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ORIGINAL ARTICLE

Thermodynamic properties of Sodium Dodecyl Sulfate aqueous solutions with Methanol, Ethanol, *n*-Propanol and *iso*-Propanol at different temperatures

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Abstract The thermodynamic activation parameters such as, free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) change for the viscous flow of the ternary systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005 and 0.01 M aqueous Sodium Dodecyl Sulfate (SDS) were determined by using viscosity at 298.15–323.15 K with an interval of 5 K for the entire range of composition. The critical micelle concentration (CMC) of Sodium Dodecyl Sulfate (SDS) in water was found to be 0.0085 mol L^{-1} at 303.15 K. The concentration of SDS in pre-micellar and post-micellar regions of 0.005 and 0.01 M was used for the thermodynamic measurements. Free energy ($\Delta G^{\#}$), increases rapidly with alcohol concentration and shows maxima in aqueous SDS rich region at 0.2–0.3 mol fraction of alcohols. The position of maxima virtually does not change remarkably with the variation of temperature. The excess free energy, ($\Delta G^{\#E}$) values are found to be positive and large in magnitude, indicating that the aqueous SDS solutions of alcohols are highly non ideal. The heights of the maxima are in the order:

iso-Propanol + aqueous SDS > *n*-Propanol + aqueous SDS > Ethanol + aqueous SDS > Methanol + aqueous SDS.

The $\Delta H^{\#}$ values that are positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. The variation of $\Delta S^{\#}$ is reversing the variation of the $\Delta H^{\#}$. The excess parameters ($\Delta G^{\#E}$, $\Delta H^{\#E}$) data have been fitted by the least square

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method to the four parameter Redlich–Kister equation and the values of the parameter a_j have been reported. The observed increase of thermodynamic values in the aqueous SDS region are thought to be mainly due to the combined effect of hydrophobic hydration and hydrophilic effect.

1. Introduction

This research is a part of our ongoing project on the physical properties and the molecular interactions in ternary mixtures. The solution of highly surface-active materials exhibits unusual physical properties. In a dilute solution the surfactant acts as a normal solute. By increasing the concentration of the surfactant, an abrupt change in several physico-chemical properties of the solution, such as osmotic pressure, electrical conductance, surface tension, viscosity etc. is observed. Micelle formation of surfactant molecules in water solution is a typical hydrophobic process (Tanford, 1973). In water medium, surfactant molecules with their long hydrophobic tails undergo hydrophobic hydration. Alcohols are self-associated liquids through H-bonding. Alcohols possess hydrophilic-OH group as well as hydrophobic group. Interactions between aqueous SDS and alcohols are extremely complex. The mode of interaction of these two groups toward SDS is completely different. The hydrophilic –OH group of an alcohol forms H-bond with aqueous SDS through hydrophilic interactions and disrupts the aqueous SDS structure, while the alkyl group promotes the structure of aqueous SDS molecules surrounding this group, through hydrophobic hydration. The densities and excess molar volumes of alcohols in water Surf Excel solution (Kabir et al., 2004), the volumetric and viscometric properties of carbohydrates in water Surf Excel (Dey et al., 2003) and the electrolytes in water SDS (Afroz et al., 2003) systems were reported. Research on some binary alcohol systems the thermophysical properties has been reported by several authors (Al-Azzawi and Awwad, 1990; Awwad et al., 2000, 2001; Sacco and Rakshit, 1975; Karvo, 1982; Jannelli et al., 1984; Liu and Hai, 2010; Lide, 1992). Here, we report the effect of some simple alcohols on the structure of water SDS systems based on the thermodynamic properties. Micelle-forming molecules in SDS may force water to be in a certain structural form in the water SDS system. The perturbations of this forced structure in water SDS system by some alcohols are expected to be more appreciable than the perturbation caused by these alcohols only in the water system. The knowledge of interactions of simple smaller hydrophobic molecules with water and with water surfactant solvent systems may be useful sometimes to interpret many complex systems. The data are also useful for the design of mixing, storage and process equipments.

2. Experimental

The chemicals used were purchased from Aldrich chemical Co. with the quoted purities: Methanol (99.5%), Ethanol (99.0%), *n*-Propanol (99.0%), *iso*-Propanol (99.5%) and Sodium Dodecyl Sulfate (SDS) (99.5%). The measures of purity check, the densities and viscosities of pure liquids were compared with the available literature values shown in Table 1 (Lide, 1992; Roy et al., 2005; Zarei et al., 2009; Timmermans, 1950; Kabir et al., 2004; Sovilj and Barjaktarovic, 2000; Radovic et al., 2009; Acevedom, 1988; Nikam et al., 1988, 1996; Marigliano and Solimo, 2002; Motin et al., 2005; Wei and Rowley, 1984). Our measured values of densities and viscosities of pure liquids have been found to be very satisfactory with the literature (Table 1). These alcohols were used without any further purification, except that they were allowed to stand over molecular sieves (4A) about one week before measurements. Deionized and doubly distilled water were used in the preparation of all the alcohol solutions. The viscosities were measured by calibrated U-type Ostwald viscometer of the British standard institution with sufficiently long efflux time to avoid kinetic energy correction. Temperatures were controlled by a thermostatic water bath fluctuating to ±0.05 K. A HR-200 electronic balance with an accuracy of ±0.0001 g was used for the mass determination. Reproducibility of the results was checked by taking each measurement three times. The densities and viscosities of the systems, Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005 and 0.01 M aqueous SDS, over the whole composition range at 298.15–323.15 K with an interval of 5 K were reported in our previous studies (Motin et al., 2011). The experimental procedure for measuring density and viscosity of the systems has been described in detail elsewhere (Kabir et al., 2004; Dey et al., 2003; Afroz et al., 2003). The free energy ($\Delta G^{\#}$) of activation for the viscous flow was calculated by using the following form of Eyring equation.

$$\therefore \Delta G^{\#} = RT \ln\left(\frac{\eta V_{\mathrm{m}}}{Nh}\right) \tag{1}$$

where, η = viscosity of the mixture, V_{m} = molar volume of solution, h = Plank's constant, N = Avogadro's constant and R = gas constant. Energy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution were calculated,

$$\ln\left(\frac{\eta V_{\mathrm{m}}}{Nh}\right) = \frac{\Delta H^{\#}}{RT} - \frac{\Delta S^{\#}}{R} \tag{2}$$

Assuming $\Delta H^{\#}$ and $\Delta S^{\#}$ are almost independent of temperature in this range, a plot of $\ln \frac{\eta V_{\mathrm{m}}}{Nh}$ against $\frac{1}{T}$ will give a straight line with slope $= \frac{\Delta H^{\#}}{R}$ and intercept $= -\frac{\Delta S^{\#}}{R}$ from which, $\Delta H^{\#} = \text{slope} \times R$ and $\Delta S^{\#} = -\text{intercept} \times R$.

The thermodynamic activation parameters for the viscous flow are represented by a common polynomial equation of the type,

$$Y = \sum_{i=0}^{n} a_i x_2^i \tag{3}$$

where, a_i is the ith coefficient, Y stands for $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ and x_2 for the mole fraction of alcohols.

The excess values, Y^{E}, of the above functions, i.e. $\Delta G^{\#\mathrm{E}}$, $\Delta H^{\#\mathrm{E}}$ and $\Delta S^{\#\mathrm{E}}$ have been calculated by the following general additive equation.

$$Y^{E} = Y - (x_1 Y_1 + x_2 Y_2) \tag{4}$$