The NMR of Benzene/Water Emulsion

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To date, no paper has reported the application of the high-resolution NMR technique to the investigation of emulsion except that of Cratin and Robertson.1) Since the emulsion state is heterogeneous and thermodynamically-metastable, its complete analysis is very difficult. In this communication, some information obtained with the NMR technique concerning the benzene/water emulsion will be reported.

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1) P. D. Cratin and B. K. Robertson, *J. Phys. Chys. Chem.*, **69**, 1087 (1965).

Experimental

The emulsions were prepared by shaking portions of benzene with equal amounts of water containing an emulsifier in various concentrations. As the emulsifier sodium dodecyl sulfate (SDS) was used. The emulsions thus obtained were of the o/w type. The freshly-prepared emulsion was left to stand for about 24 hr. before the NMR investigation was started in order to secure the state of the emulsion which was stable enough during the NMR measurement.

The chemical shifts of the proton in water, benzene and SDS were measured at constant temperatures, but the shifts of the latter two were so small as to fall within the range of experimental error; therefore, the final measurements were made solely with the water proton peaks. The shifts were measured by using a Japan Electron Optics JNM-3 high-resolution NMR spectrometer, with dioxane as the external reference. The experimental error was less than 0.5 c. p. s.

Results and Discussion

Figure 1 shows the water proton chemical shifts in SDS solutions of various concentrations and temperatures. The water proton gave a single but somewhat broad resonance line; this line shifted towards the higher applied field with an increase in the SDS concentration and temperature. The single line in this case represents the rapid proton exchange between different species, and the higher field shift is assumed to show that the structure of water is increasingly destroyed by the increase in the concentration of SDS, as well as by the rise in temperature, the shift per mole of SDS nearly corresponding to that per ten degrees of temperature. There should be a kink at the critical micelle concentration (CMC) on the curve of the shift vs. SDS concentration, as was shown by Pethica,[2] but in this experiment the range of the SDS concentration is so high that the kink at the CMC is not clear. However, it may be said from Fig. 1 that the slope of the curve below the CMC decreases with the temperature, while that above the CMC is independent of the temperature.

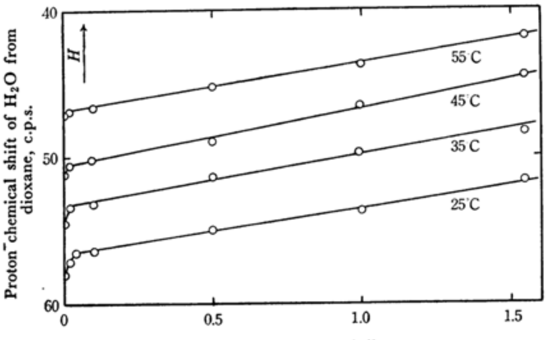

Fig. 1. Proton chemical shift of H_2O vs. SDS concentration at various temperatures.

The concentration of the SDS solution used for preparing the emulsion in this experiment was far above the CMC, and the amount of benzene added was large enough so that the bulk solution should have been saturated with benzene (solubilization). The chemical shift of the water proton in the SDS solution saturated with benzene was, therefore, measured. The results are shown in Fig. 2. In the presence of solubilized benzene, the water proton shifts to a higher field than in the absence of benzene; this shift increases with the amount of benzene solubilized. When Wiedmann's theory is applied, the chemical shift due to the change in bulk susceptibility is less than 0.4 c. p. s. at the SDS concentration of 1.0 mol./l. The observed value is much larger than this. Therefore, the higher field shift due to solubilized benzene may be attributed to the magnetic anisotropy of benzene. If the solubilized benzene is only in the central part of micelles, this effect can not be expected. It is, therefore, reasonable to consider that the solubilized benzene is, as Eriksson[3] proposed, near the micelle surface, or that, as Nakagawa et al.[4] showed, benzene molecules in the micelle exchange with those in the bulk solution.

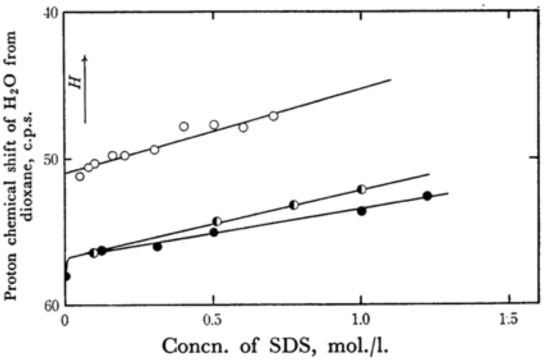

Fig. 2. Proton chemical shift of H_2O vs. SDS concentration at 25°C.
○ In emulsion ● In SDS solution
◐ In SDS solution saturated with benzene

Also in Fig. 2, the chemical shift of the water proton in the benzene/water emulsion is plotted against the SDS concentration, the latter being determined after the destruction of the emulsion. It may be seen that the shift of the water proton in the emulsion state containing SDS as an emulsifier is further towards the higher magnetic field than in the case of the SDS solution containing solubilized benzene. This higher field shift can not be due to the magnetic anisotropy of benzene, since we found a similar shift in the case of the cyclohexane/water

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[2] J. Clifford and B. A. Pethica, *Trans. Faraday Soc.*, **60**, 1483 (1964).

[3] J. C. Eriksson, *Acta Chem. Scand.*, **17**, 1478 (1963).

[4] T. Nakagawa and K. Tori, *Kolloid-Z. u. Z. Polymere*, **194**, 143 (1964).

emulsion. The observed difference between the chemical shift of the water proton in the SDS solution, which has solubilized benzene, and that in the benzene/water emulsion state is to be attributed to the surface effect of the emulsion particles.

At the oil/water interface the SDS molecules are considered to form an adsorbed layer. Accordingly, the water molecules near the interface are different in structure from those of the bulk water due to the charge as well as to the dipole effect of the adsorbed SDS molecules. It is difficult to distinguish the true interface effect (without an adsorbed emulsifier) from the effect of the adsorbed layer of the emulsifier, but it would be natural to consider that the higher field shift of the water proton in the emulsion state over the shift of that in the bulk solution containing benzene is caused chiefly by the breaking of the hydrogen bond structure of water at the interface. Again, it is assumed that the exchange of water between the surface and the bulk is rapid. When the chemical shifts of water protons in the emulsion state, at the interface, and in the bulk solution, are denoted by δ_e, δ_s, and δ_b respectively, then:

$$\delta_e = X_s\delta_s + (1 - X_s)\delta_b \tag{1}$$

where X_s is the mole fraction of water near the interface causing δ_s. From Eq. 1 we have:

$$\varDelta\delta/X_s = \delta_s - \delta_b \tag{2}$$

where $\varDelta\delta=\delta_e-\delta_b$. We have attempted to determine the particle-size distribution of the benzene droplets in the emulsion by microscopic observations as a function of the SDS concentration. From this we can estimate the value corresponding to X_s at each SDS concentration, assuming that X_s is proportional to the interfacial area between benzene droplets and water. For δ_b the chemical shift of the water proton in the SDS solution saturated with benzene can be used. From these data the $\varDelta\delta/X_s$ vs. δ_b plot can be obtained. Unfortunately, due to errors accompanying the particle-size distribution of the emulsion, we could only roughly confirm the linear relationship between $\varDelta\delta/X_s$ vs. δ_b. We are expecting to reach a more precise conclusion after the particle-size distribution has been improved.