Effect of Salt on the Structure and Properties of Sonicated Emulsions Stabilized by a Tertiary Oil Recovery Formulation

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ABSTRACT

Structure of sonicated emulsions obtained by varying sodium chloride concentration in surfactant formulations containing 5% (w/w) TRS 10–410 (a petroleum sulfonate), 3% (w/w) isobutanol and equal volumes of aqueous and dodecane oil phases was studied by scanning electron microscopy. The microstructure of these emulsions together with that of the mutually equilibrated oil and aqueous phases was investigated by electron spin resonance (ESR) technique. Extensive physical property data for the emulsion system and for the equilibrated phases were measured. The phase inversion of emulsions from O/W type at low salinities to W/O type at high salinities was confirmed by ESR, viscosity and electrical conductivity measurements. With increasing salt concentration, the macroemulsion passed through a series of structural changes as revealed by the electron microscopy results. A detailed analysis of viscosity and electrical conductivity of the emulsions is presented. The anomalous behavior of the emulsion at optimal salinity is highlighted. A discussion to correlate the structure, stability and type of emulsions with physical property behavior as a function of electrolyte concentration is included.

INTRODUCTION

In a tertiary oil recovery process employing surfactant and polymer fooding techniques, one of the factors that may affect the efficiency of recovery is the formation of emulsions. Formation of macroemulsions with a high degree of stability entails deemulsification outside the reservoir (1). Emulsification or the presence of emulsions within the reservoir has been reported to facilitate oil recovery (2). Thus, a macroemulsion signifies two opposing trends, an advantageous one within the reservoir and a deleterious effect outside it. In order to understand those optimal conditions with respect to stability and phase-separation, structure and extent of cosolubilization and the consequent rheological behavior, we undertook a detailed physicochemical investigation of such macroemulsions. The system chosen contained a petroleum sulfonate, TRS 10–410, isobutanol as the cosurfactant, dodecane oil, water and varying amounts of sodium chloride. The objective of the study was to choose relatively stable macroemulsions and to characterize them in terms of their equilibrium physical properties as a precursor to the study of flow-through-porous-media behavior of these emulsions.

The equilibrium phase behavior of the system containing water + NaCl (X %) + TRS 10-410 + IBA with dodecane oil has been characterized by the presence of microemulsions (3). It was found that these microemulsions possess a high degree of structure and contain appreciable amounts of oil and water. The variables involved are surfactant and alcohol concentrations, water-to-oil ratio and electrolyte concentration. In our studies, we chose electrolyte concentration as the variable, keeping other parameters constant.

At low salinity (NaCl), the mixture separates into two phases: an oil phase and a water-external microemulsion phase containing oil. At intermediate salinities, the mixture separates into three phases: an aqueous phase, a middle-phase microemulsion (containing water, oil, cosolvent and majority of surfactant) and an oil phase. At high salinities, reversal to a two-phase system occurs containing an aqueous phase and an oil-external microemulsion phase. For a given system, there is a specific NaCl concentration defined as "optimal salinity," in which ultralow values for interfacial tensions for both the oil/microemulsion phase and the brine or water/microemulsion phase are obtained.

Field operations have generally favored low salinities due to the presence of water-external microemulsions. The oil phase in this case is less contaminated with surfactant or other species. However some amount of oil is lost in the microemulsion. Studies using middle-phase microemulsions also have been reported (4).

It is evident that salinity is an important factor in the formation and type of microemulsions and possibly macroemulsions. This study is an attempt to correlate the structure, stability and type of emulsions with physical property behavior as a function of electrolyte concentration.

EXPERIMENTAL

Materials

The surfactant used, a petroleum sulfonate, TRS 10-410 (∿60% active) was obtained from Witco Chemical Company and used as such. Isobutanol (IBA) and sodium chloride were of high purity grade (>99%) from Fisher Scientific. Dodecane oil (99% pure) was obtained from Chemical Sample Company. Water used in these systems was deionized distilled water obtained by passing doubly distilled water through a Barnstead mixed-bed ion exchange resin column and had a specific conductivity less than 2 μS/cm. All spin labels were purchased from Syva Company, Palo Alto, CA, and were used as such.

Preparation of Emulsions

Aqueous solutions were prepared by dissolving 5% (w/w) of TRS 10-410, 3% (w/w) IBA and desired quantities of sodium chloride in distilled water. While the concentrations of surfactant and alcohol are expressed in weight percent (wt %) based on total weight of aqueous phase, sodium chloride concentration is based on total weight of aqueous phase minus the weight of surfactant and alcohol. To these aqueous solutions an equal volume of dodecane was added and sonicated at 30 W sonic-power for ca. 5 min. Cooling of the samples was provided in order to eliminate any heating by sonication.

In order to study the different phases, an equal volume of dodecane was added to aqueous solutions and equilibrat-

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ed at 30 C in graduated cylinders. The spin label was incorporated either in the oil or surfactant formulation.

Measurement of Physical Properties

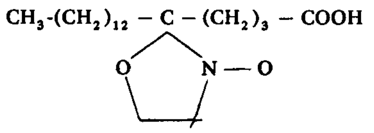
Specific conductance and kinematic viscosity measurements using 1:1 oil/aqueous sonicated emulsions. The kinematic viscosity of the emulsions was measured with an Ostwald-type Cannon Viscometer at 25 ± 1 C for low salt concentrations. Because the viscosity was high, a relatively large capillary diameter viscometer was used. In these experiments, measurements showed reproducibility within ± 0.5 cS.

The specific conductance of the macroemulsions was measured with a Beckman conductivity meter. The cell constant was 1.00 ± 10%. For salt concentrations less than 2 wt % this cell was used. Because at higher salt concentrations (3.5-8 wt %) conductivity vaules were found to be much smaller than 1 μS/cm, no further attempt was made to resolve the values by using an electrode system having lower cell constant. In all of these experiments, conductance values were recorded immediately after sonication was completed. Leaving the sample for a prolonged period of time decreased the conductance values. This is conceivably the consequence of separation of the phases at a microscopic level, although no observable phase boundary was formed. The emulsion system containing 1.5% NaCl was relatively unstable, posing a problem in the measurement of conductivity. However, we attempted to carry out the measurement by keeping the entire mixture in suspension by adequately mixing the liquid mixture. There were fluctuations in conductivity values, in general, with the three-phase systems. The values reported are average values with respect to time. The conductivity values were all recorded at 1,000 Hz.

Macroscopic structure of 1:1 sonicated emulsions by scanning electron microscopy. In order to get some insight into the packing characteristics and dispersed phase droplet size, we employed scanning electron microscopy. The object here was to use this technique effectively for liquid systems. The freeze-fracture method has been adapted by Chan and Shah (5) for a middle-phase microemulsion system. Davis et al. (6) used a carbon-replica palladium-gold shadowing technique in conjunction with an electron microscope to study the fluorocarbon emulsions. The freeze-fracture method for systems containing electrolytes has been criticized by Hatfield et al. (7) for its ability to accurately discern the difference between a salt-water and a surfactant-salt-water system. Despite the difficulties of the freeze-fracture method, with awareness, we have used this technique to understand, at least, qualitatively, the differences, if any, among the emulsions containing different amounts of sodium chloride.

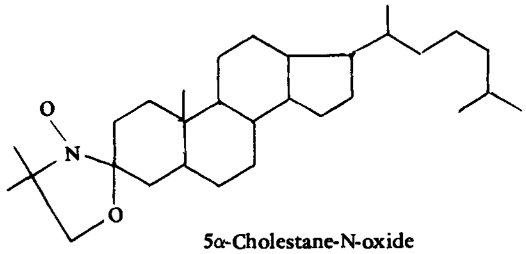
Because we had no experimental facility to study in situ frozen samples, an "image transfer" procedure was used. Here, the emulsions were poured into 1 cm diameter and 5 cm long cylindrical paper tubes and were frozen in liquid nitrogen. The frozen sample was removed and cracked into two halves to produce a fresh surface. A polyvinyl acetate paper strip (3×3 mm^2) was soaked in an image-fixing solution and the strip was placed on the fresh surface for ca. 2 min. The strip was now removed and placed onto the electron microscope sample holder and glued onto the holder by means of silver paint. Moisture was removed under vacuum, and the samples were coated with gold-palladium by vapor phase deposition. The samples were then scanned.

Electron spin resonance measurements. The labels used are.



5-Ketostearic acid

PROBE I



5α-Cholestane-N-oxide

PROBE II

Choosing an optimal label concentration is important in the electron spin resonance (ESR) studies, as the labels may adversely interact with the system under study. In general, the sensitivity of the ESR technique is controlled by the magnitude of the concentration of the spin-labeled substance in the system. Extensive investigations dealing with this aspect of the subject have been done by various authors in the literature (8-15). In the current study, we have chosen concentrations of the labels, by trial and error, such that at least one molecule of the label per micelle or aggregate is available. However, it is essential that this concentration of the label also be able to yield sufficient intensity of signal for observation and recording. Many aspects of this subject with respect to impure petroleum sulfonate formulations have been discussed elsewhere (16).

In this study, the probe concentration was maintained around 10^{-4} M in the mixture. Probe I was first dissolved in a 5:3 TRS 10-410/IBA mixture and then appropriate amounts of brine and oil were added. Probe II was dissolved in dodecane and then added to the desired aqueous solutions of the surfactant-alcohol mixture.

Samples of ESR were gently withdrawn using a syringe and transferred to pyrex capillary tubes of uniform id of 1 mm and then sealed. Deoxygenation of samples of equilibrated phases was not attempted due to the adverse effect concomitant with foaming. All spectra were recorded using a Varian E-9 spectrometer operating at a frequency of 9.5 GHz. Microwave power used was 32 mW and the ambient temperature was 25 ± 1 C. The modulation frequency used was 100 KHz and modulation amplitude was well below the limit where broadening occurs. Scan ranges were 100 and 40 gauss for order parameter and correlation time determinations, and 4 to 10 gauss for linewidth measurements. The scan rate was ca. 2 gauss/min. At least two sets were run for a single sample. Reproducible spectra were obtained under these conditions. The maximal error in order parameter determination was ± 0.5 G whereas, in most cases, the error in correlation time was ± 5%.

RESULTS AND DISCUSSION

Physical Properties of Emulsions

Electrical conductivity. Electrical conductivity of emulsions has been widely used as a convenient property to distinguish O/W and W/O emulsions. In general, emulsions in which water is the continuous medium are expected to show a high conductivity. Similarly, emulsions in which the oil phase is the continuous medium are expected to show very low conductance values.

Based on this evidence, our results shown in Figure 1 indicate the presence of water-external macroemulsions below optimal salinity (1.5%) and an oil-external type above optimal salinity concentration. The low value of conductance above 2 wt % NaCl clearly demonstrates the formation of O/W emulsions. Because of the constraints in the current experimental measurements for conductance values less than 1 μS/cm, we have not attempted to resolve these values further. The conductivity of emulsions increases with the increase of NaCl concentration up to 1.0 wt %. This increase can be attributed to the electrolytic effect of NaCl in the continuous phase. The conductivity of 2% NaCl emulsions shows much higher conductance than the 3.5% NaCl emulsion system.

The striking conductance behavior can be seen with 1.5% NaCl emulsions. This value (2,500 μS/cm) appears to lie in between 1 and 2% NaCl emulsions. It should be mentioned, however, that the measurement of conductance for such three-phase emulsion systems is indeed difficult because of the unstable nature of such emulsions. What we have reported is the average value of several measurements taken immediately after the emulsion is formed.

Viscosity of emulsions. From a theoretical point of view, viscosity measurements are capable of giving considerable information about the structure of emulsions. It has been reported that the viscosity values are often a clue to the emulsion stability.

Sherman (17) has reported the factors which may affect the rheological properties of an emulsion: (a) viscosity of the external phase; (b) volume concentration of the dispersed phase; (c) viscosity of the internal phase; (d) nature of the emulsifying agent and the interfacial film formed at the interface; (e) electroviscous effect; and (f) particle size distribution.

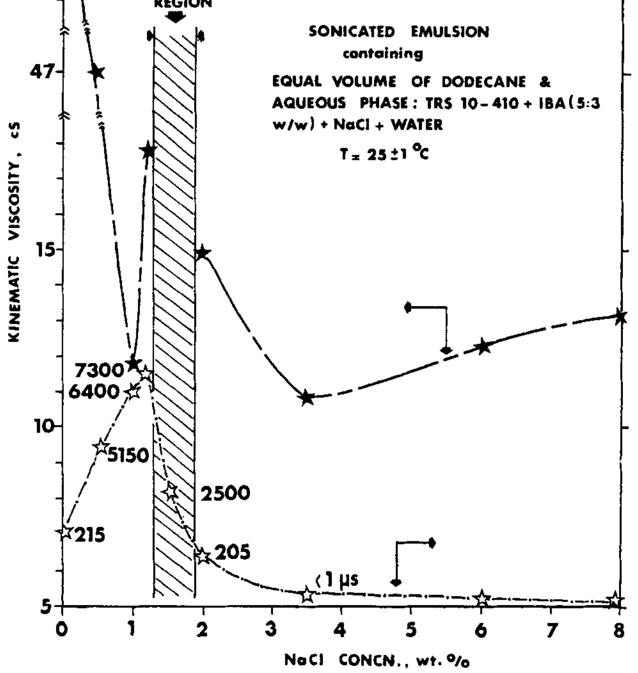


FIG. 1. Variation of kinematic viscosity and specific conductance of sonicated emulsions (aq/oil, 1:1) of TRS 10-410/isobutanol (5:3, w/w) with varying amounts of sodium chloride.

The viscosity changes observed in our system as the NaCl concentration is increased (Fig. 1) can be attributed to a number of factors. First of all, below 1.5% NaCl (optimal salinity), kinematic viscosity of the emulsions decreases as NaCl concentration is increased. From electron microscopic pictures, we can say qualitatively that the average particle size increases although the increase is not appreciable. If we conclude from the electrical conductivity data that these are water-external macroemulsions, then it is conceivable that the addition of electrolyte could considerably affect the double layer, i.e., the addition of NaCl can decrease the double-layer effects. Under these circumstances, one ought to consider the phenomenon of electroviscous effect in emulsions. In brief, the electroviscous effect was first investigated theoretically for lyophobic colloids by Smouluchowski (18). This study has shown that lyophobic particles bearing an electric charge exhibit a viscosity exceeding that of a similar system of uncharged particles. Taking this into consideration, Smouluchowski modified Einstein's equation:

$$[\eta_E = \eta_o (1 + 2.5\phi)]$$

$$\frac{\eta_E - \eta_o}{\eta_o} = 2.5\,\phi\;[1 + \frac{1}{\eta_o \kappa a^2}\;(\frac{\epsilon\zeta}{2\pi})^2],$$

where η_E = viscosity of emulsion; η_o = viscosity of external phase, ϕ = volume fraction of dispersed phase, a = radius of particles, κ = specific conductivity of suspension or emulsion, ϵ = dielectric constant of the dispersed medium and ζ = the electrokinetic potential of charged particles (called zeta potential).

It can be seen from this equation that the particle size effect is incorporated as a reciprocal term. That is, for a given ϕ, ϵ, ζ and η_o, an increase in particle size would reduce η_E. In the current study, η_o (viscosity of external phase) of equilibrated aqueous phase (Table I) varies from 1.2 to 6.9 cP corresponding to a NaCl concentration variation of 0–1.2 wt %. Also, the specific conductance of emulsions increases from 200 μS/cm to 7,300 μS/cm (see Fig. 1). Because of the large conductance values, we did not measure the dielectric constant of the medium over the NaCl concentration range. However, some measurements are being done at present for relatively low conductance systems and the results will be reported in the near future. For the present, we can intuitively say that the ϵ values will be relatively higher than water and can be assumed to be constant over the NaCl concentration range of 0–1.2 wt %. With this picture, it can be deduced now that as η_o, κ and "a" increase with NaCl concentration for a given ϕ (0.5), η_E will decrease. This is essentially the observation – η_E decreases from 75 cS to 11.8 cS when NaCl concentration is increased from 0 to 1 wt %. An abrupt increase of η_E (17.8 cS) at 1.2% NaCl could very well be due to the foam-type structure. One other possibility for the increase in emulsion viscosity at 1.2% NaCl could be the high external phase viscosity of the equilibrated aqueous phase (6.8 cP). Of course, this is only a speculation and warrants further study.

The experimental emulsion viscosity reduction with NaCl (up to 1 wt %) obviously cannot be explained by the increases in conductivity, external phase viscosity and particle size alone. It is our contention that double-layer suppression or discharge is equally important in this region. That is, ζ could decrease considerably and thus influence the viscosity decrease. With regards to the nature of charge on the surface, it is evident from the equation that it is unimportant. Both negative and positive charges yield the same results.

TABLE I

Physical Properties of Equilibrated Phases: Aqueous Phase: TRS 10-410 + IBA (5:3, w/w) + NaCl (X%); Oil Phase: Dodecane; Aqueous/Oil = 1:1 (v/v) at 30 C

NaCl conc. (wt %)	Bulk density (g/cm^3)			Absolute viscosity of aqueous phase (cP)	Absolute viscosity of oil phase (cP)	At 25 C specific conductance of aqueous phase (mS/cm)	Interfacial tension (dyne/cm)
	Aqueous phase	Middle phase	Oil phase				
0	0.9883		0.7410	1.26	1.20		0.422
0.5	0.9851		0.7410	1.21	1.24	19.45	0.105
1.0	0.9729		0.7422	2.33	1.26		0.0178
1.2	0.9612		0.7434	6.86	1.25	15.5	0.0056
1.5	1.0018	0.9079	0.7417	0.89	1.24	25.0	–
1.8	1.0060					26.0	–
2.0	1.0494	0.80	0.7518	0.96		31.30	0.00975[a]
3.5	1.0174		0.7664	0.84	2.77	53.0	0.083
6.0	1.0362		0.7581	0.83	1.56	75.0	0.243
8.0	1.0490		0.7664	0.93	1.72	102.0	0.39

[a] Middle phase/oil interface.

For the case of 1.5% NaCl, we could not produce any sonicated emulsion at 25 C. The system was very unstable and separated almost immediately. However, mild-hand-shake experiments gave a milky emulsion which was again unstable. Because of these difficulties, no viscosity measurements could be made.

Some experiments using a continuously sonicated system of 1.5% NaCl with constant stirring when allowed to flow through a given porous media gave pressure drops much lower than other emulsions with different NaCl concentrations. It is appropriate to mention here that the pressure drop value was ca. 2 times greater than that of water. This leaves us with an interesting problem. Probably, the mixture viscosity or emulsion viscosity (if it was formed) must be in the vicinity of 1 or 2 cP. If we take the maximum viscosity phase as the external phase, then η_o (now middle phase) will be 5.0 cP (see Table I). If we assume that the double-layer forces are completely minimized and take the condition $\zeta=0$, then we are left with the Einstein equation $\eta = \eta_o (1 + 2.5\phi)$. This equation would predict a viscosity of ca. 11 cP, which is much too large for the observed pressure drops. Evidently, the question to be posed would be: if an emulsion is produced, what is the phase which is dispersed and what is the volume fraction dispersed? As a lower limit, if we take viscosity of aqueous or oil phase (saturated) as the external phase, then η_o will become 0.9 or 1.2 cP, respectively. With these values, the emulsion viscosity would be of the order of 2.2 or 2.8 cP, respectively. These values agree quite well, considering the pressure drop results.

Obviously, we have a problem using Einstein's Equation because it is a limiting law. It has been reported (19) that the equation probably is invalid for values of ϕ greater than 0.02. In the literature, therefore, several modifications were made to improve this equation for higher dispersed phase volume emulsions. One important equation applicable to emulsions containing more than 50% of dispersed phase has been derived by Hatschek (20):

$$\eta_E = \eta_o \left[\frac{1}{1-\phi^{1/3}}\right]$$

If the several combinations of η_o values discussed for this emulsion are substituted in the above expression, one would again have large values for η_E based on $\phi = 0.5$. Once more, these results are not favorable in the context of pressure drop results. More study is evidently needed using the three-phase systems and, therefore, further discussion will not ensue.

Macroscopic structure of emulsions. The macroscopic structure of sonicated emulsions (aq/oil = 1:1) was determined for sodium chloride concentrations 0, 0.5, 1, 1.5, 2, 3.5, 6 and 8 wt %. The scanning electron microscope pictures taken by the "frozen-sample replica" method are given in Figures 2 and 3. The droplet configurations existing in the emulsions can be classified according to the next three sections.

I. A relatively closely packed emulsion of nonuniform size droplets. This type of behavior is exhibited by emulsions containing 0% sodium chloride (Fig. 2, plate A), 2% NaCl (Fig. 3, plate E), 3.5% NaCl (Fig. 3, plate F) and most likely by 6% NaCl (plate G). In the case of 6% NaCl emulsions, the droplet configuration is not clearly revealed (plate G). We believe that the presence of large amounts of salt is disadvantageous in the use of the current technique. The freezing action can produce NaCl crystals at certain locations of the emulsion matrix. Because of the experimental limitation (e.g., overheating of acetate paper by a high intensity electron beam) only a 20,000 x magnification was used.

Despite the limitations of this technique, it is possible to obtain order-of-estimates of the droplet size in the emulsion systems. Emulsions containing 0% NaCl, 2% NaCl and 3.5% NaCl have droplets of diameters in the range of 0.3–1.5 μm, 1.2–2.5 μm and 0.5–1 μm, respectively. It is possible that the droplet size of the 6% NaCl emulsion is in the vicinity of 0.1 μm.

II. A closely packed emulsion of polyhedral droplets. Emulsions with 1% NaCl (Fig. 2, plate C) and 8% NaCl (Fig. 3, plate H) appear to be in this category. An estimate of the maximal dimensions of the polyhedral droplets gives values of ca. 1.4–2.4 μm in the case of 1% NaCl and ca. 1.3–1.9 μm with 8% NaCl emulsions. It is interesting to observe replicas of sodium chloride crystals inside the droplet phase (water containing 8% NaCl). This type of emulsion has been identified by Manegold (21) in his studies of the relationship between volume and the droplet form required for emulsion stability. Furthermore, Manegold recognized the morphologic similarity between emulsions of this type and drained polyhedral foams. He considered the polyhedral form of emulsions as an extreme case in which the concentration of dispersed phase is so high that the droplets are subjected to deformation. This state of the emulsion possesses an additional source of instability. (It should be noted

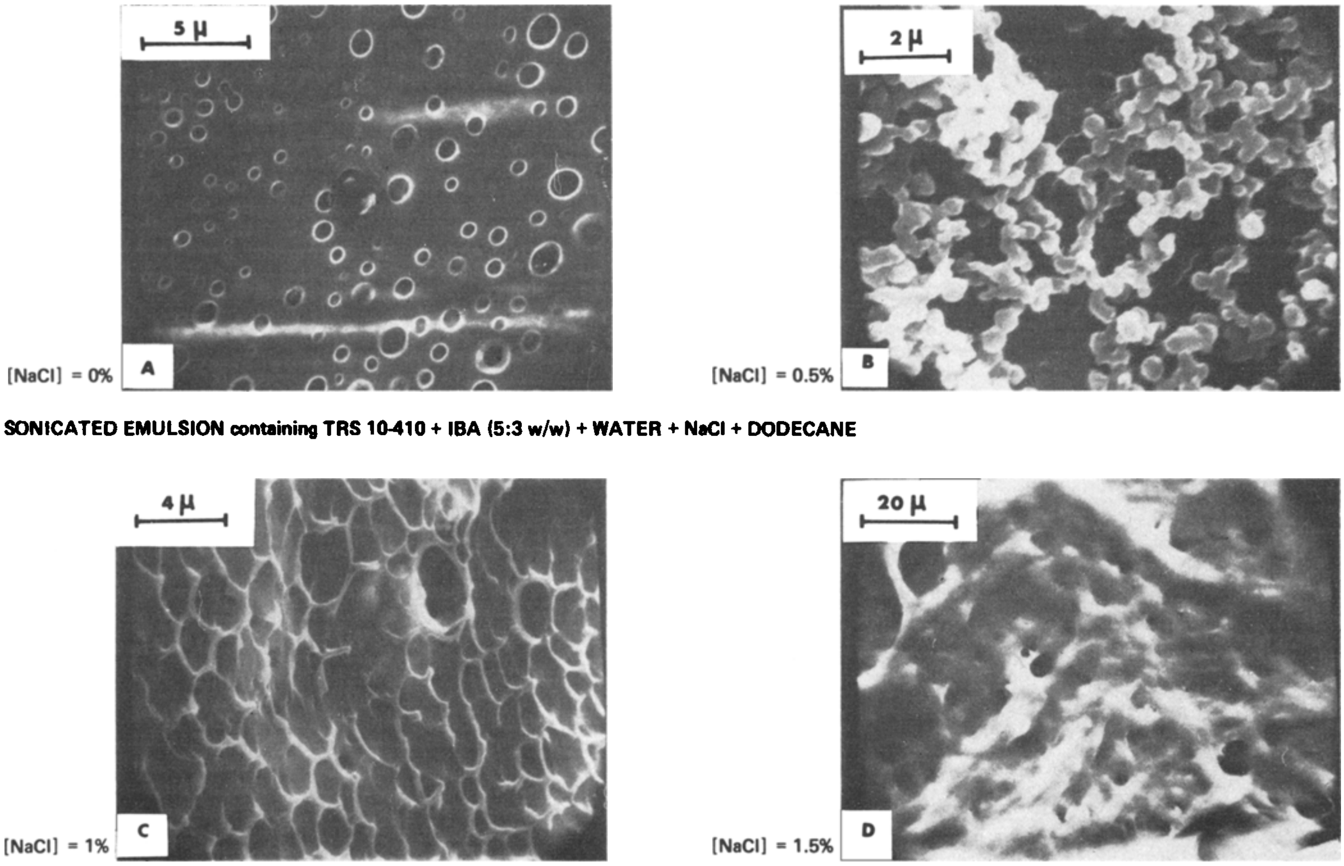


FIG. 2. Scanning electron micrographs of sonicated emulsions (aq/oil, 1:1) of TRS 10-410/IBA (5:3, w/w) for various sodium chloride concentrations.

that the polyhedra have a greater surface area than the undistorted spheres).

It is evident in the current study that we have a similar situation as that of Manegold's observations, except that, instead of phase volume we have salt concentration as the variable.

III. Microemulsion-type structure. Electron micrograph shown in Figure 2, (plate B) for sonicated emulsions with 0.5 wt % sodium chloride closely resembles that of Prince's (22) alkyd-in-water microemulsions. The cause for this similarity, is, however, unclear at present. The sample preparing procedure used to photograph these structures is quite different – Prince (23) took a dilute solution of an O/W alkyd microemulsion and exposed it to the vapors of osmium tetroxide in a vacuum desicator. In this operation, the droplets were converted into little cannon balls. Now the dispersion was mounted on the stage of the electron microscope and vacuum was applied. The organic material was burned off, leaving behind osmium skeletons of the original spheres. Prince remarked that this technique is applicable only to unsaturated oils as alkyds or other materials of this kind in the form O/W microemulsions. In order to illustrate the behavior of W/O emulsions, he used the same method but now with carnauba wax and carotene W/O emulsions and no pictures were obtained.

Note on 1.5% NaCl Emulsions

This system yields three phases after complete separation. Forming a suitable emulsion for study has been a problem with this system. Mild hand-shaking has been found to yield milky, short-lived, unstable emulsions. Typical time taken for complete separation of these three-phase system-emulsions was found to be of the order of 5 min. When this system was sonicated, strata of liquid layers were found to move in the container with "patches of white mass" at random position. Careful sonication with adequate temperature control (23 ± 1 C) also gave similar results. Even if some emulsions were produced by this method, it disappeared soon after the sonication was stopped. These observations thus present the question of the true state and the formation of emulsions in three-phase systems. (A similar effect was also observed with a 1.8% NaCl three-phase system). By alternately sonicating and hand-shaking this system for several cycles, we could get what we thought was an emulsion, which was immediately frozen in liquid nitrogen for electron microscopy studies.

The result obtained using this emulsion is given in Figure 2 (plate D). It is evident from the picture that macroemulsion droplets do not appear to exist and no further analysis is made.

Microstructure of Sonciated Emulsions (Aq/Oil = 1:1) by ESR Studies

Cholestane-N-oxide label. This label is insoluble in water and therefore can be present either in an oil or surfactant environment. The spectra obtained were isotropic, indicating that anchoring of the label via the nitroxide group at the oil-water interface is weak. This imparts rotational freedom averaging any axial symmetry. Correlation time for rotational tumbling motion can be used as a monitor of the label environment. These parameters were calculated accord-

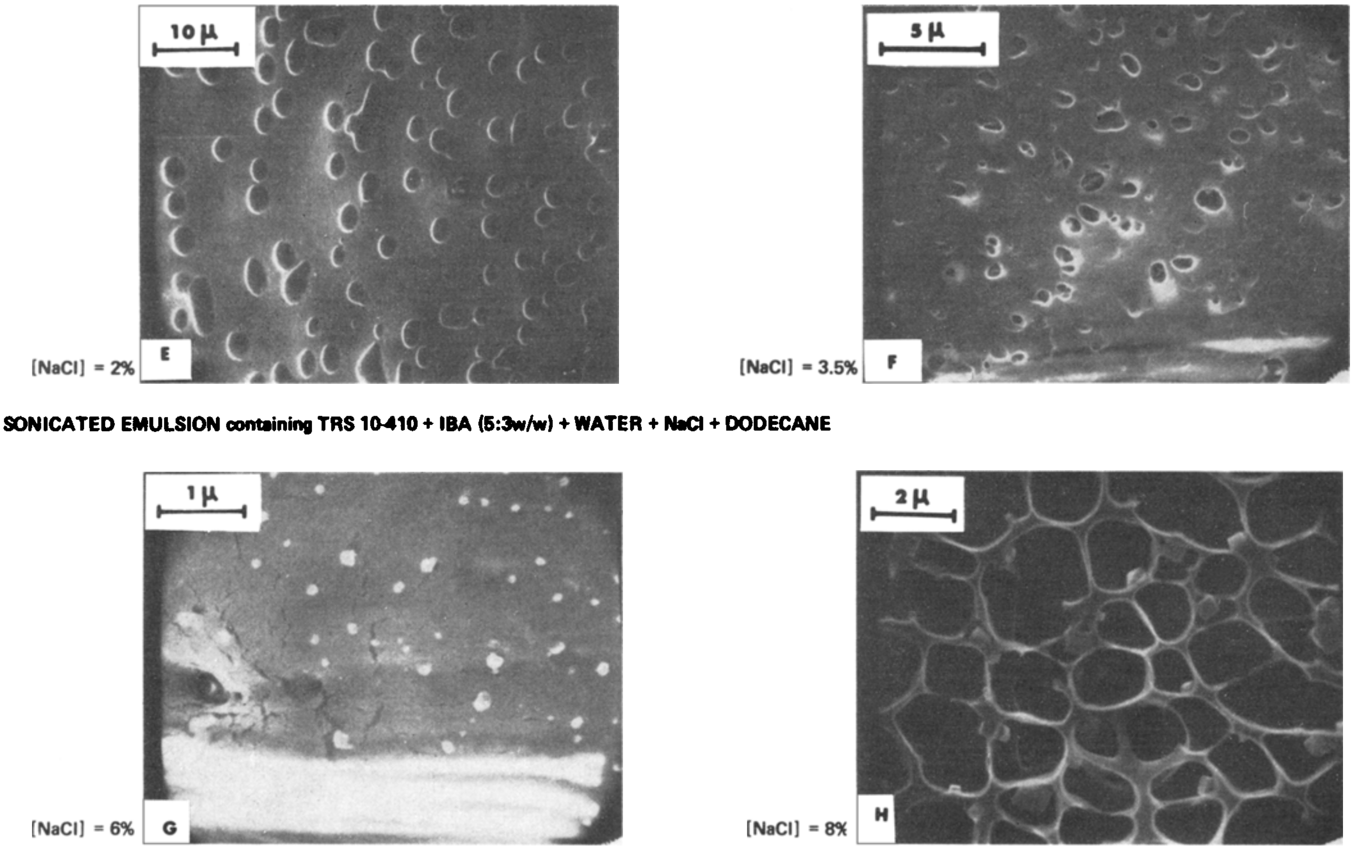


FIG. 3. Scanning electron micrographs of sonicated emulsions (aq/oil, 1:1) of TRS 10-410/isobutanol (5:3, w/w) for various sodium chloride concentrations.

ing to the method of Stone et al. (8) using the equation:

$$\tau_\theta = 6.5 \times 10^{-10} \times W_o \times \left[\left(\frac{h_o}{h_{-1}}\right)^{1/2} + \left(\frac{h_o}{h_{+1}}\right)^{1/2} - 2 \right] \text{ sec},$$

where W_o = width of central line, h_{+1}, h_o, and h_{-1} are peak heights of the low field, central and high field lines. The results are plotted in Figure 4 for emulsions and Figure 5 for equilibrated phases.

The emulsion studies indicate that, as the salinity increases: $\tau\theta$ decreases up to 1%; increases slightly at 2%; and thereafter gradually decreases up to 8%. Therefore, the probe molecule experiences maximal restriction to motion at 0%, which decreases greatly as salinity increases. At 2%, this restriction is slightly enhanced but remains almost constant up to 8% NaCl.

To explain these results, it is necessary to fix the location of the probe. Upon equilibration, almost all of the probe molecules preferred an oil phase to a surfactant-rich phase. This rules out the location of the probe at the interface. The label is known to reflect the fluidity of one phase if the other phases are too rigid (9). The hyperfine splitting constant is always 14.2 gauss, the value in pure oil, indicating that the label is in the oil phase. Isotropy of spectra reflects an isotropic label environment (10). It is evident, therefore, that cholestane-N-oxide prefers an oil environment.

The abnormally high correlation time for emulsions at 0 and 0.5% NaCl (∿400–450 psec) cannot be explained by either invoking bulk viscosity or packing at the interfaces.

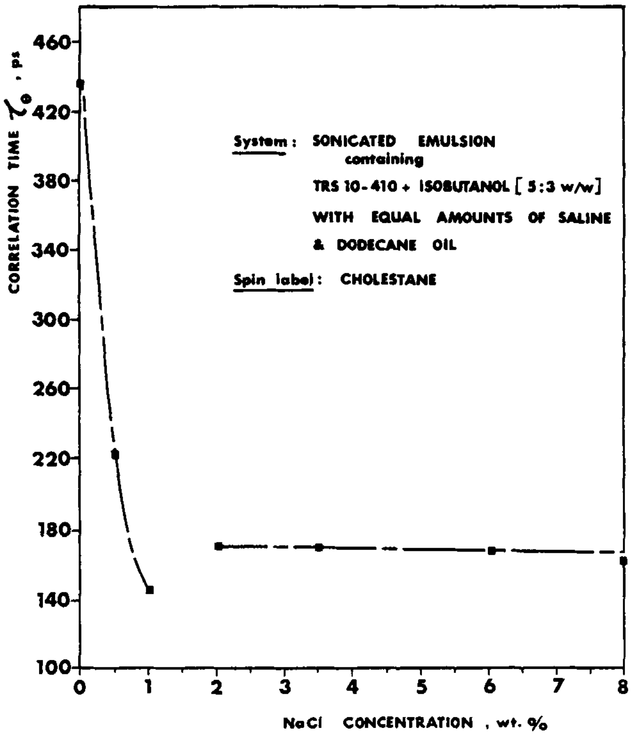


FIG. 4. Correlation time, τ_θ, of cholestane label in sonicated emulsions (aq/oil, 1:1) of TRS 10-410/isobutanol (5:3, w/w) for various sodium chloride concentrations.

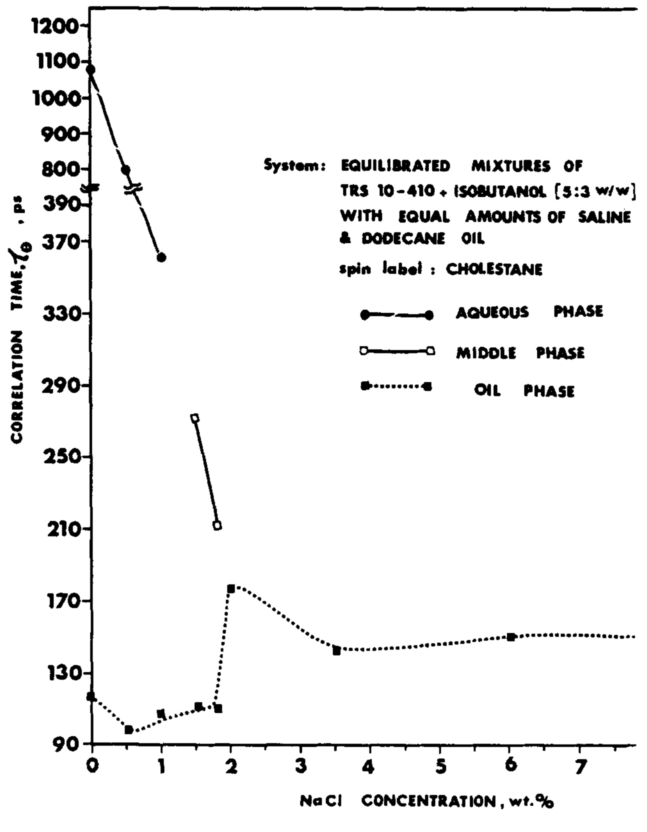


FIG. 5. Correlation time, τ_θ, of cholestane label in different phases of equilibrated mixtures of TRS 10-410/isobutanol (5:3, w/w) with equal amounts of brine and dodecane.

SCEM results show that the size of an average macroemulsion droplet is of the order of thousands of angstroms. Because an oil-external macroemulsion is ruled out on the basis of phase volumes, one can only picture a water-external macroemulsions system with oil solubilized in the core. The label has molecular dimensions of the order of 50 Å and could not be expected to be restricted so highly in a macroemulsion oil droplet. High correlation times can result only if the probe is trapped in a cage having micellar dimensions. Swollen micelles of the water-external type are strongly indicated. To test this, the equilibrated aqueous phase was analyzed. It was found that, at 0 and 0.5% NaCl, the correlation times of the probe in aqueous phases was of the order of 800–1,100 psec. This value is ca. 3–4 times the value for the emulsions. We believe that a sonicated emulsion consists of both macro- and microemulsions and that they are of the same type. The decrease in τ_θ for the emulsions is therefore due to increase in core volume in the macro and micro droplets. Beyond 2%, the trend is one of constancy. This is expected, because the system is an oil-external type and has a constant environment in both types of emulsions. It is not surprising that the emulsion correlation time parameters are about the same (∿160–170 psec). From these studies as well as the data from electrical conductivity studies, we believe that, at low salinities, a water-external macroemulsion exists whereas at high salinities, an oil-external type is found. Swollen micellar systems co-exist with the macroemulsions and have the same external phase. Studies on middle phases obtained under different conditions for the same formulation has indicated that a transition from water-external to oil-external does occur.

5-Ketostearic acid label. The spectra obtained with this label in these systems exhibit an anisotropic behavior with well defined extrema. Similar spectra have been obtained for spin-labeled phospholipid dispersions (11), egg lecithin vesicles (10) and normal sarcoplasmic vesicles (13) for stearic acid labels. The observed shape of such spectra has been identified with that arising mainly due to the strong anchoring of the label via the carboxylic group at the oil-water interface. The theory associated with the motion of fatty acid labels in membranes, dispersions and vesicles is well documented (10–15, 24–26) and will not be described here. The order parameter S is obtained from the experimental values of $T_{\|}$ and $T_{\perp}$ as shown in Figure 6. S is given by:

$$S = \frac{T_{\|} - T_{\perp}}{T_{zz} - T_{xx}}$$

Values for T_{zz} and T_{xx} have been taken from the literature for this label. The quantity $T_{\|} - T_{\perp}$ is denoted by ΔT and can be used as a measure of the degree of order. The hyperfine splitting constant A_N is given by $A_N = (T_{\|} + 2T_{\perp})/3$. $T_{\|}$ is inversely related to mobility in the system.

The variation in the order parameter ΔT of the emulsions as a function of salinity is plotted in Figure 6. It is seen that ΔT is high at 0% NaCl and decreases significantly up to 1.0% NaCl. At 2% NaCl, the order parameter increases and increasing the salinity decreases ΔT gradually but steadily up to 8.0% NaCl. Analyses of the spectra show that $T_{\|}$ follows ΔT closely and indicates that the mobility of the fatty acid chain increases from 0→1% NaCl, shows a decrease at 2% followed by a gradual increase beyond up to 8.0% NaCl. These results tally well with those obtained using the cholestane label. Studies of the equilibrated phases with 5-ketostearic acid label essentially underscore the importance of the contribution of the swollen micelles to the packing and order in sonicated emulsions. The results are tabulated in Table II. The oil phase analysis shows that as salinity increases, an increasing amount of surfactant is found in the oil phase. A saturation value would be expected before transition to a two-phase at high salinities. Furth-

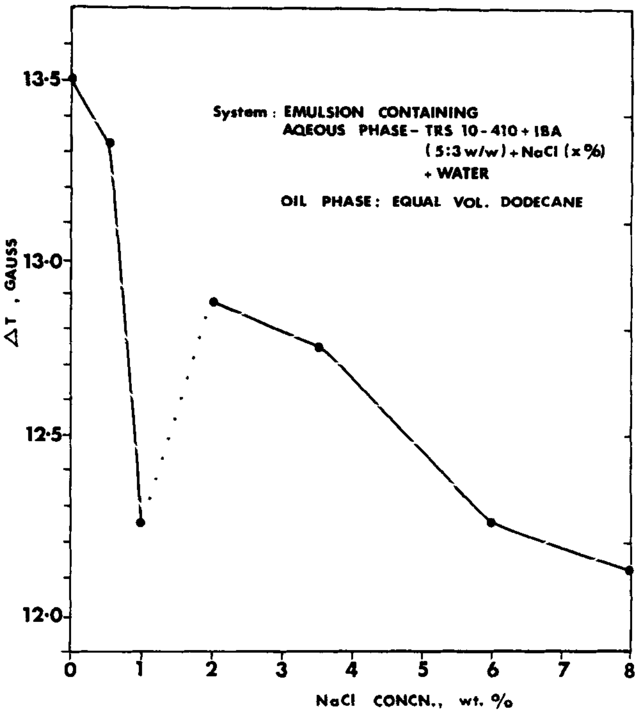


FIG. 6. Variation of order parameter ΔT and $T_{\|}$ of 5-ketostearic acid label in sonicated emulsions (aq/oil, 1:1) of TRS 10-410/isobutanol (5:3, w/w) with varying amounts of sodium chloride.

TABLE II

Spin Label Studies on the Different Aqueous, Middle and Oil Phases of Equilibrated Mixtures of 1:1 Aqueous Solutions of 5:3 (% w/w) TRS 10-410: Isobutanol with Dodecane Oil Using 5-Ketostearic Acid Label

Salinity (%)	0.5	1.0	1.5	6.0	8.0
Aqueous phase	$\Delta T = 12.00$	$\Delta T = 12.375$	Negligible concentration of label	Negligible concentration of label	Negligible concentration of label
Middle phase	–	–	$\Delta T = 12.5$ Gauss	–	–
Oil phase	$\tau_\theta = 88$ ps	$\tau_\theta = 132$ ps	$\tau_\theta = 150$ ps	$\Delta T = 12.375$ Gauss	$\Delta T = 11.625$ Gauss

er, the order parameters at very low and very high salinities are lower for equilibrated phases than the respective sonicated emulsions. At intermediate salinities, these values are about the same in either equilibrated phases or emulsions.

Preliminary experiments on ascorbic acid treatment, which destroys the nitroxide moiety, of surfactant-rich equilibrated phases of these systems revealed distinct differences. The interfacial component (immobile) of the signal disappeared relatively slowly at low salinities whereas at higher salinities, this signal was destroyed almost immediately. It is evident that the nitroxide moiety is buried within the core in the first case and exposed in an oil environment in the second. This lends evidence to the existence of a water-external emulsion at low salinities and an oil-external one at high salinities.

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