769±.083	2.48	2.563±1.29	-10.32	-10.21±.38	47.25	44.68±13.5
SF ₆	277.15	11.58	11.548±.008	-12.53	-13.531±.298	-24.11	-25.08±.30	49.56	65.81±8.9
	298.15	12.33	12.330±.010	-8.01	-8.040±.074	-20.34	-20.38±.08	53.50	63.01±1.5
	323.15	12.78	12.764±.005	-3.13	-2.616±.352	-15.91	-15.38±.36	56.35	61.37±9.0
	358.15	12.79	12.708±.101	2.79	3.572±1.64	-10.00	-9.13±1.74	58.29	60.24±17.6
neo-C ₅ H ₁₂	277.15	10.42	10.400±.087	-16.97	-17.276±2.0	-27.39	-27.66±1.94	65.09	69.73±22.6
	298.15	11.44	11.441±.010	-11.00	-11.306±0.6	-22.44	-22.75±.58	69.97	65.58±14.2
	323.15	12.07	12.114±.015	-4.61	-5.499±0.23	-16.68	-17.61±.22	72.90	63.47±8.4
	358.15	12.14	12.366±.045	3.04	1.152±1.26	-9.10	-11.19±1.30	73.96	62.33±17.5

Table IIIA2

Thermodynamic Properties of Solution of Gaseous Hydrocarbons

Solute	T(°K)	$\frac{\Delta \bar{G}_{\text{cal}}^{\circ}}{RT}$	$\frac{\Delta \bar{G}_{\text{exp}}^{\circ}}{RT}$	$\frac{\Delta \bar{H}_{\text{cal}}^{\circ}}{RT}$	$\frac{\Delta \bar{H}_{\text{exp}}^{\circ}}{RT}$	$\frac{\Delta \bar{S}_{\text{cal}}^{\circ}}{R}$	$\frac{\Delta \bar{S}_{\text{exp}}^{\circ}}{R}$	$\frac{\Delta \bar{C}_p^{\circ}}{R}$	$\frac{\Delta \bar{C}_p^{\circ}}{R}$
CH ₄	277.15	10.05	10.104±.005	-8.84	-7.954±.30	-13.88	-18.057±.30	27.17	26.709±5.7
	298.15	10.60	10.596±.004	-6.19	-5.549±.05	-16.79	-16.145±.04	30.04	25.551±2.5
	323.15	10.98	10.946±.003	-3.28	-3.188±.07	-14.26	-14.137±.07	32.78	24.484±1.5
	358.15	11.12	11.134±.008	0.40	-0.526±.28	-10.73	-11.661±.29	35.80	23.845±5.1
C ₂ H ₆	277.15	9.62	9.601±.008	-11.13	-11.441±.43	-20.76	-21.042±.42	40.54	38.777±8.3
	298.15	10.31	10.307±.006	-7.69	-7.952±.07	-18.00	-18.259±.06	35.28	37.091±3.6
	323.15	10.79	10.807±.003	-4.55	-4.535±.10	-15.34	-15.340±.11	30.93	35.496±2.1
	358.15	11.09	11.072±.010	-1.29	-0.683±.41	-12.38	-11.751±.42	26.87	34.580±7.4
C ₃ H ₈	277.15	9.73	9.078±.009	-12.91	-13.284±.53	-22.64	-22.995±.52	48.03	47.700±10.2
	298.15	10.52	10.521±.007	-8.90	-9.052±.08	-19.42	-19.577±.08	40.63	45.591±4.4
	323.15	11.09	11.081±.006	-5.33	-4.909±.13	-16.42	-15.989±.13	34.00	43.598±2.6
	358.15	11.45	11.342±.010	-1.86	-0.248±.50	-13.30	-11.590±.51	26.80	42.416±9.0
C ₄ H ₁₀	277.15	9.79	9.809±.011	-15.47	-14.824±.54	-25.26	-24.635±.53	62.39	48.133±10.4
	298.15	10.73	10.729±.006	-10.38	-10.452±.08	-21.10	-21.183±.08	51.85	46.059±4.5
	323.15	11.38	11.395±.005	-5.97	-6.163±.13	-17.34	-17.559±.13	41.72	44.117±2.6
	358.15	11.73	11.775±.011	-4.20	-1.325±.52	-15.93	-13.100±.52	18.50	42.989±9.2

dilution is possible using the best capacity data of Leduc, et al (1974). The data show each segment of the chain contributes about 10-10.5 to $\Delta C_p^\circ/R$. The present theory predicts about 8-8.5 for this value.

Finally, an attempt was made to predict the chain length effects for micellization for alkyl sulfates using the above methods for the hydrophobic effects and our previous models for electrostatic effects. The length effects for free energy and entropy were weaker than experiment while the enthalpies were too positive even though the electrostatic charge effects (making the values even more positive) were ignored. The inadequacies of the model are likely to include incorrect energy effects of hydrocarbon chains in micelles and restriction of the head groups to the micelle surface. Means of attacking these effects are being devised. The milestone has not been met completely.

In the rock-fluid interaction sections, it has been reported that aqueous-oleic distribution coefficients for surfactants change dramatically with chain length. A brief investigation of group contribution methods for effects of alkyl chains on aromatic rings (Tsonopoulos and Prausnitz, 1971 and Pierotti, et al., 1959) shows that this effect on the infinite dilution distribution coefficient, which goes as the ratio of activity coefficients of the surfactant in the two phases, should be given by the following relation for alkyl benzene sulfonates

$$\ln K_n^\infty - \ln K_{n'}^\infty = - .00113[(n_o - n)^2 - (n_o - n')^2] + 1.073\left[\frac{1}{n-4} - \frac{1}{n'-4}\right] - 1.34 (n - n')$$

where n_o is the oil chain carbon number and n and n' are the (effective) surfactant chain lengths. For example in the cases of sodium dodecyl benzene sulfonate ($n=18$) and sodium hexadecylbenzene sulfonate ($n' = 22$) sulfonate with n -dodecane ($n_o = 12$) as oil, $K_{12}^\infty/K_{16}^\infty = 230$ which means that if the hexadecyl is found roughly equally partitioned between the aqueous and oleic phases, the dodecyl surfactant should be found essentially completely in the aqueous phase, as it is. It may be possible to extend such arguments to systems where micellization occurs in one or more phases.

B. Experiment

1. The influence on the structural transition of the potassium oleate liquid crystal by dissolved CH_4 and CO_2 will be studied up to their saturation concentrations at 100 bar.

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

Somewhat more thorough investigation of the influence of pressure, temperature and dissolved gas on the anisotropic isotropic transition of the lyotropic potassium oleate liquid crystal has been completed. While thermal control of the system left something to be desired, we are reasonably confident that previously observed anisotropic stability at elevated pressure and dissolved gas was a transient effect.

This study will be completed within the present quarter to finally answer this question.

2. Phase Equilibrium and Temperature Effects in Concentrated Surfactant Solutions

Investigator: Ms. Charlotte Chen

Phase behavior studies of different two- and three-phase surfactant solutions at higher concentrations show unusual behavior. For example, petroleum sulfonate systems prepared as two-phase (water external) at room temperature will become three phases at higher temperatures. However, sodium stearate systems mixed as three phases at room temperature can become water external two-phase systems when the temperature is above 45°C . There is evidence that these systems may have different middle phase structures, based on electrical conductivity and dielectric behavior, the stearate system being oil-continuous. The different temperature behavior supports the possibility of more than one structure for the middle phase.

We have also found that when the above samples are returned to room temperature, only the stearate system returns to the original phases. The sulfonate system remains in the higher temperature form even through several cycles. It is possible that the initial mixture behavior of the sulfonate system is non-equilibrium, perhaps calling into question some previous conclusions based on room temperature measurements. We expect temperature cycling to aid in reaching equilibrium.

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IV. ROCK/FLUID INTERACTIONS

Research Director: Professor Robert D. Walker, Jr.

A. Surfactant/Polymer Precipitation

1. Surfactant Salting-Out: Apply Scanning Electron Microscopy, Energy Dispersive X-ray Analysis and Chemical Analysis of Surfactant to Characterize Salted-Out Material. Measure Size Distribution of Aggregates, and Explore Common Ion Effect on Extent of Ionization.

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

Scanning Electron Microscopy, EDXA, and Chemical Analysis

This work is still in progress and will be described in a later report. Preliminary results suggest that the salted-out material is the sodium salt of the surfactant, more or less poorly crystallized.

Surfactant Salting-Out By Indifferent Electrolytes

Salting-out of SUL-FON-ATE AA10 (approx. $C_{12}\phi SO_3Na$) and $2-\phi C_{12}SO_3Na$ (a pure monoisomeric surfactant made available to us by Dr. S.E. McGuire, Conoco) was carried out by the procedures described in the last quarterly report (Project Status Report Sept. 1-Dec. 31, 1978, U.S.DOE Contract No. EW-78-S-19-0008). These results are shown in Figures IVA1 and IVA2.

In Figure IVA1 the influence of both surfactant and NaCl concentration are shown for the salting-out of Cities Service SUL-FON-ATE AA10. These data indicate that no salting-out of this surfactant by 1 wt.% NaCl occurs up to 4 wt.% surfactant (higher concentrations were not studied). However, salting-out begins in 2 wt.% NaCl when the surfactant concentration reaches 0.008 wt.% and becomes almost complete when the surfactant concentration exceeds about 0.1 wt.%.

Salting-out for Conoco $2-\phi C_{12}SO_3Na$ by 1 wt.% NaCl are shown in Figure IVA2. Owing to the very limited amount of this surfactant which was available, only one NaCl concentration was studied. The general shape of the salting-out curve is similar to the curve shapes observed for SUL-FON-ATE AA10, but the entire curve is translated to a much lower surfactant concentration. Moreover, it should be recalled that SUL-FON-ATE AA10 was not salted-out by 1 wt.% NaCl. It appears, therefore, that some of the components in SUL-FON-ATE AA10 are able to resist salting-out to a very considerable degree.

Figure IVA1. Salting-Out of SUL-FON-ATE AA10

Figure IVA2. Salting-Out of $2-\phi \text{ C}_{12}\text{SO}_3\text{Na}$
in 1% NaCl

Partitioning to Oil

It may be recalled from the last quarterly report that 8- ϕ C₁₆S₃Na (UT-1) was salted-out readily by NaCl and that it partitioned to oil (n-dodecane) in a manner strongly dependent on NaCl concentration (See Figures IVA4, 5, and 6 of that report). Some partitioning to oil occurred even in distilled water and it occurred to a measurable extent for all surfactant concentrations. In contrast, neither 2- ϕ C₁₂S₃Na nor SUL-FON-ATE AAL0 partitioned to n-dodecane at any surfactant or NaCl concentration studied. It is clear, therefore, that a change in hydrocarbon chain length from 12 to 16 makes a tremendous difference in the tendency of the surfactant to salt-out. The visible evidence is striking in that the presence of oil makes no difference in the appearance or the persistence of salted-out C₁₂ surfactants whereas no salting-out is observed with the C₁₆ surfactant when oil is present.

The O/W partition coefficient is clearly near zero for the dodecylbenzene sulfonates for all surfactant and NaCl concentrations, but for 8- ϕ C₁₆S₃Na it varies from about 10⁻² in distilled water to about 10⁻¹ in 1 wt.% NaCl. This finding has obvious consequences for the surfactant-polymer flooding process, but its full implications do not yet appear clear. Incidentally, Professor J.P. O'Connell, using group contribution methods for estimation of partition coefficients, has concluded that the behavior noted is approximately that which is to be expected theoretically.

Suggested Mechanism For Surfactant Salting-Out

In a mixture containing an anionic surfactant, NA, an indifferent electrolyte, NX, water, W, and a hydrocarbon oil, O, the dissolution, ionization, micellization, salting-out, and partitioning to oil of a surfactant can be represented as follows; where A₂⁻² signifies the dimerized surfactant anion, NA₂⁻ the partially neutralized dimer, M the surfactant micelle, and where the subscripts s, w, and o signify the solid, aqueous, and oil phases, respectively:

Surfactant Dissolution and Ionization:

Note: $\alpha_{\text{NA}} = \text{fraction NA}_{(w)} \text{ ionized, } < 1 = f(C_{\text{NA}}, C_{\text{NS}}, \text{ and CMC})$

Surfactant Dimerization:

or

Surfactant Micellization:

Note 1: Partially neutralized dimers assumed to be the favored low concentration species

Note 2: CMC decreases as C_{NX} increases

Indifferent Electrolyte Dissolution and Ionization:

Note: α_{NX} = fraction $NX_{(w)}$ ionized $\doteq 1$ and $C_{NX(w)} \gg C_{NA(w)}$

for salting-out.

Surfactant Salting-Out:

Note: Salting-out not observed below CMC

Surfactant Partitioning to Oil:

or

Note: The oil/water partition coefficient, $PC_{o/w}$, depends strongly on the surfactant structure and concentration, and on the salt concentration.

It should be noted that salting out of surfactants has not been observed until the CMC is exceeded. Therefore, if the surfactant is below the Krafft point and salting-out is observed upon the addition of an indifferent electrolyte, e.g. NaCl, it is clear that the CMC at the particular electrolyte concentration is less than the equilibrium surfactant concentration, C_e . Moreover, when salting-out occurs from micellar solutions, precipitation of the solid-like materials (Scriven and co-workers at U. Minn. have characterized these and similar materials as liquid crystals) by a process such as that indicated by Equation 6 seems reasonable. Owing to the depression of surfactant ionization by the strongly ionized indifferent electrolyte and its effect on the CMC, it is apparent that these two effects can combine to produce salting-out of the surfactant as shown in Equation 6.

It seems appropriate to emphasize here that although the salted-out surfactant appears to be the solid sodium salt of the surfactant, its structure and composition are not yet firmly established.

2. Surfactant Precipitation by Multivalent Cations: Determine composition and structure of precipitated surfactant, and attempt to develop a mechanism for surfactant precipitation and precipitate dissolution by excess surfactant. Measure polymer precipitation by multivalent cations and attempt to characterize by SEM, EDXA, and chemical analysis.

Investigators: Dr. G. Rama Rao and Ms. M.J. Meister

Chemical Analysis of Calcium Salts of Surfactants

The calcium salts of several anionic surfactants were precipitated, the precipitate collected by centrifugation, washed by centrifugation and decantation, and finally collected on a filter. The precipitate was washed with distilled water, and dried at 110°C. Some of the precipitates appeared to be crystalline, but several appeared to be waxy, amorphous solids when examined microscopically. These precipitates were analyzed for C, H, S, Ca, and Na, and the results of these analyses are given in Table IVA1 along with the theoretical composition assuming that the formula of the precipitate was CaA_2 , where A denotes a surfactant anion.

These analyses indicate that the general formula is close to CaA_2 . Moreover, they demonstrate that the precipitate contains little or no sodium even through some of the solutions from which precipitation occurred contained micelles. In short, it appears that if precipitation took place from micellar solutions and the micelles contained sodium ions fixed fairly firmly on the micelles, rapid exchange between micellar sodium and calcium occurred.

Multivalent Cation Precipitation of Lauryl Sulfate

Sodium lauryl sulfate solutions were mixed with calcium chloride solutions in various proportions and the mixtures rotated at one rpm for three days in an air bath held at $25 \pm 1^\circ\text{C}$. In any given series the calcium ion concentration was held constant at selected values of 28, 50, 200 and 800 ppm (7×10^{-4} , 1.25×10^{-3} , 5×10^{-3} , and 2×10^{-2} moles Ca^{+2}/ℓ) while the lauryl sulfate concentration was varied over a considerable range. In all cases precipitation of calcium lauryl sulfate was observed, but the precipitate dissolved as excess lauryl sulfate was added.

After equilibration (precipitation and dissolution were actually very rapid-appearing to be complete within one minute) for one day with gentle agitation, the solutions were centrifuged for 15 minutes to settle any precipitate, and the

Table IVA1

Composition of Calcium Surfactant Precipitates,
Weight Percent

<u>Element</u>	<u>Calcium Lauryl Sulfate</u>	<u>Calcium Dodecyl- benzene Sulfonate</u>	<u>Calcium Pentadecyl- benzene Sulfonate</u>
<u>Carbon</u>			
Theoret.	50.48	62.60	65.11
Found	50.47	62.42	63.66
<u>Hydrogen</u>			
Theoret.	8.83	8.40	9.04
Found	8.97	8.71	9.17
<u>Sulfur</u>			
Theoret.	11.24	9.29	8.28
Found	11.42	9.02	8.01
<u>Calcium</u>			
Theoret.	7.01	5.80	5.17
Found	7.16	5.85	4.82
<u>Sodium</u>			
Theoret.	0	0	0
Found	0.55	0.25	0.21

Figure IVA3. Precipitation of Lauryl Sulfate By Calcium Ions.
 $T = 25 \pm 1^\circ\text{C}$ $\blacktriangle = 7 \times 10^{-4}$ moles Ca^{+2}/ℓ ; $*$ = 1.25×10^{-3} moles Ca^{+2}/ℓ ; $\circ$ = 200 ppm = 5×10^{-3} moles Ca^{+2}/ℓ ;
 $\bullet$ = 800 ppm Ca^{+2} = 2×10^{-2} moles Ca^{+2}/ℓ .

clear supernatant was sampled for analysis of surfactant remaining in solution. The fraction of the surfactant remaining in solution, C_e/C_o , was calculated and these results are shown in Figure IVA3, where C_e/C_o is plotted as the ordinate and the equilibrium surfactant concentration, C_e , is plotted as the abscissa.

For each of the constant calcium concentrations precipitation is first observed, then the precipitate dissolves as more surfactant is added; the surfactant concentration at which C_e/C_o is a minimum represents the onset of precipitate dissolution. As one would expect, $(C_e/C_o)_{\min}$ decreases as the calcium concentration increases. Likewise, C_e , at the minimum also decreases slightly as the calcium concentration increases.

The plateaus on the dissolution branch of the curve for 50 ppm calcium appear to be real, but their cause is not clear at this time. They do not appear at the other calcium concentrations, but this phenomenon has not been studied intensively.

The Mechanism of Precipitation and Dissolution

The fixation, or binding, of calcium ions by anionic surfactant micelles is widely discussed in the literature, and we have generally adhered to this view. However, the equilibrium surfactant concentrations in solution at the minima in the curves shown in Figure IVA3 were sufficiently small to raise a question as to whether these solutions could be micellar. Corrin and Harkins (1947) measured the effect of added salts on the CMC of several surfactants, including sodium lauryl sulfate, and found that the CMC decreases as the salt concentration increased. They showed that the counterion concentration was the principal factor in the diminution of the CMC, and they found that their data for the CMC of sodium lauryl sulfate could be represented by the equation

$$\log \text{CMC} = -0.45774 \log m^+ - 3.2485$$

where m^+ = total cation concentration, i.e., the cations from both salt and surfactant.

Corrin and Harkins did not study the effect of salts with multivalent cations, but if we assume that the precipitation reaction is

then, for each calcium lauryl sulfate molecule precipitated, two NaCl molecules will be added to the solution. We can calculate the equivalent sodium concentrations and the CMC by taking the value of C_e at the minimum (the surfactant concentration at which dissolution begins) as tabulated below.

<u>Ca⁺² Conc.</u>		<u>Na⁺ Concentration</u>			
<u>ppm</u>	<u>moles/l</u>	<u>From Ca⁺²</u>	<u>From C_e min</u>		<u>Total Na⁺</u>
		<u>moles/l</u>	<u>wt. %</u>	<u>moles/l</u>	
28	7×10^{-4}	1.4×10^{-3}	0.052	1.73×10^{-3}	3.13×10^{-3}
50	1.25×10^{-3}	2.5×10^{-3}	0.050	1.73×10^{-3}	4.23×10^{-3}
200	5×10^{-3}	1×10^{-2}	0.033	1.14×10^{-3}	1.11×10^{-2}
800	2×10^{-2}	4×10^{-2}	0.030	1.04×10^{-3}	4.10×10^{-2}

<u>Ca⁺² Conc., ppm</u>	<u>Na⁺ Conc., moles/l</u>	<u>CMC</u>		<u>C_e min., wt. %</u>	<u>C_e min/CMC</u>
		<u>moles/l</u>	<u>wt. %</u>		
28	3.13×10^{-3}	7.90×10^{-3}	0.228	0.052	0.228
50	4.23×10^{-3}	6.88×10^{-3}	0.198	0.050	0.253
200	1.11×10^{-2}	4.42×10^{-3}	0.130	0.033	0.254
800	4.10×10^{-2}	2.43×10^{-3}	0.070	0.030	0.429

These CMC values are shown on Figure IVA3; they indicate that dissolution of precipitate began at each calcium concentration before the CMC had been reached. It should be borne in mind, however, that the CMC calculated was based on the assumption that no free calcium ions remained in the solution at the onset of precipitate dissolution. This is, of course, incorrect as the calcium lauryl sulfate has a finite, though small, solubility. In view of the multivalent character of calcium ions and their demonstrated activity in anionic surfactant solutions (see, for example, Powney and Addison (1937), Shinoda and Ito (1961), Corkill and Goodman (1962), and Pearson and Lawrence (1967)), there still seems to be some question as to whether precipitate dissolution began before micellization occurred. This point obviously needs further clarification and experiments are planned for the near future to settle the matter.

However, if one accepts the data as they appear in Figure IVA3, it seems that precipitate dissolution must begin with calcium fixation in some sort of complex ion. At equilibrium surfactant concentrations above the CMC, calcium binding in the micelles can occur. With these observations in mind, one can write a set of equations which account for the experimental results. If we use the terminology of the section on Surfactant Salting-Out, we can rewrite Equations 1 through 4 for Surfactant Dissolution, Ionization, Dimerization, and Micellization, when we can add the equations for precipitation of the multivalent salt and its dissolution by excess surfactant.

or

Now if we let B^{+2} represent calcium or other divalent cation, we can write for precipitation

and for precipitate dissolution, first by complex ion formation, then, by micellar fixation

O'Brien and Wiers (1974), in a colloid symposium preprint which apparently has not yet been published, postulated precipitate dissolution by complex ion formation of several kinds. They do not appear to have postulated precipitate dissolution by direct incorporation into micelles, but they postulated reactions between micelles and complex ions which resulted in fixation of calcium in micelles.

One can, perhaps, visualize the structure of the complex ion containing the calcium as something like

Although Equations 9, 10, and 11 appear to account for the experimental observations, the existence of the complex ion is not experimentally established, nor is it yet certain that precipitate dissolution occurs in pre-micellar solutions. Additional experiments will be required to clarify these points.

B. Surfactant/Polymer Adsorption

1. Surfactant CMC

Measure CMC of Surfactants To Be Used in Adsorption Measurements as Necessary to Establish Upper Limit of Monomer Concentration at the Conditions of the Adsorption Experiment.

Investigator: Dr. G. Rama Rao

The Second CMC of Anionic Surfactants

Experiments discussed in earlier reports have demonstrated that two CMC values are observed when the surfactant is dissolved in water and equilibrated with a slight excess of oil. The CMC at the higher surfactant concentration is approximately the same as the CMC in distilled water without oil. The CMC at the lower concentration is usually about one order of magnitude less than the high concentration CMC. If salt is added, the high concentration CMC decreases in proportion to the salt concentration and the second CMC disappears; in short, the salt effect tends to dominate the behavior of the surfactant.

We have observed two CMC values for every anionic surfactant which we have studied when oil is present and when we have determined the CMC by surface tension measurements. When we have measured the electrolytic conductivity, only one CMC value (the high concentration CMC) has been found.

Other investigators have reported two CMC values before. Mino et al. (1977) reported finding two CMC values for sodium 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoate, but examination of their data indicates that they found two CMC values from electrolytic conductivity measurements (4.23×10^{-3} and 9.03×10^{-3} moles/l, respectively) while only one CMC (4.23×10^{-3} M/l) was found by surface tension measurements. Miura and Kodama (1972 and 1973) published a series of papers in which they reported two CMC values for sodium dodecyl sulfate, but the second CMC was about an order of magnitude larger than the first CMC-which is the one normally observed. Miura and Kodama cited similar findings by other investigators.

Chan (1978) reported reduced CMC values in the presence of oil but he found only a single CMC value.

It appears, therefore, that our observation of a second CMC value in the presence of a slight excess of oil at a surfactant concentration about an order of magnitude below the normal CMC for distilled water is unique. Two CMC values have been observed only by surface tension measurements, and they have been found only for surfactants dissolved in distilled water. Until confirmation by other techniques is achieved, the existence of the second CMC must remain tentative. Several experiments are planned for the near future, and we hope to be able to resolve the matter in a future report.

2. Surfactant Adsorption

Measure the influence of alcohol type and concentration on the adsorption of selected surfactants on cation exchanged kaolin, and measure the equilibrium adsorption of single and mixed anionic surfactants on cation exchanged Berea Sandstone. Run dynamic adsorption experiments with these systems

Investigator: Dr. G. Rama Rao

The Influence of Alcohol Type and Concentration on Equilibrium Surfactant Adsorption

Equilibrium adsorption experiments have been initiated with 8- ϕ C₁₆S_{0.3}Na, (UT-1) being adsorbed on cation exchanged kaolin at 25°C. The butanol series was chosen as the alcohol in this series of experiments, and the alcohol concentrations were 1, 3, and 5 weight percent. Much of this work is complete but it seems best to postpone a full report until the isotherms for the entire series can be discussed.

The data in hand indicate that both the structure and the concentration of the alcohol have a significant influence on the amount of surfactant adsorbed. Moreover, it appears that alcohol can cause either an increase or a decrease in the amount of surfactant adsorbed.

Although the kaolin used in these experiments was cation exchanged by a standard procedure, and then washed free of salt before drying, crushing, and screening to size, a nagging doubt has remained as to whether all of the multivalent cations have been removed from the clay. If calcium or magnesium ions can be extracted from the cation exchanged clay in any appreciable amount, surfactant precipitation and precipitate dissolution could influence the apparent adsorption isotherm significantly, especially for the higher equivalent weight surfactants. In view of the importance of the phenomenon for adsorption, it seemed desirable to undertake experiments on the extraction of calcium and magnesium from cation exchanged clay by distilled water and one wt. % NaCl.

Extraction of Multivalent Cations From Cation Exchanged Clay

One gram samples of cation-exchanged kaolin were weighed into screw-capped test tubes; ten ml of either distilled water or one wt.% NaCl solution were added to each test tube, the tube mouth covered with Saran Wrap, and the cap affixed. The tubes were rotated at one rpm while being maintained at a temperature of 25°C. Periodically tubes were removed, the clay centrifuged out, and an aliquot of the clear supernatant

liquid withdrawn for calcium and magnesium analysis. A distilled water blank with no clay was also analyzed after 90 hours equilibration. The results are tabulated below.

Table IVB1

Extraction of Calcium and Magnesium From
Cation Exchanged Clay, Solid/Liquid Ratio = 1g/10ml

<u>System</u>	<u>Cation</u>	<u>Cation Concentration, ppm</u>			
		<u>Equilibration Time, hrs.</u>			
		24	48	72	90
Distilled Water, No Clay	Ca ⁺²	-	-	-	0.1, 0
	Mg ⁺	-	-	-	1.0, 0.3
Distilled Water With Clay	Ca ⁺²	0,0	1.7,0	0,0	0,0
	Mg ²	0, <0.1	0.9, <0.1	0.5,0.5	0.3,0.5
1% NaCl with Clay	Ca ⁺²	27.5,27.2	26.9,27.9	26.7,25.9	-
	Mg ⁺²	0.9,1.0	1.1,1.5	1.3,1.3	-

These data demonstrate that distilled water does not extract appreciable amounts of either calcium or magnesium ions from cation exchanged kaolin, but one wt.% NaCl extracted very significant amounts of calcium ions and measurable amount of magnesium. This means that some multivalent ions still remain in the exchange sites. The concentration of the extracted multivalent cations is small, but it is sufficient to precipitate a very significant amount of surfactant, particularly if the equivalent weight of the surfactant is 400 or greater. A more plaguing question is whether continued extraction of the clay would continue to yield significant concentrations of calcium or magnesium ions (it should be borne in mind that this clay has already been extracted three times with 1N NaCl (5.8 wt.%) and washed extensively with distilled water.

A search of our files for data which might shed some light on this matter turned up several interesting sets of data. For example, successive extraction of Mississippi Montmorillonite (Ward #22A) with one wt.% NaCl gave the following results.

Table IVB2

Multivalent Cation Contents of NaCl Extracts of Clay,
Mississippi Montmorillonite (Ward #22A)
1 g. Clay per 10 ml One Wt.% NaCl

<u>Extract No.</u>	<u>Cation Concentration of Extract</u>			
	<u>Calcium</u>		<u>Magnesium</u>	
	<u>meg./10 ml</u>	<u>ppm</u>	<u>meg./10ml</u>	<u>ppm</u>
1	0.155	310	0.107	128
2	0.074	148	0.046	55
3	0.037	74	0.025	30
4	0.025	50	0.016	19

While these data are for montmorillonite, which has a cation exchange capacity several times as great as does kaolin, the possibility of continued extraction of significant amounts of multivalent cations-especially by NaCl solutions-is obvious.

The absence of any significant extraction of either calcium or magnesium by distilled water does not mean that multivalent cation precipitation cannot occur. On the contrary, the existence of relatively accessible calcium (or magnesium) ions on the clay suggests that surfactant adsorption can occur wherever a surface calcium ion rests. Furthermore, since calcium bound to a surfactant anion is in a relatively exposed site, one can conceive a mechanism for adsorption and adsorption maxima where the surface calcium-surfactant adsorbate species would be adsorbed at the exchanged sites occupied by calcium or magnesium and this could be solubilized by either surfactant complex ions or by surfactant micelles in the manner postulated in Section IVB2 of this report (p. 75).

Significance of Surface Multivalent Cations For Surfactant Adsorption

When calcium ions are in exchange sites, they can serve as bridges between a negatively charged surface site and a surfactant anion (either monomer or dimer); this is basically a Langmuir-type adsorption mechanism. Langmuir-type adsorption isotherms have been proposed by several investigators. The Langmuir-type adsorption is modified by hemimicelle formation; however, one would expect it to be further modified as calcium-surfactant adsorbate dissolved (desorption of surfactant) by complex ion formation or micellar fixation when the adsorption plateau is approached.

In the event that the solution contains an appreciable concentration of salt, cation exchange will occur and this will be followed by surfactant precipitation from solution. When the surfactant is in sufficient excess, precipitate dissolution will occur. Since the precipitated surfactant will be separated from the residual solution along with the clay or other adsorbent, the equilibrium surfactant concentration will decrease and it will appear that the precipitated surfactant is adsorbed. When the equilibrium surfactant concentration becomes large enough to initiate precipitate dissolution, the dissolved precipitate will be incorporated in the solution and it will appear that adsorption has decreased. This sort of interaction of cation exchange, precipitation and dissolution processes would lead to apparent adsorption isotherms with a maximum.

One would expect the same general isotherm shape to result from either surfactant adsorption at cation exchange sites through calcium bridges followed by desorption of the calcium-surfactant adsorbate by dissolution in excess surfactant or by cation exchange leading to surfactant precipitation and subsequent precipitate dissolution by excess surfactant. In the former case one would be dealing with a type of chemisorption; in the latter case, adsorption of the surfactant would not be involved at all.

Other adsorption sites which are positively charged also exist at crystal edges and at other locations. The same basic adsorption process could be expected to occur at these sites, i.e. attraction of the negatively charged surfactant ion to the positively charged site, along with hemimicelle formation. However, since these adsorbed surfactant anions would not be joined to the surface by a calcium bridge, one would not expect these surfactant anions to desorb as the equilibrium surfactant concentration passed the CMC, and one would expect to find an adsorption isotherm without a maximum.

Thus, one can conceive of at least two kinds of adsorption occurring, and an apparent adsorption which does not actually involve surfactant adsorption. Adsorption of surfactant anions occurs at positively charged crystal sites (edges, corners, cracks, etc.), and it appears possible for surfactant adsorption to occur at cation exchanged sites occupied by multivalent cations such as calcium or magnesium. Cation exchange can result in surfactant precipitation followed by precipitate dissolution. These processes can be visualized as shown in the schematic diagrams following:

Surfactant Adsorption at Positively Charged Crystal Sites

Surfactant Adsorption By Calcium Bridging

Cation Exchange and Surfactant Precipitation and Dissolution

(sx) indicates cation exchange site on surface of adsorbent.

In summary, it appears that multiple treatments with 1N NaCl (5.8 wt.%) is insufficient to remove all exchangeable calcium and magnesium ions, from kaolin (we have recently found that this also holds true for disaggregated Berea Sandstone), and that one wt.% NaCl will extract sufficient additional calcium and magnesium to precipitate substantial quantities of most anionic surfactants. Although negligible quantities of these multivalent cations are extracted from the cation exchanged clay by distilled water, it seems likely that the multivalent cations in the exchange sites can result in substantial surfactant adsorption by means of multivalent cation bridges between the exchange site and the adsorbed surfactant anion. These phenomena, along with dissolution of the cation-surfactant adsorbate complex or the insoluble calcium (magnesium) salt by excess surfactant, can have a strong influence on surfactant losses by adsorption and precipitation.

3. Polymer Adsorption

Measure polyacrylamide adsorption on raw and cation exchanged kaolin for a variety of salt concentrations and in the presence of oil, and evaluate the importance of degree of hydrolysis for polymer losses by adsorption.

Investigator: Mr. S.B. Balachandran

Polymer Adsorption Analysis

We have described in several earlier reports some of the difficulties we have encountered in quantitative analysis of polyacrylamides, particularly when we sought to evaluate the adsorption of the polymer on cation exchanged clay. After attempting unsuccessfully to utilize a considerable number of the methods of analysis reported in the literature, it finally appears that an analytical procedure has been found by which polymer adsorption can be studied in systems containing cation exchanged clay.

Principal of the Method:

The method of analysis is based on our observation that partially hydrolyzed polyacrylamides are precipitated quantitatively from aqueous solutions by cupric ions. The polymer can be determined indirectly by measuring the copper content of the precipitate. A modification of the neocuproine method of Gahler, A.R. (1954) has been found to yield satisfactory results, as shown by calibration curves and other measurements.

Materials:

Copper Sulphate Solution - 0.02M
Hydroxylamine Hydrochloride - 50g/450 ml DW
Sodium Citrate Solution - 150g/400 ml DW
Neocuproine Reagent - 100mg/100 ml MeOH
Chloroform
Methanol

Procedure:

The solution to be analyzed is first separated from clay or other suspended matter by centrifugation [complete clarification of polymer-clay suspensions containing more than about 500ppm polyacrylamide, even by prolonged centrifugation, has not been achieved, but the traces of clay remaining in suspension do not appear to have interfered with the subsequent polymer analysis.] The polymer concentration in the clarified solution is adjusted to not more than 1000 ppm, and the solution analyzed as follows:

- 1) Transfer a 2 ml aliquot to a 15ml screw-capped test tube, and add 5 ml of 0.02M CuSO_4 to precipitate the polymer. Cap the test tube and mix the contents well; centrifuge to insure settling of the precipitate.
Note: The precipitation reaction is very rapid and the precipitate is very sticky, so it adheres well to the walls of the test tube.
- 2) Remove test tubes from the centrifuge and pour off the supernatant liquid. Rinse well with two successive 5 ml portions of distilled water. Discard rinsings.
Note: The polymer precipitate adheres so strongly to the test tube walls that filtration of the supernatant liquid and rinsings has not been necessary.
- 3) Add 5 ml of hydroxylamine hydrochloride solution and 10 ml of sodium citrate. Mix well.
Note: $\text{NH}_2\text{OH}\cdot\text{HCl}$ dissolves the precipitate and reduces copper to the cuprous state. Citrate reduces the potential interference of other ions.
- 4) Transfer the hydroxylamine solution to a 125 ml separatory funnel. Rinse the test tube with four successive 10 ml portions of distilled water, adding the rinsings to the separatory funnel. Check the pH of the solution to make sure it is between 4 and 6 (Add NH_4OH or HCl , if necessary).
- 5) Add 10 ml of neocuproine solution and 10 ml of chloroform to the separatory funnel, and shake vigorously for about one minute. Allow the mixture to stand until separation of the aqueous and CHCl_3 layers is complete. Draw off the CHCl_3 layer into a 25 ml volumetric flask.
- 6) Repeat the extraction with second 10 ml portion of CHCl_3 . Add this CHCl_3 extract to that from the first extraction in the 25 ml volumetric flask. Make up to 25 ml with methanol, and mix well.
- 7) Measure the absorbance of the CHCl_3 extract at 457nm in an appropriate absorption cell, and determine the polymer content of the original solution from a calibration curve.
Note: In our laboratory, one cm square cuvettes are used and the absorption curve is recorded on a Perkin-Elmer spectrophotometer over the wavelength range 350-500 nm, using the CHCl_3 extract of a blank (no polymer) as the reference. The maximum absorbance occurs at 457nm, and the absorbance at this wavelength is plotted versus the polymer content of the 2ml aliquot taken for analysis.

Calibration Curve:

Polyacrylamide solutions ranging in concentration from zero to 1000 ppm (1 mg/ml) were prepared, and 2 ml aliquots analyzed by the procedure described above. When the absorbance per cm at 457 nm was plotted versus the polyacrylamide content of the 2 ml aliquot, expressed in mg of polymer, a straight line passing through the origin resulted. For Calgon 815 the relationship between the absorbance and the polymer content of the aliquot was found to be

$$A_{457} = 0.643 p$$

where p = polymer content in mg.

Equilibrium Adsorption of Polyacrylamide on Kaolin

Adsorption Procedure:

- 1) One gram portions of dry kaolin (either raw or cation exchanged to the sodium form) are weighed into 15 ml screw-capped test tubes, and a calculated amount of water is added, then the polymer solution. The amount of water to be added is calculated as follows: The final volume of aqueous solution is to be 10 ml. The polymer stock solution concentration should be chosen so that not more than 5 ml of polymer solution need be added for the highest polymer concentration to be tested. Then if X is the volume of polymer solution to be added, the water required will be $(10-X)$ ml.

Note: The reason for this procedure arises from the tendency of the clay not to wet and disperse uniformly when the polymer is added without prior wetting and dispersion in water.

- 2) The tubes are covered with Saran Wrap and capped, and they are placed on the rotator and run at one rpm while being held at $25 \pm 1^\circ\text{C}$ in an air bath.
- 3) Tubes are removed at selected intervals and centrifuged to produce a clear (or essentially so) supernatant liquid which is then sampled for polymer analysis by procedure described earlier.

Results and Discussion:

Both rate and equilibrium experiments are in progress and the evidence in hand is not sufficiently complete to warrant extended discussion. It will be more fully discussed in the next report, but several conclusions can be drawn from the data available at this time.

1. Rate of Adsorption: It appears that at least 24 hours contact is required to attain equilibrium. Some of this may be due to a tendency of raw kaolin to flocculate immediately on addition of polymer and to poor contact between the flocs and the polymer solution.

2. Equilibrium Adsorption: Polymer adsorption on raw kaolin (Ca and Mg in the cation exchange sites) is clearly significant. The mechanism may be through calcium bridging between the clay and the polymer. Adsorption of polymer on Na-kaolin appears to be very small or negligible. The results in hand are somewhat inconclusive and are complicated by the smallness of the apparent adsorption (which requires taking the difference between two much larger numbers).

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

Continue to review literature and analyze it to determine areas where precipitation processes are well understood and to identify areas where additional knowledge is needed. Seek additional unpublished information from industrial sources.

Investigators: Ms. M.J. Meister, Messrs. J. Funk, M. Cosper and G. Porcella

Our literature search has continued to turn up a considerable number of papers which touch on multivalent cation precipitation in one way or another, but few really definitive studies appear to have been published and only a small number of these really deal with dissolution of the precipitate by excess surfactant and subsequent reprecipitation as the surfactant slug becomes dispersed, depleted, and diluted.

Several very useful papers which are concerned primarily with cation exchange have been published.

The literature on salting-out of surfactants by in-different electrolytes continues to be found negligibly small. So far no definitive studies have been found, and most references consist of passing remarks to the fact that salting-out occurs when the salt concentration exceeds some limiting value.

Although several patents have been examined, relatively little new information has been found in them.

Efforts to elicit unpublished information from industrial sources have not yet been very successful but they will be continued in the hope that useful information from these sources can be found.

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