

# Modelling of membrane potential and ionic flux in weak amphoteric polymer membranes

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Model calculations concerning the membrane potential and ionic fluxes in weak amphoteric polymer membranes have been presented and the results were compared with recent experimental data obtained with a membrane which contains succinyl chitosan as ampholyte and poly(vinyl alcohol) as supporting matrix. The ion transport through the membrane has been described with the aid of the Nernst–Planck equations, and the results obtained explain satisfactorily the observed experimental trends in broad ranges of pH and electrolyte concentration. Also, the model predictions concerning the membrane isoelectric point may be useful for the analysis of future experiments. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Amphoteric crosslinked polymer networks contain both positively and negatively fixed charge groups chemically bound to the polymer chains. Most physicochemical applications of these polymer networks concern their swelling behaviour when immersed in an electrolyte bath, especially in the case of polymer hydrogels<sup>1,2</sup>. It is also possible to prepare amphoteric membranes which show ion exchange properties<sup>3–12</sup>. Recently, the membrane potential and piezodialysis properties of a weak amphoteric polymer membrane which contains succinyl chitosan (see *Figure 1*) as ampholyte and poly(vinyl alcohol) as supporting matrix were experimentally studied<sup>13,14</sup>. The membrane properties are very sensitive to the external pH.

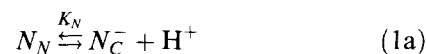
In this study, we present a theoretical model based on the Nernst–Planck equations for the ion transport through weak amphoteric membranes. The membrane characteristics studied are the ionic fluxes and the membrane potential. Comparison of the theory with experiments shows that the model is able to explain the experimental trends in broad ranges of pH and electrolyte concentration. Moreover, the model predictions concerning the membrane isoelectric point could be useful for the analysis of future experiments.

## THEORETICAL MODEL

The system considered is shown schematically in *Figure 2*. The amphoteric membrane separates two solutions of the same univalent electrolyte. The whole system is isothermal and free of convective movement. The solutions are assumed to be perfectly stirred, and  $c_i(x)$  stands for the concentration of the  $i$ th species ( $i = 1$  for salt cations,  $i = 2$  for salt anions,  $i = 3$  for hydrogen ions, and  $i = 4$  for hydroxide ions) in the membrane, which is placed between  $x = 0$  and  $x = d$ .

### Dissociation equilibria

We denote the total concentrations of acidic and basic groups in the membrane by  $N_T$  and  $P_T$ , respectively, and assume the following equilibria between neutral groups  $N_N$  or  $P_N$  and charged groups  $N_C$  or  $P_C$ :



where  $K_N$  and  $K_P$  are the respective equilibrium constants, and  $N_T = N_N + N_C$  and  $P_T = P_N + P_C$ . The concentrations of  $H^+$  and  $OH^-$  ions are assumed to verify the equilibrium condition:

$$c_3 c_4 = K_W \quad (2)$$

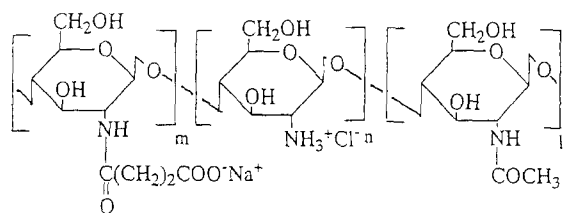
with  $K_W = 10^{-14} \text{ M}^2$  through the whole system.

From the equilibrium conditions for the acidic and

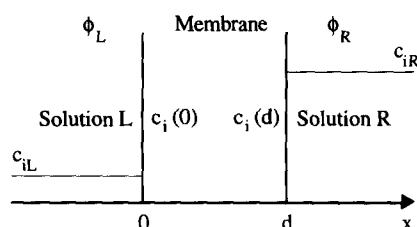
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**Figure 1** Schematic representation of *N*-succinyl chitosan. The degree of deacetylation is 0.98, and the degree of substitution from amino to carboxy groups is given by the ratio  $m/(m+n)$



**Figure 2** Schematic view of the membrane system

basic groups, we obtain

$$N_C = \frac{1}{1 + c_3/K_N} N_T \quad (3a)$$

$$P_C = \frac{c_3/K_P}{1 + c_3/K_P} P_T \quad (3b)$$

*Donnan equilibria*

From the electroneutrality condition:

$$c_1 + c_3 + P_C = c_2 + c_4 + N_C \quad (4)$$

in the membrane, and assuming that all the ions are in thermodynamic equilibrium at the membrane/solution interfaces located at  $x = 0$  and  $x = d$ , the Donnan relationships (ideal behaviour)<sup>15</sup>:

$$c_i(0) = \frac{c_{iL}}{c_{1L} + c_{3L}} \{ (-1)^{i-1} (P_C - N_C) / 2 + [(P_C - N_C)^2 / 4 + (c_{1L} + c_{3L})^2]^{1/2} \}, \quad i = 1, \dots, 4 \quad (5)$$

are valid at  $x = 0$ . A similar equation can also be written for the interface at  $x = d$ .

Note that to calculate  $c_i(0)$  in equation (5), we need to obtain  $P_C$  and  $N_C$  in equations (3), which in turn depend on  $c_3(0)$ . This leads to a fourth-order polynomial equation for each interface at  $x = 0$  and  $x = d$ , which can be solved numerically using a standard procedure. Once the inner membrane interface concentrations  $c_i(0)$  and  $c_i(d)$  have been determined, the Donnan potential differences at the left ( $x = 0$ ) and right ( $x = d$ ) interfaces,  $\Delta\phi_L$  and  $\Delta\phi_R$ , can be readily computed as

$$\Delta\phi_L = \frac{RT}{F} \log \frac{c_1(0)}{c_{1L}} \quad (6a)$$

$$\Delta\phi_R = \frac{RT}{F} \log \frac{c_{1R}}{c_1(d)} \quad (6b)$$

respectively, where  $c_{iL}$  and  $c_{iR}$  are the ionic concentrations in the left (L) and right (R) bathing solutions.

*Nernst-Planck flux equations*

The basic equations describing the membrane potential and the ion flux in an amphoteric membrane are the one-dimensional Nernst-Planck equations<sup>16</sup>:

$$J_i = -D_i \left[ \frac{dc_i}{dx} + (-1)^{i+1} c_i \frac{F}{RT} \frac{d\phi}{dx} \right], \quad i = 1, \dots, 4 \quad (7)$$

and the condition of zero total current requires

$$J_1 - J_2 + J_3 - J_4 = 0 \quad (8)$$

In equation (7),  $D_i$  and  $J_i$  stand for the diffusion coefficient in the membrane and the flux of species  $i$ , respectively,  $\phi$  is the electric potential, and the constants  $F$  and  $R$  have their usual meaning<sup>15</sup>.

*Numerical solution*

The total membrane potential and the ionic flux can be calculated as follows. Substituting equation (2) into equation (7) for  $i = 3$  and 4, and taking into account equation (8), the following relationships between the ion fluxes are derived:

$$J_3 = \frac{J_2 - J_1}{1 + K_W D_4 / D_3 c_3^2} \quad (9a)$$

$$J_4 = -\frac{D_4 K_W}{D_3 c_3^2} J_3 \quad (9b)$$

Equations (9) show that the fluxes of  $H^+$  and  $OH^-$  ions are not constant through the membrane in a general case. However, in the particular case of very low pH of the bathing solutions, equations (3) and (9) give approximately

$$N_C \approx 0 \quad (10a)$$

$$P_C \approx P_T \quad (10b)$$

$$J_3 \approx J_2 - J_1 \quad (11a)$$

$$J_4 \approx 0 \quad (11b)$$

Integrating equation (7) for  $\phi$  through the membrane and summing up the two Donnan potentials of equations (6), the membrane potential  $\Delta\phi_M = \phi_L - \phi_R$  is obtained as

$$\Delta\phi_M = -\frac{RT}{F} \log \frac{\frac{D_1 J_3}{D_3 J_1} - \frac{c_{3L}}{c_{1L}}}{\frac{D_1 J_3}{D_3 J_1} - \frac{c_{3R}}{c_{1R}}} \quad (12)$$

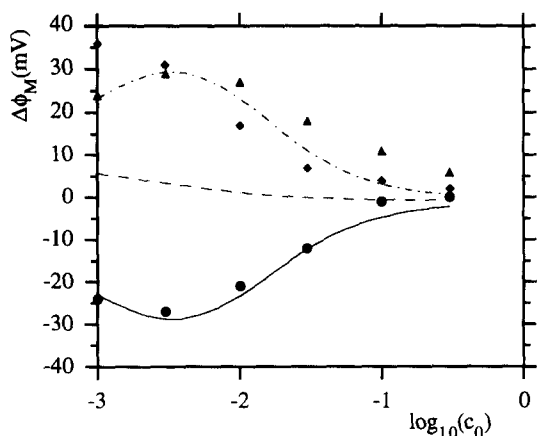
where the quotient  $J_3/J_1$  is the solution of the transcendental equation:

$$\Gamma \log \frac{c_2(d) - P_T \frac{1-\Gamma}{2}}{c_2(0) - P_T \frac{1-\Gamma}{2}} = \log \frac{\frac{D_1 J_3}{D_3 J_1} - \frac{c_{3L}}{c_{1L}}}{\frac{D_1 J_3}{D_3 J_1} - \frac{c_{3R}}{c_{1R}}} \frac{c_1(0)}{c_1(d)} \quad (13)$$

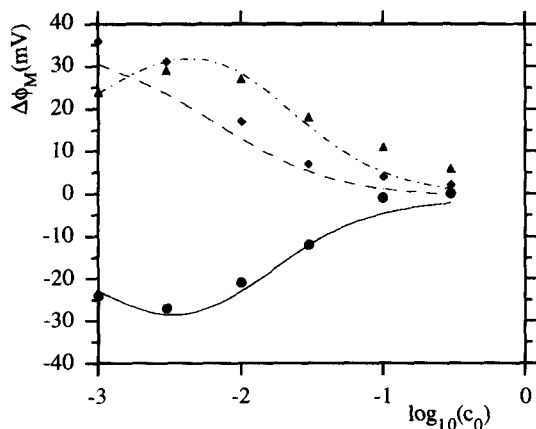
where

$$\Gamma \equiv \frac{\frac{D_2}{D_1} - 1 + \frac{J_3}{J_1} \left( \frac{D_2}{D_3} - 1 \right)}{\frac{D_2}{D_1} + 1 + \frac{J_3}{J_1} \left( \frac{D_2}{D_3} + 1 \right)} \quad (14)$$

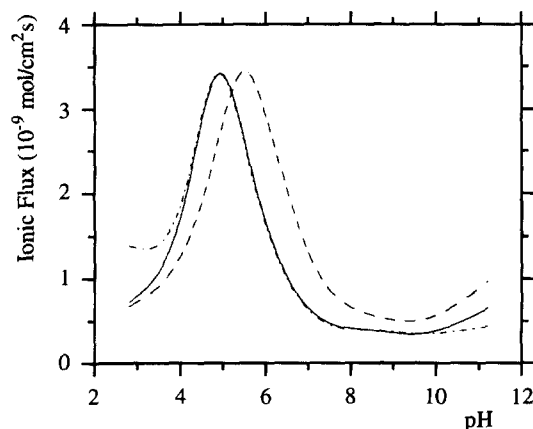
Analogously, similar equations can be derived for the case of high pH values of the bathing solutions.



**Figure 3** Membrane potential  $\Delta\phi_M$  versus salt concentration  $c_0$  for the A-50 membrane with  $H = 0.79$  (ref. 13). The KCl concentration of the left-hand solution in Figure 2 ( $c_0$ ) was initially five times lower than that of the right-hand solution ( $5c_0$ ). The symbols correspond to the experimental results of ref. 13, and the lines correspond to the theoretical calculations with  $N_T = P_T = 4 \times 10^{-2}$  M for pH 2.8 (continuous lines), pH 5.6 (dashed line) and pH 11.2 (dotted-dashed line)



**Figure 4** Membrane potential versus salt concentration  $c_0$  for the same system of Figure 3 when  $N_T = 6 \times 10^{-2}$  M and  $P_T = 4 \times 10^{-2}$  M in the theoretical calculations



**Figure 5** Calculated ion flux  $J_1$  versus pH for  $N_T = P_T = 4 \times 10^{-2}$  M (dashed line) and  $N_T = 6 \times 10^{-2}$  M and  $P_T = 4 \times 10^{-2}$  M (continuous line) in the case of  $c_0 = 10^{-3}$  M. The calculated ion flux  $J_2$  (dotted-dashed line) is also shown

In the case of intermediate pH values, however, the above equations are not valid, and a numerical procedure must be used to integrate equation (7). We have used an iterative method which assumes some

initial values for the ion fluxes and integrates numerically equation (7) with the boundary conditions at the interface  $x = 0$ . We then check if the solutions satisfy the boundary conditions at  $x = d$  or not. If not, the initial estimation is changed until the boundary conditions at  $x = d$  are satisfied.

## RESULTS AND DISCUSSION

In order to apply the above theoretical model to an experimental situation we have considered the previous results by Tanioka and co-workers<sup>13,14</sup> where the membrane potential and the solute (salt) permeability of a weak amphoteric polymer membrane of succinyl chitosan supported by poly(vinyl alcohol) (see Figure 1) were examined. Since the water content of the membranes was very high, we estimate the ion diffusion coefficients in the membrane as<sup>17,18</sup>  $D_i = H^2 / (2 - H)^2 D_{i,\text{solution}}$ , where  $D_{i,\text{solution}}$  is the diffusion coefficient in a free aqueous solution and  $H$  is the degree of hydration. For this membrane, the  $pK_a$  values are<sup>19</sup>  $pK_N = 4.65$  and  $pK_P = 6.3$ , so that the unknown parameters are only  $P_T$  and  $N_T$  in our case. In principle, the ratio  $N_T/P_T$  could be approximately estimated from the degree of substitution of carboxylic groups from amino groups<sup>13</sup>, though the experimental uncertainties in determining the cationic/anionic capacity ratio of amphoteric membranes are usually relatively high<sup>4,5</sup>.

The results of the membrane potential obtained by the above procedure are shown in Figures 3 and 4. The points are the experimental results for the A-50 membrane<sup>13</sup>, which has  $H = 0.79$ , and the lines represent the results of theoretical calculations. In the experiments, the KCl concentration of the left-hand solution in Figure 2 ( $c_0$ ) was initially five times lower than that of the right-hand solution ( $5c_0$ ). The pH of the solutions was then adjusted to the desired value by adding KOH or HCl.

The A-50 membrane had a degree of substitution from amino to carboxylic groups of 50%. However, we see from Figures 3 and 4 that we have to assume that  $N_T \neq P_T$  in order to reproduce the experimental results. Indeed, Figure 3 corresponds to effective<sup>20</sup> charge densities  $N_T = P_T = 4 \times 10^{-2}$  M and Figure 4 to  $N_T = 6 \times 10^{-2}$  M and  $P_T = 4 \times 10^{-2}$  M. These latter values give the best fitting between theory and experiment. Since the experimental uncertainties in the cationic/anionic capacity ratio of amphoteric membranes can be relatively high<sup>4,5</sup>, we conclude that a slight deviation from the equality  $N_T = P_T$  occurred in our case, and produced significant effects on the membrane potential (compare Figure 3 with Figure 4).

Figure 5 shows the calculated pH dependence of the ion flux  $J_1$ . Again, we take the salt concentration of the right-hand solution to be five times higher than that of the left-hand solution. We see that there is a maximum in the salt flux at a certain pH, which is in agreement with previous experimental results which showed that the solute permeability coefficient should reach a maximum (and then the reflection coefficient<sup>13</sup> should reach a minimum) near the isoelectric point<sup>3,14,21,22</sup>. It is also shown in this figure that the position of this maximum changes with the  $N_T/P_T$  ratio.

Figure 5 gives also the calculated ion flux  $J_2$  over a broad pH range. It is shown that the hydrogen flux  $J_3$  cannot be neglected for  $pH < 4$  (note that  $J_1 < J_2$  for pH

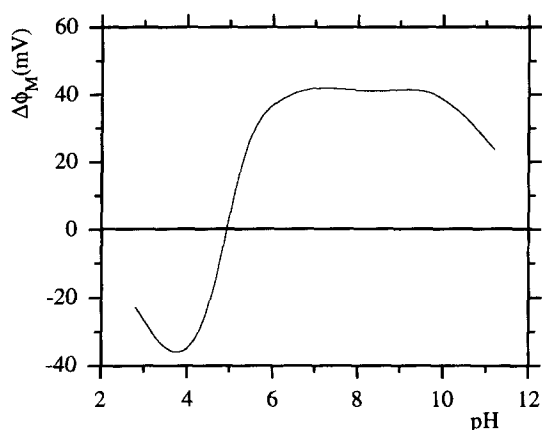


Figure 6 Calculated membrane potential versus pH for  $N_T = 6 \times 10^{-2}$  M and  $P_T = 4 \times 10^{-2}$  M in the case of  $c_0 = 10^{-3}$  M

<4 from Figure 5, and thus  $J_1 + J_3 = J_2$  to ensure the experimental condition of zero electric current). Analogously, the hydroxide flux  $J_4$  should be taken into account when  $\text{pH} > 10$ . Therefore, Figure 5 could be useful to establish the range of pH values where the salt ions are the dominant ions.

Finally, Figure 6 shows the predicted pH dependence of the membrane potential under the same conditions as in Figure 5. The S-shaped behaviour of the membrane potential over a broad range of pH value is characteristic of the weak amphoteric membrane, and is a natural consequence of the behaviour of the ion flux depicted in Figure 5. Indeed, we see that  $\Delta\phi_M = 0$  at the same pH value which makes the ion flux maximum. Also, the absolute value of  $\Delta\phi_M$  in Figure 6 decreases at lower pH ( $\text{pH} < 4$ ) and at higher pH ( $\text{pH} > 10$ ), which are just the pH values at which the flux of the hydrogen or hydroxide ions is not negligible, as shown in Figure 5. The decrease in the absolute value of  $\Delta\phi_M$  at  $\text{pH} < 4$  and  $> 10$  is due to a decrease in the Donnan potential. The latter is caused by an increase in the total ion concentration in the left-hand or right-hand bulk solution, which occurs at very low or very high pH.

In summary, we have presented a set of model calculations concerning the membrane potential and the ion fluxes in amphoteric membranes and compared the theoretical results with recent experimental data. Though we had to introduce some crude approximations concerning the diffusion coefficient, effective charge density, etc., to keep the model reasonably simple, the calculations are rather general since they are based on the original Nernst-Planck equations without any additional simplifying assumption (e.g. the Goldman constant field assumption<sup>15,23</sup>). Also, we have considered in the model equations the important fact that the pH within the membrane may be very different from the

external pH because of the membrane fixed charge<sup>1</sup>. Finally, we emphasize that the model predictions concerning the membrane isoelectric point could be useful for the analysis of future experiments.

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