JOURNAL OF MATERIALS SCIENCE **34** (1999) 1081 – 1091

Uphill transport of organic electrolytes using polyethylene films photografted with 2-(dimethylamino)ethyl methacrylate

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Uphill transport of organic electrolytes, benzoic acid, benzenesulfonic acid, and *p*-aminobenzoic acid, was examined using polyethylene films photografted with 2-(dimethylamino)ethyl methacrylate (DMA). The transport fractions had the maximum values around the grafted amount of 5.0 mmol/g at which the ungrafted layers in the inside of DMA-grafted PE (PE-g-PDMA) films disappeared. Uphill transport of organic anions from the acidic to the alkaline sides occurred most favorably only when the initial pH value in the alkaline side was adjusted to 12.0 while the initial pH values in the acidic side agreed to the pH values of each aqueous solution of the organic electrolytes at 10 mmol/dm^3. Under these conditions each organic electrolyte was concentrated by 1.7–1.8 times the initial concentration. In case either the initial H^+ or OH^- ion concentration was too high or low, the transport fractions of organic anions decreased. When the initial pH value in the acidic side was decreased to 1.5, *p*-aminobenzoic electrolytes were transported from the alkaline to the acidic sides and the transport fraction amounted to 80%. It was experimentally confirmed that the pH difference across the PE-g-PDMA films was a driving force for uphill transport of organic anions. © *1999 Kluwer Academic Publishers*

1. Introduction

Membrane separation techniques such as reverse-osmosis, ultrafiltration, electropermeation, and so on have been widely applied to various fields from chemical industry to medical treatment. In addition, much attention has been given to substrate specificities and active transport properties of biomembranes in an attempt to further functionalize synthetic membranes. One of the characteristic properties of the cell membranes of living bodies is that they recognize a specific substrate and actively transfer it against the osmotic pressure, concentration, and potential gradient.

Recently, many studies have been carried out on the development of synthetic membranes with a variety of functional carriers. Synthetic membranes that provide the uphill transport mechanism of ions usually have specific groups in the polymer structure to interact specifically and reversibly with ions, causing them to transfer from a low to a high concentration across the membranes. We have had a deep interest in the development of synthetic polymeric membranes having similar function to biomembranes such as active and selective transport. Active transport or uphill transport can occur through two types of carriers, fluid or fixed type carriers. The fluid type membranes, or liquid membranes, have the advantages of low energy barrier and high transport efficiency, whereby metal ions such as sodium (Na^+) and potassium (K^+) ions can be specifically transported [1]. On the other hand, the fixed carrier membranes are superior to the liquid membranes in their thermal stability and selectivity to the substrate. There are many membranes capable of concentrating small ions such as metal cations [2–6] and halogen anions [7–9] on the basis of the uphill transport mechanism. Several studies have been reported on synthetic membranes with more effective concentration ability for organic ions [10–15]. However, they are of little practical use in terms of mechanical strength.

We reported that 2-(dimethylamino)ethyl methacrylate (DMA) grafted polyethylene (PE) (PE-g-PDMA) films possessed good electrical conductivities and water-absorptivities, while concurrently maintaining mechanical strength in the water-swollen state [16, 17], and made it clear that their permeabilities were controlled with changes in the surrounding conditions such as pH [17, 18], temperature [17–20], and electric field [21] by making use of the expansion/contraction behavior of the grafted PDMA chains. Though one end of a grafted polymer chain is covalently bonded to a site on the polymer substrate, the other end is usually not put under restraint. Therefore, grafted polymer chains in the grafted layer possess considerable mobility in a good solvent and the ionizable groups affixed to the grafted polymer chains can be expected to function as a fixed carrier. PDMA chains consist of positively chargeable repeating units, dimethylamino groups, and can form salt-linkages with organic anions. However, encountering a strong alkali compound such as NaOH, the PDMA chains with weak electrolytic properties will liberate the organic anions. Therefore, it is supposed that the organic anions taken into the PE-g-PDMA films through salt-linkage with positively charged dimethylamino groups from one side of the film in an acidic state migrate toward the other side of the film in an alkaline state and that they are liberated from the PDMA to form organic anion-Na^+ ion pairs in the aqueous solution.

Uphill transport experiments for some organic ions were made using the difference in pH value between the two sides of the PE-g-PDMA films with positively chargeable groups as a fixed carrier. The organic ions used here were benzoic acid (weak acid), benzenesulfonic acid (strong acid), and *p*-aminobenzoic acid (ampholytic electrolyte). In addition, the concentration of organic electrolytes and their transport mechanism are also discussed in detail.

2. Experimental

2.1. Materials

A film of PE (thickness, 30 μm; density, 0.924 g/cm^3) supplied from Tamapoly Co. Ltd., (Japan) was used as a polymeric substrate. The degree of crystallinity of the PE film used was calculated on the basis of a flotation or buoyancy method to be 47.0%. DMA monomers were photografted onto the PE samples cut into 6.0 cm length and 3.0 cm width in the liquid phase [22, 23]. The detailed procedures of the photografting and membrane properties of PE-g-PDMA films were described in our previous papers [16, 17].

2.2. Colloid titration

The protonation behavior of dimethylamino groups affixed to the PDMA chains was investigated as a function of the pH value of the medium from colloid titration measurements. PDMA (0.015 g) was dissolved in twice distilled water and the solution was taken to a 1 dm^3 volume. The pH value of a 50 cm^3 sample of the PDMA solution was adjusted with 0.1–2 mol/dm^3 HCl or NaOH. An aqueous potassium poly(vinyl alcohol) sulfate (KPVS) solution containing 0.0025 mol/dm^3 of sulfate groups was used as a titrant. The PDMA solution was titrated with the aqueous KPVS solution adjusted to the pH value of the PDMA solution using an ART-3 type HIRAMA automatic recording titrator [24, 25]. The end point of the titration was determined by measuring turbidity at 420 nm. The degree of protonation of the dimethylamino groups of PDMA, α, was calculated using Equation 1.

$$\text{Degree of protonation} = \frac{C_t \cdot V_t \cdot 157.21}{C_p \cdot V_p} \qquad (1)$$

where C_t is the concentration of sulfate group of aqueous KPVS solution (mol/dm^3); C_p, the weight concentration of aqueous PDMA solution (g/dm^3); V_t, the volume of titrated aqueous KPVS solution (dm^3); and V_p, the volume of aqueous PDMA solution (0.050 dm^3). In addition, the quantity of 157.21 is the molecular weight of the repeating unit of PDMA.

TABLE I Measurements of concentration of organic electrytes in the aqueous medium

Permeant	Diluent	Wavelength (nm)
Benzoic acid	Water	219
Benzenesulfonic acid	HCl of pH 2	219
p-Aminobenzoic acid	Water	233

2.3. Uphill transport

The uphill transport experiments were carried out according to the following procedures [10–15]. PE-g-PDMA films with different grafted amounts, which had been swollen in water at 25 °C beforehand, were clamped between the two halves of the cell (100 cm^3 each). The pH values of the aqueous solutions of benzoic acid, benzenesulfonic acid, or *p*-aminobenzoic acid at 10 mmol/dm^3 were adjusted to a given value with 0.1–2 mol/dm^3 HCl or NaOH, and then a 100 cm^3 sample of the solution was put into each chamber. The concentration of individual organic electrolytes in the acidic and alkaline sides was measured using a Shimadzu UV-260 type UV-visible recording spectrophotometer. That is, a 5 mm^3 aliquot taken out from the two sides at fixed time intervals was diluted with water for benzoic acid and with HCl of pH 2 for benzenesulfonic acid up to 200 times, and then the absorbance of each solution was measured at 219 nm (Table I). For *p*-aminobenzoic acid, on the other hand, the absorbance of the solution diluted with water up to 200 times was measured at 233 nm. The concentration of sodium cations and chloride anions was determined by an IM-40S ionmeter (TOA Electronics Ltd., Japan). The transport fraction was calculated from the maximum concentration in the acidic or alkaline side, $C_{\max}$, and the initial concentration of 10 mmol/dm^3 using Equation 2.

$$\text{Transport fraction (\%)} = \frac{C_{\max} - 10}{10} \times 100 \qquad (2)$$

The positive and negative sign of the transport fraction represents the concentration increase in the alkaline side and in the acidic side, respectively.

3. Results and discussion

Since PDMA chains are considered to work as a fixed carrier, the degree of the protonation of dimethylamino groups affixed to PDMA chains was determined from colloid titration measurements with KPVS as shown in Fig. 1. The electrolytic behavior characteristic of weak electrolytes which depended on the pH value was observed. It is important that the dimethylamino groups are fully protonated below pH 4 and deprotonated above pH 10.

The PE-g-PDMA film with the grafted amount of 5.5 mmol/g was used for the first experiment on uphill

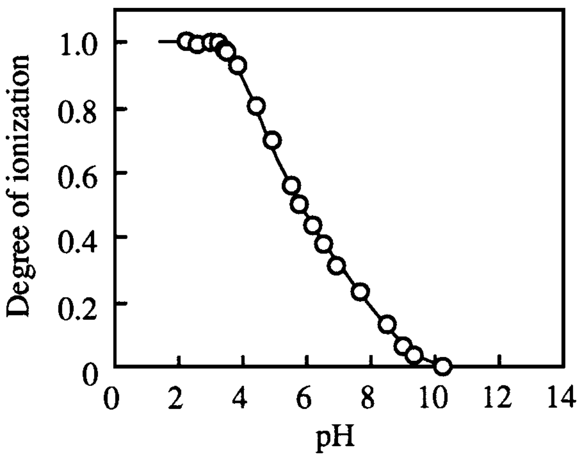

Figure 1 Change in the degree of protonation of dimethylamino group affixed to PDMA chains with pH value from colloid titration measurements with KPVS.

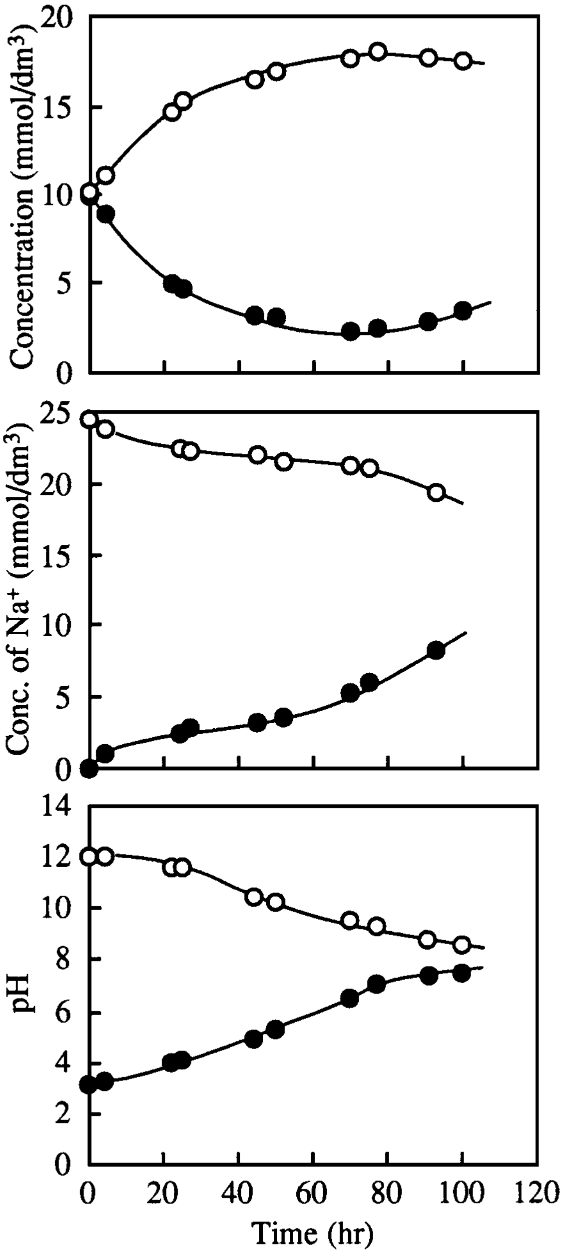

Figure 2 Changes in the concentrations of benzoic acid and Na$^+$ cation and pH values in the acidic (●) and alkaline (○) sides of PE-g-PDMA film with 5.5 mmol/g with time. (The initial pH value in the acidic side = 3.2 and the initial pH value in the alkaline side = 12.0.)

transport for benzoic acid, since no ungrafted layers in any PE-g-PDMA films could be observed at more than 5 mmol/g [16]. (The dependence of the transport fraction on the grafted amount will be discussed later.) An aqueous solution of benzoic acid at the concentration of 10 mmol/dm^3 with pH 3.2 was poured into the cell in the acidic side, while the solution in the alkaline side was adjusted to pH 12.0 by the addition of 0.1–2 mol/dm^3 NaOH. Fig. 2 shows the changes in the concentrations of benzoic acid and sodium cation and the pH values in the acidic and alkaline sides with time at the initial pH value of pH 3.2 in the acidic side using the PE-g-PDMA film. An increase in the concentration of benzoic acid in the alkaline side and its decrease in the acidic side with time indicate that benzoate anions are transferred through the PE-g-PDMA film from the acidic to the alkaline sides against the concentration gradient. The increase in concentration of sodium cation in the acidic side suggests that sodium cations are permeated to the acidic side due to its concentration gradient between the two sides of the PE-g-PDMA film. The gradual decrease in the difference in the pH values between the two sides is considered to come from the transport of benzoate anions to the alkaline side and the neutralization between hydrogen ions and hydroxyl ions across the PE-g-PDMA film. It is a noteworthy feature of the PE-g-PDMA film that it can concentrate benzoic acid to 1.8 times the initial concentration, maintaining the considerably higher value even after the passage of a long time (Fig. 3(a)). It is well known that with many other copolymer membranes [10–12] and polymer cast membranes [13–15], the concentration decreases to the original concentration due to the diffusion through the membranes in a relatively short time after the maximum concentration.

A benzoic anion is supposed to be transported from the acidic to the alkaline side through the salt-linkage with a dimethylamino group affixed to PDMA chains. Therefore, polymer chains grafted to PE films need to have some positively chargeable groups in their structure. Experiment were made on uphill transport for benzoic acid using methacrylic acid (MAA) grafted PE (PE-g-PMAA) with 15 mmol/g and methacrylamide (MAAm) grafted PE (PE-g-PMAAm) films with 35 mmol/g. The grafted amounts of the PE-g-PMAA and PE-g-PMAAm films used here are higher than that of the PE-g-PDMA film, since much higher grafted amounts are needed for the grafted PMAA and PMAAm chains to reach the center of the PE film compared to grafted PDMA chains [16]. Fig. 3(b) and (c) shows the changes in the concentrations of benzoic acid and the pH values in the acidic and alkaline sides with time using the PE-g-PMAA and PE-g-PMAAm films, that is, the films with acidic and neutral functional groups as the side groups of the grafted polymer chains. Little increase in the concentration of benzoic acid was observed for the acidic PE-g-PMAA film because the salt-linkage between benzoate anions and negatively charged carboxylate groups is impossible due to their mutual electrostatic repulsion. Since

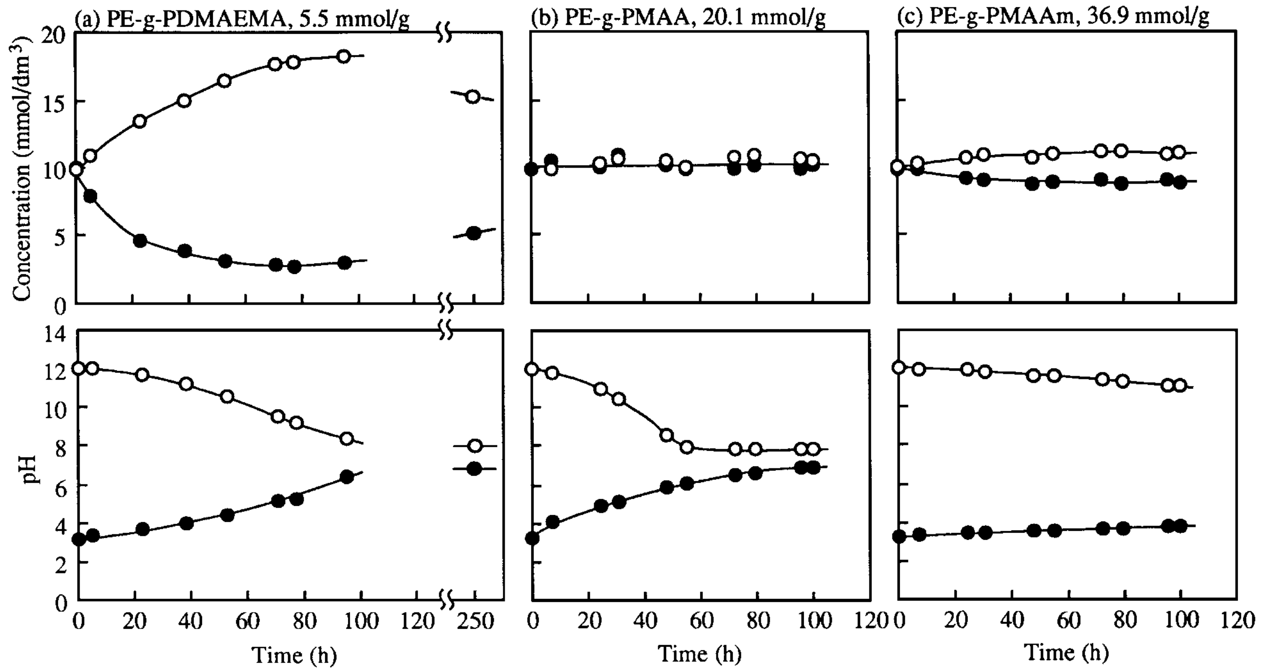

Figure 3 Changes in the concentration of benzoic acid and pH values in the acidic (●) and alkaline (○) sides with time for (a) PE-g-PDMA film with 5.5 mmol/g, (b) PE-g-PMAA film with 20.1 mmol/g, and PE-g-PMAAm film with 36.9 mmol/g.

hydrogen ions can swiftly permeate through the PE-g-PMAA film in association with anionic carboxylate groups, the concentration of hydrogen ion in the acidic side accordingly decreases. Neutralization occurs between permeated hydrogen ions and hydroxyl ions in the alkaline side, and so the pH difference between the two sides decreases with time. On the other hand, although the PE-g-PMAAm film had no ionizable groups, a slight increase in the concentration of benzoic acid was observed in the acidic side. It is considered from the above results that both conditions, that is, the presence of positively chargeable groups on the grafted polymer chains and a pH difference across the grafted PE films are required for uphill transport of benzoic acid. As an example, the mechanism of the uphill transport of benzoate anions through PE-g-PDMA film is suggested in Fig. 4. To begin with, a benzoate anion is incorporated into the PE-g-PDMA film by electrostatic attraction with a positively charged dimethylamino group at the interface between PE-g-PDMA film and the acidic medium. Secondly, the benzoate anion incorporated into the PE-g-PDMA film is transferred toward the alkaline side. And finally, the benzoate anion ionically bonded to a positively charged dimethylamino group

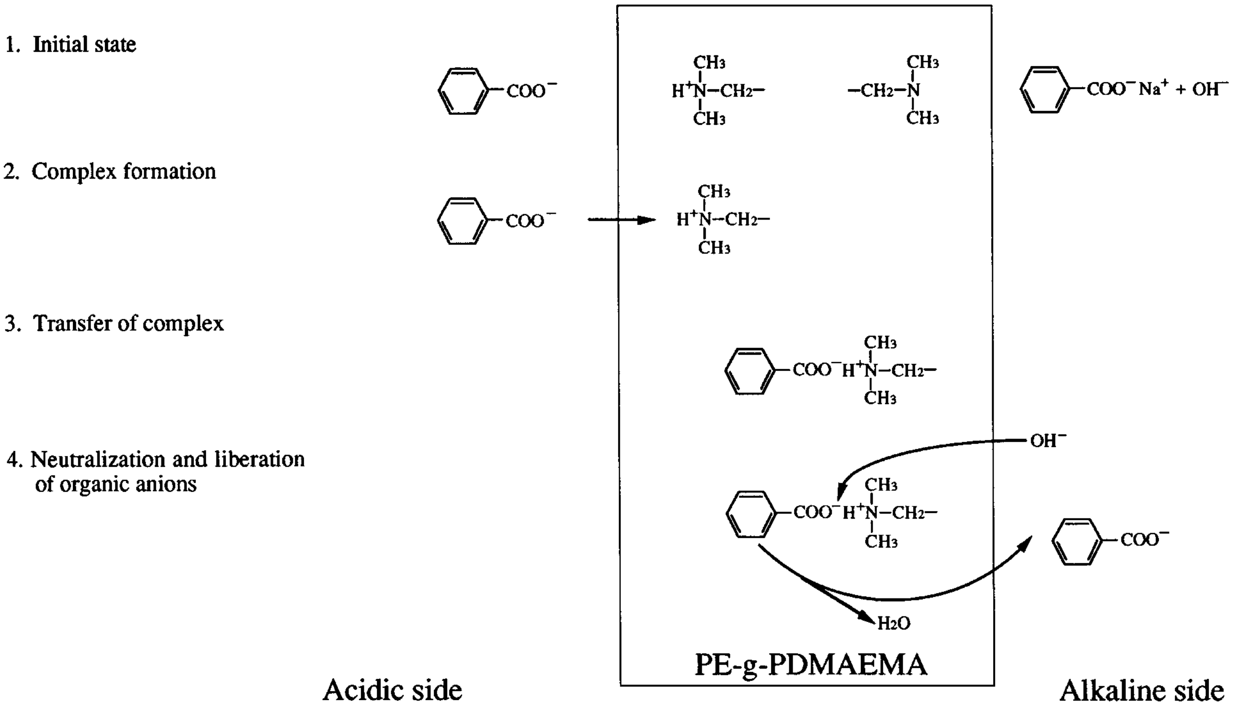

Figure 4 The mechanism of uphill transport of benzoate anions through PE-g-PDMA film.

reacts with a hydroxyl ion at the alkaline interface, and then the benzoate anion is released to the alkaline medium. The above mechanism indicates that dimethylamino groups affixed to the grafted PDMA chains act as a cationic fixed carrier and the pH difference between the two sides plays an important role in uphill transport of benzoate anions. In addition, it becomes apparent that benzoate anions are transported uphill to the alkaline side against the concentration gradient by a symport mechanism with simultaneous transfer of hydrogen ions [27].

The effect of the initial pH values in the acidic and alkaline sides on the uphill transport of benzoate anions was pursued in detail using the PE-g-PDMA film with 5.5 mmol/g. Here, the initial pH value in the acidic side was varied by the addition of HCl or NaOH to a 10 mmol/dm^3 aqueous benzoic solution and the initial pH value in the alkaline side was adjusted to 12.0 with NaOH in the same manner as the first experiment shown in Fig. 2.

First, the initial pH value in the acidic side was decreased to 2.0 by the addition of HCl. The experimental results obtained are shown in Fig. 5. The concentration of benzoic acid at the two sides remained almost unchanged during the first 20 hours, although the pH difference across the PE-g-PDMA film gradually decreased. It is found from Fig. 1 that the dimethylamino groups affixed to the PDMA chains are fully protonated below pH 4. In addition, it is understandable from the calculation of the degree of dissociation using the dissociation constant of p$K_a = 4.20$ [14] that benzoic acid molecules are little dissociated below pH 2. Therefore, benzoate anions and positively charged dimethylamino groups cannot become ionically bonded with each other at the acidic interface. However, it is evident that some benzoic acid molecules dissociate and benzoate anions begin to transport uphill to the alkaline side as the pH value in the acidic side gradually increases. The maximum concentration obtained from these conditions was lower than that obtained at the initial pH value of 3.2 shown in Fig. 2, and the concentration of benzoic acid in the alkaline side slightly decreased when the difference in the pH values between the two sides decreased. Chloride anions started to be transported from the acidic to the alkaline side immediately after the experiments were started and the concentration of chloride anion showed a maximum value in a much shorter time compared to benzoic acid. Chloride ions were also concentrated in the alkaline side through positively charged dimethylamino groups owing to the uphill transport mechanism shown in Fig. 4.

Next, the initial pH value in the acidic side was increased to 4.0 by the addition of NaOH. The results obtained are shown in Fig. 6. The increase in the pH value in the acidic side resulted in a decrease in the amount of hydrogen ions permeated from the alkaline side through the PE-g-PDMA film and the maximum concentration of benzoic acid was limited to about 14 mmol/dm^3. It is considered from Figs 5 and 6 that the decrease or increase in the pH value in the acidic side from 3.2 comes from the depression of dissociation of carboxyl groups of benzoic acid molecules or the decrease in the hydrogen ions [10].

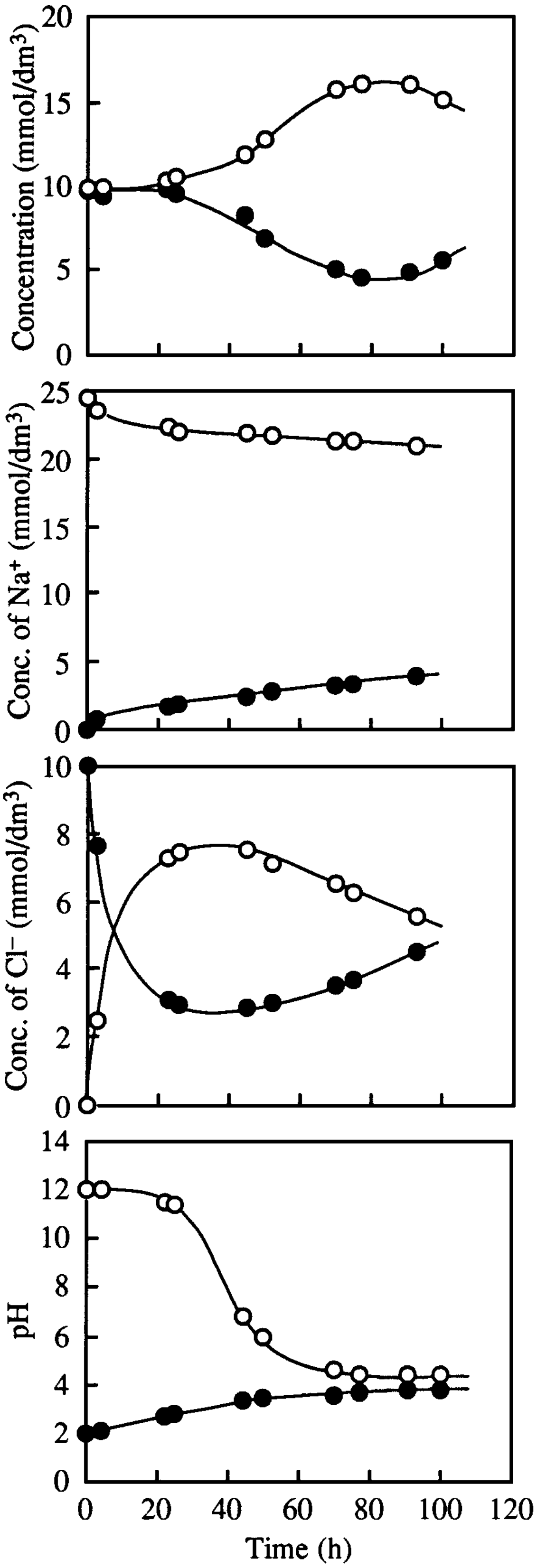

Figure 5 Changes in the concentrations of benzoic acid, Na$^+$ cation, and Cl$^-$ anion and pH values in the acidic (●) and alkaline (○) sides of PE-g-PDMA film with 5.5 mmol/g with time. (The initial pH value in the acidic side = 2.0 and the initial pH value in the alkaline side = 12.0.)

The transport fraction of benzoic acid was calculated using Equation 2 from the maximum concentrations obtained at different initial pH values either in the acidic or alkaline side. The variation in the transport fraction with the initial pH value in the alkaline side is shown

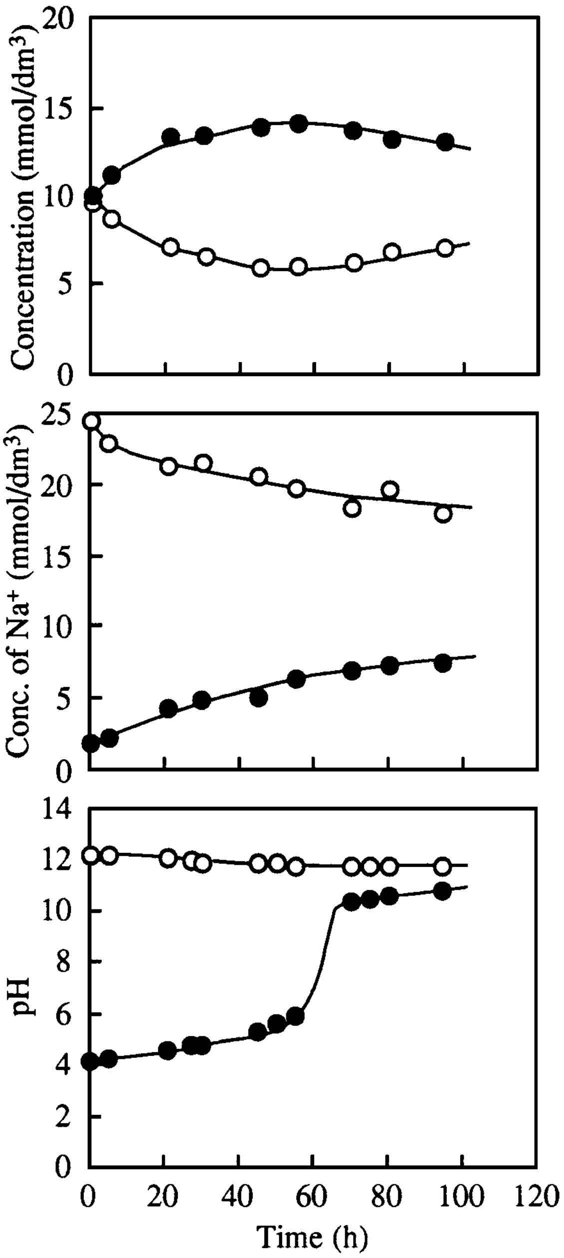

Figure 6 Changes in the concentrations of benzoic acid and Na$^+$ cation and pH values in the acidic (●) and alkaline (○) sides of PE-g-PDMA film with 5.5 mmol/g with time. (The initial pH value in the acidic side = 4.0 and the initial pH value in the alkaline side = 12.0.)

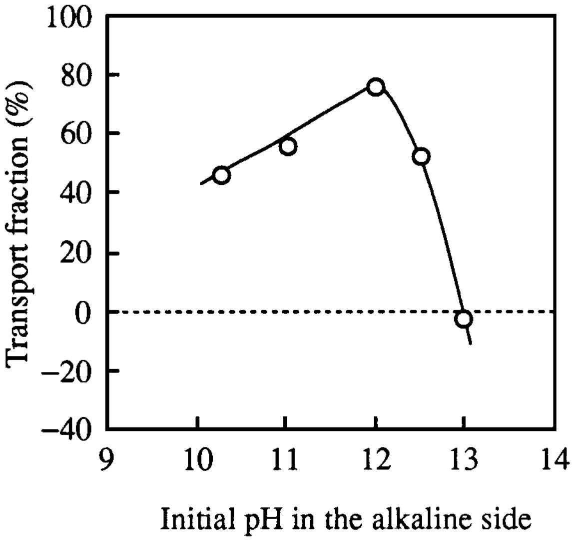

Figure 7 The effects of the initial pH value in the alkaline side on the transport fraction of benzoic acid. (The initial pH value in the acidic side = 3.2.)

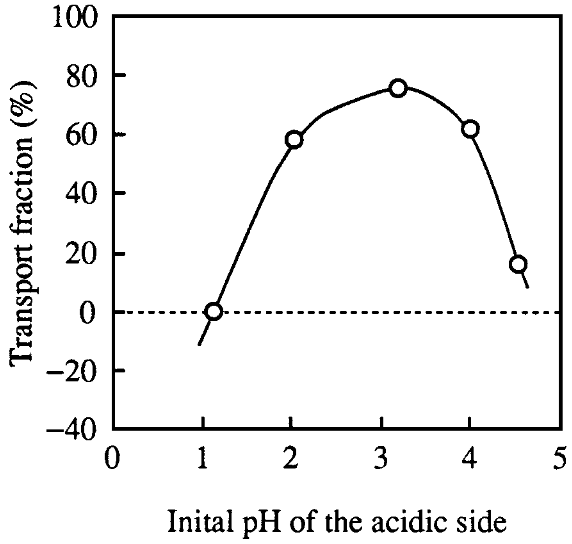

Figure 8 The effects of the initial pH value in the acidic side on the transport fraction of benzoic acid. (The initial pH value in the acidic side = 12.0.)

in Fig. 7 (the initial pH value in the acidic side = 3.2). The transport fraction increased with an increase in the initial pH value in the alkaline side and showed a maximum value at the initial pH value of 12.0. The decrease in the transport fraction below and above the initial pH value of 12.0 can be explained as follows: there are not enough of the hydroxyl ions required to release benzoate anions to the alkaline side below the initial pH value of 12.0. On the other hand, an excess of hydroxyl ions present in the alkaline side will make the pH value in the acidic side increase sharply for a relatively short time.

Experiments on the uphill transport for benzoic acid were carried out at different initial pH values in the acidic side (the initial pH value in the alkaline side = 12.0). Fig. 8 shows the variation in the transport fraction with the initial pH value in the acidic side. The increase or decrease in the initial pH value in the acidic side from 3.2 resulted in a decrease in the transport fraction of benzoic acid. The maximum transport fraction was obtained at the initial pH value of 3.2 corresponding to the pH value of an aqueous solution of benzoic acid of 10 mmol/dm^3. In the pH value range above 3.2, the pH value in the acidic side increased sharply for a short time because of the neutralization of hydrogen ions with hydroxyl ions that permeated from the alkaline side across the PE-g-PDMA film. Therefore, the increase in the pH value in the acidic side resulted in a decrease in the pH difference between the two sides across the PE-g-PDMA films. On the other hand, it is considered that when the initial pH value in the acidic side is decreased, the dissociation of carboxyl groups of benzoic acid molecules is depressed.

It is found from both Figs 7 and 8 that benzoic acid can be most successfully concentrated in the alkaline side at the initial pH values of 3.2 and 12.0 in the acidic

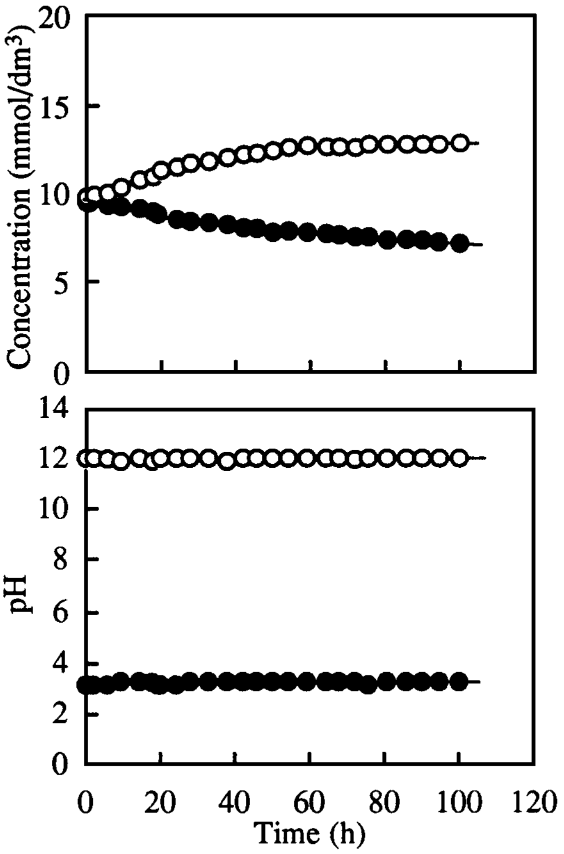

Figure 9 Changes in the concentration of benzoic acid and pH values in the acidic (●) and alkaline (○) sides of DMA-g-PE film with 5.5 mmol/g with time. (The initial pH value in the acidic side = 3.2, the initial pH value in the alkaline side = 12.0, and the initial pH values in the acidic and alkaline sides were kept constant by the addition of HCl and NaOH, respectively.)

and alkaline sides, respectively. To follow up the influence of the pH difference across the PE-g-PDMA films on the transport fraction, uphill transport experiments were carried out while the initial pH values of 3.2 and 12.0 were maintained by addition of HCl and NaOH to the acidic and alkaline sides, respectively. The results are shown in Fig. 9. The transport fraction of benzoic acid in the alkaline side is limited to 30% because the dissociation of benzoic acid molecules was depressed and the addition of HCl and NaOH favored the neutralization between hydrogen ions and hydroxyl ions.

The effect of the grafted amount of the PE-g-PDMA film on the transport fraction was also examined using benzenesulfonic acid as a strong organic electrolyte and *p*-aminobenzoic acid as an organic ampholyte. The initial pH values in the acidic side for benzenesulfonic acid and *p*-aminobenzoic acid were 2.1 and 3.8 for the aqueous solutions of 10 mmol/dm^3 and the initial pH values in the alkaline side were adjusted to 12.0 with NaOH. Fig. 10 shows the variations in the transport fraction with the grafted amount for the three types of organic electrolytes. All three types of organic electrolytes were concentrated in the alkaline side. The transport phenomena of benzenesulfonic acid and *p*-aminobenzoic acid as well as benzoic acid can also be explained in terms of the uphill transport mechanism shown in Fig. 4. The transport fractions increased with an increase in the grafted amount and reached the maximum values at about the grafted amount of 5 mmol/g irrespective of the types of organic electrolytes used. In a previous paper we reported from microscopic observations of the cross sections of PE-g-PDMA films stained with indigo carmine (5,5′-indigodisulfonic acid disodium salt) that the ungrafted layer disappeared at 5 mmol/g [16]. This means that grafted PDMA chains at this grafted amount reached the center of the PE film. The grafted amount at which the transport fraction had the maximum values agreed approximately with that at which the ungrafted layer disappeared. The transport fractions for the three types of organic electrolytes increased with the grafted amount in the range below 5 mmol/g even if an ungrafted layer remained in the center of the PE film. This supports that the progression of grafted PDMA chains into the PE film makes the PE film itself expand [16]. In order to explain the decrease in the transport fraction above 5 mmol/g the thickness of PE-g-PDMA films swollen in water at 25 °C was measured with a micrometer. Fig. 11 shows the change in the thickness of PE-g-PDMA film swollen in water with the grafted amount. The thickness of PE-g-PDMA films in the swollen state increased with an increase in the grafted amount. Since an increase in the grafted amount up to 5 mmol/g leads not only to an increase in the amount of dimethylamino groups as a fixed cationic carrier but also to a decrease in the thickness of the ungrafted layer, the transport fraction increases with an increase in the grafted amount. However, it is considered that a further increase in the grafted amount leads to an increase in the total thickness of PE-g-PDMA film, and so the transport fraction decreases.

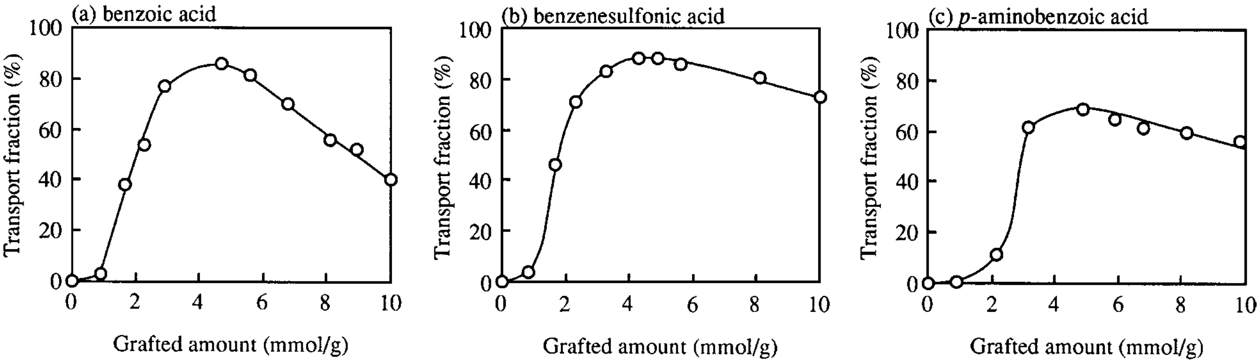

Figure 10 Changes in the transport fractions of (a) benzoic acid, (b) benzenesulfonic acid, (c) *p*-aminobenzoic acid with the grafted amount of PE-g-PDMA film.

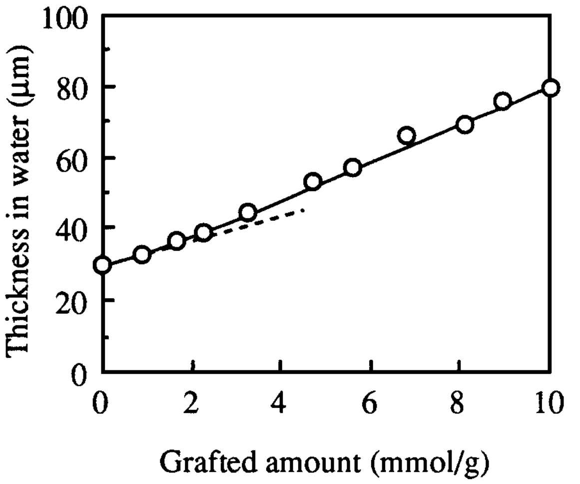

Figure 11 Change in the thickness with the grafted amount for PE-g-PDMA films swollen in water at 25 °C.

The effect of initial pH values in the acidic and alkaline sides on the uphill transport of benzenesulfonic acid and *p*-aminobenzoic acid was investigated using the PE-g-PDMA film with 5.5 mmol/g. Fig. 12 shows typical examples of the time dependence of the concentration of benzenesulfonic acid and pH values in the acidic and alkaline sides at the initial pH value in the alkaline side of 12.0. It can be seen from Fig. 12a that benzenesulfonic acid is concentrated in the alkaline side at the initial pH value of 2.1, which is the pH value of an aqueous solution of benzenesulfonic acid of 10 mmol/dm^3, although it takes a longer time compared with benzoic acid. However, benzenesulfonate anions began to penetrate to the acidic side due to the concentration gradient at 150 h, since there was little difference in the pH value between both sides. Fig. 12b shows that transport of benzenesulfonate anions to the acidic side progressed concurrently with a sharp decrease in the pH value in the alkaline side when the concentration of hydrogen ions in the acidic side was higher than that of hydroxyl ions in the alkaline side. Under these conditions, the transport fraction of benzenesulfonic acid was limited to 40%. The concentration difference among the PE-g-PDMA films is considered to decrease sharply due to the permeation of benzenesulfonate anions from the alkaline to the acidic sides. Fig. 13 shows typical examples of the time dependence of the concentration and pH values in the acidic and alkaline sides for *p*-aminobenzoic acid. Fig. 13a indicates that *p*-aminobenzoic acid is concentrated in the alkaline side at the initial pH value of 3.8 as the pH value of an aqueous solution of *p*-aminobenzoic acid of 10 mmol/dm^3. In addition, when the initial pH value in the acidic side was decreased to 1.5, an increase in the concentration to the acidic side was observed as shown in Fig. 13b and the maximum concentration amounted to 18 mmol/dm^3. During the first 20 hours there was no obvious change in the concentration of *p*-aminobenzoic acid. This can be explained by supposing that dimethylamino groups are little protonated at the alkaline interface and *p*-aminobenzoate cations and positively charged dimethylamino groups affixed to grafted PDMA chains electrostatically repel

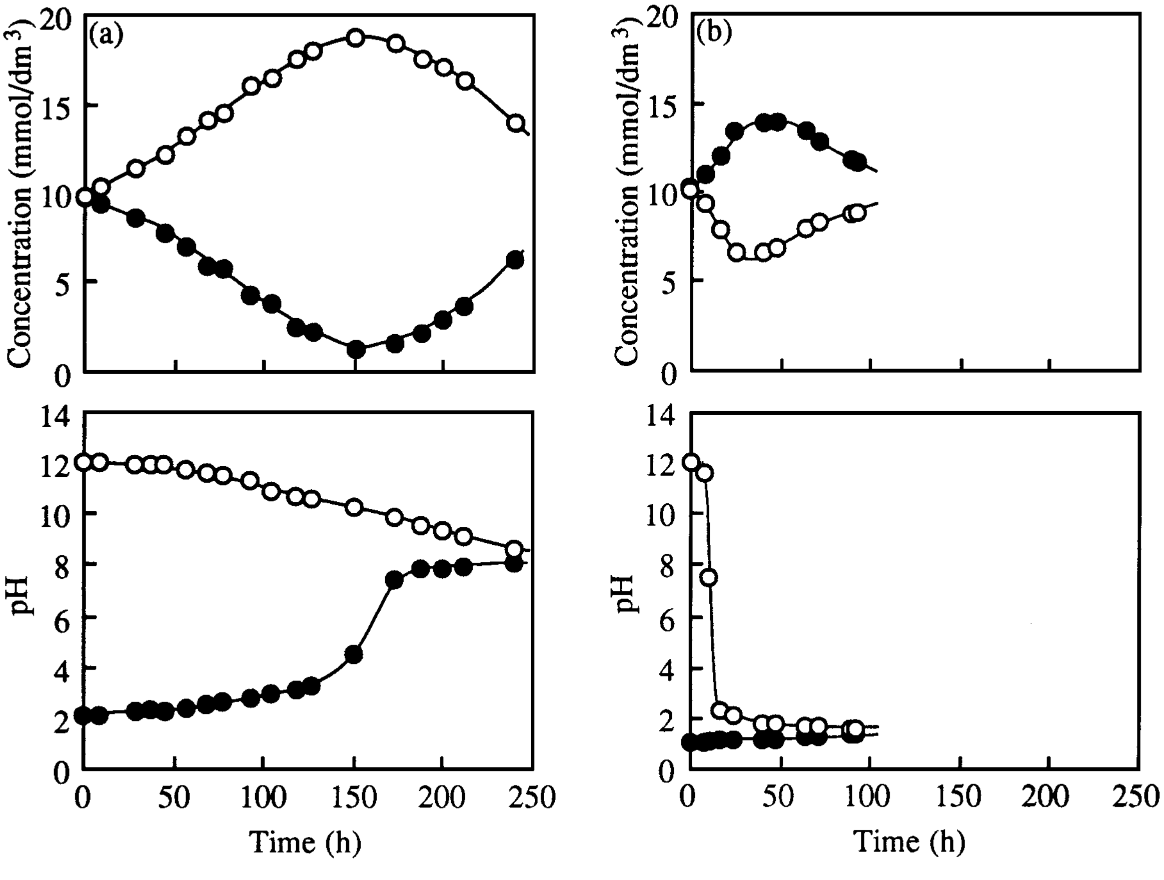

Figure 12 Changes in the concentration of benzenesulfonic acid and pH values in the acidic (●) and alkaline (○) sides of PE-g-PDMA film with 5.5 mmol/g with time. (The initial pH value in the acidic side = (a) 2.1, (b) 1.0 and the initial pH value in the alkaline side = 12.0.)

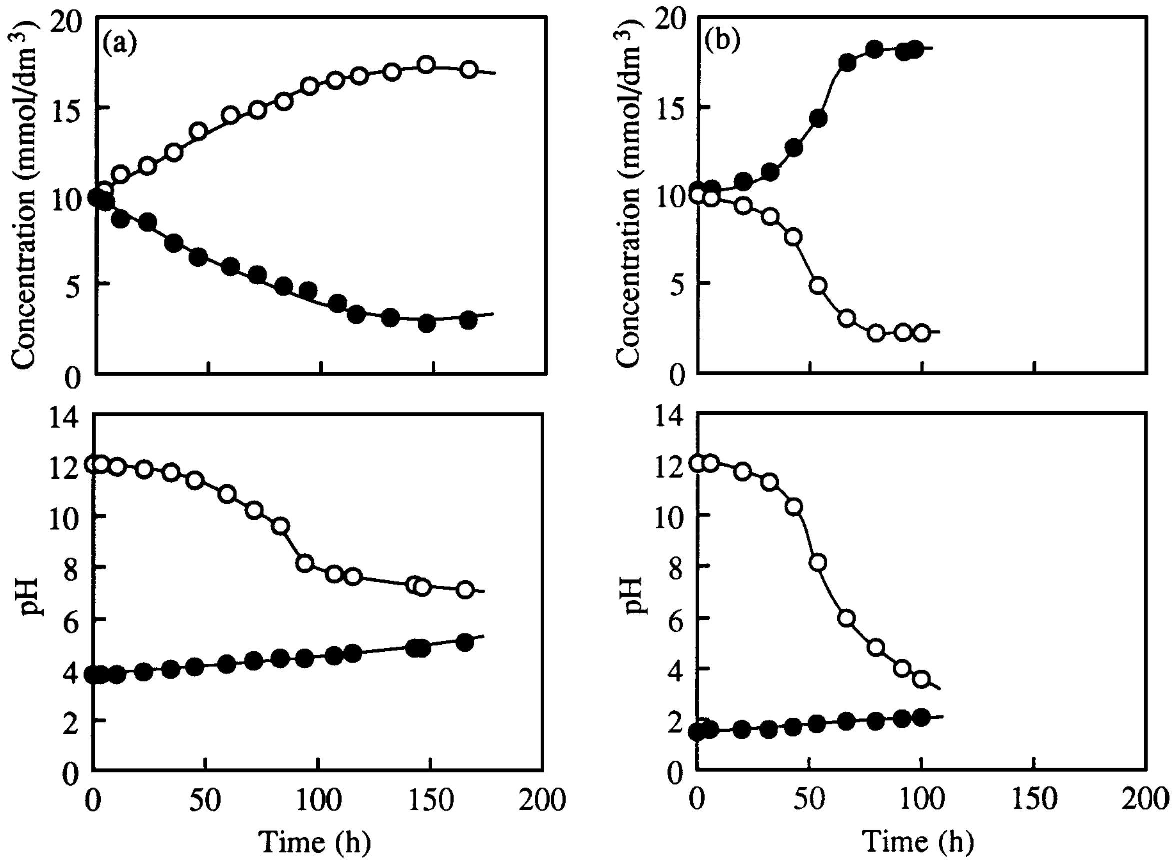

Figure 13 Changes in the concentration of *p*-aminobenzoic acid and pH values in the acidic (●) and alkaline (○) sides of PE-g-PDMA film with 5.5 mmol/g with time. (The initial pH value in the acidic side = (a) 3.8, (b) 1.5 and the initial pH value in the alkaline side = 12.0.)

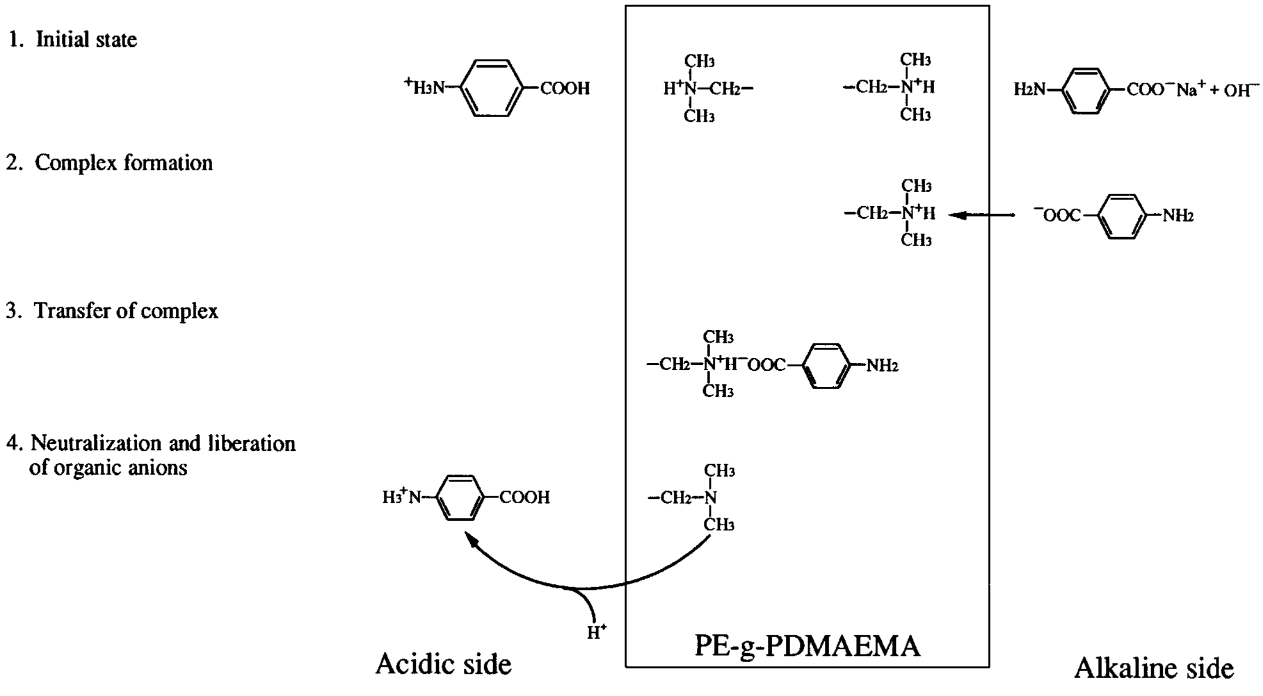

Figure 14 The mechanism of uphill transport of *p*-aminobenzoate anions through PE-g-PDMA film.

each other at the acidic interface. Therefore, it is observed that as the pH value in the alkaline side gradually decreases with the passage of time, the concentration of *p*-aminobenzoic acid in the acidic side sharply increases. The increase in the concentration of *p*-aminobenzoic acid in the acidic side shown in Fig. 13b can be explained in terms of the uphill transport mechanism shown in Fig. 14. Since the pH value in the acidic side is too low for carboxyl groups of *p*-aminobenzoic acid molecules to dissociate, the uphill transport from the acidic to the alkaline sides will not occur. On the other hand, the pH value in the alkaline side gradually decreased with the passage of time. The decrease in the pH value in the alkaline side to about 10

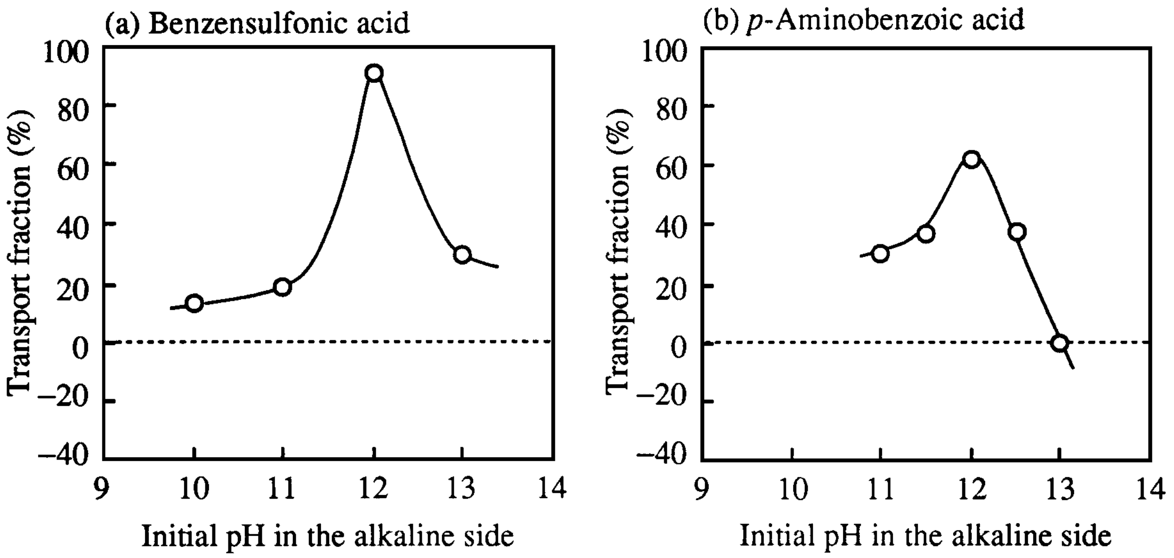

Figure 15 The effect of the initial pH value in the acidic side on the transport fraction of (a) benzenesulfonic acid and (b) *p*-aminobenzoic acid. (The initial pH value in the acidic side for benzenesulfonic acid = 2.1 and the initial pH value in the acidic side for *p*-aminobenzoic acid = 3.8.)

makes it possible for *p*-aminbenzoate anions to bond ionically to positively charged dimethylamino groups at the alkaline interface. The *p*-aminobenzoate anions incorporated into the PE-g-PDMA film are transferred though positively charged dimethylamino groups in the PE-g-PDMA film toward the acidic side. The positively charged dimethylamino group ionically bonded to a *p*-aminobenzoate anion react with hydrogen ions at the interface of the acidic side and so a *p*-aminobenzoate cation is released to the acidic side.

The transport fractions of benzenesulfonic acid and *p*-aminobenzoic acid were calculated from the maximum concentrations obtained at various initial pH values in the acidic or alkaline sides. Fig. 15 shows the variations in the transport fractions with the initial pH value in the alkaline side for benzenesulfonic acid and *p*-aminobenzoic acid. The transport fractions of both organic electrolytes had maximum values at an initial pH value of 12.0 in the same manner as benzoic acid. The drastic decrease in the transport fraction at the initial pH values below and above 12.0 is considered to arise from a shortage and an excess of hydroxyl ions in the alkaline side, respectively.

Experiments on uphill transport of benzenesulfonic acid and *p*-aminobenzoic acid were carried out at different initial pH values in the acidic side and the initial pH value of 12.0 in the alkaline side. Fig. 16 shows the variations in the transport fraction with the initial

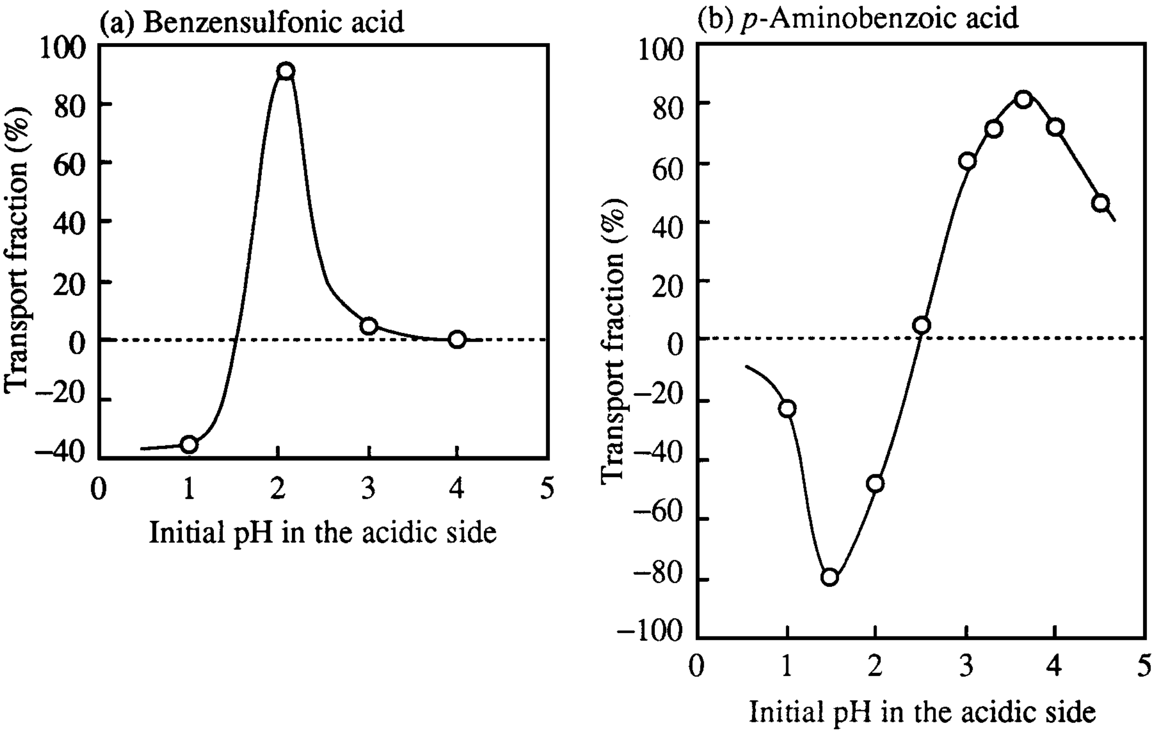

Figure 16 The effect of the initial pH value in the alkaline side on the transport fraction of (a) benzenesulfonic acid and (b) *p*-aminobenzoic acid. (The initial pH value in the alkaline side = 12.0.)

pH value in the acidic side for benzenesulfonic acid and *p*-aminobenzoic acid. The maximum concentration of two types of organic electrolytes in the alkaline side was obtained at the same initial pH values as the pH values of the original solutions of 10 mmol/dm^3. *p*-Aminobenzoate cations were transferred to acidic side at the initial pH values in the acidic side below 2.5. The transport fraction of *p*-aminobenzoic acid amounted to 80% at the initial pH value of 1.5 in the acidic side.

4. Conclusion

Experiments on uphill transport of three organic compounds, benzoic acid, benzenesulfonic acid, and *p*-aminobenzoic acid, were carried out using PE-g-PDMA films to establish the dependence of transport fraction on the grafted amount and the initial pH value in the acidic and alkaline sides. From the experimental results above, we can conclude the following:

1. Organic anions are transported uphill using dimethylamino groups affixed to grafted PDMA chains as a cationic fixed carrier by a symport mechanism with hydrogen ions.
2. The transport fractions of the three types of organic electrolytes show individual maximum values under the conditions where the initial pH values in the alkaline side are adjusted to 12.0 and the initial pH values in the acidic side are the pH values of each aqueous organic electrolyte solution of 10 mmol/dm^3.
3. The transport fractions increase with an increase in the amount of grafted DMA and reach maximum values at around 5 mmol/g at which value the ungrafted layer in the inside of PE film disappears.
4. Organic electrolytes can be effectively concentrated using PE-g-PDMA films and the transport fraction of each organic electrolyte each 70–80%.

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Received 29 April 1997
and accepted 8 October 1998