D.3: Studies on Solution Properties of Some Amino Acids in Aqueous Mixture of Catechol.

D.3.1. Introduction:

Many cations and anions of neutral salts affect the properties of proteins such as their solubility, stability and biological activity in widely different manner[1,2].It is well established that various cosolutes, cosolvents such as guanidine hydrochloride, sodium thiocyanate, magnesium chloride in different ways, act as effective probes of their conformation in solutions[3-6].

As proteins are complex macromolecules, the direct study of these important protein-water interactions are difficult. The small amino acid molecules incorporate some of the structural features found in proteins and have been used as model compounds for specific aspects of proteins in aqueous solutions[7,8].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[9,10], in order to understand the solute-solute interactions and the effects of various alcohols on proteins.

Thus the study of low molecular model compounds such as amino acids, peptides and their derivatives which represents the building block of proteins in a variety of media is of immense importance.

It has been reported[10,11], 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[12], and act as vehicles for pharmaceuticals or cosmetics when introduce into living organisms.

Ahluwalia et al[13,14]., reported apparent molar volumes of amino acids in aqueous salt and carbohydrate solutions. Ogawa, Mizutani, and Yasuda[14], has studied the viscosities and apparent molar volumes of amino acids in mixed aqueous solutions.

Accepted for Publication in Journal of Dispersion Science and Technology (In Press)

In view of the above and in continuation of our studies we have undertaken a systematic study on the volumes, viscosities and ultrasonic speeds of some amino acids in aqueous catechol solutions at 298.15 K.

D.3.2. Experimental section:

D.3.2.1. *Chemicals:*

The amino acids Glycine (Analar,>99%), L-alanine (S.D. fine Chemicals,>98.5%), L-valine (Loba Chemie, India, >99%), L-leucine (Loba Chemie, India, >99%), and catechol (S.D. fine Chemicals,>98%), were used for the present study. The amino acids were purified by re-crystallizing from methanol-water mixture and dried at 373.15 K for 12 h in a vacuum desiccator over P_2O_5 before use.

Commercial sample of catechol was purified by repeated crystallization from mixture of chloroform-methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dryed & distilled methanol was added dropwise. Fine plat like crystal separated and recovered by rapid filtration & ready for use. Deionized, doubly distilled, degassed water with a specific conductance of less than$10^{-6}\Omega$ cm^{-1} was used for all of the measurements. The purity of the solvents was ascertained by GLC.

D.3.2.2. *Measurement:*

The mass measurements were done on a digital electronic analytical balance (Mettler, AG 285, Switzerland), with a precision of ±0.01 mg. The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25cm^3 and an internal diameter of about 0.1 cm. The pycnometer with the experimental solution was equilibrated at 298.15 K with doubly distilled water and benzene. The measurements were done in a thermostat bath controlled to ±0.01 K. The pycnometer was then removed from thermostatic bath, properly dried and weighed. Adequate precautions were taken to minimize evaporation loses during the actual measurements. The precision of density measurements was ± 3×10^{-4} g cm^{-3}.

The viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature[15,16]. A thoroughly cleaned and perfectly dried viscometer filled

with experimental solution was placed vertically in a glass-walled thermostat maintained to ±0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch correct to ±0.1 s. The flow times were accurate to ± 0.1s, and the uncertainty in the viscosity measurements was ± 2 $\times 10^{-4}$ mPa.s. An average of triplicate measurement was taken into account. Viscosity of the solution, η, is given by the following equation:

$$\eta = \left(Kt - \frac{l}{t}\right)\rho \qquad (1)$$

where K and l are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ±0.003 mPa.s.

Details of the methods and techniques of density and viscosity measurements have been described elsewhere[17-19].

Ultrasonic speeds, u, were measured, with an accuracy of 0.2 %, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi, M-81) operating at 4 MHz. which is calibrated with water, methanol and benzene at 298.15K. The details of the methods have been described earlier[19].

D.3.3. Results and discussion:

D.3.3.1. *Standard partial molar volume and compressibility*:

The apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation [20]:

$$V_\phi = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0} \qquad (2)$$

where M is the molar mass of the solute, c is the molarity of the amino acids in catechol-water mixtures in mol.dm^{-3}, ρ_o and ρ are the densities of the solvent and the solution respectively in

$Kg.m^{-3}$. The experimentally measured densities (ρ), viscosities (η) and sound speed (u) at 298.15 K are given in table 1.

The apparent molar volumes and apparent molar isentropic compressibilities of the amino acids were shown in table 2 and found to be a linear function of molality over the studied entire concentration range.

The apparent molar volumes at infinite dilution, V_ϕ^0 (also known as partial molar volume at infinite dilution) were calculated using a least–squares treatment to the plots of V_ϕ versus $\sqrt{c}$ using the following Masson equation [21]:

$$V_\phi = V_\phi^0 + S_V^* \sqrt{c} \tag{3}$$

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

The V_ϕ^0 values are summarized in table 3. The experimental values of V_ϕ^0 for the amino acids in water agreed well with those reported in the literature[22-24].

The isentropic compressibility (K_S) of the solution was calculated from the Laplace's equation:

$$K_S = \frac{1}{u^2 \rho} \tag{4}$$

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

The apparent molar isentropic compressibility (K_ϕ) of the solutions was determined from the relation:

$$K_\phi = \frac{MK_S}{\rho_0} + \frac{1000\left(K_S\rho_0 - K_S^0\rho\right)}{c\rho\rho_0} \tag{5}$$

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

The limiting apparent molar isentropic compressibility (K_ϕ^0) was obtained by extrapolating the plots of K_ϕ versus the square root of molal concentration of the solute, $\sqrt{c}$ to zero concentration by a least-squares method[25]:

$$K_\phi = K_\phi^0 + S_K^* \sqrt{c} \tag{6}$$

where, S_K^* is the experimental slope.

V_ϕ^0 and K_ϕ^0 produce information regarding solute-solvent interactions and S_V^* is the experimental slope which is sometimes called volumetric pair wise interactions coefficient[24].

It has been observed from the volumetric data as well as compressibility data that most of the S_V^* and S_K^* values are positive for all amino acids studied. The positive values of S_V^* and S_K^* Simply that the interaction is dominated by the charged functional group of the zwitterionic amino acids and -OH group of catechol. The values of S_V^* and S_K^* varies with the addition of alkyl group in the side chain position of the amino acids. It indicates that the alkyl group modulates the interaction of the charged end groups in the pair wise interactions[24].

The values of V_ϕ^0 are positive for all the amino acids in catechol solution at all concentrations studied. For Glycine and L-alanine V_ϕ^0 increases but in the case of L-valine and L-leucine reverse is observed with the increase in the concentration of catechol solution.

From table 4, it is observed that the values of isentropic compressibilities at infinite dilution (K_ϕ^0) increase with the increase in concentration of catechol solution and 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 apparent molar 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< L-alanine< L-valine < L-leucine

Since the contribution of alkyl 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 molar expansibilities. Hence L-leucine may have largest hydrophobic group resulting higher negative values of K_ϕ^0.

D.3.3.2. ***Group contribution:***

The alkyl chain of the studied amino acids are CH_2- (Glycine), CH_3CH- (L-alanine), CH_3CH_3CHCH- (L-valine) and $CH_3CH_3CHCH_2CH$- (L-leucine). It was observed that the values of V_ϕ^0 of the present amino acids in catechol solutions vary linearly with the number of carbon atoms n_C, in their hydrophobic part. Similar linear correlation for the homologous series of α-amino acids has also been reported in aqueous[13], and glucose, solutions

In this way a regression analysis of the V_ϕ^0 values as a function of n_C is carried out by the following equation[22]:

$$V_\phi^0 = V_\phi^0\left(NH_3^+, COO^-\right) + n_C\left(CH_2\right) \tag{7}$$

where n_C is the number of carbon atoms in the alkyl side chain of the amino acids. $V_\phi^0\left(NH_3^+, COO^-\right)$ and $V_\phi^0\left(CH_2\right)$ are the zwitterionic end groups and the methylene side group contributions respectively.

The values of $V_\phi^0\left(CH_2\right)$ characterize the mean contribution of CH and CH_3 group to the V_ϕ^0 of the amino acids. The other alkyl chains contribution of the amino acids calculated by Hakin et al[19], as follows:-

$$V_\phi^0\left(CH_3\right) = 1.5V_\phi^0\left(CH_2\right) \tag{8}$$

$$V_\phi^0\left(CH\right) = 0.5V_\phi^0\left(CH_2\right) \tag{9}$$

The values of $V_\phi^0\left(NH_3^+, COO^-\right)$ are larger than $V_\phi^0\left(CH_2\right)$.It implies that the interactions of the functional groups of catechol with the zwitterionic groups of amino acids dominate in comparison to those of the hydrophobic group-catechol interactions. Side chain contribution increases with the increase of chain length.

D.3.3.3. *Hydration Number*:

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[23,26]:

$$V_\phi^0 = V_\phi^0(\text{int}) + V_\phi^0(\text{elec}) \tag{10}$$

where $V_\phi^0(\text{int})$ is the intrinsic partial molar volume of the amino acid and $V_\phi^0(\text{elec})$ is the electrostriction partial molar volume as a result of hydration of the amino acids. The $V_\phi^0(\text{int})$ consists of two terms: the Van der waal volume and the volume due to packing effects.

The values of $V_\phi^0(\text{int})$ for the amino acids were calculated from their crystal molar volume by Millero et al.[23] using the following relationship:

$$V_\phi^0(\text{int}) = \frac{0.7}{0.634} V_\phi^0(\text{cryst}) \tag{11}$$

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[27] at 298.15 K. The values of $V_\phi^0(\text{elec})$ were obtained from the experimentally determined V_ϕ^0 values using equation 10.

The number of water molecules hydrated to the amino acids due to electrostriction causes decrease in volume can be related to the hydration numbers[20,23]

$$N_W = \frac{V_\phi^0(\text{elec})}{\left(V_E^0 - V_B^0\right)} \qquad (12)$$

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 for every water molecules taken from the bulk phase to the surroundings of amino acid, the volume is decreased by using a value of -3.0 $cm^3.mol^{-1}$,[20] for $\left(V_E^0 - V_B^0\right)$ at 298.15 K the hydration number of the studied amino acids were calculated & reported in table 6.

From table 5, the observed values of N_W for the amino acids in catechol solutions were varied in the following order:

$$N_W \text{ (L-leucine)} > N_W \text{ (L-valine)} \approx N_W \text{ (L-alanine)} > N_W \text{ (Glycine)}$$

In the case of Glycine the N_W values decreases with the increase of concentration of catechol solution owing to reduction in the electrostriction. But in other amino acid cases namely L-alanine, L-valine & L-leucine the value of hydration numbers remain unchanged by the increase of catechol solution .This is due to the fact that with the increase of hydrophobic group[28], the interaction between the charge end group and OH group of catechol solution reduces.

The N_W values are lower than observed by Banerjee et al.[28] leads to the fact that the bulky phenyl group in the hydrophobic part are lesser solvated compared to the small size of the alkyl groups.

D.3.3.4. ***Partial Molar volume of Transfer & Partial Molar Compressibility of Transfer*:**

The values of partial molar volume of transfer and partial molar compressibility of transfer of the amino acid[24] from pure water to catechol are obtained from the eqns.

$$\Delta_{tr}V_\phi^0 = V_\phi^0(\text{catechol}) - V_\phi^0(\text{water}) \qquad (13)$$

$$\Delta_{tr}K_{\phi}^{0} = K_{\phi}^{0}(\text{catechol}) - K_{\phi}^{0}(\text{water}) \qquad (14)$$

These results are reported in table 7 and tabl 8, graphically shown in fig 1 and fig 2 respectively.

The uncertainty in the values of volume transfer and compressibility of transfer are calculated as the root mean square of the uncertainities associated with the apparent molar properties at infinite dilution. Both positive and negative results were observed from the calculation for amino acids.

The values of the $\Delta_{tr}V_{\phi}^{0}$ in the case glycine are all positive at three different concentration of catechol solution. For alanine tends to increase of catechol solution. However in the latter two amino acid cases the transfer value decreases. The calculated transfer values are explained by the cosphere model by Gurney[29] and Franks & Evans.

There are several types of interactions occurring in the ternary system of amino acid, catechol and water.

(a) Ion-polar group interactions between the NH_3^+ and COO^- groups of the Zwitterionic amino acid with the OH groups of the catechol.

(b) ion-non polar group interactions between the NH_3^+ and COO^- groups of the amino acid with the phenyl group of the catechol

(c) Nonpolar- nonpolar group of interactions between the hydrophobic parts of the acids with the hydrophobic part of the catechol.

Introducing the cosphere overlap model[30] the ion- polar group interactions would lead to a positive $\Delta_{tr}V_{\phi}^{0}$ and $\Delta_{tr}K_{\phi}^{0}$ due to decrease of electrostriction effect and the overall water structure is enhanced.

Interaction of the type (b) & (c) would lead to a negative $\Delta_{tr}V_{\phi}^{0}$ and $\Delta_{tr}K_{\phi}^{0}$. It signifies the presence of hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions resulting a reduction in the water structure due to their co spheres overlapping.

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

$$V_{\text{Intrinsic}} = V_{\text{VW}} + V_{\text{Void}} \tag{15}$$

where V_{VW} is the Van der waal volume, occupied by solute and V_{Void} is the volume of void and empty spaces present there in.

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

$$V_{\phi}^{0}(\text{int}) = V_{\text{VW}} + V_{\text{Void}} - n\sigma_{\text{S}} \tag{16}$$

where σ_{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:

$$V_{\phi}^{0} = V_{\text{VW}} + V_{\text{void}} - V_{\text{shrinkage}} \tag{17}$$

Assuming the fact that V_{VW} and V_{Void} remain unchanged in water as well as in aqueous catechol 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 catechol solute in aqueous solutions.

The observed positive values of volume transfer and compressibility of transfer 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 catechol and charge end groups (NH_3^+ and COO^-) reduces the electrostriction phenomenon resulting in an increase in volume.

But for L-alanine most of the values are negative though very small implies a balance of type (a) to (c) interactions and at higher concentration the values are positive indicating the ion-hydrophilic interactions predominant.

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 catechol resulting in a negative volume and compressibility of transfer but with the increase of the concentration of catechol the negative values are lower i.e., tend to be positive indicating (a) type of interactions tends to predominant.

But in the case of L-leucine the observed values are more &more negative strongly indicate the large hydrophobic part reside in the side chain of leucine. Similar observation shown by Bannerjee et al[28].

D.3.3.5. *Viscosity B – coefficient*:

The relative viscosities η_r are expressed by $\eta_r = \frac{\eta}{\eta_0}$, where η and η_0 signifies the viscosities of the solution and solvent respectively. The calculated η_r by the above method are listed in the table (9). These η_r values have been utilized to calculate the viscosity B coefficient by Jones- Dole equation:

$$\eta_r = 1 + Bc + A\sqrt{c} \qquad (18)$$

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

A and B are empirical constants known as 'A' and 'B' coefficients. A and B imply the solute – solute and solute – solvent interactions respectively and 'c' is the concentration of ternary solution in molarities.The values of A and B are obtained from the straight line by plotting $(\eta_r - 1)/\sqrt{c}$ against $\sqrt{c}$.

The values of B are reported in table (9). This 'B' coefficient reflect the size and shape effect as well as the structural effect caused by the Solute – Solvent interactions [31].The 'B' coefficient values for amino acids in pure water and in catechol solutions follow the order

Glycine < L-alanine < L-valine <L-Leucine.

From the above trend it is confirmed that the magnitude of the '*B*' coefficient increases with the increasing of molar mass and side chain length of the amino acids. Due to the liquid structure caused by catechol solution in amino acid supports the increasing values of '*B*' with the increasing concentration of the ternary solution. complexing nature of '*A*' are not discussed here.

The '*B*' coefficient values imply the net structural effects of the charged end group and the hydrophobic ($-CH_2$) group on the amino acids. By plotting '*B*' values with the number of carbon atoms of the alkyl chain straight line were observed. These effects can be expressed as follows.

$$B = B\left(NH_3^+COO^-\right) + N_C B\left(CH_2\right) \tag{20}$$

The regression parameters $B\left(NH_3^+COO^-\right)$ and $B\left(CH_2\right)$ reflect the charge end group contribution and methylene group contribution are listed in table (10).

Such linear correlation[32,33] has also been observed in other solute for those amino acids. It is to be mentioned that the contribution of $B\left(CH_2\right)$ is the mean contribution of CH and CH_3 groups to '*B*' coefficients of the amino acids.

It is interesting to note from table 10 that the contribution of $B\left(CH_2\right)$ group to the '*B*' coefficient is increased while $B\left(NH_3^+COO^-\right)$ group contribution decreases with the increase of concentration of catechol solution indicating the fact that ion polar interaction between the zwitterionic group and OH group of catechol reduced while increasing contribution of $B\left(CH_2\right)$ reflect the hydrophobic – hydrophobic type interaction predominant in aqueous catechol solution.

D.3.4.Conclusion:-

From the above results of transfer of volume, transfer of compressibility, number of hydrated molecules and the viscosity '*B*' coefficient it has been concluded that the partial molar quantities increases with the increase of concentration of catechol.The contribution of the zwitterions ($NH_3^+COO^-$) group to the value of the partial molar volumes is larger in comparison

to the (CH_2) group and increases with the increasing concentration of catechol solution. The standard volume of transfer & transfer compressibility for the amino acids Glycine, L-alanine and L-valine increase with increasing concentration of catechol clearly rationalize the ion-hydrophilic interaction between the hydrophilic part of the said amino acid and the cosolute and predominant over hydrophobic interaction. But for L-leucine having the large alkyl part in the side chain hydrophobic interactions develop. The hydration numbers of the amino acids increases from Glycine to L-leucine also indicate more & more water molecules solvated due to increasing number of carbon atoms in the side chain by hydrophobic interaction.

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

Molarity of catechol in water(mol.dm^{-3})	$\rho\times10^{-3}$/kg.m^{-3}	η/mPa.s	u/m.s^{-1}
c =0.05	0.9975	0.8521	1502.3
c =0.10	0.9988	0.8698	1555.6
c =0.15	0.9997	0.8893	1621.1

Table 2 Experimental concentration (c), densities (ρ), viscosities (η), sound speed (u), apparent molar volumes (V_ϕ) and apparent isentropic compressibilities (K_ϕ) along with the concentration (c) of pure aqueous catechol solutions and Glycine, L-alanine, Lvaline, L-leucine in aqueous catechol solution as a function of the molarities of amino acids

c/ mol.dm^{-3}	$\rho\times10^{-3}$/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}
		c=0.05			
		Glycine			
0.0160	0.9980	0.8715	1570.1	43.25	-23.47
0.0281	0.9984	0.8741	1621.1	43.32	-22.34
0.0402	0.9988	0.8855	1677.2	43.40	-21.86
0.0563	0.9993	0.8889	1758.4	43.51	-21.32
0.0764	0.9999	0.8914	1862.3	43.59	-20.32
0.0962	1.0005	0.9091	1974.4	43.62	-19.46
		L-alanine			
0.0200	0.9981	0.8640	1588.6	60.50	-23.42
0.0362	0.9985	0.8647	1664.9	60.53	-22.74
0.0523	0.9990	0.8750	1747.7	60.58	-22.13
0.0685	0.9995	0.8770	1836.7	60.60	-21.42
0.0846	0.9999	0.8817	1942.2	60.62	-21.06
0.1003	1.0004	0.8907	2047.9	60.64	-20.43
		L-valine			
0.0201	0.9980	0.8722	1612.6	90.19	-29.04
0.0362	0.9985	0.8793	1714.5	90.20	-28.35
0.0524	0.9989	0.8917	1832.8	90.22	-27.70
0.0686	0.9994	0.9023	1972. 6	90.23	-27.10
0.0849	0.9998	0.9082	2151.4	90.24	-26.74
0.1003	1.0000	0.9163	2347.5	90.25	-26.10

Table 2: (Continued)

c/ mol.dm^{-3}	$\rho\times10^{-3}$/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}
			L-leucine		
0.0241	0.9981	0.8675	1658.2	106.26	-32.81
0.0393	0.9985	0.8745	1779.0	106.23	-32.25
0.0546	0.9989	0.8859	1921.4	106.17	-31.50
0.0697	0.9993	0.8930	2101.0	106.15	-31.04
0.0849	0.9996	0.9010	2338.7	106.13	-30.66
0.0992	1.0000	0.9052	2643.0	106.11	-30.27
			c=0.10		
			Glycine		
0.0241	0.9996	0.8859	1653.0	43.43	-19.61
0.0401	1.0001	0.8931	1721.6	43.48	-18.92
0.0522	1.0005	0.8944	1764.1	43.49	-17.61
0.0673	1.0009	0.9023	1831.7	43.52	-17.12
0.0834	1.0014	0.9040	1900.0	43.54	-16.34
0.0991	1.0019	0.9107	1964.6	43.56	-15.56
			L-alanine		
0.0200	0.9994	0.8870	1644.7	60.60	-21.71
0.0361	0.9998	0.8956	1719.3	60.65	-20.7
0.0523	1.0003	0.9006	1793.5	60.68	-19.52
0.0684	1.00081	0.9005	1879.9	60.70	-19.00
0.0846	1.0012	0.9229	1958.8	60.72	-18.00
0.1002	1.0017	0.9199	2082.6	60.74	-18.20
			L-valine		
0.0241	0.9995	0.8814	1700.1	89.80	-27.76
0.0402	0.9999	0.8860	1808.3	89.76	-26.60
0.0564	1.0004	0.8983	1932.9	89.72	-25.71
0.0685	1.0007	0.8994	2044.4	89.69	-25.31
0.0847	1.0012	0.9083	2213.2	89.64	-24.62

Table 2: (Continued)

c/ mol.dm^{-3}	$\rho\times10^{-3}$/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}
0.1003	1.0016	0.9125	2412.4	89.62	-24.02
		L-leucine			
0.02	0.9993	0.8831	1691.5	106.33	-31.65
0.0354	0.9997	0.8935	1815.8	106.31	-30.89
0.0409	0.9998	0.8976	1866.8	106.31	-30.72
0.0666	1.0005	0.9077	2159.9	106.29	-29.76
0.0822	1.0009	0.9184	2417.0	106.28	-29.38
0.0991	1.0013	0.9317	2824.7	106.27	-29.02
		c=0.15			
		Glycine			
0.0240	1.0004	0.9025	1684.3	43.88	-11.64
0.0401	1.0009	0.9066	1719.2	43.89	-10.48
0.0521	1.0013	0.9126	1742.3	43.90	-09.77
0.0682	1.0019	0.9137	1767.0	43.91	-08.80
0.0843	1.0023	0.9169	1786.6	43.92	-07.94
0.1000	1.0028	0.9267	1793.5	43.92	-06.93
		L-alanine			
0.0200	1.0003	0.8871	1714.7	60.73	-20.10
0.0361	1.0007	0.8910	1789.3	60.76	-18.80
0.0522	1.0012	0.9026	1872.0	60.79	-18.15
0.0683	1.0016	0.9044	1949.7	60.82	-17.12
0.0846	1.0021	0.9122	2029.2	60.84	-16.21
0.1000	1.0025	0.9250	2123.9	60.86	-15.82
		L-valine			
0.0241	1.0004	0.8775	1780.4	89.72	-26.81
0.0402	1.0008	0.8886	1900.1	89.65	-25.60
0.0523	1.0011	0.8892	2003.5	89.60	-24.98
0.0684	1.0016	0.8962	2159.3	89.54	-24.16

Table 2: (Continued)

c/ mol.dm^{-3}	$\rho\times10^{-3}$/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}
0.0847	1.0020	0.9023	2349.6	89.51	-23.44
0.0970	1.0024	0.9104	2532.3	89.49	-23.07
		L-leucine			
0.0180	1.0001	0.8871	1750.2	106.30	-29.78
0.0341	1.0005	0.9008	1881.0	106.27	-28.49
0.0503	1.0009	0.9057	2043.0	106.26	-27.84
0.0665	1.0013	0.9231	2231.7	106.25	-26.88
0.0814	1.0017	0.9242	2455.3	106.24	-26.25
0.1000	1.0022	0.9508	2839.1	106.22	-25.56

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

Amino acids	Parameters	Water	$c = 0.05$	$c = 0.10$	$c = 0.15$
Glycine	$V_\phi^0 \times 10^6/m^3.mol^1$	43.14	42.97	43.315	43.842
	S_V^* $(m^9.mol^{-3})^{1/2}$	0.86	2.1718	0.7811	0.2486
L-alanine	$V_\phi^0 \times 10^6/m^3.mol^{-1}$	60.43	60.39	60.494	60.618
	S_V^* $(m^9.mol^{-3})^{1/2}$	0.73	0.8122	0.7811	0.7661
L-valine	$V_\phi^0 \times 10^6 m^3.mol^{-1}$	90.39	90.133	89.979	89.954
	S_V^* $(m^9.mol^{-3})^{1/2}$	----	0.3478	-1.1295	-1.5293
L-leucine	$V_\phi^0 \times 10^6/m^3.mol^{-1}$	107.72	106.41	106.37	106.35
	S_V^* $(m^9.mol^{-3})^{1/2}$	-----	-0.9729	-0.3326	-0.3954

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

Amino acids	Parameters	Water	$c = 0.05$	$c = 0.10$	$c = 0.15$
	K_ϕ^0 x10^{10}/				
	$m^3 \cdot mol^{-1}Pa^{-1}$	-27.0	-26.04	-23.76	-16.04
glycine	S_K^* $(m^9 \cdot mol^{-3}Pa^{-1})^{1/2}$	4.56	20.83	26.15	27.83
	K_ϕ^0 x10^{10}/				
	$m^3 \cdot mol^{-1}Pa^{-1}$	-25.26	-25.85	-24.52	-23.64
l-alanine	S_K^* $(m^9 \cdot mol^{-3}Pa^{-1})^{1/2}$	4.750	16.64	17.51	24.94
	K_ϕ^0 x10^{10}/				
	$m^3 \cdot mol^{-1}Pa^{-1}$	-30.62	-31.06	-30.83	-30.24
l-valine	S_K^* $(m^9 \cdot mol^{-3}Pa^{-1})^{1/2}$	8.430	14.42	21.10	23.20
	K_ϕ^0 x10^{10}/				
	$m^3 \cdot mol^{-1}Pa^{-1}$	-31.78	-33.61	-34.26	-35.24
l-leucine	S_K^* $(m^9 \cdot mol^{-3}Pa^{-1})^{1/2}$	13.61	6.060	16.87	23.70

Table 5. Contribution of zwitterionic groups ($NH_3^+COO^-$) and CH_2 group, and other alkyl chains to the infinite dilution apparent molar volumes in aqueous catechol solution at 298.15 K.

	$V_\phi^0 \times 10^6$/ $m^3.mol^{-1}$			
Group	Water	c=0.05	c=0.1	c=0.15
$NH_3^+COO^-$	27.68	27.989	28.361	28.885
CH_2	15.91	15.662	15.56	15.435
CH_3CH	31.82	31.324	31.12	30.87
CH_3CH_3CHCH	63.64	62.65	62.24	61.74
$CH_3CH_3CHCH_2CH$	79.45	78.31	77.8	77.18

Table 6. Hydration number (N_W) of amino acids in aqueous catechol at 298.15 K.

Amino acids	N_w		
	c=0.05	c=0.1	c=0.15
Glycine	3	2.9	2.7
L-alanine	3.8	3.8	3.7
L-valine	4	4	4
L-leucine	6	6	6

Table 7. Transfer volumes of amino acids ($\Delta_{tr}V_{\phi}^{0} \times 10^{6}$/ $m^3.mol^{-1}$) from water to aqueous catechol, at 298.15 K.

Amino acids	$\Delta_{tr}V_{\phi}^{0}$ x10^{6} / $m^3.mol^{-1}$		
	c=0.05	c=0.1	c=0.15
Glycine	0.061	0.331	0.73
L-alanine	-0.187	-0.019	0.255
L-valine	-0.681	-0.719	-0.695
L-leucine	-0.831	-0.969	-1.065

Table 8. Transfer compressibilities of amino acids ($\Delta_{tr}K_{\phi}^{0} \times 10^{6}/m^{3}.mol^{-1}$) from water to aqueous catechol, at 298.15 K.

Amino acids	$\Delta_{tr}K_{\phi}^{0}$ x10^{6} / $m^{3}.mol^{-1}$		
	c=0.05	c=0.1	c=0.15
Glycine	0.96	3.24	10.96
L-alanine	-0.59	0.74	1.62
L-valine	-0.44	-0.21	0.38
L-leucine	-1.9	-2.48	-3.46

Table 9. *A*- and *B*-coefficients for the amino acids in aqueous catechol solutions at 298.15 K.

Amino acids	B/ $m^3.mol^{-1}$			A/ $m^{3/2}.mol^{-1/2}$		
	c=0.05	*c*=0.1	*c*=0.15	*c*=0.05	*c*=0.1	*c*=0.15
Glycine	0.1534	0.1666	0.1782	0.1488	0.0943	0.0657
L-alanine	0.2684	0.2802	0.2901	0.0476	0.0963	0.0959
L-valine	0.4539	0.4715	0.4842	0.0962	0.0107	-0.0019
L-leucine	0.5564	0.6056	0.6553	0.031	0.0264	0.0658

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

Group	*c*=0.05	*c*=0.1	*c*=0.15
NH_3^+,COO^-			
	0.0607	0.06	0.0576
CH_2			
	0.0991	0.107	0.1148

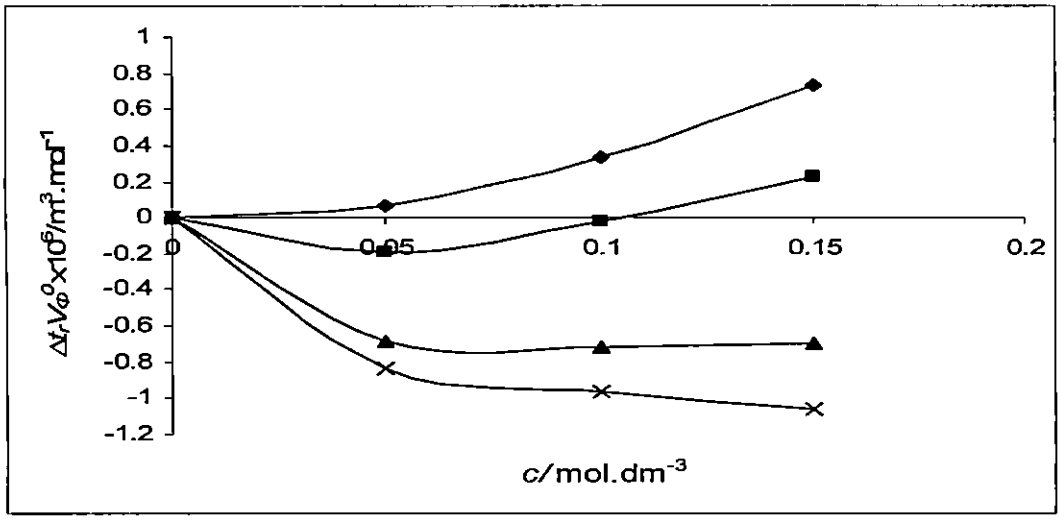

Figure1.The transfer volumes $\Delta_{tr}V_{\phi}^{0}$ of the experimental amino acids from water to aqueous catechol solutions plotted against the molarity c of the catechol solutions at 298.15 K. ♦, Glycine; ■, L-alanine; ▲, L-valine; ×, L-leucine

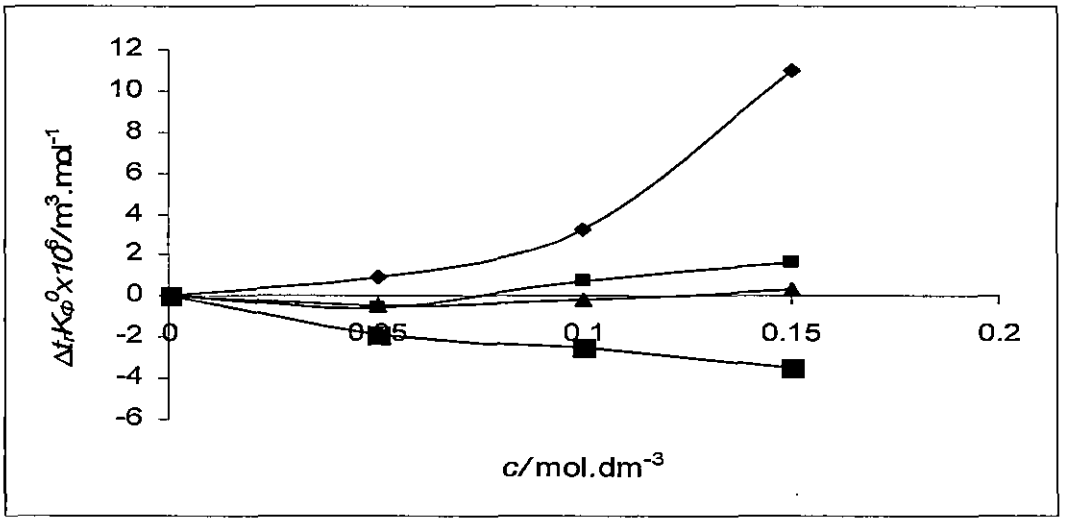

Figure2 The transfer compressibilities $\Delta_{tr}K_\phi^0$ of the experimental amino acids from water to aqueous catechol solutions plotted against the molarity *c* of the catechol solutions at 298.15 K. ♦, Glycine; ■, L-alanine; ▲, L-valine; ■, L-leucine