Preferential Solvation Studied by the Fluorescence Spectrum of Pyrene in Water-Alcohol Binary Mixtures

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The local mole fraction of an alcohol such as methanol, ethanol, and 1-propanol was determined on the basis of the polarity variation sensed by pyrene in water-alcohol binary mixtures. The data indicate that alcohol molecules preferentially solvate pyrene in water; the degree of preferential solvation increases with an increase in the extent of the hydrophobic interaction between pyrene and alcohols.

The phenomenon of solvation is of paramount importance in solution chemistry. This involves the modification of physicochemical properties of a solute due to its interaction with the solvent molecules in the immediate environment. In the case of binary solvent mixtures, due to the difference in the specificities of interaction of solute with the component solvents, the composition of the solvents in the immediate vicinity of the solute may be different from that in the bulk. This phenomenon, commonly known as preferential solvation, has been found to be important for explaining spectroscopic, equilibrium, and kinetic data in mixed binary solvents.[1] Thus, preferential solvation in mixed binary solvents is currently a topic of experimental and theoretical interest.[2,3]

Water-alcohol mixtures are frequently used as solvents in studies of chemical equilibria and reactions as well as various biological studies. Especially, water-ethanol mixtures are one of the most interesting mixtures, because of existing in various kinds of alcoholic liquors and having a sterilizing power.

Fluorescence spectra are sensitive to the properties of a solution such as viscosity and polarity. Thus, various fluorescent materials have been used as sensitive probes to investigate the properties of solutions.[3] Pyrene is one of the most useful fluorescent probes and is widely used as a probe for environmental polarity. To our best knowledge, parameters characterizing preferential solvation around pyrene in the water-alcohol mixtures have not been reported so far.

In the present work we report studies of preferential solvation based on the variation in the vibronic-band-intensity ratio of pyrene monomer fluorescence in the water-alcohol mixtures.

Pyrene (GR grade of Wako) was passed through silica gel in cyclohexane solution and recovered as white crystals. Taking account of the solubility of pyrene in water (5.3×10^{-7} and 6×10^{-7} mol dm^{-3}),[4] the concentration of pyrene was fixed at 3×10^{-7} mol dm^{-3} in all the experiments to avoid the formation of pyrene microcrystals and extrinsic phenomena. Laboratory deionized water was twice distilled. Methanol (Dotite), ethanol (Wako), and 1-propanol (Aldrich) of the highest grade available and water were used to prepare the water-alcohol solvent mixtures in volume fraction. The corrected fluorescence spectra were obtained with aerated solutions at 25 ℃ by using a Hitachi 850 spectrofluorometer with 1 nm slit at an excitation wavelength of 318 nm.

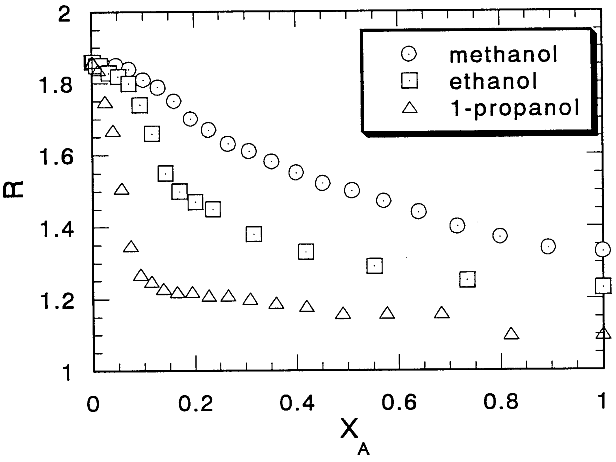

Figure 1. Variation of R of pyrene in water-alcohol mixtures with the alcohol mole fraction X_A. The alcohols investigated are indicated in the figure.

It is well known that the ratio (R) of the first-peak and third-peak intensities (I at 373 nm and III at 384 nm, respectively) in the pyrene monomer fluorescence increases drastically with increasing medium polarity.[5] The use of this ratio is expected to permit the determination of parameters characterizing preferential solvation since the water-alcohol binary mixtures present both hydrophilic and hydrophobic environments. In Figure 1, R values are plotted against the mole fraction of alcohol (X_A) in water; concave downward behavior is seen. However, the R values was not linearly dependent on the bulk properties, such as the Onsagar and Debye polarity functions,[3,6] of the water-alcohol mixtures. Thus, the downward curvatures for R in Figure 1 strongly suggest that there are specific interactions between pyrene and alcohols. Here, it should be noted that pyrene is much less soluble in water than in alcohols.

In order to interpret such behavior of R with X_A as the consequences of solvation processes, we have estimated the local mole fraction of alcohol ($X_A{}^L$) around pyrene using the following expression.[7]

$$R_{\mathrm{obsd}} = \frac{\mathrm{I}}{\mathrm{III}} = \frac{X_A{}^L \mathrm{I}_A + (1 - X_A{}^L)\mathrm{I}_W}{X_A{}^L \mathrm{III}_A + (1 - X_A{}^L)\mathrm{III}_W} \qquad (1)$$

Here, I_A and I_W, and III_A and III_W denote the values of I and III of pyrene in pure alcohol (A) and pure water (W), respectively. The measured band intensities (I_A, I_W, III_A, and III_W) were substituted into the corresponding numerator and denominator in Eq. 1. Values of $X_A{}^L$ were then computed from the measured R values (R_{obsd}) (Figure 1) for each binary solvent composition. Thus, the extent of preferential solvation, δ_{AP}, defined by $X_A{}^L - X_A$, was determined as a function of the bulk mole fraction of alcohol (X_A). The results are shown in Figure 2 for the three

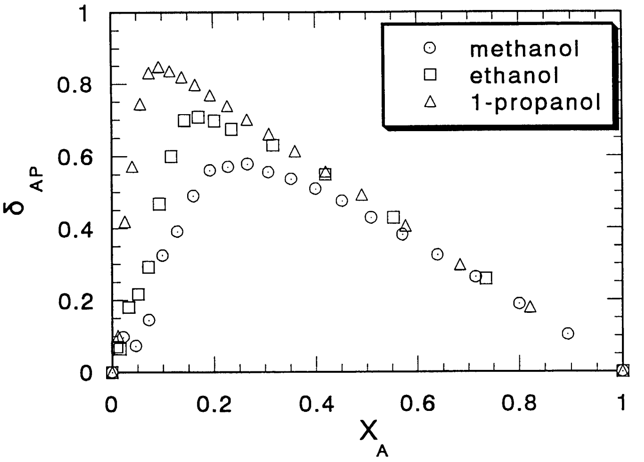

Figure 2. Plots of δ_{AP} vs. X_A for water-alcohol mixtures. The alcohols investigated are indicated in the figure.

solvent systems. A positive value of δ_{AP} indicates that pyrene is preferentially solvated by alcohol. We can see in Figure 2 that with an increase in the alcohol chain length, the δ_{AP} values increase, especially at lower X_A regions. This indicates that the degree of preferential solvation increases with an increase in the extent of the hydrophobic interaction between pyrene and the aliphatic moiety of the alcohol molecules. An another remarkable feature of Figure 2 is that after reaching the maximum value of δ_{AP}, the value of X_A^L rapidly approaches 1 in each solvent system. The present findings may be correlated to the existence of polymeric clusters of alcohol molecules in water as suggested in the literature.[8] Further detailed experiments, however, are required to clarify this point fully.

References and Notes

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