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ABSOLUTE ELECTRODE POTENTIAL AND THERMODYNAMICS OF SINGLE IONS

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ABSTRACT

A new method, relating the electrode potential to the radius of the solvated ion on whose activity the potential depends, has been developed for the determination of absolute electrode potentials and the thermodynamics of single ions in solution. It is successfully applied to the cells: $Pt|H_2$(g, 1 atm)|HX, solvent |AgX|Ag, and M|MX, solvent|AgX|Ag, in aqueous, partially aqueous, and non-aqueous solvents. The absolute electrode potentials have been computed in aqueous and methanol + water solvents. The single ion activities, activity coefficients, the radii of solvated cations, and their solvation extent have been calculated. The temperature variation of the standard absolute potential has been utilized to evaluate the standard thermodynamic functions for the electrode reactions, and the standard transfer thermodynamic quantities of single ions from water to methanolic solvents. The results are interpreted in terms of ion–solvent interactions as well as the structural features and the acid–base properties of these solvents.

INTRODUCTION

The absolute scale of single electrode potentials has long been sought by both experimental and theoretical means. The selection of the hydrogen electrode as the zero point for the measurement of electrode potentials in different solvents and at all temperatures is purely conventional, and there may be better choices [1,2]. The subject of absolute and relative electrode potentials has been reviewed by Milazzo and Bombara [3]. In spite of the work that has been made, the validity and accuracy of a basis for an absolute scale of potential have not been established.

Also, it is well-known that the thermodynamic values of single ions cannot be measured exactly [4]. All thermodynamic assumptions made for measurements, and also for calculations, furnish controversial results [4]. Although a lot of working groups all over the world have been investigating on this theme for 40 years, no generally acknowledged assertion on the thermodynamic quantities for single ions has been made so far [4]. Methods, assumptions and conceptions on this theme have recently been summarized in a

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survey article and discussed in detail by Schwabe and Queck [4]. The assumptions do not only lead to bad conformity but also contradict experimentally assured results. How divergently these results are, in fact, can be recognized with the help of the much discussed free transference enthalpy from water to methanol (from $+19.3$ to -12.3 kJ mol^{-1}) for the H^+ ion [4].

In the same manner of Izmailov [5] for the separation of solvation free energy into values for the individual ionic solvation energies of individual ions, Feakins and co-workers [6–12] made careful measurements of the transfer free energies for the halogen acids in methanol + , dioxane + and acetic acid + water solvents by EMF methods. They found that the transfer free energies (ΔG_t^0) for the halogen acids from water to a solvent medium of fixed composition, vary in an approximately linear fashion with the reciprocal of the anionic radius (r_a), although the slopes of the lines were quite different from those predicted by the Born equation [6–12]. Accordingly, they [6] fitted their data to

$$\Delta G_t^0 = \Delta G_t^0(H^+) + a r_a^{-1} \tag{1}$$

and, by the method of least-squares, arrived at transfer free energies for the H^+ ion. Similarly, a plot of the transfer free energy for LiCl, NaCl and KCl as a function of the reciprocal of the cationic radius (r_c) was used to obtain the standard free energy of the chloride ion, according to

$$\Delta G_t^0 = \Delta G_t^0(Cl^-) - b r_c^{-1} \tag{2}$$

When the individual transfer free energies for H^+ and Cl^- ions obtained in this way are added together, the calculated and observed free energies of transfer of hydrochloric acid from water to methanol + water solvents [10] differ by 3350 J on average. The results indicate that cations are more stable in methanol + water solvents than in pure water, whereas the opposite is true for anions. Feakins and co-workers [10–12] explained the curvature of the plots of ΔG_t^0 against r_a^{-1}, observed for the transfer from water to the dioxane + water solvents, in terms of the "non-electrolytic" contribution to ΔG_t^0, and their main conclusions [6] reached so far are summarized as follows.

(1) The Born approach fails every quantitative or even semi-quantitative test, and is useless as a guide to the thermodynamic properties of the ions.

(2) The free energy of transfer of all the anions studied is greater numerically than that of any of the cations, despite the smaller radii of the latter.

DeLigny and Alfenaar [13] proposed a refinement of Feakins' procedure [6]. They regarded the free energy of transfer from one solvent to another to be composed of a neutral part, ΔG_t^0(neut), and an electrostatic part, ΔG_t^0(el), which approaches zero as the radius of the ion becomes very large, in accordance with the predictions of the Born equation. In their treatment [13], ΔG_t^0(neut) was evaluated from solubility data for the noble gases and for methane in water and methanol. After subtracting this neutral part from the observed transfer free energy, using the same data as Feakins et al. [6], the residuals were extrapolated to $1/r_a = 0$, on the assumption that the Born slope will be valid when r_a exceeds 1 nm. For each solvent, two lines, which should meet in the limit of $1/r = 0$ at the value of $\Delta G_t^0(H^+)$, were constructed. The first was a plot of $\Delta G_t^0(H^+) + \Delta G_t^0(el)(X^-)$ against $1/r_a$, where X^- is a halide ion. The second was a plot of $\Delta G_t^0(H^+) - \Delta G_t^0(el)(M^+)$ against $1/r_c$, where M^+ is an alkali-metal ion.

The transfer free energy for the proton is easily converted to a medium effect [2]. Bates [2] collected the results for the medium effect of the hydrogen ion in methanol + water solvents, calculated by the previously mentioned methods [5,10,13], for comparison. Although the agreement is poor, the data of Feakins and co-workers [10] and deLigny and Alfenaar [13] indicate that the proton has a lower free energy in methanol + water solvents than in water, whereas Izmailov's values [5] (differences in the solvation energy of the proton in two different solvents are equivalent to the transfer energy of the proton) lead to the opposite conclusion [2].

Thermodynamic functions gained by different extrathermodynamic assumptions differ strongly, sometimes even in the sign. One cannot prove which value is really correct. Thus, other independent methods for the estimation of single ionic thermodynamic quantities of transfer must be sought.

In the present investigation, attempts have been made not only to provide a new method for the determination of absolute electrode potentials and thermodynamics of single ions, but also to decide its applicability in both aqueous and partially aqueous, as well as in non-aqueous media.

THEORY

Consider, for example, the cell

$$\mathrm{Pt|H_2(g, 1\ atm)|HX(m),\ solvent|AgX(s)|Ag} \tag{i}$$

consisting of a hydrogen electrode at the left (L), and a silver, silver halide electrode at the right (R), both in contact with the same solution of halogen acid. This type of cell has received much attention, and their EMF data are well-known and available in aqueous, partially aqueous, and non-aqueous solvents. Hydrogen gas is oxidized to hydrogen ions

$$\tfrac{1}{2}\mathrm{H_2(g) = H^+ + e} \tag{3}$$

at the left-hand electrode of oxidation (Ox) potential ${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}}$

$${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}} = {}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} - \frac{RT}{F}\ln a_{\mathrm{H^+}} \tag{4}$$

and silver halide is reduced to silver

$$\mathrm{AgX(s) + e = Ag(s) + X^-} \tag{5}$$

at the right-hand electrode of reduction (Red) potential ${}^{\mathrm{Red}}_{\mathrm{R}}E_{\mathrm{m}}$

$$ {}^{\mathrm{Red}}_{\mathrm{R}}E_{\mathrm{m}} = {}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}} - \frac{RT}{F}\ln a_{\mathrm{X}^-} \quad (6) $$

The oxidation potential (or reduction potential) corresponding to the reduction potential (or oxidation potential) in eqns. (4) and (6) can be obtained by reversing the sign in each case.

The complete cell reaction for the passage of one faraday is

$$ \tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{AgX(s)} = \mathrm{Ag(s)} + \mathrm{H^+} + \mathrm{X^-} \quad (7) $$

The EMF (E_{m}) of the complete cell is equal to the algebraic sum of the oxidation potential of the left electrode (${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}}$) and the reduction potential of the right electrode (${}^{\mathrm{Red}}_{\mathrm{R}}E_{\mathrm{m}}$).

$$ \left({}^{\mathrm{Ox}}_{\mathrm{L}}E_{m} + {}^{\mathrm{Red}}_{\mathrm{R}}E_{m}\right) = \left({}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{m} + {}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{m}\right) - \frac{RT}{F}\ln(a_{\mathrm{H}^+}a_{\mathrm{X}^-}) \quad (8) $$

or

$$ E_{\mathrm{m}} = E^{0}_{\mathrm{m}} - \frac{2RT}{F}\ln(m\gamma_{\pm}) \quad (9) $$

and is thus seen to be dependent upon the activities of the hydrogen and halide ions in the solution of halogen acid. The parameters of eqns. (8) or (9) have their usual significance [14], and all the EMFs are on the molal scale. It follows, therefore, that the EMF of the cell (E_{m} or E^{0}_{m}) is equivalent to the difference of two oxidation potentials or two reduction potentials.

$$ E_{\mathrm{m}} = {}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E_{\mathrm{m}} \ \text{(10-I)} \qquad \text{or } E_{\mathrm{m}} = {}^{\mathrm{Red}}_{\mathrm{R}}E_{\mathrm{m}} - {}^{\mathrm{Red}}_{\mathrm{L}}E_{\mathrm{m}} \quad \text{(10-II)} $$

$$ E^{0}_{\mathrm{m}} = {}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}} \ \text{(11-I)} \qquad \text{or } E^{0}_{\mathrm{m}} = {}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}} - {}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}} \quad \text{(11-II)} $$

Absolute electrode potentials

At any temperature, eqns. (4) or (6) show that the electrode potential is dependent only on the activity of the ion. In a series of identical half-cell reactions, for example

$\mathrm{AgCl(s)} + \mathrm{e} = \mathrm{Ag(s)} + \mathrm{Cl^-}$

$\mathrm{AgBr(s)} + \mathrm{e} = \mathrm{Ag(s)} + \mathrm{Br^-}$

$\mathrm{AgI(s)} + \mathrm{e} = \mathrm{Ag(s)} + \mathrm{I^-}$

it is seen practically that: (I) the oxidation potential varies directly with the radius of the solvated ion (r); or (II) the reduction potential varies inversely with r [6–21]. Thus, these facts may be expressed as

$$ {}^{\mathrm{Ox}}E_{\mathrm{m}} = a_1 r \ \text{(12-I)} \qquad \text{or } {}^{\mathrm{Red}}E_{\mathrm{m}} = a_2/r \quad \text{(12-II)} $$

where a_1 and a_2 are proportionality constants. Therefore, there are generally two possibilities (I and II) for the variation of the electrode potential with the radius of the solvated ion on whose activity the potential depends. Of course, for each possibility, the oxidation potential of any electrode is equal to the reduction potential of the same electrode, but with the sign reversed. Substitution of ${}^{\mathrm{Ox}}E_{\mathrm{m}}$ and ${}^{\mathrm{Red}}E_{\mathrm{m}}$ values in eqns. (10) and (11) leads to

$$E_{\mathrm{m}} = a_1 r_+ - a_1 r_- \quad \text{(13-I)} \qquad \text{or } E_{\mathrm{m}} = a_2/r_- - a_2/r_+ \qquad \text{(13-II)}$$

$$E^0_{\mathrm{m}} = a^0_1 r_+ - a^0_1 r_- \quad \text{(14-I)} \qquad \text{or } E^0_{\mathrm{m}} = a^0_2/r_- - a^0_2/r_+ \qquad \text{(14-II)}$$

where r_+ and r_- are the radii of solvated hydrogen and halide ions, respectively. The EMF of a cell and even its sign depend on the activities, and thus on the radii, of the solvated ions of the reaction taking place in the cell. It is seen, from eqns. (13) and (14), that the cell EMF (E_{m} or E^0_{m}) is positive when $r_+ > r_-$, negative when $r_- > r_+$ and zero when $r_+ = r_-$. Therefore, the cell EMF (E_{m} or E^0_{m}) is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion. Thus, at any temperature, the plot of E^0_{m} (for example) of cells (i) where X = Cl, Br and I, against r_- (method I) or $1/r_-$ (method II), would yield a straight line of (I) negative slope ($-a^0_1$) and positive intercept ($a^0_1 r_+$), or (II) positive slope (a^0_2) and negative intercept ($-a^0_2/r_+$), according to eqns (14-I) and (14-II), respectively, in any solvent. The absolute hydrogen electrode potential, and also the radius of the solvated proton, in the standard state, can thus be obtained by both possibilities, methods I and II. One would expect that different values based on different, oxidation or reduction, potential scales will be obtained. Thus, the question arising is: which method (I or II) applies to the EMF data? In the following, we arrive at the answer, taking into consideration both possibilities.

In each solvent, the absolute potential of any electrode (${}_{\mathrm{E}}E^0_{\mathrm{m}}$) obtained at different temperatures can be fitted by the method of least-squares to a quadratic equation of the form

$${}_{\mathrm{E}}E^0_{\mathrm{m}} = a - b(T - 298.15) - c(T - 298.15)^2 \qquad (15)$$

where T is the thermodynamic temperature and a, b and c are constants.

The values of the standard single electrode potential on the molar concentration (${}_{\mathrm{E}}E^0_{\mathrm{c}}$) and mole fraction (${}_{\mathrm{E}}E^0_{\mathrm{N}}$) scales can be obtained with the help of the following relations

$${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} = {}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{c}} - k \log d = {}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{N}} + k \log(10^3/M) \qquad (16)$$

$${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}} = {}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{c}} + k \log d = {}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{N}} - k \log(10^3/M) \qquad (17)$$

where $k = (RT \ln 10)/F$, d is the density, and M is the mean molar mass of the solvent.

Standard thermodynamic functions for the half-cell reactions

The standard free energy change ΔG^0 associated with the cell reaction is

$$\Delta G^0 = -nFE^0_{\mathrm{m}} \qquad (18)$$

Substitution of E^0_{m} values, from eqns. (11-I) and (11-II), into eqn. (18) yields

$$\Delta G^0 = -nF\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}\right) \quad (19\text{-I}) \text{ or } \Delta G^0 = -nF\left({}^{\mathrm{Red}}_{\mathrm{R}}E^0_{\mathrm{m}} - {}^{\mathrm{Red}}_{\mathrm{L}}E^0_{\mathrm{m}}\right) (19\text{-II})$$

i.e.

$$\Delta G^0 = \Delta G^0_{\mathrm{L}} - \Delta G^0_{\mathrm{R}} \quad (20\text{-I}) \text{ or } \Delta G^0 = \Delta G^0_{\mathrm{R}} - \Delta G^0_{\mathrm{L}} \quad (20\text{-II})$$

where ΔG^0_{L} and ΔG^0_{R} are the standard free energy changes of the half-cell reactions occurring at the left and the right, respectively. Thus

$$\Delta G^0_{\mathrm{L}} = -nF\,{}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} \quad (21\text{-I}) \text{ or } \Delta G^0_{\mathrm{L}} = -nF\,{}^{\mathrm{Red}}_{\mathrm{L}}E^0_{\mathrm{m}} \quad (21\text{-II})$$

and

$$\Delta G^0_{\mathrm{R}} = -nF\,{}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}} \quad (22\text{-I}) \text{ or } \Delta G^0_{\mathrm{R}} = -nF\,{}^{\mathrm{Red}}_{\mathrm{R}}E^0_{\mathrm{m}} \quad (22\text{-II})$$

The standard absolute electrode potentials and their temperature coefficients are essentially related to the standard free energy, enthalpy and entropy changes involved in the half-cell reaction. Hence, the standard changes of free energy could be calculated from the relation

$$\Delta G^0_{\mathrm{E}} = -nF_{\mathrm{E}}E^0 = a' - b'T + c'T^2 \quad (23)$$

The standard thermodynamic functions of the half-cell can be obtained by applying the usual thermodynamic relations [14] to eqn. (23), where all refer to the molal scale

$$\Delta S^0_{\mathrm{E}} = -\mathrm{d}\left(\Delta G^0_{\mathrm{E}}\right)/\mathrm{d}T = b' - 2c'T \quad (24)$$

$$\Delta H^0_{\mathrm{E}} = \Delta G^0_{\mathrm{E}} + T\Delta S^0_{\mathrm{E}} = a' - c'T^2 \quad (25)$$

Equations (20) show that ΔG^0, and similarly ΔH^0 and ΔS^0, values are given as the difference between those for half-cell reactions.

Standard transfer thermodynamic quantities of single ions

To understand more clearly the proton transfer equilibria as well as ionic processes in general in any solvent, the evaluation of the energetics involved should be of prime importance. For the transfer of 1 mole of HX from the standard state in water (indicated by superscript w) to the standard states of the respective solvents (superscript s)

$$\mathrm{HX}\ (\text{in water}) = \mathrm{HX}\ (\text{in respective solvents}) \quad (26)$$

the standard Gibbs free energy of transfer (ΔG^0_{t}) is given [14] by

$$\Delta G^0_{\mathrm{t}} = F\left({}^{\mathrm{w}}E^0_{\mathrm{m}} - {}^{\mathrm{s}}E^0_{\mathrm{m}}\right) \quad (27)$$

Substitution of E^0_{m} values, from eqns. (11-I) and (11-II), into eqn. (27), yields

$$\Delta G^0_{\mathrm{t}} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}\right)\right] \quad (28\text{-I})$$

or

$$\Delta G_{\mathrm{t}}^{0} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}} - {}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}} - {}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right)\right] \qquad (28\text{-II})$$

which, on rearrangement, gives

$$\Delta G_{\mathrm{t}}^{0} = \mathrm{F}\left[{}^{\mathrm{w}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right)\right] - F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right)\right] \qquad (29\text{-I})$$

or

$$\Delta G_{\mathrm{t}}^{0} = \mathrm{F}\left[{}^{\mathrm{w}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right)\right] - F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right)\right] \qquad (29\text{-II})$$

i.e.

$$\Delta G_{\mathrm{t}}^{0} = \Delta G_{\mathrm{t}}^{0}(+)_{\mathrm{m}} - \Delta G_{\mathrm{t}}^{0}(-)_{\mathrm{m}} \ (30\text{-I}) \text{ or } \Delta G_{\mathrm{t}}^{0} = \Delta G_{\mathrm{t}}^{0}(-)_{\mathrm{m}} - \Delta \mathrm{G}_{\mathrm{t}}^{0}(+)_{\mathrm{m}} \ (30\text{-II})$$

where $\Delta G_{\mathrm{t}}^{0}(+)_{\mathrm{m}}$ and $\Delta G_{\mathrm{t}}^{0}(-)_{\mathrm{m}}$ are the standard transfer thermodynamic quantities, on the molal scale, of positive and negative ions, respectively, and given by

$$\Delta G_{\mathrm{t}}^{0}(+)_{\mathrm{m}} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right)\right] = F\left[{}^{\mathrm{w}}\left(a_1^0 r_+\right) - {}^{\mathrm{s}}\left(a_1^0 r_+\right)\right] \qquad (31\text{-I})$$

or,

$$\Delta G_{\mathrm{t}}^{0}(+)_{\mathrm{m}} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Red}}_{\mathrm{L}}E^{0}_{\mathrm{m}}\right)\right] = F\left[{}^{\mathrm{w}}\left(a_2^0/r_+\right) - {}^{\mathrm{s}}\left(a_2^0/r_+\right)\right] \qquad (31\text{-II})$$

and,

$$\Delta G_{\mathrm{t}}^{0}(-)_{\mathrm{m}} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right)\right] = F\left[{}^{\mathrm{w}}\left(a_1^0 r_-\right) - {}^{\mathrm{s}}\left(a_1^0 r_-\right)\right] \qquad (32\text{-I})$$

or,

$$\Delta G_{\mathrm{t}}^{0}(-)_{\mathrm{m}} = F\left[{}^{\mathrm{w}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right) - {}^{\mathrm{s}}\left({}^{\mathrm{Red}}_{\mathrm{R}}E^{0}_{\mathrm{m}}\right)\right] = F\left[{}^{\mathrm{w}}\left(a_2^0/r_-\right) - {}^{\mathrm{s}}\left(a_2^0/r_-\right)\right] \qquad (32\text{-II})$$

Equations (15), (31) and (32) show that the standard transfer Gibbs free energy of a single ion, $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})_{\mathrm{m}}$, can be expressed as a function of temperature by

$$F\left({}^{\mathrm{w}}_{\mathrm{E}}E^{0}_{\mathrm{m}} - {}^{\mathrm{s}}_{\mathrm{E}}E^{0}_{\mathrm{m}}\right) = \Delta G_{\mathrm{t}}^{0}(\mathrm{i})_{\mathrm{m}} = A - BT + \mathrm{CT}^{2} \qquad (33)$$

The standard transfer thermodynamic quantities of single ions can then be obtained by applying the usual thermodynamic relations [14] to eqn. (33), where all refer to the molal scale.

$$\Delta H_{\mathrm{t}}^{0}(\mathrm{i})_{\mathrm{m}} = A - CT^{2} \qquad (34)$$

$$\Delta S_{\mathrm{t}}^{0}(\mathrm{i})_{\mathrm{m}} = B - 2CT \qquad (35)$$

Equation (30) shows that $\Delta G_{\mathrm{t}}^{0}$, and similarly $\Delta H_{\mathrm{t}}^{0}$ and $\Delta S_{\mathrm{t}}^{0}$, values are given by the differences between the values for the ion constituents, both based on the same type of potential (oxidation or reduction).

Hydrogen ion activity and pa_H *scale*

Various attempts [1,22] have been made to circumvent the difficulties by defining pH in terms of quantities that have thermodynamic significance. An example of such a definition is the thermodynamic scale, ptH, defined as

$$\mathrm{ptH} = -\log\left(c_{\mathrm{H_3O^+}} f_{\pm}\right) \tag{36}$$

where $c_{\mathrm{H_3O^+}}$ is the molarity of the hydrated hydrogen ions and $f_{\pm}$ is the mean molar activity coefficient [1]. However, relation (36) is limited in its applicability, and gives reasonable results for single uni-univalent electrolytes only [1,22]. Therefore, it is more accurate to define pH in terms of activity as

$$\mathrm{p}a_{\mathrm{H}} = -\log a_{\mathrm{H^+}} = -\log(m_{\mathrm{H^+}} \gamma_{\mathrm{H^+}}) \tag{37}$$

where $m_{\mathrm{H^+}}$ and $\gamma_{\mathrm{H^+}}$ are the molality and the (single ion) activity coefficient of the solvated hydrogen ions, respectively. This thermodynamically correct equation [22] can be applied since the hydrogen ion activity is now a determinable quantity. The ion activities (and thus activity coefficients) are obtained (at 25 °C, for example), from eqns. (4) and (6), by

$${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{L}}E^{0}_{\mathrm{m}} = -0.05916 \log a_{\mathrm{H^+}} = 0.05916\ \mathrm{p}a_{\mathrm{H}} \tag{38}$$

$${}^{\mathrm{Ox}}_{\mathrm{R}}E_{\mathrm{m}} - {}^{\mathrm{Ox}}_{\mathrm{R}}E^{0}_{\mathrm{m}} = 0.05916 \log a_{\mathrm{X^-}} \tag{39}$$

For calculations using reduction potentials (method II), ${}^{\mathrm{Ox}}E$ is substituted by $-{}^{\mathrm{Red}}E$. As a result, the definition of a $\mathrm{p}a_{\mathrm{H}}$ scale (eqn. 37) that has an exact thermodynamic meaning [22] can now be used from the practical standpoint. The definition contains nothing that would restrict it to aqueous solutions only. Thus, it can be used in aqueous, partially aqueous, and non-aqueous solutions.

RESULTS AND DISCUSSION

Now, it is of considerable interest to examine the results of applying the proposed relations to reported consistent EMF data of cell (i), where X = Cl, Br and I, in aqueous, partially aqueous, and non-aqueous solvents.

There is some evidence that the chloride ion is not strongly solvated by water [23], and that the hydration number of the larger bromide or iodide ion is negligible [24]. Recently, based on three sets of crystal ionic radii, Marcus calculated [25] the aqueous ionic radii of $\mathrm{Cl^-}$, $\mathrm{Br^-}$ and $\mathrm{I^-}$ ions as 1.83, 1.94 and 2.22×10^{-10} m, respectively. This set differs little from the Pauling [26] set of crystal ionic radii of 1.81, 1.95 and 2.16×10^{-10} m, respectively. However, Marcus' results [25] showed that the Pauling set [26] of crystal ionic radii is superior for the purpose of the description of the sizes of the nonsolvated aqueous ions [25]. Thus, in the present work, and for the sake of comparison with previously reported results (all based on the Pauling set [26] of radii), it is more convenient to use the Pauling set of halide radii throughout the following applications.

Standard absolute electrode potentials

Five different sets of standard EMF values [6,15–21] in aqueous medium, at 25 °C, have been used to test eqns. (14). Plots of E^0_m values (Table 1) of cells (i), where X = Cl, Br and I, against r_- (method I) or $1/r_-$ (method II) values gave practically perfect straight lines. The least-squares results are summarized in Table 1. Although only three points are available, the correlation coefficients (corr) obtained indicate that the variables are very closely related in the wider range (1.81–2.16) of case I than in the narrower range (0.463–0.552) of case II, where the extrapolation to $1/r_- = 0$ involves considerable uncertainty. The negative corr values (method I) show that the

TABLE 1

Standard molal absolute potentials and radius of a solvated proton in an aqueous medium at 25 °C, obtained from five different sets of EMF data

	Kundu et al. [16]	Robinson and Stokes [17]	Feakins et al. [6]	Bates and co-workers [18–21]	Elsemongy et al. [15]
E^0_m(V) values of					
cell (i): X = Cl	0.2223	0.22234	0.2224	0.22234	0.22236
Br	0.0713	0.07131	0.0712	0.07106	0.07105
I	−0.1523	−0.15225	−0.15225	−0.15244	−0.15235
Method I					
Corr	−0.999994	−0.999993	−0.999992	−0.999991	−0.999991
ΔE^0_m(mV): X = Cl	−0.46	−0.47	−0.53	−0.54	−0.56
Br	+0.76	+0.79	+0.88	+0.90	+0.94
I	−0.31	−0.31	−0.35	−0.36	−0.38
$10^{-10}a^0_1$(V m^{-1})	1.06985	1.06981	1.06992	1.07029	1.07006
$10^{10}r_+$ (m)	2.017	2.017	2.017	2.017	2.017
${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_m$(V)	2.15827	2.15822	2.15843	2.15902	2.15861
${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_m$(V) X = Cl	1.93643	1.93635	1.93656	1.93722	1.93682
Br	2.08621	2.08613	2.08635	2.08706	2.08662
I	2.31088	2.31079	2.31104	2.31182	2.31134
Method II					
Corr	0.998951	0.998956	0.998976	0.998980	0.998988
ΔE^0_m(mV): X = Cl	+5.54	+5.52	+5.47	+5.46	+5.44
Br	−9.94	−9.92	−9.82	−9.81	−9.77
I	+4.40	+4.39	+4.35	+4.35	+4.33
$10^{10}a^0_2$(V m)	4.19703	4.19689	4.19744	4.19887	4.19804
$10^{10}r_+$ (m)	2.007	2.007	2.007	2.007	2.007
${}^{\mathrm{Red}}_{\mathrm{L}}E^0_m$(V)	2.09097	2.09086	2.09116	2.09202	2.09156
${}^{\mathrm{Red}}_{\mathrm{R}}E^0_m$(V): X = Cl	2.31880	2.31872	2.31903	2.31982	2.31936
Br	2.15232	2.15225	2.15253	2.15327	2.15284
I	1.94307	1.94300	1.94326	1.94392	1.94354
$10^{20}(a^0_2/a^0_1)$(m^2)	3.92301	3.92302	3.92313	3.92311	3.92318

increase in E_m^0 is related to the decrease in the r_- value. The differences (ΔE_m^0) between the E_m^0 values calculated by eqns. (11) and those obtained experimentally reflect the extent of correlation. Examination of Table 1 reveals the following.

(1) In all cases, eqn. (14-I) fits better than eqn. (14-II), and the correlations are perhaps surprising.

(2) The radius (10^{-10} m) of the solvated H^+ ion $r_+^{I} = (r_+^{II} + 0.010) = 2.017$.

(3) As would be expected, the standard absolute oxidation potentials calculated by eqn. (14-I), increase in the order: ${}^{Ox}E_m^0(Ag, AgCl) < {}^{Ox}E_m^0(Ag, AgBr) < {}^{Ox}E_m^0(H_2, H^+) < {}^{Ox}E_m^0(Ag, AgI)$, whereas the standard absolute reduction potentials calculated by eqn. (14-II) decrease in the same order.

(4) The ratio a_2^0/a_1^0 was found to be constant (3.923 ± 0.001 at 25 °C) and, as will be seen later, is the same for all solvent compositions and for all solvent systems. The values of a_1^0 and a_2^0 appear to be constant for all electrodes, and dependent only on the medium and the temperature.

(5) The assumption that the solvation of Cl^-, Br^- and I^- ions is negligible [23–25] seems to be reasonable in an aqueous medium, and thus will be more reasonable as the temperature of the medium increases, the acid concentration increases, or the water content of a solvent decreases in partially aqueous media, since the extent of solvation reaches a minimum in non-aqueous media [2,6]. This will be clearly seen in the following sections.

Temperature effect on standard electrode potential

The E_m^0 values required to study the temperature effect are available from recent studies [15] in aqueous medium over a wide range of temperatures (0–55 °C), and these are also consistent with several reported [17–21] well-known, accurate E_m^0 values. The results of applying eqns. (14) to the data at each temperature are given in Table 2.

At any temperature, the same general features, as seen in Table 1, are again observed. As the temperature increases, the r_+ values, calculated by both equations, decrease, reflecting the expected decrease in the extent of solvation by raising the temperature [2,6]. The correlation coefficients calculated by method I increase as expected, whereas those calculated by method II decrease (which is not recommended), with increasing temperature.

Both the oxidation and reduction electrode potentials calculated by eqns. (14) decrease with increasing temperature. For the electrode reactions, either the oxidation potential or reduction potential would decrease, with increasing temperature. This shows that only one of these methods (I or II) can be accepted for the calculation of a single electrode potential.

The potential values (V) of each electrode obtained in an aqueous medium were fitted by the method of least-squares to eqn. (15). The values of the parameters a, b and c are recorded in Table 3, for each electrode. Values of

TABLE 2

Temperature effect on standard molal absolute electrode potential, and on the radius of a solvated H^+ ion in the aqueous medium, at 0–55 °C

Temperature (°C) =	0	5	15	25	35	45	55
Method I							
Corr	−0.999979	−0.999982	−0.999987	−0.999991	−0.999993	−0.999995	−0.999996
ΔE^0_m(mV): X = Cl	−0.86	−0.78	−0.67	−0.56	−0.48	−0.40	−0.34
Br	+1.43	+1.31	+1.11	+0.94	+0.80	+0.66	+0.57
I	−0.57	−0.52	−0.45	−0.38	−0.32	−0.26	−0.23
$10^{-10}a^0_1$(V m^{-1})	1.09295	1.08851	1.07914	1.07006	1.06077	1.05139	1.04202
$10^{10}r_+$ (m)	2.026	2.024	2.021	2.017	2.013	2.008	2.002
${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_m$(V)	2.21404	2.20352	2.18110	2.15861	2.13515	2.11091	2.08615
${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_m$(V): X = Cl	1.97825	1.97021	1.95324	1.93682	1.91999	1.90302	1.88605
Br	2.13126	2.12260	2.10431	2.08662	2.06850	2.05022	2.03194
I	2.36078	2.35118	2.33093	2.31134	2.29126	2.27101	2.25076
Method II							
Corr	0.999082	0.999059	0.999022	0.998988	0.998961	0.998932	0.998913
ΔE^0_m(mV): X = Cl	+5.29	+5.34	+5.39	+5.44	+5.46	+5.49	+5.49
Br	−9.50	−9.58	−9.68	−9.77	−9.81	−9.86	−9.86
I	+4.21	+4.25	+4.29	+4.33	+4.35	+4.37	+4.37
$10^{10}a^0_2$(V m)	4.28830	4.27075	4.23379	4.19804	4.16146	4.12455	4.08768
$10^{10}r_+$ (m)	2.016	2.014	2.011	2.007	2.003	1.997	1.992
${}^{\mathrm{Red}}_{\mathrm{L}}E^0_m$(V)	2.12728	2.12009	2.10519	2.09156	2.07804	2.06498	2.05246
${}^{\mathrm{Red}}_{\mathrm{R}}E^0_m$(V): X = Cl	2.36922	2.35953	2.33911	2.31936	2.29915	2.27876	2.25839
Br	2.19913	2.19013	2.17117	2.15284	2.13408	2.11515	2.09625
I	1.98532	1.97720	1.96009	1.94354	1.92660	1.90951	1.89245
$10^{20}(a^0_2/a^0_1)$(m^2)	3.92360	3.92348	3.92330	3.92318	3.92306	3.92295	3.92284

TABLE 3

Values of the parameters *a*, *b* and *c* of eqn. (15) for the evaluation of ${}_{\mathrm{E}}E^0_{\mathrm{m}}$ in an aqueous medium from 0 to 55 °C, and the standard absolute electrode potentials on the molar concentration (${}_{\mathrm{E}}E^0_{\mathrm{c}}$) and mole fraction (${}_{\mathrm{E}}E^0_{\mathrm{N}}$) scales, as well as the standard molal thermodynamic functions of the half-cell reactions at 25 °C

Electrode	*a* (10^{-2} V)	*b* (10^{-4} V K^{-1})	*c* (10^{-6} V K^{-2})	Δ(mV)	25 °C				
					${}_{\mathrm{E}}E^0_{\mathrm{c}}$(V)	${}_{\mathrm{E}}E^0_{\mathrm{N}}$(V)	$-\Delta G^0_{\mathrm{E}}$ (kJ mol^{-1})	$-\Delta H^0_{\mathrm{E}}$ (kJ mol^{-1})	$-\Delta S^0_{\mathrm{E}}$ (J K^{-1} mol^{-1})
Method I									
Hydrogen electrode	215.859	23.090	3.641	±0.22	2.15851	2.05539	208.3	274.7	222.8
Ag, AgX electrode: X = Cl	193.677	16.748	0.668	±0.21	1.93685	2.03997	186.9	235.0	161.6
Br	208.657	18.039	0.703	±0.23	2.08665	2.18977	201.3	253.2	174.0
I	231.128	19.984	0.793	±0.25	2.31136	2.41448	223.0	280.5	192.8
Method II									
Hydrogen electrode	209.148	13.731	−2.260	±0.25	2.09156	2.19468	201.8	241.3	132.5
Ag, AgX electrode: X = Cl	231.931	20.131	0.721	±0.26	2.31923	2.21611	223.8	281.7	194.2
Br	215.279	18.688	0.663	±0.24	2.15271	2.04959	207.7	261.5	180.3
I	194.349	16.871	0.608	±0.21	1.94341	1.84029	187.5	236.0	162.8

${}_{\mathrm{E}}E_{\mathrm{m}}^{0}$ calculated by eqn. (15) and the experimental values (Table 2) agree within ± 0.2 mV at 0–55 °C, and the maximum difference between these values (Δ(mV)) is given in Table 3, for each electrode.

The standard electrode potentials on the molar concentration (${}_{\mathrm{E}}E_{\mathrm{c}}^{0}$) and on the mole fraction (${}_{\mathrm{E}}E_{\mathrm{N}}^{0}$) scales, in the aqueous medium, were computed at 25 °C with the help of eqns. (16) and (17), and are included in Table 3.

The standard free energy, $\Delta G_{\mathrm{E}}^{0}$, enthalpy, $\Delta H_{\mathrm{E}}^{0}$, and entropy, $\Delta S_{\mathrm{E}}^{0}$ changes associated with the half-cell reactions were calculated on the molal scale using eqns. (21)–(25). The results at 25 °C are also included in Table 3. The values of $\Delta G_{\mathrm{E}}^{0}$ are accurate to ± 45 J mol^{-1}. Although the values obtained by method I are based on the oxidation potential scale, whereas those by method II are on the different reduction scale, the thermodynamic functions for the half-cell reactions are all negative. However, since the oxidation reactions of the half-cells are known to be exothermic [2,6], the $\Delta H_{\mathrm{E}}^{0}$ values must be negative, and the oxidation potentials of the single electrodes should decrease with increasing temperature. This is in agreement with the results obtained from method I calculations.

Concentration effect on electrode potential

The EMF data of Robinson and Stokes [17] of cells (i), in aqueous media of different molalities in the wide range from 0.001 to 2.5 mol kg^{-1}, which are consistent and in good agreement with the recent EMF data [15] and those of Bates and co-workers [18–21] in aqueous solution of acid molality 0.001–0.1 mol kg^{-1}, have been used to study the concentration effect on the electrode potential. The E_{m} values of cells (i) containing solutions of HX having the same molality (m), were plotted against r_- or $1/r_-$. Practically perfect straight lines were obtained for each molality, in accordance with eqns. (13), and the least-squares results are recorded in Tables 4 and 5, respectively. However, it should be pointed out that eqns. (13) must be tested for solutions of the same molalities (not activities), because if the same activities were used, $E_{\mathrm{m}} = E_{\mathrm{m}}^{0} - \text{const}$, where the constant would be the same for X = Cl, Br and I. Thus, the relationship between E_{m} and r_- or $1/r_-$ will be the same as that between E_{m}^{0} and r_- or $1/r_-$; the same corr and slope, which means the same ${}_{\mathrm{R}}E_{\mathrm{m}}(a_1 r_-$ or $a_2/r_-)$ values in solutions of different activities. This is, of course, impossible.

Now, using the electrode potentials and their standard values, the ion activities, activity coefficients and pa_{H} values have been calculated by eqns. (38) and (39), for each molality, assuming complete dissociation of halogen acid HX. The results are also included in Tables 4 and 5.

For all molalities, eqn. (13-I) fits better than eqn. (13-II) as indicated by the corr and ΔE values. The radius of the solvated proton, calculated by both methods, decreases with increasing acid concentration. This shows that as the H^{+} ion concentration increases, the extent of solvation decreases. For any solution of $m \geqslant 0.5$, the r_+^{I} value is slightly greater than the r_+^{II} value.

If we consider the left half-cell reaction, eqn. (3), one would expect a decrease in the oxidation potential (or an increase in the reduction potential) with increasing H^+ ion concentration, according to eqn. (4). This is actually obtained in Tables 4 and 5. On the other hand, for the right half-cell reaction, eqn. (5), the oxidation potential must increase (which is seen in Table 4), whereas the reduction potential must decrease (against that obtained in Table 5), with increasing X^- ion concentration, according to eqn. (6). Again, this may give additional strong evidence against the applicability of method II for such calculations.

As would be expected, the a_{H^+} and a_{X} values should increase with increasing acid concentration. Results of calculations made by method I (Table 4) support this fact. The values of a_{H^+} increase slowly, whereas the values of a_{X} increase first slowly up to 0.1 m and then rapidly, with increasing acid concentration. The activity coefficients show different trends. The γ_+ values increase to a maximum at around 1 m and thereafter decrease, whereas the γ_- values decrease to minima at around 0.7, 0.5 and 0.5 m for Cl^-, Br^- and I^- ions, respectively, and thereafter increase, with increasing acid concentration. On the other hand, results of calculations made by

TABLE 4

Absolute electrode potential, radius of solvated proton, ion activity and activity coefficients, from 0.001 to 2.5 mol kg^{-1}, at 25°C, using the data reported by Robinson and Stokes [17]

		$m = 0.001$	0.005	0.01	0.05
Corr		−0.999993	−0.999993	−0.999993	−0.999992
ΔE_{m}(mV):	X = Cl	−0.47	−0.47	−0.47	−0.52
	Br	+0.78	+0.79	+0.78	+0.87
	I	−0.31	−0.32	−0.31	−0.35
r_+ (10^{-10} m)		2.351	2.275	2.243	2.169
${}^{(0)}_{\mathrm{I}}E_{\mathrm{m}}$(V)		2.51512	2.43481	2.40087	2.32635
${}^{(0)}_{\mathrm{R}}E_{\mathrm{m}}$(V):	X = Cl	1.93651	1.93692	1.93724	1.94102
	Br	2.08629	2.08673	2.08708	2.09116
	I	2.31097	2.31146	2.31184	2.31636
a_{H^+}		9.272×10^{-7}	2.112×10^{-5}	7.914×10^{-5}	1.439×10^{-3}
γ_+		9.272×10^{-4}	4.224×10^{-3}	7.914×10^{-3}	2.878×10^{-2}
a_{X}	X = Cl	1.006	1.022	1.035	1.199
	Br	1.006	1.024	1.038	1.216
	I	1.007	1.026	1.042	1.242
γ	X = Cl	1006	204.5	103.5	23.99
	Br	1006	204.7	103.8	24.33
	I	1007	205.3	104.2	24.84
$\mathrm{p}a_{\mathrm{H}}$		6.033	4.675	4.102	2.842
γ_+ (HCl) this work		0.966	0.929	0.905	0.831
	ref. 17	0.966	0.929	0.905	0.830

method II show that the a_{H^+} and γ_+ values increase to unusually large values, whereas the a_{X^-} and γ_- values decrease with increasing acid concentration (Table 5). Thus, this may lend further support to the inapplicability of method II.

The a_{H^+} values calculated by both methods I and II, are nearly the same in the dilute solutions up to 0.02 *m*. This is reflected by the $\mathrm{p}a_{\mathrm{H}}$ values, which are accurate to ± 0.008 $\mathrm{p}a_{\mathrm{H}}$ units. The $\mathrm{p}a_{\mathrm{H}}$ values calculated by method I are all positive and decrease, whereas those calculated by method II decrease to negative values, with increasing acid concentration.

It should be mentioned that the standard state for any concentration scale is chosen so that the mean ionic activity coefficient on that scale approaches unity when the concentration is reduced to zero. Thus, at infinite dilution, $\gamma_\pm = 1$, and thus, by definition, $\gamma_+ = 1/\gamma_-$ or $\gamma_- = 1/\gamma_+$, i.e., $\gamma_+ = 0$ and $\gamma_- = \infty$, and/or, $a_+ = 0$ and $a_- = 1$. This can be concluded from Tables 4 and 5. However, recent results [27], implying an extrathermodynamic assumption, show that γ_+ differs from γ_- and both deviate from the values calculated on the basis of the hydration theory or the Debye–Hückel equation [27].

The $\gamma_\pm$ values of HCl, for example, obtained by combining the values of γ_+ with those of $\gamma_-(\gamma_\pm^2 = \gamma_+\gamma_-)$ could then be compared with the reported

$\mathrm{p}a_{\mathrm{H}}$ and $\gamma_\pm$ (HCl) values, calculated by method I, in aqueous solutions of different molalities

0.1	0.5	1.0	1.6	2.5
−0.999993	−0.999993	−0.999991	−0.999982	−0.999943
−0.48	−0.48	−0.55	−0.81	−1.45
+0.80	+0.80	+0.92	+1.35	+2.42
−0.32	−0.32	−0.37	−0.54	−0.97
2.138	2.061	2.022	1.993	1.959
2.29548	2.23543	2.21517	2.20385	2.19658
1.94358	1.96365	1.98249	2.00196	2.02982
2.09391	2.11553	2.13584	2.15681	2.18682
2.31941	2.34336	2.36585	2.38908	2.42233
4.784×10^{-3}	4.953×10^{-2}	1.090×10^{-1}	1.693×10^{-1}	2.247×10^{-1}
4.784×10^{-2}	9.906×10^{-2}	1.090×10^{-1}	1.058×10^{-1}	8.988×10^{-2}
1.325	2.894	6.025	12.85	38.02
1.354	3.140	6.923	15.66	50.35
1.399	3.553	8.525	21.06	76.81
13.25	5.788	6.025	8.034	15.21
13.54	6.280	6.923	9.786	20.14
13.99	7.105	8.525	13.160	30.72
2.320	1.305	0.963	0.771	0.648
0.796	0.757	0.810	0.922	1.169
0.796	0.757	0.809	0.916	1.147

TABLE 5

Absolute electrode potential, radius of solvated proton, ion activity and activity coefficients, pa_H and $\gamma_\pm$ (HCl) values, calculated by method II, in aqueous solutions of different molalities from 0.001 to 2.5 mol kg^{-1}, at 25 °C, using the data reported by Robinson and Stokes [17]

		m = 0.001	0.005	0.01	0.05	0.1	0.5	1.0	1.6	2.5
Corr		0.998956	0.998957	0.998955	0.998974	0.998958	0.998956	0.998981	0.999064	0.999253
ΔE_m(mV)	X = Cl	+5.53	+5.52	+5.53	+5.49	+5.54	+5.60	+5.59	+5.41	+4.90
	Br	−9.92	−9.92	−9.93	−9.86	−9.95	−10.06	−10.04	−9.71	−8.80
	I	+4.40	+4.39	+4.40	+4.37	+4.41	+4.46	+4.45	+4.30	+3.90
r_+ (10^{-10} m)		2.420	2.312	2.269	2.176	2.139	2.053	2.012	1.982	1.949
${}^{\text{Red}}_{\text{L}}E_m$(V)		1.73431	1.81551	1.85015	1.93302	1.96946	2.07355	2.13522	2.18946	2.25838
${}^{\text{Red}}_{\text{R}}E_m$(V)	X = Cl	2.31891	2.31940	2.31978	2.32436	2.32738	2.35141	2.37404	2.39757	2.43149
	Br	2.15242	2.15288	2.15323	2.15748	2.16029	2.18259	2.20360	2.22544	2.25692
	I	1.94316	1.94357	1.94389	1.94773	1.95026	1.97039	1.98936	2.00908	2.03750
a_{H^+}		9.399×10^{-7}	2.216×10^{-5}	8.534×10^{-5}	2.148×10^{-3}	8.870×10^{-3}	5.098×10^{-1}	5.621	4.642×10	6.787×10^{2}
γ_+		9.399×10^{-4}	4.433×10^{-3}	8.534×10^{-3}	4.295×10^{-2}	8.870×10^{-2}	1.020	5.621	2.901×10	2.715×10^{2}
a_{X^-}	X = Cl	0.9926	0.9739	0.9596	0.8029	0.7139	0.2802	0.1161	0.0465	0.0124
	Br	0.9934	0.9758	0.9626	0.8158	0.7313	0.3070	0.1355	0.0579	0.0170
	I	0.9938	0.9781	0.9660	0.8319	0.7538	0.3444	0.1646	0.0764	0.0253
γ_-	X = Cl	992.6	194.8	95.96	16.06	7.139	0.5603	0.1161	0.0290	0.0050
	Br	993.4	195.2	96.26	16.32	7.313	0.6140	0.1355	0.0362	0.0068
	I	993.8	195.6	96.60	16.64	7.538	0.6887	0.1646	0.0477	0.0101
pa_H		6.027	4.654	4.069	2.668	2.052	0.293	−0.750	−1.667	−2.832
$\gamma_\pm$ (HCl)	This work	0.966	0.929	0.905	0.831	0.796	0.756	0.808	0.918	1.161
	Ref. 17	0.966	0.929	0.905	0.830	0.796	0.757	0.809	0.916	1.147

values [17] to check the reliability of the calculations. Full agreement between the values is seen (Tables 4 and 5), up to 1 *m*. In more concentrated solutions, the deviations show that the EMF data are not completely reliable. This may be due to the incomplete dissociation of HX, or the functioning of the electrodes in such media.

Solvent effect on electrode potential

The EMF data [14] of cells (i), in partially aqueous and non-aqueous methanol (MeOH) solvents have been used not only to test the validity and applicability of the method proposed to determine the single electrode potential and the thermodynamic properties of single ions, but also to study the solvent effects on these properties. Application of eqns. (13) and (14) to the EMF data [14] in the standard state and in 0.01 *m* HX solutions, for example, gives rise to the least-squares results shown in Tables 6 and 7, respectively.

In the standard state, the same general features, seen before, are again observed for each methanolic solvent. The ratio (a_2^0/a_1^0) is again constant and independent of the solvent composition. Its value is 3.923 ± 0.001 at 25 °C.

Table 6 shows that, as the MeOH content of the solvent increases, the oxidation potentials of both left and right electrodes decrease, the solvation extent of H^+ ions also decreases, and thus the transfer free energies of single ions increase. However, Table 7 shows that although the extent of solvation of H^+ ions decreases in one direction, a minimum and the corresponding maximum have been observed at around 70% MeOH for ${}^{\mathrm{Red}}_{\mathrm{L}}E^0_{\mathrm{m}}$ and $\Delta G_t^0(+)$ values, respectively. For transfer free energies of ions, see Table 8.

In 0.01 *m* HX solution, almost the same corr and ΔE_{m} values found in the standard state, have been obtained, and especially in solvents of low MeOH content. This may be so because the $\gamma_\pm$ values for HCl, HBr and HI in this dilute solution of methanolic solvents are very close to each other. However, method I calculations (Table 6) show that the values of ${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}}$, ${}^{\mathrm{Ox}}_{\mathrm{R}}E_{\mathrm{m}}$ and a_{H^+} decrease, whereas the r_+, a_{X^-} and thus γ_- values increase to maxima at around 60% MeOH and thereafter decrease, with increasing MeOH content in the solvent. The $\mathrm{p}a_{\mathrm{H}}$ values increase from 4.104 in the aqueous, to 4.370 in the non-aqueous solvents. On the other hand, method II results show that while the values of ${}^{\mathrm{Red}}_{\mathrm{R}}E_{\mathrm{m}}$ decrease, the ${}^{\mathrm{Red}}_{\mathrm{L}}E_{\mathrm{m}}$, a_{X^-} and thus γ_- and $\mathrm{p}a_{\mathrm{H}}$ values decrease to minima at around 70, 60 and 50% MeOH, respectively, and thereafter increase, whereas the r_+ and a_{H^+} values increase to maxima at around 60 and 50% MeOH, respectively, and thereafter decrease, with increasing MeOH concentration in the solvent. Thus, although a maximum extent of solvation of the H^+ ion has been observed at around 60% MeOH in both cases (I and II), different trends have been noticed for the left electrode potential, a_{H^+}, a_{X^-} and $\mathrm{p}a_{\mathrm{H}}$ values in MeOH + water solvents.

TABLE 6

Absolute electrode potential, radius of solvated proton, ion activity and pa_{H} values, calculated by method I, in methanol + water solvents at 25 ° C, using the previous data [14] in these solvents

	MeOH (wt%) = 10	30	50	70	90	100
In the standard state						
Corr	−0.999997	−1.000000	−0.999999	−0.999956	−0.999955	−0.999979
ΔE^0_{m}(mV) X = Cl	−0.33	−0.10	−0.13	−1.06	−1.06	−0.68
Br	+0.55	+0.16	+0.22	+1.77	+1.77	+1.14
I	−0.22	−0.07	−0.09	−0.71	−0.71	−0.46
a^0_1(10^{10} V m^{-1})	1.05183	1.01985	0.98782	0.93739	0.92116	0.87818
r_+ (10^{-10} m)	2.015	2.009	2.003	1.989	1.932	1.798
${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}}$(V)	2.11896	2.04895	1.97841	1.86435	1.77974	1.57871
${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}$(V) X = Cl	1.90381	1.84593	1.78795	1.69667	1.66730	1.58950
Br	2.05107	1.98871	1.92625	1.82791	1.79626	1.71244
I	2.27195	2.20288	2.13369	2.02476	1.98970	1.89686
In 0.01 m *HX solution*						
r_+ (10^{-10} m)	2.244	2.246	2.249	2.251	2.203	2.086
${}^{\mathrm{Ox}}_{\mathrm{L}}E_{\mathrm{m}}$(V)	2.36346	2.29702	2.23020	2.11823	2.03578	1.83724
${}^{\mathrm{Ox}}_{\mathrm{R}}E_{\mathrm{m}}$(V) X = Cl	1.90609	1.85074	1.79495	1.70342	1.67224	1.59403
Br	2.05353	1.99389	1.93378	1.83518	1.80158	1.71733
I	2.27467	2.20862	2.14204	2.03281	1.99560	1.90227
$10^5\,a_{\mathrm{H}^+}$	7.364	6.408	5.545	5.111	4.699	4.265
pa_{H}	4.133	4.193	4.256	4.291	4.328	4.370
a_{X^-} X = Cl	1.093	1.206	1.313	1.300	1.212	1.193
Br	1.100	1.223	1.341	1.327	1.230	1.210
I	1.112	1.250	1.384	1.368	1.258	1.234

TABLE 7

Absolute electrode potential, radius of solvated proton, ion activity and pa_H values, calculated by method II, in methanol + water solvents at 25 °C, using the previous data [14] in these solvents

	MeOH (wt%) = 10	30	50	70	90	100
In the standard state						
Corr	0.998907	0.998822	0.998836	0.999201	0.999208	0.999080
ΔE^0_m(mV) X = Cl	+5.56	+5.59	+5.39	+4.23	+4.14	+4.26
Br	−9.98	−10.04	−9.67	−7.60	−7.44	−7.64
I	+4.42	+4.45	+4.28	+3.37	+3.30	+3.39
$a^0_2(10^{-10}$ V m)	4.12615	4.00034	3.87476	3.67844	3.61479	3.44559
$r_+(10^{-10}$ m)	2.004	1.999	1.992	1.978	1.923	1.804
${}^{\mathrm{Red}}_{\mathrm{L}}E^0_m$(V)	2.05861	2.00142	1.94478	1.85931	1.87946	1.90949
${}^{\mathrm{Red}}_{\mathrm{R}}E^0_m$(V) X = Cl	2.27964	2.21013	2.14075	2.03229	1.99712	1.90364
Br	2.11597	2.05146	1.98706	1.88638	1.85373	1.76697
I	1.91025	1.85201	1.79387	1.70298	1.67351	1.59518
$(a^0_2/a^0_1)(10^{-20}$ m^2)	3.9228	3.9225	3.9225	3.9241	3.9242	3.9236
In 0.01 m *HX solution*						
$r_+(10^{-10}$ m)	2.271	2.274	2.277	2.279	2.218	2.080
${}^{\mathrm{Red}}_{\mathrm{L}}E_m$(V)	1.81911	1.76390	1.70836	1.62025	1.63425	1.66087
${}^{\mathrm{Red}}_{\mathrm{R}}E_m$(V) X = Cl	2.28237	2.21589	2.14914	2.04038	2.00302	1.90902
Br	1.11850	2.05680	1.99485	1.89389	1.85921	1.77197
I	1.91254	1.85684	1.80090	1.70976	1.67845	1.59969
$10^5\, a_{H^+}$	8.946	9.662	10.09	9.100	7.163	6.273
pa_H	4.048	4.015	3.996	4.041	4.145	4.203
a_{X^-} X = Cl	0.8992	0.7992	0.7214	0.7299	0.7948	0.8111
Br	0.9062	0.8123	0.7385	0.7465	0.8079	0.8232
I	0.9147	0.8286	0.7606	0.7681	0.8251	0.8390

Standard transfer thermodynamic quantities of single ions

Ion–solvent interactions are important in accounting for acid–base equilibria in partially aqueous and non-aqueous solvents [1,6]. The variation of single electrode potential with temperature provides a useful insight into the phenomena of ion–solvent interactions. The standard transfer thermodynamic quantities of single ions from water to MeOH + water solvents were calculated using eqns. (33)–(35), and the results at 25 °C are given in Table 8. The $\Delta G_t^0(\mathrm{i})$ values are accurate to within ±90 J mol^{-1}.

TABLE 8

Standard thermodynamic quantities (molal scale) for the transfer of individual ions from water to methanolic solvents at 25 °C, calculated from the previous data [14]

MeOH (wt%) =	10	30	50	70	90	100
Method I						
$\Delta G_t^0(\mathrm{i})(\mathrm{kJ\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	3.824	10.578	17.385	28.390	36.553	55.949
Cl^-	3.180	8.764	14.359	23.166	26.000	33.506
Br^-	3.425	9.442	15.468	24.957	28.010	36.098
I^-	3.795	10.459	17.135	27.645	31.028	39.985
$\Delta H_t^0(\mathrm{i})(\mathrm{kJ\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	21.616	50.381	60.412	74.938	63.062	28.907
Cl^-	20.486	52.234	65.522	86.787	79.998	13.142
Br^-	22.063	55.434	74.800	93.500	86.154	23.158
I^-	24.427	60.237	82.639	103.595	95.431	34.350
$\Delta S_t^0(\mathrm{i})(\mathrm{J\ K^{-1}\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	59.7	133.5	144.3	156.1	88.9	−90.7
Cl^-	58.0	145.8	171.6	213.4	181.1	−68.3
Br^-	62.5	154.3	199.0	229.9	195.0	−43.4
I^-	69.2	167.0	219.7	254.7	216.0	−18.9
Method II						
$\Delta G_t^0(\mathrm{i})(\mathrm{kJ\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	3.171	8.689	14.154	22.401	20.457	17.559
Cl^-	3.828	10.534	17.228	27.693	31.086	40.106
Br^-	3.553	9.777	15.990	25.704	28.855	37.226
I^-	3.207	8.826	14.436	23.206	26.049	33.607
$\Delta H_t^0(\mathrm{i})(\mathrm{kJ\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	23.869	52.328	91.626	118.928	113.762	73.432
Cl^-	25.121	50.655	86.645	107.679	97.207	89.390
Br^-	23.324	47.070	76.941	99.917	90.235	78.846
I^-	21.068	42.463	69.355	90.201	81.468	68.133
$\Delta S_t^0(\mathrm{i})(\mathrm{J\ K^{-1}\ mol^{-1}})$						
$\mathrm{i} = \mathrm{H}^+$	69.4	146.4	259.8	323.8	312.9	187.4
Cl^-	71.4	134.6	232.8	268.3	221.8	165.3
Br^-	66.3	125.1	204.4	248.9	205.9	139.6
I^-	59.9	112.8	184.2	224.7	185.9	115.8

Table 8 shows that the transfer free energies are all positive. For the transfer of the H^+ ions from water to methanolic solvents, the values obtained by method I increase, whereas those obtained by method II increase to a maximum at around 70% MeOH and thereafter decrease, with increasing MeOH content in the solvent. The free energies of transfer of halide ions calculated by both methods increase in the same direction. The positive values of $\Delta G_t^0(i)$ support the view that the transfer of ions from water to methanolic solvents is not favoured, i.e., water is more basic than the methanolic solvents. The increase in $\Delta G_t^0(H^+)$ with increasing MeOH content in the solvent suggests that the proton is strongly stabilized by solvation with water molecules. This is also supported by the r_+ values obtained (Tables 6 and 7) and lends further support to the view that the hydrogen ion interacts strongly with water molecules in preference to methanol molecules in methanolic solvents.

The structural features of the ion–solvent interactions in MeOH + water solvents are reflected by $\Delta H_t^0(i)$ and $\Delta S_t^0(i)$ values. Although the transfer thermodynamic quantities calculated by method I are based on the oxidation potential scale, whereas those calculated by method II on the reduction potential scale, the transfer entropies and enthalpies from water to methanolic solvents show the same trend, with increasing methanol concentration in the solvent. Their values increase to maxima at around 70% MeOH and thereafter decrease with increasing MeOH content in the solvent. The transfer entropies obtained by method I in non-aqueous methanol are negative.

The positive entropy and enthalpy of transfer of ions from water to MeOH + water solvents can be attributed to a greater structure breaking by the ion in these solvents than in water. The methanolic solvent is therefore a more structured (with a maximum at 70% MeOH) solvent than water. The negative $\Delta S_t^0(i)$ values for the non-aqueous MeOH solvent assume that ions are more effective at breaking the structure in water than in this solvent. This is further supported with the view [6,24] that the structure-forming processes, including solvation of ions, are exothermic and accompanied by an entropy decrease and the structure-breaking processes are endothermic, leading to an entropy increase.

Thermodynamics of single ions in solution and Feakins' procedure

If Feakins' [6] eqns. (1) and (2) are added together, one obtains

$$\Delta G_t^0 = a r_a^{-1} - b r_c^{-1} + \text{const} \tag{40}$$

Comparing with eqn. (30-II), the constant (solvent dependent) appearing in eqn. (40) is the difference [10] between the observed free energy of HX and that calculated from the individual transfer free energies for ions (3350 J on average [10]). It is partly due to the term $2RT\ln(d_w/d_s)$ as a difference between ΔG_t^0 values on the molar [10] and molal scales, on one hand, and

TABLE 9

Absolute electrode potential, radius of solvated cation and extent of solvation in methanol + water solvents, and transfer free energies of individual ions from water to these solvents, at 25 °C, all calculated by method I, using the reported data by Feakins and Voice [12] (ΔG_t^0 values (kJ mol^{-1}) are on the molal scale)

MeOH (wt%) =		0	10	20	30	40	50	60	80	90	99
–Corr (10^{-2})		99.9994	99.9996	99.9999	99.9996	99.9991	99.9997	99.9969	99.9928	99.9856	99.9962
ΔE_m^0(mV)	X = Cl	−0.5	−0.3	−0.2	−0.3	−0.6	−0.3	−0.9	−1.3	−1.8	−0.9
	Br	+0.8	+0.5	+0.3	+0.6	+0.9	+0.5	+1.5	+2.2	+3.1	+1.6
	I	−0.3	−0.2	−0.1	−0.2	−0.4	−0.2	−0.6	−0.9	−1.2	−0.6
a_1^0(10^{10} V m^{-1})		1.0698	1.0546	1.0386	1.0185	0.9926	0.9703	0.9537	0.9116	0.8962	0.8900
r_+ (10^{-10} m)	M = Li	4.863	4.896	4.931	–	5.050	–	5.150	5.267	–	5.304
	Na	4.554	4.577	4.602	4.639	4.693	4.738	4.767	4.850	4.873	4.871
	K	4.752	4.777	4.805	–	4.905	–	4.985	5.072	–	5.094
	Rb	4.752	4.777	4.806	–	4.907	–	4.987	5.072	–	5.089
	Cs	4.750	4.777	4.806	–	4.910	–	4.991	5.076	–	–
S_e(10^{-10} m)	M = Li	4.26	4.30	4.33	–	4.45	–	4.55	4.67	–	4.70
	Na	3.60	3.63	3.65	3.69	3.74	3.79	3.82	3.90	3.93	3.92
	K	3.42	3.45	3.48	–	3.58	–	3.66	3.74	–	3.76

	Rb	3.27	3.30	3.33	–	3.43	–	3.51	3.59	–	3.61
	Cs	3.06	3.09	3.12	–	3.22	–	3.30	3.39	–	–
${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}}$(V)	M = Li	5.2033	5.1632	5.1217	–	5.0124	–	4.9119	4.8014	–	4.7200
	Na	4.8723	4.8268	4.7795	4.7245	4.6585	4.5974	4.5463	4.4217	4.3675	4.3353
	K	5.0833	5.0382	4.9908	–	4.8687	–	4.7539	4.6238	–	4.5334
	Rb	5.0833	5.0382	4.9914	–	4.8709	–	4.7564	4.6241	–	4.5294
	Cs	5.0813	5.0377	4.9920	–	4.8733	–	4.7599	4.6279	–	–
${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}$(V)	X = Cl	1.9364	1.9089	1.8799	1.8435	1.7966	1.7562	1.7262	1.6501	1.6222	1.6108
	Br	2.0862	2.0566	2.0254	1.9861	1.9356	1.8920	1.8597	1.7777	1.7477	1.7354
	I	2.3109	2.2780	2.2435	2.2000	2.1441	2.0958	2.0599	1.9692	1.9359	1.9223
$\Delta G^0_t(+)_{\mathrm{m}}$	M = Li	–	3.869	7.873	–	18.419	–	28.116	38.777	–	46.631
	Na	–	4.386	8.953	14.257	20.628	26.521	31.448	43.476	48.698	51.810
	K	–	4.351	8.925	–	20.706	–	31.782	44.335	–	53.057
	Rb	–	4.351	8.867	–	20.493	–	31.541	44.306	–	53.443
	Cs	–	4.207	8.616	–	20.069	–	31.010	43.746	–	–
$\Delta G^0_t(-)_{\mathrm{m}}$	X = Cl	–	2.655	5.450	8.962	13.488	17.393	20.288	27.628	30.319	31.415
	Br	–	2.860	5.871	9.655	14.531	18.738	21.857	29.765	32.664	33.845
	I	–	3.168	6.504	10.695	16.096	20.756	24.211	32.971	36.181	37.490

TABLE 10

Absolute electrode potential, radius of solvated cation, extent of solvation in methanol + water solvents, and transfer free energies of individual ions from water to these solvents, at 25 °C, all calculated by method II, using the reported data by Feakins and Voice [12] (ΔG_t^0 values (kJ mol^{-1}) are on the molal scale)

MeOH (wt%) =		0	10	20	30	40	50	60	80	90	99
Corr (10^{-2})		99.8951	99.8912	99.8859	99.8915	99.8988	99.8907	99.9141	99.9305	99.9478	99.9175
ΔE_m^0(mV)	X = Cl	+5.5	+5.6	+5.6	+5.4	+5.0	+5.1	+4.5	+3.9	+3.3	+4.1
	Br	−9.9	−10.0	−10.1	−9.6	−9.1	−9.2	−8.0	−6.9	−5.9	−7.3
	I	+4.4	+4.4	+4.5	+4.3	+4.0	+4.0	+3.6	+3.0	+2.6	+3.2
a_2^0(10^{-10} V m)		4.1970	4.1372	4.0742	3.9956	3.8942	3.8061	3.7421	3.5779	3.5183	3.4922
r_+ (10^{-10} m)	M = Li	4.399	4.246	4.088	–	3.642	–	3.330	3.033	–	2.948
	Na	6.736	6.484	6.226	5.883	5.440	5.117	4.936	4.472	4.362	4.365
	K	5.032	4.871	4.706	–	4.205	–	3.875	3.570	–	3.499
	Rb	5.032	4.871	4.702	–	4.195	–	3.865	3.570	–	3.513
	Cs	5.045	4.874	4.700	–	4.184	–	3.851	3.556	–	–
S_e(10^{-10} m)	M = Li	3.80	3.65	3.49	–	3.04	–	2.73	2.43	–	2.35
	Na	5.79	5.53	5.28	4.93	4.49	4.17	3.99	3.52	3.41	3.42
	K	3.70	3.54	3.38	–	2.87	–	2.54	2.24	–	2.17

	Rb	3.55	3.39	3.22	–	2.71	–	2.38	2.09	–	2.03
	Cs	3.35	3.18	3.01	–	2.49	–	2.16	1.87	–	–
$-{}^{\mathrm{Red}}_{\mathrm{L}}E^0_{\mathrm{m}}(\mathrm{V})$	M = Li	0.9541	0.9744	0.9967	–	1.0693	–	1.1238	1.1797	–	1.1848
	Na	0.6230	0.6380	0.6544	0.6792	0.7159	0.7438	0.7581	0.8000	0.8067	0.8001
	K	0.8340	0.8493	0.8657	–	0.9261	–	0.9658	1.0021	–	0.9982
	Rb	0.8340	0.8493	0.8664	–	0.9283	–	0.9683	1.0023	–	0.9942
	Cs	0.8320	0.8488	0.8669	–	0.9307	–	0.9718	1.0062	–	–
${}^{\mathrm{Red}}_{\mathrm{R}}E^0_{\mathrm{m}}(\mathrm{V})$	X = Cl	2.3188	2.2858	2.2509	2.2075	2.1515	2.1028	2.0675	1.9767	1.9438	1.9294
	Br	2.1523	2.1216	2.0893	2.0490	1.9970	1.9519	1.9190	1.8348	1.8043	1.7909
	I	1.9431	1.9154	1.8862	1.8498	1.8029	1.7621	1.7324	1.6564	1.6288	1.6168
$\Delta G^0_t(+)_{\mathrm{m}}$	M = Li	–	1.968	4.120	–	11.125	–	16.383	21.777	–	22.269
	Na	–	1.448	3.026	5.416	8.961	11.655	13.033	17.076	17.717	17.082
	K	–	1.476	3.059	–	8.886	–	12.717	16.219	–	15.843
	Rb	–	1.476	3.126	–	9.098	–	12.958	16.238	–	15.457
	Cs	–	1.621	3.367	–	9.523	–	13.489	16.808	–	–
$\Delta G^0_t(-)_{\mathrm{m}}$	X = Cl	–	3.189	6.547	10.739	16.143	20.837	24.252	33.004	36.181	37.571
	Br	–	2.960	6.077	9.968	14.984	19.341	22.510	30.634	33.583	34.873
	I	–	2.672	5.486	8.999	13.527	17.461	20.322	27.656	30.318	31.483

partly to the misuse of radii of nonsolvated cations which, as will be seen in Tables 9 and 10, are strongly solvated, on the other hand.

Feakins and co-workers [6–12] reported that ΔG_t^0 values should be additive in, i.e., the sum of, the values for the ion constituents which are positive for anions and negative for cations. This means that while the first is based on the reduction potential scale, the second is based on the oxidation scale (see eqns. 29-II and 30-II), i.e., on two different scales, which is impractical. This is equivalent to the difference between single ion values both based on the same type of potential scale (eqn. 30-II). Therefore, their [6–12] $\Delta G_t^0(\mathrm{i})$ values are actually positive for both anions and cations, and not as reported [6–12], based on the reduction potential scale. This may explain why positive and negative values were obtained by different investigators [4] for the same thermodynamic property of a single ion. In all cases, the difference between ΔG_t^0 values for two electrolytes having a common ion would be the same.

The assumption that the ionic radii of nonsolvated aqueous Cl^-, Br^- and I^- ions remain the same in MeOH + water solvents is seen to be reasonable (Tables 6 and 7). However, this assumption cannot be made for cationic radii because the cations are strongly solvated (Tables 9 and 10). Thus, eqns. (28)–(30) may be reduced to

$$\Delta G_t^0 = \Delta G_t^0(+) - \Delta G_t^0(-) = F\left[{}^{w}(a_1^0 r_+) - {}^{s}(a_1^0 r_+)\right] - F\left[{}^{w}(a_1^0) - {}^{s}(a_1^0)\right] r_- \tag{41-I}$$

or

$$\Delta G_t^0 = \Delta G_t^0(-) - \Delta G_t^0(+) = F\left[{}^{w}(a_2^0) - {}^{s}(a_2^0)\right]/r_- - F\left[{}^{w}(a_2^0/r_+) - {}^{s}(a_2^0/r_+)\right] \tag{41-II}$$

These equations show that the transfer free energies for the halogen acids from water to any solvent vary linearly with r_- or $1/r_-$, respectively.

Equation (41-II) may be compared with Feakins' [6] eqns. (1) and (2). Equation (1) is a simple form of eqn. (41-II), and must be rewritten as

$$\Delta G_t^0 = a r_a^{-1} - \Delta G_t^0(\mathrm{H}^+) \tag{42}$$

on the molal scale, whereas eqn. (2) cannot be applied to cations using the Pauling set [26] of nonsolvated ionic radii since both ${}^{w}r_+$ and ${}^{s}r_+$ (i.e., two variables) vary from one cation to another, and ${}^{s}r_+$ values vary strongly with solvent composition (Tables 9 and 10). This may be responsible for the deviation from linearity, observed in such cases [12]. Thus, plots of ΔG_t^0 against r_c^{-1}, reported by Feakins and co-workers [6–12] cannot be accepted.

Standard absolute potential of $M|M^+$ electrodes and $\Delta G_t^0(M^+)$ values in methanol + water solvents

The studies have been extended to the cell

$$\mathrm{M|MX,\ solvent|AgX|Ag} \tag{ii}$$

where M = Li, Na, K, Rb and Cs, and X = Cl, Br and I. The standard EMFs of cell (**ii**) were reported in aqueous [16] as well as in MeOH + water [12] solvents. Thus, the results of calculations by methods I and II are recorded in Tables 9 and 10, respectively.

Table 9 shows that both ${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_{\mathrm{m}}$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_{\mathrm{m}}$ values decrease with increasing MeOH content in the solvent. This is reflected by the increasing values of $\Delta G^0_{\mathrm{t}}(+)$ and $\Delta G^0_{\mathrm{t}}(-)$ in the same direction. The solvation extent (S_{e}) has been calculated as the difference between the r_+ values obtained and the Pauling [26] ionic radii (r_{P}) of nonsolvated ions in the aqueous medium [25].

$$S_{\mathrm{e}} = r_+ - r_{\mathrm{P}} \tag{43}$$

The variation of r_+ (and thus, S_{e}) with solvent composition shows a slight maximum at around 90% MeOH. A very interesting feature seen in Table 9 is that the extent of solvation, in any solvent, increases in the expected well-known order: $\mathrm{Cs}^+ < \mathrm{Rb}^+ < \mathrm{K}^+ < \mathrm{Na}^+ < \mathrm{Li}^+$, and that the Li^+ ion is always highly solvated.

Method II treatment of the data shows that the plots of E^0_{m} against $1/r_-$ gave practically perfect straight lines with positive slopes and positive intercepts, which means that the ${}^{\mathrm{Red}}_{\mathrm{L}}E^0_{\mathrm{m}}$ values are negative. The reduction potential, of course, may be positive or negative. Thus, eqn. (14-II) may be written as

$$E^0_{\mathrm{m}} = \left(a^0_2/r_-\right) - \left(-a^0_2/r_+\right) \tag{44}$$

where the reduction potential of the left electrode is $(-a^0_2/r_+)$, and so, eqn. (14-II) may be written in the more general form

$$E^0_{\mathrm{m}} = \left(\pm a^0_2/r_-\right) - \left(\pm a^0_2/r_+\right) \tag{45}$$

It is evident from Table 10 that the reduction potentials of the right electrode decrease, whereas those of the left electrode decrease negatively to minima at around 90% MeOH and thereafter increase, with increasing MeOH content in the solvent. This is reflected in the values of $\Delta G^0_{\mathrm{t}}(-)$ and $\Delta G^0_{\mathrm{t}}(+)$. For any M^+ ion, the variation of the radius of solvated cation, and thus the extent of solvation, with solvent composition shows a slight minimum at around 90% MeOH. In any solvent, the expected order of increasing solvation is inverted for Li^+ and Na^+ ions. It is well-known that this is not the case [2,6]. Thus, this interesting feature, again sheds more light on the inapplicability of method II for such calculations and gives further evidence that all thermodynamic calculations based on $1/r$ relationships may be inadequate, and need a major revision. There is now every reason that method II cannot be accepted for the calculation of thermodynamic properties of single ions.

CONCLUSION

It is now evident that the standard hydrogen electrode potential is not zero either at all temperatures or in all solvents. Keeping in mind all features covered in the text, the author feels that method I must be preferable to method II and has to apply to EMF data for the determination of absolute electrode potentials and the thermodynamics of single ions in aqueous, partially aqueous, and non-aqueous media. However, if method II, or if both methods I and II, cannot be acceptable for this aim, it should be pointed out that all thermodynamic quantities of individual ions calculated by Izmailov [5], Feakins and co-workers [6–12] and deLigny and Alfenaar [13] as well as all workers in the field following the same procedure, cannot be considered as acceptable values.

The purpose of this paper has been to present the above theoretical derivation, demonstrate the agreement of its predictions with experimental data, and to illustrate how it can provide useful insights into the thermodynamics of single ions. Thus, the author has considered the EMF data for the halogen acids and alkali-metal halides, and restricted the discussion to the aqueous and methanol + water systems. Results for other systems, including both protic and aprotic partially aqueous and non-aqueous solvents, are in general agreement with those obtained in this work, show the same general trends, and reflect the same interesting features. Discussion of these solvent systems will be deferred to later papers.

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