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THE EXTRAPOLATION OF EMF DATA TO INFINITE DILUTION IN NON- AQUEOUS AND MIXED SOLVENTS

(Technical Report)

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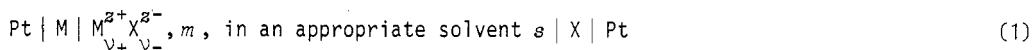
The extrapolation of EMF data to infinite dilution in non-aqueous and mixed solvents

1. INTRODUCTION

The standard electromotive force (emf) of a voltaic cell, E° , is of fundamental importance in both theoretical and applied electrochemistry. It is well known that E° is strongly dependent on the solvent of the supporting electrolyte, and this fact was rationalised in terms of the so-called primary medium effect (refs. 1-4). Among the various solvents, needless to say, water has the greatest importance and aqueous electrolyte solutions take the lion's share of practical cases. The need and convenience of reading and quoting ion-responsive electrode potentials E_i versus some reference electrode potential E_{ref} prompted the introduction of the (conventional) standard electrode potentials E_i° . The convention which IUPAC promulgated in Stockholm, 1953, of $E^\circ(\text{H}^+/\text{H}_2) = 0$ in water at all temperatures (refs. 5,6), has become generally accepted and used. Parallel electrochemical series could be set up to each and every nonaqueous or mixed solvent, by repeating the convention that $E^\circ(\text{H}^+/\text{H}_2) = 0$ in it, but with no thermodynamic basis of intercomparison. Several experimental schemes have recently been combined with extrathermodynamic assumptions for the intercomparison of E_i° 's in different solvents with ultimate reference to the conventional aqueous scale (refs. 7-10). This problem of the intercomparison of E_i° 's is, however, outside the scope of the present document and has been dealt with in specific separate documents (ref. 11).

1.1 The determination of the standard emf E° may be required for cells of the types presented below.

1.1.1 The *general cell* can be represented as:



and its emf E can be expressed by the Nernstian equation as:

$$E = E^\circ - (\nu RT / \nu_+ z_+ F) \ln(Z m \gamma_{\pm}) \quad (2)$$

where $m / (\text{mol} \cdot \{\text{kg solvent}\}^{-1})$ is the molality of the electrolyte $\text{M}_{\nu_+}^{\text{z}+} \text{X}_{\nu_-}^{\text{z}-}$, γ_{\pm} is the corresponding mean molal activity coefficient, $\nu = \nu_+ + \nu_-$, $\nu_+ z_+ = \nu_- |z_-|$, $Z = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}$, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is the gas constant, $F = 96485.3 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}$ is Faraday's constant, and T is the absolute temperature.

1.1.2 The $\text{M}^{\text{z}+}/\text{M}$ electrode, or the $\text{X}/\text{X}^{\text{z}-}$ electrode, or both, may be *gas electrodes*, in which case the partial pressure of the gas/gases involved in the measured cell emf E must be normalised to the standard pressure so that in the emf expression any term in gas pressure is eliminated.

1.1.3 If the M^{z+}/M electrode is an amalgam electrode $M^{z+}/M \text{ Hg}_{1-x}$, then E depends also on the mole fraction x of the metal M in the amalgam, and this dependence must be dealt with by an extrapolation to $x = 0$ (ref. 12).

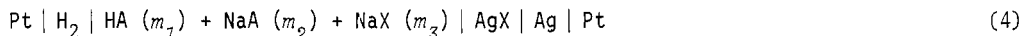
1.1.4 The X/X^{z-} electrode may be a halogen electrode with $X = \text{Cl}_2$ (gas), Br_2 (liquid), or I_2 (solid). Since the reactions $X_2 + X^- = X_3^-$ and $X_3^- + X_2 = X_5^-$ (with the respective equilibrium constants K_3 and K_5) occur in the solutions, the ions X_3^- and X_5^- must be accounted for in addition to M^{z+} and X^- . Methods were described to obtain simultaneously E° and K_3 (ref. 13).

1.1.5 If the cell is of the type:



the electrolyte of this cell has three ions (H^+ , HSO_4^- and SO_4^{2-}) due to the incomplete second ionisation (of constant K_2) of H_2SO_4 , although H_2SO_4 is formally regarded as a binary electrolyte as far as its γ_{\pm} is concerned. The HSO_4^- ion must be accounted for by preliminary knowledge of K_2 in iterative calculations, to obtain E° (ref. 14).

1.1.6 The buffered cell (refs. 15-17):



which is extensively used to determine the ionisation constant K of a weak acid HA , has an emf expression of the type:

$$E = E^\circ - (RT/F) \ln(m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{X}^-} \gamma_{\text{X}^-}) = E^\circ - (RT/F) \{ \ln(m_{\text{X}^-} m_{\text{HA}} / m_{\text{A}^-}) + \ln(\gamma_{\text{X}^-} \gamma_{\text{HA}} / \gamma_{\text{A}^-}) + \ln K \} \quad (5)$$

where the γ_{\pm} and γ_{\pm} are single-ion activity coefficients that cannot be combined in an expression of the form

$$\gamma_{+} \gamma_{-} = \gamma_{\pm}^2 \quad (6)$$

to give the mean activity coefficient γ_{\pm} of some strong acid HX . The ionisation constant K can be obtained from the measured E 's through a simple elaboration and extrapolation of equation (5) to infinite dilution of the mixed $\text{HA} + \text{NaA} + \text{NaX}$ electrolyte, provided that E° is already known. But the procedure can well be reversed to determine E° from preliminary knowledge of K . This is indeed occasionally done (ref. 18).

1.2 The procedure described in the present document is applicable when the simple expression (2) holds, with γ_{\pm} of the general binary electrolyte $M_{\nu_+}^{z+} X_{\nu_-}^{z-}$, namely for cell (1) in the general case 1.1.1 and for the subcases 1.1.2 and 1.1.3. The extrapolation to $m = 0$ of

$$E' = E + (\nu k / \nu_{+} z_{+}) \log(Zm) = E^\circ - (\nu k / \nu_{+} z_{+}) \log \gamma_{\pm}, \quad (7)$$

where $k = (\ln 10) RT/F$, should give E° as the intercept, since at infinite dilution $\log \gamma_{\pm} = 0$. Such an extrapolation is, however, seldom linear and is, hence, impractical. It is preferable, therefore, to express $\log \gamma_{\pm}$ as a function of the molality m , and include in E' that part of $\log \gamma_{\pm}$ (times the factor $\nu k / \nu_{+} z_{+}$) that does not involve unknown parameters, and leave on the right-hand side of equation (7) that part of $\log \gamma_{\pm}$ that does. It has long been common practice to invoke the Debye-Hückel theory of activity coefficients to express the dependence of $\log \gamma_{\pm}$ on the concentration.

Such theory, in its extended form, specifies that:

$$\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{\frac{1}{2}} / (1 + \alpha_0 B I^{\frac{1}{2}}) - \log(1 + \nu m M_g) + b_0 I \quad (8)$$

where A and B are parameters given by the theory, a_0 is an adjustable parameter related to the distance of closest approach of ions, b_0 is a second adjustable parameter related to short-range ion-solvent interactions, M_g is the molar mass of the solvent (the contribution of the $\log(1 + \nu m M_g)$ term becomes negligible at sufficiently low molalities m), and I is the (molal) ionic strength of the solution:

$$I = 0.5 \sum (m_i z_i^2) \quad (9)$$

where m_i is the molality of the ionic species i and z_i its charge number. (A parallel ionic strength $I_c = 0.5 \sum (c_i z_i^2)$ defined on the molar scale (c_i , in $\text{mol} \cdot \text{dm}^{-3}$) is very popular, especially in conductimetric studies, and here will be used in connection with equation (19)).

Equation (8) fits activity coefficient data very well in the range of molalities that is relevant for the extrapolations discussed here, at least in aqueous solutions where it was tested extensively. The extrapolation is then carried out according to:

$$\begin{aligned} E'' &= E + (\nu k / \nu_+ z_+) \{ \log(Zm) - |z_+ z_-| A I^{1/2} / (1 + \alpha_0 B I^{1/2}) - \log(1 + \nu m M_g) \} = \\ &= E^\circ - (\nu k / \nu_+ z_+) b_0 I \end{aligned} \quad (10)$$

where E'' is a linear function of I and, covering a relatively large I range, lends itself much better for the extrapolation than E' in equation (7). Equation (10) was employed in many studies, now classical, that established standard electrode potentials in aqueous solutions. For its application, values of the adjustable parameter a_0 were tried until satisfactory linearity of E'' with I was attained. Such studies are described, for instance, in the books of Harned and Owen (ref. 19) and of Robinson and Stokes (ref. 20). This equation is, in principle, not limited to aqueous solutions, provided that the electrolyte remains fully dissociated into ions and that the dependence of A and B on the nature of the solvent, through its relative permittivity ϵ_g and density ρ_g , is taken into account. When the provision of full dissociation of the electrolyte breaks down, as when organic solvents or aqueous-organic solvent mixtures with low permittivities are used, then equation (10) no longer yields satisfactory results. Whereas there have been no noteworthy attempts to replace equation (10) with alternative expressions to extrapolate E° in aqueous solutions, several alternatives were proposed for organic or aqueous-organic solvent mixtures. These employ expressions for $\log \gamma_{\pm}$ appearing on the right-hand side of equation (7) that differ from equation (8), examples being shown in Table 1. These expressions do, however, not take explicit cognizance of the ion association that takes place in solvents of low relative permittivity at the concentrations used in emf measurements. Harned and Owen (ref. 37) replaced equation (2) by:

$$E = E^\circ - (\nu k / \nu_+ z_+) \log(Z \alpha m \gamma_\alpha) \quad (11)$$

where α is the degree of ionisation, *i.e.* the fraction of the electrolyte dissociated into ions, and γ_α the mean molal activity coefficient of the solute as a strong electrolyte at an ionic molality m_α . Janz and coworkers (refs. 38,39) used equation (11), with $\alpha m \gamma_\alpha$ replaced by $\alpha c y_\alpha$, (c is the concentration of the electrolyte and y_α the corresponding mean activity coefficient on the molar scale, $\text{mol} \cdot \text{dm}^{-3}$) to obtain E_c° on the molar scale [$E_c^\circ = E_m^\circ + (\nu k / \nu_+ z_+) \log \rho_g$, where ρ_g is the solvent density, and the subscript m denotes the usual molal scale, $\text{mol} \cdot \text{kg}^{-1}$]. The Gronwall, LaMer and Sandved's extension (ref. 35) to the Debye-Hückel activity coefficient expression was used (refs. 38,39) to calculate y_α , and an experimental value for the (molar scale) association constant K_c to calculate α , in an iterative procedure. This approach

has, however, not seen extensive used since then.

Ion association to ion pairs has been recognized as a phenomenon that takes place in solutions of highly charged electrolytes ($|z_+z_-| \geq 3$) even in water and of even 1:1 electrolytes in solvents of low relative permittivity. The dependence of the degree of association ($1 - \alpha$) on the concentration is given by the mass-law expression

$$(1 - \alpha) = K_c \alpha^2 c y_\alpha^2 \quad (12)$$

Equation (12) can be solved for α in terms of the product $x = K_c c y_\alpha^2$

$$\alpha = \{(1 + 4x)^{\frac{1}{2}} - 1\} / (2x) \quad (13)$$

However, y_α depends on α , so that equation (13) is an implicit equation, and, furthermore, there is no general agreement on the dependence of K_c on the nature of the solvent. Table 2 shows that α values appreciably lower than unity are obtained for relatively low concentrations, $c > 0.01 \text{ mol} \cdot \text{dm}^{-3}$, at moderately low values of the relative permittivity, $\epsilon_s < 35$.

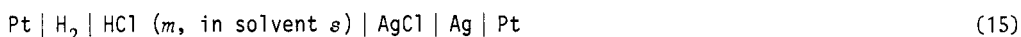
The distance of closest approach of ions, a_0 , that appears in equation (8) and in several of the expressions shown in Table 1, was generally used as a free parameter. This is true for the simpler expressions and for those that involve the terms ext, *i.e.* the extended terms expression according to Gronwall, LaMer and Sandved (ref. 35), which is very complicated. The recent trend in one branch of electrochemistry, that of pH measurements, is not to permit such freedom in a_0 . This pertains both to aqueous solutions (ref. 40) and to water-rich aqueous-organic solvent mixtures (ref. 41). [The burden of fitting individual experimental data can be left to the second adjustable parameter, b_0 , in the activity coefficient expression]. Rather than employ the theoretical value of B and a free choice of a_0 in equation (8), the product Ba_0 was fixed to have the value of $1.5 \text{ kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}}$ exactly in aqueous solutions at all temperatures $273.15 \leq T/K \leq 373.15$. In other solvents this quantity was consequently assigned (ref. 41), at the operating temperature, the value:

$$Ba_0 / (\text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}}) = 1.5 \{ \epsilon_w \rho_s / \epsilon_s \rho_w \}^{\frac{1}{2}} \quad (14)$$

where the subscript w stands for water and s for any solvent, including aqueous organic mixtures.

2. SUGGESTED PROCEDURE FOR CELLS INVOLVING A 1:1 ELECTROLYTE

It is suggested that international agreement be sought on an extrapolation procedure to obtain the standard emf E° from the measured emf's E of reversible cells under conditions where appreciable association may take place. For the sake of simplicity, the case of cells involving a 1:1 electrolyte (*i.e.* one where $z_+ = |z_-| = 1$, hence $Z = 1$ in equation (2)), is dealt with first. This is a very common case, and much work was reported on a cell such as (ref. 42) :



or similar cells involving other hydrohalic acids and the corresponding sparingly soluble salts, among others (ref. 43). The following three facts are taken into account: a multitude of extrapolation procedures have been used in the past (see Table 1), ions association prevails under the conditions of many of these studies (see Table 2), and some consensus has been reached on how to deal with water-rich organic solvent solutions involving a 1:1 electrolyte [see equation (14)].

TABLE 1 - Alternative expressions for the mean *molar* activity coefficient γ_{\pm} used for the extrapolation of standard emf E° values in the case of 1:1 electrolytes, where $z_{+} = |z_{-}| = 1$, and $I \equiv m$ and $I_c \equiv c$ for the molal-scale and molar-scale ionic-strength, respectively.

Expression for $\log \gamma_{\pm} =$	References
$-Am^{\frac{1}{2}} + b''m$	24,34
$-A_c m^{\frac{1}{2}} / (1 + a_0 B_c m^{\frac{1}{2}})$	23
$-A_c m^{\frac{1}{2}} / (1 + m^{\frac{1}{2}}) + b'_0 m$	23
$-Am^{\frac{1}{2}} / (1 + a_0 B m^{\frac{1}{2}}) - \log(1 + 2mM_s) + b_0 m$	25,26,27
$-Am^{\frac{1}{2}} / (1 + a_0 B m^{\frac{1}{2}}) - \log(1 + 2mM_s) + b_0 m + \text{ext}$	30,31,35
$-A_c c^{\frac{1}{2}} / (1 + a_0 B_c c^{\frac{1}{2}}) - \log(1 + 2mM_s) + b_0 m$	28
$-A_c c^{\frac{1}{2}} / (1 + a_0 B_c c^{\frac{1}{2}}) - \log(1 + 2mM_s) + b_0 c + \text{ext}$	29,35
$-Ac^{\frac{1}{2}} / (1 + a_0 Bc^{\frac{1}{2}}) + \log(c/m\rho_s)$	36
$-A^* m^{\frac{1}{2}} + B^* m + C^* m + \dots$	32,33
$-A^* c^{\frac{1}{2}} + b^* c + \log(c/m\rho_s)$	21,22

N.B. $A = A_c \rho_s^{\frac{1}{2}}$, $B = B_c \rho_s^{\frac{1}{2}}$, A^* , B^* , C^* , a_0 , b_0 , b'_0 , b''_0 and b^* are concentration-independent constants, M_s is the molar mass of the solvent ($\text{kg}\cdot\text{mol}^{-1}$) and ρ_s its density ($\text{kg}\cdot\text{dm}^{-3}$), and ext are further terms in the extended Debye-Hückel equation as proposed by Gronwall and coworkers (ref. 35).

TABLE 2 - Values of the degree of dissociation, α , of a 1:1 electrolyte at 298.15 K in solvents of specified permittivities, ϵ_s , and at specified molar concentrations, $c/(\text{mol}\cdot\text{dm}^{-3})$, in terms of the association constants K_c (according to equations (19) and (23) to (30)).

ϵ_s	50	45	40	35	30	25	20	15	10
$\log K_c$	0.251	0.551	0.912	1.131	1.434	1.794	2.248	2.917	4.306
	α								
c									
0.001	0.997	0.995	0.995	0.983	0.965	0.921	0.807	0.547	0.1500
0.002	0.995	0.991	0.979	0.964	0.928	0.848	0.682	0.405	0.1032
0.005	0.988	0.975	0.944	0.907	0.827	0.689	0.499	0.259	0.0616
0.01	0.973	0.947	0.886	0.826	0.702	0.541	0.356	0.177	0.0411
0.02	0.942	0.888	0.785	0.695	0.553	0.399	0.249	0.119	0.0272
0.05	0.846	0.743	0.596	0.496	0.365	0.248	0.147	0.068	0.0154
0.1	0.719	0.591	0.445	0.352	0.253	0.167	0.093	0.044	0.0100
0.2	0.562	0.437	0.314	0.242	0.172	0.109	0.062	0.028	0.0064
0.5	0.365	0.271	0.188	0.141	0.097	0.061	0.034	0.015	0.0035
1	0.249	0.182	0.124	0.092	0.063	0.039	0.021	0.009	0.0022

The present state of electrolyte theory does not provide compelling reasons for the choice of any expression for the activity coefficient $\log \gamma_{\pm}$ or for the dependence of the association constant K_c on the nature of the solvent. The criteria for the choice of the semi-empirical extrapolation procedure should therefore be its conformity with accepted practice, as far as possible, and convenience. The procedure is described in terms of *molar* concentrations, c , rather than molalities, m , since the theoretical expressions at the basis of the semi-empirical

procedure involve the number of particles per unit volume. The relationship between the two scale is:

$$c = m\rho/(1 + mM) \quad (16)$$

where ρ is the density of the solution (not of the solvent) in $\text{kg}\cdot\text{dm}^{-3}$ and M the molar mass of the solute electrolyte in $\text{kg}\cdot\text{mol}^{-1}$. Also,

$$E_m^\circ = E_c^\circ - 2k \log \rho_s \quad (17)$$

where for the 1:1 electrolyte $\nu = 2$ and $Z = 1$, and ρ_s is the density of the solvent. The E measurements reported in the literature or obtained in the laboratory as a function of m are first submitted to the m to c conversion by equation (16), then a suitable function of E is extrapolated to obtain E_c° , which is finally converted to E_m° , if so desired, by equation (17). The Nernst equation is now written in the form:

$$E = E_c^\circ - 2k \log(\alpha c) - 2k \log y_\alpha \quad (18)$$

and the mean ionic activity coefficients y_α are written in analogy with equation (8) in the form:

$$\log y_\alpha = -A_c(\alpha c)^{\frac{1}{2}} / \{1 + B_c q(\alpha c)^{\frac{1}{2}}\} + Cc \quad (19)$$

where, on the molar scale, $A_c = A\rho_s^{-\frac{1}{2}}$, $B_c = B\rho_s^{-\frac{1}{2}}$ and for the ionic strength of the partly associated 1:1 electrolyte $I_c = \alpha c$. The parameters A_c and B_c are given their values according to the Debye-Hückel theory and the quantity $B_c q$ is given its value according to the Bjerrum theory of ion association. Reasons have been presented (ref. 44) for giving preference to this theory over others. The Debye-Hückel expression (19) is seen to apply to the ionized part of the electrolyte beyond the distance $q = e^2/(8\pi\epsilon_0\epsilon_s k_B T)$ that replaces the distance of closest approach a_0 which applies for completely dissociated electrolytes. The extrapolation function is, therefore:

$$E' = E + (k'T) \log(\alpha c) - (k'T)A'(\epsilon_s T)^{-3/2}(\alpha c)^{\frac{1}{2}} \{1 + B'(\epsilon_s T)^{-3/2}(\alpha c)^{\frac{1}{2}}\}^{-1} = E_c^\circ - C'c \quad (20)$$

where C' is a free parameter (the only one in this treatment). It takes care of the linear term in electrolyte concentration in equation (8), of the activity coefficient of the unionized part of the electrolyte, and of the conversion from molal to molar activity coefficients:

$$y = (1 + mM)\rho_s \gamma_{\pm} / \rho = m\rho_s \gamma_{\pm} / c \quad (21)$$

The above parameters have the following values:

$$k' = 2(\ln 10)R/F = 3.96845 \times 10^{-4} \text{ V}\cdot\text{K}^{-1} \quad (22)$$

$$A' = A_c(\epsilon_s T)^{3/2} = e^3 N_A^{\frac{1}{2}} (5/\epsilon_0 k_B)^{3/2} / (\pi \ln 10) = 1.82482 \times 10^6 \text{ dm}^{3/2} \cdot \text{K}^{3/2} \cdot \text{mol}^{-\frac{1}{2}} \quad (23)$$

$$B' = A'(\ln 10) = B_c e^2 (\epsilon_s T)^{\frac{1}{2}} (\epsilon_0 k_B)^{-1} \times 10^2 / 8\pi = 4.20179 \times 10^6 \text{ dm}^{3/2} \cdot \text{K}^{3/2} \cdot \text{mol}^{-\frac{1}{2}}, \quad (24)$$

(the values of the fundamental constants employed are from ref. 45), and $C' = (k'T)C$ is the fitted slope of the linear extrapolation. The characterizing variable in equations (19) and (20) is α which can, through equation (13), be obtained from the value of the association constant K_c . Frequently, experimental values of K_c are unavailable, and in these cases K_c can be evaluated as a function of solvent properties by the following procedure.

According to Bjerrum's theory,

$$K_c = K'(\epsilon_s T)^{-3} Q(b) \quad (25)$$

where

$$K' = N_A e^6 (10/\epsilon_0 k_B)^3 / (4\pi)^2 = 3.53101 \times 10^{13} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{K}^3 \quad (26)$$

and

TABLE 3 - Values of some properties of water as a function of temperature

property	value	ref.
ϵ_w	= 78.46 at 298.15 K and 0.101325 MPa	46
ρ_w	= 0.997045 kg·dm ⁻³ at 298.15 K and 0.101325 MPa	47
(ϵ_w/ρ_w)	= {78.46 - 0.3595× ΔT - 0.0007×(ΔT) ² }/ /{0.997045 - 0.0002564× ΔT - 0.000004812×(ΔT) ² + + 2.8736×10 ⁻⁸ ×(ΔT) ³ - 1.4456×10 ⁻¹⁰ ×(ΔT) ⁴ } dm ³ ·kg ⁻¹ (where $\Delta T = T/K - 298.15$), valid at 0.101325 MPa pressure and 273.15 ≤ T/K ≤ 373.15	48

TABLE 4 - The standard emf's E° of some cells of the type Pt|H₂|HX (*m* or *c*) in solvent *s* | AgX|Ag|Pt, obtained by the proposed extrapolation procedure, compared with the literature values

X	solvent (mass % in H ₂ O)	ϵ_s	T/K	K_c	E°/V this work	E°/V literature	ref.	
Br (<i>m</i>)	methanol (43.12)	59.4	298.15	none	0.0565±0.0015	0.0560	25	
	(<i>m</i>) monoglyme (30)	87.1	278.15	none	0.0771±0.0000	0.0774	49	
	(<i>m</i>) monoglyme (50)	45.8	328.15	none	0.0156±0.0001	0.0163	49	
Cl (<i>c</i>)	methanol (90)	37.91	298.15	4.7	0.1034±0.0006	0.1030	29	
	(<i>m</i>) ethanol (40)	66.2	263.15	none	0.21395±0.00007	0.21395±0.00009	52	
	(<i>c</i>) ethanol (90)	29.92	288.15	21.4	0.0997±0.0006	0.0957	29	
	(m) 1,4-dioxane (70)		20.37	273.15	130.9	0.1066±0.0006	0.1058±0.0003	50
			15.37	323.15	235.0	0.0177±0.0007	0.0175±0.0003	50
	(m) 1,4-dioxane (82)		10.52	278.15	334.0	-0.0066±0.0003	0.0025±0.0010	51
			9.53	298.15	434.0	-0.0525±0.0002	-0.0415±0.0010	51
		8.62	318.15	600.0	-0.1033±0.0004	-0.0925±0.0010	51	

$$Q(b) = \int_2^b t^{-4} \exp(t) dt \quad (27)$$

The integrand contains t as an auxiliary variable, and the integral is readily evaluated numerically to the limit of integration b . This quantity is given by the theory as:

$$b = (e^2/\epsilon_0 k_B) (\epsilon_s T)^{-1} a_0^{-1} 10^2 / (4\pi) \quad (28)$$

and depends on the properties of the solvent via ϵ_s and also a_0 , which is given by equation (14). The explicit form of b is:

$$b = b' \rho_w^{1/2} \epsilon_s^{-1} \epsilon_w^{-1/2} T^{-3/2} \quad (29)$$

with

$$b' = N_A^{1/2} e^3 (5/\epsilon_0 k_B)^{3/2} (1.5\pi)^{-1} = 5.60239 \times 10^6 \text{ mol}^{-1} \cdot \text{dm}^{3/2} \cdot \text{K}^{3/2} \quad (29)$$

Input data required for the calculation are the temperature T/K , the solvent density $\rho_s / (\text{kg} \cdot \text{dm}^{-3})$, and the relative permittivity ϵ_s of the solvent at this temperature. The ratio of the

relative permittivity of water to its density, (ϵ_w/ρ_w) at the temperature T is obtained from the expression given in Table 2. These data enable b to be calculated from equations (29) and (30), hence the integral $Q(b)$ numerically from equation (27), and then the association constant K_c from equations (25) and (26). Further input data are a set of corresponding values of: m , the molality ($\text{mol}\cdot\{\text{kg solvent}\}^{-1}$) of the 1:1 electrolyte in the cell, to the ions of which the electrodes are reversible; ρ , the density ($\text{kg}\cdot\text{dm}^{-3}$) of the cell solution; and E , the measured emf (in V) of the cell. From the related m and ρ data the corresponding molar concentrations c ($\text{mol}\cdot\text{dm}^{-3}$) of the cell electrolyte above are calculated by means of equation (16). The cycle of iterative calculations involving these concentrations can be summarized as follows: (i) From K_c (whether experimental or calculated from Bjerrum's theory through equations (25) to (30), and setting initially $y_{\pm} = 1$ and $x = K_c c$, a first value of α is calculated from equation (13); (ii) This value of α is inserted into equation (19), ignoring the cC term, to obtain a first value of $\log y_{\pm}$, from which $x = K_c c y_{\pm}$ and a better α value are obtained from equation (13); (iii) This calculation is repeated iteratively until a pair of α and $\log y_{\pm}$ is obtained of a desired level of constancy. This cycle of iterations is repeated at each concentration c . Since equation (19), and hence equation (20), is semi-empirical, any inadequacies in the α values (and $\log y_{\pm}$) due to the neglect of the term in C at this stage are covered up by the final regression analysis of E' , as calculated from equation (20), as a linear function of c . Finally, equation (17) is used to obtain E_m° , the standard emf of the cell on the commonly used molal scale, from E_c° and ρ_s . Of course, if the measured E values for the cell are directly available as a function of c , then the densities ρ of the cell solutions at the various concentrations are not needed.

3. EXAMPLES OF APPLICATION OF THE PROCEDURE

The procedure was applied to several examples of emf data from the literature, as shown in Table 4. The accuracy of the E° values obtained is at least as good as, and generally better than, that of the original authors. Particularly severe tests of the procedure are the cases of 82 mass per cent of 1,4-dioxane in water, where extensive association takes place, due to the low relative permittivity. Whereas Harned and coworkers (ref. 51) obtained a curved extrapolation, the one obtained by the present procedure is a good straight line of minimal slope.

4. SUGGESTED PROCEDURE FOR CELLS WITH ELECTROLYTES OF HIGHER CHARGE TYPE

Minimal changes have to be introduced for symmetrical electrolytes (to the ions of which the electrodes are reversible) where $\nu_+ = \nu_- = 1$ and $z_+ = |z_-| > 1$. Here $\nu = 2$ is still valid, but the number of electrons involved in the cell reaction for the electrolyte $M_{\nu_-}^{z_+} X_{\nu_+}^{z_-}$ is greater than unity, so that the value of k' in equation (22) should now read $k' = 2(\ln 10)R/(z_+ F) = 2(\ln 10)R/(|z_- F|) = 3.96843 \times 10^{-4}/z_+ \text{ V}\cdot\text{K}^{-1}$. In turn, both A' and B' (equations (23) and (24)) must be multiplied by z_+^2 ; this also applies to q since $q = |z_+ z_-| e^2 / (8\pi \epsilon_0 \epsilon_s k_B T) = z_+^2 e^2 / (8\pi \epsilon_0 \epsilon_s k_B T)$. Furthermore, K' in equations (25) and (26) should now be multiplied by

$|z_+z_-|^3$. For unsymmetrical electrolytes, where $z_+ \neq |z_-|$, a further complication is introduced, in that the ion pair formed at low relative permittivities is itself charged. Hence its activity coefficient cannot be ignored in equation (12), as is justified for symmetrical electrolytes forming an uncharged ion pair. The quantity $|z_+z_-|$ should replace z_+^2 in the parameters A' and B' , and a factor γ' should be introduced on the right-hand side of equation (12). This may be calculated by means of equation (19), ignoring the C -term, with a factor of $z_i(z_j - z_i)$ multiplying A on the right-hand side, the suffix i pertaining to the ion having the lower absolute charge number. Whether the cell electrolyte is symmetrical or not, complications would arise in the presence of foreign electrolytes in the cell solution, since the activity coefficients of the ions to which the electrodes are reversible must be calculated by equations pertaining to mixed electrolytes. This is obviated in the case of 1:1 electrolytes by the specified activity coefficient equation, where all ion-specific terms are collected into the slope C determined by the regression.

5. CONCLUSIONS

It is desirable that the determination of the standard emf E° of the cell (1) in non-aqueous or aqueous-organic solvent mixtures, which is of great importance in both fundamental and applicative areas, be carried out according to more uniform criteria. In particular, E° values for a cell of the type $\text{Pt} | \text{H}_2 | \text{HX} (m, \text{ in solvent } s) | \text{AgX} | \text{Ag} | \text{Pt}$ are needed for the determination of pH_s standards according to the IUPAC-recognized procedure.

For solvents of moderate to high relative permittivities ($\epsilon > \sim 30$) the extrapolation procedure described here provides a sound independent basis for verification of E° values as obtained by the variety of existing procedures.

At low relative permittivities ($2 < \epsilon < \sim 30$), Harned's method wherein the emf E measurements on cell (1) are supplemented by conductivity measurements on the electrolyte $\text{M}_{\nu_+}^{z_+} \text{X}_{\nu_-}^{z_-}$ to obtain its degree of ionisation α for insertion in the extrapolation function of E , is seen to cover down to $\epsilon \sim 10$. The results can be verified by the present, independent procedure which covers the whole ϵ range and thus is the only hitherto available method applicable to the critical range of relative permittivities below $\epsilon \sim 10$.

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