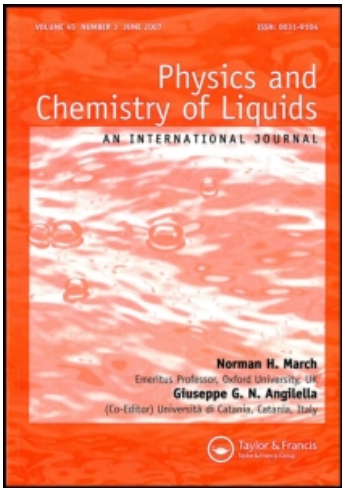

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Physicochemical investigation on interactions of some amino acids with aqueous tetra-butyl ammonium bromide solution at 298.15 K

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Physicochemical investigation on interactions of some amino acids with aqueous tetra-butyl ammonium bromide solution at 298.15 K

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Apparent molar volumes, viscosity *B*-coefficients, and apparent molar isentropic compressibilities of glycine, L-alanine, L-valine and L-leucine in 0.062, 0.125 and 0.256 mol kg^{-1} aqueous tetra-butyl ammonium bromide (TBAB) solution have been determined at 298.15 K from their experimental density, flow time and sound speed measurements, respectively. The standard partial molar volumes and compressibilities are used to calculate the corresponding volume of transfer at infinite dilution, from water to aqueous TBAB solutions. The linear correlation of partial molar volumes for a homologous series of amino acids has been utilised to calculate the contribution of charged end groups and other alkyl chains of the amino acids to partial molar volumes. The hydration numbers of amino acids have also been determined. Viscosity *B*-coefficients have been calculated using the Jones–Dole equation. The values of the charged end groups contribution to the viscosity *B*-coefficients of the amino acids are calculated.

Keywords: amino acid; tetra-butyl ammonium bromide; partial molar volumes; partial molar isentropic compressibilities; viscosity *B*-coefficients

1. Introduction

Amino acids are monomers that constitute proteins and are considered to be the model compounds of proteins. The behaviour of proteins in mixtures is highly influenced by many factors, such as pH, solvent properties, chemical structure and surface charge distribution of proteins, and type and concentration of the electrolyte. The influence of an electrolyte on the behaviour of a protein is an important topic in the physical chemistry of the substances. It has long been known that there is a strong interaction between electrolytes and proteins [1], which causes a departure from ideal behaviour. To understand the finer details, the interactions of the monomers of the protein, i.e. the interactions of the amino acids with electrolytes, must be studied owing to the complex structural organisation of the biological macromolecules.

There are investigations into the changes of the thermodynamic behaviour of proteins by the effect of various co-solutes/co-solvents, such as guanidine hydrochloride, sodium thiocyanate, magnesium chloride, urea and alcohols [2–7]. However, there are few measurements on the interactions between amino acids and organic salts [8–14].

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Better insight can be gained into the effect of electrostatic and hydrophobic interactions on the stability of proteins with the help of tetraalkylammonium salts, as these salts are expected to influence the macromolecular conformation by weakening attractive or repulsive inter- and intra-chain, charge–charge interactions, and also by affecting hydrophobic interactions through the side chains of the alkyl groups. Tetraalkylammonim salts orient water molecules around them depending on their alkyl side chain, due to their bulkiness.

In this work, we studied the volumes, viscosities and sound speeds of some amino acids in aqueous tetraalkylammonimbromide solutions. All of these properties are sensitive to specific interactive changes in solutions. In order to understand the finer details of the interactions of functional groups of amino acids with the experimentally selected salt, we studied the standard partial molar volumes, the corresponding volume of transfer at infinite dilution, and *B*-coefficients of viscosity.

2. Experiments

2.1. *Source and purity of samples*

The amino acids glycine (Analar, >99%), L-alanine (S.D. Fine Chemicals, >98.5%), L-valine (Loba Chemie, India, >99%) and L-leucine (Loba Chemie, India, >99%), and tetra-butyl ammonium bromide (TBAB; Thomas Baker, India, >98%) were used for the present study. These were used without further purification and dried over anhydrous P_2O_5 in a vacuum desiccator before use. Deionised, doubly distilled, degassed water with a specific conductance of less than $10^{-6}\,\Omega\,cm^{-1}$ was used for all of the measurements. The density, viscosity and sound speeds of the solutions were measured immediately after mixing. The purity of the samples were ascertained by GLC.

2.2. *Method*

The mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The densities (ρ) were measured with an Ostwald–Sperngel type pycnometer having a bulb volume of $25\,cm^3$ 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 the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperature. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. Averages of triplicate measurements were taken into account. The density values were reproducible to $\pm 3 \times 10^{-4}\,g\,cm^{-3}$.

The viscosity was measured by means of a suspended Ubbelohde-type viscometer calibrated at 298.15 K with doubly distilled water and purified methanol, using density and viscosity values from the literature [15–17]. A thoroughly cleaned and perfectly dried viscometer filled with 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 precision of the viscosity measurements was ± 0.003 mPa s. Details have been described earlier [18,19].

The accuracy of the viscosity measurements, based on our work on several pure liquids, was ±0.003 mPa s.

Ultrasonic speeds of sound (u) were measured with an accuracy of ±0.03% using a single crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, M-81) working at 2 MHz, which was calibrated with doubly distilled water, purified methanol and benzene at 298.15 K. The details of the methods and measurement have been described earlier [18,19].

3. Results and discussion

3.1. *Standard partial molar volume and compressibility*

The measured densities of aqueous amino acid solutions were used to calculate the value of apparent molar volume $V_{\phi,2}$, using Equation (1):

$$V_{\phi,2} = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0}, \tag{1}$$

where M is the molar mass of the solute, m is the molality of the amino acid in aqueous TBAB solution, ρ and ρ_0 are the densities of the water–TBAB–amino acid ternary mixture and aqueous TBAB solution. The experimentally measured densities (ρ) and the apparent molar volumes ($V_{\phi,2}$) are listed in Table 1.

The apparent compressibilities ($K_{\phi,2}$) of the solutions are determined from Equation (2):

$$K_{\phi,2} = \frac{M\kappa}{\rho} - \frac{(\kappa_0\rho - \kappa\rho_0)}{m\rho\rho_0}, \tag{2}$$

where κ and κ_0 are the compressibilities of the amino acid solution and the co-solute solution, respectively. The calculated $K_{\phi,2}$ values are reported in Table 1.

Compressibility (κ) values were calculated from experimental densities (ρ) and speeds of sound (u), using Equation (3):

$$\kappa = (u^2\rho)^{-1}. \tag{3}$$

We used an empirical equation for determining the apparent molar volumes and compressibilities:

$$Q_\phi = Q_\phi^0 + S_Q m, \tag{4}$$

where Q_ϕ^0 is the infinite dilution apparent molar quantity and S_q is the experimental slope.

The partial molar quantity $Q_{\phi,2}$ of the solute is calculated by using the following equation,

$$Q_{\phi,2} = Q_\phi + m\left(\frac{\partial Q_\phi}{\partial m}\right). \tag{5}$$

As $m \to 0$ the partial molar quantity becomes equal to the apparent molar quantity at infinite dilution, i.e. the standard partial molar quantity.

The $V_{2,m}^0$ and $K_{2,m}^0$ values calculated using the above-mentioned method, together with their standard deviation percents are summarised in Tables 2 and 3, along with the

Table 1. Experimental molalities (c), densities (ρ), viscosities (η), sound speed (u), apparent molar volumes ($V_{2,\phi}$) and apparent isentropic compressibilities ($K_{s,\phi}$), along with the concentration (c), of glycine, L-alanine, L-valine, L-leucine in water and in aqueous TBAB solution as a function of the molalities of amino acids.

c (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η_r	u (ms^{-1})	$V_{\phi,2} \times 10^{6}$ (m^3 mol^{-1})	$K_{\phi,2} \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})
$m_s = 0.062$					
Glycine					
0.0241	1.0070	1.0028	1583.7	41.68	−25.12
0.0320	1.0072	1.0243	1918.6	43.55	−24.88
0.0561	1.0081	1.0280	2155.2	42.72	−24.11
0.0721	1.0085	1.0308	2368.5	42.90	−23.77
0.0881	1.0091	1.0337	2638.0	41.89	−23.30
0.1001	1.0094	1.0357	2916.5	42.84	−23.06
Alanine					
0.0266	1.0072	1.0290	1861.0	60.64	−23.61
0.0354	1.0072	1.0314	1929.0	60.66	−23.31
0.0621	1.0080	1.0382	2182.9	60.71	−22.63
0.0799	1.0085	1.0424	2409.2	60.74	−22.23
0.0976	1.0091	1.0469	2717.9	60.78	−21.89
0.1109	1.0094	1.0503	3039.0	60.79	−21.64
Valine					
0.0257	1.0069	1.0136	1896.3	90.18	−28.51
0.0342	1.0071	1.0170	1982.0	90.19	−28.18
0.0599	1.0078	1.0276	2310.6	90.12	−27.06
0.0770	1.0082	1.0347	2642.5	90.22	−26.64
0.0942	1.0087	1.0417	3139.9	90.23	−26.11
0.1070	1.0090	1.0474	3759.8	90.24	−25.74
Leucine					
0.0261	1.0068	1.0214	1942.3	106.31	−32.66
0.0348	1.0070	1.0265	2052.2	106.38	−32.30
0.0609	1.0077	1.0408	2516.7	106.48	−31.24
0.0782	1.0081	1.0505	3065.2	106.52	−30.68
0.0956	1.0085	1.0604	4170.5	106.61	−30.06
0.1087	1.0088	1.0684	7170.2	106.65	−29.81
$m_s = 0.125$					
Glycine					
0.0245	1.0172	0.9854	2043.4	43.83	−16.69
0.0326	1.0175	0.9867	2097.2	43.88	−16.22
0.0570	1.0182	0.9903	2255.8	43.95	−14.63
0.0734	1.0187	0.9930	2378.2	44.01	−14.00
0.0896	1.0192	0.9956	2494.2	44.08	−13.23
0.1018	1.0196	0.9975	2585.7	44.10	−12.72
Alanine					
0.0262	1.0172	0.9899	2110.9	61.32	−21.26
0.0349	1.0175	0.9926	2198.5	61.41	−20.92
0.0611	1.0182	0.9993	2536.4	61.61	−20.27
0.0785	1.0186	1.0044	2851.5	61.72	−19.82
0.0960	1.0191	1.0092	3316.6	61.82	−19.48
0.1090	1.0195	1.0128	3836.5	61.88	−19.20
Valine					
0.0261	1.0172	1.0017	2151.9	90.42	−24.55
0.0348	1.0174	1.0047	2257.2	90.46	−23.99
0.0608	1.0180	1.0148	2672.1	90.57	−22.75
0.0782	1.0185	1.0215	3008.3	90.65	−21.35
0.0956	1.0189	1.0282	3604.8	90.70	−20.86
0.1086	1.0192	1.0337	4338.2	90.74	−20.49

(*continued*)

Table 1. Continued.

c (mol kg^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	η_r	u (ms^{-1})	$V_{\phi,2} \times 10^{6}$ (m^3 mol^{-1})	$K_{\phi,2} \times 10^{10}$ (m^3 mol^{-1} Pa^{-1})
$m_s = 0.062$					
Leucine					
0.0166	1.0169	1.0390	2103.3	106.19	−32.31
0.0222	1.0170	1.0423	2187.6	106.20	−31.85
0.0388	1.0174	1.0514	2508.8	106.23	−30.99
0.0498	1.0177	1.0582	2809.7	106.25	−30.39
0.0610	1.0179	1.0645	3246.0	106.26	−29.95
0.0692	1.0181	1.0689	3729.1	106.28	−29.62
$m_s = 0.256$					
Glycine					
0.0245	1.0186	0.9818	2146.3	45.03	−11.53
0.0326	1.0188	0.9832	2179.3	45.13	−10.62
0.0571	1.0195	0.9878	2260.6	45.38	−8.63
0.0735	1.0211	0.9915	2313.9	45.49	−7.89
0.0898	1.0205	0.9946	2323.2	45.62	−6.62
0.1021	1.0208	0.9971	2351.9	44.69	−6.26
Alanine					
0.0262	1.0186	0.9872	2196.0	61.97	−14.59
0.0349	1.0188	0.9895	2254.9	62.10	−13.96
0.0611	1.0195	0.9971	2484.3	62.47	−13.55
0.0786	1.0201	1.0024	2651.1	62.62	−13.01
0.0961	1.0204	1.0070	2833.4	62.75	−12.43
0.1092	1.0208	1.0101	2992.1	62.84	−12.09
Valine					
0.0262	1.0185	1.0020	2342.4	92.59	−24.08
0.0349	1.0188	1.0054	2481.6	89.75	−23.69
0.0611	1.0194	1.0166	3011.5	90.97	−21.90
0.0786	1.0198	1.0243	3570.7	91.34	−21.00
0.0961	1.0202	1.0318	4510.6	91.52	−20.15
0.1092	1.0205	1.0374	5904.0	91.62	−19.56
Leucine					
0.0262	1.0185	0.9956	2379.1	106.28	−26.18
0.0349	1.0187	0.9997	2516.6	106.31	−24.94
0.0612	1.0193	1.0149	3094.0	106.37	−22.75
0.0786	1.0197	1.0261	3643.8	106.38	−21.27
0.0961	1.0201	1.0356	4623.5	106.38	−20.26
0.1092	1.0204	1.0434	5711.3	106.39	−19.25

concentration dependence of the thermodynamic functions S_v and S_k. The standard deviations for all the quantities are given within the first bracket.

The slopes for the compressibility data behave similarly to the slopes of the volume data, i.e. positive S_{k_s} and S_v slopes are observed for all amino acids studied. The sign of S_q (S_v or S_{k_s}) is determined by the interaction between the solute species. It is seen from Tables 2 and 3 that the S_q values for all the amino acids are positive. The positive S_q values indicate the dominance of the interaction of the charged functional groups of the zwitterionic amino acids over the pairwise interaction. With the introduction of additional methyl groups in the side chains of the amino acids, the S_q values also change, indicating that the methyl groups modulate the interaction of the charged end groups in pairwise interactions. $V^0_{2,m}$ and $K^0_{2,m}$ values are by definition free from solute–solute interactions and therefore provide information regarding solute–solvent interactions.

Table 2. Standard partial molal volumes of amino acids in aqueous TBAB solution at 298.15 K.

Amino acids	Parameters	$V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$) Water	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	$V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)	43.14 (±0.06) [32]	42.52 (±0.01)	43.57 (±0.03)	44.40 (±0.02)
	S_v	0.86	0.9078	0.9912	0.5812
Alanine	$V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)	60.43 (±0.04) [32]	60.23 (±0.03)	60.78 (±0.01)	61.14 (±0.02)
	S_v	0.73	0.7218	0.6955	0.1045
Valine	$V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1)}$	90.39 (±0.14) [32]	90.12 (±0.01)	90.10 (±0.04)	91.01 (±0.04)
	S_v	–	0.3613	0.8618	0.6759
Leucine	$V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)	107.72 (±0.24) [32]	106.01 (±0.02)	106.11 (±0.01)	106.20 (±0.02)
	S_v	–	0.9891	0.7995	0.1589

Table 3. Standard partial isentropic compressibilities of amino acids in aqueous TBAB solution at 298.15 K.

Amino acids	Parameters	$K^0_{2,m} \times 10^{10}$ ($m^3\,mol^{-1}\,Pa^{-1}$) Water	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	$K^0_{2,m} \times 10^{10}$ ($m^3\,mol^{-1}\,Pa^{-1}$)	−27.00 [23]	−27.14 (±0.07)	−20.54 (±0.09)	−16.53 (±0.11)
	S_K	4.56	12.81	24.74	32.73
L-Alanine	$K^0_{2,m} \times 10^{10}$ ($m^3\,mol^{-1}\,Pa^{-1}$)	−25.26 [23]	−25.47 (±0.08)	−23.18 (±0.11)	−16.75 (±0.13)
	S_K	4.75	11.46	12.12	13.93
L-Valine	$K^0_{2,m} \times 10^{10}$ ($m^3\,mol^{-1}\,Pa^{-1}$)	−30.62 [23]	−31.17 (±0.11)	−30.95 (±0.09)	−28.61 (±0.07)
	S_K	8.43	16.50	23.73	27.54
L-Leucine	$K^0_{2,m} \times 10^{10}$ ($m^3\,mol^{-1}\,Pa^{-1}$)	−31.78 [23]	−35.45 (±0.09)	−34.83 (±0.11)	−32.46 (±0.12)
	S_K	13.61	17.11	19.98	40.04

The values of $V^0_{2,m}$ are positive for all the amino acids at all the concentrations of TBAB solution studied. The $V^0_{2,m}$ value increases gradually with the increase in concentration of TBAB in the aqueous solution for all the TBAB concentrations studied. For valine, there is a slight decrease in $V^0_{2,m}$ value for the 0.125 (M) TBAB concentration; however, the value finally increases.

A similar work was reported by Banerjee *et al.* in aqueous tetra-ethyl ammonium bromide solution [14]. All the $V^0_{2,m}$ values obtained by them are positive, like ours, and the trend of changes in $V^0_{2,m}$ values observed by them are similar to those observed by us.

From Table 3, it is seen that the value of isentropic compressibilities at infinite dilution ($K^0_{2,m}$) also increases gradually with the increase in concentration of TBAB in the aqueous solution for all the TBAB concentrations studied. But, the values of the isentropic compressibilities at infinite dilution are negative for all the solutions.

At neutral pH, amino acids exist as zwitterions, and on dissolution in water there is an overall decrease in the volume of the water. This is due to the contraction of the water near the end groups, and is termed 'electrostriction'. As a result, the electrostricted water is much less compressible than bulk water, and leads to a large decrease in the compressibility of the aqueous solution [20]. Thus, the values of ($K^0_{2,m}$) for all the studied amino acids are negative.

Moreover, it is seen that the negative nature of $K^0_{2,m}$values for the studied amino acids increases in the order

Glycine < L-Alanine < L-Valine < L-Leucine.

Since the contribution of a methylene group to the partial compressibility is negative at ambient temperature [21], the ions having larger hydrophobic groups may be expected to have more negative values of the partial molar compressibility. So, L-leucine, having the largest negative $K^0_{2,m}$ value.

3.2. *Group contributions*

The $V^0_{2,m}$ values of studied amino acids vary linearly with the number of C-atoms in their alkyl side chain. Similar correlation has been reported for some series of ω-amino acids in aqueous potassium thiocyanate [22] and guanidine hydrochloride solutions [9].

A linear regression analysis of $V^0_{2,m}$ values of amino acids *vs.* number of carbon atoms in 0.062, 0.125, 0.256 (M) TBAB solution was carried out using the following equation:

$$V^0_{2,m} = V^0_{2,m}\left(NH_3^+, COO^-\right) + n_c V^0_{2,m}(CH_2), \tag{6}$$

where n_c is the number of carbon atoms in the alkyl side chain of the amino acid, $V^0_{2,m}(NH_3^+,COO^-)$ and $V^0_{2,m}(CH_2)$ are the contribution of the zwitterionic end groups and methylene group to $V^0_{2,m}$ respectively. Since the alkyl side chains of the homologous series of α-amino acids studied in this work are: CH_2-(glycine), CH_3CH-(alanine), CH_3CH_3CHCH-(valine) and $CH_3CH_3CHCH_2CH-$(leucine), the value of (CH_2) obtained by this method characterises the mean contribution of the CH- and CH_3-groups to $V^0_{2,m}$ of the α-amino acids. To calculate the contribution of other alkyl chains, the method of Hakin *et al.* [19,20] was used. According to them,

$$V^0_{2,m}(CH_3) = 1.5V^0_{2,m}(CH_2), \text{ and} \tag{7}$$

$$V^0_{2,m}(CH) = 0.5V^0_{2,m}(CH_2). \tag{8}$$

$V^0_{2,m}$values of zwitterionic groups and other alkylside chains of the amino acids are listed in Table 4. It is observed from Table 4 that the contribution of the (NH_3^+, COO^-) to $V^0_{2,m}$ of the amino acids is larger compared to that of the (CH_2) group, and it increases with the increase of TBAB concentration in the solution, thereby indicating that the interaction of the ions of TBAB with the zwitterionic end groups of amino acids dominate over those of the hydrophobic group–TBAB interaction. However, the contribution from the side chain of the amino acids increases with the increase in chain length.

3.3. *Hydration of water*

The number of water molecules hydrated to amino acids (N_w) can be estimated from the electrostriction partial molar volume, using the equation [23]

$$N_w = \frac{V^0_{2,m}(\text{elect})}{\left(V^0_E - V^0_B\right)}, \tag{9}$$

where V^0_E is the molar volume of the electrostricted water and V^0_B is the molar volume of the bulk water. The value of $(V^0_E - V^0_B) \approx -3.0\,cm^3\,mol^{-1}$ [23] for electrolytes at 298.15 K. The $V^0_{2,m}$(elect) value was calculated using the following equation:

$$V^0_{2,m} = V^0_{2,m}(\text{in}) + V^0_{2,m}(\text{elect}), \tag{10}$$

Table 4. Contribution of the zwitterionic groups (NH_3^+, COO^-) and CH_2 group, and other alkyl chains, to the infinite dilution apparent molar volume in aqueous TBAB at 298.15 K.

	$V^0_{2,m} \times 10^6 (m^3\,mol^{-1})$			
Group	Water	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
NH_3^+, COO^-	27.68 (±0.92)	27.80 (±0.86)	29.07 (±0.72)	30.65 (±0.51)
CH_2	15.91 (±0.33)	15.66 (±0.29)	15.40 (±0.21)	15.17 (±0.19)
CH_3CH–	31.82 (±0.52)	31.32 (±0.44)	30.80 (±0.31)	30.34 (±0.25)
CH_3CH_2CH–	47.73 (±0.42)	93.96 (±0.36)	92.40 (±0.21)	91.02 (±0.28)
CH_3 CH_3CH CH_2CH–	79.45 (±0.41)	78.30 (±0.32)	77.00 (±0.56)	75.85 (±0.41)

Table 5. Hydration number (N_W) of amino acids in aqueous TBAB at 298.15 K.

	N_W		
Amino acids	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	3.1	2.8	2.5
L-Alanine	3.8	3.7	3.5
L-Valine	4.0	4.0	3.7
L-Leucine	6.0	6.0	6.0

where $V^0_{2,m}$(in) is the intrinsic partial molar volume due to the hydration of the amino acids. The $V^0_{2,m}$(in) term can further be divided into two terms, one for the Vanderwall's volume and the other for the volume of the packing effects. The values of $V^0_{2,m}$(in) for amino acids were obtained from their molar crystal volumes using the following relationship:

$$V^0_{2,m}(\text{in}) = \frac{0.7}{0.634} V^0_{2,m}(\text{cryst}), \tag{11}$$

where 0.7 is the packing density for the molecule in an organic crystal and 0.634 is the packing density for the randomly packed spheres. The molar volume of the crystals were calculated using the crystal densities of the amino acids represented by Berlin and Pallansh [24] at 298.15 K. The values of $V^0_{2,m}$(elect) were obtained from the intrinsic partial molar volume of the amino acid $V^0_{2,m}$(in) and the $V^0_{2,\phi}$ values determined experimentally.

Obtained N_w values are listed in Table 5. It can be seen that, for glycine, L-alanine and L-valine, the values the N_w values vary with the solvent composition, showing a tendency to decrease with the increase in the concentration of TBAB solution. This indicates that the addition of electrolytes introduces a dehydration effect on amino acids in solution [25]. However, for L-leucine, the N_w values remain unaltered by the TBAB concentration. This indicates that the hydrophobic group of leucine reduces the ion–ion interaction between the amino acid and the salt.

The N_w values obtained by us are lower than those obtained by Banerjee *et al*. [14]. This may be due to the replacement of the ethyl group of the co-solute molecule by the bulkier butyl group. A possible explanation may be that it is due to the lesser solvation of the bulkier butyl group compared to the smaller ethyl group [26].

Table 6. Transfer volumes of amino acids ($\Delta_{tr}V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)) from water to aqueous TBAB at 298.15 K.

	$\Delta_{tr}V^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)		
Amino acids	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	−0.09 (±0.03)	0.43 (±0.02)	1.26 (±0.02)
L-Alanine	−0.20 (±0.08)	0.34 (±0.07)	0.70 (±0.08)
L-Valine	−0.27 (±0.05)	−0.29 (±0.04)	0.62 (±0.05)
L-Leucine	−1.34 (±0.21)	−1.36 (±0.21)	−0.45 (±0.23)

Table 7. Transfer compressibilities of amino acids ($\Delta_{tr}K^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)) from water to aqueous TBAB at 298.15 K.

	$\Delta_{tr}K^0_{2,m} \times 10^6$ ($m^3\,mol^{-1}$)		
Amino acids	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	−0.14 (±0.06)	6.46 (±0.13)	10.47 (±0.27)
L-Alanine	−0.21 (±0.03)	2.08 (±0.08)	8.51 (±0.19)
L-Valine	−0.55 (±0.07)	−0.33 (±0.03)	2.01 (±0.13)
L-Leucine	−3.67 (±0.13)	−3.05 (±0.23)	−0.68 (±0.11)

3.4. *Transfer volume and compressibility*

Transfer volumes and transfer compressibilities ($\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$) for each amino acid [27] from pure water to TBAB solutions is determined by the equations

$$\Delta_{tr}V^0_{\phi,2} = V^0_{2,m}(\text{TBAB}) - V^0_{2,m}(\text{water}), \tag{12}$$

$$\Delta_{tr}K^0_{2,m} = K^0_{2,m}(\text{TBAB}) - K^0_{2,m}(\text{water}). \tag{13}$$

The results obtained are listed in Tables 6 and 7 and are illustrated in Figures 1 and 2.

The different types of interactions which take place in the ternary systems of amino acid + TBAB + water are: (a) ion–ion interaction between the Br^- ion of TBAB and the NH_3^+ group of the amino acid; (b) ion–ion interaction between the $(C_4H_9)_4N^+$ ion of TBAB and the COO^- group of amino acid; and (c) hydrophobic–hydrophobic interaction between the butyl group of TBAB and hydrophobic group of amino acid.

Applying the co-sphere overlap model [28] as a guideline, it may be inferred that the (a) and (b) type of interactions will lead to a positive $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$, since there is a reduction in the electrostriction effect and the overall water structure is enhanced. Interactions of the (c) type will lead to negative $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$, because the introduction of an alkyl group provides an additional scope of hydrophobic–hydrophobic and hydrophilic–hydrophobic interactions. As a result, there will be a reduction in the structure of water formed as a result of their co-spheres overlapping.

Both positive and negative values of the volume of transfer for the amino acids were observed. The $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ values for glycine and L-alanine increases with the increase in concentration of TBAB in the solution. But for L-valine, the volume of transfer increases from negative to positive values with the rise in TBAB concentration.

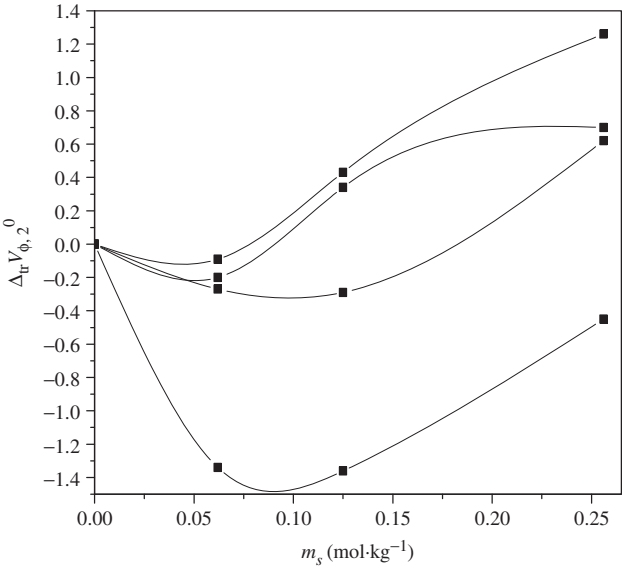

Figure 1. Transfer volumes of the amino acids from water to aqueous TBAB solution against the concentration of the TBAB solution.

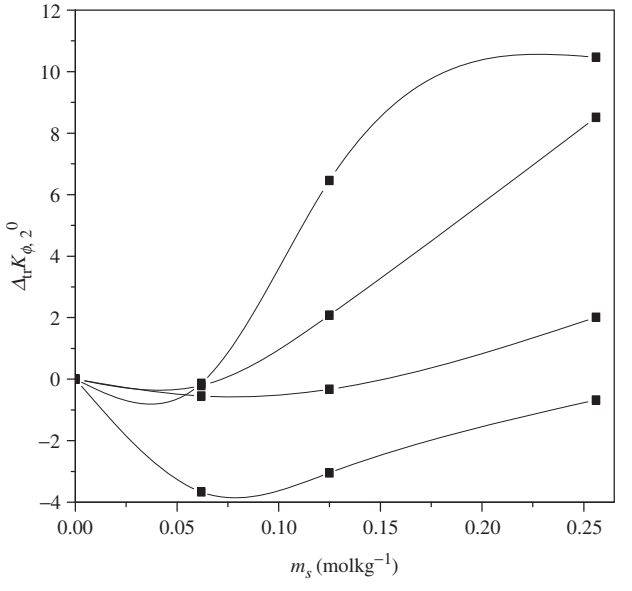

Figure 2. Transfer compressibilities of the amino acids from water to aqueous TBAB solution against the concentration of the TBAB solution.

For L-leucine, all of the $\Delta_{tr}V_{2,m}^{0}$ and $\Delta_{tr}K_{2,m}^{0}$ values are negative, but with the rise in TBAB concentration, the values shift to lower negative values.

The value of $\Delta_{tr}V_{2,m}^{0}$ for glycine from water to 0.025(M) TBAB is negative, but very small. This indicates a balance between the interactions (a) and (c). With increasing

concentration of co-solute TBAB, positive $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ results indicate an enhancement in the ion–ion interaction between the zwitterionic centres of the amino acid and the ion of the salt. Similar is the case of alanine, but here the presence of an additional alkyl group increases the hydrophobic interaction, leading to a decrease in the positive nature of $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ values. With the increase in the number of hydrophobic groups from L-valine to L-leucine, the $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ values become more and more negative. The increased number of hydrophobic groups in these amino acids interacts strongly with the hydrophobic groups of TBAB, thereby leading to negative volumes of transfer, which increases with the increasing concentration of TBAB.

The comparison of our work with the work of Banerjee *et al.* shows that the $\Delta_{tr}V^0_{2,m}$ values for amino acids shifts towards the positive side in aqueous TBAB solution. This is due to the predominance of (a) and (b) type of forces in the case of the TBAB solution.

3.5. *Viscosity* B-*coefficients*

The relative viscosities, η_r, of the studied amino acids in the selected concentrations of co-solute solutions were calculated using the following relation, and are summarised in Table 8:

$$\left(\eta_r = \frac{\eta}{\eta_0}\right), \tag{14}$$

where η and η_0 are the viscosities of solution and solvent, respectively. The *B*-coefficients of viscosity were determined by fitting the η_r values to the Jones–Dole equation by the least-squares method, as follows:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Bc, \tag{15}$$

where c is the molarity of the solution calculated from molality values. The values of the *B*-coefficients along with their standard deviation percents are listed in Table 9.

The *B*-coefficient measures the size and shape effects, as well as the structural effects, induced by solute–solvent interactions [29]. The *B*-coefficient values for amino acids in aqueous TBAB solutions follow the order

Glycine < L-Alanine < L-Valine < L-Leucine.

From the above order, it is clear that the magnitude of the *B*-coefficient increases with increasing molar mass and size of the alkyl side chains of amino acids. The values increase with the concentration of TBAB, indicating the promotion of the liquid structure in the presence of TBAB.

Table 8. Experimental densities (ρ), viscosities (η), and sound speed (u) of aqueous TBAB solutions of all the experimental concentrations at 298.15 K.

Molality of TBAB in water	$\rho \times 10^{-3}/(\mathrm{kg\,m^{-3}})$	η (mPa s)	u ($\mathrm{ms^{-1}}$)
$m_s = 0.062$	1.0062	0.9506	1685.2
$m_s = 0.125$	1.0165	0.9698	1888.4
$m_s = 0.256$	1.0179	1.0796	2016.4

Table 9. Viscosity B-coefficients, B, ($dm^3\,mol^{-1}$) for amino acids in aqueous TBAB solutions at 298.15 K.

	B ($dm^3\,mol^{-1}$)		
Amino acids	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	0.1473 (±0.09)	0.1681 (±0.06)	0.1986 (±0.06)
L-Alanine	0.2728 (±0.02)	0.2761 (±0.02)	0.2796 (±0.01)
L-Valine	0.4144 (±0.03)	0.4175 (±0.05)	0.4285 (±0.04)
L-Leucine	0.5647 (±0.05)	0.5769 (±0.04)	0.5824 (±0.02)

Table 10. Contributions of (NH_3^+, COO^-) and (CH_2) groups to viscosity B-coefficients of the amino acids in aqueous TBAB solutions at 298.15 K.

	B ($dm^3\,mol^{-1}$)		
Group	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
NH_3^+, COO^-	0.098 (±0.18)	0.096 (±0.08)	0.092 (±0.11)
CH_2	0.057 (±0.04)	0.072 (±0.05)	0.097 (±0.05)

In fact, the B-coefficient values for the amino acids reflect the net structural effects of the charged end and the hydrophobic (CH_2) groups on the amino acids. B-coefficients for the homologous series of R-amino acids vary linearly with the number of carbon atoms on their alkyl chains at a given temperature [22,30,31]. Similar to Equation (4), the linear relation can be represented by the regression parameters

$$B = B\left(NH_3^+, COO^-\right) + n_c B(CH_2). \tag{16}$$

The regression parameters $B(NH_3^+, COO^-)$ and $B(CH_2)$ indicate the contributions of the zwitterionic and the methylene groups to the B-coefficient. It should be pointed out that $B(CH_2)$ obtained here characterises the mean contribution of CH- and CH_3-groups to B-coefficients of the amino acids. Such linear correlation [20,31] has also been observed in other solutes for these amino acids. The values of the charged end groups contributions, $B(NH_3^+, COO^-)$, and the methylene group contribution, $B(CH_2)$, to the B-coefficients are given in Table 10. It can be seen from Table 10 that values of $B(NH_3^+, COO^-)$ decrease, while $B(CH_2)$ values increase, with increasing concentration of TBAB in solutions, indicating that the zwitterionic groups break while (CH_2) groups enhance the structures of the aqueous salt solutions.

4. Conclusion

In summary: volume, viscosity and compressibility data have been determined for aqueous amino acids solutions, and the results have been used to estimate the volume and compressibility of transfer, the number of hydrated water molecules, and the viscosity B-coefficient values. From the values obtained for the above-mentioned parameters, the following conclusions may be drawn.

With the increase in concentration of TBAB in solution, the partial molar quantities also increases. The contribution of the (NH_3^+, COO^-) group to $V_{2,m}^0$ of the amino acids is

larger compared to that of the (CH_2) group and increases with the increase of TBAB concentration in the solution. The number of water molecules hydrated to amino acids increases with the increase in hydrophobic content of the amino acids, indicating the predominance of hydrophobic interactions between the amino acid and TBAB, with increasing number carbon atoms in the former.

The partial isentropic compressibilities of the amino acids behave in the similar way to that of the $V^0_{2,m}$, and the same conclusions are drawn as above. From the considerations of the volume of transfer, it is concluded that, for glycine and L-alanine, with increasing concentration of co-solute TBAB, more positive $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ values result, indicating an enhancement in the ion–ion interaction. From glycine to L-leucine, the $\Delta_{tr}V^0_{2,m}$ and $\Delta_{tr}K^0_{2,m}$ values become more and more negative. The increased number of hydrophobic groups in these amino acids leads to stronger interaction between the hydrophobic groups of amino acids with the hydrophobic groups of TBAB, thereby leading to negative volumes of transfer.

The magnitude of the *B*-coefficient increases with increasing molar mass and size of the alkyl side chains of amino acids. The values increase with the concentration of TBAB, indicating the promotion of the liquid structure in the presence of TBAB.

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