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THE THERMODYNAMICS OF IONIZATION OF α-ALANINE IN METHANOL + WATER MIXTURES AND THE DETERMINATION OF SINGLE ION THERMODYNAMICS

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ABSTRACT

In order to understand the effect of solvents on the thermodynamic parameters of amino acids, the thermodynamic dissociation constants, K_1 and K_2, for the reactions

$$RH_2^+ + H_2O \overset{K_1}{\rightleftharpoons} H_3O^+ + RH^\pm \qquad (1)$$

and

$$RH^\pm + H_2O \overset{K_2}{\rightleftharpoons} H_3O + R^- \qquad (2)$$

(where $RH^\pm$ = α-alanine) have been determined pH-metrically in methanol + water mixtures. The measurements were carried out in dilute solutions and in the absence of neutral electrolytes to minimize the "salt effect" as far as practicable so that the "medium effects" on the dissociation constants of the α-alanine can be properly understood.

The enthalpy values for reactions (1) and (2) (up to 44.14 wt% of methanol) have been determined calorimetrically. It has been observed that the conversion of α-alanine into cations and anions is favourable both from enthalpic and entropic considerations, so that the reverse reactions of (1) and (2) are spontaneous. Attempts have been made to interpret the thermodynamics properties of α-alanine in terms of hydrophilic and hydrophobic interactions and other structural changes of the solvent molecules.

In order to get a better insight into the nature of specific solute–solvent interactions, we have analysed the results in terms of single ion values using the thermodynamic values from the present work and other relevant data from previous work in our laboratory.

INTRODUCTION

Extensive equilibrium studies have been made on the most abundant solvent, water. In spite of such studies, our knowledge of molecular interac-

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tions in water is extremely limited. It has been realized [1–7] that studies in other solvent media (particularly mixed aquo-organic mixtures or non-aqueous solvents) would be of great help in understanding different molecular interactions and other fundamental properties of the solvent mixtures and the solutes.

These considerations led to extensive studies [1–12] on the thermodynamics of transfer (mostly free energies of transfer) of electrolytes from water to organic or aquo-organic solvent mixtures. These studies are of importance to understand the ion–solvent interactions of electrolytes which are the controlling forces in dilute solutions where ion–ion interactions are absent. The quantitative measure of ion–solvent interactions and the factors associated with them can be obtained from the thermodynamics of transfer of ions and molecules.

With the above objects in view, Lahiri and co-workers [13–16] have undertaken systematic studies on the dissociation constants of the amino acids:

$$RH_2^+ + H_2O \rightleftharpoons H_3O^+ + RH^\pm \qquad (1)$$

and

$$RH^\pm + H_2O \rightleftharpoons H_3O^+ + R^- \qquad (2)$$

(where $RH^\pm$ represents the different amino acids) in different mixed solvent media.

The thermodynamic parameters of the amino acids in aquo-organic solvents are of great importance in understanding the thermodynamic behaviour of proteins.

This communication presents the first and second dissociation constants of α-alanine in different aquo-methanolic solutions determined pH-metrically. Calorimetric determinations of the enthalpies of ionization of α-alanine at 298 K in methanol + water mixtures (0–44.1 wt% of methanol) are also described.

EXPERIMENTAL

α-Alanine (G.R., Merck) was dried at 303 K for 1 h and kept in a desiccator. The middle fraction of the distilled methanol (A.R., B.D.H.) was utilized within 24 h. The weight percentage determinations of the mixed solvents and their dielectric constants and other experimental details were described previously [13–17]. The solutions were made with double-distilled water from an all-glass distilling set.

The pK_1 and pK_2 values of α-alanine were determined as previously described [13–17] (Table 1).

TABLE 1

pK_1 and pK_2 values of α-alanine, heats of neutralization of α-alanine by alkali and thermodynamics of the heat neutralization of H_2O in methanol + water mixtures at 298 K

Wt% of methanol	pK_1	pK_2	Heat of neutralization of α-alanine by alkali (kJ mol^{-1})	$-\Delta H^0_{H_2O}$ [a]
0.0	2.36	9.72	−10.17	55.65
8.0	2.52	9.77	−8.32	53.22
16.4	2.63	9.80	−5.07	50.21
25.2	2.67	9.84	−1.19	46.86
34.4	2.94	9.86	5.72	42.84
44.1	3.17	9.88	8.85	39.08
54.2	3.43	9.86		
64.7	3.57	9.85		
75.9	3.73	9.82		

[a] Interpolated from the data given in ref. 24.

The calorimeter was the same as that described earlier [18,19]. The performance of the calorimeter was tested repeatedly during the course of the experiment by determining the heat of neutralization of $HClO_4$ with sodium hydroxide solutions. For the measurement of heats of neutralization (ΔH) of amino acids by acid or alkali corresponding to reactions (1) or (2), 250 ml of perchloric acid solution ($HClO_4 \approx 0.5$ M l^{-1}) or sodium hydroxide solution (NaOH ≈ 0.1 M l^{-1}) in appropriate solvents were taken in the reaction flask. A definite volume of α-alanine (5 ml of 0.30–0.63 M l^{-1}) in the appropriate solvent, to avoid heat change due to mixing, was taken in a glass bulb. After proper equilibration at the desired temperature (298 K), the bulb was broken and the heat change was measured by the change in resistance which was calibrated against a known amount of heat supplied before each set of measurements. The blank titration was performed for each set of experiments. For the blank experiments, the experimental details were the same, except that the 5 ml of amino acid solution in the bulb were

TABLE 2

Thermodynamics of α-alanine ($RH^{\pm}$) [30] and for reactions (1) and (2) in methanol + water mixtures at 298 K (values in kJ mol^{-1})

Wt% of methanol	ΔG^0 ($RH^{\pm}$)	ΔH^0 ($RH^{\pm}$)	$T\Delta S^0$ ($RH^{\pm}$)	ΔG_1^0	ΔH_1^0	$T\Delta S_1^0$	ΔG_2^0	ΔH_2^0	$T\Delta S_2^0$
0.0	−1.55	9.48	11.03	13.46	7.69	−5.77	55.46	45.48	−9.98
8.0	−1.33	9.40	10.73	14.38	9.06	−5.32	55.74	44.90	−10.84
16.4	−0.99	9.14	10.13	15.01	10.91	−4.10	55.91	45.14	−10.77
25.2	0.23	3.21	2.98	15.23	12.00	−3.23	56.14	48.05	−8.09
34.4	2.12	4.73	2.61	16.77	14.06	−2.71	56.26	48.56	−7.70
44.1	2.27	6.07	3.80	18.09	15.11	−2.98	56.37	47.93	−8.44

replaced by 5 ml of the appropriate solvent. The values from the blank experiments were subtracted or added (as necessary) from the respective heat of neutralization data to obtain accurate ΔH values. The procedure was repeated with different concentrations of α-alanine and the average values are recorded in Tables 1 and 2.

RESULTS

The dissociation constants for reactions (1) and (2) are given by

$$K_1 = \frac{C_{\mathrm{H^+}} C_{\mathrm{RH^\pm}}}{C_{\mathrm{RH_2^+}}} \frac{f_{\mathrm{H^+}} f_{\mathrm{RH^\pm}}}{f_{\mathrm{RH_2^+}}} \tag{3}$$

and

$$K_2 = \frac{C_{\mathrm{H^+}} C_{\mathrm{R^-}}}{C_{\mathrm{RH^\pm}}} \frac{f_{\mathrm{H^+}} f_{\mathrm{R^-}}}{f_{\mathrm{RH^\pm}}} \tag{4}$$

In the determinations of K_1 and K_2, the alanine concentrations used were $0.5–1.0 \times 10^{-2}$ M l^{-1} whereas the $HClO_4$ or NaOH concentrations used were of the order of 10^{-3} M l^{-1}.

The $C_{\mathrm{H^+}}$ values in water have been calculated using the pH and $f_\pm$ values of the ions at these ionic strengths. In case of mixed solvents, we actually determined the $\mathrm{H^+}$ ion concentrations as described earlier [20–23]. Under the present experimental conditions, we can assume $f_{\mathrm{H^+}} = f_{\mathrm{RH_2^+}}$ and since the ionic strengths are low, $f_{\mathrm{RH^\pm}}$ can be regarded to be unity. Thus, in the case of $\mathrm{p}K_1$, the error, if any, would be marginal. But in the case of $\mathrm{p}K_2$, the error limit may be considerably greater. In calculating $\mathrm{p}K_2$ values, the autoprotolysis constants of water in methanol + water mixtures have been taken from the data of Parsons and Rochester [24] by suitable interpolations.

The enthalpy changes for reactions (1) and (2) were calculated using the relation

$$\Delta H = \frac{Q}{1000X} \ (\mathrm{kJ\ mol^{-1}})$$

where Q (J) is the heat liberated (Q negative) to neutralize X (g-mol l^{-1}) of the α-alanine by acid or alkali.

The α-alanine was completely neutralized by the acid or alkali. Since fairly dilute solutions of α-alanine were used and ΔH values were found to be within the limits of the experimental error, the experimental ΔH values were taken to be equal to ΔH^0. However, the reaction with alkali necessarily means the neutralization of $\mathrm{H^+}$ ion, and thus the enthalpy for reaction (2) changes. So we have

$$\Delta H_2^0 + \Delta H_{\mathrm{H_2O}}^0 \text{ (in water or in mixed solvents)} = \Delta H_{\mathrm{obs}}^0.$$

$\Delta H^0_{H_2O}$ (in mixed solvents) values were interpolated from $\Delta H^0_{H_2O}$ values in methanol + water mixtures given in the literature [24]. The heats of neutralization of α-alanine in different methanol + water mixtures are recorded in Table 1. The entropy values were calculated using the relation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

The thermodynamic values are given in Table 2.

DISCUSSION

Determination of the dissociation constants of α-alanine in mixed solvents is difficult. Values of the dissociation constants K_1 and K_2 of the amino acids have mostly been obtained using glass–calomel electrodes [25], which were used here. The method may involve uncertainty but the values of K_1 obtained by this method agree well with those obtained from measurements (only in a few cases) using cells without a liquid-junction potential. In the case of K_2, the differences are only marginal. However, even the accurate method involves approximations regarding the activity coefficients of the ions and the extrapolations are always non-linear.

No method can give unambiguous values of K_1 and K_2, without any approximations, for amino acids in mixed solvents with the most used solvent, water, as standard. The usual method for determining K_1 and K_2 values of the amino acids, using hydrogen and Ag/AgCl(s) electrodes, is laborious. The question of ion-association in mixed solvents cannot be neglected and extrapolations would probably be non-linear.

Even this method suffers from the following limitations:

(1) The E^0 of the hydrogen electrode $[H^+ + e \rightarrow 0.5H_2(g)]$ has been assumed to be zero in all solvents, i.e., the free energy of transfer of H^+ ion is zero, irrespective of solvent. This does not hold in view of the possible differences in ion–solvent interactions due to changes in acid–base character, dielectric constant and other fundamental properties of the solvents.

(2) The method generates a large number of thermodynamically unrelated pH or EMF scales due to the solvents, and the comparison of results having different standard states involves uncertainties [26].

Thus, in the absence of data from other methods, the thermodynamic pK_1 and pK_2 values determined in dilute solutions and in the absence of an "inert electrolyte" can be regarded as accurate. In order to test the reproducibility of the present method, we have redetermined pK_1 values, and found that they are in good agreement with previously reported values. A slight error may be observed in K_2 values where both f_{H^+} and f_{R^-} terms are in the numerator and the autoprotolysis constants are obtained using suitable interpolations [24]. Moreover, a long time is required for equilibration in alkali solutions, particularly in mixed solvents. Edsall and Blanchard

[27] also observed that the measurements in alkaline solutions gave unstable EMF readings.

It is seen that the replacement of an H atom of the CH_3 group by an NH_2^- group in propionic acid causes an enormous decrease in the pK value. The pK_1 value of α-alanine is found to increase with increasing methanol content in the mixture, but the magnitude of increase is much smaller than those of the propionic acid due to the dipolar nature of the amino acid. However, pK_2 is found to be relatively insensitive to changes in solvent composition.

The enthalpy changes ΔH_1^0 and ΔH_2^0 for reactions (1) and (2) are 7.69 and 45.48 kJ mol^{-1}, respectively, for α-alanine. The disagreement is considerable for reaction (1) if we consider the value of 3.23 kJ mol^{-1} obtained from the temperature coefficient measurements [25] but the value of 45.94 kJ mol^{-1} for reaction (2) is in very good agreement.

The results show that the conversion of amino acids into cations and anions is favourable both from enthalpic and entropic considerations so that the backward reactions of (1) and (2) are spontaneous.

It is known that α-alanine is generally solvated by large numbers of solvent molecules [28]. The forward reaction of (1) is accompanied by the conversion of RH_2^+ to $RH^\pm$ which means the immobilization of solvent molecules around the H^+ ion and $RH^\pm$ leading to an entropy decrease. Conversion of $RH^\pm$ to R^- takes place in the case of reaction (2). This causes greater immobilization of the solvent molecules leading to a considerable decrease in entropy. In both cases the forward processes are endothermic.

Table 2 shows that ΔG_1^0 and ΔH_1^0 increase continuously whereas ΔS_1^0 increases and reaches a maximum at about 34 wt% of methanol. A slight decrease is observed at about 8 wt% methanol but the maxima are observed at about 34 wt% for ΔH_2^0 and ΔS_2^0. These are reflected in the thermodynamics of transfer presented in Table 3.

It is known that ΔH_t^0 and ΔS_t^0 are governed by the structural and electrostatic contributions whereas the free energy change is governed by the electrostatic contributions only [29].

α-Alanine will undergo hydrophilic and hydrophobic interactions with H_2O molecules. With the introduction of methanol, both these types of interaction change, leading to a change in the thermodynamic values. Moreover, the change in the ratio of Zwitterions to the neutral form with the increase in methanol content may cause changes in the thermodynamic values. But recent investigations [30] show that the conversion of Zwitterions to the neutral form (on addition of methanol) is too small to have an appreciable effect on the thermodynamic values. It is evident that the abnormalities of the solvent mixtures should be properly understood in the light of hydrogen bond formation, hydrophobic interactions and other ion–solvent or solute–solvent interactions in these solvent mixtures.

TABLE 3

Thermodynamics of transfer for α-alanine ($RH^{\pm}$), and for reactions (1) and (2) (values in kJ mol^{-1})

Wt% of methanol	$\Delta G_t^0(RH^{\pm})$	$\Delta H_t^0(RH^{\pm})$	$T\Delta S_t^0(RH^{\pm})$	$\Delta G_t^0(1)$	$\Delta H_t^0(1)$	$T\Delta S_t^0(1)$	$\Delta G_t^0(2)$	$\Delta H_t^0(2)$	$T\Delta S_t^0(2)$
8.0	0.22	−0.08	−0.30	0.92	1.37	0.45	0.28	−0.58	−0.86
16.2	0.56	−0.34	−0.90	1.55	3.22	1.67	0.45	−0.34	−0.79
25.2	1.78	−6.27	−8.05	1.77	4.31	2.54	0.68	2.57	1.89
33.4	3.67	−4.75	−8.42	3.31	6.37	3.06	0.80	3.08	2.28
44.7	3.82	−3.41	−7.23	4.63	7.42	2.79	0.91	2.45	1.54

TABLE 4

Thermodynamics of transfer of H^+, RH_2^+ (α-alanine cation) and R (α-alanine anion) from water to methanol + water at 298 K (values in kJ mol^{-1}) (values in parentheses are based on $\Delta H^0(H^+)$ values reported in ref. 12)

Wt% of methanol	$\Delta G_t^0(H^+)$	$\Delta H_t^0(H^+)$	$T\Delta S_t^0(H^+)$	$\Delta G_t^0(RH_2^+)$	$\Delta H_t^0(RH_2^+)$	$T\Delta S_t^0(RH_2^+)$	$\Delta G_t^0(R^-)$	$\Delta H_t^0(R^-)$	$T\Delta S_t^0(R^-)$
8.0	−0.6	1.3	1.9	−1.30	−0.15	1.15	1.10	−1.96	−3.06
		(1.3)							
16.4	−1.3	8.8	10.1	−2.29	5.24	7.53	2.31	−9.48	−11.79
		(1.3)	(2.6)		(−2.26)	(0.03)		(−1.98)	(−4.29)
25.2	−1.8	5.0	6.8	−1.79	−5.58	3.79	4.26	−8.70	−12.96
		(2.4)	(4.2)		(−8.18)	(6.39)		(−6.10)	(−10.36)
34.4	−2.1	1.2	3.3	−1.74	−9.92	−8.18	6.57	−2.87	−9.44
		(5.2)	(7.3)		(−5.92)	(−4.18)		(−6.87)	(−13.44)
44.1	−3.2	−0.2	3.0	−4.01	−11.03	−7.02	7.93	−0.76	−8.69
		(6.3)	(9.5)		(−4.53)	(−0.52)		(−7.26)	(−15.19)

Values in water: $\Delta G^0(H^+) = -1083.2$ kJ mol^{-1}; $\Delta H^0(H^+) = -1087.4$ kJ mol^{-1}; $\Delta S^0(H^+) = -14$ J K^{-1} mol^{-1}; $\Delta G^0(RH_2^+) = -1098.21$ kJ mol^{-1}; $\Delta H^0(RH_2^+) = -1085.61$ kJ mol^{-1}; $\Delta S^0(RH_2^+) = 42.3$ J K^{-1} mol^{-1}.
$\Delta G^0(R^-) = 1137.11$ kJ mol^{-1}; $\Delta H^0(R^-) = 1142.36$ kJ mol^{-1}; $\Delta S^0(R^-) = 17.6$ J K^{-1} mol^{-1}.

The enthalpy changes for the reactions in mixed solvents may be considered to involve the following steps.

(i) Rupture of the bonds between the amino acid molecules to remove the solute to the vapour phase (ΔH and ΔS positive), i.e. enthalpy and entropy changes due to the formation of gaseous ions or molecules. This step, however, is not important for comparison of the enthalpy of transfer data from water to mixed solvents.

(ii) Creation of a cavity in the solvent molecules which means the rupture of bonds (ΔH and ΔS positive). It is known that the addition of methanol first strengthens the three-dimensional water structure, which passes through a maximum at about 0.2–0.3 mole fraction of methanol, after which structural collapse is observed. Methanol + water mixtures show a maximum in exothermic enthalpy of mixing at about $x_2 \approx 0.2$, a minimum in $T\Delta S$ at $x_2 = 0.3$ and a maximum in the free energy of mixing at ca. $x_2 = 0.5$[2]. Thus the structural changes take place in the region 0.2–0.3 mole fraction of methanol as would be apparent from the excess thermodynamic properties of mixing. The creation of a cavity initially leads to a more endothermic enthalpy and positive entropy changes, but these values decrease after maximum structuration of solvent molecules.

(iii) Placement of solute molecules into the cavity, which usually involves bond formation between the solute and the solvent molecules. However, the solute molecules involved in the equilibrium processes are the Zwitterions, anions and cations of α-alanine and H^+ ions. Thus, enthalpy changes would occur due to the solvation of the different solute molecules, due to ion–dipole, ion–quadrupole, dispersion, hydrophobic interactions, etc. In all cases, this step is usually accompanied by a decrease in entropy due to loss of degrees of freedom of the gaseous ions or molecules. Naturally, the enthalpy and entropy changes would be different for different species and vary from solvent to solvent. This step thus involves structural rearrangement leading to: (a) an endothermic process due to disordering of the original solvent structure causing an increase in entropy and (b) an exothermic process due to the ordering of the solvent molecules around the ions or molecules causing a decrease in entropy.

Consideration of the enthalpy and entropy changes due to the reaction

$$\mathrm{ROH} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{ROH_2^+} + \mathrm{H_2O}$$

should also be taken into consideration. Quantitative interpretation of the thermodynamic parameters is therefore difficult and demands an extensive collection of thermodynamic data of different systems.

However, in order to comprehend better the nature of the solute–solvent interactions, the division of the thermodynamics of transfer into single ion values is desirable and this can be achieved using the simple equations (5) and (6) derived from reactions (1) and (2).

$$\Delta X_t^0 = \Delta X_t^0(\mathrm{H^+}) + \Delta X_t^0(\mathrm{RH^\pm}) - \Delta X_t^0(\mathrm{RH_2^+})$$

or

$$-\Delta X_t^0(\text{RH}_2^+) = \Delta X_t^0(1) - \Delta X_t^0(\text{H}^+) - \Delta X_t^0(\text{RH}^\pm) \qquad (5)$$

and

$$\Delta X_t^0(\text{R}^-) = \Delta X_t^0(2) - \Delta X_t^0(\text{H}^+) + \Delta X_t^0(\text{RH}^\pm) \qquad (6)$$

where X represents the appropriate thermodynamic parameters (H, G and S).

$\Delta X_t^0(1)$ and $\Delta X_t^0(2)$ have been taken from the present investigation. $\Delta G_t^0(\text{RH}^\pm)$ and $\Delta H_t^0(\text{RH}^\pm)$ of α-alanine in water and mixed solvents have been obtained from the determinations of solubility and temperature coefficients of the solubility of α-alanine [30].

$\Delta G_t^0(\text{H}^+)$ values have been taken from our earlier works [8]. $\Delta H_t^0(\text{H}^+)$ values have been recently reported by Abraham et al. [12], using the "reference electrolytes" Ph_4PBPH_4 and $\text{Ph}_4\text{ASBPh}_4$ and assuming $\Delta H^0(\text{Ph}_4\text{P}^+, \text{Ph}_4\text{AS}^+) = \Delta H^0(\text{Ph}_4\text{B}^-)$. Though there may be some uncertainty, it is regarded as the best available method for obtaining single ion values. We have calculated $\Delta H^0(\text{H}^+)$ values utilizing enthalpy values of the "isoelectric" reaction [31]:

$\text{HPhen}^+ \rightleftharpoons \text{H}^+ + \text{Phen}$

The calculated $\Delta H_t^0(\text{H}^+)$ values (Table 4) agree well (except at 16 wt% of methanol) with those reported by Abraham et al. [12] (in parentheses in Table 4) if we consider the limitations of the widely different methods of calculation, particularly since the closest values of $\Delta H^0(\text{H}^+)$ in water are about 13 kJ mol^{-1} (ref. 6, p. 320). Moreover, it is very difficult to predict the error ranges for $\Delta H_t^0(\text{H}^+)$ values which are based on extra-thermodynamic assumptions. In spite of the limitations, it is desirable to obtain more data on single ion values based on different assumptions which would enable us to gain a deeper understanding of the mechanism of ion solvation.

The values of the thermodynamics of transfer of ions from water to methanol + water mixtures are recorded in Table 4.

We have also calculated the thermodynamics of cations and anions of α-alanine in water using the $\Delta G^0(\text{H}^+)$ and $\Delta H^0(\text{H}^+)$ values from the literature and the experimental values of amino acids determined by us. It is unfortunate that the $\Delta G^0(\text{H}^+)$ and $\Delta H^0(\text{H}^+)$ values reported by different workers differ so much (ref. 6, p. 320) and do not give the accepted value of $\Delta S^0_{\text{H}_2\text{O}}(\text{H}^+) = -5.0$ e.u. We therefore took $\Delta H^0(\text{H}^+) = -260.7$ and $\Delta G^0(\text{H}^+)_{\text{H}_2\text{O}} = -259.7$ kcal mol^{-1} (molal scale) (ref. 6, p. 320). $\Delta S^0(\text{H}^+)_{\text{H}_2\text{O}} = -14$ J K^{-1} mol^{-1} (from these data after proper conversion into the molar scale). The thermodynamics of ions in water are also recorded in Table 4.

Almost no report of the thermodynamics of transfer of organic ions has been made, and only a few data on the thermodynamics of transfer of inorganic ions are known. The values are not always consistent due to inherent limitations and it is exceedingly difficult to correlate these data with solvent structure.

Our attempt is also not without fault. The error ranges cannot be predicted properly since the evaluation of single ion values are based on several terms, errors of which are likely to be compounded. The thermodynamics of transfer of amino acids ($RH^{\pm}$) suggest that the transfer process is increasingly unfavourable on going from water to organic solvents due to endothermic enthalpy and positive entropy changes, but the $\Delta H_t^0(RH^{\pm})$ and $\Delta S_t^0(RH^{\pm})$ values suggest that the structure formation is probably maximum in the region 25.2–34.4 wt% beyond which structural collapse occurs. The single ion values in water show that the formation of the cation is favourable, accompanied by an exothermic enthalpy change and a positive entropy change, whereas the formation of the anion is accompanied by an endothermic enthalpy change and a positive entropy change. It is noted that the addition of $RH^{\pm}$ creates considerable disorder in the water structure though amino acids are usually solvated by a large number of water molecules. The H^+ ion creates slight order in the water structure, leading to a decrease in entropy.

Both RH_2^+ and R^- cause disorder in the water structure. Disorder in the water structure may be due to hydrophobic interactions of the hydrophobic groups of the amino acid and water molecules. However, ordering appears to be greater in R^- due to immobilization of a greater number of water molecules around the carboxylate ion compared to those around the NH_3^+ ion.

The free energy of transfer of the H^+ ion is favourable, with unfavourable enthalpy changes but favourable entropy changes, though the two available sets of data differ. The values based on $\Delta H_t^0(H^+)$ calculated by us show that structure breaking is at a maximum in the region of 16 wt%. Abraham et al. [12] found that structure breaking increases continuously.

The free energy of transfer of RH_2^+ is favourable whereas that of R^- is unfavourable; the formation of cations or anions is favourable from the enthalpic point of view. The entropy of transfer of cations is accompanied by an initial disorder in the solvent structure (which reaches a maximum in the region 16–25 wt%), followed by ordering. The entropy of transfer of anions is accompanied by structure formation which is maximum in the region 16–25 wt%.

It is too early to predict a generalization from these meagre data, but it can be said that the formation of cations or anions first brings about disorder in the solvent structure but subsequently strengthens structure of the solvent mixtures, whereas methanol first strengthens the water structure followed by depolymerization beyond 0.2–0.3 mole fraction of methanol.

However, it is desirable to obtain more data on single ion thermodynamics to reach a clear understanding on the nature of the ion–solvent interactions and related solvation phenomena.

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