Solubilization Equilibria of Water in Nonaqueous Solutions of Block Ionomer Reverse Micelles: An NMR Study

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ABSTRACT: Water can be solubilized into the ionic cores of reverse micelles formed by block ionomers in nonpolar solvents. The distribution coefficients of water in the reverse micellar solutions of polystyrene (440 units)-*b*-poly(sodium methacrylate) (40 units) were determined from ^{1}H NMR chemical shift measurements. For different solvents, the partition of water in favor of the reverse micelles occurs in the following order: cyclohexane > toluene ~ benzene > chloroform ≫ THF ~ DMF. From the distribution coefficients, the free energies of transfer of water from the solvent phase to the reverse micelles can be calculated. These free energies of transfer correlate linearly with the free energies of transfer of water from the solvent phase to the water phase, as calculated from the solubility data of water in the solvents. From this linear relationship, the distribution of water can be estimated for reverse micellar systems in other solvents once the solubilities of water in the solvents are known.

Introduction

The ionic domains of ionomers in bulk have received considerable attention in the last 2 decades since the presence of ionic groups in the polymer has a profound effect on its properties.[1] In studies of ionomer membranes, the understanding of the hydration microstructures of the ionic core becomes essential.[2] Some recent theoretical developments on this issue have been reviewed by Mauritz.[3] NMR spectroscopy has played a key role in understanding the hydration process in ionomer membranes.[4,5]

When an ionomer is dissolved in a solution of low-polarity solvent, the ionic groups associate, resulting in an increase in viscosity with increasing ionomer concentration.[6] For block ionomers, reverse micelles are formed in low-polarity solvents, with the ionic groups located in the interior.[7,8] Although the phenomenon of micelle formation for block copolymers dissolved in a good solvent selective for one of the blocks has been well documented,[9] the studies on block ionomer reverse micelles are limited. Reverse micelles based on polystyrene-*b*-poly(sodium methacrylate) diblock ionomers in nonaqueous solvents have recently been characterized in great detail in this laboratory by means of size-exclusion chromatography, dynamic light scattering, and other techniques.[8,10]

Reverse micelles formed by surfactant molecules in organic solvents have been the subject of intensive investigation for many years.[11,12] The most prominent feature of a reverse micellar solution lies in its ability to solubilize water in the form of a water pool inside the micelle. Thus, reverse micelles can serve as hosts for proteins and small hydrophilic molecules, and many reactions can be carried out in these "microreactors" with adjustable sizes.[13–15] It has been established that in the absence of water there is no well-defined critical micelle concentration and the aggregates formed are very small and polydisperse.[16] For the polystyrene–poly(ethylene oxide) diblock copolymer, it has also been found that the aggregate structure in cyclopentane is very sensitive to a trace amount of water.[17] The addition of water breaks up the large aggregates and yields a mixture of monodisperse spherical micelles and single chains.[17]

We have initiated a series of investigations on the reverse micelles formed by block ionomers in nonpolar solvents in the presence of water, by means of multinuclear NMR spectroscopy and small-angle X-ray scattering. In this paper we are dealing with the most fundamental aspect, the distribution equilibrium of water between the ionic cores and the nonpolar solvent, which is of great importance in block ionomer systems with low water contents.

The investigations of distribution equilibria of the solubilized water between the reverse micelles and nonpolar media were reported previously by Senō et al.[18–20] for the dodecylammonium propionate/hexane and hexadecyltrimethylammonium bromide/chloroform systems. In the near-infrared region two bands were observed for these systems, corresponding to the free water in a nonpolar media and the bound water in the reverse micelles. The distribution coefficients were obtained from the fourth-derivative spectra in the near-infrared region. However, for reverse micelles formed from anionic and zwitterionic surfactants, these two bands overlap almost completely;[21] hence, this method is not applicable to reverse micelles formed by these surfactants.

We propose here a simple NMR method to determine the distribution coefficient of water between the nonpolar solvent and the cores of the block ionomer reverse micelles, based on the proton chemical shift difference. The nonpolar solvents used in this study include chloroform, toluene, benzene, and cyclohexane.

Theory

In a reverse micellar solution, if the added water is distributed between the micelles and the solvent and if the exchange rate of the water between these two pseudophases is fast on the NMR chemical shift time scale, the observed chemical shift is a weighted average of the water chemical shifts in the reverse micelles and in the solvent. This is summarized in eq 1 where p is the fraction

$$\delta_{\text{obs}} = p\delta_{\text{mic}} + (1 - p)\delta_{\text{solv}} \qquad (1)$$

of the water in the reverse micelles and δ_{mic} and δ_{solv} are the chemical shifts of water in the reverse micelles and in the solvent, respectively. The difference between δ_{obs} and δ_{solv} can be as large as 4 ppm; δ_{solv} can be easily determined in a solution in the absence of the reverse micelles.

According to the micellar solubilization model proposed by Kwan, Atik, and Singer[22] and by Yekta, Aikawa, and

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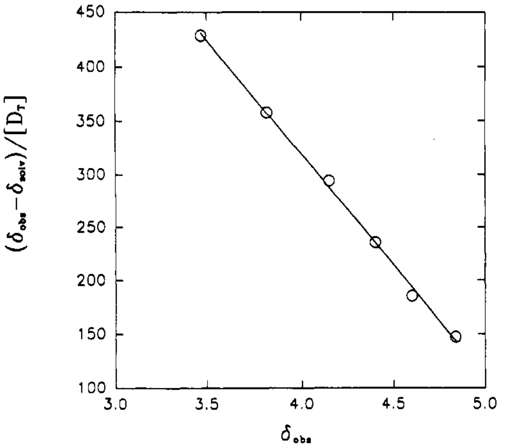

Figure 1. Plot of $(\delta_{obs} - \delta_{solv})/[D_T]$ vs δ_{obs} for water in the toluene solution of polystyrene (440 units)-*b*-poly(sodium methacrylate) (40 units) reverse micelles at 25 ± 1 °C.

Turro,[23] the equilibrium constant of the solute is given by[24]

$$K = [S_{mic}]/([S_{solv}][D_T]) \qquad (2)$$

where $[S_{mic}]$ and $[S_{solv}]$ are the concentrations of solute in the micelles and in the solvent, respectively, and $[D_T]$ is the concentration of the surfactant in solution; in this study $[D_T]$ denotes the concentration of the ionic block on a repeat unit basis (moles of repeat unit per kilogram of solvent). This model has been successfully applied to reverse micellar systems by Magid et al.[24] and recently by D'Aprano et al.[25]

According to eq 2, the fraction of solute in the micelle, p, is related to K since $[S_{mic}]/[S_{solv}] = p/(1 - p)$

$$p = K[D_T]/(1 + K[D_T]) \qquad (3)$$

Substituting eq 3 into eq 1 and rearranging, we have

$$(\delta_{obs} - \delta_{solv})/[D_T] = -K(\delta_{obs} - \delta_{mic}) \qquad (4)$$

The distribution coefficient K can be obtained from the plot of $(\delta_{obs} - \delta_{solv})/[D_T]$ vs δ_{obs}. The values of δ_{obs} are measured at different $[D_T]$ while the concentration ratios of the total water to ionic groups are kept constant. A typical plot is given in Figure 1 for water in the reverse micelles formed by polystyrene-*b*-poly(sodium methacrylate) in toluene.

The following two conditions must be satisfied when this method is applied: (1) at each step, the rate constant for the solute associating with the micelles is the same; i.e., the K value is constant, which is the basic assumption of the solubilization model;[22] and (2) the chemical shift of the water in the reverse micelles is a constant under the experimental condition. We have measured the proton chemical shift of water in toluene at different water to ionic group ratios by fixing the block ionomer concentration and increasing the water concentration. It was observed that when the total water to ionic group ratio increases from 2 water molecules per ionic group to 7 water molecules per ionic group, the proton chemical shift increases by only 0.2 ppm. This value is similar to those obtained in water–AOT–oil reverse micellar systems.[26] It is reasonable to assume that if the ratio of the total water to ionic groups is kept constant, the values of K and δ_{mic} do not vary significantly (vide infra). On the other hand, the linear plot (e.g., Figure 1) itself is a good indication that these conditions are satisfied.

In a reverse micellar solution, single surfactant molecules or single-chain polymers may be present in the solvent phase at a concentration equal to the critical micelle concentration. The chemical shift of water in the solvent phase, δ_{solv}, may be affected by the presence of these single molecules and be shifted to a new value. In principle, δ_{solv} should be measured at a surfactant or polymer concentration equal to the critical micelle concentration. However, for the block ionomer used, the critical micelle concentration should be extremely low. It was found that a fraction of block ionomers (15%) is present in the solvent phase (THF) in the form of a single chain.[8] This fraction of block ionomers was identified as polystyrene with a very short ionic block or even homopolystyrene.[8] The effect of the presence of these single-chain polymers on δ_{solv} should be proportional to $[D_T]$. We can see from eq 4 that, as long as $\Delta\delta_{solv}/[D_T]$ is a constant, the actual value used for δ_{solv} has no effect on the determination of the distribution coefficient K.

Experimental Section

The polystyrene (440 units)-*b*-poly(sodium methacrylate) (40 units) diblock polymer was synthesized by sequential anionic polymerization of styrene monomer followed by *tert*-butyl methacrylate monomer, using *n*-butyllithium as an initiator. The polymerization process was carried out in tetrahydrofuran (THF) at −78 °C under a nitrogen atmosphere. Polystyryllithium chains were capped with diphenylethylene (DPE) before introducing the *tert*-butyl methacrylate monomer in order to avoid the formation of high molecular weight contaminants. The diblock polymer in acid form was obtained by acid-catalyzed hydrolysis of the *tert*-butyl methacrylate segments in toluene at 80 °C using *p*-toluenesulfonic acid as the catalyst.[27] A detailed description of the preparation and characterization of these polymers will be given elsewhere.[28]

The sodium salt of the diblock copolymer was prepared in a benzene/methanol (90/10, v/v) mixture by adding a stoichiometric amount of a methanolic solution of NaOH. The solvent was removed by freeze-drying, and the sample was vacuum-dried at 80 °C for several days. The reverse micellar solutions used in this study (0.0050–0.0300 g/g solvent) were prepared by dissolving the dried sample in the desired solvent. Small amounts of water (0.5–3.0 μL) were added using a microsyringe, and the solutions were shaken for 20 min.

Proton NMR spectra were recorded on a Varian XL-300 (B_0 = 7.05 T) spectrometer at 299.9 MHz or a Varian XL-200 spectrometer (B_0 = 4.70 T) at 200.1 MHz. Deuterated chloroform (99.8% D; Aldrich), benzene (99.6% D; MSD), toluene (99.6% D; MSD), cyclohexane (99.5% D; MSD), dimethylformamide (DMF, 99.5% D; Aldrich), and tetrahydrofuran (THF, 99.5% D; Aldrich) were used as solvents. All the measurements were performed at 25 ± 1 °C except for the cyclohexane solutions (40 ± 1 °C). The residual proton resonance of the solvent served as an internal reference. The reference for chloroform as solvent is 7.27 ppm, for benzene 7.16 ppm, for toluene 2.09 ppm, for cyclohexane 1.38 ppm, for THF 3.58 ppm, and for DMF 8.03 ppm.

Results and Discussion

The solubilization equilibria of water in reverse micelles of polystyrene (440 units)-*b*-poly(sodium methacrylate) (40 units) in various solvents were determined by use of eq 4. The plot of $(\delta_{obs} - \delta_{solv})/[D_T]$ vs δ_{obs} for toluene is given in Figure 1, and those for cyclohexane, benzene, and chloroform are given in Figure 2. From the slopes of these plots, it is obvious that the partition of water in favor of the reverse micellar phase occurs in the order cyclohexane > toluene ~ benzene > chloroform.

The distribution coefficients, as defined by eq 2, were obtained from the slopes of the plots in Figures 1 and 2 and are given in Table I. From the distribution coefficients, the free energies of transfer of water from the solvents to the micelles can be calculated from the equation

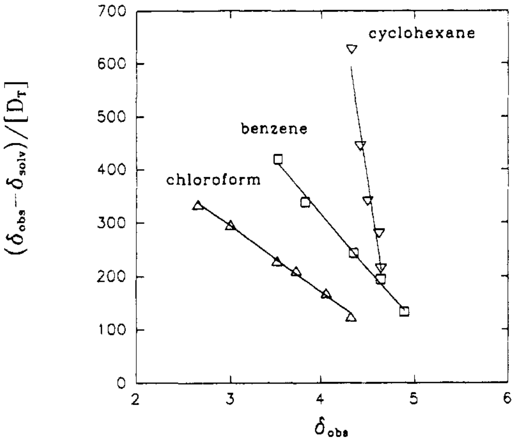

Figure 2. Plots of $(\delta_{obs} - \delta_{solv})/[D_T]$ vs δ_{obs} for water in the polystyrene-*b*-poly(sodium methacrylate) reverse micellar solutions of cyclohexane at 40 ± 1 °C (▽), benzene at 25 ± 1 °C (□), and chloroform at 25 ± 1 °C (△).

Table I
Distribution Coefficients and Free Energies of Transfer of Water in the Reverse Micellar Solutions and the Solubility Data of Water in the Relevant Solvents

solvent	$K \times 10^2$, m^{-1}	$\Delta G°$-(solv → mic), kJ/mol	$(1/X_{water}) \times 10^2$	$\Delta G°$-(solv → water), kJ/mol
cyclohexane	11.6 (40 °C)	-18.4	16.8 (38 °C)[a]	-19.3
toluene	2.1 (25 °C)	-13.2	3.4 (25 °C)[b]	-14.4
benzene	2.0 (25 °C)	-13.1	3.2 (25 °C)[b]	-14.3
chloroform	1.2 (25 °C)	-11.9	1.5 (25 °C)[a]	-12.4

[a] Calculated based on data in ref 30. [b] Calculated based on data in ref 31.

$\Delta G° = -RT \ln K$. Also shown in Table I are the solubilities of water in the corresponding solvents and the free energies of transfer of water from the solvents to the water phases, calculated from $\Delta G° = -RT \ln (1/X_{water})$, where X_{water} is the solubility of water, given as the mole fraction of water in the solvent phase. The free energies of transfer of water from the organic solvents to the reverse micelles correlate linearly with those of water from the corresponding organic solvent phase to the water phase (Figure 3). This linear relation clearly indicates that in these systems the binding of water to the ionic cores of the reverse micelles is very similar, and only the water–solvent interactions determine the distribution of water. Note that, in our studies of reverse micellar solutions, the concentrations of water in the solvent phases are well below the solubility limits of water in the solvents. According to Figure 3, predictions can be made on the solubilization of water in the reverse micellar solutions of many other solvents, once the solubilities of water in these solvents are known.

We also investigated the distribution of water in the DMF and THF solutions of reverse micelles. The chemical shift of water in DMF remains the same in both the absence and presence of the block ionomer, and the water signal is quite broad in the reverse micellar solution, indicating that only minimum amounts of water are located in the ionic cores. Similar phenomena are observed for the reverse micelles in THF. These results are very much in line with the above discussion on the relationship between solubility and water distribution in reverse micelles. DMF and THF are miscible with water as results of much more favorable interactions between these solvents and water molecules, compared to the other solvents mentioned earlier. It is more favorable, energetically, for water to stay in the DMF or THF phase instead of moving into the ionic cores in the block ionomer reverse micellar solutions, whereas in reverse micellar solutions of other nonpolar solvents such as cyclohexane and benzene, it is less favorable for water to remain in the solvent phase.

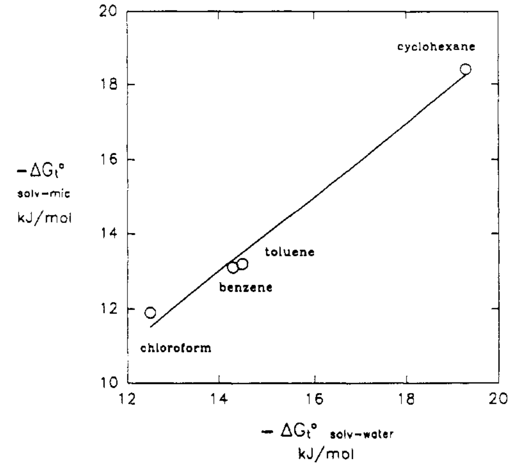

Figure 3. Relationship of the free energy of transfer of water from the solvent phase to the water phase and the free energy of transfer from the solvent phase to the reverse micelles.

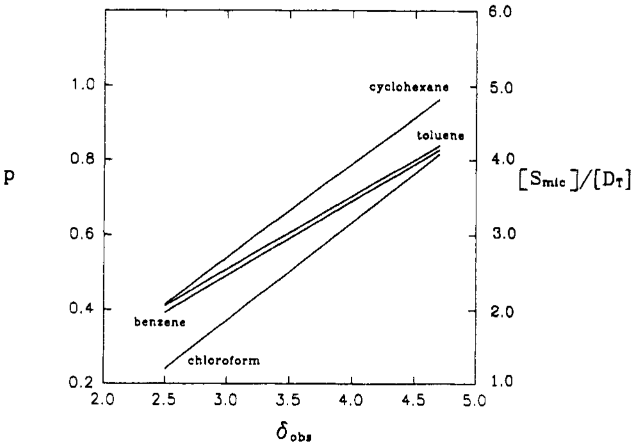

Figure 4. Fraction of water in the reverse micelles and the water to ionic group ratio in the ionic cores, as a function of observed chemical shift.

By use of eqs 1 and 2, the fraction of water in the reverse micelles, p, and the concentration ratio of water to the ionic group in the reverse micelles, $[S_{mic}]/[D_T]$, can be calculated as a function of observed chemical shift, δ_{obs}. The results for water in reverse micellar solutions of cyclohexane, toluene, benzene, and chloroform are shown in Figure 4. In these calculations, δ_{mic} values were obtained from the intercepts of $(\delta_{obs} - \delta_{mic})/[D_T]$ vs δ_{obs} plots in Figures 1 and 2. Also, $[S_{mic}]/[D_T] = pR$, where R is the concentration ratio of the total added water to the ionic groups; in Figure 4 the value of R was taken to be 5. For different R values, the $[S_{mic}]/[D_T]$ axis in Figure 4 shifts up or down proportionally. From Figure 4 we find that even when the total water to ionic group ratios, R, remain constant, the ratios of water to ionic groups in the ionic cores, $[S_{mic}]/[D_T]$, may vary. The decrease of $[S_{mic}]/[D_T]$ in toluene from 4 to 2, for instance, corresponds to a change in the observed chemical shift from 4.5 to 2.5 ppm. Similar situations were also found for the other solvents. The changes in the water to ionic group ratio in the ionic cores may lead to some variations in the values of δ_{mic}, which were assumed to be constants in the use of eq 4. However, as we pointed out earlier, the maximum change in δ_{mic} is about 0.2 ppm when the total water to ionic group ratio decreases from 7 to 2. These variations in δ_{mic} are quite small, less than 10% at maximum, compared to the changes in δ_{obs} and hence should not affect the measurements of distribution coefficients.

The amount of water in the reverse micellar solution can be obtained from the integration of the ^{1}H NMR spectrum. When the value of K is known for a particular system, the ratio of water to ionic groups in the cores of reverse micelles can be determined from a single chemical shift measurement. K values can be estimated based on the solubility data of water in the solvents (Figure 3).

The nature of water in the cores of the reverse micelles of block ionomers is also of particular interest. In an earlier publication, Matsuura and Eisenberg[29] reported that, for copolymers of ethyl acrylate and acrylic acid neutralized with sodium, when the water content increased to 15% (referred to sodium carboxylate content) or 1–2 water molecules per ionic group, the glass transition temperature decreased to less than 0 °C. In our experiments, the ionic core of the reverse micelle in the presence of water also appears to be liquidlike since only one proton NMR resonance was observed for the water molecules. This observation also indicates the fast exchange of water between the ionic core and the solvent phase on the NMR chemical shift time scale. The water molecules in the ionic cores of the reverse micelles may also be classified as those in the first and second hydration layers.[4,5,19,26,32] Similarly, the sodium ions in the cores can be divided into bound and unbound (fully hydrated) fractions.[4,5,32] In general, an equilibrium under a fast-exchange condition is assumed for the water or sodium ions between different states in the cores of reversible micelles.[4,5,19,26,32] The organization of the ionic core and the dynamics of solubilized water are currently under investigation using ^{1}H, ^{2}H, ^{17}O, and ^{23}Na NMR relaxation measurements.

Conclusions

The distribution coefficients of water between the ionic cores of the block ionomer reverse micelles and the solvents can be determined from proton NMR chemical shift measurements. This approach can, in principle, be applied to other reverse micellar systems formed by surfactants or block copolymers, e.g., polystyrene–poly(ethylene oxide). The following solvent order was obtained for the solubilization of water in the cores of the polystyrene-*b*-poly(sodium methacrylate) reverse micelles: cyclohexane $>$ toluene $\sim$ benzene $>$ chloroform $\gg$ THF $\sim$ DMF. The free energy of transfer of water from the solvent phase to the reverse micelles, as calculated from the distribution coefficients, correlates linearly with the free energy of transfer of water from the solvent phase to the water phase, as derived from the solubility data of water in the solvent, indicating that the difference in distribution of water in reverse micellar solutions of different solvents is related to the nature of interactions between the solvent and water molecules.

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