Transport Equations of Electrodiffusion Processes in the Laboratory Reference Frame

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The transport equations of electrodiffusion processes use three reference frames for defining the fluxes: Fick's reference in diffusion, solvent-fixed reference in transference numbers, and laboratory fluxes in electric conductivity. The convenience of using only one reference frame is analyzed here from the point of view of the thermodynamics of irreversible processes. A relation between the fluxes of ions and solvent and the electric current density is deduced first from a mass and volume balance. This is then used to show that (i) the laboratory and Fick's diffusion coefficients are identical and (ii) the transference numbers of both the solvent and the ion in the laboratory reference frame are related. Finally, four experimental methods for the measurement of ion transference numbers are analyzed critically. New expressions for evaluating transference numbers for the moving boundary method and the chronopotentiometry technique are deduced. It is concluded that the ion transport equation in the laboratory reference frame plays a key role in the description of electrodiffusion processes.

Introduction

Lithium secondary batteries, fuel cells for energy storage, and electrodialysis treatment of solutions have attracted a lot of attention in the past decade.[1–5] In all of these systems, a concentration gradient combines its action with an electric current, that is, an electrodiffusion processes is developed. Three kinds of transport coefficients chracterize these processes: diffusion coefficients, transference number, and electric conductivity. A lot of work has been developed to measure these coefficients in a wide variety of solutions.

The study of these processes involves the use of three reference frames for defining the fluxes: Fick's reference in diffusion, solvent-fixed reference in transference numbers, and laboratory fluxes in electric conductivity. For pure diffusion and pure electric conduction processes, no problem is found in using the different reference frame; however, this issue becomes more difficult when describing electrodiffusion processes.

The thermodynamics of irreversible processes (TIP) deduces the transport equations of a phenomenon from the dissipation function. This quantity expresses the entropy production in terms of local fluxes and thermodynamic forces. There are different ways of expressing the dissipation function of a phenomenon according to the thermodynamic forces selected for describing the local irreversibility; each one of these sets of thermodynamic forces emphasizes different coupled phemomena. In our case, we choose a set formed by independent and observable forces, which the experimental arrangements provided straightfor-wardly.[6–9]

We consider the simple case of a solution with a neutral solvent and an electrolyte $A_{\nu+}B_{\nu-}$ with two ionic constituents A^{z+} and B^{z-}; temperature and pressure are constant. We assume that the solution is locally well defined by the solute concentration, c_2; the eventual deviation with respect to the electroneutrality condition is unnecessary and strictly not evaluable.[9,10] The whole phenomenon will be described by the solute concentration gradient and the electric current density; no reference to the electric charge density is needed. We also assume that the Gibbs–Duhem's equation is expressed by $c_1 d\mu_1$

$+ c_2 d\mu_2 = 0$ where μ_i ($i = 1, 2$) are chemical potentials; subindex 1 denotes the solvent.

The constituent fluxes in the laboratory reference frame are fasten as the thermodynamics forces are by the Gibbs–Duhem's equation; a mass and volume balance provides this constraint. From this relationship, we deduce that (i) the laboratory and Fick's diffusion coefficients are identical and (ii) the value of the solvent transference number depends on the value of the ion transference number. We also verify that the methods of measuring transference numbers, such as Hittorf's, moving boundary, radiotracers, NMR, and others, provide laboratory coefficients directly. All of these results show the relevant role of transport equations in the laboratory reference frame.

The theory developed in this work provides a good base for making a critical analysis of the methods that measure ion transference numbers. Thus, four experimental methods are reviewed. New expressions are deduced to evaluate the transference number in the moving boundary method and in the chronopotentiometry technique.

Transport Equations in the Solvent-Fixed Reference Frame

In the thermodynamics of irreversible processes (TIP), the transport equations are postulated from the dissipation function.[11] The system is locally characterized by the gradient of concentration and the electric current density; temperature and pressure are uniform. Then the dissipation function, Ψ, in one-dimensional transport is given in Cartesian coordinates by[12]

$$-\Psi = j_1 \frac{d\mu_1}{dx} + j_+ \frac{d\tilde{\mu}_+}{dx} + j_- \frac{d\tilde{\mu}_-}{dx} \qquad (1)$$

where j_i is the molar flux density of species $i = 1, +, -$ in the laboratory reference frame; and $\tilde{\mu}_i$ is the electrochemical potential of the ionic species $i = +, -$.[6]

We introduce the observable electric potential, ψ_-, for electrodes reversible to the anion through the relation[9]

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$$\frac{d\psi_-}{dx} = \frac{1}{z_- F}\frac{d\tilde{\mu}_-}{dx} \tag{2}$$

where F is Faraday's constant, and z_- is the charge number of the anion. From eqs 1 and 2 we obtain

$$-\Psi = j_1 \frac{d\mu_1}{dx} + \frac{1}{\nu_+}j_+\frac{d\mu_2}{dx} + j\frac{d\psi_-}{dx} \tag{3}$$

where j is the electric current density $j = F(z_+ j_+ + z_- j_-)$ and $\mu_2 = \nu_+ \tilde{\mu}_+ + \nu_- \tilde{\mu}_-$ is the chemical potential of the electrolyte. (The equations can be modified straightforwardly if electrodes reversible to the cation are used.) By introducing the Gibbs–Duhem's equation, we can express the dissipation function as

$$-\Psi = \frac{1}{\nu_+}j_+^1 \frac{d\mu_2}{dx} + j\frac{d\psi_-}{dx} \tag{4}$$

where $j_+^1 = j_+ - (\nu_+ c_2/c_1)j_1$ is the flow density of matter of the cation constituent in a solvent-fixed reference frame.

Therefore, we can postulate the linear transport equations

$$\frac{1}{\nu_+}j_+^1 = -\Lambda_{11}\frac{d\mu_2}{dx} - \Lambda_{12}\frac{d\psi_-}{dx} \tag{5a}$$

$$j = -\Lambda_{21}\frac{d\mu_2}{dx} - \Lambda_{22}\frac{d\psi_-}{dx} \tag{5b}$$

which are valid only for the system not far away from the global equilibrium, and hence the forces should be small enough. Finally, these equations can be transformed to[9]

$$\frac{1}{\nu_+}j_+^1 = -D_2^1\frac{dc_2}{dx} + \frac{t_+^1}{\nu_+ z_+ F}j \tag{6a}$$

$$-\frac{d\psi_-}{dx} = \left(\frac{t_+^c}{\nu_+ z_+ F}\frac{d\mu_2}{dc_2}\right)\frac{dc_2}{dx} + \frac{1}{\kappa}j \tag{6b}$$

where D_2^1 is the diffusion coefficient and t_+^1 is the Hittorf's transference number, both in the solvent-fixed reference frame; t_+^c is the transference number measured from concentration cells; and κ is the electric conductivity. If the ORR $\Lambda_{12} = \Lambda_{21}$ is assumed, then we deduce that $t_+^1 \equiv t_+^c$, as already postulated by Helmholtz.[13]

Each of the variables of eq 6b is a quantity in the laboratory reference frame. But transport eq 6a has the inconvenience of working with a flux in the solvent-fixed reference frame. For determining its value, we need to carry out two measurements of fluxes in the laboratory reference frame: one for the cation and another for the solvent. Fortunately, these two fluxes are related and only a measurement will be needed, as will be shown in the following.

Relation among the Fluxes in the Laboratory Reference Frame

Because the thermodynamic forces of the dissipation function of eq 3 are related by the Gibbs–Duhem's equation, it is also expected that there is a constraint among the fluxes in laboratory reference frame $(j_1 \; j_+ \; j)$. This relationship is obtained from a mass and volume balance. The cell is shown in Figure 1: a solution is limited by two electrodes reversible to the B/B^{z-} anions. We consider a control volume limited by the left cell wall and an imaginary surface in the solution fixed with respect
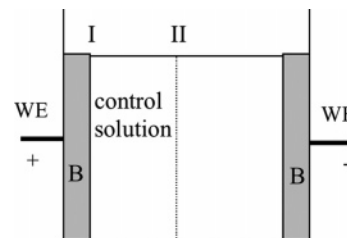

Figure 1. Sketch of the cell considered: WE working electrodes of constituent B; I and II surfaces that limit the control solution.

to the laboratory (denoted as II). The electrode/solution interface is denoted as I.

The control volume remains constant; then in time dt the changes in the solution volume, V_s, and in the electrode volume, V_e, hold

$$dV_s + dV_e = 0 \tag{7a}$$

$$dV_e = V_B dn_B \tag{7b}$$

$$dV_s = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \tag{7c}$$

where dn_B is the mole change in the anode; dn_i ($i = 1, 2$) are the mole changes in the solution inside the control volume; V_B is the molar volume of constituent B of the electrode in equilibrium with the anion; and $\bar{V}_i$ ($i = 1, 2$) are average values of the partial molar volumes in the solution.

The mole change in the anode is

$$dn_B = -\frac{j\Sigma\, dt}{z_- F} \tag{8}$$

where Σ is the area of the cell cross section. And the mole change in the solution is the balance of two contributions: (i) $dn_i' = 0$ ($i = 1, +$) through the surface I; and (ii) $dn_i'' = -j_i\Sigma\, dt$ ($i = 1, +$) through the surface II; therefore, we have

$$dn_1 = dn_1' + dn_1'' = -j_1\Sigma\, dt \tag{9a}$$

$$dn_2 = \frac{1}{\nu_+}(dn_+' + dn_+'') = -\frac{j_+}{\nu_+}\Sigma\, dt \tag{9b}$$

And finally from eqs 7–9 we deduce the following relation among the fluxes in the laboratory reference $(j_1 \; j_+ \; j)$ at surface II

$$\bar{V}_1 j_1 + \bar{V}_2 \frac{j_+}{\nu_+} + \frac{V_B}{z_- F}j = 0 \tag{10}$$

This relationship allows us to evaluate one of the fluxes from the values of the other two. For these calculations, we need to evaluate $\bar{V}_i$ ($i = 1, 2$). These quantities cannot be determined very accurately but, under many practical situations, the concentration changes are so small that the aproximation $\bar{V}_i \approx V_i$ can be accepted, where V_i are the partial molar volumes at the average concentration.

Transport Equations in the Laboratory Reference Frame

Similar to eq 6a, we can propose the following two transport equations in the laboratory reference frame

$$j_1 = -D_1\frac{dc_2}{dx} + \frac{t_1}{F}j \tag{11a}$$

$$\frac{1}{\nu_+}j_+ = -D_2\frac{dc_2}{dx} + \frac{t_+}{\nu_+ z_+ F}j \qquad (11b)$$

where D_i is the diffusion coefficient of the component $i = 1, 2$ in the laboratory reference; and t_i is the transference number of the constituent $i = 1, +$ in the laboratory reference. These transport coefficients are not independent quantities, and several relationships can be deduced. Here we consider the experimental conditions in the measurements of transport coefficients at concentration c_2 and therefore the approximation $\bar{V}_i \approx V_i$ ($i = 1, 2$) can be accepted. From eqs 6a, 10, 11a, and 11b we deduce that

$$D_1 = -\frac{V_2}{V_1}D_2 \qquad (12a)$$

$$D_2^1 = \frac{D_2}{c_1 V_1} \qquad (12b)$$

$$t_1 = \frac{\nu_- V_B - V_2 t_+}{\nu_+ z_+ V_1} \qquad (12c)$$

$$t_+^1 = \frac{t_+ - \nu_- c_2 V_B}{c_1 V_1} \qquad (12d)$$

These equations relate the three sets of transport coefficients, that is, $(D_2^1\ t_+^1)$, $(D_1\ t_1)$, and $(D_2\ t_+)$. They are equivalent, and once we have measured one set the other two are also known. But eq 11b should be emphasized because the diffusion coefficients in the Fick and laboratory reference frames are identical. Indeed, it is well known that the diffusion coefficient in Fick's reference, D_2^f, is related to the diffusion coefficient in solvent reference D_2^1 as $D_2^f = c_1 V_1 D_2^1$.[14] Therefore, eq 12b implies that $D_2^f \equiv D_2$.

Moreover, because the methods of measuring transference numbers, such as Hittorf's, moving boundary, radiotracers, NMR, and others, provide the values in the laboratory reference frame directly, the transport equation of the cation in this frame can be employed directly without any correction.

Critical Analysis of Transference Numbers in the Literature

In the literature, the transference numbers are usually given in the solvent-fixed reference frame, but not always. The theory developed above can be used to make critical analysis of the reported values. This is made on the following experimental methods for the measurement of transference numbers: (i) cell potential; (ii) moving boundary; (iii) pulse gradient spin−echo (PGSE) NMR; and (iv) chronopotentiometry. In every case, first we determine the reference frame in which the ion transference numbers have been measured and then eqs 12c and 12d are applied to obtain the values in other references.

The first system selected is an aqueous solution of MgCl$_2$.[15] The authors calculate the transference number from the values of electric potential at cells with transference reported by Phang and Stokes[16] and from the measurements of the activity coefficients of magnesium chloride by Golberg and Nuttal.[17] They have assumed the ORR; the transference number is solvent-fixed reference. To deduce the values in laboratory reference frames t_+ and t_1, partial molar volumes are needed; these are obtained from the density data reported by Miller.[15] The results are shown in Figures 2 and 3. The two ion transference numbers, t_+ and t_+^1, can differ by as much as 70%.
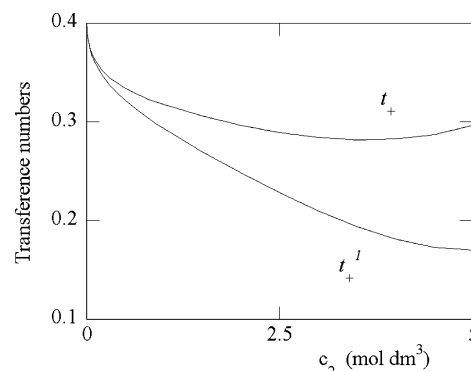

Figure 2. Transference numbers of the cation for MgCl$_2$ solutions in the laboratory reference frame, t_+, and in the solvent-fixed reference, t_+^1. Ag/AgCl electrodes have been considered. The values of t_+^1 are from Phang and Stokes.[16]
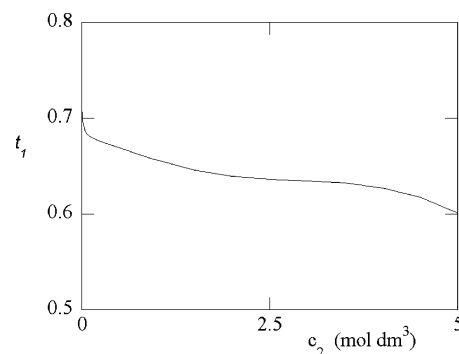

Figure 3. Transference numbers of solvent t_1 for MgCl$_2$ solutions in the laboratory reference frame. Ag/AgCl electrodes have been considered. The values of t_+^1 are from Phang and Stokes.[16]
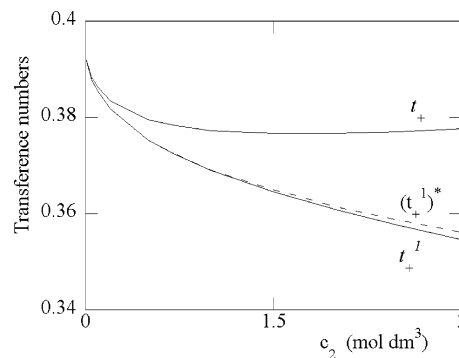

Figure 4. Transference numbers of the cation for NaCl solutions in the laboratory reference frame, t_+, and in the solvent-fixed reference, t_+^1. Ag/AgCl electrodes have been considered. Quantity $(t_+^1)^*$ is from Miller,[14] measured by Currie and Gordon[18] applying the moving boundary method and then corrected following MacInnes.[20]

In the second case, we analyze the measurement using the moving boundary method from refs 18 and 19. In this method, the direct measurements are the transference number in laboratory reference frame t_+; but the authors use the correction suggested by MacInnes[20,21] and finally they give the values of $(t_+^1)^* = (1 + c_2 V_2)t_+ - c_2 V_B$. From this quantity, we have evaluated transference numbers t_+, t_+^1, and t_1 shown in Figures 4−7 for NaCl and KCl solutions. The values of the partial molar volume have been calculated from the density data.[22] Transference numbers $(t_+^1)^*$ and t_+^1 differ by less than 0.4% and their identity can be accepted. This validates the relation among the fluxes deduced in this work; effectively the MacInnes' correction, which obtains $(t_+^1)^*$ from t_+, can practically be identified with transformation $t_+ \rightarrow t_+^1$ when eq 12d is applied.
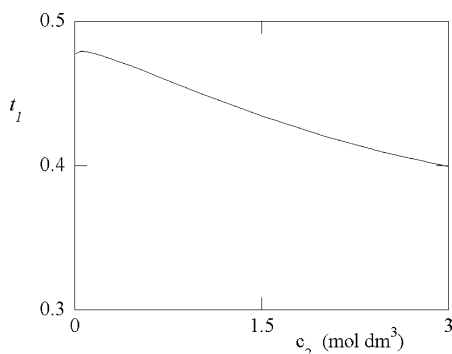
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Figure 5. Transference numbers of solvent t_1 for NaCl solutions in the laboratory reference frame. Ag/AgCl electrodes have been considered. Quantity $(t_+^1)*$ is from Miller,[14] measured by Currie and Gordon[18] applying the moving boundary method and then corrected following MacInnes.[20]
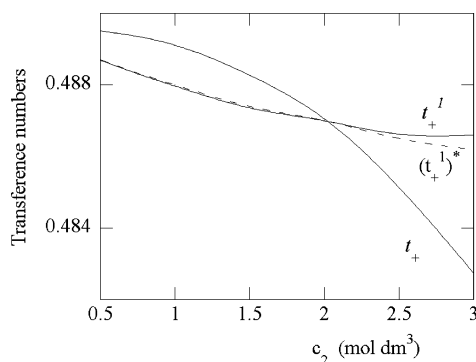

Figure 6. Transference numbers of the cation for KCl solutions in laboratory reference frame, t_+, and in the solvent-fixed reference, t_+^1. Ag/AgCl electrodes have been considered. Quantity $(t_+^1)*$ is from Miller,[14] measured by Shedlovsky and D. A. MacInnes[19] applying the moving boundary method and then corrected following MacInnes.[20]
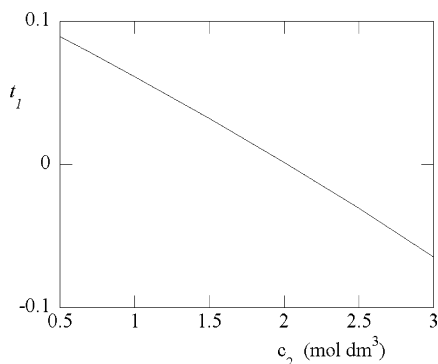

Figure 7. Transference numbers of solvent t_1 for KCl solutions in the laboratory reference frame. Ag/AgCl electrodes have been considered. Quantity $(t_+^1)*$ is from Miller,[14] measured by Shedlovsky and D. A. MacInnes[19] applying the moving boundary method and then corrected following MacInnes.[20]

Transference number t_1 for NaCl and KCl solutions was also measured by Longsworth in a different way without applying eq 10.[23] He followed the movement, on passage of an electric current, of a boundary between a solution of a salt and the same solution to which an "electrically inert" reference substance had been added. Thus, with raffinose, he obtained the values of t_1 given in Table 1. A fundamental objection can be presented to this method: the addition of raffinose modifies the solution and the transport coefficients of the constituents; therefore, we cannot compare these results with the values shown in Figures 5 and 7.

TABLE 1: Solvent Transference Numbers, t_1, Determined by Longsworth Following the Displacement of the Moving Boundary H₂O + Electrolyte/H₂O + Electrolyte + Raffinose[23]

electrolyte	c_2 (mol dm^{-3})	t_1
NaCl	0.2	1.06
NaCl	0.5	0.93
NaCl	1.0	0.80
KCl	0.2	0.59
KCl	1.0	0.42

TABLE 2: Transport Numbers in a 1 M Solution of LiN(CF₃SO₂)₂ in Ethylene Carbonate and Diethyl Carbonate (2/3 in Volume Ratio)^a

$\Delta\psi_+$ (V)	$u_+ \times 10^9$ (m²s⁻¹V⁻¹)	$u_- \times 10^9$ (m²s⁻¹V⁻¹)	$u_1 \times 10^9$ (m²s⁻¹V⁻¹)	t_+	t_1	t_+^1	$(t_1)*$
(0 < $\Delta\psi_+$ < 30)	3.6	9.4	0.0	0.28	0.0	0.0	1.61
(30 < $\Delta\psi_+$ < 60)	18.6	9.4	10.0	0.66	−3.05	1.02	0.67

^{a} The ionic mobilities u_i (i = 1, +, −) have been measured by (PGSE) NMR techniques.[4] The results change significantly with the applied cell potential, $\Delta\psi_+$

Other techniques, such as (PGSE) NMR have been used to measure transport coefficients in polymer electrolytes. In these solid materials, the traditional techniques of measuring the transference number, such as the Hittorf's method and the moving boundary method, can hardly be employed.[24] The transport numbers can be calculated from the experimental values of the ionic mobilities, u_i, using the equations

$$t_+ = \frac{u_+}{u_+ + u_-} \tag{13a}$$

$$t_1 = -\frac{c_1 u_1}{\nu_+ z_+ c_2(u_+ + u_-)} \tag{13b}$$

$$t_+^1 = \frac{u_+ + u_1}{u_+ + u_-} \tag{13c}$$

The ionic mobilities u_i (i = +, −) are definitely positive, but the solvent mobility may be positive or negative; for example, when the solvent and the anions go in the same direction $u_1 > 0$. In Table 2 we give the results obtained by Kataoka on a polymer gel electrolyte.[4] The solvent is a mixture of ethylene carbonate and diethyl carbonate (2/3 in volume ratio); the electrolyte is LiN(CF₃SO₂)₂ with the two ionic constituents Li⁺ and N(CFSO)₂⁻; a 1 M solution has been formed. Two different mobilities have been measured according to the electric potential applied $\Delta\psi_+$ to the cell between two Li/Li⁺ electrodes. This anomalous behavior is explained by the authors by the flow of lithium to compensate the lithium deposition at the electrode surface. Values of t_+ less than one are expected; nevertheless, t_+^1 may be greater than 1. Two solvent transference numbers are given in the table: (i) t_1 calculated by eq 13b; and (ii) (t_1) calculated from the constraint among the fluxes, that is, by $(t_1)* = (\nu_+ V_A - V_2[1 - t_+])/\nu_-\ z_- V_1$. The disagreement between these two last quantities evidences that transport numbers has proven difficult to measure correctly in solid polymer electrolytes.[24−26] In these calculations, $V_i \approx V_i°$ (i = 1, 2) has been assumed, where $V_i°$ is the partial molar volume of pure component i = 1, 2.[27]

Finally, we comment on another potentiometric determination of transference numbers.[24] The solvent is a copolymer of ethylene oxide and propylene oxide; and the solute is LiN(CF₃-
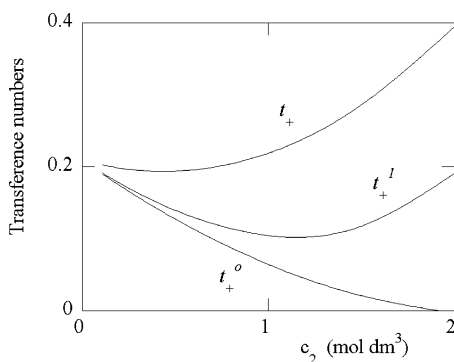
Figure 8. Transference numbers of cations t_+ and t_+^1 for a copolymer of ethylene oxide and propylene oxide and the electrolyte LiN(CF$_3$SO$_2$)$_2$. Li/Li$^+$ electrodes have been considered. The t_+^o data are given by Georen.[24]
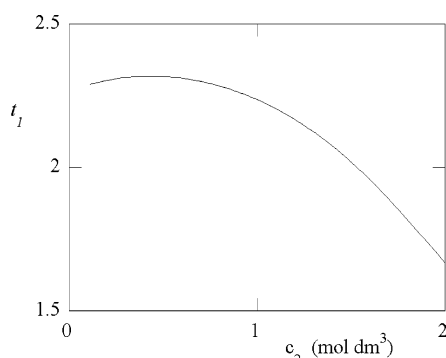

Figure 9. Transference numbers of solvent t_1 for a copolymer of ethylene oxide and propylene oxide and the electrolyte LiN(CF$_3$SO$_2$)$_2$. Li/Li$^+$ electrodes have been considered. The t_+^o data are given by Georen.[24]

SO$_2$)$_2$. The authors develop the perturbing method chronopotentiometry (CPM) based on the measurement of a response during passage of a current. They analyze three parts of the experiment: the concentration change at the working electrode (WE) during the polarization, the steady-state concentration profile in the cell, and the concentration relaxation at the WE. To relate the model results to experiment, they need to transform the quantities from solvent-fixed to room-fixed coordinates. The use of the ion transport equation in the laboratory reference frame may be used successfully in this method. We can identify the transference number reported by the authors as $t_+^o = 1 - (1 - t_+)/[1 - (c_2V_2)/(c_1V_1)]$. From this quantity, we have evaluated transference numbers t_+, t_+^1, and t_1 shown in Figures 8 and 9. In these calculations, important errors have probably been introduced because the poor approximation $V_i \approx V_i^o$ ($i = 1, 2$) has been assumed, where V_i^o is the partial molar volume of pure component $i = 1, 2$; to obtain accurate transference numbers by CPM, we need precise values on partial molar volumes.

Conclusions

The transport equations of electrodiffussion processes in the framework of nonequilibrium thermodynamics have been discussed. This theory uses three reference frames: Fick's, solvent-fixed, and laboratory. From a mass and volume balance, a relation among the fluxes of solvent, cation, and electric current in the laboratory reference frame is deduced. Thus, the solvent flux is not an independent quantity but it can be evaluated from the values of the ion flux and the electric current density.

From this constraint, relationships for diffusion coefficients and transference numbers among the three reference frames have been deduced. Two reasons emphasize the laboratory reference frame: (i) the identity of the diffusion coefficients in Fick's and laboratory references and (ii) the methods that measure the cation transference number directly, that is, Hittorf, moving boundary, (PGSE) NMR, and so forth, provide a value in the laboratory reference frame.

A critical analysis of four determination methods for ion transference numbers has been made. First, we identify the quantity reported as a transference number in each case; then the values in the other reference frames have been calculated. We also conclude that several modifications must to be introduced in the theoretical expressions usually applied: in the correction due to the solvent in the moving boundary method for evaluating the transference number in solvent-fixed reference frame, in the expression used for evaluating the transference number in the chronopotentiometry technique, and so forth.

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