Thermodynamic Studies Related to the Solvation Chemistry of Dl-A-Amino Butyric Acid in Aqueous Solution of Sodium Chloride

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Abstract

In this paper the solubilities of the amino acid, DL-α-amino butyric acid (Aba) were measured in aqueous solution with various sodium chloride (NaCl) concentrations. The solubilities were measured by 'formol titrimetry' method in the temperature range from 288.15 to 308.15 K. The standard transfers Gibbs energies and entropies have been evaluated for Aba from water to aqueous mixture of NaCl solution at 298.15 K. The chemical effects of the transfer Gibbs energies ($\Delta G^0_{t,ch}(i)$ *), as 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 chloride (NaCl) have also been reported here. The results show that the solubility is affected by the electrolyte. The solvation chemistry of Aba is guided here by different types of interactions.*

Keywords: DL-α-amino butyric acid; solubility; sodium chloride, transfer energetics; hydrophobic interaction

Introduction

Amino acids are the biomolecules. These are building block of proteins. The amino acids are not only important in protein formation, but also important due to their applications in chemical, pharmaceutical and food industries. The solubility studies of these biomolecules 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 explore 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] solvent systems.

But the detail 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. From these thermodynamic point of views in the present article efforts are given to increase the knowledge of solvation chemistry of the amino acids (here for DL-α-amino butyric acid) in aqueous sodium chloride (NaCl) solution.

Hence as a part of our systematic study of the effect of aqueous solution of NaCl, the solubility of this amino acid have been measured by formol titration in (water, 0.5(M), 1(M), 2(M), 4(M) and 5(M)) aqueous NaCl solutions at 288.15, 293.15, 298.15, 303.15 and 308.15 K and then different thermodynamic properties of the amino acid, DL-α-amino butyric acid have been evaluated and discussed.

Materials and Methods:

Chemicals and their purifications:

DL-α-amino butyric acid [> 99.5 %, E Merck] was used after drying as described in previous works [9]. Sodium chloride (NaCl) of purity 99.9 % obtained from E 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 NaCl of the concentrations of 0.0, 0.5, 1.0, 2.0, 4.0 and 5.0 (M) were made. Then the solvent (H_2O/ H_2O+NaCl) 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 co-solvent 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 0.8 %.

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 NaCl are presented in the Table 1. The solubilities of DL-α-amino butyric acid are measured on molal scale (mol·kg-1) and listed in Table 2. The standard deviations, sf are also estimated for all solubility values to know about the precision and are shown in parentheses (Table 2) only for 0.5, 1.0, 2.0, 4.0 and 5.0 (M) for the aqueous solvent of NaCl at all temperatures.

Table 1 Values of solvent parameters (Molarity of NaCl solvent system, Mole fraction of Nacl (z_s), water ((z_R), mean mol. Weight (M_S), density (d_s), hard sphere diameter of co-solvent (σ_s) (NaCl+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+NaCl system at 298.15 K

Molality of NaCl	Mole fraction of NaCl ($z_{s)}$	Mole fraction of water (z_R)	Molar mass (M_S)	10^3 d_s (kg m^{-3})	Molar Volume (V_s)	σ_s (nm)	σ_{s-x} (nm)	Dipole Moment (μ_s)	α (x 10^{-3})
0.0	0.0000	1.0000	18.015	0.99700$^{\#}$	18.0690	0.2740	0.4660	1.831	0.257*
0.5	0.0089	0.9911	18.375	1.00744	18.2393	0.2741	0.4661	1.894	0.255
1.0	0.0177	0.9823	18.732	1.01776	18.4051	0.2742	0.4661	1.956	0.253
2.0	0.0347	0.9653	19.419	1.03770	18.7135	0.2743	0.4662	2.078	0.249
4.0	0.0672	0.9328	20.736	1.07583	19.2744	0.2746	0.4663	2.311	0.243
5.0	0.0826	0.9174	21.359	1.09389	19.5257	0.2747	0.4664	2.422	0.239

* 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_chloride and from reference [22].

Table 2 Solubility (*S)* in mol·kg^{-1} of DL-α-amino butyric acid in aqueous mixtures of sodium chloride (NaCl) at different temperature (K) (b= standard deviation)

Molality of NaCl	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.0 [Water]	1.856 (1.702)[14] (1.850)[25]	2.060 (1.952)[14] (1.990)[25]	2.132 (2.205)[14] (2.199)[25]	2.360 (2.534)[14] (2.550)[25]	2.923 (2.874)[14] (2.919)[25]
0.5	1.152 (±0.003)^b	1.271 (±0.003)^b	1.343 (±0.002)^b	1.404 (±0.001)^b	1.557 (±0.001)^b
1.0	1.085 (±0.002)^b	1.156 (±0.001)^b	1.227 (±0.001)^b	1.299 (±0.001)^b	1.359 (±0.001)^b
2.0	0.892 (±0.002)^b	0.905 (±0.001)^b	0.921 (± 0.003)^b	0.988 (±0.001)^b	1.137 (±0.002)^b
4.0	0.738 (±0.001)^b	0.779 (±0.001)^b	0.819 (±0.001)^b	0.854 (±0.001)^b	0.944 (±0.001)^b
5.0	0.567 (±0.001)^b	0.622 (±0.002)^b	0.676 (±0.001)^b	0.717 (±0.001)^b	0.753 (±0.003)^b

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 (i). Here we have also measured the Gibbs energies of solutions by using the same equation as given below and presented in Table 3.

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 chloride (NaCl) 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})
1.856	-1.48154	2.060	-1.76141	2.132	-1.87429	2.360	-2.16416	2.923	-2.74535
1.152	-0.33899	1.271	-0.58523	1.343	-0.73083	1.404	-0.85451	1.557	-1.13466
1.085	-0.19544	1.156	-0.35353	1.227	-0.5075	1.299	-0.65893	1.359	-0.78739
0.892	0.274606	0.905	0.242748	0.921	0.204803	0.988	0.031703	1.137	-0.32871
0.738	0.726861	0.779	0.606812	0.819	0.494344	0.854	0.397188	0.943	0.149272
0.567	1.359299	0.622	1.158811	0.676	0.970245	0.717	0.839888	0.753	0.728504

The required diameter and other solvent parameters of H_2O and NaCl 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 α-amino butyric acid is 16.0 D [23, 25].

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

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 appropriate theoretical correlations for computing the same, these have been tacitly taken to be negligibly small, as is usually done for non-electrolytes. [28]

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

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

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 ΔG_t^0 and entropies ΔS_t^0 of the amino acids from water to aqueous sodium chloride (NaCl) mixtures were calculated at 298.15 K on mole fraction scale by using the following equations (iii) & (iv):

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

$$\text{i.e. } \Delta G_t^0(i) = (a_s - a_R) + (b_s - b_R)T + (c_s - c_R)T\ln T - RT\ln(M_s / M_R) \qquad \text{(iii)}$$

$$\text{and, } \Delta S_t^0(i) = (b_R - b_s) + (c_R - c_S)(1 + \ln T) + R\ln(M_s / M_R) \qquad \text{(iv)}$$

here the subscript 's' and 'R' refer to the aqueous sodium chloride (NaCl) 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 acids 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.

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 H_2O-NaCl mixture at 298.15 K

Molality of Nacl	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]	-454.34	10.5156	-1.57924	0	0
0.5	-892.61	20.0661	-2.99649	1.6344	-17.3513
1.0	39.76	-70.7332	0.10529	1.7584	-9.9487
2.0	-364.46	8.3601	-1.25265	1.8316	-9.4137
4.0	-67.87	1.6911	-0.25658	1.9589	-9.2839
5.0	130.48	-2.7292	0.40277	2.2675	-8.5760

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

Now here the term $\Delta P_t^0(i)$ (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].

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

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 H2O and aqueous sodium chloride (NaCl) 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, $\Delta P^{0}_{t,ch}(i)$ 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 $\Delta P^{0}_{t,cav}(i)$ 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:

$$\Delta G^{0}_{cav}(i) = G_C + RT\ln(RT/V_S) \qquad \text{(vi)}$$

Where

$$G_C = RT[-\ln(1-Z) + \{3X/(1-Z)\}\sigma_x + \{3Y/(1-Z)\}\sigma_x{}^2 + \{9X^2/4(1-Z)^2\}\sigma_x{}^2]$$
$$Z = \pi N_A/6V_s(z_R\sigma_R{}^3 + z_s\sigma_s{}^3)$$
$$X = \pi N_A/6V_s(z_R\sigma_R{}^2 + z_s\sigma_s{}^2)$$
$$Y = \pi N_A/6V_s(z_R\sigma_R + z_s\sigma_s)$$
$$V_s = \mathrm{M}_s/d_s$$

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 $\Delta G^{0}_{t,cav}(i)$ represents the difference,

$$\Delta G^{0}_{t,cav}(i) = {}_s\,\Delta G^{0}{}_{cav}(i) - {}_R\,\Delta G^{0}{}_{cav}(i) = {}_s\,G_C - {}_R\,G_C + RT\ln(V_R/V_s) \qquad \text{(vii)}$$

Again $\Delta G^{0}_{t,d-d}(i) = ({}_s\Delta G^{0}_{d-d}(i) - {}_R\Delta G^{0}_{d-d}(i))$ (viii)

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

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

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

$${}_s\Delta S^{0}_{d-d}(i) = -\{\delta\,{}_s\Delta G^{0}_{d-d}(i)/\delta\mathrm{T}\}_p \qquad \text{(x)}$$

i.e. $\mathrm{T}\,{}_s\Delta S^{0}_{d-d}(i) = {}_s\Delta G^{0}_{d-d}(i)[1+\mathrm{T}\alpha]$, where N stands for Avogadro's number, μ_s, μ_x are the dipole moment of aqueous sodium chloride mixtures and amino acid respectively (Table 1).

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 of the solvent and given by the following equation-

$$\alpha = \delta \ln V_s / \delta \mathrm{T})_P = -(\delta \ln d_s / \delta \mathrm{T}) \qquad \text{(xi)}$$

The enthalpy change due cavity forming interaction in water to aqueous sodium chloride (NaCl) mixtures is measured by the equation-

$$\Delta H^0_{t,cav}(i) = {}_s\Delta H^0_{cav}(i) - {}_R\Delta H^0_{cav}(i) \qquad \text{(xii)}$$

$$\Delta H^0_{cav}(i) = (\mathrm{A}+\mathrm{H}+\mathrm{K}+\mathrm{E}) \times \mathrm{B} \qquad \text{(xiii)}$$

where $\mathrm{A} = (\Pi \mathrm{N}_A / 6V_s) \times (\mathrm{Z}_R \sigma_R{}^3 + \mathrm{Z}_S \sigma_S^3)$; $B = \sigma_S R\mathrm{T}^2 / 1 - A$;

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

$\mathrm{X} = (\Pi \mathrm{N}_A / 6V_s) \times (\mathrm{Z}_R \sigma_R{}^2 + \mathrm{Z}_S \sigma_S^2)$; and $\mathrm{Y} = (\Pi \mathrm{N}_A / 6V_s) \times (\mathrm{Z}_R \sigma_R + \mathrm{Z}_S \sigma_S)$.

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

$$\mathrm{X}_{s1} = \mathrm{X}_s (\mu_s / \sigma_s^3) / (\mu_R / \sigma_R^3) \qquad \text{(xiv)}$$

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.

Table 5 Gibbs energies of transfer $\Delta G^0_t(i)$, $\Delta G^0_{t,cav}(i)$, $\Delta G^0_{t,dd}(i)$, $\Delta G^0_{t,ch}(i)$ and enthalpy of transfer, $\Delta \mathrm{H}^0_{t,cav}(i)$ and entropies of transfer $\mathrm{T}\Delta S^0_t(i)$, $\mathrm{T}\Delta S^0_{t,cav}(i)$, $\mathrm{T}\Delta S^0_{t,dd}(i)$ and $\mathrm{T}\Delta S^0_{t,ch}(i)$ of DL-α-amino butyric acid from H_2O to H_2O-NaCl at 298.15 K (on mole fraction scale) in $\mathrm{kJ \cdot mol^{-1}}$.

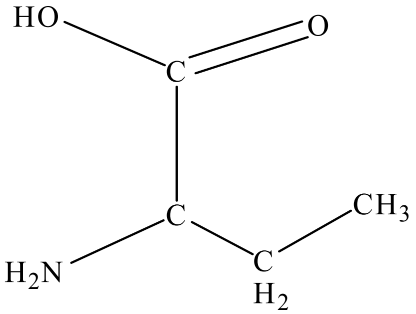
Molality of NaCl	$\Delta G^0_t(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta G^0_{t,cav}(i$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta G^0_{t,dd}(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta G^0_{t,ch}(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\mathrm{T}\Delta S^0_t(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta \mathrm{H}^0_{t,cav}(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\mathrm{T}\Delta S^0_{t,cav}(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\mathrm{T}\Delta S^0_{t,dd}(i)$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\mathrm{T}\Delta S^0_{t,ch}(i$ ($\mathrm{kJ \cdot mol^{-1}}$)
0.0 [Water]	0	0	0	0	0	0	0	0	0
0.5	1.6344	-0.0990	-0.0632	1.7966	-17.3513	-0.1730	-0.0740	-0.0674	-17.2099
1.0	1.7584	-0.1950	-0.8230	2.7764	-9.9487	-0.3390	-0.1440	-0.8830	-8.6347
2.0	1.8316	-0.3680	-1.1000	3.2996	-9.4137	-0.6370	-0.2690	-1.1700	-7.9747
4.0	1.9589	-0.6680	-4.7900	7.4169	-9.2839	-1.1000	-0.4320	-5.1000	-3.7519
5.0	2.2675	-0.7970	-7.7100	10.7745	-8.5760	-1.3200	-0.5230	-8.1900	0.1370

Discussion:

4.1 Analysis of solubility data:

The solubility values of DL-α-amino butyric acid increases with increasing temperature in a particular composition of water-NaCl mixed solvent system but with the increased concentration of NaCl solubility values decreased at a particular temperature (Fig. 1).

As shown in Fig. 1, the presence of NaCl in water has a drastic effect on the solubility of amino acid, Aba. The gradual decrement of solubility of DL-α-amino butyric acid (Aba.) in presence of NaCl may be due to the 'salting out effect'. This effect arises due to the interactions of the ions and water molecules with the hydrocarbon backbone and charged amino and carboxyl group of the zwitterionic amino acid. Here the chemical structure as well as structural orientation of the amino acid (**Structure 1**) may play an important role for the 'salting out effect'.



Structure 1: Chemical structure of DL-α-amino butyric acid

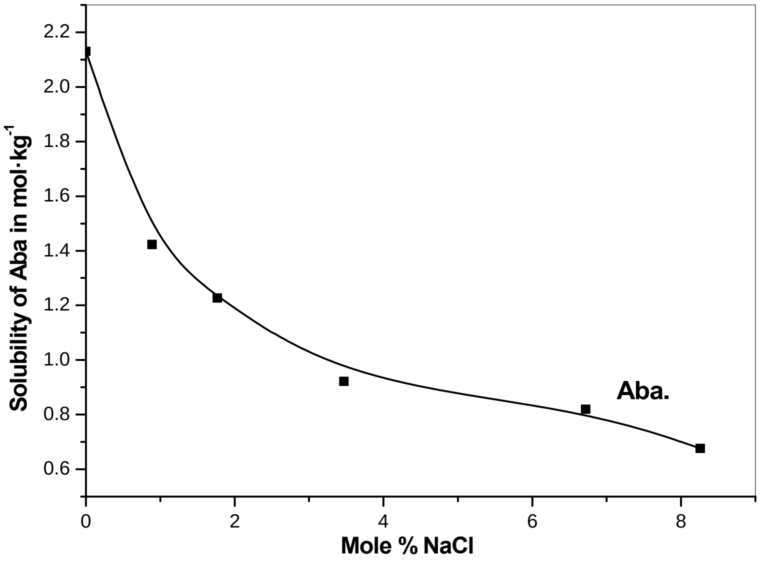


Fig 1. Variation of solubility of DL-alpha-amino butyric acid in aqueous solution of NaCl at 298.15 K

Interactions involved between solute and solvent mixtures:

In the present study different types of interactions involved between solute and solvent molecules are presented graphically and discussed. Here Fig. 2 represents the variation of $\Delta G_t^0(i)$ for DL-α-amino butyric acid against the mole % of NaCl at 298.15 K.

The positive increment of $\Delta G_t^0(i)$ values indicates that DL-α-amino butyric acid will be destabilized with the increased concentration of the electrolyte. Actually the $\Delta G_t^0(i)$ is composed of $\Delta G_{t,cav}^0(i)$, $\Delta G_{t,d-d}^0(i)$ and $\Delta G_{t,ch}^0(i)$.

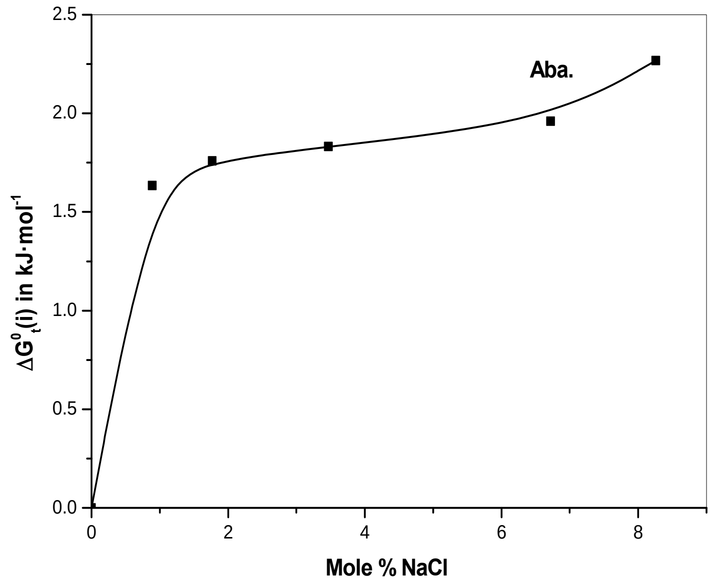


Fig 2. Variation of $\Delta G_t^0(i)$ in kJ·mol^{-1} of DL-alpha-amino butyric acid in aqueous solution of NaCl at 298.15 K

Such 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 NaCl mixed solvent system.

The $\Delta G_{t,cav}^0(i)$, values are gradually decreased with NaCl concentration (Table 5) which indicates that the involved amino acid acquire more stability with the increased mole % of NaCl i.e. it should be easily accommodated in NaCl water system than H_2O with release of concerned energy due to the comparatively larger size of aqueous NaCl (0.283Å) [22] than H_2O (0.274 Å) [17, 22]. During the introduction of amino acid in aqueous NaCl solvent system, there may form an ion-pair complexes between the zwitterionic amino acid and the cation (Na^+) / anion (Cl^-) of the electrolyte, NaCl. This factor may responsible for the stability of DL-α-amino butyric acid during transfer from water to water-NaCl solvent system.

The $\Delta G^0_{t,d-d}(i)$ (Table 5) values of DL-α-amino butyric acid are decreased gradually with increased mole % of NaCl. The dipole moment of NaCl (9.0 D) [24] is higher than H_2O (1.83 D) [22] which may support such type of variation.

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

Fig. 3 shows the variation of $\Delta G^0_{t,ch}(i)$ with mole % of NaCl. The $\Delta G^0_{t,ch}(i)$ values gradually become positive with the increased concentration of NaCl in NaCl-water system. This indicates the destabilization of DL-α-amino butyric acid. Though $\Delta G^0_{t,cav}(i)$ and $\Delta G^0_{t,d-d}(i)$ stabilised the amino acid 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 positive increment i.e. DL-α-amino butyric acid becomes destabilized with the increased concentration of NaCl in water-NaCl solution system.

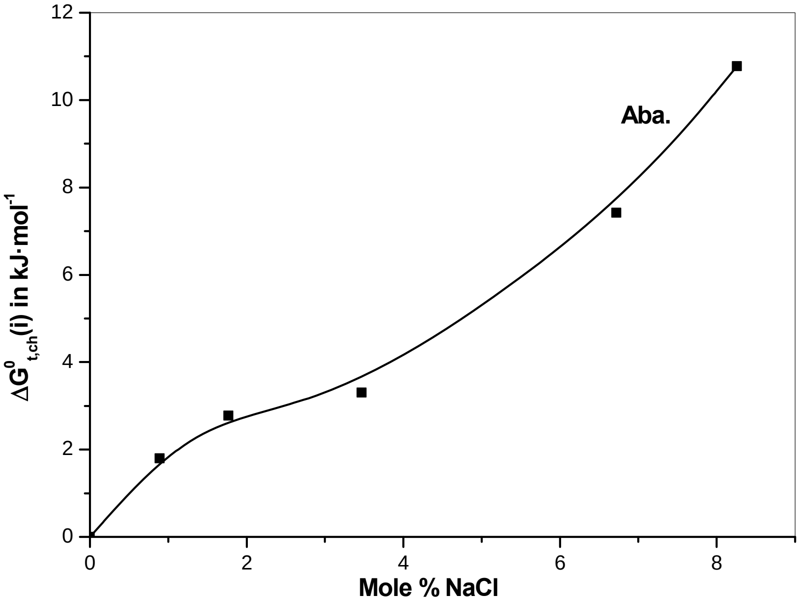


Fig 3. Variation of $\Delta G^0_{t,ch}(i)$ in kJ·mol^{-1} of DL-alpha-amino butyric acid in aqueous solution of Nacl at 298.15 K

With the increase concentration of the electrolyte in the water-NaCl solution system the salt and non-polar hydrophobic moiety (CH_3-CH_2-) interaction increases, this disrupts the hydrophobic hydration co-sphere between the water and amino acid molecules, consequently the hydrophobic interaction between the hydrophobic moiety of the amino acid increases in a greater extent resulting in the more positive

$\Delta G_t^0(i)$ value that makes the $\Delta G_{t,ch}^0(i)$ value in favour of positive increment. Thereby the chemical stability of DL-α-amino butyric acid will fall as shown in Fig. 3. From these observations one may conclude that NaCl may stabilize the hydrophobic interactions among the non-polar groups within the proteins as well as in the bio-macromolecules.

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

In the present study Fig. 4 & Fig. 5 represent the variations of total transfer entropy, $T\Delta S_t^0(i)$ and entropy of transfer, due chemical interactions, $T\Delta S_{t,ch}^0(i)$ with mole % NaCl respectively and Fig. 6 represents the variation of enthalpy of transfer, $\Delta H_{t,cav}^0(i)$ due to cavity forming interaction. Both the figures 4 & 5 show a complicated nature of variations of $T\Delta S_t^0(i)$ & $T\Delta S_{t,ch}^0(i)$ respectively.

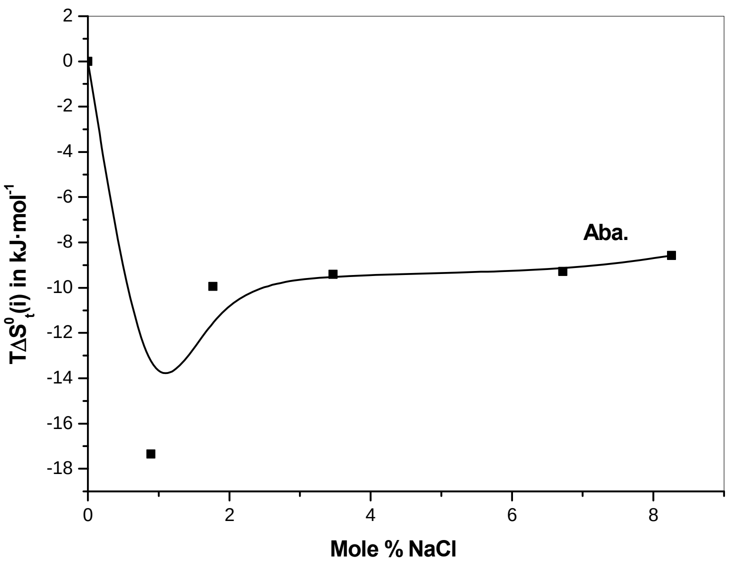


Fig 4. Variation of $T\Delta S_t^0(i)$ in kJ·mol^{-1} of DL-alpha-amino butyric acid in aqueous mixturesofNaCl at 298.15 K

Actually $T\Delta S_t^0(i)$ is composed of transfer entropy due to cavity, dipole-dipole and chemical interaction effects i.e. $T\Delta S_t^0(i) = T\Delta S_{t,cav}^0(i) + T\Delta S_{t,d-d}^0(i) + T\Delta S_{t,ch}^0(i)$

Now combined effect in $T\Delta S_t^0(i)$ value may represents such behaviour as shown in Fig. 4.

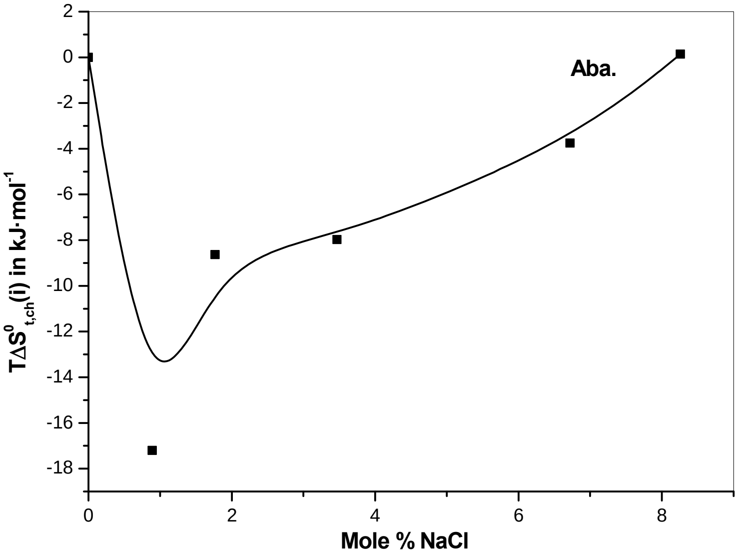


Fig 5. Variation of $T\Delta S^0_{t,ch}(i)$ in kJ·mol^{-1} of DL-alpha amino butyric acid in aqueous mixtures of NaCl at 298.15 K

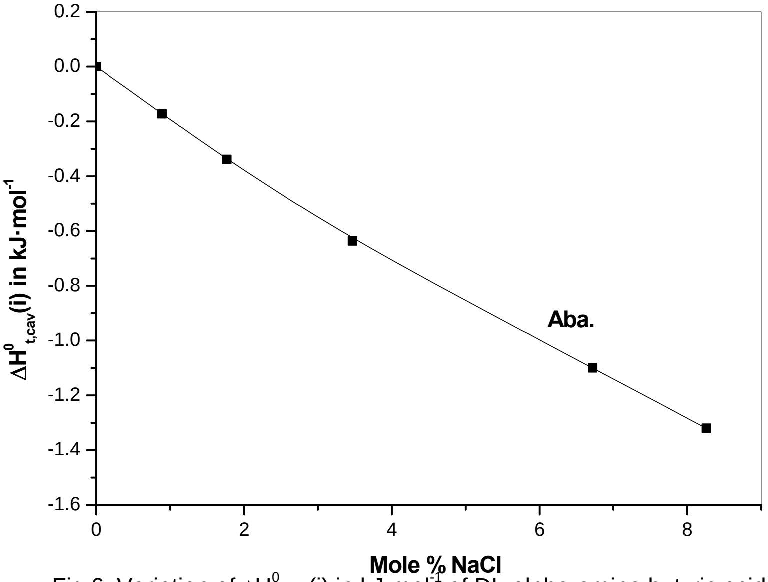


Fig 6. Variation of $\Delta H^0_{t,cav}(i)$ in kJ·mol^{-1} of DL-alpha-amino butyric acid in aqueous solution of NaCl at 298.15 K

On the other hand, the similar negative variation of $T\Delta S^0_{t,ch}(i)$ is observed in aqueous sodium chloride solution system. In low content of NaCl (about 1% NaCl) the $T\Delta S^0_{t,ch}(i)$ value shows maximum negative value. With the increased concentration of NaCl in the solvent system the $T\Delta S^0_{t,ch}(i)$ value increases. In the initial stage there may be strong hydrophilic and hydrogen bonding interactions between the zwitterionic amino acid and water molecules and hydrophobic hydration may also happens in a greater extent in the water rich region which leads significantly decrease of the number of free solvent molecules, as a result the $T\Delta S^0_{t,ch}(i)$ value become highly negative. But as the concentration of NaCl content increases the hydrogen bonds between the water molecules and amino acid molecules are broken down i.e. the hydrophobic hydration co-sphere disrupted and hence large number of free molecules of water, cation and anion of the electrolyte and amino acid molecules are responsible for positive increment of $T\Delta S^0_{t,ch}(i)$ value.

As shown in Fig. 6 enthalpy of transfer, $\Delta H^0_{t,cav}(i)$ due to cavity formation shows gradual decrement with mole % NaCl which manifests that during the introduction of larger amino acid in NaCl-water system, formation of ion-pair complexes 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.

Conclusion

The solubility studies shows that electrolyte affect the solubility of the amino acid as well as other biomolecules having hydrophobic side chains. The α-amino butyric acid is destabilised in aqueous sodium chloride solution as its solubility decreases with the increasing concentration of NaCl content. Sodium chloride disrupt the hydrophobic hydration sphere between the hydrophobic moiety and water molecules and increases hydrophobic interaction between the hydrophobic groups which indicates NaCl may stabilize the hydrophobic interactions among the non-polar groups within the proteins as well as in the bio-macromolecules.

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