

The Effect of Counterions on Coacervation and Solubilization in Oil-External and Middle-Phase Microemulsions

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The effect of hydrated radii, valency, and concentration of counterions on the coacervation of aqueous petroleum sulfonate solutions and on the solubilization capacity of oil-external and middle-phase microemulsions was investigated. The critical electrolyte concentration (CEC) for coacervation increased with Stokes' hydrated radii of monovalent counterions. The CEC for CaCl_2 was much lower than that predicted by either the Stokes' hydrated radii or the ionic strength. For mixed electrolytes containing NaCl and CaCl_2 , it was concluded from the shift in CEC that 1 mole of CaCl_2 is equivalent to 16 to 19 moles of NaCl . The changes in relative concentrations of NaCl and CaCl_2 for coacervation exhibited additive behavior. The maximum solubilization of brine in oil-external microemulsions occurred at a specific salt concentration. For mixed electrolytes containing NaCl and CaCl_2 , the shift in electrolyte concentration for maximum solubilization showed that 1 mole of CaCl_2 is equivalent to about 4 moles of NaCl . These results suggest that the equivalence ratio of CaCl_2 to NaCl is strikingly different in aqueous solutions and oil-external microemulsions. For solubilization in middle-phase microemulsion containing mixed NaCl and CaCl_2 , it was concluded from the shift in optimal salinity that 1 mole of CaCl_2 is equivalent to about 16 moles of NaCl . Here also the changes in NaCl and CaCl_2 concentrations showed additive behavior. The equivalence ratio of CaCl_2 and NaCl appears to be independent of oil chain length in the present study. As shown by the equivalence ratio of CaCl_2 to NaCl , the formation of middle-phase microemulsions appears to be similar to coacervation of aqueous surfactant solutions and quite different from the solubilization of water in oil-external microemulsions.

INTRODUCTION

Microemulsions and micellar solutions in brine or oil have been employed as injection fluids for a number of tertiary oil recovery processes (1-7). These solutions may produce ultra low interfacial tensions at oil/microemulsion and microemulsion/brine interfaces under favorable conditions. One of the key variables in designing the surfactant flooding process is the salinity of reservoir brine. Of particular importance is the deleterious effect of divalent cations when petroleum sulfonates are used (8, 9).

When the salinity of a homogeneous aqueous surfactant solution is increased, phase

separation occurs after reaching a critical electrolyte concentration in which a colloid-rich liquid phase is in equilibrium with a colloid-lean liquid phase. This process, known as coacervation (10, 11), bears a close resemblance to the coagulation of lyophobic colloids. It is well known that the stability of lyophobic colloids is critically dependent on the valency of counterions (12-14), which can be qualitatively described by the DLVO theory (15, 16). Approximately, 1 mole of divalent ions can be as effective as 20 to 80 moles of monovalent ions depending on the surface potential of the colloidal particles (16).

Micellar solution or microemulsion upon mixing with oil and brine may form a middle-phase microemulsion in equilibrium with excess oil and brine depending on the salin-

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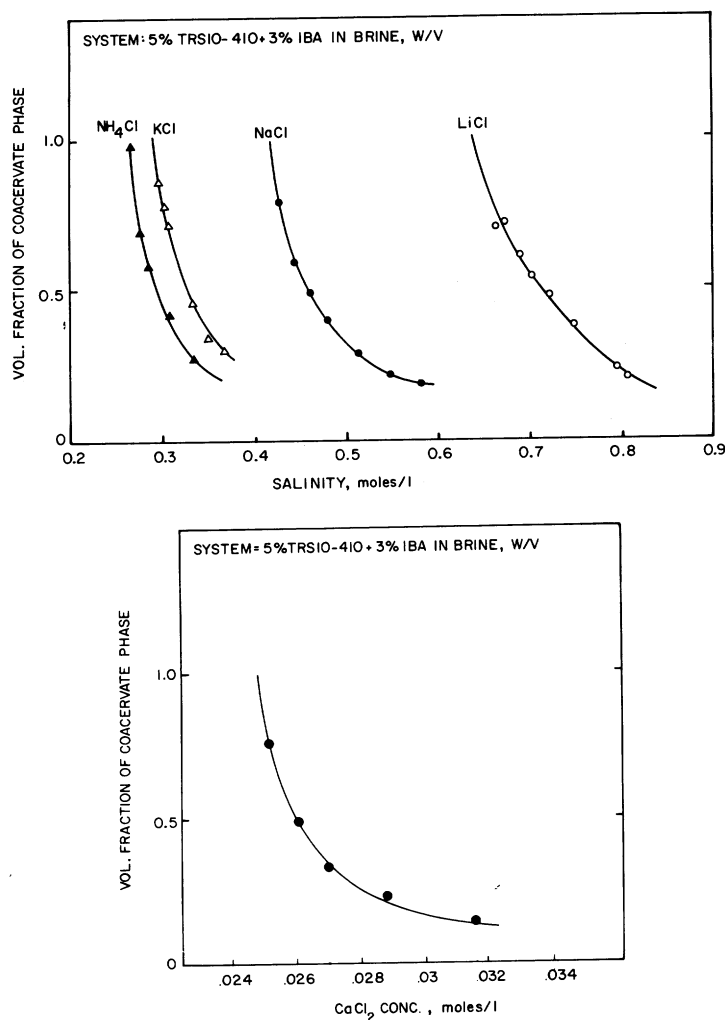


FIG. 1. (a) The effect of different 1-1 electrolytes on the coacervation of aqueous surfactant solution. (b) The effect of CaCl_2 on the coacervation of aqueous surfactant solution. The CEC is 0.275% (0.0248 M) for CaCl_2 and 0.42 M for NaCl .

ity. It has been shown (17) that the amount of oil and brine solubilized in the microemulsion can correlate with the interfacial tension; namely, the higher the solubilization, the lower the interfacial tension. Although the solubilization capacity or the stability of microemulsions has been treated theoretically by a number of investigators (18–22), the effect of counterion valency is not well described. The difference between O/W and W/O type microemulsions regarding the effect of counterions is not elucidated.

The solubilization limit of water in inverted Aerosol OT micellar solution was reported to correlate with the ion–dipole interaction energy between the water molecules and the cation of the surfactant in the micelle (23).

In this paper, we report the effect of hydrated radii, valency, and concentration of counterions on three phenomena: the coacervation of aqueous surfactant solutions, solubilization capacity of oil-external microemulsions, as well as solubilization in middle-phase microemulsions. The following

electrolytes, LiCl, NaCl, KCl, NH_4Cl , and CaCl_2 were employed with particular emphasis on the effect of mixed NaCl and CaCl_2 .

MATERIALS AND METHODS

A petroleum sulfonate, TRS 10-410 (Witco Chemical Company), was used as received. The surfactant has an average molecular weight 418. Isobutanol (99.9% pure), dodecane, and hexadecane (99% pure) were obtained from Chemical Samples Company. Deionized, distilled water was used in all experiments.

Coacervation of aqueous surfactant solution and solubilization capacity of brine in oil-external microemulsion experiments were performed at room temperature ($23 \pm 1^\circ\text{C}$). For solubilization in middle-phase microemulsion, the samples were vigorously shaken, and put on a rotating tumbler for 2 days before allowing for phase separation in a constant temperature bath maintained at $25 \pm 0.1^\circ\text{C}$ for about 1.5 month. Interfacial tension between the microemulsion and the excess oil or brine phase in equilibrium was measured by a spinning drop tensiometer.

RESULTS AND DISCUSSION

1. Coacervation of Aqueous Surfactant Solution

The surfactant solution of 5% TRS 10-410 and 3% IBA in 0.5% NaCl brine is optically isotropic. Upon adding NaCl, the solution becomes anisotropic. However, further addition of NaCl causes the formation of two isotropic liquid phases. The upper surfactant-rich phase is called coacervate phase. Upon further increasing salinity, the volume fraction of coacervate phase decreases. Other electrolytes such as LiCl, KCl, NH_4Cl , and CaCl_2 exhibited similar behavior, except that in the CaCl_2 system the coacervate phase is the lower phase in equilibrium with upper phase brine. In all cases including the CaCl_2 system, the coacervate phase is a transparent liquid phase. The results are plotted in Figs. 1a and 1b as volume fraction of the coacervate phase versus the electro-

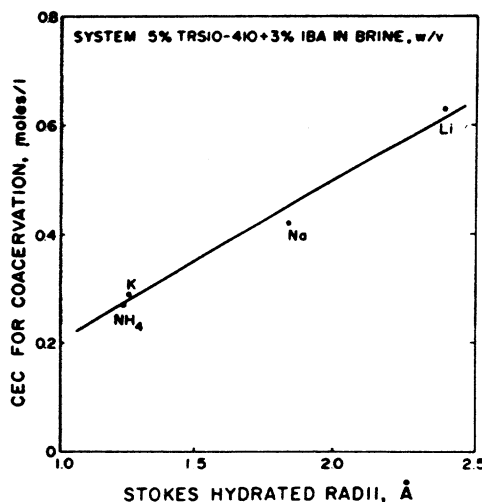


FIG. 2. The correlation of CEC with the Stokes hydrated radii of counterions.

lyte concentration. The minimum electrolyte concentration required for the onset of coacervation is defined as the critical electrolyte concentration (CEC). In the present system, the CEC is in the order: $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{NH}_4\text{Cl} > \text{CaCl}_2$. For the monovalent ions, this order is the same as the lyotropic series (24) which is typical of sulfates or sulfonates surfactant system (10). Except for CaCl_2 , the CEC can correlate with the Stokes hydrated radii of counterions (25) as shown in Fig. 2. It seems that counterions with smaller Stokes radii are more effective in reducing the surface potential (via the Stern region) of micelles. Alternatively, one can interpret the results based on the refined version of DLVO theory (26) in which systems with smaller counterions have lower critical Stern potential and hence have smaller CEC.

The effect of mixed NaCl and CaCl_2 on coacervation was studied. The results are plotted in Fig. 3 as the volume fraction of coacervate phase versus NaCl concentration at various CaCl_2 concentrations. As CaCl_2 content increases, the NaCl concentration necessary to cause coacervation decreases. The data in Fig. 3 can be presented in a different manner as shown in Fig. 4 where

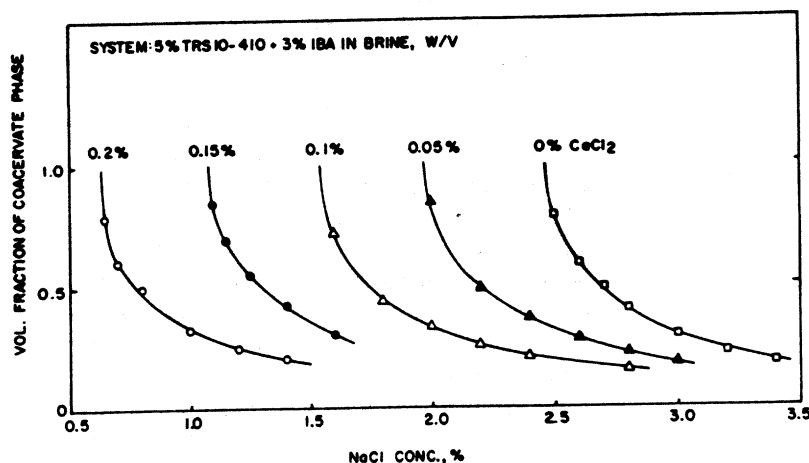


FIG. 3. The effect of NaCl concentration on the coacervation of aqueous surfactant solution at different CaCl_2 contents.

the CEC of NaCl, the NaCl concentration necessary to produce a 50 or 30% volume fraction of coacervate is plotted against the CaCl_2 concentration. Within the accuracy of

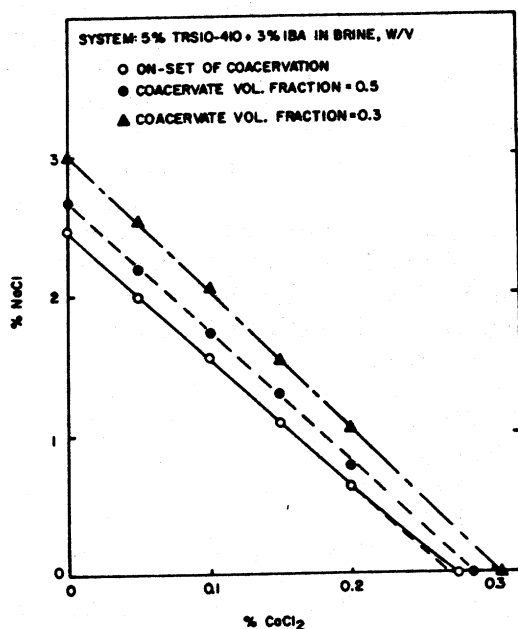


FIG. 4. Coacervation of aqueous surfactant solution by mixed NaCl and CaCl_2 . The same data in Fig. 3 are shown here for CEC (O), and NaCl concentration required to produce a 50% (●), or 30% (▲) volume fraction of coacervate vs CaCl_2 conc. From the slope of the lines, it is shown that 1 mole of CaCl_2 is equivalent to 16 to 19 moles of NaCl in coacervation.

experiments, these lines can be considered additive. It should be mentioned that the additive behavior observed here may not hold for other systems such as coacervation of some cationic surfactants (11). From the slope of the lines, it was found that 1 mole of CaCl_2 is equivalent to 16 to 19 moles of NaCl in coacervation.

The large difference between NaCl and CaCl_2 can be considered as due to their effectiveness in reducing the electric double layer repulsion between micelles. In the kinetic sense, there are basically two effects of electrolyte concentration and valency on the stability of colloidal dispersions (27). One is the compression of the diffuse double layer thus reducing the range of repulsion forces. Another is due to the reduction of surface potential. It is difficult to separate out these two effects, however, because the compression of double layer leads to a reduction of surface potential if the surface charge density is held constant during a Brownian collision which is probably the case for surfactant micelles (28). The compression of the diffuse double layer can be important only in aqueous dispersions where the double layer thickness and consequently the shape of the electrostatic potential energy curve are critically dependent on the valency and concentration of counterions.

The overall potential energy of interaction of two neighboring particles can be obtained by summing up the electrostatic and van der Waals attraction potentials which may have a maximum vs distance of separation. In the classical version of the DLVO theory, the lyophobic colloid system was considered as kinetically stable when the potential energy maximum is higher than about 10 kT . According to this model, Overbeek (16) calculated the critical electrolyte concentration for coagulation of lyophobic colloids as a function of surface potential (held constant during collision) and counterion valency. For surface potential of 100 mV, the ratio of coagulation concentration of 1-1 electrolyte to 2-2 electrolyte is about 16. It is more appropriate, however, to use the refined version of DLVO theory (26) for the present system in which the interactions of micelles are taking place at constant surface charge density and the distance of nearest approach of neighboring particles is at least twice the thickness of the Stern region during a Brownian collision. The colloidal system can be thermodynamically stable if the Stern potential of the colloidal particle (which is a function of electrolyte concentration and valency) is greater than some critical value characteristic of each system (26). According to this model, the critical Stern potential (Stern potential at the onset of coacervation) was calculated to be approximately 38 mV for the NaCl system and 47 mV for the CaCl_2 system such that 1 mole of CaCl_2 would be equivalent to 16 moles of NaCl.

The difference between the effects of NaCl and CaCl_2 might also be in part due to the influence on the free energy of formation of electrical double layer. As a first approximation, one can calculate the free energy of formation of the electrical double layer using the flat-plate approximation of the Gouy-Chapman theory (29) which is valid for $\kappa a \gg 1$. Assuming a surface charge density of one unit charge per 120 \AA^2 (\sim complete ionization of surfactant molecules), the electrical term of the free energy of formation of the

double layer $\int \psi_0 d\sigma$, in the presence of 0.42 M NaCl (CEC of NaCl), was calculated to be 5.08 erg/cm². While in the presence of 0.0248 M CaCl_2 (CEC of CaCl_2), it was 6.19 erg/cm². By interpolation, it was found that about 0.055 M CaCl_2 corresponded to a free energy of formation of the double layer of 5.08 erg/cm². Thus in terms of the free energy of formation of the double layer and neglecting the contribution of specific adsorption, 1 mole of CaCl_2 was equivalent to only about 8 moles of NaCl in the present system.

The equilibrium between Ca^{2+} and the surfactant anion (RSO_3^-) to form $(\text{RSO}_3\text{Ca})^+$ might be another source for the difference between the effects of NaCl and CaCl_2 on coacervation. Since in the present system, practically all the surfactant molecules are at the micellar surfaces, this equilibrium merely addresses the specific adsorption of calcium ions in the Stern region. This equilibrium appears to be of minor importance as the effect of mixed NaCl and CaCl_2 on coacervation is additive in this study (see Fig. 4). A preferential adsorption of the more effective counterions (Ca^{2+}) will lead to significant negative deviation from additivity (27).

2. Solubilization in Oil-External Microemulsions

In this study, an inverted micellar solution of 10.7% TRS 10-410 (w/w) and 3.74% IBA (w/w) in dodecane was prepared. The maximal amount of brine that can be solubilized by the inverted micellar solution as a function of electrolyte concentration was measured. The composition was chosen here such that the IBA concentration in dodecane was 3% g/ml which was the same as that used in coacervation studies. The surfactant concentration was raised to a higher value so that appreciable amount of brine could be solubilized in order to improve the experimental accuracy. It has been reported (30) that the surfactant concentration does not change the optimal salinity (will be defined in next section) of the present system.

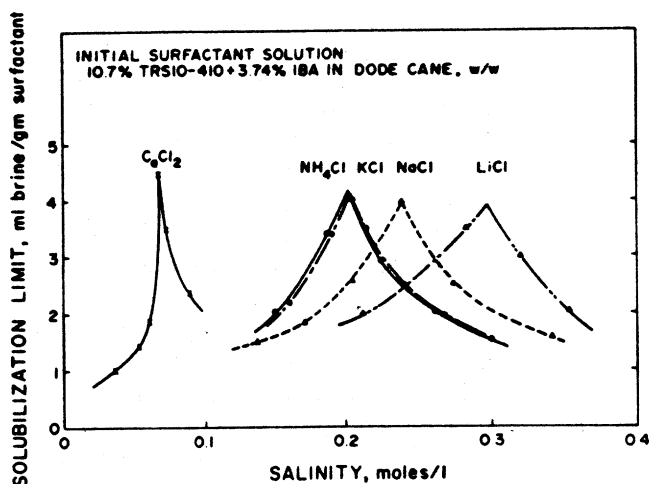


FIG. 5. The maximal amount of brine that can be solubilized by an inverted micellar solution vs the brine salinity for different electrolytes. The curves represent the single phase boundary of oil-external microemulsion.

Figure 5 shows the effect of different electrolytes and their concentrations on the solubilization limit. As salinity increases, the solubilization limit increases, passes through a maximum then decreases. Although possible structural transition may occur near or beyond the phase boundary, the structure of the microemulsion was considered to be oil-external within the single-phase boundary.^{1,2}

Figure 5 shows the specific ion effect on solubilization in oil-external microemulsion.

¹ The oil-external structure is supported by the following experimental observations: the single phase region is continuously connected to the inverted micellar solution region and that no abrupt changes in viscosity, electrical resistance, or hydrodynamic radius were observed upon increasing the brine content; the volume fraction of brine is less than 0.25; the Schlieren peak in ultracentrifuge moves toward the bottom of the cell; the hydrodynamic radii (100 to 250 Å) is consistent with the oil-external model but too small for the water-external model based on the oil and brine contents of the system; and the viscosity increases with the volume fraction of brine.

² Beyond the solubilization limit, middle-phase microemulsions may be produced upon further increase of the brine content. However, the compositions of these middle-phase microemulsions are distinctly different from those shown in section 3, since the amounts of oil and brine are significantly different in these systems.

The optimal salinity for maximal solubilization is in the order: $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{NH}_4\text{Cl} > \text{CaCl}_2$, which is the same as that of CEC but the difference between each electrolyte is much smaller in this case. The effect of mixed NaCl and CaCl_2 on solubilization in oil-external microemulsion is shown in Fig. 6 as a function of NaCl concentration at various CaCl_2 contents. The addition of CaCl_2 shifted the solubilization curves to the left. Unlike those observed in coacervation, the difference between each curve or equivalently, the effect of CaCl_2 , is fairly small. The data in Fig. 6 were reproduced as a function of ionic strength as shown in Fig. 7, in which all the data fall more or less on the same curve. Thus the effect of counterion valency on the solubilization limit in oil-external microemulsion is nearly an ionic strength effect in the present system. This is further demonstrated in Fig. 8 where the NaCl concentration corresponding to maximal solubilization of brine is plotted vs CaCl_2 concentration. Similar to those found in coacervation, the effect of mixed NaCl and CaCl_2 is also additive, but in this case, 1 mole of CaCl_2 is only equivalent to about 4 moles of NaCl . The small deviation

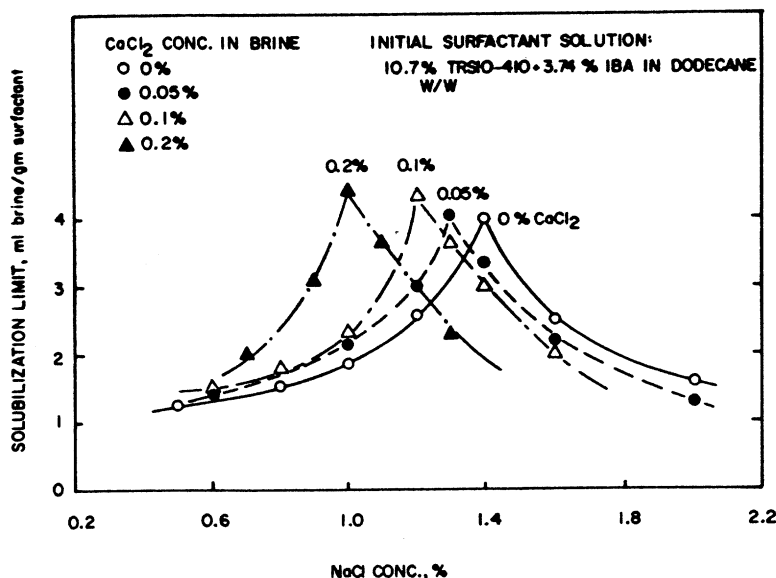


FIG. 6. The effect of NaCl concentration on the solubilization limit of brine in oil-external microemulsion at different CaCl₂ contents.

from the ionic strength effect (1 mole of CaCl₂ is equivalent to 3 moles of NaCl) can be considered as due to the difference in the hydrated radii of Na⁺ and Ca²⁺ ions (1.84 and 1.54 Å, respectively).

It was noted that in the study of solubilization limit of pure CaCl₂ brine in oil-external microemulsion (Fig. 5), minute precipitation was observed. While for the solubilization of mixed NaCl and CaCl₂ brine (Fig. 6), no precipitation was observed.

Since for colloidal dispersions in oil such as oil-external microemulsions, the electrolyte concentration in oil is extremely low and the double layer thickness approaches infinity, the electrolyte valency and concentration have negligibly small effects on the shape of potential energy curve outside the water droplet vs particle separation (31). Under this circumstance, the potential energy due to double layer repulsion is usually small (32). Thus the difference between NaCl and CaCl₂ is presumably related to their influence on surface potential and the free energy of formation of the electrical double layer inside the water droplet.

It is interesting to note, as shown in Fig. 6, that the maximal solubilization limit is slightly higher in the presence of CaCl₂ when the NaCl concentration is decreased correspondingly. This point will be discussed further in the next section.

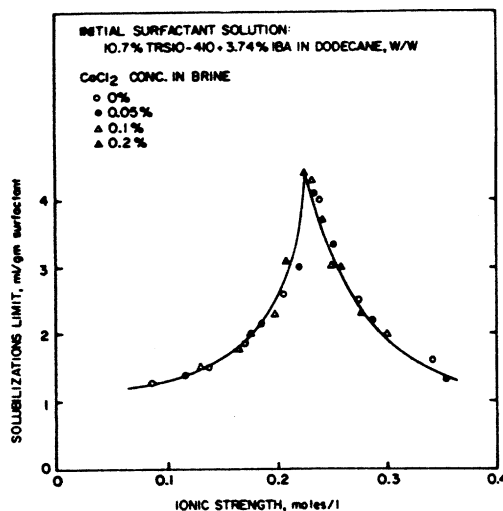


FIG. 7. The effect of ionic strength of brine on the solubilization limit of oil-external microemulsion. The same data in Fig. 6 are shown here.

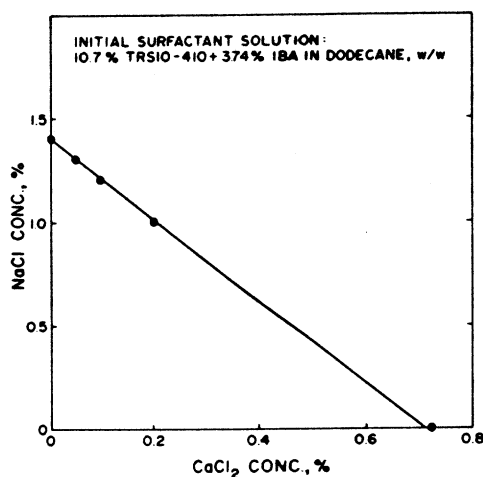


FIG. 8. The NaCl concentration corresponding to maximum solubilization limit at various CaCl_2 concentrations. The linear relationship indicates additive behavior and that 1 mole of CaCl_2 is equivalent to 3.8 moles of NaCl in this study.

3. Solubilization in Middle-Phase Microemulsions

In this section, the surfactant solution of 6.25% TRS 10-410 and 3.75% IBA (w/w) in dodecane or hexadecane was equilibrated with equal volumes of brine at $25 \pm 0.1^\circ\text{C}$.

The concentration expressed in g/ml would be 5% TRS 10-410 and 3% IBA which is the same as those used in Section 1. At equilibrium, the solubilized volume of oil, V_o , and water, V_w , in the microemulsion phase was measured. Figure 9 shows the effect of different 1-1 electrolytes on solubilization (dodecane was used in this study). For each electrolyte, there is a certain range of salinity where a middle-phase microemulsion is formed in equilibrium with excess oil and excess water. The salinity at which V_o is equal to V_w in middle-phase microemulsion was defined as the optimal salinity (17). As shown in Fig. 9, the optimal salinity is also in the order: $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{NH}_4\text{Cl}$. The correlation of (a) CEC, (b) optimal salinity for solubilization in middle phase microemulsion, and (c) optimal salinity for maximal solubilization limit of brine in oil-external microemulsion with the Stokes radii of counter ions is shown in Fig. 10. It is clear that the dependency of CEC and optimal salinity for middle-phase formation on the Stokes radii of counterions are nearly the same, while the optimal salinity for maximum solubilization of brine in oil-external microemulsions is distinctly different.

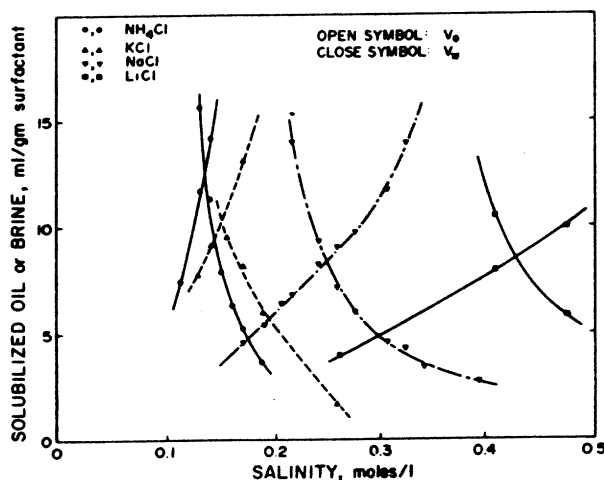


FIG. 9. The effect of salinity on the solubilized oil (V_o) or brine (V_w) in microemulsions in equilibrium with excess oil or excess brine or both. In the last case, the microemulsion is called a middle-phase microemulsion. The salinity at which equal solubilization of oil and brine occurs (intersection of V_o and V_w curves) in the middle-phase microemulsion is called the optimal salinity.

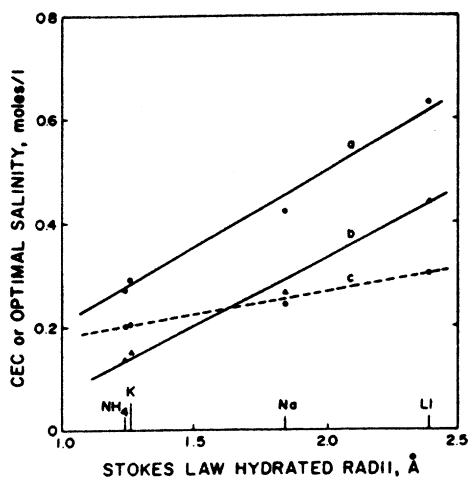


FIG. 10. Correlation of (a) CEC for coacervation in aqueous surfactant solution (Figs. 1 and 2), (b) optimal salinity for solubilization in middle-phase microemulsion (Fig. 9), and (c) optimal salinity for maximum solubilization limit in oil-external microemulsion (Fig. 5) with the Stokes hydrated radii of counterions. Based on the slope of lines, the effect of counterions on phenomena (a) and (b) is similar but distinctly different from that on (c).

The effects of CaCl_2 and mixed NaCl and CaCl_2 on solubilization in middle phase microemulsion were also determined. Figures 11 and 12 are for the dodecane system

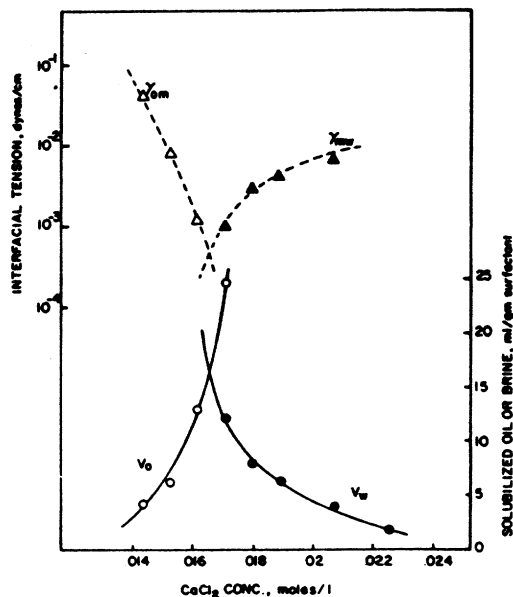


FIG. 12. The effect of CaCl_2 concentration on solubilization and interfacial tension of middle phase microemulsions (dodecane system). Here γ_{ow} is the interfacial tension between excess oil and microemulsion while γ_{mw} is that between microemulsion and excess brine.

and Figs. 13 and 14 for the hexadecane system. At each CaCl_2 content, there is a corresponding optimal NaCl concentration

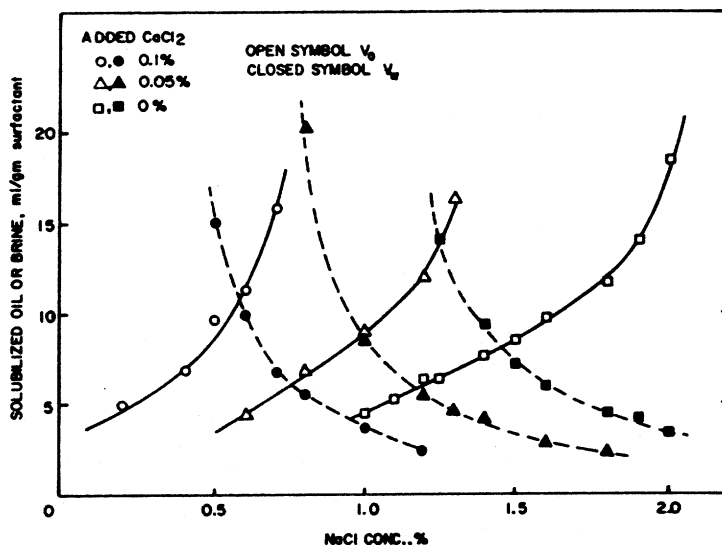


FIG. 11. The effect of NaCl concentration on solubilization in middle-phase microemulsions at different CaCl_2 contents (dodecane system).

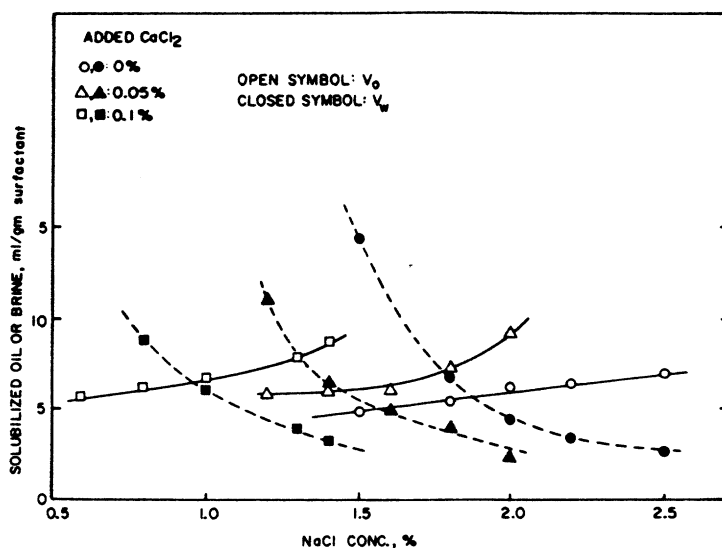


FIG. 13. The effect of NaCl concentration on solubilization in middle-phase microemulsions at different CaCl_2 contents (hexadecane system).

(where V_o equals V_w) as shown in Fig. 11 or 13. The results are reproduced in Fig. 15 plotting optimal NaCl concentration vs CaCl_2 concentration, which decreases linearly. The upper line corresponds to the hexadecane system while the lower line is for the dodecane system. The two lines are al-

most parallel to each other indicating that the results are independent of oil chain length. From the slope of the lines, it was found

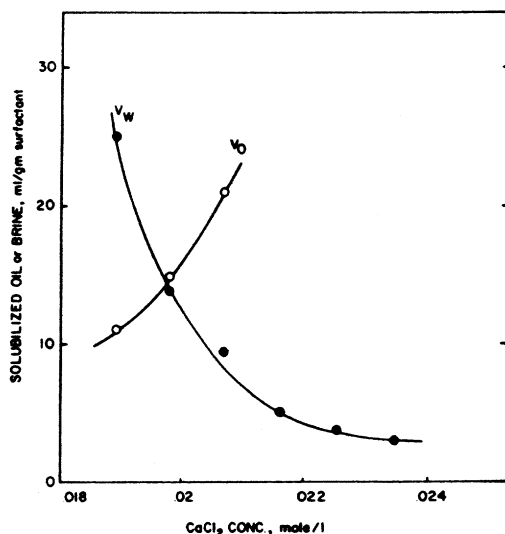


FIG. 14. The effect of CaCl_2 concentration on solubilization in middle-phase microemulsion (hexadecane system).

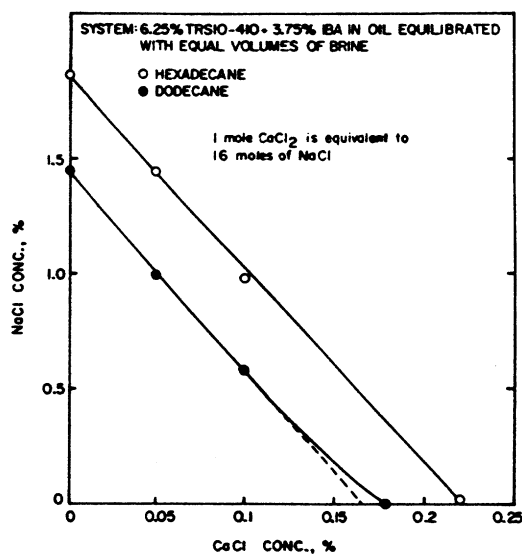


FIG. 15. The optimal NaCl concentration for solubilization in middle-phase microemulsion vs corresponding CaCl_2 concentration. The data were extracted from Figs. 11–14. From the slope of the two lines for dodecane or hexadecane system, it is shown that 1 mole of CaCl_2 is equivalent to 16 moles of NaCl in this study.

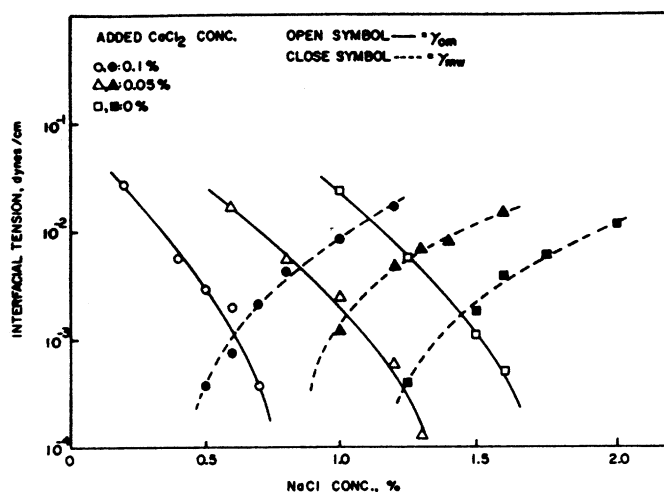


FIG. 16. The effect of mixed NaCl and CaCl_2 on the interfacial tensions of middle-phase microemulsion. This is the same system as that shown in Fig. 11.

that 1 mole of CaCl_2 was equivalent to about 16 moles of NaCl. Therefore, the effect of counterion valency on solubilization in middle-phase microemulsion is similar to the coacervation of aqueous surfactant solution and distinctly different from that for solubilization in oil-external microemulsion. The results suggest that the middle-phase microemulsion³ behaves like a water-continuous system with respect to the effect of counterions.

Interfacial tension for the dodecane system was also measured. Figure 16 indicates that the addition of CaCl_2 does not change the interfacial tension appreciably. In fact, the interfacial tension of CaCl_2 containing systems was slightly lower, consistent with the solubilization data shown in Fig. 11, namely, the solubilization of oil and brine in the middle-phase microemulsion is higher in the presence of CaCl_2 at corresponding optimal NaCl concentrations. Similar effect of CaCl_2 on solubilization in oil-external microemulsions was observed (Section 2).

³ It is emphasized that the composition of middle-phase microemulsions can vary significantly over the entire range of salinity in which three phases exist and the structure of these middle-phase microemulsions need not be the same.

Since the calcium salt of surfactant is more soluble in oil than the sodium salt of surfactant, one might expect that the interfacial surfactant molecules would be less in CaCl_2 -containing systems. This would lower the solubilization capacity of microemulsions contrary to the experimental observations. Whether this phenomenon is due to the partitioning of alcohol which in turn influences the partitioning of surfactant or due to the lower optimal salinity in CaCl_2 containing systems remains to be determined. It is noted in this study, that the solubilization capacity in oil-external or in middle-phase microemulsion is always higher when the optimal salinity is lower. This seems to indicate that the solubilization capacity is closely related to the surface charge density or equivalently, the apparent surface area per surfactant molecule.

CONCLUSIONS

The effect of hydrated radii, valency, and concentration of counterions on coacervation of aqueous surfactant solution, solubilization in middle-phase microemulsion, and solubilization in oil-external microemulsion has been reported. Additive behavior was observed for all three phenomena when

a mixture of NaCl and CaCl₂ was used. From the shift of CEC and optimal salinity, it was found that 1 mole of CaCl₂ was equivalent to 16 to 19 moles of NaCl in coacervation and solubilization in middle-phase microemulsions. While for solubilization in oil-external microemulsion, 1 mole of CaCl₂ was equivalent to only 4 moles of NaCl. As for the effect of different 1-1 electrolytes, the CEC and the optimal salinity for solubilization in oil-external and middle-phase microemulsion are in the same order: LiCl > NaCl > KCl > NH₄Cl, which correlates with the Stokes radii of hydrated counterions. The dependency of CEC and optimal salinity for middle-phase microemulsions on Stokes radii of counterions is nearly the same, which is distinctly different from the solubilization in oil-external microemulsions. The large difference in counterion effect between the two types of phenomena seems to be related to the nature of the external phase and the surface potential of colloidal dispersions. It is concluded that the middle-phase microemulsion behaves like a water-continuous system with respect to the effect of counterions.

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