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Transfer entropies of solvation of a series of homologous α-amino acids in aqueous mixtures of protic ethylene glycol

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ABSTRACT

Standard transfer entropies, $\Delta S_t^0(i)$ of a series of homologous α-amino acids (i) like glycine (gly), dl-alanine (ala), dl-α-amino butyric acid (aba) and dl-nor-valine (nor-val) from water to aqueous mixture of protic ethylene glycol (EG) with 0, 20, 40, 60, 80 and 100wt% EG compositions have been evaluated at 25°C. For this purpose the solubility of the amino acids measured using 'formol titrimetry' at 15°, 20°, 30°, and 35°C and that of 25°C reported earlier. $\Delta S_t^0(i)$ of the acids as well as their chemical effects, $\Delta S_{t,ch}^0(i)$ obtained after correcting for the cavity effects, $\Delta S_{t,cav}^0(i)$ and dipole-dipole interaction effect, $\Delta S_{t,d-d}^0(i)$. The chemical contributions of transfer entropies, $T\Delta S_{t,ch}^0(i)$ of amino acids are guided by the superimposed effects of increased acidity affecting the $RCOO^-$ part, decreased basicity affecting the NH_3^+ part and decreased H_bH affecting R′ group of Zwitterionic amino acids $R'CH(NH_3^+)COO^-$, and the complex structural interactions of EG-H_2O mixtures.

KEYWORDS

Zwitter-ion;
α-amino acids;
Transfer entropy;
Hydrophobic hydration (H_bH).

INTRODUCTION

It is well established that proteins exert key role in nearly all biological processes. The basic structural units of proteins are amino acids. Different studies on structuring and destructuring ability of co solvent on amino acids in some mixed aqua-organic solvents are also reported[1-8]. In this context, it is recognized that polyols (i.e. glycerol) cause folding of native conformation of proteins. Although several mechanism of these effects have been proposed from different viewpoints[1-8]. A successful explanation appears to be that the effects of polyols on proteins may be mediated through the changes in solvation properties or alternation of water structure. From the free energy of transfer studies obtained from solubilities of amino acids and peptides at 25°C in aqueous urea[2a] and ethanol[2c], Nozaki and Tanford concluded that while both non-polar and polar side chains are preferentially solvated in UH + H_2O mixtures, the effect was much reduced in EtOH + H_2O mixtures. On the other hand similar experiments by Gekko[8b] led him to conclude that polyol can stabilize the protein conformation through hydrophobic interactions. Also in our previous paper[9] we have reported

Regular Paper

$\Delta G_t^0(i)$ of some homologous series of α-amino acids (Gly. to Val.) in EG + H_2O solvent system at 25°C and have gathered important reflections of short-range chemical solvation of the acids in this unique solvent system.

Though the free energy of transfer data of these solvents are seemingly useful in imparting information's regarding denaturation processes, a more detailed understanding may be possible by evaluating entropies, $\Delta S_t^0(i)$ or enthalpies, $\Delta H_t^0(i)$ of transfer data, since these quantities in general reflect more sensitively the structural[10-12] and interactional parts of the solvents. But till to date relatively little works have been reported regarding these quantities[8,13,15-17]. Though, previously Gekko[8] has reported $\Delta S_t^0(i)$ and $\Delta H_t^0(i)$ of some amino acids including glycine and also of peptide like diglycine in some low concentrations of polyols including GL. Such studies on $\Delta S_t^0(i)$ and $\Delta H_t^0(i)$ are still lacking for a series of homologous amino acids. Keeping this in mind herein, we therefore in the present paper report the transfer entropies, $\Delta S_t^0(i)$ and other related quantities of a homologous series of α-amino acids in aqueous mixtures of structure making protic EG by measuring solubilities using formal titrimetry at five equi-distant temperatures at 0, 20, 40, 60, 80, and 100wt% EG compositions.

EXPERIMENTAL

α-aminoacids like glycine(gly) (E Merck) and dl-alanine(ala), amino butyric acid (aba) and nor-valine (n-val) were used after drying as described earlier[9]. Purification of ethylene-glycol (EG) was performed as usual method[9]. Aqueous mixtures of co-solvent that have been used were 20, 40, 60, 80 and 100 wt%. The solubility of these four amino acids were measured by the same method as described in our previous paper[9].These measurements were taken at 15, 20, 30 and 35°C temperatures and that at 25°C were reported earlier[9]. The low-cum-high temperature thermostat used for all measurements was capable of registering temperatures having an accuracy of ±0.1°C. These 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 measurements were made for all the solvents and the solubilities were found to agree to within ±1 to 1.5%.

RESULTS

The measured solubilities (m) of the amino acids (on molal scale) are listed in TABLE 1. As in the previous studies by Bates and coworkers on Tris[11] and by Kundu and coworkers[11,12] on non–electrolytes like pNA, HBz and amino acids[15]: glycine $\Delta G_t^0(i)$, 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 eq (1):

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

Where y is the molar activity coefficient of the solutes but taken tentatively to be unity in each solvent. True, since these amino acids are likely to be mostly in zwitter ionic forms as in water[18,19], the involved activity coefficient factor -RTlny in ΔG_s^0 arising from interactions of dipolar solutes with large dipole moments may not be that 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[11a,14,15]. This is because the effective contribution of activity coefficient factor $-RT\ln y_s/y_w$ in the transfer free energetics $\Delta G_t^0(t) = \Delta G_s^0(i) - \Delta G_w^0(i)$ 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 form;

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

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 $kJmol^{-1}$. Transfer Gibbs energies ΔG_t^0 and entropies ΔS_t^0 of the amino acids from water to ethylene-glycol were calculated at 25°C on mole fraction scale by using the following equations:

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

i.e.

$$\Delta G_t^0(i) = (a_s - a_w) + (b_s - b_w)T + (c_s - c_w)T \ln T - RT \ln\left(\frac{M_s}{M_w}\right) \quad (3)$$

Regular Paper

TABLE 1: Solubilities (m) of glycine, dl-alanine, dl-amino butyric acid and dl-nor-valine in aqueous mixtures of protic ethylene glycol at different temperature (°C)

Wt% solvent	Glycine					dl-alanine				
	Temp. (°C)					Temp. (°C)				
	15°	20°	25°[9]	30°	35°	15°	20°	25°[9]	30°	35°
Water	2.720 (2.690)[a]	3.060	3.340 (3.315)[a]	3.720	4.060 (4.04)[a]	1.634 (1.650)[a]	1.720	1.800 (1.800)[a]	2.300	2.400 (2.390)[a]
20%EG	1.735	1.905	2.070	2.250	2.400	1.304	1.450	1.610	1.700	1.860
40%EG	1.010	1.100	1.230	1.380	1.570	1.060	1.140	1.301	1.450	1.530
60%EG	0.550	0.670	0.810	0.884	0.960	0.510	0.640	0.773	0.850	0.905
80%EG	0.299	0.340	0.360	0.415	0.456	0.360	0.450	0.540	0.600	0.630
100%EG	0.143	0.149	0.170	0.178	0.186	0.126	0.133	0.140	0.154	0.160
Wt% solvent	dl-amino butyric acid					dl-nor-Valine				
	Temp. (°C)					Temp. (°C)				
	15°	20°	25°[9]	30°	35°	15°	20°	25°[9]	30°	35°
Water	1.850 (1.850)[a]	2.020	2.190 (2.199)[a]	2.540	2.915 (2.919)[a]	0.618 (0.590)[a]	0.650	0.677 (0.683)[a]	0.702	0.718 (0.715)[a]
20%EG	1.280	1.506	1.790	1.850	1.928	0.520	0.538	0.560	0.620	0.654
40%EG	1.010	1.260	1.390	1.500	1.670	0.450	0.470	0.500	0.544	0.602
60%EG	0.680	0.812	0.980	1.150	1.330	0.360	0.400	0.430	0.500	0.536
80%EG	0.480	0.604	0.790	0.804	0.880	0.320	0.350	0.360	0.422	0.464
100%EG	0.190	0.210	0.220	0.238	0.255	0.122	0.126	0.130	0.134	0.138

'a' for ref. 16

and $\Delta S_t^0(i) = (b_w - b_s) + (c_w - c_s)(1 + \ln T) + R \ln\left(\frac{M_s}{M_w}\right)$ **(4)**

here the subscripts s, w refer to the solvent and water respectively and M is the molar mass of the pure and mixed solvent. $\Delta G_t^0(i)$ and $T\Delta S_t^0(i)$ values of amino acids thus obtained and presented in the TABLE 2. The estimated values shows an uncertainties in $\Delta G_t^0(i)$ and $\Delta S_t^0(i)$ are about ±0.05kJ mol^{-1} and 2 Jk^{-1} mol^{-1}, respectively.

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

$$\Delta P_t^0(i) = \Delta P_{t,cav}^0(i) + \Delta P_{t,dd}^0(i) + \Delta P_{t,ch}^0(i) \quad (5)$$

here, $\Delta P_{t,cav}^0(i)$ means for the transfer energy contribution of the cavity effect which is involved due to creation of cavities for the species in water and aquo-organic solvent and $\Delta P_{t,dd}^0(i)$ stands for the dipole-dipole interaction effect involving interaction between dipolar-zwitter-ionic amino acids and the solvents molecules, on the other hand, $\Delta P_{ch}^0(i)$ includes that for all other effects such as those arising from acid-base or short-range dispersion interaction, hydrophilic (H_1H) or hydrophobic hydration and structural effects. Here $\Delta P_{t,cav}^0(i)$ values were computed by using Scaled particle theory (SPT)[9], assuming the solutes and solvent molecules as equivalent hard-sphere models as dictated by their respective diameter (Vide TABLE 3).

$\Delta G_{t,dd}^0(i) = ({}_s\Delta G_{dd}^0(i) - {}_w\Delta G_{dd}^0(i))$

and $\Delta S_{t,dd}^0(i) = ({}_s\Delta S_{dd}^0(i) - {}_w\Delta S_{dd}^0(i))$ were calculated by means of the Keesom-orientation expression[20] for ${}_s\Delta G_{dd}^0(i)$ in a solvent S, as given below

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

where $A = -\left(\frac{8\pi}{9}\right)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(k)^{-1}$ and $V_s = \frac{M_s}{d_s}$ and that of $\Delta S_{dd}^0(i)$ as follows:

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

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 solvent and amino acid molecules respectively (TABLE 3). σ_{SX} is the distance at which the attractive and repul-

Regular Paper

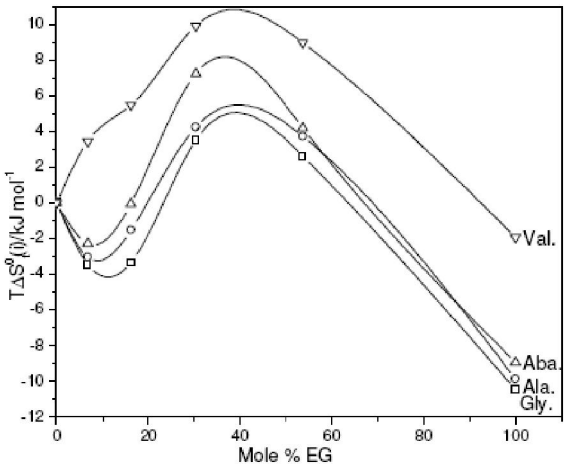

Figure 1 : Variation of $T\Delta S_t^0(i)$ of glycine, dl-alanine, dl-alpha-amino butyric acid and dl-nor-valine in aqueous ethylene glycol mixture

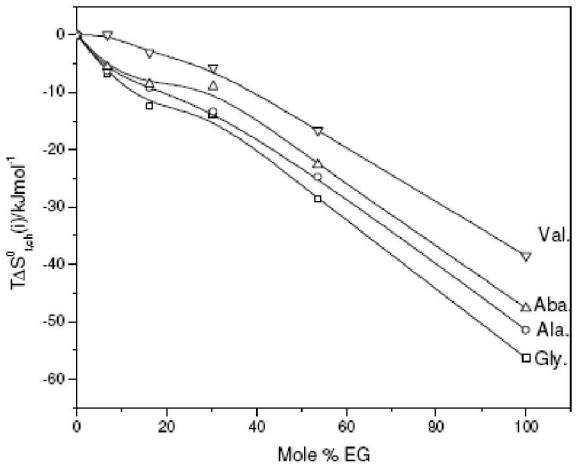

Figure 2 : Variation of $T\Delta S_{t,ch}^0(i)$ of glycine, dl-alanine, dl-alpha-amino butyric acid and dl-nor-valine in aqueous ethylene glycol mixture

sive interactions between the solvent and solute molecules are equal and is generally equal to $\frac{1}{2}(\sigma_s + \sigma_x)$ where σs and σs are the hard sphere diameter of solvent and solute molecules respectively (TABLE 3) and α is the isothermal expansibility of the solvent and given by $(\delta \ln V_s / \delta T)_P = -(\delta \ln d_s / \delta T)$ (TABLE 3). Following Kim et al.[21] and Marcus[20] in order to get these $\Delta P_{t,dd}^0(i)$ term on mole fraction scale the quantity was again multiplied by the term X_{s1}.

$$X_{s1} = X_s(\mu_s / \sigma_s^3)/(\mu_w / \sigma_w^3) \quad (7)$$

Which is the real mole fraction contribution due to dipole-dipole interaction[20]. Subtraction of $\Delta S_{t,cav}^0(i)$ and $\Delta S_{t,d-d}^0(i)$ from the total we can get $\Delta S_{t,ch}^0(i)$ of amino acids. The values of $\Delta S_{t,cav}^0(i)$, $\Delta S_{t,d-d}^0(i)$ and $\Delta S_{t,ch}^0(i)$ are presented in TABLE 3.

DISCUSSION

Figure 1 and 2 reflect the variation of $T\Delta S_t^0(i)$ and $T\Delta S_{t,ch}^0(i)$ of homologous amino acids with mole % of co solvent in EG-water mixtures. $T\Delta S_t^0(i)$-composition profiles of figure 1 shows that the variation follow the same pattern for all amino acids. A clear maxima is obtained for all acids in almost 40 mole% EG. Similar maximum appears in various other structure related properties[22,23]. Somewhat downward but similar variations are also shown for Glycine, Alanine and Amino butyric acid at about 10 mole% EG.

This may reflect the effects of the well known 3D-structure making propensity of ethylene glycol besides reducing effects of H_bH. Similar nature of $T\Delta S_t^0(i)$-composition profiles have also been obtained previously with amino acids glycine, diglycine and triglycine in aqueous glycerol[15] as co solvents which are related with opposing structural interactions of the co solvents.

The present results (TABLE 3 & Figure 2) show that the entropy of transfer of amino acids from water to aqueous EG sensitively depends on the polarity of the solutes and on the solvent composition. Also, the thermodynamic function of transfer (here $T\Delta S_t^0$) should reflect the difference of solute-solvent and solvent-solvent interaction in the two solvent systems (e.g. water & water-EG mixtures). This difference may be generated mainly from four steps in transfer process i.e, cavity formation to accommodate the solute molecule in the mixed solvent $T\Delta S_{tra}^{cav}$, and the interaction of mixed solvent with non polar groups $T\Delta S_{tra}^{non-polar}$, polar groups $T\Delta S_{tra}^{polar}$, and charged groups of the solute molecules $T\Delta S_{tra}^{el}$.

Thus the observed transfer entropy of a solute between two solvents, $T\Delta S_{tra}$ may be expressed as-

$$T\Delta S_{tra} = T\Delta S_{tra}^{cav} + T\Delta S_{tra}^{non-polar} + T\Delta S_{tra}^{polar} + T\Delta S_{tra}^{el}$$

For such transfer process of a solute (here, α-amino acids) between aqueous media differing primarily by the degree of structuredness, such as our solvent systems, the changes in solvent structure taking place in the complex of the solute may be more sensitively re-

Regular Paper

TABLE 2 : Coefficients a, b and c of glycine, dl-alanine, dl-amino butyric acid and dl-nor-valine and Gibbs energies ΔG^0_t and entropies $T\Delta S^0_t$ of transfer of the acids (on mole fraction scale) in kJmol^{-1} from water to aqueous mixtures of ethylene-glycol at 25°C

Solvents	a (kJmol^{-1})	b (kJmol^{-1}K^{-1})	c (kJmol^{-1}K^{-1})	ΔG^0_t (kJmol^{-1})	$T\Delta S^0_t$ (kJmol^{-1})
Glycine					
Water	41.55	-0.6639	0.09029	0	0
20%EG	59.76	-1.1189	0.16015	0.844	-3.463
40%EG	-130.91	3.2534	-0.49425	1.675	-3.348
60%EG	397.68	-8.5423	1.26552	2.219	3.516
80%EG	-36.59	1.1250	-0.17446	3.401	2.605
100%EG	-145.06	-3.0343	0.44978	4.388	-10.461
dl-Alanine					
Water	-238.73	5.6586	-0.85356	0	0
20%EG	91.52	-1.8154	0.26408	0.073	-3.048
40%EG	66.27	-1.2165	0.17412	0.121	-1.524
60%EG	511.23	-11.0827	1.6446	0.887	4.246
80%EG	516.82	-11.2121	1.66453	1.048	3.733
100%EG	-23.26	0.7155	-0.10904	3.363	-9.871
dl-α-amino butyric acid					
Water	-235.44	5.6075	-0.84675	0	0
20%EG	466.51	-10.1989	1.51460	0.207	-2.293
40%EG	292.46	-6.2420	0.9229	0.317	-0.038
60%EG	92.86	-1.6101	0.22795	0.638	7.239
80%EG	644.59	-14.0604	2.08875	0.614	4.197
100%EG	25.76	-0.3657	0.05111	2.455	-8.950
dl-nor-valine					
Water	74.52	-1.5669	0.23170	0	0
20%EG	-134.30	3.1925	-0.48045	0.057	3.450
40%EG	-185.23	4.3739	-0.65763	-0.067	5.470
60%EG	-23.53	0.8235	-0.12948	-0.278	9.912
80%EG	-191.39	4.5718	-0.6883	-0.574	8.962
100%EG	3.020	0.03593	-0.00511	1.039	-1.934

TABLE 3 : The enthalpy of transfer, ΔH^0t,cav(i) and entropies of transfer $T\Delta S^0$t(i), $T\Delta^0$t,cav(i), $T\Delta S^0$t,dd(i) and $T\Delta S^0$t,ch(i) of glycine, dl-alanine, dl-amino-butyric acid and dl-nor valine from water to aqueous ethylene-glycol at 25°C (on mole fraction scale in kJmol^{-1}

Solvents	$T\Delta S^0_t(i)$	$\Delta H^0_{t,cav}(i)$	$T\Delta S^0_{t,cav}(i)$	$T\Delta S^0_{t,dd}(i)$	$T\Delta S^0_{t,ch}(i)$
Glycine					
Water	0	0	0	0	0
20%EG	-3.463	1.309	2.059	1.14	-6.662
40%EG	-3.348	2.540	4.176	4.86	-12.385
60%EG	3.516	3.425	6.238	12.10	-13.779
80%EG	2.605	4.620	8.860	22.30	-28.555
100%EG	-10.461	5.380	11.738	34.10	-56.298
dl-Alanine					
Water	0	0	0	0	0
20%EG	-3.048	1.519	2.292	0.932	-6.272
40%EG	-1.524	2.940	4.624	4.09	-9.174
60%EG	4.246	3.951	6.850	10.10	-13.372
80%EG	3.733	5.317	9.670	18.80	-24.737
100%EG	-9.871	6.166	12.676	28.90	-51.447
α-amino butyric acid					
Water	0	0	0	0	0
20%EG	-2.293	1.699	2.492	0.811	-5.596
40%EG	-0.037	3.385	5.011	3.56	-8.608
60%EG	7.239	4.404	7.378	8.80	-8.939
80%EG	4.197	5.915	10.366	16.40	-22.569
100%EG	-8.950	6.838	13.484	25.20	-47.634
dl-nor-vline					
Water	0	0	0	0	0
20%EG	3.450	1.853	2.664	0.721	0.065
40%EG	5.470	3.577	5.374	3.160	-3.030
60%EG	9.912	4.788	7.827	7.830	-5.745
80%EG	8.962	6.423	10.959	14.600	-16.597
100%EG	-1.934	7.407	14.169	22.400	-38.503

flected by $T\Delta S_{tra}$.

In figure 2, $T\Delta S^0_{t,ch}(i)$ -composition profiles of α-amino acids in EG-H_2O mixtures show that $T\Delta S^0_{t,ch}(i)$ values are increasingly negative and their relative order is Gly.> Ala.> Aba.> Val. Elimination of largely positive dipole-dipole interaction effects (TABLE 3) but non-elimination of the expected more largely negative dipole-induced dipole and dispersion effects[20] may be to some extent responsible for such observations. The relative order of $T\Delta S^0_{t,ch}(i)$ values of homologous α-amino acids with gradual increase of (-CH_2-) group from Glycine to nor-Valine reflects that the co-solvent EG is a hydrophobic hydration (H_bH) reducer which is expected from its 3D-structure making capability due to its hydrogen bond forming ability.

The results (TABLE 3) indicate the increasingly positive values of $T\Delta S^0_{t,ch}(i)$ of the concerned amino acids (from Gly. to Val.) in aqueous mixtures of structure making and more acidic EG. Therefore, it supports that the involved increasingly reduced H_bH-effect of EG will overcomes the opposing increased acidity and dispersion effects of co-solvent, ethylene glycol.

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In conclusion, from the observations of cavity forming effect, dipole-dipole interactions, dispersion interactions, hydrogen bond forming capacity, acidity-basicity interactions, hydrophilic hydration, hydrophobic hydration etc in between solute-solvent and solvent-solvent it may be considered that ethylene glycol will be a good stabilizer of amino acids as well as proteins.

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