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Transport Numbers of Ions in Charged Membrane Systems

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Abstract

Transport numbers have been extensively used over the last decades to characterize ion transport in charged membranes. In spite of their conceptual simplicity, a number of difficulties arise in the interpretation of experimental results because of the influence of the operating conditions. The meaning of the transport numbers measured with different methods is here explained by relating them to the local migrational transport numbers and the concentration profiles. The important effects of the diffusion boundary layers and the electric current density used (in the case of Hittorf's method) are then analyzed. Although electromembrane processes often involve multicomponent systems, the characterization of the transport properties of the membrane is often made in terms of binary electrolyte systems. The definitions of potentiometric transport numbers in ternary systems are worked out and these numbers are computed from the solution of the transport equations. These transport numbers are compared to the apparent potentiometric transport numbers used in the literature (i.e., those obtained by assuming that the ternary system behaves as a binary system), and the benefits of their use are clearly shown. Finally, a brief account of the difference between transport numbers in the membrane-fixed and solvent-fixed reference systems is given, and a recent modification of Hittorf's method that makes use of countercurrent convective flow is reviewed.

I. INTRODUCTION

The efficiency of electromembrane processes requires quantitative information on transport of both ions and solvent in the membrane system. The counterion transport number (TN) and water transference number are then important characteristics provided by manufacturers of industrial membranes. The counterion TN is often found by Hittorf's method or by measuring concentration potentials. Hittorf's TN represent the fraction of current transported by a charged species in an ionic solution when no concentration gradients are present [1,2]. Thus, by Hittorf's method, the concentration change in the cathode and anode compartments is measured when a known amount of electrical current passes through the membrane system by the use of reversible electrodes. However, when electric conduction takes place across a membrane system, concentration gradients are inevitably present and this can lead to errors in TN determinations due to back diffusion. Modifications of Hittorf's method that avoid correction for back diffusion [3,4] and the use of radiotracers [5] have been suggested, though they are not easy to use in practice. Furthermore, the ordinary methods for TN determination in charged membranes are such that they actually measure properties of the membrane system,

influence of which is difficult to estimate [6].

The TN found by the emf method are known as potentiometric TN, and quite frequently do not coincide with Hittorf's TN because these two methods characterize the membrane system as a whole and the values they yield depend on the experimental conditions [7]. Since there is no satisfactory way at present to reliably determine TN, and Hittorf's method or its modifications are relatively laborious, the potentiometric method is often used.

One of the reasons why more extensive use of ion-exchange membranes has not been made is the lack of knowledge of their transport properties in the multicomponent case. Counterion TN measured when binary electrolyte solutions bath the membrane are then of limited value in the performance analysis of electromembrane process, where at least ternary systems are always involved. For instance, in the case of acid and alkali production with bipolar membranes, it is important to determine the TN through the monopolar membranes in systems such as NaCl–HCl or NaCl–NaOH [8].

The scope of this chapter is restricted to the theory of TN in dilute solutions of strong electrolytes. The details of experimental methods by means of which TN are determined will not be discussed. The literature on TN in charged membranes is very extensive and the early developments have been properly reviewed in authoritative monographs [5]. Thus, only a few pioneering works will be cited. The aim of the chapter is not to provide a complete account of the subject matter, but to explain the origin of important effects, such as that of the polarization layers, the electric current density or the changes in pH, and to show how they can be accounted for in terms of the Nernst–Planck formulation.

Section II is intended to serve as an introduction to the different TN definitions. The connection between TN and concentration profiles will be worked out in detail, which will enable for a relatively simple explanation of the effects of the diffusion boundary layers, and the driving forces (electric current density or concentration difference) used in the TN determination.

Section III endeavors to define potentiometric TN in ternary systems and presents simple theoretical expressions for their evaluation. The current use of apparent TN and the consequences of the fixed charge estimation are also discussed.

Finally, Sec. IV gives a brief account of the difference between TN in the membrane-fixed and solvent-fixed reference systems. A recent modification of Hittorf's method that makes use of a countercurrent convective flow is also reviewed.

II. BINARY ELECTROLYTES

A. Model System

Figure 1 presents a schematic view of the membrane system considered. The

charge groups within the membrane is c_m and their charge number is z_m. The bathing solutions are of the same binary electrolyte at different concentrations, c_L and c_R. The electrolyte is considered to be completely dissociated and of $1:-1$ type. The two diffusion boundary layers (DBL) adjacent to the membrane have the same thickness δ.

The transport of ions is described by the Nernst–Planck equation [9]

$$J_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{\mathrm{F}}{RT}\frac{d\phi}{dx}\right) \tag{1}$$

where J_i, D_i and c_i are the flux density, diffusion coefficient and molar concentration of species i, respectively, ϕ is the local electric potential, F the Faraday constant, R the gas constant and T the absolute temperature. Alternatively, J_i can be presented as the sum of the salt flux density, J_{12}, and the ionic contribution to the electric current density [10]

$$J_i = -\frac{D_1 D_2}{D_1 c_1 + D_2 c_2}\frac{d(c_1 c_2)}{dx} + \frac{z_i D_i c_i}{D_1 c_1 + D_2 c_2}\frac{I}{F} = J_{12} + \frac{t_i}{z_i}\frac{I}{F} \tag{2}$$

where

$$t_i(x) \equiv \frac{z_i^2 D_i c_i(x)}{\sum_j z_j^2 D_j c_j(x)} \tag{3}$$

is the (differential) TN of species i [11], also called the *local migrational TN* because of its dependence on position within the membrane system.

In the absence of concentrations gradients, ion transport can be described

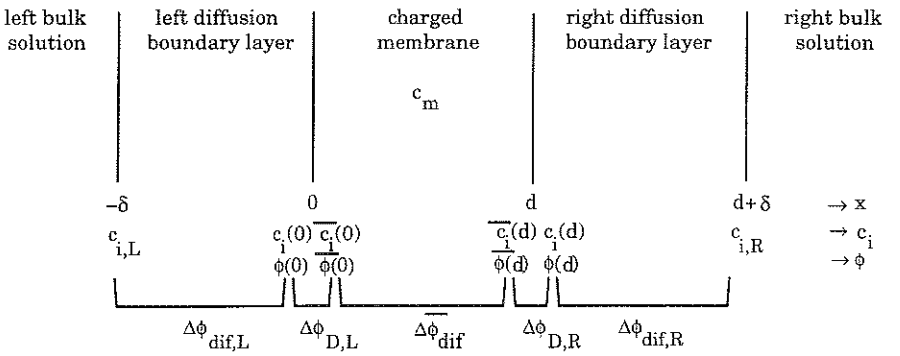

FIG. 1 Sketch of the membrane system and notations used for the ion concentrations and electric potential. Overbars denote membrane phase. The different potential drops in the system are also shown.

as a conduction process following Ohm's law, where every mobile charged species carries a fraction t_i of the electric current density. This statement, however, does not hold in the presence of concentration gradients. First, the electric current density

$$I = \mathrm{F} \sum_i z_i J_i \tag{4}$$

does not obey Ohm's law but [2]

$$I = -\kappa\left(\frac{d\phi}{dx} - \frac{d\phi_{\mathrm{dif}}}{dx}\right) \tag{5}$$

where

$$\kappa = \frac{\mathrm{F}^2}{RT} \sum_j z_j^2 D_j c_j \tag{6}$$

is the electric conductivity and

$$\frac{d\phi_{\mathrm{dif}}}{dx} = -\frac{RT}{\mathrm{F} \sum_j z_j^2 D_j c_j} \sum_i z_i D_i \frac{dc_i}{dx} = -\frac{RT}{\mathrm{F}} \sum_i \frac{t_i}{z_i} \frac{\mathrm{d} \ln c_i}{dx} \tag{7}$$

is the gradient of the diffusion potential. That is, even in the absence of electric current, there may be ion migration due to the gradient of the diffusion potential. And second, the migrational TN $t_i(x)$ does not represent the fraction of current carried by species i [12], but the relative contribution of species i to the local electrical conductivity.

B. Permselectivity and Integral Transport Numbers

The permselectivity is the property of ion-exchange membranes most often used to describe its quality. Permselective membranes are those that exhibit selectivity with respect to the passage of charged species. In particular, an ideal permselective membrane only allows the passage of counterions (i.e., those having the opposite sign from the fixed groups). Due to Donnan exclusion, counterions have a concentration in the membrane which is higher than in the bathing solution, while coions (i.e., those having the same sign as the fixed groups) have a lower concentration than in the bathing solution. The permselectivity of a nonideal membrane is defined as the difference between the counterion TN in the membrane T_i and that in solution t_i divided by the same difference in the case of an ideal permselective membrane [13–15]

$$S = \frac{T_i - t_i}{1 - t_i} \tag{8}$$

But this simple statement requires a careful definition of the TN T_i.

Some authors consider that the TN T_i should only be defined in pure conduction processes (i.e., in absence of concentration gradients and convective flow) [1,16]. Then, the TN would represent the fraction of current transported by the species i [13]

$$T_i \equiv \left(\frac{z_i \mathrm{F} J_i}{I} \right)_{dc_i/dx = 0} \tag{9}$$

Unfortunately, concentration gradients develop in the membrane and in the adjacent DBL under nonequilibrium conditions, and Eq. (9) cannot be used in connection with Eq. (8). Therefore, another definition which provides an *integral* characterization of the fraction of current that is transported *in the membrane system as a whole* must be introduced; the migrational TN are position dependent and they cannot provide this integral characterization. It is then proposed to use

$$T_i \equiv \frac{z_i \mathrm{F} J_i}{I} \tag{10}$$

where no restrictions apply [7], except for the requirement that current is transported under steady-state conditions, since only then the ion fluxes are constant throughout the membrane system.

Hittorf's method is intended to use directly the definition of integral TN. The membrane separates two electrolyte solutions of the same molarity, $c_{\mathrm{L}} = c_{\mathrm{R}}$ initially, and some electric current is passed across the system. Even though the passage of current causes slight changes in these concentrations, it is considered that Hittorf's method provides the result

$$T_i \equiv \left(\frac{z_i \mathrm{F} J_i}{I} \right)_{c_{\mathrm{L}} = c_{\mathrm{R}}} \tag{11}$$

Thus, Eq. (11) is taken in the next section as the definition of the integral TN of species i.

The reliability of TN as permselectivity and fixed charge estimates depends on our ability to eliminate the influence of the experimental method used in their determination. In particular, the TN in the limit of small fluxes, T_i^{eq} (i.e., where the two bathing solutions are the same and no electric current crosses the membrane system) have to be extracted from the measurements. Since the ion concentrations are constant throughout the membrane in this limit, the migrational TN are also constant. However, the difference between the local migrational TN in the membrane and in the bathing solutions means that they are different from the integral TN T_i^{eq}. Note that T_i^{eq} characterizes the membrane system as a whole and taking the limit of small fluxes does not imply the disappearance of the DBL effects.

It is also very important to consider how well the permselectivity given by

Eqs. (8) and (11) describe the behavior of the membrane system under given operating conditions. The membrane permselectivity is routinely measured in laboratories without taking into account the particular electromembrane technique for which the membranes are to be used. The Hittorf's and potentiometric methods provide the permselectivity at the static or "zero gradient" condition. This means that the counterion TN for a membrane separating electrolyte solutions of the same molarity ($c_L = c_R$ at $t = 0$ in Hittorf's experiments) or at zero current ($I = 0$ in potentiometric experiments) are obtained. Unlike these laboratory experiments, the molarities of bathing solutions differ and an external electric field introduces an electric current to the operating electromembrane systems. As a result, the membrane permselectivity under operating conditions differs from that obtained in laboratory experiments [17]. Simple methods for the determination of the membrane performance for any concentration difference and current density have been presented by A. Narebska and S. Koter [14,17,18].

Note, however, that when the bathing solutions are of different concentrations, $c_L \neq c_R$, the ion fluxes are no longer proportional to the electric current and the TN T_i include a contribution from the salt flux. Furthermore, if this diffusional component is predominant, the TN T_i can be smaller than zero or larger than unity [7,19]. Obviously, they cease to represent the fraction of current transported by the species i.

To summarize, the permselectivity and the integral TN are in fact parameters which characterize the membrane system as a whole, i.e., they incorporate a contribution from the DBL. Furthermore, their values are not the same under equilibrium and nonequilibrium conditions, which means that the effect of electric current (in the case of Hittorf's method) or differences in electrolyte concentration in the bathing solutions (in the case of potentiometric method) must be studied.

Finally, it is interesting to comment that the homogeneity of the membrane also affects its permselectivity. In order to increase the membrane permselectivity either the diffusion coefficients or the concentration of fixed charged groups must be modified. The former requires changes in the membrane structure and the results are very limited. The latter (i.e., the increase in the fixed charge concentration) requires increasing cross-linking, with a prohibitive increase in the electrical resistance of the membrane. However, the total concentration of fixed charges is not the only factor influencing the ion permselectivity. The particular distribution of these groups inside the membrane can play a significant role [20]. The possibility of having permselectivities exceeding that of a homogeneous distribution was first considered by H. Reiss [21,22]. This pioneering work was followed by other studies which were able to predict the distributions that would lead to higher permselectivities [23,24]. More recently, the significant influence of the DBL has been demonstrated [20,25].

C. Integral Transport Number in Hittorf's Experiment

The condition $c_L = c_R \equiv c_b$ enables an important conclusion on membrane permselectivity to be made from Eq. (2). Since the product $c_1 c_2$ is constant across the membrane boundaries, Eq. (2) can be integrated from $x = -\delta$ to $x = d + \delta$ to yield

$$T_i = \frac{z_i^2 D_i \langle c_i \rangle}{\sum_j z_j^2 D_j \langle c_j \rangle} \tag{12}$$

where

$$\langle c_i \rangle = \frac{1}{d + 2\delta} \int_{-\delta}^{d+\delta} c_i(x)\, dx \tag{13}$$

is the average concentration of species i over the membrane system. Hence, T_i *is a constant which depends on the actual concentration profiles across the membrane system.* Moreover, its value lies between the migrational TN in solution (where $c_1 = c_2$)

$$t_i = \frac{D_i}{D_1 + D_2} \tag{14}$$

and the migrational TN in the membrane (where $\bar{c}_1 \neq \bar{c}_2$)

$$\bar{t}_i(x) = \frac{D_i \bar{c}_i(x)}{D_1 \bar{c}_1(x) + D_2 \bar{c}_2(x)} \tag{15}$$

which is position dependent.

When the diffusion coefficients in the membrane phase differ from those in the bathing solutions, Eq. (12) takes the form

$$T_i = \frac{\langle c_i / D_{3-i} \rangle}{\langle c_1 / D_2 \rangle + \langle c_2 / D_1 \rangle} \tag{16}$$

where the diffusion coefficients are considered to be position dependent in the form

$$D_i(x) = \begin{cases} D_i, & -\delta < x < 0,\ d < x < d + \delta \\ \bar{D}_i, & 0 < x < d \end{cases} \tag{17}$$

Equation (16) can be further simplified because the local electroneutrality condition $c_1 = c_2 = c$ implies that the concentration gradient is constant in the DBL and

$$\int_{-\delta}^{0} c_i(x)\, dx + \int_{d}^{d+\delta} c_i(x)\, dx = 2c_b \delta \tag{18}$$

Therefore

$$T_i = \frac{t_i r + \dfrac{\bar{\tau}_i \langle \bar{c}_i \rangle}{c_m}}{r + \dfrac{\bar{\tau}_1 \langle \bar{c}_1 \rangle + \bar{\tau}_2 \langle \bar{c}_2 \rangle}{c_m}} \quad \text{(counterion)} \tag{19}$$

where

$$\bar{\tau}_i \equiv \frac{\bar{D}_i}{\bar{D}_1 + \bar{D}_2} \tag{20}$$

is a constant (not to be confused with $\bar{t}_i$), and

$$\langle \bar{c}_i \rangle = \frac{1}{d} \int_0^d \bar{c}_i(x)\, dx \tag{21}$$

is the average concentration of species i within the membrane. The parameter r is defined as

$$r = \frac{2\bar{D}_{12} c_b \delta}{D_{12} c_m d}, \tag{22}$$

with $D_{12} = 2D_1 D_2/(D_1 + D_2)$ and $\bar{D}_{12} = 2\bar{D}_1 \bar{D}_2/(\bar{D}_1 + \bar{D}_2)$ being the salt diffusion coefficients in solution and in the membrane, respectively.

The concentration $\langle \bar{c}_i \rangle$ can be easily evaluated in the limit of small fluxes. In particular, Eqs. (A1) and (A14) (see Appendix) yield

$$\langle \bar{c}_i^{eq} \rangle = \bar{c}_i^{eq} = -\frac{z_m c_m}{2z_i} + \left[\left(\frac{c_m}{2} \right)^2 + c_b^2 \right]^{1/2} \tag{23}$$

where $c_b = c_L = c_R$. The counterion TN given by Eq. (19) in this limit has been represented in Fig. 2, against $\bar{D}_{12}\delta/D_{12}d$ which represents the ratio between the diffusional permeability of the DBL, D_{12}/δ, and that of the membrane, $\bar{D}_{12}/d$. The effect of both the membrane fixed charge concentration and the DBL thickness have been analyzed in Fig. 2. It is shown that $T_{\text{counterion}}$ varies from the migrational TN in the membrane to the migrational TN in the DBL when $\bar{D}_{12}\delta/D_{12}d$ decreases.

The concentration $\langle \bar{c}_i \rangle$ is also easily evaluated for the case of ideal permselective membranes, where total coion exclusion takes place. The local counterion TN within the membrane $\bar{t}_i$ equals unity, and

$$T_i = \frac{t_i r + \bar{\tau}_i}{r + \bar{\tau}_i} \quad \text{(counterion)} \tag{24}$$

Thus, the integral counterion TN varies between 1 when $r \ll 1$, i.e., when the DBL effects are negligible, and t_i when $r \gg 1$, i.e., when the transport across the membrane system is controlled by the DBL. In terms of the membrane permselectivity, which in this case takes the form $S = 1/(1 + r/\bar{t}_i)$, these two limits correspond to $S = 1$ and $S = 0$, respectively.

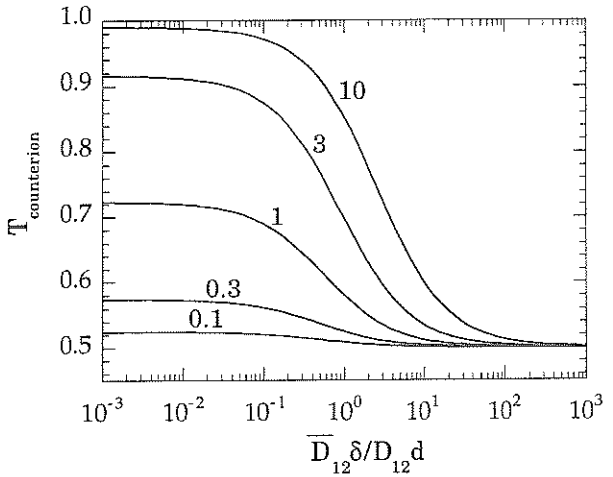

FIG. 2 Counterion transport number in the limit of small fluxes against the diffusional permeability of the DBL (relative to that of the membrane). The values of c_m/c_b are shown on the curves, and equal diffusion coefficients have been considered for coions and counterions, i.e., $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$.

The application of Eq. (19) to nonideal membranes requires calculating $\langle \bar{c}_i \rangle$ from the solution of the Nernst–Planck equations. The description of this problem is conveniently made in terms of the TN ratio

$$\eta = \frac{T_1}{T_2} \tag{25}$$

Equations (A4) and (A5) in the Appendix can be easily transformed into

$$\eta = \frac{\bar{D}_1}{\bar{D}_2} \frac{\bar{c}_1(d) - e\bar{c}_1(0)}{\bar{c}_2(d) - e\bar{c}_2(0)} \tag{26}$$

where

$$e \equiv \exp\left\{ \frac{2[\bar{c}_1(d) - \bar{c}_1(0)] + d \sum_i \frac{J_i}{\bar{D}_i}}{\frac{z_m c_m}{z_1} \frac{\eta + \bar{D}_1/\bar{D}_2}{\eta - \bar{D}_1/\bar{D}_2}} \right\} \tag{27}$$

and the concentrations $\bar{c}_1(0)$ and $\bar{c}_1(d)$ are given by Eqs. (A14) and (A11). In particular, Eqs. (A11) take in this case the form

$$c_1(0) = c_b(1 - I/I_{lim}) \tag{28a}$$

$$c_1(d) = c_b(1 + I/I_{lim}) \tag{28b}$$

where

$$I_{\lim} = \frac{\eta + 1}{\eta - D_1/D_2} \frac{2FD_1 c_b}{\delta} \tag{29}$$

is the limiting current density [26]. Equations (26) and (27) can be solved iteratively to obtain η, and thus also the TN T_i. This implies that the average concentrations $\langle \bar{c}_i \rangle$ are known [see Eq. (19)].

In Fig. 3, the local migrational TN is compared to the integral TN for different values of the DBL thickness. In the limit of high diffusional permeability of the DBL (relative to that of the membrane), $T_{\text{counterion}}$ equals the local migrational TN at $x = d$, i.e., the minimum value of $\bar{t}_i(x)$ inside the membrane. The explanation for this behavior can be found in Eqs. (2) (applied to membrane phase) and (10)

$$J_i = -\frac{\bar{D}_1 \bar{D}_2}{\bar{D}_1 \bar{c}_1 + \bar{D}_2 \bar{c}_2} \frac{d(\bar{c}_1 \bar{c}_2)}{dx} + \frac{\bar{t}_i}{z_i} \frac{I}{F} = \frac{T_i}{z_i} \frac{I}{F} \tag{30}$$

Since T_i is constant and the terms representing the diffusional salt flux inside the membrane and the ion migration have different signs, the local migrational TN has to be larger than T_i. Equality is possible only when there is no diffusional contribution to the ion flux, i.e., when the concentration profiles inside the membrane are flat. Indeed, Fig. 4 shows that the concentration profiles

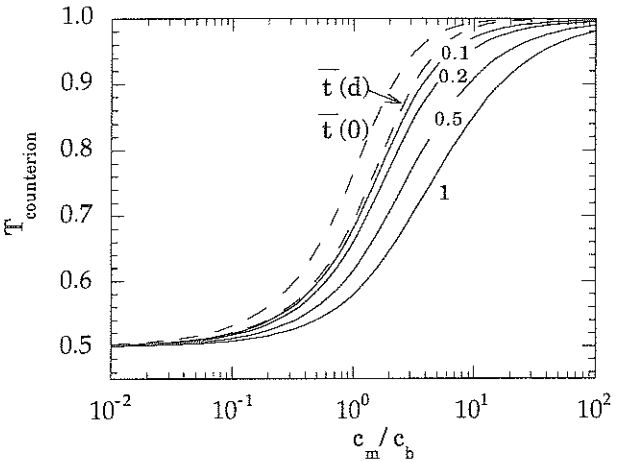

FIG. 3 The effect of the diffusional permeability of the DBL (values of $\bar{D}_{12}\delta/D_{12}d$ shown on the curves) on the counterion transport number in Hittorf's experiment. The electric current density amounts to 20% of the limiting value, $I/I_{\lim} = 0.2$. Other parameters are $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$. The dashed lines show the migrational counterion transport number at the membrane ends.

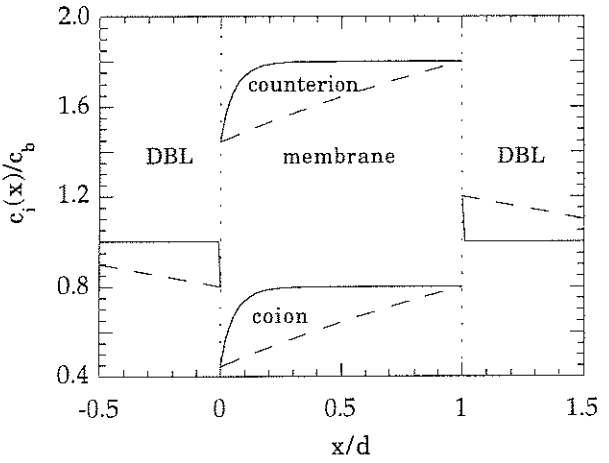

FIG. 4 The effect of the DBL thickness, at constant polarization ratio $I/I_{lim} = 0.2$, on the concentration profiles for $c_m/c_b = 1$, $\bar{D}_{12}/D_{12} = 1$, $D_1/D_2 = 1$, and $\bar{D}_1/\bar{D}_2 = 1$. The dashed lines correspond to $\delta/d = 1$ and show practically linear profiles. In this case, $\langle \bar{c}_{counterion} \rangle = 1.636$ and $T_{counterion} = 0.580$. The continuous lines correspond to $\delta/d = 0.01$, and show nonlinear concentration profiles inside the membrane, leading to an average concentration larger than in the case $\delta/d = 1$. In particular, $\langle \bar{c}_{counterion} \rangle = 1.780$ and $T_{counterion} = 0.692$. These values are to be compared to $\bar{c}_{counterion}(0) = 1.443$, $\bar{c}_{counterion}(d) = 1.800$, $\bar{t}_{counterion}(0) = 0.765$, $\bar{t}_{counterion}(d) = 0.692$.

inside the membrane are flat (except for the region in the close vicinity of $x = 0$) when $\bar{D}_{12}\,\delta/D_{12}\,d$ is very small. Furthermore, since $\langle \bar{c}_i \rangle$ approaches $\bar{c}_i(d)$ in the limit $\bar{D}_{12}\,\delta/D_{12}\,d \to 0$, Eq. (19) clearly explains that $T_{counterion}$ approaches $\bar{t}_i(d)$.

It was mentioned in Sec. II.B that TN have to be measured under nonequilibrium conditions (e.g., in the presence of electric current in Hittorf's method) and that the observed TN might depend on how far away is the system from the equilibrium state. In particular, since T_i depends on the actual concentration profiles across the membrane system [see Eq. (12)] and these are affected by the current density, T_i is also a function of the current density [20,24, 27]. For instance, Fig. 5 shows that the changes in the counterion transport are of the order of 10% when $\bar{D}_{12}\,\delta/D_{12}\,d = 0.1$, which is a common practical situation. This is in agreement with the relatively low values of counterion TN measured under limiting current conditions [28].

Experimentally, the TN may be observed to increase with increasing current density at low current densities [5,29]. This effect is due to back diffusion and cannot be accounted for by the above equations because of the condition $c_R = c_L$ imposed here.

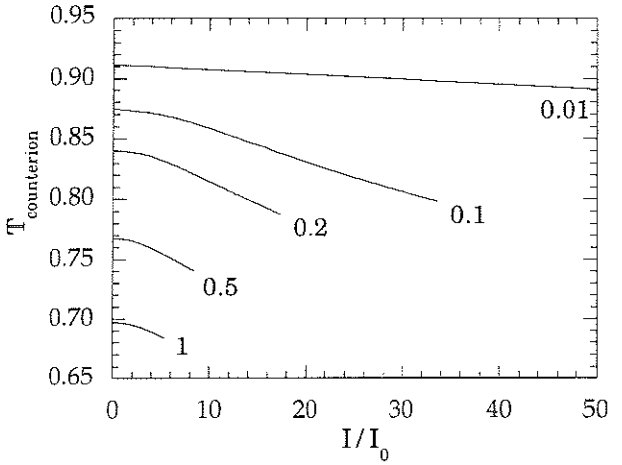

FIG. 5 The effect of the electric current on the counterion transport number in Hittorf's experiment for different values of the diffusional permeability of the DBL (values of $\bar{D}_{12}\delta/D_{12}d$ shown on the curves). The fixed charge concentration is $c_m/c_b = 3$, and the diffusion coefficients satisfy $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$. The current has been normalized to $I_0 = FD_{12}c_b/d$, and ranges from zero to I_{lim}/I_0 (except for the case $\bar{D}_{12}\delta/D_{12}d = 0.01$, where $I_{lim}/I_0 = 333$).

D. Potentiometric Transport Numbers

In Sec. II.C, the integral TN under Hittorf's conditions, i.e., with $c_L = c_R = c_b$ and an electric current passing through the system, were introduced. In this section, a membrane system under zero electric current and where $c_L \neq c_R$ is considered and the integral TN under potentiometric conditions are introduced.

The diffusion potential drop in the membrane can be formally obtained by integrating Eq. (7)

$$\Delta\bar{\phi}_{dif} = -\frac{RT}{F}\int_0^d \sum_i \frac{\bar{t}_i}{z_i}\, d \ln \bar{c}_i \tag{31}$$

The actual integration requires the solution of the transport equations to find the concentration profiles, and therefore, the variation of t_i throughout the membrane. Alternatively, the variables t_i can be replaced by some average (constant) values, $\overline{T}_i$, which give the same diffusion potential. Thus, Eq. (31) is used to introduce the potentiometric TN $\overline{T}_i$ by means of the equation

$$\Delta\bar{\phi}_{dif} = -\frac{RT}{F}\sum_i \frac{\overline{T}_i}{z_i} \ln \frac{\bar{c}_i(d)}{\bar{c}_i(0)} \tag{32}$$

The property

$$\sum_i \bar{T}_i = 1 \tag{33}$$

together with Eqs. (A14) in Appendix for the Donnan potential drops, allows us to write

$$\Delta\phi_{\mathrm{D,L}} + \Delta\bar{\phi}_{\mathrm{dif}} + \Delta\phi_{\mathrm{D,R}} = -\frac{RT}{\mathrm{F}} \sum_i \frac{\bar{T}_i}{z_i} \ln \frac{c_i(d)}{c_i(0)} \tag{34}$$

In the presence of DBL effects, the total potential drop across the membrane system (or membrane potential) also incorporates contributions from the diffusion potential in these layers. Integration of Eq. (7) yields

$$\Delta\phi_{\mathrm{dif,L}} = -\frac{RT}{\mathrm{F}} \sum_i \frac{t_i}{z_i} \ln \frac{c_i(0)}{c_{\mathrm{L}}} \tag{35a}$$

and

$$\Delta\phi_{\mathrm{dif,R}} = -\frac{RT}{\mathrm{F}} \sum_i \frac{t_i}{z_i} \ln \frac{c_{\mathrm{R}}}{c_i(d)} \tag{35b}$$

so that the membrane potential is given by

$$\Delta\phi_{\mathrm{M}} = -\frac{RT}{\mathrm{F}} \sum_i \frac{\bar{T}_i}{z_i} \ln \frac{c_i(d)}{c_i(0)} - \frac{RT}{\mathrm{F}} \sum_i \frac{t_i}{z_i} \ln \frac{c_i(0)c_{\mathrm{R}}}{c_i(d)c_{\mathrm{L}}} \tag{36}$$

where the concentrations $c_i(0)$ and $c_i(d)$ are

$$c_1(0) = c_2(0) = c_{\mathrm{L}} - J_{12}\,\delta/D_{12} \tag{37a}$$

$$c_1(d) = c_2(d) = c_{\mathrm{R}} + J_{12}\,\delta/D_{12} \tag{37b}$$

Equation (36) can be written, similarly to Eq. (34), in the form

$$\Delta\phi_{\mathrm{M}} = -\frac{RT}{\mathrm{F}} \sum_i \frac{T_i}{z_i} \ln \frac{c_{\mathrm{R}}}{c_{\mathrm{L}}} \tag{38}$$

which serves as a definition for the potentiometric TN T_i of the membrane system. Evidently, these TN are also required to satisfy the condition $\sum_i T_i = 1$. From a practical point of view, the TN T_i are evaluated by arranging Eq. (38) in the form

$$T_i = \frac{1}{2}\left[1 - \frac{z_i \mathrm{F}\,\Delta\phi_{\mathrm{M}}/RT}{\ln(c_{\mathrm{R}}/c_{\mathrm{L}})}\right] \tag{39}$$

Note that the membrane potential $\Delta\phi_{\mathrm{M}}$ must be calculated by subtracting the electrode potentials from the cell potential [15,30]. Comparison with Eq. (36) clearly shows that Eq. (39) must yield values between $\bar{T}_i$, when $J_{12}\,\delta/D_{12}\,c_{\mathrm{L}} \ll 1$, i.e., when the DBL effects are negligible, and t_i, when the membrane effects are negligible and $c_i(0) \approx c_i(d)$.

From a theoretical point of view, the evaluation of T_i requires the solution of the transport equations in a binary system to calculate $\Delta\phi_M$. This solution can be easily derived from that worked out in the Appendix for a ternary system. In particular, the application of Eqs. (A4) and (A5) to a binary case gives

$$\Delta\bar{\phi}_{dif} = \frac{1}{z_1}\frac{RT}{F}\frac{\bar{D}_2 - \bar{D}_1}{\bar{D}_1 + \bar{D}_2}\ln\frac{\bar{c}_1(d) + \bar{\tau}_2\dfrac{z_m c_m}{z_1}}{\bar{c}_1(0) + \bar{\tau}_2\dfrac{z_m c_m}{z_1}} \tag{40}$$

and

$$J_{12} = -\frac{\bar{D}_{12}}{d}\left[\bar{c}_1(d) - \bar{c}_1(0) - \frac{z_m c_m}{2}\frac{F\,\Delta\bar{\phi}_{dif}}{RT}\right] \tag{41}$$

These equations, when combined to Eqs. (35), (37) and (A14), lead to the desired $\Delta\phi_M$ evaluation by following a simple iterative procedure.

The counterion TN given by Eq. (39) has been represented in Fig. 6, where both the effects of the membrane fixed charge concentration (values of c_m/c_L shown on the curves) and the DBL thickness have been analysed. When the diffusional permeability of the DBL (relative to that of the membrane) is small,

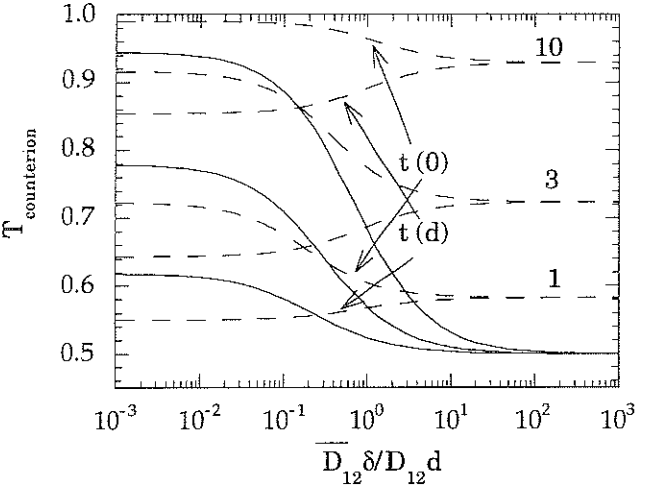

FIG. 6 Counterion potentiometric transport number in the limit of small fluxes against the diffusional permeability of the DBL (relative to that of the membrane) for membranes of different charge concentration (the values of c_m/c_L are shown on the curves). The concentration ratio has been set to $c_R/c_L = 5$, and the diffusion coefficients satisfy $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$. The dashed lines show the migrational transport number of the counterion at the two ends of the membrane.

the concentration gradient is in the DBL, and $c_i(0) \approx c_i(d)$. The local migrational TN is constant within the membrane and the potentiometric TN equals the bulk value t_i. On the contrary, when the diffusional permeability of the DBL (relative to that of the membrane) becomes larger, the membrane phase is also polarized and $\bar{t}_i(x)$ can vary significantly over the membrane. In particular, it can be read from the curves with $c_m/c_b = 3$ that $\bar{t}_{counterion}(0) = 0.916$ and $\bar{t}_{counterion}(d) = 0.644$ when $\bar{D}_{12}\,\delta/D_{12}\,d \to 0$. The potentiometric TN $T_{counterion}$ takes approximately the average value of $\bar{t}_{counterion}(0)$ and $\bar{t}_{counterion}(d)$ at this limit. Note that this situation is different to that observed in the case of Hittorf's method, where $T_{counterion}$ approaches $\bar{t}_{counterion}(d)$ in the limit $\bar{D}_{12}\,\delta/D_{12}\,d \to 0$. The difference can be more easily appreciated by comparing Figs. 3 and 7.

Similarly to the Hittorf's integral TN, which is a function of the current density (see Fig. 5), the potentiometric TN varies with the concentration ratio c_R/c_L. This effect is more pronounced (see Fig. 8) in the case of high diffusional permeability of the DBL (relative to the membrane), i.e., low $\bar{D}_{12}\,\delta/D_{12}\,d$ values.

Figure 8 shows that the potentiometric TN depend on the two external concentrations and should be denoted as $T_i(c_R, c_L)$. It can be easily shown that,

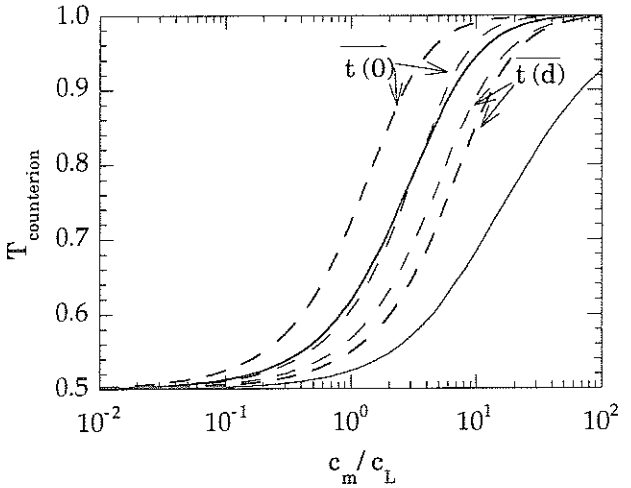

FIG. 7 The effect of the diffusional permeability of the DBL on the potentiometric transport number (continuous lines). The concentration ratio has been set to $c_R/c_L = 5$, and the diffusion coefficients satisfy $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$. The dashed lines show the migrational transport number of the counterion at the two membrane ends. The bold lines correspond to $\bar{D}_{12}\,\delta/D_{12}\,d = 0.01$ and the thin lines to $\bar{D}_{12}\,\delta/D_{12}\,d = 1$.

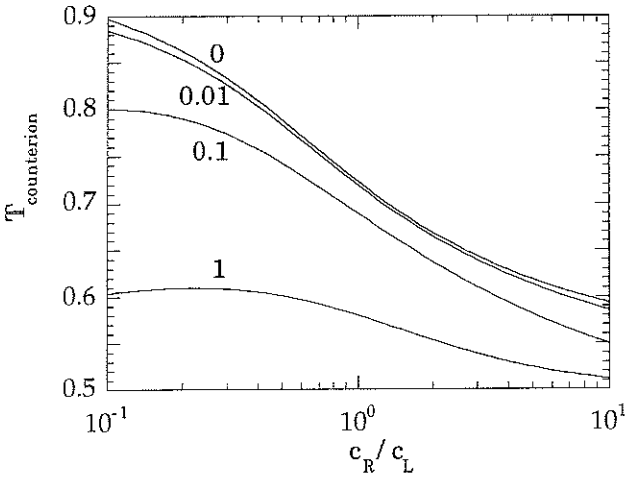

FIG. 8 The effect of the bulk concentration ratio on the potentiometric transport number for different values of the diffusional permeability of the DBL ($\bar{D}_{12}\delta/D_{12}d$ values are shown on the curves). The fixed charge concentration is $c_m/c_L = 1$, and the diffusion coefficients satisfy $D_1/D_2 = 1$ and $\bar{D}_1/\bar{D}_2 = 1$.

when $c_R > c_L$,

$$t_i^{eq}(c_R) < T_i(c_R, c_L) < t_i^{eq}(c_L) \quad \text{(counterion)} \tag{42}$$

where $t_i^{eq}(c)$ is the migrational TN inside the membrane corresponding to an equilibrium situation where the two external solution have the same concentration c. Equation (42) suggests that, in principle, the potentiometric TN could be referred to just one external solution concentration c_{av} such that

$$T_i(c_R, c_L) = T_i^{eq}(c_{av}, c_{av}) = t_i^{eq}(c_{av}) \quad \text{with} \quad c_L < c_{av} < c_R \tag{43}$$

In practice, this is not so straightforward due to the complicated dependence of $\Delta\phi_M$ on the ionic concentration differences [see Eq. (36)]. Several estimates have been proposed for c_{av} (e.g., c_R, c_L, $(c_R + c_L)/2$, $(c_R c_L)^{1/2}$, etc.) but they all lead to important systematic errors [31]. This problem can be easily overcome by using two potentiometric TN. In particular, it has been suggested [6,7] that $t_i^{eq}(c)$ could be estimated as

$$t_i^{eq}(c) = \tfrac{1}{2}[T_i(r_c c, c) + T_i(c/r_c, c)] + \varepsilon(t_i^{eq}) \tag{44}$$

where r_c is the ratio of external concentrations and $\varepsilon(t_i^{eq})$ is the error of this estimation. Since $T_i(r_c c, c)$ can be considered a linear function of $\ln r_c$ for small values of r_c, Eq. (44) leads then to an accurate determination of $t_i^{eq}(c)$. From the experimental point of view, however, it is required that r_c is not close to one, as $\Delta\phi_M$ would be small and could not be determined with sufficient accu-

racy. Satisfactory values of r_c for the estimation of $t_i^{eq}(c)$ are between 2 and 5. Other interpolation techniques to obtain $t_i^{eq}(c)$ are also possible [5], but only those accurate to second order in $\ln r_c$ should be used [31].

III. TERNARY ELECTROLYTES

A. Introduction

The counterion TN measured to characterize a given charged membrane is often obtained with binary electrolyte solutions. In electromembrane process, however, ternary systems are often involved. Moreover, even in systems where the bathing solutions are intended to be binary [32], the minimal presence of hydrogen ions from the autoprotolysis of water makes them ternary systems at high dilution [33]. The incorporation of the third ion (H^+) in the calculation of the membrane potential is then of great importance [34–38].

The measured TN are also used to estimate the membrane fixed charge concentration [28,33,39,40] as well as the presence of any intrinsic asymmetry present in the membrane [41–43]. Particularly interesting is the case of biological membranes such as cornea or skin. The recent interest in electro-assisted transdermal drug delivery processes has recalled the need for accurate determination methods of the TN of drugs [44]. Since biological membranes are often amphoteric, a change in bathing solution pH can alter the ratio of negatively charged to positively charged groups in the membrane [45] (see also Chap. 12). The TN determination is then carried out in the presence of an acid or a base that is added to adjust the pH of the bathing electrolyte solutions. The bathing solutions become then (at least) ternary systems, e.g., KCl–HCl or KCl–KOH.

The aim of this section is to study the effect of the acid or base addition on the potentiometric determination of TN. For the sake of clarity, the DBL effects will not be considered here. Firstly, the definition of potentiometric TN in ternary systems are worked out. Then, the local concentration and electrical potential profiles obtained from the solution of the transport equations are used to evaluate the potentiometric TN. These are compared to the apparent potentiometric TN, i.e., those obtained by assuming that the ternary system behaves as a binary system. Finally, some comments on the estimation of the membrane fixed charge concentration are given.

B. Apparent Potentiometric Transport Numbers

The analysis of TN in ternary electrolyte systems will be restricted to potentiometric TN. By extending Eq. (38) to the ternary case, the membrane potential can be written as

$$\Delta\phi_M = -\frac{RT}{F}\sum_i \frac{T_i}{z_i}\ln\frac{c_{i,R}}{c_{i,L}} \tag{45}$$

where $c_{i,R}$ and $c_{i,L}$ denote the ion concentrations in the bathing solutions, which are formed by mixing two completely dissociated binary electrolytes with a common ion. The common ion is denoted by subscript $i = 1$ and subscript $i = 3$ is used for the minority ion.

The potentiometric TN evaluation in ternary systems is complex both from a theoretical point of view as well as from an experimental point of view; note that the two independent TN cannot be obtained from a single membrane potential measurement. Then, some authors [45] have resolved to interpret the membrane potential measurements of ternary systems by using Eq. (45) in the binary system form, thus neglecting the effect of the acid or base added to adjust the pH. The potentiometric TN are then obtained as

$$T_{i,\text{app}} \equiv \frac{1}{2}\left[1 - \frac{z_i \mathrm{F}\,\Delta\phi_M/RT}{\ln(c_{i,R}/c_{i,L})}\right] \tag{46}$$

and are named *apparent potentiometric TN*. This procedure constitutes an oversimplification in the study of ternary systems. The apparent TN so determined are not properties of the ions constituting the binary salt in the membrane but they also incorporate the effect of the acid or base added. Indeed, the introduction of Eq. (45) into Eq. (46) leads to

$$T_{1,\text{app}} = \frac{T_1}{2}\left[1 + \frac{\ln(c_{1,R}/c_{1,L})}{\ln(c_{2,R}/c_{2,L})}\right] + \frac{T_3}{2}\left[1 - \frac{\ln(c_{3,R}/c_{3,L})}{\ln(c_{2,R}/c_{2,L})}\right] \tag{47}$$

which coincides with T_1 only when $c_{1,R}/c_{1,L} = c_{2,R}/c_{2,L} = c_{3,R}/c_{3,L}$. Note, however, that $T_{2,\text{app}}$ does not coincide with T_2 unless $c_3 = 0$.

The apparent counterion TN in the ternary systems KCl–HCl and KCl–KOH is presented in Figs. 9 and 10. The two bathing solutions have the same pH, so that $c_{3,R} = c_{3,L} \equiv c_T = 10^{-\text{pH}}$ M. The membrane potential is calculated as described in the Appendix [see Eq. (A15)] for the particular case $\delta = 0$, i.e., in absence of DBL effects. Equation (46) is then used to obtain $T_{2,\text{app}}$. The infinite dilution values [46] have been employed for the diffusion coefficients: $D_{Cl^-} = 2.03 \times 10^{-5}$ cm^2/s, $D_{K^+} = 1.95 \times 10^{-5}$ cm^2/s, $D_{H^+} = 9.30 \times 10^{-5}$ cm^2/s, and $D_{OH^-} = 4.50 \times 10^{-5}$ cm^2/s.

Figure 9 corresponds to a negatively charged membrane ($z_m = -1$) and KCl–HCl bathing solutions. The fixed charge concentration is $c_m = c_{2,L}$, where subscript $i = 2$ is used for the potassium ion. It is observed that $T_{2,\text{app}}$ changes considerably with $c_T/c_{2,L}$ when $c_{2,R}/c_{2,L} = 0.1$ but not so much when $c_{2,R}/c_{2,L} = 10$ because these TN tend to ~ 0.5 at high bathing solution concentrations. Still, Fig. 10 shows that the influence of the third ion (H^+ or OH^-) on $T_{2,\text{app}}$ becomes more pronounced when higher values of the fixed charge concentration are considered. In this figure the situation of K^+ as coion ($z_m = 1$) has also been considered.

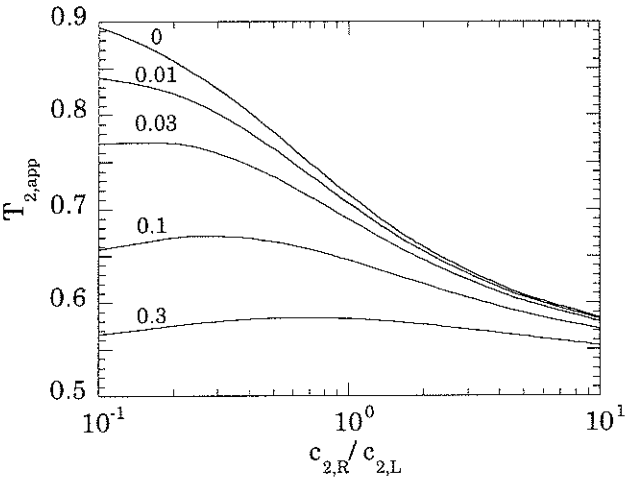

FIG. 9 Apparent transport numbers of potassium ion against its bulk solution concentration ratio $c_{2,R}/c_{2,L}$. The numbers on the curves give the value of $c_T/c_{2,L}$, where c_T is the H^+ concentration in the bathing solutions.

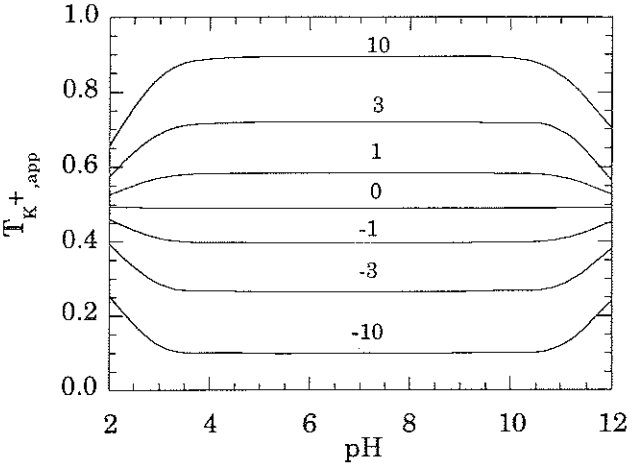

FIG. 10 The influence of the third ion (H^+ or OH^-) on the apparent transport number of potassium ion corresponding to $c_{2,R}/c_{2,L} = 10$. The values of $-z_m c_m/c_{2,L}$ are shown on the curves.

C. Potentiometric Transport Numbers

Even though Eq. (45) is sound due to its similarity to Eq. (38), the definition of the TN T_i is not straightforward. In contrast to the case for binary electrolytes, where there is only one independent TN and Eq. (38) constitutes the definition of the potentiometric TN, additional expressions are required when ternary systems are considered.

It has been shown [47] that Eq. (31) can be written in the form

$$\Delta\bar{\phi}_{\text{dif}} = -\frac{RT}{\text{F}}\left(\int_0^d \frac{d\ln\bar{c}_1}{z_1} + \int_0^d \frac{\bar{t}_2\, d\ln\bar{p}_{12}}{z_2} + \int_0^d \frac{\bar{t}_3\, d\ln\bar{p}_{13}}{z_3}\right) \tag{48}$$

where $\bar{p}_{12} \equiv \bar{c}_1\bar{c}_2$ and $\bar{p}_{13} \equiv \bar{c}_1\bar{c}_3$ are the ideal salt activities [48]. Equation (49) allows us to introduce the potentiometric TN in membrane phase as

$$\bar{T}_2 \equiv \frac{\int_0^d \bar{t}_2\, d\ln\bar{p}_{12}}{\ln[\bar{p}_{12}(d)/\bar{p}_{12}(0)]} \tag{49a}$$

$$\bar{T}_3 \equiv \frac{\int_0^d \bar{t}_3\, d\ln\bar{p}_{13}}{\ln[\bar{p}_{13}(d)/\bar{p}_{13}(0)]} \tag{49b}$$

while $\bar{T}_1$ is determined from Eq. (33).

In the DBL, equations similar to (48) and (49) can be obtained for the potentiometric TN and the diffusion potential drop. The membrane potential is then given by

$$\Delta\phi_{\text{M}} = -\frac{RT}{\text{F}}\left(\frac{1}{z_1}\ln\frac{c_{1,\text{R}}}{c_{1,\text{L}}} + \frac{T_2}{z_2}\ln\frac{p_{12,\text{R}}}{p_{12,\text{L}}} + \frac{T_3}{z_3}\ln\frac{p_{13,\text{R}}}{p_{13,\text{L}}}\right) \tag{50}$$

where

$$T_2 \equiv \frac{\int_{-\delta}^{d+\delta} t_2\, d\ln p_{12}}{\ln(p_{12,\text{R}}/p_{12,\text{L}})} \tag{51a}$$

$$T_3 \equiv \frac{\int_{-\delta}^{d+\delta} t_3\, d\ln p_{13}}{\ln(p_{13,\text{R}}/p_{13,\text{L}})} \tag{51b}$$

are the potentiometric TN in the membrane system. Note that Eq. (50) coincides with Eq. (45).

The T_i values where $c_{i,\text{R}} \neq c_{i,\text{L}}$ cannot be obtained from membrane potential measurements and require the solution of the transport equations for their evaluation (see Appendix). Figure 11 shows the apparent and exact TN of potassium ion for $c_{2,\text{R}}/c_{2,\text{L}} = 0.1$, 1 and 10. Once again, for the sake of clarity, DBL effects are not considered (i.e., $\delta = 0$). It is observed that the exact TN

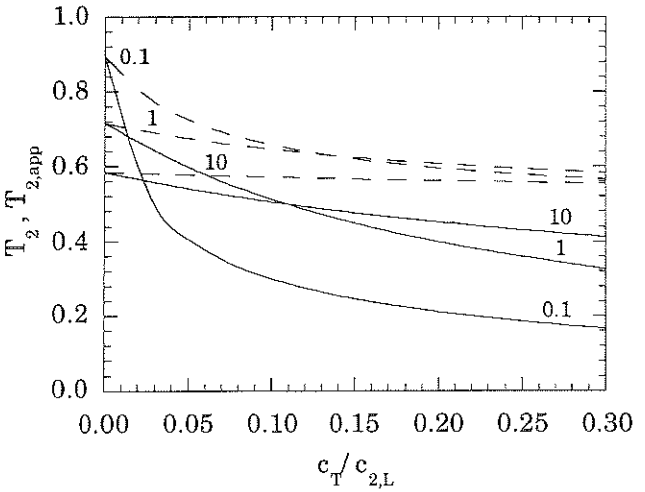

FIG. 11 Apparent (dashed lines) and exact (continuous lines) potentiometric transport number of potassium ion in the system KCl–HCl vs. $c_T/c_{2,L}$ for different values of $c_{2,R}/c_{2,L}$ (shown on the curves), $z_m = -1$ and $c_m/c_{2,L} = 1$.

take low values when $c_T/c_{2,L}$ increases, while the apparent TN remain close to 0.5 in this limit. It is also seen that the difference between exact and apparent values is significant, and increases with decreasing $c_{2,R}/c_{2,L}$.

D. Fixed Charge Estimation

The differences noted in the previous sections between the exact and the apparent TN suggest that the use of apparent TN to estimate the membrane fixed charge concentration could also lead to significant errors even when the third ion present has a relatively low concentration [47]. It is therefore necessary to identify the effect of the third ion by determining the relation between apparent and exact TN. However, this relation is very complicated (see Eq. (47) and note that T_1 and T_3 depend also on the ionic concentrations in the bathing solutions as well as on the unknown fixed charge concentration), and requires the solution of the transport equations (see Fig. 11). Fortunately, this situation changes when the limit of small fluxes (i.e., the equilibrium limit) is considered.

The equilibrium concentrations can be easily obtained from Eqs. (A1) and (A14) as

$$\bar{c}_1^{eq} = -\frac{z_m}{z_1}\frac{c_m}{2} + \left[\left(\frac{c_m}{2}\right)^2 + (c + c_T)^2\right]^{1/2} \tag{52a}$$

$$\frac{\bar{c}_2^{eq}}{\bar{c}_3^{eq}} = \frac{c}{c_T} \tag{52b}$$

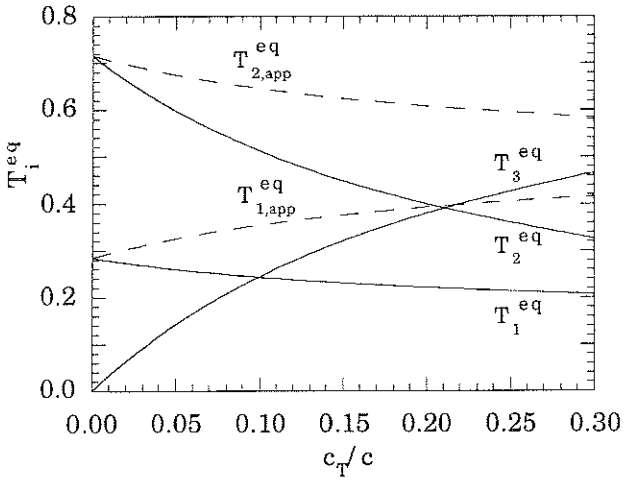

FIG. 12 Apparent (dashed lines) and exact (continuous lines) potentiometric transport numbers in the limit of small fluxes for the system KCl–HCl ($i = 1$ Cl^-, $i = 2$ K^+, $i = 3$ H^+).

where $c = c_{2,R} = c_{2,L}$ and $c_T = c_{3,R} = c_{3,L}$. Since no DBL effects are taken into account, the integral TN coincide with the migrational TN in the membrane, $T_i^{eq} = \bar{t}_i^{eq}$. Then, Eq. (52b) implies

$$\frac{T_2^{eq}}{\bar{D}_2 c} = \frac{T_3^{eq}}{\bar{D}_3 c_T} \tag{53}$$

Moreover, in the limit $c_{2,R}/c_{2,L} \to 1$, Eq. (47) reduces to

$$T^{eq}_{1,app} = T_1^{eq}\left(1 - \frac{1}{2}\frac{c_T}{c + c_T}\right) + \frac{T_3^{eq}}{2} \tag{54}$$

It is now possible to solve for T_1^{eq} and obtain

$$T_1^{eq} = \frac{2\left(1 + \dfrac{\bar{D}_2 c}{\bar{D}_3 c_T}\right)T^{eq}_{1,app} - 1}{2\left(1 + \dfrac{\bar{D}_2 c}{\bar{D}_3 c_T}\right)\left(1 - \dfrac{1}{2}\dfrac{c_T}{c + c_T}\right) - 1} \tag{55a}$$

and

$$T_2^{eq} = \frac{1 - T_1^{eq}}{1 + \dfrac{\bar{D}_3 c_T}{\bar{D}_2 c}} \tag{55b}$$

while T_3^{eq} is given by the condition $\sum_i T_i^{eq} = 1$. Figure 12 shows the comparison of the equilibrium values for the apparent TN and the exact ones for the case $z_m = -1$ and $c_m = c$. Note that $T_i^{eq} \to T_{i,app}^{eq}$ $(i = 1,2)$ and $T_3^{eq} \to 0$ when $c_T \to 0$. However, the differences between apparent and exact values become significant even for relatively low values of c_T/c.

Finally, the membrane fixed charge concentration can be determined from Eqs. (52) and $T_i^{eq} = \bar{t}_i^{eq}$ as

$$c_m = \frac{2z_1}{z_m}(c + c_T)\sinh\left\{\frac{1}{2}\ln\left[\left(\frac{1}{T_1^{eq}} - 1\right)\frac{D_1(c + c_T)}{D_2 c + D_3 c_T}\right]\right\}, \tag{56}$$

where T_1^{eq} is determined from Eq. (55a), and $T_{i,app}^{eq}(c)$ can be obtained from two membrane potential measurements as

$$T_{i,app}^{eq} \approx \tfrac{1}{2}[T_{i,app}(r_c c, c) + T_{i,app}(c/r_c, c)] \tag{57}$$

where $r_c \equiv c_{2,R}/c_{2,L}$.

IV. CONVECTIVE FLOW

A. Reference System

Thus far the absence of bulk convective flow has been implicitly assumed. It is considered here the case of dilute solutions with nonzero solvent velocity. The reference system used to describe the relative average velocities of the different species now becomes of primary importance for the interpretation of experimental results [49]. The aim of this section is to briefly describe the effects of convective flow on ion transport in charged membranes. More thorough studies on the flux equations in these systems and the choice of reference frame can be found in Refs. 50–52.

Whenever the reference system is not made explicit, it must be assumed that the membrane-fixed or laboratory reference system is being used. In this reference system, the flux densities are given by

$$J_i = c_i v_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{F}{RT}\frac{d\phi}{dx}\right) + c_i v_0 \tag{58}$$

where v_i is the velocity of species i and v_0 the solvent velocity (both defined with respect to the membrane).

The presence of bulk solvent flow inside a charged membrane gives rise to electrokinetic phenomena [16,53] (see also Chap. 15). Since the solution inside the membrane is not electrically neutral and has an electric charge per unit volume $-Fz_m c_m$, the mass transport also implies the presence of an electric current density, $I_{str} = -Fz_m c_m v_0$, which is called the *streaming current*.

When electric potential and concentration gradients are also present, the total current density is given by

$$I = -\kappa\left(\frac{d\phi}{dx} - \frac{d\phi_{\text{dif}}}{dx}\right) - \text{F}z_{\text{m}}c_{\text{m}}v_0 = -\kappa\left(\frac{d\phi}{dx} - \frac{d\phi_{\text{dif}}}{dx} - \frac{d\phi_{\text{str}}}{dx}\right) \tag{59}$$

where κ was defined in Eq. (6) (some authors, however, use different definitions [53,54]). If the total current density is zero, the bulk flow inside the membrane implies that an electric potential gradient $d\phi_{\text{str}}/dx$ must appear, in addition to the diffusion potential gradient, to slow down the counterions and accelerate the coions and thus maintain electroneutrality. The electric potential drop in the membrane due to the bulk flow is called *streaming potential*, $\Delta\phi_{\text{str}}$.

In the next sections, the bulk flow is also described in terms of the velocity v_0 and the question of its origin is avoided. For the present discussion, it is sufficient to state that the velocity v_0 is proportional to the net force (other than viscous forces) acting on an elementary volume of the solution [55]

$$v_0 = d_{\text{h}}\left(-\frac{dp}{dx} + \text{F}z_{\text{m}}c_{\text{m}}\frac{d\phi}{dx}\right) \tag{60}$$

where d_{h} is the hydrodynamic permeability. The electric potential gradient may be externally imposed but can also arise because of the solvent flow (i.e., the streaming potential gradient) or because of the concentration gradients (i.e., the diffusion potential gradient). Similarly, the pressure gradient maybe externally imposed or result from osmotic and electrosmotic phenomena. Further discussions on these topics maybe be found elsewhere [49,53].

In a reference system moving at velocity v with respect to the laboratory (i.e., with respect to the membrane), the flux density is [16]

$$J_i^{(v)} = c_i(v_i - v) = J_i - c_i v \tag{61}$$

In contrast to Eq. (58), Eq. (61) must also be applied to the charged groups fixed to the membrane matrix. Indeed, the electric current density is given by

$$I = \text{F}\sum_i z_i J_i^{(v)} \tag{62}$$

where the sum index runs over all charged species including the fixed groups, whose flux density inside the membrane is $J_{\text{m}}^{(v)} = -c_{\text{m}}v$. The local electroneutrality condition [Eq. (A1)] then leads to the important result that the electric current density is independent of the reference system used. Equation (59) is thus valid in any reference system.

Most of the classical experimental methods yield TN in the solvent-fixed reference system. The solvent velocity should then be determined by additional experimental arrangements for each particular case to provide a full description of the TN measured. Since the ion flux density in this reference system

takes the form

$$J_i^{(0)} = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{\mathrm{F}}{RT}\frac{d\phi}{dx}\right) \tag{63}$$

it could be thought that the expressions obtained in the previous sections were derived for the solvent-fixed reference system. However, this conclusion is valid only in the solution outside the membrane, where there is no contribution from the fixed charge (and no electrokinetic phenomena). Inside the membrane, $J_{\mathrm{m}}^{(0)} = -c_{\mathrm{m}} v_0$ and this means that their TN is not zero [56,57]. In fact, one of the difficulties associated with reference systems other than the membrane-fixed reference system is that TN change discontinuously at the membrane boundaries. But these reference systems must be used because TN measurements in the membrane-fixed system are extremely difficult.

B. Hittorf's Transport Numbers

The integral TN in any reference system is defined as [1,16]

$$T_i^{(\mathrm{v})} \equiv \frac{z_i \mathrm{F} J_i^{(\mathrm{v})}}{I} \tag{64}$$

The TN in the membrane-fixed and solvent-fixed reference systems thus follow the relationship

$$T_i^{(0)} = T_i - \frac{z_i \mathrm{F} c_i v_0}{I} = T_i - \frac{z_i c_i \tau_0}{c_0} \approx T_i - \left(0.018 \frac{L}{\mathrm{mol}}\right) z_i c_i \tau_0 \tag{65}$$

where $\tau_0 \equiv \mathrm{F} c_0 v_0 / I$ and c_0 are the transference number and molar concentration of water, respectively.

The continuity equation (i.e., the mass conservation equation) requires that J_i be independent of position under steady-state conditions. Hence, the TN in membrane-fixed reference system, T_i, are constant. On the contrary, Eqs. (61) and (64) show that $T_i^{(v)}$ is only independent of position if the concentration is homogeneous. When using TN such as $T_i^{(0)}$ it must therefore be understood that reference is made to the value at the bulk solution concentration. Accordingly, the concentration c_i in Eq. (65) is replaced by the bulk value.

From the experimental point of view, the flux $J_i^{(0)}$ is easily obtained from the observed change in concentration Δc_i in a time interval Δt as

$$J_i^{(0)} \approx \frac{V}{A}\frac{\Delta c_i}{\Delta t} \tag{66}$$

where A is the effective membrane area and V the volume of the compartment where Δc_i is measured. Transport numbers in solvent-fixed reference system are then reported from Hittorf's experiments [58].

The relevant question, however, is whether T_i or $T_i^{(0)}$ provides a value which characterizes the membrane. To answer this question, the transport equations [obtained from Eqs. (58) and (59)]

$$J_i = \bar{J}_{12} + \frac{\bar{t}_i}{z_i}\frac{I - I_{str}}{F} + \bar{c}_i v_0 \quad \text{(membrane)} \tag{67a}$$

$$J_i = J_{12} + \frac{t_i}{z_i}\frac{I}{F} + c_i v_0 \quad \text{(DBL)} \tag{67b}$$

are integrated from $x = -\delta$ to $x = d + \delta$, where the ion concentrations are $c_L = c_R \equiv c_b$. For the sake of simplicity, the diffusion coefficients are assumed to take the same value inside and outside the membrane. It is then obtained

$$T_i = \frac{z_i^2 D_i \langle c_i \rangle}{\sum_j z_j^2 D_j \langle c_j \rangle} + \frac{F v_0 \langle \bar{\kappa} \rangle}{I \langle \kappa \rangle}\left(z_i \langle c_i \rangle + \frac{d}{d + 2\delta} z_m c_m \bar{T}_i\right) \tag{68}$$

where

$$\bar{T}_i \equiv \frac{z_i^2 D_i \langle \bar{c}_i \rangle}{\sum_j z_j^2 D_j \langle \bar{c}_j \rangle} \tag{69}$$

The average values $\langle c_i \rangle$ and $\langle \bar{c}_i \rangle$ were defined in Eqs. (13) and (21), respectively. Similarly, $\langle \kappa \rangle$ and $\langle \bar{\kappa} \rangle$ are the average values of the electrical conductivity in the membrane system and inside the membrane.

Neglecting DBL effects, Eq. (68) simplifies to

$$T_i = \bar{T}_i + \frac{F v_0}{I}(z_i \langle \bar{c}_i \rangle + z_m c_m \bar{T}_i) \tag{70}$$

For the case of highly charged membranes, the sum inside brackets in Eq. (70) is of the order of c_b^2/c_m and can be neglected, thus giving $T_i \approx \bar{T}_i$ (see Fig. 13). However, for the case of weakly charged membranes, the sum inside brackets contributes to T_i and this number ceases to characterize accurately the migrational transport inside the membrane. On the contrary, the TN in the solvent-fixed reference system

$$T_i^{(0)} = T_i - \frac{z_i F c_b v_0}{I} \tag{71}$$

can be shown to be approximately equal to $\bar{T}_i$ for both highly and weakly charged membranes, thus providing a good characterization of the membrane.

C. Modified Hittorf's Method

The polarization of the DBL is responsible for the observed dependence of the TN determined by Hittorf's method on the current density (see Fig. 5) [5,59].

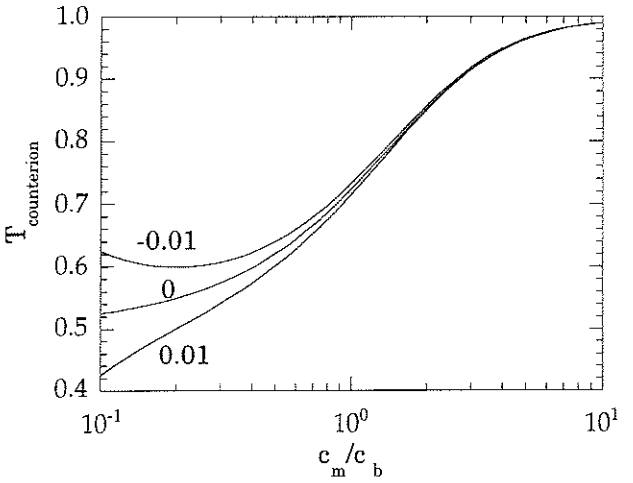

FIG. 13 Counterion Hittorf transport number in membrane-fixed reference system vs. c_m/c_b for different values of the ratio I_{str}/I (shown on the curves) and $\bar{D}_1/\bar{D}_2 = 1$. The central line corresponds to $\bar{T}_i$. DBL effects have not been incorporated.

Either the use of extrapolation methods or an estimation of the diffusional contribution are then required to obtain a value representative of the membrane system (which still would incorporate the effect of DBL) [60]. The problem of concentration polarization can be avoided by using a stack of membranes, but this method is tedious to use in practice [56,61] (see also Chap. 13, Sec. IV.B). More recently, the use of a convective flow opposed to the electric current has been proposed [4]. This modified Hittorf's method significantly reduces the concentration polarization and prevents the development of a concentration difference between the two bulk solutions.

When the conventional Hittorf's method is applied to a membrane system, the concentration changes in the two compartments are due to both the transport through the membrane system and the electrode reactions. Consider, e.g., a membrane bathed by KCl solutions where Ag/AgCl electrodes are immersed. Since the electrode reactions only involve chloride ions, there is a net salt flux $T_{K+}I/F$ from the anode to the cathode compartment, where T_{K+} is the integral TN of potassium ions. Then, the bulk concentrations change with time (i.e., the system is not under true steady-state conditions) and there is a contribution from back diffusion to the ion transport. In the modified Hittorf's method [4] the integral TN of the cation is zero due to the countercurrent convective flow, $T_{K+} = 0$, i.e. for any given current density I, the convective velocity v_0 is adjusted so that $T_{K+} = 0$ is satisfied. Obviously, the TN characterizing the membrane, $\bar{T}_{K+}$ in Eq. (70), must be extracted from the current

and convective flow measurements. When the fixed charge concentration is of the order or smaller than the bathing solution concentration, Eq. (71) gives $\bar{T}_{K^+} = -Fc_b v_0/I$ where v_0 and I have opposite signs because the flow is opposed to the current. The determination of $\bar{T}_{K^+}$ by this method consists then in adjusting the convective velocity v_0, for a given current density I, so that $T_{K^+} = 0$ is satisfied and calculating $\bar{T}_{K^+} \approx -Fc_b v_0/I$. Moreover, since the diffusional contribution to the ion transport through the membrane system is small, this TN $\bar{T}_{K^+}$ does not depend on the electric current used in its determination.

D. Potentiometric Transport Numbers

The relationship between potentiometric TN and the reference system is difficult to make in practice because they are defined from the membrane potential expression and not from Eq. (64). In electrolyte solutions, it has long been discussed that potentiometric TN are essentially identical to Hittorf's TN, and therefore they are also relative to the solvent [62]. In the case of membrane systems, a good correlation between the TN determined by these two methods has also been observed [63], and thus it is widely accepted that both potentiometric and Hittorf's methods provide TN in the solvent-fixed reference system [17].

Equation (59) shows that in the presence of convective flow (and $I = 0$), the membrane potential is given by

$$\Delta\phi_M = \Delta\phi_{dif} + \Delta\phi_{str} = -\frac{RT}{F}\sum_i \frac{\bar{T}_i}{z_i} \ln \frac{c_R}{c_L} - Fz_m c_m v_0 \, d\langle\bar{\rho}\rangle \tag{72}$$

where $\bar{\rho} = 1/\bar{\kappa}$ is the local electrical resistivity in membrane phase, and $\langle\bar{\rho}\rangle$ its average value. In Eq. (72), DBL effects have been neglected for the sake of simplicity. This equation, however, if often written in the form

$$\Delta\phi_M = -\frac{RT}{F}\sum_i \frac{\bar{T}_{i,\,app}}{z_i} \ln \frac{c_R}{c_L} \tag{73}$$

where $\bar{T}_{i,\,app}$ is the so-called apparent potentiometric TN [5] note that the term apparent is used here for a different reason than in Sec. III.B).

The membrane potential $\Delta\phi_M$ can also be evaluated from nonequilibrium thermodynamics and written in the Scatchard–Staverman form [64–66]

$$\Delta\phi_M = -\frac{1}{F}\int \sum_{i=0}^{2} \tau_i \, d\mu_i = -\frac{RT}{F}\int \sum_{i=0}^{2} \tau_i \, d \ln c_i \tag{74}$$

where τ_0 is the transference number of water and $\tau_i \equiv \bar{T}_i/z_i$ is the transference number of ion species i (see also Chap. 10, Sec. II.A). Activities have also been replaced by concentrations for the sake of consistency with the above

expressions. By using the Gibbs–Duhem equation, Eq. (74) can be transformed into Eq. (73), where $\bar{T}_{i,\,\mathrm{app}}$ takes the form of a TN in the solvent-fixed reference system

$$\bar{T}^{(0)}_{i,\,\mathrm{app}} = \bar{T}_{i,\,\mathrm{app}} - z_i c_{\mathrm{av}} \tau_0 / c_0 \tag{75}$$

and c_{av} represents here the average $(c_{\mathrm{R}} + c_{\mathrm{L}})/2$.

The equivalence of these two formulations [Eqs. (72) and (74)] can be shown by equating the convective terms in the Nernst–Planck and nonequilibrium thermodynamics formulations

$$c_i v_0 = -l_{i0} \frac{d\mu_0}{dx} \tag{76}$$

where l_{i0} is a phenomenological coefficient. It then follows that

$$\begin{aligned} \frac{d\phi_{\mathrm{str}}}{dx} &= -\frac{\mathrm{F} z_{\mathrm{m}} c_{\mathrm{m}} v_0}{\kappa} = \frac{\mathrm{F}}{\kappa} \sum_i z_i c_i v_0 \\ &= -\frac{\mathrm{F}}{\kappa} \left(\sum_i z_i l_{i0} \right) \frac{d\mu_0}{dx} = -\frac{\tau_0}{\mathrm{F}} \frac{d\mu_0}{dx} \end{aligned} \tag{77}$$

V. CONCLUDING REMARKS

Transport numbers have been extensively used over the last decades to characterize ion transport in charged membranes. In spite of their conceptual simplicity, a number of difficulties arise in the interpretation of experimental results because of the influence of the operating conditions. More effort should therefore be put to identify the effect of polarization layers and the driving force (i.e., the electric current density and/or the concentration difference) on the experimental results. Also, the use of simplified expressions for the TN (e.g., the application to ternary systems of equations valid only for binary systems) should be avoided.

Finally, attention must be called to the restrictions applying to the theoretical approach presented in this chapter. First, activities have been replaced by concentrations throughout, which limits the applicability of the equations to dilute solutions. Second, chemical partition coefficients have not been included, which amounts to consider only membranes with high water content. More important are the limitations associated with the homogeneous membrane assumption. Homogeneity is a spatial scale-dependent concept and all membranes deviate to some extent from homogeneity. If the membrane is inhomogeneous on a plane normal to the axis along which transport occurs, the introduction of a distribution of pore radii and charge densities will prove necessary when attempting to interpret experimental data [28]. Recent accounts of the effect of structural membrane inhomogeneity on transport properties can be found in Refs. 67–70.

APPENDIX: THE INTEGRATION OF THE NERNST–PLANCK EQUATIONS OVER THE MEMBRANE SYSTEM FOR THE CASE OF TERNARY ELECTROLYTE SOLUTIONS AND $|z_i| = 1$

In this appendix a procedure for the integration of the Nernst–Planck equations in ternary systems, under the assumption of local electroneutrality

$$\sum_i z_i \bar{c}_i(x) + z_m c_m = 0 \tag{A1}$$

is presented. The equations corresponding to binary systems can be easily obtained by taking $c_3 = 0$. Alternatively, the Schlögl integration procedure could also be used [36,71,72].

Since the electric potential gradient inside the membrane can be written as [73]

$$\frac{d\bar{\phi}}{dx} = \frac{RT}{F} \frac{\bar{\Gamma}}{\sum_j z_j^2 \bar{c}_j + \bar{\Gamma} z_m c_m} \sum_i \frac{d\bar{c}_i}{dx} \tag{A2}$$

where

$$\bar{\Gamma} \equiv \frac{\sum_j z_j J_j / \bar{D}_j}{\sum_j J_i / \bar{D}_i} \tag{A3}$$

the diffusion potential drop in the membrane $\Delta\bar{\phi}_{dif}$ is given by

$$\Delta\bar{\phi}_{dif} \equiv \bar{\phi}(d) - \bar{\phi}(0) = \frac{RT}{F} \bar{\Gamma} \ln \frac{\sum_i \bar{c}_i(d) + \bar{\Gamma} z_m c_m}{\sum_j \bar{c}_j(0) + \bar{\Gamma} z_m c_m} \tag{A4}$$

Alternatively, $\Delta\bar{\phi}_{dif}$ can also be obtained by integration of $\sum_i J_i/\bar{D}_i$ as

$$\Delta\bar{\phi}_{dif} = \frac{RT}{F} \frac{1}{z_m c_m} \sum_i \left[\bar{c}_i(d) - \bar{c}_i(0) + d \frac{J_i}{\bar{D}_i} \right] \tag{A5}$$

Equations (A4) and (A5) contain the sum $\sum_i \bar{c}_i$, which can be transformed into

$$\sum_i \bar{c}_i(x) = 2\bar{c}_1(x) + \frac{z_m c_m}{z_1} \tag{A6}$$

with the help of Eq. (A1) and observing that $z_2 = z_3 = -z_1$ because $i = 1$ is the common ion. The ion fluxes in Eqs. (A4) and (A5) are obtained by integration of the Nernst–Planck equations in Kramers' form [20,73–75] as

$$J_i = -\bar{D}_i \frac{\bar{c}_i(x) \exp\{z_i F[\bar{\phi}(x) - \bar{\phi}(0)]/RT\} - \bar{c}_i(0)}{\int_0^x \exp\{z_i F[\bar{\phi}(\xi) - \bar{\phi}(0)]/RT\}\, d\xi} \tag{A7}$$

and

$$\frac{J_2}{J_3} = \frac{\bar{D}_2}{\bar{D}_3} \frac{\bar{c}_2(d)\exp(z_2 \mathrm{F}\, \Delta\bar{\phi}_{\mathrm{dif}}/RT) - \bar{c}_2(0)}{\bar{c}_3(d)\exp(z_3 \mathrm{F}\, \Delta\bar{\phi}_{\mathrm{dif}}/RT) - \bar{c}_3(0)} \tag{A8}$$

where the equality $z_2 = z_3$ has been used.

In the DBL, the diffusion potential drops are given by

$$\Delta\phi_{\mathrm{dif,\,L}} = \frac{RT}{\mathrm{F}} \Gamma \ln \frac{c_1(0)}{c_{1,\mathrm{L}}} \tag{A9a}$$

and

$$\Delta\phi_{\mathrm{dif,\,R}} = \frac{RT}{\mathrm{F}} \Gamma \ln \frac{c_{1,\mathrm{R}}}{c_1(d)} \tag{A9b}$$

where

$$\Gamma \equiv \frac{\sum_j z_j J_j/D_j}{\sum_i J_i/D_i} \tag{A10}$$

$$c_1(0) = c_{1,\mathrm{L}} - \frac{\delta}{2} \sum_i \frac{J_i}{D_i} \tag{A11a}$$

and

$$c_1(d) = c_{1,\mathrm{R}} + \frac{\delta}{2} \sum_i \frac{J_i}{D_i} \tag{A11b}$$

The other two ion concentrations at the external side of the membrane/DBL interfaces are given by the local electroneutrality condition

$$c_1(x) = c_2(x) + c_3(x) \tag{A12}$$

and the analogous to Eq. (A8), i.e.

$$\frac{J_2}{J_3} = \frac{D_2}{D_3} \frac{c_2(0)\exp(z_2 \mathrm{F}\, \Delta\phi_{\mathrm{dif,\,L}}/RT) - c_{2,\mathrm{L}}}{c_3(0)\exp(z_3 \mathrm{F}\, \Delta\phi_{\mathrm{dif,\,L}}/RT) - c_{3,\mathrm{L}}} \tag{A13a}$$

and

$$\frac{J_2}{J_3} = \frac{D_2}{D_3} \frac{c_{2,\mathrm{R}} \exp(z_2 \mathrm{F}\, \Delta\phi_{\mathrm{dif,\,R}}/RT) - c_2(d)}{c_{3,\mathrm{R}} \exp(z_3 \mathrm{F}\, \Delta\phi_{\mathrm{dif,\,R}}/RT) - c_3(d)} \tag{A13b}$$

At the membrane/DBL interfaces, the Donnan potential drops are given by

$$\Delta\phi_{\mathrm{D,\,L}} = -\frac{RT}{\mathrm{F}} \frac{1}{z_i} \ln \frac{\bar{c}_i(0)}{c_i(0)} = \frac{1}{z_1} \operatorname{arcsinh}\left(\frac{z_{\mathrm{m}} c_{\mathrm{m}}}{2 z_1 c_1(0)}\right) \tag{A14a}$$

$$\Delta\phi_{\mathrm{D,\,R}} = -\frac{RT}{\mathrm{F}} \frac{1}{z_i} \ln \frac{c_i(d)}{\bar{c}_i(d)} = -\frac{1}{z_1} \operatorname{arcsinh}\left(\frac{z_{\mathrm{m}} c_{\mathrm{m}}}{2 z_1 c_1(d)}\right) \tag{A14b}$$

where Eqs. (A1) and (A9) have been used to obtain the last equalities.

The above equations form a closed system which enables the determination of values for ion fluxes and the different potential drops. The membrane potential is then obtained as

$$\Delta\phi_M = \Delta\phi_{dif,L} + \Delta\phi_{D,L} + \Delta\bar{\phi}_{dif} + \Delta\phi_{D,R} + \Delta\phi_{dif,R} \tag{A15}$$

The distributions of electric potential and the common ion concentration inside the membrane can be calculated from the system

$$\bar{\phi}(x) - \bar{\phi}(0) = \frac{RT}{F}\bar{\Gamma}\ln\frac{c_1(x) + (\bar{\Gamma} + 1/z_1)z_m c_m/2}{c_1(0) + (\bar{\Gamma} + 1/z_1)z_m c_m/2} \tag{A16}$$

and

$$\bar{\phi}(x) - \bar{\phi}(0) = \frac{RT}{F}\frac{1}{z_m c_m}\left\{2[c_1(x) - c_1(0)] + x\sum_i \frac{J_i}{\bar{D}_i}\right\} \tag{A17}$$

which are obtained by integration of Eq. (A2), and integration of $\sum_i J_i/\bar{D}_i$, respectively. The other two ion concentration profiles can be calculated from Eq. (A7).

The corresponding distributions in the DBL are finally given by

$$c_1(x) = c_{1,L} - \frac{x}{2}\sum_i \frac{J_i}{D_i}, \quad -\delta < x < 0 \tag{A18a}$$

$$c_1(x) = c_{1,R} + \frac{x}{2}\sum_i \frac{J_i}{D_i}, \quad d < x < d + \delta \tag{A18b}$$

$$\phi(x) - \phi(-\delta) = \frac{RT}{F}\Gamma\ln\frac{c_1(x)}{c_{1,L}}, \quad -\delta < x < 0 \tag{A19a}$$

$$\phi(x) - \phi(d+\delta) = \frac{RT}{F}\Gamma\ln\frac{c_1(x)}{c_{1,R}}, \quad d < x < d + \delta \tag{A19b}$$

$$\frac{J_2}{J_3} = \frac{D_2}{D_3}\frac{c_2(x)\exp\{z_2 F[\phi(x) - \phi(-\delta)]/RT\} - c_{2,L}}{c_3(x)\exp\{z_2 F[\phi(x) - \phi(-\delta)]/RT\} - c_{3,L}}, \quad -\delta < x < 0 \tag{A20a}$$

$$\frac{J_2}{J_3} = \frac{D_2}{D_3}\frac{c_2(x)\exp\{z_2 F[\phi(x) - \phi(d+\delta)]/RT\} - c_{2,R}}{c_3(x)\exp\{z_2 F[\phi(x) - \phi(d+\delta)]/RT\} - c_{3,R}}, \quad d < x < d + \delta \tag{A20b}$$

LIST OF SYMBOLS

c	molar concentration [mol/cm^3]
D	diffusion coefficient [cm^2/s]

d	membrane thickness [cm]
e	auxiliary constant defined in Eq. (27)
F	Faraday constant [C/mol]
I	electric current density [A/cm^2]
J	flux density [mol/cm^2/s]
p	ideal salt activity [mol^2/cm^6 in the case of 1 : $-$ 1 electrolytes]
R	gas constant [J/(mol K)]
r	auxiliary constant defined in Eq. (22)
r_c	ratio of bulk solution concentrations
S	membrane permselectivity
T	absolute temperature [K]
t	local migrational TN
T_i	integral TN of species i
v	velocity [cm/s]
x	position [cm]
z	charge number
δ	DBL thickness [cm]
ϕ	local electric potential [V]
Γ	auxiliary constant defined in Eqs. (A3) and (A10)
η	TN ratio
κ	electrical conductivity [Ω^{-1}/cm]
ρ	electrical resistivity [Ω cm]
τ	transference number
$\bar{\tau}_i$	auxiliary constant defined in Eq. (20)
ξ	dummy integration variable
$\tilde{\mu}$	electrochemical potential [J/mol]
μ	chemical potential [J/mol]
$\langle\ \rangle$	average value
Δ	difference over the bulk or interfacial region (right minus left)
DBL	diffusion boundary layer
TN	transport number
$\bar{}$	membrane phase

Subscripts/Superscripts

0	solvent
12	binary electrolyte formed by ion species 1 and 2
13	binary electrolyte formed by ion species 1 and 3
app	apparent
b	bulk solution in L and R compartments
c	concentration ratio

D	Donnan
dif	diffusion potential
eq	small fluxes limit (i.e., equilibrium limit)
i	ion species i (i = 1,2,3)
L	left compartment
lim	limiting current density
M	membrane potential
m	fixed charge groups within the membrane
R	right compartment
str	streaming
°	standard

REFERENCES

1. N. Ibl, Pure & Appl. Chem. *53*: 1827 (1979).
2. J. Newman, *Electrochemical Systems*, Prentice Hall, Englewood Cliffs, New Jersey, 1973, Sec. 70.
3. K. Kontturi, P. Forsell, and A. Ekman, Acta Chem Scand. *A39*: 271 (1985).
4. K. Kontturi, S. Mafé, J. A. Manzanares, J. Pellicer, and M. Vuoristo, J. Electroanal. Chem. *378*: 111 (1994).
5. N. Lakshminarayanaiah, *Transport Phenomena in Membranes*, Academic Press, New York, 1969, p. 232.
6. K. A. Lebedev, V. I. Zabolotsky, and V. V. Nikonenko, Sov. Electrochem. *23*: 555 (1987).
7. K. A. Lebedev, V. V. Nikonenko, and V. I. Zabolotsky, Sov. Electrochem. *23*: 459 (1987).
8. N. V. Shel'deshov, V. I. Zabolotsky, M. V. Shadrina, and M. V. Solov'eva, J. Appl. Chem. USSR *63*: 831 (1990).
9. R. P. Buck, J. Membrane Sci. *17*: 1 (1984).
10. V. M. Aguilella, J. A. Manzanares, and J. Pellicer, Langmuir *9*: 550 (1993).
11. F. Helfferich, *Ion Exchange*, Dover, New York, 1995, p. 326 and footnote.
12. Ref. 2, Sec. 4 and 70.
13. R. Hattenbach, *Terminology for Electrodialysis*, European Society of Membrane Science and Technology, 1988.
14. A. Narebska and S. Koter, in *Advances in Membrane Phenomena and Processes* (A. M. Mika and T. Z. Winnicki, eds.), Wroclaw Technical University Press, Wroclaw, 1989, pp. 111–127.
15. N. Rossignol, D. E. A. Thesis, Univ. Pierre et Marie Curie (Paris VI), 1995.
16. R. Haase, *Thermodynamics of Irreversible Processes*, Dover, New York, 1990, Sec. 4–16.
17. A. Narebska and S. Koter, Electrochim. Acta *38*: 815 (1993).
18. S. Koter and A. Narebska, Sep. Sci. Technol. *24*: 1337 (1989/90).
19. J. Goodisman, *Electrochemistry: Theoretical Foundations*, Wiley, New York, 1987, p. 35.
20. A. V. Sokirko, J. A. Manzanares, and J. Pellicer, J. Colloid Interface Sci. *168*: 32 (1994).

21. H. Reiss and I. C. Bassignana, J. Membrane Sci. *11*:219 (1982).
22. C. Selvey and H. Reiss, J. Membrane Sci. *23*:11 (1985).
23. S. Mafé, J. A. Manzanares, M. J. Hernández, and J. Pellicer, J. Colloid Interface Sci. *145*:433 (1991).
24. J. A. Manzanares, S. Mafé, and J. Pellicer, J. Chem. Soc. Faraday Trans. *88*:2355 (1992).
25. S. Koter, J. Membrane Sci. *108*:177 (1995).
26. J. A. Manzanares, W. D. Murphy, S. Mafé, and H. Reiss, J. Phys. Chem. *97*:8524 (1993).
27. Ref. 11, p. 408.
28. K. Kontturi, S. Mafé, J. A. Manzanares, L. Murtomäki, and P. Viinikka, Electrochim. Acta *39*:883 (1994).
29. T. R. E. Kressman, P. A. Stanbridge, and F. L. Tye, Trans. Faraday Soc. *59*:2129 (1963).
30. S. Koter, Polish J. Chem. *69*:1213 (1995).
31. N. I. Zharkikh, Sov. Electrochem. *27*:123 (1991).
32. T. S. Sørensen and J. B. Jensen, J. Non-Equilib. Thermodyn. *9*:1 (1984).
33. J. B. Jensen, T. S. Sørensen, B. Malmgren-Hansen, and P. Sloth, J. Colloid Interface Sci. *108*:18 (1985).
34. T. S. Sørensen, J. B. Jensen, and B. Malmgren-Hansen, J. Non-Equilib. Thermodyn. *13*:57 (1988).
35. B. Malmgren-Hansen, T. S. Sørensen, and J. B. Jensen, J. Non-Equilib. Thermodyn. *13*:193 (1988).
36. S. Laursen, B. Malmgren-Hansen, and T. S. Sørensen, J. Non-Equilib. Thermodyn. *15*:223 (1990).
37. F. Skácel, B. Malmgren-Hansen, T. S. Sørensen, and J. B. Jensen, J. Chem. Soc. Faraday Trans. *86*:341 (1990).
38. T. S. Sørensen, J. B. Jensen, and B. Malmgren-Hansen, Desalination *80*:293 (1990).
39. N. Lakshminarayanaiah, *Equations of Membrane Biophysics*, Academic Press, New York, 1984, p. 124.
40. Y. Toyoshima and H. Nozaki, J. Phys. Chem. *74*:2704 (1970).
41. T. S. Sørensen and V. Compañ, J. Phys. Chem. *100*:7623 (1996).
42. T. S. Sørensen and V. Compañ, J. Phys. Chem. *100*:15261 (1996).
43. V. Compañ, T. S. Sørensen, A. Andrio, M. L. López, and J. de Abajo, J. Membrane Sci. *123*:293 (1997).
44. S. Numajiri, K. Sugibayashi, and Y. Morimoto, Chem. Pharm. Bull. *44*:1351 (1996).
45. Y. Rojanasakul and J. R. Robinson, Int. J. Pharm. *55*:237 (1989).
46. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1959.
47. J. A. Manzanares, G. Vergara, S. Mafé, K. Kontturi, and P. Viinikka, J. Phys. Chem. B *102*:1301 (1998).
48. J. Garrido, V. Compañ, and M. L. López, J. Phys. Chem. *98*:6003 (1994).
49. A. I. Gorshkov and O. V. Oshurkova, Sov. Electrochem. *26*:135 (1990) [Élektrokhimiya *26*:144 (1990)].
50. D. C. Mikulechy and S. R. Caplan, J. Phys. Chem. *70*:3049 (1966).

51. J. W. Lorimer, J. Membrane Sci. *14*: 275 (1983).
52. B. Baranowski, J. Membrane Sci. *57*: 119 (1991).
53. Ref. 5, Chapter 6.
54. P. Schaetzel, E. Favre, B. Auclair, and Q. T. Nguyen, Electrochim. Acta *42*: 2475 (1997).
55. R. Schlögl, Discuss. Faraday Soc. *21*: 46 (1956) and references therein.
56. P. Forssell, K. Kontturi, and A. Ekman, Acta Chem. Scand. *A39*: 279 (1985).
57. G. Scatchard, J. Am. Chem. Soc. *75*: 2883 (1953).
58. A. I. Gorshkov and O. V. Oshurkova, Sov. Electrochem. *24*: 1292 (1988) [Élektrokhimiya *24*: 1292 (1988)].
59. H. P. Gregor and M. A. Peterson, J. Phys. Chem. *68*: 2201 (1964).
60. T. R. E. Kressman and F. L. Tye, Discuss. Faraday Soc. *21*: 185 (1956).
61. K. Kontturi, P. Forssell, and A. Ekman, Acta Chem. Scand. *A39*: 271 (1985).
62. M. J. Pikal and D. G. Miller, J. Phys. Chem. *74*: 1337 (1970).
63. Y. Hirata, M. Date, Y. Yamamoto, A. Yamauchi, and H. Kimizuka, Bull. Chem. Soc. Jpn *60*: 2215 (1987).
64. G. Scatchard, J. Am. Chem. Soc. *75*: 2883 (1953).
65. F. Danes, S. Sternberg, and S. Danes, Rev. Roumaine Chim. *26*: 11 (1981).
66. T. S. Sørensen and J. B. Jensen, J. Non-Equilib. Thermodyn. *9*: 1 (1984).
67. J. H. Petropoulos, J. Membrane Sci. *52*: 305 (1990).
68. V. I. Zabolotsky and V. V. Nikonenko, J. Membrane Sci. *79*: 181 (1993).
69. I. Tugas, G. Pourcelly, and C. Gavach, J. Membrane Sci. *85*: 183 (1993) and *85*: 195 (1993).
70. N. P. Berezina, N. P. Gnusin, O. Dyomina, and S. Timofeyev, J. Membrane Sci. *86*: 207 (1994).
71. R. Schlögl, Z. phys. Chem. N. F. *1*: 305 (1954).
72. H. U. Demisch and W. Pusch, J. Colloid Interface Sci. *69*: 247 (1979).
73. A. Guirao, S. Mafé, J. A. Manzanares, and J. A. Ibáñez, J. Phys. Chem. *99*: 3387 (1995).
74. H. A. Kramers, Physica *7*: 284 (1940).
75. K. Kontturi, J. A. Manzanares, and L. Murtomäki, Electrochim. Acta *40*: 2979 (1995).