

01 Jan 1980

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Recommended Citation

H. Christenson et al., "NMR Investigations Of Aggregation Of Nonionic Surfactants In A Hydrocarbon Medium," *Journal of Physical Chemistry*, vol. 84, no. 26, pp. 3633 - 3638, American Chemical Society, Jan 1980.

The definitive version is available at <https://doi.org/10.1021/j100463a028>

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NMR Investigations of Aggregation of Nonionic Surfactants in a Hydrocarbon Medium

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Proton NMR, carbon-13 NMR, light-scattering, and density measurements were used to investigate association structures and molecular interactions during water solubilization in polyoxyethylene dodecyl ether/benzene systems at high surfactant concentrations. The results indicated an absence of association aggregates at low water concentrations. At water contents between 10 and 20%, association structures started to form, probably micelles of the inverse type, in which the water-polyoxyethylene chain interaction is the predominant feature. There is evidence that the average chain conformation changes with water content, and that bound water molecules are distributed evenly along the polyethoxyethylene chain. At higher water concentration, the results indicated a water-rich core to be formed, supported by the close resemblance of the water properties to those of native water.

Introduction

There have been numerous studies of the phase behavior and water solubilization by nonionic surfactants of the polyoxyethylene type. Investigations have been concerned both with polydisperse commercial surfactants¹⁻⁸ and monodisperse substances of high purity.⁹⁻¹¹

Characteristic of these nonionic surfactants is the pronounced dependence of phase behavior on the temperature and the nature of the hydrocarbon. Shinoda²⁻⁵ has systematized this complex behavior by introducing the concept of the HLB temperature. In order to clarify the dependence of water solubilization upon temperature and hydrocarbon, it is necessary to determine the conditions for water-free surfactant molecules in hydrocarbon solution. Such investigations have shown that polyoxyethylene surfactants do not form micelles in hydrocarbon solution,^{1,12-17} at least not unless large amounts of water and surfactant are present. However, there is evidence that small amounts of water may, in some systems, promote micellization.^{18,19}

These investigations have mainly been concerned with the determination of micellar size; information about specific solubilization sites for different hydrocarbon structures and about their molecular interactions with water and surfactants has so far been lacking.

We found such information to be necessary for a complete understanding of the water solubilization in hydrocarbons by nonionic surfactants of the polyoxyethylene alkyl ether type. Preliminary results demonstrated the interpretational difficulties of NMR spectra in concentrated systems due to the complex intermolecular interactions of the surfactant molecules. Against this background, our first investigation¹¹ was limited to sufficiently small concentrations for the surfactant molecules to exist as monomers. Under these conditions, the NMR resonances could be given an unambiguous interpretation and the changes brought about by addition of water to the solution could be analyzed.

Our results showed the aromatic hydrocarbon to be concentrated along the polar part of the surfactant. Addition of small amounts of water gave spectral changes that revealed a preferential water adsorption hydrogen bonded to the hydroxide group of the surfactant. Further addition of water gave a gradual retraction of the aromatic hydrocarbon from the polar chain caused by the advancing water.

The understanding gained from the dilute solution studies gave a firm basis for an analysis of more concentrated solutions with micellization. Hence it appeared logical to consider conditions at higher surfactant/hydrocarbon ratios as a sequel to the preceding work. The object of the present article is to consider molecular interactions and associations in systems of benzene/polyoxyethylene dodecyl ethers/water at benzene/surfactant ratios giving maximum water solubilization.

Experimental Section

Materials. The polyoxyethylene dodecyl ethers, obtained from Nikkol Co., Japan, were well-defined compounds of purities $\geq 98\%$, as determined by gas chromatography. The polyoxyethylene dodecyl ethers will henceforth be referred to only by their prefixes, i.e., penta for pentaoxyethylene dodecyl ether, etc. The benzene was Fischer certified and used without further purification, and the water was doubly distilled.

Determination of Solubility Areas. The extensions of the water-poor isotropic liquid-phase regions were determined by direct titration of surfactant-benzene solutions with water. A short time (15 min-1 h) was allowed for equilibration at 30 °C. At least 15 points were used for the determination of each solubility area.

The following measurements were all done on the system penta/benzene/water with a penta/benzene ratio of approximately 3:1. This is the ratio that gives maximum water solubilization, 55% at 30 °C. The exact ratio varies between 76:24 and 74:26 depending on the lot number of

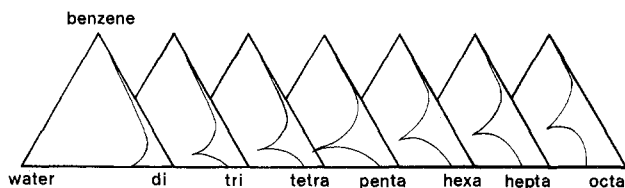


Figure 1. The extension of the isotropic liquid phase at 30 °C as determined by titration for well-defined polyoxyethylene dodecyl ethers, water, and benzene. Diagrams are constructed on a weight basis.

the surfactant. A sufficient number of complementary measurements with surfactants of differing oxyethylene chain lengths were performed so as to allow generalization to systems of polyoxyethylene dodecyl ethers/benzene/water at surfactant/benzene ratios giving optimum solubilization of water.

Light Scattering. A Wippler & Scheibling photogometer was used to measure the intensity of scattered light ($\lambda = 5460 \text{ \AA}$) at 90° relative to that of benzene. Toluene was used as a bath liquid at a temperature of 30 °C.

Density Measurements. Densities were measured with a Mettler/Par DMA 40 digital density meter at 30.0 °C.

Proton NMR Spectra. The proton magnetic resonance spectra were obtained with a Perkin-Elmer R-20 instrument operating at 60 MHz with water as an external lock. The probe temperature was maintained at 30 °C by a variable-temperature accessory. Spectra from selected compositions were also run on an EM-390 spectrometer at 90 MHz and ambient temperature (34 °C) with benzene as internal lock. No reference was used; in all cases shifts were determined relative to the alkyl proton resonances.

Carbon-13 NMR Spectra. Measurements were performed on a Jeol FX 100 Fourier transform spectrometer at 25 MHz with a probe temperature of 30 °C. Water was used as an internal lock; no internal reference was employed. Typical settings were as follows: spectral width, 5000 Hz; acquisition time, 0.8 s; pulse angle, 45°; number of transients, 100–600; 8K data points.

Results

The results will be presented in the following order: First, the variation of water solubilization with oxyethylene chain length and the benzene/surfactant ratio giving optimum water solubilization will be presented. These values give information about the variation in benzene/surfactant ratios for maximum water solubilization for the different surfactants. They are used to select the benzene/surfactant ratio for determination of association conditions as a function of the water content. This information is obtained from the results of light-scattering and density measurements, which are presented sequentially. These will be used to interpret the molecular phenomena involved in the association process.

Figure 1 presents the phase diagrams for the polyoxyethylene dodecyl ether/water/benzene system. It can be seen that the location of the water solubilization maximum shifts toward higher benzene/surfactant ratios on increasing the number of oxyethylene groups in the polar chain of the surfactant, which is in agreement with previous results.^{9,10} This is especially apparent if one considers molecular ratios since the diagrams were constructed on a weight basis. The penta homologue showed the highest solubilization of water, 55%, at a hydrocarbon/surfactant ratio 1/3 and also a minimum water solubilization in the surfactant isotropic liquid with no hydrocarbon present.

At high benzene/surfactant ratios the general features were similar for all surfactants and the amount of solubilized water was very small, a few tenths of a percent at

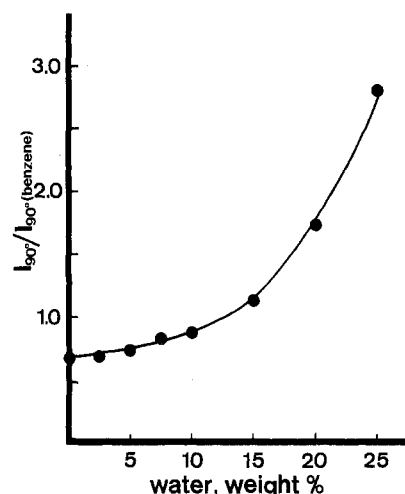


Figure 2. The ratio of the intensity of scattered light at 90° for penta-oxyethylene dodecyl ether and benzene (3:1) to that for pure benzene as a function of water content.

ratios of 10 and greater. The results also indicated that there is no linear solubilization limit at a constant water/surfactant ratio; instead, the solubility border seemed to approach the benzene/surfactant side of the phase triangle asymptotically.

Results from the light-scattering measurements are plotted in Figure 2. The intensity of scattered light increased gradually with increasing water content; no discontinuity in the curvature, indicating a critical micellization concentration, was observed.

For the calculation of partial molal volumes of water the following approach was employed: Taking an initial amount of 1.000 g of water-free penta/benzene solution 76:24, we calculated the change in the difference between the actual volume V (calculated from density values) and a theoretical volume, V_{add} , based on the addition of water and benzene/penta volumes. Letting this difference in volume be ΔV , one obtains

$$\Delta V = V_{\text{add}} - V$$

Since $V_{\text{add}} = V_0 + V_w$ = the sum of the initial volume of 1.000 g of penta/benzene solution and the volume of added water, the partial molal volume may be expressed as

$$\left(\frac{\partial V}{\partial n_{\text{H}_2\text{O}}}\right)_{T,p} = \left(\frac{\partial V_0}{\partial n_{\text{H}_2\text{O}}}\right)_{T,p} + \left(\frac{\partial V_w}{\partial n_{\text{H}_2\text{O}}}\right)_{T,p} - \left(\frac{\partial \Delta V}{\partial n_{\text{H}_2\text{O}}}\right)_{T,p}$$

where $(\partial V_0/\partial n_{\text{H}_2\text{O}})_{T,p} = 0$ since V_0 is constant and $(\partial V_w/\partial n_{\text{H}_2\text{O}})_{T,p}$ is the partial molal volume of bulk water at 30 °C which is 180941 cm^3 , so that

$$\left(\frac{\partial V}{\partial n_{\text{H}_2\text{O}}}\right)_{T,p} = 180941 - M_{\text{H}_2\text{O}}\left(\frac{\partial \Delta V}{\partial m_{\text{H}_2\text{O}}}\right)_{T,p}$$

$M_{\text{H}_2\text{O}}$ is the molecular weight of water, and $(\partial \Delta V/\partial m_{\text{H}_2\text{O}})_{T,p}$ can be estimated from the slopes in a plot of ΔV vs. $m_{\text{H}_2\text{O}}$. The resulting values of $(\partial V/\partial n_{\text{H}_2\text{O}})_{T,p}$ as a function of weight percent water are plotted in Figure 3.

Proton NMR spectra of polyoxyethylene dodecyl ethers in benzene solution have been reported and assigned in a previous article.¹¹ The oxyethylene resonance signal of penta in 24% benzene is presented in Figure 4 (dashed line). Solubilization of water caused the resonance peak to shift downfield and broaden. At high water content, the resonances were split into four distinct peaks (Figure 4, full line). The total downfield shift observed for the most downfield peak when water content was varied from 0 to 50% water was 0.19 ppm relative to the alkyl signal. This was the largest observed shift. The observed peak

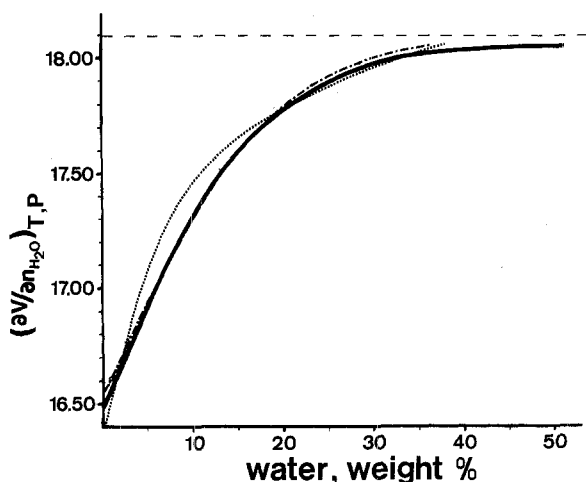


Figure 3. Partial molal volumes (cm^3) of water at 30°C as functions of water content: (—) 3:1 pentaoxyethylene dodecyl ether and benzene; (····) 31:19 heptaoxyethylene dodecyl ether and benzene; (---) 4:1 tetraoxyethylene dodecyl ether and benzene; (---) value for bulk water (18.094).

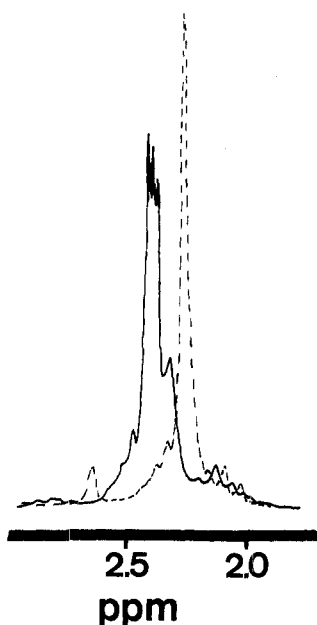


Figure 4. Oxethylene proton resonances of NMR spectra of (---) pentaoxyethylene dodecyl ether and benzene 24% and (—) the same with 20% solubilized water. Shifts in ppm downfield from the alkyl resonances.

TABLE I: Proton NMR Downfield Shifts (in ppm) of Oxethylene Groups on Increasing Water Content from 0 to 25% by Weight

	CH_2	O	EO_1	EO_2	EO_3	EO_4	EO_5	EO_6
tri	0.04		0.07	0.09				
tetra			0.07	0.12	0.13			
penta	0.04		0.07	0.11	0.13	0.15		
hexa			0.06	0.14	0.15	0.16	0.18	

positions are plotted in Figure 5. The samples studied at 90 MHz with benzene as an internal lock indicated that the alkyl protons exhibit a maximum downfield shift of 0.02 ppm under the same conditions as for Figure 5.

Similar behavior was observed for tri, tetra, and hexa when water was added to solutions with the respective benzene/surfactant ratios giving maximum water solubilization. These results are tabulated in Table I. Tri split into two peaks, tetra into three, and hexa into five peaks.

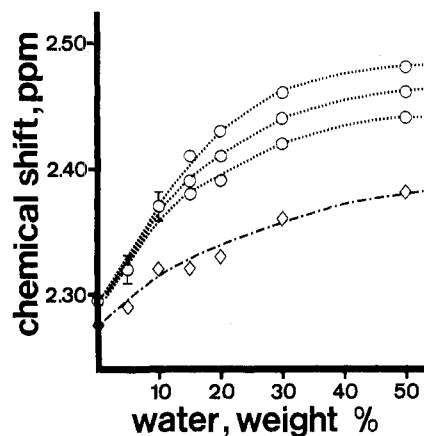


Figure 5. Proton chemical shifts of the oxyethylene resonances for pentaoxyethylene dodecyl ether and benzene (24%) as a function of water content. Shifts in ppm downfield from the alkyl resonances. Error bars have been drawn for the first two points to indicate that these resonances are much broader than the following ones.

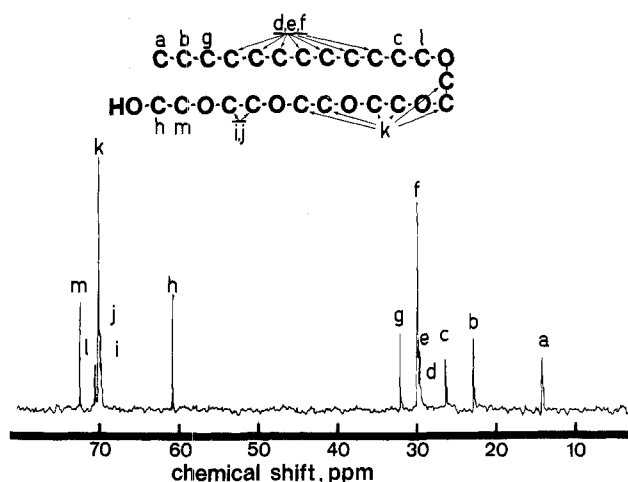


Figure 6. The carbon-13 NMR spectrum of neat pentaoxyethylene dodecyl ether with assignment of peaks. Scale constructed by assuming shift of CH_3 to be 14.3 ppm.

Comparison of the downfield shifts observed between 0 and 25% water solutions showed that each peak corresponds to one unit. The group next adjacent (β) to the hydroxyl end experiences the greatest apparent downfield shift. This is only because the outer most oxyethylene group (α) is spin-spin split and is not observed at 60 MHz.¹¹ Thus we observe the downfield shift to be greatest for the resonances of the oxyethylene units closest to the hydroxyl group and to decrease progressively with decreasing distance from the alkyl chain. In addition, the signal of the inner most oxyethylene group (that adjacent to the alkyl chain) was considerably broadened (Figure 4).

The C-13 spectrum of penta is shown in Figure 6. Ribeiro and Dennis²⁰ have recently reported and assigned the C-13 spectrum of octaoxyethylene dodecyl ether in D_2O and CDCl_3 solution. On the basis of their assignment and comparison with spectra of the monotetra homologues we have reached the assignment given in Figure 6.

Ribeiro and Dennis assignment of the last two methylene carbons of the oxyethylene groups (peak h and m in our spectra, Figure 6) is as they point out in disagreement with earlier results^{21,22} and literature data.²³

Addition of 25% benzene caused negligible changes in the spectrum; the shift differences were for all carbons ≥ 0.10 ppm. Addition of water to this penta/benzene caused upfield shifts for the oxyethylene carbons whereas the terminal methylene carbon of the alkyl chain exhibited

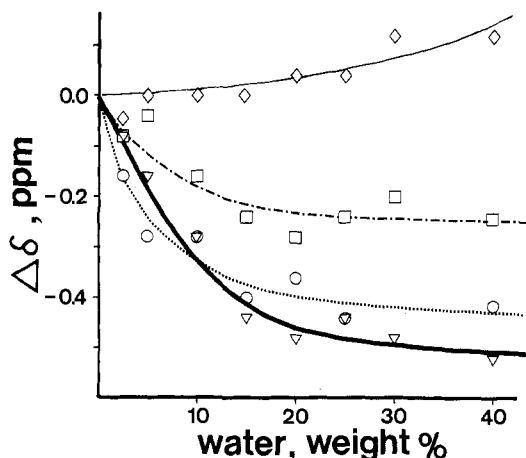


Figure 7. Carbon-13 chemical shift changes for oxyethylene carbons of pentaerythylene dodecyl ether and benzene upon successive addition of water. Negative shift is upfield. Surfactant to benzene ratio 3:1 by weight. (\diamond , —) C_{12} peak, l; (\square , - - -) one of C_{13} - C_{20} peak, k; (\circ , ····) C_{22} peak, h; (∇ , —) C_{21} peak, m.

a slight downfield shift. A plot is given in Figure 7. The upfield shift was greatest for the two carbons of the terminal oxyethylene group. The alkyl carbons did not shift relative to one another and they were used as internal references to determine shift changes in Figure 7.

The main oxyethylene carbon resonance, peak k, split into several well-resolved resonances at higher concentrations of water, two of which are visible as shoulders on the upfield side of peak j in Figure 6.

Discussion

The results of the solubility-area determinations demonstrated the exceedingly sharp maximum in water solubilization and its initial dependence upon the surfactant/benzene ratio.

The extent of water solubilization at high benzene concentrations tends to preclude the possibility of any larger aggregates of the inverse micellar type in this region of the phase diagram, supporting previous work.^{7,8,10,11} At benzene concentrations of 90%, only a few tenths of a percent of water are solubilized, which on a molecular scale is equivalent to less than one molecule of water per molecule of surfactant. This behavior is also in marked contrast to that of aliphatic hydrocarbons, for which numerous phase diagrams reported in the literature¹⁰ give water solubilization of a few percent at 90% hydrocarbon and 30 °C. For these hydrocarbons the solubility border is also more or less a straight line of constant water/surfactant ratio.

The insignificant solubilization at high benzene content support our earlier¹¹ interpretation of a preferential location of benzene molecules close to the polyoxyethylene chain. With only aliphatic hydrocarbon present or with only water and surfactant well-recognizable hydrates are formed²⁴ containing several water molecules per oxyethylene group. Similar conditions have also been detected for polyethylene oxide.²⁵ The benzene present obviously gave a sufficient interaction with the polyoxyethylene chain to prevent the formation of the water clusters.

Increasing the surfactant/benzene ratio caused the water solubilization suddenly to reach a sharp maximum and then decline (Figure 1).

The tendency has so far been to treat this solubilization maximum as a question of stability of the inverse micellar structure. Such a treatment is justified for W/O microemulsions stabilized by an ionic surfactant and a cosurfactant.²⁶ For such systems the pronounced solubilization

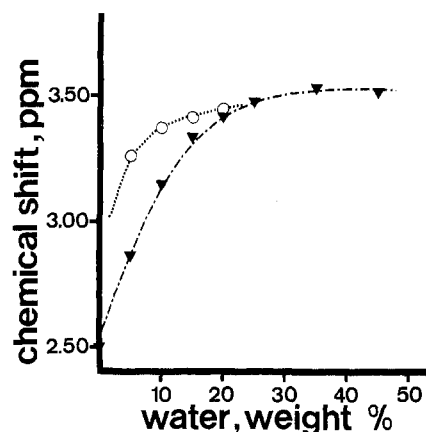


Figure 8. Chemical shift of water/hydroxyl protons (\blacktriangledown) as a function of water content in a 24% benzene-76% penta solution. (\circ) denotes a shift calculated by assuming the shift of added water to be equal to that of bulk water. Shifts relative to alkyl resonances (downfield = positive shift).

maximum as function of the surfactant/cosurfactant ratio is not accompanied by a change in the structure of the phase in equilibrium with the microemulsion.

This is not the case for the present microemulsions stabilized by nonionic surfactants. At the maximum water solubilization the phase in equilibrium with the hydrocarbon/surfactant solution with solubilizing water changed from being liquid water to become a lamellar liquid crystalline phase. At surfactant/hydrocarbon ratios less than the optimal one for water solubilization the equilibrium phase at excess water content was water; at surfactant/hydrocarbon ratio in excess of the optimal water solubilization the "equilibrium phase" was a liquid crystal.

These equilibrium conditions offer a rational explanation for the fact that the surfactants with longer polyoxyethylene chains show a higher hydrocarbon/surfactant ratio for maximum water solubilization. The longer polyoxyethylene part permits more hydrocarbon to be present without destabilization of the lamellar structure.

This does not mean a maximally stable lamellar structure; the long polyoxyethylene chain facilitates a change to a liquid crystalline structure of hexagonally close-packed cylinders.¹⁰ The optimum polar chain length for stabilization of the lamellar structure at 30 °C appears to be the five oxyethylene groups. The penta compound showed a minimum of water solubilization in the pure surfactant demonstrating a phase transition to the lamellar phase at the smallest amount of water. It also gave the highest water solubilization at the optimum surfactant/hydrocarbon ratio; this is a further indication of the stability of the lamellar structure.

The light-scattering data and the partial molal volumes of water both showed the absence of a critical micellization concentration with increased water content. This is in agreement with earlier expressed opinions.²⁷

The partial molal volume curves of water vs. water content gave further information about the state of water. The partial molal volume of bulk water is 18.09 cm³ at 30 °C and this value was approached fairly closely already at 30% water (Figure 3). This fact indicated the water at high content to be accumulated in an environment similar to that of bulk water. A model of water-rich core in an inverse micelle or microemulsion droplet appears justified.

This model is further corroborated by the ¹H chemical shifts of the water/hydroxyl protons in Figure 8. Figure 8 shows this shift for the samples and also for comparison a curve of the chemical shift for simple addition of the contribution from different components in pure form. For

the latter the signal composition was calculated as a weighted average of the number of protons from water and surfactants. The signal positions were measured as the shift from the methylene frequency in the pure surfactant and in a dilute solution of the surfactant in water. The two curves coincide at 30% showing that above this concentration the system behaved as a mixture of the two protic solvents without specific interactions.

The results from three independent experimental methods hence agree showing gradual association to take place with increased water content, with the water aggregates reaching sufficient size closely to approach the properties of liquid water at 30% per weight. It is essential to understand the value of 30% to be related to a point where the water aggregates reached a size to give properties similar to those of pure water. Figures 3, 5, 7, and 8 reflect different properties of the aggregates. Figure 3 describes the properties of water alone showing its partial molal density to approach that of pure water steeply to about 30%, then slowly. Figure 8 reflects a similar relationship. Figure 5, on the other hand, describes the properties of the surfactant showing the gradual water penetration along the surfactant layer of the aggregates. This penetration increased with increased radius leaving a slope with the chemical shift also at water contents in excess of 30%.

The NMR spectra gave further information about the molecular interactions accompanying aggregation. These will be discussed after the interpretation of the spectral features has been discussed in the following sections.

The downfield shift experienced by the oxyethylene proton resonances upon addition of water may have its origin among several factors. Benzene, water, and the ether linkages all give rise to highly anisotropic shielding effects. Hence, a change from a benzene environment or even a chain conformational change can give rise to chemical shift changes. Also, coordination at oxygen is expected to give rise to deshielding. Alternatively, one might adopt a simplified approach in which the downfield shifts experienced by the oxyethylene proton resonances upon addition of water are explained in terms of the so-called polar effect.^{28,29} A non-hydrogen bonded proton experiences a downfield shift on transfer to a more polar environment, provided bulk susceptibility effects and changes in the diamagnetic anisotropy of the solvent may be ignored.

The fact that the magnitude of the downfield shift (Figure 5 and Table I) is dependent upon the proximity to the hydroxyl-bearing end of the molecule might be attributed to a difference in the degrees of contact with water along the oxyethylene chain, the influence of water being successively greater on going from the alkyl chain to the terminal hydroxyl group. However, the shapes of the curves in Figure 5 suggest that an alternate explanation should be sought. The curves appear to be essentially the same shape (within experimental error), only the asymptotic values are different. This suggests that binding constants for water along the oxyethylene chain are all of similar magnitude. Hence, it is probably correct to view the water molecules as undergoing rapid exchange along the chain (and with "bulk" water), with no preference for binding site. The fact that the asymptotic values in Figure 5 differ with chain position may then be a result of different average conformations at the various positions.

A postulate such as this appears to be required to explain the fact that single resonances are observed for each oxyethylene group. Since binding with water occurs at the ether linkage, one might expect the protons within a given oxyethylene group to constitute an A_2B_2 case, giving rise to a complex multiplet. The slightly broadened singlet that

is observed appears to be the result of very small splittings (second-order effects) due to almost zero chemical shift difference between A and B nuclei. We anticipate spin coupling constants $J \approx 5-7$ Hz and thus the chemical shift $\nu_0\delta \leq 1-2$ Hz is required for the observed singlets. The small chemical shift may be attributed to the fact that chain conformation is a dynamic process and the average appears to be dependent on water content, as discussed above.

Since the rate of the downfield shifting is greatest at low concentrations of water and the separation between the individual peaks remains constant above 20% water, a conclusion that the oxyethylene chain becomes saturated with water is reasonable. This suggests that further addition of water results in water entering a new environment, presumably a "core" surrounded by the oxyethylene portions of the surfactant molecule.

With the present state of knowledge of C-13 chemical shifts and especially medium effects^{30,31} an interpretation of the shift changes (Figure 7) must only be tentative. Only very recently have C-13 NMR studies of micelle-forming compounds and micellization been conducted. Some studies have been done on ionic surfactants³²⁻³⁵ in which case the shifts have been interpreted as due to conformational changes in the alkyl chains, others have performed on nonionic surfactants in aqueous systems,²⁰⁻²² in which case the authors have refrained from giving interpretations of the shift changes encountered.

It is known³⁶ that increasing the fraction of gauche conformers in a long carbon chain causes an upfield shift. This is a steric effect due to interactions between a carbon and its γ carbon neighbor, in the case of alkyl chains resulting from steric crowding of hydrogens.³⁴

Hence, it is difficult to separate possible conformational effects from medium effects on the C-13 shift changes encountered in the present investigation. The shift changes are upfield which qualitatively agrees with the results of Dennis and Rieiro,²⁰ who reported upfield shifts for octaoxyethylene dodecyl ether and different ethylene glycols on transfer from $CDCl_3$ to D_2O .

Nevertheless, it appears obvious that the C-13 shift changes upon addition of water do indicate an initially rapid change in environment and/or conformation for the oxyethylene carbons. This change is greatest for the penultimate methylene and almost as large for the terminal group, whereas the main resonance originating from the three or four other groups experience this change to a lesser extent. Moreover, the asymptotic values appear to be reached by $\approx 20\%$ water.

This value is lower than the one estimated from other methods (Figures 3, 5, 7, and 8), a difference that is reasonable taking the basis for the signal position into account. The signal position of the C-13 spectra is determined partly by the conformation of the molecule. It appears reasonable to assume the conformational changes caused by the micellization to be obtained during the initial association; the growth of the micelles should then have little influence.

Combining the above results we may present the following general picture of the change in molecular association upon addition of water. Initially, the surfactant/benzene solution is a more or less disordered liquid; the surfactant molecules are hydrogen bonded to each other.¹¹ At this concentration, 25%, the effect of benzene upon the oxyethylene groups is still very slight.¹¹ Small amounts of water are distributed along the oxyethylene chains hydrogen bonded to the ether oxygens, possibly with a slight preference for the terminal oxyethylene(s). Larger

amounts of water begin to induce aggregation by bonding from surfactant molecule to another with hydrogen bonds. This process starts at 10% water (light-scattering results) and proceeds gradually with addition of further water until the surfactant molecules are associated into large aggregates, inverse micelle. At 20% water this process has led to a saturation of the oxyethylene chains by water, and additional water starts to enter a water-rich core.

Acknowledgment. This research was funded by the National Science Foundation, Grant No. DMR76-23569, and the Department of Energy, Grant No. ET 78 G 01 3428.

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Thioketyls. 7. Anisotropic ESR Parameters and Line Width Variations in the Thio- and Selenoketyl Series¹

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The spin density distribution in thioketyl radical anions has been determined from the anisotropic ESR parameters of frozen solutions. Obviously, aliphatic thioketyls are alkyl rather than thiy radical; the ratio of π spin populations ρ^π at the thiocarbonyl carbon and sulfur atoms is ca. 3:1. Spin delocalization into adjacent aryl groups occurs mainly at the expense of the carbon spin population ρ_C^π . The π spin density distribution of selenoketyl radical anions is analogous to that in thioketyls. The s spin population on the Se atom is, however, extremely small (0.0003). This is the reason for the absence of ⁷⁷Se satellites in solution ESR spectra of even ⁷⁷Se-enriched selenoketyls. The anisotropic Zeeman interaction observed in selenoketyls can be explained by d orbital participation in the ground state. Evaluation of line width variations of the main and satellite ESR lines of thioketyls yields anisotropic ³³S and ¹³C coupling constants, which agree well with the parameters obtained from frozen solutions. An effective hydrodynamic radius of 270 pm for the thioketyl molecule 1⁻ can be calculated from these results. The width of the central ESR line of aliphatic thioketyls in dimethylformamide at room temperature is mainly due to spin rotation, whereas modulation of the anisotropic Zeeman interaction predominates below 240 K.

Introduction

In a recent publication² we have shown that the radical anions of aliphatic thioketones ("thioketyls") are quite persistent species. From their ESR spectra some conclusions concerning the spin density distribution in these molecules could be drawn. However, the information remained incomplete, as only the isotropic case, i.e., the solution spectra, was taken into consideration, whereas the study of single crystals and powders or glasses³ would yield

the g and hyperfine tensor \bar{g} and \bar{A} . We have therefore measured the ESR spectra of thio- and selenoketyls 1⁻-12⁻ in frozen solutions as well as the line width variations in liquid solutions, from which independent and additional data are available.

Experimental Section

The preparation of thioketones 1,⁴ 2a-c,⁵ 3a,⁶ 3b,⁷ 4a,⁶ 4b,⁷ 5-7,² selenoketones 8,⁸ 9,² dithio- β -lactones 10,⁶ 11,⁷