CHAPTER VII

Partial molal volumes, viscosity *B*-coefficients and adiabatic compressibilities of some amino acids in aqueous resorcinol solutions at 298.15 K

Keywords: Partial molal volume, Viscosity *B*-coefficient, Isentropic compressibility, Amino acid.

7.1. Introduction

Globular proteins form a class of macromolecules which have well-defined physicochemical properties and functions in biological systems. They have a marginally stable native structure that results from a fine balance among various non-covalent forces: ionic and dipolar interactions, hydrogen bonding, and hydrophobic forces, etc.[1] The process of denaturation of a globular protein in aqueous solutions involves a change from the native state, in which the protein adopts its characteristic folded conformation, to the denatured state where the protein is predominantly in an extended form.[2,3] During this process, substantial changes in protein solvation will occur, and these changes will make an important contribution to the energetics of protein denaturation. The study of these protein-solvent interactions is difficult because of the complexity of the interactions in such a large molecule. However, one useful approach, which can be of help in our understanding of these interactions, is to study simple compounds such as amino acids and peptides, which model some specific aspects of the protein structure.

The rigid nature of α helix structure of proteins and peptides are affected by alcohols via dissolution of peptide aggregates. Amino acids exist as zwitterions in aqueous solution. These dipolar ions should reflect structural interactions with water molecules as in the case of electrolytes. The properties of amino acids in aqueous alcohol solutions have been studied by some workers [4-6] in order to understand the solute-solute interactions and the effects of various alcohols on proteins. It has been reported [6,7] that

polyhydric alcohols increase the thermal stability of proteins or reduce the extent of their denaturation by other reagents. The properties of solutions of polyols in aqueous and mixed solutions are important in many areas of applied chemistry and are essential for understanding the chemistry of biological systems [8,9] and act as vehicles for pharmaceuticals or cosmetics when introduce into living organisms. Resorcinol is an important organic compound, used externally as an antiseptic and disinfectant .It is also used as a chemical intermediate for the synthesis of pharmaceuticals and some organic compounds. An emerging use of resorcinol is as a template molecule in supramolecular chemistry .The -OH groups on resorcinol form hydrogen bonds to target molecules holding them in the proper orientation for a reaction.. Resorcinol is readily soluble in water through hydrogen bonding

Among the various physical parameters, the standard partial molal volume has been recognized as a quantity that is sensitive to structural changes occurring in solutions. In the present work we have studied the standard partial molal volumes of transfer of a homologous series of four amino acids in three different concentrations of aqueous Resorcinol solutions and interpreted the results in terms of possible interactions between solute and solvent molecules.

7.2. Experimental section

7.2.1 Source and purity of samples

The amino acids Glycine (Analar,>99%), DL-Alanine (S.D. fine Chemicals,>98.5%), L-valine (Loba Chemie, India, >99%), L-leucine (Loba Chemie, India, >99%). The amino acids were purified by re-crystallizing from methanol-water mixture and dried at 373.15 K for 12 h in vacuum desiccators over P_2O_5 before use. Resorcinol was purchased from Sd. Fine Chemical Limited. Resorcinol was purified by a reported procedure [10,11] and the compound was dried and stored in a vacuum desiccators. Freshly distilled conductivity water was used for the preparation of different aqueous resorcinol solutions. The physical properties of different aqueous resorcinol solutions are listed in Table 1. Stock solutions of resorcinol in different aqueous resorcinol solutions were prepared by mass and the working solutions were prepared by mass

dilution. The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in molarity of the resorcinol solutions is evaluated to ± 0.0001 mol dm^{-3}.

7.2.2. Apparatus and Procedure

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 measurements were done in a thermo stated bath controlled to ± 0.01 K. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was ± 2×10^{-4} mPa s. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation loses during the actual measurements. The reproducibility in mole fraction was within ± 0.0002 units. The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The precision of density measurements was ± 3×10–4 g cm^{-3}.

Ultrasonic speeds of sound (u) were determined by a multifrequency ultrasonic interferometer (Mittal enterprise, New Delhi, M-81) working at 2 MHz, calibrated with triply distilled and purified water, methanol and benzene at 298.15 K. The precision of ultrasonic speed measurements was ± 0.2 m s^{-1}. The details of the methods and techniques had been described elsewhere.[12, 13]

7.3. Results and discussion

Standard partial molar volume and compressibility:

Densities of aqueous solutions of amino acids containing resorcinol determined at 298.15K are given in Table 2. These data were used to calculate the partial molal volume of the solute V_ϕ using the following equation, [13, 14]

$$V_\phi = M/\rho - 1000(\rho - \rho_o)/m\rho_o \qquad (1)$$

where M is the molar mass of the solute in $g \cdot mol^{-1}$, m is the molality of solute in $mol \cdot kg^{-1}$ in the resorcinol-water mixture, and ρ and ρ_o are the densities of the solution and the solvent, respectively. The partial molal volumes of the amino acids were found to be a linear function of molality over the studied concentration range. Hence, values of the standard partial molal volume, V_ϕ^0 were calculated by least-squares fitting using the following Masson equation: [15]

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

where V_ϕ^0 is the partial molal volume at infinite dilution and S_v^* is the experimental slope, which is sometimes called volumetric pair wise interactions coefficient.[16] The regression coefficients V_ϕ^0 and S_v^* of Eq. 2 for the amino acids in aqueous resorcinol are presented in Table 3., where values of V_ϕ^0 and S_v^* for the amino acids in pure water are adapted from the literature .[17, 18]

The isentropic compressibility, K_ϕ, of the solution was calculated from the Laplace's equation:

$$K_S = 1/(u^2\rho) \qquad (3)$$

where ρ is the solution density and u is the ultrasonic speed in the solution.

The partial molal isentropic compressibility, K_ϕ , of the solutions was determined from the relation:

$$K_\phi = M K_S/\rho_0 + 1000 (K_S \rho_0 - K_S^0 \rho)/(m \rho \rho_0) \qquad (4)$$

K_S^0 is the isentropic compressibility of the solvent mixture, M is the molar mass of the solute, and m is the molality of the solution.

The standard partial molal isentropic compressibility, K_ϕ^0, was obtained by extrapolating the plots of K_ϕ versus the square root of molal concentration of the solute, $\sqrt{m}$ to zero concentration by a least-squares method, [19]

$$K_\phi = K_\phi^0 + S_K^* \sqrt{m} \qquad (5)$$

where, S_K^* is the experimental slope. The regression coefficients K_ϕ^0 and S_K^* of Eq. 5 for the amino acids in aqueous resorcinol are presented in Table 4.

V_ϕ^0 and K_ϕ^0 values are by definition free from solute-solute interactions and thus provide information regarding solute- solvent interactions. Solute- solute interactions can be understood from the S_v^* and S_K^* values.

It is seen from Table 3 and Table 4 that, the S_v^* and S_K^* values for all the amino acids are positive. The positive S_v^* and S_K^* 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_v^* and S_K^* values also change indicating that, the methyl groups modulates the interaction of the charged end groups in pair wise interaction.

The values of V_ϕ^0 are positive for all the amino acids under study in aqueous resorcinol at all molalities studied. The V_ϕ^0 value increases gradually with the increase in concentration of aqueous resorcinol over the studied concentration range, except for the case of valine where V_ϕ^0 value decreases with the increase in the molality of resorcinol.

From Table 4, it is observed that the value of standard partial molal isentropic compressibility K_ϕ^0 increases with the increase in concentration of resorcinol solution for all the concentration studied but all the values are negative.

At neutral pH, amino acid exist as zwitterions when dissolution in water and there is an overall decrease in the volume of water. This is due to the contraction of water near the end charged groups and termed as electrostriction. Hence the electrostricted water is much less compressible than bulk water and accounts for the partial molal compressibilities for the amino acids in mixed ternary solutions being larger than the

corresponding ones in water. It is also observed that the negative values of K_ϕ^0 for the studied amino acids follow the order -

Glycine < DL-alanine < L-valine < L-leucine

Since the contribution of methylene group to the partial compressibility is negative, it implies that the ions having the larger hydrophobic group may have more negative values for the partial molal expansibilities. Hence L-leucine may have largest hydrophobic group resulting higher negative values of K_ϕ^0.

Contributions of the zwitterionic end group, CH_2 groups and other alkyl chains of the α-amino acids to V_ϕ^0

At each molality, the V_ϕ^0 value varies linearly with the number of carbon atoms in the alkyl chain (R) of the amino acids. Similar correlations have been reported earlier by a number of workers,[17, 18] and this linear variation can be represented as follows:

$$V_\phi^0 = V_\phi^0 (NH_3^+,COO^-) + N_C (CH_2) \qquad (6)$$

where N_C is the number of carbon atoms in the alkyl chain of the amino acids and V_ϕ^0 (NH_3^+,COO^-) and V_ϕ^0 (CH_2) are the zwitterionic end group and methylene group contribution to V_ϕ^0, respectively. The values of V_ϕ^0 (NH_3^+,COO^-) and V_ϕ^0 (CH_2), calculated by a least-square regression analysis, are listed in Table 5, where those values in pure water are also provided from the literature.[19] It is well described in the literature [20] that V_ϕ^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.[21, 22]

$$V_\phi^0 (CH_3) = 1.5\ V_\phi^0 (CH_2) \qquad (7)$$

$$V_\phi^0 (CH) = 0.5\ V_\phi^0 (CH_2) \qquad (8)$$

and are listed in Table 5. It 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 the cosolute, which indicates that the interactions between the cosolute and charged

end groups (NH_3^+,COO^-) of amino acids are much stronger that those between the cosolute and CH_2.

Partial molal volumes of transfer of the zwitterionic end group, V_ϕ^0 (NH_3^+,COO^-), and other alkyl chain groups, V_ϕ^0 (R), of amino acids from water to cosolute solutions have been calculated as follows,

$$\Delta_{tr}V_\phi^0 (NH_3^+,COO^-) \text{ or } \Delta_{tr}V_\phi^0 (R) = V_\phi^0 (NH_3^+,COO^-) \text{ or } V_\phi^0 (R) \text{ [in aqueous cosolute]} - V_\phi^0 (NH_3^+,COO^-) \text{ or } V_\phi^0 (R) \text{ [in water]} \quad (9)$$

and are included in Table 5 and illustrated in Fig. 2. The contribution of (NH_3^+,COO^-) to $\Delta_{tr}V_\phi^0$ 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 $\Delta_{tr}V_\phi^0$ is negative for all the amino acids, and their contribution decreases with the increase in the number of carbon atoms.

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

$$V_\phi^0 (R) = V_\phi^0 (\text{amino acid}) - V_\phi^0 (\text{glycine}) \quad (10)$$

where V_ϕ^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 6.

The number of water molecule hydrated to the amino acids (N_w) in aqueous resorcinol solutions

The number of water molecules hydrated to the amino acids, N_w, calculated from the value of measured standard partial molar volume by the following manner.

The values of V_ϕ^0 of the studied amino acids can be expressed as,[17, 23]

$$V_\phi^0 = V_\phi^0 (\text{int}) + V_\phi^0 (\text{elect}) \quad (11)$$

where V_ϕ^0 (int) is the intrinsic partial molar volume of the amino acid and V_ϕ^0 (elect) is the electrostriction partial molar volume as a result of hydration of the amino acids .the V_ϕ^0 (int) consists of two terms: the Vander waal volume and the volume due to packing effects. The values of V_ϕ^0 (int) for the amino acids were calculated from their crystal molar volume by Millero et al [17] using the following relationship,

$$V_\phi^0 \text{(int)} = (0.7/0.634)\, V_\phi^0 \text{(cryst)} \qquad (12)$$

where, 0.7 is the packing density in an organic crystal and 0.634 is the packing density of randomly packed spheres. The molar volume of crystals was calculated using the crystal densities of the amino acids represented by Berlin and Pallansch [24] at 298.15 K. The values of V_ϕ^0 (elect) were obtained from the experimentally determined V_ϕ^0 values using Eq.11.

The number of water molecules hydrated to the amino acids due to electrostriction causes decrease in volume can be related to the hydration numbers,[17]

$$N_w = \frac{V_\phi^0 \text{ (elect)}}{V_E^0 - V_B^0} \qquad (13)$$

where V_E^0 is the molar volume of electrostricted water and V_B^0 is the molar volume of bulk water.

This model implies that the for every water molecules taken from the bulk phase to the surroundings of amino acid, the volume is decreased by $V_E^0 - V_B^0$, using a value of -3.0 $cm^3.mol^{-1}$.[17]

The obtained N_w values are listed in Table 7, where N_w varies with the solvent composition, showing a tendency to decrease with an increase in the concentration of resorcinol for glycine and L-alanine under investigation. The observed decreasing tendency of N_w for glycine and L-alanine supports the view [25] that the resorcinol has a dehydration effect on these amino acids in aqueous resorcinol solutions. In case of L-valine, a slight increase of N_w 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 hydration

number, N_w . However, for L-Leucine, the N_w values remain unaltered by resorcinol concentration. This indicates that, the hydrophobic group of leucine reduces the ion-ion interaction between the amino acid and the salt.

Partial molar volume of transfer from water to aqueous resorcinol solution

The values of partial molar volume of transfer and partial molar compressibility of transfer of the amino acid [18] from pure water to resorcinol are obtained from the eqns.

$$\Delta_{tr}V_{\phi}^{0} \text{ (water to aqueous resorcinol)} = V_{\phi}^{0} \text{ (in aqueous resorcinol)} - V_{\phi}^{0} \text{ (in water)} \quad (14)$$

$$\Delta_{tr}K_{\phi}^{0} \text{ (water to aqueous resorcinol)} = K_{\phi}^{0} \text{ (in aqueous resorcinol)} - K_{\phi}^{0} \text{ (in water)} \quad (15)$$

These results are reported in Table 8 and Table 9, graphically shown in Fig 1 and Fig 3 respectively. Since the solute-solute interactions are absent at infinite dilution, the observed transfer volume reflects the solute-solvent interactions. In general, the interactions between amino acids and resorcinol can be classified into: (i) Ion-polar group interactions between the NH_3^+ and COO^- groups of the Zwitterionic amino acid with the OH groups of the resorcinol; (ii) ion-non polar group interactions between the NH_3^+ and COO^- groups of the amino acid with the phenyl group of the resorcinol; (iii) Nonpolar- nonpolar group of interactions between the hydrophobic parts of the acids with the hydrophobic part of the resorcinol.. According to the cosphere overlap model of Gurney,[26] interactions of type (i) and (ii) lead to a positive $\Delta_{tr}V_{\phi}^{0}$ value, whereas type (iii) would lead to a negative $\Delta_{tr}V_{\phi}^{0}$ value because the introduction of alkyl groups provides an additional tendency for hydrophilic-hydrophobic and hydrophobic-hydrophobic group interactions leading to a reduction in the overall structure of water formed as a result of their cosphere overlap. Positive and negative values of volume transfer were observed for the studied amino acids (Table 8). The values of $\Delta_{tr}V_{\phi}^{0}$ for glycine, alanine increase positively with the increasing concentration of resorcinol. However for valine and leucine, the transfer value decreases.

The intrinsic volume is expressed by the following two types of terms

$$V_{intrinsic} = V_{vw} + V_{void} \qquad (16)$$

Where V_{vw} is the Vanderwaal volume,[27] occupied by solute and V_{void} is the volume of void and empty spaces present there in.[28]

Shahidi et al [29] modified the above equation to express the contribution of the solute molecules to its partial molar volume.

$$V_{\Phi}^{0}(\text{int}) = V_{vw} + V_{void} - n\,\delta_s \qquad (17)$$

Where δ_s is the shrinkage in the volume due to the interaction of hydrogen bonding groups present in the solute with water molecules and 'n' is the number of potential hydrogen bonding sites in the molecule.

Hence, the V_{ϕ}^{0} of the amino acid can be expressed as:

$$V_{\phi}^{0} = V_{vw} + V_{void} - V_{shrinkage} \qquad (18)$$

Assuming the fact that V_{vw} and V_{void} remain unchanged in water as well as in aqueous resorcinol solution the positive volume transfer of the amino acid can be documented from a decrease in the volume of shrinkage in the presence of the resorcinol solute in aqueous solutions.

The observed positive values of $\Delta_{tr}V_{\phi}^{0}$ and $\Delta_{tr}K_{\phi}^{0}$ of glycine indicate that the ion-hydrophilic and hydrophilic-hydrophilic interactions mask the ion-hydrophobic and hydrophobic-hydrophobic group interactions. The ion-hydrophilic interaction takes place between OH group resorcinol and charge end groups (NH_3^+ and COO^-) reduces the electrostriction phenomenon resulting in an increase in volume.

But for DL-alanine most of the values are negative though very small implies a balance of type (i) to (iii) interactions and at higher concentration 0.15(M) the values are positive indicates the predominance of ion-hydrophilic interactions.

But in the case of L-valine owing to large hydrophobic part in the side chain leading to hydrophobic – hydrophobic group interaction, with the hydrophobic part of resorcinol resulting in a negative volume and compressibility of transfer but with the increase of

the concentration of resorcinol the negative values are lower i.e., tend to be positive indicating (i) type of interactions tends to predominant.

But in the case of L-leucine the observed values, being more and more negative, strongly indicate the large hydrophobic part reside in the side chain of leucine. Similar observation shown by Bannerjee et al [30] and in lit.[31]

Viscosity B-Coefficient.

The experimental viscosity data for the systems studied are listed in Table 2. The relative viscosity (η_r) has been analyzed using the Jones-Dole equation [32]

$$\eta_r = \eta / \eta_o = 1 + A\sqrt{c} + B c \qquad (19)$$

where η and η_o are the viscosities of the ternary solutions (amino acid +resorcinol+ water) and binary solvents (resorcinol+water)and c is the molarity of the amino acids in ternary solutions. A and B are empirical constants known as viscosity A- and B-coefficients, which are specific to solute-solute and solute solvent interactions, respectively. Eq.19 can be rearranged

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad (20)$$

Values of A- and B-coefficients are obtained from a linear plot of the left-hand side of Eq.20 vs $\sqrt{c}$. The values of A- and B-coefficients are listed in Table 10. Due to the complex nature of A-coefficients, they are not discussed in the present work. Table 10 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

$$B = B(NH_3^+, COO^-) + N_C B(CH_2) \qquad (21)$$

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 11. It shows that $B(NH_3^+, COO^-)$) values decrease while $B(CH_2)$ values increase with

increasing concentration of resorcinol in ternary solutions, indicating that the zwitterionic groups break while the CH_2-group enhances the structure of the aqueous salt solutions. The side chain contributions to *B*-coefficients, *B*(R), have also been derived using the same scheme as that of V_ϕ^0 (R) and are listed in Table 5, which shows that *B*(R) values are positive and follow the order: L-leucine > L-valine > DL-alanine. This order is due to the greater structure breaking tendency of L-leucine as compared to L-valine and DL-alanine, and these findings are in line with our volumetric results discussed earlier.

The viscosity data are also analyzed on the basis of transition state theory for relative Viscosi ty of the acetate solutions as suggested by Feakins et al.[33] using Eq 22:

$$\Delta\mu^o{}_2^* = \Delta\mu^o{}_1^* + (RT/V^o{}_1)(1000B + V^o{}_2 - V^o{}_1) \qquad (22)$$

where $\Delta\mu^o{}_2^*$ is the contribution per mole of the solute to free energy of activation for viscous flow of solutions and $\Delta\mu^o{}_1^*$ is the free energy of activation per mole of solvent mixture . The values are reported in Table 12 . $V^o{}_1$ is the partial molal volume of the solvent mixture, $V^o{}_2$ is the partial molal volume of the solute. $\Delta\mu^o{}_1^*$ is calculated from

$$\Delta\mu^o{}_1^* = \Delta G^o{}_1^* = RT \ln(\eta_o V^o{}_1 / h N_A) \qquad (23)$$

where *h* is Planck's constant and N_A is Avogadro's number. From Table 12, it is seen that $\Delta\mu^o{}_1^*$ is almost constant at all solvent compositions. It means that $\Delta\mu^o{}_2^*$ is dependent mainly on the values of viscosity *B*-coefficients and $(V^o{}_2 - V^o{}_1)$ terms. It is also evident from Table 12 that the $\Delta\mu^o{}_2^*$ values are positive and much larger than the $\Delta\mu^o{}_1^*$ values. This may be due to the fact that amino-acid-solvent interactions in the ground state are stronger than in the transition state. In other words, the solvation of amino acids in the transition state is unfavourable in terms of free energy. Furthermore, as $\Delta\mu^o{}_2^* > \Delta\mu^o{}_1^*$, for solutes having positive viscosity *B*-coefficients indicates a stronger solute–solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.[34] The $\Delta\mu^o{}_2^*$ values (Table 12) of the amino acids were found to increase from Glycine to Leucine. This indicates that the solvation of the amino acids

in the transition state becomes increasingly unfavourable as the hydrophobicity (number of carbon atoms) of the side chain increases from Glycine to Leucine.

7.4. Conclusion

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

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Table 1. Experimental densities (ρ), viscosities (η), sound speed (u) of aqueous resorcinol solutions at all experimental concentration at 298.15 K

Molality of resorcinol in water mol kg^{-1}	$\rho \times 10^{-3}$ $kg.m^{-3}$	η mPa.s	u ms^{-1}
$m_s = 0.05$	0.9992	0.9013	1572.3
$m_s = 0.10$	1.0003	0.9102	1721.1
$m_s = 0.15$	1.0012	0.9208	1908.3

Table 2. Experimental molalities m/mol.kg^{-1}, densities $\rho\times10^{-3}$/Kg.m^{-3}, viscosities η/mPa.s, sound speed u/ms^{-1}, partial molar volume of the solute $V\phi\times10^{6}$/m^{3}.mol^{-1} and partial molal isentropic compressibility $K\phi$ $\times10^{10}$/m^{3}.mol^{-1}Pa^{-1} along with the concentration m_s of Glycine, DL-Alanine, L-Valine and L-Leucine in aqueous resorcinol solutions as a function of the molalities of Amino Acids.

m mol.kg^{-1}	$\rho\times10^{-3}$ Kg.m^{-3}	η mPa.s	u ms^{-1}	$V\phi\times10^{6}$ m^{3}.mol^{-1}	$K\phi\times10^{10}$ m^{3}.mol^{-1}Pa^{-1}
			m_s=.05		
			Glycine		
0.0246	1.0000	0.9066	1710.7	43.64	-25.78
0.0322	1.0002	0.9082	1757.7	43.99	-25.34
0.0566	1.0010	0.9123	1933.4	43.83	-24.41
0.0726	1.0014	0.9143	2077.0	44.01	-23.97
0.0888	1.0020	0.9169	2268.1	43.95	-23.82
0.101	1.0023	0.9191	2451.8	44.11	-23.72
			DL-Alanine		
0.0258	0.9999	0.9088	1704.8	60.29	-23.66
0.0358	1.0002	0.9118	1761.6	60.35	-23.20
0.0632	1.0010	0.9185	1947.5	60.43	-22.47
0.0793	1.0015	0.9220	2081.5	60.32	-22.07
0.0978	1.0020	0.9262	2280.7	60.38	-21.85
0.1114	1.0024	0.9296	2455.5	60.44	-21.55
			L-Valine		
0.0263	0.9999	0.9087	1741.2	90.43	-28.63
0.0337	1.0001	0.9119	1793.5	90.45	-28.01
0.0596	1.0008	0.9208	2029.5	90.50	-27.32
0.0762	1.0012	0.9271	2225.1	90.46	-26.74
0.0951	1.0018	0.9346	2527.6	90.48	-26.21
0.1101	1.0021	0.9405	2862.8	90.52	-25.77
			L-Leucine		
0.0252	0.9998	0.9097	1762.3	106.12	-32.99
0.0360	1.0001	0.9143	1856.9	106.20	-32.01
0.0619	1.0007	0.9226	2174.1	106.18	-31.34
0.0753	1.0011	0.9282	2398.0	106.21	-30.78
0.0954	1.0016	0.9394	2923.5	106.27	-30.26
0.1091	1.0019	0.9507	3565.7	106.24	-29.97
			m_s=0.10		
			Glycine		
0.0243	1.0011	0.9149	1858.2	43.78	-19.91
0.0325	1.0013	0.9163	1902.7	43.81	-19.04
0.0573	1.0021	0.9201	2074.9	44.02	-18.51
0.0731	1.0026	0.9228	2179.0	43.90	-17.49
0.0897	1.0031	0.9247	2274.2	43.84	-16.19
0.1018	1.0034	0.9271	2366.4	44.09	-15.72
			DL-Alanine		
0.0253	1.0010	0.9173	1873.2	60.46	-20.94
0.035	1.0013	0.9196	1935.4	60.49	-20.32

Contd.....

0.0617	1.0021	0.9261	2149.6	60.48	-19.75
0.0768	1.0025	0.9299	2298.5	60.51	-19.41
0.0969	1.0031	0.9348	2541.6	60.52	-18.94
0.1104	1.0034	0.9371	2739.1	60.56	-18.57
			L-Valine		
0.0258	1.0010	0.9163	1933.8	89.42	-27.34
0.0344	1.0013	0.9195	2007.9	89.55	-26.16
0.0621	1.0020	0.9269	2336.3	89.46	-24.95
0.0784	1.0025	0.9343	2575.3	89.34	-23.90
0.0964	1.0030	0.9420	3007.3	89.18	-23.60
0.1102	1.0034	0.9468	3428.6	89.12	-22.95
			L-Leucine		
0.0248	1.0009	0.9067	1954.9	106.30	-30.74
0.0349	1.0012	0.9115	2073.4	106.36	-30.19
0.0613	1.0018	0.9220	2536.5	106.35	-29.79
0.0760	1.0022	0.9276	2934.8	106.39	-29.20
0.0941	1.0026	0.9370	3826.2	106.38	-28.65
0.1068	1.0029	0.9440	4649.0	106.40	-27.30
			m_s=0.15		
			Glycine		
0.0243	1.0020	0.9247	2027.1	43.84	-12.98
0.0326	1.0022	0.9260	2073.2	43.76	-12.98
0.0573	1.0030	0.9294	2176.9	43.98	-11.20
0.0732	1.0035	0.9323	2230.3	43.72	-10.15
0.09	1.0040	0.9348	2266.5	44.09	-8.98
0.1024	1.0044	0.9367	2252.3	43.86	-7.67
			DL-Alanine		
0.0258	1.0019	0.9267	2059.8	60.72	-15.18
0.0346	1.0022	0.9294	2116.2	60.76	-14.92
0.0619	1.0029	0.9356	2310.8	60.79	-14.18
0.0792	1.0034	0.9385	2450.0	60.84	-13.70
0.0972	1.0039	0.9431	2603.0	60.76	-13.12
0.1098	1.0043	0.9469	2723.7	60.81	-12.78
			L-Valine		
0.0257	1.0019	0.9260	2169.2	89.08	-24.22
0.0353	1.0022	0.9279	2291.4	89.03	-23.89
0.0627	1.0030	0.9370	2674.1	88.98	-21.52
0.0791	1.0034	0.9430	3040.2	89.01	-21.05
0.0968	1.0039	0.9495	3669.7	88.99	-20.69
0.1108	1.0043	0.9556	4098.9	88.95	-19.4
			L-Leucine		
0.0246	1.0018	0.9038	2195.7	106.53	-27.36
0.0352	1.0021	0.9101	2336.7	106.55	-26.02
0.0627	1.0027	0.9196	2878.6	106.58	-24.56
0.0792	1.0031	0.9274	3321.8	106.55	-23.23
0.0975	1.0036	0.9365	4208.9	106.61	-22.36
0.1107	1.0039	0.9436	5232.3	106.58	-21.78

Table 3. Standard partial molar volumes of amino acids in aqueous resorcinol solution at 298.15 K.

Amino acids	Parameters	water	m_s =0.05	m_s =0.10	m_s =0.15
Glycine	$V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$	43.14(±.06)[34]	43.28	43.59	43.72
	S_v*	0.86	2.35	1.26	0.58
DL-Alanine	$V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$	60.43(±.73)[34]	60.18	60.21	60.59
	S_v*	0.73	0.69	0.12	0.05
L-Valine	$V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$	90.39(±.14)[34]	90.37	89.87	89.15
	S_v*	-	0.41	-2.12	-0.58
L-Leucine	$V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$	107.72(±.24)[34]	106.04	106.25	106.48
	S_v*	-	0.65	0.47	0.33

Table 4. Standard partial isentropic compressibilities of amino acids in aqueous resorcinol solution at 298.15

Amino acids	Parameters	water	m_s =0.05	m_s =0.10	m_s =0.15
Glycine	$K_\phi^0 \times 10^{10}$ $m^3 \cdot mol^{-1} \cdot Pa^{-1}$	-27.00 [17]	-27.70	-23.80	-18.52
	S_k^*	4.56	13.11	24.55	32.15
DL- Alanine	$K_\phi^0 \times 10^{10}$ $m^3 \cdot mol^{-1} \cdot Pa^{-1}$	-25.26 [17]	-26.32	-22.87	-17.52
	S_k^*	4.75	11.13	12.73	13.96
L-Valine	$K_\phi^0 \times 10^{10}$ $m^3 \cdot mol^{-1} \cdot Pa^{-1}$	-30.62 [17]	-31.12	-30.95	-28.71
	S_k^*	8.43	15.97	24.23	27.24
L-Leucine	$K_\phi^0 \times 10^{10}$ $m^3 \cdot mol^{-1} \cdot Pa^{-1}$	-31.78 [17]	-35.45	-33.61	-32.11
	S_k^*	13.61	16.79	17.18	31.13

Table 5. Contribution of the Zwitterionic End Group ($NH_3^+COO^-$), CH_2- Group, and Other Alkyl Chain Groups (R) to Standard Partial Molar Volume, V_ϕ^0, and Transfer Volumes, $\Delta_{tr}V_\phi^0$ in Different Aqueous Resorcinol Solutions at 298.15 K

group	$V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$				$\Delta_{tr}V_\phi^0 \times 10^6$ $m^3 \cdot mol^{-1}$		
	Water	m_s=0.05	m_s=0.10	m_s=0.15	m_s=0.05	m_s=0.10	m_s=0.15
$NH_3^+COO^-$	27.68	28.25	28.49	28.76	0.57	0.81	1.08
CH_2	15.91	15.57	15.50	15.41	-0.34	-0.41	-0.50
CH_3CH	31.82	31.14	31.00	30.82	-0.68	-0.82	-1.00
$(CH_3)_2CHCH$	63.64	62.28	61.99	61.63	-1.36	-1.65	-2.01
$(CH_3)_2CHCH_2CH$	79.45	77.86	77.49	77.04	-1.60	-1.96	-2.41

Table 6. Contribution of the Alkyl Chain Group (R) to Standard Partial Molar Volume, $V_\phi^0(R)$, and Viscosity *B*-Coefficient *B*(R) in Different Aqueous Resorcinol Solutions at 298.15 K

group	V_ϕ^0(R)$\times 10^6$ $m^3 \cdot mol^{-1}$			*B*(R) $m^3 \cdot mol^{-1}$		
	m_s=0.05	m_s=0.10	m_s=0.15	m_s=0.05	m_s=0.10	m_s=0.15
DL- Alanine	16.90	16.62	16.87	0.094	0.09	0.08
L-Valine	47.09	46.28	45.43	0.312	0.31	0.30
L-Leucine	62.76	62.66	62.76	0.430	0.46	0.50

Table 7. Hydration number (N_w) of amino acids in aqueous resorcinol at 298.15 K.

Amino acids	N_w		
	m_s=0.05	m_s=0.10	m_s=0.15
Glycine	2.9	2.8	2.7
DL-Alanine	3.9	3.8	3.7
L-Valine	4.0	4.2	4.4
L-Leucine	6.0	6.0	6.0

Table 8. Transfer volumes of amino acids ($\Delta_{tr}V_{\phi}^{0}$ $\times10^{6}/m^{3}\cdot mol^{-1}$) from water to aqueous resorcinol, at 298.15 K.

Amino- acids	$\Delta_{tr}V_{\phi}^{0}\times10^{6}/m^{3}\cdot mol^{-1}$		
	m_s=0.05	m_s=0.1	m_s=0.15
Glycine	0.24	0.39	0.58
DL-Alanine	-0.10	-0.02	0.08
L-Valine	-0.78	-0.84	-0.93
L-Leucine	-1.02	-1.15	-1.33

Table 9 Transfer compressibilities of amino acids ($\Delta_{tr}K_{\phi}^{0}\times10^{6}/m^{3}\cdot mol^{-1}$) from water to aqueous resorcinol, at 298.15 K

Amino- acids	$\Delta_{tr}K_{\phi}^{0}\times10^{6}/m^{3}\cdot mol^{-1}$		
	m_s=0.05	m_s=0.1	m_s=0.15
Glycine	-0.70	3.20	8.48
DL-Alanine	-1.06	2.39	7.74
L-Valine	-0.50	-0.33	1.91
L-Leucine	-3.67	-1.83	-0.33

Table 10. *A*- and *B*-coefficients for the amino acids in aqueous resorcinol solutions at 298.15 K.

Amino-acids	$B/m^{3}\cdot mol^{-1}$			$A/m^{3/2}\cdot mol^{-1/2}$		
	m_s=0.05	m_s=0.1	m_s=0.15	m_s=0.05	m_s=0.1	m_s=0.15
Glycine	0.140	0.148	0.165	0.020	0.013	0.003
DL-Alanine	0.234	0.241	0.247	0.016	0.011	0.002
L-Valine	0.453	0.456	0.463	-0.020	-0.031	-0.045
L-Leucine	0.571	0.604	0.660	-0.037	-0.047	-0.052

Table 11. Contributions of (NH_3^+, COO^-) and CH_2 groups to viscosity B-coefficients of the amino acids in aqueous resorcinol solutions at 298.15 K.

group	$B/m^3 \cdot mol^{-1}$		
	m_s=0.05	m_s=0.10	m_s=0.15
NH_3^+,COO^-	0.026	0.024	0.022
CH_2	0.108	0.113	0.121

Table12. Values of $(V^o_2 - V^o_1) \cdot 10^6/(m^3 \cdot mol^{-1})$, free energy of activation for the solvent, $\Delta\mu^o_1$*/(kJ·mol^{-1}), and solute $\Delta\mu^o_2$*/(kJ·mol^{-1}), for the amino acids in aqueous resorcinol at 298.15 K.

Parameters	Glycine	DL-Alanine	L-Valine	L-Leucine
m_s=0.05				
$(V^o_2 - V^o_1) \cdot 10^6$ $m^3 \cdot mol^{-1}$	25.20	42.09	72.25	87.91
$\Delta\mu^o_1$* kJ·mol^{-1}	9.20	9.20	9.20	9.20
$\Delta\mu^o_2$* kJ·mol^{-1}	19.23	32.11	61.98	78.13
m_s=0.10				
$(V^o_2 - V^o_1) \cdot 10^6$ $m^3 \cdot mol^{-1}$	25.48	42.07	71.68	88.04
$\Delta\mu^o_1$* kJ·mol^{-1}	9.22	9.23	9.23	9.24
$\Delta\mu^o_2$* kJ·mol^{-1}	20.29	32.95	62.22	82.32
m_s=0.15				
$(V^o_2 - V^o_1) \cdot 10^6$ $m^3 \cdot mol^{-1}$	25.57	42.40	70.89	88.18
$\Delta\mu^o_1$* kJ·mol^{-1}	9.26	9.26	9.27	9.28
$\Delta\mu^o_2$* kJ·mol^{-1}	22.57	33.73	62.85	89.50

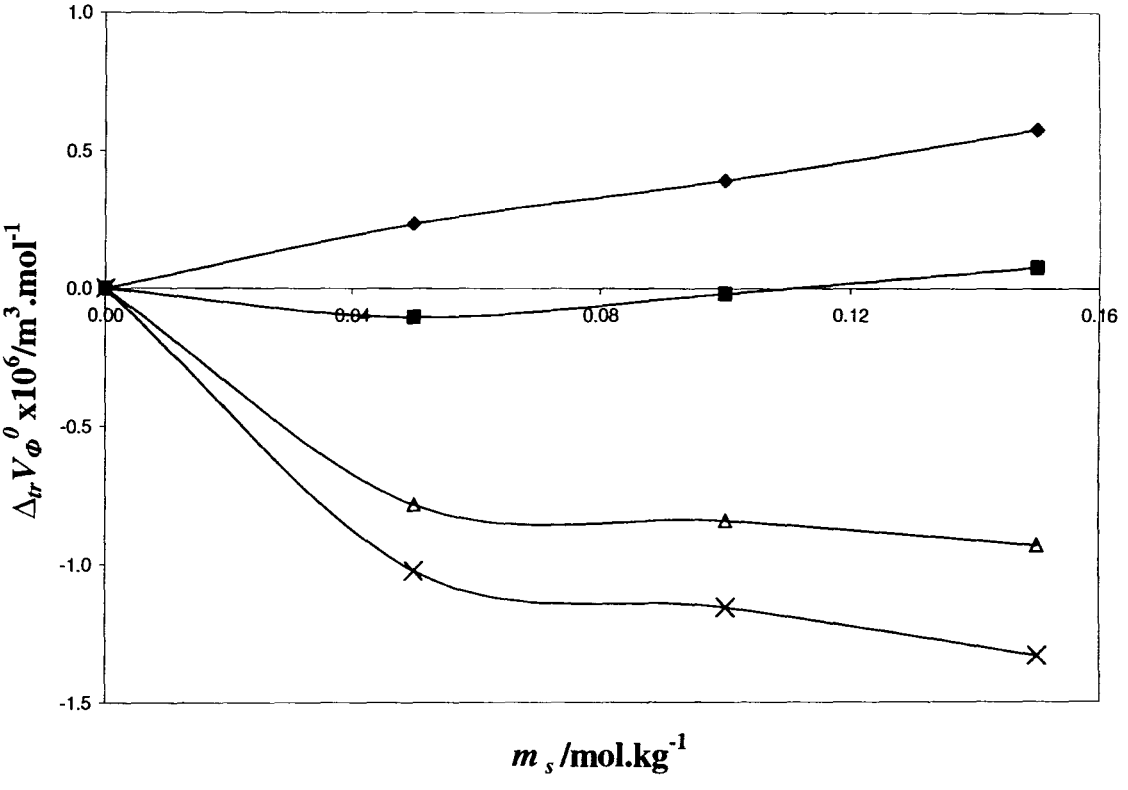

Fig. 1. The transfer volumes of Glycine(♦), DL-Alanine (■), L-Valine (△), L-Leucine (×), from water to aqueous resorcinol solutions plotted against the molarity m_s of the resorcinol solutions at 298.15 K.

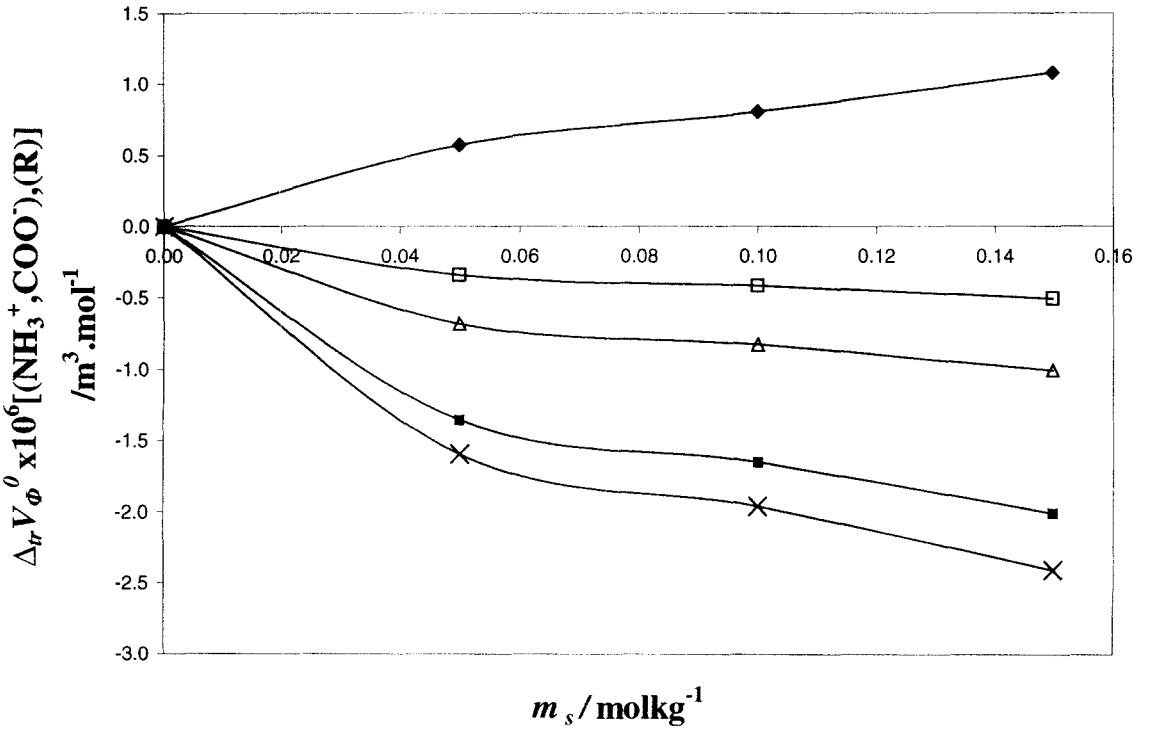

Figure 2. Contribution of $NH_3^+COO^-$ (♦) and CH_2 (□), CH_3CH (△),$(CH_3)_2CHCH$ (■), or -$(CH_3)_2CHCH_2CH$ (×) groups to standard volumes of transfer, $\Delta_{tr}V\phi^0$, vs molality, m_s, at 298.15 K.

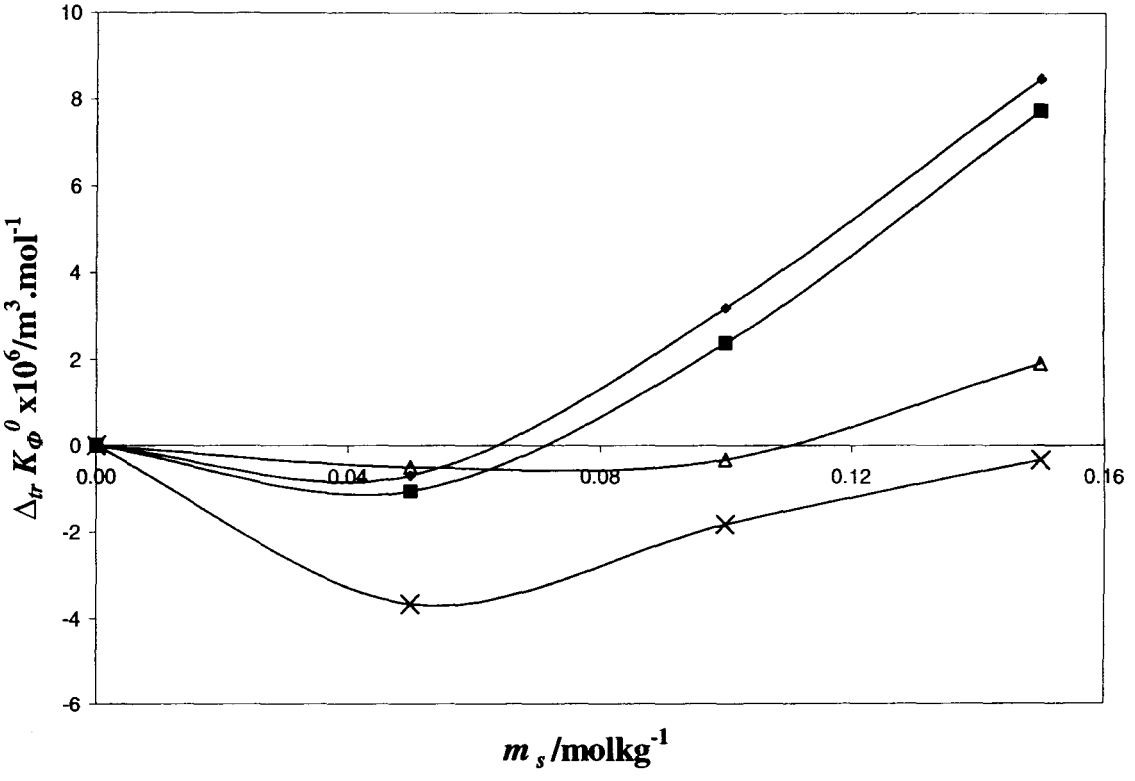

Fig. 3. The transfer compressibiltites of Glycine(♦), DL-Alanine (■), L-Valine (△), L-Leucine (×), from water to aqueous resorcinol solutions plotted against the molarity, m_s, of the resorcinol solutions at 298.15 K.