

The Effect of H_2O and D_2O on Colloidal Properties of Surfactant Solutions and Microemulsions

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The effects of hydration on solubilization and colloidal phenomena have been studied by comparing the differences between two oil-brine-surfactant-alcohol systems containing H_2O or D_2O . The H_2O system was significantly more hydrophilic than the D_2O system in relation to coacervation of aqueous surfactant solutions, formation of middle phase microemulsions, surfactant partitioning in oil and brine, and solubilization capacity of brine in oil-external microemulsions. The two oil-brine-surfactant-alcohol systems appeared to be macroscopically similar if the salinity of the D_2O system was decreased by about 0.3% NaCl. Electrical resistance and dielectric relaxation measurements showed that the surface charge density of H_2O -in-oil microemulsions was three times higher than that of the corresponding D_2O -in-oil microemulsions. The higher surface charge density of the H_2O system caused its higher interfacial alcohol concentration, which was confirmed by alcohol titration measurements. It is interesting to note that the interfacial alcohol concentration of the two systems can have similar values if the salinity of D_2O is decreased by about 0.3% NaCl. The higher surface charge density of the H_2O system can be explained by the lower (more negative) free energy of hydration of surfactant ions and counterions in H_2O than in D_2O , which leads to a higher degree of dissociation of the surfactant polar groups in the H_2O system. An expression is given to estimate the free energy of transfer (from H_2O to D_2O) of interfacial surfactant anions from surface charge density measurements.

INTRODUCTION

Petroleum sulfonates used in tertiary oil recovery often form a microemulsion (surfactant rich) phase upon mixing with alcohol, oil, and brine, which may be in equilibrium with excess oil phase or excess brine phase or both (1-3). The interfacial tensions between these phases, which are critical for tertiary oil recovery process, depend on the type of phase equilibria as well as on the solubilization capacity and droplet size in microemulsions (3-6). Theories for the thermodynamic stability and solubilization capacity of microemulsions (6-10) show the importance of electrostatic effects on size and stability. A significant factor generally neglected may be the hydration of surfactant anions and

counterions similar to that on micelles (11), hydrophobic colloids (12), and emulsions (13). Although H_2O and D_2O are chemically similar and their dielectric constants are nearly identical, there may be differences in hydrogen (vs deuterium) bonding (14) of H_2O or D_2O with the surfactant headgroups or counterions. Such differences have been postulated to account for their interactions with phospholipids (15) and proteins (16).

In this study, the effect of hydration on microemulsion properties was investigated by comparing the differences between two oil-brine-surfactant-alcohol systems containing H_2O or D_2O , in the following processes: solubilization in middle phase microemulsions, coacervation of aqueous surfactant solutions, surfactant distribution between oil and brine at low surfactant concentrations, and solubilization capacity of brine in oil-external microemulsions. The

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differences between these two systems, at a microscopic level, were further investigated by measuring the interfacial alcohol concentration and surface charge density of oil-external microemulsions by alcohol titration, electrical resistance and dielectric relaxation methods. An expression relating the surface charge density to the free energies of transfer from H_2O to D_2O of interfacial surfactant anions and counterions is also given.

EXPERIMENTAL

A petroleum sulfonate TRS 10-410 (Witco Chemical Co.) was used as received. This surfactant has an average molecular weight of 418. Isobutanol (IBA) of 99.9% purity and dodecane of 99% purity were obtained from Chemical Samples Co. Deionized distilled H_2O and D_2O (>99.8% deuterium, Stohler Isotope Chemicals) were used to prepare the brine. Samples were prepared by first making solutions of surfactant and alcohol in oil of desired concentrations and subsequently mixed with H_2O or D_2O brine. In the study of solubilization in middle phase microemulsions, coacervation, and surfactant partitioning, the samples were vigorously shaken, put on a rotating tumbler for 2 days before allowing for phase separation in a constant temperature bath ($25 \pm 0.1^\circ C$). Other experiments involving single phase, oil-external microemulsions were performed at room temperature ($23 \pm 1^\circ C$) using freshly prepared samples.

The surfactant concentration in the equilibrated phases was determined by UV optics or by a two-phase, two-dye titration method (17) when the surfactant concentration is high. Electrical resistance was measured by a Beckman AC bridge (model RC 16B2) at 1000 Hz. Dielectric measurements were made by a Hewlett-Packard RX meter (model 250B) at $25^\circ C$. A variable electrode distance dielectric cell, similar to the one used by Schwan *et al.* (18), was employed. The calculation of

the dielectric constant and dielectric loss from the measured capacitance and resistance has been described in detail elsewhere (19, 20). The accuracy of dielectric constant was estimated to be 2 to 10% and that of dielectric loss 5 to 15%.

RESULTS

Middle Phase Formation, Coacervation, Surfactant Distribution, and Solubilization Capacity

Within specific range of salinity, the oil-brine-surfactant-alcohol system forms three phases, in which the middle phase microemulsion is in equilibrium with excess oil and excess brine phases. The amount of oil and brine solubilized in the middle phase microemulsion is shown in Fig. 1. As salinity increases, the amount of oil solubilized (V_o) increases while the amount of brine solubilized (V_w) decreases. The salinity at which equal solubilization of oil and water occurs was defined as the optimal salinity of the system (4). The optimal salinity of the D_2O system is 0.27% NaCl smaller than that of the H_2O system. The onset of the formation of the middle phase microemulsion in the D_2O system also occurs at a lower salinity.

The formation of the middle phase microemulsion bears a close resemblance to the coacervation of aqueous surfactant solution (3). In the coacervation process (21), a homogeneous, isotropic aqueous surfactant solution becomes anisotropic upon adding NaCl. However, further addition of NaCl causes the formation of two isotropic liquid phases in equilibrium. The upper surfactant phase is called the coacervate phase. Upon further increasing salinity, the volume fraction of the coacervate phase decreases as shown in Fig. 2. The onset of coacervation as well as the salinity required to form a certain volume fraction of coacervate phase is higher for the H_2O system. The difference between H_2O and D_2O system in coacervation salinity is about

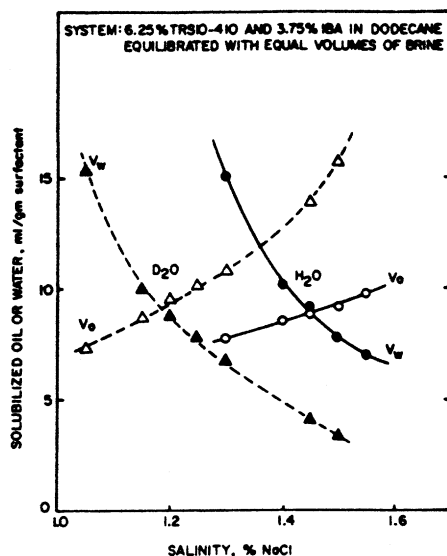


FIG. 1. Solubilization in middle-phase microemulsions containing H_2O or D_2O brine as a function of brine salinity.

0.3% NaCl, approximately the same as the 0.27% NaCl difference in the optimal salinity of these two systems.

Figure 3 shows the solubilization limit of brine (1.5% NaCl) in oil-external microemulsions as a function of alcohol/surfactant ratio. In this study, a surfactant and alcohol solution in oil was prepared and the amount of brine that can be solubilized (without causing phase separation) was determined. As shown in Fig. 3, the solubilization limit of each system initially increases with the alcohol/surfactant ratio, passes through a maximum then decreases. The optimal alcohol/surfactant ratio for maximum solubilization of brine is higher for the H_2O system. It should be noted that IBA is more soluble in oil than in brine, and hence increasing the IBA concentration in an oil-brine-surfactant-alcohol system will increase its lipophilic character (22). The mechanism of the occurrence of a maximum solubilization capacity at the optimum alcohol concentration is very complicated and will not be discussed here. Phenomenally, it can be said that the surfactant-

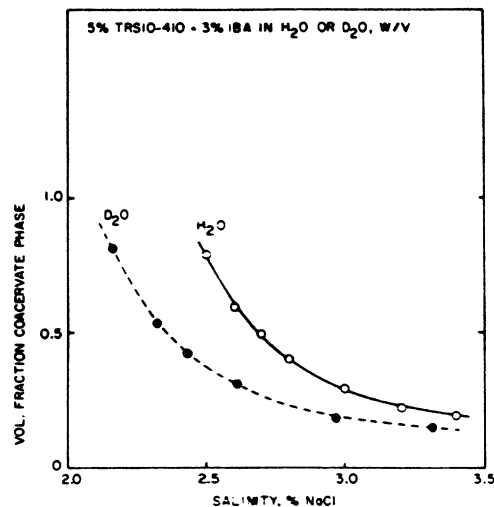


FIG. 2. Coacervation of surfactant solution in H_2O or D_2O brine by increasing the NaCl concentration.

alcohol-oil-brine system has achieved a proper hydrophilic-lipophilic balance (HLB) at the optimum alcohol concentration similar to the effect of temperature on the solubilization capacity in nonionic surfactant systems (23, 24).

The surfactant distribution between oil and brine was also distinctly different for

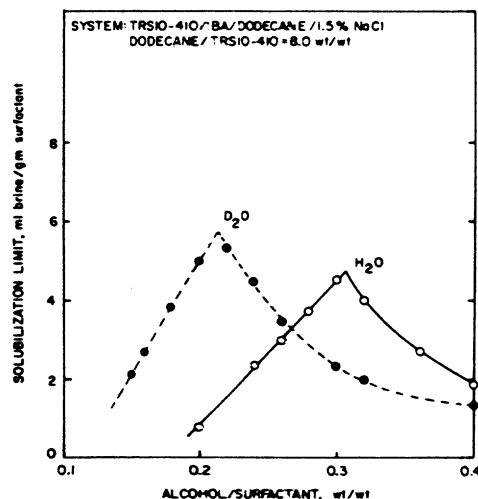


FIG. 3. Solubilization limit of H_2O or D_2O brine in oil-external microemulsions as a function of alcohol-to-surfactant ratio. The data represent the single phase boundaries for the two systems.

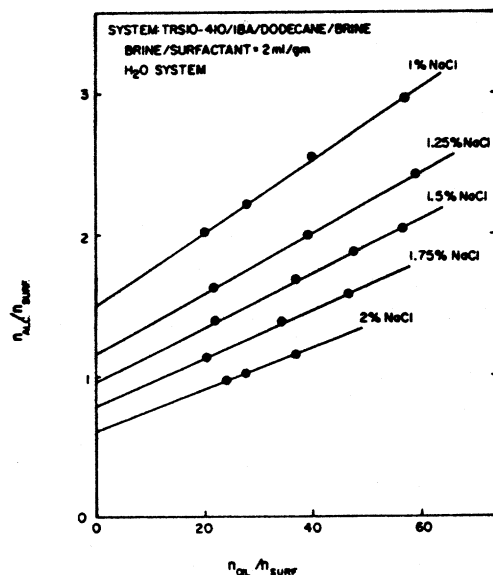


FIG. 4. Minimum amount of alcohol required to form oil-external microemulsions as a function of oil/surfactant ratio at different brine salinities (H₂O system).

the two surfactant-oil-brine systems. At low surfactant concentrations (below about 0.1%), the system forms two phases at equilibrium. For a given salinity and overall surfactant concentration, it was found that the surfactant concentration in the equilibrated oil phase was always higher for the D₂O system than the corresponding H₂O system. The surfactant partition coefficient (defined as the ratio of the surfactant concentration in oil to that in the aqueous phase) was 1.3 to 3.5 times higher in the D₂O system than that of the H₂O system (25).

Interfacial Alcohol Concentration and Surface Charge Density

The alcohol to surfactant molar ratio at the microemulsion droplet surface can be estimated by the alcohol titration method (26). At a constant brine/surfactant ratio (2 ml/g surfactant), the amount of alcohol required to titrate an oil-brine-surfactant emulsion from turbid to transparent was

measured as a function of oil/surfactant ratio at several salinities of brine. As shown in Figs. 4 and 5 for the H₂O and D₂O system, respectively, the amount of alcohol required for the formation of oil-external microemulsions increases linearly with the oil/surfactant ratio. The intercept is regarded as alcohol/surfactant ratio at the microemulsion droplet surface and the slope as the alcohol/surfactant ratio in the bulk oil phase, assuming negligible partitioning of alcohol into brine (26). The interfacial alcohol/surfactant molar ratios taken from the intercepts of these plots are shown in Table I. For each system, the interfacial alcohol concentration decreases with the salinity; and for a given salinity, the interfacial alcohol concentration is higher in the H₂O system. It is interesting to note that the interfacial alcohol concentration in these two systems can be approximately equal if the salinity of the D₂O system is decreased, on the average, by about 0.3% NaCl.

The higher interfacial alcohol concentration in the H₂O-in-oil microemulsions could

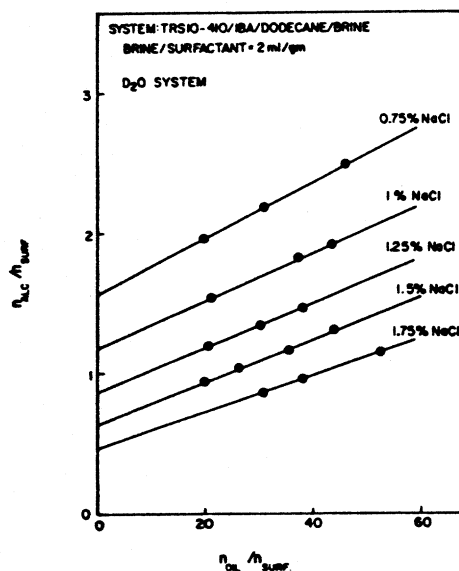


FIG. 5. Minimum amount of alcohol required to form oil-external microemulsions as a function of oil/surfactant ratio at different brine salinities (D₂O system).

imply that the surface charge density is also higher in the H₂O system, which is supported by the electrical resistance of the two systems. As shown in Fig. 6, the specific electrical resistance of the D₂O-in-oil microemulsions is more than one order of magnitude higher than that of the H₂O-in-oil microemulsions for all compositions studied. On the otherhand, for a given H₂O or D₂O system, increasing the overall alcohol concentration thereby increasing the interfacial alcohol concentration would increase the electrical resistance (25). The electric resistance was also found to increase with the salinity of brine (25).

The following dielectric relaxation studies give a more quantitative measure of the surface charge density in oil-external microemulsions. Figure 7 shows the dielectric constant (ϵ') and dielectric loss (ϵ'') over a frequency range from 0.5 to 100 MHz. While the dielectric constants of H₂O and D₂O are nearly identical, the dielectric properties of oil-external microemulsions containing H₂O or D₂O brine are distinctly different. From the shape of the dielectric loss curve, it is evident that the H₂O system undergoes two consecutive relaxation processes. The dielectric relaxation of the D₂O-in-oil microemulsion was not so apparent because, as it will be shown later, its surface charge den-

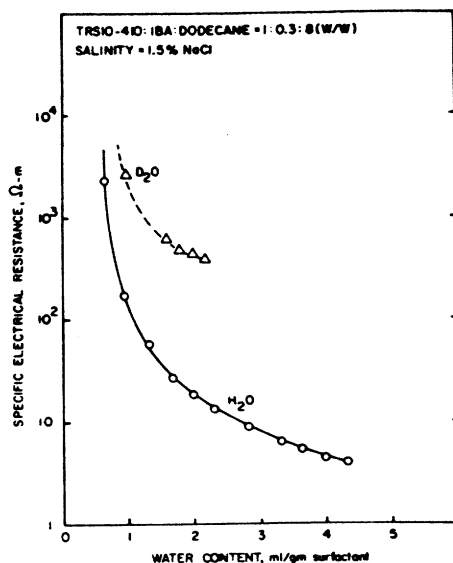


FIG. 6. Specific electrical resistance of microemulsions containing H₂O or D₂O as a function of the amount of solubilized brine. Only single phase regions were studied and the range of single phase regions was different for the two systems (see Fig. 3).

sity was much lower than that of the H₂O system.

It has been shown (27, 28) that, for a system exhibiting two consecutive Debye type relaxation processes, the complex dielectric constant ϵ^* can be described by

$$\epsilon^* = \epsilon_h + \frac{\epsilon_1 - \epsilon_i}{1 + (j\omega\tau_s)^\alpha} + \frac{\epsilon_i - \epsilon_h}{1 + (j\omega\tau_2)^\beta} + \frac{K_1}{j\omega\epsilon_v}, \quad j = -1^{1/2}, \quad [1]$$

where ϵ_1 , ϵ_i , and ϵ_h are the low, intermediate, and high frequency limits of dielectric constant, τ_s and τ_2 are the low-frequency and high-frequency relaxation times, $(1-\alpha)$ and $(1-\beta)$ characterize the width of the distribution of τ_s and τ_2 , respectively, K_1 is the low-frequency limit of conductance, ω is the angular frequency, and ϵ_v is the absolute permittivity of vacuum (8.8541×10^{-14} f/cm). One can determine the above parameters by fitting the ϵ' and ϵ'' data to Eq. [1]. The details of calculation are described

TABLE I

The Alcohol/Surfactant Molar Ratio (n_s/n_a)_i at Microemulsion Droplet Surface^{a,b}

Percentage NaCl in brine	H ₂ O system	D ₂ O system
0.75	—	1.58
1.00	1.5	1.18
1.25	1.17	0.89
1.50	0.96	0.65
1.75	0.78	0.48
2.00	0.61	—

^a System: TRS 10-410/IBA/dodecane/1.5% NaCl brine; brine/surfactant ratio = 2 ml/g.

^b (n_s/n_a)_i was determined by the alcohol titration method (26) (see Figs. 4 and 5). The accuracy of (n_s/n_a)_i was estimated to be ± 0.05 .

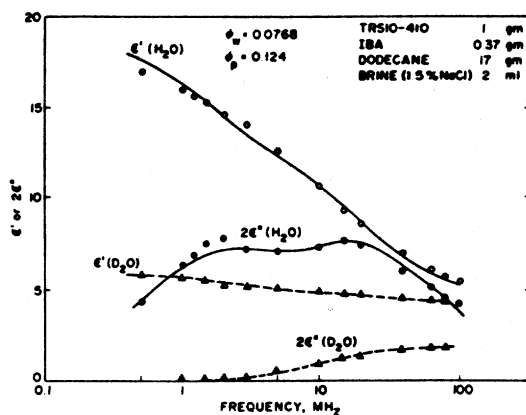


FIG. 7. Dielectric relaxation of oil-external microemulsions from 0.5 to 100 MHz. The volume fraction of water, ϕ_w , is 0.0768.

elsewhere (29). The results are listed in Table II. The solid curves (H_2O system) in Fig. 7 were calculated according to Eq. [1] using the parameters listed in Table II. The fitting with experimental data appears to be very good.

We have proposed a model to describe the dielectric phenomena of oil-external microemulsions (29), which is based on the triphasic model of interfacial polarization (27, 28) and the theory of Schwarz (30) for double layer polarization.¹ This model reduces to the classical Maxwell-Wagner theory (31, 32) when the surface charge den-

¹ Schwarz (30) treated the double layer as an infinitely thin surface of bound ions on which the diffusion currents of counterions respond to the tangential component of the electromigration flux in an applied electric field. This model should be applicable for systems with $\kappa R \gg 1$. For the present system, $\kappa R = 20.6$.

sity approaches zero. The low-frequency relaxation time (τ_1) is related to the diffusion of counterions in the electrical double layer while the high-frequency relaxation time (τ_2) corresponds to the relaxation between the equivalent particle (particle with its double layer) and the medium. They are given by the following expressions (29):

$$\tau_1 = \frac{e_0^2 R^2 \sigma_0}{2kT\lambda_0}, \quad [2]$$

and

$$\tau_2 \sim \frac{\epsilon_p}{K_p} \epsilon_v + \frac{e_0^2 R \sigma_0}{kTK_p}, \quad [3]$$

where e_0 is the charge of one electron, R the radius of the water droplet, σ_0 the surface charge density, λ_0 the surface conductivity, ϵ_p and K_p are the dielectric constant and specific conductance of the dispersed phase (1.5% NaCl brine), respectively, and kT the thermal energy term. The radius of the water droplet in oil-external microemulsions of the present system was determined to be 125 Å using a variety of techniques (33). According to Eqs. [2] and [3], τ_1 is proportional to R^2 and τ_2 proportional to R . Both relationships were established (29). Using Eqs. [2] and [3], one can calculate σ_0 and λ_0 from the measured values of τ_1 and τ_2 . The results are also listed in Table II. The surface charge density of the H_2O system was found to be $2.1 \times 10^{13} \text{ cm}^{-2}$ while that of the D_2O system was $0.69 \times 10^{13} \text{ cm}^{-2}$. For a surface area of 42 Å^2 per interfacial surfactant molecule (33), the degrees of ionization of surfactant

TABLE II
Dielectric Parameters of Oil-External Microemulsions^a

System	ϵ_1	ϵ_2	ϵ_3	τ_1 (sec)	τ_2 (sec)	β	α	σ_0 (cm^{-2})	λ_0 (mho)
H_2O	19.0	11.9	4.4	1.04×10^{-7}	7.1×10^{-9}	0.86	0.87	2.1×10^{13}	9.5×10^{-10}
D_2O	5.7	5.4	3.2	0.43×10^{-7}	2.7×10^{-9}	0.78	0.83	6.8×10^{12}	8.6×10^{-10}

^a Composition of oil-external microemulsion: TRS 10-410/isobutanol/dodecane/1.5% NaCl brine = 1/0.37/17/2 (g/g/g/ml).

molecules at oil-external microemulsion droplet surface were only 9 and 3%, respectively. The surface conductivity of the H₂O system ($\lambda_0 = 0.95 \times 10^{-9}$ mho) was only 15% higher than that of the D₂O system ($\lambda_0 = 0.86 \times 10^{-9}$ mho) which could be explained as due to the lower viscosity of H₂O than D₂O (34).

DISCUSSION

The results reported in this study can be consistently explained as follows. The surfactant-alcohol-oil-brine system containing H₂O is significantly more hydrophilic due to its higher surface charge density than the corresponding D₂O system. According to Winsor's *R* theory (22), the formation of middle phase microemulsion (Winsor's type III equilibria) signals the achievement of a proper hydrophilic-lipophilic balance (HLB) of the oil-brine-surfactant-alcohol system. Since, in general, increasing the salinity of an ionic surfactant system will increase its lipophilic character (22) and since the H₂O system is more hydrophilic than the D₂O system, a higher salinity is required to achieve the proper HLB resulting in a higher optimal salinity for the H₂O system. Similarly, the H₂O system requires a higher concentration of IBA (which is preferentially oil soluble) to acquire the proper HLB for maximum solubilization of brine in oil-external microemulsions. In the coacervation process, the H₂O system having a higher surface charge density would require a higher concentration of counterions to reduce the surface potential of surfactant micelles to induce phase separation. When a system is more hydrophilic, the surfactant molecules will preferentially partition into the aqueous phase in a low surfactant concentration system at equilibrium. Moreover, a higher system charge density would favor the adsorption of more alcohol molecules into the microemulsion droplet surface to reduce the electrostatic repulsion between ionized

surfactant polar groups. The results reported in this paper are indeed in agreement with the above mentioned expectations.

The higher surface charge density in the H₂O system can be explained by the lower (more negative) free energy of hydration of ionic species in H₂O than in D₂O (35, 36). The difference between the free energy of hydration of a species in the two solvents is the free energy of transfer of the species from H₂O to D₂O. Although the values of the free energy of transfer have been reported for many simple electrolytes (35), no such values are available for surfactant ions. However, it is possible to estimate the free energy of transfer of interfacial surfactant anions from the ratio of surface charge density in microemulsions as shown below.

Consider the following dissociation equilibrium of interfacial surfactant molecules (RSO₃Na) in H₂O and D₂O,



and



where the subscripts 1 and 2 denote the H₂O and D₂O system, respectively. The equilibrium constant for the dissociation and hydration process (neglecting the activity coefficient as a first approximation) is

$$K_i = \frac{[\text{RSO}_3^-]_i [\text{Na}^+]_i}{[\text{RSO}_3\text{Na}]_i}, \quad i = 1, 2. \quad [6]$$

When the degree of ionization of surfactant molecules is small and when in the presence of excess NaCl in brine, the concentration of counterions and undissociated surfactant molecules can be regarded as constant, hence

$$\frac{K_1}{K_2} = \frac{[\text{RSO}_3^-]_1}{[\text{RSO}_3^-]_2}. \quad [7]$$

The equilibrium constant is related to the free energy of dissociation ΔG^d , hydration of interfacial surfactant anions ΔG^s and hy-

dration of counterions ΔG^c by

$$\ln K_i = - \frac{(\Delta G^d + \Delta G_i^f + \Delta G_i^c)}{N_A kT} \quad [8]$$

$i = 1, 2.$

Thus

$$\ln \frac{K_1}{K_2} = - \frac{(\Delta G_1^f - \Delta G_2^f) - (\Delta G_1^c - \Delta G_2^c)}{N_A kT} \quad [9]$$

Since $(\Delta G_2 - \Delta G_1)$ is simply the free energy of transfer from H_2O to D_2O (ΔG_t) and the ratio $[RSO_3^-]_1/[RSO_3^-]_2$ is simply the ratio of surface charge density σ_1/σ_2 (neglecting the very small amount of surfactant ions partitioned into the bulk phases) we have

$$\ln \frac{\sigma_1}{\sigma_2} = \frac{\Delta G_1^f + \Delta G_1^c}{N_A kT} \quad [10]$$

According to Eq. [10], the surface charge density of the H_2O system (σ_1) is higher whenever the sum of free energies of transfer of interfacial surfactant anions and counterions is positive. This is expected since the degree of ionization, as well as the solubility of weak electrolytes, is in general higher in H_2O than in D_2O (35). For the present system, the free energy of transfer of interfacial surfactant anions was calculated to be 560 cal/mole, assuming $\Delta G_i^f = 90$ cal/mole (35) and using $\sigma_1/\sigma_2 = 3.0$ (Table II). Since the standard enthalpy of transfer (ΔH_t) of methyl sulfonate is only 130 cal/mole (35), it is seen that the effect of hydration of surfactant anions is much enhanced at microemulsion droplet surface. One of the reasons may be that the interfacial alcohol concentration is higher in the H_2O system leading to higher disorder of the interfacial surfactant/alcohol film as has been detected by ESR measurements of similar systems (20). The transfer of an interfacial surfactant anion from the more disordered H_2O -in-oil microemulsion droplet surface to the less dis-

ordered D_2O -in-oil microemulsion droplet surface would decrease its entropy and hence the entropy of transfer (ΔS_t) is negative. This would then lead to a higher value of ΔG_t as $\Delta G_t = \Delta H_t - T\Delta S_t$. Thus the entropy effects may contribute to rather than compensating (37) the free energy of transfer in microemulsion systems. Another possible explanation for the higher value of ΔG_t (than the value of ΔG_t at infinite dilution) is that the activity coefficients of interfacial surfactant anions and counterions could be smaller in the H_2O system due to its higher surface potential.

The results have important implications for the validity of the approach of determining the molecular interactions in lipid/water or surfactant/oil/water systems by substituting D_2O for H_2O , as is commonly done for NMR studies of such systems (37-40).

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