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# THERMODYNAMICS OF INDIVIDUAL IONS IN ETHYLENE GLYCOL–WATER SOLVENTS

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## ABSTRACT

A new equation, correlating the cell (or electrode) potential with the dielectric constant of the solvent, has been developed and used to compute the chemical contribution to the transfer thermodynamic quantities of individual ions in various solvents. The results show that the electrostatic contribution to the transfer free energies should in fact account for all the interactions between the charge on the ion and the overall charge on the solvent molecules, of which the Born contribution plays but a minor role. The thermodynamic properties of individual ions have been discussed in the light of ion–solvent interactions as well as the structural effects of the solvents on the transfer process.

## INTRODUCTION

The transfer process, HX (in water) = HX (in respective solvents), is associated with a transfer of charged species, i.e., of $H^+$ and $X^-$ ions from water to respective solvents. It is generally agreed [1–8] that the standard Gibbs energy of transfer $\Delta G_t^\circ$, (and similarly the entropy and enthalpy of transfer) consists of a non-electrostatic or chemical part, $\Delta G_{ch}^\circ$, and an electrostatic part, $\Delta G_{el}^\circ$, which is estimated by Born's eqn. (1).

$$\Delta G_{el}^\circ = \tfrac{1}{2}Ne^2\left(D_s^{-1} - D_w^{-1}\right)\left(r_+^{-1} + r_-^{-1}\right) \tag{1}$$

where $N$ is Avogadro's number, $D_s$ and $D_w$ are the dielectric constants of the solvent and water, respectively, and $r_+$ and $r_-$ are the radii of the cation and anion, respectively. While the electrostatic transfer free energy arises from the differences in the dielectric constants of the solvents, the non-electrostatic transfer free energy reflects the contributions of solvation and other specific ion–solvent interactions which depend on the basicity of the solvent [1–8].

The electrostatic part of the entropy of transfer is obtained [2,3,6–8] by differentiating eqn. (1)

$$\Delta S_{el}^\circ = -\tfrac{1}{2}Ne^2\left[D_w^{-1}(\mathrm{d}\ln D_w/\mathrm{d}T) - D_s^{-1}(\mathrm{d}\ln D_s/\mathrm{d}T)\right]\left(r_+^{-1} + r_-^{-1}\right) \tag{2}$$

where the values of (d ln $D_w$/d$T$) and (d ln $D_s$/d$T$) are evaluated from the

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simple empirical eqn. (3), in which $\theta$ is a constant characteristic of the medium [1–3,6–10].

$$d \ln D/dT = -1/\theta \tag{3}$$

Thus, eqn. (2) can be rewritten [1–8] as

$$\Delta S^\circ_{el} = -\tfrac{1}{2}Ne^2\left(D_s^{-1}\theta_s^{-1} - D_w^{-1}\theta_w^{-1}\right)\left(r_+^{-1} + r_-^{-1}\right) \tag{4}$$

From the slopes of the linear plots of $\ln D$ against $T$ for the respective solvents [2,3,7–11], the values of $\theta$ can be calculated. From a knowledge of $\Delta G^\circ_{el}$ and $\Delta S^\circ_{el}$, the electrostatic part of the enthalpy change, $\Delta H^\circ_{el}$, can be computed. The chemical contributions, $\Delta G^\circ_{ch}$, $\Delta S^\circ_{ch}$ and $\Delta H^\circ_{ch}$, can then be obtained by subtracting the respective electrostatic contribution values from the total [2,3,5–8].

Previous evidence [3–8] has proved the inadequacy of the Born theory in providing a guide to the thermodynamic properties of ions in solution. This raises doubts [4] about the validity of the electrostatic contribution calculated from the Born equation and thus, the chemical contribution to the transfer thermodynamic quantities. In view of these unreliable data [3–8], another independent method for determination of chemical contributions must be sought.

Also, several trials have been made to correlate the standard potential $E^\circ$ of a cell with the dielectric constant $D$ of the medium [1,4–8,11]. In all cases, the plots of $E^\circ$ values vs. $1/D$ approached linearity in the higher dielectric regions of the solvents but became more noticeably curved in the lower dielectric regions.

In the present investigation, a new equation, correlating the cell (or electrode) potential with the dielectric constant of the solvent, has been developed and used to compute the chemical contribution to the standard transfer thermodynamic quantities.

## THEORY

The change with temperature of the dielectric constant of the pure solvents and the solvent–water mixtures is expressed with considerable accuracy by Åkerlöf and Short [9,10] as

$$\ln D = \ln a_1 - b_1 T \tag{5}$$

where $a_1$ and $b_1$ ($b_1 = 1/\theta$, see eqn. (3)) are empirical constants [9,10]. This equation was tested in literature using a lot of data and the results indicate its validity within the experimental errors, over a temperature range of at least 150° [9,10]. Thus, eqn. (5) has long been used [1–3,5–8,11–13] in electrochemical studies for evaluation of $\theta$ by eqn. (3), and then $\Delta S^\circ_{el}$ by eqn. (4).

In any solvent, the cell (or electrode) potentials at different temperatures are usually expressed by quadratic equations of the form

$$E_m^\circ = a - bT + cT^2 \tag{6}$$

It is always reported [1–15] that eqn. (6) is valid and accurate within the experimental errors over a wide temperature range.

Thus, in order to correlate the cell (or electrode) potential $E_m^\circ$, on the molal scale, with the dielectric constant of the solvent, then by substitution of the value of $T$ from eqn. (5), into eqn. (6) gives eqns. (7) and (8) as follows

$$E_m^\circ = A_1 + B_1(\ln D) + C_1(\ln D)^2 \tag{7}$$

$$(E_m^\circ)^{1/2} = a_2 + b_2(\ln D) \tag{8}$$

These equations are general relations which represent the variation of $E_m^\circ$ at various temperatures with the corresponding dielectric constants of the solvent. Equation (8) predicts that, for any solvent at different temperatures, $(E_m^\circ)^{1/2}$ will vary linearly with $(\ln D)$. As will be seen later, this has been verified in all solvents over all wide ranges of $D$ values.

The standard Gibbs transfer free energy $\Delta G_t^\circ$, on the molal scale, is given [1–8] by eqn. (9).

$$F({}^{w}E_m^\circ - {}^{s}E_m^\circ) = \Delta G_t^\circ = \Delta G_{ch}^\circ + \Delta G_{el}^\circ \tag{9}$$

where the superscripts w and s refer to water and solvent, respectively. Substitution of the value of $E_m^\circ$, using eqn. (7), into eqn. (9) leads to

$$\Delta G_t^\circ = F\left[{}^{w}(A_1 + B_1L + C_1L^2) - {}^{s}(A_1 + B_1L + C_1L^2)\right] \tag{10}$$

or

$$\Delta G_t^\circ = F\left[({}^{w}A_1 - {}^{s}A_1) + ({}^{w}B_1{}^{w}L - {}^{s}B_1{}^{s}L) + ({}^{w}C_1^{w}L^2 - {}^{s}C_1^{s}L^2)\right] \tag{11}$$

where $(\ln D)$ is written as $L$, for simplicity.

Equations (10) and (11) reflect the dependence of $\Delta G_t^\circ$ values on the dielectric constant, for the transfer process from water to any (aqueous or non-aqueous) solvent. However, when the water (at a temperature) and the solvent (at another temperature) both have the same dielectric constant $D$, i.e., a transfer process from water of dielectric constant $D$ to a solvent (at another temperature) of the same $D$, the electrostatic contribution to the transfer free energy would be zero, and the chemical contribution $\Delta G_{ch}^\circ$ is thus given, from eqn. (11), by

$$\Delta G_{ch}^\circ = F({}^{w}A_1 - {}^{s}A_1) + F({}^{w}B_1 - {}^{s}B_1)L + F({}^{w}C_1 - {}^{s}C_1)L^2 \tag{12}$$

or

$$\Delta G_{ch}^\circ = A_2 + B_2L + C_2L^2 \tag{13}$$

where $A_2 = F({}^{w}A_1 - {}^{s}A_1)$, $B_2 = \mathrm{F}({}^{w}B_1 - {}^{s}B_1)$ and $C_2 = F({}^{w}C_1 - {}^{s}C_1)$. Thus, eqn. (13) can be used to evaluate the chemical contribution to the transfer free energy at any dielectric constant $D$.

The transfer entropy $\Delta S_t^\circ$ can be obtained by applying the usual thermodynamic relationships to eqn. (11). Thus,

$$-\Delta S_t^\circ = \frac{\mathrm{d}(\Delta G_t^\circ)}{\mathrm{d}\ln D}\,\frac{\mathrm{d}\ln D}{\mathrm{d}T} \tag{14}$$

$$= F\left[({}^{s}b_1{}^{s}B_1 - {}^{w}b_1{}^{w}B_1) + 2({}^{s}b_1{}^{s}C_1{}^{s}L - {}^{w}b_1{}^{w}C_1{}^{w}L)\right] \tag{15}$$

where $(\mathrm{d}\ln D/\mathrm{d}T)$ or $(\mathrm{d}L/\mathrm{d}T) = -\mathrm{b}_1$, from eqn. (5). The chemical contribution $\Delta S_{ch}^\circ$, to the transfer entropy can thus be obtained, for the transfer process from water to any solvent both have the same $D$ (or $L$), since eqn. (15) reduces to

$$-\Delta S_{ch}^\circ = F\left[({}^{s}b_1{}^{s}B_1 - {}^{w}b_1{}^{w}B_1) + 2({}^{s}b_1{}^{s}C_1 - {}^{w}b_1{}^{w}C_1)L\right] \tag{16}$$

or

$$\Delta S_{ch}^\circ = A_3 + B_3L \tag{17}$$

where $A_3 = F({}^{w}b_1{}^{w}B_1 - {}^{s}b_1{}^{s}B_1)$ and $B_3 = 2F({}^{w}b_1{}^{w}C_1 - {}^{s}b_1{}^{s}C_1)$. Equation (17) can, therefore, be utilized for computing $\Delta S_{ch}^\circ$ values at any dielectric constant.

Equation (16) can be rewritten as

$$\Delta S_{ch}^\circ = F\left[{}^{w}b_1({}^{w}B_1 + 2{}^{w}C_1L) - {}^{s}b_1({}^{s}B_1 + 2{}^{s}C_1L)\right] \tag{18}$$

$$= {}^{w}(-\Delta S_{ch}^\circ) - {}^{s}(-\Delta S_{ch}^\circ) \tag{19}$$

Thus, for the transfer process from water at ${}^{w}T$, ${}^{w}T = (\ln {}^{w}a_1 - L)/{}^{w}b_1$, to any solvent at ${}^{s}T$, ${}^{s}T = (\ln {}^{s}a_1 - L)/{}^{s}b_1$, both of the same $D$ (or $L$) value

$$\Delta H_{ch}^\circ - \Delta G_{ch}^\circ = {}^{w\to s}(T\Delta S_{ch}^\circ) \tag{20}$$

$$= {}^{w}(-T\Delta S_{ch}^\circ) - {}^{s}(-T\Delta S_{ch}^\circ) \tag{21}$$

From eqns. (18) and (19), and substitution of the values of ${}^{w}T$ and ${}^{s}T$ in eqn. (21), one obtains

$$\Delta H_{ch}^\circ - \Delta G_{ch}^\circ = F\left[(\ln {}^{w}a_1 - L)({}^{w}B_1 + 2{}^{w}C_1L) - (\ln {}^{s}a_1 - L)({}^{s}B_1 + 2{}^{s}C_1L)\right] \tag{22}$$

which rearranges to

$$\begin{aligned}\Delta H_{ch}^\circ - \Delta G_{ch}^\circ = {} & F\left[{}^{w}(B_1\ln a_1) - {}^{s}(B_1\ln a_1)\right] - F\left[{}^{w}(B_1 - 2C_1\ln a_1)\right.\\ & \left. - {}^{s}(B_1 - 2C_1\ln a_1)\right]L - 2F({}^{w}C_1 - {}^{s}C_1)L^2\end{aligned} \tag{23}$$

$\Delta H_{ch}^\circ$ is thus obtained from eqns. (12) and (23) as

$$\begin{aligned}\Delta H_{ch}^\circ = {} & F\left[{}^{w}(A_1 + B_1\ln a_1) - {}^{s}(A_1 + B_1\ln a_1)\right] + 2F\left[{}^{w}(C_1\ln a_1)\right.\\ & \left. - {}^{s}(C_1\ln a_1)\right]L - F({}^{w}C_1 - {}^{s}C_1)L^2\end{aligned} \tag{24}$$

or

$$\Delta H_{ch}^\circ = A_4 + B_4L - C_2L^2 \tag{25}$$

where $A_4 = F[^{w}(A_1 + B_1 \ln a_1) - {}^{s}(A_1 + B_1 \ln a_1)]$ and $B_4 = 2F[^{w}(C_1 \ln a_1) - {}^{s}(C_1 \ln a_1)]$. Therefore, eqn. (25) can be used for the evaluation of the chemical contribution to the transfer enthalpy, at any dielectric constant.

Also, in the same manner, the chemical contribution to the heat capacity $(\Delta C_p^{\circ})_{ch}$, can be obtained from eqns. (26) and (27).

$$(\Delta C_p^{\circ})_{ch} = 2F[^{s}(b_1 C_1 \ln a_1) - {}^{w}(b_1 C_1 \ln a_1)] - 2F[^{s}(b_1 C_1) - {}^{w}(b_1 C_1)]L \quad (26)$$

$$= A_5 + B_3 L \quad (27)$$

where $A_5 = 2F[^{s}(b_1 C_1 \ln a_1) - {}^{w}(b_1 C_1 \ln a_1)]$.

## RESULTS AND DISCUSSION

### *Electrode potential and dielectric constant*

Equations (7) and (8) correlate the cell (or electrode) potential at different temperatures with the dielectric constant, in any solvent. This relation has been tested in an aqueous medium and in several solvent systems [1–8,11–18], including both protic and aprotic, partially aqueous and non-aqueous solvents. In all cases, as expected from eqn. (8), plots of $(E_m^{\circ})^{1/2}$ against $L$ (where $L = \ln D$) gave practically perfect straight lines with slopes $(b_2)$ and intercepts $(a_2)$, in any solvent, over a wide range of dielectric constant values.

### *Chemical contribution to the standard transfer thermodynamic quantities of individual ions*

Now, it is of interest to compute the chemical contribution to the standard thermodynamic properties of individual ions. However, calculations have been made using the recently reported [16] EMF data in ethylene glycol (EG)–water solvents, as an example, since the transfer thermodynamic quantities of single ions from water to respective glycolic solvents have been calculated, in the preceding paper [17] by Elsemongy's methods [18]; the discussion is reserved until the chemical contributions have been computed.

As previously reported [17,18], there are two possibilities for the variation of electrode potential with the radius $(r)$ of the solvated ion on whose activity the potential depends: I—the oxidation potential varies directly with $r$ (method I), or II—the reduction potential varies inversely with $r$ (method II). It is evident [17,18] that method I must be applied to the EMF data for the determination of absolute electrode potentials as well as the thermody-

TABLE 1

Chemical contribution to the standard thermodynamic quantities (molal scale) for the transfer of individual ions from water to glycolic solvents at $D = 40$, calculated by methods I and II, using the recently reported EMF data [16]

| Glycol wt.% | Ion | $\Delta G^{\circ}_{ch}$ (kJ mol$^{-1}$) |  | $\Delta H^{\circ}_{ch}$ (kJ mol$^{-1}$) |  | $\Delta S^{\circ}_{ch}$ (J K$^{-1}$ mol$^{-1}$) |  |
|---|---|---|---|---|---|---|---|
|  |  | I | II | I | II | I | II |
| 20 | $H^+$ | 11.18 | 14.87 | −54.55 | −67.01 | −173.5 | −198.8 |
|  | $Cl^-$ | 11.72 | 14.35 | −54.52 | −67.02 | −167.2 | −205.1 |
|  | $Br^-$ | 12.66 | 13.35 | −58.92 | −62.40 | −180.7 | −190.9 |
|  | $I^-$ | 14.02 | 12.02 | −65.28 | −56.15 | −200.2 | −171.8 |
| 40 | $H^+$ | 3.85 | 10.61 | −2.06 | −26.58 | −52.8 | −102.1 |
|  | $Cl^-$ | 6.52 | 7.95 | −12.52 | −16.07 | −69.1 | −85.7 |
|  | $Br^-$ | 7.06 | 7.39 | −13.68 | −15.04 | −75.0 | −79.9 |
|  | $I^-$ | 7.81 | 6.66 | −15.09 | −13.51 | −82.9 | −72.0 |
| 60 | $H^+$ | 2.48 | 10.12 | 24.72 | −4.04 | −1.4 | −50.9 |
|  | $Cl^-$ | 5.68 | 6.95 | 10.25 | 10.39 | −21.5 | −31.0 |
|  | $Br^-$ | 6.14 | 6.47 | 10.97 | 9.49 | −23.3 | −29.2 |
|  | $I^-$ | 6.78 | 5.82 | 12.25 | 8.73 | −25.6 | −26.0 |
| 80 | $H^+$ | 1.69 | 9.58 | 49.14 | 14.45 | 42.0 | −5.7 |
|  | $Cl^-$ | 5.11 | 6.16 | 29.87 | 33.66 | 19.1 | 16.8 |
|  | $Br^-$ | 5.53 | 5.74 | 32.11 | 31.17 | 20.4 | 15.4 |
|  | $I^-$ | 6.10 | 5.17 | 35.63 | 28.19 | 22.7 | 14.0 |
| 100 | $H^+$ | 7.44 | 2.12 | 92.06 | 32.55 | 123.7 | 71.3 |
|  | $Cl^-$ | 4.28 | 5.29 | 56.68 | 68.16 | 88.4 | 106.9 |
|  | $Br^-$ | 4.64 | 4.93 | 60.96 | 63.17 | 95.0 | 99.0 |
|  | $I^-$ | 5.12 | 4.44 | 67.61 | 57.10 | 105.5 | 89.6 |

namics of single ions in solution, all the results showed that the plots of standard transfer free energy or entropy against $r^{-1}$, used earlier [5,6] to obtain the thermodynamic properties of single ions, cannot be accepted. Nevertheless, the results of calculations by both methods I and II are considered in the present work, in order to provide further proof of these conclusions.

The chemical parts of the standard transfer thermodynamic quantities of the individual ions from water to respective glycolic solvents have been calculated, by eqns. (13), (17) and (25), and the results at $D = 40$, for example, are recorded in Table 1. The values of $\Delta G^{\circ}_{ch}$ are all positive and show maxima at around 20% EG. Thereafter, for the $H^+$ ions, the $\Delta G^{\circ}_{ch}(H^+)$ values of method I decrease to minima at around 80% EG and thereafter increase, whereas those of method II decrease; for the halide ions, the $\Delta G^{\circ}_{ch}(X^-)$ values calculated by both methods I and II, decrease, with increasing EG content in the solvent.

As chemical contributions to the Gibbs energy of transfer of an ion in solution arise mainly from the solvation of the ion, $\Delta G^\circ_{\text{ch}}$ of the ions should reflect the solvating capacities of the solvent concerned and water toward the ion [14]. The resulting positive magnitudes of $\Delta G^\circ_{\text{ch}}$ for all ions presumably indicate that water possesses a larger solvating capacity toward the ions than the glycolic solvents.

The values of $\Delta H^\circ_{\text{ch}}$ and $\Delta S^\circ_{\text{ch}}$ for the individual ions, which are negative in the water-rich regions, pass through minima at around 20% EG, thereafter increase with increasing EG content in the solvent and become positive in the EG-rich solvents. Now, all structure-forming processes including solvation of ions are exothermic and are accompanied by a decrease in entropy, whereas structure-breaking processes including desolvation of ions are endothermic, entailing an increase in entropy [14]. The transfer of an ion from water to another solvent involves the following structural changes [14,15]: (1) dehydration of the ions, releasing water of hydration to form an assembly of non-interacting molecules, (2) return of this de-structured water to a normal water structure, (3) the partial breakdown of solvent structure, if any, and cavity formation, if required and (4) solvation of the ion. For the respective steps $\Delta H^\circ$, as well as $\Delta S^\circ$, is positive for (1) and (3), and negative for (2) and (4). The sign and magnitude of the overall entropy or enthalpy changes will depend on the relative magnitudes of the individual steps [14,15]. Obviously, the minima at 20% EG show that at least two opposing factors are operating. The minimum solvating capacities of glycolic solvents toward the ions at 20% EG are reflected by the minima in the chemical entropy and enthalpy of transfer, at this composition. The large negative $\Delta H^\circ_{\text{ch}}$ value, for the 20% EG solvent, reflect the smaller enthalpy changes involved in creating a correct configurational change of the solvent on the transfer process. This view is further supported by the large negative value of $\Delta S^\circ_{\text{ch}}$, which is associated with the structural changes as far as the chemical interaction or solvation on the transfer process is concerned. This phenomenon produces an overall order and hence $\Delta S^\circ_{\text{ch}}$ is negative.

The transfer thermodynamic properties of single ions in EG–water solvents have been computed and given in the preceding paper [17]. In any solvent, the values of $\Delta G^\circ_{\text{t}}$ or $\Delta G^\circ_{\text{ch}}$ of individual ions calculated by method I increase in the order: $\Delta G^\circ_{\text{t}}(\text{Cl}^-) < \Delta G^\circ_{\text{t}}(\text{Br}^-) < \Delta G^\circ_{\text{t}}(\text{I}^-)$, whereas those calculated by method II decrease in the same direction. On the other hand, in any aqueous solvent, while $\Delta S^\circ_{\text{t}}$ (and also in water-rich solvents, $\Delta S^\circ_{\text{ch}}$) values of method I decrease in the order: $\Delta S^\circ_{\text{t}}(\text{Cl}^-) > \Delta S^\circ_{\text{t}}(\text{Br}^-) > \Delta S^\circ_{\text{t}}(\text{I}^-)$, those of method II increase in the same direction. In the non-aqueous EG, the $\Delta S^\circ_{\text{t}}$ (and also in EG-rich solvents, $\Delta S^\circ_{\text{ch}}$) values of method I increase positively in the order: $\Delta S^\circ_{\text{t}}(\text{Cl}^-) < \Delta S^\circ_{\text{t}}(\text{Br}^-) < \Delta S^\circ_{\text{t}}(\text{I}^-)$, whereas those of method II decrease positively, also in the same direction.

Generally, for various solvent systems, one observes, in the respective structurally critical regions, either of the sequences: (i) $\Delta S^\circ_{\text{t}}(\text{Cl}^-) > \Delta S^\circ_{\text{t}}(\text{Br}^-) > \Delta S^\circ_{\text{t}}(\text{I}^-)$, or (ii) $\Delta S^\circ_{\text{t}}(\text{I}^-) > \Delta S^\circ_{\text{t}}(\text{Br}^-) > \Delta S^\circ_{\text{t}}(\text{Cl}^-)$.

Both sequences have been observed before and are known for various solvent systems [15]. Evidently, besides the physicochemical properties of the solvents, pronounced structural contributions are responsible for the observed nature and sequence of $T\Delta S_t^\circ(\text{HX})$ against composition profiles. The question arising is which of these two orders is in better accord with the

TABLE 2

Standard thermodynamic quantities for the transfer of HX from water to glycolic solvents at 25°C, and their chemical contributions at two different dielectric constants ($D = 40$ and 60), computed from recently reported EMF data [16] ($\Delta G^\circ$ and $\Delta H^\circ$ (kJ $\text{mol}^{-1}$); $\Delta S^\circ$ (J $\text{K}^{-1}$ $\text{mol}^{-1}$))

| Glycol wt.% | Method | $\Delta G_t^\circ$ | $\Delta H_t^\circ$ | $\Delta S_t^\circ$ | $D = 40$ | | | $D = 60$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $-\Delta G_{ch}^\circ$ | $\Delta H_{ch}^\circ$ | $\Delta S_{ch}^\circ$ | $-\Delta G_{ch}^\circ$ | $\Delta H_{ch}^\circ$ | $\Delta S_{ch}^\circ$ |
| HCl | | | | | | | | | | |
| 20 | I | 1.14 | 0.20 | −3.1 | 0.53 | −0.03 | −6.3 | 0.23 | 2.15 | 2.0 |
| | II | 1.15 | 0.19 | −3.3 | 0.52 | −0.02 | −6.3 | 0.22 | 2.14 | 2.0 |
| 40 | I | 2.43 | −0.42 | −9.5 | 2.68 | 10.46 | 16.3 | 0.49 | 6.74 | 11.6 |
| | II | 2.46 | −0.45 | −9.7 | 2.67 | 10.50 | 16.4 | 0.48 | 6.73 | 11.5 |
| 60 | I | 4.05 | −2.50 | −21.9 | 3.19 | 14.47 | 20.1 | 0.53 | 8.49 | 11.8 |
| | II | 4.09 | −2.53 | −22.2 | 3.18 | 14.43 | 19.9 | 0.53 | 8.47 | 11.6 |
| 80 | I | 7.01 | −4.11 | −37.3 | 3.42 | 19.27 | 22.9 | 0.58 | 12.30 | 15.9 |
| | II | 7.07 | −4.09 | −37.4 | 3.41 | 19.21 | 22.5 | 0.57 | 12.41 | 16.0 |
| 100 | I | 19.05 | 3.66 | −51.6 | −3.16 | 35.37 | 35.3 | −6.16 | 23.96 | 19.1 |
| | II | 19.15 | 3.90 | −51.2 | −3.17 | 35.61 | 35.6 | −6.18 | 24.02 | 18.9 |
| HBr | | | | | | | | | | |
| 20 | I | 0.80 | 0.22 | −1.9 | 1.47 | 4.37 | 7.2 | 0.47 | 3.40 | 7.1 |
| | II | 0.78 | 0.21 | −1.9 | 1.52 | 4.61 | 7.9 | 0.48 | 3.45 | 7.4 |
| 40 | I | 1.75 | −0.05 | −6.0 | 3.21 | 11.62 | 22.2 | 0.77 | 7.21 | 15.5 |
| | II | 1.70 | −0.03 | −5.8 | 3.22 | 11.54 | 22.2 | 0.79 | 7.17 | 15.6 |
| 60 | I | 3.00 | −1.29 | −14.4 | 3.65 | 13.75 | 21.9 | 0.82 | 9.64 | 19.2 |
| | II | 2.93 | −1.21 | −13.9 | 3.65 | 13.53 | 21.7 | 0.83 | 9.67 | 19.5 |
| 80 | I | 5.35 | −3.80 | −30.7 | 3.84 | 17.03 | 21.6 | 0.72 | 14.40 | 28.9 |
| | II | 5.23 | −3.79 | −30.2 | 3.84 | 16.72 | 21.1 | 0.72 | 14.47 | 29.6 |
| 100 | I | 16.79 | −1.10 | −60.0 | −2.80 | 31.10 | 28.7 | −5.90 | 24.21 | 30.6 |
| | II | 16.63 | −1.44 | −60.7 | −2.81 | 30.62 | 27.7 | −5.87 | 24.08 | 30.9 |
| HI | | | | | | | | | | |
| 20 | I | 0.29 | 0.24 | −0.1 | 2.84 | 10.74 | 26.7 | 0.81 | 5.19 | 14.5 |
| | II | 0.30 | 0.23 | −0.3 | 2.85 | 10.86 | 27.0 | 0.80 | 5.22 | 14.6 |
| 40 | I | 0.72 | 0.51 | −0.6 | 3.96 | 13.02 | 30.1 | 1.20 | 7.80 | 21.0 |
| | II | 0.74 | 0.48 | −0.9 | 3.95 | 13.06 | 30.1 | 1.19 | 7.80 | 20.9 |
| 60 | I | 1.44 | 0.51 | −3.1 | 4.30 | 12.47 | 24.2 | 1.23 | 11.27 | 30.0 |
| | II | 1.47 | 0.43 | −3.5 | 4.30 | 12.76 | 24.9 | 1.22 | 11.21 | 29.6 |
| 80 | I | 2.85 | −3.36 | −20.9 | 4.42 | 13.50 | 19.3 | 0.92 | 17.37 | 48.0 |
| | II | 2.91 | −3.41 | −21.2 | 4.41 | 13.74 | 19.7 | 0.92 | 17.16 | 47.0 |
| 100 | I | 13.41 | −8.24 | −72.6 | −2.32 | 24.44 | 18.2 | −5.52 | 24.43 | 47.3 |
| | II | 13.47 | −8.17 | −72.7 | −2.32 | 24.55 | 18.3 | −5.49 | 24.27 | 46.4 |

fundamental tenets of ion-solvation and solvent structure theory.

After a comprehensive treatment of the arguments and detailed discussion, Bose et al. [15] concluded that the ideal order is: $\Delta S_t^\circ(\mathrm{I}^-) > \Delta S_t^\circ(\mathrm{Br}^-) > \Delta S_t^\circ(\mathrm{Cl}^-)$, as envisaged in case (ii), in a solvent more structured than water (here, the non-aqueous EG or the EG-rich solvents, as indicated by $\Delta S_t^\circ$ or $\Delta S_{\mathrm{ch}}^\circ$, respectively); it is in the opposite direction, as in case (i), in solvents less structured than water (the aqueous glycolic or water-rich solvents, as indicated by $\Delta S_t^\circ$ or $\Delta S_{\mathrm{ch}}^\circ$, respectively). This conclusion [15] is in agreement with the results obtained from method I calculations based on the oxidation potential scale. This lends further support to the validity and general applicability of method I for determination of thermodynamic properties of single ions in solution.

Now, one could predict the relative order of variation of $\Delta G_t^\circ(\mathrm{HX})$ and $\Delta S_t^\circ(\mathrm{HX})$ as well as $\Delta G_{\mathrm{ch}}^\circ(\mathrm{HX})$ and $\Delta S_{\mathrm{ch}}^\circ(\mathrm{HX})$ values, in any solvent. The transfer thermodynamic quantities of HX are obtained from the differences between those for the ion constituents, both based on the same type of potential (oxidation or reduction) scale [17,18]. These are collected in Table 2. The values of methods I and II could be then compared with each other to check the reliability of the calculations. Full agreement between the values, within the experimental errors, is generally seen. Whatever the method of calculation (I or II) used, the same value of $\Delta G_t^\circ(\mathrm{HX})$, $\Delta H_t^\circ(\mathrm{HX})$ or $\Delta S_t^\circ(\mathrm{HX})$, is always obtained [18].

## *Standard transfer thermodynamic quantities of HX*

For HCl, HBr and HI, $\Delta G_t^\circ$ values are all positive and increase in magnitude as the proportion of glycol increases. The rate of increase is slow up to about 80% EG, beyond which there is a sharp rise at 100% EG. Thus, the transfer of HCl, HBr or HI from water to the glycolic solvents is non-spontaneous and becomes more unfavourable as the proportion of EG increases, particularly in the glycol-rich region. In any solvent, the value of $\Delta G_t^\circ(\mathrm{HX})$, as expected, decreases in the order: $\Delta G_t^\circ(\mathrm{HCl}) > \Delta G_t^\circ(\mathrm{HBr}) > G_t^\circ(\mathrm{HI})$. On the other hand, the relative order of increasing $\Delta S_t^\circ(\mathrm{HX})$ value, in any aqueous solvent, is: $\Delta S_t^\circ(\mathrm{HCl}) < \Delta S_t^\circ(\mathrm{HBr}) < \Delta S_t^\circ(\mathrm{HI})$. This order is reversed in the non-aqueous EG. The standard entropy changes of transfer of HX are found to be increasingly negative, with increasing EG content in the solvent, showing the net structure-making effect of the ions which is aided by strong ionic fields in aqueous media of low dielectric constant. In any aqueous solvent, while the value of $\Delta H_t^\circ$ increases in the order: $\Delta H_t^\circ(\mathrm{HCl}) < \Delta H_t^\circ(\mathrm{HBr}) < \Delta H_t^\circ(\mathrm{HI})$; it decreases, in the non-aqueous EG, in the same direction.

However, it should be pointed out that $\Delta S_t^\circ(\mathrm{HCl})$ values obtained by Sen et al. [19] do not exhibit any maximum at the water-rich portion of the mixed media, as do the data of Stern and Nobilione [20], and in any case, the values of $\Delta S_t^\circ$(HCl) obtained from the two different sources are in somewhat poor agreement with each other especially at extreme regions [14].

According to Franks and Ives [21] and Feakins and Voice [5], the effect of ionic fields on the structure of the solvent will appear as a compensating contribution in $\Delta H_t^\circ$ and $T\Delta S_t^\circ$, and the structural effects of the solvents on the transfer process are revealed through these quantities. For HCl and HBr, the value of $\Delta H_t^\circ$ passes over an endothermic maximum at around 20% EG and then becomes increasingly negative up to an exothermic minimum at around 80% EG, and thereafter increases, with increasing EG content in the solvent. For HI, the value of $\Delta H_t^\circ$ increases positively to an endothermic maximum at around 50% EG and thereafter decreases to negative values in the EG-rich region. Such extrema are considered [4] to occur in the region of composition where the order–disorder relationships in the structure of the mixed solvents are undergoing the most pronounced changes. In the case of inflexions there are grounds for suggesting [4] that they are real and do in fact reflect solvent structural changes.

The change in $\Delta H_t^\circ$ is, however, overshadowed by a large decrease of $T\Delta S_t^\circ$ with increasing EG content. This is most possibly [22] due to the increased effect of ionic fields on the solvent molecules in aqueous media of lower dielectric constant to produce ordered structures. This is also consistent with the heat evolution on transfer, i.e., a lowering of structural enthalpy associated with structure-making ion–solvent interactions after 20% EG for HCl and HBr, and 60% EG for HI.

### *Chemical contributions to standard transfer thermodynamic quantities of HX*

The chemical contributions have been computed (Table 2) at two different dielectric constants ($D = 40$ and 60, for example), for comparison. For the transfer to media of high dielectric constant ($D = 60$), the values of $\Delta G_{ch}^\circ$ are increasingly negative, pass through minima (at around 80, 75 and 70% EG for the data of method I, and 70, 65 and 60% EG for those of method II, for HCl, HBr and HI, respectively) and thereafter increase to large positive values in the non-aqueous EG. This indicates that the transfer of the acid to aqueous solvents is increasingly favourable, with increasing proportions of EG, to a maximum at 60–80% EG, but it is not favoured to non-aqueous EG, as far as chemical interactions are concerned. This suggests that all aqueous glycolic solvents are more basic than water, and water is more basic than the non-aqueous EG. This conclusion was reported by Sen et al. [19] on the basis of their acid–base studies in EG–water solvents. The values of $\Delta H_{ch}^\circ$ and $\Delta S_{ch}^\circ$ for the transfer of HCl, HBr or HI, increase positively with increasing the EG content in the solvent.

For the transfer to media of low dielectric constant ($D = 40$), while the $\Delta G_{ch}^\circ$ values show the same trend observed at $D = 60$ (the minima are displaced to 70, 65 and 60% EG for the data of method I, and 80, 80 and

75% EG for those of method II, for HCl, HBr and HI, respectively), those of $\Delta H^\circ_{\mathrm{ch}}$ and $\Delta S^\circ_{\mathrm{ch}}$ show different trends as follows. (1) For HCl, the values of $\Delta H^\circ_{\mathrm{ch}}$ and $\Delta S^\circ_{\mathrm{ch}}$ decrease to negative minima at around 20% EG, and thereafter increase positively. (2) For HBr, the values of $\Delta S^\circ_{\mathrm{ch}}$ increase positively to a maximum at around 40% EG, then decrease to a minimum at around 80% EG and finally increase again, while those of $\Delta H^\circ_{\mathrm{ch}}$ increase positively in one direction. (3) For HI, the value of $\Delta S^\circ_{\mathrm{ch}}$ increases to a maximum at around 40% EG, and thereafter decreases, while the $\Delta H^\circ_{\mathrm{ch}}$ value increases positively to a maximum at around 40% EG, then decreases to a minimum at 60% EG, and thereafter increases.

Now, it is evident that different trends are observed, if the values of $\Delta G^\circ_{\mathrm{ch}}$, $\Delta H^\circ_{\mathrm{ch}}$ and $\Delta S^\circ_{\mathrm{ch}}$ are compared with those of $\Delta G^\circ_{\mathrm{t}}$, $\Delta H^\circ_{\mathrm{t}}$ and $\Delta S^\circ_{\mathrm{t}}$, respectively, for any ion or acid. This reflects the importance of computing the chemical contribution to the standard transfer thermodynamic quantities from water to any solvent.

*Born's equation and thermodynamics of single ions in solution*

Born's equation suggests that plots of $E^\circ$ against $1/D$ should be linear [23]. However, sharp deviations from the Born line were observed especially when water percentages are low [23]. The departure from theoretical Born plots was attributed in part to the uncertainty in the radius of the solvated ion-complexes, especially in the water-poor solvents, which is different in different solvents, invalidates the very basis of the well-known linear relationship. Besides, it is well known [7] that the Born equation only takes care of the so-called secondary solvation energy. Even if the solvated ion species happens to be the same in the different aqueous organic media, the primary solvation energy may not necessarily remain constant. Differences in $E^\circ$ values may not, therefore, be rightly equated to the Born free energy change [23].

However, the electrostatic contribution to the standard Gibbs energy of transfer $\Delta G^\circ_{\mathrm{el}}$, given by Born's eqn. (1), could be separated into two parts for the individual ions, i.e.

$$\Delta G^\circ_{\mathrm{el}}(+) = \tfrac{1}{2}Ne^2(r_+^{-1})(D_{\mathrm{s}}^{-1} - D_{\mathrm{w}}^{-1}) \tag{28}$$

$$\Delta G^\circ_{\mathrm{el}}(-) = \tfrac{1}{2}Ne^2(r_-^{-1})(D_{\mathrm{s}}^{-1} - D_{\mathrm{w}}^{-1}) \tag{29}$$

In solution, $r_+$ and $r_-$ should refer to the radii of solvated positive and negative ions, respectively. It is always assumed that the radii of the ions do not change with changing solvent or temperature [1–8], which is not the case [18]. Now, it is evident that the radii of ions vary with temperature and solvent type and composition [17,18], and the extent of solvation varies from an ion to another. Therefore, eqns. (28) and (29) should be rewritten as

$$\Delta G^\circ_{\mathrm{el}}(+) = \tfrac{1}{2}Ne^2\left[{}^{\mathrm{s}}(r_+^{-1})(D_{\mathrm{s}}^{-1}) - {}^{\mathrm{w}}(r_+^{-1})(D_{\mathrm{w}}^{-1})\right] \tag{30}$$

$$\Delta G^\circ_{\mathrm{el}}(-) = \tfrac{1}{2}Ne^2\left[{}^{\mathrm{s}}(r_-^{-1})(D_{\mathrm{s}}^{-1}) - {}^{\mathrm{w}}(r_-^{-1})(D_{\mathrm{w}}^{-1})\right] \tag{31}$$

TABLE 3

Electrostatic contribution, $\Delta G_{el}^{\circ}$ (J mol$^{-1}$), to the standard transfer free energy for the individual ions as well as for the hydrdohalic acids, all calculated at 25°C on the basis of the corrected Born equation, and its percent (%) of the $\Delta G_t^{\circ}$ value

| Glycol wt.% | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| $H^+$ | 17.6 | 35.9 | 57.4 | 82.7 | 112.2 | 149.4 | 203.0 | 279.0 | 383.0 | 561.4 |
| % | 0.84 | 0.88 | 0.91 | 1.01 | 1.11 | 1.24 | 1.39 | 1.50 | 1.61 | 3.54 |
| $Cl^-$ | 18.7 | 38.3 | 60.9 | 87.3 | 118.3 | 157.1 | 212.6 | 289.5 | 389.2 | 528.9 |
| % | 0.70 | 0.73 | 0.75 | 0.82 | 0.89 | 0.97 | 1.07 | 1.13 | 1.14 | 1.51 |
| $Br^-$ | 17.4 | 35.5 | 56.5 | 81.1 | 109.8 | 145.9 | 197.4 | 268.7 | 361.2 | 490.9 |
| % | 0.70 | 0.73 | 0.75 | 0.82 | 0.89 | 0.97 | 1.07 | 1.13 | 1.14 | 1.51 |
| $I^-$ | 15.7 | 32.1 | 51.0 | 73.2 | 99.1 | 131.7 | 178.2 | 242.6 | 326.1 | 443.2 |
| % | 0.70 | 0.73 | 0.75 | 0.82 | 0.89 | 0.97 | 1.07 | 1.13 | 1.14 | 1.51 |
| HCl | 1.1 | 2.4 | 3.5 | 4.6 | 6.1 | 7.7 | 9.6 | 10.5 | 6.2 | −32.5 |
| % | 0.19 | 0.21 | 0.19 | 0.19 | 0.19 | 0.19 | 0.18 | 0.15 | 0.06 | 0.17 |
| HBr | −0.2 | −0.4 | −0.9 | −1.6 | −2.4 | −3.5 | −5.6 | −10.3 | −21.8 | −70.5 |
| % | 0.05 | 0.05 | 0.07 | 0.09 | 0.11 | 0.12 | 0.15 | 0.20 | 0.28 | 0.42 |
| HI | −1.9 | −3.8 | −6.4 | −9.5 | −13.1 | −17.7 | −24.8 | −36.4 | −56.9 | −118.2 |
| % | 1.34 | 1.25 | 1.30 | 1.29 | 1.25 | 1.20 | 1.21 | 1.25 | 1.20 | 1.88 |

In view of the Born approach eqns. (30) and (31) can now be used to compute the electrostatic contribution to the standard Gibbs free energy of transfer of the individual ions. According to the results obtained from calculations by method II, the value of $\Delta G^\circ_{\mathrm{el}}$ for the electrolyte transfer must be given as the difference between those for the individual ions, both based on the same type of (the reduction) potential scale [18]. Thus

$$\Delta G^\circ_{\mathrm{el}} = \Delta G^\circ_{\mathrm{el}}(-) - \Delta G^\circ_{\mathrm{el}}(+) \tag{32}$$

$$= \tfrac{1}{2}Ne^2\left[D_{\mathrm{s}}^{-1}\,{}^{\mathrm{s}}\left(r_-^{-1} - r_+^{-1}\right) - D_{\mathrm{w}}^{-1}\,{}^{\mathrm{w}}\left(r_-^{-1} - r_+^{-1}\right)\right] \tag{33}$$

eqn. (33) is the corrected Born equation, where the solvation of ions in solution should be taken into account, on one hand, and the value of $\Delta G^\circ_{\mathrm{el}}$ for the electrolyte is the difference (and not the sum, as given before [6]) between those of the single ions, on the other. The values so computed, by eqns. (30), (31) and (33), at 25°C are collected in Table 3. The values of the radii of the solvated $H^+$ ion in various EG–water solvents were evaluated before [17], and those of $X^-$ ions were given earlier [18].

Table 3 shows that the values of $\Delta G^\circ_{\mathrm{el}}$ for all ions increase positively; those of $\Delta G^\circ_{\mathrm{el}}(\mathrm{HCl})$ increase positively also to a maximum at around 80% EG, thereafter decrease, and become negative in the non-aqueous EG, while those of $\Delta G^\circ_{\mathrm{el}}(\mathrm{HBr})$ and $\Delta G^\circ_{\mathrm{el}}(\mathrm{HI})$, which are all negative, decrease, with increasing EG content in the solvent.

In aqueous glycolic solvents, the $\Delta G^\circ_{\mathrm{el}}$ values for ions are 0.7–1.6% of the total $\Delta G^\circ_{\mathrm{t}}$ value for the ion, and those in the non-aqueous EG are 1.5–3.5%. Also, the $\Delta G^\circ_{\mathrm{el}}(\mathrm{HX})$ contribution to $\Delta G^\circ_{\mathrm{t}}(\mathrm{HX})$ is found to be 0.1–1.3% over the entire solvent composition range. Similar results have been obtained in several solvent systems [24]. Thus, the values of $\Delta G^\circ_{\mathrm{ch}}$ evaluated on the basis of Born's equation would show the same trends given by $\Delta G^\circ_{\mathrm{t}}$ values. Therefore, in view of Born's equation, there is no need for splitting of $\Delta G^\circ_{\mathrm{t}}$ values into $\Delta G^\circ_{\mathrm{el}}$ and $\Delta G^\circ_{\mathrm{ch}}$ parts. As seen from the previous sections, this is not the case. Thus, the results show that the $\Delta G^\circ_{\mathrm{el}}$ values, should in fact account for all the interactions between the charge on the ion and the totality of charges on the solvent molecules, of which the Born contribution plays but a minor role [4].

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