

## Potentiometric Determination of Transport Numbers of Ternary Electrolyte Systems in Charged Membranes

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*Received: January 14, 1997; In Final Form: November 25, 1997*

The potentiometric determination of transport numbers in charged membranes for the case of ternary systems is critically analyzed, and expressions are derived to evaluate these transport numbers close to equilibrium conditions. The apparent potentiometric transport number (i.e., that obtained by assuming that the ternary system behaves as a binary system) is also studied and the conditions that make it reliable for the estimation of the membrane fixed charge concentration are given. Particular attention is paid to the case of amphoteric membranes where the pH adjustment is necessary and the bathing solutions are often ternary systems. However, our theoretical study is general, and can also be applied to estimate the effect of any impurity ion present in the bathing solution. The main conclusion is that the interpretation of ion transport data in terms of the binary system equations can be an erroneous procedure even when the third ion present has a relatively low concentration.

### Introduction

The electric conduction process in an ionic solution is often described in terms of Hittorf's transport numbers which represent the fraction of the total current density transported by every charged species in the absence of concentration gradients.<sup>1,2</sup> However, when the electric conduction takes place across a membrane system of finite conductivity, concentration gradients are always present and this can lead to errors in the transport number determination due to back diffusion. Modifications of Hittorf's method that avoid the correction for back diffusion<sup>3,4</sup> and the use of radiotracers<sup>5</sup> have been suggested, though they are not easy to use in practice. Furthermore, diffusion boundary layers exert also an important effect whose influence is difficult to estimate.<sup>6</sup>

Alternatively, the transport numbers may be found by measuring concentration potentials.<sup>7</sup> These are known as potentiometric transport numbers, and quite frequently do not coincide with those obtained by Hittorf's method because these two methods characterize the membrane system as a whole and the values they yield depend on the experimental conditions. Since there is no satisfactory way at present to determine transport numbers reliably, and Hittorf's method or its modifications are relatively laborious, the potentiometric method is often used.

The determination of transport numbers through charged membranes is required to study the performance of electromembrane processes. The counterion transport number is then one of the characteristics provided by the manufacturers of industrial membranes. However, this information is of limited value because it has been obtained with binary electrolyte solutions, a situation that differs often from that in the electromembrane process. For instance, in the case of acid and alkali production with bipolar membranes, it is important to determine the transport numbers through the monopolar membranes in systems

such as NaCl–HCl or NaCl–NaOH.<sup>8</sup> Even in systems where the bathing solutions are intended to be binary,<sup>9</sup> the minimal presence of hydrogen ions from the autoprotolysis of water makes them at least ternary systems at high dilution.<sup>10</sup> The incorporation of the third ion ( $H^+$ ) in the calculation of the emf is then of great importance.<sup>11–15</sup>

The measured transport numbers are also used to estimate the membrane fixed charge concentration,<sup>9,16–18</sup> as well as the presence of any intrinsic asymmetry present in the membrane.<sup>19–21</sup> 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 transport numbers of drugs.<sup>22</sup> 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.<sup>23</sup> The transport number 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. However, the effect of this acid or base addition on the potentiometric determination of transport numbers has not been analyzed in detail, except for a few studies.<sup>10–15</sup> On the contrary, the theoretical expression of the membrane potential corresponding to a binary system is sometimes used and the comparison with the observed membrane potential yields then the apparent potentiometric transport numbers.<sup>9</sup> The use of this procedure is not surprising: the relations between the transport data of binary and ternary electrolyte solutions are not trivial,<sup>24</sup> and these relations become even more complicated in the case of charged membranes.

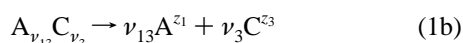
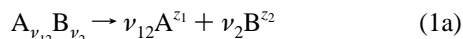
The expression of the membrane potential in a ternary system is known, e.g., from thermodynamics of irreversible processes

(TIP).<sup>25</sup> Evidently, this expression involves two independent transport numbers and this implies that the transport numbers cannot be obtained from a single membrane potential determination but from a series of measurements. However, a clear procedure to conduct this series of measurements is lacking in the literature. Furthermore, the TIP approach uses the potentiometric transport numbers as some kind of average values of the migrational transport numbers, which represent the fraction of the electrical conductivity of the system due to every ionic species and depend on the space coordinate in the presence of concentration gradients.<sup>6</sup> The relation between the potentiometric transport numbers and the local migrational transport numbers is an important problem which apparently have been neglected so far.

The aim of this contribution is to study theoretically the effect of the acid or base addition on the potentiometric determination of transport numbers. First, the membrane potential is derived as a function of the potentiometric transport numbers, and an expression for these numbers in terms of the local migrational transport numbers is given. Second, the Nernst–Planck equations are solved for a ternary system in order to evaluate the membrane potential. For the sake of clarity, no correction for bulk solvent flow is considered. The local concentration and electrical potential profiles obtained from the solution of the Nernst–Planck equations are then used to evaluate the potentiometric transport numbers. Finally, the apparent potentiometric transport number (i.e., that obtained by assuming that the ternary system behaves as a binary system) is also studied and the conditions that make it reliable for the estimation of the membrane fixed charge concentration are given.

## Theory

**(a) Membrane Potential and Potentiometric Transport Numbers of Ternary Systems.** Let us consider a ternary electrolyte solution formed by mixing two binary electrolytes with a common ion. These electrolytes are considered to be completely dissociated according to the equations



where  $\nu_i$  and  $z_i$  denote the stoichiometric coefficients and charge numbers, respectively. (Note that the common ion may have different stoichiometric coefficients in the two binary electrolytes.) Charge neutrality then requires

$$\nu_{12}z_1 + \nu_2z_2 = 0 \quad (2a)$$

$$\nu_{13}z_1 + \nu_3z_3 = 0 \quad (2b)$$

We are interested in obtaining the expression of the steady-state membrane potential under the conditions that characterize the potentiometric method. That is, the electric current density  $I$  will be zero and the bulk solution concentrations will be

$$c_{1,L} = \nu_{12}c_{12,L} + \nu_{13}c_{13,L}, \quad c_{2,L} = \nu_2c_{12,L}, \quad c_{3,L} = \nu_3c_{13,L} \quad (3a)$$

$$c_{1,R} = \nu_{12}c_{12,R} + \nu_{13}c_{13,R}, \quad c_{2,R} = \nu_2c_{12,R}, \quad c_{3,R} = \nu_3c_{13,R} \quad (3b)$$

in the left (L) and right (R) compartments, respectively. No diffusion boundary layer effects will be considered here for the sake of simplicity.

In the homogeneous membrane model, the flux density of species  $i$  is given by the Nernst–Planck equation<sup>26</sup>

$$J_i = -D_i \left( \frac{dc_i}{dx} + z_i c_i \frac{F}{RT} \frac{d\phi}{dx} \right) \quad (4)$$

where  $D_i$  and  $c_i$  are the diffusion coefficient and molar concentration of species  $i$ , respectively,  $\phi$  is the local electric potential,  $R$  is the gas constant, and  $T$  is the absolute temperature. The membrane extends from  $x = 0$  to  $x = d$ , where  $d$  is the membrane thickness. Since the electric current density is

$$I = F \sum_i z_i J_i = 0 \quad (5)$$

the diffusion potential takes the form

$$\Delta\phi_{\text{dif}} \equiv \phi(d) - \phi(0) = -\frac{RT}{F} \int_0^d \sum_i \frac{t_i}{z_i} \frac{1}{c_i} dc_i \quad (6)$$

where

$$t_i \equiv \frac{z_i^2 D_i c_i}{\sum_j z_j^2 D_j c_j} \quad (7)$$

is the local migrational transport numbers of species  $i$ . Equation 6 cannot be integrated unless the concentration profiles (and therefore the variation of  $t_i$  throughout the membrane) are known, e.g., by solving the Nernst–Planck equations. However, the numbers  $t_i$  can be replaced by some average (constant) values  $T_i$  which give the same diffusion potential. Thus, we introduce the potentiometric transport numbers  $T_i$  by means of the equation

$$\Delta\phi_{\text{dif}} = -\frac{RT}{F} \sum_i \frac{T_i}{z_i} \ln \frac{c_i(d)}{c_i(0)} \quad (8)$$

The concentrations that appear in eq 8 are those inside the membrane close to the interfaces with the right and left bulk solutions. Their values are determined from the local electro-neutrality assumption

$$\sum_i z_i c_i(x) + z_X X = 0, \quad 0 \leq x \leq d \quad (9)$$

and the expressions for the Donnan potential at these interfaces

$$\Delta\phi_{D,L} = -\frac{RT}{F} \frac{1}{z_i} \ln \frac{c_i(0)}{c_{i,L}} \quad (10a)$$

$$\Delta\phi_{D,R} = -\frac{RT}{F} \frac{1}{z_i} \ln \frac{c_{i,R}}{c_i(d)} \quad (10b)$$

where the Nernst distribution coefficients<sup>14</sup> have not been incorporated for the sake of simplicity. In eq 9,  $X$  stands for the concentration of fixed charge groups and  $z_X$  for their charge number. The introduction of eqs 10a and 10b into eq 9 for  $x = 0$  and  $x = d$  leads to algebraic equations which require frequently a numerical solution.

It is interesting to note that the transport number property

$$\sum_i T_i = 1 \quad (11)$$

together with the Donnan equilibrium relationship for each ionic species, allows us to write the membrane potential as

$$\Delta\phi \equiv \Delta\phi_{D,L} + \Delta\phi_{dif} + \Delta\phi_{D,R} = -\frac{RT}{F} \sum_i \frac{T_i}{z_i} \ln \frac{c_{i,R}}{c_{i,L}} \quad (12)$$

Equation 12 is the most representative result of the potentiometric method and can also be obtained from quasi-thermodynamic arguments.<sup>9</sup>

We address now the question of how to evaluate the potentiometric transport numbers  $T_i$  from the local migrational transport numbers  $t_i$  so that eq 8 (and then eq 12) is satisfied. The choice

$$T_i \equiv \frac{\int_0^d t_i d \ln c_i}{\ln[c_i(d)/c_i(0)]} \quad (13)$$

is not suitable because it does not satisfy eq 11. Therefore, alternative definitions in terms of the salt variables are sought.

Let us introduce the ideal salt activities

$$p_{12} \equiv c_1^{v_{12}} c_2^{v_2} \quad (14a)$$

$$p_{13} \equiv c_1^{v_{13}} c_3^{v_3} \quad (14b)$$

Equation 6 can then be rewritten as

$$\Delta\phi_{dif} = -\frac{RT}{F} \left( \int_0^d \frac{d \ln c_1}{z_1} + \int_0^d \frac{t_2 d \ln p_{12}}{z_2 v_2} + \int_0^d \frac{t_3 d \ln p_{13}}{z_3 v_3} \right) \quad (15)$$

which allows to introduce the potentiometric transport numbers

$$T_2 \equiv \frac{\int_0^d t_2 d \ln p_{12}}{\ln[p_{12}(d)/p_{12}(0)]} \quad (16a)$$

$$T_3 \equiv \frac{\int_0^d t_3 d \ln p_{13}}{\ln[p_{13}(d)/p_{13}(0)]} \quad (16b)$$

while  $T_1$  is determined from eq 11. Note that eq 15 is now

$$\Delta\phi_{dif} = -\frac{RT}{F} \left( \frac{1}{z_1} \ln \frac{c_1(d)}{c_1(0)} + \frac{T_2}{z_2 v_2} \ln \frac{p_{12}(d)}{p_{12}(0)} + \frac{T_3}{z_3 v_3} \ln \frac{p_{13}(d)}{p_{13}(0)} \right) \quad (17)$$

which coincides with eq 8 because of eqs 2, 14a, and 14b.

**(b) Integration of the Steady-State Nernst–Planck Equations for  $|z_i| = 1$ .** The use of the ratio<sup>27</sup>

$$\Gamma \equiv \frac{\sum_j z_j J_j / D_j}{\sum_i J_i / D_i} \quad (18)$$

leads to the following expression for the electric potential gradient

$$\frac{d\phi}{dx} = \frac{RT}{F} \frac{\Gamma}{\sum_j z_j^2 c_j + \Gamma z_X X} \sum_i \frac{dc_i}{dx} \quad (19)$$

In the case  $|z_i| = 1$  ( $i = 1, 2, 3$ ), eq 19 can be integrated to give

$$\Delta\phi_{dif} = \frac{RT}{F} \Gamma \ln \frac{\sum_i c_i(d) + \Gamma z_X X}{\sum_j c_j(0) + \Gamma z_X X} \quad (20)$$

Alternatively,  $\Delta\phi_{dif}$  can also be obtained by integration of  $\sum_i J_i / D_i$  as

$$\Delta\phi_{dif} = \frac{RT}{F} \frac{1}{z_X X} \sum_i \left[ c_i(d) - c_i(0) + d \frac{J_i}{D_i} \right] \quad (21)$$

Equations 20 and 21 contain the sum  $\sum_i c_i$ , which can be transformed into

$$\sum_i c_i = 2c_1 + (z_X/z_1)X \quad (22)$$

with the help of eq 9 and observing that  $z_2 = z_3 = -z_1$  because  $i = 1$  is the common ion. Equations 20 and 21 contain also the ion fluxes, which can be calculated by multiplying eq 4 by  $\exp(z_i F \phi / RT)$  and integrating it to give<sup>28</sup>

$$J_i = -D_i \frac{c_i(d) \exp(z_i F \Delta\phi_{dif} / RT) - c_i(0)}{\int_0^d \exp\{z_i F [\phi(x) - \phi(0)] / RT\} dx} \quad (23)$$

Again, since  $z_2 = z_3$ , eq 23 leads to

$$\frac{J_2}{J_3} = \frac{D_2 c_2(d) \exp(z_2 F \Delta\phi_{dif} / RT) - c_2(0)}{D_3 c_3(d) \exp(z_3 F \Delta\phi_{dif} / RT) - c_3(0)} \quad (24)$$

The values of  $J_1$ ,  $J_2$ ,  $J_3$ ,  $\Gamma$ , and  $\Delta\phi_{dif}$  can now be obtained as solutions to the equation system 5, 18, 20, 21, and 24, while the membrane potential is obtained from eqs 10a, 10b, 20, and 22 as

$$\Delta\phi = \frac{RT}{F} \left[ -\frac{1}{z_1} \ln \frac{c_1(0)c_{1,R}}{c_1(d)c_{1,L}} + \Gamma \ln \frac{c_1(d) + (\Gamma + 1/z_1)z_X X/2}{c_1(0) + (\Gamma + 1/z_1)z_X X/2} \right] \quad (25)$$

Finally, in order to obtain the potentiometric transport numbers from eqs 16a and 16b, the concentration profiles are needed. The integration of eq 19 from  $x = 0$  to  $x$  yields

$$\phi(x) - \phi(0) = \frac{RT}{F} \Gamma \ln \frac{c_1(x) + (\Gamma + 1/z_1)z_X X/2}{c_1(0) + (\Gamma + 1/z_1)z_X X/2} \quad (26)$$

Also, similarly to eq 21 we can obtain

$$\phi(x) - \phi(0) = \frac{RT}{F} \frac{1}{z_X X} \left\{ 2[c_1(x) - c_1(0)] + x \sum_i \frac{J_i}{D_i} \right\} \quad (27)$$

Equations 26 and 27 describe the distributions of electric potential and the common ion concentration. The other two ion concentrations are obtained from the values of  $J_i$  and

$$J_i = -D_i \frac{c_i(x) \exp\{z_i F[\phi(x) - \phi(0)]/RT\} - c_i(0)}{\int_0^x \exp\{z_i F[\phi(\xi) - \phi(0)]/RT\} d\xi}, \quad i = 2, 3 \quad (28)$$

## Results

The results presented in the next sections have been obtained for the systems KCl–HCl and KCl–KOH. The infinite dilution values<sup>29</sup> have been employed for the ion diffusion coefficients:  $D_{K^+} = 1.95 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $D_{H^+} = 9.30 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $D_{Cl^-} = 2.03 \times 10^{-5} \text{ cm}^2/\text{s}$ , and  $D_{OH^-} = 4.50 \times 10^{-5} \text{ cm}^2/\text{s}$ .

**(a) Apparent Transport Numbers.** Figure 1 shows the membrane potential computed from eq 25 for the system KCl–HCl ( $i = 1$  for  $Cl^-$ ,  $i = 2$  for  $K^+$ , and  $i = 3$  for  $H^+$ ). The membrane fixed groups are negatively charged ( $z_X = -1$ ) and their concentration has been set equal to  $X = c_{2,L}$ . The two bathing solutions have the same pH, so that  $c_{3,R} = c_{3,L} \equiv c_T = 10^{-\text{pH}} \text{ M}$ .

The membrane potential of a ternary system like this is given by eq 12 in terms of the potentiometric transport numbers. Equation 11 reduces to two the number of independent transport numbers (see eq 17), but still they cannot be obtained from a single membrane potential measurement. Then, some authors<sup>23</sup> have resolved to interpret the membrane potential measurements of ternary systems by using eq 12 in the binary system form, neglecting thus the effect of the acid or base added to adjust the pH. The potentiometric transport numbers are then obtained as

$$T_{2,\text{app}} \equiv \frac{1}{2} \left[ 1 - \frac{F\Delta\phi}{RT} \frac{z_2}{\ln(c_{2,R}/c_{2,L})} \right] \quad (29a)$$

$$T_{1,\text{app}} = 1 - T_{2,\text{app}} \quad (29b)$$

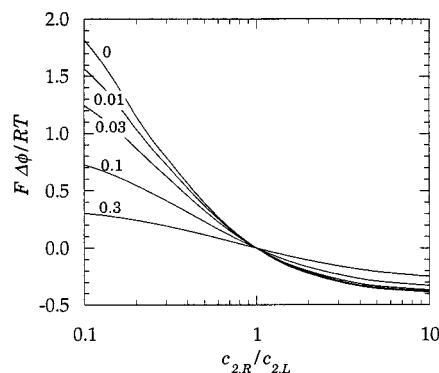
and will be denoted here as apparent transport numbers. This procedure constitutes an oversimplification in the study of ternary systems and has the important shortcoming that the apparent transport numbers are not properties of the binary salt in the membrane system because they incorporate implicitly the effect of the acid or base added. Indeed, the introduction of eq 12 into eqs 29a and 29b leads to

$$T_{1,\text{app}} = \frac{T_1}{2} \left[ 1 + \frac{\ln(c_{1,R}/c_{1,L})}{\ln(c_{2,R}/c_{2,L})} \right] + \frac{T_3}{2} \left[ 1 - \frac{\ln(c_{3,R}/c_{3,L})}{\ln(c_{2,R}/c_{2,L})} \right] \quad (30)$$

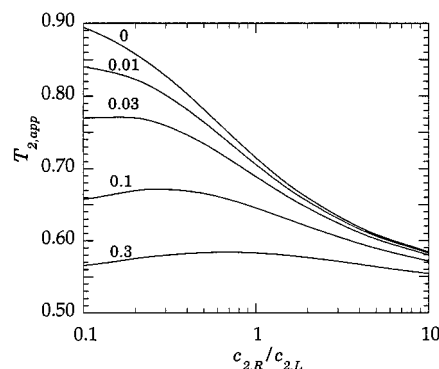
which coincides with  $T_1$  only when  $c_{1,R}/c_{1,L} = c_{2,R}/c_{2,L} = c_{3,R}/c_{3,L}$ . Note, however, that  $T_{2,\text{app}}$  does not coincide with  $T_2$  unless  $c_3 = 0$ .

Figure 2 shows the apparent transport numbers of potassium ion calculated from the membrane potential data in Figure 1 and eq 29a. The apparent transport numbers change considerably with  $c_T/c_{2,L}$  when  $c_{2,R}/c_{2,L} = 0.1$  but not when  $c_{2,R}/c_{2,L} = 10$  because these transport numbers tend to ca. 0.5 in the limit of high bathing solution concentration. Note also the important changes of  $T_{2,\text{app}}$  with  $c_T/c_{2,L}$  even for relatively low values of  $c_T/c_{2,L}$ .

**(b) Potentiometric Transport Numbers in the Limit of Small Fluxes.** The practical importance of transport numbers in charged membranes comes from the fact that they characterize the membrane permselectivity and allow for an estimation of the fixed charge concentration. However, the measured transport numbers also contain information on the particular experimental conditions. Hence, the reliability of potentiometric transport numbers to estimate the fixed charge depends on our



**Figure 1.** Membrane potential of the system KCl–HCl|negatively charged membrane|KCl–HCl vs the ratio of potassium ion concentration in the bathing solutions,  $c_{2,R}/c_{2,L}$ , for  $z_X = -1$  and  $X/c_{2,L} = 1$ . The numbers on the curves give the values of  $c_T/c_{2,L}$ , where  $c_T$  is the hydrogen ion concentration in the bathing solutions.



**Figure 2.** Apparent transport numbers of potassium ion vs the ratio of its bulk solution concentration  $c_{2,R}/c_{2,L}$ . Other values as in Figure 1.

ability to evaluate the limiting values  $t_i^{\text{eq}}$  for small concentrations differences and small fluxes. The migrational transport numbers  $t_i^{\text{eq}}$  are then constant throughout the membrane and coincide with the potentiometric transport numbers  $T_i^{\text{eq}}$ . However, no experimental determination of  $T_i^{\text{eq}}$  is possible because  $\Delta\phi = 0$  when the two external solutions are the same.

In the case of 1:–1 binary systems, the potentiometric transport numbers

$$T_i = \frac{1}{2} \left[ 1 - \frac{z_i F \Delta\phi}{RT \ln(c_R/c_L)} \right] \quad (31)$$

depend on the two external concentrations and will be denoted here as  $T_i(c_R, c_L)$ . It can be easily shown that, when  $c_R > c_L$

$$t_i^{\text{eq}}(c_R) < T_i(c_R, c_L) < t_i^{\text{eq}}(c_L) \quad (32)$$

where  $t_i^{\text{eq}}(c)$  is the migrational transport number inside the membrane corresponding to an equilibrium situation where the two external solution have the same concentration  $c$ . Equation 32 suggests that, in principle, the potentiometric transport numbers could be referred to just one external solution concentration  $c_m$  such that

$$T_i(c_R, c_L) = T_i^{\text{eq}}(c_m, c_m) = t_i^{\text{eq}}(c_m) \quad \text{with } c_L < c_m < c_R \quad (33)$$

In practice, this is not so simple due to the complicated dependence of  $\Delta\phi$  on the ionic concentration differences (see eq 25). Several estimates have been proposed for  $c_m$  (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.<sup>30</sup> This problem can be solved by using two

potentiometric transport numbers. In particular, it has been suggested<sup>6,7</sup> that  $t_i^{\text{eq}}(c)$  could be estimated as

$$t_i^{\text{eq}}(c) = \frac{1}{2}[T_i(rc, c) + T_i(c/r, c)] + \epsilon(t_i^{\text{eq}}) \quad (34)$$

where  $r$  is the ratio of external concentrations and

$$\epsilon(t_i^{\text{eq}}) \approx \frac{1}{2} \left( \frac{\partial^2 T_i(rc, c)}{\partial (\ln r)^2} \right)_{r=1} (\ln r)^2 \quad (35)$$

is the error of this estimation of  $t_i^{\text{eq}}(c)$ . Since  $T_i(rc, c)$  can be considered a linear function of  $\ln r$  for small values of  $r$ , eq 35 shows that eq 34 leads to an accurate determination of  $t_i^{\text{eq}}(c)$ . From the experimental point of view, however, it is required that  $r$  is not close to 1, since  $\Delta\phi$  is small then and cannot be determined with sufficient accuracy. Satisfactory values of  $r$  for the estimation of  $t_i^{\text{eq}}(c)$  are between 2 and 5. Other interpolation techniques to obtain  $t_i^{\text{eq}}(c)$  are also possible,<sup>5</sup> but only those accurate to second order in  $\ln r$  should be used.<sup>30</sup>

In the case of ternary systems in homogeneous membranes (with no explicit dependence of the transport properties on position), eq 34 can be used for the apparent potentiometric transport numbers

$$T_{i,\text{app}}^{\text{eq}}(c, c) = \frac{1}{2}[T_{i,\text{app}}(rc, c) + T_{i,\text{app}}(c/r, c)] + \epsilon(T_{i,\text{app}}^{\text{eq}}) \quad (36)$$

where  $r \equiv c_{2,R}/c_{2,L}$ . Figure 3 shows the values of  $\epsilon(T_{2,\text{app}}^{\text{eq}})$  obtained from the numerical solution of the transport equations. It is concluded that in the cases here considered eq 36 introduces an error smaller than 0.02 when  $r < 6$ .

It has been mentioned in the previous section that the apparent transport numbers incorporate the effect of the third ion. Furthermore, since the relation between apparent and exact transport numbers is very complicated (see eq 30 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), it is not possible to evaluate the potentiometric transport numbers  $T_i$  from the apparent transport numbers under nonequilibrium conditions. Fortunately, this situation changes when we consider the equilibrium state.

In the case  $|z_i| = 1$ , the equilibrium concentrations can be easily obtained from eqs 9, 10a, and 10b as

$$c_1^{\text{eq}} = -\frac{z_X X}{z_1} \frac{X}{2} + \left[ \left( \frac{z_X X}{z_1} \frac{X}{2} \right)^2 + (c + c_T)^2 \right]^{1/2} \quad (37a)$$

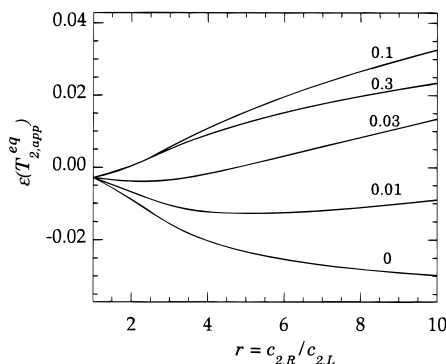
$$c_2^{\text{eq}} = \frac{c(c + c_T)}{c_1} \quad (37b)$$

$$c_3^{\text{eq}} = \frac{c_T(c + c_T)}{c_1} \quad (37c)$$

where  $c = c_{2,R} = c_{2,L}$  and  $c_T = c_{3,R} = c_{3,L}$ . Since the concentrations given by eqs 37a, 37b, and 37c are constant throughout the membrane, the migrational transport numbers are also constant and  $T_i^{\text{eq}} = t_i^{\text{eq}}$ . Then, the following relationship is easily derived

$$\frac{T_2^{\text{eq}}}{D_2 c} = \frac{T_3^{\text{eq}}}{D_3 c_T} \quad (38)$$

Taking the limit  $c_{2,R}/c_{2,L} \rightarrow 1$ , eq 30 reduces to



**Figure 3.** Error in the estimation of  $T_{i,\text{app}}^{\text{eq}}(c_{2,L}, c_{2,L})$  from eq 36. Other values as in Figure 1.

$$T_{1,\text{app}}^{\text{eq}} = T_1^{\text{eq}} \left( 1 - \frac{1}{2} \frac{c_T}{c + c_T} \right) + \frac{T_3^{\text{eq}}}{2} \quad (39)$$

Introducing now eqs 11 and 38 into eq 39 and solving for  $T_1^{\text{eq}}$  we obtain

$$T_1^{\text{eq}} = \frac{2 \left( 1 + \frac{D_2 c}{D_3 c_T} \right) T_{1,\text{app}}^{\text{eq}} - 1}{2 \left( 1 + \frac{D_2 c}{D_3 c_T} \right) \left( 1 - \frac{1}{2} \frac{c_T}{c + c_T} \right) - 1} \quad (40a)$$

and

$$T_2^{\text{eq}} = \frac{1 - T_1^{\text{eq}}}{1 + \frac{D_3 c_T}{D_2 c}} \quad (40b)$$

while  $T_3^{\text{eq}}$  is given by eq 11. Figure 4 shows the comparison of the equilibrium values for the apparent transport numbers and the exact ones for the same case considered in Figure 1. Note that  $T_i^{\text{eq}} \rightarrow T_{i,\text{app}}^{\text{eq}}$  ( $i = 1, 2$ ) and  $T_3^{\text{eq}} \rightarrow 0$  when  $c_T \rightarrow 0$ . However, the differences between apparent and exact values become significant even for relatively low values of  $c_T/c$ .

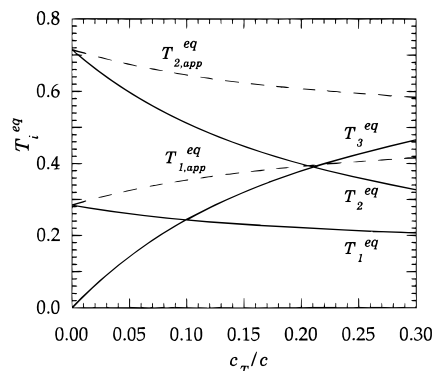
### (c) Determination of the Fixed Charge Concentration.

Figure 5 shows the apparent transport number of potassium ion calculated for the system KCl–HCl, with  $c_{2,R}/c_{2,L} = 10$  and different values of the fixed charge concentration (for both  $z_X = 1$  and  $z_X = -1$ ). This kind of plots can be used for the determination of the fixed charge concentration.<sup>7,9</sup> When the membrane potential is measured for a given ratio  $c_{2,R}/c_{2,L}$  (and  $c_{3,R} = c_{3,L} = c_T$ ), the calculated transport number can be used to read the fixed charge concentration from the corresponding curve in Figure 5. It is evident, however, that this procedure requires to obtain other plots when the experimental conditions are different, and cannot thus be considered satisfactory.

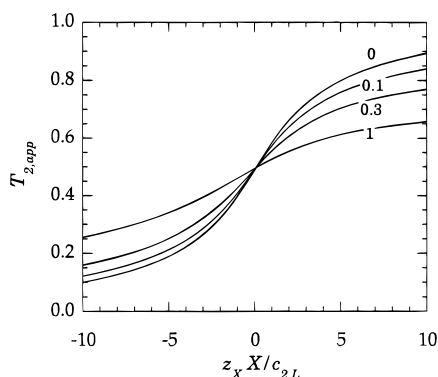
The membrane fixed charge concentration can also be determined from eqs 37a, 37b, 37c and  $T_i^{\text{eq}} = t_i^{\text{eq}}$  as

$$X = \frac{z_1}{z_X} 2(c + c_T) \sinh \left\{ \frac{1}{2} \ln \left[ \left( \frac{1}{T_1^{\text{eq}}} - 1 \right) \frac{D_1(c + c_T)}{D_2 c + D_3 c_T} \right] \right\} \quad (41)$$

Equation 41 is very important from the practical point of view, since it tells us how to estimate the fixed charge concentration from two membrane potential measurements carried out for  $c_R = rc_L$  and  $c_R = c_L/r$  (see eq 36).



**Figure 4.** Equilibrium values of the apparent (dashed lines) and exact (continuous lines) potentiometric transport numbers (obtained from eqs 36 and 40) vs  $c_T/c$  for the membrane system of Figure 1.



**Figure 5.** Apparent transport numbers of potassium ion vs  $z_X X/c_{2,L}$  for the membrane system of Figure 1. The numbers on the curves give the value of  $c_T/c_{2,L}$ , where  $c_T$  is the concentration of hydrogen ion in the bathing solutions.

The fixed charge concentration should not be directly determined from the equilibrium apparent transport numbers, since these numbers are based on the idea of interpreting the measurements of ternary systems by using the equations for binary systems. In a binary system, a similar procedure leads to

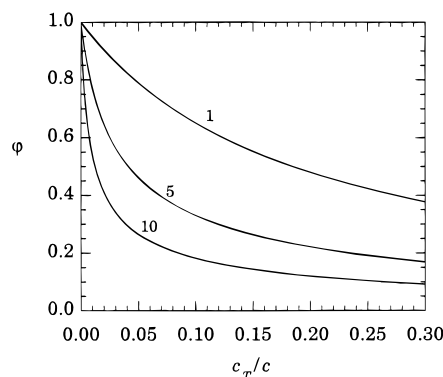
$$X_{\text{app}} = \frac{z_1}{z_X} 2c \sinh \left\{ \frac{1}{2} \ln \left[ \left( \frac{1}{T_{1,\text{app}}^{\text{eq}}} - 1 \right) \frac{D_1}{D_2} \right] \right\} \quad (42)$$

where the subscript app has been added to  $X$  in order to make explicit that this is an apparent value, obtained from the apparent transport number, which differs from the exact  $X$  when  $c_T \neq 0$ . In order to show the error in the fixed charge estimation from the apparent transport numbers, we can write

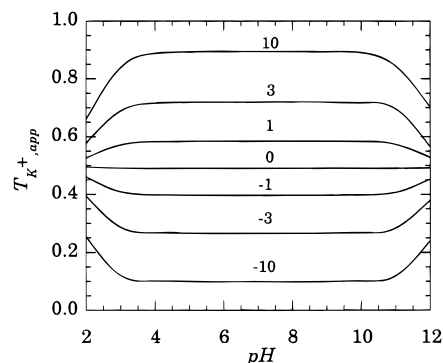
$$X_{\text{app}} = \varphi X \quad (43)$$

where  $\varphi$  ( $0 < \varphi < 1$ ) is a proportionality factor that indicates the “effectiveness” of the fixed charge concentration in relation to the apparent transport numbers. Figure 6 shows the variation of  $\varphi$  with  $c_T/c$  for different values of the fixed charge concentration. Note that since  $T_{1,\text{app}}^{\text{eq}}$  tends to  $T_1^{\text{eq}}$  when  $c_T/c \rightarrow 0$  (see Figure 4), then  $\varphi$  tends to 1 in this limit. For relatively low values of  $c_T/c$ , however,  $\varphi$  deviates significantly from unity. This means that ignoring the presence of the third ion leads to the need of introducing an “effective” or “apparent” fixed charge concentration.

Alternatively, the apparent fixed charge concentration can be obtained from the curve  $c_T/c_{2,L} = 0$  in Figure 5 by reading the



**Figure 6.** The ratio  $\varphi \equiv X_{\text{app}}/X$  vs  $c_T/c$  for the system KCl–HCl. The numbers on the curves give the value of  $X/c$ , and  $z_X = -1$ .

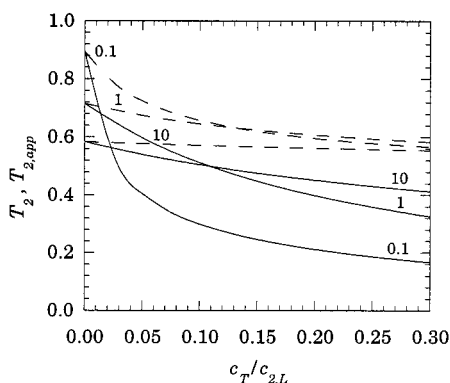


**Figure 7.** Apparent transport number of potassium ion vs pH obtained from membrane potential calculations corresponding to  $c_{2,R}/c_{2,L} = 10$  and  $c_{2,L} = 10$  mM. The numbers on the curves refer to the value of  $z_X X/c_{2,L}$ .

fixed charge concentration which agrees with the value of  $T_{2,\text{app}}$ .

**(d) Fixed Charge Concentration of Amphoteric Membranes.** The fixed charge concentration of amphoteric membranes can be studied as a function of pH by, e.g., measuring the membrane potential at different pH values for the fixed concentrations  $c_{2,R}/c_{2,L} = 10$  and  $c_{2,L} = 10$  mM, and evaluating the apparent transport number of a given ion from eqs 28a or 28b. The results obtained should then be represented in Figure 7 (which can be prepared with as many curves as the precision of the fixed charge determination requires). In particular, the intercept of the experimental data with the curve  $X/c_{2,L} = 0$  would give the isoelectric point, which is a parameter of great experimental interest. The above procedure is more exact than considering just the variation of the apparent transport number vs pH on the basis of only one experimental curve.<sup>23</sup>

**(e) Computed Potentiometric Transport Numbers.** We have shown in subsection c above how to determine the potentiometric transport numbers in the equilibrium situation  $c_{i,R} = c_{i,L}$ . The values corresponding to  $c_{i,R} \neq c_{i,L}$ , however, cannot be obtained from membrane potential measurements. Nevertheless, it is worth considering the behavior of these numbers as obtained from the numerical solution of the transport equations. Figure 8 shows the apparent and exact transport numbers of potassium ion for  $c_{2,R}/c_{2,L} = 0.1, 1$ , and 10. As in Figure 4, it is observed that the exact transport numbers take low values when  $c_T/c_{2,L}$  increases, while the apparent transport numbers remain close to 0.5 in this limit. It is also seen that the difference between exact and apparent values is very significant and increases with decreasing  $c_{2,R}/c_{2,L}$ .



**Figure 8.** 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),  $z_X = -1$ , and  $X/c_{2,L} = 1$ .

## Conclusions

The potentiometric determination of transport numbers for ternary systems in charged membranes has been studied theoretically. First, the use of apparent transport numbers is critically analyzed. Second, a procedure for obtaining the (more meaningful) equilibrium values is discussed. Then, expressions are proposed to evaluate the exact transport numbers under equilibrium conditions.

The estimation of the fixed charge concentration is also studied. The use of the exact equilibrium transport numbers is suggested, and the errors resulting from the use of apparent values are analyzed. Particular attention is paid to the case of amphoteric membranes where the pH adjustment is necessary and the bathing solutions are often ternary systems. However, the study presented here is general and can also be applied to estimate the effect of any impurity ion present in the bathing solution.

The differences found between the exact and the apparent transport numbers are very significant and suggest clearly that the theoretical analyses of the measured transport numbers must be carried out carefully. The same conclusion can be drawn for the membrane fixed charge concentration obtained from the transport numbers. Therefore, the interpretation of ion transport data in terms of the binary system equations can lead to erroneous conclusions even when the third ion present has a relatively low concentration.

**Acknowledgment.** J.A.M. and S.M. thank the DGICYT, Ministry of Education and Science of Spain for financial support (Project No. PB 95-0018).

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