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Convective electrodiffusion processes through graft-modified charged porous membranes

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Abstract

Convective diffusion and electrophoresis across a charged porous membrane showing variable permeability properties were studied. The membrane used was prepared by grafting poly(acrylic acid) (PAA) onto a porous polyvinylidene fluoride (PVDF) membrane. The degree of grafting was selected to be relatively low, 18 wt%, to compromise between the ion selectivity and hydraulic permeability of the membrane. The possible electric field induced effects on the membrane permselectivity were examined after the membrane had been characterized by convective diffusion and concentration cell potential measurements. The measured electrophoresis data, however, could be modelled using the extended Teorell–Meyer–Sievers theory, which indicates that the membrane studied shows no variable permeability behaviour with respect to a weak applied external electric field. This conclusion was also further confirmed by separation experiments carried out with ternary salt solutions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Variable permeability membranes; Convective separation processes; Membrane electrochemistry

1. Introduction

Charged porous membranes prepared by radiation [1]or plasma induced [2] graft-copolymerization of different monomers into porous films is an emerging field in membrane science which is receiving increasing attention. The grafting method is very attractive from the point of view of membrane preparation, and enables easy control of the membrane properties through the degree of grafting [3,4]. More importantly, the permeability of the grafted membranes is sensitive to their environment, as are biological membranes, and can be controlled by changes in temperature [5], pH [6,7], salt concentration [8] and by applying an external electric field [9,10]. This behaviour is explained by the conformational changes of the polyacid groups attached to the membrane pore walls, which affect the transport properties by opening or closing the pores [11–13].

In previous studies [3,10,13], we prepared variable permeability membranes (VPM) by grafting poly(-acrylic acid) (PAA) onto porous polyvinylidene fluoride (PVDF) membranes and found that their mechanical permeability changed by several orders of magnitude when the ionic strength and the pH of the permeate was varied. Since the VPM behaviour enables the control of mechanical permeability and permselectivity, the use of this kind of membrane in convective electrodiffusion processes becomes appealing. Continuous convective electrophoresis in porous membranes has been studied extensively in our laboratory as a separation method for small ions [14–16] and charged proteins [17]. The use of the PVDF/PAA VPM for this application requires knowledge of its permselective properties in current-driven processes. Moderate changes in the membrane permselectivity due to the effect of an elec-

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tric current have been previously observed [10]. However, these membranes have not yet been studied under the simultaneous influence of electric current and convective flow. The present studies have been carried out as a preliminary investigation on the applicability of the PVDF/PAA membranes to convective electrodiffusion separation processes.

A key parameter in convective diffusion processes is the so-called membrane constant A/l (effective membrane area/membrane thickness). If an electrokinetic phenomenon is studied by measuring a force with respect to a flux or vice versa, the ratio A/l must be known, which in practice means that this constant has to be determined in a separate measurement. The standard procedure consists of analysing the concentration gradient established by a convective flow under steady-state, open-circuit conditions [18]. The membrane constant is then obtained from the slope of a logarithmic plot of the concentration ratio versus flow rate. However, the electrical charges bound to the membrane matrix are known to induce important effects during this determination [19] and comparison with results from other methods is recommended. The experimental approach is then followed by potentiometric determination of the membrane fixed charge [20]. Since diffusion boundary layers affect this determination, the convective diffusion cell is replaced in this case by a rotating diffusion cell [3]. Convective electrophoresis and separation experiments are finally analysed, paying particular attention to the effects of the electric current on the effective membrane area to gain insight into possible electric-field induced opening or closing of pores.

2. Theoretical description

Mass transport through charged membranes can be described either by using the Teorell–Meyer–Sievers (TMS) theory [20,21], which considers the membrane as a homogenous phase, or by using the space-charge capillary model (SCM), which considers the membrane as a bank of parallel cylindrical pores bearing a uniformly spread surface charge [22–24]. The SCM takes into account radial and axial variations of ion concentration, electrical potential, and pressure inside the membrane. The counterpart of this theoretical completeness is that the solution procedure of the SCM requires a numerical integration of the Poisson–Boltzmann (PB) equation along the radial direction of the pore, coupled to a different numerical integration of the Nernst–Planck and Navier–Stokes equations along the pore length. Thus, the SCM is used in practice with approximate analytical expressions for the transport coefficients. In the case of low electrical potentials, the PB equation is linearized. In the case of high electrical potentials, total co-ion exclusion is assumed. In practical applications, however, the electrical potential falls within a range where neither of these two hypotheses is valid over the whole pore radius. Westermann–Clark and Christoforou [23] and Cwirko and Carbonell [25] have compared the TMS and SCM models and showed that these two models yield similar results in the case of weakly and very highly charged membranes. Since the grafted membranes considered here are weakly charged, the large computational effort of the SCM does not seem to be justified. In fact, an extended TMS theory explains satisfactorily the results reported in this paper under different experimental conditions.

Fig. 1 shows a sketch of the system considered. The membrane is modelled as a homogeneous phase bearing a uniform molar concentration c_m of fixed groups of charge number z_m. The membrane thickness and the effective membrane area are denoted by l and A, respectively. Due to the high membrane porosity, no chemical partition coefficients are included in the modelling, and the same values for the ionic diffusion coefficients, D_i, are used inside and outside the membrane. Moreover, ionic concentrations inside the membrane are defined considering the whole swollen membrane as the phase volume. The electrolyte solutions bathing the membrane are considered to be ideal, i.e. activity coefficients are set equal to unity. The bathing solutions are either binary or ternary, formed by two binary electrolytes with a common ion, depending on the experiments considered. Superscripts α and β denote bulk concentrations in the respective compartments. Diffusion boundary layers (DBL) of equal thickness δ are considered at each side of the membrane. Hence, one-dimensional transport is described from $x = -\delta$ (α compartment) to $x = l + \delta$ (β compartment). The solvent flow takes place at a rate V^c in the opposite direction to the electric current I.

The analytical solution for this type of convective electrodiffusion problem was first given by Schlögl [21] in parametric form. The integration method used in this work is described in the Appendix A.

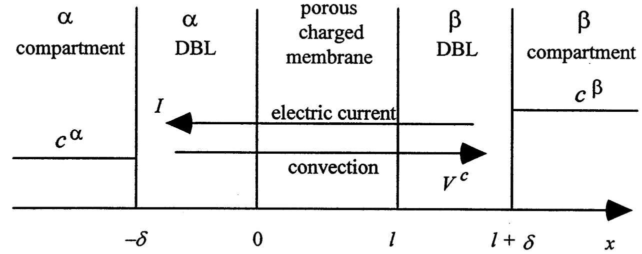

Fig. 1. A schematic drawing of the model membrane system.

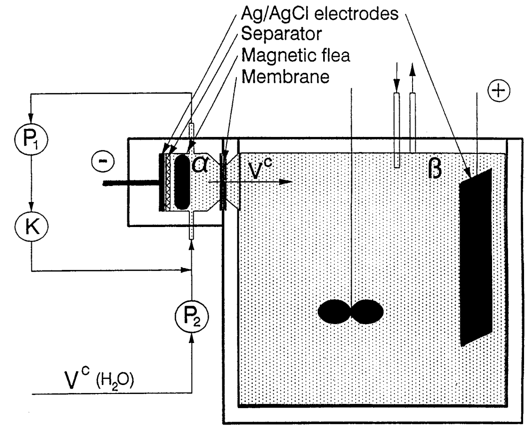

Fig. 2. A schematic drawing of the convective electrodiffusion cell used. P_1 and P_2 are peristaltic pumps and K is a conductometer.

3. Experimental

3.1. Membrane and chemicals

The charged porous membranes required for convective electrodiffusion processes must exhibit a good compromise between permselectivity and hydrodynamic permeability. Based on previous studies [3,10,13], a PVDF membrane with original pore size of 5.0 μm grafted with PAA to 18%-weight was employed. All solutions were prepared from pa chemicals and deionized water (Millipore MilliQ).

3.2. Mass transport experiments

Convective electrodiffusion experiments were carried out in the cell described in Fig. 2. The cell was made of Perspex glass and had an exposed membrane area of 0.28 cm^2. The volume of the α compartment was small (ca. 10 ml) compared with that of the β compartment (ca. 1000 ml), so there were virtually no concentration changes in the bigger compartment. The solution in the α compartment was fed and circulated by two peristaltic pumps (Ismatec IPN) and its concentration was monitored with a conductivity meter (Phillips PW9527) thermostated with a Haake DC3 thermostat. The convective flow through the membrane was measured by weighing. The Ag | AgCl electrode in the α compartment was separated by a porous membrane (Millipore GS 0.22 μm) to prevent possible precipitation of colloidal silver chloride onto the membrane studied. The electric current was controlled by a potentiostat (Sycopel Scientific Ministat 40) and electrodes were re-electrolysed when needed. Bulk solution concentrations were determined either from the conductivity or in the case of ternary solutions by AAS.

The rotating diffusion cell used in the concentration cell potential measurements has been described elsewhere [26].

3.3. SEM studies of membrane morphology

The membrane morphology was investigated using a JEOL JSM-840A scanning electron microscope at an accelerating voltage of 15 kV. The membrane sample was precoated with gold to increase its electrical conductivity.

4. Results

4.1. SEM studies of membrane morphology

SEM micrographs of the membrane studied at 1000-fold and 2300-fold magnifications are presented in Fig. 3a and b, respectively. The inhomogenity of the membrane structure and lack of well-defined pores is clearly seen from these pictures, especially from the latter one.

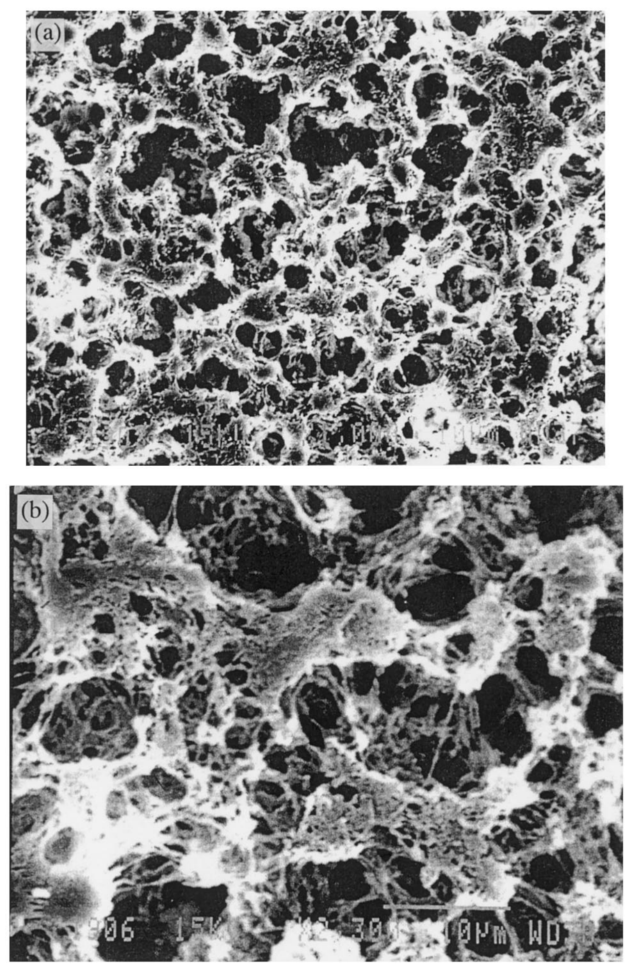

Fig. 3. SEM micrographs of the grafted membrane with an original pore size of 5.0 μm. (a) Magnification 1000 × and (b) magnification 2300 × .

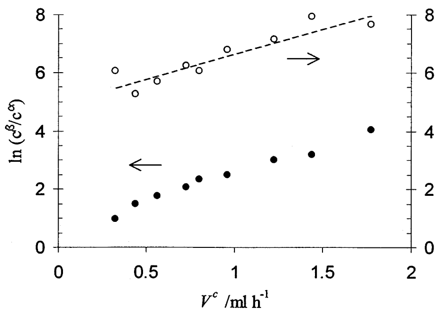

Fig. 4. Determination of the membrane constant from convective diffusion experiments using NaCl ($D_{NaCl} = 1.61 \times 10^{-5}$ cm^2 s^{-1} [28]). From the slope of the logarithmic concentration ratios versus convective flow rate (full symbols), a value of 5.9 cm was determined for the membrane constant. Open symbols correspond to membrane constant values determined from single measurements.

4.2. Convective diffusion measurements

A first estimation of the geometric parameter A/l can be obtained from convective diffusion experiments, in which a convective flow is opposed by a diffusive flow of binary salt under steady-state, open-circuit conditions. These experiments are known to be ruled by [18]

$$\ln \frac{c^{\beta}}{c^{\alpha}} = \frac{V^{c}(l+2\delta)}{DA} \tag{1}$$

where $D = 2D_{+}D_{-}/(D_{+} + D_{-})$ is the salt diffusion coefficient and V^c is the solvent flow rate. It is evident from Eq. (1) that the magnitude actually determined in these experiments is $A/(l+2\delta)$, where δ is the DBL thickness.

Fig. 4 shows the results obtained for NaCl with $c^{\beta} \approx 20$ mM and varying V^c. The deviations of the plot ln (c^{β}/c^{α}) versus V^c from a straight line (full symbols) might be explained by changes in the DBL thickness with convective flow. However, it has been shown that the experimental data deviate from Eq. (1) due to a combined effect of fixed charges and pore geometry [19].

The experimental values of c^{β}, c^{α} and V^c can be used to evaluate the membrane constant $A/(l+2\delta)$ from Eq. (1). The values obtained are in the range 5.2–7.8 cm and show increasing behaviour with respect to the flow rate (open symbols and dashed line in Fig. 6). In the measurements reported in section 4.4, a convective flow rate of 1.1 ml h^{-1} has been used and the membrane constant $A/(l+2\delta)$ is 6.0 cm, approximately.

4.3. Concentration cell potential measurements

The measurement of the membrane constant from convective electrophoresis and separation experiments requires knowledge of the fixed charge concentration. This is routinely determined from electrical potential measurements in a concentration cell [20], which follow Eq. (A18) in the Appendix A. In the case of KCl solution in a concentration cell with Ag | AgCl electrodes and a negatively charged membrane, Eq. (A18) reduces to [20]

$$-f\Delta\phi_{\text{cell}} = \ln \frac{c^{\beta}c(0)c_{-}(l)}{c^{\alpha}c(l)c_{-}(0)} + (t_{+}^{\text{b}} - t_{-}^{\text{b}}) \ln \frac{c^{\beta}c_{-}(0)[c_{-}(l) + t_{+}^{\text{b}}c_{\text{m}}]}{c^{\alpha}c_{-}(l)[c_{-}(0) + t_{+}^{\text{b}}c_{\text{m}}]} \tag{2}$$

where the concentrations involved are given by

$$c_{-}(0) = -c_{\text{m}}/2 + [c_{\text{m}}^2/4 + c(0)^2]^{1/2} \tag{3a}$$

$$c_{-}(l) = -c_{\text{m}}/2 + [c_{\text{m}}^2/4 + c(l)^2]^{1/2} \tag{3b}$$

$$c(0) = c^{\alpha} + \frac{\delta}{l}\left\{c_{-}(l) - c_{-}(0) + (t_{-}^{\text{b}} - t_{+}^{\text{b}})\frac{c_{\text{m}}}{2} \ln \frac{c_{-}(l) + t_{+}^{\text{b}}c_{\text{m}}}{c_{-}(0) + t_{+}^{\text{b}}c_{\text{m}}}\right\} \tag{4a}$$

$$c(l) = c^{\alpha} + c^{\beta} - c(0) \tag{4b}$$

In Eq. (2), $f = F/RT = 38.94$ V^{-1}, and $t_i^{\text{b}} = D_i/(D_{+} + D_{-})$ $(i = +, -)$ is the transport number of species i in bulk solution.

In order to keep the DBL effects under control, a rotating diffusion cell is used for these potential measurements. The ratio of DBL to membrane thickness can then be written as $\delta/l = a/\sqrt{f}$, where f is the rotation frequency in Hz and a is a proportionality coefficient. The measurements are carried out in ascending order of rotation frequencies to reduce the effect of changes in solution concentrations.

Fitting the experimental data to Eq. (2) allows us to determine the fixed charge concentration c_{m} and the constant a. Notice that these two fitting parameters have different effects on $\Delta\phi_{\text{cell}}$; its magnitude is determined by c_{m} and its dependence on f is determined by a, so that the fitting yields a reliable value for c_{m}. In particular, the solid line shown in Fig. 5 has been obtained from Eq. (2) with $c_{\text{m}} = 34$ mM and $a = 0.152$.

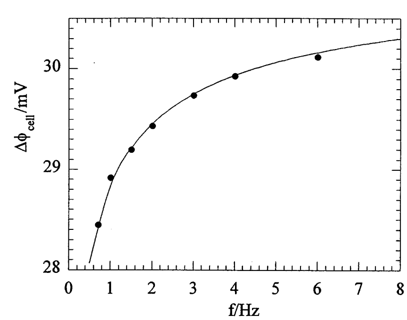

Fig. 5. Cell potentials determined in a rotating diffusion cell working as concentration cell with 10 and 20 mM KCl solution ($t_{+}^{\text{b}} = 0.50$, $D_{KCl} = 1.87 \times 10^{-5}$ cm^2 s^{-1}) [28] and Ag | AgCl electrodes. The full circles represent experimental data, and the solid line is the best fit to Eq. (2), obtained with the fixed charge concentration $c_{\text{m}} = 34$ mM and the proportionality coefficient $a = 0.152$.

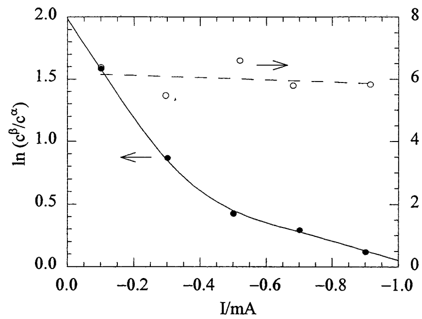

Fig. 6. Concentration ratio as a function of electric current in convective electrophoresis experiments using NaCl ($D_{NaCl} = 1.61 \times 10^{-5}$ cm^2 s^{-1}, $t_+^b = 0.40$) [28] with $c^\beta \approx 18$ mM and $V^c = 1.1$ ml h^{-1}. The solid line has been obtained from Eq. (5) with $l/\delta = 2.0$ and the experimental values of concentration c^α and c^β. The open symbols are membrane constant estimations from Eq. (5) and the applied electric currents.

4.4. Convective electrophoresis measurements

In convective electrophoresis experiments, a convective flow is opposed to a migrational flow so that the cation flux is zero and the anion (in this case, the coion) carries the electric current density; obviously, diffusive transport also plays an important role in this situation [27]. When the solvent flow rate V^c is kept constant and the electric current density is varied, the concentration difference between the two compartments changes according to the Eqs. (3a), (3b), (A11a) and (A13a), which are rewritten here for the case of a negatively charged membrane and $J_+ = 0$

$$\ln \frac{c_-(l) + c_m}{c_-(0) + c_m} + \left(1 + \frac{2c_i}{c_m}\right) \ln \frac{c_-(l) - c_i}{c_-(0) - c_i} = \left(1 + \frac{c_i}{c_m}\right) \frac{2V^c l}{DA} \quad (5)$$

$$\ln \frac{c(0) - c_i}{c^\alpha - c_i} = \ln \frac{c^\beta - c_i}{c(l) - c_i} = \frac{V^c \delta}{DA} \quad (6)$$

where $c_i = -t_+^b I/FV^c$ [18,25].

Fig. 6 shows the experimental results obtained with NaCl and $c^\beta \approx 18$ mM (full symbols). The theoretical analysis of these data has been carried out in two ways. First, the membrane constant was fixed at 6.0 cm, as determined in section 4.2, and the ratio l/δ was used as a fitting parameter of the experimental results to the above equations. The best fit was obtained for $l/\delta = 2.0$, which is a reasonable value. The fitting results are shown in the form of a cubic spline (solid line). Second, the ratio l/δ was fixed at 2.0 and the membrane constant was obtained from the above equations to match every datum point. The results (open symbols and dashed line) show that the membrane constant does not vary significantly with the current density, a conclusion that could also be drawn from the fact that the agreement between theory and experiment using a single value for the membrane constant (solid line) was excellent.

4.5. Separation factor measurements

When the negatively charged membrane is bathed by NaCl + KCl solutions, an electric current can be used to vary the concentration ratio of these two electrolytes in the bulk compartments. In particular, experiments are run where an electric current is carried by the anions (i.e. the cation fluxes are zero) and a convective flow is opposed to the current. The concentrations in the α and β compartments are measured and the separation factor $S = c^\beta_{Na+} c^\alpha_{K+} / c^\alpha_{Na+} c^\beta_{K+}$ is calculated. It is easy to show (see Appendix A) that the theoretical expressions of the separation factor is

$$\ln S = \frac{V^c(l + 2\delta)}{A} \frac{D_{K+} - D_{Na+}}{D_{K+} D_{Na+}} \quad (7)$$

Fig. 7 shows the separation factors observed (full symbols) when the concentrations in the β compartment were $c^\beta_{Na+} \approx 20$ mM and $c^\beta_{K+} \approx 1.1$ mM and the flow rate was fixed at $V^c = 1.1$ ml h^{-1}. From the ion diffusion coefficients $D_{K+} = 1.86 \times 10^{-5}$ cm^2 s^{-1} and $D_{Na+} = 1.33 \times 10^{-5}$ cm^2 s^{-1} [28] and the average value of the separation factor, $S = 1.7$ (solid line), Eq. (7)) yields the result $A/(l + 2\delta) = 12.3$ cm. The reason why the separation experiments yield an effective membrane constant larger than convective diffusion or convective electrophoresis experiments remains unclear. Nevertheless, the slight changes observed in S when the electric current is varied are indirect evidence for the lack of effect of the electric current on the effective membrane constant. This can also be shown by estimating the membrane constant from Eq. (7) and the observed separation factors (open symbols). The slightly increasing tendency observed (dashed line) cannot be judged as significant because of its relatively low correlation coefficient ($r = 0.53$).

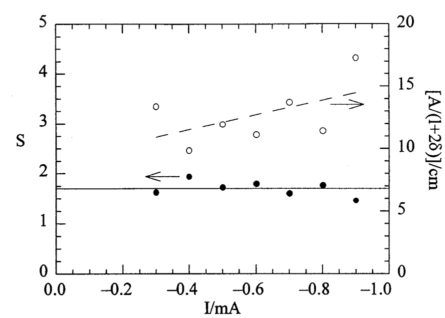

Fig. 7. Separation factor $S = c^\beta_{Na+} c^\alpha_{K+} / c^\alpha_{Na+} c^\beta_{K+}$ in a NaCl + KCl experiment with $c^\beta_{Na+} \approx 20$ mM, $c^\beta_{K+} \approx 1.1$ mM and $V^c = 1.1$ ml h^{-1} as a function of the applied electric current. The membrane constant values (open symbols) have been obtained from Eq. (7).

5. Conclusions

Variable permeability membranes (VPM) prepared by grafting poly(acrylic acid) on porous polyvinylidene fluoride membranes have been used in the presence of simultaneous diffusion, convection and electric current. Thus, this kind of membrane is shown for the first time to be suitable for practical applications requiring both permselectivity and high mechanical permeability, such as electroassisted separation processes with forced convection through the membrane.

The membrane fixed charge has been measured from concentration cell potential measurements in a rotating diffusion cell, yielding a result in agreement with previous studies [3,10,13]. The grafted membranes behave in convective diffusion experiments in a similar way to that observed for non-grafted porous membranes with charge due to ion adsorption [19]. The membrane constant determined from these convective diffusion experiments leads to an excellent agreement between continuous convective electrophoresis experimental data and theoretical expressions derived from an extended TMS theory. This result is considered as evidence for the absence of effects, within the experimental range considered here, of the electric current on the effective membrane area, which means that the electric fields involved are too weak to induce an observable opening or closing of the membrane pores. This conclusion is further confirmed from the analysis of separation factor experiments, since no significant variation of the separation factor with the applied electric current is observed.

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Appendix A

In this appendix, the integration procedure of the steady-state transport equations

$$J_i = -D\left(\frac{dc_i}{dx} + z_i c_i f \frac{d\phi}{dx}\right) + c_i v \quad (A1)$$

is described for the case of binary and ternary electrolyte solutions of univalent ions in the presence of a homogeneous distribution of charged groups bound to the membrane matrix. In Eq. (A1), J_i is the ionic flux density and v is the solvent velocity, which is related to flow rate by $v = V^c/A$. The local electroneutrality assumption

$$\sum_i z_i c_i + z_m c_m = 0 \quad (A2)$$

is employed in the solution procedure, and no activity and partition coefficients are included.

Introducing the magnitudes $g_i = (J_i - c_i v)/D_i$, the flux equations take the form

$$-g_i = \frac{dc_i}{dx} + z_i c_i f \frac{d\phi}{dx} \quad (A3)$$

The position derivative of Eq. (A2)

$$\sum_i z_i \, dc_i/dx = 0 \quad (A4)$$

allows us to solve for the electric potential gradient as

$$-f\frac{d\phi}{dx} = \sum_i z_i g_i / \sum_i c_i \quad (A5)$$

Thus, Eq. (A3) become a system of equations where only ion concentrations appear. The system, however, requires numerical integration for most cases [29].

When applied to a *ternary electrolyte solution* formed by mixing two 1:1 binary electrolytes with a common ion, the transport equations become

$$\frac{dc_2}{dx} = -g_2 + \frac{c_2(g_2 + g_3 - g_1)}{c_1 + c_2 + c_3} \quad (A6a)$$

$$\frac{dc_3}{dx} = -g_3 + \frac{c_3(g_2 + g_3 - g_1)}{c_1 + c_2 + c_3} \quad (A6b)$$

where subscript 1 has been used for the common ion (i.e. the charge numbers satisfy $z_2 = z_3 = -z_1$). No equation is needed for dc_1/dx due to Eq. (A4).

In the separation ratio measurements considered in Section 4.5, the cation fluxes are zero, $J_2 = J_3 = 0$, and the following relation can be derived from Eqs. (A6a) and (A6b)

$$\frac{c_3 e^{-vx/D_3}}{c_2 e^{-vx/D_2}} = \text{constant} \quad (A7)$$

which can be used over the membrane and the two DBL to yield Eq. (7).

The above equations can also be applied to *binary electrolyte solutions* by taking $c_3 = 0$ and $g_3 = 0$. Eq. (A6a) reduces then to

$$\frac{dc_2}{dx} = \frac{c_1 g_2 + c_2 g_1}{c_1 + c_2} \quad (A6c)$$

which can be combined with Eq. (A5) to give

$$z_1 f d\phi = \frac{g_1 - g_2}{c_2 g_1 + c_1 g_2} dc_2 = \frac{t_2^b(c_1 - J_1/v) - t_1^b(c_2 - J_2/v)}{c_1 c_2 - c_1 t_1^b J_2/v - c_2 t_2^b J_1/v} \quad (A8)$$

where $t_i^b = D_i/(D_1 + D_2)$ is the transport number of species i in bulk solution. The potential drop results from integration of Eq. (A8)

$$z_1 f\Delta\phi = \frac{t_2^{\rm b} - t_1^{\rm b}}{c_{1+} - c_{1-}} \Delta \ln \frac{(c_1 - c_{1+})^{c_{1+}}}{(c_1 - c_{1-})^{c_{1-}}} + \frac{t_1^{\rm b}(J_2/v - z_{\rm m}c_{\rm m}/z_1) - t_2^{\rm b}J_1/v}{c_{1+} - c_{1-}} \Delta \ln \frac{c_1 - c_{1+}}{c_1 - c_{1-}} \quad \text{(A9a)}$$

where c_{1+} and c_{1-} are the roots of equation $c_1c_2 - c_1t_1^{\rm b}J_2/v - c_2t_2^{\rm b}J_1/v = 0$, and $c_2 = c_1 + z_{\rm m}c_{\rm m}/z_1$. Symbol Δ denotes the right ($x = l$) minus left ($x = 0$) value.

Furthermore, the ion flux densities can be obtained from the electric current

$$I = AF(z_1 J_1 + z_2 J_2) \quad \text{(A10)}$$

and the integral of Eq. (A6c) over the membrane length l

$$\left(c_{1+} + \frac{z_{\rm m}c_{\rm m}}{2z_1}\right)\Delta \ln(c_1 - c_{1+}) - \left(c_{1-} + \frac{z_{\rm m}c_{\rm m}}{2z_1}\right)\Delta \ln(c_1 - c_{1-}) = (c_{1+} - c_{1-})\frac{vl}{D}. \quad \text{(A11a)}$$

Eqs. (A9a) and (A11a) require the concentration c_1 at the membrane boundaries, $x = 0$ and $x = l$. These are related to the ion concentrations outside the membrane (at these same positions) by the Donnan equilibrium equations

$$c_1(0) = -z_{\rm m}c_{\rm m}/2z_1 + [c_{\rm m}^2/4 + c(0)^2]^{1/2} \quad \text{(A12a)}$$

$$c_1(\rm l) = -z_{\rm m}c_{\rm m}/2z_1 + [c_{\rm m}^2/4 + c(\rm l)^2]^{1/2} \quad \text{(A12b)}$$

Notice that no subscript is needed in c outside the membrane because both ions have the same local concentration in the DBL. In fact, the difference between concentrations inside and outside the membrane is made here through the use of subscripts. The values of $c(0)$ and $c(l)$ can be obtained from the bulk concentrations in the α and β compartments by

$$\frac{c(0) - (t_1^{\rm b}J_2 + t_2^{\rm b}J_1)/v}{c^\alpha - (t_1^{\rm b}J_2 + t_2^{\rm b}J_1)/v} = \frac{c^\beta - (t_1^{\rm b}J_2 + t_2^{\rm b}J_1)/v}{c(l) - (t_1^{\rm b}J_2 + t_2^{\rm b}J_1)/v} = {\rm e}^{v\delta/D} \quad \text{(A13a)}$$

which is easily obtained from Eq. (A11a) by setting $c_{\rm m} = 0$ and replacing the membrane thickness l by the DBL thickness δ.

In the limit of zero convective flow, Eqs. (A9a), (A11a) and (A13a) reduce to

$$f\Delta\phi = \Gamma \Delta \ln[c_1 + (1 + z_1\Gamma)z_{\rm m}c_{\rm m}/2z_1] \quad \text{(A9b)}$$

$$z_{\rm m}c_{\rm m}\Delta\phi - 2\Delta c_1 = (J_1/D_1 + J_2/D_2)l \quad \text{(A11b)}$$

$$c^\alpha - c(0) = c(l) - c^\beta = (J_1/D_1 + J_2/D_2)\delta/2 \quad \text{(A13b)}$$

where $\Gamma = (z_1J_1/D_1 = z_2J_2/D_2)/(J_1/D_1 = J_2/D_2)$.

Finally, the electrical potential drop in each DBL is obtained from Eq. (A9a) with $c_{\rm m} = 0$ as

$$f\Delta\phi_{\rm DBL} = \Gamma \Delta \ln c - (\Gamma - \gamma)v\delta/D \quad \text{(A14)}$$

where $\gamma = z_1(t_2^{\rm b} - t_1^{\rm b})$, and the sum of the Donnan potentials is given by

$$z_1 f(\Delta\phi_D^\alpha + \Delta\phi_D^\beta) = \ln \frac{c(0)c_1(l)}{c(l)c_1(0)}. \quad \text{(A15)}$$

The above equations can now be applied to the different experiments reported. First, in the case of the convective diffusion measurements, both ionic fluxes are zero and the integration of Eq. (A6c) yields Eq. (1). Second, in the case of the concentration cell potential measurements, the electric current and the solution velocity are both zero, and the total potential drop across the membrane system is

$$z_1 f(\gamma\Delta\phi_{\rm DBL}^\alpha + \Delta\phi_D^\alpha + \Delta\phi_M + \Delta\phi_D^\beta + \Delta\phi_{\rm DBL}^\beta) = \ln \frac{c(0)c_1(l)}{c(l)c_1(0)} + (t_2^{\rm b} - t_1^{\rm b})\ln \frac{c^\beta c_1(0)[c_1(l) + t_2^{\rm b}z_{\rm m}c_{\rm m}/z_1]}{c^\alpha c_1(l)[c_1(0) + t_2^b z_{\rm m}c_{\rm m}/z_1]} \quad \text{(A16)}$$

If the electrodes are reversible to species 1, their contribution to the cell potential is

$$z_1 f\Delta\phi_{\rm e} = -\ln(c^\alpha/c^\beta) \quad \text{(A17)}$$

and Eq. (A16) takes the form

$$z_1 f\Delta\phi_{\rm cell} = \ln \frac{c^\beta c(0)c_1(l)}{c^\alpha c(l)c_1(0)} + (t_2^{\rm b} - t_1^{\rm b})\ln \frac{c^\beta c_1(0)[c_1(l) + t_2^{\rm b}z_{\rm m}c_{\rm m}/z_1]}{c^\alpha c_1(l)[c_1(0) + t_2^{\rm b}z_{\rm m}c_{\rm m}/z_1]}. \quad \text{(A18)}$$

And third, in the case of convective electrophoresis measurements, the cation flux is zero and Eqs. (A11a) and (A13a) reduce to Eqs. (5) and (6).

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