$E_T(30)$ Values of AOT Reverse Micelles Prepared in Supercritical Ethane

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The $E_T(30)$ values in the core region of water/AOT/SC ethane micelles were determined for the first time as functions of pressure and water content of micelles (W_0, $[H_2O]/[AOT]$) at 310 K. The $E_T(30)$ values increased with increasing W_0, but remained independent of pressure after system changed to a homogeneous micellar solution. The $E_T(30)$ values ranging from that observed in pure ethanol to 1, 3-propanediol were obtained, with increasing W_0 from 1 to 8.

The reverse micelles in supercritical fluids have a large variety of uses as extraction and reaction media because the physical properties such as diffusion coefficients, viscosity, and density of supercritical fluids can be widely varied by operating temperature and pressure.[1] Sodium bis (2-ethylhexyl) sulfosuccinate (AOT) is known to form reverse micelles in conventional nonpolar solvents [2] and in supercritical ethane (SC ethane) and propane [3-5] on the addition of water. Ikushima et al.[6] have investigated the conformational characteristics and hydration process of AOT reverse micelles in SC ethane. The qualitative polarity change within the core of AOT micelles was examined by measuring the peak shifts in the UV-vis spectra of polarity sensitive probes as functions of W_0 and pressure in SC ethane.[7,8] The polarity of the micellar core had a strong influence on the fading rate of crystal violet when AOT micelles prepared in SC ethane were used as a reaction medium.[9] The solvent polarity parameter, $E_T(30)$ values, of AOT reverse micelles have been determined in ordinary solvents such as hexane,[10] heptane,[11] and benzene[12] at atmospheric pressure by using various solvatochromic probes. However, no quantitative determination of the polarity within the core of supercritical fluid micelles has been carried out.

We first determine the $E_T(30)$ values of the aqueous core of AOT reverse micelles in SC ethane as functions of W_0 and pressure by using the charge-transfer bands of the probes solubilized in the aqueous core of reverse micelles. 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate commonly known as $E_T(30)$ reagent (Figure 1a) and 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI) (Figure 1b) were used as probes. The charge-transfer bands observed in the absorption spectra of these probes are very sensitive to the polarity of the local environment. An increase in the polarity of the medium stabilizes the dipolar ground state, leading to an increase in the value of transition energy of these bands.[13,14] The probe molecules are localized at the vicinity of water/AOT interface in the aqueous core of reverse micelles owing to electrostatic interaction between the polar head groups of AOT and probe molecules.[15,16] Therefore, the values of the transition energies of charge-transfer bands can be considered representing the polarity of the micellar core at the interface region. The $E_T(30)$ reagent is a large molecule, it can not be solubilized in the small micellar core of $W_0<4$, while EMCPI of smaller size can be used to determine the $E_T(30)$ values for micelles of $W_0<4$. $E_T(30)$ and E_T values correspond to the transition energies of charge-transfer bands observed in the spectrum of $E_T(30)$ reagent and EMCPI, respectively.

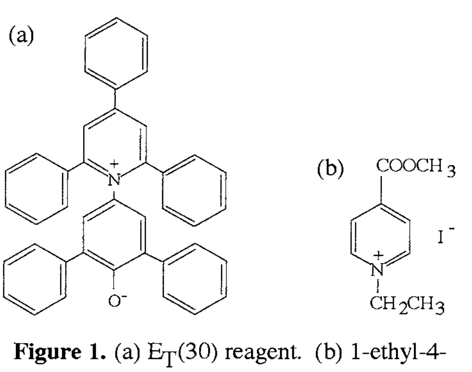

Figure 1. (a) $E_T(30)$ reagent. (b) 1-ethyl-4-methoxycarbonyl pyridinium iodide.

$E_T(30)$ values (kcal mol^{-1}) were calculated from the λ_{max} (nm) of the charge-transfer band of $E_T(30)$ reagent by using the following equation.

$$E_T(30) = 2.859\times10^4/\lambda_{max} \qquad (1)$$

Similarly, E_T values were determined from the λ_{max} of the charge-trasfer band of EMCPI with the above equation. There is a linear correlation between $E_T(30)$ and E_T values (kcal mol^{-1}) according to Eq. 2 (n=54 solvents; correlation coefficient r= 0.978).[14]

$$E_T = 1.337\times E_T(30) + 9.80 \qquad (2)$$

AOT reverse micelles containing probe molecule were prepared as follows. The stock solution of the probe in methanol was added to the high pressure cell maintained at a temperature of 333 K. A gentle stream of N_2 was passed through the cell to remove residual methanol. The cell was allowed to cool at an experimental temperature of 310 K. AOT (50.8 mg) and a measured volume of water were put in the cell. At last, ethane was pressurized inside the cell to a desired pressure for the formation of micelles. The solution was stirred for 30 min and equilibrated for 30 min before recording the spectrum.

Figure 2 shows the pressure dependence of the $E_T(30)$ values of AOT reverse micelles formed in SC ethane for W_0=2, 5, and 7 at 310 K. The $E_T(30)$ values initially increase with increasing pressure up to 31.1 and 32.3 MPa for W_0=5 and W_0=7, respectively. Further increase in pressure has no effect on the

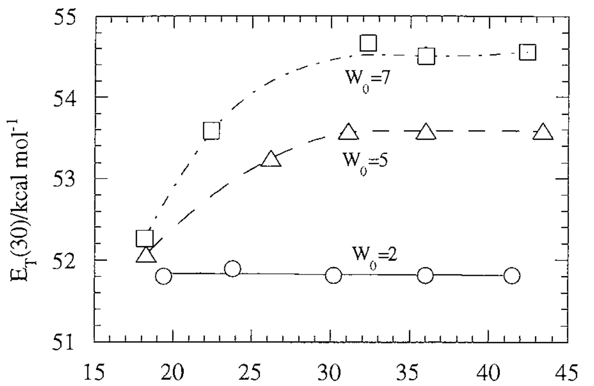

Figure 2. Pressure dependence of $E_T(30)$ values of water/AOT/SC ethane micelles at 310 K.

$E_T(30)$ values. The initial increase in the $E_T(30)$ values is attributed to the existence of 2-phases in the system where AOT is not completely solubilized to form micelles at low pressures. As the pressure increases up to 31.1 MPa for W_0=5 and 32.3 MPa for W_0=7, the system changes to a homogeneous micellar solution in which no influence of increasing pressure on the $E_T(30)$ values was observed. For W_0=2, the $E_T(30)$ values remain independent of pressure as the system changes to a single micelles solution at pressure as lower as 19.4 MPa. The transition from heterogeneous to homogeneous phase was also confirmed visually through the windows of high pressure cell. The heterogeneous phase observed at lower pressures was turbid and it changed to a trasparent single micelles solution at higher pressures of ethane. The authors [6,17] have also confirmed visually and by F T-IR spectroscopy the existence of 2-phases at intermediate pressures. The pressure dependence of the $E_T(30)$ values shows that in a homogeneous micellar solution of any W_0 value, an increase in the pressure (or density) of SC ethane phase does not change the polarity at the interface region in the aqueous core.

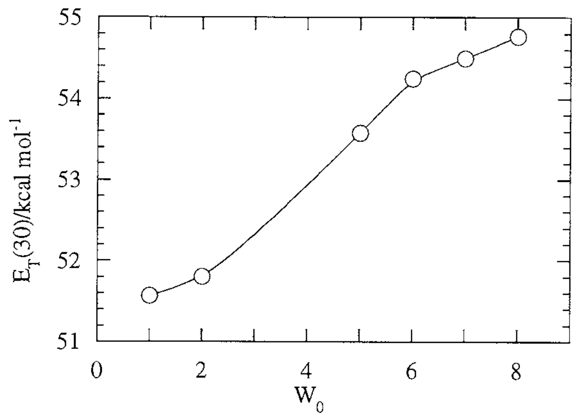

Figure 3. $E_T(30)$ values of water/AOT/SC ethane micelles as a function of W_0 at 36.0 MPa and 310 K.

Figure 3 shows the effect of W_0 on $E_T(30)$ values of water/AOT/SC ethane reverse micelles in a homogeneous solution at 36.0 MPa and 310 K. The $E_T(30)$ values increase with increasing W_0. These results represent that the polarity of the aqueous core at the interface region is adjustable by controlling W_0. The $E_T(30)$ value varies from 51.57 to 54.77 kcal mol^{-1} by increasing W_0 from 1 to 8, approximately corresponding to that of pure ethanol and to that of 1,3-propanediol. In conclusion, the polarity of the aqueous core of AOT reverse micelles in SC ethane can be tuned by controlling W_0. Therefore, these micellar solutions may have important applications in separation and chemical reactions.

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