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Adsorption and Desorption Properties of Cationic Polyethylene Film Gels to an Anionic Compound

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An investigation was undertaken on the adsorption and desorption properties of DMAEMA grafted (PE-g-PDMAEMA) PE films using indigocarmine (IC) as an anionic organic compound at different pH values and 25 °C. The amount of IC anions adsorbed onto PE-g-PDMAEMA films had the maximum at about pH 3. This is due to an increase in the protonation of dimethylamino groups with a decrease in the pH value. However, the adsorbed amount decreased below pH 3, since the ionic strength increased by the addition of HCl to adjust the initial pH value. It was found from analysis according to Langmuir adsorption isotherm equation that IC anions were electrostatically bonded to protonated dimethylamino groups in the 1:1 stoichiometry. The desorption of IC anions from PE-g-PDMAEMA films had the maximum at the initial pH value of 11.0. The cyclic process of adsorption at the initial pH value of 3.0 and desorption at the initial pH of 11.0 was alternately repeated without any appreciable fatigue of the PE-g-PDMAEMA film. It was made clear that the PE-g-PDMAEMA films were used as a repeatedly regenerative weakly basic ion-exchange membrane for adsorption and desorption of IC anions.

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

1. INTRODUCTION

It is possible to prepare functional membranes with practical mechanical strength by photografting various monomers throughout the bulk of polyethylene (PE) films [1,2]. PE films grafted with ionic monomers could absorb a considerable amount of water and possessed reasonable mechanical properties in the swollen state [1-3].

The grafted PE films have been shown to have promise for various membrane separation techniques such as uphill transport [4-8] and selective separation [7]. The pH [4-6] and electric potential [7,8] differences across the grafted PE films were applied to the source of the driving force.

In addition, membrane separation of anionic or cationic compounds by adsorption and desorption with ion exchange membranes is a potentially attractive process for the removal of undesirable ions, purification of waste water, and concentration or recovery of valuable materials with low energy and operating cost. However, few studies have been reported on the equilibrium isotherms for adsorption of anionic and cationic compounds on weakly basic or weakly acidic ion-exchange membranes. Here, weakly basic or weakly acidic polyelectrolytes play an important role in the membrane separation by adsorption and desorption because the positively charged or negatively charged functional groups can be changed reversibly and rapidly in the response to a pH change of the surrounding solution.

In this study, an investigation was undertaken on adsorption and desorption properties of PDMAEMA-grafted PE (PE-g-PDMAEMA) films using indigocarmine (IC) as a model anionic compound (strong electrolyte) at different pH values and 25 °C. In addition, the reusabilities of PE-g-PDMAEMA film were examined by alternately repeating the cyclic process of adsorption and desorption experiments.

2. EXPERIMENTAL

2.1 Photografting

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 photografting of DMAEMA onto PE films was carried out by the same method described previously [2].

2.2 Ion exchange capacity

PE-g-PDMAEMA films equilibrated in a 1.0

mol/dm^3 NaOH were immersed in a 0.1 mol/dm^3 of HCl (volume 100 cm^3) with an appropriate stirring at 25 °C for 36 hrs. The PE-g-PDMAEMA films were then removed and the outer solutions were titrated with a 0.1 mol/dm^3 of NaOH. The ion exchange capacity was calculated on the basis of specific weight of the PE-g-PDMAEMA film (mmol/g-dry membrane).

2.3 Adsorption and desorption

PE-g-PDMAEMA films of the grafted amount of 10.5 mmol/g cut into 10 × 10 mm square were immersed in the aqueous IC solutions of 50 cm^3 at the initial pH values of 2.0 to 12.0 with an appropriate stirring at 25 °C. The amount of IC anions adsorbed onto the PE-g-PDMAEMA films was spectrophotometrically determined at 610 nm at a regular time interval.

The PE-g-PDMAEMA films adsorbed IC anions were immersed in a 50 cm^3 of aqueous HCl or NaOH solution at the initial pH values of 2.0-12.0. The solutions were stirred at 25 °C and the amount of desorbed IC anions was determined in the same way as described above.

3. RESULTS and DISCUSSION

3.1 Ion-exchange properties

PE-g-PDMAEMA films of different grafted amounts were immersed in a 0.1 mol/dm^3 of HCl at 25 °C, and then the HCl concentration was determined by the titration with NaOH at a regular time interval. Figure 1 shows the ion-exchange properties of PE-g-PDMAEMA films. The ion-exchange capacities increased with the passage of time, and then became constant. The time required for the equilibrium to be reached increased with an increase in the grafted amount due to the formation of the thicker and closer grafted layers at higher grafted amounts. The equilibrium was reached by the immersion of PE-g-PDMAEMA films in HCl for 36 hrs. The ion-exchange capacity increased with the grafted amount. We reported in ref. [2] that the ungrafted layers in the inside of the PE films were disappeared at 5 mmol/g by the photografting of DMAEMA. The ion-exchange capacities of PE-g-PDMAEMA films with more than 5 mmol/cm^2 were higher than those of commercially available ion-exchange membranes (1.5-2.5 meq/g) [9]. In addition, the degree of ion-exchange, ie., the ratio of the grafted amount to the ion-exchange capacity, went up to over 97% regardless of the grafted amount. This indicates that most of the dimethylamino groups are protonated by immersing them in a 0.1 mol/dm^3 of HCl for 36 hrs.

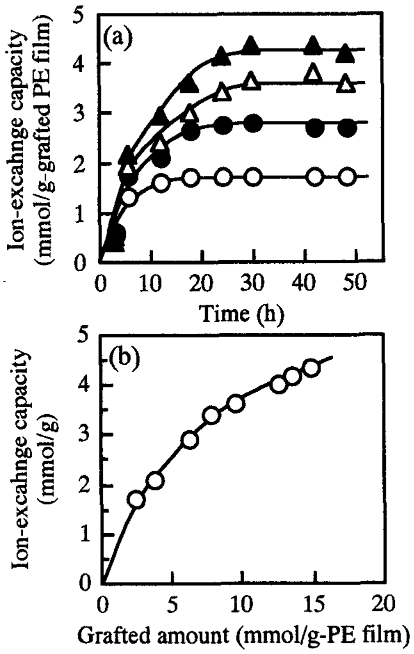

Figure 1 The ion-excahnge properties of PE-g-PDMAMEA films
Grafted amount (mmol/g)-
○:2.5, ●:5.0, △:10.0, ▲:15.0

3.2 Langmuir adsorption isotherm

PE-g-PDMAEMA films of 10.5 mmol/g swollen to the equilibrium state in distilled water were immersed in an aqueous IC solution without the adjustment of the pH values in the IC concentration ranging 0.05 to 1.0 mmol/dm^3 at 25 °C. The amount of IC anions was kept constant above the equilibrium concentration of 0.2 mmol/dm^3. The adsorption of IC anions onto PE-g-PDMAEMA films was analyzed according to the Langmuir adsorption isotherm equation:

$$\frac{Ceq}{Qeq} = \frac{1}{Q \cdot b} + \frac{Ceq}{Q} \qquad (1)$$

where Ceq is the free IC concentration in the outer solution at equilibrium; Qeq, the amount of adsorbed IC anions per gram of PE-g-PDMAEMA film; Q, the maximum amount of adsorbed IC anions; and b, the Langmuir constant [10]. The equilibrium concentration of IC and the amount of adsorbed IC anions bore a linear relationship in Langmuir adsorption isotherm equation as shown in Figure 2 [11]. The maximum amount of adsorbed IC anions, Q, and the Langmuir constant, b, were calculated to be 1.02 mmol/g-dry membrane and 70.9 dm^3/mmol, respectively, from the slope and intercept of the straight line. These results mean that IC anions are electrostatically bonded to protonated

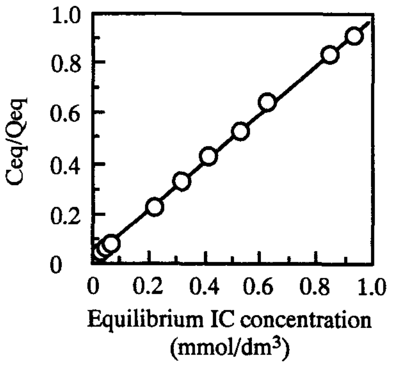

Figure 2 Langmuir isotherm for adsorption of IC anions on PE-g-PDMAEMA film of 10.5 mmol/g in an aqueous IC solution.

dimethylamino groups in the 1:1 stoichiometry.

3.3 pH dependence of adsorption

The pH dependence of the adsorption of IC anions on a PE-g-PDMAEMA film of 10.5 mmol/g was investigated in the aqueous IC solutions of 0.1, 0.3, and 0.5 mmol/dm^3 at the initial pH values of 2.0 to 12.0. The PE-g-PDMAEMA films were equilibrated in an aqueous solution of HCl or NaOH the pH values of which were equal to those of the aqueous IC solutions prior to the adsorption experiments. Figure 3 shows the variations in the adsorbed amount with the equilibrium pH value. The adsorbed amount increased with a decrease in the equilibrium pH value and passed through the maximum values at pH 3. The pH-dependence of the adsorbed amount can be explained in terms of the fact that the degree of protonation of dimethylamino groups increase with a decrease in the pH value [6]. On the other hand, the decrease in the adsorbed amount below pH 3 is mainly due to the increase in the ionic strength by the addition of HCl to adjust the initial pH values of the aqueous IC solutions.

The adsorption of IC anions onto PE-g-PDMAEMA films was assumed to proceed in the first order-like reaction and the kinetic constants of adsorption, k, were calculated using eq (2):

$$\ln(1-\frac{Q_t}{Q_{eq}}) = -k\cdot t \qquad (2)$$

where Qt was the adsorbed amount at time t [12]. Since a plot of ln(1−Qt/Qeq) against t gave a straight line, the kinetic constant of adsorption was calculated from its slope. Figure 4 shows the variations of the kinetic constant of adsorption with the equilibrium pH value. The kinetic constants of adsorption at 0.1 and 0.3 mmol/dm^3 increased with a decrease in the pH value and passed through the maximum values at pH 3. On the other hand, the kinetic constant of adsorption at 0.5 mmol/dm^3 ranged from 1 to 3×10^{-5} (1/s) independent of the equilibrium pH value. It can be understandable from Figures 3 and 4 that as the IC concentration increases below pH 6, the adsorbed amount increases and the kinetic constant of adsorption decreases. In addition, the adsorbed amount at 0.5 mmol/dm^3 and pH 3.0 was in close agreement with the ion-exchange capacity. This fact supposes that adsorption of IC anions onto PE-g-PDMAEMA films proceeds stoichometrically. It is considered that IC anions adsorb onto protonated dimethylamino groups located not only in the vicinity of the outer surface region of the grafted layers but also in the inside of the grafted layers in the equilibrium pH range of 2 to 7.

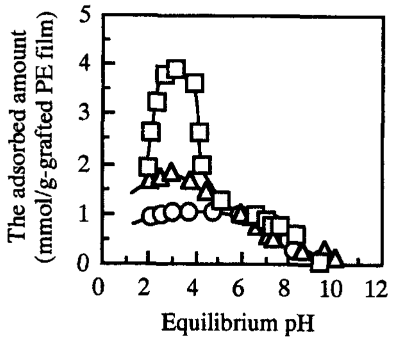

Figure 3 Variations in the absorbed amount with the equilibrium pH value at the initial IC concentrations of 0.1 (○), 0.3 (△), and 0.5 (□)mmol/dm^3.

3.4 pH dependence of desorption

After the adsorption of IC anions onto PE-g-PDMAEMA films of 10.5 mmol/g was equilibrated, the PE-g-PDMAEMA films were immersed in the aqueous HCl or NaOH solution at pH 2 to 11. Figure 5 shows the variations in the degree of desorption of IC anions and the kinetic constant of desorption with the equilib-

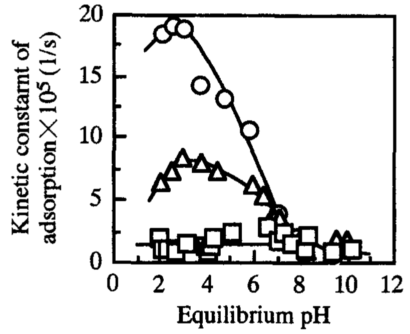

Figure 4 Variations in the kinetic constant of adsorption with the equilibrium pH value at the initial IC concentrations of 0.1 (○), 0.3 (△), and 0.5 (□) mmol/dm^3.

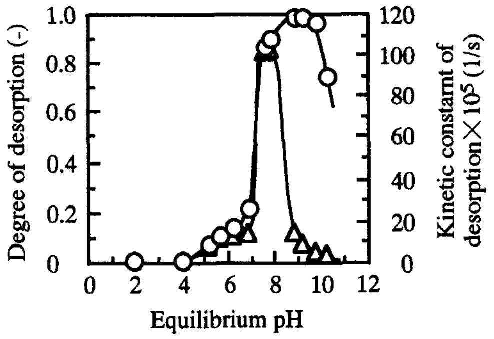

Figure 5 Variations in the degree of desorption of IC anions (○) and kinetic constant of desorption (△) with the equilibrium pH value.

rium pH value. The degree of desorption increased with the equilibrium pH value, since the degree of protonation of dimethylamino groups decreased with an increase in the pH value. Although the degree of desorption had the maximum value and almost all IC anions desorbed at the initial pH value was adjusted to 11.0 (equilibrium pH value = 8.9), it took a long time for the desorption equilibrium to be reached. It is considered that when the deprotonation of protonated dimethylamino groups proceeds, the dense layers form in the vicinity of the surface of PE-g-PDMAEMA film due to the contraction of grafted PDMAEMA chains. On the other hand, the maximum value of the kinetic constant of desorption was obtained at the initial pH value of 10.5 (equilibrium pH value = 7.6). However, the degree of desorption was limited to 90 % because the degree of protonation of dimethylamino groups at pH 7.6 was higher than at pH 8.9.

3.5 Repetitive cycles of adsorption and desorption

The usabilities of PE-g-PDMAEMA films were examined by alternately repeating the cyclic process of adsorption at the initial pH value of 3.0 and desorption at the initial pH value of 11.0. Figure 6 shows the three successive IC anion adsorption-desorption cycles. When the PE-g-PDMAEMA film of 10.5 mmol/g was put back in a aqueous IC solution after the first desorption process, IC anions immediately started to adsorb onto the PE-g-PDMAEMA film. The amounts of adsorbed and desorbed IC anions were almost equivalent in each cyclic process of adsorption and desorption. This indicates that the PE-g-PDMAEMA film is practically acid- and alkali-proof and can endure several cycles of adsorption and desorption experiments without a considerable fatigue.

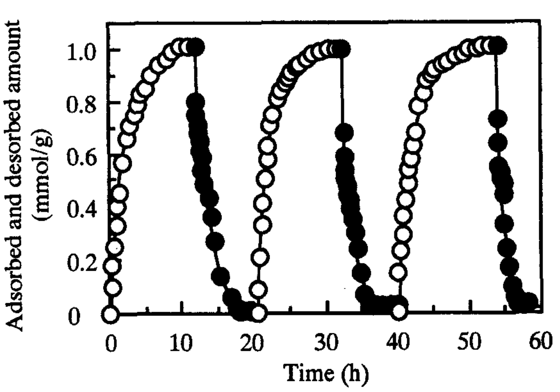

Figure 6 Alternately repeated cyclic process of adsorption at the initial pH value of 3.0 (○) and desorption at the initial pH value of 11.0 (●).

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 anionic compounds.

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