

# Volumetric and viscometric studies on dodecyltrimethylammonium bromide in aqueous and in aqueous amino acid solutions in premicellar region

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**Abstract** The densities and viscosities of dodecyltrimethylammonium bromide (DTAB), glycine, and *rac*-alanine in water and DTAB in glycine/alanine aqueous solutions have been determined at 288.15, 296.15, 304.15, 312.15, and 320.15 K. The apparent molar volumes ( $\varphi_v$ ) were obtained from these density data. The limiting apparent molar volumes ( $\varphi_v^0$ ) and experimental slopes ( $S_v$ ) were derived from the Masson equation and interpreted in terms of solute–solute and solute–solvent interactions. The sign of  $[\delta^2(\varphi_v^0)/\delta T^2]_p$ , which corresponds to structure-making or structure-breaking properties of solutes, was determined. The viscosity coefficients *A*, *B*, and *D* were obtained from viscosity data on the basis of the Jones–Dole equation. Glycine/alanine in aqueous solutions exhibit structure-breaking behavior. In premicellar region, DTAB in aqueous solutions exhibits structure-breaking behavior, and DTAB in aqueous glycine/alanine solutions exhibits structure-making behavior. The free energy, enthalpy, and entropy of activation were calculated using the Nightingale and Benck, and Eyring equations. The values of  $(\Delta\mu_1^\ddagger - \Delta\mu_0^\ddagger)$  for solutions were calculated. The effects of solutes on the structure of water were interpreted in terms of viscosities and the thermodynamic parameters.

**Keywords** Apparent molar volume · Partial molar volume · Viscosity coefficient · Activation parameter

## Introduction

Volumetric, viscometric, and other thermodynamic data provide valuable information regarding solute–solvent, solute–solute, and solvent–solvent interactions [1, 2]. Although volumetric, viscometric, and related thermodynamic parameter values in binary systems are abundantly available, data on ternary systems are limited. Physicochemical studies on aqueous ternary systems are gaining importance, because sometimes it is difficult to arrive at a definite conclusion regarding structure and properties of solutions from studies on binary systems alone. DTAB–water and amino acid–water mixtures are of great importance in protein stability and denaturation phenomena [3–10].

The effect of DTAB and amino acids on protein structure is now recognized to be more complex than simply disruption of hydrogen bonds and, in particular, causes the breaking of hydrophobic bonds [11–13]. The effects of added DTAB and amino acids upon the properties of water are continuously investigated in order to understand the mechanism of protein stability and denaturation by DTAB and amino acids. These effects are reported to be intimately connected with the local liquid structure [14, 15]. In this study we made an attempt to: (a) interpret the apparent and partial molar volume and the viscosity coefficients *A*, *B*, and *D* in terms of ion–ion, solute–solvent, and solute–solute interactions; (b) study the effect of DTAB on these interactions; (c) investigate the structure-making/breaking properties of the amino acids; and (d) discuss the species

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involved in viscous flow by their characteristic activation parameters  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ , and  $(\Delta\mu_1^\ddagger - \Delta\mu_0^\ddagger)$  in the pre-micellar region of DTAB.

## Results and discussion

Volumetric properties of glycine, alanine, and DTAB in aqueous solutions and DTAB in aqueous amino acid solutions were determined at 288.15, 296.15, 304.15, 312.15, and 320.15 K. The apparent molar volume ( $\varphi_v$ ) and partial molar volume of binary and ternary solutions are shown in Tables 1, 2, and 3 (alanine solution data are not shown because they are very similar to glycine data). The apparent molar volumes depend on solute

concentration as well as on temperature [16]. In aqueous glycine solutions, the apparent molar volumes show linear variation with concentration [17] (Fig. 1). Similar behavior was also seen in case of temperature rise. Comparatively higher apparent molar volumes ( $\varphi_v$ ) for DTAB in aqueous amino acid solutions are more progressively structure than in the aqueous system alone.

The variation of apparent molar volume of DTAB in aqueous and in aqueous amino acid solutions in the low-concentration region ( $\varphi_v - \sqrt{m}$  plots) shows a sudden change in the  $\varphi_v$  value at a particular molality (Figs. 2, 3). The apparent molar volume of DTAB in aqueous and in aqueous amino acid solutions may have two components, viz. the true size of the molecule and the free space between the molecules. In pre-micellar region, the

**Table 1** Concentration dependence of apparent molar volumes and partial molar volumes for glycine in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

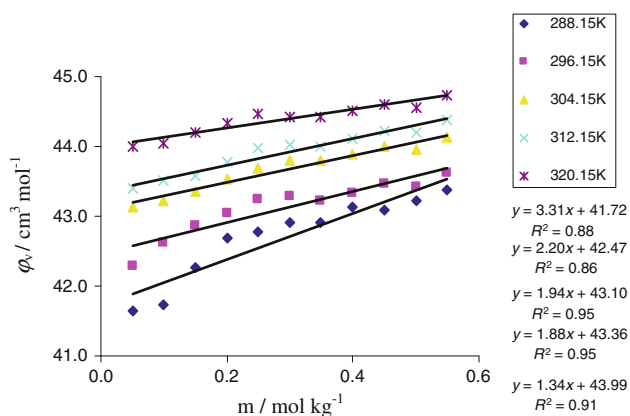
Conc. m (mol kg <sup>-1</sup> )	Apparent molar volume $\varphi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )					Partial molar volume $\bar{V}_2$ (cm <sup>3</sup> mol <sup>-1</sup> )				
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K
0.0499	41.51	42.29	43.14	43.39	44.00	41.56	42.36	43.48	43.48	44.06
0.1003	41.49	42.62	43.23	43.51	44.04	41.58	42.78	43.68	43.68	44.15
0.1501	41.90	42.88	43.35	43.57	44.21	42.04	43.10	43.83	43.83	44.37
0.1997	42.20	43.05	43.54	43.77	44.32	42.38	43.35	44.11	44.11	44.54
0.2504	42.17	43.24	43.68	43.98	44.47	42.40	43.62	44.40	44.40	44.74
0.2998	42.19	43.29	43.81	44.02	44.42	42.47	43.74	44.53	44.53	44.75
0.3486	42.07	43.23	43.80	44.00	44.43	42.40	43.76	44.59	44.59	44.80
0.3985	42.18	43.34	43.89	44.11	44.52	42.55	43.94	44.79	44.79	44.95
0.4498	42.00	43.46	43.99	44.22	44.60	42.42	44.14	44.99	44.99	45.09
0.4998	42.03	43.42	43.95	44.19	44.56	42.50	44.17	45.04	45.04	45.10
0.5488	42.07	43.61	44.13	44.38	44.74	42.58	44.44	45.31	45.31	45.33

**Table 2** Concentration dependence of apparent molar volumes and partial molar volumes for DTAB in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

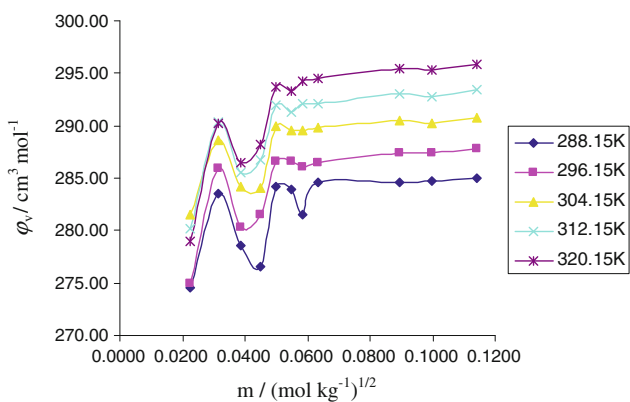
Conc. m (mol kg <sup>-1</sup> )	Apparent molar volume $\varphi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )					Partial molar volume $\bar{V}_2$ (cm <sup>3</sup> mol <sup>-1</sup> )				
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K
0.0005	274.56	274.93	281.52	280.19	278.96	275.62	276.32	282.89	282.19	281.78
0.0010	283.57	285.98	288.58	290.34	290.20	284.99	287.70	290.17	292.50	293.15
0.0015	278.55	280.28	284.21	285.60	286.45	280.29	282.39	286.14	288.25	290.02
0.0020	276.55	281.45	284.03	286.78	288.15	278.54	283.83	286.20	289.70	292.04
0.0025	284.16	286.58	289.99	291.96	293.67	286.35	289.16	292.24	294.99	297.67
0.0030	283.89	286.64	289.58	291.34	293.26	286.29	289.45	292.02	294.63	297.58
0.0034	281.49	286.03	289.58	292.12	294.22	284.04	289.01	292.15	295.56	298.73
0.0040	284.55	286.47	289.83	292.10	294.53	287.30	289.67	292.59	295.78	299.35
0.0080	284.65	287.45	290.44	292.97	295.40	288.50	291.88	294.17	297.92	301.89
0.0100	284.71	287.44	290.25	292.83	295.27	289.01	292.36	294.38	298.31	302.45
0.0130	284.95	287.77	290.69	293.40	295.88	289.84	293.35	295.35	299.56	303.95

**Table 3** Concentration dependence of apparent molar volumes and partial molar volumes for DTAB in 0.25 m aqueous glycine solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

Conc. m (mol kg <sup>-1</sup> )	Apparent molar volume $\phi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )					Partial molar volume $\bar{V}_2$ (cm <sup>3</sup> mol <sup>-1</sup> )				
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K
0.0005	527.06	526.37	516.16	518.21	524.64	512.68	512.24	502.77	504.89	510.90
0.0010	342.66	341.33	342.19	345.26	352.56	322.32	321.34	323.26	326.42	333.13
0.0015	296.96	301.41	304.08	305.60	309.28	272.06	276.94	280.90	282.52	285.49
0.0020	296.30	299.27	300.93	302.77	307.27	267.54	271.01	274.16	276.12	279.79
0.0025	288.41	292.04	294.67	296.27	300.42	256.26	260.44	264.74	266.47	269.70
0.0030	273.93	276.66	278.55	281.59	285.45	238.71	242.05	245.76	248.95	251.80
0.0035	267.82	272.46	274.43	276.25	280.22	229.78	235.07	239.01	241.00	243.87
0.0040	272.12	275.25	278.05	280.25	283.85	231.45	235.28	240.19	242.56	244.99
0.0080	294.92	297.52	299.93	302.51	305.25	237.41	241.00	246.38	249.21	250.29
0.0099	289.79	292.66	295.32	297.84	301.03	225.81	229.79	235.75	238.55	239.89
0.0130	287.21	289.73	292.36	294.92	297.94	213.89	217.69	224.10	226.97	227.88

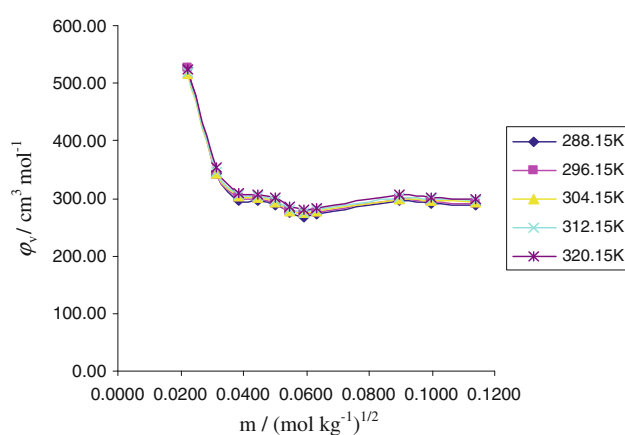


**Fig. 1** Plots of apparent molar volume versus molality of glycine in aqueous solutions at different temperatures



**Fig. 2** Apparent molar volume versus (molality)<sup>1/2</sup> of DTAB in aqueous solutions at different temperatures

molecules exist as monomers, and the monomer-monomer interaction may account for  $\phi_v$  with concentration having the free space between the molecules [18].



**Fig. 3** Apparent molar volume versus (molality)<sup>1/2</sup> of DTAB in 0.25 m aqueous glycine solutions at different temperatures

For DTAB, glycine, and alanine in aqueous solutions, the value of  $\bar{V}_2$  increases with increasing molality and the value of  $\bar{V}_1$  slightly decreases. This suggests that ion-solvent interactions increase with increasing molality of the solute. On the other hand, DTAB in aqueous amino acid solutions shows the opposite effect.

The apparent molar volume at infinite dilution ( $\phi_v^0$ ) was calculated using a least-squares fit to the linear plots of experimental values of  $\phi_v$  versus the square root of molar concentration ( $\sqrt{m}$ ) using the Masson equation [19]:

$$\phi_v = \phi_v^0 + S_v \sqrt{m}, \tag{1}$$

where  $S_v$  is the experimental slope, which is sometimes considered to be the volumetric pairwise interaction coefficient [20, 21]. The limiting apparent molar volume ( $\phi_v^0$ ) and  $S_v$  values along with standard errors are given in Table 4. It is evident from the table that the values of  $S_v$  are positive for DTAB in water at different temperatures. Since

**Table 4** Limiting apparent molar volumes ( $\phi_v^0$ ) and experimental slopes ( $S_v$ ) for binary and ternary solutions at different temperatures

System	Temperature (K)	$\phi_v^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (cm <sup>3</sup> dm <sup>3/2</sup> mol <sup>-1</sup> )	$[\delta^2 \phi_v^0 / \delta T^2]_p$
DTAB + water	288.15	276.93 ( $\pm 5.36E-04$ )	84.52 ( $\pm 2.06E-02$ )	-1.2428 ( $\pm 8.57E-07$ )
	296.15	279.14 ( $\pm 4.79E-04$ )	94.55 ( $\pm 1.86E-02$ )	
	304.15	283.87 ( $\pm 4.32E-04$ )	75.66 ( $\pm 1.67E-02$ )	
	312.15	284.54 ( $\pm 3.73E-04$ )	99.39 ( $\pm 1.49E-02$ )	
	320.15	284.41 ( $\pm 3.16E-04$ )	130.02 (1.34E-02)	
Glycine + water	288.15	41.72 ( $\pm 6.99E-03$ )	3.31 ( $\pm 8.19E-01$ )	-0.0928 ( $\pm 4.21E-04$ )
	296.15	42.47 ( $\pm 9.10E-03$ )	2.20 ( $\pm 7.84E-01$ )	
	304.15	43.10 ( $\pm 8.97E-03$ )	1.93 ( $\pm 7.75E-01$ )	
	312.15	43.36 ( $\pm 8.92E-03$ )	1.88 ( $\pm 7.75E-01$ )	
	320.15	43.99 ( $\pm 8.04E-03$ )	1.34 ( $\pm 7.73E-01$ )	
<i>rac</i> -Ala + water	288.15	58.64 ( $\pm 8.06E-03$ )	3.25 ( $\pm 6.00E-01$ )	-0.2828 ( $\pm 1.83E-04$ )
	296.15	59.76 ( $\pm 6.92E-03$ )	2.06 ( $\pm 5.92E-01$ )	
	304.15	60.54 ( $\pm 6.21E-03$ )	1.32 ( $\pm 5.88E-01$ )	
	312.15	60.66 ( $\pm 6.62E-03$ )	1.46 ( $\pm 5.89E-01$ )	
	320.15	61.12 ( $\pm 6.20E-03$ )	1.37 ( $\pm 5.87E-01$ )	
DTAB + 0.25 m Gly + water	288.15	390.52 ( $\pm 7.38E-04$ )	-1,286.07 ( $\pm 1.99E-02$ )	2.2186 ( $\pm 5.21E-06$ )
	296.15	391.67 ( $\pm 6.87E-04$ )	-1,263.80 ( $\pm 1.79E-02$ )	
	304.15	388.72 ( $\pm 6.16E-04$ )	-1,197.30 ( $\pm 1.60E-02$ )	
	312.15	390.64 ( $\pm 5.66E-04$ )	-1,191.80 ( $\pm 1.45E-02$ )	
	320.15	397.12 ( $\pm 5.41E-04$ )	-1,228.90 ( $\pm 1.29E-02$ )	
DTAB + 0.25 m <i>rac</i> -Ala + water	288.15	373.92 ( $\pm 7.07E-04$ )	-1,156.60 ( $\pm 2.22E-02$ )	0.7872 ( $\pm 2.50E-06$ )
	296.15	373.94 ( $\pm 6.57E-04$ )	-1,120.80 ( $\pm 2.04E-02$ )	
	304.15	375.81 ( $\pm 6.03E-04$ )	-1,111.10 ( $\pm 1.85E-02$ )	
	312.15	374.65 ( $\pm 5.44E-04$ )	-1,066.70 ( $\pm 1.68E-02$ )	
	320.15	378.94 ( $\pm 5.14E-04$ )	-1,085.80 ( $\pm 1.55E-02$ )	

$S_v$  is a measure of solute–solute/ion–ion interactions, the result indicates the presence of very strong ion–ion interactions. For DTAB in aqueous amino acid solutions, the values of  $S_v$  are negative, which indicates the very weak ion–ion interactions in this region.

The limiting apparent molar volume ( $\phi_v^0$ ), which is taken to be the partial molar volume at infinite dilution of DTAB in aqueous and in aqueous amino acid solutions, reflects the true volume of the solute and the volume change arising from solute–solvent interactions. The variation of  $\phi_v^0$  with the molality of DTAB can be rationalized in terms of the cosphere overlap model [22].

According to the model, the overlap of the cospheres of two ions or polar groups or an ion with that of a hydrophilic group always produces a positive volume change. On the other hand, the overlap of the cosphere of an ion with that of hydrophobic groups results in a negative volume change. On the overlap of the cospheres of DTAB–DTAB and DTAB–hydrophilic groups, zwitterionic interactions may take place. The overlap of the cospheres of DTAB gives a positive change in volume due to relaxation of the electrostricted water molecules due to strongly localized ion–zwitterion

interactions from the cospheres of amino acid and DTAB, which may cause an increase in volume [23].

The positive volume change due to the overlap of the cospheres of amino acids with those of the hydrophilic groups of DTAB outweighs the negative volume change due to the overlap of cospheres of amino acids and hydrophobic groups of DTAB (negligible), giving a greater  $\phi_v^0$  value in amino acid compared with that in water in this region (Table 4). The water–water and water–amino acid interactions are assumed to be the same and do not produce a considerable change in volume. An increase in the molality of DTAB increases the ion–zwitterion and also the DTAB–DTAB interactions, giving rise to increased  $\phi_v^0$  values.

The increase of  $\phi_v^0$  with temperature may be due to the result of the following effects [24]:

- (1) At higher temperature the thermal energy of the water molecules is increased, causing fast movement of the bulk electrostricted water molecules from the interaction region of  $(\text{CH}_3)_3\text{N}^+$  and  $-\text{COOH}$  groups, resulting in a positive volume change.

- (2) An increase in temperature decreases the DTAB–DTAB interaction, giving rise to a small negative volume change.
- (3) A decrease in DTAB–water interactions causes a positive volume change.
- (4) The water–water interactions decrease with increasing temperature, giving rise to a small negative change in volume.

In DTAB in aqueous and in aqueous amino acid solutions, the DTAB–DTAB and DTAB–zwitterion interactions increase, giving rise to an increased  $\phi_v^0$  value.

The  $\phi_v^0$  value of DTAB in ternary solution can alternatively be thought of as arising from four constituents [25]:

$$\phi_v^0 = V_w + V_f + V_n + V_s, \tag{2}$$

where  $V_w$  and  $V_f$  are van der Waals volumes [26] and volume of empty spaces present therein.  $V_n$  and  $V_s$  represent contributions due to hydrophobic and hydrophilic hydration.

**Table 5** Concentration dependence of viscosity for glycine in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

Conc. m (mol kg <sup>-1</sup> )	Viscosity $\eta$ (cP)				
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K
0.0499	1.137880	0.942678	0.793556	0.673591	0.580944
0.1003	1.147339	0.948971	0.797374	0.676478	0.582315
0.1501	1.150220	0.954667	0.802681	0.683000	0.587100
0.1997	1.165109	0.960280	0.808677	0.687347	0.591364
0.2504	1.167401	0.966909	0.813114	0.691004	0.595743
0.2998	1.172076	0.973330	0.819991	0.701196	0.599757
0.3486	1.186965	0.979896	0.825447	0.707964	0.608078
0.3985	1.192241	0.986627	0.829158	0.703235	0.607041

$V_w$  and  $V_f$  are assumed to be the same in aqueous amino acids as in water. The variation of  $\phi_v^0$  is therefore due to the change in ( $V_n + V_s$ ) resulting from DTAB–amino acid, amino acid–amino acid, and amino acid–water interactions; the contribution from water–water is assumed to be negligible.

The temperature dependence of the limiting apparent molar volume  $\phi_v^0$  for binary and ternary solution can be expressed by the expression

$$\phi_v^0 = a + bT + cT^2. \tag{3}$$

The sign of  $\left[\frac{\partial^2 \phi_v^0}{\partial T^2}\right]_p$ , i.e., the second derivative of the limiting apparent molar volume of the solution with respect to temperature at constant pressure, which correspond to structure-making or structure-breaking properties of solution, was determined [27]. For binary and ternary solutions, the values of  $\left[\frac{\partial^2 \phi_v^0}{\partial T^2}\right]_p$  are shown in Table 4.

Glycine, alanine, and DTAB in aqueous solutions show negative values of  $\left[\frac{\partial^2 \phi_v^0}{\partial T^2}\right]_p$ , indicating that glycine, alanine, and DTAB act as structure breakers for water solvent systems [28]. Similar information was reported by Devine and Lowe [29]. Again, the value of  $\left[\frac{\partial^2 \phi_v^0}{\partial T^2}\right]_p$  was found to be positive for DTAB in aqueous amino acid solutions, corresponding to structure-making property of water [27].

Viscosity properties of glycine and DTAB in aqueous and DTAB in aqueous amino acid solutions were measured at 288.15, 296.15, 304.15, 312.15, and 320.15 K. The relevant data are shown in Tables 5 and 6.

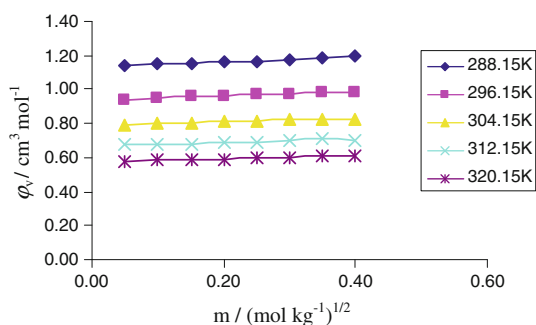
The representative curves (viscosity versus molality) for binary and ternary systems are linear and are shown in

**Table 6** Concentration dependence of viscosity for DTAB in aqueous and DTAB in 0.25 m glycine aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

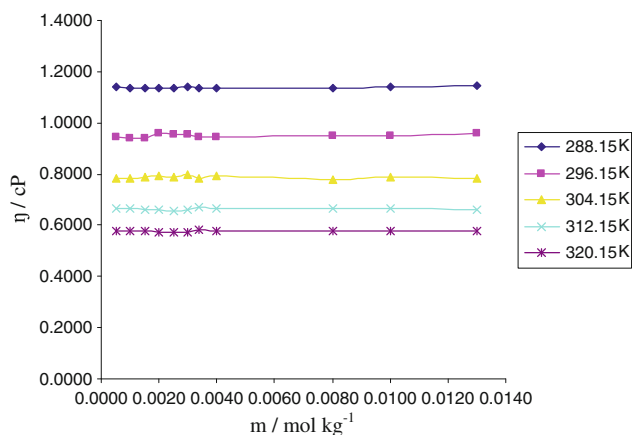
DTAB Conc. m (mol kg <sup>-1</sup> )	Viscosity $\eta$ (cP)					DTAB + 0.25 m glycine Viscosity $\eta$ (cP)				
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K
0.0005	1.140515	0.942544	0.780821	0.666754	0.578572	1.163237	0.966766	0.818132	0.685966	0.603104
0.0010	1.137853	0.940308	0.784959	0.664363	0.576847	1.174014	0.972239	0.817642	0.689824	0.598130
0.0015	1.137689	0.942212	0.787145	0.660770	0.576553	1.169530	0.977138	0.814032	0.688972	0.593354
0.0020	1.136180	0.957896	0.790749	0.660949	0.574375	1.169226	0.981347	0.820553	0.691945	0.593703
0.0025	1.135044	0.955332	0.789985	0.658062	0.573453	1.172392	0.976990	0.812960	0.693833	0.594558
0.0030	1.138992	0.954772	0.797780	0.661215	0.574824	1.180319	0.971528	0.817157	0.688168	0.593483
0.0034	1.134168	0.945214	0.782197	0.669451	0.582811	1.168365	0.972365	0.814383	0.686140	0.597807
0.0040	1.137100	0.946604	0.794392	0.663339	0.579485	1.174915	0.970780	0.814982	0.687410	0.583213
0.0080	1.136934	0.947222	0.780352	0.663789	0.578529	1.174910	0.970893	0.815146	0.682075	0.590829
0.0100	1.140350	0.951443	0.787082	0.667042	0.579036	1.176227	0.970982	0.821448	0.682591	0.592583
0.0130	1.144537	0.959352	0.783562	0.662832	0.576318	1.183795	0.972362	0.827889	0.683742	0.594707

Figs. 4, 5, and 6. The values of  $\eta$  increase with increase in molality and decrease with temperature. According to the “flickering cluster” [30] models of water, there are large void spaces within the hydrogen-bonded framework of the water structure. The linear increase of  $\eta$  with concentration may be interpreted by the fact that the molecules may have penetrated into the void spaces and may have a positive interaction with water.

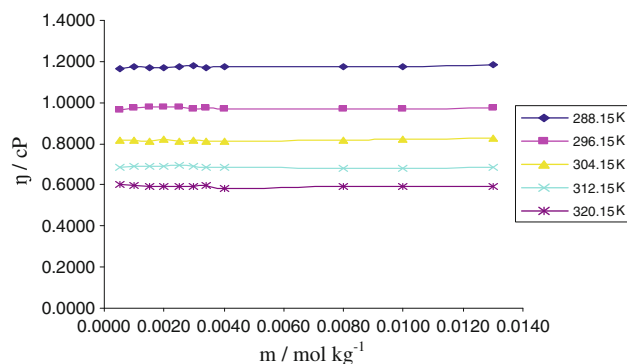
To calculate the viscosity coefficient  $B$ , the viscosity data were analyzed in terms of the semi-empirical Jones–Dole equation [31]. The viscosity coefficient  $B$  represents information regarding solute–solvent interaction and shape and size effect on the solvent structure [32, 33]. The calculated values of the  $B$  coefficient are presented in Table 7. The  $B$  coefficient values of the studied electrolyte in aqueous solutions are based on the fact that there exists around an ion a region of modified solvent differing from the bulk in structure and in properties. Gurney’s [34] co-sphere, Frank and Wens [30] A, B, and C zones, and Nightingale’s hydrated radius are recent reflections of this idea. From the above approaches, Kaminsky indicated that the observed viscosity changes result from competition



**Fig. 4** Viscosity versus molality of glycine in aqueous solutions at different temperatures



**Fig. 5** Viscosity versus molality of DTAB in aqueous solutions at different temperatures



**Fig. 6** Viscosity versus molality of DTAB in 0.25 m aqueous glycine solutions at different temperatures

between various effects occurring in the neighborhood of the ion. The viscosity of a dilute electrolyte solution can be equated to that of the solvent plus the contributions from four other sources in the following manner [35]:

$$\eta - \eta_0 = \Delta\eta^* + \Delta\eta^E + \Delta\eta^A + \Delta\eta^D, \quad (4)$$

where  $\Delta\eta^*$  is the positive increment in the viscosity caused by coulombic interactions, and  $\Delta\eta^E$  is the viscosity increment arising from the size and shape of an ion, which is closely related to the Einstein effect; it is always positive and normally increases with increasing ion size [36, 37].  $\Delta\eta^A$  is the increment due to the alignment or orientation of polar molecules by the ionic field. Since the freedom of movement of these molecules is restricted, this generally results in a “stiffening” of the solution, and the increment will again be positive.  $\Delta\eta^D$  is the viscosity change associated with distortion of the solvent structure leading to greater fluidity. This distortion can be thought of as due to competing forces from the solvent structure in the bulk and from the ionic field and/or the oriented molecules associated with the ion. In mixed solvents,  $\Delta\eta^D$  is of considerable magnitude due to significant distortion in the solvent molecules present in the vicinity of the ionic field [38].

Substituting equation (4) into the following Jones–Dole [21] equation one obtains

$$\eta - \eta_0 = \eta_0 (A\sqrt{C} + BC)$$

or

$$\Delta\eta^* + \Delta\eta^E + \Delta\eta^A + \Delta\eta^D = \eta_0 (A\sqrt{C} + BC). \quad (5)$$

Eliminating the contributions due to the ionic interaction from both sides we obtain

$$\Delta\eta^E + \Delta\eta^A + \Delta\eta^D = \eta_0 BC. \quad (6)$$

Thus, at a given concentration ( $C$ ), the coefficient  $B$  can be interpreted in terms of a competition between these specialized viscosity effects. The charged cations strongly orient with water molecules and in fact are believed to have

**Table 7** The viscosity coefficient values  $A/D$ ,  $B$ , and  $\left[\frac{dB}{dT}\right]$  for binary and ternary solutions as functions of temperature

System	Temperature (K)	$A$ (coefficient)	$B$ (coefficient)	$[dB/dT]$
DTAB + water	288.15	$-0.0894 (\pm 1.50E-03)$	$0.7710 (\pm 2.84E-04)$	$0.3707 (\pm 3.44E-04)$
	296.15	$0.3552 (\pm 9.87E-04)$	$-1.5858 (\pm 2.47E-03)$	
	304.15	$0.0898 (\pm 4.98E-04)$	$-0.1300 (\pm 1.12E-03)$	
	312.15	$-0.2788 (\pm 2.56E-03)$	$2.1265 (\pm 9.76E-04)$	
	320.15	$-0.0804 (\pm 1.45E-03)$	$0.7684 (\pm 2.86E-04)$	
DTAB + 0.25 m (aq) Gly	288.15	$-0.2114 (\pm 2.07E-04)$	$2.5888 (\pm 9.06E-06)$	$-0.0093 (\pm 3.55E-06)$
	296.15	$-0.2390 (\pm 1.04E-04)$	$2.7845 (\pm 6.58E-05)$	
	304.15	$-0.1010 (\pm 6.21E-04)$	$1.7190 (\pm 3.42E-04)$	
	312.15	$-0.5489 (\pm 1.06E-03)$	$4.0708 (\pm 5.58E-04)$	
	320.15	$-0.2329 (\pm 1.27E-04)$	$1.8993 (\pm 2.73E-04)$	
DTAB + 0.25 m (aq) Ala	288.15	$-0.2523 (\pm 2.08E-03)$	$4.6372 (\pm 2.57E-04)$	$-0.0196 (\pm 3.98E-05)$
	296.15	$-0.2758 (\pm 2.18E-03)$	$5.4044 (\pm 3.73E-04)$	
	304.15	$0.3495 (\pm 4.92E-04)$	$-2.9214 (\pm 1.74E-03)$	
	312.15	$0.1195 (\pm 4.90E-04)$	$0.3120 (\pm 9.21E-04)$	
	320.15	$0.1739 (\pm 2.57E-04)$	$6.4004 (\pm 6.26E-04)$	
Glycine + water	288.15	$0.1191 (\pm 1.13E-04)$	$0.0365 (\pm 1.59E-04)$	$0.0077 (\pm 2.16E-04)$
	296.15	$0.1162 (\pm 1.34E-04)$	$0.0401 (\pm 7.65E-05)$	
	304.15	$0.1274 (\pm 5.07E-05)$	$0.0192 (\pm 5.58E-04)$	
	312.15	$0.1848 (\pm 3.77E-04)$	$-0.0745 (\pm 2.72E-03)$	
	320.15	$0.1235 (\pm 7.97E-05)$	$0.0468 (\pm 7.78E-05)$	
Alanine + water	288.15	$0.0832 (\pm 6.04E-04)$	$0.1655 (\pm 1.11E-03)$	$0.0242 (\pm 2.56E-04)$
	296.15	$0.2526 (\pm 2.02E-04)$	$0.0406 (\pm 4.82E-04)$	
	304.15	$0.2391 (\pm 1.38E-04)$	$0.0092 (\pm 8.83E-04)$	
	312.15	$0.2906 (\pm 3.83E-04)$	$-0.0611 (\pm 1.78E-03)$	
	320.15	$0.1852 (\pm 1.19E-04)$	$0.1158 (\pm 4.76E-04)$	

a primary sheath of firmly attached molecules which moves with them as a kinetic entity [39].  $\Delta\eta^E$  will therefore be large because the ion plus primary sheath can be visualized as a single entity. It is also probable that, at room temperature, water molecules beyond this inner layer are oriented to some extent, giving positive  $\Delta\eta^A$ . The sum  $\Delta\eta^E + \Delta\eta^A$  will not outweigh the decrement due to  $\Delta\eta^D$ , because it is thought to be small for these ions and the fixed outward-pointing hydrogen atoms fit reasonably well into the tetrahedral water structure. Thus, in this case of ions,  $\Delta\eta^E + \Delta\eta^A \gg \Delta\eta^D$ , and the  $B$  coefficient is large and positive. The sign of  $\frac{dB}{dT}$ , i.e., the first derivative of the viscosity coefficient of  $B$  with respect to temperature, which corresponds to structure-making or structure-breaking properties of solutes, was determined [40]. The values of  $\frac{dB}{dT}$  are presented in Table 7.

For glycine, alanine, and DTAB in aqueous solutions the values of  $\frac{dB}{dT}$  are positive, which corresponds to structure-breaking behavior [41]. Although glycine and alanine have high values of  $B$ , the simplest amino acids are classified as

structure breakers [33, 42, 43]. It is seen that  $\frac{dB}{dT}$  is negative for DTAB in aqueous amino acid solutions, which indicates that DTAB acts as a structure maker in the aqueous amino acid solvent system [44].

The viscosity coefficient  $A$  represents the ion-ion interactions coupled with the size and shape effect of the solute and to some extent solute-solvent interactions. In this study, irregular variation in the values of  $A$  was found, which may be due to

- (1) Incomplete dissociation and ion association of electrolyte in aqueous and in aqueous amino acid solvent, and
- (2) The size of ions which differ in degree of hydration or solvation [45].

The decrease of  $A$  with rising temperature is probably due to greater thermal agitation and reduction of attractive forces between the ions. The increase in  $A$  value can be explained by the interpenetration effect, which brings the ions closer together [46]. It is found that more  $A$  coefficient

values are negative for DTAB in aqueous glycine solutions than in aqueous alanine solutions. This indicates that DTAB has less solute–solute interaction in the aqueous glycine solvent system. On the other hand the viscosity coefficient  $D$  also represents the solute–solute interaction, but it is related to nonelectrolyte solutions. In aqueous glycine and alanine solutions, the coefficient  $D$  shows negative values at 312.15 K (Table 7). The negative  $D$  contributions indicate that amino acid–amino acid interactions are decreased compared with amino acid–water interactions.

The thermodynamic properties of glycine, alanine, and DTAB in aqueous and DTAB in aqueous amino acid solutions were calculated at the mentioned temperatures using the Nightingale and Benck [47] and Eyring equations [48] and are shown in Tables 8, 9, and 10. The  $\Delta G^\ddagger$  value is positive for all the studied systems. The positive free energy of activation for viscous flow can be interpreted with the help of the Furth model [49], which states that the

kinetic species involved in forming cavities or holes in the liquid medium are given by the work required in forming the hole against surface tension of the solution. The solute–solvent interaction, interstitial incorporation, and hydrophilic hydration interaction render the binary and ternary aqueous systems more structured. This is reflected in the positive  $\Delta G^\ddagger$  value.

It is seen that the  $\Delta G^\ddagger$  value of glycine in aqueous solutions increases very slowly with increasing solute concentration and decreases with increasing temperature (Fig. 7). The slow increase in  $\Delta G^\ddagger$  for aqueous amino acid solutions indicates that the structure-destroying property is decreased with increasing solute concentration. Similar structure-making results have been reported by other authors as well [32, 50–52]. For aqueous DTAB solutions, overall decrease of  $\Delta G^\ddagger$  is shown with increasing solute concentrations at all studied temperatures. This indicates that DTAB acts as a structure breaker for the water system (Fig. 9).

**Table 8** Concentration dependence of activation parameters for viscous flow of glycine in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

Conc. m (mol kg <sup>-1</sup> )	Free energy $\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )					$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K		
0.0499	9.4346	8.9878	8.5807	8.1951	7.8485	22.3979	15.8745
0.1003	9.4573	9.0067	8.5953	8.2083	7.8572	22.7845	16.0085
0.1501	9.4662	9.0240	8.6141	8.2343	7.8799	22.2375	15.8621
0.1997	9.5000	9.0410	8.6350	8.2526	7.9003	22.5068	15.9671
0.2504	9.5075	9.0606	8.6512	8.2685	7.9211	22.1468	15.8746
0.2998	9.5199	9.0794	8.6744	8.3065	7.9402	21.6264	15.7401
0.3486	9.5528	9.0983	8.6933	8.3324	7.9762	21.3803	15.6934
0.3985	9.5664	9.1178	8.7071	8.3195	7.9752	22.1618	15.9377

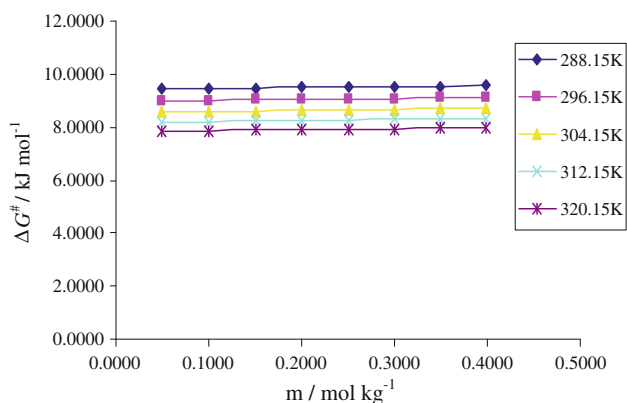
**Table 9** Concentration dependence of activation parameters for viscous flow of DTAB in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

Conc. m (mol kg <sup>-1</sup> )	Free energy $\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )					$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K		
0.0005	9.4424	9.2390	9.0182	8.8527	8.7107	23.3540	16.1548
0.0010	9.4371	9.2335	9.0319	8.8437	8.7031	23.4297	16.1750
0.0015	9.4371	9.2388	9.0392	8.8300	8.7021	23.6858	16.2524
0.0020	9.4342	9.2798	9.0511	8.8311	8.6924	24.2968	16.4466
0.0025	9.4322	9.2735	9.0491	8.8201	8.6885	24.4082	16.4754
0.0030	9.4408	9.2724	9.0742	8.8328	8.6952	24.2627	16.4415
0.0034	9.4309	9.2479	9.0246	8.8652	8.7322	22.4694	15.8934
0.0040	9.4375	9.2519	9.0642	8.8419	8.7175	23.2975	16.1475
0.0080	9.4397	9.2562	9.0218	8.8465	8.7160	23.4363	16.1833
0.0100	9.4481	9.2684	9.0449	8.8606	8.7198	23.4995	16.2148
0.0130	9.4588	9.2908	9.0356	8.8463	8.7094	24.4922	16.5165



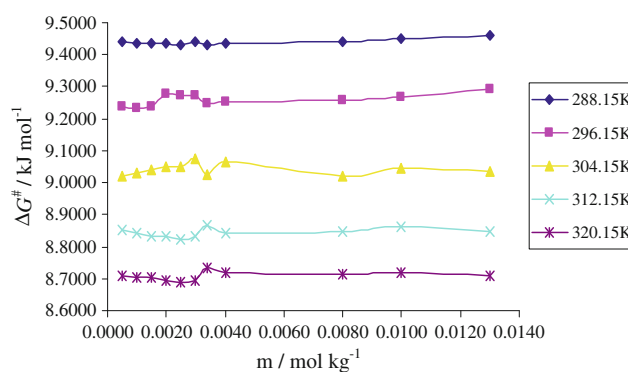
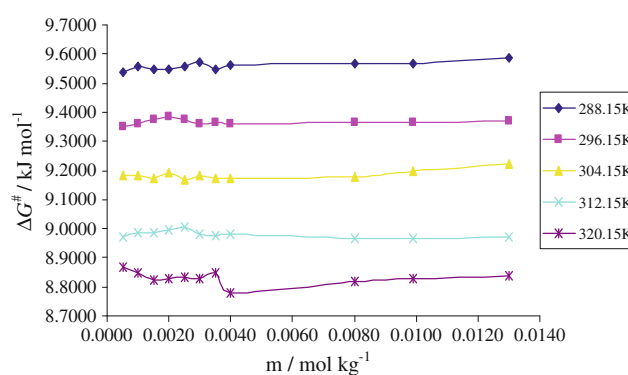
**Table 10** Concentration dependence of activation parameters for viscous flow of DTAB in 0.25 m glycine aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

Conc. m (mol kg <sup>-1</sup> )	Free energy $\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )					$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
	288.15 K	296.15 K	304.15 K	312.15 K	320.15 K		
0.0005	9.5362	9.3481	9.1830	8.9732	8.8681	21.3961	15.65952
0.0010	9.5585	9.3623	9.1817	8.9880	8.8462	22.4744	15.99311
0.0015	9.5495	9.3749	9.1707	8.9850	8.8251	22.9400	16.12851
0.0020	9.5492	9.3859	9.1913	8.9966	8.8270	22.8369	16.10609
0.0025	9.5560	9.3752	9.1680	9.0040	8.8312	22.7247	16.06876
0.0030	9.5724	9.3616	9.1813	8.9829	8.8266	23.3615	16.26074
0.0035	9.5482	9.3640	9.1730	8.9755	8.8463	22.3963	15.9635
0.0040	9.5620	9.3603	9.1752	8.9807	8.7807	24.1954	16.50107
0.0080	9.5649	9.3636	9.1788	8.9636	8.8186	23.6350	16.33571
0.0099	9.5687	9.3650	9.1996	8.9669	8.8279	23.4604	16.29143
0.0130	9.5861	9.3705	9.2215	8.9734	8.8397	23.5893	16.34311


**Fig. 7** Free energy of activation versus molality of glycine in aqueous solutions at different temperatures

For DTAB in aqueous glycine solutions, there is an overall increase of  $\Delta G^\ddagger$  with increasing DTAB concentration (Figs. 8, 9). This indicates that DTAB acts as a structure maker for H<sub>2</sub>O–amino acid solvent systems. The change may be attributed to the fact that  $\Delta G^\ddagger$  controls the rate of flow, which is governed by the slowest step in the fluid process. Similar structure-making results for electrolytes have been reported by other authors earlier [49, 53–55].

The variations of entropy of activation ( $\Delta S^\ddagger$ ) with the concentration of binary and ternary systems are noted in Tables 8, 9, and 10. The  $\Delta S^\ddagger$  values for the flow process are positive in all cases but do not follow any specific pattern. It is also found that the values of  $\Delta S^\ddagger$  for DTAB in the aqueous glycine system are higher than those in the aqueous alanine system, indicating that in the aqueous alanine system the DTAB is more structured than in the aqueous glycine system [51]. This corresponds to the structure-breaking property of solute. The positive values


**Fig. 8** Free energy of activation versus molality of DTAB in aqueous solutions at different temperatures

**Fig. 9** Free energy of activation versus molality of DTAB in 0.25 m aqueous glycine solutions at different temperatures

of  $\Delta H^\ddagger$  indicate that positive work has to be done to overcome the energy barrier for the flow process. That is, viscous flow is not thermodynamically favored for the systems studied. According to Freemantle and Lawrence

**Table 11** Change of chemical potential ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) for glycine in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

288.15 K		296.15 K		304.15 K		312.15 K		320.15 K	
Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )
0.0497	21.29	0.0497	21.56	0.0496	23.77	0.0494	32.50	0.0493	33.93
0.0998	21.22	0.0996	21.54	0.0994	23.70	0.0991	32.37	0.0988	29.09
0.1490	21.21	0.1488	21.51	0.1484	23.64	0.1480	32.22	0.1475	27.47
0.1978	21.18	0.1975	21.47	0.1971	23.59	0.1965	32.11	0.1959	26.62
0.2476	21.12	0.2471	21.43	0.2466	23.53	0.2458	31.99	0.2450	26.09
0.2958	21.06	0.2952	21.37	0.2946	23.47	0.2937	31.85	0.2928	25.69
0.3432	20.98	0.3426	21.31	0.3418	23.40	0.3408	31.71	0.3397	25.40
0.3915	20.93	0.3908	21.26	0.3899	23.34	0.3887	31.58	0.3875	25.17
0.4410	20.85	0.4401	21.21	0.4391	23.28	0.4378	31.46	0.4364	24.97
0.4891	20.79	0.4880	21.14	0.4868	23.20	0.4854	31.32	0.4838	24.79
0.5359	20.74	0.5347	21.11	0.5334	23.15	0.5319	31.21	0.5301	24.66

**Table 12** Change of chemical potential ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) for DTAB in aqueous solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

288.15 K		296.15 K		304.15 K		312.15 K		320.15 K	
Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )	Molarity	$(\Delta\mu_1^\# - \Delta\mu_0^\#)$ (kJ mol <sup>-1</sup> )
0.0005	139.00	0.0005	-178.93	0.0005	21.19	0.0005	344.23	0.0005	153.19
0.0010	140.16	0.0010	-177.48	0.0010	22.17	0.0010	345.47	0.0010	154.80
0.0015	139.46	0.0015	-178.32	0.0015	21.56	0.0015	344.59	0.0015	154.21
0.0020	139.16	0.0020	-178.22	0.0020	21.54	0.0020	344.56	0.0020	154.42
0.0025	140.13	0.0025	-177.58	0.0025	22.37	0.0025	345.09	0.0025	155.19
0.0030	140.06	0.0030	-177.63	0.0030	22.31	0.0030	344.81	0.0030	155.09
0.0034	139.72	0.0034	-177.76	0.0034	22.31	0.0034	344.75	0.0034	155.20
0.0040	140.08	0.0040	-177.77	0.0040	22.34	0.0040	344.51	0.0040	155.19
0.0080	139.81	0.0080	-178.12	0.0079	22.42	0.0079	343.02	0.0079	155.01
0.0100	139.68	0.0099	-178.36	0.0099	22.39	0.0099	342.21	0.0099	154.83
0.0129	139.50	0.0129	-178.67	0.0129	22.45	0.0129	341.10	0.0128	154.69

[32], the viscosity coefficient  $B$  is related to the difference in chemical potential for the flow of 1 mol of solute. The change in chemical potential values ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) indicates the solute–solvent interactions in the solution (shown in Tables 11, 12, 13). A positive and high value of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) indicates strong interaction between ions and solvents, whereas a low and negative value of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) indicates structure disorder [53]. Calculated values obtained from the  $B$  coefficient data for all systems studied are presented in Table 7. An examination of the data indicates that positive values of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) are obtained for glycine and alanine in aqueous solutions, corresponding to strong solute–solvent interaction. For DTAB in aqueous solvent systems the values of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) are negative at 296.15 K, indicating a weak interaction, and positive at 288.15, 304.15, 312.15, and

320.15 K, indicating a strong interaction between ion and solvent. For DTAB in amino acid solvent systems the values of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) are positive at the studied temperatures, indicating a strong interaction between ion and solvent.

However, for DTAB in the aqueous amino acid solvent system, the values of ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) decrease with increasing DTAB concentration. This indicates that the structure-disordering properties of DTAB increase in the amino acid solvent system.

## Conclusions

The studies on the solution properties of dodecyltrimethylammonium bromide, glycine, and *rac*-alanine in aqueous

**Table 13** Change of chemical potential ( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) for DTAB in 0.25 m aqueous glycine solutions at 288.15, 296.15, 304.15, 312.15, and 320.15 K

288.15 K		296.15 K		304.15 K		312.15 K		320.15 K	
Molarity	( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) (kJ mol <sup>-1</sup> )	Molarity	( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) (kJ mol <sup>-1</sup> )	Molarity	( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) (kJ mol <sup>-1</sup> )	Molarity	( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) (kJ mol <sup>-1</sup> )	Molarity	( $\Delta\mu_1^\# - \Delta\mu_0^\#$ ) (kJ mol <sup>-1</sup> )
0.0005	85.99	0.0005	68.44	0.0005	85.70	0.0005	55.76	0.0005	58.85
0.0010	61.61	0.0010	43.35	0.0010	61.53	0.0010	31.16	0.0010	33.83
0.0015	55.57	0.0015	37.94	0.0015	56.23	0.0015	25.52	0.0015	27.54
0.0020	55.48	0.0020	37.65	0.0020	55.79	0.0020	25.12	0.0020	27.25
0.0025	54.43	0.0025	36.66	0.0025	54.91	0.0025	24.19	0.0025	26.25
0.0030	52.51	0.0030	34.58	0.0030	52.67	0.0030	22.11	0.0030	24.08
0.0035	51.70	0.0035	34.01	0.0035	52.09	0.0035	21.35	0.0035	23.32
0.0040	52.27	0.0040	34.38	0.0040	52.59	0.0040	21.92	0.0040	23.84
0.0080	55.23	0.0080	37.38	0.0080	55.59	0.0080	25.07	0.0080	26.94
0.0099	54.54	0.0099	36.72	0.0099	54.93	0.0099	24.41	0.0098	26.33
0.0130	54.17	0.0130	36.31	0.0130	54.49	0.0130	23.99	0.0129	25.87

solution and DTAB in amino acid solutions (glycine/alanine) reveal the following:

- (1) DTAB + water: the behavior of DTAB in aqueous solution is temperature dependent. In pre-micellar region it appears to be a structure breaker for the water solvent system.
- (2) Glycine/*rac*-alanine + water: glycine and *rac*-alanine in aqueous solutions exhibit similar behavior. Both of the solutes act as structure breakers at all studied temperatures (15–47 °C).
- (3) DTAB + 0.25 m glycine/*rac*-alanine: DTAB in aqueous glycine solution acts as a structure maker in pre-micellar region at all temperatures studied.

## Experimental

The surfactant dodecyltrimethylammonium bromide (DTAB, purity  $\geq 98\%$ ) was purchased from Fluka, Switzerland; the reported critical micellar concentration (cmc) value of DTAB in water is close to 0.015 m at 25 °C. Glycine (mass fraction  $\geq 0.99$ ) and *rac*-alanine (mass fraction  $\geq 0.99$ ) were procured from Fluka chemical company, Switzerland. The chemicals were used without further purification. Supplied distilled water was redistilled and deionized by passing through two ion-exchange columns. The deionized water was distilled again in alkaline  $\text{KMnO}_4$  medium and was used for preparation of all solutions. Conductivity of this water was found to be 1.00  $\mu\text{S}$ . The cmc of DTAB in water was determined from conductance measurements. The concentration dependence of molar conductivity of aqueous solutions of DTAB was observed. The molar conductivity decreases with increasing DTAB concentration and shows a sharp break in its value

where micelles start to form, determined by extrapolating the molar conductivity data in the pre-micellar region to intersect with a straight line drawn through the data in the post-micellar region. The estimated cmc value thus obtained for DTAB is  $1.5 \times 10^{-2}$  mol  $\text{kg}^{-1}$  at 23 °C, in good agreement with the values reported earlier in literature [52, 56, 57].

An electric balance with accuracy of  $\pm 0.0001$  g was used for weighing. Viscosities of various liquids were measured using a calibrated Ostwald-type viscometer. The flow time of liquids was recorded by a timer able to read up to 0.01 s. Temperature was controlled by a water thermostat with accuracy of  $\pm 0.1$  °C. A densitometer (DSA-5000; Anton Paar, Austria) was used for density measurements.

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