Solubilization in AOT–Water Reverse Micelles. Effect of the External Solvent

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The partition of 1-pyrenemethanol (PyM) between the external medium and AOT/water reverse micelles formed in several organic solvents has been measured and compared with its partition between bulk solvents. The organic solvents employed were n-heptane, cyclohexane, isooctane, dodecane, benzene, chlorobenzene, toluene, and tetrachloroethylene. The partition of PyM in AOT/water/nonpolar solvent reverse micelles is dominated by the free energy of the probe in the external solvent. To evaluate the stability of the probe in micelles dispersed in different solvents, the micellar data were referred to a common (water) solvent. A weakly positive correlation was obtained for the partition of the probe between the different micelles and water. Furthermore, the polarity sensed by PyM is higher in AOT/alkane/water than in AOT/organic solvent/water reverse micelles. These results can be explained in terms of two opposite driving forces whose relative importance is determined by the characteristics of the solute and the external solvent. One of them, solvation of the surfactant head by the polar group of PyM, will be disfavored by the surfactant head interaction with the external solvent, would be determined by the solvent/probe affinity, measured by the solvent/water partition constant.

Introduction

The incorporation of solutes to reverse micellar aggregates is a matter of current interest.1 The partition of different solutes between the micellar aggregates and the external solvent has been determined for a variety of solvents employing different experimental techniques.2–23 Most of these studies have been performed in sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micellar systems, although some data have been also obtained employing other surfactants. In principle, it can be expected that the distribution of a solute, measured at a given temperature and pressure, will be determined by the type of surfactant employed, the [internal solvent]/[surfactant] mole ratio (W), the properties of the internal polar solvent, and the characteristics of the external solvent. In most of the previously reported studies, the partitioning of a variety of solutes as a function of W has been determined in AOT–water–hydrocarbon systems. There are considerably fewer studies in which different surfactants13–15,24 and/or different internal polar solvents were considered.5,9–12 With regard to the effect of the external solvent upon the distribution of solutes, the studies are even more scarce.5,18–20 and to the best of our knowledge, there are not systematic studies comprising solvents of different characteristics. In the present work, we attempt to fill this gap by measuring the partitioning of a solute (1-pyrenemethanol) between AOT–water reverse micelles and the external solvent employing solvents of different characteristics. External solvents considered were n-heptane, cyclohexane, isooctane, dodecane, benzene, toluene, chlorobenzene, and tetrachloroethylene. To correctly interpret the results, the partitioning of the solute between bulk water–external solvents in the absence of micelles was also determined. Partitioning studies either in the presence or in the absence of micelles have been performed following fluorescence techniques. The results obtained emphasize the importance of the external solvent–AOT headgroup interaction and the localization of the solute in determining the extent of solute association to the micellar aggregates.

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Experimental Section

All solvents employed were spectroscopic grade or of the highest purity available. 1-Pyrenemethanol (PyM) (Molecular Probes) was employed as received. The probe was incorporated to the solutions from a concentrated stock solution in methanol or n-heptane. The concentration was estimated from the fluorescence intensity (excitation, 337 nm; emission, 376 nm). Low amounts of the probe were employed in order to ensure a linear fluorescence intensity vs concentration relationship. All measurements were carried out at room temperature (25 ± 1°C).

Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) (Sigma, > 99% purity) was dried by heating at 50 °C under vacuum and kept under vacuum over P2O5. Reverse micelles were prepared (W10) using ultrapure water obtained from a Labconco equipment model 90901-01.

Micelle/external solvent partition constants were evaluated from the changes in fluorescence intensity of a sample containing a fixed PyM concentration as a function of the AOT concentration. The surfactant concentration was changed, at the constant W = 10, from 0 to 0.2 M. The mixtures were strongly shaken until attaining constant readings.

Organic solvent/water partition constants were evaluated by shaking an aqueous solution of the probe (PyM) with increasing amounts of the organic solvent. The volume of the organic solvent was adjusted to extract between ca. 10 and 90% of the probe initially present in the aqueous solution. The amount of probe remaining in the aqueous phase was evaluated from the fluorescence intensity remaining in the aqueous layer. The partition of the probe was attained in the same cuvette employed for the fluorescence measurements or in closed tubes. After the centrifugation of these tubes to obtain a clear aqueous phase with a neat phase separation, an aliquot of the aqueous phase was taken, and the amount of remaining PyM was estimated from the fluorescence intensity. The tubes (or cuvettes) were manually shaken until constant fluorescence intensities were attained.

Fluorescence measurements were carried out with an 1681 Spex-Flurolog fluorescence spectrometer. Fluorescence lifetimes were determined using an Edinburgh Instruments O8900 time-correlated single-photon-counting fluorometer.

Results and Discussion

1-Pyrenemethanol Fluorescence Spectra in the Neat Solvents and in the Micellar Solutions. Addition of AOT/water to a PyM solution in a given external solvent produces a sustained increase in fluorescence intensity and a change in the I/IIII ratio, characteristic of the average polarity sensed by the probe. Typical fluorescence spectra obtained in neat n-heptane and in an AOT/water/n-heptane micellar solution are shown in Figure 1. A plot of the fluorescence intensity, measured at a fixed wavelength, as a function of the AOT concentration is given in Figure 2A. In Figure 2B is shown the dependence of the I/IIII ratio with the surfactant concentration. The behavior of both parameters is indicative of a progressive association of the probe to the micelles. The obtained plateaus would indicate that, at high AOT concentrations, the probe is almost quantitatively associated with the micellar pseudophase. The values of the I/IIII ratio obtained under these conditions are collected in Table 1. In this table are also given the values obtained in the neat solvents. It can be observed that in all the solvents considered the value increases in the presence of the micelles, as expected if the emission arises from a more polar environment. However, the data of Table 1 clearly show that there is

Figure 1. Fluorescence spectra of 1-pyrenemethanol: (A) spectra in AOT/n-heptane/water (AOT = 0.2 M; W = 10); (B) spectra in neat n-heptane. Excitation wavelength: 337 nm.

Figure 2. Changes in PyM fluorescence spectra elicited by AOT–water incorporation. Data obtained in n-heptane as solvent. (A) Change in fluorescence intensity measured at 376 nm. (B) I/IIII ratio.

not a direct relationship between the values obtained in the neat solvents and in the micellar solutions. In fact, there seems to be a poor inverse correlation between both sets of values (Figure 3). The reasons for this apparent anomaly will be discussed later.

Distribution of 1-Pyrenemethanol between the Micellar Pseudophase and the External Solvent.

The data given in Figure 2A can be employed to evaluate the partition constant of PyM between the micellar pseudophase and the corresponding external solvent. The partition constant ($K$) can be defined as

$$ K = \frac{n}{[PyM]_S} $$

where $n$ is the number of PyM molecules associated with the micelles per molecule of AOT and $[PyM]_S$ is the probe concentration remaining in the organic solvent. Taking into account that, at the surfactant concentrations employed most of the AOT is in the micellar pseudophase, the value of $n$ is given by

$$ n = \frac{[PyM]_M}{[AOT]} $$

where $[PyM]_M$ is the (analytical) concentration of PyM associated with the micelles and $[AOT]$ is the analytical concentration of micellized AOT. The local concentration of the probe in the organic pseudophase can be related to its analytical concentration in the surrounding solvent $[PyM]_SA$ by eq 3

$$ [PM]_S = f [PyM]_SA $$

where $f$ is a factor determined by the relative volumes of both pseudophases:

$$ f = \frac{(V_M + V_S)}{V_S} $$

Under the conditions employed, $f$ is a factor close to one that can be easily obtained if it is assumed additivity of the volumes.

The observed fluorescence ($F$) can be related to the fraction ($\alpha$) of solute associated with the micellar pseudophase by

$$ F = \alpha F^o_M + (1 - \alpha) F^o_S $$

where $F^o_M$ and $F^o_S$ are the fluorescence intensities if all the probes were present in the micellar or organic pseudophase, respectively. Taking into account that

$$ \alpha = \frac{[PyM]_M}{[PyM]} $$

it can be derived that

$$ F^o_S/(F - F^o_S) = F^o_S/((F^o_M - F^o_S) + F^o_S/(F^o_M - F^o_S)) 1/K (f [AOT])^{-1} $$

A plot of the left-hand side of eq 8 against the reciprocal of the $f [AOT]$ product allows an evaluation of $K$ as the quotient between the intercept and the slope. A typical plot is shown in Figure 4. The values of $K$ obtained by this procedure are collected in Table 2.

The partition constant evaluated from fluorescence measurements corresponds to the distribution of the solute in its ground state if it does not exchange between both pseudophases during its excited lifetime. In the other limiting situation, in which the solute equilibrates during its excited lifetime, the measured partition constant would

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Table 1. Values of the $I_{II}/I_{III}$ Ratio Obtained in the Organic Neat Solvents and in AOT/Water/External Solvent Micellar Solutions

<table>
<thead>
<tr>
<th>organic solvent</th>
<th>neat</th>
<th>AOT micelles$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>0.76</td>
<td>1.46</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>0.72</td>
<td>1.42</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.74</td>
<td>1.44</td>
</tr>
<tr>
<td>isooctane</td>
<td>0.73</td>
<td>1.47</td>
</tr>
<tr>
<td>toluene</td>
<td>1.18</td>
<td>1.31</td>
</tr>
<tr>
<td>benzene</td>
<td>1.25</td>
<td>1.34</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>1.18</td>
<td>1.28</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>0.96</td>
<td>1.23</td>
</tr>
</tbody>
</table>

$^a$ Values obtained at $W = 10$ and at high AOT concentrations.

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correspond to that of the electronically excited state. The assumption that the data given in Table 2 reflect the partition of the probe in the ground state is supported by results obtained in time-resolved fluorescence measurements employing isoctane as solvent. Because of the presence of oxygen, the lifetime of the probe in neat isoctane is relatively short (ca. 10 ns). In 0.2 M AOT (W = 10), conditions under which most of the probe is associated with the micelles, a monoeponential decay is observed, with a lifetime of 21.3 ns. This longer lifetime can be associated with a slower quenching by oxygen when the probe is associated with the micellar pseudophase. In solutions with lower AOT concentrations, where the probe partitions between both pseudophases, the data were well fitted to a biexponential decay with lifetimes very close to those obtained in bulk isoctane and in the concentrated AOT solution. Furthermore, the contribution of the long-lived component increases when the AOT concentration increases. All these results are compatible with a compartmentalization of the probe between the two phases. Furthermore, it can be argued that, for aromatic compounds such as PyM, the change in polarity associated with the excitation should be low, and hence the distribution of the probe will be rather similar in the ground and in the excited state.27

The data collected in Table 2 show that K values change almost 10-fold among the different solvents considered. Furthermore, they show that the incorporation of the probe is more efficient in the saturated hydrocarbons than in more polar-polarizable solvents. This difference can reflect both differences in the free energies of the probes in the external solvent and/or in the micelles formed in the different solvents. To establish which of these factors is the dominant, we have measured the partitioning of the probe between a common solvent (water) and the organic solvents employed in the present work in the absence of micelles. Solute partitioning between bulk phases can be quantified by a pseudo partition constant, $K_{\text{solvent/water}}$, defined by

$$K_{\text{solvent/water}} = \frac{[\text{PyM}]_S}{[\text{PyM}]_W}$$

where $[\text{PyM}]_S$ and $[\text{PyM}]_W$ are the analytical solute concentrations equilibrated between the two nearly insoluble solvents. This partition constant can be related to the fluorescence intensity remaining in the aqueous phase ($F_{\text{water}}$) when a volume $V_W$ of an aqueous solution of fluorescence $F$ is shaken with a volume $V_S$ of the corresponding organic solvent:

$$\left(\frac{F_{\text{water}}}{F_{\text{water}}} - 1\right) F_{\text{water}} = K_{\text{solvent/water}} V_S/V_W$$

A plot of the left-hand side of eq 10 against $V_S/V_W$ allows then the evaluation of the partition constant. A typical plot is shown in Figure 5. The values of the partition constants so obtained are included in Table 2. The data of this table show that the low values of $K$ measured in the polar solvents are due to the low free energy of the probe in these solvents. In fact, the partition constant is more than an order of magnitude higher in the aromatic solvents than in the saturated hydrocarbons.

To evaluate the thermodynamic stability of the probe in the micelles formed in the different solvents, we have calculated the distribution constant between a common solvent (water) and the micellar pseudophase formed in the different organic solvents. The (hypothetical) partition constant between water and the micelles in a given solvent, $K_{\text{M/water}}$, can be obtained from the product of K and $K_{\text{solvent/water}}$:

$$K_{\text{M/water}} = K K_{\text{solvent/water}}$$

Differences in $K_{\text{M/water}}$ reflect only the relative stability of the solute in the micelles formed in the different solvents. The values so obtained are collected in Table 2. A comparison of these data with $K$ values shows smaller differences among the tested solvents. However, noticeable differences remain among the different solvents. In particular, the data show that PyM solubilizes better in the micelles formed in the aromatic solvents than in those formed in the saturated hydrocarbons. In fact, it seems that the major factor relating the stability of the solute in the micelles is the quality of the external solvent/solute interaction. To test this proposal, $K_{\text{M/water}}$ values are plotted against the $K_{\text{solvent/water}}$ in Figure 6. This figure shows that, although there is a weak positive correlation, micelles formed in the more polar and polarizable solvents (such as chlorobenzene and tetrachloroethylene) are poorer solvents than could be expected from their solvent/solute affinities.

The characteristics of the micellar aggregates, and hence their capacity to incorporate solutes, can be extremely dependent on the external solvent. The most extensive comparative study has been performed for AOT/hydrocarbon/water and AOT/benzene/water micelles.28 In particular, the thermodynamics of micellization shows that

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the clustering of benzene molecules around the AOT headgroups appears to be more ordered than is the case for saturated alkanes.\textsuperscript{29} It turns out that, at the same value of $W$, the aggregation number of AOT is 5 times greater in \textit{n}-hexane than in benzene.\textsuperscript{30,31} Furthermore, while AOT reverse micelles in saturated hydrocarbons are able to solubilize large amounts of water, those formed in benzene solubilize only small amounts of water.\textsuperscript{32} Despite this, \textsuperscript{1}H NMR studies\textsuperscript{33} show that free water can be detected in AOT--benzene reverse micelles, even at low $W$ values. All these studies give evidence of a specific interaction between the AOT polar headgroups and the aromatic (more polarizable) solvent.

To interpret the effect of the external solvent upon the solubilization of a given solute in the micellar pseudophase, two extreme models can be envisaged:

(i) The solvent and the solute compete for surfactant-head solvation. This model would predict that $K_{\text{M/water}}$ should decrease when the affinity of the solvent toward the heads increases. In other words, more polar (or more polarizable) solvents should decrease the water/micelle partition constant. This is opposite to the relative values obtained for the aromatic and aliphatic hydrocarbons.\textsuperscript{29,31}

(ii) The solvent at (or near) the interface solvates the protuberant aromatic moiety of the surface-associated probe. This interaction would stabilize the solute associated with the micellar pseudophase. The fact that the lowest $K_{\text{M/water}}$ values are obtained when the micelles are formed in saturated hydrocarbons (the solvents with the lowest $K_{\text{solvent/water}}$ values) would support this description. This proposal can then explain the high and similar $K_{\text{M/water}}$ values obtained in toluene and benzene. However, this model cannot explain the lower value observed in chlorobenzene. We think that the whole of the data can be qualitatively described in terms of two driving forces whose relative importance is determined by the characteristics of the solute and the external solvent. One of them, solvation of the surfactant head by the polar group of PyM, will be disfavored by polar solvents. The second one, interaction of the aromatic part of the associated PyM molecules with the external solvent, would be determined by the solvent/probe affinity, measured by the $K_{\text{solvent/water}}$ partition constant. The interplay of these two effects can explain, at least qualitatively, all the data obtained in the present work.

The data of Table 1 regarding $I_{\text{II}}/I_{\text{II}}$ values measured in the bulk solvents and in the micellar solutions at high AOT concentrations support the above considerations. So, while higher $I_{\text{II}}/I_{\text{II}}$ values are obtained in bulk aromatic solvents, the opposite is observed in the presence of high AOT concentrations. In fact, the data of Table 1 show that the values obtained in the aromatic solvents are very close in the presence and absence of the micelles, indicating a minimum interaction with the surfactant polar heads. On the other hand, the values measured in the saturated hydrocarbons are considerably higher (ca. 1.44) than those measured in the micelles when these are generated in more polar (polarizable) solvents. This can be explained in terms of a stronger interaction with the surfactant polar heads when they are poorly solvated by solvents of very low polarity and/or polarizability. Correa et al.\textsuperscript{28} have interpreted on similar grounds data obtained regarding the microenvironments sensed by 1-methyl-8-oxyquinolinium betaine in AOT/hexane/water and AOT/benzene/water micelles.\textsuperscript{34}

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