

# Recent advances in the electromotive force method for determining transference numbers of electrolytes and characterizing new salt bridges\*

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Recent transference-cell e.m.f. data sets for various 1:1 electrolytes in aqueous-organic solvent mixtures obtained in these laboratories for the determination of ionic transference numbers have been aggregated with earlier sets for 1:1 electrolytes in aqueous solutions and reexamined in the light of a new theoretical approach accounting for the solvent transfer phenomena accompanying ionic transfer. The potentialities and the precision of the transference-cell e.m.f. method have been highlighted, and new salt bridges, for use in aqueous-organic solvents, have been thereby characterized.

Keywords: *concentration cells, salt bridges, transference numbers*

## 1. Introduction

In a key review by Spiro [1] the three main methods of determining transference numbers of electrolytes (moving-boundary electrolysis, Hittorf electrolysis and electromotive force) were compared, and the accuracy of the electromotive force method was considered somewhat lower than that of the other two methods. However, significant advances in the e.m.f. method have been obtained since 1990 [2, 3] for both basic theory and experimental procedures.

The intrinsic precision of the potentiometric measurement of the e.m.f.s of the relevant cells, and the zero-current condition classifies the e.m.f. method among 'nondestructive' methods, whereas the Hittorf method and the moving-boundary method, both being electrolysis-based are, as such, 'destructive'.

In pIon-metric and pH-metric cells it is established practice to insert a *salt bridge* (i.e., an appropriate 'concentrated equitransferent' strong binary salt [4–8]) between the sample solution and the reference electrode solution to reduce the diffusion potential (liquid junction potential) arising at the solution junction. The salt bridge reducing the liquid junction potential to zero is a sort of 'electrolytic short circuit', in the terminology used by Professor Bianchi [9], who promoted systematic search of new salt bridges for use in studies of metal corrosion in aqueous-organic media.

For aqueous solutions very little or no problems remain because of the wealth of good salt bridges now available following recent work [2, 3, 10–12].

The nonavailability of salt bridges in nonaqueous or aqueous-organic solvents prompted our recent research, leading to the characterization of symmetrical-valence (alkali chlorides) bridges as well as unsymmetrical valence ( $\text{Li}_2\text{SO}_4$ ) bridges in a number of solvent mixtures of water with methanol, ethanol, ethylene glycol, acetonitrile and 1,4-dioxane [12–14].

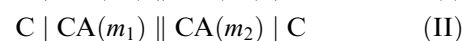
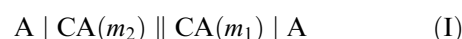
One of the two key features of a salt bridge  $\text{C}_{\nu_C}^{z_C} \text{A}_{\nu_A}^{z_A}$  is its *equitransference*, which in general terms implies [8]:

$$\nu_C t_C = \nu_A t_A \quad (1a)$$

or equivalently

$$t_C/z_C = t_A/|z_A| \quad (1b)$$

where  $t_C$  and  $t_A$  are the transference numbers of the cation  $\text{C}^{z_C}$  and the anion  $\text{A}^{z_A}$ , respectively. Equation 1(b) reduces to the familiar condition,  $t_C = t_A$  (which originated the equitransference terminology [5, 6]) if  $\text{C}_{\nu_C}^{z_C} \text{A}_{\nu_A}^{z_A}$  is symmetrical (i.e.,  $\nu_C = \nu_A$ ). Characterization of a new salt bridge requires a systematic study of transference numbers over a wide range of  $\text{C}_{\nu_C}^{z_C} \text{A}_{\nu_A}^{z_A}$  'concentrations' in the appropriate solvent S. A powerful method of doing this is based on measuring the electromotive force (e.m.f.) of transference cells of the following types:



where  $m_2 > m_1$  are CA molalities ( $\text{mol kg}^{-1}$ ) in solvent S; CA is a simplified notation for  $\text{C}_{\nu_C}^{z_C} \text{A}_{\nu_A}^{z_A}$ ; A and C denote electrodes reversible to the anion  $\text{A}^{z_A}$  and to

\* This paper is dedicated to memory of Professor Giuseppe Bianchi.

the cation  $C^{z_C}$ , respectively,  $v_C + v_A = v$ , and  $v_C z_C = v_A |z_A|$ . In the traditional scheme of treatment, the e.m.f.s  $E_A$  and  $E_C$  of cells (I) and (II), respectively, are interpreted in the following terms:

$$E_A = (vk/v_C z_C) \int_{m_1}^{m_2} t_C d \ln \{m\gamma\} \\ = (vk/v_A |z_A|) \int_{m_1}^{m_2} t_C d \ln \{m\gamma\} \quad (2a)$$

$$E_C = (vk/v_A |z_A|) \int_{m_1}^{m_2} t_A d \ln \{m\gamma\} \\ = (vk/v_C z_C) \int_{m_1}^{m_2} t_A d \ln \{m\gamma\} \quad (2b)$$

where  $t_C$  and  $t_A$  are (molality-dependent) transference numbers of the cation and the anion, respectively;  $E_A$  and  $E_C$  are the e.m.f. measured with anion-reversible and cation-reversible electrode pairs, respectively;  $\gamma$  denotes the mean-molal activity coefficient of CA at molality  $m$ ;  $k = RT/F$ ,  $R =$  gas constant,  $F =$  Faraday constant and  $T =$  absolute temperature.

The method requires combining the e.m.f.s  $E_A$  and/or  $E_C$  with the parallel e.m.f.  $E_{MAX}$  of double cell (type III) without transference:



It can be shown that for either configuration of cell (III)  $E_{MAX}$  has one identical expression, that is,

$$E_{MAX} = (vk/v_C z_C) \int_{m_1}^{m_2} d \ln \{m\gamma\} \\ = (vk/v_A |z_A|) \int_{m_1}^{m_2} d \ln \{m\gamma\} \\ = (vk/v_C z_C) \ln \{m_2 \gamma_2 / m_1 \gamma_1\} \\ = (vk/v_A |z_A|) \ln \{m_2 \gamma_2 / m_1 \gamma_1\} \quad (3)$$

As shown by Equation 3, if accurate  $\gamma$  values at the appropriate molalities  $m$  are available, there is no need to measure  $E_{MAX}$ , which can be simply and conveniently computed.

If  $E_A$ ,  $E_C$ , and  $E_{MAX}$  are measured for the same molality differences. With, for example,  $m_1 =$  fixed  $= m_f$  and  $m_2 =$  variable  $= m$ , the textbook scheme of treatment leads to

$$dE_A/dE_{MAX} = t_C; \quad \text{and} \quad dE_C/dE_{MAX} = t_A \quad (4)$$

where  $t_C + t_A = 1$  and

$$dE_A + dE_C = dE_{MAX}; \quad \text{and} \quad E_A + E_C = E_{MAX} \quad (5)$$

Equation 4 is unfortunately incomplete, and so are Equations 2(a) and 2(b), because they consider only transfer of ions ( $C^{z^+}$  or  $A^{z^-}$ ) and ignore transfer of solvent S; for their complete forms, *vide infra*. Equation 5 is exact and permits conversion of  $E_A$  into  $E_C$  data and vice versa through  $E_{MAX}$ . This procedure implies that experimental results for  $E_A$  against  $E_{MAX}$  be fitted to an empirical polynomial of the type

$$E_A = aE_{MAX} + b(E_{MAX})^2 + \dots \quad (6)$$

and the first derivative

$$dE_A/dE_{MAX} = t_C = a + 2bE_{MAX} + \dots \quad (7)$$

(which is a function of molality  $m$  through  $E_{MAX}$  and Equation 2) was (wrongly) identified with the 'true'  $t_C$  and (rightly) attributed to the variable molality  $m$  of CA. Although popular, Equations 6 and 7 have two key drawbacks:

- (i) They assume a rather unrealistic parabolic  $E_A$  vs  $E_{MAX}$  correlation. Recent results confirm a rather common typology of the experimental  $E_A$  vs  $E_{MAX}$  correlation: namely, a straight line at low and intermediate CA molalities which becomes a flat curve at higher molalities, that is, it really has an oblique asymptote (cf. Figs 1-4).
- (ii) They cannot be extrapolated to infinite dilution ( $m = 0$ ) because  $E_{MAX}$  would become indeterminate, as equation (2) shows.

For a few salts the  $E_A$  vs  $E_{MAX}$  diagram is a straight line covering the whole molality range: this happens typically with those CAs (typically 1:1 electrolytes [8]) that fulfil the equitransference requirements of salt bridges, namely, having approximately both  $t_C^o = t_A^o = 0.5$  at infinite dilution and  $t_C = t_A = 0.5$  at finite concentrations, a feature that is fully justified in terms of the Stokes-Robinson equation (13).

Since Equation 2(a) suggests that

$$d(E_A/[vk/v_A |z_A|])/d \ln \{m\gamma\} = t_C \quad (8)$$

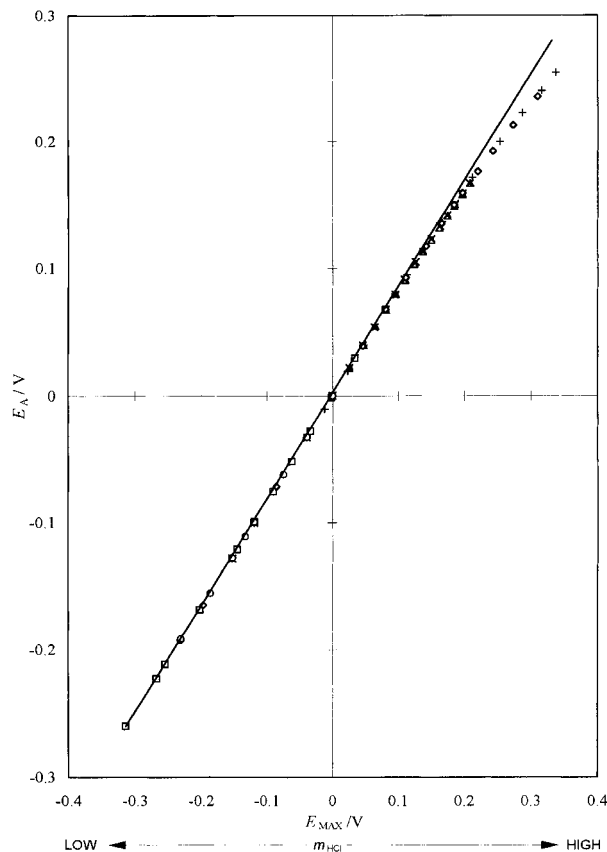


Fig. 1.  $E_A$  vs  $E_{MAX}$  relationship for aqueous HCl [16, 23-27] at 25°C.

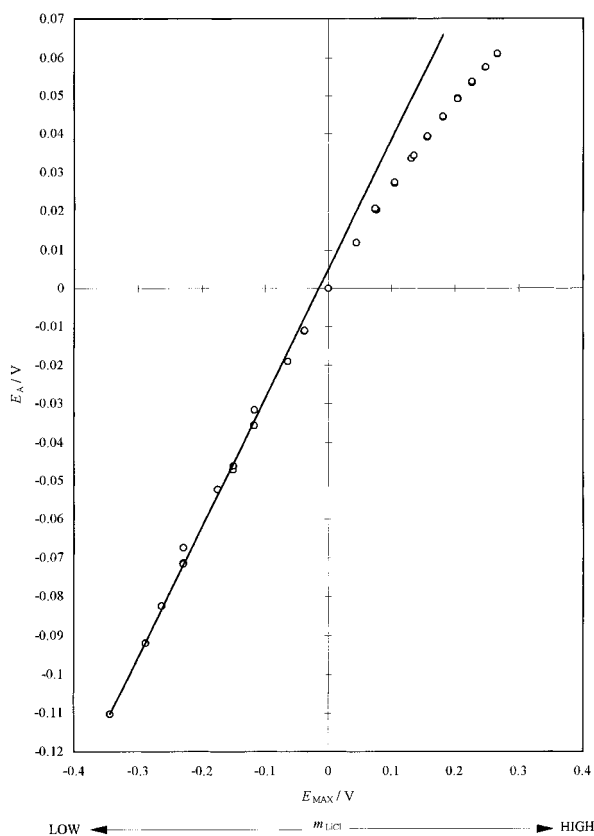


Fig. 2.  $E_A$  vs  $E_{MAX}$  relationship for aqueous LiCl [15, 29, 30] at 25°C.

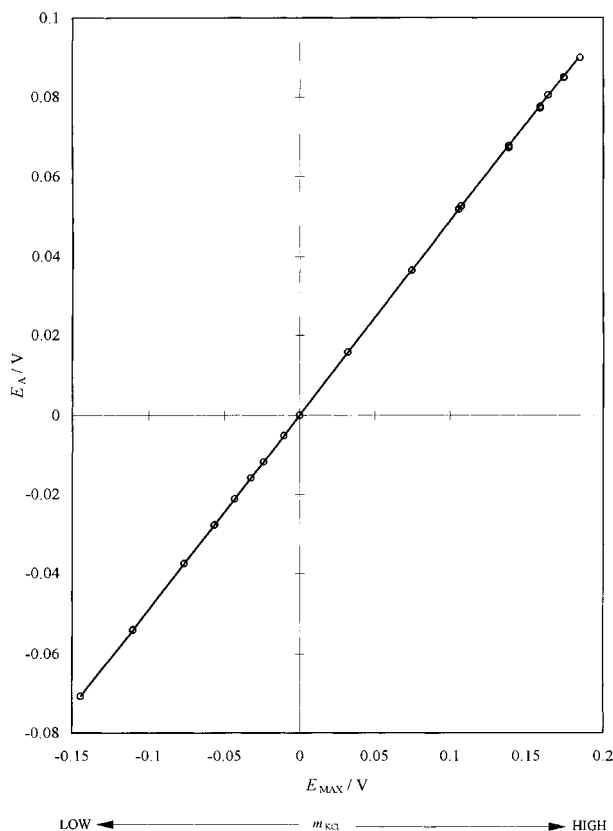


Fig. 4.  $E_A$  vs  $E_{MAX}$  relationship for aqueous KCl [34] at 25°C.

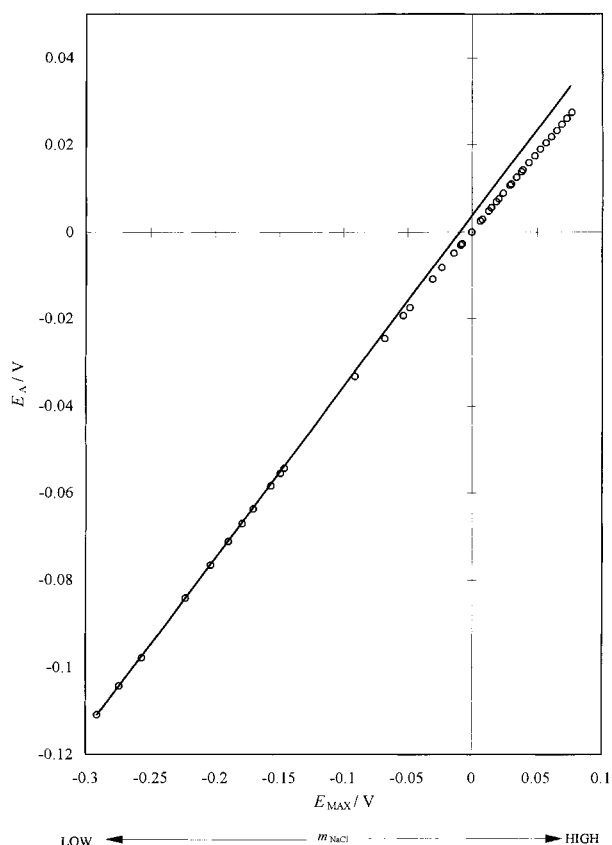


Fig. 3.  $E_A$  vs  $E_{MAX}$  relationship for aqueous NaCl [31–33] at 25°C.

MacInnes and Beattie [15] represented  $E_A$  as a polynomial in  $\ln\{m\gamma\}$  of the type

$$E_A/[vk/v_A|z_A|] = a + b \ln \{m\gamma\} + c \ln^2 \{m\gamma\} + \dots \tag{9}$$

so that by differentiation

$$\begin{aligned} d(E_A/[vk/v_A|z_A|])/d \ln \{m\gamma\} \\ = t_C = b + 2c \ln \{m\gamma\} + \dots \end{aligned} \tag{10}$$

which was, however, good for interpolation but again clearly not for extrapolation to  $m = 0$ . This kind of drawback was not removed even by the later, more refined treatment introduced by Harned and Dreby [16] working with aqueous as well as aqueous-organic solutions of hydrochloric acid.

Mussini *et al.* [3], in an extensive study of 1:1-valent CA electrolytes in  $S = \text{water}$ , showed that  $t_C$  in Equations 4 and 7 is an *apparent* transference number (hereafter denoted as  $(t_C)_{APP}$ ) and the correct, complete forms of Equations (2a) and (2b) are

$$\begin{aligned} E_A &= (vk/v_C z_C) \int_{m_1}^{m_2} (t_C - v_C z_C \tau_S M_S m) d \ln \{m\gamma\} \\ &= (vk/v_A |z_A|) \int_{m_1}^{m_2} (t_C - v_C z_C \tau_S M_S m) d \ln \{m\gamma\} \end{aligned} \tag{11a}$$

$$\begin{aligned} E_C &= (vk/v_A |z_A|) \int_{m_1}^{m_2} (t_A + v_A |z_A| \tau_S M_S m) d \ln \{m\gamma\} \\ &= (vk/v_C z_C) \int_{m_1}^{m_2} (t_A + v_A |z_A| \tau_S M_S m) d \ln \{m\gamma\} \end{aligned} \tag{11b}$$

respectively, and that of Equations 4 is

$$dE_A/dE_{MAX} = (t_C)_{APP} = t_C - v_C z_C \tau_S M_S m \quad (12a)$$

and

$$dE_C/dE_{MAX} = (t_A)_{APP} = t_A + v_A |z_A| \tau_S M_S m \quad (12b)$$

where  $\tau_S M_S m$  is the hitherto neglected solvent-transfer contribution,  $M_S$  is the molar mass ( $\text{kg mol}^{-1}$ ) of solvent S, and  $t_C$  complies with the Stokes–Robinson equation, which for a 1:1 electrolyte is

$$\begin{aligned} t_C &= [\lambda_C^\circ - \frac{1}{2} B_2 \sqrt{m} / (1 + a_0 B \sqrt{m})] \\ &\quad / [\Lambda_{CA}^\circ - B_2 \sqrt{m} / (1 + a_0 B \sqrt{m})] \\ &= [t_C^\circ - 0.5] / \{ (1 - B_2 \sqrt{m}) \\ &\quad / [(1 + a_0 B \sqrt{m}) / \Lambda_{CA}^\circ] \} + 0.5 \end{aligned} \quad (13)$$

where  $t_C^\circ = \lambda_C^\circ / \Lambda_{CA}^\circ$  is the limiting (infinite dilution) cation transference number,  $B_2$  and  $B$  are classical constants of the Debye–Hückel–Onsager theory,  $a_0$  is the ion-size parameter, and  $\lambda_C^\circ$  and  $\Lambda^\circ$  are the limiting molar conductivities of  $C^+$  and CA, respectively, in S. In turn, the solvent transfer number  $\tau_S$  (moles of S transferred per faraday inside the cell from negative pole to positive pole) can be expressed [2, 3] as

$$\tau_S = \tau_S^\circ (1 - h M_S m) \quad (14)$$

where  $\tau_S^\circ$  is the limiting (infinite dilution) transference number of solvent S, and  $h = h_C + h_A$  is the primary solvation (hydration) number of CA, which can be obtained by some of the existing independent methods for the determination of the ionic hydration numbers  $h_C$  and  $h_A$ . Here it is worthwhile to remember that by definition [5, 17–22]:

$$t_C = \tau_C z_C \quad \text{and} \quad t_A = \tau_A z_A \quad (15)$$

where  $t_C$  and  $t_A$  are ionic transference numbers in the current ‘unsigned’ definition (i.e., fraction of charge carried by the relevant ion),  $\tau_C$  and  $\tau_A$  are the corresponding ‘signed’ ionic transference numbers (moles of relevant ion transferred per mole of electrons (i.e., per faraday) inside the cell from negative pole to positive pole, so that  $\tau_C$  is always positive and  $\tau_A$  always negative), and the ionic charge numbers  $z_C$  and  $z_A$  are taken with sign.

With regard to the above aspects, in the present work Equation 6 is replaced with a new form of  $E_A$  vs  $E_{MAX}$  correlation which proves outstandingly better than anything tried earlier:

$$E_A = a E_{MAX} + b [1 - \exp(c E_{MAX})] \quad (16)$$

From Equations 16 and 12,

$$\begin{aligned} dE_A/dE_{MAX} &= (t_C)_{APP} = t_C - v_C z_C \tau_S M_S m \\ &= a - bc \exp(c E_{MAX}) \end{aligned} \quad (17)$$

and, introducing Equation 3 for  $E_{MAX}$ ,

$$\begin{aligned} dE_A/dE_{MAX} &= (t_C)_{APP} = t_C - v_C z_C \tau_S M_S m \\ &= a - Q [(m\gamma)_{CA}]^{2kc} \end{aligned} \quad (18)$$

where  $Q = bc [(m_f \gamma_f)_{CA}]^{-2kc} = \text{constant}$ . Now, Equation 18 can be extrapolated to the limiting conditions

of infinite dilution ( $m = 0, \gamma = 1$ ), where  $\tau_S M_S m = 0$  for the solvent-transfer term, and thus gives  $t_C^\circ$  as the limiting slope:

$$(dE_A/dE_{MAX})_{m=0} = a = (t_C^\circ)_{APP} \equiv t_C^\circ \quad (19)$$

Clearly, the transference number at infinite dilution ( $t_C^\circ$ ) is the key quantity; once it is determined, the transference numbers  $t_C$  at finite molalities can be obtained through the Stokes–Robinson Equation 13. It is also clear that, in case of rectilinear experimental  $E_A$  vs  $E_{MAX}$  correlation over the whole molality range, Equation 6 would read  $E_A = a E_{MAX}$  and the result for  $dE_A/dE_{MAX}$  would be identical with that from Equation 19.

## 2. Results and discussion

If  $m_3$  denotes another possible fixed molality of CA in cell (I), while  $m_2$  still denotes the varied molality, and  $\Psi$  is an abbreviation for  $(t_C - v_C z_C \tau_S M_S m)$ , from Equation 11(a):

$$\begin{aligned} E_A &= (vk/v_C z_C) \int_{m_1}^{m_2} \Psi \, d \ln \{m\gamma\} \\ &= (vk/v_C z_C) \int_{m_3}^{m_2} \Psi \, d \ln \{m\gamma\} \\ &\quad + (vk/v_C z_C) \int_{m_1}^{m_3} \Psi \, d \ln \{m\gamma\} \end{aligned} \quad (20)$$

Thus a set of  $E_A$  values measured (at varied molalities  $m_2$ ) with reference to a certain fixed molality  $m_3$ , can be converted into a new, wholly significant set referred to a fixed molality  $m_1$  by correcting the original e.m.f. values by addition of the quantity  $(vk/v_C z_C) \int_{m_1}^{m_3} \Psi \, d \ln \{m\gamma\}$ , which is obviously the e.m.f. measurable with the same cell (I) with molalities  $m_3$  and  $m_1$  instead of  $m_2$  and  $m_1$ . This procedure is convenient when different  $E_A$  sets by different authors must be referred to the same fixed molality for comparison or consolidation, and has also been used in the present work. Of course, a parallel correction must be made for the corresponding  $E_{MAX}$  set, in the following terms, derived from Equation 3:

$$\begin{aligned} E_{MAX} &= (vk/v_C z_C) \int_{m_1}^{m_2} d \ln \{m\gamma\} \\ &= (vk/v_C z_C) \ln \{m_2 \gamma_2 / m_1 \gamma_1\} \\ &= (vk/v_C z_C) \int_{m_3}^{m_2} d \ln \{m\gamma\} \\ &\quad + (vk/v_C z_C) \int_{m_1}^{m_3} d \ln \{m\gamma\} \\ &= (vk/v_C z_C) \ln \{m_2 \gamma_2 / m_3 \gamma_3\} \\ &\quad + (vk/v_C z_C) \ln \{m_3 \gamma_3 / m_1 \gamma_1\} \end{aligned} \quad (21)$$

and the correction term  $(vk/v_C z_C) \ln \{m_3 \gamma_3 / m_1 \gamma_1\}$  can be either measured or computed from known  $\gamma$  values.

Various sets of  $E_A$  and  $E_C$  data as functions of  $E_{MAX}$  for various aqueous as well as aqueous-organic electrolytes are considered here. When necessary, the  $E_C$  vs  $E_{MAX}$  sets have been converted to  $E_A$  vs  $E_{MAX}$

sets by Equation 5 and referred to the same fixed molality  $m_1$  by Equations 20 and 21. For the following electrolytes, single- or multi-author  $E_A$  vs  $E_{MAX}$  data sets covering substantially the whole respective molality range, are available: (i) in pure aqueous medium HCl [16, 23–27], HBr [28], LiCl [15, 29, 30], NaCl [31–33], KCl [34], CsCl [2, 3, 35], RbCl [11], RbBr, RbI and  $NH_4I$  [10], and  $NH_4Cl$  [36]; (ii) in ethanol/water solvent mixtures NaCl, KCl and CsCl [13]; (iii) in methanol/water solvent mixtures LiCl, NaCl [37]; (iv) in ethylene glycol/water, acetonitrile/water and 1,4-dioxane/water solvent mixtures NaCl [14], KCl [38], and  $Li_2SO_4$  [12].

The typology of the relevant  $E_A$  vs  $E_{MAX}$  dependence is of key importance in the present discussion, and is best illustrated by the Figs 1–6. It is evident that two limiting forms emerge: the first, strictly linear over the whole molality range, and the second, linear at low, and intermediate, molalities and asymptotically curvilinear at higher molalities. To the first type belong such electrolytes as aqueous CsCl, RbCl, RbBr, RbI, KCl,  $NH_4Cl$  and  $NH_4I$ , as well as CsCl and KCl in alcohol/water solvents, that show more or less close equitransference and, as such, can be used as salt bridges. To the second type belong those that do not. There are certain salts, such as NaCl in methanol/water and in ethanol/water solvent mixtures, that shift from the second type to the first type as the proportion of organic component increases, as shown by Figs 5 and 6: for 80% mass of methanol [14] or ethanol [13], and for 60% mass of acetonitrile, NaCl behaves as an acceptable salt bridge, thus approaching the behaviour of the popular saturated-aqueous KCl [34]. (The case of NaCl in 80% mass of acetonitrile was not considered for the too low solubility of NaCl). However, as shown in the comparative Fig. 7, in ethylene glycol/water the NaCl behaviour is constantly far from equitransference and shows no salt-bridge quality, just as in pure aqueous medium. This points to the opportunity of extension of systematic studies to different families of organic solvents, in

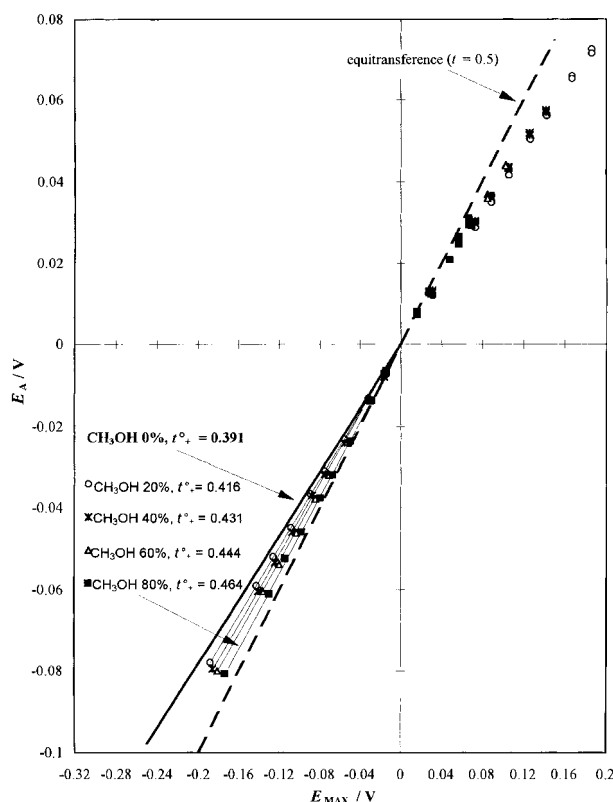


Fig. 5.  $E_A$  vs  $E_{MAX}$  plots for aqueous NaCl in various methanol + water solvent mixtures [37] at 25 °C.

particular diols and nitriles, to clarify the role of such key properties as relative permittivity, viscosity and preferential solvation on the ionic mobilities and related transference numbers.

For the aqueous 1:1 electrolytes the following results emerge:

- (i) By the procedure of multiple non-linear regression already described [2, 3], if the  $E_A$  vs  $E_{MAX}$  data set processed is complete and accurate, it is possible to optimize all of the key parameters involved by Equations 12–19, especially  $t_C^0$ ,  $\tau_S^0$ , and  $h$  (=moles of water firmly bound to one

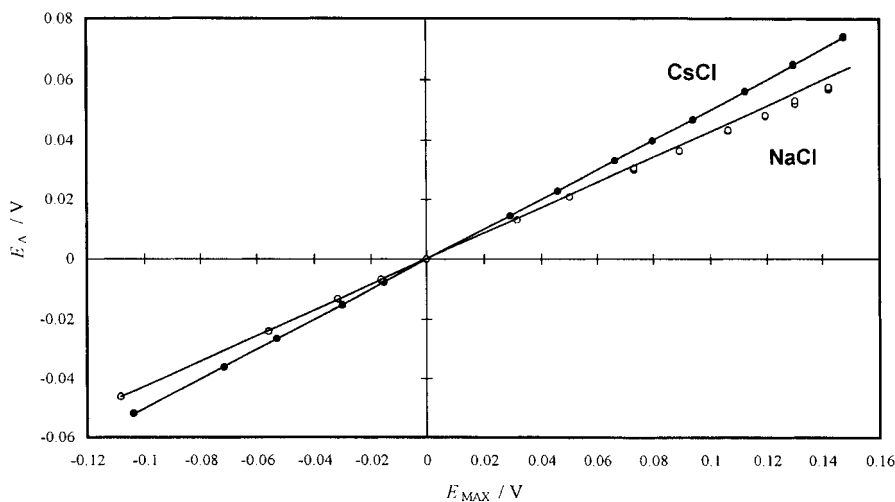


Fig. 6. Limiting  $E_A$  vs  $E_{MAX}$  patterns in ethanol + water solvent mixtures [13] at 25 °C: (○) asymptotic (NaCl in 20 mass % ethanol), and (●) linear (CsCl in 40 mass % ethanol).

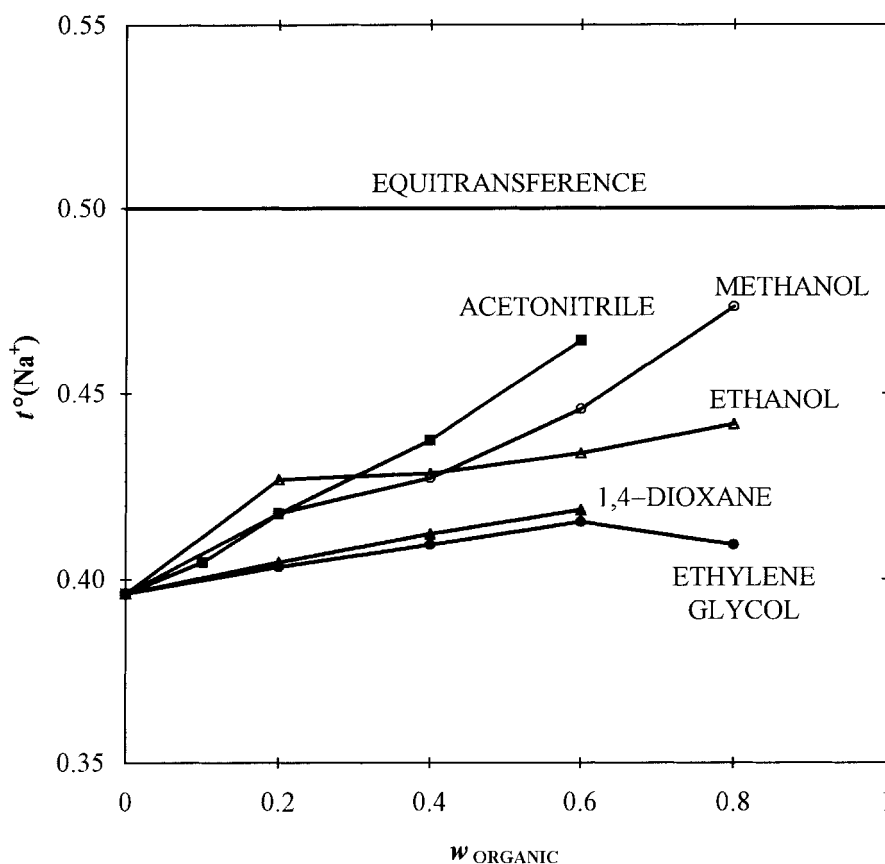


Fig. 7. Dependence of the limiting value  $t_{\text{Na}^+}^{\circ}$  of the transference number of  $\text{Na}^+$  in  $\text{NaCl}$  on the mass fraction  $w$  of the organic solvent in admixture with water.

mole of CA electrolyte). As Table 1 shows, the  $\tau_S^{\circ}$  values are close to zero for those salts that closely approach equitransference (i.e.,  $t_C^{\circ} = t_A^{\circ} = 0.5$ ), but  $\tau_S^{\circ}$  increases up to 1.36 (limiting case of  $\text{HCl}$ ) with increasing difference between  $t_C^{\circ}$  and  $t_A^{\circ}$ .

- (ii) In this context, it is noteworthy that the values of the whole-electrolyte primary hydration numbers  $h = h_C + h_A$  found fulfil satisfactorily the additivity rule and are in good agreement with those obtained, for the single ions  $\text{C}^+$  and  $\text{A}^-$  by independent methods, by Mussini *et al.* [39–41] which are representable empirically by

$$h_i = 26.05 - 19.90 \sqrt{(r_i/\text{\AA})} \quad (22)$$

(where  $r_i$  for the cations (excluding  $\text{H}^+$ ) denotes Pauling's crystal radii, and for the anions the crystal radii diminished by  $0.047 \text{ \AA}$ ), and are confirmed by

the general analysis of Bockris *et al.* [42, 43] as well as by the theoretical study of Azzam [44, 45] based on a statistical-mechanical model. For instance, for  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{KF}$ , and  $\text{CsCl}$ ,  $h = 8.2\{9.4\}$ ,  $7.5\{6.1\}$ ,  $11.1\{10.4\}$ , and  $3.3\{3.2\}$ , respectively (in braces are quoted the values estimated by Equation 22).

For the *aqueous-organic 1:1 electrolytes* the determination of  $\tau_C^{\circ}$  causes no more difficulties than in pure aqueous medium, but the determination of  $\tau_S^{\circ}$  really requires simultaneous determination of  $\tau_W^{\circ}$  (for water) and  $t_O^{\circ}$  (for the organic component of the mixed solvent  $\text{S} = \text{W} + \text{O}$ ); and besides the primary hydration numbers  $h$ ,  $h_C$  and  $h_A$ , there will be the primary solvation numbers  $o$ ,  $o_C$  and  $o_A$ : therefore it will be quite unlikely that the purpose by the aforementioned procedure of multiple nonlinear regression will be attained with so many determinands. The difficulty can be overcome either by combining the

Table 1. Comparison of infinite-dilution transference numbers at  $25^\circ\text{C}$  for the cation ( $t_C^{\circ}$ ) and for the solvent ( $\tau_S^{\circ}$ ) of various aqueous 1:1 electrolytes

	<i>HCl</i>	<i>HBr</i>	<i>LiCl</i>	<i>NaCl</i>	<i>KF</i>	<i>KCl</i>
$t_C^{\circ}$	0.8359	0.8112	0.3414	0.3959	0.5728	0.4891
$\tau_S^{\circ}$	1.36	0.92	0.60	0.21	0.82	-0.082
	<i>NH<sub>4</sub>Cl</i>	<i>NH<sub>4</sub>I</i>	<i>RbCl</i>	<i>RbBr</i>	<i>RbI</i>	<i>CsCl</i>
$t_C^{\circ}$	0.4938	0.4906	0.5007	0.4958	0.5071	0.5018
$\tau_S^{\circ}$	-0.026	-0.036	0.004	-0.017	-0.021	0.008

present e.m.f. measurements with an *ad hoc* independent method of determining  $h$ ,  $h_C$  and  $h_A$  and  $o$ ,  $o_C$  and  $o_A$ , or by setting up an appropriate model for the interpretation of concurrent hydration and solvation for the situation when the components of the solvent mixture have nonzero dipole moments. Work is in progress, and efforts are being made towards the above aim.

### 3. Conclusions

The transference-cell e.m.f. method of determining ionic transference numbers is a powerful, convenient, and accurate one and is especially suitable for determinations extending over wide ranges of electrolyte concentrations, mixed solvent compositions and temperatures; its limitation is the availability of appropriate reversible electrodes. The complete theory requires taking solvent transfer and ionic solvation parameters into account together with ionic transfer parameters. For aqueous-organic solvent mixtures, it may be necessary to combine e.m.f. measurements with *ad hoc* independent methods of determining ionic solvation numbers, or to introduce an appropriate model for the interpretation of concurrent hydration and solvation when the components of the solvent mixture have nonzero dipole moments.

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