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Studies of Polystyrene-based Ion-exchange Fiber. III. A Novel Fiber-form Chelating Exchanger and Its Adsorption Properties for Heavy-metal Ions†

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Fibrous chelating exchangers with $-N(CH_2COOH)_2$ and $-N(CH_2CH_2COOH)_2$ groups have been prepared for the first time by using a polystyrene–polypropylene composite fiber as the starting material. They have large surface areas per unit of weight and can be utilized in various forms. The properties of adsorbing Cu^{2+} are compared between these chelating fibers and an ordinary chelating resin. The former groups form more stable complexes with Cu^{2+} than the latter, probably because of their different chelating structure. The rate of the adsorption of Cu^{2+} to the fibers is dependent upon their water content and is from ten to fifty times as high as that to the resin. These results are explained by assuming that the diffusion within the exchangers is the major rate-controlling step in the adsorption process. The diffusion equation of isotopic ion exchange for a cylindrical endless fiber was solved in the case of ideal particle-diffusion control by modifying the method used for a spherical resin. The experimental data are interpreted in terms of their theoretical solutions. For practical application, the removal of Cu^{2+} and Mn^{2+} from various solutions was also carried out by using fixed-beds of these chelating fibers.

The preparation methods, fundamental characteristics, and acid-base catalytic properties of a polystyrene-based ion-exchange fiber (IONEX) have already been reported by the present author and his co-worker.[1,2] This ion-exchanger based on a polystyrene–polypropylene composite fiber has high mechanical strengths and can be used in various forms. The ion-exchange fiber also has two fundamental characteristics because of its larger surface areas; the ion exchange rate for metal ions is extremely high, and the capacity for adsorbing the macromolecular ionic substances is exceedingly large, compared with ordinary ion-exchange resins. Taking the latter characteristic into account, we have also studied the adsorption or immobilization to IONEX of biologically-active substances, such as enzyme, protein, and microorganism cell. These results have been published in preliminary reports.[3] Polystyrene is suitable for the addition not only of ionic groups, but also of various functional groups. The introduction of special functional groups to crosslinked polystyrene–polypropylene composite fibers is of especial interest. The quaternary phosphonium ions and crown ethers supported on the polystyrene–polypropylene composite fiber have been investigated as phase-transfer catalysts for numerous organic reactions by Tomoi and Kakiuchi.[4]

Recently selective chelating resins based on a styrene–divinylbenzene polymer have been intensively studied[5–8] and used for the separation, removal, and recovery of heavy-metal ions in the fields of waste-fluid treatment, the atomic-power industry, the food industry, and analytical chemistry. The use of chelating resins, however, has the disadvantage that the adsorption rate is very low because of their small ion dissociation in comparison with strong cation- and anion-exchange resins.[9–13] Although the adsorption rate is enhanced by using fine or crushed resins, the treatment of such resins becomes difficult.[11,13] It is also well-known that adsorption properties are affected by the physical structure of polymers supporting chelating groups.

In order to enhance the adsorption rate and to make the treatment easier, we have undertaken an investigation of fibrous chelating exchangers, which have large surface areas per unit of weight and which can be used in various forms. An iminodicarboxylic-acid-type chelating fiber has been prepared, for the first time, by using the polystyrene–polypropylene composite fiber as the starting material; it has then been used in the adsorption of Cu^{2+}.[14] In this paper the author would like to report on this chelating fiber and its ability to adsorb Cu^{2+}. The results of the adsorption rate will be discussed in terms of the kinetic theory of isotopic ion exchange for fiber systems, which is introduced in detail here. The results of removing Cu^{2+} and Mn^{2+} from various solutions by fixed-beds of the chelating fiber will also be described.

Experimental

Polystyrene–Polypropylene Composite Fiber. Forty-nine parts of polystyrene and 12 parts of polypropylene as the *sea* ingredient and 39 parts of polypropylene as the *island* ingredient were melt-spun at 255 °C into composite filaments with an *islands-in-a-sea* type sectional structure, as is shown in Fig. 1. The composite filaments were drawn five times as long as their original length in a conventional manner. The diameters of the *sea* and the *islands* of the resulting filaments were 20 and 3.1 μm respectively. Their tensile strength was 2.5 g d^{-1}.[14]

Crosslinked Polystyrene–Polypropylene Composite Fiber. Ten grams of the fiber were high-(or low-) crosslinked in 100 ml of a solution consisting of 5 wt% paraformaldehyde, 25 (45) wt% acetic acid, and 70 (50) wt% concd sulfuric acid

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† A preliminary report of this work was presented in *Polym. Prepr. Jpn.*, **33**, 1615 (1984).

at 80 °C for 2 h.[14]

Iminodiacetic-acid(IDA)-type Chelating Fiber. Ten grams of the crosslinked fiber were acrylamidomethylated in a solution comprising 20 g of bis(acrylamidomethyl) ether, 200 ml of nitrobenzene, and 140 g of concd sulfuric acid at room temperature for 20 h. After being extracted with methanol, the fiber was treated in 450 ml of concd hydrochloric acid at 105 °C for 20 h; it was thus hydrolyzed into an aminomethylated fiber.[15] The IDA-type chelating IONEX was obtained by treating the aminomethylated fiber (10 g) with a solution consisting of 27 g of chloroacetic acid, 11 g of sodium hydroxide, 19 g of sodium carbonate, and 130 g of water at 100 °C for 8 h.[14] The structure of the IDA chelating group is shown in Fig. 2.

Iminodipropionic-acid(IDP)-type Chelating Fiber. Ten grams of the crosslinked fiber were chloromethylated in a solution comprising 100 ml of chloromethyl methyl ether and 10 ml of tin(IV) chloride at 30 °C for 1 h. Ten grams of the chloromethylated fiber were treated in a solution consisting of 160 g of *N, N, N″, N″*-tetrakis(2-cyanoethyl)diethylenetriamine and 350 ml of dioxane at 70 °C for 6 h. The IDP-type chelating IONEX was obtained by treating the fiber with 450 ml of concd hydrochloric acid at 60 °C for 6 h.[14,16] The structure of the IDP chelating group is also shown in Fig. 2.

Adsorption Capacity of Cu^{2+}. A chelating IONEX (0.25 g in the Na form) was added to 100 ml of a 0.013 M[††] Cu^{2+} solution containing 0.5 M NaCl and a Clark Lubs buffer of pH 6.0, and then the mixture was strongly shaken at 20 °C for 24 h. The adsorption capacity of Cu^{2+} to the fiber was evaluated by measuring the concentration of Cu^{2+} in the solution before and after the adsorption treatment.

Water Content. A chelating IONEX in the Na form was immersed in a bath of deionized water at room temperature for a sufficient period of time to reach saturation. The fiber was then centrifugally dehydrated at 3000 r.p.m. for 5 min. Immediately thereafter, the wet weight (W) of the fiber was measured. The water content of the fiber was determined from the following equation:

$$\text{Water content} = (W - W_0)/W_0,$$

where W_0 is the absolutely dry weight of the fiber.

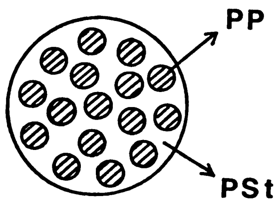

Fig. 1. Schematic cross section of composite fiber. Pst: Polystyrene, *sea* ingredient; PP: polypropylene, *island* ingredient.

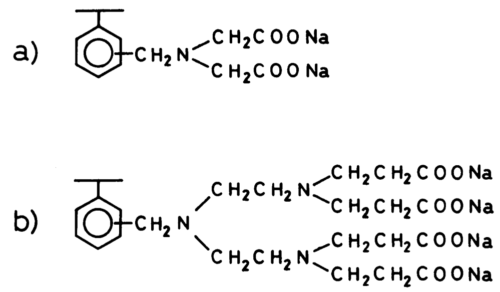

Fig. 2. Structures of the iminodicarboxylic-acid chelating groups. a) IDA-Na, b) IDP-Na.

Chelating Resin and Measurements. The bead chelating resin (Diaion CR-10, IDA-type resin based on styrene-divinylbenzene copolymer) with a diameter of *ca.* 400 μm and a water content of 1.7 was obtained from the Mitsubishi Kasei Kogyo Co., Ltd. (Japan). The concentrations of Cu^{2+} and Mn^{2+} were determined by using an atomic absorption photometer.

Results and Discussion

Fibrous Chelating Exchanger. The process of preparing the chelating fiber is shown in Fig. 3. The chelating fiber in various forms, such as filament, cut fiber, knitted fabric, woven fabric, braid, felt, nonwoven fabric, chip, and paper, can be obtained by processing the polystyrene-polypropylene composite fiber before crosslinking reactions, as the fiber reinforced with polypropylene has high mechanical strengths. Figure 4 shows the polystyrene–poly-

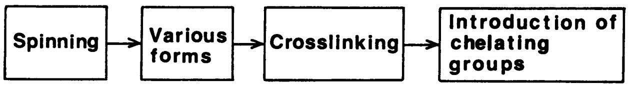

Fig. 3. Process of preparing the polystyrene-based chelating fiber.

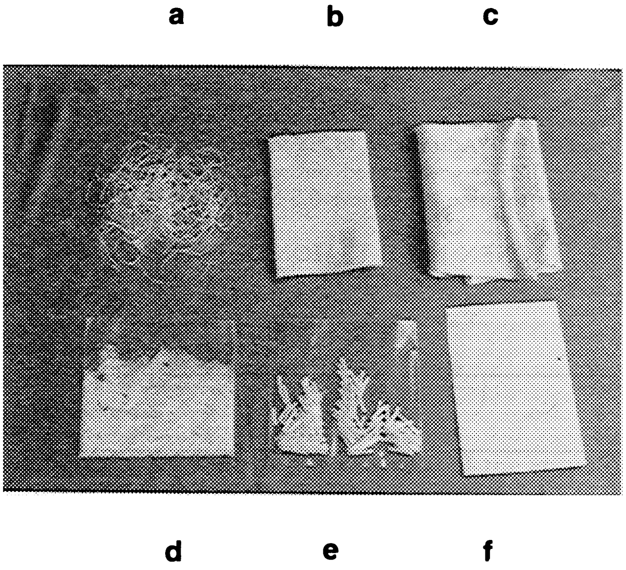

Fig. 4. Polystyrene-polypropylene composite fiber in various forms of filament (a), needle punched felt (b), knitted fabric (c), cut fiber (d), chip (e), and paper (f).

[††] 1 M=1 mol dm^{-3}.

propylene composite fiber in the various forms. The characteristic data of the chelating IONEX are summarized in Table 1. The chelating filaments had a diameter of *ca.* 30 μm and exhibited a tensile strength of *ca.* 1.0 g d^{-1}. It was found that the low-crosslinked fibers have larger adsorption capacities and water contents than the high-crosslinked ones. The former result is explained by the fact that the amount of the aminomethyl or chloromethyl group introduced in the synthetic process is larger in the case of the low-crosslinked fiber because of its high reactivity.

Equilibrium Adsorption. The correlation between the adsorption capacity of Cu^{2+} and the pH in the solution for various chelating exchangers is shown in Fig. 5. The IDA-type fiber exhibits the same pH dependence as the CR-10 resin. The half-pH, where the adsorption capacity becomes half of pH 5.2, is 1.7. On the other hand, the IDP-type fiber exhibits a different pH dependence from the IDA-type; here, the half-pH is 2.9. These results indicate that the IDA type forms more stable complexes with Cu^{2+} than the IDP type.[7] This fact can be explained by assuming that the former coordinates to Cu^{2+} by forming five-members rings while the latter does so by forming six-members rings.

Adsorption Rate Ion exchange between the Na form of a chelating exchanger (0.25 g) and a 0.013 M Cu^{2+} solution containing 0.5 M NaCl and a Clark Lubs buffer of pH 6.0 (100 ml) was examined. Figure 6 displays the fractional attainment of the equilibrium as a function of the time. The fibers do not require ten minutes to attain 50% of equilibrium, whereas the resin requires more than one hour. Besides, the exchange rate becomes higher as the water content of the fibers increases, that is, as the degree of crosslinking is lowered. This means that the diffusion within the exchangers is the major rate-controlling step in the adsorption process. The plots of t_R/t_F *vs.* the water content of the fibers is given in Fig. 7, where t_R and t_F are the half-times of ion exchange for the resin and the fiber respectively. It can be seen from Fig. 7 that the exchange rate of the fiber is forty times higher than that of the resin when

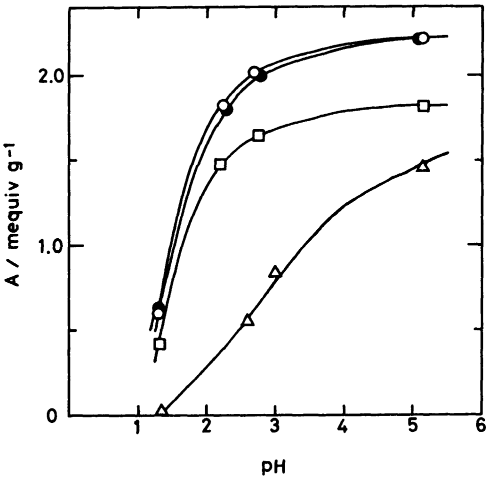

Fig. 5. Effect of pH in solution on adsorption capacity of Cu^{2+}. Adsorption to Na form of chelating exchanger (0.25 g) was carried out with 100 ml of 0.013 M Cu^{2+} solution containing 0.5 M NaCl and Clark Lubs buffer (20 °C, 24 h).
○: IONEX No. 1, □: IONEX No. 2, △: IONEX No. 4, ●: Diaion CR-10.

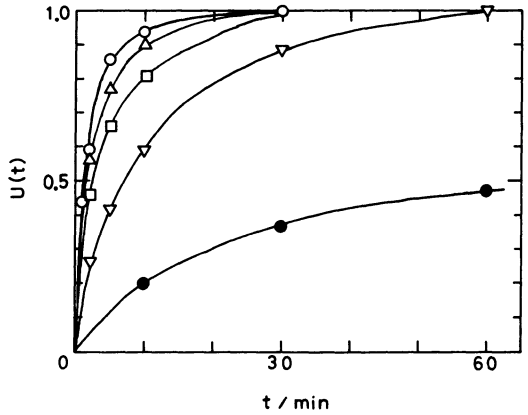

Fig. 6. Fractional attainment of equilibrium as a function of time. Ion exchange between Na form of chelating exchanger (0.25 g) and 0.013 M Cu^{2+} solution containing 0.5 M NaCl and Clark Lubs buffer of pH 6.0 (100 ml).
○: IONEX No. 1, □: IONEX No. 2, △: IONEX No. 4, ▽: IONEX No. 5, ●: Diaion CR-10.

Table 1. Characteristic data of chelating IONEX

No.	Chelating group	Fiber form[a]	Degree of crosslinking	Capacity[b] / mequiv g^{-1}	Water[c] content
1	IDA-Na	filament	low	2.2	2.6
2		filament	high	1.8	1.4
3		felt	high	1.8	—
4	IDP-Na	filament	low	1.5	1.7
5		filament	high	1.4	1.0

a) Diameter and composition of original fiber: 20 μm, *Sea*(PSt//PP)/*Islands*(PP) = (49//12)/39. b) Adsorption capacity for Cu^{2+}. c) $(W-W_0)/W_0$. W: wet weight, W_0: dry weight.

the fiber has the same water content (1.7) as the resin and that the exchange rate is independent of the structure of the chelating groups because of the diffusion control.

Theoretical Considerations. The theoretical solution of ion exchange[1,6,9] in a simple system (isotopic exchange) can be applied to our experimental results as a first-order approximation. We solve the diffusion equation in the case of an endless fiber with a radius of r_f and a length of l ($l \gg r_f$) by modifying the method used for a spherical resin.[1] The diffusion equation for the fiber systems in the case of an ideal particle-diffusion control is given by:

$$\frac{\partial \bar{C}_A}{\partial t} = \bar{D}_f\left(\frac{\partial^2 \bar{C}_A}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{C}_A}{\partial r}\right), \tag{1}$$

where r is the radial coordinate of the fiber; t, the time; $\bar{C}_A$, the concentration of the A ion at r and t, and $\bar{D}_f$, the interdiffusion coefficient in the fiber. Hereafter, quantities with bars will refer to the interior of the fiber. A schematic drawing of the fiber systems is shown in Fig. 8. The general solution of Eq. 1 can be described as follows:

$$\bar{C}_A = \sum_{n=1}^{\infty} A_n J_0(a_n r) \exp(-\bar{D}_f a_n^2 t), \tag{2}$$

where A_n is derived as:

$$A_n = \frac{2}{x_0^2[J_{i+1}(a_n x_0)]^2}\int_0^{x_0} x J_i(a_n x) f(x)\mathrm{d}x,$$

when $f(x) = \sum_{n=1}^{\infty} A_n J_i(a_n x)$ and $J_i(a_n x_0) = 0$, in which $J_i(x)$ is the ith-order Bessel function.

The simple initial conditions are assumed to be:

$$\begin{array}{ll} r > r_f,\ t = 0 & \bar{C}_A(r) = 0, \\ 0 \leqq r \leqq r_f,\ t = 0 & \bar{C}_A(r) = \bar{C}_A{}^0 = \text{const.} \end{array} \tag{3}$$

Secondly we assume that the concentrations at the fiber surface are the same as in the bulk solution. The infinite solution volume condition is then postulated as:

$$r = r_f,\ t > 0 \qquad \bar{C}_A(t) = 0. \tag{4}$$

The conditions of Eqs. 3 and 4 give, respectively:

$$\bar{C}_A{}^0 = \sum_{n=1}^{\infty} A_n J_0(a_n r), \tag{5}$$

$$J_0(a_n r_f) = 0. \tag{6}$$

The A_n coefficients can, therefore, be determined from Eqs. 5 and 6 as follows:

$$A_n = \frac{2}{r_f^2[J_1(a_n r_f)]^2}\int_0^{r_f} \bar{C}_A{}^0 r J_0(a_n r)\mathrm{d}r = \frac{2\bar{C}_A{}^0}{a_n r_f J_1(a_n r_f)}. \tag{7}$$

The fractional attainment of the equilibrium, $U(t)$, is obtained from the integration of the solution $\bar{C}_A(r,t)$ throughout the fiber as:

$$U(t) = 1 - \frac{\int_0^{r_f} 2\pi r l \bar{C}_A \mathrm{d}r}{\pi r_f^2 l \bar{C}_A{}^0}. \tag{8}$$

By substituting Eqs. 2 and 7, Eq. 8 is finally reduced to:

$$U(t) = 1 - \sum_{n=1}^{\infty} \frac{4}{a_n^2 r_f^2}\exp(-\bar{D}_f a_n^2 t) = 1 - \sum_{n=1}^{\infty}\frac{4}{x_n^2}\exp\left(-\frac{\bar{D}_f x_n^2 t}{r_f^2}\right), \tag{9}$$

where the x_n quantities are the roots of the equation $J_0(x) = 0$, as was preliminarily described in Ref. 1. From this equation, $U(t)$ is found to depend only on the magnitude of the dimensionless time parameter, $\bar{D}_f t/r_f^2$, which is plotted in Fig. 9 as a function of the parameter. The numerical values are tabulated in Table 2. The half-time of ion exchange is also

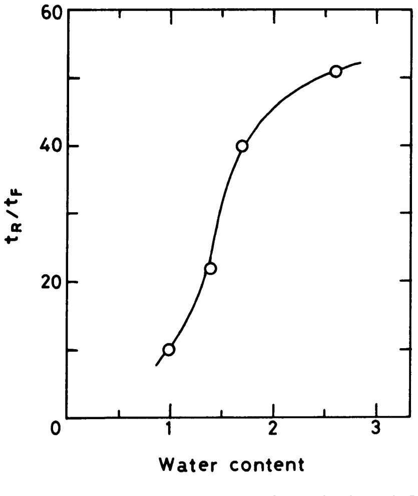

Fig. 7. t_R/t_F *vs.* water content of chelating IONEX. t_R: The half-time of ion exchange with Diaion CR-10, t_F: the half-time of ion exchange with chelating IONEX.

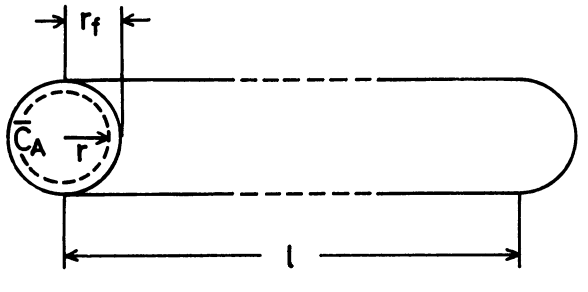

Fig. 8. Schematic drawing of fiber systems (Eq. 1).

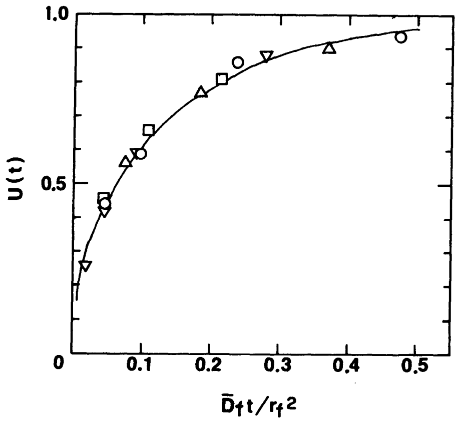

Fig. 9. Fractional attainment of equilibrium as a function of $\bar{D}_f t/r_f^2$. The solid line represents the theoretical curve for particle-diffusion controlled isotopic exchange in the case of cylindrical endless fiber (Eq. 9). Experimental points are plotted by use of empirical $\bar{D}_f$ obtained from Eq. 13. The notations for the points are used in the same meanings as Fig. 6.

TABLE 2. NUMERICAL VALUES OF $U(\tau) = 1 - \sum_{n=1}^{\infty} \frac{4}{x_n^2} \exp(-x_n^2 \tau)$ (Eq. 9)

τ	$U(\tau)$	τ	$U(\tau)$	τ	$U(\tau)$
0.005	0.155	0.05	0.452	0.20	0.782
0.01	0.215	0.06	0.489	0.25	0.837
0.02	0.299	0.08	0.553	0.30	0.878
0.03	0.360	0.10	0.606	0.40	0.932
0.04	0.410	0.15	0.708	0.50	0.962

readily derived from Eq. 9 as follows:

$$t_F = 0.065 r_f^2/\bar{D}_f. \tag{10}$$

The fractional attainment of the equilibrium, $U(t)$, within a spherical resin with a radius of r_0 has been described in the case of ideal particle-diffusion control by the following equation:

$$\begin{aligned} U(t) &= 1 - \sum_{n=1}^{\infty} \frac{6}{X_n^2} \exp\left(-\frac{\bar{D}X_n^2 t}{r_0^2}\right) \\ &= 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\bar{D}\pi^2 n^2 t}{r_0^2}\right), \end{aligned} \tag{11}$$

where $\bar{D}$ is the interdiffusion coefficient in the resin and where the quantities $X_n = \pi n$, the roots of the equation $J_{1/2}(x)=0$. The half-time of ion exchange has been calculated from Eq. 11 as follows:

$$t_R = 0.030 r_0^2/\bar{D} \tag{12}$$

The equations derived for the fractional attainments and the half-times do not involve $\bar{C}_A$ and remain unchanged under our experimental conditions.[6] Now, let us theoretically compare the ion-exchange rate of our fibers with that of the CR-10 resin, assuming that no polymer for the reinforcement in our fibers exists. The volume of the resin with r_0=0.02 cm corresponds to that of the fiber with r_f=0.0015 cm and l=4.74 cm. The theoretical $U(t)$ for the fiber and resin can be plotted as a function of the time parameter ($\bar{D}_f t$ and $\bar{D}t$) in Fig. 10 by using Eqs. 9 and 11 respectively. The half-times of ion exchange can also be obtained from Eqs. 10 and 12 respectively as:

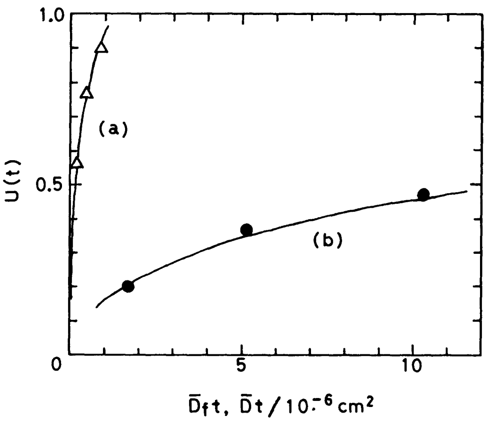

Fig. 10. Fractional attainment of equilibrium as a function of $\bar{D}_f t$ and $\bar{D}t$. The solid lines represent the theoretical curves for particle-diffusion controlled isotopic exchange. (a) Fiber with r_f=0.0015 cm and l=4.74 cm (Eq. 9), and (b) resin with r_0=0.02 cm (Eq. 11). Experimental points are plotted by use of empirical $\bar{D}_f$ and $\bar{D}$ obtained from Eqs. 13 and 14 respectively. The notations for the points are used in the same meanings as Fig. 6.

$$t_F = 1.46 \times 10^{-9}/\bar{D}_f \tag{13}$$

$$t_R = 120 \times 10^{-9}/\bar{D}. \tag{14}$$

The ratio of the half-time of the resin to that of the fiber can be calculated to be 82 from Eqs. 13 and 14, as $\bar{D}_f = \bar{D}$ can be expected when the water contents are the same, that is, when there are the same degrees of crosslinking. The ratio obtained from the experimental data is, however, 40, about half the calculated ratio. This discrepancy can be interpreted on the assumption that the interdiffusion coefficients in our fibers are lowered because the polymer for reinforcement disturbs the diffusion of ions. The apparent $\bar{D}_f$ values for the fibers with the water contents of 1.0, 1.4, 1.7, and 2.6 can be directly evaluated from Eq. 13 to be 0.35, 0.80, 1.39, and 1.78×10^{-9} cm² s⁻¹ respectively by using the half-times obtained from the experimental curves. Similarly, the apparent $\bar{D}$ value for the resin with the water content of 1.7 can be evaluated to be 2.86×10^{-9} cm² s⁻¹ from Eq. 14. In Fig. 9, the experimental $U(t)$—$\bar{D}_f t/r_f^2$ data obtained by the use of these empirical interdiffusion coefficients are given, together with the theoretical curve. The experimental $U(t)$—$\bar{D}_f t$ and —$\bar{D}t$ data obtained by the use of $\bar{D}_f=1.39\times10^{-9}\,\mathrm{cm^2\,s^{-1}}$ and $\bar{D}=2.86\times10^{-9}\,\mathrm{cm^2\,s^{-1}}$ are also compared with the theoretical curves in Fig. 10. Although the interpretation does not include direct comparisons of the observed rates with the results of calculations based on independent measurements, the experimental results are in fairly good agreement with the theoretical curves.

Practical Applications

Removal of Cu^{2+} from a Solution by Fix-bed Methods. A 830 mg dm^{-3} Cu^{2+} solution containing 0.5 M NaCl was passed through a column packed with a chelating exchanger at a space velocity (S. V.) of 10 h^{-1}. The breakthrough curves of the filamentary IONEX No. 4 and Diaion CR-10 columns are given in Fig. 11. The ion leaks through the resin column in the early stage, while the fiber column represents the breakthrough curve of a roughly *S* form. From this curve, the band length and utilization of the ion exchange can be evaluated to be 7.8 cm and 0.71 respectively. The band length for the resin column is estimated to be more than 30 cm. These results show that the utilization of the fiber is high, since the band length is short because of its rapid adsorption properties, even if the Cu^{2+} concentration is high.

The breakthrough volume of a cylindrical module made of the felt IONEX No. 3 was examined by using a feed solution of 100 mg dm^{-3} Cu^{2+} and compared with those of the felt IONEX No. 3 and filamentary IONEX No. 2 columns. The felt column is superior to the others, as is shown in Fig. 12. The breakthrough volume of the module, which has seventy times as large a filtrating area as the felt column, is 30% lower than that of the felt column. From the observation of the module colored with Cu^{2+}, it was found that some of its parts are not utilized because of an irregular flow. The breakthrough volume of the module is, however, almost equal to that of the filamentary column. It can be concluded that the cylindrical module is a suitable one for a rapid fluid treatment since it has a large filtrating area and a low pressure drop.

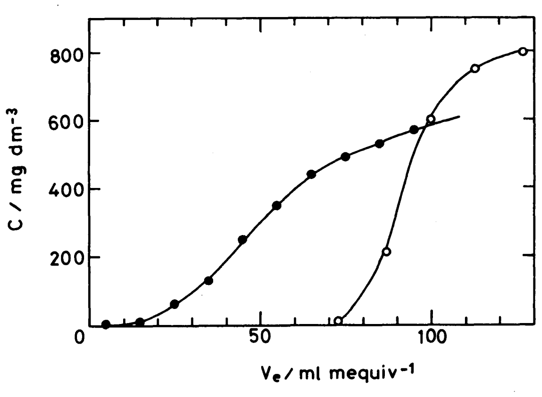

Fig. 11. Concentration of Cu^{2+} in effluent *vs.* effluent volume.
Feed solution, 830 mg dm^{-3} (0.013 M) Cu^{2+} solution containing 0.5 M NaCl and Clark Lubs buffer of pH 6.0; bed volume, 10 ml (1 cm × 13 cm); packed weight of chelating exchanger in Na form, 2.5 g; flow rate, 100 ml h^{-1} (S.V. 10 h^{-1}).
○: Filamentary IONEX No. 4, ●: Diaion CR-10.

Removal of Mn^{2+} from a Solution by Fix-bed Methods. A 100 mg dm^{-3} Mn^{2+} solution containing 0.5 M NaCl was passed through columns of various chelating exchangers. The results are shown in Fig. 13. The breakthrough volume of the felt column is superior to that of the filamentary column, as was found in the case of Cu^{2+}. The minimum Mn^{2+} concentrations in the effluent for the resin columns are 0.2 mg dm^{-3} at S. V. 20 h^{-1} and 0.1 mg dm^{-3} at S. V. 10 h^{-1}, while those for the fiber columns are below 0.02 mg dm^{-3} at S. V. 20 h^{-1}.

Next, a 137.5 mg dm^{-3} Mn^{2+} solution containing 30 wt/vol% lysine was passed through the felt and resin columns at various space velocities. Figure 14 presents the space velocity dependence of the breakthrough volume. The minimum concentrations for the resin and felt columns are 0.05 mg dm^{-3} and below 0.02 mg dm^{-3} respectively at S. V. 5 h^{-1}. In the case of the resin column, the breakthrough volume decreases rapidly as the space velocity is raised, and the ion leak takes place in the early stage at S. V. 20 h^{-1}. On the other hand, even at S. V. 80 h^{-1}, the felt column gives 72% as large a

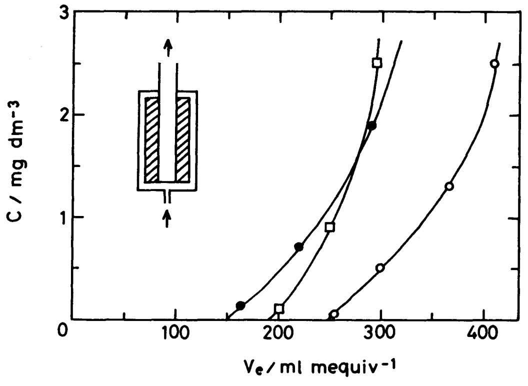

Fig. 12. Concentration of Cu^{2+} in effluent *vs.* effluent volume.
Removal of Cu^{2+} by using fixed-bed of chelating felt IONEX in H form. Feed solution, 100 mg dm^{-3} Cu^{2+} solution (pH 4.0); flow rate, S. V. 40 h^{-1}.
○: Felt IONEX No. 3 (1.1 g) in 5 ml (1.8 cm × 2 cm), □: felt IONEX No. 3 of cylindrical module (55 g) in 340 ml (inner diameter, 2.5 cm; outer diameter, 6.5 cm; height, 12 cm., see above side view), ●: filamentary IONEX No. 2 (1.25 g) in 5 ml (1 cm × 6.5 cm).

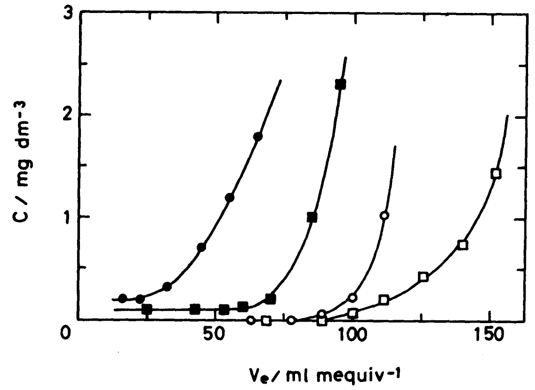

Fig. 13. Concentration of Mn^{2+} in effluent *vs.* effluent volume.
Removal of Mn^{2+} by using fixed-bed of chelating exchanger in H form. Feed solution, 100 mg dm^{-3} containing 0.5 M NaCl and Clark Lubs buffer (pH 6.0).
○: Filamentary IONEX No. 2 (1.25 g) in 5 ml (1 cm × 6.5 cm), S. V. 20 h^{-1}, □: felt IONEX No. 3 (1.1 g) in 5 ml (1.8 cm × 2 cm), S. V. 20 h^{-1}, ●: Diaion CR-10 (4.5 g) in 10 ml (1 cm × 13 cm), S. V. 20 h^{-1}, ■: Diaion CR-10 (9 g) in 20 ml (1 cm × 26 cm), S. V. 10 h^{-1}.

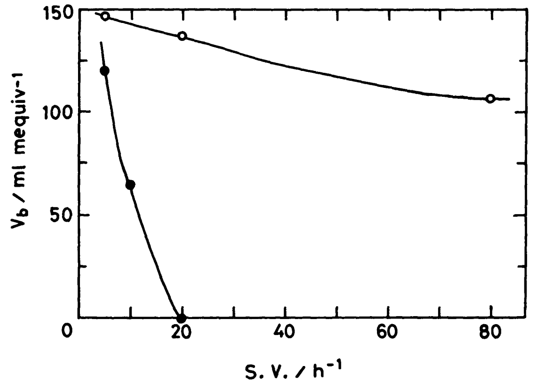

Fig. 14. Space velocity dependence of breakthrough volume in removal of Mn^{2+} from highly concentrated lysine solution. Breakthrough point, 1 mg dm^{-3} as Mn^{2+} in effluent; feed solution, 137.5 mg dm^{-3} Mn^{2+} solution containing 30 wt/vol% lysine (pH 5.4).
○: Lysine form of felt IONEX No. 3 (1.1 g) in 5 ml (1.8 cm × 2 cm), ●: lysine form of Diaion CR-10 (2.5 g) in 10 ml (1 cm × 13 cm).

breakthrough volume as at S. V. 5 h^{-1}, and its minimum concentration is still below 0.02 mg dm^{-3}. These results indicate that the chelating fiber can be utilized in various fields which require a rapid treatment or a high removal ratio, since it has such a high adsorption rate.

Conclusion

1. A fibrous chelating exchanger based on polystyrene has been prepared by using an *islands-in-a-sea* type composite fiber as the starting material. This fibrous chelating exchanger can be used in various forms because of its high mechanical strength.
2. This chelating fiber has from ten to forty times as high an adsorption rate for Cu^{2+} as the ordinary chelating resin. These results are interpreted in terms of the rate laws of ion exchange for the limiting case of ideal particle-diffusion control in a simple system.
3. A column packed with this chelating fiber has excellent removal properties for heavy-metal ions. A cylindrical module made of felt is a suitable one for a rapid fluid treatment.

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