

Thermodynamic Solvation of α -Amino Butyric Acid in Aqueous Mixture of Dipolar Aprotic N,N-Dimethyl formamide

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Standard transfer free energies ($\Delta G_t^0(i)$) and entropies ($\Delta S_t^0(i)$) of α -amino butyric acid from water to aqueous mixture of cationophilic dipolar aprotic N,N-dimethyl formamide have been evaluated at 25 °C from solubility measurements of the amino acid at five equidistant temperatures *i.e.*, from 15 to 35 °C. The chemical effects of the transfer Gibbs energies [$\Delta G_{t, ch}^0(i)$] and entropies of transfer [$\Delta S_{t, ch}^0(i)$] have been obtained after elimination of cavity effect, estimated by the scaled particle theory and dipole-dipole interaction effects, computed by the use of Keesom-orientation expression. The chemical contribution of transfer energetics of α -amino butyric acid are guided by the composite effects of increased dispersion interaction, basicity effect and decreased acidity, hydrogen bonding effects, hydrophilic hydration and hydrophobic hydration of aqueous DMF mixtures as compared to that of reference solvent, water.

Key Words: Transfer energetics, Zwitter ions, Aqua-organic solvent, Amino acid, Hydrophobic hydration.

INTRODUCTION

It is well known that amino acids are fundamental structural units of proteins. The native state of a protein is determined by the nature and sequence of its constituent's amino acids as well as by the solvent environment. Much attention has been paid¹⁻⁵ to determine the various thermodynamic properties of amino acids in aqua-organic mixed solvent system.

The purposes of such studies were to gain the various aspects of protein folding - unfolding processes and protein hydration^{6,7}. In this regard Tanford, Nozaki and other authors^{8,9} reported free energies of some amino acids from water to urea from solubility measurements. Transfer free energies and entropies data of some amino acids, dipeptide, tripeptides and other biomolecules in aqueous glycerol^{10,11} and ethylene glycol^{12,13} are also available in literature. All these experiments tried to give an idea about the relative stabilization of those amino acids and other biomolecules in aqua-organic media with respect to water and the complex solute-solvent and solvent-solvent interactions therein. In fact the environment in which the different biological processes occur may be much more 'amide like' than 'water like'. Therefore relevant data in amide solvents, like DMF in particular, are likely to be very much useful to understand biochemical processes better¹⁴.

With that end in view, in the present paper we are reporting the transfer free energies [$\Delta G_t^0(i)$] and entropies [$\Delta S_t^0(i)$] at

25 °C of α -amino butyric acid (Aba.) from water to aqueous mixture of cationophilic dipolar aprotic N,N-dimethyl formamide (H₂O + DMF), as determined from solubility measurements using 'formol titrimetry' at five equidistant temperatures ranging from 15-35 °C.

After eliminating effects due to cavity formation and dipole-dipole interactions and neglecting dipole-induced dipole interactions the results have been discussed in terms of dispersion interaction, acidity-basicity, hydrophilic and hydrophobic hydration and in the case of transfer entropies in terms of relative structuredness as well.

EXPERIMENTAL

α -Amino butyric acid (Aba) (E Merck) is used after drying as described earlier¹⁴. N,N-Dimethyl formamide (LR, BDH) and water are purified by the usual method¹⁵. Aqueous mixtures of co-solvent (H₂O + DMF) that have been used were 20, 40, 60, 80 and 100 wt %. The solubility of α -amino butyric acid is measured by formol titrimetry method. These measurements were taken at 15, 20, 25, 30 and 35 °C temperatures. The low-cum-high temperature thermostat used for all measurements was capable of registering temperatures having an accuracy of ± 0.1 °C. Three sets of measurements were made for all the solutes by equilibrating the solutions from both above and below the required temperatures and at least two sets of

TABLE-1
SOLUBILITIES (mol kg⁻¹) OF α -AMINO BUTYRIC ACID IN AQUEOUS MIXTURES OF DMF AT DIFFERENT TEMPERATURES (°C)

Wt % of DMF	15 °C	20 °C	25 °C	30 °C	35 °C
0	1.702 (1.850) ^a	1.952	2.205 (2.199) ^a	2.534	2.874 (2.919) ^a
20	1.091	1.195	1.359	1.458	1.621
40	0.762	0.833	0.934	1.101	1.201
60	0.467	0.549	0.638	0.711	0.814
80	0.206	0.326	0.409	0.533	0.601
100	0.039 (0.036) ^b	0.044	0.048 (0.045) ^b	0.052	0.057 (0.056) ^b

^aReference²⁰, ^bReference²⁴.

measurements were made for all the solvents and the solubilities were found to agree to within ± 1.0 -1.5 %.

RESULTS AND DISCUSSION

The measured solubility (m) of the amino acid, α -amino butyric acid on molal scale is listed in Table-1. Bates and coworkers on Tris¹⁶ and by Kundu and coworkers^{16,17} on non-electrolyte like pNA, HBz and amino acids¹⁵, glycine (G), diglycine (DG) and triglycine (TG), the Gibbs energies of solutions (ΔG_s^0) of these amino acids on molal scale were calculated for each solvent using eqn. 1.

$$\Delta G_s^0(i) = -RT \ln C\gamma = -RT \ln C = -RT \ln m \quad (1)$$

where γ is the molar activity coefficient of the solutes but taken tentatively to be unity in each solvent. Since α -amino butyric acid is likely to be mostly in zwitter ionic forms as in non-aqueous solvent mixtures^{18,19}, the involved activity coefficient factor $-RT \ln \gamma$ in ΔG_s^0 arising from interactions of dipolar solutes with large dipole moments 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- electrolytes²⁰. This is because the effective contribution of activity coefficient factor $-RT \ln \gamma_s/\gamma_R$ in the transfer free energetics; $\Delta G_t^0(i) = \Delta G_s^0(i) - \Delta G_R^0(i)$ in particular which is our main concern likely to be hardly significant.

The free energies, ΔG_s^0 at different temperatures are fitted by the method of least squares to an equation of the form¹¹,

$$\Delta G_s^0 = a + bT + cT \ln T \quad (2)$$

where T is the temperature in Kelvin scale. The values of the coefficients a, b, c are presented in Table-2. These are found to reproduce the experimental data within ± 0.04 kJ mol⁻¹. Transfer Gibbs energies and entropies of the amino acids from water to N,N-dimethylformamide mixtures were calculated at 25 °C on mole fraction scale by using the following eqns. 3 and 4:

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

$$i.e., \quad \Delta G_t^0(i) = (a_s - A_R) + (b_s - b_R)T + (c_s - c_R)T \ln T - RT \ln \left(\frac{M_s}{M_R} \right) \quad (3)$$

$$and \quad \Delta S_t^0(i) = (b_R - b_s) + (c_R - c_s)(1 + \ln T) + R \ln \left(\frac{M_s}{M_R} \right) \quad (4)$$

TABLE-2
COEFFICIENTS a, b AND c, GIBBS ENERGIES $\Delta G_t^0(i)$ AND ENTROPIES $\Delta S_t^0(i)$ OF TRANSFER OF α -AMINO BUTYRIC ACID (ON MOLE FRACTION SCALE) IN kJ mol⁻¹ FROM H₂O TO H₂O-DMF MIXTURE AT 25 °C

Wt % of DMF	a	b	C	$\Delta G_t^0(i)$	$\Delta S_t^0(i)$
0	-17.73	0.7615	-0.12437	0	0
20	19.71	-0.1656	0.01704	0.839	-5.561
40	-71.81	1.9497	-0.29985	0.841	-2.602
60	97.40	-1.7984	0.25897	1.602	-0.765
80	763.91	-16.4168	2.43296	1.775	17.415
100	64.54	-1.2530	0.18400	6.015	-11.685

here the subscript 's' and 'R' refer to the co- solvent (H₂O + DMF) mixtures and reference solvent (H₂O), respectively and M_R and M_s are the molar mass of the pure and mixed solvent, respectively. $\Delta G_t^0(i)$ and $\Delta S_t^0(i)$ values of amino acid, α -amino butyric acid thus obtained and presented in the Table-2. The involved uncertainties in $\Delta G_t^0(i)$ and $\Delta S_t^0(i)$ are ca. ± 0.05 kJ mol⁻¹ and 2 J K⁻¹ mol⁻¹, respectively.

Now $\Delta X_t^0(i)$ (where X = G or S) may be ascribed as the sum of the following terms (assuming dipole induced dipole term to be negligibly small).

$$i.e., \quad \Delta X_t^0(i) = \Delta X_{t,cav}^0(i) + \Delta X_{t,dd}^0(i) + \Delta X_{t,ch}^0(i) \quad (5)$$

Here, $\Delta X_{t,cav}^0(i)$ indicates the transfer energy contribution of the cavity effect which is involved due to creation of cavities for the species in H₂O and H₂O + DMF mixed solvent system and $\Delta X_{t,d-d}^0(i)$ stands for the dipole-dipole interaction effect involving interaction between dipolar-zwitter-ionic amino acids and the solvent molecules. On the other hand, $\Delta X_{t,ch}^0(i)$ includes all other effects such as those arising from acid-base or short-range dispersion interaction, hydrophilic or hydrophobic hydration and structural effects *etc.* Here $\Delta X_{t,cav}^0(i)$ values were computed by using Scaled particle theory (SPT)^{16,21}, assuming the solutes and solvent molecules as equivalent to hard-sphere models as dictated by their respective diameter (Table-3).

$\Delta G_{t,dd}^0(i) = ({}_s\Delta G_{dd}^0(i) - {}_R\Delta G_{dd}^0(i))$ and $\Delta S_{t,dd}^0(i) = ({}_s\Delta S_{dd}^0(i) - {}_R\Delta S_{dd}^0(i))$ are calculated by means of the Keesom-orientation expression²² for ${}_s\Delta G_{dd}^0(i)$ in a solvent S, as given below

$${}_s\Delta G_{dd}^0(i) = -\left(\frac{8\pi}{9}\right) N^2 \mu_s^2 \mu_x^2 \sigma_{sx}^{-3} (kT)^{-1} v_s^{-1} = \frac{A}{T} V_s \quad (6)$$

where $A = -\left(\frac{8\pi}{9}\right) N^2 \mu_s^2 \mu_x^2 \sigma_{sx}^{-3} (k)^{-1}$ and $V_s = M_s/d_s$ and that of as follows:

TABLE-3
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 α -AMINO BUTYRIC
ACID FROM H₂O TO H₂O-DMF AT 25 °C (ON MOLE FRACTION SCALE) IN kJ mol⁻¹

Wt % of DMF	$\Delta G_t^0(i)$	$\Delta G_{t,cav}^0(i)$	$\Delta G_{t,dd}^0(i)$	$\Delta G_{t,ch}^0(i)$	$T\Delta S_t^0(i)$	$\Delta H_{t,cav}^0(i)$	$T\Delta S_{t,cav}^0(i)$	$T\Delta S_{t,dd}^0(i)$	$T\Delta S_{t,ch}^0(i)$
0	0	0	0	0	0	0	0	0	0
20	0.839	-1.62	0.073	2.386	-5.561	-1.042	0.578	0.0008	-6.140
40	0.841	-4.40	4.27	0.971	-2.602	-2.760	1.64	4.31	-8.552
60	1.602	-4.98	5.41	1.172	-0.765	-1.949	3.031	4.86	-8.656
80	1.775	-6.87	10.6	-2.045	17.415	-0.824	6.046	9.19	2.179
100	6.015	-8.46	18.2	-4.275	-11.685	14.573	23.033	15.0	-49.718

$${}_s\Delta S_{dd}^0(i) = \left\{ \frac{\delta_s \Delta G_{dd}^0(i)}{\delta T} \right\}_p \quad (7)$$

i.e. $T_s \Delta S_{dd}^0(i) = {}_s \Delta G_{dd}^0(i) [1 + T\alpha]$, where N stands for Avogadro's number, μ_s , μ_x are the dipole moment of solvents and amino acid molecules, respectively (Table-3).

σ_{sx} is the distance at which the attractive and repulsive interactions between the solvent and solute molecules are equal and is generally equal to $1/2(\sigma_s + \sigma_x)$ where σ_s and σ_x are the hard sphere diameter of co-solvent and solute molecules, respectively (Table-3) and α is the isothermal expansibility of the solvent and given by $(\delta \ln V_s / \delta T)_p = -(\delta \ln d_s / \delta T)$. Following Marcus²² and Kim *et al.*²³ in order to get this $\Delta X_{t,dd}^0(i)$ term on mole fraction scale the quantity was again multiplied by the term X_{s1} .

$$X_{s1} = \frac{X_s \left(\frac{\mu_s}{\sigma_s^3} \right)}{\left(\frac{\mu_R}{\sigma_R^3} \right)} \quad (8)$$

which is the real mole fraction contribution due to dipole-dipole interaction¹⁹. Subtraction of $\Delta X_{t,cav}^0(i)$ and $\Delta X_{t,dd}^0(i)$ from the total we can get $\Delta X_{t,ch}^0(i)$ of amino acid, α -amino butyric acid. The values of $\Delta X_{t,cav}^0(i)$, $\Delta X_{t,dd}^0(i)$ and $\Delta X_{t,ch}^0(i)$ are presented in Table-3.

The required diameter and other solvent parameters of H₂O and DMF mixtures are taken from Ref.²². The required diameter of α -amino butyric acid (Aba.) is 6.58 Å as given in Ref.⁶. Dipole-moment value of α -amino butyric acid (Aba.) is 16 D⁶.

Type of interactions between α -amino butyric acid and solvent mixtures: Fig. 1. Represents the variation of $\Delta G_t^0(i)$ of α -amino butyric acid against the mole % of DMF at 25 °C. The gradual increment of $\Delta G_t^0(i)$ value indicates that α -amino butyric acid will be destabilized with the increased concentration of DMF in aqueous-DMF system.

Here, $\Delta G_t^0(i)$ is composed of $\Delta G_{t,cav}^0(i)$, $\Delta G_{t,dd}^0(i)$ and $\Delta G_{t,ch}^0(i)$. [$\Delta G_{t,d-id}^0(i)$] *i.e.*, free energy change due to dipole-induced dipole interaction, it is considered negligible].

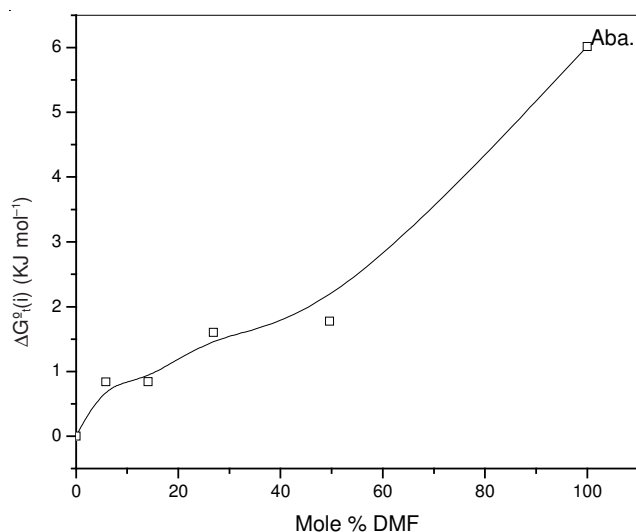


Fig. 1. Variation of $\Delta G_t^0(i)$ α -amino butyric acid in aqueous DMF at 25 °C

The $\Delta G_{t,cav}^0(i)$, values are gradually decreased with DMF concentration (Table-3). The α -amino butyric acid should easily be accommodated in DMF than H₂O with release of concerned energy due to the greater size of DMF (0.498 Å) than H₂O (0.274 Å).

On the other hand $\Delta G_{t,dd}^0(i)$ (Table-3) values are increased gradually with increased mol % of DMF. The dipole moment of DMF (3.82D)²³ is greater than H₂O (1.85D) but the involved hard sphere diameter difference of DMF and H₂O supports such variation. $\Delta G_{t,ch}^0(i)$ of α -amino butyric acid can be computed after subtraction of $\Delta G_{t,cav}^0(i)$, $\Delta G_{t,dd}^0(i)$ from $\Delta G_t^0(i)$.

$\Delta G_{t,ch}^0(i)$ involves the chemical interaction (*i.e.*, H-bonding, acid-base, hard-soft, dispersion, hydrophilic hydration and hydrophobic hydration etc) between solute (α -amino butyric acid) and solvent molecules in this water-DMF mixture.

Fig. 2 represents the variation of $\Delta G_{t,ch}^0(i)$ with DMF concentration. The $\Delta G_{t,ch}^0(i)$ value increases up to around 10 mol % of DMF in the H₂O-DMF system. This indicates the destabilization of α -amino butyric acid. This occurs due to the breaking of extensive hydrogen bond between protic water and hydrophilic head of α -amino butyric acid with the introduction of DMF in water. After that the gradual stabilization of α -amino butyric acid occurs with the sharp decrement of $\Delta G_{t,ch}^0(i)$

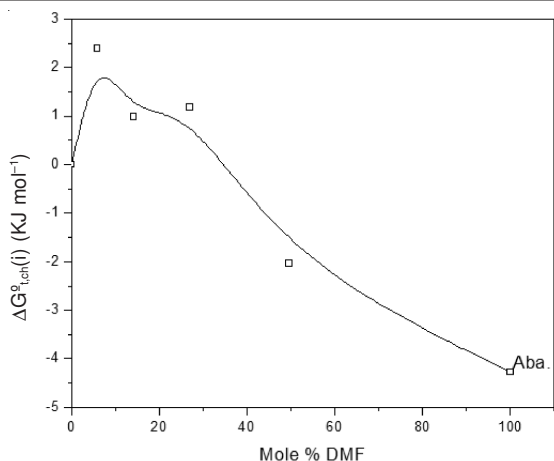


Fig. 2. Variation of $\Delta G_{t, ch}^0(i)$ of α -amino butyric acid in aqueous DMF at 25 °C

values with DMF concentration. Here hydrogen bonding capacity of DMF is weaker than water. This factor will destabilize the α -amino butyric acid with the increased concentration of DMF. But the greater size of DMF²⁴ introduces very strongly the soft-soft as well as dispersion interaction among DMF and α -amino butyric acid [*i.e.*, $\text{CH}_3\text{-CH}_2\text{-CH}(\text{NH}_3^+)(\text{COO}^-)$] having larger $R = \text{-CH}_2\text{-CH}_3$.

The hydrophilic as well as hydrophobic hydration interactions are gradually reduced with decreased concentration of H_2O in H_2O -DMF mixture. This factor may destabilize α -amino butyric acid in aqueous DMF system.

But the increased dispersion interaction may play more dominating role over the reduced acid-base, H-bonding, hydrophilic and hydrophobic interaction involved between α -amino butyric acid and DMF in H_2O -DMF mixture compared to the reference solvent, H_2O .

Role of α -amino butyric acid for controlling solvent-solvent interactions: Fig. 3 represents the variation of $T\Delta S_{t, ch}^0(i)$, of α -amino butyric acid against mol % of DMF in aqueous DMF. A broad minimum is shown at about 8 mol % of DMF. Also broad maxima are obtained at about 50 mol % DMF. Like $\Delta G_{t, ch}^0(i)$, $T\Delta S_{t, ch}^0(i)$ is composed of cavity, dipole-dipole and chemical interaction effects *i.e.*,

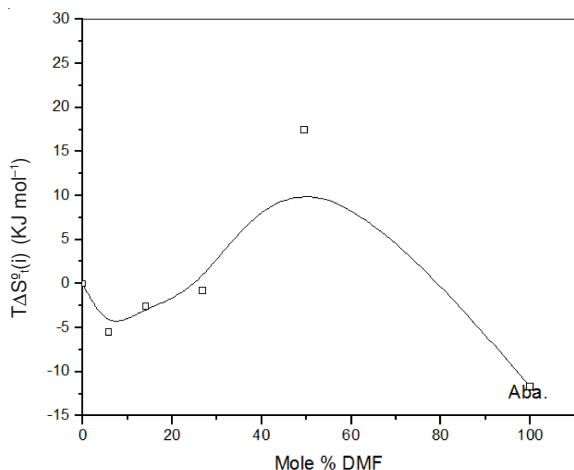


Fig. 3. Variation of $T\Delta S_{t, ch}^0(i)$ of α -amino butyric acid in aqueous DMF at 25 °C

$$T\Delta S_{t, ch}^0(i) = T\Delta S_{t, cav}^0(i) + T\Delta S_{t, dd}^0(i) + T\Delta S_{t, ch}^0(i)$$

Now combined effect in $T\Delta S_{t, ch}^0(i)$ value may represent

such behaviour as shown in Fig. 3. $T\Delta S_{t, cav}^0(i)$ values (Table-3) are gradually increased with the mol % DMF. This indicates that in presence of α -amino butyric acid the co-solvent (DMF) and reference solvent (H_2O) become separated. With the increased DMF concentrations the water molecule becomes free from α -amino butyric acid to allow it to be accommodated by *N,N*-dimethyl formamide. $T\Delta S_{t, dd}^0(i)$ values (Table-3) are also gradually increased with the DMF concentration. Here with the increased concentration of DMF the dipolar α -amino butyric acid become less associated with dipolar co-solvent due to the larger size of DMF (0.498 Å) and therefore α -amino butyric acid allow water as well as DMF molecules to be more free as the concentrations of DMF gradually increased. $T\Delta S_{t, ch}^0(i)$ is computed after subtraction of $T\Delta S_{t, cav}^0(i)$ and $T\Delta S_{t, dd}^0(i)$ from $T\Delta S_{t, ch}^0(i)$. Fig. 4 represents the variation of $T\Delta S_{t, ch}^0(i)$ of α -amino butyric acid with increased DMF concentration in aqua-DMF mixture at 25 °C. A broad minimum at *ca.* 20 mol % DMF indicates that water molecules adopt 3-D structure due to its extensive intermolecular hydrogen bonding (Fig. A) at lower concentration of DMF.

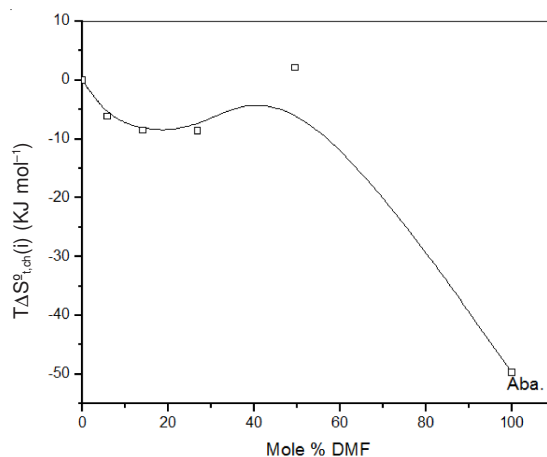
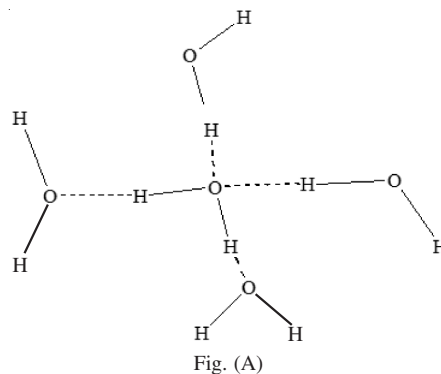


Fig. 4. Variation of $T\Delta S_{t, ch}^0(i)$ of α -amino butyric acid in aqueous DMF at 25 °C



On the other hand a broad maximum at *ca.* 40 mol % DMF indicates that the breaking of intermolecular hydrogen bond may also be occurred as the concentration of DMF increases in this solvent mixture. With increase of DMF concentration from 40-100 mol % the $T\Delta S_{t, ch}^0(i)$ values are decreased sharply. This indicate that the large sized α -amino butyric acid induces dipolar aprotic N,N-dimethylfomamide to be dimerized (Fig. B).

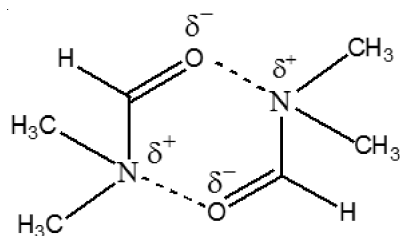


Fig. (B)

Here, the α -amino butyric acid also induces the hydrophilic hydration and hydrophobic hydration to be decreased with the increased DMF concentration.

But the solute induced dispersion interaction among large size DMF molecules being the predominant factor over others the overall decrement of $T\Delta S_{t, ch}^0(i)$ values occur throughout the higher concentration of DMF in this aqua-DMF mixed solvent system.

Conclusion

It may be concluded that due to chemical interaction the larger α -amino butyric acid will be stabilized in larger solvent DMF, with dipolar aprotic character. The zwitterionic α -amino butyric acid induces to adopt 3-D-structuredness of water at water rich concentration in aqua-DMF solvent system.

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