Journal of Thermal Analysis, Vol. 29 (1984) 815–820

Thermometry — enthalpimetry

ENTHALPY AND ENTROPY OF TRANSFER OF HYDROGEN ION FROM WATER TO MIXED SOLVENTS

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(Received November 5, 1983; in revised form March 28, 1984)

Attempts have been made to determine the enthalpy and entropy of transfer of H^+ ion from water to mixed solvents using the calorimetric data of earlier experiments. The results are in qualitative agreement with the facts that $\Delta H_t^0(H^+)$ passes through an exothermic maximum and $T\Delta S_t^0$ passes through a minimum at about 20 to 30 wt% of organic solvent indicating the initial structure formation and the ultimate breakdown of the solvent structure with the addition of organic solvent.

The importance and use of the free energies of transfer $[\Delta G_t^0(H^+)]$ or medium effects of the H^+ ion in different mixed or non-aqueous solvents are well-known. The medium effect of the H^+ ion is a quantitative measure of the differences in ion-solvent interactions which are the controlling factors in dilute solutions where ion—ion interactions are absent. Moreover, medium effects of H^+ ions in different solvents would measure the relative basicities of the solvents directly.

Measurements of the medium effects of electroneutral combinations are relatively simple, but the thermodynamics provide no method to divide them into single-ion contributions. Though a number of theoretical and semi-empirical extrathermodynamic methods have been attempted to divide the free energies of transfer into single-ion contributions, all the methods have some inherent limitations and the results obtained are usually divergent [1—5].

However, it has been widely admitted that the free energy of transfer of ions can be regarded as composed of a neutral part and an electrostatic part, i.e.

$$\Delta G_t^0(\text{ion}) = \Delta G_{t(\text{neut})}^0 + \Delta G_{t(\text{el})}^0(\text{ion})$$

The values of the free energies of transfer of ions from one solvent to another are reliable in view of the compensation of the ΔH_t^0 and $T\Delta S_t^0$ terms, where the structural contributions of unknown magnitudes largely cancel out [5].

However, the separation of ΔH_t^0 into single-ion contributions is difficult, as the enthalpies of solvation are mainly dependent on complex structural contributions arising from the making or breaking of bonds. Considerable disagreements (as high as 50 Kcal) in the single-ion enthalpy values in water have been reported [5]. Consistent results are not given by methods such as [6]

i) extrapolations of enthalpy values of alkali metal halides or tetraalkylammonium halides with respect to ionic radius or ionic volume to zero reciprocal radius, or

ii) the assumption that the enthalpies of transfer of both cryptates of alkali ions and the corresponding free ligands are identical [6–8].

Very few determinations of ΔH_t^0 of ions, mainly based on $\Delta H_t^0(\mathrm{Ph_4As^+}) = \Delta H_t^0(\mathrm{BPh_4^-})$, have been made [9. 10]. Friedman and co-workers [10] recommended the use of propylene carbonate (pc) as an ideal solvent for ions, and transfer enthalpies of ions from pc to other solvents have been evaluated and explained in terms of structural effects. However, serious deficiencies of the model $\Delta H_t^0(\mathrm{Ph_4As^+}) = \Delta H_t^0(\mathrm{BPh_4^-})$ have also been reported [10].

Generally, ΔH is determined calorimetrically, but in most cases the determinations have been made for relatively concentrated solutions, so that it is hardly justifiable to consider ΔH to be truly ΔH^0. Measurements of ΔH at various ionic strengths to yield ΔH^0 by suitable extrapolations are rarely made. However, accurate ΔH_t^0 values demand the accurates determination of ΔH^0 values in very dilute solutions, where ion–ion interactions are absent and the ions are in their respective standard states. In view of the importance of ΔH_t^0 ion values, but at the same time the lack of such data in different mixed and non-aqueous solvents, we have attempted to evaluate $\Delta H_t^0(H^+)$ from water to different aquo-organic mixtures.

We have assumed

$$\Delta H_t^0(\mathrm{ion}) = \Delta H_{t(\mathrm{neut})}^0 + \Delta H_{t(\mathrm{el})}^0(\mathrm{ion})$$

similarly as in the evaluation of the free energies of transfer of ions. $\Delta H_{t(\mathrm{neut})}^0$ of an ion has been assumed to be equal to $\Delta H_{t(\mathrm{neut})}^0$ of the corresponding uncharged species of similar size and structure as the ion.

Thus, for an isoelectric reaction of the type

$$\mathrm{LH^+} \rightleftharpoons \mathrm{L} + \mathrm{H^+} \tag{1}$$

where L is either 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), we have

$$\begin{aligned} \delta\Delta H_t^0(1) &= \Delta H_t^0(\mathrm{L}) + \Delta H_t^0(\mathrm{H^+}) - \Delta H_t^0(\mathrm{LH^+}) = \\ &= \Delta H_t^0(\mathrm{H^+}) - \Delta H_{t(\mathrm{el})}^0(\mathrm{LH^+}) \end{aligned} \tag{2}$$

or

$$\Delta H_t^0(\mathrm{H^+}) = \Delta H_t^0(1) + \Delta H_{t(\mathrm{el})}^0(\mathrm{LH^+}) \tag{3}$$

$\Delta H_{t(\mathrm{el})}^0(\mathrm{LH^+})$ has been calculated using the Born equation [11]:

$$\Delta H_{t(\mathrm{el})}^0(\mathrm{LH^+}) = \\ = \frac{N(Ze)^2}{2r}\left[\frac{1}{\epsilon_M} - \frac{1}{\epsilon_W}\right] + \frac{N(Ze)^2}{2r}T\left[\frac{1}{\epsilon_M}\frac{\mathrm{d}\ln\epsilon_M}{\mathrm{d}T} - \frac{1}{\epsilon_W}\frac{\mathrm{d}\ln\epsilon_W}{\mathrm{d}T}\right]$$

r has been calculated to be 3.70 A°. The dielectric constant values at different temperatures have been taken from the data of Akerlof and Short [12]. The calculated

Table 1 Thermodynamics of transfer of H^+ ion from water to aquo-organic mixture at 298 K

Wt% of organic solvent	$-\Delta H_t^0$, kJ/mole				$-\Delta G_t^0$, kJ/mole				$-T\Delta S_t^0$, kJ/mole			
	MeOH	EtOH	t-BuOH	Glycerol	MeOH	EtOH	t-BuOH	Glycerol	MeOH	EtOH	t-BuOH	Glycerol
5	–	–	1.20 (0.20)	0.84 (0.09)	–	–	1.22	0.57	–	–	– 0.0	0.3
10	4.06 (0.21)	1.48 (0.23)	2.62 (0.36)	1.96 (0.16)	0.60	1.25	1.73	0.94	3.5	0.2	0.9	1.0
20	8.76 (0.48)	2.68 (0.30)	9.03 (0.71)	7.08 (0.26)	1.30	2.15	3.24	1.65	7.5	0.5	5.8	5.4
30	3.24 (0.02)	1.85 (0.52)	11.29 (1.50)	6.16 (0.47)	1.80	3.00	4.04	2.28	1.4	– 1.2	7.3	3.9
40	2.49 (1.03)	–	9.49 (2.84)	4.60 (0.63)	2.10	–	3.71	2.45	0.4	–	5.8	2.2
45	–	2.06 (1.01)	–	–	–	4.60	–	–	–	– 2.5	–	–
50	2.72 (1.34)	–	9.48 (4.17)	1.38 (0.38)	3.20	–	2.83	–	– 0.5	–	6.7	–
60	4.04 (1.74)	4.15 (1.84)	–	–	4.00	5.10	–	–	– 0.0	– 1.0	–	–

values of $\Delta H^0_{t(el)}$(LH+) in different solvent mixtures are given in brackets (Table 1). The enthalpy changes for reaction (1) in water and mixed solvents were determined by measuring calorimetrically the heat changes accompanying the complete conversion of bipy or phen to bipyH+ or phenH+ [13–16], from which the ΔH^0_t values of bipy and phen were calculated.

In view of the isoelectric nature of the reactions, the effects due to ionic strengths and the dielectric constants are eliminated to a large extent. The limitations of the Born equation in the calculation of $\Delta H^0_{t(el)}$ are well known. The equation cannot account for the structural changes in solution, but $\Delta H^0_{t(neut)}$ should account for the structural changes occurring in solution. The use of the Born equation in the case of unsymmetrical molecular ions such as bipyH+ or phenH+ may introduce considerable error.

It has been observed that there is considerable disagreement between the ΔH^0_t(H+) values obtained using bipy and phen, and we prefer the ΔH^0_t(H+) values based on phen rather than bipy for the reasons given below.

In spite of the similar linkages N → H+, the important differences between phen and bipy are the resonance stabilization and fixed coplanarity, leading to a high pK value of phenH+ compared to that of bipyH+ [17]. Due to the free rotation in bipy, the molecule may be twisted. The addition of acid to neutral *trans*-bipy leads to *cis*-bipyH+, which is subsequently converted to the *trans* dication bipyH_2^{++} in excess acid [17]. The pK value of bipy is rather low in mixed solvents; the acidity of the medium is kept low (~ 0.2 *M*) so as to convert bipy completely to bipyH+. However, this acidity is sufficient to convert bipyH+ to bipyH_2^{++} to different extents in different mixed solvents. This structural change obviously involves enthalpy changes. Moreover, considerable disagreement exist between the reported ΔH^0 values for bipyH+ in water [14, 16]. Therefore, we prefer the ΔH^0_t(H+) values based on the dissociation reaction of phenH+.

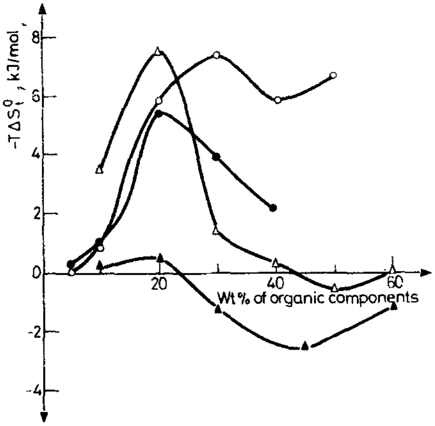

Fig. 1 Plots of wt% *vs.* $-TS^0_t$ of organic components: methanol–water, ethanol–water, t-BuOH–water, glycerol–water

The values of $\Delta H_t^0(\mathrm{H}^+)$ in different solvents (based on phenH+) are presented in Table 1. Considering the uncertainty in the calculated values of $\Delta H_{t(\mathrm{el})}^0(\mathrm{phenH}^+)$, we estimate the uncertainty in the $\Delta H_t^0(\mathrm{H}^+)$ values to be ±1.0 kJ. The $T\Delta S_t^0(\mathrm{H}^+)$ values calculated using $\Delta G_t^0(\mathrm{H}^+)$ values determined previously [18–20], are also presented in Table 1. The usefulness of the method could not be tested due to the lack of data. However, the trends appear to be reasonable.

It has been found that the enthalpies of transfer of the H+ ion form water to mixed solvents are exothermic [21]. It is well known that the H+ ion is solvated by water. Though enthalpy is gained by ion–water interactions in the first hydration sphere, hydrogen-bonds in the bulk–water structure must be broken due to introduction of the H+ ion. On the transfer to mixed solvents, the exothermic enthalpy changes are due to strong H+–water interactions in the more structured solvents. The structure ultimately breaks down, leading to enthalpy gain from the ion-solvent interactions as compared to the enthalpy loss due to the destruction of solvent–solvent interactions. The enhancement of the ordered structure due to the addition of organic solvent and the subsequent destruction of the structure can be fully corroborated from the $T\Delta S_t^0$ *vs.* wt% of organic solvent profile (Fig. 1).

However, it is desirable to acquire single-ion values from different methods in order to test the applicability of the present method. The single-ion values would definitely be of great help in elucidating the solvent structure and the different aspects of the ion–solvent interactions.

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The authors wish to thank the U. G. C., Government of India, for the award of a Junior Research Scholarship to S. K. C.

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Zusammenfassung — Es wurden Versuche zur Bestimmung der Enthalpie und Entropie der Übertragung von H^+ von Wasser auf Lösungsmittelgemische unter Benutzung kalorimetrischer Daten früherer Experimente unternommen. Die Ergebnisse sind in qualitativer Übereinstimmung mit den Tatsachen, daß $\Delta H_t^0(H^+)$ bei etwa 20–30 Gew.-% an organischem Lösungsmittel durch ein exothermes Maximum und $T\Delta S_t^0$ durch ein endothermes Minimum gehen, was den Beginn der Strukturausbildung und den endgültigen Zusammenbruch der Lösungsmittelstruktur mit der Zugabe des Lösungsmittels anzeigt.

Резюме — На основе проведенных ранее калориметрических измерений сделаны попытки определить энтальпию и энтропию переноса протона из воды в смешанные растворители. Результаты качественно согласуются с теми фактами, что $\Delta H_t^0(H^+)$ проходит через экзотермический максимум, а $T\Delta S_t^0$ — через минимум при содержании около 20—30 вес. % органических растворителей. Все это указывает на начальное образование структуры и конечное разрушение структуры растворителя при добавлении органических растворителей.