

Effect of Salt and Aging on Aqueous Surfactant Formulations for Tertiary Oil Recovery: A Correlation of Physical Properties with Microstructure Using Spin-Labels

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ABSTRACT

Physical properties and molecular packing in surfactant aggregates of the surfactant formulation 5% (w/w) TRS 10-410 (a petroleum sulfonate), 3% (w/w) isobutanol and desired quantities of sodium chloride in distilled water were studied using electron spin resonance (ESR) technique and pH, density, viscosity, screen factor, specific conductance, surface tension and free sodium ion measurements of fresh and aged solutions. The results suggested that both salt concentration and aging lead to changes in molecular packing of surfactant aggregates. At optimal salinity, the order parameter was a maximum. With increasing salt concentration, the correlation time increases initially and decreases at higher salt concentration. Various physical property data substantiate the observed microstructural changes. A detailed discussion is presented of the interrelations of these parameters operative in this complex surfactant formulation.

INTRODUCTION

Micellar solutions of various surfactants have been employed as injection fluids to improve oil recovery. These solutions produce ultra-low interfacial tension at the oil/micellar solution interface (1). The aqueous solution of the surfactant formulation, usually a mixture of surfactant and cosurfactant has therefore to be characterized before we can attribute physical property behavior to special structural alterations in the presence of oil. It will be useful to find out if structural changes in the aqueous solution alone influences phase behavior in the presence of oil. Salinity is an important factor in all these processes, and hence, a study of aqueous solutions of the formulation as a function of salinity is warranted. Factors that are affected by salinity changes include low interfacial tension, salt tolerance limits (which has a direct bearing on phase changes), solubilization capacity changes in micellar size and shape, rheological and flow properties. The extent to which aging affects the structural architecture of these solutions is one of many parameters that would be important in field operations. We therefore undertook a detailed study of the structural and physical property behavior of aqueous solutions of a surfactant formulation as a function of salinity.

The objectives of this investigation are: (a) to characterize structural changes in aqueous solutions, (b) to correlate these structural changes to other physical property behavior, (c) to assess the effect of aging of these solutions on physical property behavior and structure, and (d) to elucidate changes in structure when small amounts of oil are solubilized.

EXPERIMENTAL

Materials

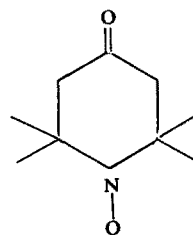
The surfactant was Petroleum Sulfonate TRS 10-410 (\cong 62% active), obtained from Witco Chemical Co. Isobutanol (IBA) and sodium chloride were of high purity grade (> 99%) from Fisher Scientific. Dodecane (99% pure) was obtained from Chemical Sample Co. Water used in these solutions was doubly distilled and deionized by passing through a Barnstead mixed-bed ion exchange resin column. The specific conductance was less than 2 μ S/m.

Preparation of Solutions

Aqueous solutions were prepared by freshly dissolving 5% (w/w) of TRS 10-410, 3% (w/w) IBA and desired quantities of sodium chloride in distilled water. The concentrations of surfactant and alcohol are expressed as percentage of weight based on total weight of aqueous phase, whereas the concentration of sodium chloride is based on total weight minus the weight of surfactant and alcohol. The solutions prepared at every instant, by the procedure just described, are referred to as "fresh solutions" and are arbitrarily assigned a zero bulk-solution age. Aging of the fresh solutions was achieved by allowing them to stand in closed-glass containers for periods up to 15 months. In this study, measurements of various physical properties were done using fresh and aged solutions.

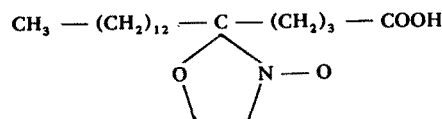
Electron Spin Resonance Measurements

The labels used were:



2,2,6,6-Tetramethyl piperid-4-one-N-oxide (TEMPO)

PROBE I



5-Ketostearic acid

PROBE II

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Probe I was readily soluble in water and all solutions were prepared from a stock solution of Probe I in water. Probe II was dissolved in the 5:3 mixture of TRS 10-410:IBA and the appropriate amounts of brine were added to make the desired solution.

Samples for electron spin resonance (ESR) were withdrawn gently using a syringe, and then transferred to pyrex capillary tubes of uniform id 1 mm which were sealed, leaving a minimum of vapor space. Deoxygenation of solutions was not attempted because of the adverse effects of foaming.

All spectra were recorded using a Varian E-9 spectrometer operating at a frequency of 9.5 GHz. Microwave power was 32 mW for Probe II and 2 mW for Probe I in order to avoid saturation. The modulation frequency used was 100 KHz and modulation amplitude was maintained well below the limit where broadening of lines occurred. Scan ranges were 100 and 40 gauss (G) for order parameter and correlation time determinations and 10 and 2 gauss for line width estimation. The scan rate was 2 G/min. Ambient temperature was 25 ± 1 C and at least two sets were run for a single sample. Reproducible spectra were obtained under these conditions. Maximum error in order parameter determination was ± 0.5 G and for correlation time estimation it was often within $\pm 5\%$. The reproducibility of line widths was within 10-15 mG.

Measurement of Physical Properties

Density. The density of the aqueous surfactant solutions was measured by 1-ml and 5-ml specific gravity bottles.

Viscosity. The bulk viscosity was measured with a Ostwald-type Cannon viscometer. The time taken for the solution to flow through a standard capillary of fixed hydrostatic head was recorded at desired temperatures. The kinematic viscosity thus obtained, knowing the cell constant of the viscometer, was then converted to absolute viscosity by using the density data. The relative accuracy of the apparatus was ± 0.1 cP. In some cases, foaming occurred when the solutions were drawn through the capillary. For these systems, capillaries with larger diameters were used. This minimized the foam formation but increased the measurement error. Nevertheless, duplicate mixtures and measurements showed reproducibility to within ± 0.01 cP in the current measurements.

Electrical conductivity. The electrical conductivity of the solutions were measured with a Beckman conductivity meter. The cell constant was $1.00 \pm 10\%$. No special precaution was taken in these measurements as the system conductivity was very high. Nevertheless, conductivity values were recorded at 50 and 1000 Hz. Steady readings were obtained within 5 min. The reproducibility of the measurements were estimated to be within 1% error.

pH measurements. The pH measurements were done at 25 ± 1 C with an Orion pH meter equipped with an immersion glass electrode system. Prior to the measurements, the pH meter was calibrated using standard pH buffers. The precision of the readings were within ± 0.02 pH. Several measurements were taken for each concentration of a solution for different solution ages. The measurements were reproducible within a relative error of ± 0.02 pH. No special care was taken either to eliminate the carbon dioxide from the measuring cell or to exclude carbon dioxide during the preparations of all solutions.

Screen factor measurements. Screen factor measurements were done using a standard set-up consisting of a fine steel mesh constriction. The time taken for flow of various aqueous systems through the wire mesh constriction

was measured. The ratio of the time taken for the flow of aqueous systems to that for water is expressed as the relative screen factor. The results are the average of at least 10-20 measurements.

Sodium activity. Free sodium activity in aqueous solutions was measured by sodium ion selective electrodes with a digital pH/mv Orion meter, model 801A. It has been recommended that for the use of this technique, the pH of the solutions should be a constant; otherwise, buffer solutions would be employed to achieve pH consistency. In the current measurements with fresh aqueous solutions, the pH remained constant ($\cong 10$ units) throughout the NaCl concentration range. Hence, no pH adjustment was necessary. However, in the aged solutions ($\cong 1$ yr), as discussed in the earlier section, the pH changed from one solution to the other with a local maximum at 1.5% NaCl. Overall, the variation was within 2 pH units. As our primary objective was to study the counterion effect in fresh and in aged solutions, it was decided to measure the sodium activity without introducing a buffer. In order to study the effect of addition of buffer, we tried some experiments with a buffer. There was no significant difference in the results between the buffered and unbuffered systems. The only difference, however, was that the time taken to read a steady potential was accelerated in the buffered systems. Extensive calibration of the ion-specific sodium electrode was done in standard salt solutions containing 2 ml of ionic adjuster (20 g NH_4Cl + 5 ml NH_4OH diluted to 100 ml of water). Appropriate activity correction was employed. Thus, free sodium ion activity in the solution was measured.

Relative errors in the measurements were of the order $\pm 7\%$ and $\pm 4\%$ for NaCl concentrations of 0 and 0.5%, respectively, and ± 1 to 2% for higher concentration. The error limits were of the same order for both fresh and aged solutions. Total sodium concentration was measured by flame photometry. From the total and free sodium ion concentration, the amount of sodium bound to the micellar structures was determined.

RESULTS AND DISCUSSION

Microstructure Studies of Aqueous Surfactant Formulation by Electron Spin Resonance (ESR) Technique

Spin probe studies of Probe I in fresh aqueous solutions of 5:3 TRS 10-410:IBA indicates that, as the salinity increases, the correlation time initially increases at 0.5% followed by a gradual decrease up to 1.8%. Beyond this salinity the correlation time is essentially constant. Aged solutions of the same system behave differently. The correlation time in these solutions shows an initial increase up to 1%, followed by a steep drop at 1.5%. The trend beyond 1.5% salinity also is different from those of fresh solutions in that, instead of a leveling effect, we observed a significant increase at 1.8% followed by a decrease at 2% (Fig. 1). Our results for the stearate label indicate that the order parameter (which is a direct reflection of the packing and the rigidity, as seen in the separation of the outermost peaks) increases as the salinity increases. This is a maximum at around 1.5% and then shows a slight decrease (Fig. 2). The polarity of the label, as seen through A_N values does not vary significantly, reflecting an environment that does not change with salinity. The line width, on the other hand, remains constant up to 1.25% NaCl, increasing enormously at 1.5-1.9%. The line width drops as abruptly beyond these salinities as those obtained below 1.25% NaCl (Fig. 3).

It is known from literature (2) that fresh solutions of

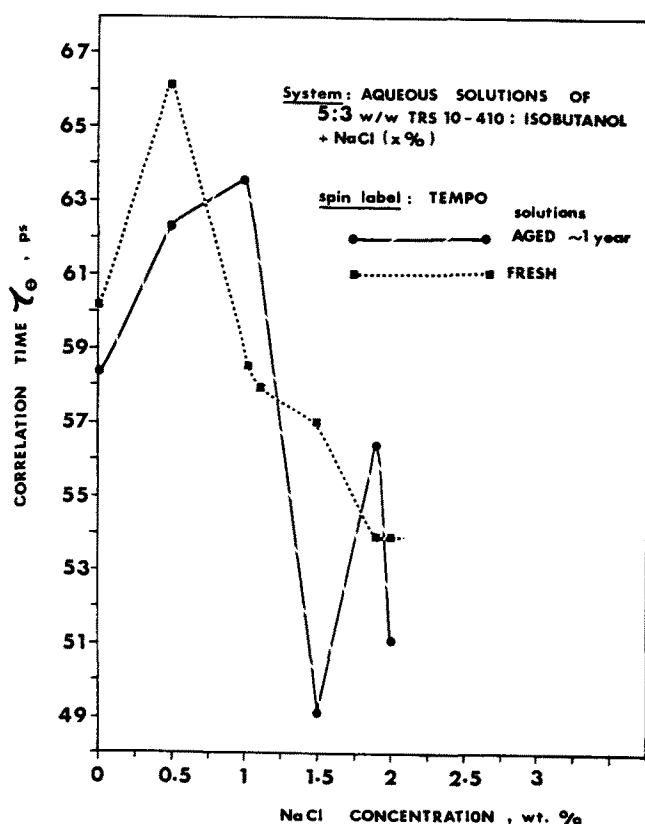


FIG. 1. Correlation time, τ_{θ} , of TEMPO label in fresh and aged aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with varying amounts of sodium chloride.

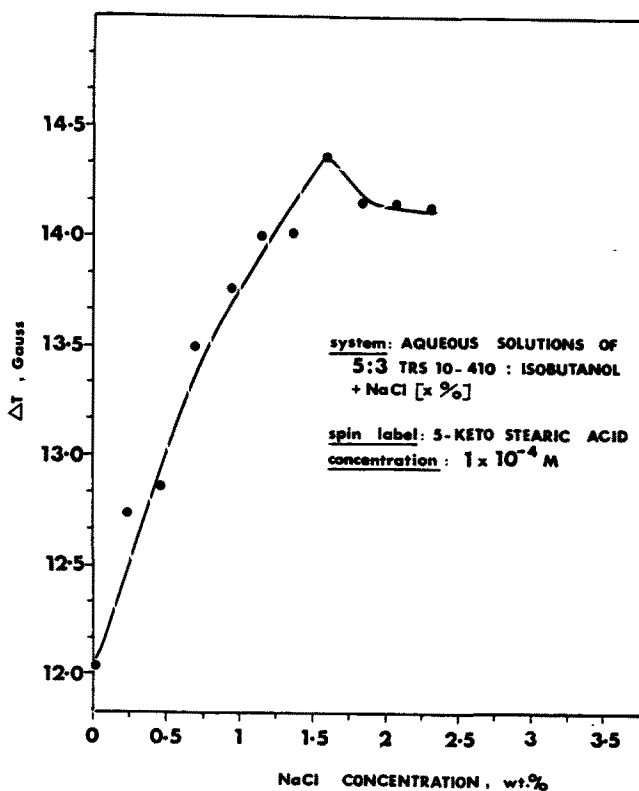


FIG. 2. Variation of order parameters ΔT of 5-ketostearic acid label in fresh aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol and varying amounts of sodium chloride.

these systems are birefringent beyond 1.5% NaCl. Liquid crystalline lamellar structures might be involved. The maximum order parameter obtained around 1.5% might be the region where the tightest packing of surfactant molecules are possible. Viscosity, screen factor and line width all support this possibility. Our previous studies on similar systems using the stearate label (3) and nuclear magnetic resonance (NMR) (4) also support the view that birefringence is a maximum where packing is tightest. Apparently, the decrease in the order parameter above this salinity is the result of a more fluid structure. A closely packed structure is indicated at 1.5-1.6% whereas beyond this a less rigid structure exists.

The decrease in correlation time obtained with a TEMPO label at concentrations where the tightest packing is expected leads us to the conclusion that the TEMPO molecule would be excluded from such structures. Partition studies of TEMPO in equilibrated mixtures of equal volumes of water and dodecane oil with and without 3% isobutanol in the total absence of surfactant and salt indicates that the correlation time is almost unchanged in aqueous solutions; the slight amount of TEMPO that does partition into the oil phase has greatly reduced correlation times and is drastically affected in the presence of alcohol. Therefore, low concentrations of alcohol are not expected to alter correlation times in aqueous solution greatly. If we assume that TEMPO is included in the structures formed around 1.5 NaCl, the correlation time ought to be significantly high compared to aqueous solutions of the surfactant without these special structures. Also the hyperfine splitting constant of TEMPO should at the least reflect an average of an aqueous and hydrocarbon environment. Both of these observations are conspicuous by their absence. Indeed, the correlation time shows a marked decrease and

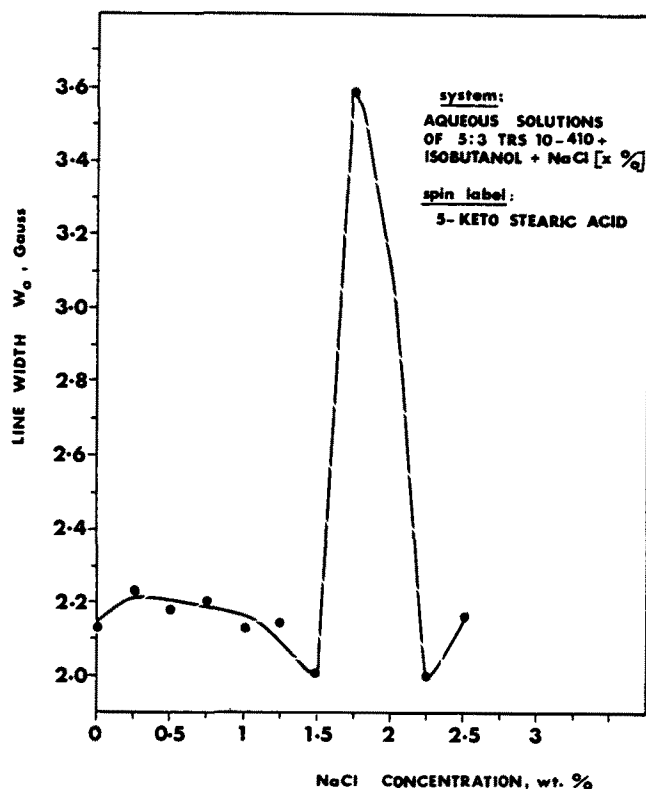


FIG. 3. Variation of line width, W_0 , of 5-ketostearic acid label in fresh aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with varying amounts of sodium chloride.

the hyperfine splitting constant exhibits water values. It is highly improbable, therefore, that TEMPO is included either as it is or along with alcohol molecules.

Correlation times without any added salt are on the order of ca. 60 psec. This value is typical of micellar systems. The inclusion of TEMPO in these micellar structures seems highly probable since the hyperfine splitting constant A_N is ca. 14.9 G, which is 0.2 G less than the water value. This situation exists even at low salt concentrations. It is known that the addition of an electrolyte would decrease the electrical double layer around the micelle and facilitate growth of the micelle. The presence of alcohol would further enhance this tendency. The fact that A_N in a water-alcohol mixture is only slightly changed precludes the possibility that TEMPO is not included in the micelle. Our results therefore reflect an inclusion of TEMPO in the micelles at low salt concentrations. The increase of τ_β with addition of salt indicates that the micelle has grown in size. Further addition of salt induces structural changes and, also, the exclusion of TEMPO from such structures. Closer packing of the spherical micelles leading to the eventual formation of a closely packed anisotropic structure around 1.5% is indicated by the gradual decrease in τ_β and the gradual increase in order parameter ΔT . The hyperfine splitting constant is identical to the water value around 1.65% NaCl, the concentration where ΔT is a maximum, indicating the complete and total exclusion of TEMPO at this concentration. The decrease in hyperfine splitting constant, A_N , of TEMPO beyond these concentrations also supports the theory that the structures are less rigid. Flow-through porous media studies further corroborate this observation (5).

In summary, fresh aqueous solutions of 5:3 (%w/w) TRS 10-410:isobutanol exhibit structural changes upon the addition of sodium chloride. Starting from a micellar system, we have initial growth of the micelles which pack themselves tightly as salt is added, finally transforming into closely packed structures. Birefringence begins around 1.5% and continues up to 2.25%, this region also being the region of maximum order and line width. There is a possibility that these structures are completely destroyed prior to phase separation as indicated by the return to normal line widths. However, the order parameter is only slightly changed, inviting the possibility of bilayer structures. The continuance of birefringence even at 2.5% does not exclude this possibility while negating the notion of complete disorder.

The basic difference in behavior between fresh and aged systems may be attributed to the difference between a kinetically controlled process in the first case and a thermodynamically stable state in the second. Recent studies of equilibrium phase-behavior of these systems with respect to temperature cycles (6) further substantiate this basic behavioral difference between fresh and aged solutions.

Effect of Addition of Small Amounts of Dodecane

The petroleum sulfonate TRS 10-410 used in the aqueous formulation consists of ca. 62% sulfonate, 33% oil, 5% water and less than 0.1% salt (as reported by the manufacturers). That is, the aqueous formulations contain some oil (ca. 1.5 wt%) in the solubilized form. As the exact amount of oil present was unknown, the solubilization limit of the oil in the formulation could not be ascertained readily. However, in an attempt to understand the role of small amounts of oil in the fresh surfactant formulation and the effect on the structural perturbations, we added ca. 0.1-0.2 ml of dodecane/20 ml of aqueous solution in addition to the oil present inherently in the surfactant. The correlation time data as a function of salt concentra-

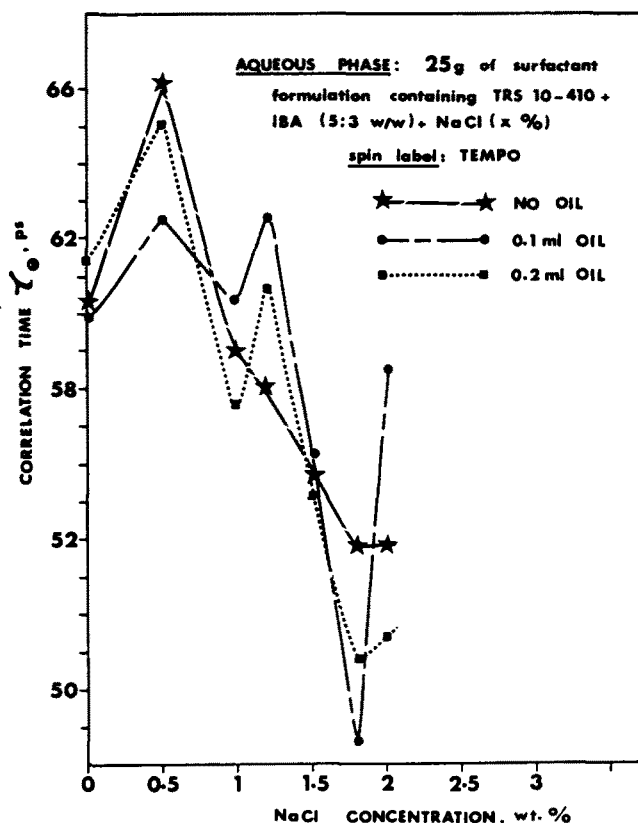


FIG. 4. Effect of addition of small amounts of dodecane on correlation time, τ_β , of TEMPO label in fresh aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol and varying amounts of sodium chloride.

tion for systems without any added dodecane oil (no oil system) and those with dodecane are shown in Figure 4. All curves follow essentially the same pattern with slight quantitative changes. The micellar region and the subsequent tight packing of these spherical micelles should now be considered as microemulsions.

Evidence for the presence of light packing of the spherical micelles is shown by the high correlation times (700-1,300 psec) obtained using an oil-soluble cholestane label in these systems (Table I). It can be seen that the correlation time for rotational tumbling motion of the label decreases with increasing salinity. This indicates an increase in solubilization of oil with addition of salt. TEMPO studies (Fig. 4) reveal that the packing of micelles is tight when smaller amounts of oil are solubilized, but is fluidized when oil solubilization is enhanced.

Eriksson and Gillberg (7) observed that solubilization of oils in a micelle extended the hydrocarbon chains, increasing the chain interactions within the micelle. Smith and Alexander (8) reported that solubilization makes the

TABLE I

Correlation Time, τ_β , of Cholestane Label Solubilized in Varying Amounts of Oil As a Function of Salinity

NaCl (%)	Correlation time τ_β psec)	
	Amount of oil	
	0.1 ml	0.2 ml
0.5	1270	1320
1.0	1120	793

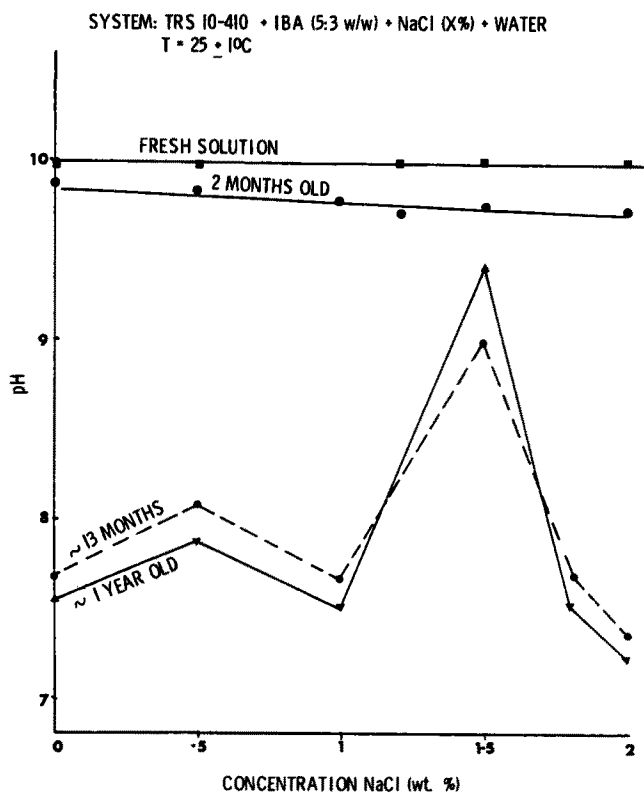


FIG. 5. Variation of pH in aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with sodium chloride concentration.

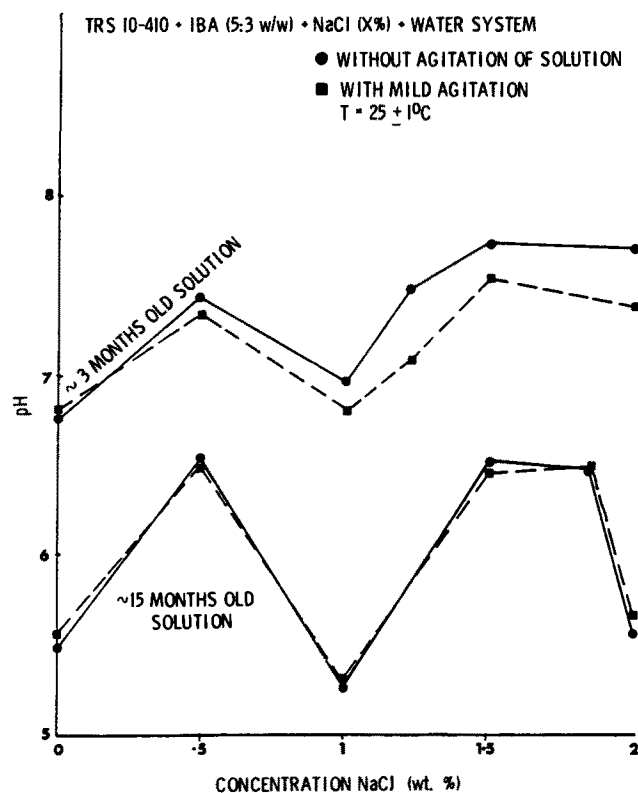


FIG. 6. Variation of pH in aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with sodium chloride concentration.

micelles more compact. Eriksson and Gillberg further stated that increasing the amount of solubilized oil made the micelles more fluid. The behavior of aqueous surfactant solutions equilibrated with 0.1 ml and 0.2 ml oil follow this trend as observed by TEMPO as well as cholestane studies. Beyond these salinities it is probable that a tightly packed micelle could give rise to tightly packed anisotropic structures.

CONCLUSIONS

Correlation time from TEMPO studies gave values typical of micelles (cf. sodium dodecyl sulfate \cong 40-50 psec beyond cmc) at low concentrations of sodium chloride. This region is extended when the system is aged.

The decrease in correlation time resulting from exclusion of TEMPO at intermediate salinities indicates a transition to tightly packed structures. This transition is more pronounced upon aging.

At much higher concentrations, a probable transition to

anisotropic structures exists. Apparently, this structure exists almost up to a concentration of salt where phase separation (of surfactant and alcohol/brine) occurs. This transition is clearly indicated in aged systems.

Spin label studies using the stearate label show a marked increase in ordering characteristics and a gradual decrease in mobility as salt concentration increases. The maximal order is obtained at concentrations where TEMPO correlation time is a minimum. A gradual packing is indicated with the tightest packing corresponding to an anisotropic structure, possibly of the lamellar type.

Order parameter for the stearate label decreases slightly at higher concentrations. This is indicative of an increase in chain mobility of these structures.

The line width of the central line W_0 , increases almost two-fold in the concentration range 1.5-2.0% NaCl. The line width is normal beyond these concentrations. Such an increase follows the tight packing observed in TEMPO studies as well as in stearate label order parameters.

The line width beyond 2.0% salt concentration does not

TABLE II

Physical Properties of Fresh and Aged Aqueous Solutions of TRS 10-410 + IBA (5:3% w/w) + NaCl (X%) at 24 ± 1 C

NaCl concn. (wt %)	Density (g/cm ³)		Absolute viscosity (cP)		Specific conductance (mS/cm)			
	Fresh	~1 yr old	Fresh	~1 yr old	Fresh	~3 mos. old	~7 mos. old	~20 mos. old
0	0.9924	1.0170	1.2	1.23	2.275	2.6	2.63	2.75
0.5	0.9955	0.9974	1.1	1.14	9.7	10.0	10.45	11.55
1.0	0.9981	1.0008	1.6	1.84	5.9	—	12.6	17.25
1.2	0.9998	—	2/8	—	7.2	6.6	9.4	—
1.5	1.0015	1.0064	3.7	3.9	8.08	8.8	8.82	10.0
1.8	—	1.0084	—	2.82	9.30	—	—	11.23
2.0	1.0047	1.0064	2.4	2.92	9.0	11.3	13.5	12.0

reflect tight packing. A lamellar structure with the chains having motional freedom is indicated. The partial inclusion of TEMPO in these solutions, as reflected by a slight decrease in hyperfine splitting constant A_N , supports a fluid structure. Order parameter for the stearate label is still large, indicating that the polar groups are anchored strongly at the interface.

Aqueous solutions equilibrated with different amounts of oil indicated in TEMPO studies that the initial solubilization of small amounts of oil made the micelles more compact or rigid. This is in agreement with previous studies. Increased solubilization fluidized the micelle.

Spin label studies using an oil-soluble cholestane label did indeed indicate that small amounts of solubilized oil decreased the fluidity of the micelle and that increased solubilization increased the fluidity of the micelle.

For a given volume of oil being solubilized, cholestane label studies indicate that with increasing salt concentration, the core is more rigid at low oil contents, whereas with higher oil amounts, the core becomes highly fluid.

Finally, the changes in behavior of aqueous solutions in terms of structural changes upon varying salt concentration seem to be induced by solubility parameters. The role of alcohol is not very clear but preliminary studies indicate that, besides playing a role as a stabilizer and one that accelerates the structural changes, the alcohol very definitely resides at the interface, as well, but it is doubtful if any oil molecules are cosolubilized along with the alcohol.

Physical Properties of Fresh and Aged Aqueous Solutions of TRS 10-410 + Isobutanol (5:3 w/w) + NaCl (X%)

In this section, we present physical property data for the surfactant formulation under study. The various physical property results will be considered in succession.

pH. Fresh solutions have essentially constant pH values over the entire sodium chloride concentration range. Aging of solutions brought down the pH values for all sodium chloride concentrations except 1.5% NaCl (Fig. 5). With aged solutions (3 months, 1 yr, and 13 months) pH increased for NaCl concentrations for 0 to 0.5% and then decreased at 1%, and again increased over the concentration range of 1.2, 1.5 and 1.8%. Finally a mild decrease occurred at 2%. Aged solutions (\approx 15 months old, see Fig. 6) with 0.5, 1.5 and 1.8% NaCl show almost identical pH values. From all these results we see, in general, that the pH values to go down from 10 to almost 5.5 when aged for long periods of time. It is likely that the carbon dioxide intake could adequately explain the observed change. The dissolution of carbon dioxide is possible, considering the number of times the solutions are exposed to the atmosphere. The slow decrease of pH at certain NaCl concentrations seems to reflect the more structured state of these solutions. A typical concentration is 1.5% NaCl. One can possibly visualize these structural states in terms of their "barrier action" for carbon dioxide diffusion.

Density. Density values of fresh aqueous surfactant formulations show an increase with the increase of sodium chloride. For the sodium chloride concentration 0-2 wt% studied, the density increase is ca. 1.2%. Although this increase is not appreciable, there is evidently a consistent increase when NaCl concentration is increased (Table II). In solutions that are about 1 yr old, again density increased but there was a local minimum at 0.5% NaCl. This decrease was ca. 1.9% from that of 0% NaCl. In general, densities of aged solutions are greater than those of fresh solutions in the lower and higher NaCl concentration regions, respectively. If we consider the density increase for sodium chloride concentrations from 0 to 2% in water alone, we

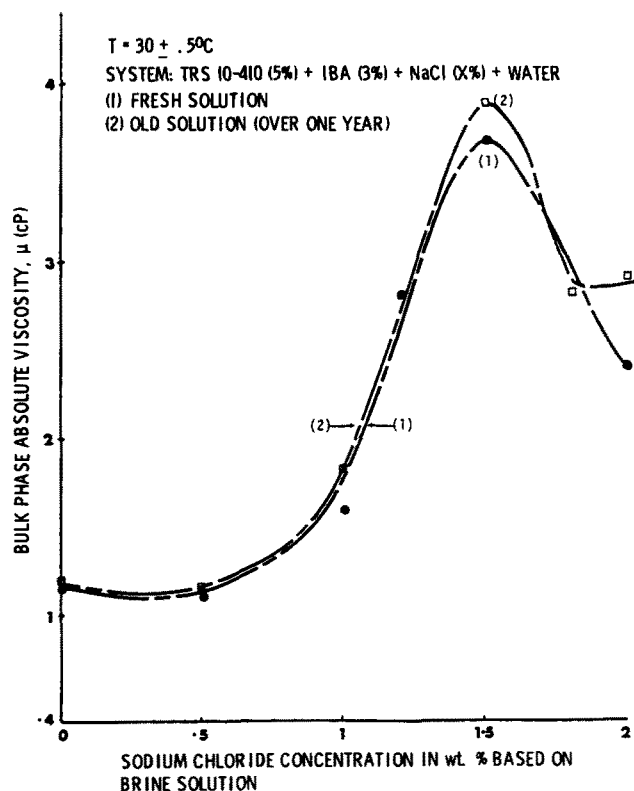


FIG. 7. Variation of bulk viscosity of aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with sodium chloride concentration.

observe a density increase of ca. 1.5% over this concentration range. Taking this effect into consideration, it appears that the increase in the density values observed for the surfactant formulation under study can be attributed to the electrolyte effect. The differences in the density values between aged and fresh solutions (aged solutions ca. 2-2.5% higher density) for the NaCl concentration range of 0-0.5% are worth noting. A further discussion will be taken up in a later section where we analyze all the property data together.

Viscosity. Absolute viscosity values of fresh and aged solutions are presented in Figure 7. Viscosity values do not seem to differ much between fresh and aged solutions. However, a small increase at 1.5% with aged solutions can be seen. For both sets of solutions, viscosity values go through a distinct maximum at 1.5%.

Screen factor. From the data given in Table III, it is evident that the relative screen factor values go through a pronounced maximum at 1.5% NaCl. This variation is parallel

TABLE III

Screen Factor Variation with Sodium Chloride Concentration

System	Time (sec)	Relative screen factor/ with respect to water
Water	8.65	1
NaCl (%)		
0	10.87	1.256
0.5	9.26	1.070
1	14.41	1.665
1.2	18.45	2.133
1.5	27.49	3.178
1.8	20.4	2.358
2	18.23	2.107

with the absolute viscosity value discussed earlier.

Specific conductance. Specific conductance values with the addition of sodium chloride increase up to 0.5% NaCl in the case of fresh surfactant formulation (Fig. 8) and essentially remain constant with further addition of NaCl. However, with aged solutions, the specific conductance increases up to 2 wt% NaCl and then decreases, showing a minimum at ca. 1.2-1.5% NaCl, and then increases thereafter. Evidently, the magnitude of conductance of over 1-yr-old solutions show about a 20% increase in the value to that of fresh aqueous solutions.

Surface tension. The equilibrium surface tension data of fresh and aged aqueous solutions determined by the Wilhelmy plate method are shown in Figure 9. These data were obtained with great care and the error in the measurements was within ± 0.3 dyne/cm. Figure 9 shows a mild decrease of surface tension (from 33 dyne/cm to 31 dyne/cm) with fresh aqueous solutions when the sodium chloride concentration is increased. In the aged solutions, surface tension starts at 33 dyne/cm at 0% NaCl, decreases rapidly to 30.5 dyne/cm at 1.0% NaCl, then increases to 32.1 dyne/cm at 1.5% NaCl and finally decreases to 31.5 dyne/cm. Thus, in terms of absolute values, there is a basic difference between fresh and aged solutions. Such age-dependent tension behavior has been reported by Cash et al. (9) for similar systems. A satisfactory explanation for this effect is currently unavailable. Attempts to measure interfacial tension of aged systems with dodecane oil proved unsuccessful. Around optimal salinity, we could not form any oil droplets in the aqueous phase that were stable enough for spinning drop measurements. Generally, the drops immediately broke up and/or adhered to the glass tube wall. This behavior probably results from very low tension values of solutions when aged. However, with the fresh solutions,

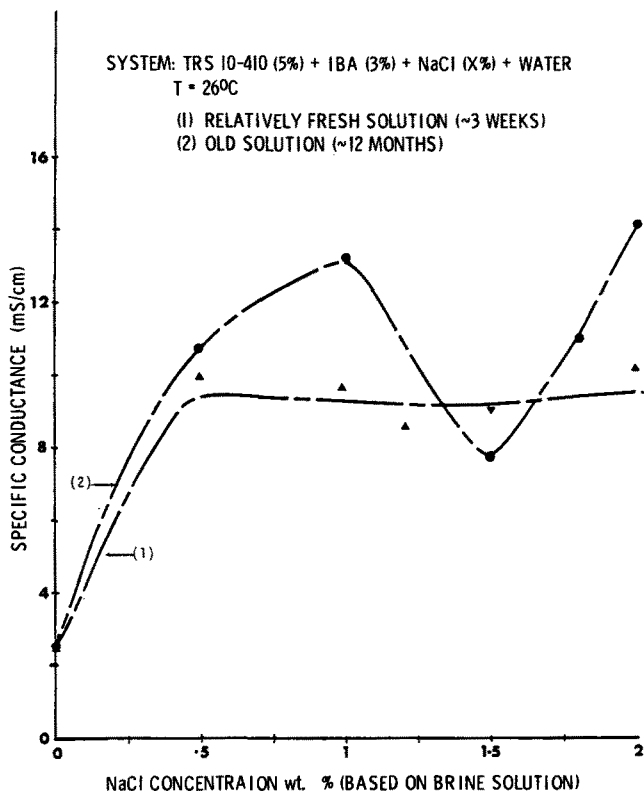
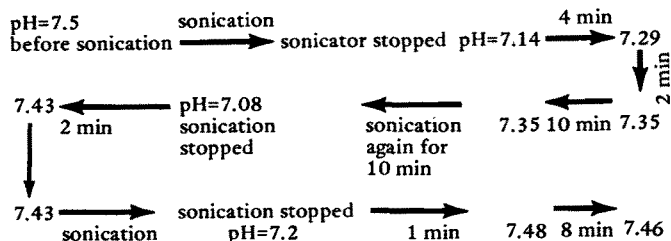


FIG. 8. Variation of specific conductance of aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with sodium chloride concentration.

the interfacial tension measurement was relatively simple and stable drops could be formed in the spinning tube. Detailed data for fresh systems have been reported elsewhere (10).

Figure 10 shows that bound sodium decreases with the addition of sodium chloride up to 1.2-1.5% NaCl in the fresh solutions and up to 1.8% in the aged solutions, and then increases. In both samples, the decrease is pronounced in the region 0-1% NaCl. The decrease of bound sodium ions in the aqueous solutions (fresh and aged) can be explained by invoking the structural state of the micelles in these systems. Our earlier discussion of microstructure results by spin labeling studies have indicated that the spherical micelles at 0% NaCl pack together more and more as the NaCl concentration is increased. Up to 1.5% and thereafter, the addition of NaCl transforms the structure to a lamellar type. Evidently, the binding sites for counterion is reduced when closely packed structures are present. However, formation of lamellar structures again create more sites and, consequently, the counter-ion binding increases.

In an attempt to study this effect with respect to pH changes, we used 1.8% NaCl aged, aqueous solutions which initially possessed a lamellar structure. The pH was 7.1. Then, with the intention of destroying the structure, we sonicated the solution for ca. 10 min, stopped the sonication and measured the pH change with time. This operation was performed repeatedly. The results are summarized in Scheme I:



SCHEME I

This preliminary experiment apparently shows that hydrogen ion binding is more pronounced in a lamellar-structured system than in a disrupted system.

An Overall Comparison of the Physical Properties and Microstructures: The Effect Adding Sodium Chloride to Fresh Aqueous Solutions

pH essentially remains constant (10 units) over the NaCl concentration range studied.

Density increases gradually, showing the effect of adding salt.

Viscosity shows a mild local minimum at 0.5% NaCl and gradually increases. At 1.5% NaCl, a pronounced maximum occurs and then viscosity decreases.

The screen factor essentially follows the viscosity pattern.

Specific conductance increases, passing through a local minimum at 1% NaCl, and finally levels off after 1.8% NaCl at a value of 9.3 mS/cm.

Bound sodium ion first decreases gradually, reaching a minimum in the NaCl concentration range of 1.2-1.5 wt% and then increases.

Structural order parameter by stearate label studies show that the order parameter increases, reaching a maximum at around 1.6% NaCl and decreases thereafter mildly.

Correlation time studies using TEMPO label further substantiate the results.

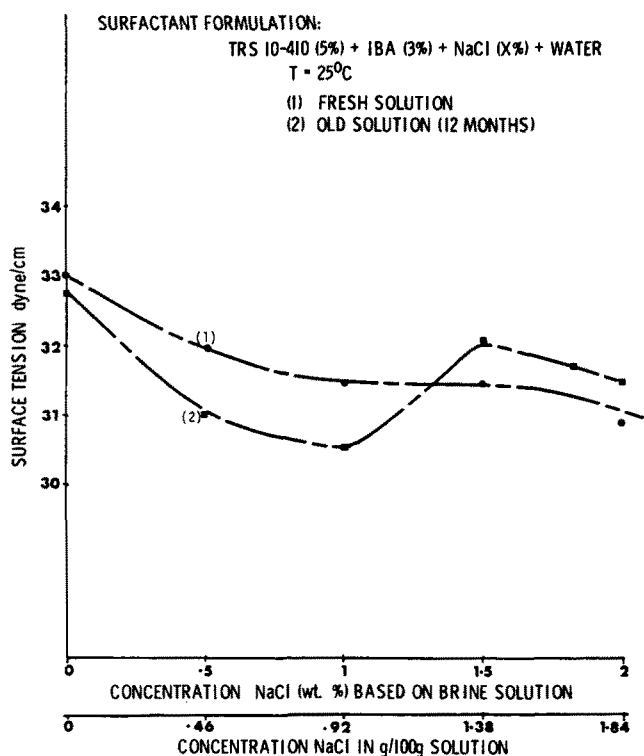


FIG. 9. Variation of surface tension of aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with sodium chloride concentration.

The conductance increase up to 1.5% NaCl can be explained in terms of the free sodium ion increase. Viscosity and screen factor maxima around 1.5% NaCl can be substantiated by microstructure studies which reveal the presence of very tight packing of micelles. The decrease of bound sodium ions at lower concentrations of NaCl (less than 1.5%) can be explained in terms of the formation of more and more packed structures of micelles starting from the state of spherical micelles at 0% NaCl. The mild increase of sodium binding above 1.5% NaCl may result from lamellar structures in which one expects to have more counter-ion binding sites.

Aged Aqueous Solutions

The behavior of aged solutions is essentially the same as that of the fresh solutions except that the micellar region at low concentrations of NaCl is extended when the system is aged. pH and conductance results show some unexpected variations with NaCl addition. A definitive reasoning for the observed pH effect is not possible presently. However, an explanation based on carbon dioxide diffusion should not be overlooked. Correlation time by TEMPO studies reveal tightly packed structures at ca. 1.8% NaCl. Similarly, bound sodium ions show a minimum at 1.5% NaCl. Surface tension values of aged solutions show a minimum at 1% and a maximum at 1.5% NaCl. It is notable that specific conductance values show an opposite effect to that of surface tension. In general, both total and free sodium content in aged solutions are higher than that in fresh solutions. It is likely that prolonged storage of solutions in glass vessels might be the cause of increased sodium content in aged solutions. The discussions thus far reveal that aging of impure surfactant solutions is a complex phenomenon. A unified interpretation of the various mechanisms operative in the aging phenomena can be

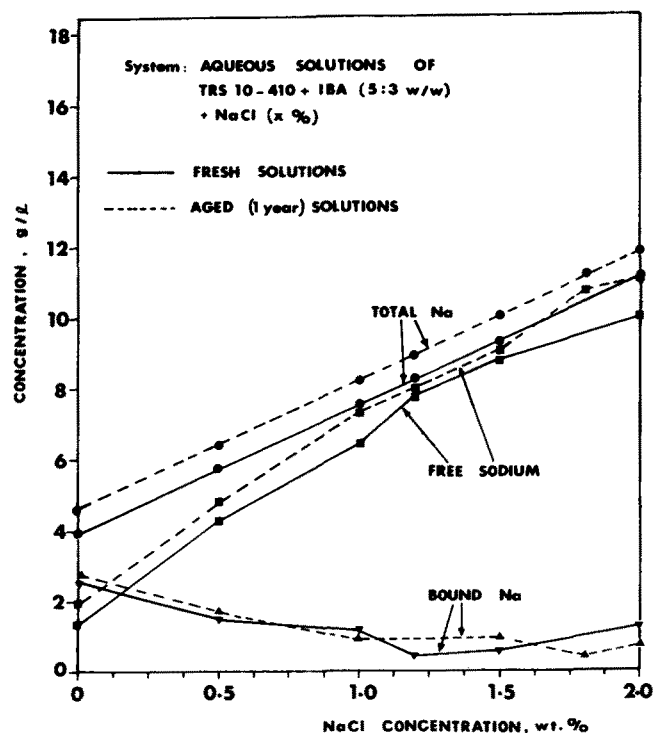


FIG. 10. Amounts of total sodium, free sodium and bound sodium in aqueous solutions of 5:3 (w/w) TRS 10-410: isobutanol with added sodium chloride.

achieved by further studying systems of known impurities and their interactions.

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