

Research Article

**Kosmotropicity And
Cheiotropicity Of Various
Neutral Amino Acids In
Water With The
Temperature Range
(T=288.15-318.15) K Using
Cosphere Overlap Model**

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Abstract

Apparent molar volumes, $V_{2,\phi}$ of glycine, DL- α -alanine, DL- α -amino-*n*-butyric acid, L-valine and L-leucine in water solutions have been determined from densities measurements at various temperatures (T= 288.15, 298.15, 308.15 and 318.15)K. The standard partial molar volumes, $V_{2,\phi}^0$ obtained from $V_{2,\phi}$ have been used to calculate on the basis of Mason equation. The structure making / breaking capacities of these amino acids in water have been discussed. The structure making/breaking capacities of these amino acids in water have also been discussed on the basis of Hepler equation. Apparent molar volumes of glycine in water as a function of concentration and density change at T=288.15K will be shown as octagon whereas the values at different corners while values of different densities shown at inner of octagon depict apparent molar volumes with the change in concentration of glycine at fixed temperature T=288.15K. Similar observations were noted for other amino

acids at different temperatures also. The values of glycine at different concentrations will show heptagonal pattern which means that density of solution varies with concentration as well as temperatures which further effect molar volumes.

Key words: Glycine · DL- α -amino-*n*-butyric acid·L-valine· L-leucine·Partial molar volumes

INTRODUCTION

The detailed study of proteins is very difficult as they denatured with the mild change in temperature, PH of solution and other thermodynamic factors. There in order to study these proteins we are using model approach which is nothing but taking small amino acids as model compounds and they were studies individually and then using additive property the nature of protein will be determined. The amino acids are either kosmotropic or cheiotropic in nature. Remarkable experimental work has been done by many scientists in solution thermodynamics [1-3] but very little explained the structure making and breaking tendencies of different amino acids.

MATERIALS AND METHODS

The amino acids selected for the present study are glycine (G-7126, 99 %), DL- α -alanine(A-7502, 99 %), DL- α -amino-*n*-butyric acid(A-1754, 98 %), L-valine(V-0500, 99 %) and L-leucine (L-8000, 98 %) were obtained from sigma chemicals co. were used without further purification and dried over anhydrous CaCl₂ in a vacuum desiccator before use. Deionized, doubly distilled degassed water with a specific conductance of less than $1.3 \times 10^{-4} \Omega \cdot m^{-1}$ was used for all of the measurements. All solutions were prepared by mass using a mettler balance with an accuracy of ± 0.01 mg.

Results and discussion

Apparent molar volumes of amino acids have been calculated as follows:

$$V_{2,\phi} = M/\rho - [(\rho - \rho_0) \cdot 1000/m \cdot \rho \cdot \rho_0] \quad (1)$$

where M is the molar mass of the amino acid, m (mol·kg⁻¹) is the molality of amino acid in aqueous solution of various nitrates and ρ, ρ_0 are the densi-

ties of solution and solvent (water), respectively. At infinite dilution, the apparent molar volumes, $V_{2,\phi}$ and partial molar volumes, $V_{2,\phi}^0$ are identical ($V_{2,\phi} = V_{2,\phi}^0$). In the case of negligible concentration dependence of $V_{2,\phi}$, $V_{2,\phi}^0$ was determined by taking the average of all the data points. However, where finite concentration dependence was observed, $V_{2,\phi}^0$ was determined by least-squares fitting of the data using the following equation;

$$V_{2,\phi} = V_{2,\phi}^0 + S_v m \quad (2)$$

where S_v is the experimental slope. The $V_{2,\phi}^0$ values along with their standard deviations are summarized in Table 1.

The present values of $V_{2,\phi}^0$ for the amino acids in water agreed well with those reported in the literature [1-6]. Franks et al. have shown that the partial molar volume of non-electrolyte is a combination of two types of contributions given by the follow-

ing equation:

$$V_{2,\phi}^0 = V_{int} + V_s \quad (3)$$

where, V_{int} is the intrinsic volume of non-electrolyte and V_s volume due to its interactions with the solvent. It has been considered that V_{int} is made up of two types of contributions.

$$V_{int} = V_{vw} + V_{void} \quad (4)$$

Where, V_{vw} , is the van der Waals volume and V_{void} is the associated void or empty volume. The contribution of interactions of a non-electrolyte solute with the solvent is given as below:

$$V_{2,\phi}^0 = V_{vw} + V_{void} + n\sigma \quad (5)$$

Where σ is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with water molecules and n is the potential number of hydrogen bonding sites in the molecule.

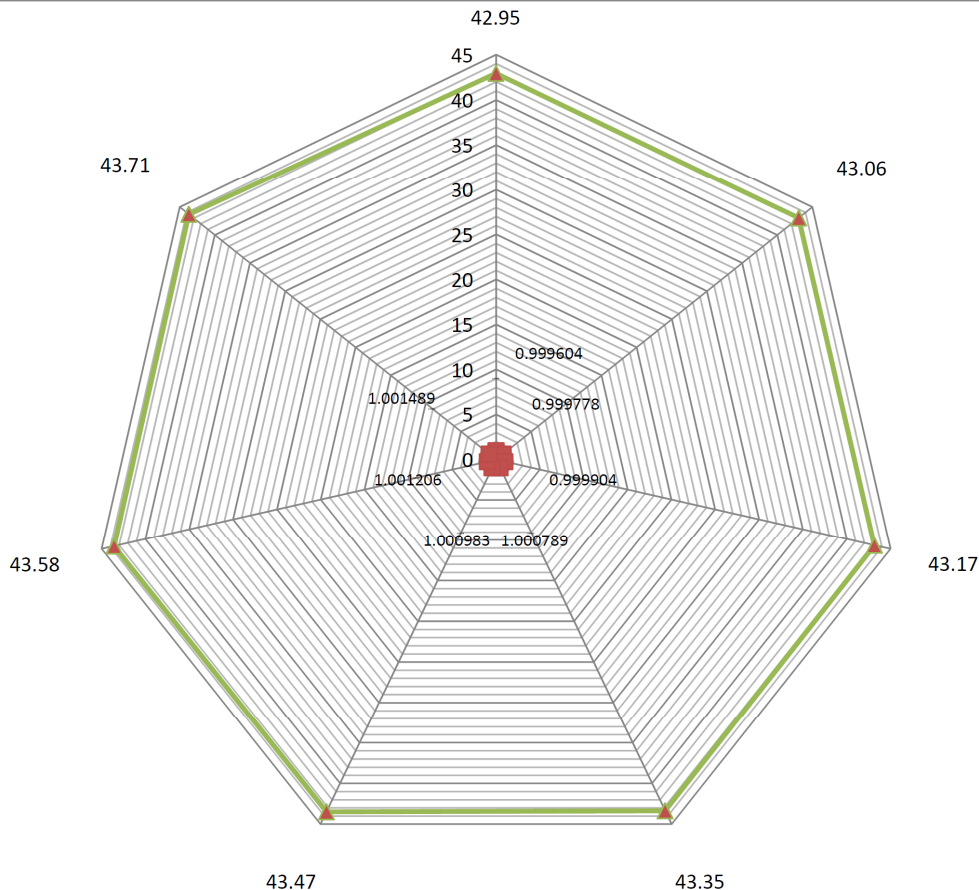


Table 1 Standard Partial Molar Volumes, V_2^0 , at Infinite Dilution for Some Amino Acids in Water from T= (288.15 to 318.15)K

Amino acids	Water
T/K= 288.15	
Glycine	42.81 ± 0.05 ^b (11.31) 42.84 ^c 42.40 ^d
DL- α -alanine	59.89 ± 0.04 ^b (8.03) 59.67 ^c 59.90 ^d
DL- α -amino- <i>n</i> -butyric acid	75.62 ± 0.09 (3.51) 74.67 ^e
L-valine	90.02 ± 0.05 (5.05) 90.08 ^c
L-leucine	107.08 ± 0.09 (2.0) 106.81 ^f
T/K = 298.15	
Glycine	43.17±0.02 ^b (1.66) 43.20 ^d 43.14 ^e 43.23 ^f
DL- α -alanine	60.40 ± 0.03 ^b (0.95) 60.30 ^d 60.62 ^e
DL- α -amino- <i>n</i> -butyric acid	75.97 ± 0.03 (0.72) 75.92 ^e
L-valine	90.76 ± 0.02 (0.92) 90.98 ^e
L-leucine	107.44±0.03 (1.77) 107.96 ^e
T/K = 308.15	
Glycine	44.34 ±0.05 ^b (2.37) 43.85 ^d 44.80 ^g
DL- α -alanine	61.31±0.12 (3.68) 61.06 ^d 60.90 ^g 61.01 ^h
DL- α -amino- <i>n</i> -butyric acid	76.47±0.12 (4.51) 76.61 ^h
L-valine	91.22±0.07 (1.86) 91.55 ^h
L-leucine	107.78±0.03 (1.19) 108.41 ^h
T/K = 318.15	
Glycine	45.28 ±0.12 ^b (8.80) 44.17 ^h
DL- α -alanine	62.20 ± 0.24 (8.73) 61.31 ^h
DL- α -amino- <i>n</i> -butyric acid	77.00 ± 0.22 (8.68) 76.82 ^h
L-valine	91.81 ±0.16 (14.05) 91.93 ^h
L-leucine	108.19 ± 0.7 (5.70) 109.38 ^h

'a' our work, 'b' standard deviation, 'c-h' ref. 1-3

The figure 1 illustrates the change in apparent with the change in concentration of an amino acid at fixed temperature (T=288.15K).

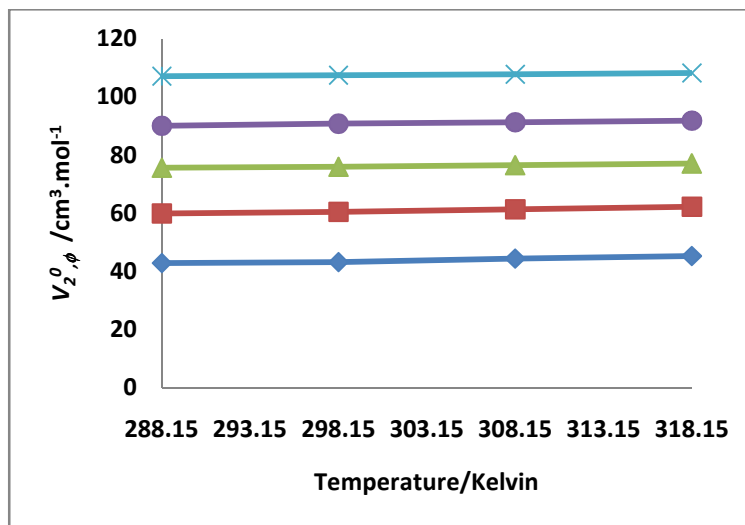


Figure 1 Standard partial molar volumes $V_{2,\phi}^0$ of some amino acids in water vs temperature: (♦), Glycine; (■), DL- α -Alanine; (▲), DL- α -Amino-*n*-butyric acid; (●), L-Valine; (×), L-Leucine.

For non-electrolytes and zwitterionic solutes the shrinkage is caused by electrostriction and finally $V_{2,\phi}^0$ can be evaluating as:

$$V_{2,\phi}^0 = V_{vw} + V_{void} - V_{shrinkage} \quad (6)$$

The increase of $V_{2,\phi}^0$ values with the increase in temperature may also be attributed to the reduction in electrostriction with temperature.

$$V_{2,\phi}^0 = V_{2,\phi}^0(\text{int}) + n_{\text{H}}(V_{E^0} - V_{B^0}) \quad (7)$$

Where $V_{2,\phi}^0(\text{int})$ is the intrinsic volume of a solute molecule, V_{E^0} and V_{B^0} are the partial molar volumes of water in the bulk state and in the hydration shell of a solution. Following the procedure described by Miller et al. ($V_{E^0} - V_{B^0} = (-2.9, -3.3, -4.0) \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ at 288.15 K, 298.15 K and 308.15 K, respectively). Therefore, as an approximation, the hydration number n_{H} can be obtained by Eq.(8), and the results are listed in Table 2.

The number of water molecules bound to the amino acids was calculated using the method reported by Miller et al.

$$n_{\text{H}} = V_{2,\phi}^0(\text{elect}) / (V_{E^0} - V_{B^0}) \quad (8)$$

Where V_{E^0} is the molar volume of electrostricted water and V_{B^0} is the molar volume of bulk water. The electrostriction partial molar volume, $V_{2,\phi}^0(\text{elect})$ can be estimated from experimentally measured $V_{2,\phi}^0$ using following equation:

$$V_{2,\phi}^0(\text{elect}) = V_{2,\phi}^0(\text{amino acid}) - V_{2,\phi}^0(\text{int}) \quad (9)$$

where $V_{\text{shrinkage}}$ is the volume due to shrinkage caused by the interaction of hydrogen bonding groups present in the solute with water molecules.

The intrinsic volume, $V_{2,\phi}^0(\text{int})$, consists of two terms: the vander Waals volume and the void volume. $V_{2,\phi}^0(\text{int})$ can be obtained from crystal volume data. The n_{H} values are given studied amino acids in water have been found and shown in the Table 5. Other workers have also reported the similar observations.

The partial specific quantities are:

$$V_{2,\phi}^0 = a + b \cdot T + c \cdot T^2 \quad (10)$$

Using the general thermodynamic expression;

$$(\partial C_p / \partial p)_T = - (\partial^2 V_{2,\phi}^0 / \partial T^2)_p \quad (11)$$

On the basis of this expression it has been deduced that structure making solutes should have positive values, whereas structure breaking solutes should have negative values. It has been suggested that for a structure breaking solute, the left side of the equation should be positive, and therefore $(\partial^2 V_{2,\phi}^0 / \partial T^2)_p$ values should be negative for structure breaking and positive for structure making solutes. This equation is useful for making a distinction ionic or polar solutes and those for making a distinction between ionic or polar solutes and those for which hydrophobic hydration is dominant. The presently

obtained $(\partial^2 V_{2,\phi}^0 / \partial T^2)_p$ values are positive for all amino acids which suggests that studied amino acids are structure maker in water.

Table 2: Hydration number, n_H , for Some Amino Acids in Water at 288.15, 298.15 and 308.15K.

Amino acids	$0.0^3 m_s$
T/K = 288.15	
Glycine	3.12
DL- α -alanine	4.13
DL- α -amino- <i>n</i> -butyric acid	5.78
L-valine	4.16
L-leucine	5.81
T/K = 298.15	
Glycine	2.63 2.63 [§]
DL- α -alanine	3.46 3.41 [§]
DL- α -amino- <i>n</i> -butyric acid	4.95
L-valine	3.44
L-leucine	5.04 4.96 [§]
T/K = 308.15	
Glycine	1.93
DL- α -alanine	2.58
DL- α -amino- <i>n</i> -butyric acid	4.0
L-valine	2.72
L-leucine	4.11

§Ref. [2-6] Conclusion

Partial molar volumes, $V_{2,\phi}^0$ of glycine, DL-amino-*n*-butyric acid, L-valine, L-leucine in water have been determined at T = (288.15 to 318.15)K. From these data, transfer volumes, hydration numbers, and side chain contributions have been determined. These parameters suggest that ion-ion interactions between charged ends of amino acids dominate over the ion-hydrophobic interactions in these systems. The positive $(\partial^2 V_{2,\phi}^0 / \partial T^2)_p$ values for all amino acids in water suggest that studied amino acids are structure makers.

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