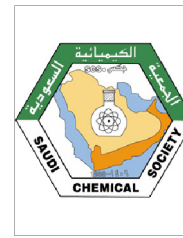




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## ORIGINAL ARTICLE

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



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Received 6 October 2011; accepted 23 January 2012

Available online 31 January 2012

## KEYWORDS

Thermodynamic activation parameters;  
SDS;  
Alcohols

**Abstract** The thermodynamic activation parameters such as, free energy ( $\Delta G^\ddagger$ ), enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) 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<sup>-1</sup> 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 ( $\Delta G^\ddagger$ ), 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, ( $\Delta G^{\ddagger E}$ ) 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  $\Delta H^\ddagger$  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  $\Delta S^\ddagger$  is reversing the variation of the  $\Delta H^\ddagger$ . The excess parameters ( $\Delta G^{\ddagger E}$ ,  $\Delta H^{\ddagger E}$ ) 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.

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## 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 thermo-physical 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  $\pm 0.05$  K. A HR-200 electronic balance with an accuracy of  $\pm 0.0001$  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 ( $\Delta G^\ddagger$ ) of activation for the viscous flow was calculated by using the following form of Eyring equation.

$$\therefore \Delta G^\ddagger = RT \ln \left( \frac{\eta V_m}{Nh} \right) \quad (1)$$

where,  $\eta$  = 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 ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) for viscous flow for the solution were calculated,

$$\ln \left( \frac{\eta V_m}{Nh} \right) = \frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R} \quad (2)$$

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

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

$$Y = \sum_{i=0}^n a_i x_2^i \quad (3)$$

where,  $a_i$  is the  $i$ th coefficient,  $Y$  stands for  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  and  $x_2$  for the mole fraction of alcohols.

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

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2) \quad (4)$$

**Table 1** Comparison of experimental and literature values of density,  $\rho$  ( $\text{g cm}^{-3}$ ) and viscosity,  $\eta$  (mPa s) of pure components at different temperatures.

Component	Temperature (K)	Density ( $\text{g cm}^{-3}$ )		Viscosity (mPa s)	
		$\rho_{\text{lit}}$	$\rho_{\text{exp}}$	$\eta_{\text{lit}}$	$\eta_{\text{exp}}$
Methanol	298.15	0.787200	0.787323	0.5530	0.5523
	303.15	0.782420	0.782764	0.5100	0.5108
	308.15	0.777100	0.777426	0.4837	0.4902
	313.15	0.772500	0.772540	0.4542	0.4577
	318.15	0.769285	0.766700	0.4256	0.4280
	323.15	0.762800	0.758600	0.4000	0.4055
Ethanol	298.15	0.801900	0.808867	1.0900	1.1355
	303.15	0.798255	0.804509	1.1808	1.2060
	308.15	0.794517	0.799029	1.0638	1.0871
	313.15	0.780157	0.793200	0.9646	0.9655
	318.15	0.785760	0.788300	0.8714	0.8708
	323.15	0.771336	0.783558	0.8010	0.7952
<i>n</i> -Propanol	298.15	0.799692	0.800501	1.9340	1.9233
	303.15	0.795840	0.796323	1.6626	1.6951
	308.15	0.797499	0.791910	1.5422	1.5234
	313.15	0.787500	0.787892	1.3000	1.3430
	318.15	0.789183	0.782407	1.2440	1.2060
	323.15	0.778500	0.779224	1.1091	1.0690
<i>iso</i> -Propanol	298.15	0.780000	0.778306	2.0360	2.0257
	303.15	0.777100	0.774467	–	1.7639
	308.15	0.772460	0.771190	1.5420	1.5220
	313.15	–	0.766972	–	1.3179
	318.15	–	0.762585	–	1.1516
	323.15	–	0.758129	–	1.0075

Here, each term has its usual significance and the subscripts 1 and 2 refer to solvent and alcohol, respectively. Each of the excess properties has been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^E = x_1 x_2 \sum_{i=0}^n a_i (1 - 2x_1)^i \quad (5)$$

where,  $a_i$  is the  $i$ th coefficient,  $Y^E$  stands for each of  $\Delta G^{\#E}$ ,  $\Delta H^{\#E}$  and  $\Delta S^{\#E}$  and  $x_1$  and  $x_2$  are the mole fractions of solvent and alcohol, respectively.

### 3. Results and discussion

The critical micelle concentration (CMC) of Sodium Dodecyl Sulfate (SDS) in water was determined from the conductance

and viscosity measurements. The conductance and viscosity data of SDS have been reported (Lide, 1992 and Motin et al., 2011). The estimated value of CMC was found to be  $0.0085 \text{ mol L}^{-1}$  at  $29^\circ\text{C}$ . The concentration of SDS in pre-micellar and post-micellar regions of 0.005 and 0.01 M respectively was used for these measurements.

Free energy change ( $\Delta G^{\#}$ ) and excess free energy ( $\Delta G^{\#E}$ ) change of activation for the viscous flow of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005 and 0.01 M SDS solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K except Methanol over the entire composition range are shown in Tables 2–5 (for similar nature data of 0.005 M SDS containing alcohol systems are not shown). Methanol system was studied at 298.15, 303.15 and 308.15 K owing to its low boiling point. The variation of free energy ( $\Delta G^{\#}$ ) at

**Table 2** Change of free energy ( $\Delta G^{\#}$ ) and excess free energy ( $\Delta G^{\#E}$ ) of Methanol + 0.01 M SDS system at 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K respectively.

$X_2$	$\frac{\Delta G^{\#}}{\text{kJ mol}^{-1}}$			$\frac{\Delta G^{\#E}}{\text{kJ mol}^{-1}}$		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.0000	12.2772	12.1749	12.1412	0.0000	0.0000	0.0000
0.1002	11.9559	11.7951	11.6978	0.9732	0.9209	0.8640
0.2000	12.3124	12.1169	12.0126	1.4395	1.3421	1.2652
0.3001	12.3164	12.1525	12.0607	1.5538	1.4775	1.4000
0.4006	12.1863	12.0450	11.9720	1.5342	1.4702	1.3984
0.5012	11.9525	11.7971	11.7625	1.4111	1.3224	1.2761
0.6006	11.6535	11.5444	11.5004	1.2214	1.1688	1.1001
0.7012	11.3086	11.2461	11.2105	0.9872	0.9708	0.8974
0.8004	10.9256	10.8802	10.8660	0.7134	0.7037	0.6388
0.8991	10.4640	10.4450	10.4576	0.3603	0.3668	0.3159
1.0000	9.9926	9.9776	10.0542	0.0000	0.0000	0.0000

**Table 3** Change of free energy ( $\Delta G^\#$ ) and Excess free energy ( $\Delta G^{\#E}$ ) of Ethanol + 0.01 M SDS system at 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K respectively.

$X_2$	$\frac{\Delta G^\#}{\text{kJ mol}^{-1}}$						$\frac{\Delta G^{\#E}}{\text{kJ mol}^{-1}}$					
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	12.2772	12.1749	12.1412	12.0845	12.0378	11.9905	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1005	13.6429	13.4472	13.3100	13.1642	13.0119	12.8846	1.5471	1.4472	1.3480	1.2685	1.1709	1.0945
0.1997	14.1448	13.9252	13.7468	13.5662	13.4124	13.3004	1.9477	1.8161	1.6752	1.5628	1.4630	1.3991
0.2992	14.1859	13.9938	13.8679	13.7245	13.5729	13.4554	1.8871	1.7753	1.6865	1.6130	1.5146	1.4426
0.3989	14.1140	13.9240	13.8192	13.6600	13.5440	13.4246	1.7134	1.5958	1.5277	1.4401	1.3768	1.3000
0.4988	13.9806	13.8171	13.7318	13.6032	13.4680	13.3834	1.4780	1.3790	1.3300	1.2748	1.1916	1.1468
0.6005	13.8197	13.6887	13.6011	13.5113	13.4075	13.3205	1.2132	1.1387	1.0870	1.0724	1.0199	0.9699
0.7019	13.6183	13.4938	13.4301	13.3335	13.2578	13.1751	0.9082	0.8323	0.8041	0.7844	0.7594	0.7109
0.8017	13.4203	13.3279	13.2715	13.2011	13.1034	13.0490	0.6083	0.5566	0.5353	0.5435	0.4959	0.4729
0.9002	13.2782	13.1751	13.1361	13.0681	12.9992	12.9579	0.3656	0.2955	0.2912	0.3035	0.2840	0.2714
1.0000	13.0145	12.9894	12.9551	12.8730	12.8243	12.7984	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

**Table 4** Change of free energy ( $\Delta G^\#$ ) and excess free energy ( $\Delta G^{\#E}$ ) of *n*-Propanol + 0.01 M SDS system at 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K respectively.

$X_2$	$\frac{\Delta G^\#}{\text{kJ mol}^{-1}}$						$\frac{\Delta G^{\#E}}{\text{kJ mol}^{-1}}$					
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	12.2772	12.1749	12.1412	12.0845	12.0378	11.9905	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1006	14.6115	14.4220	14.2990	14.1730	14.0465	13.9484	1.7630	1.6629	1.5665	1.4910	1.4122	1.3572
0.2005	15.1738	14.9780	14.8658	14.7628	14.6232	14.5210	2.1304	2.0208	1.9343	1.8788	1.7904	1.7317
0.2991	15.2753	15.0907	14.9980	14.8816	14.7623	14.6464	2.0394	1.9378	1.8701	1.7982	1.7335	1.6616
0.3990	15.2456	15.0726	14.9916	14.8613	14.7635	14.6504	1.8149	1.7216	1.6648	1.5760	1.5362	1.4676
0.5026	15.1524	15.0092	14.9090	14.8178	14.7135	14.6289	1.5195	1.4527	1.3757	1.3230	1.2803	1.2407
0.6011	15.0480	14.9013	14.8445	14.7721	14.6732	14.5759	1.2228	1.1493	1.1151	1.0781	1.0442	0.9923
0.7022	14.9285	14.8203	14.7711	14.6944	14.6255	14.5361	0.9061	0.8677	0.8404	0.7960	0.7957	0.7521
0.7993	14.8337	14.7332	14.6950	14.6312	14.5541	14.4728	0.6218	0.5880	0.5709	0.5365	0.5313	0.4963
0.8998	14.7137	14.6450	14.6027	14.5681	14.4859	14.4399	0.3058	0.3005	0.2784	0.2702	0.2634	0.2641
1.0000	14.6035	14.5434	14.5238	14.5006	14.4216	14.3745	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

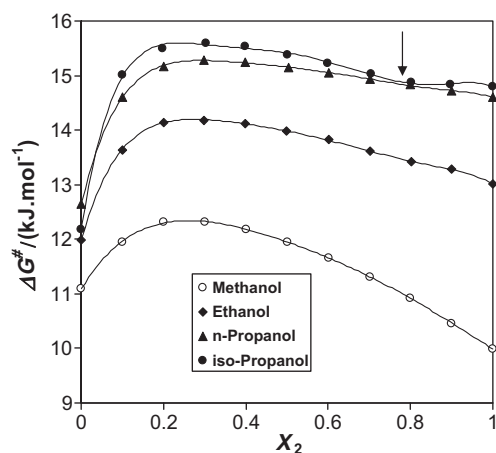
**Table 5** Change of free energy ( $\Delta G^\#$ ) and excess free energy ( $\Delta G^{\#E}$ ) of *iso*-Propanol + 0.01 M SDS system at 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 K respectively.

$X_2$	$\frac{\Delta G^\#}{\text{kJ mol}^{-1}}$						$\frac{\Delta G^{\#E}}{\text{kJ mol}^{-1}}$					
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	12.2772	12.1749	12.1412	12.0845	12.0378	11.9905	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1004	15.0200	14.7354	14.5827	14.3946	14.2364	14.0972	2.5711	2.3947	2.2864	2.1574	2.0469	1.9604
0.1988	15.4998	15.2451	15.0916	14.9349	14.7630	14.6534	2.7935	2.6449	2.5444	2.4539	2.3366	2.2869
0.3042	15.5879	15.3934	15.2585	15.1084	14.9253	14.7963	2.6060	2.5152	2.4427	2.3664	2.2452	2.1837
0.3990	15.5428	15.3224	15.1934	15.0309	14.8936	14.7488	2.3129	2.1941	2.1359	2.0541	1.9853	1.9149
0.5003	15.3883	15.1754	15.0528	14.8963	14.7754	14.6291	1.8935	1.7799	1.7371	1.6685	1.6233	1.5587
0.6000	15.2158	15.0292	14.9336	14.7778	14.6514	14.5122	1.4601	1.3706	1.3638	1.3031	1.2594	1.2091
0.7031	15.0378	14.8791	14.7865	14.6529	14.5308	14.4099	1.0126	0.9486	0.9539	0.9228	0.8906	0.8660
0.8026	14.8797	14.7544	14.6694	14.5675	14.4570	14.3534	0.5942	0.5614	0.5832	0.5909	0.5773	0.5772
0.8975	14.8291	14.6941	14.6124	14.4856	14.3736	14.2578	0.2953	0.2508	0.2842	0.2740	0.2655	0.2600
1.0000	14.8018	14.7137	14.5894	14.4655	14.3548	14.2371	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

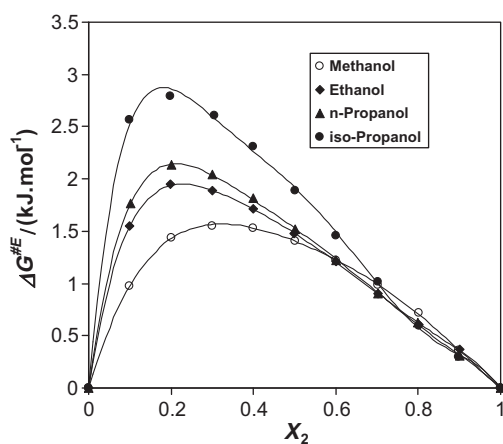
303.15 K as a function of the mole fraction of the all studied alcohols is shown in Fig. 1. Fig. 2 represents the variation of  $\Delta G^{\#E}$  of the systems against the mole fraction of the alcohols at 303.15 K. The excess free energy ( $\Delta G^{\#E}$ ) was fitted by least squares method to a polynomial equation. The values of the fitting parameters along with the standard deviation of

Ethanol system are presented in Table 6 as sample. The following characteristic features of  $\Delta G^\#$  and  $\Delta G^{\#E}$  are observed:

- The change of free energy ( $\Delta G^\#$ ) increases rapidly with alcohol concentration and shows maxima in the aqueous SDS rich region at 0.2–0.3 mol fraction of alcohol and



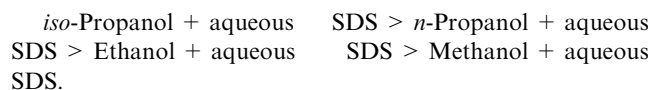
**Figure 1** Plots of free energy change ( $\Delta G^\#$ ) vs mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.01 M aqueous SDS system at 303.15 K.



**Figure 2** Plots of excess free energy change ( $\Delta G^{\#E}$ ) vs mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.01 M aqueous SDS system at 303.15 K.

then declines up to the pure state of alcohols. In each system, values of  $\Delta G^\#$  are found to decrease with the increase in temperature (Tables 2–5).

- (ii) At the alcohol rich region shallow minima of  $\Delta G^\#$  are observed for *iso*-Propanol at  $\sim 0.7$ – $0.8$  mol fraction of alcohol only at 303.15 K (Table 5 and Fig. 1). The minima seem to disappear with the rise in temperature (Table 5).
- (iii) The  $\Delta G^{\#E}$  values are positive for the whole range of composition and are large in magnitude, all the values being fitted well to the Redlich Kister polynomial Eq. (5) (Table 6). This indicates that the solutions are highly non ideal, and the species formed in the solutions have to surmount a large additional energy barrier in order to flow. This implies that the species experience enhanced resistance to flow. The order of increment of  $\Delta G^{\#E}$  in the aqueous SDS rich region is as follows:



- (iv) Variation of  $\Delta G^{\#E}$  with composition for all the systems under investigation is more or less similar in nature, all being associated with maxima (Fig. 2).
- (v) The effect of temperature on both  $\Delta G^\#$  and  $\Delta G^{\#E}$  is seen to be significant, particularly in the region at or around the maximum, though the positions of maxima apparently remain almost unchanged with the variation of temperature.

The rapidly ascending parts of free energy  $\Delta G^\#$  curves (Fig. 1) in the dilute region of alcohols can be explained primarily in terms of the phenomenon called hydrophobic hydration. In the study, all four alcohols are polar by virtue of the presence of an unshared electron pair on oxygen atoms. The value of dipole moments ( $\mu$ ) are being 1.7, 1.69, 1.68, 1.66 D for Methanol, Ethanol, *n*-Propanol and *iso*-Propanol, respectively (Kosower, 1969). Therefore, hydrogen bonding is thought to be formed by the polar group of the alcohols and aqueous SDS due to the hydrophilic effect. However, the large positive  $\Delta G^{\#E}$  can not be explained by hydrophilic effect only and it is possible that the hydrophobic hydration is playing a role here. According to hydrophobic hydration, aqueous SDS molecules form a long range of structural aggregate around the hydrocarbon moieties; with the continued addition of alcohols; such aggregates increase causing a rapid rise in  $\Delta G^{\#E}$ . These are variously known as ice-burges, clusters or cages. There is a large body of experimental evidence which suggest the existence of such cages (Sovilj

**Table 6** Coefficient,  $a_i$ , of Redlich–Kister equation express in  $\Delta G^{\#E}$  and standard deviation,  $\sigma$  for the Ethanol, +0.005 M SDS, +0.01 M SDS systems.

Systems	$T$ (K)	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
0.005 M SDS + Ethanol systems	298.15	6.5979	−5.5982	7.1574	−5.8617	0.0298
	303.15	6.2108	−5.2615	6.7407	−5.9216	0.0363
	308.15	5.9969	−5.2642	5.9416	−4.2669	0.0255
	313.15	5.8616	−5.0179	5.4471	−3.4696	0.0258
	318.15	5.6418	−4.6676	4.9169	−3.4490	0.0246
	323.15	5.3591	−4.6927	4.4689	−2.7266	0.0263
0.01 M SDS + Ethanol systems	298.15	5.7613	−5.0345	6.7355	−5.0343	0.0341
	303.15	5.3990	−4.6805	6.0189	−5.1600	0.0335
	308.15	5.1928	−4.4223	5.3454	−4.4081	0.0364
	313.15	4.9908	−3.9815	5.0657	−4.0788	0.0402
	318.15	4.7450	−3.7424	4.5053	−3.7030	0.0341
	323.15	4.5221	−3.6469	4.1988	−3.2461	0.0296

and Barjaktarovic, 2000; Radovic et al., 2009; Acevedo, 1988; Nikam et al., 1988; Marigliano and Solimo, 2002; Roy et al., 2005; Motin et al., 2005). With a further increase in solute concentration, a composition is reached when solute molecules cannot find enough aqueous molecules to be surrounded. After attaining the state of maximum free energy ( $\Delta G^\ddagger$ ) further addition of alcohol continuously breaks down both the ordered structure and alcohol–aqueous association, and instead, alcohol–alcohol association is inequitably formed, which results in the continual decrease in free energy ( $\Delta G^\ddagger$ ). Therefore, the appearance of free energy ( $\Delta G^\ddagger$ ) maxima is expected as a result of these competing processes i.e. the result of a balance between the formation and decay of the aggregates formed by the aqueous molecules. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, while the hydrophilic effect is expected to be almost same for all the studied alcohols. As the long chain alcohols are more hydrophobic than short chain alcohols and their hydrophobicity decreases with increasing degree of unsaturation. The hydrophobic hydration varies according to hydrocarbon groups such as  $\text{CH}_3\text{CH}_2 > \text{CH}_3 > \text{CH}_2 > \text{CH}$  (Andini et al., 1990; Motin et al., 2011). Again the branched alcohols are more viscous than the unbranched alcohols. Hence by considering hydrophobic hydration, Andini's principle and the structural features of the alcohols, it is possible to predict that the free energy and their maxima should vary in the following order: *iso*-Propanol + aqueous SDS > *n*-Propanol + aqueous SDS > Ethanol + aqueous SDS > Methanol + aqueous SDS, which is in complete agreement with the present observations (Covington and Jones, 1968).

The values of free energy,  $\Delta G^\ddagger$  for the systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol are higher in post-micellar region than those of pre-micellar region (data are not shown). This indicates that alcohols may be more structured in post-micellar region than in the pre-micellar region.

In the present investigation at 303.15 K, the maximum values of  $\Delta G^{\ddagger E}$  have been found to be 1.5 (at  $x_2 = 0.30$ ), 1.95 (at  $x_2 = 0.2$ ), 2.15 (at  $x_2 = 0.2$ ), 2.79 (at  $x_2 = 0.2$ ) for the aqueous SDS + Methanol, aqueous SDS + Ethanol, aqueous SDS + *n*-Propanol and aqueous SDS + *iso*-Propanol mixtures, respectively. The height of the maxima has been found to be in the order similar to water systems:

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

As suggested by the author (Timmermans, 1950), a large negative excess free energy,  $\Delta G^{\ddagger E}$  indicates the presence of weak interactions, whereas a large positive excess free energy,  $\Delta G^{\ddagger E}$  suggests a specific association between the molecules in the solvent mixture. The positive  $\Delta G^{\ddagger E}$  values in our studied systems are also indicative of the strong molecular interaction among the aqueous SDS and alcohol systems.

The difference in maxima of  $\Delta G^\ddagger$  over the temperature range ( $\Delta\Delta G_{max}^\ddagger$ ) of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol–aqueous SDS association, the aqueous SDS–aqueous SDS association in the cage structure is assumed to be more fragile to heat. Examination of  $\Delta G^\ddagger$  curves of different alcohol solutions shows that  $\Delta\Delta G_{max}^\ddagger$  varies in the order,

*iso*-Propanol (0.84 kJ mol<sup>-1</sup>) > *n*-Propanol (0.79 kJ mol<sup>-1</sup>) > Ethanol (0.68 kJ mol<sup>-1</sup>) > Methanol (0.63 kJ mol<sup>-1</sup>).

The values, therefore, indicate the extent of the destruction of the cage structures by thermal effect which, in turn, reflects the extent of cage formation. Therefore, the effect of temperature on  $\Delta G^\ddagger$  and  $\Delta G^{\ddagger E}$ , particularly in the region at or around the maxima is significant (Tables 2–5). This may be due to the structures formed by hydrophobic hydration that are considered to be much more labile and thermally less stable than the normal water structure (Covington and Jones, 1968; Franks, 1983), i.e. the cages formed by the water–water association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than water–water association in normal water.

The shallow minima occurring at 0.7–0.8 mol fraction of alcohol are shown in the *iso*-Propanol at 303.15 K (Fig. 1). This observation is in agreement with the viscosity of aqueous mixtures of *t*-Butanol in the temperature range at 288–318 K also confirmed this phenomenon (Kipkemboi and Easteal, 1994). In the study of the viscosity of aqueous solutions of isomeric butanol, similar minima are noticed (Scanayake et al., 1987). Incidentally, the minima of static dielectric constants of alcohol–water mixtures occur at about the same composition where the shallow minima of viscosity are observed (Spink and Wyckoff, 1972). They explained these minima in terms of the formation of so called “centrosymmetric” associates which are thought to be composed of one water and four alcohol molecules. At the alcohol rich region shallow minima are observed prominently for *iso*-Propanol at 0.7–0.8 mol fraction in water and 0.005 M SDS solutions. But the minima at the post micellar concentration (0.01 M SDS) for *iso*-Propanol in SDS solutions are not so noticeable. This may be due to the centrosymmetric association (one water and four alcohol molecules) that is not available on the addition of higher concentration of SDS.

Table 7 lists enthalpy  $\Delta H^\ddagger$ , entropy  $\Delta S^\ddagger$ , excess enthalpy  $\Delta H^{\ddagger E}$  and excess entropy  $\Delta S^{\ddagger E}$  values for the studied system for different molar ratios. Figs. 3 and 4 show the plots of  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  as a mole fraction of alcohols, respectively. The  $\Delta H^\ddagger$  curves show that, on addition of alcohols to aqueous SDS  $\Delta H^\ddagger$  rise up sharply, pass through maxima in the aqueous SDS region and then decline monotonously. But  $\Delta S^\ddagger$  with the addition of alcohols decrease sharply, passes through minima and then increases regularly. The variation of  $\Delta S^\ddagger$  is just reversing the variation of the  $\Delta H^\ddagger$ . The positive  $\Delta S^\ddagger$  for all the alcohol systems indicate that probably rupturing of hydrogen bonds formed through –OH groups of alcohols in the activation process for viscous flow occurs, resulting in the structural disorder.

From careful examination of the excess enthalpy ( $\Delta H^{\ddagger E}$ ) and excess entropy ( $\Delta S^{\ddagger E}$ ) (Table 7), the following characteristic features are observed:

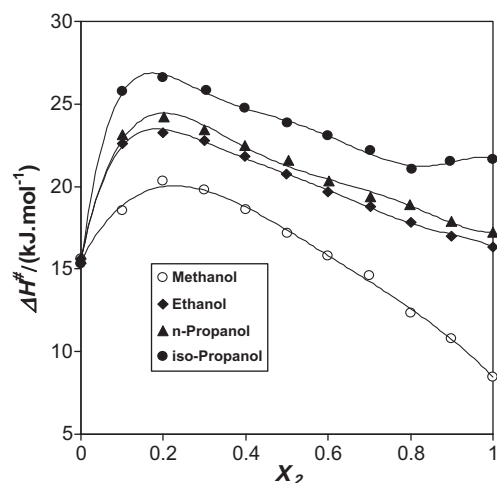
- $\Delta H^{\ddagger E}$  values rise sharply on the addition of alcohols and show pronounced maxima in the aqueous SDS regions and then decline gradually.
- $\Delta H^{\ddagger E}$  values are positive but  $\Delta S^{\ddagger E}$  values are negative for the whole composition range.
- $\Delta S^{\ddagger E}$  values decrease on the addition of alcohols and show minima and then increases gradually.
- The order of increment of  $\Delta H^{\ddagger E}$  in the aqueous SDS region is as follows:

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

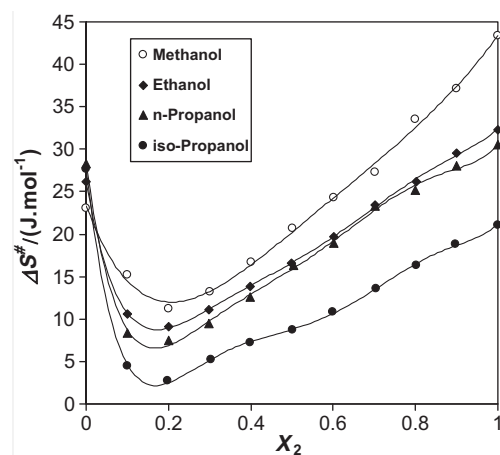
**Table 7** Change of enthalpy ( $\Delta H^\#$ ), excess enthalpy ( $\Delta H^{\#E}$ ), Entropy ( $\Delta S^\#$ ) and excess entropy ( $\Delta S^{\#E}$ ) of Methanol, Ethanol, *n*-Propanol, *iso*-Propanol + 0.01 M SDS systems.

$X_2$	$\frac{\Delta H^\#}{\text{kJ.mol}^{-1}}$	$\frac{\Delta H^{\#E}}{\text{kJ.mol}^{-1}}$	$\frac{\Delta S^\#}{\text{kJ.mol}^{-1}}$	$\frac{\Delta S^{\#E}}{\text{kJ.mol}^{-1}}$
<i>Methanol + 0.01 M SDS</i>				
0.0000	15.5953	0.0000	23.1209	0.0000
0.1002	18.5226	3.6413	15.2000	-8.9799
0.2000	20.3459	6.1758	11.2438	-15.9257
0.3001	19.7945	6.3377	13.1686	-16.0273
0.4006	18.6259	5.8854	16.6553	-14.5750
0.5012	17.1893	5.1657	20.6350	-12.6318
0.6006	15.8037	4.4881	24.3150	-10.9631
0.7012	14.5965	3.9981	27.2592	-10.0562
0.8004	12.3189	2.4275	33.5625	-5.7610
0.8991	10.8099	1.6218	37.1105	-4.2110
1.0000	8.4690	0.0000	43.3641	0.0000
<i>Ethanol + 0.01 M SDS</i>				
0.0000	15.5953	0.0000	26.1405	0.0000
0.1005	22.5726	6.9520	10.6000	-18.1531
0.1997	23.2400	8.6312	9.1000	-22.4925
0.2992	22.8007	7.1300	11.1000	-17.6301
0.3989	21.8100	6.5008	13.8000	-16.1226
0.4988	20.7300	5.3462	16.6000	-13.0248
0.6005	19.6575	3.9108	19.7000	-9.1011
0.7019	18.7586	2.9863	23.4000	-7.0381
0.8017	17.8462	2.0487	26.2000	-4.8715
0.9002	17.0174	1.1950	29.5000	-2.8753
1.0000	16.3400	0.0000	32.3000	0.0000
<i>n-Propanol + 0.01 M SDS</i>				
0.0000	15.5953	0.0000	28.3508	0.0000
0.1006	23.1300	6.6360	8.4000	-16.3975
0.2005	24.2400	6.7972	7.5000	-15.7181
0.2991	23.4600	6.4218	9.5000	-14.7487
0.3990	22.5000	5.8721	12.6000	-13.6549
0.5026	21.5700	4.8723	16.3000	-11.2893
0.6011	20.3428	3.7803	19.0000	-8.6269
0.7022	19.3868	2.6616	23.2962	-5.9078
0.7993	18.9195	2.0381	25.2000	-4.7663
0.8998	17.9122	0.8690	28.0000	-1.8949
1.0000	17.2044	0.0000	30.5000	0.0000
<i>iso-Propanol + 0.01 M SDS</i>				
0.0000	15.5953	0.0000	27.6109	0.0000
0.1004	25.7468	9.7714	4.5000	-24.2565
0.1988	26.6000	8.8417	2.7000	-20.3821
0.3042	25.8400	7.7097	5.2000	-17.1141
0.3990	24.7400	6.9042	7.2389	-15.4666
0.5003	23.8500	5.6551	8.7611	-12.6989
0.6000	23.0500	4.2605	10.7933	-9.4410
0.7031	22.1600	2.6011	13.5950	-5.3717
0.8026	21.0509	0.6356	16.3000	-0.1769
0.8975	21.5428	0.5275	18.8000	-0.8235
1.0000	21.6634	0.0000	21.1000	0.0000

In order to explain this behavior similar to  $\Delta G^\#$  and  $\Delta G^{\#E}$ , hydrophobic hydration may be considered as the major cause in which it is assumed that in the very dilute solution a hydrophobic solute molecule is encaged by a network of highly structured water molecules. Studies on viscometric properties (Kipkemboi and Eastaer, 1994; Saleh et al., 2000) and FTIR spectrophotometric properties (Gojlo et al., 2005) of aqueous solutions of these alcohols unambiguously indicated that the studied alcohols are hydrophobic in nature. The bulkier



**Figure 3** Plots of enthalpy change ( $\Delta H^\#$ ) vs mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.01 M aqueous SDS system.



**Figure 4** Plots of entropy change ( $\Delta S^\#$ ) vs mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.01 M aqueous SDS system.

species so formed by hydrophobic hydration may be supposed to use large energy for their passage to activated state and hence the large positive  $\Delta H^{\#E}$  in the aqueous SDS regions. An investigation of the  $\Delta H^\#$  values of alcohols indicate that the  $\Delta H^\#$  of *iso*-Propanol is higher than that of studied other alcohol systems. It might be due to the structure of *iso*-Propanol in aqueous SDS, is much hydrophobic and more rigid than that of Methanol, Ethanol or *n*-Propanol requiring greater energy during the viscous flow. The  $\Delta H^\#$  values are positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. That is, the viscous flow is not thermodynamically favored for the systems studied. All these concepts can equally be applied to explain the positive values of excess free energy, excess enthalpy functions in the aqueous SDS regions of the present systems (Saleh et al., 2000).

In the solute rich region, on the other hand, the cage structures as mentioned above are thought to be destroyed completely, and new structures ensue. These structures could not

be understood clearly, but it is thought that some kind of centrosymmetric species are formed in highly alcohol rich region- a concept used to explain the fall of dielectric constant of aqueous branched alcohols in highly alcohol rich region (Kipkemboi and Easteal, 1994). These species possibly because of their spheroidal structure, are thought to face much less resistance to flow, and hence less energy of activation is required in this particular region of composition. The structural rearrangement that takes place in the activation process for the viscous flow in this region is believed to be associated with either loss or gain of some degree of structural order, resulting in a small increase or decrease of entropies as observed experimentally.

The value of entropy of activation,  $\Delta S^\ddagger$  for different systems is shown in Table 7. The  $\Delta S^\ddagger$  value is positive for all the systems studied here. The  $\Delta S^\ddagger$  measures the randomness or dis-orderness of the systems. The  $\Delta S^\ddagger$  values for the flow process are positive in all cases. A number of H-bonds formed between aqueous SDS and alcohol as a result of hydrophilic effect are also disrupted in the activation process, which is supposed to contribute to the positive  $\Delta S^\ddagger$ . The  $\Delta S^\ddagger$  decrease rapidly with alcohol concentration and show minima in the aqueous SDS rich region at 0.2–0.25 mol fraction of alcohol and then increases up to the pure state of alcohols. This indicates that the mixtures of alcohols with aqueous SDS are more ordered at 0.2–0.25 mol fraction of alcohols. The  $\Delta S^\ddagger$  value of *iso*-Propanol is lower than the studied other alcohols, also indicating that *iso*-Propanol is more organized in SDS solutions than other alcohols. It is found that the  $\Delta S^\ddagger$  values of flow process of SDS–alcohol systems are less than for alcohol–water systems. This also indicates that the environment of water–alcohol systems is more random than SDS–alcohol systems. The values of excess entropy of activation,  $\Delta S^{\ddagger E}$  for the studied systems are shown in Table 7. The  $\Delta S^{\ddagger E}$  value is negative for all the systems studied here.

#### 4. Conclusion

The studies on the solution properties of ternary mixtures of Methanol + 0.005 M SDS and 0.01 M aqueous SDS, Ethanol + 0.005 M SDS and 0.01 M aqueous SDS, *n*-Propanol + 0.005 M SDS and 0.01 M aqueous SDS and *iso*-Propanol + 0.005 M SDS and 0.01 M aqueous SDS solutions, show strong solute–solvent interactions in aqueous-SDS region, the aqueous SDS molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. The free energy ( $\Delta G^\ddagger$ ) increases with alcohol concentration and show maxima in the aqueous-SDS rich region. The position of maxima does not change with the variation of temperature. The shallow minima occurred at ~0.7–0.8 mol fraction of *iso*-Propanol at 303.15 K. This is due to the formation of “centrosymmetric” association. The excess free energy ( $\Delta G^{\ddagger E}$ ) and excess enthalpy ( $\Delta H^{\ddagger E}$ ) values are found to be positive and large in magnitude, indicating that the aqueous solutions of alcohols are highly non ideal. The  $\Delta H^\ddagger$  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  $\Delta S^\ddagger$  values decrease on the addition of alcohols and show a minima and then increases gradually. A hydrophobic hydration and hydrogen bonds formed as a result of hydrophilic effect are also disrupted in the activation process, which is supposed to contribute the positive  $\Delta S^\ddagger$ . The  $\Delta S^{\ddagger E}$  indicates that the mixture

of alcohols with aqueous SDS is more ordered at 0.2–0.3 mol fraction of alcohols. The thermodynamic data are consistent with the volumetric and viscometric properties data. Although the value of free energy,  $\Delta G^\ddagger$  of the studied systems in pre-micellar and post-micellar aqueous SDS solutions (0.005 M SDS and 0.01 M SDS) is higher than the pure water solutions, but the nature of curves are almost similar as to SDS systems.

#### Acknowledgement

We are grateful for the financial support by the CASR of Khulna University of Engineering & Technology (KUET), Bangladesh in the form of Research Project.

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