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Polyamphoteric membrane study: 2. Piezodialysis in weakly amphoteric polymer membranes

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Piezodialysis in weakly amphoteric polymer membranes is discussed from the viewpoint of non-equilibrium thermodynamics. Succinyl chitosans were used as the weak polyampholytes. With varying pH in the outer solution, the apparent isoelectric point of the membrane was defined as the point of zero membrane potential, where solute permeation is much enhanced. Piezodialysis was confirmed from the phenomenological hydraulic permeability coefficients, reflection coefficients and solute permeability coefficients of the membrane, which were based on non-equilibrium thermodynamics. Permeation experiments with mixed ion systems were also performed. The permeation behaviour was in accordance with that expected for the interactions of ions with polyampholytes in aqueous solutions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: piezodialysis; amphoteric membrane; polyampholyte)

INTRODUCTION

It was first suggested by Sollner[1–3] that an ion exchange membrane with both negatively and positively charged groups should show distinctive ion transport phenomena. The existence of circulating currents within an amphoteric membrane was predicted theoretically, as the basis of non-equilibrium thermodynamics, by Kedem and Katchalsky[4] and investigated experimentally by Weinstein *et al.*[5]. The piezodialysis phenomenon was confirmed for a charged mosaic membrane where a cationic exchange layer and an anionic layer were arranged alternately and parallel to each other with a neutral layer between them. An amphoteric membrane composed of strong polyelectrolytes, where both negatively and positively charged groups were distributed randomly in the membrane, was also investigated for piezodialysis by Yamauchi and coworkers[6–9]. It is very important to know the behaviour of ions within an amphoteric ion exchange membrane when it is used for the concentration of saline water or the separation of salt from organic solutes in mixed aqueous solution. However, piezodialysis by a weakly amphoteric polymer membrane has not been studied until now. If it is possible to change the dissociation state of the dissociative groups by varying the pH, the utility of charged amphoteric membranes will be expanded not only to salt separation but also to sensors and drug delivery systems controlled by changes in pH. An advanced knowledge of these membranes will contribute much towards the progress of biology, physiology and polymer science.

The weakly amphoteric polymer membranes were prepared from mixed solutions of poly(vinyl alcohol) (PVA) and succinyl chitosans composed of carboxy and amino groups as the dissociative groups. In the first paper[10] of this series, the investigation of dilute aqueous solutions of succinyl chitosans was carried out in order to determine the interactions occurring between the charged groups on the polyampholyte chain and the counter ions. In this paper, the possibility of piezodialysis and the ionic behaviour within the membrane will be discussed from the viewpoint of non-equilibrium thermodynamics.

EXPERIMENTAL

Samples

Succinyl chitosans, whose potentiometric behaviour in dilute aqueous solution was investigated in the first paper[10] of this series, were used to prepare the polyamphoteric membranes. The degrees of substitution (*DS*) from the amino to carboxy groups for A-29 and A-78 were 29% and 78%, respectively. As the supporting matrix of each membrane, we used poly(vinyl alcohol) (PVA, degree of polymerization of 2000) purchased from Wako Chemical Co. Ltd. PVA was saponified before preparation of the membranes.

Membrane preparation was performed according to the following procedure. For A-78 membranes, 5.00 g of PVA, 0.517 g of the succinyl chitosan and 8×10^{-3} mol of KCl were dissolved in 80 ml of 3 vol% acetic acid. The solution was then heated to above 90°C and mixed well. (Because it was difficult to dissolve the A-29 sample in water, an aqueous solution of acetic acid and KCl was employed in place of pure water when the A-29

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membrane was made.) Then the solution was cast onto a flat poly(methyl methacrylate) plate to dry at 25°C for more than 7 days. To increase the physical strength of the membranes, we annealed some of them at a temperature between 90°C and 100°C. Finally, the prepared membranes were soaked in deionized water for more than 24 h to permit swelling. In the case of the A-29 membranes, they were repeatedly washed with water to remove any excess acetic acid left within the membrane phase. Deionized water and reagent grade chemicals were used in all the experiments.

Measurements of membrane potential

The apparatus used for measurements of membrane potential is shown in *Figure 1*. The salt used as solute was KCl. The concentration of the external solution on the lower concentration side was 10^{-2} M, while that on the higher concentration side was 0.1 M. The pH values on both sides of the membrane were kept equal at all times for each measurement. Series of measurements were carried out while varying the pH equally on both sides of the membrane.

Piezodialysis measurements

The experimental set-ups used in the piezodialysis measurements are shown in *Figures 2a–c*. On the basis of non-equilibrium thermodynamics, the phenomenological coefficients were determined after measurements of volume flux (J_V) and solute flux (J_S). A practical method of determining the coefficients can be found elsewhere[9]. It should be noted that no hydrodynamic pressure was imposed in this study and the osmotic pressure was controlled by adding saccharose. The volume flux of water (J_V) through the membrane was determined using a capillary. To determine the solute flux through the membrane (J_S), we measured the variation in salt concentration in the outer solution by ion chromatography. The ion chromatograph used was a Hitachi L-3720 equipped with a Shodex YD-521 column. Series of experiments were performed while varying the pH of the outer solution.

RESULTS AND DISCUSSION

For a general description of transport through synthetic membranes, one may use the phenomenological relationships of the thermodynamics of irreversible processes[11–16]. Treatment by means of the method of the thermodynamics of irreversible processes yields linear relationships between general fluxes (J_i) and conjugated general forces (X_i) such as

$$J_i = \sum_k L_{ik} X_k \qquad (1)$$

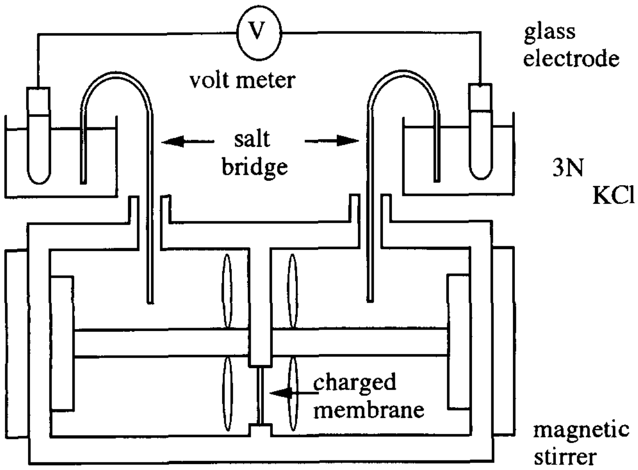

Figure 1 Apparatus used for measurements of membrane potential

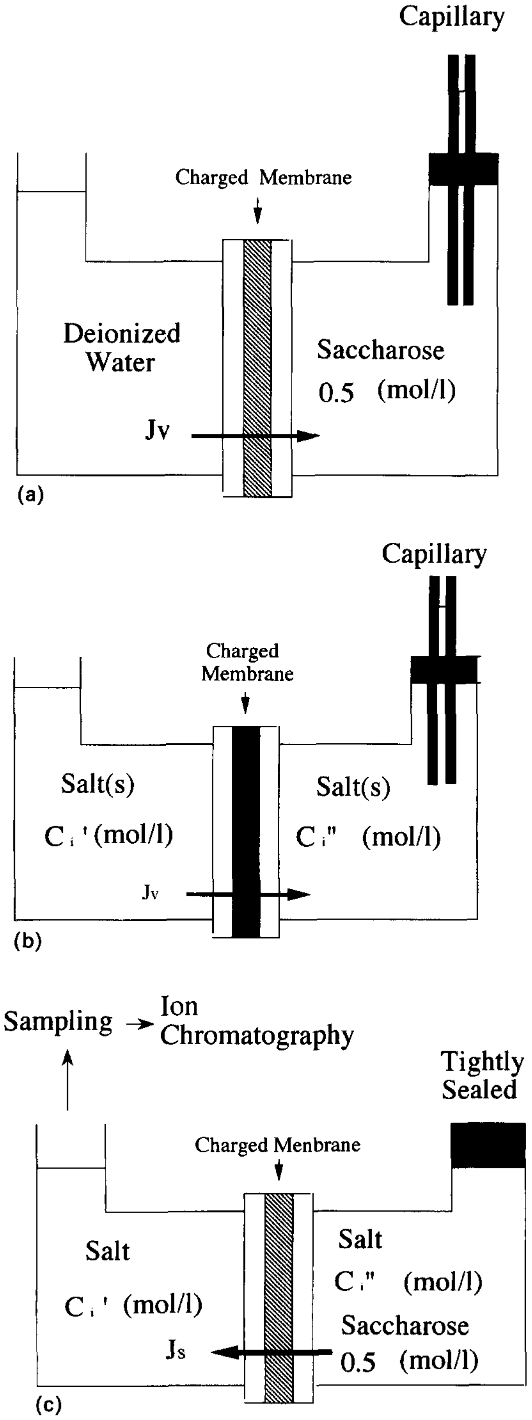

Figure 2 (a) Experimental set-up used to determine the hydraulic permeability coefficients. (b) Experimental set-up used to determine the reflection coefficients. C_i' is 3×10^{-3} M and C_i'' is 10^{-2} M. (c) Experimental set-up used to determine the solute permeability coefficients. C_i' is 3×10^{-3} M and C_i'' is 10^{-2} M

Experimentally accessible fluxes are the volume flux (J_V) and the chemical fluxes of the different neutral species and salts (J_D), in addition to the electric current (I). From an experimental point of view, the electric current (I) is more easily kept constant than the potential difference (ΔE) across the membrane. Therefore, it is more convenient to use I instead of ΔE as the independent variable. Thus, the following equivalent relationships are yielded[13]

$$\begin{aligned} -\Delta E &= -r_e I + l_{ep}\Delta P + l_{e\pi}\Delta\Pi \\ J_V &= l_{pe} I + L_p\Delta P + l_{p\pi}\Delta\Pi \\ J_D &= l_{\pi e} I + l_{\pi p}\Delta P + l_{\pi}\Delta\Pi \end{aligned} \tag{2}$$

The transport coefficients are usually measured under the additional condition that $I = 0$. The following two relationships are then obtained

$$\begin{aligned} J_V &= l_p(\Delta P - \sigma\Delta\Pi) \\ J_D &= -\sigma l_p\Delta P + l_\pi\Delta\Pi \end{aligned} \tag{3}$$

where $l_p(= L_p - (L_{EP}^2/L_E))$ is the hydrodynamic permeability of the membrane at $I = 0$, $l_\pi(= L_\Pi - (L_{E\Pi}^2/L_E))$ is the osmotic permeability of the membrane at $I = 0$ and $l_{\pi p}(= L_{\Pi P} - (L_{EP}L_{E\Pi}/L_E))$ is the coupling coefficient at $I = 0$. If an impermeable solute such as saccharose is mixed in solution with permeable solutes such as ions, the practical phenomenological relationships which correlate the solute flux (J_S) with the volume flux (J_V), the osmotic pressure difference ($\Delta\Pi$) and the solute permeability coefficient (ω) are written as

$$\begin{aligned} J_V &= l_p(\Delta P - \Delta\Pi_i) - \sigma l_p\Delta\Pi_s \\ J_s &= \tilde{c}_s(1 - \sigma)J_V + \omega\Delta\Pi_s \end{aligned} \tag{4}$$

where $\Delta\Pi_i$ and $\Delta\Pi_s$ are the osmotic pressure differences across the membrane caused by concentration differences in the impermeable solutes and permeable solutes, respectively, and $\tilde{c}_s$ is the mean concentration of solute. In these equations, if one of the driving forces is not assumed, the hydrodynamic permeability coefficient (l_p), the reflection coefficient (σ)[17] and the solute permeability coefficient (ω) are given by

$$l_p = \left(\frac{J_V}{\Delta P - \Delta\Pi_i}\right)_{\Delta\Pi_s, I} \tag{5}$$

$$\sigma = -\frac{1}{l_p}\left(\frac{J_V}{\Delta P_s}\right)_{\Delta P - \Delta\Pi_i, I} \tag{6}$$

$$\omega = \left(\frac{J_s}{\Delta\Pi_s}\right)_{J_V, I} \tag{7}$$

The apparatus used to determine l_p is shown in *Figure 2a*. In accordance with equation (5), the hydraulic permeability coefficient of the membrane was measured using a capillary in the system containing no electrolytic solute. The pH of the outer solution was also varied in order to alter the dissociation state of the dissociative groups in the membrane. The value of l_p gives a measure of the ability of the solvent to permeate through the membrane. The reported l_p values in *Figures 5* and *6* this paper are of the order of those reported previously[9,18]. The plots of l_p against pH in the outer solution for A-78 and A-29 membranes are shown in *Figures 5a* and *6a*. As shown in another report of ours[10], the pH in the outer solution should alter the dissociation state of the fixed dissociative groups within the membrane. Therefore, the dependence of l_p on the pH in the outer solution originates from the structural changes in the membrane caused by the dissociation of the fixed dissociative groups. In *Figures 3* and *4*, plots of membrane potential against pH in the outer solution are shown for the A-78 and A-29 membranes. It is obvious that a pH exists where the membrane potential becomes zero in both cases. At the point of zero membrane potential, the membrane resistance should be a minimum; therefore, this point is defined as the apparent isoelectric point. In another paper of ours[10], we reported that it was impossible to determine the isoelectric point by potentiometric titration, but by the membrane potential procedure the isoelectric point of an aqueous solution of a polyampholyte was easily found. However, it is possible to discuss the isoelectric point of a polyamphoteric membrane in terms of the above definition. In *Figures 3* and *4*, the isoelectric points of the membrane appear at pH 3.8 for A-78 and pH 4.5 for A-29. These points are qualitatively in accordance with the points where l_p becomes a minimum in both cases, but especially in the case of A-78.

The reflection coefficient (σ) characterizes the velocity of the solute relative to the solvent; that is, the solute should permeate the membrane completely if $\sigma = 1$ and

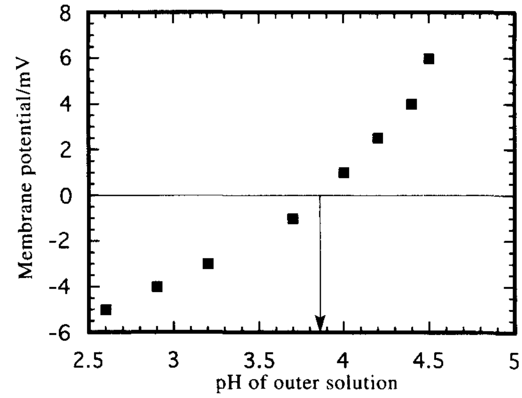

Figure 3 Plot of membrane potential of A-78 against pH in the outer solution

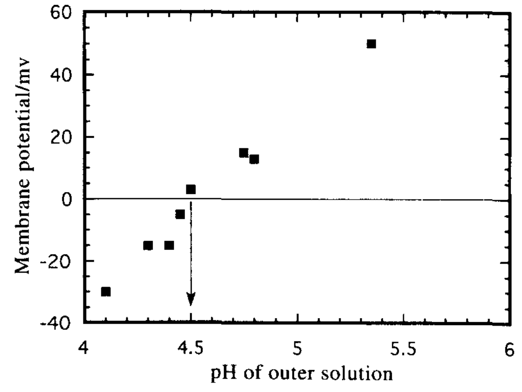

Figure 4 Plot of membrane potential of A-29 against pH in the outer solution

not at all if $\sigma = 0$. The apparatus used to determine σ is shown in *Figure 2b*. In accordance with equation (6), the reflection coefficient of the membrane was measured using a capillary in the system containing no impermeable solute (saccharose). The pH in the outer solution was also varied in order to alter the dissociation state of the fixed dissociative groups in the membrane. Plots of σ against pH in the outer solution for a variety of salts are shown in *Figure 5b* for the A-78 membrane and in *Figure 6b* for the A-29 membrane. At the apparent isoelectric point, the σ of each salt was found to be a minimum. This means that the permeation of the salt should be much enhanced at this point.

The solute permeability coefficient (ω) characterizes the permeability of the solute through the membrane. The apparatus used to determine ω is shown in *Figure 2c*. In accordance with equation (7), the solute permeability coefficients of the membranes were measured with an ion chromatograph while neglecting J_V. The pH in the outer solution was also varied in order to alter the dissociation state of the fixed dissociative groups in the membrane. The larger the ω value is, the more the salt permeates. Plots of ω against pH in the outer solution for a variety of salts are shown in *Figure 5c* for the A-78 membrane and in *Figure 6c* for the A-29 membrane. At the apparent isoelectric point, the ω value of each salt was found to be a maximum, meaning that the solute was more permeable at the apparent isoelectric point.

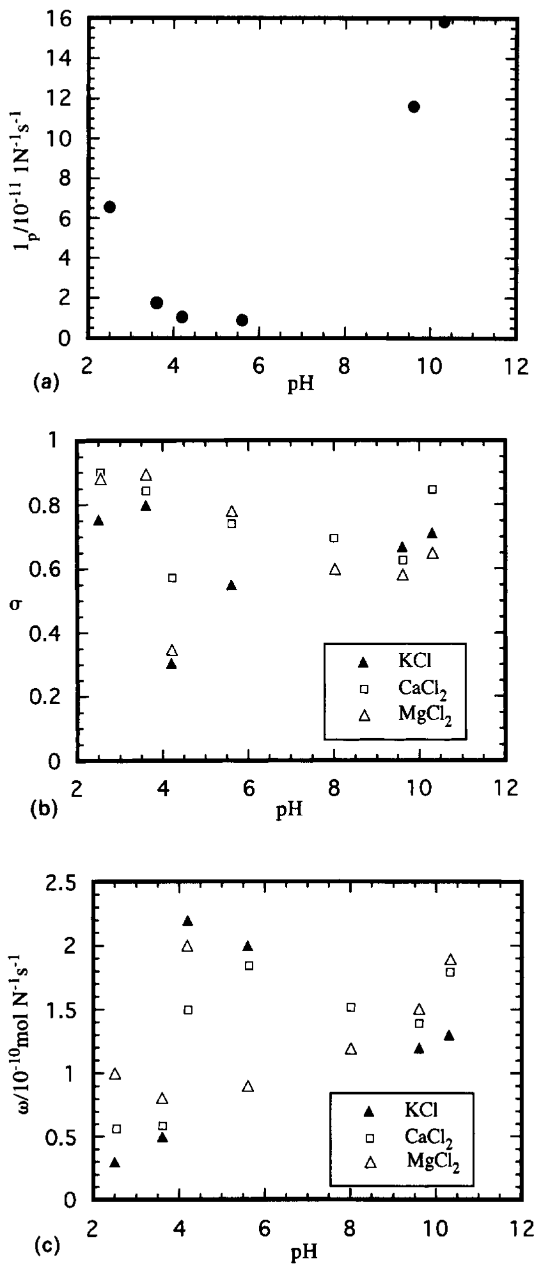

Figure 5 (a) Dependence of the hydraulic permeability coefficient of the A-78 membrane on the pH in the outer solution. (b) Dependence of the reflection coefficient of the A-78 membrane on the pH in the outer solution. (c) Dependence of the solute permeability coefficient of the A-78 membrane on the pH in the outer solution

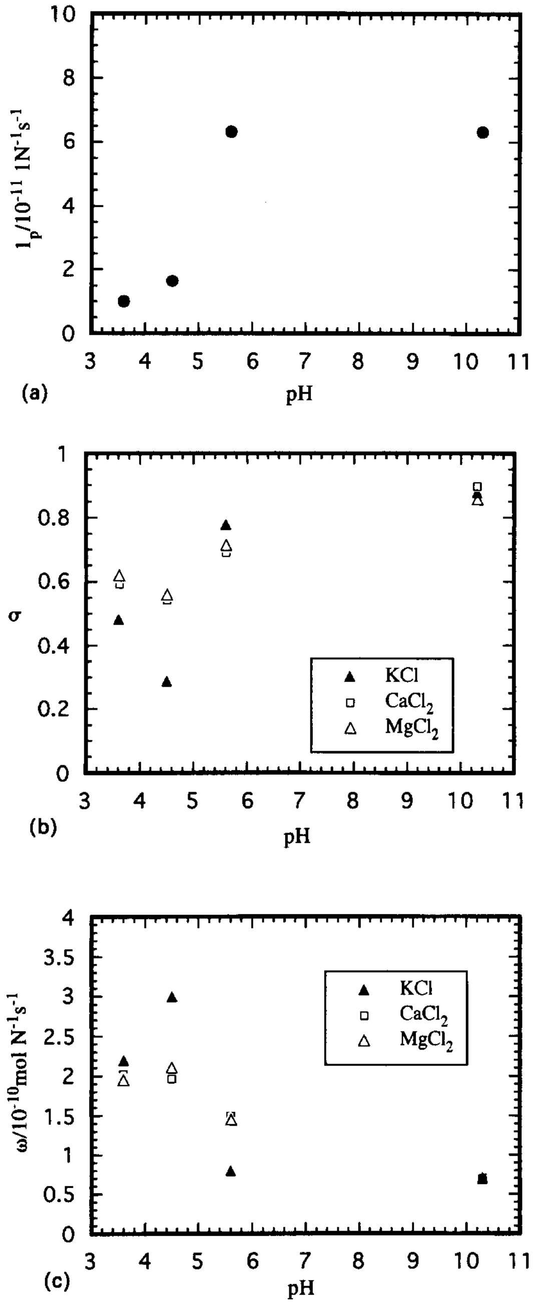

Figure 6 (a) Dependence of the hydraulic permeability coefficient of the A-29 membrane on the pH in the outer solution. (b) Dependence of the reflection coefficient of the A-29 membrane on the pH in the outer solution. (c) Dependence of the solute permeability coefficient of the A-29 membrane on the pH in the outer solution

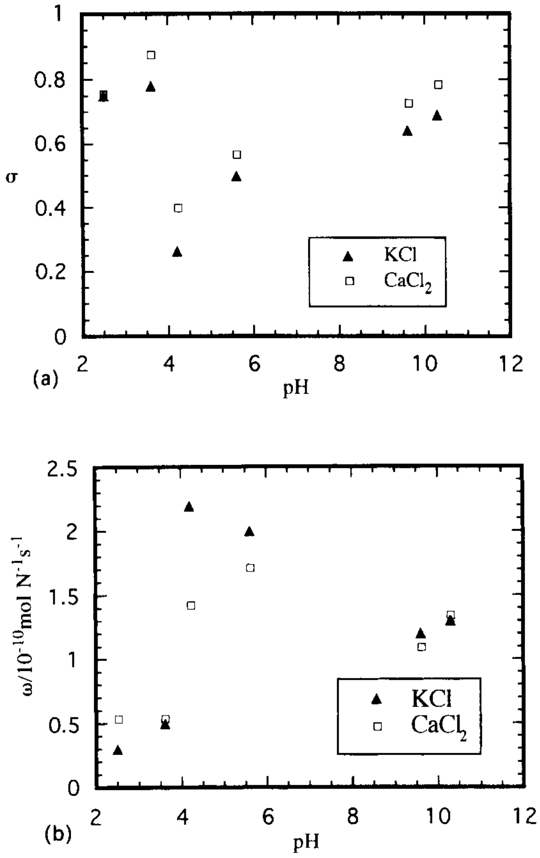

Figure 7 (a) Dependence of the reflection coefficient of the A-78 membrane on the pH in the outer solution for a mixed solute system containing KCl and $CaCl_2$. (b) Dependence of the solute permeability coefficient of the A-78 membrane on the pH in the outer solution for a mixed solute system containing KCl and $CaCl_2$

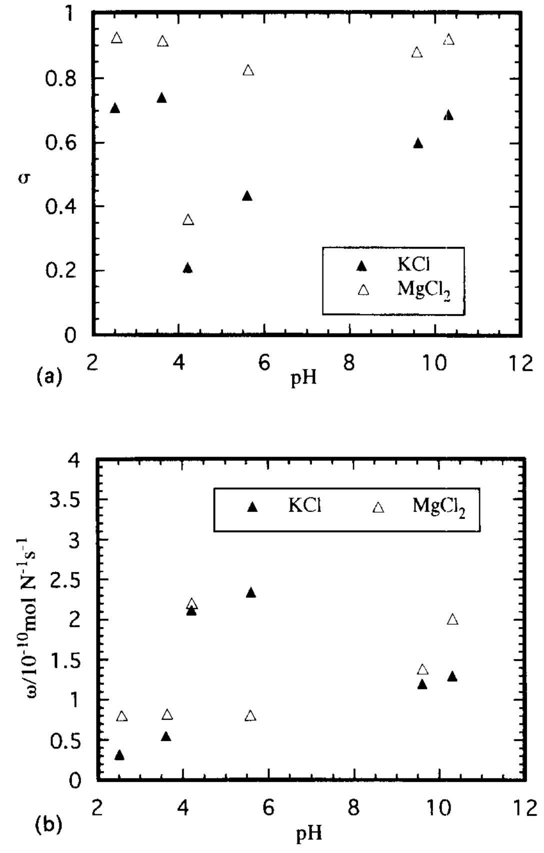

Figure 8 (a) Dependence of the reflection coefficient of the A-78 membrane on the pH in the outer solution for a mixed solute system containing KCl and $MgCl_2$. (b) Dependence of the solute permeability coefficient of the A-78 membrane on the pH in the outer solution for a mixed solute system containing KCl and $MgCl_2$

Considering together the results for l_p, σ and ω, we can say that the permeation of the solute through the membrane should be much enhanced at the isoelectric point of the membrane, which indicates the occurrence of piezodialysis. *Figures 7* and *8* show some results relating to permeation of mixed ion systems through the A-78 membrane. From *Figures 7a* and *7b*, $CaCl_2$ permeates faster than KCl over the whole range of pH in the outer solution. From Figures *8a* and *8b*, $MgCl_2$ permeates faster than KCl. In our previous work[10], the differences in the interactions of various positive ions with the A-78 membrane at pH levels higher than the isoelectric point were enhanced, probably as a result of the dissociation of carboxy groups. In addition, Ca^{2+} has been reported to participate in peculiar interactions, such as in the formation of ionic bridges between CO_2^- groups[19,20]. Accordingly, it is expected that the permeation of Ca^{2+} through a membrane having a high proportion of CO_2^- groups will be discouraged. Thus, it can be readily understood that the order of ionic permselectivity through the membrane corresponds to the reciprocal order of ionic interaction with A-78 in aqueous solution, as reported in our previous paper[10].

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