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SHORT COMMUNICATION

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Micropolarity of sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles prepared in supercritical ethane and near-critical propane

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Abstract The micropolarity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles prepared in supercritical ethane and near-critical propane has been determined in terms of a solvent polarity parameter, $E_T(30)$ values, by using absorption probes, 1-ethyl-4-methoxycarbonyl pyridinium iodide and 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate as a functions of pressure and the molar ratio of water to AOT, W_0, at a constant temperature of 310 K. The micropolarity comparable to that of ethanol was observed for reverse micelles containing water of $W_0 = 2$. The micropolarity increased with the water content and became independent of pressure after the system changed to a one-phase reverse micelle solution. For a given W_0 value, no difference in the micropolarity was noticed in the micelles prepared in ethane and propane. Phase behaviour investigations have revealed that complete dissolution of 50 mM AOT occurred at 20 MPa in supercritical ethane, while a much lower pressure of 1 MPa was required in near-critical propane. The amount of water solubilized in reverse micelles formed in supercritical ethane was relatively low, reaching a W_0 value of 7 at 36 MPa. In contrast, the amount of water solubilized in near-critical propane reverse micelles was $W_0 = 11$ at a much lower pressure of 6 MPa. A higher pressure was required to solubilize larger amount of water in reverse micelles prepared in both ethane and propane.

Key words Sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles – Supercritical ethane – Near-critical propane – $E_T(30)$ values – 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate

Introduction

Reverse micelles in supercritical fluids (SCFs) have a large variety of uses as extraction and reaction media because properties such as diffusion coefficients [1], viscosity [2], and density [3] of SCFs can be widely varied by manipulation of temperature or pressure. Ikushima et al. [4] have observed that the alkaline fading rate of crystal violet was accelerated by several orders of magnitude when water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/ethane reverse micelles were used as a reaction medium under supercritical (SC) conditions. In 1987 Gale et al. [5] first observed the formation of reverse micelles in SC ethane and propane using AOT. Since then, several researchers have carried out physicochemical investigations of these aggregates [2, 6–8]. Beckman et al. [9] and Zemanian et al. [10] have reviewed the properties of reverse micelles and microemulsions in near-critical fluids (NCFs) and in SCFs. Solvatochromic probe studies have been carried out to examine qualitatively the environment of the core of micelles in SCFs [11, 12]; however, no quantitative determination of the polarity within the core of SCF micelles has been carried out. The polarity of the medium has been known to have a strong influence on the reaction rate, extraction, and separation processes [13–15]. A linear dependence of rate constants for the Diels–Alder reaction of isoprene and methyl acrylate on the polarity of SC carbon dioxide was observed [13]. A similar relationship was observed when Menschutkin reactions of pyridine with methyl iodide in acetone [14] and in methanol [15] were carried out under high pressure.

Here, we determine for the first time the micropolarity of the aqueous core of AOT reverse micelles in SC ethane and in NC propane in terms of $E_T(30)$ values as a functions of pressure and water content, W_0, of micelles. 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI) (Fig. 1a) and $E_T(30)$ reagent[1] (Fig. 1b) have been used as probes for micropolarity determination. We have observed that the $E_T(30)$ reagent was not soluble in the micelles of small core of $W_0 < 4$ because of its large size; therefore, for micelles of $W_0 < 4$ the smaller-sized probe EMCPI was used. Due to low solubility of the $E_T(30)$ reagent in water and alkanes, its preferential position is at water/surfactant interface [17, 18]. EMCPI is also localized in the vicinity of interface owing to its hydrophilic nature. There exist electrostatic interactions between the polar head groups of AOT and the probe molecules. The $E_T(30)$ value is the transition energy of the charge-transfer (CT) band of the $E_T(30)$ reagent, while the E_T value is the transition energy of the CT band of EMCPI. The transition energy of the CT band observed in the $E_T(30)$ reagent and EMCPI changes with the polarity of the solvent [16, 19]. Increasing the polarity of the solvent stabilizes the dipolar ground state of these probe molecules, leading to an increase in the transition energy.

Experimental

Materials

Ethane (>99.7%) and propane (>99%) obtained from Nippon Sanso Co. and Sumitomo Seika Co., respectively, were used as received. Fluka AOT was purified according to the method of Polity et al. [20] and stored over anhydrous $CaSO_4$. It was assumed that after purification 1 mol AOT had 1 mol water of hydration. Reichardt's dye and 1-ethyl-4-methoxy carbonyl pyridinium iodide were obtained from Sigma and Tokyo Chemical Industry Co., respectively. Deionized and distilled water was used.

Apparatus

The high-pressure UV cell consisted of a stainless-steel block with two sapphire windows. It had a volume of 2.2 cm^3 and could withstand a pressure of 45 MPa. The mixture in the cell was stirred by a Teflon-coated bar driven by an outside magnet. The temperature was controlled with a temperature controller attached to the cell. A schematic diagram of the high-pressure cell and apparatus has been given in a previous publication [11].

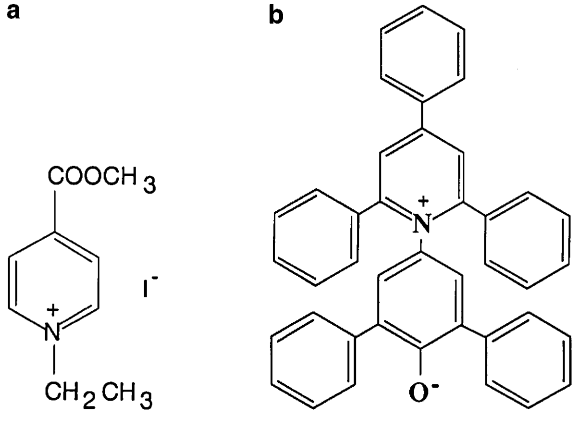

Fig. 1a Molecular structure of 1-ethyl-4-methoxycarbonyl pyridinium iodide (EMCPI) and **b** molecular structure of the $E_T(30)$ reagent

Procedure

Stock solutions of EMCPI and $E_T(30)$ reagent were prepared daily in methanol. A stock solution of the probe was poured into the high-pressure cell maintained at a temperature of 60 °C. A gentle stream of N_2 was passed through the cell to remove residual methanol. AOT (50.8 mg) and a measured volume of water were put inside the cell. The reverse micelles were obtained by pressurizing ethane or propane inside the cell to the desired pressures. The solution was stirred for 30 min and equilibrated for 30 min before recording the spectrum. All measurements were carried out at a fixed temperature of 310 K. W_0 represents the molar ratio of water to AOT. We considered that the amount of water added was solubilized inside the core of the micelles because of the negligibly small solvating power of these alkanes for water [21, 22]. Absorption spectra were recorded with a Jasco V-570 spectrophotometer. E_T values were calculated from the λ_{max}(nm) of the CT band of EMCPI by using the following equation.

$$E_T = 2.859 \times 10^4/\lambda_{max} \quad (\text{kcal mol}^{-1}) \qquad (1)$$

Similarly, $E_T(30)$ values were determined from the λ_{max} of the CT band of the $E_T(30)$ reagent using Eq. (1).

The phase behaviour investigation was carried by recording the UV-vis spectrum of AOT and looking through the windows of the high-pressure UV cell. The heterogeneous phase observed at lower pressures was a turbid phase and at higher pressures the system changed to a single micellar phase which was a transparent solution.

Results and discussion

Phase behaviour investigation

The effect of pressure on the phase behaviour of water/AOT/NC propane system was examined by comparing the absorption spectra of AOT at various pressures. The band observed in the 200–245 nm region is characteristic of acyloxy group of the polar head of AOT molecule and

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[1] 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate also known as Reichardt's dye [16]

this band was sensitive to pressure and W_0. The absorption spectra of 50 mM AOT recorded at 1, 3, and 6–38 MPa for $W_0 = 11$ at 310 K is shown in Fig. 2. The spectrum showed a pressure dependence at low pressures. Red shift in the absorption maxima along with increase in absorbance were noticed as the pressure increased. The effect of pressure on λ_{max} and the absorbance of AOT for $W_0 = 1$ and $W_0 = 11$ at 310 K is shown in Fig. 3. For $W_0 = 11$, no change in λ_{max} or the absorbance was observed on increasing the pressure above 6 MPa. The pressure dependence of the spectrum at low pressures has been attributed to the existence of a two-phase region. Above 6 MPa the system changed to a single reverse micellar phase where no influence of pressure on the spectrum was noticed. The spectral changes were due to an increase in the number of aggregated AOT molecules as a result of micelle formation as the pressure was increased. The two-phase region has been identified as being composed of a transparent fluid phase containing dissolved AOT and a viscous turbid phase of melted AOT. The existence of three phases at lower pressures and two phases at intermediate pressures in which AOT is not completely solubilized in micellar form has also been confirmed by other authors [6, 23]. It was further proved that 50 mM AOT containing water of $W_0 = 1$ was completely solubilized in propane at 1 MPa and 310 K (Fig. 3). In a previous paper [11], we reported the phase behaviour of the water/AOT/SC ethane system as a functions of pressure and W_0 at 310 K. In brief, 50 mM AOT with $W_0 = 1$ and $W_0 = 7$ was solubilized to form a single reverse micellar phase at 20 MPa and 36 MPa, respectively. The pressure dependence of water solubilization in AOT micelles in SC ethane and NC propane is shown in Fig. 4. The region under the plot consists of an optically transparent homogeneous micellar solution. A larger amount of water could be solubilized in micelles prepared in propane than in ethane. The water/AOT/NC propane system containing water of $W_0 = 12$ was transformed to a homogeneous micellar solution at a pressure of 9.3 MPa; however, by increasing the pressure above 9.3 MPa, a larger amount of water can be solubilized. Larger uptake of water in propane has been attributed to the decrease in the interfacial curvature as a result of decreased penetration of the surfactant tails by propane compared to ethane. The phase behaviour investigation revealed that at a constant temperature of 310 K the state of the water/AOT/SC ethane and water/AOT/NC propane systems was dependent on the pressure and W_0, and the amount of water solubilized in both systems increased with pressure.

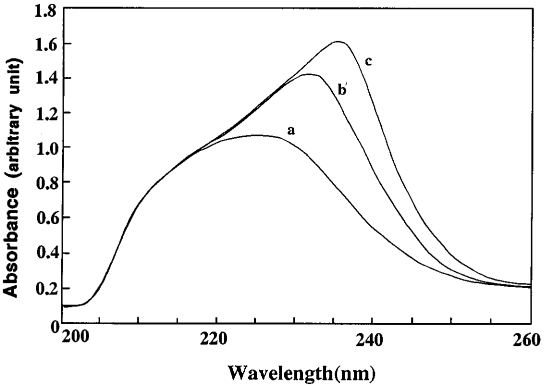

Fig. 2 Absorption spectra of 50 mM *AOT* in water/AOT/NC propane reverse micelles for $W_0 = 11$ at pressures of 1 (a), 3 (b), and 6–38 MPa (c) at 310 K

E_T values of the micellar core

The micropolarity of the aqueous core of AOT micelles prepared in SC ethane and in NC propane was

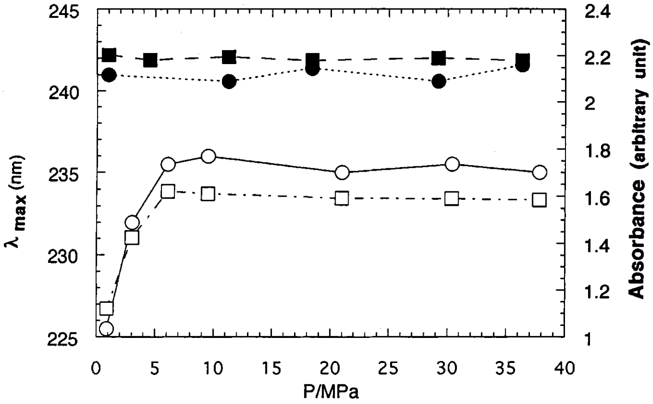

Fig. 3 Effect of pressure on the absorption spectra of 50 mM AOT in water/AOT/NC propane micelles at 310 K. λ_{max} (●) and absorbance (■) for $W_0 = 1$; and λ_{max} (○) and absorbance (□) for $W_0 = 11$

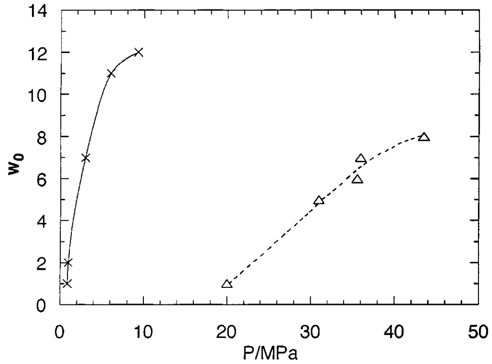

Fig. 4 Pressure-dependent water solubilization diagram of water/AOT/SC ethane (△) and water/AOT/NC propane (x) systems showing the boundary between the single phase and the turbid multiphase region

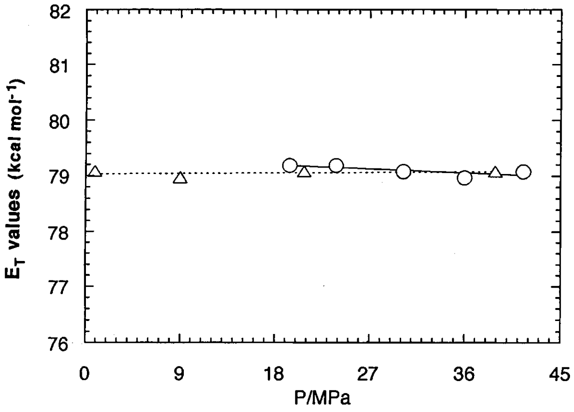

Fig. 5 Pressure dependence of the E_T values of the CT band of EMCPI in micelles of water/AOT/SC ethane (○) and water/AOT/NC propane (△) at 310 K for $W_0 = 2$

determined for $W_0 = 1$ and $W_0 = 2$ by solubilizing the EMCPI probe. The transition energy (E_T value) of the CT band of EMCPI depends on the polarity of the environment [19]. The polarity of the core can be represented in terms of the E_T values. Figure 5 shows the pressure independence of the E_T values of water/AOT/SC ethane and water/AOT/NC propane micelles in one-phase region for $W_0 = 2$ at 310 K. A similar pressure independence of E_T values was observed for micelles formed in the above mentioned fluids at $W_0 = 1$. The pressure independence of the E_T values suggests that in the one-phase region pressure has no influence on the polarity. For $W_0 = 1$ and $W_0 = 2$, the micropolarity remained the same when micelles were prepared in ethane and in propane.

There is a satisfactory linear correlation between E_T and $E_T(30)$ values according to Eq. (2) (54 solvents, correlation coefficient $r = 0.978$) [16].

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

The $E_T(30)$ values were calculated from E_T values using Eq. (2) for micelles of $W_0 = 1$ and $W_0 = 2$. The $E_T(30)$ value of 51.81 kcal mol^{-1} was obtained for micelles of $W_0 = 2$, which is comparable to that of ethanol.

$E_T(30)$ values of water/AOT/SC ethane micelles

The pressure dependence of the $E_T(30)$ values for water/AOT/SC ethane micelles is shown in Fig. 6 for various W_0 at a fixed temperature of 310 K. The micropolarity of the micelles increased with pressure in two-phase region and in one-phase region it remained independent of pressure. However, for $W_0 = 8$ the micropolarity showed a continuous increase with pressure because the system maintained two phases until a pressure of 43.5 MPa was reached. The $E_T(30)$ value increases with W_0, suggesting that the micropolarity of the aqueous core increases with increasing W_0.

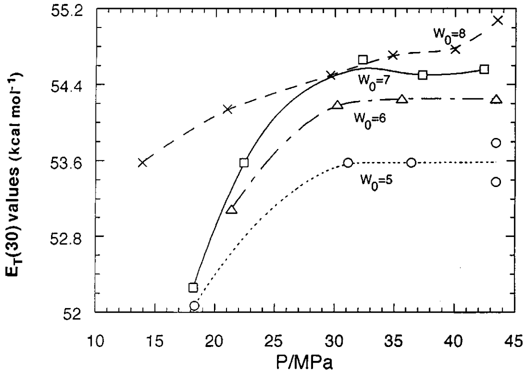

Fig. 6 The pressure dependence of the $E_T(30)$ values in water/AOT/SC ethane reverse micelles at 310 K for various W_0

The pressure dependence of the absorbance of the CT band of the $E_T(30)$ reagent in water/AOT/SC ethane micelles for W_0 = 5, 6, and 8 at 310 K is shown in Fig. 7. In two-phase region the absorbance increased with pressure as the amount of the $E_T(30)$ reagent dissolved into the micelles increased. For $W_0 = 5$ and $W_0 = 6$ at pressures of 31 and 35.6 MPa, respectively, the maximum absorbance corresponded to the formation of one-phase micellar solution observed visually.

$E_T(30)$ values of water/AOT/NC propane micelles

The micropolarity of water/AOT/propane micellar core was not influenced by pressure in one-phase region for a given W_0 values as the $E_T(30)$ values were independent of pressure (Fig. 8); however, the micropolarity significantly increased with the W_0 value. The CT band of the $E_T(30)$ reagent at 1 and 3–36.7 MPa for $W_0 = 7$ at 310 K is shown in Fig. 9. Increasing the pressure above 3 MPa had no influence on the absorbance, which

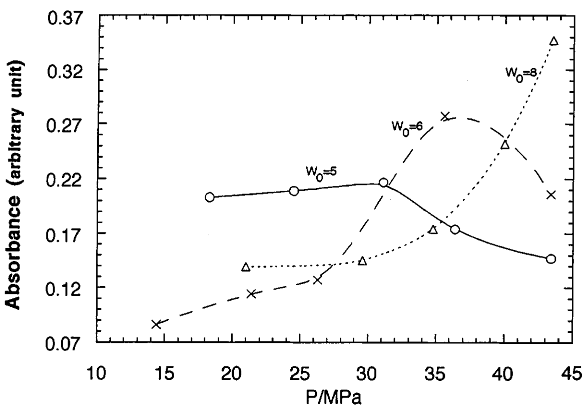

Fig. 7 Effect of pressure on the absorbance of the CT band of the $E_T(30)$ reagent in water/AOT/SC ethane reverse micelles for various W_0

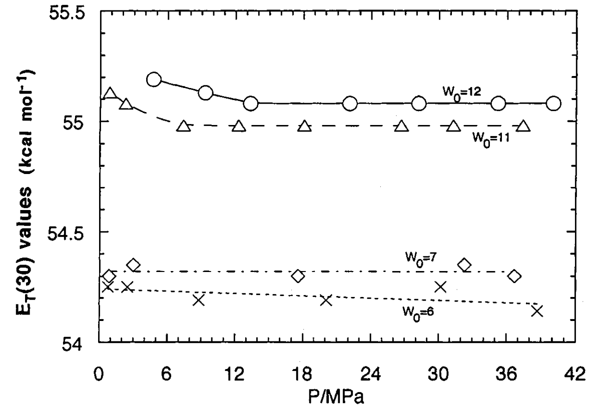

Fig. 8 The pressure dependence of the $E_T(30)$ values in water/AOT/NC propane micelles at 310 K for various W_0

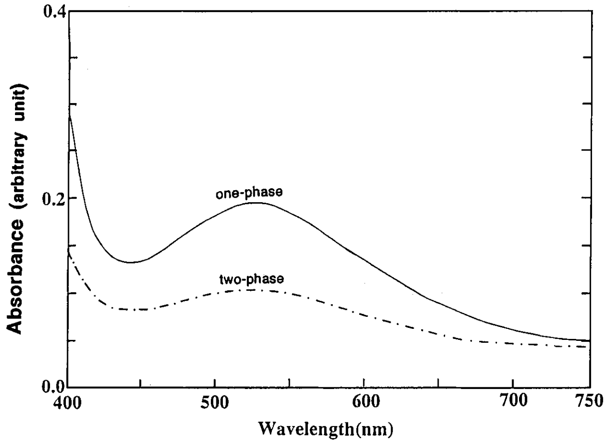

Fig. 9 The CT band of the $E_T(30)$ reagent in water/AOT/NC propane micelles at 1 MPa (–·–) and at 3–36.7 MPa (—) for W_0 = 7 and 310 K

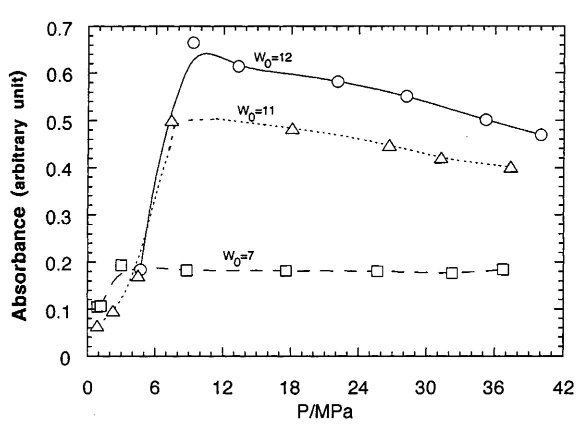

Fig. 10 Effect of pressure on the absorbance of the CT band of the $E_T(30)$ reagent in water/AOT/NC propane micelles for various W_0

suggests that at a pressure of 3 MPa the system changed to a homogeneous micellar solution. The pressure dependence of the absorbance is shown in Fig. 10 for different W_0 values. At low pressures, where the system existed in two phases, the absorbance increased with pressure and attained a maximum value at the pressure where the system changed to one phase. In each case of W_0 = 7, 11, and 12 at pressures of 3, 7.4, and 9.3 MPa, respectively, a maximum absorbance was observed which corresponded to the transition from a turbid to a clear phase as observed visually. The increase in the absorbance with pressure in two-phase region has been ascribed to an increase in the solubilization of AOT in reverse micellar form which enables a large amount of dye to be dissolved inside the micelles. The absorbance was higher at higher W_0 values as the amount of dye solubilized increased with increasing size of the core. Figure 11 compares the micropolarity of water/AOT/SC ethane and water/AOT/NC propane micelles in one-phase micellar solution at 310 K. The micropolarity was the same for the micelles formed in ethane and propane for a given W_0 and increased with increasing W_0 values. The results of micropolarity measurements show that the micellar size for a given W_0 remains the same in ethane and propane and increases with increasing W_0 values. In a wide range of liquid alkanes the micellar size was found to be the same for equivalent W_0 values and increased linearly with W_0 [24]. In one-phase micellar solutions, the micropolarity can be varied between values close to those obtained in ethanol and methanol solvents by adjusting the W_0 values. The micropolarity and the size of the micelles could be tuned by controlling W_0 and pressure for separation and reaction processes in SCFs.

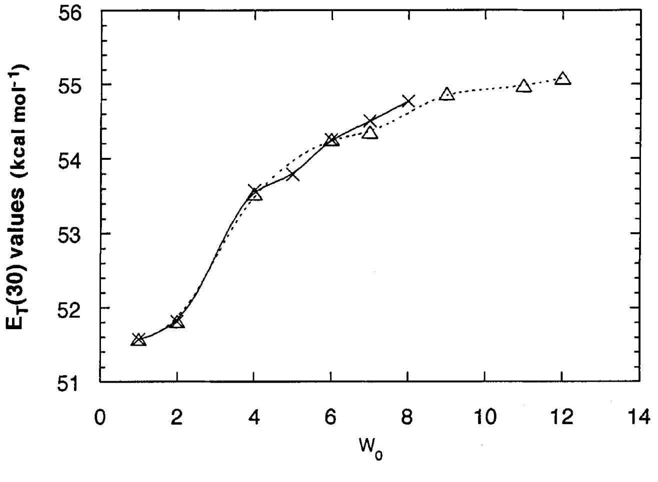

Fig. 11 $E_T(30)$ values in water/AOT/SC ethane (x) and water/AOT/NC propane (△) micelles as a function of W_0 in one-phase micellar solutions at 310 K

Conclusions

The phase behaviour investigation of AOT reverse micelles in SC ethane and NC propane shows that the amount of water solubilized in the reverse micelles increases by increasing the fluid pressure at a constant temperature of 310 K. The amount of water solubilized in the reverse micelles in NC propane is larger than in SC ethane. The results of micropolarity determination show that

1. Pressure has no effect on the micropolarity of the micellar core after the system changes to one phase.
2. The micropolarity increases with the water content of the micelles.
3. In one-phase region the micropolarity is the same for the micelles prepared in ethane and propane for a given W_0 value.
4. The micropolarity can be adjusted between the values obtained in ethanol and methanol by changing W_0 value and pressure of the system.

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