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Apparent Molar Volumes and Viscosity *B*-Coefficients of Some Amino Acids in Aqueous Tetramethylammonium Iodide Solutions at 298.15 K

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Apparent molar volumes and viscosity *B*-coefficients of glycine, L-alanine, and L-valine in 0.05, 0.10, and 0.15 mol·dm^{-3} aqueous tetramethylammonium iodide (TMAI) solutions have been determined at 298.15 K from density and viscosity measurements. The standard partial molar volumes, standard volumes of transfer, and hydration number of the amino acids have been calculated for rationalizing various interactions in the ternary solutions. It has been found that the partial molar volume and viscosity *B*-coefficient varies linearly with the number of carbon atoms in the alkyl chain of the amino acids, and they were split into contributions from charged end groups (NH_3^+, COO^-) and the CH_2- group of amino acids. Furthermore, the side chain contribution to the partial molar volume and viscosity *B*-coefficient of the amino acids has been determined using a group additivity approach. The results have been discussed in terms of ion−dipolar, hydrophobic−hydrophobic, and hydrophilic−hydrophobic group interactions.

Introduction

Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes.[1,2] Proteins are complex molecules, and their behavior in solutions is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interactions in systems containing smaller biomolecules, such as amino acids and peptides. Some studies[3,4] have revealed that the presence of an electrolyte drastically affects the behavior of amino acids in solutions, and this fact can be used for their separation and purification. Thermodynamic properties of amino acids in aqueous electrolyte solutions thus provide valuable information about solute−solvent and solute−solute interactions. Hence there has been a number of works[5−9] revealing the effect of electrolytic solutions on amino acids. Salts such as tetramethylammonium halides can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of proteins as these salts are known to influence macromolecular conformations by weakening attraction or repulsion of inter and intra charge−charge interactions and by affecting hydrophobic interactions through the side chain of the alkyl groups. Tetraalkylammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain.[10,11] Therefore, in this paper, an attempt has been made to unravel the various interactions prevailing in the ternary systems of amino acid + TMAI + water at 298.15 K.

Experimental Section

Materials. The amino acids glycine (Analar, BDH, purity > 99 %), L-alanine (S.D. Fine Chemicals, India, purity > 98.5 %), L-valine (Loba Chemie, India, purity > 99 %), and tetramethylammonium iodide (Thomas Baker, India, purity > 98 %) were used for the present study. The amino acids were

Table 1. Density, ρ, and Viscosity, η, of Different Aqueous TMAI Solutions at T = 298.15 K

aqueous TMAI solution	$\rho \cdot 10^{-3}$	η	
mol·dm^{-3}	kg·m^{-3}	mPa·s	pH
0.05	1.001	0.805	5.14
0.10	1.003	0.812	4.77
0.15	1.009	0.819	4.52

recrystallized from the methanol−water mixture and dried at 373.15 K for 12 h in an infrared drier and then in vacuo over P_2O_5 at room temperature. TMAI was purified by dissolving it in mixed alcohol medium and recrystallized from solvent ether medium. After filtration, the salt was dried in vacuo for a few hours. Triply distilled, degassed water with a specific conductance < 10^{-6} S·cm^{-1} was used for the preparation of different aqueous TMAI solutions. The physical properties of different aqueous TMAI solutions are listed in Table 1.

Apparatus and Procedure. A stock solution of each amino acid in different aqueous TMAI solutions was prepared by mass ,and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of the amino acid solutions is evaluated to ± 0.0001 mol·dm^{-3}.

Densities (ρ) were measured with an Ostwald−Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with a precision of ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurements was taken into account. The density values were reproducible to ± 3·10^{-4} g·cm^{-3}. The viscosity was measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water

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Table 2. Molarity, c, Density, ρ, Viscosity, η, Apparent Molar Volume, V_ϕ, and $(\eta_r - 1)/\sqrt{c}$ of Amino Acids in Aqueous TMAI Solutions at T = 298.15 K

c	ρ·10⁻³	η	V_φ·10⁶	(η_r − 1)	c	ρ·10⁻³	η	V_φ·10⁶	(η_r − 1)
mol· dm⁻³	kg· m⁻³	mPa· s	m³· mol⁻¹	√c	mol· dm⁻³	kg· m⁻³	mPa· s	m³· mol⁻¹	√c
				0.05ᵃ					
				Glycine					
0.0364	1.0021	0.814	44.80	0.060	0.1092	1.0044	0.825	43.89	0.078
0.0485	1.0025	0.816	44.10	0.063	0.1334	1.0052	0.829	43.54	0.084
0.0849	1.0037	0.822	43.22	0.073	0.1516	1.0057	0.832	44.02	0.087
				L-Alanine					
0.0297	1.0019	0.814	58.73	0.066	0.0892	1.0036	0.828	59.88	0.098
0.0396	1.0021	0.816	61.25	0.072	0.1090	1.0041	0.833	60.59	0.107
0.0693	1.0030	0.823	60.17	0.088	0.1238	1.0045	0.837	60.76	0.113
				L-Valine					
0.0235	1.0016	0.811	91.53	0.052	0.0704	1.0029	0.827	90.07	0.104
0.0312	1.0018	0.814	91.42	0.063	0.0860	1.0033	0.832	90.31	0.115
0.0547	1.0025	0.821	89.64	0.089	0.0977	1.0036	0.836	90.45	0.124
				0.10ᵃ					
				Glycine					
0.0356	1.0041	0.819	44.04	0.045	0.1066	1.0063	0.829	43.98	0.064
0.0474	1.0045	0.821	43.29	0.050	0.1304	1.0071	0.832	43.50	0.069
0.0829	1.0056	0.826	43.58	0.059	0.1481	1.0076	0.835	43.88	0.075
				L-Alanine					
0.0311	1.0039	0.821	59.97	0.062	0.0935	1.0056	0.836	61.10	0.096
0.0415	1.0042	0.823	59.99	0.069	0.1142	1.0062	0.841	60.89	0.104
0.0727	1.0051	0.831	60.02	0.086	0.1297	1.0067	0.845	60.38	0.111
				L-Valine					
0.0243	1.0037	0.820	88.08	0.064	0.0728	1.0050	0.837	89.41	0.115
0.0323	1.0039	0.823	89.02	0.076	0.0889	1.0054	0.843	89.88	0.129
0.0566	1.0045	0.832	90.38	0.101	0.1011	1.0058	0.848	89.19	0.139
				0.15ᵃ					
				Glycine					
0.0361	1.0098	0.825	44.21	0.039	0.1082	1.0120	0.835	44.19	0.060
0.0481	1.0102	0.826	43.51	0.044	0.1323	1.0128	0.838	43.70	0.065
0.0841	1.0113	0.831	43.77	0.053	0.1503	1.0133	0.840	44.08	0.069
				L-Alanine					
0.0296	1.0095	0.827	61.53	0.056	0.0889	1.0112	0.841	60.44	0.091
0.0395	1.0098	0.829	60.71	0.063	0.1087	1.0117	0.845	60.96	0.099
0.0691	1.0106	0.836	61.06	0.080	0.1235	1.0122	0.849	60.23	0.105
				L-Valine					
0.0214	1.0093	0.825	88.34	0.057	0.0642	1.0104	0.840	89.89	0.105
0.0285	1.0095	0.828	88.31	0.067	0.0785	1.0108	0.846	89.62	0.119
0.0500	1.0100	0.835	90.36	0.092	0.0892	1.0111	0.850	89.47	0.127

ᵃ = molarity of TMAI in water in mol·dm⁻³.

and purified methanol using density and viscosity values from the literature.[12–14] A thoroughly cleaned and perfectly dried viscometer filled with the experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The accuracy of the viscosity measurements, based on our work on several pure liquids, was ± 0.003 mPa·s. The details of the methods and measurement techniques have been described elsewhere.[15–17] The pH values of the experimental solvent and solutions were measured by a Systronics MK-VI 5631 digital pH meter, calibrated with a commercially available buffer capsule (Merck, India) of pH = 4.00 at 298.15 K. pH values of the aqueous TMAI solutions are listed in Table 1. Although pH ranges for glycine were found to be 5.20 to 5.78, 5.56 to 5.73, and 5.48 to 5.71, those for L-alanine were 5.80 to 6.08, 5.54 to 5.68, and 5.29 to 5.62 and those for L-valine were 5.72 to 5.82, 5.49 to 5.64, and 5.27 to 5.54 in 0.05, 0.10, and 0.15 mol·dm⁻³ aqueous TMAI solutions, respectively, at 298.15 K. Experimental values of molarity (c), densities (ρ), viscosities (η), and derived parameters at 298.15 K are listed in Table 2.

Results and Discussion

Apparent Molar Volume. Apparent molar volumes (V_ϕ) were determined from solution densities using the following equation[18]

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0} \tag{1}$$

where M is the molar mass of the solute; c is the molarity of the solution; and ρ_0 and ρ are the densities of the solvent (TMAI + water) and solution, respectively. The limiting apparent molar volumes or partial molar volumes (V_ϕ^0) at infinite dilution were calculated using a least-squares treatment of plots of V_ϕ vs $\sqrt{c}$ using the Masson equation[19]

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \tag{2}$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* is the experimental slope.

Values of V_ϕ^0 and S_V^* along with their standard errors are listed in Table 3, where values of V_ϕ^0 and S_V^* for the amino acids in pure water are adapted from the literature.[20,21] The parameter S_V^* is the volumetric virial coefficient, and it characterizes the pairwise interaction of solvated species in solution.[4,6,7,9] The sign of S_V^* is determined by the interaction between the solute species, and in the present study, S_V^* is found to be positive for the amino acids under investigation. For zwitterionic amino acids, the positive values of S_V^* suggest that the pairwise interaction is dominated by the interaction of the charged functional groups. The variation of S_V^* values with side chain of the amino acids indicates that the methyl group modulates the interaction of the charged end groups in the pairwise interaction.

The values of V_ϕ^0 are positive for all the amino acids under study in aqueous TMAI solutions at all the molarities studied. At each molarity, the V_ϕ^0 value varies linearly with the number of carbon atoms in the alkyl chain (R) of the amino acids. Similar correlations have been reported earlier by a number of workers,[20,21] and this linear variation can be represented as follows:

$$V_\phi^0 = V_\phi^0(NH_3^+, COO^-) + N_C V_\phi^0(CH_2) \tag{3}$$

where N_C is the number of carbon atoms in the alkyl chain of the amino acids and $V_\phi^0(NH_3^+, COO^-)$ and $V_\phi^0(CH_2)$ are the zwitterionic end group and methylene group contribution to V_ϕ^0, respectively. The values of $V_\phi^0(NH_3^+, COO^-)$ and $V_\phi^0(CH_2)$, calculated by a least-square regression analysis, are listed in Table 4, where those values in pure water are also provided from the literature.[24] It is well described in the literature[24] that $V_\phi^0(CH_2)$ obtained by this scheme characterizes the mean contribution of the CH− and CH₃− groups to V_ϕ^0 of the amino acids. The contribution of the other alkyl chains of the amino acids has been calculated using a scheme, as suggested by Hakin et al.[25,26]

$$V_\phi^0(CH) = 0.5 V_\phi^0(CH_2) \tag{4}$$

$$V_\phi^0(CH_3) = 1.5 V_\phi^0(CH_2) \tag{5}$$

and are listed in Table 4. Table 4 shows that the contribution of (NH₃⁺, COO⁻) to V_ϕ^0 is larger than that of the CH₂− group and increases with the increase in the concentration of the

Table 3. Standard Apparent Molar Volume, V_ϕ^0, and Experimental Slopes, S_V^*, for Amino Acids in Different Aqueous TMAI Solutions with Standard Errors at $T = 298.15$ K

amino acid	$V_\phi^0 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$				$S_V^* \cdot 10^6/(\text{m}^9 \cdot \text{mol}^{-3})^{1/2}$			
	0.00[a]	0.05[a]	0.10[a]	0.15[a]	0.00[a]	0.05[a]	0.10[a]	0.15[a]
glycine	43.19[20]	43.24 ± 0.03	43.40 ± 0.02	43.81 ± 0.04	0.864[20]	1.49 ± 0.01	1.12 ± 0.01	0.37 ± 0.02
L-alanine	60.12[21]	60.17 ± 0.01	60.46 ± 0.05	60.50 ± 0.02	0.778[21]	0.59 ± 0.02	0.47 ± 0.01	0.20 ± 0.06
L-valine	90.78[20]	90.21 ± 0.02	89.97 ± 0.04	89.61 ± 0.01	0.250[20]	0.23 ± 0.02	−1.48 ± 0.01	−0.27 ± 0.02

[a] = molarity of TMAI in water in mol·dm⁻³.

Table 4. Contribution of the Zwitterionic End Group (NH_3^+, COO^-), CH_2- Group, and Other Alkyl Chain Groups (R) to Standard Partial Molar Volume, V_ϕ^0, and Transfer Volumes, ΔV_ϕ^0, in Different Aqueous TMAI Solutions at $T = 298.15$ K

group	$V_\phi^0 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$				$\Delta V_\phi^0 \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$		
	0.00[a]	0.05[a]	0.10[a]	0.15[a]	0.05[a]	0.10[a]	0.15[a]
(NH_3^+, COO^-)	27.68[24]	28.22	28.64	29.25	0.54	0.96	1.57
CH_2-	15.91[24]	15.56	15.41	15.16	−0.35	−0.50	−0.75
CH_3CH-	31.82[24]	31.12	30.82	30.32	−0.70	−1.00	−1.50
CH_3CH_3CHCH-	63.64[24]	62.24	61.64	60.64	−1.40	−2.00	−3.00

[a] = molarity of TMAI in water in mol·dm⁻³.

Table 5. Contribution of the Alkyl Chain Group (R) to Standard Partial Molar Volume, $V_\phi^0(R)$, and Viscosity B-Coefficient $B(R)$ in Different Aqueous TMAI Solutions at $T = 298.15$ K

amino acid	$V_\phi^0(R) \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$			$B(R)/\text{m}^3 \cdot \text{mol}^{-1}$		
	0.05[a]	0.10[a]	0.15[a]	0.05[a]	0.10[a]	0.15[a]
L-alanine	16.93	17.06	16.69	0.127	0.125	0.122
L-valine	46.97	46.57	45.80	0.311	0.313	0.310

[a] = molarity of TMAI in water in mol·dm⁻³.

cosolute, which indicates that the interactions between the cosolute and charged end groups (NH_3^+, COO^-) of amino acids are much stronger that those between the cosolute and CH_2. Partial molar volumes of transfer of the zwitterionic end group, $\Delta V_\phi^0(NH_3^+, COO^-)$, and other alkyl chain groups, $\Delta V_\phi^0(R)$, of amino acids from water to cosolute solutions have been calculated as follows

$$\Delta V_\phi^0(NH_3^+, COO^-) \text{ or } \Delta V_\phi^0(R) = \Delta V_\phi^0(NH_3^+, COO^-) \text{ or }$$
$$\Delta V_\phi^0(R)[\text{in aqueous cosolute}] - \Delta V_\phi^0(NH_3^+, COO^-) \text{ or }$$
$$\Delta V_\phi^0(R)[\text{in water}] \quad (6)$$

and are included in Table 4. The contribution of (NH_3^+, COO^-) to ΔV_ϕ^0 is positive throughout the studied concentration range of the cosolute and increases with the increase in the concentration of the cosolute. The contribution of the alkyl chain groups to ΔV_ϕ^0 is negative for all the amino acids, and their contribution decreases with the increase in the number of carbon atoms.

The side chain contribution to the partial molar volume of the amino acids can be derived from the difference between the V_ϕ^0 values of each amino acid and that of glycine using the following scheme

$$V_\phi^0(R) = V_\phi^0(\text{amino acid}) - V_\phi^0(\text{glycine}) \quad (7)$$

where $V_\phi^0(R)$ defines the side chain contribution to V_ϕ^0 of the respective amino acid relative to the H-atom of glycine. In this scheme, it is assumed that the volume contribution of the H-atom in glycine is negligible. The results are listed in Table 5.

Hydration Number. The number of water molecules (N_H) hydrated to the amino acids can be estimated from the

Table 6. Hydration Number N_H of Amino Acids in Aqueous TMAI Solutions at $T = 298.15$ K

amino acid	N_H		
	0.05[a]	0.10[a]	0.15[a]
glycine	3.0	2.8	2.7
L-alanine	3.9	3.8	3.7
L-valine	3.9	4.0	4.1

[a] = molarity of TMAI in water in mol·dm⁻³.

electrostriction partial molar volume $V_\phi^0(\text{elect})$[20] using the relation

$$N_H = \frac{V_\phi^0(\text{elect})}{(V_e^0 - V_b^0)} \quad (8)$$

where V_e^0 is the molar volume of the electrostricted water and V_b^0 is the molar volume of bulk water. The value of $(V_e^0 - V_b^0)$ is calculated[20] to be -3.3 cm³·mol⁻¹ at 298.15 K. The $V_\phi^0(\text{elect})$ values can be calculated[27] from the intrinsic partial molar volumes of the amino acids, $V_\phi^0(\text{int})$,[28,29] and experimentally determined V_ϕ^0 values, as follows:

$$V_\phi^0(\text{amino acid}) = V_\phi^0(\text{int}) + V_\phi^0(\text{elect}) \quad (9)$$

The obtained N_H values are listed in Table 6, where N_H varies with the solvent composition, showing a tendency to decrease with an increase in the concentration of TMAI for the amino acids under investigation except L-valine. The observed decreasing tendency of N_H for glycine and L-alanine supports the view[30] that the TMAI has a dehydration effect on these amino acids in aqueous TMAI solutions. However, a slight increase of N_H for L-valine indicates that the increase in the interaction of hydrophobic groups of L-valine with those of the salt does not reduce the electrostriction of water molecules to it, but leads to a slight increase in the hydratuion number, N_H.

Standard Transfer Volume. The standard transfer volume of each amino acid, ΔV_ϕ^0, from pure water to aqueous TMAI solutions is defined by

$$\Delta V_\phi^0 = V_\phi^0(\text{amino acid} + \text{TMAI} + \text{water}) - V_\phi^0(\text{water}) \quad (10)$$

The results are illustrated in Figure 1 as a function of molarity of aqueous TMAI solutions. The value of ΔV_ϕ^0 is, by definition, free from solute–solute interactions and therefore provides information regarding solute–cosolute interactions.[9] Figure 1 shows that ΔV_ϕ^0 values are positive for all the amino acids under investigation except L-valine. This discrepancy among the amino acids can be explained by the co-sphere model, as developed by Friedman and Krishnan,[31] according to which the effect of overlap of the hydration co-spheres is destructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume, but that of hydration co-spheres of hydrophobic–hydrophobic groups and ion–hydrophobic groups results in a net volume decrease. As amino acids exist

Table 7. Viscosity A- and B-Coefficient for the Amino Acids in Aqueous TMAI Solutions with Standard Errors at T = 298.15 K

	$A/\text{m}^{3/2}\cdot\text{mol}^{-1/2}$			$B/\text{m}^3\cdot\text{mol}^{-1}$		
amino acid	0.05[a]	0.10[a]	0.15[a]	0.05[a]	0.10[a]	0.15[a]
glycine	0.033 ± 0.011	0.018 ± 0.005	0.011 ± 0.011	0.139 ± 0.011	0.144 ± 0.003	0.149 ± 0.003
L-alanine	0.019 ± 0.002	0.014 ± 0.003	0.010 ± 0.014	0.265 ± 0.010	0.269 ± 0.013	0.272 ± 0.006
L-valine	−0.016 ± 0.010	−0.007 ± 0.013	−0.010 ± 0.003	0.450 ± 0.005	0.457 ± 0.023	0.460 ± 0.012

[a] = molarity of TMAI in water in $\text{mol}\cdot\text{dm}^{-3}$.
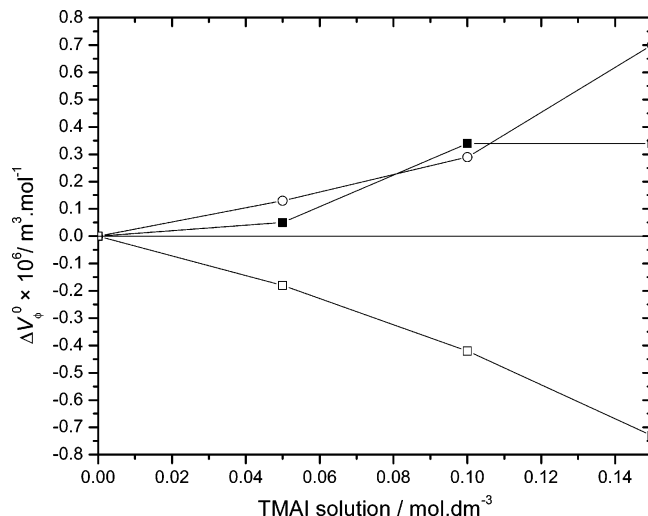
Figure 1. Transfer volume of amino acids from water to aqueous TMAI solutions ΔV_ϕ^0 at T = 298.15 K. Graphical points: ○, glycine; ■, L-alanine; □, L-valine.

predominantly as zwitterions in pure water and there is an overall decrease in volume of water due to electrostriction, the observed increasing positive volumes of transfer for glycine and alanine indicate that in the ternary solutions (amino acid + TMAI + water) the ion−hydrophilic and hydrophilic−hydrophilic group interactions predominate over the ion−hydrophobic and hydrophobic−hydrophobic groups interactions, and the contribution increases with the molarity of TMAI in solutions. However, the negative ΔV_ϕ^0 values for L-valine indicate that ion−hydrophobic and hydrophobic−hydrophobic interactions predominate over the ion−hydrophilic and hydrophilic−hydrophilic interactions. The observed trend can also be explained with the following equation[4,32]

$$V_\phi^0 = V_{VW} + V_V - V_S \tag{11}$$

where V_{VW} is the van der Waals volume; V_V is the volume associated with voids or empty space; and V_S is the shrinkage volume due to electrostriction. Assuming the V_{VW} and V_V have the same magnitudes in water and in aqueous TMAI solutions for the same class of solutes,[33] the observed positive ΔV_ϕ^0 values for glycine and L-alanine can be attributed to the decrease in the volume of shrinkage, whereas negative ΔV_ϕ^0 values for L-valine may be attributed to an increase in shrinkage volume due to its branched alkyl chain. Figure 1 shows that the ΔV_ϕ^0 values are in the order: glycine > L-alanine > L-valine. The introduction of a CH_3- group in L-alanine provides an additional tendency for hydrophobic−hydrophilic and hydrophobic−hydrophobic group interactions, and as a result, greater electrostriction of water is produced leading to smaller values of ΔV_ϕ^0. Similarly, when the H-atom of glycine is replaced by the $(CH_3)_2CH-$ group in L-valine, the additional propensity for hydrophobic−hydrophilic and hydrophobic−hydrophobic group interactions increases further and thus leads to negative ΔV_ϕ^0 values.

Table 8. Contributions of the Zwitterionic Group (NH₃⁺, COO⁻) and CH₂− Group to the Viscosity B-Coefficient in Aqueous TMAI Solutions at T = 298.15 K

	$B/\text{m}^3\cdot\text{mol}^{-1}$		
group	0.05[a]	0.10[a]	0.15[a]
(NH_3^+, COO^-)	0.077	0.076	0.074
CH_2-	0.087	0.089	0.092

[a] = molarity of TMAI in water in $\text{mol}\cdot\text{dm}^{-3}$.

Viscosity B-Coefficient. The experimental viscosity data for the systems studied are listed in Table 2. The relative viscosity (η_r) has been analyzed using the Jones−Dole equation[34]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \tag{12}$$

where η and η_0 are the viscosities of the ternary solutions (amino acid + TMAI + water) and binary solvents (TMAI + water) and c is the molarity of the amino acids in ternary solutions. A and B are empirical constants known as viscosity A- and B-coefficients, which are specific to solute−solute and solute−solvent interactions, respectively. Equation 12 can be rearranged as

$$\frac{(\eta_r - 1)}{\sqrt{c}} = A + B\sqrt{c} \tag{13}$$

Values of A- and B-coefficients are obtained from a linear plot of the left-hand side of eq 13 vs $\sqrt{c}$. The values of A- and B-coefficients are listed in Table 7. Due to the complex nature of A-coefficients, they are not discussed in the present work. Table 7 shows that B-coefficients are positive for all the amino acids and increase with the increase of the size of the side chains. The B-coefficients reflect the net structural effects of the charged groups and the hydrophobic CH_2- groups on the amino acids. As B-coefficients vary linearly with the number of carbon atoms of the alkyl chain (N_C), these two effects can be resolved as follows

$$B = B(NH_3^+, COO^-) + N_C B(CH_2) \tag{14}$$

The regression parameters, i.e., the zwitterionic group contribution, $B(NH_3^+, COO^-)$, and the methylene group contribution, $B(CH_2)$, to B-coefficients are listed in Table 8. It shows that $B(NH_3^+, COO^-)$ values decrease while $B(CH_2)$ values increase with increasing concentration of TMAI in ternary solutions, indicating that the zwitterionic groups break while the CH_2- group enhances the structure of the aqueous salt solutions.

The side chain contributions to B-coefficients, $B(R)$, have also been derived using the same scheme as that of $V_\phi^0(R)$ and are listed in Table 5, which shows that $B(R)$ values are positive and follow the order: L-valine > L-alanine. This order is due to the greater structure breaking tendency of L-valine as compared to L-alanine, and these findings are in line with our volumetric results discussed earlier.

Conclusion

In summary, the study reveals that although ion−ion or hydrophilic−hydrophilic group interactions are predominant for glycine and L-alanine, ion−hydrophobic or hydrophobic−hydrophobic group interactions are predominant for L-valine in aqueous TMAI solutions. These interactions are a function of the molarity of TMAI in the ternary solutions. Also, it is evident that TMAI has a dehydration effect on these amino acids in aqueous TMAI solutions. The size and number of carbon atoms of the alkyl chain groups of the amino acids also play a pivotal role in determining the nature and strength of the interactions in these solvent media.

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