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Ionic behaviour and membrane potential in weakly amphoteric polymer membranes

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The membrane potential of a weakly amphoteric polymer membrane was measured by varying the dissociation state of the dissociative groups within the membrane through control of the pH of the outer aqueous solution, and the effective charge density of the membrane was evaluated. On the basis of a modification of the Teorell–Meyer–Sievers equation, we concluded that the difference between the charge densities of the positively and negatively charged dissociative groups seemed to play an important role in the permeation behaviour through the membrane. From the results of a study of the potentiometric behaviour of aqueous polyamphoteric solutions, it was confirmed that the ratio of the effective charge density to the net value could be estimated to be the same as that found previously. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ionic behaviour; membrane potential; amphoteric membrane)

INTRODUCTION

Amphoteric membranes are characterized by the presence of both positively and negatively charged dissociative groups within the membrane phase. Early investigations were carried out by Sollner[1–3] and Weinstein *et al.*[4] and can be referred to elsewhere[5].

The potentiometric behaviour of succinyl chitosans in aqueous solution has been studied[5], and the possibility of piezodialysis in polyamphoteric membranes has been discussed from the point of view of the apparent isoelectric point[6]. In this paper, the basic properties, especially the charge densities of the polyamphoteric membranes, are examined. Measurements of the membrane potential and pH titrations were performed to determine the charge densities. From these charge densities, the properties of the membrane and the ionic behaviour within the membrane were evaluated. These characteristics will be related to the process of piezodialysis through the membrane in another paper[6].

EXPERIMENTAL

Samples

The succinyl chitosans used in this study to prepare amphoteric membranes were the same as those used in previous work[5,6]. The degrees of substitution (DS) from amino to carboxy groups for A-29, A-50 and A-78 were 29%, 50% and 78% in that order. As a supporting matrix for the prepared membranes, poly(vinyl alcohol) (PVA) was used. Membrane preparation followed the same procedure as given elsewhere[5]. The amount of each chitosan mixed with 5.0 g of PVA was 0.412 g for A-29, 0.486 g for A-50 and 0.517 g for A-78 for each kind of membrane.

Measurements of degree of hydration

The samples were soaked in deionized water for more than 24 h, and then they were wiped with filter paper and weighed quickly. The degree of hydration was determined according to

$$H = \frac{\text{water within membrane}}{\text{volume of membrane}} = \frac{(w_{\mathrm{W}} - d_{\mathrm{W}})/1.0}{(d_{\mathrm{W}}/1.3) + (w_{\mathrm{W}} - d_{\mathrm{W}})/1.0} \quad (1)$$

where w_{W} and d_{W} are the weights of swollen and dried membrane in that order, and 1.3 and 1.0 are the densities of PVA and water. The density of chitosan was assumed to be equal to that of PVA in this study.

Measurements of membrane potential

The apparatus used for measurements of membrane potential was the same as that used elsewhere[6]. The salt used was KCl and the measurements were made at three pH levels in order to vary the dissociation states of the dissociative groups. The concentration ratio of the KCl solutions across the two sides of the membrane was always kept at 5, and measurements were carried out for concentrations on the lower KCl concentration side of 10^{-3} M, 3×10^{-3} M, 10^{-2} M, 3×10^{-2} M, 0.1 M and 0.3 M. The pH levels at which the measurements were made were 2.8, 5.6 and 11.2, and these were kept constant on both sides of the membrane at the beginning of each experiment. The solutions on both sides of the membrane were stirred with a magnetic stirrer to minimize the effect of the boundary layer on the potential. A pair of Ag–AgCl electrodes (HS-205C,

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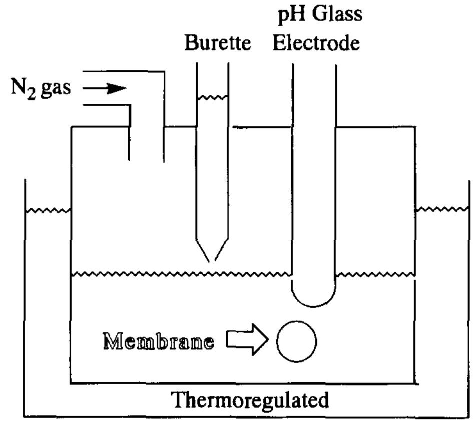

Figure 1 Apparatus used for pH titration of a membrane

TOA Electric) with a KCl salt bridge and a pH meter (HM-20E, TOA Electric) were used to measure the potential differences. For pH measurements, a complex electrode (GST-5211C, TOA Electric) and a pH meter (HM-20E, TOA Electric) were used.

The pH titration of membranes

The apparatus used for pH titration is shown in *Figure 1*. All the following procedures were carried out under N_2 according to the method given elsewhere[7]. Firstly, the membranes were soaked in HCl solution (approximately 3 N) for more than 24 h to allow all the dissociative groups to be converted to NH_3^+ and CO_2H. Secondly, the membranes were washed with deionized water to remove excess HCl. Repeated washings were carried out until the pH of the cleansing water became higher than 4. Finally, the membranes were immersed in 1 M KCl solution, and a precise amount of KOH solution (0.1 M or 10^{-2} M) was used to carry out the pH titration. At the end of a titration experiment, all the dissociative groups were assumed to be fully dissociated, and calculations of the total amounts of fixed dissociative groups were carried out for both amino and carboxy groups.

RESULTS AND DISCUSSION

The dependence of membrane potential on the pH of the outer solution is shown in *Figure 2*. Although the pH of the aqueous phase within the membrane is not equal to the pH of the outer solution because of the Donnan effect, the dissociation state of the dissociative groups can be considered as follows. The net charge should be positive if the pH of the outer solution is low and becomes zero at the isoelectric point (IEP)[6]; conversely, the net charge should be negative if the pH is high. *Figure 2* makes it clear that the dissociation state of the dissociative groups within the membrane is subject to change along with the pH of the outer solution. As the pH of the outer solution is lowered or increased, corresponding to a pH of 2.8 or 11.2, the results obtained clearly show that the system cannot be analysed within the framework of the Teorell–Meyer–Sievers (TMS) theory, which applies to a uniformly charged membrane[8–10]. In our system, an excess of H^+ or OH^- raises the ionic strength, so that a modified TMS theory, in which the flux of H^+ or OH^- is considered, should be used.

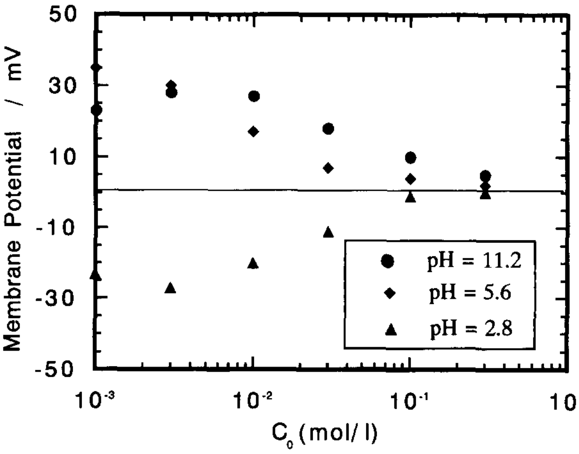

Figure 2 Dependence of the membrane potential on the pH of the outer solution (A-50, $H = 0.79$). C_0 (M) is the KCl concentration of the solution on one side of the membrane, while $5C_0$ is the KCl concentration on the other side of the membrane

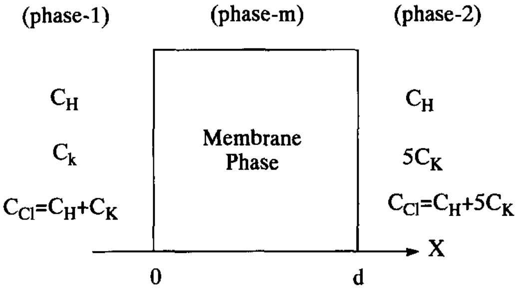

Figure 3 Schematic representation of the membrane–solution system. This scheme shows the case where the pH of the outer solution is less than 7. C_i is the concentration of the ith ion (i = H, K, Cl)

Taking this discussion into account, we can derive an expression for the membrane potential that includes the flux of HCl or KOH involved in varying the dissociation state of the fixed dissociative groups. The membrane–solution system considered in this section is shown in *Figure 3*, where phases 1 and 2 indicate the aqueous outer solution and phase m is the membrane phase of thickness d.

Firstly, we can express the Donnan potential difference[11,12] at the interface for $X = 0$ in *Figure 3*

$$\Delta\phi_{\mathrm{Don}(1\rightarrow \mathrm{m})} = -\frac{RT}{F}\ln\frac{a_{\mathrm{K}}}{(a_{\mathrm{K}})_0} \qquad (2)$$

where the subscript 0 denotes the membrane phase just inside the interface at $X = 0$. The Donnan equilibrium is assumed to operate over the interfaces of the membrane phase and the outer solution at both $X = 0$ and d, and the relationships between the electrolyte concentrations based on the Donnan equilibrium can then be expressed as follows, where the activity coefficients are assumed to be unity

$$(C_{\mathrm{K}})_0(C_{\mathrm{Cl}})_0 = C_{\mathrm{K}}C_{\mathrm{Cl}} \qquad (3)$$

$$(C_{\mathrm{H}})_0(C_{\mathrm{Cl}})_0 = C_{\mathrm{H}}C_{\mathrm{Cl}} \qquad (4)$$

In addition, the electroneutrality condition within the membrane phase has to be used

$$P + (C_{\mathrm{H}})_{\mathrm{m}} + (C_{\mathrm{K}})_{\mathrm{m}} = M + (C_{\mathrm{Cl}})_{\mathrm{m}} + (C_{\mathrm{OH}})_{\mathrm{m}} \qquad (5)$$

where P and M characterize the densities of positively and negatively charged dissociative groups within the membrane and the subscript m denotes the membrane phase. For our experiments, the following two cases are considered.

(1) If the pH of the outer solution in phase 1 and phase 2 is less than 7, $C_{\mathrm{H}} \gg C_{\mathrm{OH}}$ is assumed. In this case, equation (5) can be modified to

$$P + (C_{\mathrm{H}})_{\mathrm{m}} + (C_{\mathrm{K}})_{\mathrm{m}} = M + (C_{\mathrm{Cl}})_{\mathrm{m}} \tag{6}$$

Using equations (3) and (6), we can write equation (2) as

$$\Delta\phi_{\mathrm{Don}(1\to\mathrm{m})} = -\frac{RT}{F}\ln\frac{P-M+\sqrt{(P-M)^2+4(C_{\mathrm{K}}+C_{\mathrm{H}})^2}}{2(C_{\mathrm{K}}+C_{\mathrm{H}})} \tag{7}$$

Along the same lines, $\Delta\phi_{\mathrm{Don}(\mathrm{m}\to2)}$ can also be obtained as

$$\Delta\phi_{\mathrm{Don}(\mathrm{m}\to2)} = -\frac{RT}{F}\ln\frac{2(5C_{\mathrm{K}}+C_{\mathrm{H}})}{P-M+\sqrt{(P-M)^2+4(5C_{\mathrm{K}}+C_{\mathrm{H}})^2}} \tag{8}$$

Accordingly, the sum of the Donnan potential differences at both interfaces can be expressed as follows for the case where the pH of the outer solution is low

$$\begin{aligned}\Delta\phi_{\mathrm{Don}} &= \Delta\phi_{\mathrm{Don}(1\to\mathrm{m})} + \Delta\phi_{\mathrm{Don}(\mathrm{m}\to2)}\\ &= -\frac{RT}{F}\ln\frac{P-M+\sqrt{(P-M)^2+4(C_{\mathrm{K}}+C_{\mathrm{H}})^2}}{P-M+\sqrt{(P-M)^2+4(5C_{\mathrm{K}}+C_{\mathrm{H}})^2}}\end{aligned} \tag{9}$$

(2) In the case where the pH of the outer solution is higher than 7, $C_{\mathrm{OH}} \gg C_{\mathrm{H}}$ is assumed and equation (5) is modified to

$$P + (C_{\mathrm{K}})_{\mathrm{m}} = M + (C_{\mathrm{Cl}})_{\mathrm{m}} + (C_{\mathrm{OH}})_{\mathrm{m}} \tag{10}$$

By the same method adopted in the case where the pH of the outer solution is low, the Donnan potential differences of both interfaces can be calculated and their sum is given by

$$\Delta\phi_{\mathrm{Don}} = -\frac{RT}{F}\ln\frac{M-P+\sqrt{(M-P)^2+4(C_{\mathrm{Cl}}+C_{\mathrm{OH}})^2}}{M-P+\sqrt{(M-P)^2+4(5C_{\mathrm{Cl}}+C_{\mathrm{OH}})^2}} \tag{11}$$

Secondly, the diffusion potentials within the membrane phase can be estimated from the Nernst–Planck equation

$$J_i = u_iC_i\frac{\mathrm{d}\phi}{\mathrm{d}x} - u_iC_i\frac{RT}{F}\ln\frac{\mathrm{d}\ln a_i}{\mathrm{d}x} \tag{12}$$

$$J_j = u_jC_j\frac{\mathrm{d}\phi}{\mathrm{d}x} + u_jC_j\frac{RT}{F}\ln\frac{\mathrm{d}\ln a_j}{\mathrm{d}x} \tag{13}$$

where i is either H or K and j is either OH or Cl, and a_i is the activity of the ith ion. Accordingly, the fluxes of the ions within the membrane phase can be expressed as

$$J_{\mathrm{K}}J_{\mathrm{H}} = J_{\mathrm{Cl}} + J_{\mathrm{OH}} \tag{14}$$

For our experiments, the following two cases should be considered.

(1) If the pH of the outer solution is less than 7, J_{H} should be much larger than J_{OH}, so equation (14) can be modified to

$$J_{\mathrm{K}} + J_{\mathrm{H}} = J_{\mathrm{Cl}} \tag{15}$$

Considering the electroneutrality within the membrane phase as represented by equation (6), we can express the potential drop over a small distance dx as

$$\begin{aligned}\frac{\mathrm{d}\phi}{\mathrm{d}x} &= \frac{1}{(u_{\mathrm{H}}+u_{\mathrm{Cl}})C_{\mathrm{H}}+(u_{\mathrm{K}}+u_{\mathrm{Cl}})C_{\mathrm{K}}+u_{\mathrm{Cl}}(P-M)}\\ &\times\frac{RT}{F}\left[(u_{\mathrm{Cl}}-u_{\mathrm{H}})\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}x}+(u_{\mathrm{Cl}}-u_{\mathrm{K}})\frac{\mathrm{d}C_{\mathrm{K}}}{\mathrm{d}x}\right]\end{aligned} \tag{16}$$

(2) If the pH of the outer solution is greater than 7, J_{OH} should be much larger than J_{H}, so equation (14) can be modified to

$$J_{\mathrm{K}} = J_{\mathrm{Cl}} + J_{\mathrm{OH}} \tag{17}$$

Considering the electroneutrality within the membrane phase as represented by equation (10), we can express the potential drop as

$$\begin{aligned}\frac{\mathrm{d}\phi}{\mathrm{d}x} &= -\frac{1}{(u_{\mathrm{K}}-u_{\mathrm{Cl}})C_{\mathrm{K}}+(u_{\mathrm{OH}}+u_{\mathrm{Cl}})C_{\mathrm{OH}}-u_{\mathrm{Cl}}(P-M)}\\ &\times\frac{RT}{F}\left[(u_{\mathrm{K}}-u_{\mathrm{Cl}})\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}x}+(u_{\mathrm{Cl}}-u_{\mathrm{OH}})\frac{\mathrm{d}C_{\mathrm{OH}}}{\mathrm{d}x}\right]\end{aligned} \tag{18}$$

Accordingly, the integration of equation (16) or equation (18) across a membrane from $X = 0$ to d can give the diffusion potential within the membrane. However, more information about the ionic mobility of each ion within the membrane phase is required to carry out this integration.

Although the direct expression of the membrane potential as a function of charge density, ionic mobility and solute concentration in the outer aqueous solution needs further refinement, the derived equations, namely equations (9), (11), (16) and (18), have a common characteristic. All of them are expressed as a function of the density of charged groups, with P as the density of positively charged groups and M as the density of negatively charged groups. These charge densities are introduced into the equations as differences, i.e. $P - M$ and $M - P$. The differences $P - M$ and $M - P$ denote the absolute values of the net density of fixed charges within a polyamphoteric membrane. Therefore, the net charge density might be one of the important parameters characterizing the ionic behaviour within the membrane. Although the charge density, effective or net, can be obtained experimentally for a membrane that is a strong polyelectrolyte, such as one made from poly(styrenesulfonic acid)[13], it is not easy to estimate the charge density for a weakly polyamphoteric membrane. In order to estimate the net charge density within the membrane, we adopted a pH titration method developed in a previous study[13]. However, it was difficult to determine the end point of the titration curve in this case. In addition, membrane potentials were reported earlier in this paper not to obey the TMS theory if the pH of the outer solution is as low as 2.8 or as high as 11.2. Therefore, the effective charge density is also not available in the case where the pH of the outer solution is much lower or higher. However, if the pH of the outer solution is intermediate, such as 5.6, the TMS theory

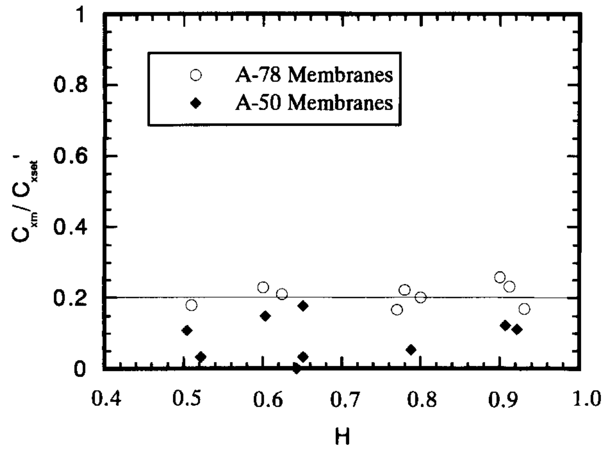

Figure 4 Plots of C_{xm}/C_{xset}' vs. degree of hydration (H)

seems applicable to the experimental results for membrane potentials. Only in this case are the membrane potential data assumed to obey the theory, and the effective charge density is obtained. Attention should be paid to the fact that the effective charge density obtained by the method above, called C_{xm} hereafter, would be the net value. This value can be compared with another net charge density, called C_{xset} hereafter, which is calculated from the volume of water in the membrane phase and the amount of charged groups in the chitosan sample after it is mixed with the PVA matrix in preparing the membrane. C_{xset} is expressed as

$$C_{xset} = P_{set} - M_{set} \qquad (19)$$

where P_{set} is the density of positively charged dissociative groups and M_{set} is the density of negatively charged dissociative groups. The ratio of C_{xm} to C_{xset} was found to be less than 5×10^{-2}, which is smaller than such ratios given in previous reports[14–20]. However, in this case it should be emphasized that the dissociative groups are weak electrolytes, and the dissociation constants should be taken into account. As mentioned earlier, the potentiometric titration experiments were found not to offer meaningful information on the ionic states within the membrane phase. Therefore, the dissociation constants of the fixed dissociative groups were also not available. Based on results discussed in an earlier report on the potentiometric behaviour of aqueous polyamphoteric solutions[5], we can deduce that the dissociation constants of NH_3^+ and CO_2H in the membrane cannot be obtained independently. However, the quantitative relationships between pH and the degree of dissociation can be found. If we neglect the Donnan effects occurring at the interfaces between the membrane phase and the outer solution, i.e. we assume that the pH values of the membrane phase and the outer solution are equal, then we can obtain the dissociation state of the fixed dissociative groups. The degrees of dissociation (α) were found to be 0.45 for A-78 and 0.55 for A-50 at pH 5.6. The estimation of α for A-29 was not possible because the entire range of the titration curve was not obtained. Using these results, we estimated the net charge density of dissociative groups, called C_{xset}' hereafter, and compared it with C_{xm}. C_{xset}' was calculated according to

$$C_{xset}' = P_{set} - \alpha(P_{set}M_{set}) \qquad (20)$$

The ratio of C_{xm} to C_{xset}' is shown in *Figure 4* as a function of the degree of hydration for A-50 and A-78. This ratio remains at 0.2 for A-78 at various degrees of hydration, and is much less than 0.2 for A-50. The value of 0.2 for A-78 is in accordance with the values given in other reports for the same ratio but for uniformly charged membranes[13,20]. The results obtained indicate that the ratio of the effective charge density to the existing charge might generally be 0.2 for charged membranes.

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