

## CHAPTER IX

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

#### 9.1. Introduction

Amino acids are monomers that constitute proteins and are considered to be the model compounds of proteins. The behavior of proteins in mixtures is highly influenced by many factors such as  $p_H$ , solvent properties, chemical structure and surface charge distribution of proteins, and type and concentration of the electrolyte. The influence of electrolyte on the behavior of protein is one of the important topics in physical chemistry of the substances. It has long been known that there is a strong interaction between electrolytes and proteins,<sup>1</sup> which causes a departure from ideal behavior. 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 organization of the biological macromolecules.

There are investigations on the changes of thermodynamic behaviour of proteins by the effect of various co-solutes/co-solvents, such as guanidine hydrochloride, sodium thiocyanate, magnesium chloride, urea and alcohols.<sup>2-7</sup> However, there are few measurements on interactions between amino acid and organic salts.<sup>8-4</sup>

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 by affecting hydrophobic interactions through the side chains of the alkyl groups. Tetraalkylammonium 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 tetraalkylammoniumbromide 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.

## 9.2. Experimental Section

### 9.2.1 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%), Tetra butyl ammonium bromide (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. Deionized, doubly distilled, degassed water with a specific conductance of less than  $10^{-6} \Omega \text{ cm}^{-1}$  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.

### 9.2.2 Method

The mass measurements accurate to  $\pm 0.01$  mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The densities ( $\rho$ ) were measured with an Ostwald-Sperngel type pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 0.1cm. 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  $\pm 0.01\text{K}$  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  $\pm 3 \times 10^{-4} \text{ g.cm}^{-3}$ .

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<sup>15-17</sup>. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to  $\pm 0.01\text{K}$ . After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to  $\pm 0.1\text{s}$ . At least three repetitions of each data reproducible to  $\pm 0.1\text{s}$  were taken to average the flow times. The precision of the viscosity measurements was  $\pm 0.003\text{mPa.s}$ . Details have been described earlier.<sup>18-19</sup>

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

Ultrasonic speeds of sound ( $u$ ) were measured with an accuracy of  $\pm 0.03\%$  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.<sup>18,19</sup>

### 9.3 Results and Discussion

#### 9.3.1 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)

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

Where,  $M$  is the molar mass of the solute,  $m$  is the molality of the amino acid in aqueous TBAB solution,  $\rho$  and  $\rho_0$  are the densities of the water-TBAB-amino acid ternary mixture and aqueous TBAB solution. The experimentally measured densities ( $\rho$ ) and the apparent molar volumes ( $V_{\phi,2}$ ) are listed in table 1.

The apparent molar isentropic compressibility ( $K_{\phi,2}$ ) of the solutions is determined from equation (2):

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

where,  $\kappa$  and  $\kappa_0$  are the isentropic compressibilities of the amino acid solution and the co-solute solution respectively. The calculated  $K_{\phi,2}$  values are reported in table 1.

Isentropic compressibility ( $\kappa$ ) values were calculated from experimental densities ( $\rho$ ) and speeds of sound ( $u$ ), using equation (3)

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

In the case of negligible concentration dependence (i.e., within the uncertainty limits of the measurements) the variation of the apparent molar quantities  $Q_{\phi,2}$ , with molality can adequately be represented by equation (4):

$$Q_{\phi,2} = Q_{2,m}^0 + S_q m \quad (4)$$

Where  $Q_{\phi,2}^0$  is the infinite dilution value that is equal to the partial molar quantity  $Q_{\phi,2}$  at infinite dilution and  $S_q$  is the experimental slope.

Equation 4 was fitted to our  $V_{\phi,2}$  and  $K_{\phi,2}$  data by the least squares method outlined earlier<sup>20</sup>. The  $V_{2,m}^0$  and  $K_{2,m}^0$  values together with their standard deviation percents are summarized in table 2 and table 3 along with the concentration dependence of these thermodynamic functions  $S_v$  and  $S_k$ . The standard deviations for all the quantities are given within 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 table 2 and table 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 pair wise 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 modulates the interaction of the charged end groups in pair wise interaction.

$V_{2,m}^0$  and  $K_{2,m}^0$  values are by definition free from solute-solute interactions and therefore provide information regarding solute-solvent interactions.

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

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

From, table3, it is seen that, the value of isentropic compressibilities at infinite dilution ( $K_{2,m}^0$ ) also increases gradually with the increase in concentration of TBAB in the aqueous solution for all the TBAB concentration 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 as electrostriction. As a result, the electrostricted water is much less compressible than bulk water and leads to a large decrease in the compressibility of aqueous solution.<sup>20</sup> Thus, the values of ( $K_{2,m}^0$ ) for all the studied amino acids are negative.

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



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 group shows the highest negative  $K_{2,m}^0$  value.

### 9.3.2 Group contributions:

The  $V_{2,m}^0$  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  $\omega$ -amino acids in aqueous potassium thiocyanate<sup>22</sup> and guanidine hydrochloride solutions.<sup>9</sup>

A linear regression analysis of  $V_{2,m}^0$  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

$$V_{2,m}^0 = V_{2,m}^0(\text{NH}_3^+, \text{COO}^-) + n_c V_{2,m}^0(\text{CH}_2) \quad (5)$$

where,  $n_c$  is the number of carbon atoms in the alkyl side chain of the amino acid,  $V_{2,m}^0(NH_3^+, COO^-)$  and  $V_{2,m}^0(CH_2)$  are contribution of the zwitterionic end groups and methylene group to  $V_{2,m}^0$  respectively. Since the alkyl side chains of homologous series of  $\alpha$ -amino acids studied in this work are:  $CH_2$ -(glycine);  $CH_3CH$ -(alanine),  $CH_3CH_2CHCH$ -(valine),  $CH_3CH_2CHCH_2CH$ -(leucine), the value of  $(CH_2)$  obtained by this method characterizes the mean contribution of the  $CH$ - and  $CH_3$ - groups to

$V_{2,m}^0$  of the  $\alpha$ -amino acids. To calculate the contribution of other alkyl chains, the method of Hakin et.al.<sup>19,20</sup> was used. According to them,

$$V_{2,m}^0(CH_3) = 1.5V_{2,m}^0(CH_2) \quad (6)$$

$$V_{2,m}^0(CH) = 0.5V_{2,m}^0(CH_2) \quad (7)$$

$V_{2,m}^0$  values of amino acids are listed in table 4. It is observed from table 4 that, the contribution of the  $(NH_3^+, COO^-)$  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, 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 amino acids increases with the increase in chain length.

### 9.3.3 Water of hydration

The number of water molecules hydrated to amino acids ( $N_w$ ) can be estimated from the electrostriction partial molar volume, using the equation,<sup>23</sup>

$$N_w = \frac{V_{2,m}^0(elect)}{(V_E^0 - V_B^0)} \quad (8)$$

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

$$V_{2,m}^0 = V_{2,m}^0(in) + V_{2,m}^0(elect) \quad (9)$$

where  $V_{2,m}^0(in)$  is the intrinsic partial molar volume due to the hydration of the amino acids. The  $V_{2,m}^0(in)$  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  $V_{2,m}^0(in)$  for amino acids were obtained from their molar crystal volumes using the following relationship,

$$V_{2,m}^0(in) = \frac{0.7}{0.634} V_{2,m}^0(cryst) \quad (10)$$

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 <sup>24</sup> at 298.15 K. The values of  $V_{2,m}^0(elect)$  were obtained from the intrinsic partial molar volume of the amino acid  $V_{2,m}^0(in)$  and the  $V_{2,\phi}^0$  values determined experimentally.

The 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, with the addition of electrolytes introduces dehydration effect on amino acids in solution.<sup>25</sup> However, for L-Leucine, the  $N_w$  values remain unaltered by 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 co-solute molecule by the bulkier butyl group. The possible explanation may be due to lesser solvation of the bulkier butyl group compared to the smaller ethyl group.<sup>26</sup>

### 9.3.4 Transfer volume and compressibility

Transfer volumes and transfer compressibilities ( $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$ ) for each amino acid <sup>27</sup> from pure water to TBAB solutions is determined by the equations,

$$\Delta_{tr}V_{\phi,2}^0 = V_{2,m}^0(TBAB) - V_{2,m}^0(water) \quad (11)$$

$$\Delta_{tr}K_{2,m}^0 = K_{2,m}^0(TBAB) - K_{2,m}^0(water) \quad (12)$$

The results obtained are listed in table 6 and table 9 and are illustrated in figure 1 and figure 2.

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; (c) hydrophobic-hydrophobic interaction between the butyl group of TBAB and hydrophobic group of amino acid.

Applying the co-sphere overlap model<sup>28</sup> as the guideline, it may be inferred that, (a) and (b) type of interactions will lead to a positive  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  since there is a reduction in the electrostriction effect and the overall water structure is enhanced. Interactions of type (c) will lead to a negative  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  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 volume of transfer for the amino acids were observed. The  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  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 rise in TBAB concentration. 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, a positive  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  results indicating an enhancement in the ion-ion interaction between the zwitterionic centers 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  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  values. With the increase in the number of hydrophobic group from L- valine to L-leucine, the  $\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  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  $\Delta_{tr}V_{2,m}^0$  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 case of TBAB solution

### 9.3.5 Viscosity *B* coefficients

The relative viscosities,  $\eta_r$ , of the studied amino acids in the selected concentrations of co-solute solutions were calculated using the following relation and are summarized in table 1.

$$\eta_r = \frac{\eta}{\eta_0} \quad (13)$$

where  $\eta$  and  $\eta_0$  are the viscosities of solution and solvent, respectively. The *B* coefficients of viscosity were determined by fitting the  $\eta_r$  values to the Jones-Dole equation by least squares method as follows,

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Bc \quad (14)$$

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 8.

The *B*-coefficient measures the size and shape effects as well as the structural effect induced by solute-solvent interactions.<sup>29</sup> The *B*-coefficient values for amino acids in aqueous TBAB solutions follow the order



From the above order, it is clear that 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 liquid structure in the presence of TBAB.

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.<sup>22, 30, 31</sup> Similar to equation 4, the linear relation can be represented by the regression parameters

$$B = B(NH_3^+, COO^-) + n_c B(CH_2) \quad (15)$$

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 characterizes the mean contribution of  $CH-$  and  $CH_3-$  groups to  $B$ -coefficients of the amino acids. Such linear correlation<sup>20, 31</sup> has also been observed in other solutes for these amino acids. The values of the charged end-groups contribution,  $B(NH_3^+, COO^-)$  and the methylene group contribution,  $B(CH_2)$  to the  $B$ -coefficients are given in table 9. It can be seen from table 7 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.

#### 9.4. 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, 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 aqueous 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 as that of the  $V_{2,m}^0$  and 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

$\Delta_{tr}V_{2,m}^0$  and  $\Delta_{tr}K_{2,m}^0$  values result indicating an enhancement in the ion-ion interaction.

The increased number of hydrophobic groups in these amino acids leads to stronger interaction between the hydrophobic groups of amino acids with hydrophobic groups of TBAB thereby leading to negative volumes of transfer.

The magnitude of the  $B$  coefficient values increase with the concentration of TBAB indicating the promotion of liquid structure in the presence of TBAB.

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**Table 1**  
 Experimental densities ( $\rho$ ), viscosities ( $\eta$ ), sound speed ( $u$ ) of aqueous TBAB solutions at all the experimental concentration at 298.15 K

Molality of TBAB in water	$\rho \times 10^{-3} / \text{kg}\cdot\text{m}^{-3}$	$\eta / \text{mPa}\cdot\text{s}$	$u / \text{ms}^{-1}$
$m_s = 0.062$	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 2**

Experimental molalities ( $c$ ), densities ( $\rho$ ), viscosities ( $\eta$ ), 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.

$m_s = 0.062$					
$c / \text{mol}\cdot\text{kg}^{-1}$	$\rho \times 10^{-3} / \text{kg}\cdot\text{m}^{-3}$	$\eta_r$	$u / \text{ms}^{-1}$	$V_{\phi,2} \times 10^6 / \text{m}^3\cdot\text{mol}^{-1}$	$K_{\phi,2} \times 10^{10} / \text{m}^3\cdot\text{mol}^{-1}\text{Pa}^{-1}$
<b>Glycine</b>					
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
<b>Alanine</b>					
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

Contd.

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
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
<b>Alanine</b>					
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
<b>Valine</b>					
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
<b>Leucine</b>					
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

Table 3.  
Standard partial molal volumes of amino acids in Aqueous TBAB solution at 298.15 K

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

Table 4.  
Standard partial isentropic compressibilities of amino acids in Aqueous TBAB  
solution at 298.15 K

Amino Acids	Parameters	$K_{2,m}^0 \times 10^{10} / \text{m}^3 \cdot \text{mol}^{-1} \text{Pa}^{-1}$			
		Water	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	$K_{2,m}^0 \times 10^{10} / \text{m}^3 \cdot \text{mol}^{-1} \text{Pa}^{-1}$	-27.00 <sup>23</sup>	-27.14(±0.07)	-20.54(±0.09)	-16.53(±0.11)
	$S_K$	4.56	12.81	24.74	32.73
L-alanine	$K_{2,m}^0 \times 10^{10} / \text{m}^3 \cdot \text{mol}^{-1} \text{Pa}^{-1}$	-25.26 <sup>23</sup>	-25.47(±0.08)	-23.18(±0.11)	-16.75(±0.13)
	$S_K$	4.75	11.46	12.12	13.93
L-valine	$K_{2,m}^0 \times 10^{10} / \text{m}^3 \cdot \text{mol}^{-1} \text{Pa}^{-1}$	-30.62 <sup>23</sup>	-31.17(±0.11)	-30.95(±0.09)	-28.61(±0.07)
	$S_K$	8.43	16.50	23.73	27.54
L-leucine	$K_{2,m}^0 \times 10^{10} / \text{m}^3 \cdot \text{mol}^{-1} \text{Pa}^{-1}$	-31.78 <sup>23</sup>	-35.45(±0.09)	-34.83(±0.11)	-32.46(±0.12)
	$S_K$	13.61	17.11	19.98	40.04

Table 5.

 Contribution of zwitterionic groups ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) and  $\text{CH}_2$  group, and other alkyl chains to the infinite dilution apparent molar volume in aqueous TBAB at 298.15 K.

Group	$V_{2,m}^0 \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$			
	Water	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
$\text{NH}_3^+$ , $\text{COO}^-$	27.68( $\pm 0.92$ )	27.80( $\pm 0.86$ )	29.07( $\pm 0.72$ )	30.65( $\pm 0.51$ )
$\text{CH}_2$	15.91( $\pm 0.33$ )	15.66( $\pm 0.29$ )	15.40( $\pm 0.21$ )	15.17( $\pm 0.19$ )
$\text{CH}_3\text{CH}-$	31.82( $\pm 0.52$ )	31.32( $\pm 0.44$ )	30.80( $\pm 0.31$ )	30.34( $\pm 0.25$ )
$\text{CH}_3\text{CH}_2\text{CH}-$	47.73( $\pm 0.42$ )	93.96( $\pm 0.36$ )	92.40( $\pm 0.21$ )	91.02( $\pm 0.28$ )
$\text{CH}_3\text{CH}_3\text{CHCH}_2\text{CH}-$	79.45( $\pm 0.41$ )	78.30( $\pm 0.32$ )	77.00( $\pm 0.56$ )	75.85( $\pm 0.41$ )

Table 6

 Hydration number ( $N_w$ ) of amino acids in aqueous TBAB at 298.15 K

Amino Acids	$N_w$		
	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
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

Table 7

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

Amino Acids	$\Delta_{tr}V_{2,m}^0 \times 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$		
	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
Glycine	-0.09( $\pm 0.03$ )	0.43( $\pm 0.02$ )	1.26( $\pm 0.02$ )
L-alanine	-0.20( $\pm 0.08$ )	0.34( $\pm 0.07$ )	0.70( $\pm 0.08$ )
L-valine	-0.27( $\pm 0.05$ )	-0.29( $\pm 0.04$ )	0.62( $\pm 0.05$ )
L-leucine	-1.34( $\pm 0.21$ )	-1.36( $\pm 0.21$ )	-0.45( $\pm 0.23$ )

Table 8

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

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

Table 9

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

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

Table 10

 Contributions of ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) and  $\text{CH}_2$  groups to viscosity B-coefficients of the amino acids in aqueous TBAB Sasolutions at 298.15 K

Group	$B / \text{dm}^3 \text{mol}^{-1}$		
	$m_s = 0.0622$	$m_s = 0.125$	$m_s = 0.256$
$\text{NH}_3^+$ , $\text{COO}^-$	0.098( $\pm 0.18$ )	0.096( $\pm 0.08$ )	0.092( $\pm 0.11$ )
$\text{CH}_2$	0.057( $\pm 0.04$ )	0.072( $\pm 0.05$ )	0.097( $\pm 0.05$ )

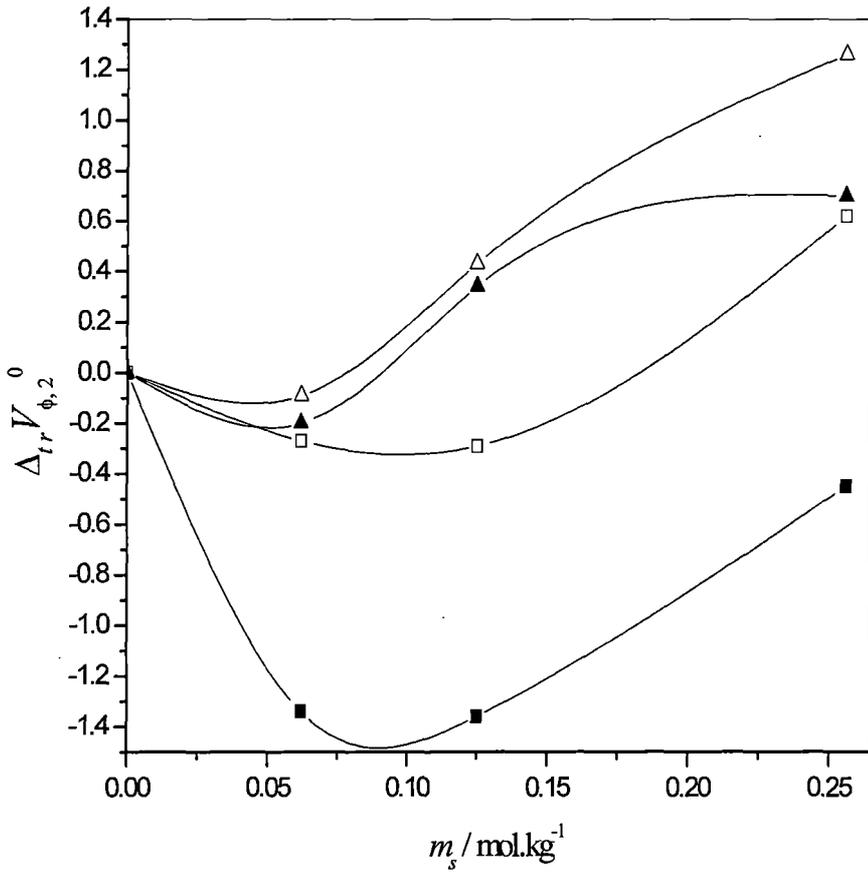


Figure1: The transfer volumes of the experimental amino acids from water to aqueous TBAB solutions plotted against the molarity  $m_s$  of the TBAB solutions at 298.15 K.  
 $\Delta$ , Glycine;  $\blacktriangle$ , L-Alanine;  $\square$ , L-Valine;  $\blacksquare$ , L-Leucine.

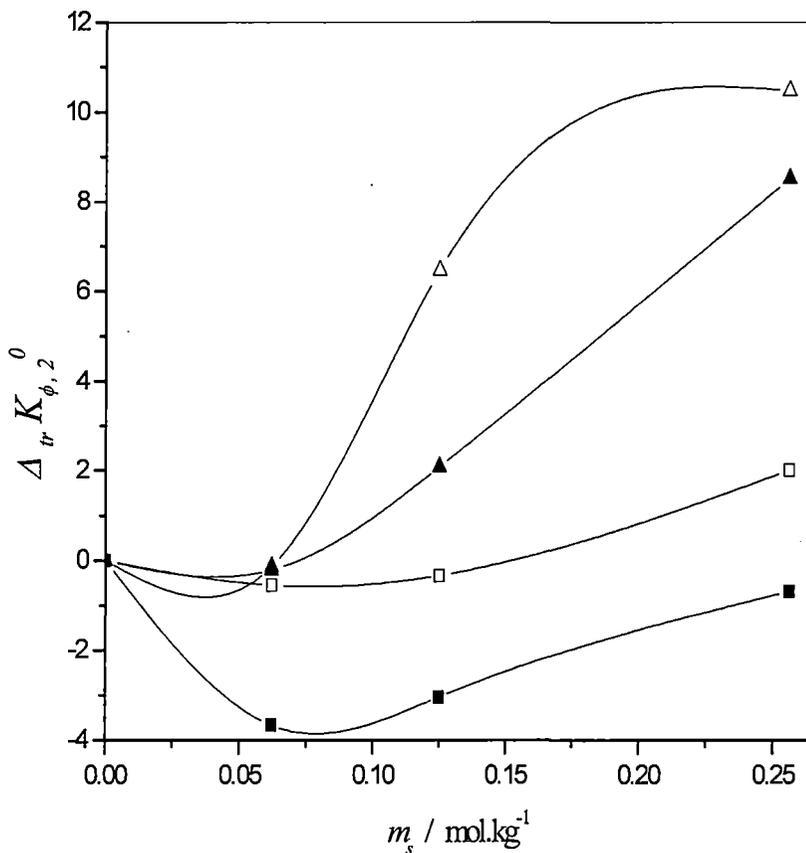


Figure 2: The transfer volumes of the experimental amino acids from water to aqueous TBAB solutions plotted against the molarity  $m_s$  of the TBAB solutions at 298.15 K.  $\Delta$ , Glycine;  $\blacktriangle$ , L-Alanine;  $\square$ , L-Valine;  $\blacksquare$ , L-Leucine.