Investigations of Various Amino acids in different Aqueous Solutions of Potassium Nitrate at Various Temperatures in terms of Partial Molar Volumes

Vaneet Dhirand, R. P. Singh Grewal

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 and in (0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1}aqueous potassium nitrate solutions have been determined from densities measurements at various temperatures (288.15, 298.15, 308.15 and 318.15) K. The standard partial molar volumes,$V_2^{0}{}_{,\phi}$ obtained from$V_{2,\phi}$have been used to calculate the corresponding volume of transfer at infinite dilution,$V_{2,\phi}$from water to aqueous potassium nitrate. The hydration number,n_H, side chain contributions of amino acids, and concentration effect of potassium nitrate as well as temperature effects have been discussed in terms of various interactions. The structure making / breaking capacities of these amino acids in water and also in aqueous potassium nitrate investigated have been discussed.**

***Index Terms*— Amino acids; Potassium nitrate; Partial molar volume; Transfer volumes; Hydration numbers; Interaction coefficients; Partial molar expansibilities.**

I. INTRODUCTION

Proteins are large complex molecules. The detailed three-dimensional structure of proteins and nucleic acids provides critical information about the molecules but they provide no information about the stability of a molecule or the energetic of its interactions[Haq et al., 2000].The interactions of water with the various functional groups of proteins play crucial role in determining the conformational stability of proteins.[2-4] Due to the complex conformational and configurationally three-dimensional structures of protein direct investigations of the solute/solvent effect on these biological macromolecules are very challenging. However their constituent molecules, the amino acids are very small biomolecules, which have been extensively used as model compounds to characterize the detailed interactions of the atomic groups that comprise proteins.

The main advantage comes out from the fact that such model studies readily allow one to systemically alter the structure so that the contribution of a chosen atomic group can be addressed.[5]The other important aim of such studies lies in the understanding of solute-solvent interactions and about the effects of amino acids on the structure of water. There are strong evidences of the controlling influence of aqueous solvent in membrane permeability, intercellular structure, function and molecular biology of proteins.[6]The most important behaviors of protein molecule is hydration which is very important in the structure and function of protein in aqueous solutions, in order to get an idea about the role of hydration in protein folding/unfolding, it is necessary to study both the native and denatured states of a protein. The side chain groups of the amino acids residues provide a very important range of properties, from hydrophilic to hydrophobic groups. The side chain groups are involved in a wide range of interactions. These interactions are affected by the surrounding solutes and solvent of macromolecules; for this reason, the physicochemical behaviors of proteins are strongly influenced by the presence of solutes.[7] For example; the phenomenon of electrostriction that is caused by the polar end groups; the structure enforcing influences of the hydrophobic alkyl groups; the interactions in between the hydrophilic and hydrophobic groups, hydrogen bonds that provides the peptide bonds in the polypeptide backbone.

All these wide ranges of interactions are being affected with the change in the concentration of aqueous electrolyte that is being studied. Attempts are being made for the systematic study of the volumetric in aqueous solutions of potassium nitrate at various temperatures (288.15, 298.15, 308.15 and 318.15)K. Salt induced electrostatic forces are known to play a important role in modifying the protein structure by affecting the properties like solubility, denaturation, and activity of enzymes[Chalikian et al., 1994]

Despite the ample use and importance of amino acids in many industries, their interactions with electrolytes and physicochemical properties in electrolyte solutions have been the subject of few investigations.The role of K^+ ions as components of all body fluids are indispensable, among others (Ca^{2+}, Mg^{2+},Na^+) for a correct functioning of the nervous system. Therefore, in continuation of our work we have undertaken a systematic study on the volumes of some amino acids in aqueous potassium nitrate solutions at different temperatures. These properties are sensitive to specific interactive changes in solutions. Consequently, in the present paper, the apparent molar volumes,$V_{2,\phi}$of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine and L-leucine in water and in aqueous potassium nitrate(0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1} have been determined by measuring the densities using a vibrating-tube digital densimeter at various temperatures (288.15, 298.15, 308.15 and 318.15) K. From these data, the partial molar volumes,$V_{2,\phi}$and the hydration number,n_H, side chain contributions of amino acids and concentration effect of potassium nitrate have been discussed in terms of various interactions. The structure making/breaking capacities of these amino acids in water and also in aqueous potassiumnitrate investigated have been discussed.

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II. EXPERIMENTAL SECTION

The amino acids selected for the present study glycine (G-7126), DL-α-alanine (A-7502), DL-α-amino-*n*-butyric acid (A-1754), L-valine (V-0500) and L-leucine (L-8000) were obtained from sigma chemicals co. these along with potassium nitrate (AR, S.d. fine chemicals Ltd., India), were used without further purification and dried over anhydrous $CaCl_2$ 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.

The solution densities were measured using a vibrating tube digital densimeter (model DMA 60/602, Anton paar), with precision of $\pm 1 \times 10^{-3}$ kg·m^{-3} accuracy of $\pm 3 \times 10^{-3}$ kg·m^{-3}. Densities function was checked by measuring the densities of aqueous sodium chloride solutions, which agreed well with the literature values[Millero et al. (1978)[literature values of density are: (1005.571, 1017.344, 1036.690, 1054.672, 1071.353 and 1087.608) kg·m^{-3} at 0.20918, 0.50653, 1.01279, 1.50262, 1.97403, and 2.44952) mol·kg^{-1}of sodium chloride, respectively] at 298.15 K. The temperature of water around the densimeter cell was controlled to within ±0.01K.

III. RESULTS AND DISCUSSION

The standard partial molar volumes,$V_{2,\phi}$of amino acids in water and ion aqueous potassium nitrate solutions of various molalities (m_s, molality of potassium nitrate solutions, mol·kg^{-1}) at (288.15, 298.15, 308.15 and 318.15) K are given in Table 1.

Standard Partial molar volumes of transfer, $\Delta_t V^0$, at infinite dilution for some amino acids from water to aqueous potassium nitrate solutions at 288.15, 298.15, 308.15 and 318.15 K

$\Delta_t V^0$ x 10^6 /m^{3}mol^{-1} at various m_S/mol·kg^{-1}[a]						
T=288.15 K						
Amino acids	0.25 m	0.5 m	0.75 m	1.0 m	1.5 m	2.0 m
Glycine	0.81 ± 0.08	0.86 ±0.09	1.40 ± 0.08	2.11 ± 0.09	2.23 ± 0.09	3.18 ±0.08
DL-α-alanine	0.31 ± 0.08	0.43 ± 0.09	0.64 ± 0.05	1.40 ± 0.23	1.72± 0.06	2.22 ±0.05
DL-α-amino-*n*-butyric acid	0.20 ± 0.11	0.31 ± 0.10	0.56 ± 0.10	1.43 ±0.10	1.61 ±0.09	1.98 ±0.10
L-valine	0.13 ± 0.06	0.17 ± 0.06	0.29 ± 0.05	0.79 ± 0.08	1.12 ±0.06	1.33 ±0.06
L-leucine	0.11 ± 0.11	0.20 ± 0.13	0.29 ± 0.09	0.58 ± 0.09	0.75 ± 0.09	0.95 ± 0.09
T = 298.15 K						
Glycine	0.38 ± 0.10	0.91 ± 0.04	1.27 ± 0.03	1.93 ± 0.02	2.31 ± 0.04	2.46 ± 0.11
DL-α-alanine	0.28 ± 0.04	0.58 ± 0.04	0.90 ± 0.06	1.67 ± 0.04	1.97 ± 0.04	2.47 ± 0.10
DL-α-amino-*n*-butyric acid	0.54 ± 0.04	0.80 ± 0.04	1.06 ± 0.04	1.40 ± 0.04	2.06 ± 0.05	2.43 ± 0.04
L-valine	0.14 ± 0.03	0.27 ± 0.04	0.58 ± 0.03	0.75 ± 0.03	1.10 ± 0.07	1.47 ± 0.04
L-leucine	0.43 ± 0.06	0.56 ± 0.05	0.65 ± 0.04	0.80 ± 0.04	1.14 ± 0.06	1.62 ± 0.07
T= 308.15 K						
Glycine	0.29 ± 0.08	0.37 ± 0.06	1.08 ± 0.09	1.72 ± 0.12	2.04 ± 0.09	2.55 ± 0.09
DL-α-alanine	0.19 ± 0.18	0.42 ± 0.14	0.74 ± 0.14 `	1.14 ± 0.13	2.01 ± 0.18	2.25 ± 0.24
DL-α-amino-*n*-butyric acid	0.19 ± 0.14	0.27 ± 0.13	0.45 ± 0.13	0.98 ± 0.13	1.47 ± 0.14	2.19 ± 0.16
L-valine	0.02 ± 0.08	0.34 ± 0.11	0.36 ± 0.12	0.87 ± 0.08	1.03 ± 0.08	2.0 ± 0.13
L-leucine	0.16 ± 0.14	0.25 ± 0.09	0.29 ± 0.08	0.80 ± 0.05	1.16 ± 0.04	1.77 ± 0.07
T = 318.15 K						
Glycine	1.40 0.15	1.49 ±0.15	1.44 ± 0.15	2.56 ± 0.16	2.78 ± 0.19	3.74 ± 0.22
DL-α-alanine	0.52 ± 0.24	0.50 ± 0.31	1.24 ± 0.26	2.21 ± 0.34	2.50 ± 0.27	3.17 ± 0.25
DL-α-amino-*n*-butyric acid	0.04 ± 0.24	0.50 ± 0.25	1.26 ± 0.25	1.33 ± 0.26	1.99 ± 0.22	2.84 ± 0.23
L-valine	0.29 ± 0.16	0.53 ± 0.18	1.13 ± 0.19	1.30 ± 0.21	1.70 ± 0.18	2.47 ± 0.20
L-leucine	0.04 ± 0.21	0.27 ± 0.21	0.94 ± 0.20	1.11 ± 0.18	1.24 ± 0.20	1.73 ± 0.23

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

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

Where M is the molar mass of amino acid, m (mol·kg^{-1}) is the molality of amino acid, and ρ, ρ^0 are the densities of solution and solvent, respectively. At infinite dilution, the apparent molar volumes, and partial molar volumes, are identical ($V_{2,\Phi} = V_2^{0},_{\Phi}$). In the case of negligible concentration dependence of$V_{2,\Phi} = V_{2,}{}^{0}{}_{\Phi}$was determined by taking the average of all the data points. However, where finite concentration dependence was observed,$V_2^{0},_{\Phi}$was determined by least-squares fitting of the data using the following equation:

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

Where $V_{2,\phi}^{0}$ is the infinite dilution apparent molar volume and has the same meaning as the standard partial molar volume, and S_v is the experimental slope. The $V_{2,\phi}^{0}$ values along with their standard deviations are summarized in Table 2 at (288.15, 298.15, 308.15and 318.15) K. The $V_{2,\phi}^{0}$ values for the amino acids increases with the increase in the concentration of potassiumnitrate.

From the $V_{2,\phi}^{0}$ data, the standard partial molar volumes of transfer, $\Delta_t V^0$, at infinite dilution from water to aqueous potassium nitrate solutions have been evaluated as follows: $\Delta_t V^0 = V_{2,\phi}^{0}$ (in aqueous potassium nitrate) - $V_{2,\phi}^{0}$ (in water) (3)

The $\Delta_t V^0$ values for the amino acids are illustrated in Figures 1 [a-d]. The $\Delta_t V^0$ values for the studied amino acids are positive and increase almost linearly with the increase in concentration of aqueous potassiumnitrate solutions. The more positive $\Delta_t V^0$ values in the case of glycine indicate the dominance of the effect of charged end groups (NH_3^+ and COO^-), whereas less positive $\Delta_t V^0$ values in the case of DL-α-amino-*n*-butyricacid, L-valine and L-leucine indicate the effect of the hydrophobic parts.

The cosphere model can be utilized to rationalize the $\Delta_t V^0$ values in terms of solute-cosolute interactions. According to this model, when two solute particles come close enough together so that their cosphere overlap some cosphere material is displaced, and this is accompanied by the change in thermodynamic parameters. The following types of interactions can occur between amino acids and KNO_3 in solutions:

i. Ion-ion interactions occurring between K^+ ions and COO^- groups of amino acids and between NO_3^- ions of potassium nitrate and NH_3^+ groups of amino acids.

ii. Interactions between ions (K^+, NO_3^-) of potassium nitrate and nonpolar (hydrophobic) groups of amino acids.

The ion-ioninteractions dominate the ion-hydrophobic group interactions. Because of the first types of interactions, the electrostriction of water in the neighborhood of charged end groups (NH_3^+, COO^-) of amino acids gets reduced, and this will contribute positively to the volumes of transfers. Furthermore, the increase in $\Delta_t V^0$ values with increasing potassium nitrate concentration strengthens this view. This is a qualitative interpretation of the results. The decreasing magnitude of transfer volumes from glycine to L-leucine indicates the building up of the ion-hydrophobic interactions that contribute negatively to $\Delta_t V^0$ values.

Franks et al. have shown that the partial molar volume of non-electrolyte is a combination of two types of contributions given by the following equation:

$V_2^0 = V_{int} + V_S$ (4)

where, V_{int} is the intrinsic volume of non-electrolyte and V_S volume due to it's interactions with the solvent.It has been consideredthat V_{int} is made up of two types of contributions.

$V_{int} = V_{vw} + V_{void}$ (5)

Where, V_{vw}, is the van der Waals volume and V_{void} is the associated void or empty volume.Shahidi et al. further modified above equation to include the contribution of interactions of a non-electrolyte solute with the solvent.

$V_2^0 = V_{vw} + V_{void} + n\sigma_S$ (6)

Where σ_S 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. For non-electrolytes and zwitterionic solutes the shrinkage is caused by electrostriction and finally V_2^0 can be evaluatingas:

$V_2^0 = V_{vw} + V_{void} - V_{shrinkage}$ (7)

Where $V_{shrinkage}$ is the volume due to shrinkage caused by the interaction of hydrogen bonding groups present in the solute with water molecules. It has been reported that V_{vw} and V_{void} have the same magnitude in water and in mixed solvents for the same class of compounds. Therefore positive $\Delta_t V^0$ values can be attributed to a decrease in the shrinkage volume in the presence of aqueous solutions of KNO_3. Because of the stronger interactions of K^+ and NO_3^- with COO^- and NH_3^+ in the amino acids, the electrostriction of neighboring water molecules due to these charged centers/peptide backbone will be reduced which will result into a reduction in the shrinkage volume.

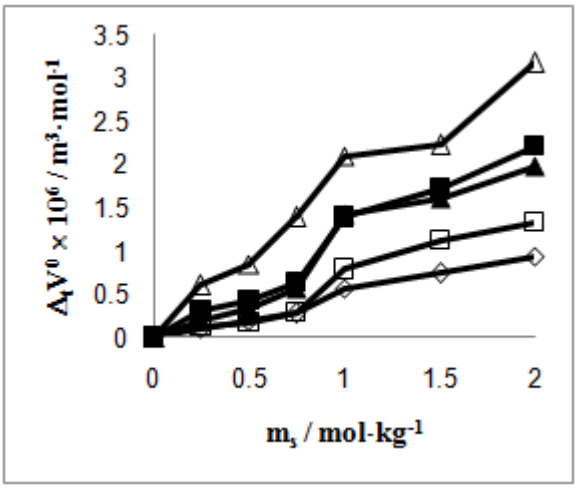

Figure 1 [a]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. different molalities, m_S, of potassium nitrate solutions at 288.15K: Δ, glycine; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; □, L- valine; ◊, L-leucine.

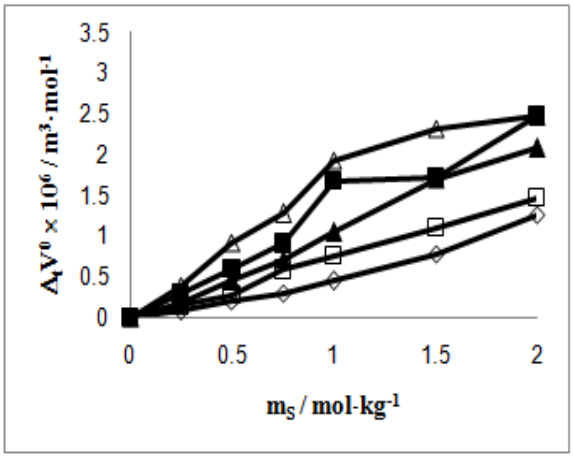

Figure 1 [b]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. different molalities, m_S, of potassium nitrate solutions at 298.15K: Δ, glycine; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; □, L- valine; ◊, L-leucine.

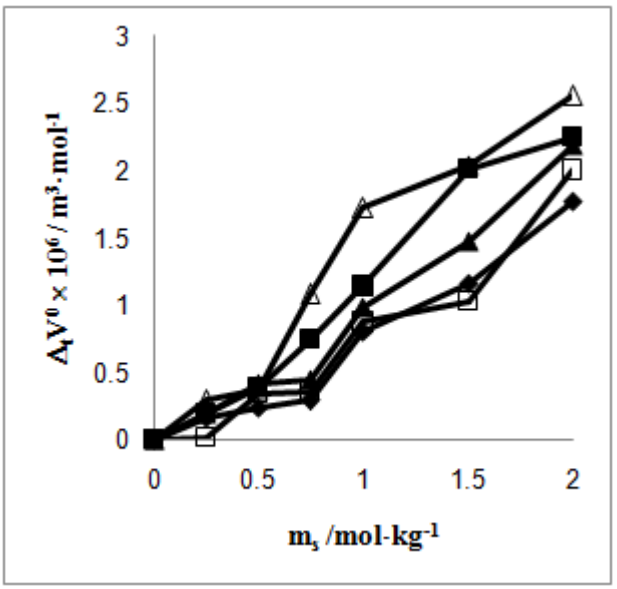

Figure 1[c]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. different molalities, m_S, of potassium nitrate solutions at 308.15K: Δ, glycine; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; □, L- valine; ◊, L-leucine.

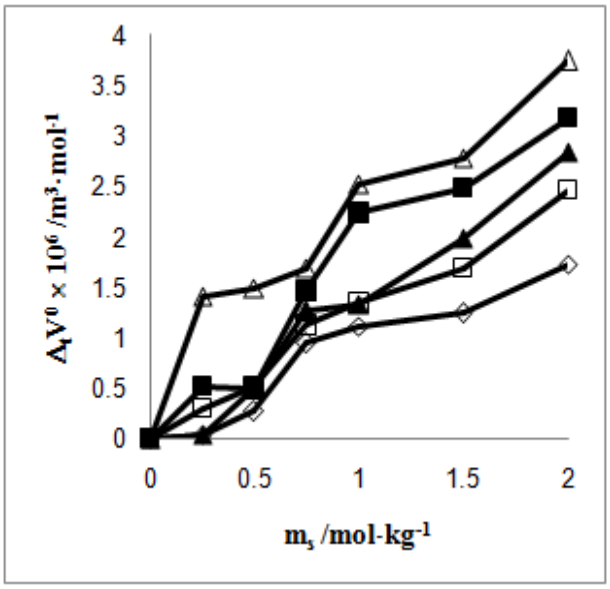

Figure 1[d]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. different molalities, m_S, of potassium nitrate solutions at 318.15K: Δ, glycine ; ■, DL-α-alanine; ▲, DL-α-amino-*n*-butyric acid; □, L- valine; ◊, L-leucine.

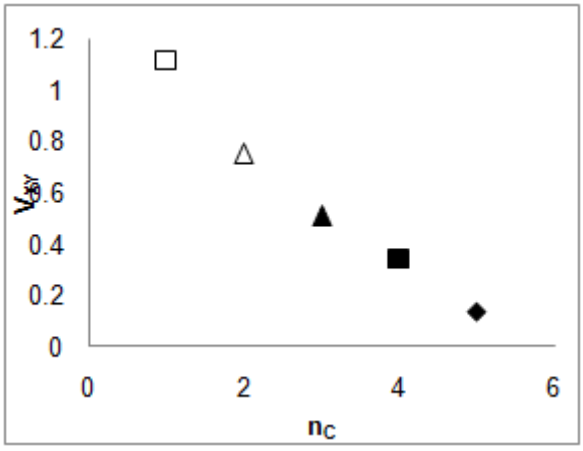

Figure 2[a]. Pair interaction coefficient, V_{XY}, of some amino acids vs. number of carbon atoms, n_C, in the alkyl chain of amino acids at 298.15K: (□), Glycine; (Δ), DL-α-alanine; (▲), DL-α-amino-*n*-butyric acid; (■), L-valine; (♦), L-leucine.

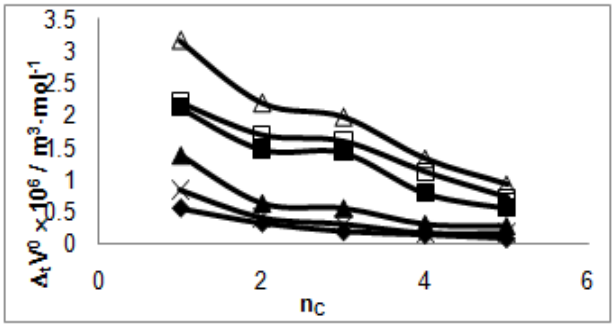

Figure 3[a]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. number of carbon atoms, n_C, in the alkyl chain of amino acids at 288.15K: (♦), 0.25m_S; (×), 0.5m_S; (▲), 0.75m_S; (■), 1.0m_S; (□), 1.5 m_S; (Δ), 2.0 m_s.

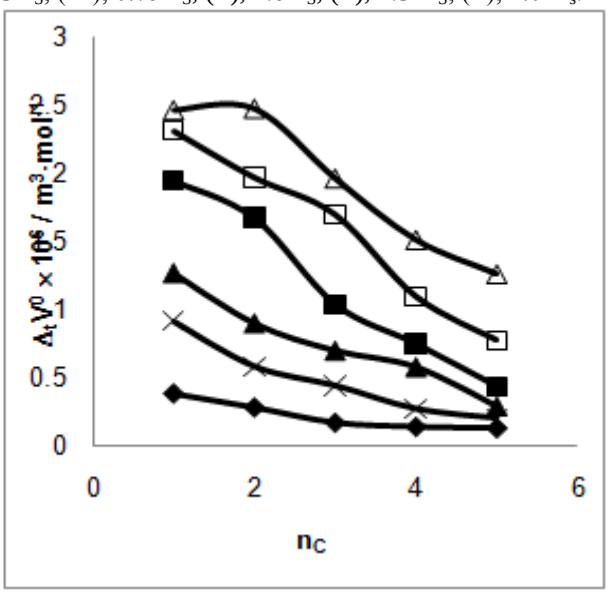

Figure 3[b]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. number of carbon atoms, n_C, in the alkyl chain of amino acids at 298.15K: (♦), 0.25m_S; (×), 0.5m_S; (▲), 0.75m_S; (■), 1.0m_S; (□), 1.5 m_S; (Δ), 2.0 m_s.

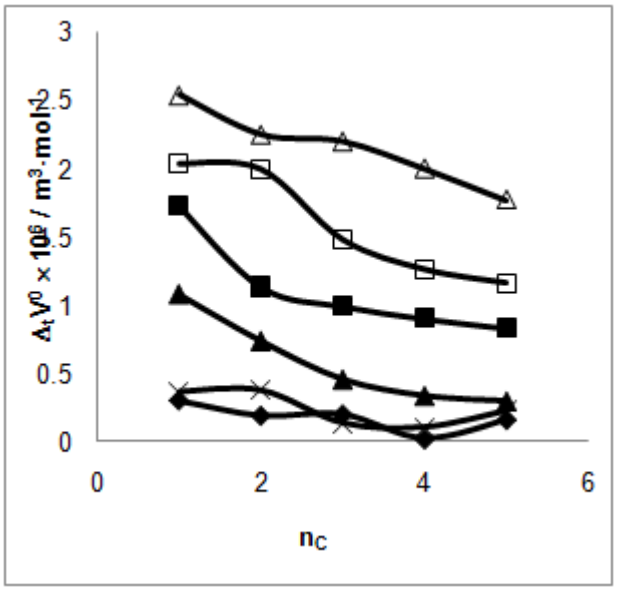

Figure 3[c]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. number of carbon atoms, n_C, in the

alkyl chain of amino acids at 308.15K: (♦), 0.25m_S; (×), 0.5m_S; (▲), 0.75m_S; (■), 1.0m_S; (□), 1.5 m_S; (Δ), 2.0 m_s.

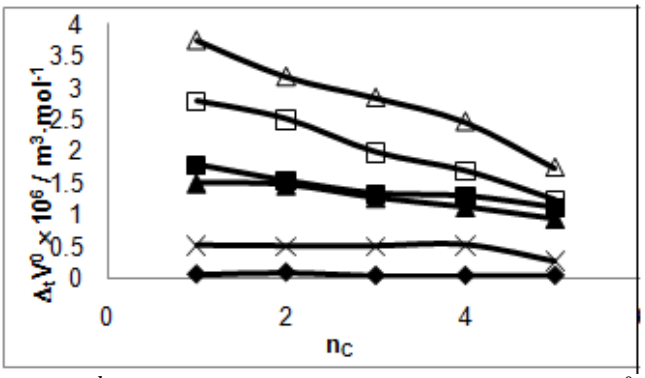

Figure 3[d]. Standard partial molar volumes of transfer, $\Delta_t V^0$, of some amino acids vs. number of carbon atoms, n_C, in the alkyl chain of amino acids at 318.15K: (♦), 0.25m_S; (×), 0.5m_S; (▲), 0.75m_S; (■), 1.0m_S; (□), 1.5 m_S; (Δ), 2.0 m_s.

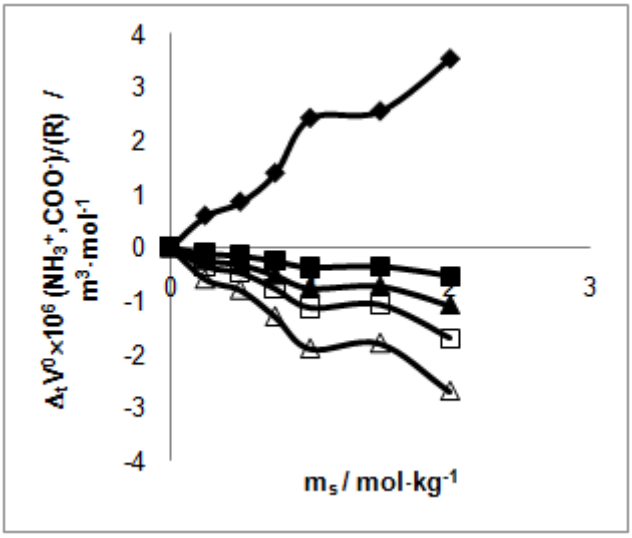

Figure 4[a]. Contributions of :(♦) NH_3^+, COO^- ;(■) -CH_2, (▲)-$CHCH_3$; (□) - $CHCH_2CH_3$;(Δ) -$CHCH_2CH$ $(CH_3)_2$ groups to standard partial molar volumes of transfer, $\Delta_t V^0$ vs. different molalities, m_S of potassium nitrate solutions at 288.15K.

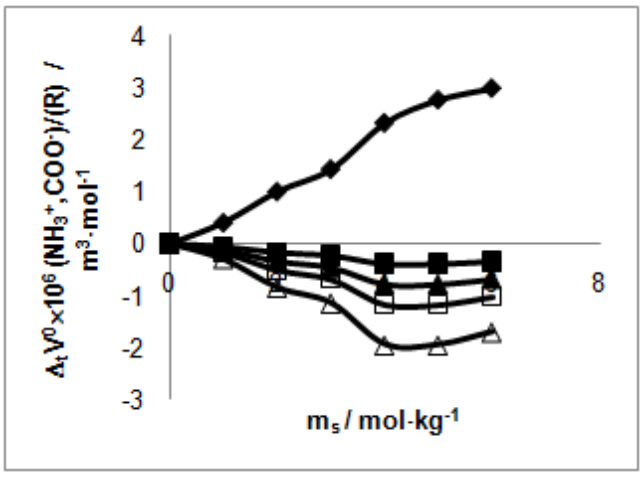

Figure 4[b]. Contributions of :(♦) NH_3^+, COO^- ;(■) -CH_2, (▲)-$CHCH_3$; (□) - $CHCH_2CH_3$;(Δ) -$CHCH_2CH$ $(CH_3)_2$ groups to standard partial molar volumes of transfer, $\Delta_t V^0$ vs. different molalities, m_S of potassium nitrate solutions at 298.15K.

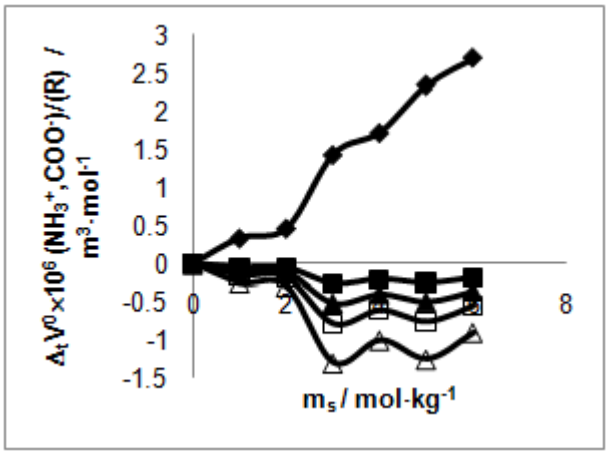

Figure 4[c]. Contributions of :(♦) NH_3^+, COO^- ;(■) -CH_2, (▲)-$CHCH_3$; (□) - $CHCH_2CH_3$;(Δ) -$CHCH_2CH$ $(CH_3)_2$ groups to standard partial molar volumes of transfer, $\Delta_t V^0$ vs. different molalities, m_S of potassium nitrate solutions at 308.15K.

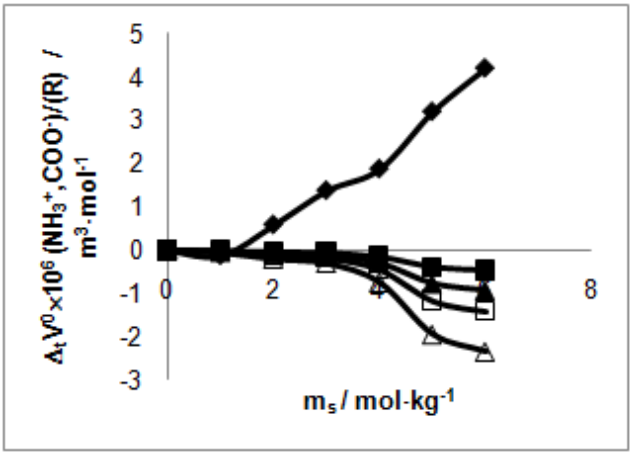

Figure 4[d]. Contributions of :(♦) NH_3^+, COO^- ; (■) -CH_2, (▲)-$CHCH_3$; (□) - $CHCH_2CH_3$; (Δ) -$CHCH_2CH$ $(CH_3)_2$ groups to standard partial molar volumes of transfer, $\Delta_t V^0$ vs. different molalities, m_S of potassium nitrate solutions at 318.15K.

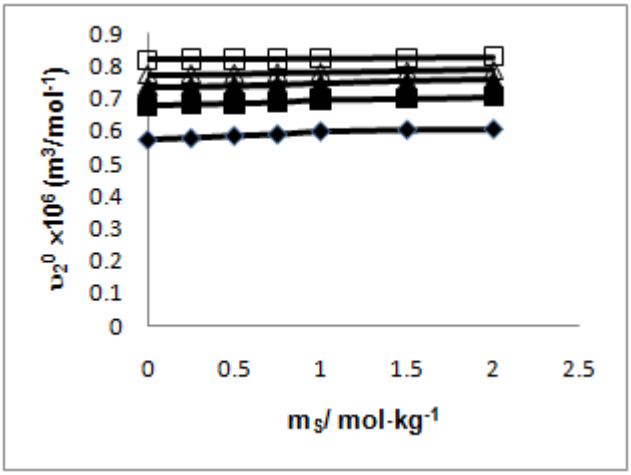

Figure 5[a]. Partial specific volumes, υ_2^0, of amino acids vs. different molalities, m_s, of sodium nitrate solutions at 298.15K: (□), Glycine; (Δ), DL-α-alanine; (▲), DL-α-amino-*n*-butyric acid; (■), L-valine; (♦), L-leucine.

The increase of V_2^0 values with the increase in temperature may also be attributed to the reduction in electrostriction with

temperature. This also gets support from the volumetric and compressibility studies of glycine and DL-α-alanine in aqueous sodium sulfate solutions by Wadi and Ramasami, who reported that the hydration number of amino acids decreases with increasing temperature and concentration of sodium sulfate. The increase in positive V_2^0 values of studied amino acids with the increase in the concentration of KNO_3 may further be attributed to the formation of non-covalent ion-pairs between the charged groups of the amino acids and the cation (K^+) and the anion (NO_3^-) of the electrolyte. This increases the apparent molar volume of amino acid and decreases electrostriction of water around amino acids in the presence of KNO_3. Further the formation of the ion-pairs also decreases the hydrophobicity of amino acid molecules arising from the interactions of the hydrocarbon portion of amino acids with water molecules.

The decrease in the magnitude of $\Delta_t V^0$ values with the increase of temperature can be attributed to the enhanced thermal agitation and weakening of various interactions involving ions resulting in the relaxation to the bulk more of the electrostricted water molecules from the mutually interacting regions.

Kozak et al. have proposed formalism on the basis of McMillan-Mayer theory of solutions which permits the formal separation of the effects due to interactions between pairs of solute molecules and those due to interactions involving three or more solute

molecules. Friedman and Krishnan and Franks et al. have further discussed this approach to include the solute-cosolute interactions in the solvation sphere. Various workers used this approach to study the interactions of amino acids and cosolutes in aqueous medium. The various transfer functions of the amino acids can be expressed by the following equation:

$$\Delta_t V^0 = 2V_{AB}\cdot m_s + 3\, V_{ABB}\cdot m_s^2 + 4\, V_{ABBB}\cdot m_s^3 \quad (8)$$

Where V_{AB}, V_{ABB} and V_{ABBB} are respectively, pair, triplet and quartet interaction coefficients (where A stands for the amino acids, B stands for KNO_3). Using above equation volumetric interaction parameters was calculated and are illustrated in Figure 2[a] at 298.15K. The data reveal that all pair volumetric interaction parameters V_{AB} are positive for the five amino acids studied and are larger than corresponding V_{ABB} values. This shows that the interactions between the amino acids and KNO_3 are mainly pair interactions. The pair, triplet and quartet interactions coefficients from volumes in case of various α-amino acids (glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine and L-leucine) are summarized in Table 4. The pair and quartet coefficients are all positive while triplet negative. This shows that the pair and quartet interactions in case of two thermodynamic properties contribute positively while triplet contributions are negative. The positive values of pair interactions occur due to the overlap of hydration spheres of the various α-amino acids (glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-valine and L-leucine) and KNO_3 molecules, which supports the conclusion drawn earlier from the cosphere overlap model.

$$V_{2,\phi}^0 = V_{2,\phi}^0(\text{int}) + n_H\,(V_E^0 - V_B^0) \quad (9)$$

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 Milleroet al.[41] $(V_E^0 - V_B^0)$ = -2.9, -3.3, -4.0 $cm^3\cdot mol^{-1}$ 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. (9). As explained earlier, addition of KNO_3 decreases the electrostriction of water and this also means that n_H decreases as the electrostricted water becomes more like bulk water.

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

$$n_H = V_2^0(\text{elect}) / V_E^0 - V_B^0 \quad (10)$$

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_2^0(elect) can be estimated from experimentally measured V_2^0 using following equation:

$$V_2^0(\text{elect}) = V_2^0(\text{amino acid}) - V_2^0(\text{int}) \quad (11)$$

The intrinsic volume, V_2^0(int), consists of two terms: the vander Waals volume and the void volume. V_2^0(int) can be obtained from crystal volume data. Then n_H values for the amino acids in the presence of KNO_3 are less than in water and decrease with increasing concentration of KNO_3, which suggests that potassium nitrate has a dehydration effect on the amino acids. Other workers also have reported the similar observations that electrolytes have a dehydration effect on amino acids. The $V_{2,\phi}^0$ increases with increasing temperature from 288.15 to 318.15K. An increase in temperature reduces the electrostriction and hence increases $V_{2,\phi}^0$. The reduction in the electrostriction with increasing temperature is confirmed by the decreased n_H. Therefore, temperature effect on the electrostriction of water by the zwitterionic centers of the amino acids is a predominant factor in determining temperature dependence of $V_{2,\phi}^0$ of the amino acids. Proposed by Hakin et al. for the infinite dilution apparent molar volumes of amino acids at all temperatures, these linear relations could be reasonably represented by:

$$V_{2,\phi}^0 = V_{2,\phi}^0(NH_3^+, COO^-) + n_C V_{2,\phi}^0(CH_2) \quad (12)$$

Where n_C is the number of carbon atoms in the alkyl chain of the amino acids. A linear regression analysis of $V_{2,\phi}^0$ values at any given temperature using equation gives $V_{2,\phi}^0$ values at any given temperature using Eq. (12) gives $V_{2,\phi}^0(NH_3^+, COO^-)$, the zwitterionic end group and $V_{2,\phi}^0(CH_2)$, the methylene group contributions. These results are illustrated in Figures 3[a-d]. However, it should be pointed out that $V_{2,\phi}^0(CH_2)$ value obtained here characterizes the mean contribution of CH and CH_3 groups to $V_{2,\phi}^0$ of the α- amino acids. The alkyl chain of the homologous series of α-amino acids investigated in this work and its contributions have been obtained using the following equation proposed by Hakinet al.

$$V_{2,\phi}^0(CH_3) = 1.5\, V_{2,\phi}^0(CH_2) \quad (13)$$

$$V_{2,\phi}^0(CH) = 0.5\, V_{2,\phi}^0(CH_2) \quad (14)$$

It can be seen that the contributions of (NH_3^+, COO^-), groups to $V_{2,\phi}^0$ is larger than that of the CH_2 group and increases with the increasing concentration of potassium nitrate which indicates that of the interactions between potassium nitrate and charged end groups (NH_3^+, COO^-) of amino acids are stronger than those between potassium nitrate and CH_2 groups. The $V_{2,\phi}^0(CH_2)$ values are almost insensitive to the concentration of potassium nitrate, and similar observations have been reported by other worker in sodium acetate. However, the contribution from side chains increases with the increasing size of side chains of amino acids. The standard partial molar volumes of transfer of zwitterionic end groups $[\Delta_t V_0(NH_3^+, COO^-)]$ and alkyl side chain groups $[\Delta_t V^0(R)]$ of amino acids from water to aqueous

potassiumnitratesolutionsare illustrated in Figures 4[a-d]for different temperatures and have been calculated as follows:

$\Delta_t V^0(NH_3^+, COO^-$ or $\Delta_t V_2^0(R) = V_2^0(NH_3^+, COO^-)$ or $V_2^0(R)$(in aqueous potassium nitrate) – $V_2^0(NH_3^+, COO^-)$ or $V_{2,\phi}^0(R)$(in water) (15)

The contribution of charged end groups(NH_3^+,COO^-)are positive, and those of CH_2 groups are negative. From these observations, the overall positive $\Delta_t V^0$ values suggest that the effect of charged end groups dominates that of alkyl side chains.

The partial specific quantities are primarily independent of the size of the solute and reflect the ratio of the effect of the hydrophilic hydration on the hydrophobic hydration, whereas the partial molar quantities are the reflection of the net changes in both hydrations. The standard partial molar specific molar volumes, υ_2^0 ($\upsilon_2^0 = V_2^0/M$, where M is the molar mass for studied amino acids) in aqueous potassium nitrate solutions are given in υ_2^0values from glycine to L-leucine both in water and in aqueous potassium nitrate solutions due to the effect of the size of the side chains of the amino acids are illustrated in Figures 5[a]at 298.15K. Furthermore, the value of υ_2^0 increases with the concentration of potassium nitrate and a slight increase is also noted with the increase in temperature, again suggesting the dominance of the interactions between ions of potassiumnitrate for the studied amino acids tends to be linear as the size of side chains increases. This may be attributed to the negative contribution from the alkyl side chains of amino acids whose magnitude increases with the size of the side chain.

The temperature dependence of $V_\phi^0$for various amino acids in water and in aqueous potassium nitrate solutions, studied here can be expressed by the general equation as follows:

$V_\phi^0 = a + b \cdot T + c \cdot T^2$ (16).

The partial molar (limiting apparent molar) expansibilities, $\phi_E^o = (\partial V_\phi^o/\partial T)_p$, calculated from the general equation are given in Table 7. It is found that Table 7 that ϕ_E^ovalues for glycine, DL-α-alanine and DL-α-amino-*n*-butyric acid increases in magnitude with increase in temperature while for L-valine at0.25 mol·kg^{-1} (KNO_3) and L-leucineat 0.25, 2.0 mol·kg^{-1} (KNO_3) decreases with rise in temperature indicating thereby that the behavior of L-valine and L-leucineat this molalitiesare just like that of common salts, because in the case of common salts the molar expansibility should decrease with rise in temperature. It is also evident from Table 7 that the value of ϕ_E^oincrease in temperature for glycine, DL-α-alanine and DL-α-amino-*n*-butyric acid in water. During the past few years it has been emphasized by different workers that $S_v^*$is not the sole criterion for determining the structure making or structure breaking nature of any solute. Heplerdeveloped a technique of examining the sign of $(\partial^2 V_\phi^0/\partial T^2)$pfor various solutes in terms of long-range structure making and breaking capacity of the solutes in aqueous solutions using the general thermodynamic expression;

$(\partial Cp/\partial p)T = -(\partial^2 V_\phi^0/\partial T^2)_p$(17)

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 $(\partial^2 V_\phi^0/\partial T^2)_p$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 $(\partial^2 V_\phi^0/\partial T^2)_p$ values are positive for all amino acids which suggests that studied amino acids are structure maker in water as well as in aqueous KNO_3.

IV. Conclusion

Partial molar volumes, $V_{2,\phi}^0$, of glycine, DL-amino-*n*-butyric acid, L-valine, L-leucine in aqueous and in mixed aqueous solutions of KNO_3 (0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1}, 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. The $\Delta_t V^0$values are positive in all the cases, and these increase with an increase in the concentration of KNO_3 and temperature. V_{XY} values are positive, and V_{XYY} values are negative in all cases, which suggest that interactions between amino acids and KNO_3 are mainly pair wise. n_H values also decrease with concentration of KNO_3 and temperature. These parameters suggest that ion-ion interactions between charged ends of amino acids and ions of KNO_3 dominate over the ion-hydrophobic interactions in these systems. The positive $(\partial^2 V^0/\partial T^2)_p$ values for all amino acids in aqueous KNO_3suggest that studied amino acids are structure breakers in aqueous KNO_3solutions.

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