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Ion and solvent transfers at homoionic junctions between concentrated electrolyte solutions

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A unified treatment of liquid junction potentials and membrane potentials which accounts for both ionic and solvent transfers at homoionic junctions between ultra concentrated electrolyte solutions, also in terms of the primary hydration parameters and the Stokes-Robinson hydration theory, is described. Application to the determination of cation transference numbers, τ_+, water transference numbers, τ_w, and primary hydration numbers, h, is described as a rational scheme for characterization of concentrated electrolytes as possible new salt bridges for the minimization of liquid junction potentials in electroanalysis. Examples of application of this scheme are presented based on multiple regression analysis of electromotive force measurements of such homoionic concentration cells as $\mathrm{Ir}\,|\,\mathrm{Cl_2}\,|\,\mathrm{HCl}\ (m_2)\ \|\ \mathrm{HCl}\ (m_1)\,|\,\mathrm{Cl_2}\,|\,\mathrm{Ir}$ and $\mathrm{Hg}\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{Li_2SO_4}\ (m_2)\ \|\ \mathrm{Li_2SO_4}\ (m_1)\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{Hg}$, with fixed m_1 molality and varied m_2 molality. Based on the electromotive force of analogous homoionic transference cells but with interposed membranes, application of the present procedure can be extended to the determination of ion and solvent transport parameters, notably the degree of permselectivity, of membranes for use either as selective sensors in electroanalysis or selective separators in industrial electrochemistry.

1. Introduction

The liquid junction potential (E_L) and the membrane potential (E_M) are notorious among the electrochemist's delights and, although physically the latter is simply an extreme case of the former, textbooks of electrochemistry have long since developed two distinct lines of approach, with distinct networks of operational equations, probably for didactic reasons. E_L and E_M, however, are expressions of the same phenomenology of irreversible diffusional processes and, as components of the electromotive force (e.m.f.) E of homoionic transference cells (or Helmholtz cells) with and without interposed membranes, respectively, they are usefully amenable to the same basic equations, as will be seen later.

Both E_L and E_M originate from the overlap of an ion transfer contribution E_{IT} and a solvent transfer contribution E_{ST} (whose determination offers some recurrent problems) and, while E_{IT} is generally the object of critical and exhaustive analysis, it is not so with E_{ST}. In fact, in textbooks of electrochemistry (almost without exception [1]) E_{ST} is ignored altogether when dealing with E_L, probably relying tacitly on the dilution level of solutions forming the liquid junctions in practical cases. (Although when dealing with E_M, the E_{ST} contribution is ignored only within the sector of high-selectivity membranes used as sensors in ion-selective electrodes). Neglect of E_{ST} in E_L, however, is no longer tolerable when the e.m.f. E of the Helmholtz cell is, for example, used for the characterization of new highly-concentrated salt bridges. This also will be shown later on.

2. General equations for the e.m.f. of homoionic transference cells with and without interposed membranes

Let us consider the following homoionic transference cell:

$$\mathrm{C}\,|\,\mathrm{CA}\ (m)\ \text{in solvent S}\ \|$$
$$\mathrm{CA}\ (m + \mathrm{d}m)\ \text{in solvent S}\,|\,\mathrm{C} \qquad (1)$$

where the double bars $\|$ indicate the location of the liquid junction potential, E_L (or of the membrane potential E_M, if there is inserted an appropriate membrane); CA is a simplified notation for the strong binary electrolyte $\mathrm{C}_{n+}^{z+}\mathrm{A}_{n-}^{z-}$, one mole of which forms n_+ moles of cations C^{z+} of valency z_+ and n_- moles of anions A^{z-} of valency z_- (here taken with sign), with $n = n_+ + n_-$; and C denotes a first-kind electrode reversible to the above cation C^{z+}. The cell diagram is written in compliance with the Stockholm Convention of IUPAC [2–4]. Considering the ion transfer processes and the solvent transfer process occurring at $\|$, in combination with the two Faradaic reactions at the above electrodes C, with reference to 1 faraday of charge (that is, equivalent to a mole of electrons [5]),

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one can write the overall cell reaction. The latter implies that, from the upper molality m + dm to the lower molality, m, $(\tau_- z_- / z_+ n_+)$ moles of CA are transferred together with $-\tau_s$ moles of solvent S, the definition of the transference numbers τ's cited being [6, 7] the number of moles of the denoted species that are transferred from the anode (negative terminal of cell) to the cathode (positive terminal of cell) per faraday (or, per mole of electrons). Thus for the electrolyte CA we have:

$$z_+ \tau_+ + z_- \tau_- = 1 \qquad (2)$$

where all of the ionic products $z\tau$ are positive because τ_- is negative by definition and z_- is taken with its (negative) sign; for the solvent S, τ_s may be either positive or negative according to experimental conditions, to be ascertained by independent tests [8–10]. This is known as the 'signed' definition of transference numbers [6, 7], which is equally valid for charged species (the ions) and uncharged species (the solvent S) [8–10]. The alternative, traditional, and much more popular 'unsigned' or 'electric' [7] definition (the transference number, t_+ or t_-, of an ion in a given electrolyte solution is the fraction of the total electric current carried in the solution by that ion) leads to the well known relation $t_+ + t_- = 1$ where both t's are positive, and are obviously inapplicable to uncharged species. For the ions of the above binary electrolyte CA we have:

$$t_+ = z_+ \tau_+ ; \quad t_- = z_- \tau \qquad (3)$$

From the overall reaction of the homoionic transference Cell (1) we can write for the related infinitesimal e.m.f. dE_1:

$$\begin{aligned} \mathrm{d}E_1 &= nk_e \left(\frac{z_- \tau_-}{n_+ z_+} \right) \mathrm{d} \ln (m\gamma) - k_e \tau_s \, \mathrm{d} \ln (a_s) \\ &= nk_e \left[\left(\frac{z_- \tau_-}{n_+ z_+} \right) + \tau_s M_s m \right] \mathrm{d} \ln (m\gamma) \qquad (4) \end{aligned}$$

where $k_e = RT/F$ (with R = gas constant, F = Faraday's constant, and T = absolute temperature), γ is the mean molal activity coefficient of CA, and M_s the molar mass (kg mol^{-1}) of the solvent S. Since τ_+ and τ_- are complementary quantities through Equation 2, the alternative homionic transference cell (5), with electrodes now reversible to the anion A^{z-}, could be used instead of Cell (1) for their determination:

$$\begin{gathered} \mathrm{A} \,|\, \mathrm{CA}\ (m + \mathrm{d}m) \text{ in solvent S} \,\|\, \\ \mathrm{CA}\ (m) \text{ in solvent S} \,|\, \mathrm{A} \qquad (5) \end{gathered}$$

In this case the overall cell reaction implies that, from the upper molality m + dm to the lower molality m, there is the transfer of $(z_+ \tau_+ / n_- |z_-|)$ moles of CA together with $+\tau_s$ moles of solvent S, per faraday. Thus for the corresponding infinitesimal e.m.f. dE_5 we have:

$$\begin{aligned} \mathrm{d}E_5 &= nk_e \left(\frac{z_+ \tau_+}{n_- |z_-|} \right) \mathrm{d} \ln (m\gamma) + k_e \tau_s \, \mathrm{d} \ln (a_s) \\ &= nk_e \left[\left(\frac{z_+ \tau_+}{n_- |z_-|} \right) - \tau_s M_s m \right] \mathrm{d} \ln (m\gamma) \qquad (6) \end{aligned}$$

Unification of Equations 4 and 6 can be best achieved by using the same terminology of membrane potentials, in terms of the cell (7). That is,

$$\mathrm{J} \,|\, \mathrm{IJ}\ (m) \text{ in S} \,\|\, \mathrm{IJ}\ (m + \mathrm{d}m) \text{ in S} \,|\, \mathrm{J} \qquad (7)$$

where IJ is simplified notation for the general strong binary electrolyte $\mathrm{I}_{n_\mathrm{I}}^{z_\mathrm{I}} \mathrm{J}_{n_\mathrm{J}}^{z_\mathrm{J}}$ where the ion $\mathrm{J}^{z_\mathrm{J}}$ to which the electrodes J are reversible is called the coion, and the ion $\mathrm{I}^{z_\mathrm{I}}$ of opposite charge sign is called the counterion (and is the ion whose transference number τ_I is actuallly determined from the cell e.m.f.). Of course, we have $n = n_\mathrm{I} + n_\mathrm{J}$ and, for the ion transference numbers involved:

$$\begin{gathered} z_\mathrm{I} \tau_\mathrm{I} + z_\mathrm{J} \tau_\mathrm{J} = 1; \quad t_\mathrm{I} + t_\mathrm{J} = 1; \\ t_\mathrm{I} = z_\mathrm{I} \tau_\mathrm{I}; \quad t_\mathrm{J} = z_\mathrm{J} \tau_\mathrm{J} \qquad (8) \end{gathered}$$

It may be noted that the cell (7) diagram is, as such, written in keeping with the Stockholm Convention only if $\mathrm{J}^{z_\mathrm{J}}$ is a cation; if instead $\mathrm{J}^{z_\mathrm{J}}$ is an anion, the left-hand terminal of cell would be positive, and the cell diagram should be reversed, namely, the (m + dm) molality should be written on the left-hand side [2–4].

The general expression for the infinitesimal e.m.f. dE of Cell (7), which comprises both Equations 4 and 6, remembering that $n_\mathrm{J} |z_\mathrm{J}| = n_\mathrm{I} |z_\mathrm{I}|$, is:

$$\begin{aligned} \mathrm{d}E &= k_e \left[\left(\frac{n z_\mathrm{I} \tau_\mathrm{I}}{n_\mathrm{I} |z_\mathrm{I}|} \right) \mathrm{d} \ln (m\gamma) - \left(\frac{z_\mathrm{J}}{|z_\mathrm{J}|} \right) \tau_s \, \mathrm{d} \ln (\mathrm{a}_s) \right] \\ &= \left(\frac{nk_e}{n_\mathrm{J} |z_\mathrm{J}|} \right) (z_\mathrm{I} \tau_\mathrm{I} + n_\mathrm{J} z_\mathrm{J} \tau_s M_s m) \, \mathrm{d} \ln (m\gamma) \qquad (9) \end{aligned}$$

It is clear that in the limit at $z_\mathrm{I} \tau_\mathrm{I} = 1$ and $\tau_s = 0$ the cell e.m.f. reaches its maximum value d$E_{\max}$, where

$$\mathrm{d}E_{\max} = \left(\frac{nk_e}{n_\mathrm{J} |z_\mathrm{J}|} \right) \mathrm{d} \ln (m\gamma) = \left(\frac{nk_e}{n_\mathrm{I} |z_\mathrm{I}|} \right) \mathrm{d} \ln (m\gamma) \qquad (10)$$

a value which, in finite terms, can be conveniently calculated from known γ values, thus dispensing with direct e.m.f. measurements. From Equations 9 and 10 we have the thermodynamically exact relation:

$$\begin{aligned} dE/\mathrm{d}E_{\max} &= z_\mathrm{I} \tau_\mathrm{I} + n_\mathrm{J} z_\mathrm{J} \tau_s M_s m \\ &= t_\mathrm{I} + n_\mathrm{J} z_\mathrm{J} \tau_s M_s m = \phi \qquad (11) \end{aligned}$$

which is the basis for the determination of transference numbers τ_I and τ_s from the finite e.m.f. E of Cell (7) and finite $E_{\max}$, namely, working with finite molalities m_2 and m_1 (instead of m + dm and m), with $m_2 > m_1$ and one of these (say m_1) fixed and the other varied. Representing E as a function of $E_{\max}$, for example, by a least-squares polynomial of the type

$$E = bE_{\max} + cE^2_{\max} + dE^3_{\max}\cdots \qquad (12)$$

(where the curve passes through the origin of axes as $E = 0 = E_{\max}$ at $m_2 = m_1$), one then gets

$$\mathrm{d}E/\mathrm{d}E_{\max} = b + 2cE_{\max} + 3\mathrm{d}E^2_{\max}\cdots = \phi \qquad (13)$$

which can be inserted into (11) for the optimization of τ_I and τ_s (or of t_I and τ_s) by also programming the respective first derivatives of the function ϕ:

$$\mathrm{d}\phi/\mathrm{d}\tau_I = z_I \quad \text{and} \quad \mathrm{d}\phi/\mathrm{d}\tau_s = n_J z_J M_s m, \qquad (14)$$

as resulting from Equation 11. It can be shown that the molality m in Equations 11 and 14 to which τ_I and τ_s must be referred is the variable one (m_2, in the example chosen above).

Interpretation of E in finite terms proceeds through integration of Equation 9 and requires assuming τ_I and τ_s to be constant in the m_1 to m_2 interval, where m_1 and m_2 are the lower and the upper limit of integration, respectively. Thus, noting that m d ln $(m\gamma)$ = dm + m d ln γ and that the lower solvent activity a_{s1} corresponds to the upper electrolyte molality m_2, we have from (9):

$$\begin{aligned} E &= k_e\left[\left(\frac{nz_I\tau_I}{n_I|z_I|}\right)\int_{m_1}^{m_2}\mathrm{d}\ln(m\gamma) - \left(\frac{z_J}{|z_J|}\right)\tau_s\int_{m_1}^{m_2}\mathrm{d}\ln(a_s)\right] \\ &= k_e\left[\left(\frac{nz_I\tau_I}{n_I|z_I|}\right)\ln\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right) + \left(\frac{z_J}{|z_J|}\right)\tau_s\ln\left(\frac{a_{s_2}}{a_{s_1}}\right)\right] \\ &= \left(\frac{nk_e}{n_J|z_J|}\right)\left[\int_{m_1}^{m_2} z_I\tau_I\,\mathrm{d}\ln(m\gamma) + \int_{m_1}^{m_2} n_Jz_J\tau_sM_sm\,\mathrm{d}\ln(m\gamma)\right] \\ &= \left(\frac{nk_e}{n_J|z_J|}\right)\left[z_I\tau_I\ln\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right) + n_Jz_J\tau_sM_s\left\{(m_2-m_1) + \int_{m_1}^{m_2} m\,\mathrm{d}\ln\gamma\right\}\right] \qquad (15)\end{aligned}$$

where the integral $\int_{m_1}^{m_2} m$ d ln γ is easily solved graphically from knowledge of γ as a function of electrolyte IJ, molality m. Of course, integration of Equation 10 for $E_{\max}$ is immediate and gives:

$$\begin{aligned} E_{\max} &= \left(\frac{nk_e}{n_J|z_J|}\right)\int_{m_1}^{m_2}\mathrm{d}\ln(m\gamma) \\ &= \left(\frac{nk_e}{n_J|z_J|}\right)\ln\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right) \\ &= \left(\frac{nk_e}{n_I|z_I|}\right)\ln\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right) \qquad (16)\end{aligned}$$

3. Liquid junction potentials, or membrane potentials, from the e.m.f. of homoionic transference cells, in terms of the Stokes-Robinson theory of ionic hydration

In terms of the Stockholm Convention the (finite) e.m.f. E of Cell (7) can be written as $E = E_{\text{right}} - E_{\text{left}} + E_L$ (or $E = E_{\text{right}} - E_{\text{left}} + E_M$, if a membrane is interposed at ‖), where E_{right} and E_{left} are the potentials of the terminal J^{z_J}-reversible electrodes, and the intrinsic, positive or negative, sign of E_L (or of E_M) shall be ascertained by independent criteria. For the corresponding infinitesimal e.m.f. dE, the terminal electrode potentials differ from each other by an infinitesimal amount because of the infinitesimal gradient between m + dm and m, and thus one can write:

$$\begin{aligned} \mathrm{d}E &= E_{\text{right}} - E_{\text{left}} + \mathrm{d}E_L \\ &= (k_e/|z_J|)\,\mathrm{d}\ln(m_J\gamma_J) + \mathrm{d}E_L \qquad (17)\end{aligned}$$

where γ_J is the activity coefficient of the single coion J^{z_J} at molality m_J. Therefore, from Equations 9 and 17 we have for dE_L (or, analogously, dE_M):

$$\mathrm{d}E_L = (k_e/|z_J|)\,[n(z_I\tau_I/n_J + z_J\tau_sM_sm)\,\mathrm{d}\ln(m\gamma) - \mathrm{d}\ln(m_J\gamma_J)] \qquad (18)$$

If IJ is a symmetrical electrolyte (that is, $n_+ = n_-$) and S = Water (henceforth denoted by subscript w), in terms of the Gibbs-Duhem equation we have:

$$\mathrm{d}\ln(a_w) = -2mM_w\,\mathrm{d}\ln(m\gamma) \qquad (19)$$

(γ = mean molal activity coefficient of IJ) and, from the Stokes-Robinson theory of ionic hydration [11–13, 14], for the single-cation and the single-anion activity coefficients, respectively:

$$\begin{aligned} \mathrm{d}\ln\gamma_- &= \mathrm{d}\ln\gamma + [(h_+ - h_-)/2]\,\mathrm{d}\ln(a_w) \\ \mathrm{d}\ln\gamma_+ &= \mathrm{d}\ln\gamma - [(h_+ - h_-)/2]\,\mathrm{d}\ln(a_w) \qquad (20)\end{aligned}$$

where h_+, h_-, and $h = h_+ + h_-$ would be the primary hydration numbers of the cation, the anion, and the whole (symmetrical) electrolyte, respectively. (The significance of these hydration numbers as resulting from the Stokes-Robinson treatment has been discussed recently [12–15]). Therefore, since

$$\mathrm{d}\ln m_+ = \mathrm{d}\ln m_- = \mathrm{d}\ln m \qquad (21)$$

from (19), (20) and (21) we obtain:

$$\begin{aligned} \mathrm{d}\ln(m_-\gamma_-) &= \mathrm{d}\ln(m\gamma) - 2mM_w\,[(h_+ - h_-)/2]\,\mathrm{d}\ln(m\gamma) \\ &= [1 - 2mM_w\,(h_+ - h_-)/2]\,\mathrm{d}\ln(m\gamma) \\ \mathrm{d}\ln(m_+\gamma_+) &= \mathrm{d}\ln(m\gamma) + 2mM_w\,[(h_+ - h_-)/2]\,\mathrm{d}\ln(m\gamma) \\ &= [1 + 2mM_w\,(h_+ - h_-)/2]\,\mathrm{d}\ln(m\gamma) \qquad (22)\end{aligned}$$

Now, introducing (22) into (18), with I = cation, we have:

$$\begin{aligned} (\mathrm{d}E_L)_{I=+} &= k_e\,\{\tau_+ + \tau_- - 2mM_w\,[\tau_w - (h_+ - h_-)/2]\} \times \mathrm{d}\ln(m\gamma) \\ &= k_e\,\{t_+ - t_- - 2mM_w \times [\tau_w - (h_+ - h_-)/2]\}\,\mathrm{d}\ln(m\gamma) \qquad (23)\end{aligned}$$

and, with I = anion, we have:

$$\begin{aligned}(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=-} &= k_\mathrm{e}\{-\tau_- - \tau_+ + 2mM_\mathrm{w} \\ &\quad \times[\tau_\mathrm{w} - (h_+ - h_-)/2]\}\ \mathrm{d}\ln(m\gamma) \\ &= k_\mathrm{e}\{t_- - t_+ + 2mM_\mathrm{w} \\ &\quad \times[\tau_\mathrm{w} - (h_+ - h_-)/2]\}\ \mathrm{d}\ln(m\gamma)\end{aligned} \tag{24}$$

From (23) and (24) it is clear that $(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=+} = -(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=-}$, as expected. Moreover, the condition for $(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=+} = 0$, or $(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=-} = 0$, for a uni : univalent salt-bridge is:

$$t_+ - t_- - 2mM_\mathrm{w}[\tau_\mathrm{w} - (h_+ - h_-)/2] = 0, \tag{25}$$

or, identically:

$$\tau_+ + \tau_- - 2mM_\mathrm{w}[\tau_\mathrm{w} - (h_+ - h_-)/2] = 0 \tag{26}$$

to be compared with the traditional textbook condition $t_+ - t_- = 0$, which evidently neglects the solven-transfer contribution to E_L and thus could be used only to a first approximation.

For unsymmetrical salt bridges, which are seldom considered for application [16], the Stokes-Robinson hydration theory leads to much more complicated equations than (22) and (23) above. However, still neglecting the solvent-transfer contribution, it was shown [17] that for a general IJ salt bridge (either symmetrical or unsymmetrical) the condition for $(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=+} = 0$, or $(\mathrm{d}E_\mathrm{L})_{\mathrm{I}=-} = 0$, is:

$$\tau_+ - |\tau_-| = 0,$$

or identically: $n_+t_+ - n_-t_- = 0$ (27)

4. Results and discussion

In terms of the above rationale, cation transference numbers $t_+ = \tau_+$ and water transference numbers τ_w have been determined here for two aqueous electrolytes, one symmetrical (HCl) and one unsymmetrical (Li_2SO_4), for which e.m.f. E sets are available over large concentration ranges up to the highest concentrations practicable. The largest data set for HCl is that of Davies and Steel [18] concerning the e.m.f. (E_{28}) of the transference cell:

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,|\,\mathrm{HCl}\ (m_1)\ \|\ \mathrm{HCl}\ (m_2)\,|\,\mathrm{H_2}\,|\,\mathrm{Pt} \tag{28}$$

at 298.15 K, with m_1 = fixed = 1.0012 mol kg^{-1} and m_2 varying from 0.00995 up to 13.6 mol kg^{-1}. These data are consistent with those (E_{28} and E_{29}) of King and Spiro [19], which were obtained at m_2's up to 8 mol kg^{-1} with a fixed m_1 = 1.0000 mol kg^{-1} (practically coincident with Davies and Steel's) with the chlorine-electrode cell:

$$\mathrm{Ir}\,|\,\mathrm{Cl_2}\,|\,\mathrm{HCl}\ (m_2)\ \|\ \mathrm{HCl}\ (m_1)\,|\,\mathrm{Cl_2}\,|\,\mathrm{Ir}, \tag{29}$$

together with parallel measurements with the hydrogen-electrode Cell (28). Harned and Dreby [20] used the Cell (30):

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{HCl}\ (m_2)\ \|\ \mathrm{HCl}\ (m_1)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag}, \tag{30}$$

whose e.m.f. is equivalent to that of Cell (29) and can still be referred to as E_{29}, to cover the range from 0.002 to 3 mol kg^{-1} HCl, the solution being carefully deoxygenated by hydrogen flow to avoid mixed potentials. Cell (30) was also used by Lengyel *et al.* [21] but their results were criticized [19] for apparent non-deoxygenation of solutions and for excessive solubility of AgCl leading to formation of $AgCl_2^-$ and $AgCl_3^{2-}$ ions at concentrations increasing from 3 to 8 mol kg^{-1}. The e.m.f. data for Li_2SO_4 have been obtained in the present work and concern the transference cell:

$$\mathrm{Hg}\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{Li_2SO_4}\ (m_2)\ \|\ \mathrm{Li_2SO_4}\ (m_1)\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{Hg} \tag{31}$$

at 298.15 K, with m_2 = fixed = 0.1 mol kg^{-1} and m_1 varying from 0.1 up to 3 mol kg^{-1}, and are to be found in Table 1. Details for the preparation of the Hg_2SO_4 electrodes and the Li_2SO_4 solutions, the temperature control, and the potentiometric measuring apparatus are exactly as in a recent paper [22]. Davies and Steel's, King and Spiro's and Harned and Dreby's e.m.f. data have been aggregated into one set referring to Cell (29), noting that $E_{29} = E_{29,\,\mathrm{max}} - E_{28}$, for the same m_1 and m_2 pair. The activity coefficient data required to calculate E_max along with Equation 10 have been taken from Robinson and Stokes's compilation [35]. Table 1 also reports values of transference numbers as a function of the m_2 molality for the H^+ and Li^+ ions simply in keeping with the traditional scheme, which neglects the solvent transfer term in Equation 11, as

$$\begin{aligned} t_{\mathrm{H}^+} \equiv \tau_{\mathrm{H}^+} &= \mathrm{d}E_{29}/\mathrm{d}E_{29,\,\mathrm{max}}; \\ t_{\mathrm{Li}^+} \equiv \tau_{\mathrm{Li}^+} &= \mathrm{d}E_{31}/\mathrm{d}E_{31,\,\mathrm{max}}, \end{aligned} \tag{32}$$

respectively.

To account for the simultaneous concentration-dependence of t_+ and τ_w implied by Equation 11, t_+ is here functionally expressed in terms of the interionic attraction theory by means of Stokes's [23, 24] equation:

$$\begin{aligned} t_+ &= \lambda_+/\Lambda = [\lambda_+^0 - \tfrac{1}{2}(|z_+|)\mathrm{f}(I)]/ \\ &\qquad [\Lambda^0 - \tfrac{1}{2}(|z_+| + |z_-|)\mathrm{f}(I)] \\ &= [t_+^0 - 1/(|z_+| + |z_-|)]/[1 - \tfrac{1}{2}(|z_+| + |z_-|)\mathrm{f}(I)/\Lambda^0] \\ &\qquad + 1/(|z_+| + |z_-|), \end{aligned} \tag{33}$$

where $\mathrm{f}(I) = B_2I^{\frac{1}{2}}/(1 + a_0BI^{\frac{1}{2}})$ and for the ionic strength, I, (here on the molal scale) we have $I = m_2$ for HCl and $I = 3m_2$ for Li_2SO_4, a_0 is the ion-size parameter (already known for both HCl and Li_2SO_4, [25, 26], B and B_2 are known Debye-Hückel constants, $t_+^0 = \lambda_+^0/\Lambda^0$ is the limiting (that is, infinite-dilution) transference number of the cation, and the limiting equivalent conductivity Λ^0 of the electrolyte is known accurately from the literature [27]. In turn, τ_w is expressed by the equation

$$\tau_\mathrm{w} = \tau_\mathrm{w}^0(1 - hm_2M_\mathrm{w}) \tag{34}$$

based on the assumption of constancy of the ratio of τ_w to the number of moles of unbound water [28], τ_w^0 is the limiting value of the water transference number and h is the primary hydration number (assumed to be

Table 1. Cation transference numbers (τ_+) and water transference numbers (τ_w) at various molalities m_2 for aqueous Li_2SO_4 (from the present e.m.f. measurements on the transference cell (31), with fixed $m_1 = 0.1\ mol\,kg^{-1}$) and HCl (transference cell (29), whose e.m.f.'s are not requoted here, as systematized from Refs. [18–21] to a fixed $m_1 = 1.0012\ mol\,kg^{-1}$), as optimized by multiple nonlinear regression based on Equations 11, 13, 33, 34, columns B. The τ_+'s obtained by Equation 32, which neglects water transference, are quoted for comparison in columns A. The values at infinite dilution ($\tau_+^0 \equiv t_+^0$), together with the constants for the relevant least-squares parabolas $E = bE_{max} + cE_{max}^2$ (Equation 12) are also quoted for convenience

m_2 (mol kg^{-1})	E_{31} (V)	$E_{31,\,max}$ (V)	τ_{Li^+}		τ_w	τ_{H^+}		τ_w
			A	B		A	B	
0.1	0.00000	0.00000	0.314	0.308	1.23	0.836	0.838	0.88
0.2	0.00633	0.02042	0.299	0.306	1.20	0.831	0.840	0.87
0.3	0.00939	0.03237	0.290	0.305	1.18	0.827	0.841	0.87
0.4	0.01217	0.04075	0.284	0.304	1.16	0.825	0.843	0.86
0.5	0.01411	0.04728	0.279	0.303	1.14	0.824	0.844	0.86
0.6	0.01552	0.05274	0.275	0.302	1.11	0.822	0.844	0.85
0.7	0.01662	0.05742	0.271	0.302	1.09	0.821	0.845	0.85
0.8	0.01777	0.06154	0.268	0.301	1.07	0.820	0.846	0.84
1.0	0.01985	0.06854	0.263	0.300	1.02	0.818	0.847	0.84
1.1	0.02089	0.07166	0.260	0.300	1.00	0.817	0.847	0.83
1.2	0.02157	0.07474	0.258	0.300	0.98	0.816	0.848	0.83
1.5	0.02330	0.08264	0.253	0.299	0.91	0.813	0.849	0.82
2.0	0.02620	0.09330	0.245	0.298	0.80	0.810	0.850	0.79
2.5	0.02840	0.10344	0.237	0.297	0.69	0.807	0.851	0.77
3.0	0.03047	0.11235	0.230	0.297	0.58	0.805	0.851	0.75
$\tau_+^0 \equiv t_+^0$ (this work)			0.3140 ± 0.0020			0.8263 ± 0.0026		
$\tau_+^0 \equiv t_+^0$ (from [27])			0.3259			0.8208		
b			0.3140 ± 0.0020			0.8176 ± 0.0019		
c (V^{-1})			-0.372 ± 0.030			-0.0783 ± 0.0066		
Electrolyte:			Li_2SO_4			HCl		

concentration-independent) of the electrolyte, respectively. Inserting (33) and (34) into (11) combined with (13) and explicit expressions for the three derivatives $d\phi/d\tau_+^0$, $d\phi/d\tau_w^0$ and $d\phi/dh$, by using the SAS Statistical Package [29], the values of τ_+^0, τ_w^0, and h have been optimized as:

$$\tau_{Li^+}^0 = 0.3140 \pm 0.0020, \quad \tau_w^0 = 1.25 \pm 0.16,$$

$$\text{and} \qquad h = 10 \pm 1 \quad \text{for } Li_2SO_4; \qquad (35a)$$

$$\tau_{H^+}^0 = 0.8263 \pm 0.0026, \quad \tau_w^0 = 0.880 \pm 0.071,$$

$$\text{and} \qquad h = 2.5 \pm 0.2 \quad \text{for HCl} \qquad (35b)$$

From this, τ_+ and τ_w have been calculated as functions of m_2 through (33) and (34), with the results shown in Table 1.

The h values found reflect a remarkable hydration (at least considering the firmly-bound water molecules of the primary hydration sheaths of ions) for both HCl and Li_2SO_4, and are reasonably consistent with observed single-ion values as $h_{Cl^-} = 3.0$ [15, 30, 31] and $h_{Li^+} = 10.9$ [15, 32, 33].

The τ_w^0 and τ_w values obtained are of the same order of 1 mole per faraday as found by several researchers [8–10] for the so-called Washburn numbers, and are of the expected positive sign, that is $\simeq$ 1 mole of water per faraday is transferred from the anode (that is, negative terminal of cell) to the cathode, and the secondary hydration sheath of ions is likely involved, at least partly, together with the primary one in this process [28], considering also the peculiar features of structure and mobility mechanism of the aqueous H^+ ion. Obviously, the τ_w's decrease with increasing molality m_2 of the electrolyte.

Finally, the infinite-dilution $\tau_{Li^+}^0$ and $\tau_{H^+}^0$ values optimized through the present multiple non-linear regression analysis of E data are close to the literature values resulting from the limiting equivalent conductivities in the literature [27], which confirms the soundness of the present treatment. Furthermore, if one considers the finite-concentration τ_{Li^+} and τ_{H^+} values in Table 1, one sees at once that between those obtained neglecting the water transfer (columns A, Equation 32) and those accounting for the water transfer (columns B, optimized by multiple regression through Equations 11, 12, 33, 34) there is a significant deviation, measured by the $n_j z_j \tau_w M_w m_2$ term in Equation 11, which increases with m_2 and amounts to -0.067 for τ_{Li^+} and to -0.047 for τ_{H^+}, at the upper molality quoted for both Li_2SO_4 and HCl, that is, $m_2 = 3\,mol\,kg^{-1}$. But for τ_{H^+} in HCl at 8 and 13.6 mol kg^{-1} (not quoted in Table 1) such deviation would rise to -0.070 and -0.087, respectively. These amounts are of the same order (and must be so) as the corrections performed when converting Hittorf 'apparent' into 'true' transference numbers [34] based on the traditional technique of adding to the electrolyte solutions being electrolyzed appropriate aliquots of sucrose, raffinose or urea as a 'reference' substance uninfluenced by the passage of the electrolyzing current. The present treatment based on the above $n_j z_j \tau_w M_w m_2$ deviation term is, in fact, equivalent to converting 'apparent' into 'true' transference numbers also in the hitherto untouched area of the transference cell method.

The procedure described above can be equally well applied to determinations of τ_i and τ_s in membranes from the e.m.f. of homoionic transference cells of the type:

$$J\,|\,IJ\;(m_1)\text{ in }S\,|\,I\text{-selective membrane}\,|\,IJ\;(m_2)\text{ in }S\,|\,J \qquad (36)$$

In this context, it is to be noted that the expected incidence of the solvent transfer contribution $n_J z_J \tau_s M_s m_2$, reference being made to the same m_2 molality and the same $m_2 - m_1$ gradient, is here often much greater than at a simple homoionic junction without membrane. In fact, the solvent transference number τ_s in membranes for industrial electrochemistry or electrodialysis is typically of the order of 10 moles of water per faraday, or even more. In turn, the counterion transference number τ_I is a parameter of paramount importance in membrane science because it represents the degree of ionic permselectivity of a membrane, the ideal (limiting) permselectivity being obviously reached when $t_I = 1$, namely, $|\tau_I| = 1/|z_I|$. This applies to natural and artificial membranes used in various areas, notably in industrial electrochemistry, electroanalytical chemistry, and bioelectrochemistry.

5. Conclusions

A definite correlation exists between ion transference number (τ_J), water transference number (τ_w) and primary hydration number (h) of any electrolyte, as can be shown through the method of the e.m.f. of homoionic transference cell. Such a correlation must be duly considered when concentrated binary electrolytes are studied to single out possible equitransference properties ($\tau_+ = |\tau_-|$) $= 1/(z_+ + |z_-|)$, see [17]) for use as salt bridges for application in electrochemistry and electroanalysis. It is desirable that independent methods be set up and tried systematically to evaluate the above transference and hydration parameters in cases where the transference cell method is inapplicable due to the unavailability of electrodes reversible to the ions being studied. Furthermore, the accumulation of such data for solvents other than water is even more urgently awaited. Finally, it is worth noting that the procedure described here for the determination of transport parameters at homoionic junctions from the e.m.f. of homoionic transference cells, is equally applicable to the determination of such parameters in natural or artificial membranes: for example, those used in industrial electrochemistry and electroanalytical chemistry.

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