Electrotransport of Organic Electrolytes Through 2-(Dimethylamino)ethyl Methacrylate–Grafted Polyethylene Films and Their Separation and Concentration

Kazunori Yamada, Takayuki Taki, Kimihito Sato, Mitsuo Hirata

Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Izumi-Cho 1-2-1, Narashino-Shi, Chiba 275-8575, Japan

ABSTRACT: Organic electrolytes with negatively chargeable functional groups such as benzoic acid (BA, weak acid), benzenesulfonic acid (BSA, strong acid), and *p*-aminobenzoic acid (*p*-ABA, ampholyte) were concentrated through polyethylene (PE) films photografted with 2-(dimethylamino)ethyl methacrylate (DMAEMA) by electrotransport. The permeabilities of DMAEMA-grafted PE (PE-*g*-PDMAEMA) films to BA and BSA were considerably increased by the application of direct current at pH 6. BA and BSA could be selectively permeated from the respective binary BA/phenyl-1,2-ethandiol (PhED, neutral) and BSA/PhED mixtures by making use of the difference in their permeabilities. In addition, BSA was selectively permeated from the binary BSA/BA mixtures. The organic electrolytes mentioned above were transported against their concentration gradient toward the anode side and their degrees of concentration went up to 90% by the continuous application of direct current. The degrees of concentration for organic electrolytes obtained by electrotransport in this study were slightly higher than those obtained by the uphill transport using the pH difference across the PE-*g*-PDMAEMA film, and the concentration time was considerably shortened. It was made clear that the electrotransport through the PE-*g*-PDMAEMA films is one of the effective techniques to selectively separate or concentrate organic electrolytes with negatively chargeable functional groups. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2535–2544, 2003

Key words: graft copolymers; electrotransport; permeability; films; photografting

INTRODUCTION

Membrane-separation techniques recently have attracted interest in various fields such as energy saving, resources recovery, and environmental preservation. Synthesized polymer membranes have been developed in many studies, mainly for the separation of metal or halogen ions in solution systems by electrotransport,[1–3] pH difference across the polymer membrane,[4–6] and adsorption processes.[7–9] However, the separation and concentration of organic ions have not been given much consideration during the development of synthesized polymer membranes. In addition, most of these membranes are highly crosslinked to improve their mechanical stability and to avoid excessive water swelling, and the increased crosslinking generally causes a decrease in the membrane permeabilities. A variation in the "mesh" size of a crosslinked polymer membrane is considered to have an influence on the permeability of organic ions with relatively high molecular weights. Therefore, the adjustment of the degree of crosslinking and the chain length of the crosslinking agent is important in improving the membrane permeabilities because loosening the network would yield increased permeability to organic ions.

Because a graft copolymer consists of a long sequence of one monomer referred to as a backbone, with branches of a long sequence of another monomer, compatibilization of a pair of polymers with different characteristics can be achieved without any crosslinking agents. The hydrophobic polymer substrates such as polyethylene (PE),[10–16] polypropylene (PP),[17–19] and polytetrafluoroethylene (PTFE)[20–25] can be modified by various grafting techniques using UV radiation,[11,16,17,20] ⁶⁰Co γ-rays,[12,15,18,22–24] plasma,[13,19–21,25] or corona discharge[14] as an energy source. Their surface properties such as wettability, adhesivity, and autohesivity were highly modified by the graftings of various hydrophilic monomers,[10,11,26–28] and modified surface properties would be durably preserved. The grafted PE films, prepared by the photografting of hydrophilic, ionic, or reactive monomers throughout the bulk of the PE films used in place of the PE plates, were applied to various functional membranes.[29,30]

The grafted PE films possess reasonable mechanical properties in the water-swollen state. In addition, one end of each grafted polymer chain is covalently bonded to the substrate polymer chains and the other end is usually not placed under restraint. Therefore, grafted polymer chains possess considerable mobility in a good solvent. For the PE films grafted with ionic monomers, positively or negatively ionizable functional groups successively affixed to the grafted polymer chains can function as a fixed carrier to transport ionic species across the grafted PE films, and the permeabilities of the grafted PE films can be controlled in response to a change in the pH value,[29] temperature,[29] or electrical field.[30,31]

Mechanical strength is also one of the important factors in the practical use of the grafted PE films as the functional membranes. The PE films grafted with methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (PE-g-PMAA and PE-g-PDMAEMA) possess practical strength in the water-swollen state.[32] Membrane properties such as electrical conductivity, water adsorptivity, and mechanical strength in the swollen state for the PE-g-PMAA and PE-g-PDMAEMA films were described in detail in our previous study.[29] Negatively chargeable organic electrolytes such as benzoic acid (BA), benzenesulfonic acid (BSA), and p-aminobenzoic acid (p-ABA) were transported uphill by the use of the pH difference across the PE-g-PDMAEMA films against their concentration gradients.[33] Although the concentrations of these organic electrolytes were increased by 1.7–1.8 times their initial concentrations, it took 100–150 h to concentrate them. We have aimed at decreasing the time required for organic electrolytes to be concentrated and further increasing the degree of concentration by electrotransport.[34]

In this study, we discuss the electropermeabilities of the PE-g-PDMAEMA films to BA, BSA, and p-ABA and their selective separation and concentration by electrotransport.

EXPERIMENTAL

Photografting

A PE film (thickness, 30 μm; density, 0.924 g/cm^3) supplied from Tamapoly Co. Ltd. (Japan) was used as a polymer substrate. The photografting was carried out in the manner described in our previous studies.[29,32] The PE films (60 × 30 mm) were dipped in an acetone solution containing benzophenone (BP) as a sensitizer (0.0275 mol/dm^3) for 1 min to coat their surfaces with BP. DMAEMA monomer was photografted onto the PE films by applying UV rays emitted from a 400-W high-pressure mercury lamp to an aqueous DMAEMA monomer solution in which the BP-coated PE films were immersed in Pyrex glass

TABLE I
Spectrophotometric Determination of the Amounts of Permeated Phenyl Compounds for the Simple Systems

Compound		Wavelength (nm)	log ε (dm^3/mol^{-1}/cm^{-1})
BA	weak acidic	219	3.850
BSA	strong acidic	219	3.750
PhAN	weak basic	212	3.807
p-ABA	ampholytic	216.5	3.899
PhED	neutral	205	3.883

tubes at 60°C.[29,32] Before the photografting, the pH value of an aqueous DMAEMA monomer solution was adjusted to 8.0 with concentrated HCl to increase the solubility of PDMAEMA in water.[35] The amount of grafted DMAEMA was calculated from the weight increase of the samples in mmol/g-PE-film after the photografting.[29,32]

Permeation control in response to direct current

Two platinum mesh electrodes and the PE-g-PDMAEMA films swollen in NH$_4$Cl/HCl or NH$_4$Cl/NaOH buffer solutions of the pH values ranging from 4 to 10 were arranged in order of one platinum electrode, the PE-g-PDMAEMA film, and the other platinum electrode between the permeation cells.[29,30,34] Buffer solution (100 cm^3) containing the organic electrolytes such as BA, BSA, and p-ABA at the concentration of 2.0 mM was put in one side of the cell (feed side) and 100 cm^3 of the buffer solution was put in the other side of the cell (permeate side). Then, direct current was alternately turned on and off with moderate stirring. During the application of the direct current, 0.5–2M HCl or NaOH was added to the feed and permeate solutions to keep their initial pH values. The amounts of permeated organic compounds were determined by measuring the absorbances of the aliquots taken from the permeate solutions at regular time intervals at the wavelengths shown in Table I, and then each aliquot was immediately returned to the permeate solutions.

Selective permeation by electrotransport

The binary mixtures of BA/phenyl-1,2-ethanediol (PhED, neutral), BSA/PhED, and BA/BSA in the buffer solutions of different pH values were put in one side of the cell and 100 cm^3 of the buffer solution in the other side of the cell, and then a 10-mA direct current was continuously applied with moderate stirring. The amounts of two phenyl compounds, designating one phenyl compound as A and the other as B, permeated from the binary mixtures through the PE-g-PDMAEMA films were determined by measuring the absorbances of the aliquots taken from the permeate solutions at two different wavelengths, λ_1 and λ_2, as shown in

TABLE II
Spectrophotometric Determination of the Amounts of Permeated Phenyl Compounds for the Binary Systems

Binary Compound		λ_1 (nm)	$\log \varepsilon_1$ $(dm^3/mol^{-1}/cm^{-1})$	λ_2 (nm)	$\log \varepsilon_2$ $(dm^3/mol^{-1}/cm^{-1})$
BA/PhED	BA	212	3.769	219	3.876
	PhED		3.769		3.101
BSA/PhED	BSA	209	3.864	220	3.676
	PhED		3.864		2.855
BA/BSA	BA	218	3.864	229	4.028
	BSA		3.864		1.959

Table II. The absorbances, Abs_1 and Abs_2, were measured at one wavelength λ_1 at which the molar absorption coefficients of phenyl compounds A and B were equal ($\epsilon_{A1} = \epsilon_{B1}$) and at the other wavelength λ_2 at which their molar absorption coefficients were quite different ($\epsilon_{A2} \neq \epsilon_{B2}$).[34,36] Each permeated amount of phenyl compounds A and B was calculated using eqs. (1) and (2):

$$Abs_2 = C_A \varepsilon_{A2} L + C_B \varepsilon_{A2} L$$
$$= C_A \varepsilon_{A2} L + (C_{A+B} - C_A) \varepsilon_{B2} L \quad (1)$$

$$C_{A+B} = C_A + C_B \quad (2)$$

where C denotes the molar concentration of the phenyl compounds, and L is the cell length (1 cm). In addition, the separation factor was calculated using eq. (3):

$$\text{Separation factor} = (Y_A/Y_B)/(X_A/X_B) \quad (3)$$

where X and Y denote the molar fractions of the phenyl compounds in the feed and permeate solutions, respectively.

Concentration by electrotransport

The PE-g-PDMAEMA films swollen in water sandwiched between two platinum mesh electrodes were laid out in the middle of the two chambers of the cell. An aqueous solution (100 cm^3) of BA, BSA, or p-ABA at 10 mM was put in both chambers of the cell, and then direct current was continuously applied. The molar concentration of organic electrolytes was spectrophotometrically determined at regular intervals at the wavelengths shown in Table I after appropriate dilution of the aliquots taken from the solutions in the anode and cathode sides with distilled water. The bubbles generated near the electrodes were removed to retain the direct current value during the application of the direct current. The degrees of concentration for the organic electrolytes used were calculated from their maximum molar concentration C_{max} and the initial molar concentration C_{int}, using eq. (4):

$$\text{Degree of concentration (\%)} = \frac{C_{max} - C_{int}}{C_{int}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Permeability of anionic organic electrolytes

The permeabilities to BA and BSA were estimated for a PE-g-PDMAEMA film of the grafted amount of 7.5 mmol/g-PE film during application of the direct current, given that the BA and BSA permeabilities showed the maximum values at about 7–8 mmol/g-PE film.[30] Figure 1 shows the BA and BSA permeabilities of the PE-g-PDMAEMA film when the direct current of 5 mA was alternately turned on and off at pH 6. BA and BSA were slightly permeated because of the concentration gradient across the PE-g-PDMAEMA film even without the application of direct current. When direct current was applied under the conditions where the platinum mesh electrode in the permeate side was used as the anode, the BA and BSA permeabilities sharply increased, as shown in Figure 1(a) and (b). In addition, the on-off regulations of BA and BSA permeation were observed by turning the direct current on and off. To the contrary, when the platinum mesh electrode in the permeate side was set as the cathode, the BA and BSA permeabilities were depressed, as shown in Figure 1(c) and (d). These results indicate that the increased permeabilities of BA and BSA were caused by the migration of benzoate and benzenesulfonate anions toward the permeate (anode) side in addition to the concentration gradient. The permeability of PhED as a neutral phenyl compound was also investigated during the application of direct current. Here, the platinum mesh electrode in the permeate side was used as the anode. Figure 2 shows the PhED permeability at pH 6 on alternately turning on and off the direct current of 10 mA. The PhED permeability slightly increased by turning on the direct current. Because the PhED molecules receive no electrostatic interaction, the slight increase in the PhED permeability would be caused by the enlargement of the pore sizes attributed to the orientation of grafted PDMAEMA chains with positively charged dimethylamino groups toward the cathode in the feed
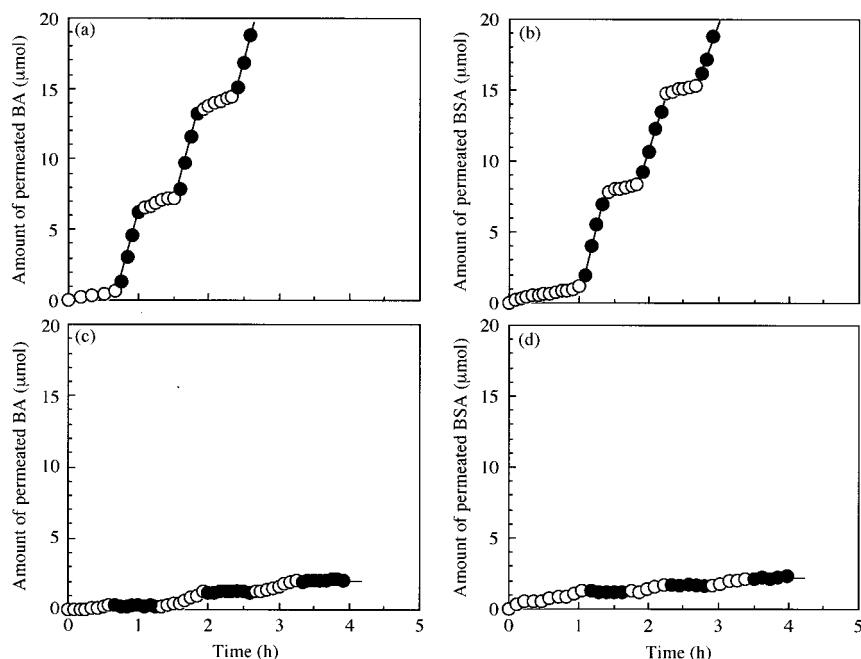
Figure 1 Reversible permeation of BA (a and c) and BSA (b and d) through a PE-g-PDMAEMA film of 7.5 mmol/g in a NH$_4$Cl/NaOH buffer of pH 6.0 by repeatedly turning on and off the direct current between 0 (○) and 5 (●) mA. (a), (b): the platinum mesh electrode in the permeate side was used as the anode. (c), (d): the platinum mesh electrode in the permeate side was used as the cathode.

solution. On the basis of the results of the colloid titration of an aqueous PDMAEMA solution with an aqueous potassium poly(vinyl alcohol)sulfate (KPVS) solution, about 50% of dimethylamino groups affixed to the PDMAEMA are protonated at pH 6.[34]

This behavior also exerts a favorable influence on the increase in the permeation of BA and BSA during the application of direct current. In addition, the BA and BSA permeabilities were examined in the buffer solutions of different pH values. Figure 3 shows the variations in the BA and BSA permeabilities with the pH value. The BA and BSA permeabilities had maximum values at pH 6. This result can be explained in

terms of the visocometric behavior of an aqueous PDMAEMA solution (ionic strength = 0.01M, NaCl) and the protonation of dimethylamino groups affixed
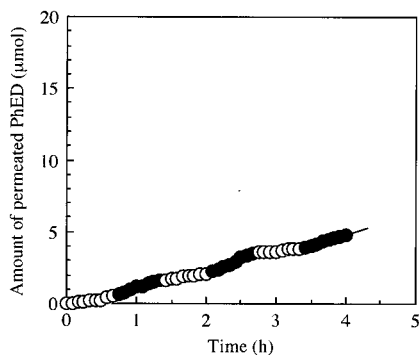

Figure 2 Reversible permeation of PhED through a PE-g-PDMAEMA film of 7.5 mmol/g in a NH$_4$Cl/NaOH buffer of pH 6.0 by repeatedly turning on and off the direct current between 0 (○) and 10 (●) mA. The platinum mesh electrode in the permeate side was used as the anode.
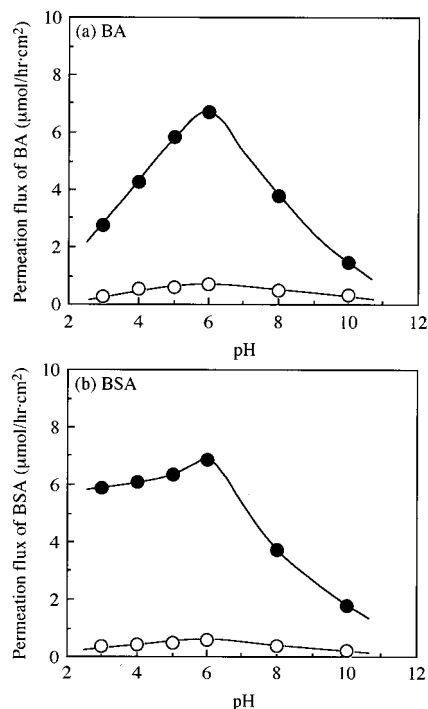

Figure 3 Variations in the permeation flux of (a) BA and (b) BSA with the pH value of the buffer solution for a PE-g-PDMAEMA film of 7.5 mmol/g at the applied direct current of 0 (○) and 5 (●) mA.
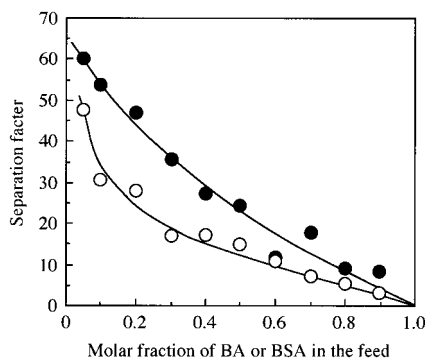
Figure 4 Effects of the feed composition on the separation factor for the permseparation of BA from the BA/PhED (○) and BSA from the BSA/PhED (●) mixtures at the total concentration of 2.0 mM on applying the direct current of 10 mA for a PE-g-PDMAEMA film of 7.5 mmol/g in a buffer solution of pH 6.0.

to PDMAEMA as a function of the pH value.[29,34] The maximum value of the reduced viscosity of PDMAEMA was observed at pH 6. The decrease in the BA permeability in the pH range below 6 is considered to be the result of the contraction of grafted PDMAEMA chains in addition to the decrease in the dissociation of carboxyl groups of BA molecules.[29] The degree of dissociation of 83% for BSA as a strong organic acid determined from the pH = 2.78 for an aqueous BSA solution of 10 mM was regarded as being kept constant as a function of the pH value. Therefore, in the pH range below 6 the permeation of BSA gradually increased with an increase in the pH value. The decrease in the BA and BSA permeabilities in a higher pH region would be attributable to the decrease in the degree of protonation of dimethylamino groups affixed to the grafted PDMAEMA chains[34] because the degree of dissociation for BA calculated from the pK_a value of 4.20 increased to over 99% at pH 7 and the dissociation behavior of BSA was independent of the pH value.

Selective permeation by electrotransport

The permselectivities of the PE-g-PDMAEMA film by electrotransport were followed up in the binary BA/PhED and BSA/PhED mixture systems at pH 6 by the differences in the permeabilities between two phenyl compounds during the application of direct current, as shown in Figures 2 and 3. In both binary mixture systems, the organic electrolytes were selectively permeated through the PE-g-PDMAEMA film irrespective of the chemical compositions of the feed solutions. Figure 4 shows the effect of the feed composition of BA and BSA on the separation factor. The molar fraction of BA or BSA in the permeate solutions became higher than those in the feed solutions and the permeate solutions enriched with BA or BSA were obtained even from the feed solutions with low molar fractions of BA and BSA. The high permselectivities to benzoate

and benzenesulfonate anions were attributed to their migration toward the anode and the electrostatic attraction between organic anions and grafted PDMAEMA chains with protonated dimethylamino groups. The permselectivity to BSA in the BSA/PhED mixture system was slightly higher than that to BA in the BA/PhED mixture system because most of the BSA molecules as a strong organic acid would dissociate into the anions (degree of dissociation = 83%).

In addition, the permselectivity was examined in the binary equimolar BSA/BA mixture system at different pH values. Because the permeability to BSA is higher than that to BA in the pH range below 6, as seen from Figure 3, BSA is expected to be selectively permeated through the PE-g-PDMAEMA film from the binary BSA/BA mixtures. Figure 5 shows the change in the separation factor with the pH value for the binary BSA/BA mixture system. BSA was selectively permeated through the PE-g-PDMAEMA film and the separation factor increased with a decrease in the pH value. The increase in the separation factor for the binary BSA/BA mixture systems arises from the decrease in the dissociation of BA with a decrease in the pH value, and selective permeation of BSA by electrotransport is caused by the difference in the degree of dissociation between BA and BSA.

Concentration of BA and BSA by electrotransport

The concentration of BA and BSA by electrotransport was investigated for the PE-g-PDMAEMA films. An aqueous solution of BA or BSA of 10 mM was put into both chambers of the cell, and then a 10-mA direct current was continuously applied. Figures 6 and 7 show the changes in the molar concentration and the pH value in the anode and cathode sides with the time for the concentration of BA and BSA by electrotransport, respectively. The concentrations of BA and BSA increased with time in the anode side because benzoate and benzenesulfonate anions migrated toward the an-
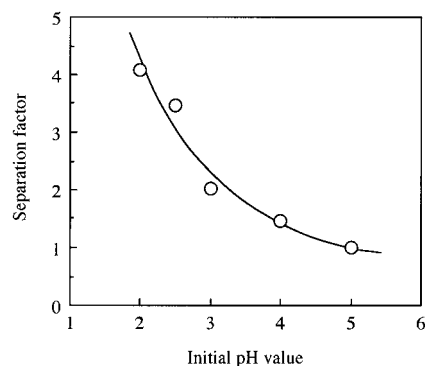

Figure 5 Effect of the initial pH value on separation factor for the permseparation of BSA from the BSA/BA mixtures at the total concentration of 2.0 mM on applying the direct current of 10 mA for a PE-g-PDMAEMA film of 7.5 mmol/g.
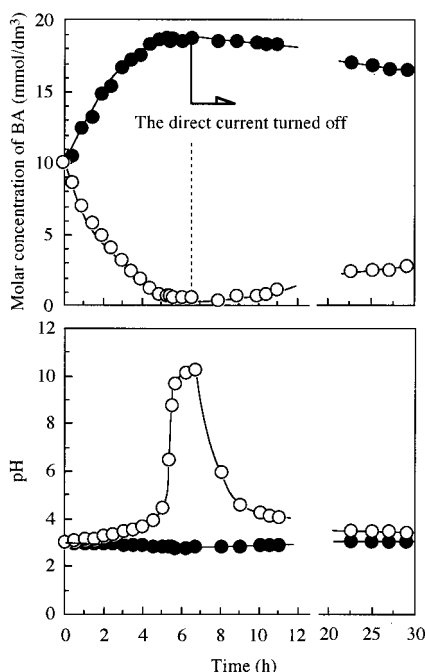
Figure 6 Changes in the concentration of BA and the pH values in the anode (●) and cathode (○) sides with the time on the continuous application of the direct current of 10 mA in an aqueous BA solution using a PE-*g*-PDMAEMA film of 7.5 mmol/g.

ode in the permeate side through the PE-*g*-PDMAEMA film. After the continuous application of direct current for 6 and 4 h, the degrees of concentration for BA and BSA obtained from eq. (4) were 90 and 95%, respectively. The degree of concentration of about 80% remained even at 25 h after the application of direct current was stopped. The time required for BSA to be concentrated (referred to as the concentration time below) was shorter than that for BA. Because most of the BSA molecules exist in the anionic form in water medium, BSA is more effectively transported than BA toward the anode side.[30] It took 100 and 150 h for BA and BSA to be concentrated by 1.8 to 1.9 times their initial concentrations by uphill transport using the pH difference across the PE-*g*-PDMAEMA film, respectively.[31] The concentration time was reduced by as much as one twenty-fifth and the degree of concentration further increased by electrotransport used instead of the pH difference across the PE-*g*-PDMAEMA film.

The pH values in the anode sides slightly decreased as a result of an increase in the molar concentrations of BA and BSA. On the other hand, the pH values in the cathode sides sharply increased, probably because of water splitting. During the application of direct current, the concentration gradient is formed in the vicinity of the cathode medium contacting the membrane interface because of a large difference between the mobilities of organic ions in the solutions and in the membrane phase.[37,38] In addition, under severe conditions of con-

centration polarization, the ion concentration at the membrane interface tends to a zero value. Therefore, water splitting occurs and the pH value of the solution changes significantly.[39] When the direct current was applied to an aqueous solution of PhED at 10 m*M*, the pH values in the anode and cathode sides changed without the change in the PhED concentration. This result supports the occurrence of water splitting.

The dependencies of the degree of concentration of BA by electrotransport and the concentration time on the grafted amount were assessed for PE-*g*-PDMAEMA films with the grafted amounts ranging from 1 to 15 mmol/g at the initial BA concentration of 10 m*M*. Figure 8 shows the variations in the degree of concentration of BA and the concentration time with the grafted amount. In the range of the grafted amounts below 5 mmol/g, it took a considerably longer time for BA anions to be concentrated because the ungrafted layers remained in the insides of the PE-*g*-PDMAEMA films. The degree of concentration passed the maximum value around 7.5 mmol/g, and then decreased with an increase in the grafted amount. The PE films are made hydrophilic by the photografting of DMAEMA, and the amount of dimethylamino groups increases with the grafted amount. Therefore, the degree of concentration of BA increases and the concentration time decreases with an increase in the grafted amount. However, a further increase in the grafted amount results in an increase of the total thickness of
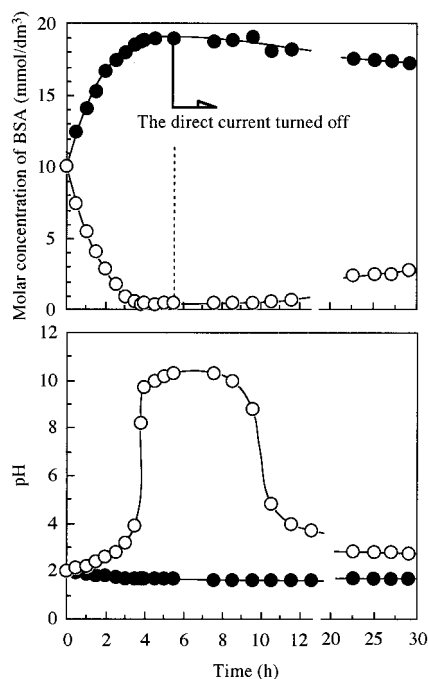

Figure 7 Changes in the concentration of BSA and the pH values in the anode (●) and cathode (○) sides with the time on the continuous application of the direct current of 10 mA in an aqueous BA solution using a PE-*g*-PDMAEMA film of 7.5 mmol/g.
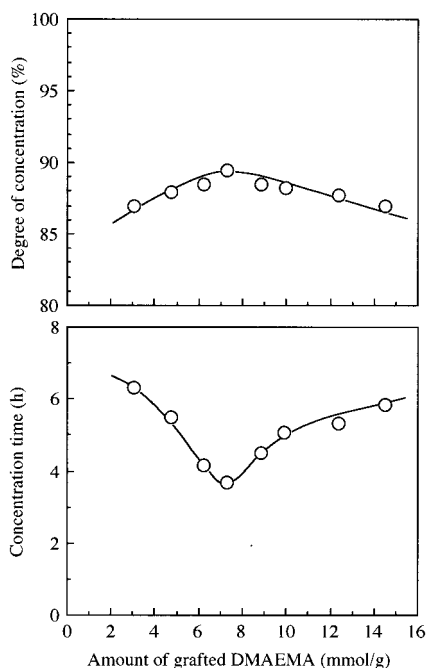
Figure 8 Variations in (a) the degree of concentration of BA and (b) the time required to reach the maximum concentration (concentration time) with the grafted amount of PE-*g*-PDMAEMA films at the initial BA concentration of 10 mM.
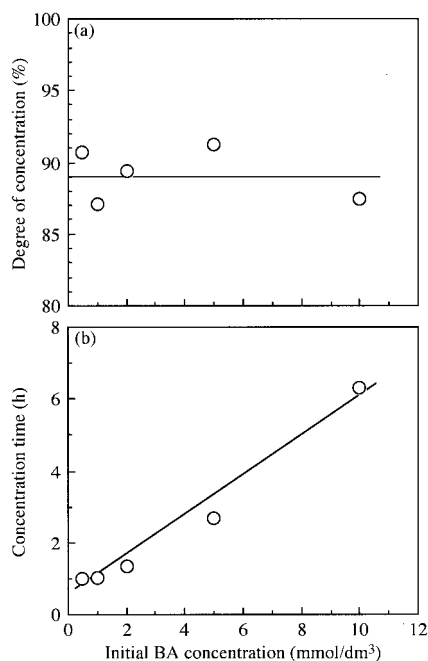

Figure 9 Changes in the degree of concentration of BA and the concentration time with the initial BA concentration at the applied direct current of 10 mA for a PE-*g*-PDMAEMA film of 7.5 mmol/g.

the PE-*g*-PDMAEMA film, and so the BA permeabilities decrease. Because the increase in the thickness of the PE-*g*-PDMAEMA films depresses the electropermeation of BA anions mainly as a result of membrane resistance, the concentration time is considered to increase with an increase in the grafted amount. In addition, the dependency of the degree of concentration and concentration time on the initial BA concentration and applied direct current value were followed up for a PE-*g*-PDMAEMA film of 7.5 mmol/g. Figures 9 and 10 show the changes in the degree of concentration and concentration time with the initial BA concentration and applied direct current value, respectively. Although the concentration time increased with an increase in the initial BA concentration, the degree of concentration for BA was 88 to 90%. The concentration time was considerably decreased and the degree of concentration gradually increased with an increase in the applied direct current in an aqueous BA solution of 10 mM. These results suggest that an increase in the applied direct current leads to an increase in the rate of migration of benzoate anions through the PE-*g*-PDMAEMA film per the unit time and an increase in the total amount of BA anions migrated into the permeate side during the application of the direct current.

Concentration of *p*-ABA

The pH dependency of the concentration of an ampholytic organic compound, *p*-ABA, by electrotrans-

port was investigated for a PE-*g*-PDMAEMA film of 7.5 mmol/g in the aqueous *p*-ABA solutions of 10 mM with different pH values. Figures 11 and 12 show the changes in the molar concentration of *p*-ABA and pH
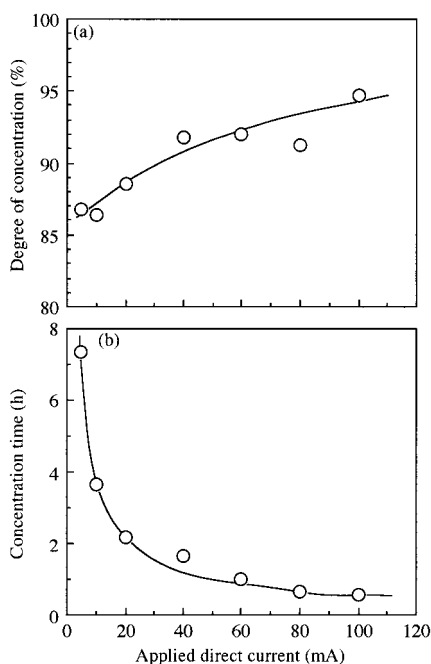

Figure 10 Changes in the degree of concentration and the concentration time with the applied direct current at the initial BA concentration of 10 mM for a PE-*g*-PDMAEMA film of 7.5 mmol/g.
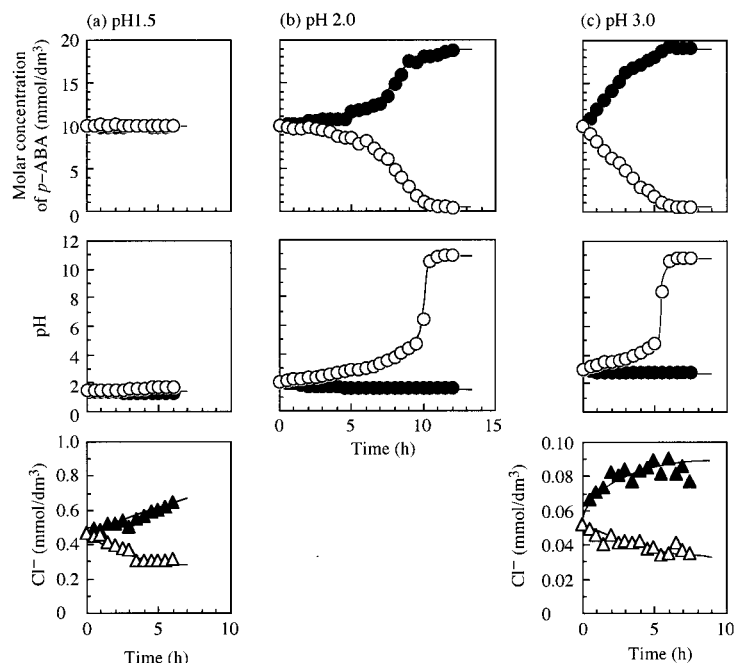
Figure 11 Changes in the concentration of p-ABA, the pH values, and concentration of Na^+ or Cl^- ions in the anode (shaded) and cathode (open) sides with the time for a PE-g-PDMAEMA film of 7.5 mmol/g at the applied direct current of 10 mA in the aqueous p-ABA solutions of 10 mM at the initial pH values of (a) 1.5, (b) 2.0, and (c) 3.0.

value in the anode and cathode sides with the time at different initial pH values. At the initial pH value adjusted to 1.5 with HCl, the p-ABA concentration changed only slightly, and Cl^- ions electrically mi-
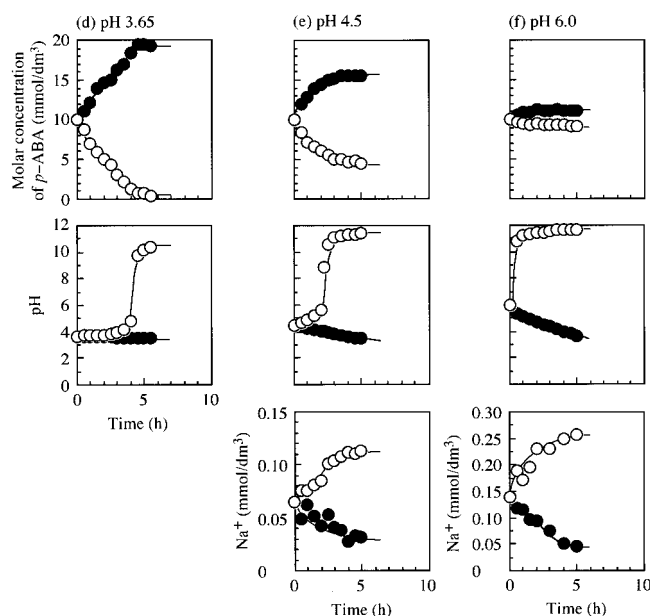

Figure 12 Changes in the concentration of p-ABA, the pH values, and concentration of Na^+ or Cl^- ions in the anode (shaded) and cathode (open) sides with the time for a PE-g-PDMAEMA film of 7.5 mmol/g at the applied direct current of 10 mA in the aqueous p-ABA solutions of 10 mM at the initial pH values of (d) 3.65, (e) 4.5, and (f) 6.0.

grated into the anode side with the time. At the initial pH value of 2.0, the p-ABA concentrations in both sides were left constant within the starting 5 h after the application of direct current, probably because of the electrical repulsion between p-ABA anions and protonated dimethylamino groups affixed to the grafted PDMAEMA chains. However, p-aminobenzoate anions were permeated into the cathode side by electrotransport through the PE-g-PDMAEMA film, when the pH value in the cathode increased to about 3. This comes from a gradual increase in the dissociation of carboxyl groups for p-ABA molecule with an increase in the pH value (pK_a = 2.41, pK_b = 4.85).[40] When the initial pH value increased to 3.0, the concentration time was significantly decreased mainly as a result of the increase in the degree of dissociation of carboxyl groups for p-ABA and the decrease in the amount of HCl added to adjust the initial pH value. Because the initial pH value was higher in the pH range between 1.5 and 3.65, p-ABA was concentrated in the anode side in a shorter time. The pH value in the cathode side sharply increased probably because of water splitting, when the molar concentration of p-ABA became considerably low. The molar concentration of p-ABA in the anode side reached the maximum value by the continuous application of direct current for about 5 h at the initial pH value of 3.65 (without adding any HCl and NaOH). The addition of NaOH to an aqueous p-ABA solution resulted in the decrease in the electrical migration of p-aminobenzoate anions
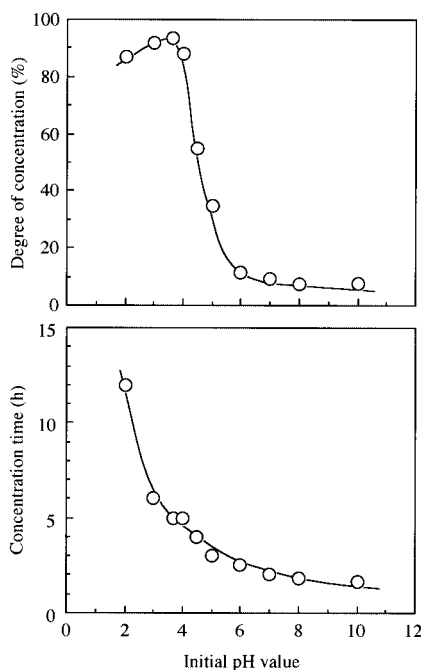
Figure 13 Variations in (a) the degree of concentration and (b) the concentration time with the initial pH value at the *p*-ABA concentration of 10 m*M* for a PE-*g*-PDMAEMA film of 7.5 mmol/g.

into the anode side and at the same time Na^+ ions effectively migrated into the cathode side. In addition, the decrease in the degree of the protonation of dimethylamino groups affixed to the grafted PDMAEMA chains is one of the factors leading to a decrease in the electrical migration of *p*-ABA anions.

Figure 13 shows the variation in the degree of concentration of *p*-ABA and the concentration time with the initial pH value. The degree of concentration passed the maximum value of 94% at the initial pH value of 3.65. It can be seen that *p*-ABA as an organic ampholyte can also be highly concentrated by electrotransport. As the initial pH value increased from 3.65 to 6.0, the degree of concentration of *p*-ABA sharply decreased. This indicates that negatively chargeable organic electrolytes can be concentrated by electrotransport using a PE-*g*-PDMAEMA film. The addition of HCl or NaOH to adjust the pH value of an aqueous *p*-ABA solution resulted in a decrease in the degree of concentration of *p*-ABA. In particular, the addition of NaOH caused a considerable decrease in the degree of concentration of *p*-ABA. This result confirms that the protonation of dimethylamino groups affixed to the grafted PDMAEMA chains is one of the important factors for *p*-ABA to be concentrated.

CONCLUSIONS

We pursued the concentration and selective separation of organic electrolytes by electrotransport using

PE-*g*-PDMAEMA films. From the experimental results above, we can conclude the following: in case the platinum mesh electrode in the permeate side was used as the anode, the on-off regulations of permeation of organic electrolytes such as BA and BSA were observed by alternately turning on and off the direct current. The organic electrolytes with higher permeability can be selectively permeated from the binary mixture systems such as BA/PhED, BSA/PhED, and BSA/BA by making use of the difference in their permeabilities. For a PE-*g*-PDMAEMA film of 7.5 mmol/g, the degrees of concentration for BA and BSA have the maximum values and each concentration time is the shortest. *p*-ABA in addition to BA and BSA can be more highly concentrated at a shorter time through electrotransport than through the uphill transport using the pH difference across the PE-*g*-PDMAEMA film.

It has been made apparent from the obtained results that electrotransport using the PE-*g*-PDMAEMA films is one of the effective techniques to selectively separate or concentrate organic electrolytes with negatively chargeable functional groups and this technique can be expected to be applied for recovery and reuse of organic electrolytes.

References

1. Elmidaoui, A.; Belcadi, S.; Houdus, Y.; Cohen, T.; Gavach, C. J Polym Sci Part A: Polym Chem 1992, 30, 1407.
2. Sata, T.; Yamaguchi, T.; Matsusaki, K. J Phys Chem 1995, 99, 12875.
3. Sata, T.; Teshima, K.; Yamaguchi, T.; J Polym Sci Part A: Polym Chem 1996, 34, 1475.
4. Uragami, T.; Nakamura, R.; Sugihara, M. Polymer 1983, 24, 559.
5. Ogata, N.; Sasui, K.; Fujimura, H. J Appl Polym Sci 1981, 26, 4149.
6. Nonaka, T.; Ogawa, H.; Egawa, H. J Appl Polym Sci 1990, 41, 2869.
7. Tan, H. K. S. Sep Sci Technol 1996, 31, 2209.
8. Heitz, C.; Binana-Limbele, W.; François, J.; Biver, C. J Appl Polym Sci 1999, 72, 455.
9. Arica, M. Y.; Testereci, H. N.; Denizli, A. J Chromatogr A 1998, 799, 83.
10. Yamada, K.; Kimura, T.; Tsutaya, H.; Hirata, M. J Appl Polym Sci 1992, 44, 993.
11. Yamada, K.; Tsutaya, H.; Tatekawa, S.; Hirata, M. J Appl Polym Sci 1992, 46, 1065.
12. Kostov, G. K.; Turmanova, S. C. J Appl Polym Sci 1997, 64, 1469.
13. Johnsen, K.; Kirkhorn, S.; Olafsen, K.; Redford, K.; Stori, A. J Appl Polym Sci 1998, 59, 1651.
14. Lei, J.; Lion, X. J Appl Polym Sci 2001, 81, 2881.
15. Gupta, B.; Anjum, N.; Gupta, A. P. J Appl Polym Sci 2000, 77, 1331.
16. Lei, J.; Gao, J.; Zhou, R.; Zhang, B.; Wang, J. Polym Int 2000, 49, 1492.
17. Shukla, S. R.; Athalye, A. R. J Appl Polym Sci 1994, 51, 1567.
18. Kaji, K.; Abe, Y.; Murai, M.; Nishioka, N.; Kosai, K.; J Appl Polym Sci 1993, 47, 1427.
19. Poncin-Epaillard, F.; Nédard, N.; Soutif, J.-C. Macromol Chem Phys 2000, 201, 212.

20. Yamada, K.; Hayashi, K.; Sakasegawa, K.; Onodera, H.; Hirata, M. Nippon Kagaki Kaishi [J Chem Soc Jpn Chem Ind Chem] 1994, 1994, 427.

21. Yamada, K.; Ebihara, T.; Gondo, T.; Sakasegawa, K.; Hirata, M. J Appl Polym Sci 1996, 61, 1899.

22. Bozzi, A.; Chapiro, A. Radiat Phys Chem 1988, 32, 193.

23. Hegazy, E. A.; El-Assy, N. B.; Taher, N. H.; Desouki, A. M. Radiat Phys Chem 1989, 33, 539.

24. Hegazy, E. A.; Taher, N. H.; Kamal, H. J Appl Polym Sci 1989, 38, 1229.

25. Kang, E. T.; Shi, J. L.; Neoh, K. G.; Tan, K. L.; Liaw, D. J. J Appl Polym Sci 1998, 36, 3107.

26. Yamada, K.; Isoda, J.; Ebihara, T.; Hirata, M. In: Interfacial Aspects of Multicomponent Polymer Materials; Sperling, L. H., Ed.; Plenum Press: New York, 1997; pp. 173–194.

27. Yamada, K.; Kimura, J.; Hirata, M. J Photopolym Sci 1998, 11, 263.

28. Yamada, K.; Kimura, J.; Hirata, M. J Appl Polym Sci, in press.

29. Yamada, K.; Sato, T.; Tatekawa, S.; Hirata, M. Polym Gels Networks 1994, 2, 323.

30. Yamada, K.; Sasaki, K.; Hirata, M. In: Field Responsive Polymers; ACS Symposium Series 726; American Chemical Society: Washington, DC, 1999; p. 16.

31. Taki, T.; Yamada, K.; Hirata, M. Trans Mater Res Soc Jpn 1999, 24, 553.

32. Yamada, K.; Tatekawa, S.; Hirata, M. J Colloid Interface Sci 1994, 164, 427.

33. Yamada, K.; Sasaki, K.; Hirata, M. In: Field Responsive Polymers; ACS Symposium Series 726; American Chemical Society: Washington, DC, 1999; Chapter 21, pp. 16–21.

34. Yamada, K.; Sato, K.; Hirata, M. J Mater Sci 1999, 34, 1081.

35. Hayashi, K.; Tatekawa, S.; Igi, F.; Yamada, K.; Ebihara, T.; Hirata, M. In: Proceedings of the Annual Meeting of Chemical Society of Japan, 1992, Abstr. 1 C8 31 (in Japanese).

36. Yamada, K.; Hirata, M. In: Recent Research Development in Polymer Science, Pandalai, S. G., Ed.; Recent Research Development: Trivandrum, India, 1997; pp. 1, 19.

37. Mani, K. M. J Membr Sci 1991, 58, 117.

38. Tanaka, Y. J Membr Sci 1991, 57, 217.

39. Elmidaoui, A.; Pourcelly, G.; Gavach, C. J Chim Phys 1996, 93, 386.

40. Handbook of Chemistry: Pure Chemistry, 3rd ed.; Chemical Society of Japan, Vol. II, 1991; p. 339.