

## Adsorption and Desorption Properties of Cationic Polyethylene Film Gels To Anionic Organic Compounds and Their Regeneration

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An investigation was undertaken on adsorption and desorption properties of 2-(dimethylamino)ethyl methacrylate (DMAEMA)-grafted PE (PE-g-PDMAEMA) films using anionic dye molecules with 1 to 3 sulfonic groups at different pH levels and 25 °C. The amounts of dye anions adsorbed onto the PE-g-PDMAEMA films passed the maximum values at about pH 3. This is due to an increase in the protonation of dimethylamino groups with a decrease in the pH level. However, the adsorbed amounts decreased below pH 3, since the ionic strength increased by the addition of HCl to adjust the initial pH level. The adsorbed amounts decreased with an increase in the number of sulfonic groups in the dye molecules, because free sulfonic groups in the adsorbed dye anions would prevent dye anions in the solutions from diffusing into the PE-g-PDMAEMA films due to the electrostatic repulsion. A large portion of dye anions adsorbed were desorbed at above the initial pH level of 11.0. The cyclic processes of adsorption at pH 3.0 and desorption at pH 11.0 were repeated without considerable fatigue. The above results show that the PE-g-PDMAEMA films can be used as a repeatedly regenerative ion-exchange membrane for adsorption and desorption of anionic compounds.

Key words: polyethylene, photografting, 2-(dimethylamino)ethyl methacrylate, adsorption, desorption

### 1. INTRODUCTION

It has been stressed, recently, that color compounds such as dyes and pigments discharged from several industries are very harmful to aquatic life in rivers. Therefore, it is very important to get rid of them from the effluents not only for removal of the color of water but also for environmental preservation. However, most of them are considered to be non-oxidizable substances by conventional, biological, and physical treatments because of their complex structure and larger molecular size [1, 2].

The methods of color removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation, hyperfiltration, and so on. Among these treatment options, adsorption appears to have considerable potential for the removal of color from industrial effluents. The possibility of an adsorption process to remove color compounds has been investigated with ion exchange membranes. The advantages of an adsorption system for controlling water pollution are less space, lower capital investment, simple design and easy operation of the equipments, and efficient removal of organic waste constituents as compared with the conventional biological treatment process [3].

We have prepared various functional membranes with practical mechanical strength by the photograftings of ionic monomers throughout the bulk of polyethylene (PE) films [4]. The grafted PE films have been shown to have promise for various membrane separation techniques such as uphill transport [5, 6] and selective separation [7]. Then, the pH [5] and electric potential [6, 7] differences were applied to the source of the driving force. In addition, weakly basic or weakly acidic

polyelectrolytes play an important role in the membrane separation by the adsorption and desorption processes, because the positively or negatively charged functional groups can be changed reversibly and rapidly in response to a pH change of the surrounding solution.

In this study, an investigation was undertaken on adsorption and desorption properties of 2-(dimethylamino)ethyl methacrylate (DMAEMA)-grafted PE (PE-g-PDMAEMA) films using anionic dye molecules with 1 to 3 sulfonic groups at different pH levels and 25 °C. In addition, the reusabilities of PE-g-PDMAEMA film was examined by alternatively repeating the cyclic processes of adsorption and desorption.

### 2. EXPERIMENTAL

#### 2.1 Photografting

A PE film (thickness, 30  $\mu\text{m}$ ; density, 0.924  $\text{g}/\text{cm}^3$ ) supplied from Tamapoly Co. Ltd., (Japan) was used as a polymeric substrate. The photografting of DMAEMA onto the PE films and membrane properties of the PE-g-PDMAEMA films prepared were described in our previous papers in detail [4, 8-10]. The PE films (60  $\times$  30 mm) were dipped in an acetone solution containing 0.25 g benzophenone (BP) as a sensitizer to coat their surfaces. DMAEMA were photografted onto the BP-coated PE films at 60 °C by applying UV rays emitted from a 400 W high pressure mercury lamp in an aqueous PDMAEMA monomer solution adjusted to pH 8 with conc. HCl to obtain PE-g-PDMAEMA films with a high grafted amount.

#### 2.2 Adsorption and desorption

PE-g-PDMAEMA films of the grafted amount of 10.5 mmol/g-PE film cut into 10  $\times$  10 mm<sup>2</sup> were immersed in

the aqueous dye solutions at different pH levels of 2.0 to 12.0 with an appropriate stirring at 25 °C [9]. The dye molecules with 1 to 3 sulfonic groups were used as model anionic organic compounds (1 : metanil yellow (MY), 2 : indigo-carmin (IC), 3 : amaranth (AM)). The amounts of adsorbed dye anions were spectrophotometrically determined at 466, 610, and 475 nm for MY, IC, and AM, respectively. The dye anion-adsorbed PE-g-PDMAEMA films were immersed in the aqueous HCl or NaOH solutions ( $V = 50 \text{ cm}^3$ ) at the initial pH levels of 2.0 to 12.0. The solutions were stirred at 25 °C and the amounts of desorbed dye anions were spectrophotometrically determined in the same way as described above.

### 3. RESULTS and DISCUSSION

#### 3.1 Langmuir adsorption isotherm

The ion-exchange capacities of PE-g-PDMAEMA films increased with the grafted amount and were higher than those of commercially available ion-exchange membranes at the grafted amounts more than 5 mmol/g-PE film. The degree of ion-exchange went up to over 97 % regardless of the grafted amount.

The PE-g-PDMAEMA films with the grafted amount of 10.5 mmol/g-PE film swollen to the equilibrium state in distilled water were immersed in the aqueous solutions of MY, IC, and AM without the adjustment of the pH levels in the dye concentration ranging 0.05 ~ 3.0 mM at 25 °C. The adsorption of three kinds of dye anions onto the PE-g-PDMAEMA film was analyzed according to the Langmuir adsorption isotherm equation:

$$C_{eq}/Q_{eq} = 1/Qb + C_{eq}/Q \quad (1)$$

where  $C_{eq}$  is the free dye concentration in the outer solution at equilibrium;  $Q_{eq}$ , the amount of adsorbed dye anions per gram of PE-g-PDMAEMA film;  $Q$ , the maximum amount of adsorbed dye anions; and  $b$ , the Langmuir constant [11, 12]. The equilibrium concentration and the adsorbed amount bore a linear relationship in Langmuir adsorption isotherm equation for three kinds of dyes as shown in Figure 1. The maximum amounts of adsorbed dye anions,  $Q$ , determined from the slopes and intercepts of the straight lines shown in Figure 1 increased with an increase in the number of sulfonic groups in the dye molecules. Some of the IC and AM anions adsorbed on the protonated dimethylamino groups through ionic bonding can have

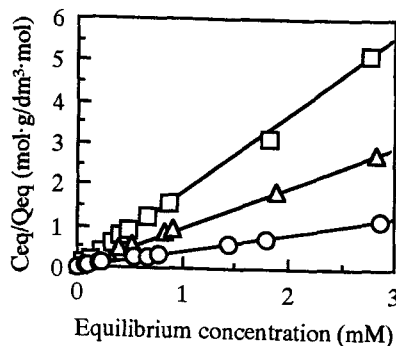


Figure 1 Change in the  $C_{eq}/Q_{eq}$  value with the equilibrium concentration of MY (O), IC ( $\Delta$ ), and AM ( $\square$ ) for a PE-p-PDMAEMA film of 10.5 mmol/g at 25 °C.

free sulfonic groups. Therefore, the ionic repulsion can be brought about between the adsorbed IC and AM anions and free IC and AM anions, and consequently the diffusion of IC and AM anions into the grafted layers would be depressed.

#### 3.2 pH dependence of adsorption

The pH dependence of the adsorption of three kinds of dye anions on a PE-g-PDMAEMA film of 10.5 mmol/g-PE film was investigated in the aqueous solutions of MY, IC, and AM of 0.5 mM at the pH levels ranging 2.0 to 12.0. The PE-g-PDMAEMA films were equilibrated in an aqueous solution of HCl or NaOH, the pH levels of which were equal to those of the aqueous dye solutions prior to the adsorption experiments. Figure 2 shows the variations in the amount of adsorbed dye anions with the equilibrium pH level. The adsorbed amounts for three kinds of dye anions used here increased with a decrease in the equilibrium pH level and passed through the maximum values at about pH 3. This pH-dependence of adsorption for the dye anions can be explained from the fact that the degree of protonation of dimethylamino groups of PDMAEMA determined by the colloid titration described in ref. [5] increases with a decrease in the pH level. On the other hand, the decrease in the adsorbed amounts below pH 3 is probably due to an

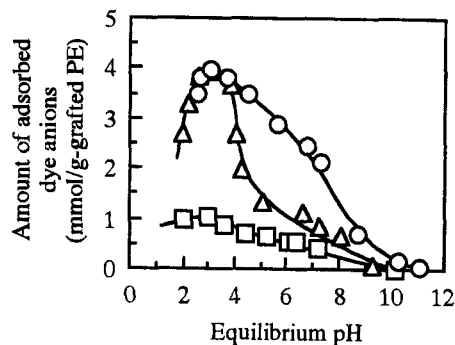


Figure 2 Variations in the amount of adsorbed MY (O), IC ( $\Delta$ ), and AM ( $\square$ ) anions with the equilibrium pH level for a PE-p-PDMAEMA film of 10.5 mmol/g at 25 °C : initial dye concentration = 0.5 mM.

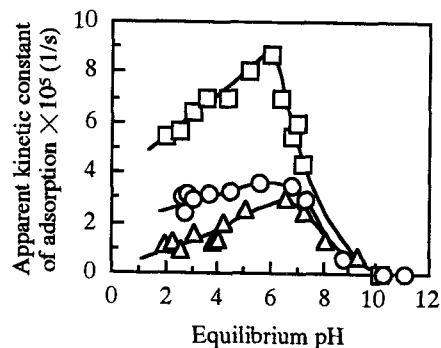


Figure 3 Variations in the apparent kinetic constant of adsorption of MY (O), IC ( $\Delta$ ), and AM ( $\square$ ) anions with the equilibrium pH level for a PE-p-PDMAEMA film of 10.5 mmol/g at 25 °C: initial dye concentration = 0.5 mM.

increase in the ionic strength by the addition of HCl to badjust the initial pH levels of the dye solutions. The lower the number of the sulfonic groups in a dye molecule, the more the adsorbed amount irrespective of the equilibrium pH level. The decrease in the adsorbed amount for IC and AM anions would be mainly attributable to the electrostatic repulsion between free sulfonic groups of dye anions adsorbed onto the protonated dimethylamino groups and free dye anions in the medium.

The adsorption of dye anions onto protonated dimethylamino groups was assumed to proceed in the first order-like reaction, and the kinetic constants of adsorption,  $k$ , were calculated using eq. (2):

$$\ln(1-Q_t/Q_{eq}) = -kt \quad (2)$$

where  $Q_t$  was the adsorbed amount at the immersion time  $t$  [12]. Since a plot of  $\ln(1-Q_t/Q_{eq})$  against the immersion time,  $t$ , gave a straight line, the apparent kinetic constant of adsorption was calculated from its slope. Figure 3 shows the variations of the kinetic constant of adsorption with the equilibrium pH level. The kinetic constants of adsorption passed through the maximum values at around pH 6. At this pH level, the reduced viscosity of an aqueous PDMAEMA solution had the maximum value [13]. The expansion of grafted PDMAEMA chains caused by the electrostatic repulsion between protonated dimethylamino groups would facilitate the adsorption of dye anions. The value of kinetic constant of adsorption for AM anion was much higher than those for MY and IC anions, since the adsorption of AM anions with three sulfonic groups would be restricted to the surface region of the grafted layers, and so the adsorption equilibrium was reached at shorter times as compared with MY and IC anions.

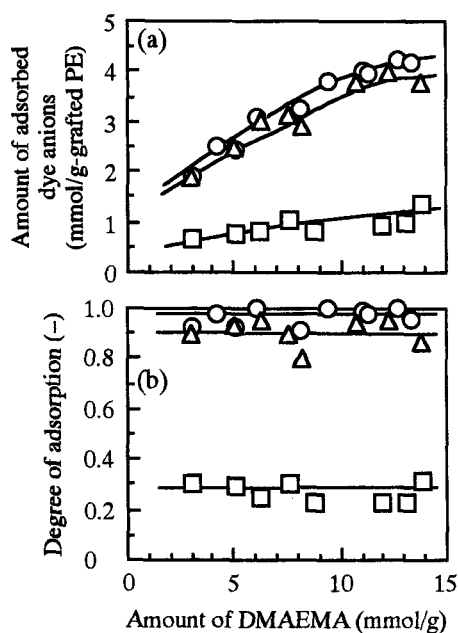


Figure 4 Variations in (a) the amount of adsorbed MY (○), IC (△), and AM (□) anions and (b) the degree of adsorption with the grafted amount at the initial pH level of 3.0 and 25 °C : initial dye concentration = 0.5 mM.

### 3.3 Grafted amount dependence of adsorption

The adsorption of the dye anions was investigated using PE-g-PDMAEMA films with 3 to 15 mmol/g-PE film at the initial pH level of 3.0 at which their adsorbed amounts had the maximum values as shown in Figure 2.

Figure 4 (a) and (b) shows the changes in the adsorbed amount and degree of adsorption with the grafted amount, respectively. The adsorbed amounts increased with an increase in the grafted amount and the degree of adsorption was kept almost constant. The increase in the number of sulfonic groups in the dye molecules resulted in the decrease in the degree of adsorption (95 % for MY, 85 % for IC, and 30 % for AM). It is understandable from the value of the degree of adsorption for MY anions that most of the protonated dimethylamino groups act as the adsorption site for MY anions. The degree of adsorption of 85 % for IC anions was higher than the calculated value of 50 % obtained for the adsorption of all sulfonic groups in the IC molecules onto the protonated dimethylamino groups through the ionic bonding. Therefore, free sulfonic groups in the adsorbed IC anions can be considered to slightly decrease the adsorption as compared with the adsorption of MY anions due to the electrical repulsion. In addition, the degree of adsorption was considerably low for an AM anion with 3 sulfonic groups because of the effective repulsive interaction between the adsorbed AM anions and free AM anions in the medium and the relatively large molecular size. It can be safely said that the adsorption of AM anions is restricted to the surface region of the grafted layers. Figure 5 shows the changes in the kinetic constant of adsorption obtained from the slopes of the straight lines of  $\ln(1-Q_t/Q_{eq})$  against the immersion time with the grafted amount for the dye anions used here. The kinetic constant of adsorption for AM anions decreased with an increase in the grafted amount. On the other hand, the kinetic constants of adsorption for MY and IC anions were lower than that of AM anion and ranged from 1 to  $2.5 \times 10^{-5}$  (1/s) independent of the grafted amount. It is considered that the adsorption of AM anions is restricted in the vicinity of the outer surface region of the grafted layers and the adsorption equilibrium is reached at a short time.

### 3.4 pH dependence of desorption

After the adsorption of dye anions onto the PE-g-

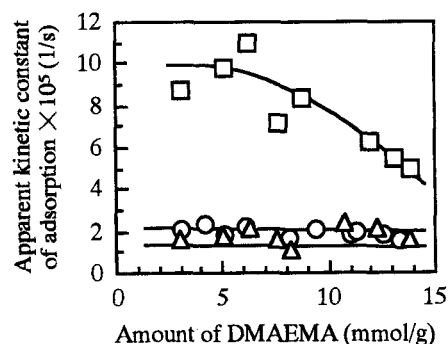


Figure 5 Variations in the apparent kinetic constant of adsorption of MY (○), IC (△), and AM (□) anions with the grafted amount at the initial pH level of 3.0 and 25 °C : initial dye concentration = 0.5 mM.

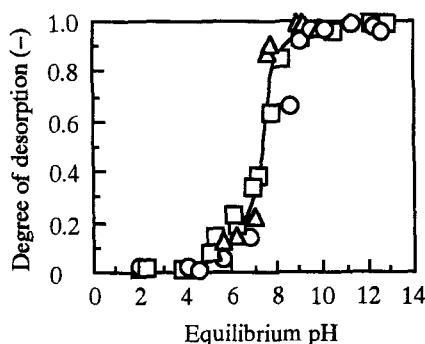


Figure 6 Changes in the degree of desorption of MY (○), IC (△), and AM (□) anions with the equilibrium pH level for a PE-p-PDMAEMA film of 10.5 mmol/g at 25 °C : initial dye concentration = 0.5 mM.

PDMAEMA films of 10.5 mmol/g-PE film was equilibrated, the PE-g-PDMAEMA films were immersed in an aqueous solution of HCl or NaOH at pH 2 to 13. Figure 6 shows the changes in the degree of desorption that represents the ratio of the desorbed amount to the adsorbed amount with the equilibrium pH level. The degree of desorption increased with an increase in the equilibrium pH level and the quantities of dye anions desorbed of about 100 % were desorbed at the equilibrium pH levels above 9, because a decrease of protonation of dimethylamino groups promote the liberation of dye anions adsorbed on the grafted PDMAEMA chains through the ionic interaction [8].

### 3.5 Repetitive cycles of adsorption and desorption

The reusabilities of the PE-g-PDMAEMA films were examined by alternately repeating the cyclic process of adsorption at the initial pH level of 3.0 and desorption at the initial pH level of 11.0. Figure 7 shows the three successive MY anion adsorption-desorption cycles. When the PE-g-PDMAEMA film of 10.5 mmol/g-PE film was put back to a aqueous MY solution at the initial pH level of 3.0 after the first desorption process, MY anions immediately started to adsorb onto the PE-g-PDMAEMA film. The amounts of adsorbed and desorbed dye anions were almost equivalent in each cyclic process of adsorption and desorption. This

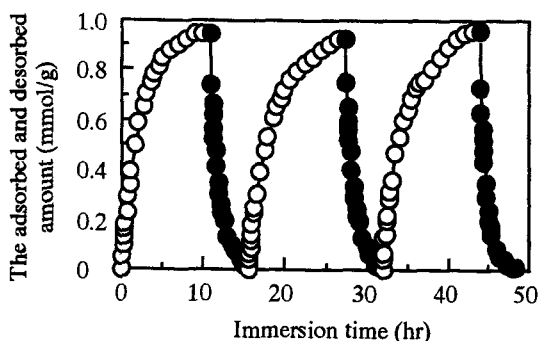


Figure 7 Alternately repeated cyclic process of adsorption at the initial pH level of 3.0 (○) and desorption (●) at the initial pH level of 11.0 for a PE-p-PDMAEMA film of 10.5 mmol/g at 25 °C.

indicates that the PE-g-PDMAEMA films are practically acid- and alkali-proof and can endure several cycles of adsorption and desorption experiments without considerable fatigue.

It becomes apparent from the above results that the PE-g-PDMAEMA films can be used as a repeatedly regenerative weakly basic ion-exchange membrane for adsorption and desorption of dye anions.

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