CHAPTER V

Apparent molar volumes and viscosity *B*-coefficients of Some Amino Acids in Aqueous Tetramethylammonium Iodide Solutions at 298.15 K*

5.1. 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 behaviour 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 behaviour 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 like 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 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.

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5.2. Experimental Section

5.2.1. Chemicals

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 recrystalised from 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 recrystallised from solvent ether medium. After filtration, the salt was dried in vacuo for 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.

5.2.2. Measurements

A stock solution of each amino acid in different aqueous TMAI solutions were 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 loses during the time of measurements. An average of triplicate measurement 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 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 ± 0.1s. At least three repetitions of each data reproducible to ± 0.1s 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 had been described elsewhere.[15-17] pH of the experimental solvent and solutions were measured by a Systronics MK-VI 5631 digital pH meter, calibrated with 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. While pH ranges for glycine were found to be 5.20-5.78, 5.56-5.73 and 5.48-5.71; those for L-alanine were 5.80-6.08, 5.54-5.68 and 5.29-5.62 and those for L-valine were 5.72-5.82, 5.49-5.64 and 5.27-5.54 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.

5.3. Results and Discussion

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

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

where M is the molar mass of the solute, c the molarity of the solution, ρ_0 and ρ 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 versus $\sqrt{c}$ using the Masson equation:[19]

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \qquad (2)$$

where V_ϕ^0 is the partial molar volume at infinite dilution and S_V^* 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 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, V_ϕ^0 value varies linearly with the number of carbon atoms in the alkyl chain (R) of the amino acids. Similar correlations have reported earlier by a number of workers[20,21] and this linear variation can be represented as follows:

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

where N_C is the number of carbon atoms in the alkyl chain of the amino acids, $V_\phi^0(NH_3^+, COO^-)$ 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 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 CH_3- 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]

$$V_\phi^0(CH) = 0.5 V_\phi^0(CH_2) \quad (4)$$

$$V_\phi^0(CH_3) = 1.5 V_\phi^0(CH_2) \quad (5)$$

and are listed in Table 4. Table 4 shows that the contribution of (NH_3^+, COO^-) to V_ϕ^0 is larger than that of the CH_2- group and increases with the increase

in the concentration of cosolute, which indicates that the interactions between cosolute and charged end groups (NH_3^+, COO^-) of amino acids are much stronger that those between 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 group, $\Delta V_\phi^0(R)$ of amino acids from water to co-solute solutions have been calculated as follows:

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

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 from that of glycine using the following scheme:

$$V_\phi^0(R) = V_\phi^0(\textit{Amino acid}) - V_\phi^0(\textit{Glycine}) \quad (7)$$

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.

The number of water molecules (N_H) hydrated to the amino acids, can be estimated from the electrostriction partial molar volume $V_\phi^0(elect)$[20] using the relation:

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

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

$cm^3.mol^{-1}$ at 298.15 K. The $V_\phi^0(elect)$ values can be calculated[27] from the intrinsic partial molar volumes of the amino acids, $V_\phi^0(int)$[28, 29] and experimentally determined V_ϕ^0 values, as follows:

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

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 of each amino acid, ΔV_ϕ^0 from pure water to aqueous TMAI solutions is defined by:

$$\Delta V_\phi^0 = V_\phi^0(Amino\ acid + TMAI + Water) - V_\phi^0(Water) \qquad (10)$$

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, is free from solute-solute interactions and therefore provides information regarding solute-cosolute interaction.[9] Figure 1 shows that ΔV_ϕ^0 values are positive for all the amino acid 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 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 contributions 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 Vander Waals volume, V_V is the volume associated with voids or empty space, and V_S 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 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 $(CH_3)_2CH$- 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.

The experimental viscosity data for the systems studied are listed in Table 2. The relative viscosity (η_r) has been analyzed using 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), 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:

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

Values of *A*- and *B*-coefficients are obtained from a linear plot of the left hand side of equation 13 versus $\sqrt{c}$. The values of *A*- and *B*- coefficients are listed in Table 7. Due to 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:

$$B = B(NH_3^+, COO^-) + N_C B(CH_2) \qquad (14)$$

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 CH_2- group enhance the structure of the aqueous salt solutions.

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

5.4. Conclusion

In summary, the study reveals that while 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.

References

[1] P. H. Von Hippel, T. Schleich, Acc. Chem. Res. 2 (1969) 257.

[2] W. P. Jencks, W. P. *Catalysis in Chemistry and Enzymology*, McGraw-Hill: New York, 1969; p 351.

[3] M. K. Khoshkbarchi, J. H. Vera, J. H. Ind. Eng. Chem. Res., 35 (1996) 87.

[4] M. Natarajan, R. K. Wadi, H. C. Gaur, J. Chem. Eng. Data., 35 (1990) 87.

[5] Z. N. Yan, Z. J. J. Wang, J.S. Lu, BioPhys. Chem., 99(2002)199.

[6] R. K. Wadi, P. Ramasami, J. Chem. Soc. Faraday Trans., 93 (1997) 243.

[7] T. S. Banipal, D. Kaur, P. K. Banipal, J. Chem. Eng. Data., 49 (2004) 1236.

[8] X. Wang, L. Xu, R. S. Lin, R. D. Z. Sun, Acta. Chim. Sin., 62,(2004)1405.

[9] K. Belibagli, E. Agranci, J. Sol. Chem., 19 (1990) 867.

[10] M. N. Roy, B. Sinha, V. K. Dakua, A. Sinha, Pak. J. Sci. Ind. Res., 49 (2006) 153.

[11] L. H. Blanco, E. F. Vargas, J. Sol. Chem., 35 (2006) 21.

[12] Marsh, K. N. *Recommended Reference Materials for the Realisation of Physicochemical Properties*, Blackwell Scientific Publications, Oxford, U. K, 1987.

[13] J. A. Dean, *Lange's Handbook of Chemistry*, 11th ed.; McGraw-Hill Book Company: New York, 1973.

[14] A. Chatterjee, B. Das, B. J. Chem. Eng. Data., 51 (2006)1352.

[15] M. N. Roy, D. K. Hazra, Indian J. Chem. Technol., 1 (1994) 93.

[16] P. S. Nikam, M. J. Hosan, J. Chem. Eng. Data., 33 (1998) 165.

[17] M. N. Roy, A. Sinha, Fluid Phase Equilib., 243 (2006)133.

[18] M. N. Roy, B. Sinha, R. Dey, A. Sinha, Int. J. Thermophys., 26 (2005)1549.

[19] D. O. Masson, *Philos. Mag.*, 8, (1929)218.

[20] F. J. Millero, A. L. Surdo, C. Shin, J. Phys. Chem., 82 (1978) 784.

[21] Li. Xu, C. Ding, R. Lin, J. Sol. Chem., 35 (2006) 191.

[22] R. K. Wadi, R. K. Goyal, J. Sol. Chem, 21 (1992) 163.

[23] Z. Yan, J. Wan, H. Zhang, D. Liu,, J. Sol. Chem., 27 (1998) 473.

[24] T. Banerjee, N. Kishore, J. Sol. Chem., 35 (2005) 137.

[25] A. W. Hakin, M. M. Duke, J. L. Marty, K. E. Preuss, J. Chem. Soc. Faraday Trans, 90 (1994) 2027.

[26] A. W. Hakin, M. M. Duke, L. L. Groft, J. L. Marty, M. L. Rashfeldt, Can. J. Chem. 73 (1995) 725.

[27] F. Franks,M. A. Quickenden, D. S. Reid, B. Watson, B. Trans Faraday Soc., 66 (1970) 582.

[28] E. Berlin, M. J. Pallansch, *J. Phys. Chem.*, 72 (1968) 1887.

[29] F. T. Gucker, W. L. Ford, C. E. Moser, J. Phys. Chem., 3 (1939)153.

[30] T. Owaga, K. Mizutami, M. Yasuda, Bull. Chem. Soc. Jpn., 57 (1984) 2064.

[31] H. L. Friedman, C. V. Krishnan, *In Water: A comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 3, Chapter 1.

[32] R. Bhat, J. C. Ahluwalia, J. Phys. Chem., 89 (1985) 1099.

[33] A. K. Mishra, J. C. Ahluwalia, J. Chem. Soc. Faraday Trans 1, 77 (1981) 1469.

[34] G. Jones, D. Dole, *J. Am. Chem. Soc.*, 51 (1929) 2950.

[35] T. S. Banipal, A. Bhatia, P. K. Banipal, G Singh, D Kaur, J. Ind. Chem. Soc., 81 (2004) 126.

Table 1.

Densityρ, and viscosity η of different aqueous TMAI solutions at T = 298.15K

Aqueous TMAI solution /(mol·dm^{-3})	$\rho \times 10^{-3}$/kg·m^{-3}	η/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

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 /(mol·dm^{-3})	$\rho \times 10^{-3}$/kg·m^{-3}	η/mPa·s	$V_\phi \times 10^6$ /m^3·mol^{-1}	$\frac{(\eta_r - 1)}{\sqrt{c}}$
		0.05 [a]		
		Glycine		
0.0364	1.0021	0.814	44.80	0.060
0.0485	1.0025	0.816	44.10	0.063
0.0849	1.0037	0.822	43.22	0.073
0.1092	1.0044	0.825	43.89	0.078
0.1334	1.0052	0.829	43.54	0.084
0.1516	1.0057	0.832	44.02	0.087
		L-Alanine		
0.0297	1.0019	0.814	58.73	0.066
0.0396	1.0021	0.816	61.25	0.072
0.0693	1.0030	0.823	60.17	0.088
0.0892	1.0036	0.828	59.88	0.098
0.1090	1.0041	0.833	60.59	0.107
0.1238	1.0045	0.837	60.76	0.113
		L-valine		
0.0235	1.0016	0.811	91.53	0.052
0.0312	1.0018	0.814	91.42	0.063
0.0547	1.0025	0.821	89.64	0.089
0.0704	1.0029	0.827	90.07	0.104
0.0860	1.0033	0.832	90.31	0.115
0.0977	1.0036	0.836	90.45	0.124
		0.10 [a]		
		Glycine		
0.0356	1.0041	0.819	44.04	0.045
0.0474	1.0045	0.821	43.29	0.050
0.0829	1.0056	0.826	43.58	0.059
0.1066	1.0063	0.829	43.98	0.064
0.1304	1.0071	0.832	43.50	0.069
0.1481	1.0076	0.835	43.88	0.075
		L-alanine		
0.0311	1.0039	0.821	59.97	0.062
0.0415	1.0042	0.823	59.99	0.069
0.0727	1.0051	0.831	60.02	0.086
0.0935	1.0056	0.836	61.10	0.096
0.1142	1.0062	0.841	60.89	0.104
0.1297	1.0067	0.845	60.38	0.111
		L-valine		
0.0243	1.0037	0.820	88.08	0.064
0.0323	1.0039	0.823	89.02	0.076
0.0566	1.0045	0.832	90.38	0.101
0.0728	1.0050	0.837	89.41	0.115
0.0889	1.0054	0.843	89.88	0.129
0.1011	1.0058	0.848	89.19	0.139

Contd...

		0.15 [a]		
		Glycine		
0.0361	1.0098	0.825	44.21	0.039
0.0481	1.0102	0.826	43.51	0.044
0.0841	1.0113	0.831	43.77	0.053
0.1082	1.0120	0.835	44.19	0.060
0.1323	1.0128	0.838	43.70	0.065
0.1503	1.0133	0.840	44.08	0.069
		L-alanine		
0.0296	1.0095	0.827	61.53	0.056
0.0395	1.0098	0.829	60.71	0.063
0.0691	1.0106	0.836	61.06	0.080
0.0889	1.0112	0.841	60.44	0.091
0.1087	1.0117	0.845	60.96	0.099
0.1235	1.0122	0.849	60.23	0.105
		L-valine		
0.0214	1.0093	0.825	88.34	0.057
0.0285	1.0095	0.828	88.31	0.067
0.0500	1.0100	0.835	90.36	0.092
0.0642	1.0104	0.840	89.89	0.105
0.0785	1.0108	0.846	89.62	0.119
0.0892	1.0111	0.850	89.47	0.127

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

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	$V_\phi^0 \times 10^6 / m^3 \cdot mol^{-1}$				$S_V^* \times 10^6 / (m^9 \cdot mol^{-3})^{1/2}$			
	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 ± .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 ± .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 $mol \cdot dm^{-3}$.

Table 4.
Contribution of zwitterionic end group (NH_3^+, COO^-), CH_2 - group and other alkyl chain group (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	$V_\phi^0 \times 10^6 / m^3 \cdot mol^{-1}$				$\Delta V_\phi^0 \times 10^6 / m^3 \cdot mol^{-1}$		
	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 $mol \cdot dm^{-3}$.

Table 5.
Contribution of 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	$V_\phi^0(R) \times 10^6 / m^3 \cdot mol^{-1}$			$B(R) / m^3 \cdot mol^{-1}$		
	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 $mol \cdot dm^{-3}$.

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 $mol \cdot dm^{-3}$.

Table 7.
Viscosity *A*- and *B*-coefficient for the amino acids in aqueous TMAI solutions with standard errors at T = 298.15 K

Amino acid	A /$m^{3/2} \cdot mol^{-1/2}$			B /$m^3 \cdot mol^{-1}$		
	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 $mol \cdot dm^{-3}$.

Table 8.
Contributions of zwitterionic group (NH_3^+, COO^-) and CH_2 - group to viscosity *B*-coefficient in aqueous TMAI solutions at T = 298.15 K

Group	B /$m^3 \cdot mol^{-1}$		
	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 $mol \cdot dm^{-3}$.

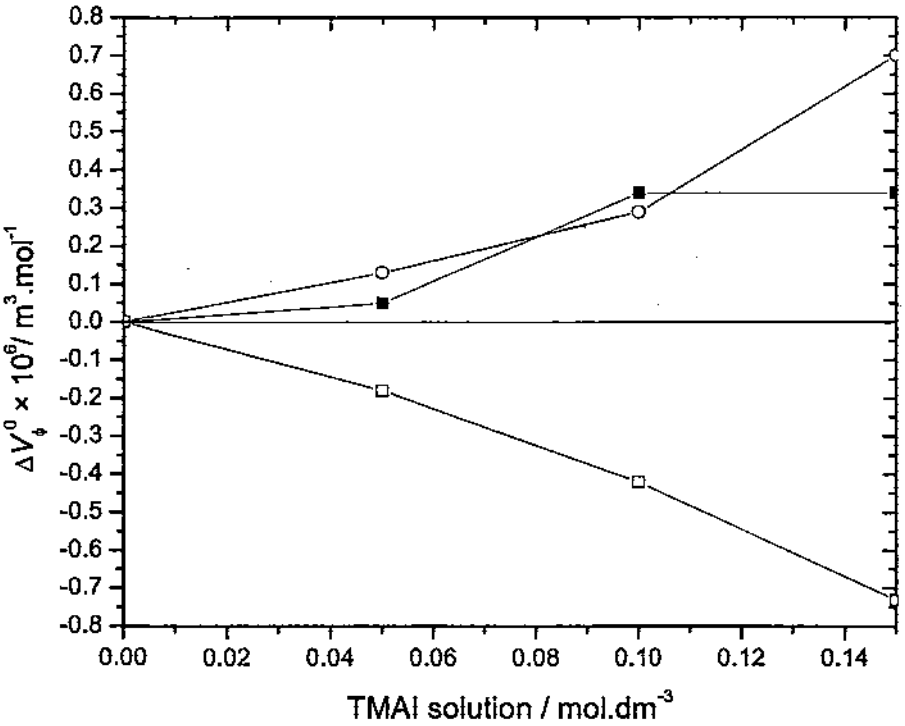

Figure 1.

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 (□).