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Solvation Changes Induced In A Lyotropic Lamellar Liquid Crystal Containing Solubilized Benzene

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Deuterium NMR quadrupole splittings of deuterated benzene and water were studied as a function of their composition in the aqueous lamellar phase of pentaethylene glycol *n*-dodecyl ether. An interpretation of the results is given in terms of hydration changes of the poly(oxyethylene) chains related to changes in the benzene solvation and location within the head-group region.

Introduction

The lamellar liquid crystal phase formed by nonionic surfactants (pentaethylene glycol *n*-dodecyl ether, $C_{12}E_5$) and water has been shown[1,2] to be remarkable in its ability to incorporate a larger amount of water in the presence of solubilized aromatic hydrocarbon. For the system water/pentaethylene glycol *n*-dodecyl ether, an increase from approximately 45% (w/w) at zero benzene content to 80% water content has been observed at an approximately 1:1 mol ratio of benzene to surfactant.[2] This contrasts the behavior exhibited by the lamellar phase in the presence of solubilized nonpolar alkanes where no extension of the phase to higher water contents is observed.[2]

This behavior was found sufficiently interesting to justify an investigation as to the cause of it. As a first approach, a determination of the location of the aromatic hydrocarbon molecule in the liquid crystalline layers was considered optimal, considering the factors that decide the shape of surfactant association structures.[3,4] For micellar solutions there is evidence[5-8] that aromatic molecules are located in the polar interface layer in preference to the more hydrophobic regions of the aliphatic hydrocarbon chains of the surfactant. It is probable, therefore, that the solubilized benzene will preferentially be found in the region occupied by the poly(oxyethylene) chains at the bilayer surface also in a liquid crystalline phase. The driving force for this being the favored solubilization site is presumably some interaction between the π electrons of the benzene molecules and the ether oxygen of the oxyethylene groups.[7-10] It is expected that there will be direct competing interactions between water molecules from the interbilayer phase and the solubilized benzene in a somewhat analogous way to that recently discussed[11] for a lipid system containing both water and ethylene glycol. These interactions should involve variations in the head-group solvation as the relative amounts of solvent and solubilizate are changed. Such variations in the intermolecular interactions are expected to cause distinctive changes in the dynamics of the solvent molecules and the present study was instigated in order to detect such effects using deuteron magnetic resonance. This paper will present some preliminary results of this study.

Experimental Section

Pentaethylene glycol *n*-dodecyl ether (Nikko Ltd., Japan) was used to form the lamellar phase at 25 °C. ^2H_2O (99.8 atom %) and perdeuterobenzene (99.5 atom %), both from MSD Isotopes, were used as received. Samples were mixed as described elsewhere[1,8] and low-angle X-ray reflections[12] gave the characteristic lamellar repeat distance. The deuterium NMR quadrupole splitting measurements were made at 25 °C and resonant fre-

quency of 30 MHz, using a Bruker Spectrospin CXP-200 pulsed NMR spectrometer. The observed spectra were of the form of Pake powder doublets[13,14] as expected for unoriented lamellar dispersion.

Results and Discussion

The quadrupolar splitting of benzene solubilized in the aqueous lamellar phase of $C_{12}E_5$ is shown in Figure 1 as a function of the water content at a fixed benzene/surfactant ratio. As water is added the splitting passes through a maximum value at a water content within the range of formation of the lamellar phase in the absence of solubilizate.

The increase in $\Delta\nu$ of the benzene as water is added reflects an increased ordering of the solubilized molecule since the quadrupole splitting, $\Delta\nu$, is related to the order parameter S, as

$$\Delta\nu = \tfrac{3}{4}\chi|S|$$

where χ is the quadrupole coupling constant and S is the order parameter associated with a C–D bond.

In contrast, the quadrupole splittings of the water molecules measured under the same conditions decreased monotonically as the water content increased (Fig. 2). The reduction of the order parameter of the water molecules over the concentration range where the benzene is apparently becoming more ordered was only insignificantly reduced remaining at a level consistent with that typically found for hydrated lipids and surfactants.[15,16] In the

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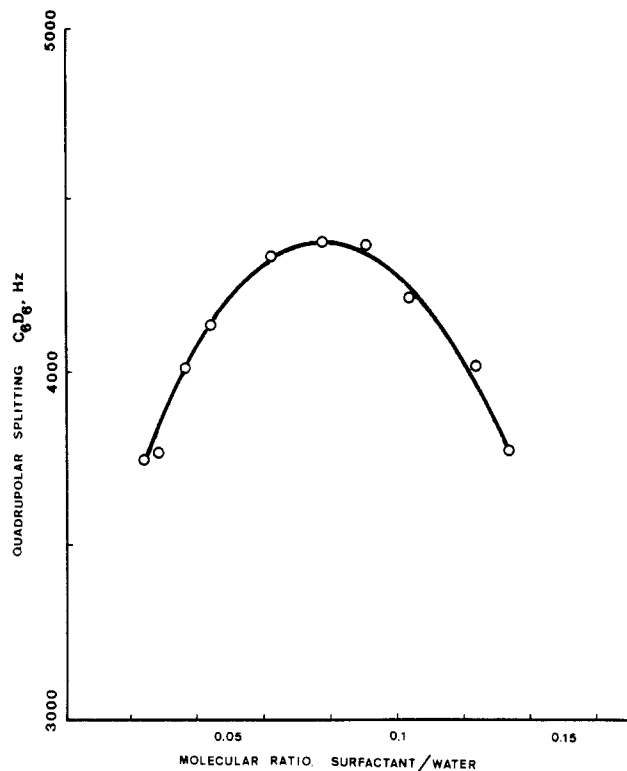*Permanent address: Chemistry Department, University College, Belfield, Dublin 4, Ireland.

Figure 1. Benzene deuterium quadrupolar splitting vs. surfactant/water ratio for samples with benzene/surfactant mole ratio of 1.06.
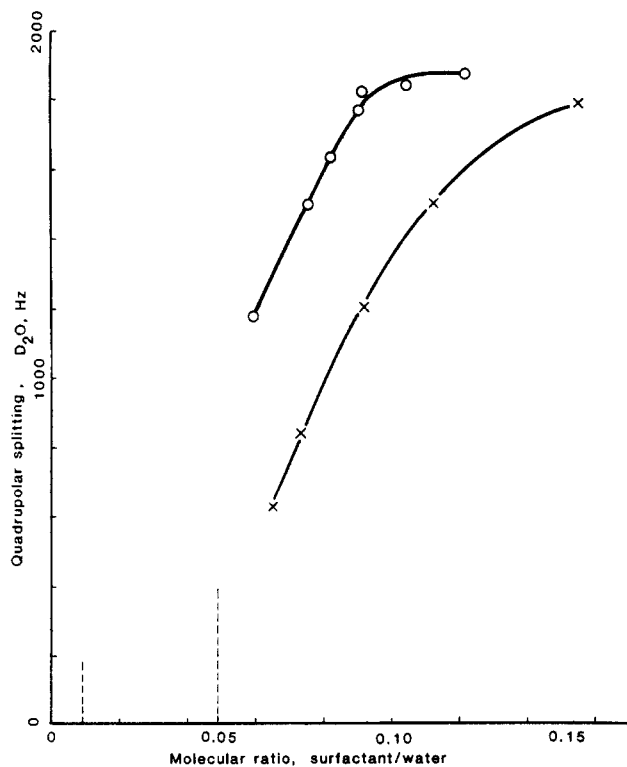

Figure 2. Water quadrupolar splittings vs. surfactant/water ratio for samples with benzene/surfactant mole ratio of 1.06 (O) and 0 (×).

higher water content range where a decrease in the benzene order was found, the water splitting may be described by
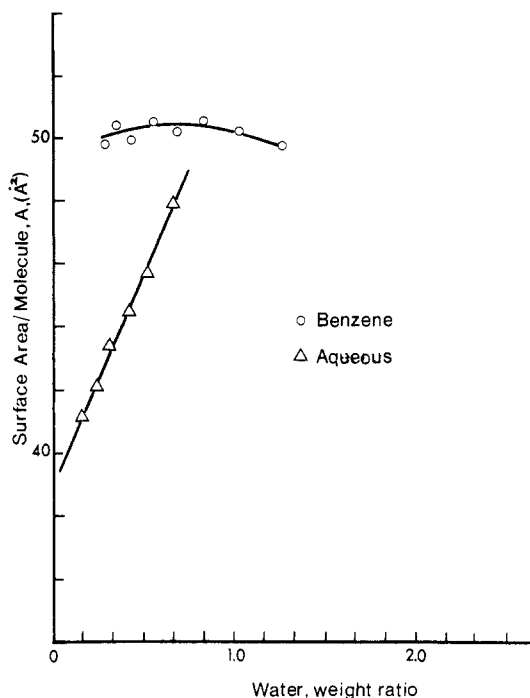
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Figure 3. Surface area/molecule ($Å^2$) vs. water weight ratio ($C_w/(1 - C_w)$) for benzene/surfactant mole ratio of 0 ($\triangle$) and 1.06 (O) (C_w, weight of water).

a fast exchange between bound and isotropic water molecules ($\Delta\nu \sim 0$), i.e.,

$$\Delta\nu_{obsd} = n(C_s/C_w)\Delta\nu_b$$

where n is the number of bound water molecules per surfactant, $\Delta\nu_b$ is the weighted average value of the bound water, and C_s/C_w is the molar ratio of surfactant to water. It should be noted that at fixed C_s/C_w the system containing benzene shows an apparent higher order parameter over the entire composition range. This implies the number of water and benzene molecules penetrated in between the oxyethylene chains is to be higher in the latter system. Such a change in environment of the benzene should be related to changes in the surface area available per surfactant head group, A,[12] at the bilayer surface. The values of A calculated from low-angle X-ray data by using the treatment of Francois et al.,[18] assuming the benzene molecules to reside in the region (among the poly(oxyethylene) chains), are presented in Figure 3. This shows that when there is no oil solubilized, the added water penetrates the surface region resulting in an observed increase in A (from 41 to 48 $Å^2$). On the other hand, in the presence of benzene, the A values are larger (ca. 51 $Å^2$) and their variation with water content is insignificant.

It appears, therefore, that at a benzene/surfactant mole ratio of ca. 1:1, the overall structure of the interfacial region is largely unaffected by the water content, i.e., the total amount of penetration of the two solvents into the bilayer has reached some limiting state. The implication is that the changes reflected in the benzene order parameter with water content are a result of some reorganization of the molecular structure in this region connected with the filling of the water hydration shell. This assumption is supported by the correspondence between the position of the maximum in the benzene quadrupolar splitting and the filling of the hydration shell at approximately 11 water molecules/molecule of $C_{12}E_5$.[17]

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A possibility which has to be considered is that the data could be interpreted purely in terms of a binding model. Such a model has been proposed[15] for the case of the water quadrupole splittings in the lamellar and gel phases of a series of polyethylene glycol alkyl ethers. The model was found to give reasonable values for the binding constants and the hydration numbers and was capable of accounting for the presence of a maximum in the water splittings with increased water content. The data presented here for the $C_{12}E_5$/water lamellar phase are in good agreement with those of Tiddy[15] and could obviously be curve-fitted in the same way. However, if the system with oil solubilized is considered, in fact the system considered here contained only ca. 1 mol of oil/mol of surfactant, a description of the observed behavior in terms of cooperative binding does not appear as well justified.

Instead, a picture is preferred in which the benzene molecules become more ordered in the alkyl chain polyethylene glycol inteface region as the primary hydration of the ethylene oxide groups is occurring. The NMR data on the isotropic liquid hydrocarbon solution[7] showed hydration to proceed from the terminal OH group of the surfactant. With the area per molecule remaining constant (Figure 3) with water content, a reasonable interpretation is that the order parameter variations arise from positional and orientational changes within the solvated E-chain region due to restricted space for the benzene molecules after the water penetration.