

Volumetric, Viscometric and Refractive Index Behavior of Some α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

A. Ali* and Shahjahan

Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi-110 025, India

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Densities, ρ , viscosities, η , and refractive indices, n_D , of glycine (Gly), DL-alanine (Ala), DL-valine (Val) (0.05, 0.10, 0.15, 0.20, 0.25 mol kg⁻¹), and L-leucine (Leu) (0.02, 0.05, 0.10 mol kg⁻¹) in water and in 0.20 mol kg⁻¹ aqueous tetrapropylammonium bromide (TPAB) have been measured at 298.15, 303.15, 308.15, and 313.15 K. The density data have been utilized to calculate apparent molar volumes, ϕ_v , partial molar volumes at infinite dilution, ϕ_v° , and partial molar volumes of transfer, $\phi_{v(tr)}^\circ$ of amino acids. The viscosity data have been analyzed by means of Jones-Dole equation to obtain Falkenhagen coefficient, A , and Jones-Dole coefficient, B , free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{*o}$, and solute, $\Delta\mu_2^{*o}$, and enthalpy, ΔH^* , and entropy of activation, ΔS^* , of viscous flow. The refractive index data have been used to calculate molar refractivity, R_D , of amino acids in aqueous tetrapropylammonium bromide solutions. It has been observed that ϕ_v° , B -coefficient and $\Delta\mu_2^{*o}$ vary linearly with increasing number of carbon atoms in the alkyl chain of amino acids, and they were split to get contributions from the zwitterionic end groups (NH₃⁺, COO⁻) and methylene group (CH₂) of the amino acids. The behavior of these parameters has been used to investigate the solute-solute and solute-solvent interactions as well as the effect of tetrapropylammonium cation (C₃H₇)₄N⁺ on these interactions.

Keywords: Amino acids, Tetrapropylammonium bromide, Partial molar volume, A and B-coefficients, Activation parameters, Refractive index, Solute-solute and solute-solvent interactions

INTRODUCTION

Proteins are the biomolecules, which play a vital role in all the biochemical processes occurring in living organisms. Their behavior can be governed by their interactions with the surrounding environment. Due to the structural complexity of these biomolecules, direct thermodynamic study is somewhat difficult. Thus, amino acids are being extensively used as model compounds as they are structural units of proteins. The study of these model compounds in aqueous electrolytic media helps to understand the effects of electrolytes on the

biomolecules [1-6]. Most of these electrolytes studied in the earlier works possessed smaller ions of hydrophilic nature. The viscosity B -coefficients of these smaller ions suggested that they are weak structure-makers/structure-breakers [7]. On the other hand, the bulky tetraalkylammonium ions (R₄N⁺) have large positive values of B -coefficients and are strong structure-makers [7]. These ions with a weak field (low charge and large size) are identified as good models for studying hydrophobic interactions; such interactions play a vital role in the very existence of biological systems. The aqueous solutions of these electrolytes are found to be highly viscous [8], have high apparent molal heat capacities [9,10] and apparent molar volume [11] with peculiar activity coefficients

*Corresponding author. E-mail: anwar_jmi@yahoo.co.in

[12].

The present study is a continuation of our earlier work on the study of solute-solvent and solute-solute interactions of amino acids in mixed solvents [13-15]. Literature survey indicates that the study of amino acids in aqueous tetraalkylammonium bromides is rare. In their recent study, Badarayani and Kumar [16] reported the volumetric behavior of glycine, L-alanine and glycyglycine in aqueous tetraalkylammonium bromides (R_4NBr ; $R = CH_3, C_2H_5, C_4H_9$) at a single temperature, 298.15 K. These considerations led us to investigate the volumetric, viscometric and refractive index behaviors of Gly, Ala, Val, and Leu in aqueous tetrapropylammonium bromide ($(C_3H_7)_4NBr$) at different temperatures.

In this paper we report the experimental values of densities, viscosities and refractive indices of glycine, DL-alanine, DL-valine, and L-leucine in aqueous tetrapropylammonium bromide solution at 298.15, 303.15, 308.15, and 313.15 K. The density data has been utilized to obtain apparent molar volumes, ϕ_v . From apparent molar volumes, partial molar volumes, ϕ_v° and transfer molar volumes, $\phi_v^{\circ(tr)}$ of amino acids have been evaluated. The viscosity data have been used to obtain viscosity coefficients, A and B of Jones-Dole equation [17], the free energies of activation of viscous flow per mole of solvent, $\Delta\mu_1^{\circ*}$, and solute, $\Delta\mu_2^{\circ*}$, respectively; enthalpy, ΔH^* , and entropy of activation, ΔS^* , of viscous flow. The refractive index data have been used to compute molar refractivity, R_D , of the amino acid solutions. The side chain group contributions to ϕ_v° , B -coefficient and $\Delta\mu_2^{\circ*}$ have been reported based on the linear correlation of these properties with the number of carbon atoms in the alkyl chain of amino acids. The results have been discussed in terms of solute-solute and solute-solvent interactions in electrolytic media.

EXPERIMENTAL

Glycine (Merck, mass fraction 0.99), DL-alanine and DL-valine (both from Loba Chemie, mass fractions 0.99, and 0.996, respectively), and L-leucine (Thomas Baker, mass fraction 0.99) were used after recrystallization from ethanol-water mixtures and were dried in vacuum over P_2O_5 at room temperature for about 72 h. Analytical reagent grade

tetrapropylammonium bromide (Aldrich Chem. Co., mass fraction 0.98) was used after recrystallization in order to attain maximum purity and was dried in vacuum. All the solutions were prepared by weight. The 0.20 molal solution of tetrapropylammonium bromide in water was prepared and used as solvent to prepare 0.05, 0.10, 0.15, 0.20, and 0.25 mol kg^{-1} solutions of Gly, Ala, and Val and 0.02, 0.05, and 0.10 mol kg^{-1} solutions of Leu (as 0.10 mol kg^{-1} is the maximum solubility of Leu in 0.20 mol kg^{-1} TPAB), using doubly distilled and deionized water. The weighings were done on a Precisa XB-220A, Swiss made electronic balance with a precision of ± 0.0001 g. Great care was taken to prepare clear solutions. The solutions were stored in special airtight bottles to minimize absorption of atmospheric moisture and carbondioxide.

The densities of amino acid solutions were measured at 298.15, 303.15, 308.15, and 313.15 K using a single stem pycnometer made of Borosil glass with a bulb capacity 8×10^{-6} m^3 . The capillary had graduated marks and a well-fitted glass cap. The suspended level Ubbelohde viscometer [15] was employed for viscosity measurements. The viscosities were averaged from three readings for each solution. The calibration of both pycnometer and viscometer were done using doubly distilled water. The pycnometer and viscometer containing the test solution were allowed to stand for about 20 min in an electronically controlled (± 0.02 K) thermostated water bath (Julabo, Model: MD GMBH Germany), so as to minimize thermal fluctuations in the test solution. The accuracies in density and viscosity measurements were found to be ± 0.01 $kg\ m^{-3}$ and $\pm 3 \times 10^{-6}$ $N\ s\ m^{-2}$, respectively. Refractive index measurements were made with the help of thermostated Abbe-refractometer after calibrating it with distilled water and toluene at known temperatures. The uncertainty in the measured values of n_D was not more than ± 0.0002 unit.

RESULTS AND DISCUSSION

The measured densities, ρ , viscosities, η , and refractive indices, n_D , for amino acids in aqueous tetrapropylammonium bromide solutions at 298.15, 303.15, 308.15, and 313.15 K are presented in Tables 1, 2, and 3, respectively. The apparent molar volumes, ϕ_v of amino acids in ternary mixtures were

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Table 1. Densities, ρ , of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

<i>m</i>	ρ (kg m ⁻³)			
	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous TPAB				
0.00	1002.7	1001.1	999.4	997.8
0.05	1004.4	1002.8	1001.1	999.4
0.10	1006.0	1004.3	1002.6	1000.9
0.15	1007.4	1005.7	1003.9	1002.3
0.20	1008.7	1007.0	1005.2	1003.5
0.25	1009.9	1008.2	1006.4	1004.7
Ala + aqueous TPAB				
0.00	1002.7	1001.1	999.4	997.8
0.05	1004.3	1002.6	1000.9	999.3
0.10	1005.6	1004.0	1002.2	1000.6
0.15	1006.9	1005.2	1003.4	1001.8
0.20	1008.0	1006.3	1004.5	1002.9
0.25	1009.1	1007.4	1005.5	1003.9
Val + aqueous TPAB				
0.00	1002.7	1001.1	999.4	997.8
0.05	1004.1	1002.5	1000.8	999.2
0.10	1005.4	1003.8	1002.0	1000.3
0.15	1006.5	1004.9	1003.1	1001.4
0.20	1007.6	1005.9	1004.1	1002.4
0.25	1008.5	1006.8	1005.0	1003.3
Leu + aqueous TPAB				
0.00	1002.7	1001.1	999.4	997.8
0.02	1003.3	1001.7	1000.0	998.4
0.05	1004.1	1002.5	1000.7	999.1
0.10	1005.3	1003.6	1001.9	1000.3

Table 2. Viscosities, η , of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

<i>m</i>	η (10 ⁻³ N s m ⁻²)			
	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous TPAB				
0.00	1.0386	0.9206	0.8224	0.7406
0.05	1.0436	0.9243	0.8251	0.7425
0.10	1.0508	0.9305	0.8302	0.7468
0.15	1.0587	0.9369	0.8361	0.7517
0.20	1.0665	0.9439	0.8418	0.7568
0.25	1.0740	0.9507	0.8481	0.7629
Ala + aqueous TPAB				
0.00	1.0386	0.9206	0.8224	0.7406
0.05	1.0495	0.9289	0.8290	0.7458
0.10	1.0632	0.9406	0.8394	0.7542
0.15	1.0773	0.9526	0.8499	0.7637
0.20	1.0911	0.9648	0.8603	0.7731
0.25	1.1049	0.9772	0.8714	0.7828
Val + aqueous TPAB				
0.00	1.0386	0.9206	0.8224	0.7406
0.05	1.0597	0.9362	0.8339	0.7489
0.10	1.0859	0.9578	0.8530	0.7643
0.15	1.1131	0.9819	0.8734	0.7826
0.20	1.1386	1.0047	0.8928	0.7993
0.25	1.1659	1.0283	0.9141	0.8184
Leu + aqueous TPAB				
0.00	1.0386	0.9206	0.8224	0.7406
0.02	1.0444	0.9242	0.8246	0.7412
0.05	1.0629	0.9397	0.8382	0.7525
0.10	1.0972	0.9699	0.8646	0.7755

determined from density measurements using the following relation

$$\phi_v = \frac{M}{\rho} - \left[\frac{1000(\rho - \rho_0)}{m\rho\rho_0} \right] \quad (1)$$

where M , m , and ρ_0 are molar mass, molality of solute (amino acid), and density of the solvent (0.20 m aqueous TPAB), respectively. The calculated values of apparent molar volume,

ϕ_v are listed in Table 4.

The partial molar volume at infinite dilution, ϕ_v° is obtained by least-squares method using the relation

$$\phi_v = \phi_v^\circ + S_v^* m^{1/2} \quad (2)$$

where ϕ_v° is the apparent molar volume of amino acid at infinite dilution, which is the same as the partial molar volume, \bar{V}_2° . S_v^* is the experimental slope which is sometimes

Table 3. Refractive Indices, n_D , of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

m	n_D			
	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous TPAB				
0.00	1.3381	1.3377	1.3373	1.3371
0.05	1.3389	1.3385	1.3381	1.3379
0.10	1.3398	1.3394	1.3390	1.3388
0.15	1.3407	1.3403	1.3399	1.3397
0.20	1.3416	1.3412	1.3408	1.3406
0.25	1.3425	1.3421	1.3418	1.3415
Ala + aqueous TPAB				
0.00	1.3381	1.3377	1.3373	1.3371
0.05	1.3398	1.3394	1.3390	1.3386
0.10	1.3408	1.3404	1.3400	1.3396
0.15	1.3417	1.3413	1.3409	1.3405
0.20	1.3426	1.3422	1.3418	1.3414
0.25	1.3438	1.3434	1.3429	1.3425
Val + aqueous TPAB				
0.00	1.3381	1.3377	1.3373	1.3371
0.05	1.3400	1.3395	1.3393	1.3390
0.10	1.3412	1.3409	1.3405	1.3402
0.15	1.3424	1.3420	1.3417	1.3413
0.20	1.3436	1.3432	1.3430	1.3425
0.25	1.3451	1.3448	1.3444	1.3440
Leu + aqueous TPAB				
0.00	1.3381	1.3377	1.3373	1.3371
0.02	1.3393	1.3390	1.3386	1.3382
0.05	1.3406	1.3403	1.3400	1.3397
0.10	1.3432	1.3429	1.3425	1.3421

considered to be the volumetric pairwise interaction coefficient [18,19]. The partial molar volume provides information regarding solute-solvent interactions, whereas, S_v^* is indicative of solute-solute interactions. The evaluated values of ϕ_v° and S_v^* along with their standard errors, are summarized in Table 5. Table 5 shows that the observed values of ϕ_v° for Gly, DL-Ala, DL-Val, and L-Leu in aqueous solutions at 298.15/308.15 K are 43.25/43.79, 60.49/61.02, 90.96/91.55, and 107.78/108.41 $\text{cm}^3 \text{mol}^{-1}$, respectively, which compare

Table 4. Apparent Molar Volumes, ϕ_v° , of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

m	$\phi_v^\circ (10^{-5} \text{ m}^3 \text{ mol}^{-1})$			
	298.15 K	303.15 K	308.15 K	313.15 K
Gly + aqueous TPAB				
0.05	4.0583	4.0993	4.1706	4.2221
0.10	4.2306	4.2921	4.3440	4.3962
0.15	4.3765	4.4185	4.4743	4.5236
0.20	4.4861	4.5285	4.5915	4.6244
0.25	4.5893	4.6281	4.6834	4.7187
Ala + aqueous TPAB				
0.05	5.7927	5.8570	5.9219	5.9669
0.10	5.9833	6.0383	6.0939	6.1385
0.15	6.1079	6.1601	6.2196	6.2589
0.20	6.2164	6.2723	6.3239	6.3603
0.25	6.3187	6.3650	6.4241	6.4588
Val + aqueous TPAB				
0.05	8.8262	8.8798	8.9504	9.0066
0.10	8.9838	9.0340	9.0952	9.1612
0.15	9.1091	9.1531	9.2183	9.2764
0.20	9.2168	9.2630	9.3254	9.3874
0.25	9.3200	9.3738	9.4388	9.4830
Leu + aqueous TPAB				
0.02	10.2173	10.2530	10.3067	10.3489
0.05	10.3652	10.3955	10.4488	10.4814
0.10	10.5196	10.5525	10.5964	10.6296

well with the reported values 43.19 [20]/43.79 [21], 60.50 [20]/61.01 [21], 90.98 [21]/91.55 [21], and 107.74 [20]/108.44 [21] $\text{cm}^3 \text{mol}^{-1}$ for the corresponding amino acids.

The observed results in Table 5 show large positive ϕ_v° values for all the amino acids at all the temperatures studied, thereby, suggesting the presence of strong solute-solvent interactions. The increase in ϕ_v° values is in the order Gly < Ala < Val < Leu indicating the trend of the strength of solute-solvent interactions. It can be seen from the Table 5 that ϕ_v° values increase with temperature. The reduction in electrostriction occurs with increase in temperature, hence, an increase in ϕ_v° .

The S_v^* values (Table 5) for all the amino acids are found

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Table 5. Partial Molar Volumes, ϕ_v° , in Aqueous and Aqueous Tetrapropylammonium Bromide, Transfer Volumes, ϕ_v° , and S_v^* of α -Amino Acids at Different Temperatures

T (K)	ϕ_v° ($10^{-5} \text{ m}^3 \text{ mol}^{-1}$)		ϕ_v° ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)	S_v^* ($10^{-5} \text{ m}^3 \text{ mol}^{-2} \text{ kg}$)
	Expt.	Lit.		
	Aqueous Gly		Gly + aqueous TPAB	Gly + aqueous TPAB
298.15	4.3249 \pm 0.004	4.3240 ^a	3.6260 \pm 0.06	-6.9887
303.15	4.3535 \pm 0.002	–	3.6818 \pm 0.013	-6.7164
308.15	4.3787 \pm 0.006	4.3790 ^b	3.7545 \pm 0.005	-6.2429
313.15	4.4009 \pm 0.003	4.4000	3.8260 \pm 0.008	-5.7484
	Aqueous Ala		Ala + aqueous TPAB	Ala + aqueous TPAB
298.15	6.0494 \pm 0.006	6.0490 ^a	5.3778 \pm 0.012	-6.7162
303.15	6.0807 \pm 0.012	–	5.4519 \pm 0.009	-6.2867
308.15	6.1019 \pm 0.016	6.1010 ^b	5.5198 \pm 0.005	-5.8210
313.15	6.1247 \pm 0.021	6.1200	5.5751 \pm 0.007	-5.4960
	Aqueous Val		Val + aqueous TPAB	Val + aqueous TPAB
298.15	9.0966 \pm 0.010	9.0980 ^b	8.4239 \pm 0.009	-6.7273
303.15	9.1333 \pm 0.013	–	8.4769 \pm 0.018	-6.5648
308.15	9.1556 \pm 0.014	9.1550 ^b	8.5481 \pm 0.022	-6.0751
313.15	9.1677 \pm 0.030	9.1670	8.6184 \pm 0.010	-5.4928
	Aqueous Leu		Leu + aqueous TPAB	Leu + aqueous TPAB
298.15	1.0778 \pm 0.01	1.0777 ^a	9.9749 \pm 0.009	-8.0274
303.15	1.0808 \pm 0.003	–	10.0114 \pm 0.002	-7.9697
308.15	1.0841 \pm 0.013	1.0841 ^b	10.0746 \pm 0.009	-7.6633
313.15	1.0900 \pm 0.002	1.0900	10.1220 \pm 0.008	-7.7801

^aRef. [20]. ^bRef. [21].

to be positive but smaller than ϕ_v° values, suggesting the presence of weak solute-solute interactions with increase in temperature. The trend of S_v^* is Leu < Val < Ala < Gly which, in turn, supports the behavior of ϕ_v° .

In recent years, group additivity principle [15,22,23] is successfully applied to aqueous amino acid systems. It is found that ϕ_v° values of the studied homologous series of α -amino acids vary linearly with the number of carbon atoms in the alkyl chain of amino acids. Similar linear correlations have also been reported for α -amino acids [24,25], α -amino acids and glycine peptides in aqueous sodium dodecyl sulfate and cetyltrimethylammonium bromide [26], α - ω -amino acids in aqueous ammonium chloride [27], α -amino acids in aqueous calcium chloride [28], and for homologous series of

α - and α - ω -amino acids in guanidium chloride and potassium thiocyanate solutions [29]. This linear variation was represented by the relation

$$\phi_v^\circ = \phi_v^\circ(\text{NH}_3^+, \text{COO}^-) + n_c \phi_v^\circ(\text{CH}_2) \quad (3)$$

where n_c is the number of carbon atoms in the alkyl chain of amino acids. The linear regression analysis of the above equation at any given temperature gives $\phi_v^\circ(\text{NH}_3^+, \text{COO}^-)$, the zwitterionic end groups contribution and $\phi_v^\circ(\text{CH}_2)$, the methylene group contribution to ϕ_v° . It should be noted that $\phi_v^\circ(\text{CH}_2)$ values evaluated characterize the mean contribution of CH and CH₃ groups to ϕ_v° of α -amino acids. The results are summarized in Table 6. The alkyl chains of homologous series

Table 6. Contributions of (NH₃⁺, COO⁻), CH₂ Groups and other Alkyl Chains to Partial Molar Volumes, ϕ_v° and of (NH₃⁺, COO⁻) and CH₂ Groups to *B*-Coefficients and $\Delta\mu_2^{\circ*}$ of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

	<i>T</i> (K)			
	298.15	303.15	308.15	313.15
	$\phi_v^\circ (10^{-5} \text{ m}^3 \text{ mol}^{-1})$			
NH ₃ ⁺ , COO ⁻	2.1275	2.2003	2.2736	2.3448
CH	0.7872	0.7842	0.7834	0.7818
CH ₂	1.5744	1.5684	1.5669	1.5635
CH ₃	2.3616	2.3526	2.3503	2.3453
CH ₃ CH	3.1488	3.1368	3.1337	3.1271
CH ₃ CH ₃ CHCH	6.2976	6.2736	6.2675	6.2541
CH ₃ CH ₃ CHCH ₂ CH	7.8720	7.8420	7.8344	7.8176
	<i>B</i> (10 ⁻¹ dm ³ mol ⁻¹)			
NH ₃ ⁺ , COO ⁻	-0.00003	-0.0224	-0.0404	-0.0304
CH ₂	1.5128	1.5519	1.5715	1.5751
	$\Delta\mu_2^{\circ*}$ (kJ mol ⁻¹)			
NH ₃ ⁺ , COO ⁻	9.9586	9.6241	9.3509	9.4641
CH ₂	21.9070	22.7515	23.3506	23.7371

of α -amino acids investigated in this work are CH₂- (Gly), CH₃CH- (Ala), CH₃CH₃CHCH- (Val), and CH₃CH₃CHCH₂CH- (Leu). The contributions of these alkyl chains of α -amino acids to ϕ_v° were computed using the following relations proposed by Hakin *et al.* [30,31]

$$\phi_v^\circ(\text{CH}_3) = 1.5 \phi_v^\circ(\text{CH}_2) \quad (4)$$

$$\phi_v^\circ(\text{CH}) = 0.5 \phi_v^\circ(\text{CH}_2) \quad (5)$$

These results are also listed in Table 6. As can be seen from Table 6, $\phi_v^\circ(\text{NH}_3^+, \text{COO}^-)$ are larger than $\phi_v^\circ(\text{CH}_2)$ values and increase with temperature, thereby, suggesting that the interactions between zwitterionic end groups (NH₃⁺, COO⁻) and (C₃H₇)₄NBr are much stronger than those between methylene group (CH₂) and (C₃H₇)₄NBr.

The standard partial molar volumes of transfer of amino acids from aqueous to aqueous TPAB were computed using the equation

$$\phi_{v(ir)}^\circ = \phi_v^\circ(\text{aqueous TPAB}) - \phi_v^\circ(\text{water}) \quad (6)$$

The transfer volumes for all amino acids studied are also included in Table 5. From Table 5, it is observed that all the amino acids have negative $\phi_{v(ir)}^\circ$ values. It is well known that solute-solute interactions vanish at infinite dilution, hence, the transfer volumes observed are the result of solute-solvent interactions. In general, the interactions which might be occurring in the ternary mixtures (amino acids + aqueous TPAB) are:

- (i) ion-ion interactions between zwitterionic end groups (NH₃⁺, COO⁻) of amino acids and cations [(C₃H₇)₄N⁺]/anions (Br⁻) of (C₃H₇)₄NBr.
- (ii) ion-nonpolar group interactions between (NH₃⁺, COO⁻) and hydrophobic side chain -(C₃H₇)₄ of (C₃H₇)₄NBr, and between (C₃H₇)₄N⁺/Br⁻ and hydrophobic side chain of amino acids.
- (iii) nonpolar-nonpolar group interactions, i.e., the interactions involving hydrophobic side chains of amino acids and (C₃H₇)₄ of (C₃H₇)₄NBr.

The results can be explained on the basis of cosphere overlap model proposed by Friedman and Krishnan [32], which states that the effect of overlap of hydration cospheres is destructive.

Table 7. Falkenhagen Coefficients, A , Jones-Dole Coefficients, B , Free Energies of Activation per Mole of Solvent, $\Delta\mu_1^{\circ*}$, and Solute, $\Delta\mu_2^{\circ*}$, of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

T (K)	A ($10^{-2} \text{ dm}^{3/2} \text{ mol}^{-1/2}$)	B ($10^{-1} \text{ dm}^3 \text{ mol}^{-1}$)	$\Delta\mu_1^{\circ*}$ (kJ mol^{-1})	$\Delta\mu_2^{\circ*}$ (kJ mol^{-1})
Gly + aqueous TPAB				
298.15	-1.6608 ± 0.086	1.7033 ± 0.022	9.6504	34.2696
303.15	-2.0209 ± 0.029	1.7141 ± 0.007	9.5123	34.7193
308.15	-2.4508 ± 0.070	1.7325 ± 0.018	9.3850	35.3062
313.15	-2.8734 ± 0.019	1.7525 ± 0.051	9.2689	35.9372
Ala + aqueous TPAB				
298.15	-1.8214 ± 0.145	2.9312 ± 0.037	9.6504	52.6721
303.15	-2.5743 ± 0.060	2.9794 ± 0.015	9.5123	53.9229
308.15	-3.0164 ± 0.143	2.9882 ± 0.036	9.3850	54.6581
313.15	-3.6316 ± 0.077	3.0022 ± 0.019	9.2689	55.4667
Val + aqueous TPAB				
298.15	-3.2796 ± 0.300	5.5695 ± 0.077	9.6504	91.2720
303.15	-5.2695 ± 0.266	5.7520 ± 0.068	9.5123	94.8678
308.15	-6.6022 ± 0.269	5.7833 ± 0.069	9.3850	96.5161
313.15	-8.0259 ± 0.354	5.7919 ± 0.091	9.2689	97.8829
Leu + aqueous TPAB				
298.15	-7.3100 ± 0.023	7.9481 ± 0.009	9.6504	124.5045
303.15	-8.6864 ± 0.234	8.0872 ± 0.098	9.5123	128.0041
308.15	-9.7301 ± 0.091	8.1924 ± 0.038	9.3850	131.1301
313.15	-11.1695 ± 0.186	8.2334 ± 0.078	9.2689	133.4143

Further, Mishra *et al.* [33] used this model and observed that the overlap of cospheres of two ionic species produces an increase in volume, whereas, overlap of hydrophobic-hydrophobic groups and ion-hydrophobic groups results in net decrease in volume. In the light of the above facts, it is interpreted that interactions of type (ii) and (iii) contribute negatively to the volume transfer because of the reduced water structure that is formed around those groups as a result of cosphere overlap. Thus, it is evident from the observed results that the decrease in magnitude of transfer volumes is due to the dominance of ion-nonpolar and nonpolar-nonpolar interactions over ion-ion interactions.

The viscosity data were analyzed by means of Jones-Dole equation [17]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad (7)$$

where η_r is the relative viscosity, C is the molar concentration, η and η_0 are the respective viscosities of solution and solvent. A is the Falkenhagen coefficient, which accounts for solute-solute interactions and B , the Jones-Dole coefficient is empirical and is a measure of the structural modification induced by solute-solvent interactions [34]. The viscosity coefficients, A and B , were obtained from the intercepts and slopes of the plots $(\eta_r - 1)/C^{1/2}$ vs. $C^{1/2}$. The values of A and B are listed in Table 7.

Table 7 shows that B values are larger as compared to A values, supporting the behavior of ϕ_v° and S_v^* , respectively.

This again suggests the dominance of solute-solvent interactions over solute-solute interactions. Further, the magnitude of B -coefficient increases with increase in molar mass and size of alkyl side chain of amino acids. The B values reflect the net structural effects of charged end groups and hydrophobic CH_2 groups of amino acids. These effects can be separated by observing the linear relationship of B -coefficients with the number of carbon atoms, n_c in the amino acids [29,35,36]:

$$B = B(\text{NH}_3^+, \text{COO}^-) + n_c B(\text{CH}_2) \quad (8)$$

The contributions of charged end groups, $B(\text{NH}_3^+, \text{COO}^-)$ and that of methylene group, $B(\text{CH}_2)$ to B -coefficients are also included in Table 6. It is found that contribution of $B(\text{CH}_2)$ group to B -coefficients is greater than that of $B(\text{NH}_3^+, \text{COO}^-)$ groups. This further reinforces our findings based on $\phi_{v(tr)}$ values of the present amino acids.

Feakins *et al.* [37] proposed the transition state theory of relative viscosity, according to which B -coefficient was computed from the following relation

$$B = \frac{1}{1000} \left[\left(\bar{V}_1^0 - \bar{V}_2^0 \right) + \frac{\bar{V}_1^0 (\Delta\mu_2^{0*} - \Delta\mu_1^{0*})}{RT} \right] \quad (9)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of solvent (aqueous TPAB) and solute (amino acids), respectively.

Eyring and coworkers [38] used the following relation for calculating $\Delta\mu_1^{0*}$, the free energy of activation of viscous flow per mole of pure solvent

$$\eta_0 = \left(\frac{hN}{\bar{V}_1^0} \right) \exp \left(\frac{\Delta\mu_1^{0*}}{RT} \right) \quad (10)$$

which on rearrangement gives

$$\Delta\mu_1^{0*} = RT \ln \left(\frac{\eta_0 \bar{V}_1^0}{hN} \right) \quad (11)$$

The combination of equations (9) and (11) yields:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \left(\frac{RT}{\bar{V}_1^0} \right) [1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \quad (12)$$

where R is the universal gas constant and T is the absolute temperature, h is the Planck's constant and N is the Avogadro's number.

Table 7 also includes the values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ for the systems under study. The observed results in Table 7 show that $\Delta\mu_2^{0*}$ values are greater than $\Delta\mu_1^{0*}$ values for all the ternary solutions at all the temperatures studied, suggesting that the formation of the transition state is less favored in presence of electrolyte (TPAB) since it is accompanied by the breaking and distortion of intermolecular bonds. The $\Delta\mu_2^{0*}$ values are found to increase from Gly to Leu, indicating that the solvation of amino acid becomes unfavorable as the hydrophobic character of the side chain increases.

Like ϕ_v^0 and B -coefficient, $\Delta\mu_2^{0*}$ is also found to vary linearly with the number of carbon atoms in the alkyl chain of amino acids. The regression of $\Delta\mu_2^{0*} - n_c$ data using equation (13)

$$\Delta\mu_2^{0*} = \Delta\mu_2^{0*}(\text{NH}_3^+, \text{COO}^-) + n_c \Delta\mu_2^{0*}(\text{CH}_2) \quad (13)$$

gives $\Delta\mu_2^{0*}(\text{NH}_3^+, \text{COO}^-)$ and $\Delta\mu_2^{0*}(\text{CH}_2)$ contributions of the charged end groups and of methylene group to $\Delta\mu_2^{0*}$, respectively, and are included in Table 6 along with the side chain contributions to B -coefficients. It is observed that $\Delta\mu_2^{0*}(\text{CH}_2)$ values are larger than $\Delta\mu_2^{0*}(\text{NH}_3^+, \text{COO}^-)$ values and increase with increase in temperature, whereas, $\Delta\mu_2^{0*}(\text{NH}_3^+, \text{COO}^-)$ values exhibit reverse trend with temperature. This again supports that the presence of hydrophobic part of the amino acids does not favour their solvation in the transition state.

The free energy of activation of viscous flow of solutions, $\Delta\mu^{0*}$ was calculated by using the equation [39]

$$\Delta\mu^{0*} = n_1 \Delta\mu_1^{0*} + n_2 \Delta\mu_2^{0*} \quad (14)$$

where n_1 and n_2 are the number of moles of mixed solvent and solute, respectively. The enthalpy, ΔH^* and entropy, ΔS^* of activation of viscous flow were computed using the equation [40]

$$\Delta\mu^{0*} = \Delta H^* - T\Delta S^* \quad (15)$$

The values ΔH^* and ΔS^* are obtained from the intercepts and

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Table 8. Enthalpies, ΔH^* , Entropies, ΔS^* of Activation of Viscous flow and Molar Refractive Index, R_D , of α -Amino Acids in Aqueous Tetrapropylammonium Bromide at Different Temperatures

<i>m</i>	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	R_D (10 ⁻⁶ m ³ mol ⁻¹)			
			<i>T</i> (K)			
			298.15	303.15	308.15	313.15
Gly + aqueous TPAB						
0.00	3.4448	0.0051	3.9394	3.9415	3.9439	3.9481
0.05	3.4900	-0.0005	3.9478	3.9499	3.9524	3.9566
0.10	3.5344	-0.0061	3.9573	3.9594	3.9619	3.9662
0.15	3.5789	-0.0117	3.9668	3.9689	3.9715	3.9757
0.20	3.6234	-0.0173	3.9763	3.9784	3.9810	3.9852
0.25	3.6678	-0.0229	3.9858	3.9879	3.9915	3.9948
Ala + aqueous TPAB						
0.00	3.4448	0.0051	3.9394	3.9415	3.9439	3.9481
0.05	3.3678	-0.0040	3.9519	3.9541	3.9567	3.9589
0.10	3.2909	-0.0132	3.9631	3.9654	3.9680	3.9702
0.15	3.2139	-0.0223	3.9733	3.9755	3.9782	3.9804
0.20	3.1369	-0.0314	3.9835	3.9857	3.9884	3.9906
0.25	3.0600	-0.0405	3.9933	3.9956	3.9972	3.9995
Val + aqueous TPAB						
0.00	3.4448	0.0051	3.9394	3.9415	3.9439	3.9481
0.05	1.6390	-0.0164	3.9548	3.9559	3.9606	3.9639
0.10	-0.1667	-0.0379	3.9684	3.9716	3.9743	3.9776
0.15	-1.9724	-0.0594	3.9820	3.9842	3.9879	3.9902
0.20	-3.7781	-0.0808	3.9956	3.9972	4.0026	4.0038
0.25	-5.5838	-0.1023	4.0074	4.0107	4.0135	4.0158
Leu + aqueous TPAB						
0.00	3.4448	0.0051	3.9394	3.9415	3.9439	3.9481
0.02	2.3817	-0.0069	3.9502	3.9534	3.9559	3.9580
0.05	0.7871	-0.0248	3.9646	3.9678	3.9714	3.9746
0.10	-1.8706	-0.0546	3.9909	3.9941	3.9967	3.9989

slopes of the plots of $\Delta\mu^{\rho*}$ vs. T . These parameters contribute to the structural information regarding solute species and solute-solvent interactions. The results are summarized in Table 8.

It is observed from Table 8 that ΔH^* values show small decrease with increase in concentration of Ala, Val and Leu, while the reverse is observed for Gly. As expected, the values of ΔS^* are negative and show a pronounced decrease as the

concentration of amino acid in the mixture increases. This maybe due to the fact that the formation of the activated species necessary for viscous flow appears easy as the amount of solute increases in the mixture. Further, the values of ΔH^* and ΔS^* (Table 8) of amino acid + aqueous TPAB solutions at a given concentration of amino acid are much smaller than their values in aqueous amino acid solution. This implies that, in the presence of TPAB, the aqueous amino acid solution is

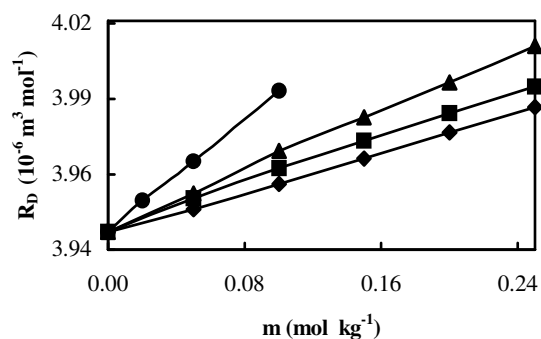


Fig. 1. Plots of R_D vs. concentration, m of amino acids (◆) Glycine, (■) DL-alanine, (▲) DL-valine, and (●) L-leucine in aqueous tetrapropylammonium bromide at 30 °C.

more structured during the viscous flow rather than in the initial state. This indicates the presence of significant solute-solvent interactions in the systems under investigation.

The molar refractivity, R_D , of the systems under study can be computed from the refractive index data using Lorentz-Lorenz equation

$$R_D = \left[\frac{(n_D^2 - 1)}{(n_D^2 + 2)} \right] \left(\frac{\sum_{i=1}^3 x_i M_i}{\rho} \right) \quad (16)$$

where x_i and M_i are the mole fraction and molecular weight of the i th component of the mixture, respectively. The values of R_D are included in Table 8 and the plots of R_D versus concentration are found to increase linearly with increasing amount of solute in aqueous tetrapropylammonium bromide. As R_D is directly proportional to molecular polarizability, Fig. 1 reveals that overall polarizability of the four systems under study increases with increasing amount of amino acid in the mixtures. This is in good agreement with the results reported by Ali *et al.* [15] for α -amino acids in aqueous D-glucose solution.

From the above reported results, it has been interpreted that the long chain hydrophobic electrolytes (tetraalkylammonium bromides) have strong interactions with the amino acids such as Gly, Ala, Val, and Leu. Due to this property these electrolytes are extensively employed in pharmaceuticals [41], softener for textile and paper products,

conditioners, algacides, detergents and others. Such study maybe extended to predict the properties of other amino acids, peptides and proteins in aqueous tetraalkylammonium bromides.

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