Asian Journal of Chemistry Vol. 15, No. 2 (2003), 675–678

Study of Solute-Solute and Solute-Solvent Interaction of Sodium Dodecyl Sulfate and Cetyl Pyridinium Bromide in Aqueous Medium

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The density, viscosity and apparent molar volume (ϕ_V) of sodium dodecyl sulfate (SDS) and cetyl pyridinium bromide (CPB) in aqueous solution at 298.15 K are reported. The experimental results of viscosity and density have been analyzed using Jones-Dole and Masson equations, respectively. The values of constants A and B of the Jones-Dole equation and those of ϕ_V and S_V of Masson equation are explained in terms of solute-solute and solute-solvent interactions. The data indicate that there is negligible solute-solute interaction and strong solute-solvent interaction.

Key Words: Solute-solute interaction, Solute-solvent Interaction, Sodium dodecyl sulfate, Cetyl pyridinium bromide.

INTRODUCTION

The solution characterization and interaction engineering investigations of some surface active substances in aqueous system have been studied. Such studies are supposed to be landmarking in the field of interaction of medicinal solution, antiseptic, agrochemicals, genetic engineering, etc. The interactions of surfactants with macromolecules in aqueous solutions have been studied during the past several years[1–13]. In the present study the simple binary systems of water + surfactant have been selected to investigate the solute-solute and solute-solvent interactions by viscosity measurement at 298.15 K. The viscometric measurements provide valuable information regarding molecular interaction in the pure liquids as well as in mixture and mechanism of these interactions. It has been reported by a number of workers that addition of a solute could either make or break the structure of the solvent[14] since viscosity is a property of the liquid which depends upon the intermolecular interactions. The present study is undertaken to examine the structural changes in the water on addition of surfactant by the measurement of density and viscosity of water + surfactant at different concentration of surfactant. The viscosity data have been analyzed for the Falkenhagen[15] constant A, Jones-Dole[16] B-coefficient and apparent molar volume to interpret the nature of the interaction existing below the critical micelle concentration (CMC) of the sodium dodecyl sulfate (SDS) and cetyl pyridinium bromide (CPB).

EXPERIMENTAL

Sodium dodecyl sulfate and cetylpyridinium bromide used were of AR grade. Ths solutions were prepared in the doubly distilled water. Densities and viscosities of the various solutions of different concentrations of SDS and CPB were measured with the help of a pyknometer and Ostwald viscometer at 298.15 K. The measurements were made in the water bath whose temperature was controlled to ±0.01 K.

RESULTS AND DISCUSSION

Densities and viscosities of water + sodium dodecyl sulfate and water + cetylpyridinium bromide binary systems have been measured at 298.15 K and recorded in Table-1. The density of water changes by the addition of the surfactant. The values of densities for these systems decreases with increase in concentration of the surfactant. This may be attributed to the fact that there might be some change in the structure of water by the addition of the SDS or CPB.

The values of viscosities of these systems have been measured at different concentrations of the surfactants (Table-1). The viscosity of these systems increases with increase in concentration of the added surfactant. The viscosity data indicate that the values are higher in case of SDS than CPB. The change in viscosity of solvent (water in the present case) is proportional to the concentration of the solute at low concentration and with further increase in concentration changes the viscosity more rapidly. The increase in viscosity with concentration is due to hydration of solute and volume of these particles may play an important role in viscosity. This can be explained on the basis of hydrodynamic theory according to which the solute particles lie across the fluid streamlines and are subject to torsional forces. They tend to rotate and thus absorb energy and this causes the increased viscosity for the solution. The viscosity data have been analyzed to calculate the value of constants A and B to interpret the nature of interaction with the help of well known Jones-Dole[16] equation (1).

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad (1)$$

The plot of $(\eta/\eta_0 - 1)/\sqrt{C}$ *vs.* is linear upto the critical micelle concentration value for water + SDS system. Similar curve was observed for water + CPB. The behaviour of SDS and CPB in aqueous system below the CMC value has been discussed on the basis of Jones-Dole equation. The values of A and B constants of this equation have been determined from the intercept and slope of the plots of $(\eta/\eta_0 - 1)/\sqrt{C}$ *vs.* $\sqrt{C}$. The values of A and B constants are presented in Table-2. The Falkenhagen constant A is negative in case of SDS while positive in case of CPB. The A (+0.57) values of CPB indicate that there is weak solute-solute interaction, while A (–0.095) values of SDS show almost no interaction. Thus A-computation shows that interactions are ranging between negligible solute-solute interaction to weak solute-solute interaction in water + SDS and water + CPB systems respectively. The value of constant B is positive in both the systems. Value of B is higher in case of SDS. This indicates that SDS shows stronger interaction with water than CPB.

The apparent molar volume (ϕ_v) was calculated from the density data using the following equation[17] (2).

$$\phi_v = 1000(d_0 - d)/C \cdot d_0 + M_2/d_0 \qquad (2)$$

where symbols have their usual meaning. The values of apparent molar volume (ϕ_v) are also presented in Table-1. The values of ϕ_v decrease with increase in the concentration of the surfactants. The decrease in the ϕ_v values with increase in concentration of solute indicates the hydrophobic nature of surfactant. The positive values of ϕ_v suggest the presence of solute-solvent interactions. Variation of apparent molar volume has been found to vary linearly with the square root of the concentration in conformity with Masson's[18] equation (3)

$$\phi_v = \phi_v^0 + S_v\sqrt{C} \qquad (3)$$

The plot of ϕ_v *vs.* $\sqrt{C}$ is linear for water + SDS system. The limiting apparent molar volume (ϕ_v^0), which is also equal to partial molar volume (v_2), at infinite dilution, has been determined easily from the plot. The values of ϕ_v are recorded in Table-2. The values of ϕ_v^0 are positive which indicates the presence of solute-solvent interaction. The values of S_v are negative (Table-2) and indicative of the absence of solute-solute interactions[19].

In order to know that what kinds of solute-solute interactions are taking place here, whether strong, weak or negligible interactions? For this purpose we calculated the A constant and took the help of these data to interpret the type of interaction. In our case CPB shows weak solute-solute interaction in aqueous system and there is negligible solute-solute interaction in case of SDS + water system.

The Jones-Dole B-coefficient values of SDS are higher than CPB. The high positive value of B-coefficient (Table-2) indicates that there is solute-solvent interaction and the solute involved in the solution behaves as a structure marker or promoter[20, 21]. In the studied system this behaviour has been observed below the CMC. These results are in conformity with earlier analyzes reported elsewhere[22–23].

Reported high positive value of B-coefficient indicates that there is strong solute-solvent interaction such that the solute behaves like a structure-forming solute. For this confirmation, we further take the help of our analyzed data and compute the value of B/ϕ_v^0. Tyrrell *et al.*[23] have shown that high values of B-coefficient and B/ϕ_v^0 ratio are indicative of solute as structure promoter. In the present case as per Table-2 all the values of B and B/ϕ_v^0 are found to be positive and higher also. The values of B and B/ϕ_v^0 in case of SDS + water system are higher than these of CPB + water. Thus it clearly shows that in case of SDS + water system the solute-solvent interactions have been found to be strong and the solute involved is acting as structure-forming.

ACKNOWLEDGEMENT

The author is thankful to Dr. D.P. Singh, Department of Physics, F.G.M.G.C., Adampur for his valuable suggestions.

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(*Received*: 21 August 2002; *Accepted:* 7 November 2002) AJC-2910