

## Concentration of Organic Electrolytes by Electrotransport using Polyethylene Films Photografted with Ionic Monomers

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The concentration of organic electrolytes by electrotransport was investigated using polyethylene (PE) films photografted with 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methacrylic acid (MAA). Organic anions and cations were uphill transported against their concentration gradient toward the anode and cathode sides, respectively. Benzoic acid (BA, weak acid), benzenesulfonic acid (BSA, strong acid) and *p*-aminobenzoic acid (*p*-ABA, ampholyte) were concentrated by use of DMAMMA-grafted PE (PE-g-PDMAEMA) films and their degrees of concentration amounted to more than 90%. L-phenylalanine (PhAN, weak base) was concentrated using MAA-grafted PE (PE-g-PMAA) films and its degree of concentration went up to 95%. For a PE-g-PDMAEMA at the grafted amount of 7.5 mmol/g and PE-g-PMAA at 12.5 mmol/g, the time required for organic electrolytes to be concentrated was the shortest and their degrees of concentration had the maximum values. Organic electrolytes were effectively concentrated in a considerably short time, when the charge sign of their ionizable functional groups was opposite to that of ionizable functional groups affixed to the grafted polymer chains. Organic electrolytes were highly concentrated by the application of a low direct current in water medium with ionic grafted PE films.

**Key words:** polyethylene, photografting, methacrylate monomer, electrotransport, concentration

### 1. INTRODUCTION

Recently the interest toward the preparation of grafted polymeric membranes and membrane separation techniques using them is growing rapidly. Researchers have drawn attention to polyethylene (PE) films photografted with hydrophilic monomers in their excellent water absorptivities and reasonable mechanical strength in the water-swollen state [1,2]. Understanding carrier-mediated transport across membranes is of great importance in the development of novel chemical separation systems.

Since the grafted polymer chains are covalently bonded to the polymer substrate at one of the ends, they have good mobilities dependent on the nature of an aqueous medium such as pH, ionic strength, electric field, and temperature. Charge of inorganic and organic electrolytes also plays an important role in their transport in synthetic membrane systems. In such systems, the mobilities of ions were strongly affected by the fixed charge of the membranes. In addition, positively or negatively charged functional groups affixed to the grafted polymer chains may act as a highly mobile fixed carrier, whereby the mechanism that contributes to uphill transport of electrolytes through the membrane is formed.

In our previous studies, organic electrolytes with positively charged groups such as benzoic acid (BA), benzenesulfonic acid (BSA), and *p*-aminobenzoic acid (*p*-ABA) were uphill transported using the pH difference across PE films grafted with 2-(dimethylamino)ethyl methacrylate (PE-g-PDMAEMA) as a driving force and their concentrations were increased by 1.7~1.8 times their initial concentrations [3-5]. However, it took as long as 100-150 hrs to concentrate the above organic electrolytes. Accordingly, we paid attention to the concentration of organic electrolytes by electrotransport in an attempt to shorten the time required for organic electrolytes to be concentrated and increase further their degrees of concentration.

In this study, we have carried out the concentration of organic electrolytes with charged functional groups by electrotransport using PE-g-PDMAEMA and methacrylic acid (MAA) grafted PE (PE-g-PMAA) films and studied the dependence of the grafted amount, direct current, and initial concentration on the degree of concentration.

### 2. EXPERIMENTAL

#### 2.1 Photografting

A PE (thickness : 30  $\mu\text{m}$ , density : 0.924  $\text{g}/\text{cm}^3$ )

film, cut into 6.0 cm length and 3.0 cm width, was dipped for 1 min in a 50 cm<sup>3</sup> of an acetone solution containing 0.25 g benzophenone (BP) as a sensitizer to coat the PE surface with BP. The photograftings of DMAEMA and MAA onto the BP-coated PE films were carried out by applying UV rays emitted from a 400 W high pressure mercury lamp to each aqueous monomer solution at 1.0 mol/dm<sup>3</sup> in the Pyrex glass tubes. The pH value of the aqueous DMAEMA solution was adjusted to 8.0 with conc. HCl before the photografting [6]. The grafted amounts were calculated from the weight increase in the PE films in mmol/g [1].

## 2.2 Electrotransport

Concentration experiments by electrotransport were carried out in a cell consisting of two chambers at 25 °C. A grafted PE film was swollen in water prior to use. The grafted PE film sandwiched between two platinum mesh electrodes was laid out in the middle of the two chambers of the cell [7]. A 100 cm<sup>3</sup> of aqueous solution of BA (weak acid), BSA (strong acid), phenylalaninol (PhAN, weak base), or *p*-ABA (ampholyte) at 10 mmol/dm<sup>3</sup> was put in both chambers of the cell, and then the direct current was continuously applied. The concentration of organic electrolytes was spectrophotometrically measured after an appropriate dilution of the aliquotes taken from the solutions in the anode and cathode sides with distilled water at a regular time interval (at 219 nm for BA and BSA, at 216.5 nm for *p*-ABA, and at 212 nm for PhAN). The degrees of concentration of organic electrolytes used were calculated from their maximum concentration,  $C_{max}$ , and the initial concentration,  $C_{int}$ , using eq. (1),

$$\text{Degree of concentration (\%)} = \frac{C_{max} - C_{int}}{C_{int}} \cdot 100. \quad (1)$$

## 3. RESULTS AND DISCUSSION

### 3.1 Electrotransport using a PE-g-PDMAEMA film

The direct current was applied to the aqueous solutions of BA and BSA using a PE-g-PDMAEMA film with the grafted amount of 7.5 mmol/g. Figure 1 shows the changes in the BA and BSA concentrations and the pH values in the anode and cathode sides with the time. The BA and BSA concentrations in the anode sides increased because benzoate and benzenesulfonate anions migrated toward the anode through the PE-g-PDMAEMA film.

Bubbles produced in the vicinity of the electrodes during the application of the direct current were frequently removed lest the electrical resistance should increase. The degrees of concentration of BA and BSA calculated from equation 1 amounted to 89 % and 96 % by the continuous application of the direct current for 6 hrs and 4 hrs,

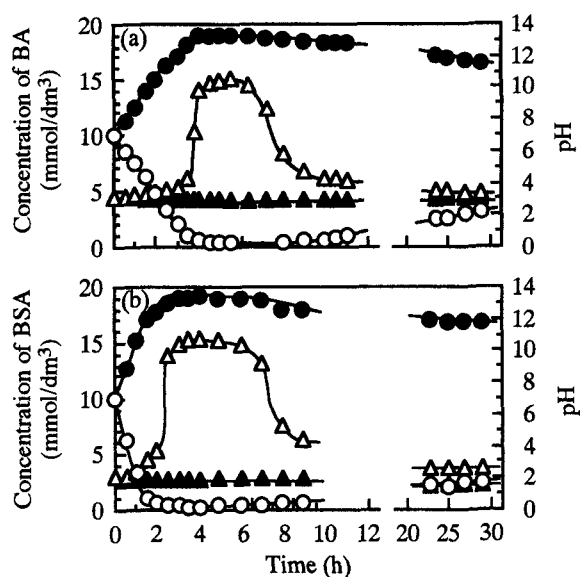


Figure 1 Changes in the concentrations (○,●) of (a) BA and (b) BSA and the pH values (△,▲) in the cathode (shaded) and anode (open) sides with the time for a PE-g-PDMAEMA film of 7.5 mmol/g.

respectively. The time required for BSA to be concentrated (referred as the concentration time below) was shorter than that for BA. The degree of dissociation of BSA was calculated to be 0.83 from the pH value of 2.08 for an aqueous BSA solution at 10 mmol/dm<sup>3</sup>. This indicates that most of BSA molecules exist in the anionic form in water solution. Therefore, BSA is more effectively transported toward the anode side than BA as a weak acid with the pK<sub>a</sub> value of 4.20 [8]. It took as long as 100 hrs and 150 hrs for BA and BSA to be concentrated by 1.8 to 1.9 times their initial concentrations even under the optimum conditions by uphill transport using the pH difference across the PE-g-PDMAEMA film [4,5]. The concentration time was reduced by one twenty-fifth and the degrees of concentration further could increase by use of electrotransport instead of the pH difference across PE-g-PDMAEMA films as driving force to concentrate BA and BSA.

The pH values in the anode sides slightly decreased due to an increase in the BA and BSA concentrations. On the other hand, the pH values in the cathode sides sharply increased due probably to water splitting. During the application of the direct current, concentration gradients are built in the membrane interface because of a large difference between the mobilities of ions in the solution and in the membrane phase [9,10]. In addition, under severe conditions of the concentration polarization, the ion concentration at the membrane interface tend to zero, and then water splitting occurs and the pH value of the solution changes remarkably [11].

When the direct current was applied to an aqueous solution of phenyl-1,2-ethanediol (PhED) as a neutral phenyl compound at 10 mmol/dm<sup>3</sup> using the PE-g-

PDMAEMA film, the pH values in the anode and cathode side changed without the change in the PhED concentration. This means the occurrence of water splitting.

### 3.2 Electrotransport using a PE-g-PMAA film

Electrotransport of PhAN was carried out using a PE-g-PMAA film of 12.5 mmol/g. Figure 2 shows the changes in the PhAN concentrations and the pH values in the anode and cathode sides with the time. The PhAN concentration in the cathode side increased with the passage of time and the degree of concentration went up to 97%. When the direct current was turned off after the BA and PhAN concentrations reached the maxima as shown in Figures 1 and 2, the pH difference across the grafted PE films became smaller because the neutralization occurred between permeated  $\text{OH}^-$  and  $\text{H}^+$  ions in the anode sides and the BA and PhAN concentrations gradually decreased due to the diffusive permeation across the grafted PE films. The degrees of concentration had still 70% for BA and 75% for PhAN even in 20 hrs after the direct current was turned off. The relatively high concentrations of BA and PhAN are maintained due to low permeabilities to BA of the PE-g-PDMAEMA film and to PhAN of the PE-g-PMAA film, even if the direct current is turned off.

The concentration of BA and PhAN by electrotransport was carried out using a PE film grafted with methacrylamide (MAAm) as a neutral hydrophilic monomer. The MAAm-grafted PE (PE-g-PMAAm) film of 40 mmol/g possessed little electrical conductivity [1]. As a result, BA and BSA were not electrically transported. It can be understandable from the above results that positively or negatively chargeable functional groups on the grafted polymer chains are needed in order to concentrate organic electrolytes by electrotransport.

When the direct current was applied to an aqueous *p*-ABA solution using a PE-g-PDMAEMA film of 7.5 mmol/g, *p*-ABA was transported to the anode side in the same manner as BA and BSA and the degree of concentration of *p*-ABA amounted to 95% by the application of the direct current for 4 hrs. The pH value of

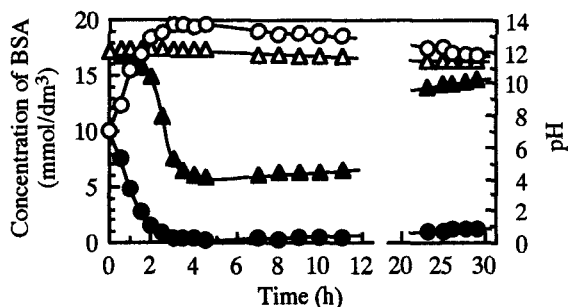


Figure 2 Changes in the concentrations of PhAN (○,●) and the pH values (△,▲) in the cathode (shaded) and anode (open) sides with the time for a PE-g-PMAA film of 12.5 mmol/g.

an aqueous *p*-ABA solution of 10 mmol/dm<sup>3</sup> was 3.8 which was higher than the isoelectric point, pI, of 3.63 of *p*-ABA. Therefore, some of *p*-ABA molecules existed in the negative charged form (pH 3.8 at 10 mmol/dm<sup>3</sup>).

In the case the direct current was applied to the aqueous solutions of BA, BSA, and *p*-ABA using the PE-g-PMAA films, the concentrations of the three kinds of organic electrolytes described above and the pH values in the cathode and anode sides underwent no changes. The main reason for the above results is as follows: benzoate and benzenesulfonate anions have the same charge sign as carboxylate anions produced by dissociation of carboxyl groups affixed to grafted PMAA chains. Some of *p*-ABA molecules exist in the anionic form, since the pH value of an aqueous *p*-ABA solution of 3.7 is higher than the pI value of *p*-ABA of 3.63 [8]. It is apparent from these phenomena that the electric current flows without the migration of phenyl anions by electrotransport through PE-g-PMAA film and no water splitting takes place.

### 3.3 Dependence of concentration on the grafted amount, initial concentration, and direct current

The dependence of the degrees of concentration of BA and PhAN on the grafted amounts of PE-g-PDMAEMA and PE-g-PMAA films, respectively, was examined. Figure 3 shows the variations in the degrees of concentration of BA and PhAN and the concentration time with the grafted

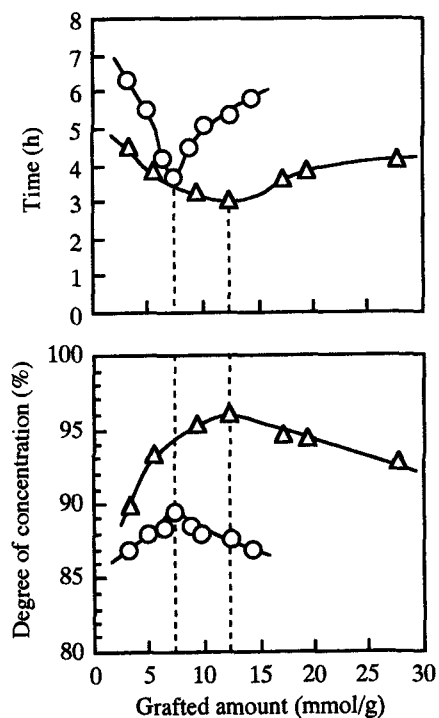


Figure 3 Variations in the concentration time and the degree of concentration with the grafted amount for the BA/PE-g-PDMAEMA film (○) and PhAN/PE-g-PMAA film (△) systems.

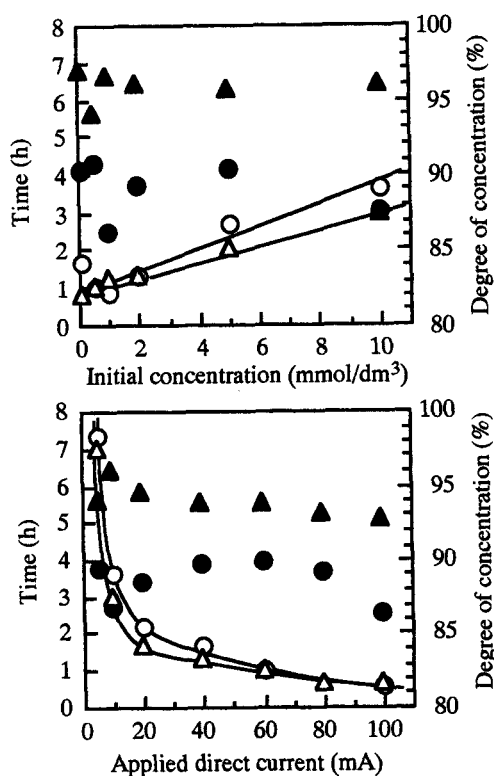


Figure 4 Changes in the concentration time (open) and the degree of concentration (shaded) with (a) the initial concentration and (b) the applied direct current for the BA/PE-g-PDMAEMA film (○,●) and PhAN/PE-g-PMAA film (△,▲) systems.

amounts. The degrees of concentration had the maximum values and the concentration time was the shortest at 7.5 mmol/g for the BA/PE-g-PDMAEMA film systems and at 12.5 mmol/g for PhAN/PE-g-PMAA film systems. Since the PE films are made hydrophilic by the photograftings of ionic monomers, the amount of positively or negatively chargeable functional groups increases with the grafted amount. Therefore, the degrees of concentration of BA and PhAN increase and their concentration time shorten with an increase in the grafted amount. However, since an increase in the grafted amount is accompanied by an increase in the thickness of the grafted PE films [1,4], the transport rate decreases with an increase in the grafted amount and the concentration time of BA and PhAN become longer above the grafted amount of 7.5 mmol/g for PE-g-PDMAEMA films and 12.5 mmol/g for PE-g-PMAA films.

The effects of the initial concentrations of BA and PhAN and the applied direct current on the degree of concentration and their concentration time were also examined using a PE-g-PDMAEMA film of 7.5 mmol/g and a PE-g-PMAA film of 12.5 mmol/g. Figure 4 (a) and (b) shows the changes in the degree of concentration and the concentration time with the initial concentrations of BA and PhAN and the direct current, respectively. It is understandable that the transport efficiency of BA and

PhAN decreases with an increase in their initial concentrations at a constant direct current of 10 mA. Therefore, the concentration time became longer, as their initial concentrations increased. The degrees of concentration ranging from 88 to 90 % for BA and ranging from 93 to 95 % for PhAN were obtained regardless of their initial concentrations. In addition, as the applied direct current was increased at a constant concentration of 10 mmol/dm<sup>3</sup> for BA and PhAN, their concentration time was shortened. The values of both degrees of concentration were kept almost constant in the range of the direct current of 5-100 mA. This suggests that the rates of migration of benzoate anions and phenylalaninol cations through the grafted PE films per unit time increase with an increase in the applied direct current and the total amounts of the phenyl ions migrated during the application of the direct current are almost independent of the applied direct current.

Organic electrolytes could be highly concentrated in a short time over a wide concentration range of 0.1 to 10 mmol/dm<sup>3</sup> by electrotransport using the PE-g-PDMAEMA and PE-g-PMAA films. The concentration time was further shortened by the application of increased direct current. Electrotransport using the PE-g-PDMAEMA and PE-g-PMAA films is one of the effective techniques to concentrate organic electrolytes and this technique can be expected to be applied for the recovery and reuse of organic electrolytes.

#### 4. REFERENCES

1. K. Yamada, S. Tatekawa, and M. Hirata, *J. Colloid Interface Sci.*, **162**, 144-50 (1994).
2. K. Yamada, T. Sato, S. Tatekawa, and M. Hirata, *Polym. Gels Networks*, **2**, 323-31 (1994).
3. K. Yamada, K. Sato, and M. Hirata, *Function & Materials (Ki no Zai ryo)*, **16** (11), 5-12 (1996) [in Japanese].
4. K. Yamada, K. Sato, M. Hirata, *J. Mater. Sci.*, **34**, 1081-91 (1999).
5. K. Yamada and M. Hirata, "Recent Research Development in Polymer Science", Ed by S. G. Pandalai, Trans world Research Network, Trivandrum (1997) pp. 19-36.
6. K. Hayashi, S. Tatekawa, F. Igi, K. Yamada, T. Ebihara, and M. Hirata, *Chem. Soc. Jpn., Annu. Mtg. Abstr.*, **1 C8 31** (1992) [in Japanese].
7. K. Yamada, K. Sasaki, and M. Hirata, *ACS Symp. Ser.*, in press.
8. Handbook of Chemistry: Pure Chemistry, 3rd Ed., Ed. by Chem. Soc. Jpn., Vol. II, p339 (1991).
9. K. M. Mani, *J. Membrane Sci.*, **58**, 117-38 (1991).
10. Y. Tanaka, *J. Membrane Sci.*, **57**, 217-35 (1991).
11. M. Taky, A. Elmidaoui, G. Pourcelly, C. Gavach, *J. Chim. Phys.*, **93**, 386-401 (1996).