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Solubility of α-amino butyric acid in water-$NaNO_3$ mixture and analysis of related thermodynamic parameters

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ABSTRACT

Solubility data of DL-α-amino butyric acid are obtained, using the 'formal titrimetry' method in water and aqueous solution with various sodium nitrate ($NaNO_3$) concentrations in the temperatures 288.15, 293.15, 298.15, 303.15 and 308.15 K. The standard transfers Gibbs energies and entropies have been evaluated for this amino acid from water to aqueous mixture of sodium nitrate solution at 298.15 K. The chemical effects of the transfer Gibbs energies ($\Delta G^0_{t,ch}(i)$), obtained by subtracting theoretically computed $\Delta G^0_t(i)$ due to cavity and dipole-dipole interactions effects from the total transfer free energies, $\Delta G^0_t(i)$. Again $T\Delta S^0_{t,ch}(i)$ have been evaluated after elimination of cavity effect and dipole-dipole interaction effects from total transfer ($T\Delta S^0_t(i)$) entropies. The various solvent parameters as well as thermodynamic parameters like molar volume, densities, dipole moment and solvent diameter of aqueous solution of sodium nitrate ($NaNO_3$) have also been reported in this manuscript. The results show that the solubility is affected by the electrolyte ($NaNO_3$) and the stability of the amino acid is affected by the electrolyte which is discussed in terms of various types of thermodynamic interactions.

KEYWORDS

DL- α-amino butyric acid;
Solubility;
Sodium nitrate;
Transfer energetics;
Hydrophobic interaction.

INTRODUCTION

The biomolecules such peptides and proteins are made up of simple blocks, the amino acids. The amino acids are not only important in biochemical processes, but also important due to their applications in chemical, pharmaceutical, cosmetics and food industries. The solubility studies of the amino acids in different solvents systems, such as aquo-organic, non-aqueous and aqueous electrolyte solutions are very important. This type of studies may help in the understanding of the solubility behaviour of other biomolecules.

It has been observed that the addition of salts modify the structure of proteins[1] by affecting properties like solubility, denaturation and activity of enzymes. That is why for better understanding of the effect of electrolytes on the thermodynamic properties of amino acids in aqueous solutions is of vital importance because these studies give valuable information regarding the protein folding and unfolding processes[2, 3] and the extent of hydrophobic interaction of the hydrophobic moiety of the amino acids.

In considering these points of views and to clarify the solvation mechanisms of various amino acids, the solubility and thermodynamic studies were carried out by different group of researchers in different aquo-organic[4-15] and non-aqueous solvent systems[9,16]. In this regard Tanford, Nozaki and other authors[10,11] reported solubilities, transfer free energies and entropies of some amino acids from water to urea, water-sodium sulphate[7], water to sodium chloride[26], water-glycerol[27], water-DMSO[28] and water-DMF[29] solvent systems.

But the details study about the solvation mechanisms of various amino acids in aqueous electrolyte solution, in terms of thermodynamic point of view is still lack of interest for the solution, pharmaceutical and industrial chemists.

In such situation the main objective of this study is the presentation of new experimental data for the solubility in various temperatures and thermodynamic parameters of DL- α-amino butyric acid in aqueous solution of sodium nitrate in different compositions.

MATERIALS AND METHODS

Chemicals and their purifications

DL- α-amino butyric acid, of 99% purity, was supplied by Merck and used after drying as described in previous work[9]. Sodium nitrate ($NaNO_3$), of 99.5 % purity was supplied by Merck, Bombay, India. The salt is was oven dried for 3-4 days and cooled in a vacuum desiccator for 2 days prior to use. For formol titration standardized NaOH [E Merck] solution and phenolphthalein indicator [LR, BDH] were used. Neutral formaldehyde [E Merck] was used to mask before titration. Triple distilled water was used for the preparation of solution and for other experimental works.

Preparations of saturated solutions

The aqueous solvent of $NaNO_3$ of the concentrations of 0.0, 0.25, 0.50, 1.0, 2.0, 3.0 and 5.0 (M) were made. Then the solvent (H_2O/ H_2O+ $NaNO_3$) and excess amount of amino acid was placed in well fitted stoppered glass tubes. Glass tubes were incompletely filled to facilitate good mixing. A low-cum-high temperature thermostat was used for all measurements which is capable of registering temperatures having an accuracy of ±0.02 K. A known mass of filtered saturated solution was transferred to a dry conical flask. The solubility of DL- α-amino butyric acid is measured by formol titrimetry method. [9, 17] The measurements were taken at 288.15, 293.15, 298.15, 303.15 and 308.15 K temperatures. Four sets of measurements for all the cosolvent mixtures were made for all temperatures by equilibrating the solutions from both above and below (± 0.02 K) the required temperatures and the solubilities were found to agree to within ±0.2 to 0.5 %.

RESULTS

Calculation of total transfer Gibbs energy and entropy of solution from solubility

The important parameters of the amino acid, DL-α-amino butyric acid and aqueous solvent of $NaNO_3$ are presented in the TABLE 1. The solubilities of DL-α-amino butyric acid are measured on molal scale ($mol{\cdot}kg^{-1}$) and listed in TABLE 2. The standard deviations (s_f) are also estimated for all solubility values to know about the precision and these are shown in parentheses (TABLE 2) at all temperatures.

In the previous studies by Bates and coworkers on Tris[18] and by Kundu and coworkers[19] and Dolui et al [12,17] for various types of biomolecules, the standard Gibbs energies of solutions (ΔG_s^0) on molal scale were calculated for each solvent using Equation (1). Here we have also measured the Gibbs energies of solutions by using the same equation as given below and presented in TABLE 3.

$$\Delta G_s^0(i) = -RT\ln C\gamma = -RT\ln m \qquad \textbf{(1)}$$

Where γ is the molar activity coefficient of the solutes but taken tentatively to be unity in solvent since α-amino acid likely to be mostly in zwitterionic form in solvent mixtures[20], the involved activity coefficient factor -RTlnγ in ΔG_s^0 arising from interactions of dipolar solute with large dipole moment may not be so small. But as there is neither the required experimental data nor any ap-

TABLE 1 : Values of solvent parameters (Molarity of $NaNO_3$ solvent system, Mole fraction of $NaNO_3$ (z_s), water ((z_R), mean mol. Weight (M_S), density (d_s), hard sphere diameter of co-solvent (σ_s) ($NaNO_3$+H_2O) and σ_{s-x} (= ½($\sigma_s + \sigma_x$)), Dipole moment of co-solvent (μ_s), and isobaric thermal expansibility constant (α) of the H_2O+ $NaNO_3$ system at 298.15 K

Molality Of $NaNO_3$	Mole Fraction Of $NaNO_3$ (z_s)	Mole Fraction of water (z_R)	Molar mass (M_S) (kg· mol^{-1})	10^3 d_s (kg· m^{-3})	Molar Volume (V_s) ($dm^{3·}$ mol^{-1})	σ_s (nm)	σ_{s-x} (nm)	Dipole Moment (μ_s)	α (x 10^{-3})
0.0	0.000	1.000	18.015	$0.9970^{\#}$	18.0692	0.274	0.466	1.831*	0.257*
0.25	0.009	0.991	18.618	1.0081	18.4684	0.275	0.467		
0.50	0.018	0.982	19.219	1.0197	18.8477	0.276	0.467		
1.00	0.036	0.964	20.426	1.0424	19.5952	0.278	0.468		
2.00	0.072	0.928	22.837	1.0877	20.9957	0.282	0.470		
3.00	0.107	0.893	25.181	1.1318	22.2486	0.287	0.473		
5.00	0.179	0.821	30.004	1.2225	24.5432	0.296	0.477		

*** for the references[22]; Density, molar mass, thermal expansibility constant, size and dipole-moment values are taken from the website: http://en.wikipedia.org/wiki/Sodium_nitrate and from reference[22].**

TABLE 2 : Solubilities (*S)* in mol·kg^{-1} of DL- α-amino butyric acid in aqueous mixtures of sodium nitrate ($NaNO_3$*)* at different temperature (K)

Molality of $NaNO_3$	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.0 [Water]	1.880 (1.652)[17] (1.634)[15]	2.008 (1.715)[17] (1.720)[15]	2.221 (1.800)[17] (1.800)[15]	2.356 (2.100)[17] (2.300)[15]	2.908 (2.350)[17] (2.400)[15]
0.25	1.935 (±0.001)^b	2.150 (±0.003)^b	2.345 (±0.001)^b	2.743 (±0.001)^b	3.045 (±0.001)^b
0.50	2.557 (±0.001)^b	2.697 (±0.001)^b	2.764 (±0.001)^b	2.939 (±0.001)^b	3.288 (±0.001)^b
1.00	2.622 (±0.002)^b	2.908 (±0.001)^b	3.342 (± 0.002)^b	3.511 (±0.002)^b	3.661 (±0.002)^b
2.0	3.146 (±0.002)^b	3.308 (±0.001)^b	3.935 (±0.001)^b	4.307 (±0.002)^b	4.409 (±0.001)^b
3.0	3.880 (±0.002)^b	4.020 (±0.003)^b	4.506 (±0.001)^b	4.612 (±0.002)^b	4.893 (±0.002)^b
5.0	4.408 (±0.001)b	4.930 (±0.002)b	5.304 (±0.001)b	5.428 (±0.002)b	5.528 (±0.001)b

b= standard deviation;

TABLE 3 : Standard Gibbs energies of solutions (ΔG_s^0) on molal scale in their respective solubilities of DL- α-amino butyric acid in aqueous mixtures of sodium nitrate ($NaNO_3$) at different temperature (K)

288.15 K		293.15 K		298.15 K		303.15 K		303.18 K	
S (mol·kg^{-1})	ΔG_s^0 (kJ·mol^{-1})	*S* (mol·kg^{-1})	ΔG_s^0 (kJ·mol^{-1})	*S* (mol·kg^{-1})	ΔG_s^0 (kJ·mol^{-1})	*S* (mol·kg^{-1})	ΔG_s^0 (kJ·mol^{-1})	*S* (mol·kg^{-1})	ΔG_s^0 (kJ·mol^{-1})
1.880	-1.5123	2.008	-1.6991	2.221	-1.9779	2.356	-2.1598	2.908	-2.7348
1.935	-1.5814	2.150	-1.8656	2.345	-2.1126	2.743	-2.5432	3.045	-2.8527
2.557	-2.2491	2.697	-2.4181	2.764	-2.5201	2.939	-2.7171	3.288	-3.0494
2.622	-2.3092	2.908	-2.6016	3.342	-2.9908	3.511	-3.1653	3.661	-3.3247
3.146	-2.7457	3.308	-2.9157	3.935	-3.3957	4.307	-3.6803	4.409	-3.8010
3.880	-3.2481	4.020	-3.3909	4.506	-3.7316	4.612	-3.8523	4.893	-4.0678
4.408	-3.5538	4.930	-3.8882	5.304	-4.1358	5.428	-4.2634	5.528	-4.3805

TABLE 4 : Coefficients a, b and c, Gibbs energies ΔG_t^0 and entropies $T\Delta S_t^0$ of transfer of DL- α-amino butyric acid on mole fraction scale from H_2O to aqueous mixtures of sodium nitrate ($NaNO_3$) at 298.15 K

Molality of $NaNO_3$	a (kJ·mol^{-1})	b (kJ·mol^{-1}·K^{-1})	c (kJ·mol^{-1}·K^{-1})	$\Delta G_t^0(i)$ (kJ·mol^{-1})	$T\Delta S_t^0(i)$ (kJ·mol^{-1})
0.0 [Water]	-329.75	7.6955	-1.15767	0	0
0.25	-101.92	2.6080	-0.39901	-0.325	1.960
0.50	-205.36	4.7727	-0.71829	-0.811	-0.383
1.00	256.70	-5.5370	0.81897	-1.337	-1.699
2.00	163.13	-3.4122	0.50089	-2.009	-1.884
3.00	47.00	-0.8989	0.12794	-2.585	-4.211
5.00	289.68	-6.3690	0.94488	-3.483	-4.397

propriate theoretical correlations for computing the same, these have been tacitly taken to be negligibly small, here.

The free energies, ΔG_s^0 at different temperatures are fitted by the method of least squares to an equation of the form (Equation 2)[11],

$$\Delta G_s^0 = a + bT + cT\ln T \qquad \textbf{(2)}$$

where T is the temperature in Kelvin scale. The values of the coefficients a, b, c are presented in TABLE 4. These are found to reproduce the experimental data within ±0.04 (kJ·mol^{-1}/ (kJ·mol^{-1}·K^{-1}) respectively.

Transfer Gibbs energies and entropies of the amino acids from water to aqueous Sodium nitrate ($NaNO_3$) mixtures were calculated at 298.15 K on mole fraction scale by using the following equations (3) & (4):

$$\Delta G_t^0(i) = {}_s\Delta G_{sol}^0(i) - {}_R\Delta G_{sol}^0(i)$$

i.e.

$$\Delta G_t^0(i) = (a_s - a_R) + (b_s - b_R)T + (c_s - c_R)T\ln T - RT\ln(M_s/M_R) \quad \textbf{(3)}$$

and,

$$\Delta S_t^0(i) = (b_R - b_s) + (c_R - c_S)(1 + \ln T) + R\ln(M_s/M_R) \quad \textbf{(4)}$$

here the subscript ‘s’ and ‘R’ refer to the aqueous Sodium nitrate ($NaNO_3$) mixtures and reference solvent (H_2O) respectively and M_R and M_s are the molar mass of the pure and mixed solvent respectively. $\Delta G_t^0(i)$ and $T\Delta S_t^0(i)$ values of α-amino acid thus obtained and presented in the TABLE 4. The involved uncertainties in $\Delta G_t^0(i)$ and $\Delta S_t^0(i)$ are about ±0.05 kJ·mol^{-1}and 2J·K^{-1} mol^{-1}, respectively.

Computation of cavity, transfer dipole-dipole interactions, enthalpy due to cavity formation, chemical parts of transfer Gibbs energy and entropy

Now here the term (where P=G or S) may be ascribed as the sum of the following terms (assuming dipole induced dipole term to be negligibly small)[17].

$$\text{i.e } \Delta P_t^0(i) .= \Delta P_{t,cav}^0(i) + \Delta P_{t,d-d}^0(i) + \Delta P_{t,ch}^0(i) \qquad \textbf{(5)}$$

Here, $\Delta P_{t,cav}^0(i)$ indicates the transfer energy contribution of the cavity effect which is involved due to creation of cavities for the species, DL- α-amino butyric acid in H_2O and aqueous Sodium nitrate ($NaNO_3$) mixtures and $\Delta P_{t,d-d}^0(i)$ stands for the dipole-dipole interaction effect involving interaction between dipolar-zwitter-ionic amino acid and the solvent molecules.

On the other hand, $\Delta P_{t,ch}^0(i)$ includes all other effects such as those arising from acid-base or short-range dispersion interaction, hydrophilic or hydrophobic hydration and structural effects, etc. scaled particle theory (SPT)[11,17,19] has been applied for computation of $\Delta P_{t,cav}^0(i)$ as earlier[17,19], assuming the solutes and solvent molecules as equivalent to hard-sphere models as are dictated by their respective diameters.(Vide TABLE 1).

The involved equations are given as follow:

$$\Delta G_{cav}^0(i) = G_C + RT\ln(RT/V_S) \qquad \textbf{(6)}$$

$$G_C = RT[-\ln(1-Z) + \{3X/(1-Z)\}\sigma_x + \{3Y/(1-Z)\}\sigma_x{}^2 + \{9X^2/4(1-Z)^2\}\sigma_x{}^2]$$

$$Z = \pi N_A/6V_s(z_R\sigma_R{}^3 + z_s\sigma_s{}^3)$$

Where
$$X = \pi N_A/6V_s(z_R\sigma_R{}^2 + z_s\sigma_s{}^2)$$

$$Y = \pi N_A/6V_s(z_R\sigma_R + z_s\sigma_s)$$

$$V_s = M_s/d_s$$

TABLE 5 : Gibbs energies of transfer $\Delta G_t^0(i)$, $\Delta G_{t,cav}^0(i)$, $\Delta G_{t,dd}^0(i)$, $\Delta G_{t,ch}^0(i)$ and enthalpy of transfer, $\Delta H_{t,cav}^0(i)$ and entropies of transfer $T\Delta S_t^0(i)$, $T\Delta S_{t,cav}^0(i)$, $T\Delta S_{t,dd}^0(i)$ and $T\Delta S_{t,ch}^0(i)$ of DL-α-amino butyric acid from H_2O to aqueous mixtures of sodium nitrate ($NaNO_3$) at 298.15 K (on mole fraction scale) in kJ·mol^{-1}

Mola lity of $NaNO_3$	$\Delta G_t^0(i)$ (kJ·mol^{-1})	$\Delta G_{t,cav}^0(i)$ (kJ·mol^{-1})	$\Delta G_{t,dd}^0(i)$ (kJ·mol^{-1})	$\Delta G_{t,ch}^0(i)$ (kJ·mol^{-1})	$T\Delta S_t^0(i)$ (kJ·mol^{-1})	$\Delta H_{t,cav}^0(i)$ (kJ·mol^{-1})	$T\Delta S_{t,cav}^0(i)$ (kJ·mol^{-1})	$T\Delta S_{t,dd}^0(i)$ (kJ·mol^{-1})	$T\Delta S_{t,ch}^0(i)$ (kJ·mol^{-1})
0.0 [Water]	0	0	0	0	0	0	0	0	0
0.25	-0.325	-0.213	0.013	-0.123	1.960	-0.291	-0.078	0.027	2.011
0.50	-0.811	-0.423	0.071	-0.459	-0.383	-0.546	-0.123	0.104	0.402
1.0	-1.337	-0.811	0.308	-0.834	-1.699	-0.990	-0.179	0.385	-1.905
2.0	-2.009	-1.460	1.140	-1.689	-1.884	-1.650	-0.190	1.320	-3.014
3.0	-2.585	-1.970	2.270	-2.885	-4.211	-2.100	-0.130	2.590	-6.671
5.0	-3.483	-2.760	4.940	-5.665	-4.397	-2.680	+0.080	5.540	-10.017

The required diameter and other solvent parameters of H_2O and $NaNO_3$ mixtures are taken from Ref. [22] .The required diameter of DL-α-amino butyric acid is 6.58 Å as given in Ref.[14, 17]. Dipole-moment value of DL- α-amino butyric acid is 16.0 D[23,25].

In this expression N_A is Avogadro's number, z_R and z_s are the mole fraction of reference solvent water and co-solvent respectively. 'σ_x, 'σ_R, and 'σ_s' are the hard sphere diameters of amino acid, water and aqueous sodium chloride mixtures respectively. Where the terms M_s, d_s represent for molar mass and molar density of the solvent.

Therefore, the required $\Delta G_{t,cav}^0(i)$ represents the difference,

$$\begin{aligned}\Delta G_{t,cav}^0(i) &= {}_s\Delta G^0{}_{cav}(i) - {}_R\Delta G^0{}_{cav}(i)\\ &= {}_sG_C - {}_RG_C + RT\ln(V_R/V_s)\end{aligned} \qquad (7)$$

Again $\Delta G_{t,d-d}^0(i) = ({}_s\Delta G_{d-d}^0(i) - {}_R\Delta G_{d-d}^0(i))$ **(8)**

and $\Delta S_{t,d-d}^0(i) = ({}_s\Delta S_{d-d}^0(i) - {}_R\Delta S_{d-d}^0(i))$ are calculated by means of the Keesom-orientation expression[14,21], for ${}_s\Delta G_{d-d}^0(i)$ in a solvent S, as given below:

$${}_s\Delta G_{d-d}^0(i) = (8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(kT)^{-1}v_s^{-1} = A/T\,V_s \qquad (9)$$

Where A = - $(8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(k)^{-1}$ and $V_s = M_s/d_s$ and that of $\Delta S_{d-d}^0(i)$ as follows-

$${}_s\Delta S_{d-d}^0(i) = -\{\delta_s\Delta G_{d-d}^0(i)/\delta T\}_p \qquad (10)$$

i.e. $T_s\Delta S_{d-d}^0(i) = {}_s\Delta G_{d-d}^0(i)[1+T\alpha]$, where N stands for Avogadro's number, μ_s, μ_x are the dipole moment of aqueous Sodium nitrate ($NaNO_3$) mixtures and amino acid respectively (TABLE 1). In this study we considered the dipole moment of aqueous Sodium nitrate solution is similar to that off reference solvent, water.

σ_{s-x} is the distance at which the attractive and repulsive interactions between the solvent and solute molecules are equal and is generally equal to ½($\sigma_s + \sigma_x$) where σ_s and σ_x are the hard sphere diameter of cosolvent and solute molecules respectively (TABLE 1) and α is the isobaric thermal expansibility constant (α value is taken same in whole compositions Sodium nitrate as water) of the solvent and given by the following equation-

$$\alpha = (\delta\ln V_s/\delta T)_P = -(\delta\ln d_s/\delta T)_P \qquad (11)$$

The enthalpy change due cavity forming interaction in water to aqueous Sodium nitrate mixtures is measured by the equation-

$$\Delta H_{t,cav}^0(i) = {}_s\Delta H_{cav}^0(i) - {}_R\Delta H_{cav}^0(i) \qquad (12)$$

$$\Delta H_{cav}^0(i) = (A+H+K+E)\times B \qquad (13)$$

where $A = (\Pi N_A/6V_s)\times(Z_R\sigma_R{}^3 + Z_S\sigma_S^3)$; $B = \sigma_S RT^2/1-A$;

$H = \sigma_x\times 3Y/1-A$; $K = \sigma_x\times 3X/1-A$; $E = 9\sigma_x{}^2\times X^2/(1-A)^2$;

$X = (\Pi N_A/6V_s)\times(Z_R\sigma_R{}^2 + Z_S\sigma_S^2)$; and

$Y = (\Pi N_A/6V_s)\times(Z_R\sigma_R + Z_S\sigma_S)$.

Following Marcus[22] and Kim *et al.*[21] in order to get this $\Delta P_{t,d-d}^0(i)$ term on mole fraction scale the quantity was again multiplied by the term X_{s1}.

$$X_{s1} = X_s(\mu_s/\sigma_s^3)/(\mu_R/\sigma_R^3) \qquad (14)$$

This is the real mole fraction contribution due to dipole-dipole interaction[22]. Subtraction of $\Delta P^0_{t,cav}(i)$ and $\Delta P^0_{t,d-d}(i)$ from the total we get $\Delta P^0_{t,ch}(i)$ of the solute amino acid. The values of $\Delta P^0_{t,cav}(i)$, $\Delta P^0_{t,d-d}(i)$ and $\Delta P^0_{t,ch}(i)$ are presented in TABLE 5.

DISCUSSION

Analysis of solubility data

The solubility of DL-α-amino butyric acid increases with temperature in a particular composition of water-$NaNO_3$ mixed solvent system and with the increased concentration of $NaNO_3$ solubility of the same also increased at a particular temperature (TABLE 2).

As shown in Figure 1, the presence of $NaNO_3$ in water has a drastic effect on the solubility of DL-α-amino butyric acid. The gradual increment of solubility of DL-α-amino butyric acid in presence of $NaNO_3$ may be due to the 'salting in effect'. The amino acid existing as zwitterions in the system may form complexes with cation and anion of the electrolyte. The solubility behaviour of the said amino acid confirms the strong effect of the nitrate anion on its solubility.

Involved Gibbs free energy between solute and solvent mixtures

Figure 2 represents the variation of $\Delta G^0_t(i)$ for DL-α-amino butyric acid against the mole % of $NaNO_3$ at 298.15 K.

The negative increment of values indicates that DL-α-amino butyric acid will be stabilized with the increased concentration of the electrolyte, having nitrate anion.

Actually $\Delta G^0_t(i)$ the is composed of, $\Delta G^0_{t,cav}(i)$, $\Delta G^0_{t,d-d}(i)$ and $\Delta G^0_{t,ch}(i)$ i.e. the nature of stability may be guided by the gradual change in cavity interaction, dipole-dipole interaction and hydrophobic/hydrophilic interactions between the ions and water molecules with the hydrocarbon backbone and charged amino and carboxyl group of the zwitterionic amino acid in this aqueous $NaNO_3$ mixed solvent system.

The, $\Delta G^0_{t,cav}(i)$ values are gradually become negative with $NaNO_3$ concentration (TABLE 5) which indicates that the involved amino acid gain more stability with the increased mole % of $NaNO_3$ i.e. it should be easily accommodated in aqueous $NaNO_3$ than in pure H_2O with release of concerned energy due to the comparatively larger size of aqueous $NaNO_3$ (3.97Å)[22,24] than H_2O (2.74 Å)[17,22]. During the introduction of amino acid in aqueous $NaNO_3$ solvent system, there may form strong ion-pair between the zwitterionic amino acid and the cation (Na^+) / anion (NO_3^-) of the electrolyte, $NaNO_3$. This factor may responsible for the stability of DL- α-amino butyric acid during transfer from water to water- $NaNO_3$ solvent system.

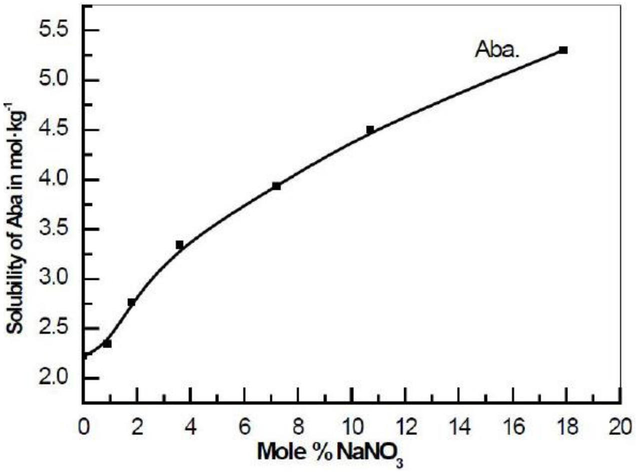

Figure 1 : Variation of solubility of DL-alpha amino butyric acid in mol·kg^{-1} in aqueous solution of $NaNO_3$ at 298.15 K

The $\Delta G^0_{t,d-d}(i)$ (TABLE 5) values of DL- α-amino butyric acid are increased gradually with increased mole % of $NaNO_3$. The values depend on hard sphere diameter of cosolvent and solute molecules, dipole moment of solvent and on molar volume of the co-solvent

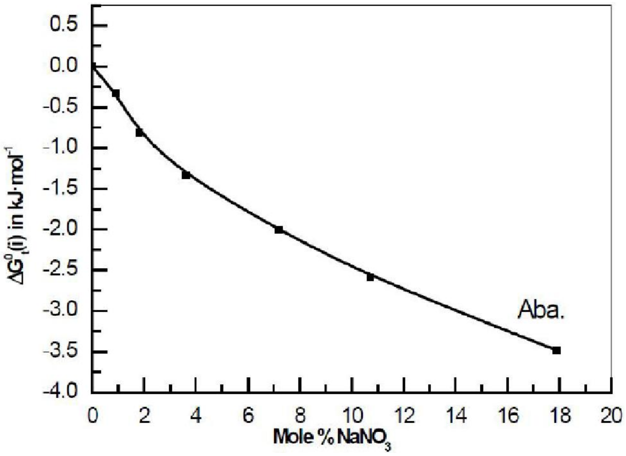

Figure 2 : Variation of $\Delta G^0_t(i)$ in kJ·mol^{-1} of DL-alpha-amino butyric acid in aqueous mixtures of $NaNO_3$ at 298.15K

(as equation IX).

The variation of values indicates that amino acid becomes unstable in higher content of sodium nitrate due to dipolar interaction.

$\Delta G^{0}_{t,ch}(i)$ values for the solute, DL- α-amino butyric acid have been computed after subtraction of [17] $\Delta G^{0}_{t,cav}(i)$ from $\Delta G^{0}_{t}(i)$.

Figure 3 shows the variation of $\Delta G^{0}_{t,ch}(i)$ with mole % of $NaNO_3$. The $\Delta G^{0}_{t,ch}(i)$ values gradually become negative with the increased concentration of $NaNO_3$ in $NaNO_3$-water system. The downward trend of $\Delta G^{0}_{t,ch}(i)$ value as shown in Figure 3 indicates the stabilization with increased concentration of sodium nitrate. Here it is important to note that due to $\Delta G^{0}_{t,cav}(i)$ the amino acid becomes stabilized and due to $\Delta G^{0}_{t,d-d}(i)$ the amino acid becomes unstable but the other factors associated with total transfer free energy, $\Delta G^{0}_{t}(i)$ make $\Delta G^{0}_{t,ch}(i)$ value as a negative increment i.e. DL-α-amino butyric acid becomes stabilized with the increased concentration of $NaNO_3$ in water- $NaNO_3$ solution system. With the increase concentration of the electrolyte in the water-$NaNO_3$ solution system the salt (cation and anion) and zwitterions interaction increases i.e. formation of ion- pair occurs, which suppress the long range electrostatic forces and, at the same time the ion-pair formation shield the hydrophobic interaction between the water and amino acid molecules, consequently the hydrophobic interaction effect between the hydrophobic moiety of the amino acid decreases in a greater extent resulting in the more negative $\Delta G^{0}_{t}(i)$ value that makes the $\Delta G^{0}_{t,ch}(i)$ value in favour of negative increment. Thereby the chemical stability of DL-α-amino butyric acid is reached as shown in Figure 3. From these observations one may conclude that $NaNO_3$ may stabilize the amino acid as well as proteins and the bio-macromolecules.

Entropy and enthalpy of transfer of DL-α-amino butyric acid in aqueous solution of sodium nitrate

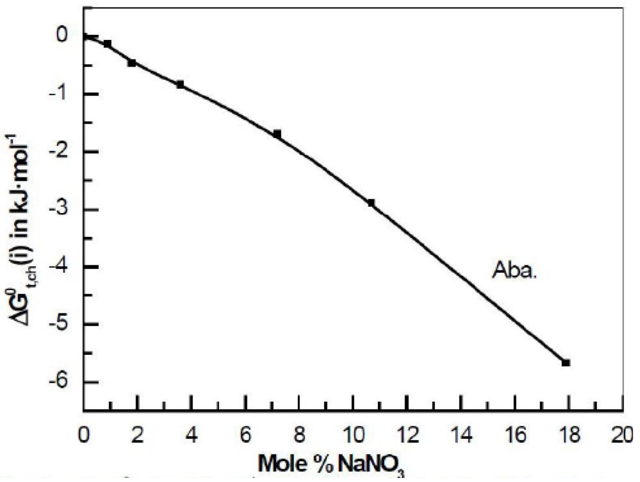

Figure 3 : Variation of $\Delta G^{0}_{t,ch}(i)$ in kJ·mol^{-1} of DL-alpha amino butyric acid in aqueous mixtures of $NaNO_3$ at 298.15K

In the present study Figure 4 represents the variations of total transfer entropy, $T\Delta S^{0}_{t}(i)$ with mole % $NaNO_3$ and Figure 5 represents the entropy of transfer, due to chemical interactions, $T\Delta S^{0}_{t,ch}(i)$.

Figure 6 represents the variation of enthalpy of transfer, $\Delta H^{0}_{t,cav}(i)$ due to cavity forming interaction. Both the Figures 4 & 5 show a complicated nature of variations of $T\Delta S^{0}_{t}(i)$ & $T\Delta S^{0}_{t,ch}(i)$ respectively.

Actually $T\Delta S^{0}_{t}(i)$ is composed of transfer entropy due to cavity, dipole-dipole and chemical interaction effects i.e.

$$T\Delta S^{0}_{t}(i) = T\Delta S^{0}_{t,cav}(i) + T\Delta S^{0}_{t,d-d}(i) + T\Delta S^{0}_{t,ch}(i)$$

Now combined effect in $T\Delta S^{0}_{t}(i)$ value may represents such behaviour as shown in Figure 4.

In Figure 5 it is observed that at about 1 % mole concentration of $NaNO_3$ in the solvent system the $T\Delta S^{0}_{t,ch}(i)$ value shows clear maxima but after that concentration the $T\Delta S^{0}_{t,ch}(i)$ values gradually become negative. It is indicates that in water there is very strong intermolecular hydrogen bonding interaction between the water molecules. But with the increased concentration of sodium nitrate in presence of amino acid the hydrogen bonds between the water molecules are broken i.e. in the lower content of the electrolyte there may be breakdown of 3D water structure occurs. In this region the number of free water molecules as well as

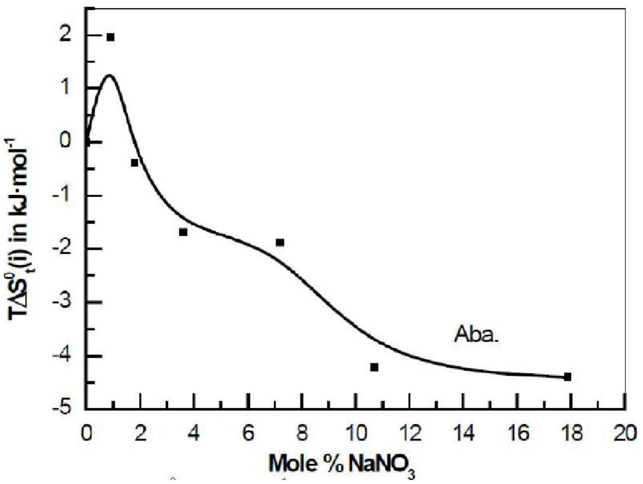

Figure 4 : Variation of $T\Delta S^0_t(i)$ in kJ·mol^{-1} of DL-alpha amino butyric acid in aqueous mixtures of $NaNO_3$ at 298.15K

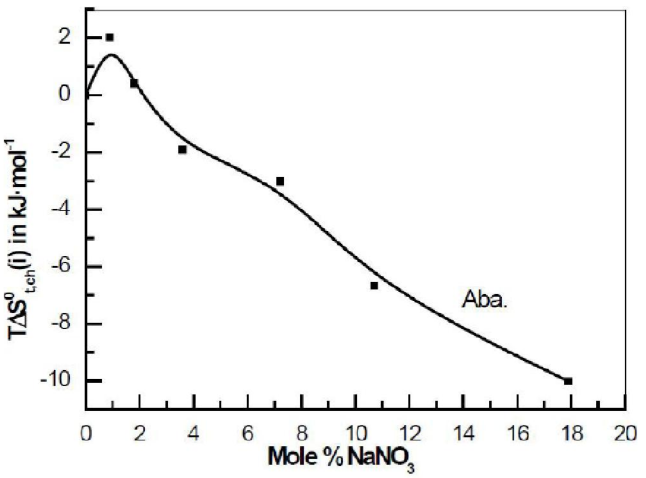

Figure 5: Variation of $T\Delta S^0_{t,ch}(i)$ in kJ·mol $^{-1}$ of DL-alpha amino butyric acid in aqueous mixtures $NaNO_3$ at 298.15K

cation and anion of the electrolyte increases which are responsible for the positive maximum of entropy change. But as the concentration of $NaNO_3$ increased, the monomeric H_2O molecules become induced by solute amino acid to be interacted by hydrogen bonding as well as hydrophilic interaction with the electrolyte cation (Na^+) and anion ($_{NO3}^-$) i.e. association with the free H_2O molecules occurs extensively. At the same time ion-pair formation occurs between the cation/ anion and zwitterions of the amino acid in a greater extent resulting less number of free molecules in the system which is mainly responsible for sharp decrement of values. As shown in Figure 6 enthalpy of transfer, $\Delta H^0_{t,cav}(i)$ due to cavity formation shows gradual decrement with mole % $NaNO_3$ which manifests that during the introduction of the amino acid in $NaNO_3$-water system, formation of ion-pair associated species occur between the zwitterionic amino acid and cation and anion of the salt. This factor may responsible for negative variation of $\Delta H^0_{t,cav}(i)$ value.

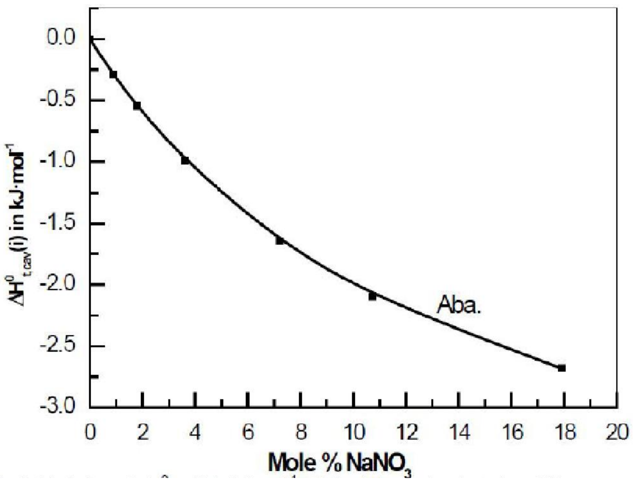

Figure 6 : Variation of $\Delta H^0_{t,cav}(i)$ in kJ·mol^{-1} of DL-alpha amino butyric acid in aqueous mixtures of $NaNO_3$ at 298.15K

CONCLUSIONS

The solubility studies shows that electrolyte affect the solubility of the amino acid as well as other biomolecules having hydrophobic side chains. The presence of nitrate anion is mainly responsible for higher solubility with the increase concentration of the electrolyte in a particular temperature. The DL- α-amino butyric acid is stabilised in aqueous sodium nitrate solution as its solubility increases with the increasing concentration of $NaNO_3$ content. Stability of the amino acid arises mainly due to cavity forming interactions, ion-pair formation, and other chemical types of interactions. The electrolyte shows water 3D-structure breaking propensity in the presence of amino acid, DL-α-amino butyric acid. The amino acid shows more disorderness in lower content of electrolyte and more orderness is found in higher content of the electrolyte.

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