

Volumetric studies of some amino acids in aqueous 1,4- dioxane solution at 308.15K

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(Received: April 12, 2007; Accepted: June 04, 2007)

ABSTRACT

The Density measurement was carried out in aqueous solution of glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine in 10% 1,4- dioxane solution at 308.15 K. The values of apparent molar volume, limiting apparent molar volume have been evaluated from density data. These values are used for calculating the number of water molecule hydrated (n_H) to the amino acids. Transfer volumes at infinite dilution from water to aqueous 1,4- dioxane solution have been also calculated. Group contribution to partial molar volumes has been determined for the amino acids. Transfer parameter have been interpreted in terms of solute-co solute interaction on the basis of co-sphere overlap model. All these parameters are related to type and extent of intermolecular interactions in binary liquid mixtures. All the results were interpreted in the light of ion-ion and ion-solvent interactions and of structural effect of solutes in solutions.

Key Words: AMINO acids, transfer function, co-sphere overlap model interaction coefficients.

INTRODUCTION

Knowledge of various solute-solvent and solute-solute interaction this interactions is very important to understand various fundamental phenomenon like stability of proteins, folding/unfolding processes, denaturation of proteins aggregation, several biochemical process such as protein dehydration in aqueous solutions¹⁻⁴. The interaction of amino acids with electrolyte in the aqueous solutions and there temperature dependence of these interactions also play a important role in understanding nature of action of bioactive molecule, the thermodynamic behavior of biochemical process in the body and the stability of the organism found in submarine hot springs⁵⁻⁷. Extensive ultrasonic data have been reported at 298.15K. We understand that much more relevance and significance can be achieved by studied compounds of biological importance at temperature close to physiological temperature 308.15K being close to the optimum temperature of several living

species offers a better choice for such experimentation.

One can notice that there is lack of volumetric data up to high concentration range of amino acids and electrolytes. Very less data are available for amino acids in 1,4- dioxane systems⁸. There is need of examining the effect of amino acids on the properties of electrolyte. So it is preferred to study properties of model compounds like amino acids instead of complex bio-molecules. In order to understand the effects of ionic species on amino acids in general, various properties of amino acids in aqueous 1,4- dioxane solutions are studied.

MATERIAL AND METHODS

Five amino acids namely glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine of highest purity were obtained from Sigma chemicals Co. Amino acids were dried in vacuum oven for 24 hrs on kept over P_2O_5 in vacuum

desiccators. 1,4- dioxane was refluxed and then distilled over sodium metal using a fractionating glass column. The middle fraction distilling at 373 K was collected for use. All the solutions were prepared on the molarity basis. The samples were weighted on a mettler balance having accuracy of 0.01mg. Water used to prepare solutions was obtained by distilling deionised water over alkaline KMnO_4 and it was thoroughly degassed prior to its use. The specific conductance of the water used was less than $0.055 \times 10^{-6} \text{ s cm}^{-1}$

The densities of the solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb of total volume of 8 cm^3 and capillary with internal diameter of 0.1 cm was chosen⁹⁻¹⁵ for the present work. The details pertaining to calibration experimental set up and operational procedure have been previously described⁹⁻¹⁵. An average of triplicate measurement was taken in to account. The reproducibility of density measurement was $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$. The temperature was constantly maintain by controlled temperature water bath (Gemini scientific instruments, Madras) having accuracy of $\pm 0.01^\circ \text{C}$.

RESULTS AND DISCUSSION

Density (ρ), apparent molar volume (V_ϕ), limiting apparent molar volume (V_ϕ^0), experimental slopes (S_v), transfer volume ΔV_ϕ^0 at infinite dilution from water to aqueous 10% 1,4- dioxane solutions of amino acids viz. glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine in 10% aqueous 1,4-dioxane at 308.15 K. as a function of molarity are included in table 1.

In the present study, densities of these solutions are increasing with increase in concentration of amino acids. The plot of density with the concentration amino acids in 10% aqueous 1,4-dioxane are found to be linear in all the cases.

The apparent molar volumes (V_ϕ) were calculated from the density data using well-known expression^{16,17,18}

$$V_\phi = \frac{1000(\rho_0 - \rho_s)}{C \cdot \rho_0} + \frac{M}{\rho_0} \quad \dots(1)$$

Where ρ_0 and ρ_s are densities of solutions and solvent respectively. C is molarity and M is the molar mass of solute. The resulting values of apparent molar volumes (V_ϕ) with the molar concentration (M) of the amino acids in 10% aqueous 1,4-dioxane at 308.15 K are reported in table. 1.1. Comparison with earlier results¹⁹ shows that Values of V_ϕ increase with increase in temperature in aqueous 1,4-dioxane. It is also found that V_ϕ increases linearly with increase in size of alkyl V_ϕ side chain of the amino acids in aqueous 1,4-dioxane. It indicates that the solute-solvent interactions increases with increase in size of the alkyl side chain of amino acids and with the concentration of amino acids²⁰⁵. It is accordance with earlier results¹⁹

The variation of apparent molar volumes with the square root of molar concentration can be represented by Mason's equation²⁰.

$$V_\phi = V_\phi^0 + S_v \cdot C^{1/2} \quad \dots(2)$$

Where V_ϕ^0 is the limiting value of the apparent molar volume (equal to the partial molar volume at infinite dilutions) and S_v is the experimental slope. The Values of V_ϕ^0 and S_v obtained by least square fitting of the V_ϕ values to equation 2 for various amino acids in aqueous 1, 4-dioxane, which are reported in table 1.

Limiting apparent molar Volume (V_ϕ^0) and the experimental slope have been employed to indicate the type of interaction²⁰⁷⁻²⁰⁸. The effect of temperature on V_ϕ^0 has been interpreted in terms of the solute-solvent interactions while that on experimental slope in terms of solute-solute and solute-solvent interaction^{21,22}. The positive value of S_v suggesting that the added electrolyte behave as a structure maker in the solvent while negative value of S_v suggest the structure breaker capacity in the solvent.

All the amino acids studied have positive V_ϕ^0 value in binary aqueous solution of aqueous 1,4-dioxane. It is also found that V_ϕ^0 increase linearly with the size of alkyl side chain of amino acids and increases with increase in temperature. It indicates that the co-solute-solvent interaction increase both

on increasing temperature and the size of alkyl side chain of amino acids²³.

Since S_v is related to solute-solute interaction. It is evident from table 1 that the values of the slope S_v for all amino acids in aqueous 1,4-dioxane are negative suggesting weak solute-solute interaction in the system. The experimental slope S_v increases with increase in temperature, suggest that more and more solute is accommodated in void space left in packing the large associated solvent molecule and such enhance the structure of the solvent. However S_v is found to decrease with increase in temperature of L-valine in aqueous 1,4-dioxane, suggesting the decrease in solute-solute interaction with the rise in temperature indicating structure-breaking effect of L-valine in aqueous 1,4-dioxane. It is found from table 4.6 that the values of S_v are more negative for L-alanine and L-valine at different temperature when compared with the values of S_v of other amino acids.

The partial molar volumes of transfer (ΔV_ϕ^0) from water to aqueous have been calculated by using the equation 3. Banipal et al.⁸ reported values of V_ϕ^0 in water; these values were used to calculate ΔV_ϕ^0 .

$$\Delta V_\phi^0 = V_\phi^0(1,4\text{-dioxane}) - V_\phi^0(\text{in water}) \quad \dots(3)$$

The value of ΔV_ϕ^0 at 308.15 are illustrated in table 1. The more positive value for glycine and L-alanine indicates the dominance of the charged group NH_3^+ and COO^- while negative ΔV_ϕ^0 values in case of L-valine L-leucine and L-phenyl alanine indicates the effect of hydrophobic parts. That is the interactions between the 1,4-dioxane and zwitter ionic center of amino acids increase with increase in temperature. For L-valine the interaction between non-polar group of L-valine and 1,4-dioxane are predominant. The overall effect is that the charged end group of glycine and L-alanine influence electrostatically the surrounding water molecule the so-called electrostriction²³. In other word, the hydration co-sphere of $\text{NH}_3^+100^-$. Which are more hydrated than that of aqueous 1,4-dioxane will be affected to greater extent than the later. The positive ΔV_ϕ^0 values results that the dehydration of solute and co-solute occurs more in case of glycine and L-alanine²³.

S. Li. et al.,²⁴ also reported positive ΔV_ϕ^0 values for different amino acids from water to aqueous glucose solutions.

Now to explain partial molar volume data, different models have been used. Franks et. al.,²⁵ have shown that partial molar volume at infinite dilution of a non electrolyte is a combination of two factors by the following equation.

$$\Delta V_\phi^0 = V_{\text{int}} + V_s \quad \dots(4)$$

Where is V_{int} the intrinsic molar volume of the non-hydrated solute V_s is the contribution due to the interaction of the solute with water. Some workers^{26,27} have suggested that the V_{int} is made of the following type of contribution.

$$V_{\text{int}} = V_{v,w} + V_{\text{void}} \quad \dots(5)$$

Where V_{v_1} is the Van der walls volume^{28,29} and V_{void} is the volume associated with void or empty space. For electrolyte zwitter ionic solutes, this equation was modified by Shahidi et. al.²⁶ to find contribution of one molecule to partial molar volume of a hydrophobic solutes as

$$V_\phi^0 = V_{v,w} + V_{\text{void}} - V_{\text{shrinkage}} \quad \dots(6)$$

Where $V_{\text{shrinkage}}$ is the volume due to shrinkage this is due to interaction of hydrogen bonding sites with water molecules. Assuming that $V_{v,w}$ and V_{void} have the same magnitude in water and aqueous 1,4-dioxane positive ΔV_ϕ^0 values of glycine and L-alanine might arise from the decrease in $V_{\text{shrinkage}}$ in aqueous 1,4-dioxane. The interaction 1,4-dioxane with the zwitter ionic center of amino acids (glycine and L-alanine) reduces the effect electrostriction of water, thereby causing a decrease in $V_{\text{shrinkage}}$. In other words some water molecule may be released as bulk water in presence of 1,4-dioxane. It brings about the increase in volume of the solvent³⁰ thereby the reducing the strong interactions between amino acids and water. This results in positive volume of transfer from water to aqueous 1,4-dioxane solution observed in case of glycine and L-alanine. Thus a positive ΔV_ϕ^0 for glycine and L-alanine results from

the decreased effect of 1,4-dioxane and glycine or L-alanine on water structure, which arises due to glycine or L-alanine — 1,4-dioxane. The negative ΔV_{ϕ}^0 values of L-valine, L-Leucine and L-phenyl alanine might arise from the smaller decrease in $V_{\text{shrinkage}}$ in 1,4-dioxane solution.

ΔV_{ϕ}^0 Values can further be rationalized by

co-sphere overlap model developed by Gurney³¹ and Frank and Evans³². According this property of water molecules in the hydration co sphere depend on the nature of solute molecule. When two solute particles come close enough such that their co-sphere overlap. Some of the co sphere material is displaced and this is accompanied by changes in the thermodynamic parameters.

Table 1: Densities(ρ), apparent molar volume(V_{ϕ}), limiting apparent molar volume (V_{ϕ}^0), experimental slope (Sv), transfer molar volume (ΔV_{ϕ}^0) and dehydration number (nH) of some amino acids in 10% aqueous 1,4-dioxane at 308.15K

Conc.	ρ	V_f	V_{ϕ}^0	Sv	ΔV_{ϕ}^0	nH
Glycine						
0.00	1.01252		44.67	-1.35	1.99	3.46
0.025	1.01327	44.50				
0.075	1.01478	44.38				
0.125	1.01630	44.31				
0.175	1.01782	44.25				
0.225	1.01938	44.02				
L-alanine						
0.00	1.02152		60.08	-1.56	0.31	4.64
0.025	1.01320	60.99				
0.075	1.01458	60.83				
0.125	1.01597	60.70				
0.175	1.01736	60.65				
0.225	1.01878	60.50				
L-valine						
0.00	1.01252		89.28	1.47	-1.00	5.16
0.025	1.01317	89.98				
0.075	1.01448	89.92				
0.125	1.01581	89.74				
0.175	1.01714	89.62				
0.225	1.01840	89.50				
L-leucine						
0.00	1.01252		106.67	-1.43	-0.90	6.72
0.025	1.01308	107.44				
0.075	1.01421	107.34				
0.125	1.01535	107.22				
0.175	1.01699	107.12				
0.225	1.01765	107.02				
L-phenyl alanine						
0.00	1.01252		119.74	-1.34	-1.50	7.91
0.025	1.01339	120.76				
0.075	1.01579	120.70				
0.125	1.01791	120.60				
0.175	1.02008	120.48				
0.225	1.02260	120.38				

The interaction between aqueous 1,4-dioxane and amino acids can be classified as follows 1) hydrophilic-ionic interaction occurring between zwitter ionic centers of amino acids and dipolar parts of 1,4-dioxane 2) Hydrophilic – hydrophobic interaction occurring between non polar parts of amino acids and hydrophobic parts of 1,4-dioxane.

According to the co sphere model in terms of solute-co solute interactions, hydrophilic-ionic group interaction contributes positively, whereas hydrophilic-hydrophobic group interaction contributes negatively to the Δv_{ϕ}^0 values. In case of glycine and L-alanine, the former type of interactions is predominant over the latter and for L-valine, L-leucine, L-phenyl alanine hydrophilic-hydrophobic group interaction are dominating over the hydrophilic-ionic group interaction. It may noted from A. Pal and S. Kumar's³³ findings that values of L alanine are less than those of glycine and L-valine in solutions. This is in line with the earlier conclusion drawn on the basis of volume of shrinkage that varies solute-co-solute interactions occur in these system which contribute to different extents, depending on the particular amino acids solution. The overall effect is that the solute – co solute interactions are predominant over the solute-solvent interaction as obtained in glycine and L-alanine .

The hydration of solute molecule in water is explained on the basis of Frank and Wen³⁴ model of solute-solvent interaction, which pictures three different solvent interactions, which pictures three different solvents structure regions in the neighborhood of the solute. Just out side the molecule, there is layer of immobilized and compressed water as a result of electrostrictive and other attractive forces exerted the solute. The solute this is surrounded by slightly less compressed or “structure broken” region of water molecule distantly affected by these forces. The outermost layer is bulk water, which possesses the typical tetra coordinated hydrogen- bonded structure not affected by any of the above forces. Compressibility measurements indicate the changes in the first two layers of solvent around the solute molecule. In case of carbohydrate molecule, the water structure is slightly disturbed by the hydrogen -bonded network around the solute; this holds the water around the solute firmly, making

the hydration layer even less compressible.

The number of water molecule n_H hydrated to the amino acids were calculated using the method given by^{35,36,37}

$$n_H = V_{\phi}^0(\text{Elect}) / (V_{\phi}^0 - V_{\phi}^0) \quad \dots(7)$$

Where v_{ϕ}^0 is the molar volume of electrostricted water and v_{ϕ}^0 is the molar volume of bulk water [$18.069 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ at 298.15K]. The reported values²³⁴ of $(v_{\phi}^0 - v_{\phi}^0) = -3.3 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ at 308.15K. The electrostriction partial molar volume $v_{\phi}^0(\text{Elect})$ can be estimated from values of v_{ϕ}^0 [amino acids].

$$V_{\phi}^0(\text{Elect}) = V_{\phi}^0(\text{amino acids}) - V_{\phi}^0(\text{int}) \quad \dots(8)$$

where $v_{\phi}^0(\text{int})$ ²³⁴ has been calculated from the following expression

$$V_{\phi}^0(\text{int}) = (0.7/0.6) V_{\phi}^0(\text{cryst}) \quad \dots(9)$$

Where $v_{\phi}^0(\text{cryst})$ (= mol.wt./ d_{cryst}) is the crystal molar volume, 0.7 is the packing density for molecules in the organic crystals and 0.6 is the packing density for random packing spheres. The values of $v_{\phi}^0(\text{int})$ for the amino acids have been estimated from equation 8 & 9 using d_{cryst} values for glycine ,L-alanine and L-valine ,L-leucine ,L-phenyl alanine taken from work of Berlin and Pallansch^{38s}. Using the value of $(v_{\phi}^0 - v_{\phi}^0)$ and values of $v_{\phi}^0(\text{Elect})$ calculated from above method are given in table 1.

From the computed values of n_H , It is found that in all the concentration, each in aqueous 1,4-dioxane molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecules.

Conclslon

In summary, we have shown ion-amino acid interaction parameters from volumetric properties of glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine in 10% aqueous 1,4-dioxane at 308.15 K. The partial molar volumes of transfer (Δv_{ϕ}^0) from water to aqueous have been calculated

from measured quantities. The more positive value of Δv_{ϕ}^0 for glycine and L-alanine indicates the dominance of the charged group NH_3^+ and COO^- while negative Δv_{ϕ}^0 values in case of L-valine, L-leucine and L-phenyl alanine indicates the effect of hydrophobic parts. That is the interactions between the 1,4-dioxane and zwitter ionic center of amino acids increase with increase in temperature. For L-valine the interaction between non-polar group of L-valine and 1,4-dioxane are predominant. The overall effect is that the charged end group of glycine and L-alanine influence electrostatically the

surrounding water molecule the so-called electrostriction¹⁵¹. Also from the computed values of n_H , it is found that in all the concentration, each in aqueous 1,4-dioxane molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecules.

ACKNOWLEDGMENTS

Authors are thankful to the principal J E S College, Jalna for providing laboratory facilities and encouragement.

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