functions; for rigid molecules, $\hat{w}_{\alpha\gamma}(k) = \sin(kL_{\alpha\gamma})/kL_{\alpha\gamma}$, where $L_{\alpha\gamma}$ is the distance between sites α and γ; $\hat{c}$ is the matrix of direct correlation functions and $\hat{c}^* = \hat{c} - \hat{k}'$; k_γ is the matrix of solvent density; and U^* is a short-range potential which usually, but not necessarily, takes the Lennard-Jones 6-12 form. The symbol A is a numerical factor introduced to impose consistency between the calculated *solvent* correlation functions and a given value of the *solvent* dielectric constant, ϵ_0. It is given by[53-55]

$$A = \frac{1 + \epsilon_0(3y - 1)}{3y(\epsilon_0 - 1)} \quad \text{with} \quad y = \frac{4\hat{\beta}\rho_v\langle d_v^2\rangle}{9} \quad \text{(A.4)}$$

where $\langle d_v^2\rangle$ is the average squared dipole moment of the solvent molecule.

By solving eqs A.1–A.3 self-consistently one can obtain $h_{\alpha\gamma}^{(0)}(r)$ and $c_{\alpha\gamma}^{(0)}(r)$ from which the excess solvation free energy, ΔG_s, of introducing a solute into the solvent at infinite dilution can be calculated by using the expression[56,57]

$$\Delta G_s = \frac{\rho_v}{\beta}\sum_{\alpha=1}^{n_u}\sum_{\gamma=1}^{n_v}\int d\vec{r}\,\{\tfrac{1}{2}[h_{\alpha\gamma}^{(0)}(r)]^2 - c_{\alpha\gamma}^{(0)}(r) - \tfrac{1}{2}h_{\alpha\gamma}^{(0)}(r)c_{\alpha\gamma}^{(0)}(r)\}$$

$$\text{(A.5)}$$

where n_u is the number of solute sites and n_v is the number of solvent sites, equal to 3 in the present case.

The solvent model used in the XRISM method is the rigid three-site TIP3P[58] water with minor modifications of the hydrogen Lennard-Jones interaction parameters to avoid a Coulombic singularity in the interaction potential due to the absence of repulsive cores on the hydrogen sites.[59] The empirical potential is characterized by the experimental water geometry ($R_{OH} = 0.9572$ Å, $\angle HOH = 104.52°$) and charges of -0.834 on the oxygen and 0.417 on the hydrogen. The Lennard-Jones parameters are $(\sigma, \epsilon) = (3.15$ Å, 0.152 kcal/mol) for the oxygen site and $(0.40$ Å, 0.046 kcal/mol) for the hydrogen site. For the Lennard-Jones interaction between oxygen and hydrogen sites, the combination rules, $\epsilon_{\alpha\gamma} = (\epsilon_\alpha\epsilon_\gamma)^{1/2}$ and $\sigma_{\alpha\gamma} = (\sigma_\alpha + \sigma_\gamma)/2$, are used. At 25 °C

and $\rho_{H_2O} = 0.997$ g/cm^3, the A of eq A.4 is 0.959 to match the experimental water dielectric constant of $\epsilon_0 = 78.4$.[60]

B. Results and Discussion. The XRISM results in Table XI show that the order of the solution pK_a is $pK_a(MeNH_3^+) > pK_a(ImH^+) > pK_a(MeOH) > pK_a(HCOOH)$ for parameter set QC; $pK_a(ImH^+) > pK_a(MeNH_3^+) > pK_a(HCOOH) > pK_a(MeOH)$ for parameter set CC; and $pK_a(ImH^+) > pK_a(MeOH) > pK_a(MeNH_3^+) > pK_a(HCOOH)$ for parameter set OO. Thus for all three parameter sets, XRISM fails to predict the order of the absolute and relative pK_a values; this results from XRISM overestimating ΔG_s of anions by 16–36% and underestimating ΔG_s of cations by 27–51%. It also underestimates ΔG_s of neutral compounds and often yields positive ΔG_s values. These trends are also manifested in ΔG_s of water, Cl$^-$ and Na$^+$ obtained by Yu and Karplus,[20] though the errors are smaller (≈ 10%).

A reason for the discrepancy between the calculated and experimental ΔG_s can be inferred from the work of Yu and Karplus.[20] They have used XRISM to obtain the solute–solvent radial distribution functions for a cation (g_+), an anion (g_-), and a Lennard-Jones nonpolar particle (g_0), with water oxygen and hydrogen sites, respectively, at 300 K; the nonbonded parameters for cation, anion, and nonpolar particle are the same and correspond to those of a chloride ion. The nearest-neighbor peak in the pair distribution function of a cation with the oxygen site of water, g_{O+}, is positioned 1.28 Å further than that of an anion with the hydrogen site of water, g_{H-}. Thus XRISM would predict a more favorable solvation energy for an anion relative to a cation, which lacks favorable hydrogen-bonding interactions. The overestimation of anion ΔG_s and underestimation of cation ΔG_s may be mainly due to the inadequacy of the HNC closure.[11,20] Furthermore, a comparison of the enthalpic and entropic contribution to ΔG_s of the model chloride *neutral* atom shows that both terms are unfavorable with the entropy term dominant. Since solvation free energies for neutral molecules are underestimated, and their experimental values are all negative, it appears that the magnitude of the entropy term is overestimated and/or there is a lack of stabilizing energetic interactions with the solvent which would make the enthalpy negative. The latter is supported by an integral equation calculation[20] of the solvation free energy of methane using the Percus–Yevick closure where a large $\epsilon(CH_4–O)$ of 0.412 was needed in order to obtain the correct experimental value.

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Transport Phenomena and Asymmetry Effects in Membranes with Asymmetric Fixed Charge Distributions

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Transport phenomena through membranes with asymmetric fixed charge distributions varying linearly with position inside the membrane are theoretically studied. The limits of applicability of previous models based on Henderson's assumption have been established, and the effects that the asymmetry exerts on the flux and the membrane potential have been found to be of minor importance for the physical model employed. The theory is based on the Nernst–Planck equations, and the numerical solution derived does not show the doubtful results arising from the use of the approximated Henderson's assumption: the nonzero, steady-state values of the flux and the membrane potential for a situation in which two identical external solutions are separated by an asymmetric membrane, and the occurrence of steady-state reverse transport. Some comments on the temporary nature of the experimentally observed asymmetry effects are also included.

Introduction

The problem of ion transport through membranes with inhomogeneous charge distributions has received some attention recently.[1-4] The description of the physical phenomena related to

the existence of a structural or chemical inhomogeneity in a membrane requires the revision and extension of the classical

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models of transport in homogeneous membranes.[3] A case of special importance is that of asymmetric membranes.[1-3] Some of the transport models proposed so far for asymmetric membranes have now been reviewed by Mafé and Manzanares.[1] One of the more relevant approaches to the problem seems to be that of Takagi and Nakagaki,[2] who extended the classical Teorell–Meyer–Sievers theory[3] to account for the asymmetry in fixed charge concentration and partition coefficients. They used the Nernst–Planck equation for the transport of uni–univalent ions, the local electroneutrality condition, and Henderson's assumption[3] for the concentration profiles inside the membrane. More recently, Higuchi and Nakagawa[5] have proposed the inclusion of the standard chemical potential gradient in inhomogeneous membranes as a new force for ion transport. They also claimed that Henderson's assumption leads to some doubtful results in Takagi and Nakagaki's theory: the nonzero steady-state values of the flux and the membrane potential for a situation in which two identical external solutions are separated by the asymmetric membrane, and the occurrence of steady-state reverse transport (matter transport opposite to that expected from the concentration difference imposed between the two bulk solutions (Note that the gradient of the asymmetric fixed charge concentration within the membrane can be opposite to that of concentration imposed externally between the two bulk solutions.)) are two theoretical conclusions violating the basic laws of thermodynamics.

The paper by Higuchi and Nakagawa has prompted us to go deeper into Takagi and Nakagaki's model in order to study the limits of applicability of this theory. Some comments on the nature of the experimentally observed asymmetry effects are also included. Our analysis is based on the numerical solution of the original (simplified[9]) form of the Nernst–Planck equations, and Henderson's assumption for the concentration profiles is not included. Reiss and co-workers[6,7] have recently paid attention to the effects of an inhomogeneous charge distribution on the membrane current efficiency on the basis of a model containing also the above mentioned Nernst–Planck equations.

Formulation of the Problem

The basic equations describing our problem are the steady-state Nernst–Planck equations for uni–univalent ions

$$J_i = -D_i\left[\frac{dc_i}{dx} + (-1)^{i+1}c_i\frac{d\psi}{dx}\right] \quad i = 1, 2 \qquad (1)$$

the local electroneutrality assumption

$$c_1 - c_2 + \theta = 0 \qquad (2)$$

and the conditions of zero electric current (eq 3a) and steady-state (constant) fluxes through the membrane (eq 3b)

$$J_1 - J_2 = 0 \qquad (3a)$$

$$J_1 \equiv J(\text{const}) \qquad (3b)$$

Equations 1–3 are the basis of many simplified treatments for one-dimensional transport phenomena in charged membranes, and their origin and limitations can be found elsewhere.[9] Here J_i, D_i, and c_i denote the flux, the diffusion coefficient, and the local molar concentration of the ith species, respectively. Subscript 1 refers to cations, and subscript 2 to anions. On the other hand, ψ stands for the local electric potential in RT/F units, θ for the local fixed

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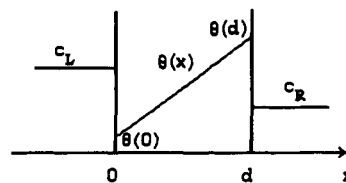(9) Buck, R. P. *J. Membr. Sci.* **1984**, *17*, 1.

Figure 1. Schematic diagram of the membrane system. Parameters $\theta(0)$ and $\theta(d)$ are the fixed charge concentrations at the membrane boundaries, c_L and c_R being the external bulk solution concentrations.

charge concentration, and x for the spatial coordinate inside the membrane (the membrane–solution interfaces are located at the points $x = 0$ and $x = d$; see Figure 1 for details). Constants F, R, and T have the usual meanings. According to previous models,[2] we define the parameters r and r_θ as $r \equiv c_L/c_R$ and $r_\theta \equiv \theta(x=0)/\theta(x=d)$ where c_L and c_R are the left and right bulk solution concentrations, respectively.

Our study will be confined to the case of an asymmetric fixed charge distribution varying linearly with x:

$$\theta(x) = \theta(0) + (\Delta\theta/d)x \qquad \Delta\theta \equiv \theta(d) - \theta(0) \qquad (4)$$

The boundary conditions for the concentrations c_i can be obtained from a simplified form of the Donnan equilibrium relationship[2,3] at the membrane–solution interfaces (partition coefficients are taken equal to unity)

$$c_1(0) = -\theta(0)/2 + [(\theta(0)/2)^2 + c_L^2]^{1/2} \qquad (5a)$$

$$c_2(0) = c_1(0) + \theta(0) = c_L^2/c_1(0) \qquad (5b)$$

$$c_1(d) = -\theta(d)/2 + [(\theta(d)/2)^2 + c_R^2]^{1/2} \qquad (5c)$$

$$c_2(d) = c_1(d) + \theta(d) = c_R^2/c_1(d) \qquad (5d)$$

In eqs 2 and 5 we have assumed, without loss of generality, that the membrane has a positive fixed charge. Note also that single bathing salts are considered at the two sides of the membrane so that anion and cation concentrations are both equal to c_L in the left compartment and to c_R in the right one.

The above equations have no analytical solution as they stand. To overcome this problem, Takagi and Nakagaki solve first for $d\psi/dx$ and J_i (eqs 5 and 3 in their paper[2]), and then *assume* the ion concentrations within the membrane to be given by the Henderson equation:

$$c_i = c_i(0)[1 - \delta(x)] + c_i(d)\delta(x) \quad i = 1, 2 \qquad (6)$$

where $\delta(x)$ is the same for the two mobile ions and then for the fixed charge groups, and verifies $\delta(0) = 0$ and $\delta(d) = 1$. Substitution of eqs 6 into eqs 5 and 3 of ref 2 leads (after integration) to the membrane potential and the flux, respectively. However, these expressions show two rather surprising results:[2] (i) the existence of nonzero, steady-state values of flux and membrane potential for a situation in which the two external bulk solution concentrations are *identical* ($r = 1$) and (ii) the possibility of steady-state reverse transport for certain values of r and r_θ. It seems that these results violate the first[5] and second laws of thermodynamics.

A transport theory should give the correct equilibrium limit,[10] and this equilibrium limit seems to correspond to $r = 1$ in our case. To check this point, consider eqs 1, 2, and 3. From eq 1 for $i = 1, 2$, it is readily obtained that

$$-\frac{d(c_1c_2)}{dx} = J(c_2/D_1 + c_1/D_2) \qquad (7)$$

Integration of eq 7 from $x = 0$ to $x = d$ yields

$$c_1(0)c_2(0) - c_1(d)c_2(d) = J\int_0^d (c_2/D_1 + c_1/D_2)\,dx \equiv JI \qquad (8)$$

where I is the final value of the integral. Note that I is a *nonzero*

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positive number. Now, according to eqs 5b and 5d, the left side of eq 8 can be written as

$$c_L{}^2 - c_R{}^2 = JI \tag{9}$$

Thus, the case $r = 1$ ($c_L = c_R$) leads to $J = 0$, that is, to a strictly zero flux.

On the other hand, substitution of $J_2 = 0$ in eq 1 would give the well-known Nernstian potential difference through the membrane

$$\psi(d) - \psi(0) = -\ln c_2(0)/c_2(d) \tag{10}$$

And the sum of the interfacial Donnan potentials is simply

$$[\psi(0) - \psi_L] + [\psi_R - \psi(d)] = \ln c_2(0)/c_L + \ln c_R/c_2(d) = \\ \ln c_2(0)/rc_2(d) \tag{11}$$

Therefore, it is clear from eqs 10 and 11 that the total membrane potential $\Delta\psi \equiv \psi_R - \psi_L$ is also strictly zero for $r = 1$, and we conclude that the case $r = 1$ corresponds indeed to the *equilibrium* state. But eq 9 contains even more information: J and ($c_L - c_R$) will always have the same sign, and then steady-state reverse transport *cannot* occur in our model. (It is worth noting that all these conclusions *do not* depend on the particular fixed charge distribution assumed within the membrane.)

It becomes clear at this point that the above discussed results in Takagi and Nakagaki's theory come from the use of Henderson's assumption (eqs 6) to calculate the flux and the membrane potential, as anticipated by Higuchi and Nakagawa.[5] Indeed, eqs 6 have been *imposed onto* eqs 1–3 rather than *derived from* them.

However, taking into account the wide use of Henderson's assumption in membrane transport theory,[3] it seems necessary to go a step further and try to show which are the sufficient conditions for the validity of eqs 6 in transport through membranes with an asymmetric fixed charge distribution. (Studies on the validity of Henderson's assumption are not very usual in the literature even for the case of homogeneous membranes.) Hereafter we will consider, for the sake of simplicity, a linear relationship for $\delta(x)$, $\delta(x) = x/d$, for the approximate distribution of the mobile ions. From eqs 1 and 6, we have that

$$-\frac{c_1}{c_2} = \frac{J_1/D_1 + dc_1/dx}{J_2/D_2 + dc_2/dx} = \text{const} \tag{12}$$

Thus, the following relationship can be obtained

$$c_2(0)/c_1(0) = c_2(d)/c_1(d) \tag{13}$$

and eqs 5b and 5d lead then to

$$c_1(0)/c_1(d) = r_\theta \tag{14}$$

Finally, eqs 5a, 5c, and 14 give

$$r = r_\theta \tag{15}$$

as the sufficient condition for the validity of Henderson's assumption. This condition is very restrictive since r and r_θ are two *independent* parameters for each experimental situation (r_θ has a characteristic value for a given asymmetric membrane, while r has to do with the concentration difference externally imposed between the two bulk solutions). Fortunately, the equality $r = r_\theta$ is *not a necessary condition* for the validity of eq 6. It can be expected that for $\theta(0)$, $\theta(d) \gg c_{L,R}$ (fixed charge concentration within the membrane much greater than external bulk solution concentrations), the concentration profiles c_1 and c_2 would follow the linear relationship imposed to θ (eq 4) because of the electroneutrality condition (eq 2). Thus, Henderson's assumption should also be valid for this limiting case.

Now, the next step is to solve numerically the "exact" eqs 1–3 according to the boundary conditions imposed onto concentrations (eqs 5) and electric potential ($\psi_L = 0$). This numerical solution is necessary in order to (i) overcome all the mentioned shortcomings arising from the use of Henderson's assumption, (ii) check the previously suggested applicability conditions for this assumption, and (iii) establish theoretically which are the actual effects that the asymmetric charge distribution exerts on the flux

and the membrane potential in the particular model used.

Numerical Solution

Equations 1–3 can be solved numerically by applying previous finite-difference algorithms[11,12] to the case of an inhomogeneous charge distribution within the membrane. This is probably a reasonable procedure to study multiionic systems[11-13] where ions of different charge numbers can occur, as well as for treating problems involving space charge effects via the Poisson equation.[12] However, only two ions are considered here, and the space charge effects can be ignored since the membrane thickness is much greater than a typical Debye length.[9] Moreover, according to previous work,[1-5] a detailed treatment[14] of the double layer at the membrane–solution interface is not included. Thus, we will show that the relative simplicity of our transport problem finally leads to a set of transcendental equations whose solution can be accomplished by means of trivial numerical procedures.

First, we solve for the electric potential gradient from eqs 1 and 2

$$\frac{d\psi}{dx} = \frac{1}{\theta}\left(2\frac{dc_1}{dx} + \frac{d\theta}{dx} + \frac{J_1}{D_1} + \frac{J_2}{D_2}\right) \tag{16}$$

Equation 16 is introduced now in eq 1 for $i = 1$. In order to simplify the resulting expression, we make use of the new variable $y \equiv c_1/\theta$. The final nonlinear differential equation for y is

$$2y^2\frac{d\theta}{dx} + \left(2\frac{d\theta}{dx} + \frac{J_1}{D_1} + \frac{J_2}{D_2}\right)y + \frac{J_1}{D_1} + \theta(1 + 2y)\frac{dy}{dx} = 0 \tag{17}$$

which can be rearranged in the form

$$\frac{y + 1/2}{y^2 + (1 + g_1 + g_2)y + g_1} dy = -\frac{d\theta}{\theta} \tag{18}$$

where

$$g_i \equiv \frac{J_i}{2D_i(d\theta/dx)} \quad i = 1, 2 \tag{19}$$

Solving for the quadratic algebraic equation in y that appears in the denominator of eq 18 yields the two roots

$$y_1 = -\frac{1 + g_1 + g_2 + [(1 + g_1 + g_2)^2 - 4g_1]^{1/2}}{2} \tag{20a}$$

$$y_2 = g_1/y_1 \tag{20b}$$

Equation 18 can now be rewritten as

$$\frac{y + 1/2}{(y - y_1)(y - y_2)} dy = -\frac{d\theta}{\theta} \tag{21}$$

whose integration is immediate

$$(y - y_1)^A (y - y_2)^{1-A}\theta = \text{const}$$

$$A \equiv \frac{y_1 + 1/2}{y_1 - y_2} \tag{22}$$

In terms of concentrations c_1 and θ, eq 22 takes the form

$$(c_1 - y_1\theta)^B(c_1 - y_2\theta) = \text{const}$$

$$B \equiv \frac{A}{1 - A} = -\frac{1 + 2y_1}{1 + 2y_2} \tag{23}$$

The flux J can now be obtained by imposing the appropriate boundary conditions (eqs 5) to eq 23

$$(c_1(d) - y_1\theta(d))^B(c_1(d) - y_2\theta(d)) = \\ (c_1(0) - y_1\theta(0))^B(c_1(0) - y_2\theta(0)) \tag{24}$$

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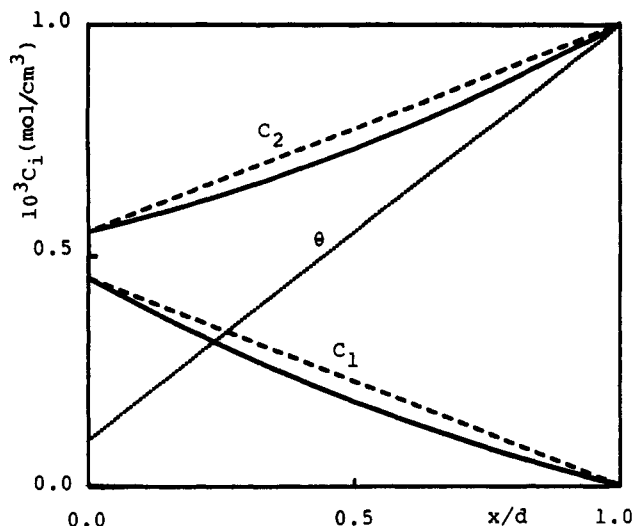(14) Bassignana, I. C.; Reiss, H. *J. Phys. Chem.* **1983**, *87*, 136.

Figure 2. Concentration profiles inside the membrane: (—) exact computed profiles; (- - -) Henderson's profiles; (···) assumed fixed charge distribution. Bulk solution concentrations are $c_L = 5 \times 10^{-4}$ mol/cm³ and $c_R = 5 \times 10^{-5}$ mol/cm³. Fixed charge concentrations at $x = 0$ and $x = d$ are $\theta(0) = 10^{-4}$ mol/cm³ and $\theta(d) = 10^{-3}$ mol/cm³, respectively.

Equation 24 is a transcendental equation in J that can be solved, e.g., by the standard bisection method.[15] Once the value for J is calculated, the constant appearing in eq 23 becomes determined and this equation can be used to compute the concentration profile $c_1(x)$ for a set of points between $x = 0$ and $x = d$. Our solution procedure makes use of Newton's rule[15] for each point within the membrane (a total number of some 10^4 points was considered). Finally, when the concentration profile $c_1(x)$ and the flux J are known, the diffusion potential within the membrane can be computed by Romberg's numerical integration[15] of the electric potential gradient obtained from eqs 1 and 2

$$\psi(d) - \psi(0) = \left(\frac{\Delta\theta}{d} + J\frac{D_1 - D_2}{D_1 D_2} \right) \int_0^d \frac{dx}{2c_1 + \theta} \quad (25)$$

Equation 25 is to be added to eq 11 for the Donnan potentials in order to calculate the total (dimensionless) membrane potential.

It should be noted that eqs 24 and 23 are not valid for $r_\theta = 1$. In this case, they should be written in the form

$$\frac{\Delta c_1}{\theta(d)} + \frac{h_2 - h_1}{2(h_1 + h_2)} \ln \left[\frac{(h_1 + h_2)c_1(d) + h_1\theta(d)}{(h_1 + h_2)c_1(0) + h_1\theta(d)} \right] + h_1 +$$
$$h_2 = 0 \quad (26)$$

$$\frac{c_1 - c_1(0)}{\theta(d)} + \frac{h_2 - h_1}{2(h_1 + h_2)} \ln \left[\frac{(h_1 + h_2)c_1 + h_1\theta(d)}{(h_1 + h_2)c_1(0) + h_1\theta(d)} \right] +$$
$$(h_1 + h_2)\frac{x}{d} = 0 \quad (27)$$

respectively. In eqs 26 and 27, $\theta(d)$ has been taken as the (constant) fixed charge concentration, and $h_i \equiv J_i d/2D_i\theta(d)$.

The numerical procedure briefly outlined above was implemented on a HP-9000/330 computer under the latest FORTRAN version. When the initial values for the bisection method are properly chosen, the solution procedure lasts less than one minute.

Results

Transport of an ideal electrolyte with charge numbers $z_1 = +1$ and $z_2 = -1$ and diffusion coefficients $D_1 = 10^{-5}$ cm²/s and $D_2 = 2 \times 10^{-5}$ cm²/s is considered throughout this section. Results have also been obtained for other diffusion coefficient values, but no significant qualitative changes were found. Two groups of results are presented. The first one corresponds to the values of J and $\Delta\psi$ derived from the "exact" eqs 1–4; the second one is that
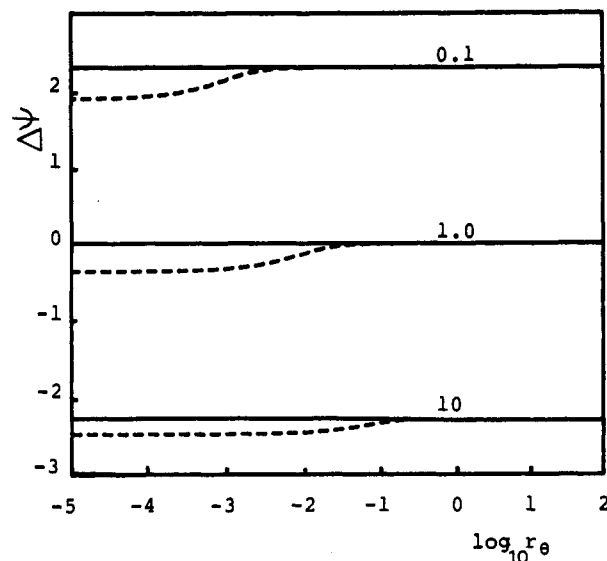
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Figure 3. Membrane potential vs log r_θ: (—) exact computed results; (- - -) results obtained by using Henderson's assumption. The figures on the curves refer to values of r. The values $c_R = 10^{-5}$ mol/cm³ and $\theta(d) = 10^{-3}$ mol/cm³ have been used in the computations.
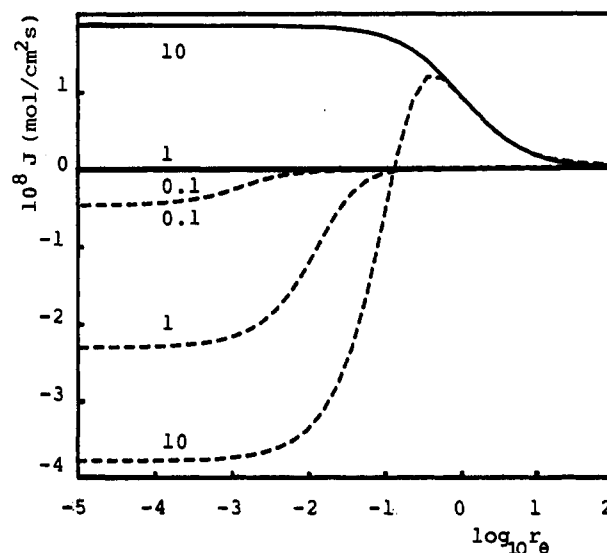

Figure 4. Flux vs log r_θ: (—) exact computed results; (- - -) results obtained by using Henderson's assumption. The figures on the curves refer to values of r. The values $c_R = 10^{-5}$ mol/cm³ and $\theta(d) = 10^{-3}$ mol/cm³ have been used in the computations.

of the values obtained by using Henderson's assumption for the concentration profiles in the equations of J and $\Delta\psi$ (see ref 2 for details).

Figure 2 shows the concentration profiles inside the membrane for the case $r = 10$ and $r_\theta = 0.1$. The exact profiles show some curvature, and the observed deviations from Henderson's profiles are important. Note that if the profiles were to vary linearly with x, eq 12 could never be fulfilled since c_2 increases and c_1 decreases with x in Figure 2. The numerical solution for other values of parameters r and r_θ showed that the smaller the difference between r and r_θ, the more linear the exact concentration profiles, as was anticipated in the previous section.

Figures 3 and 4 are plots of the membrane potential and flux vs log (r_θ) for different values of r, respectively. It is important to note that Henderson's assumption leads to steady-state nonzero values for the membrane potential and the flux for $r = 1$. In addition, the cases $r = 10$ and $r_\theta \ll r$ show reverse transport (this reverse transport cannot be obtained for a sufficiently high value of r; we obtained that this value was $r \approx 20$ in our case). The exact results show neither nonzero steady-state values for membrane potential and flux in the case $r = 1$ nor permanent

steady-state reverse transport, according to our previous analysis.

In addition, the values obtained by means of Henderson's assumption agree with our exact computed results when r_θ is of the order of or greater than r, i.e., when the sufficient condition $r = r_\theta$ is fulfilled or the fixed charge concentration is high compared to bulk solution concentrations. (The computations carried out with smaller fixed charge concentrations showed that agreement between the exact results and those obtained by using Henderson's assumption was only possible for $r \approx r_\theta$.)

The exact membrane potential is nearly constant, irrespective of the fixed charge asymmetry. Henderson's assumption leads to values of membrane potential lower than the exact ones for $r_\theta < r$. The exact fluxes and those obtained via Henderson's assumption are also quite different. On the other hand, we see for the case $r = 10$ that the exact fluxes in the range $r_\theta \ll 1$ are almost twice those corresponding to a homogeneous membrane with $\theta(x) = \theta(d)$. This is not an asymmetry effect, since the mean fixed charge concentration in this range is approximately $\theta(d)/2$.

Discussion

We have considered a simple model for ion transport through inhomogeneous membranes whose asymmetric fixed charge distribution varies linearly with position inside the membrane. The numerical solution worked out here does not show the doubtful results arising from the use of the popular Henderson assumption in Takagi and Nakagaki's model and establishes some restrictive conditions for this assumption to be valid. However, the effects that the asymmetry exerts on the flux and the membrane potential have been found to be very small in our case, and more elaborate theories incorporating other asymmetry effects are now under development.

When we compare our results to experiment, a case of particular importance is that of $r = 1$. Experimental results[2,16] have shown nonzero values for the flux and membrane potential under this condition. According to our computations, these results should be regarded as of *transient* (not permanent) nature, as previously pointed out by Higuchi and Nakagawa.[5] This question deserves more attention. A necessary experimental condition for a nonzero asymmetric membrane potential when $r = 1$ is[16] "no permeation of ions across the membrane". (Under this condition the membrane potential is simply the sum of the two interfacial Donnan potentials, and this sum is not zero for $r = 1$ because of the fixed charge distribution asymmetry; see eqs 11 and 5.) This is an ideal limiting condition that can be approximated in practice with asymmetric membranes of high *compactness*. Just two examples: in ref 16, the membrane was so compact that "the membrane resistance was high and hardly depended on the salt concentration", and in ref 2, inspection of Figure 6B leads to the estimation $D_s \approx 10^{-9}$ cm^2/s for the membrane salt diffusion coefficient (this value is to be compared to the typical one, $D_s \approx 10^{-5}$ cm^2/s, for diffusion in a free electrolyte solution). Therefore, given an initial thermodynamic state of the membrane system, it would take a typical relaxation time $\tau_d = d^2/D_s \approx 10^5$ s (one day, approximately) for the diffusion through a membrane of thickness $d = 10^{-2}$ cm to reach the steady state (this state would be that of *equilibrium* for $r = 1$).

The above facts may suggest that the asymmetry effects observed for J and $\Delta\psi$ when $r = 1$ are not permanent, steady-state properties of the membrane system but depend on the initial thermodynamic state of this system. Thus, these effects will eventually vanish after some (long) relaxation time has passed, even if the external bulk solution concentration (the same at both sides of the membrane) is kept constant. (However, a complete theory for this transient behavior is clearly beyond the scope of the simple model considered here, and calls for a careful experimental analysis to guide it. Therefore, we prefer not to insist on these tentative comments at this stage.)

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Estimation of Minimal Heat Consumption for Heat-Driven Separation Processes via Methods of Finite-Time Thermodynamics

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An analytical expression is obtained for a minimal average heat consumption of a separation process driven by heat from constant-temperature reservoirs. The classical equilibrium expression for heat consumption is obtained in the limit of an average feed flow of zero. A numerical method is proposed for computing the minimal heat consumption for reservoirs with variable temperatures. The analysis is based on energy, entropy, and material balances and on analogy with finite-time thermodynamics analysis of a heat engine with a nonuniform working fluid.

Introduction

Among all the categories of physical and chemical procedures, separation processes are probably the most wasteful of energy, when they are evaluated by free energy change from feed to products, per unit of energy used to drive the process, i.e., by the natural generalization of efficiency. The purpose of this paper is to lay the groundwork for analyzing the performance of separation processes and then to optimize that performance, especially when the process must operate at a nonzero rate.

Many heat-driven separation processes can be analyzed as heat engines, working between two reservoirs at different temperatures T_H and T_L and producing enthalpy and energy flows out of the system (instead of power output of conventional heat engines). In finite-time thermodynamics it is well-known that the average power output of a heat engine is bounded.[1,2] The analogue of this result for a separation process is the existence of an upper limit on the average enthalpy flow through the system when the average entropy flow through the system is fixed or a lower limit on the average entropy flow if the average enthalpy flow is fixed. With some additional assumptions on inputs and outputs this is equivalent to the existence of an upper limit for the average feed

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