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The Study of Surfactant-Alcohol Mixed Micelles Using Conductance, Viscosity, and Electromotive Force Measurements

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Conductance, viscosity, and EMF measurements were used to characterize solutions containing surfactant–alcohol micelles. The materials studied included sodium dodecyl sulfate (SDS), sodium octyl sulfate (SOS), decyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (CTAB) and the alcohols 1-pentanol through 1-octanol. The addition of alcohols caused the conductance of a 2% SDS solution to increase, and of a 3% solution of DTAB and of a 7% solution of SOS to decrease. CTAB showed both increases and decreases upon addition of alcohol. The EMF measurements permitted the concentration of free surfactant monomer and of unbound counterion in equilibrium with the micelle to be determined. When combined with the viscosity data, the change in conductance upon addition of alcohol can be interpreted in terms of changes in micellar shape and in the concentration of involved ions.

The aqueous solubility of many sparingly soluble organic compounds such as long-chain alcohols, lipids or hydrocarbons can be increased considerably by the addition of surfactant.1) At surfactant concentrations above the critical level at which aggregation into micells occurs, such solubilization may have a profound influence on the physical properties of the solution. For example, the conductance of such mixed micellar solutions can decrease or increase by as much as 50% upon the addition of aliphatic alcohols. In spite of the importance of mixed micellar solutions in many industrial and biological processes such as detergency, polymeric synthesis and digestion, they have received far less attention than the simple binary surfactant–water systems. In order to study mixed micellar solutions in more detail we have carried out conductance, viscosity, and EMF measurements upon alkyltrimethylammonium bromide and sodium alkyl sulfate solutions as a function of added aliphatic alcohols.

Experimental

Apparatus and Technique. The conductance measurements were carried out in two cells: a Kraus-Erlenmeyer-type cell2) with a cell constant equal to 2.383 for dilute solutions and a Mysels donut-type cell3) with a cell constant equal to 47.87 for concentrated solutions. The electrodes were slightly platinized in order to minimize the frequency dependence of the measured resistance. The solution in the cell was stirred with a Teflon-coated magnetic stirring bar, to facilitate the dissolution of alcohol. The conductance cells were immersed in a constant temperature oil bath controlled to 25±0.005 °C. A 100 W light bulb was placed above the cell in order to prevent condensation of water in the top of the conductance cell. A shielded Shedlowsky conductance bridge was used to measure the solution resistance.

A conductance run was made by placing the surfactant solution in the cell and adding small increments of alcohol to the surfactant solution using a 10 ml Pyrex weight burette. After each addition the conductance was followed until a steady resistance reading was obtained. When the mole fraction of alcohol was small, approximately half an hour was required to dissolve the alcohol. As the alcohol concentration was increased, a considerably longer time was required.

The viscosity of the surfactant–alcohol solutions was measured using Cannon-Ubbelohde viscometers. The measurements were carried out in a constant temperature water bath at 25 °C±0.01 °C.

EMF measurements were carried out on the surfactant solution using surfactant and counterion electrodes.4) The liquid membrane surfactant electrodes contained an ion exchanger, tributylhexadecylammonium ion for the anion surfactant and cholanate ion for cation surfactant. The ion exchanger was dissolved in a membrane solution consisting of a mixture of *o*-dichlorobenzene–hexachlorobenzene–bromoacetanilide. An Orion 92-00-00 electrode body with an Orion porous membrane support comprised the surfactant electrode. The EMF concentration cell for the dodecyl sulfate, an ion (Ds^-), is given by

$$\begin{array}{c|c|c|c|} \mathrm{Ag/AgCl} & \begin{array}{c}\mathrm{NaCl}\\ \mathrm{SDS}\end{array} & \begin{array}{c}\mathrm{Bu_3N(C_{16}H_{33})Ds}\\ \text{in}\\ o\text{-dichlorobenzene}\end{array} & \begin{array}{c}\mathrm{SDS}\\ \text{sample}\end{array} \end{array}$$

$$\begin{array}{c|c|c} \begin{array}{c}\mathrm{NH_4NO_3}\\ \mathrm{(5M)}\end{array} & \begin{array}{c}\text{Orion}\\ \#90\text{-}00\text{-}02\\ \text{inner filling solution}\end{array} & \mathrm{Ag/AgCl} \end{array}$$

The sodium, bromide and reference electrodes were Orion #94-11A, #94-35A, and #90-02-00 respectively.

The EMF's were measured with an Orion Research Meter (Model 801A). In pure surfactant solution and in SDS–alcohol solution steady and reproducible values of EMF were obtained with the surfactant electrodes. However, reproducible results for DTAB–alcohol solution could not be obtained with the surfactant electrode. The counterion electrodes, however, did give satisfactory results in all surfactant–alcohol combinations studied. Reproducibility was determined by repeatedly measuring the EMF in pure micellar and mixed micellar solutions. This was conveniently done with an Orion Research Manual Electrode Switch (Model 605) which permitted up to six ion electrodes to be used with one common reference electrode. Detailed procedures are given elsewhere.4)

Results and Discussion

Conductance measurements were carried out on sodium dodecyl sulfate (SDS), sodium octyl sulfate (SOS), decyltrimethylammonium bromide (DTAB), and hexadecylmethylammonium bromide (CTAB) as a function of added alcohol. The results are given in

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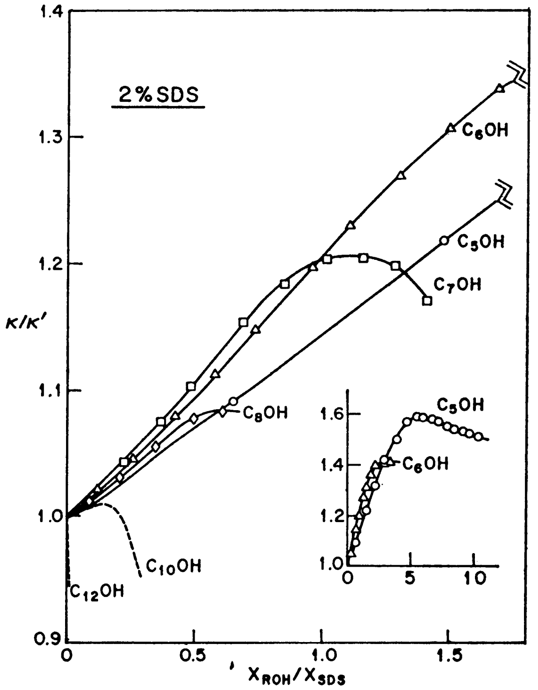

Fig. 1. The change in specific conductance of a 2% sodium dodecyl sulfate (SDS) solution upon addition of the aliphatic alcohols, pentanol through 1-octanol. The small insert shows the behavior upon addition of 1-pentanol and 1-hexanol up to the concentration at which the solution becomes cloudy.

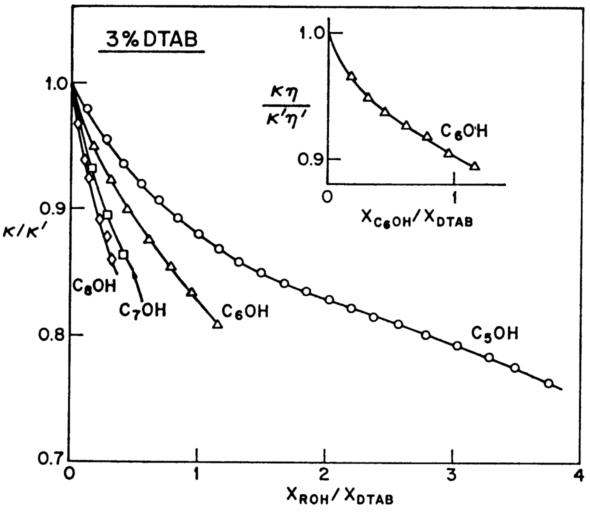

Fig. 2. The change in specific conductance of a 3% decyltrimethylammonium bromide (DTAB) solution upon addition of the aliphatic alcohols, 1-pentanol through 1-octanol. The small insert shows how the specific conductance-viscosity product for DTAB–1-hexanol solutions changes with composition.

Figs. 1—4. The initial concentration of surfactant was in all cases above the critical micelle concentration. The measurements extend up to the concentration of alcohol at which the solution becomes cloudy. Viscosity measurements were carried out on 21% SDS (0.069M), 3% DTAB (0.107M), and 2% (0.055M) and 5% (0.137M) CTAB as a function of added 1-hexanol or 1-octanol and are shown in Fig. 5. EMF measurements were carried out on 2% SDS and 3% DTAB solutions as a function of added 1-hexanol and are given in Figs. 6 and 7 below.

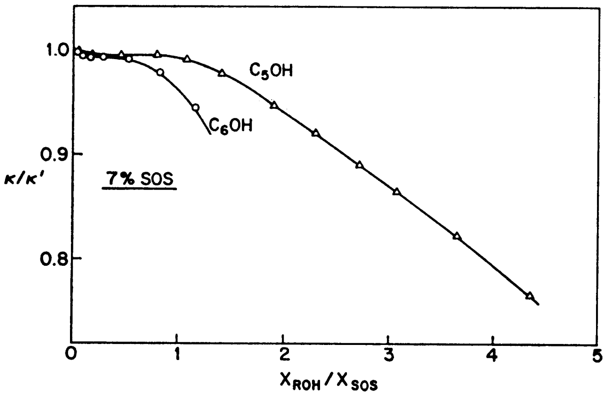

Fig. 3. The change in specific conductance of a 7% sodium octylsulfate (SOS) solution upon addition of 1-pentanol and 1-hexanol.

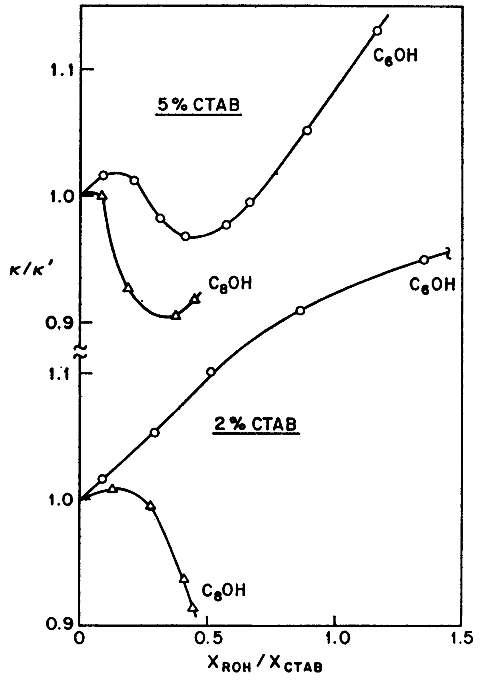

Fig. 4. The effect of surfactant concentration and alcohol chain length upon the specific conductance of hexadecyltrimethylammonium bromide (CTAB).

In Figs. 1—4 the changes in specific conductance of the surfactants as a function of added alcohol are shown. The ratio of the specific conductance with and without added alcohol, κ/κ', is plotted *versus* the molar ratio of the alcohol to surfactant, x_{ROH}/x_S. If the change in surfactant concentration upon addition of alcohol is ignored, the value of κ/κ' can be replaced by the corresponding ratio of equivalent conductances. The figures show that the conductance curves are complex with initial slopes that increase in some cases, decrease in others and which may have maxima and minima.

Although it is unlikely that a single simple explanation will account for the variety of behavior, we will delineate the main factors that are responsible for the observed conductance.

In SDS solutions, while the conductance increases for all of the alcohols studied, the rate of increase and the maximum value attained depend upon the alcohol chain length. Our results for pentanol through heptanol are in agreement with the results given in graphical form by Lawrence and Pearson.[5] They measured the conductance of SDS upon addition of the alcohols, 1-ethanol through 1-heptanol. Their results show that the maximum conductance is observed for the SDS–1-pentanol solution at a mole ratio of 6 and that a 60% increase in conductance is observed. Our results show that the maximum initial slope is observed for 1-heptanol.

The conductance may be analyzed in more detail by taking into account the distribution of the alcohols between bulk water and micelles. From vapor pressure measurements of alcohols in equilibrium with a micellar solution, Hayase and Hayano[6] determined a distribution coefficient defined as

$$K = x_a/y_a = j/(S-\mathrm{CMC}(C_a)+C_a j/[(1-j)/55.5])$$

where y_a and x_a are the mole fractions in the aqueous phase and the micellar phase, respectively. The values of $1-j$ and j are the alcohol fractions in the aqueous and micellar phases, S is the total concentration of SDS, CMC(C_a) is the critical micelle concentration in the presence of alcohol, and C_a is the total concentration of the alcohol. Using the results for CMC(C_a) and K, the values of j shown in Table 3 can be calculated. For 1-pentanol most of the alcohol is in the aqueous phase while for 1-heptanol most is solubilized by the micelle. The partition coefficients in Table 1 permit the amount of alcohol solubilized at each value of $x_{\mathrm{ROH}}/x_{\mathrm{SDS}}$ to be calculated. When these corrections are made, the values of the slope $\mathrm{d}(\kappa/\kappa')/\mathrm{d}(x_{\mathrm{ROH}}/x_{\mathrm{DS}})$ given in Table 1 are obtained. The corrected initial slopes for 1-pentanol, 1-hexanol, and 1-heptanol are very similar suggesting that these have identical effects upon the micelles. However, the initial slope is smaller for 1-octanol, and decreases further with increasing chain length.[7]

The initial increase in conductance of SDS upon the addition of alcohols can be attributed to the orientation of solubilized polar molecules with the polar head group remaining near the micellar surface and the hydrocarbon tails extending into the micellar interior. In pure SDS, the micelles are spherical and each surfactant molecule occupies approximately 60 Å^2 of surface.[8] The micelle exterior can thus be viewed as consisting of a number of surface sites. The incorporation of an alcohol molecule results in the surfactant molecules moving apart. This reduces the concentration of surfactant anions, lowers the surface charge density, and results in a release of bound counter ions.

Examination of the viscosity of the SDS–1-hexanol solutions supports this explanation. In Fig. 5, is shown the ratio $\eta/\eta_{\mathrm{H_2O}}$, the relative viscosity for the micellar solution to that for water, *versus* the volume fraction of surfactant or surfactant plus alcohol. The surfactant volume was taken from the density data of Desnoyers.[9] For the alcohols, volumes were estimated using density data of pure substances.[10] The data for pure SDS fall on a straight line which extrapolates back to the intercept of $\eta/\eta_{\mathrm{H_2O}}$ close to unity. The data for SDS–1-hexanol fall on the same straight line indicating no change in micellar shape upon addition of alcohol.

In order to understand the behavior of these mixed micelles in more detail, we determined the activities of the sodium ions and dodecyl sulfate ions using ion electrodes. Since such electrodes give the activities of free ions, information about the sodium ions and dodecyl sulfate ions in equilibrium with the micelle can be determined.

We first measured the EMF of pure SDS solution and in Fig. 6 EMF *versus* log concentration of SDS is shown. In dilute solution, slopes close to the Nernst value of 59 mV per decade are obtained. At the CMC (8×10^{-3} M) a sharp break is observed. Above this concentration, the sodium activity continues to increase but with a smaller slope, reflecting the binding of counter ion to the micelle. The dodecyl sulfate activity decreases above the CMC. A positive slope corresponds to a decrease in activity for this ion. Assuming that activity coefficients can be ignored, the concentration

TABLE 1. EFFECT OF ALCOHOLS ON THE CONDUCTANCE OF 2% SDS SOLUTION

Alcohols	K a)	Uncorrected slope b)	j c)	Corrected slope d)
C_5OH	722	0.14_4	0.50	0.25_5
C_6OH	2250	0.19_5	0.76	0.24_7
C_7OH	6020	0.21_0	0.90	0.23_7
C_8OH	16000	0.15_5	0.95	0.16_7

a) From Ref. 6. K for C_8OH was obtained by extrapolation of log K *vs.* alcohol-carbon-number curve. b) Initial slope of (κ/κ') *vs.* $(x_{\mathrm{ROH}}/x_{\mathrm{SDS}})$. c) (ROH, in micelle)/(ROH, total) at $x_{\mathrm{ROH}}/x_{\mathrm{SDS}}=0.3$. d) Initial slope of (κ/κ') *vs.* $(j\cdot x_{\mathrm{ROH}}/x_{\mathrm{SDS}})$.

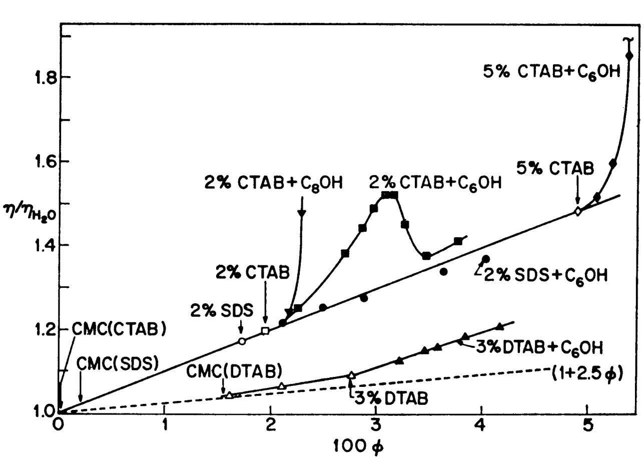

Fig. 5. The change in relative viscosity, $\eta/\eta_{\mathrm{H_2O}}$, of SDS. DTAB and CTAB solutions upon addition of aliphatic alcohols as a function of volume fraction of added solute. The open points are for pure surfactant, the closed points are for surfactant plus alcohol; the dashed line represents $\eta=\eta_{\mathrm{H_2O}}(1+2.5\,\varphi)$.

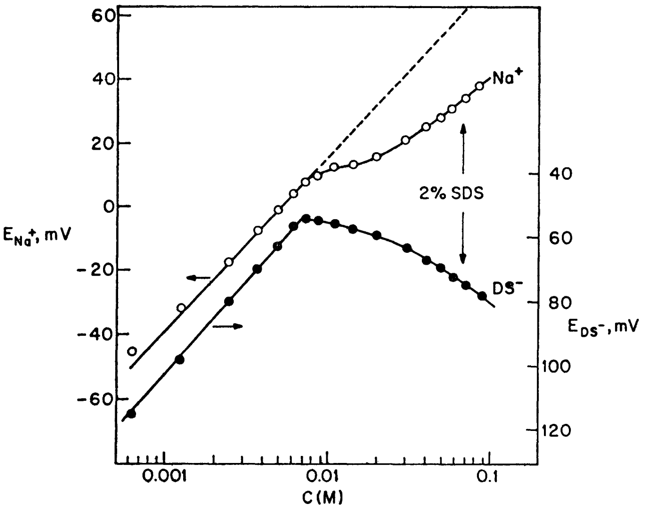

Fig. 6. The electromotive force (EMF) for sodium and dodecyl sulfate ions in 2% SDS solution. The break at 8×10^{-3} M corresponds to the CMC. Above this concentration the activities of Na^+ and Ds^- in equilibrium with the micelle can be determined.

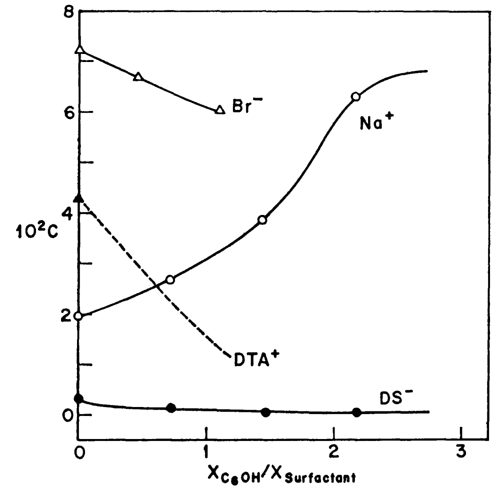

Fig. 7. The change in concentration of surfactant ions and counterions upon addition of 1-hexanol to 2% SDS and 3% DTAB as estimated from ionspecific electrodes.

of free monomer and unbound counter ion can be roughly estimated. In 2% SDS solution (0.068 M), the values of 0.02 M and 0.003 M are obtained for sodium ion and dodecyl sulfate ions respectively.

When 1-hexanol is added to 2% SDS, the ion activities change dramatically. The sodium ion concentration increases by a factor of 3 while the dodecyl sulfate concentration decreases by a factor of 10 as is seen in Fig. 7. Our results for the sodium ion activity are in substantial agreement with those of Lawrence and Pearson.[5] Since the initial concentration of free dodecyl sulfate ion is so small, even a major decrease has only a negligible effect on the conductance. However, the sodium electrode results show that the micelles release most of the bound counter ions, which results in a substantial increase in the conductance.

The conductance of DTAB–alcohol solutions is very different from that observed for SDS since it decreases upon addition of alcohol. One would expect that similarly to SDS, addition of polar compounds to DTAB should result in a release of counter ions. A decrease in the conductance of micellar solutions upon addition of non-polar solutes such as hydrocarbons is generally observed.[11] Such material appears to be solubilized entirely in the hydrocarbon interior of the micelle. The decrease in conductance arises from a corresponding increase in micellar size and perhaps by increases in counter ion binding.

One possible reason for the decrease in conductance of DTAB is that the addition of alcohol results in an increase in solution viscosity. However, the viscosity of DTAB increases by 10% up to a mole ratio, x_{ROH}/x_{DTAB}, of 1.1 while the conductance decreases by 20%. Alternatively, addition of alcohol could result in micellar reorganization such as a sphere to rod transition. This would cause the charged head groups to move closer together, increasing the micellar charge density and binding additional counter ions. That such a major reorganization does not occur can be seen from the relative viscosity shown in Fig. 5. There is a slight increase in the ratio, (η/η_{H_2O}), as 1-hexanol is added to 3% DTAB, however the increase is not as large as is usually observed for a major reorganization of micellar shape. Thus the viscosity measurements show that neither an increase in solution viscosity nor a change in micellar shape will account for the observed conductance behavior.

EMF measurements provide a clearer picture of what is happening. In a 3% (0.107M) DTAB solution the concentration of free Br^- is 0.072 M while that for DTA^+ is 0.043. Addition of 1-hexanol results in a small decrease in bromide concentration, when x_R/x_{DTAB} equals 1.1, the Br^- concentration drops to 0.060 M (see Fig. 7). Although we were not able to obtain reproducible EMF's with the DTA^+ ion electrode, the EMF decreased approximately 30±10 mV suggesting a threefold decrease of monomer surfactant concentration. Since the initial concentration of free surfactant and counter ion are reasonably large, a substantial decrease in either species will have a pronounced effect on the conductance. Even in the case of 22% (0.33 M) DTAB solution the decrease in conductance is observed (Table 1) when 1-hexanol is added. This is mainly because surfactant monomer concentration is still reasonably high (0.032 M from EMF) even in such a concentrated solution.

A comparison of the SDS and DTAB results suggests that there may be major differences in the behavior of cationic and anionic surfactants upon the addition of aliphatic alcohols. However, when 1-pentanol and 1-hexanol are added to 7% (0.306 M) sodium octyl sulfate, the specific conductance decreases (Fig. 3). Similarly to DTAB, this suggests that the decrease in surfactant monomer concentration more than compensates for any change in sodium concentration. However, when the behavior for SDS and SOS are compared, the results suggest that the relative lengths of aliphatic chains in alcohol and surfactant may be an important factor in determining whether the conductance increases or decreases. Inspection of Table 1 shows that when 1-octanol is added to SDS the increase in conductance is less than when 1-heptanol is added.

When the cationic surfactant chain becomes sufficiently long, addition of an alcohol can result in an initial increase in conductance as is shown in Fig. 4 for the addition of 1-hexanol to hexadecyltrimethylammonium bromide, CTAB. However, when 1-octanol is added the conductance increases slightly and then decreases rapidly. For 5% CTAB the addition of either 1-hexanol or 1-octanol results in both decreases and increases in the conductance. The viscosity of these solutions (Fig. 5) increases rapidly upon the addition of alcohol to either the 2% or 5% CTAB solution suggesting sphere to rod transitions.[12] In some cases the conductance rises even though the viscosity is also increasing. The behavior of 1-hexanol in 2% CTAB is pecular in this regard. Up to a mole ratio of 1.5 both the conductance and viscosity increase, above 1.5 they decrease. In general one would anticipate that an increase in viscosity would result in a decrease in conductance.

Conclusions

The results for SDS–alcohol and DTAB–alcohol micellar solutions show that when information from several experimental techniques is combined the main factors that determine the solution properties can be delineated. The two examples that we have considered in detail give reasonably simple behavior. The initial results in SOS and CTAB solution show that there are a number of complexities such as relative lengths of aliphatic chains in alcohol and surfactant, micellar reorganization and solution viscosity changes that are difficult to interpret unambiguously.

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