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Binding of ionic surfactants to charged polymer brushes grafted onto porous substrates

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Abstract

A polymer brush containing a sulfonic acid group was appended onto the pore surface of a porous hollow-fiber membrane about 1 mm thick. During the permeation of a *N*-alkylpyridinium chloride (C_nPyCl; $n=4$, 12, and 16) solution, the feed concentration of which ranged from 0.10 to 500 m*M*, through the pores at a constant transmembrane pressure of 0.2 MPa, C_{12}PyCl was bound to the charged polymer brush. Prepermeation of a magnesium chloride solution through the pores was effective in regaining the liquid permeability via ionic crosslinking of the charged groups with the magnesium ion at a degree of crosslinking of 54%. The charged polymer brush captured C_{12}PyCl without releasing the magnesium ion. At a surfactant concentration of about 70% of its critical micelle concentration, the equilibrium binding capacity of the charged polymer brush started to decrease due to micelle formation. In contrast, C_4PyCl and PyCl without micelle formation increased the equilibrium binding capacity with increasing concentration while expelling the magnesium ion.

Keywords: Charged polymer brushes; Ionic surfactants; Graft polymerization; *N*-Alkylpyridinium chloride

1. Introduction

A charged polymer brush is defined as a charged- or ionizable-group-containing polymer chain grafted onto various substrates such as polymeric films and beads [1]. The diethylamino group ($-N(C_2H_5)_2$) and sulfonic acid group ($-SO_3H$) are representative of positively and negatively charged groups, respectively. The charged polymer brush has received much attention in the control of surface properties such as wetting and adsorption [2–11].

We have so far prepared polymer brushes by radiation-induced graft polymerization of an epoxy-group-containing monomer and subsequent various ring-opening reactions [12–15]. The charged polymer brush can capture metal ions and proteins based on electrostatic interaction. Charged polymer brushes grafted uniformly onto a porous hollow-fiber mem-

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brane extend from the pore surface toward the pore interior, and capture the proteins in multilayers while changing the liquid permeability [16]. For example, diethylamino-group- and sulfonic-acid-group-containing polymer brushes adsorb urease [17] and lysozyme [18], respectively, in multilayers; the amount of urease bound onto the membrane exceeded 1 g per g of the membrane [17].

Ionic surfactants consist of an ionizable group and alkyl long chain, and form micelles with increasing concentration. The molecular masses of ionic surfactants lie between those of metal ions and proteins; the ionic surfactants are convenient as a probe to investigate the behavior of the charged polymer brush. The objective of this study was to clarify the interaction of the charged polymer brush with the ionic surfactants. The sulfonic-acid-group-containing polymer brush and *N*-alkylpyridinium chlorides were adopted as the charged polymer brush and ionic surfactants, respectively.

2. Experimental

2.1. Materials

A commercially available porous hollow-fiber membrane made of high-density polyethylene was used as a trunk polymer for grafting. This hollow fiber had inner and outer diameters of 1.9 and 3.2 mm, respectively, with an average pore diameter of 0.34 μm and porosity of 72%. Glycidyl methacrylate (GMA, CH_2=$CCH_3COOCH_2CHOCH_2$) was purchased from Nacalai Tesque Inc. and used without further purification. *N*-alkylpyridinium chloride (C_nPyCl) with n=4, 12, and 16, used as a cationic surfactant, and pyridinium chloride were purchased from Tokyo Kasei Co., and used as received. Other chemicals were of analytical grade or higher.

2.2. Preparation of charged polymer brushes onto porous substrate

Charged polymer brushes were appended onto the pore surface of the porous hollow-fiber membrane by radiation-induced graft polymerization and subsequent chemical modifications via the following three steps (Fig. 1): (1) irradiation of an electron beam onto the trunk polymer, (2) graft polymerization of GMA in a liquid phase, and (3) conversion of some of the produced epoxy group to a sulfonic acid group with sodium sulfite. The resultant porous hollow-fiber membrane containing negatively charged polymer brushes was referred to as an SS-EO fiber. For comparison, the remaining epoxy group of the polymer brushes of the SS-EO fiber was hydrolyzed into a diol group. The resultant porous hollow-fiber membrane was designated the SS-Diol fiber. Conditions for preparation are detailed in Table 1.

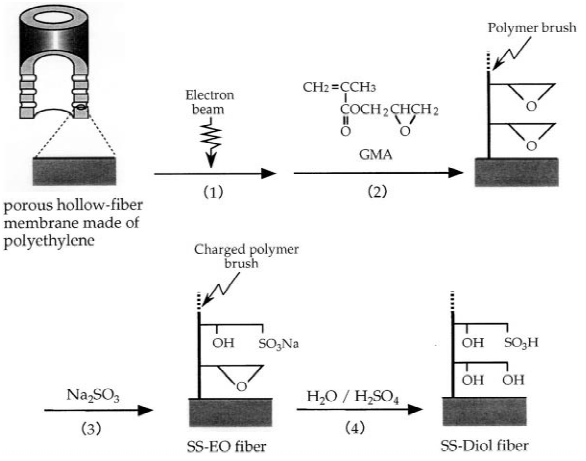

Fig. 1. Introduction of charged polymer brushes onto porous membrane of a hollow-fiber form.

Table 1
Preparation conditions of negatively charged polymer brush

Radiation-induced graft polymerization	
Irradiation dose	200 kGy
Concentration of GMA	10% (v/v) in methanol
Reaction temperature	313 K
Reaction time	12 min
Sulfonation	
Concentration of Na_2SO_3	Na_2SO_3/IPA[a]/water =10/15/75 (w/w/w)
Temperature	353 K
Reaction time	2 h
Hydrophilization	
Concentration of H_2SO_4	0.50 *M*
Temperature	353 K
Reaction time	2 h

[a] Isopropyl alcohol.

2.3. Permeation of surfactants through pores rimmed by charged polymer brush

The amount of surfactant bound to the SS-EO fiber was evaluated in the permeation mode. An SS-EO fiber 3–4 cm long was positioned in an I-shaped configuration. Before the permeation of the surfactant solution, 5.0 m*M* magnesium chloride was permeated through the pores rimmed by the charged polymer brush to raise the permeability; magnesium ions ionically crosslink the sulfonic acid groups of the extending charged polymer brush, resulting in a significant recovery of the pore size effective for liquid permeation [18].

The degree of ionic crosslinking via magnesium ion was defined as follows:

Degree of ionic crosslinking via magnesium ion
= 100(moles of bound magnesium ion)/
(initial moles of sulfonic acid group)/2 (1)

N-Dodecylpyridinium chloride (C_{12}PyCl) solution was forced to permeate outward from the inside surface of the SS-EO fiber to the outside surface, driven by transmembrane pressure (Fig. 2). The feed concentration of the surfactant ranged from 0.10 to 500 m*M*. The transmembrane pressure was maintained at 0.2 MPa. The effluent penetrating the outside surface was continuously sampled using a fraction collector equipped with vials of about 50 ml,

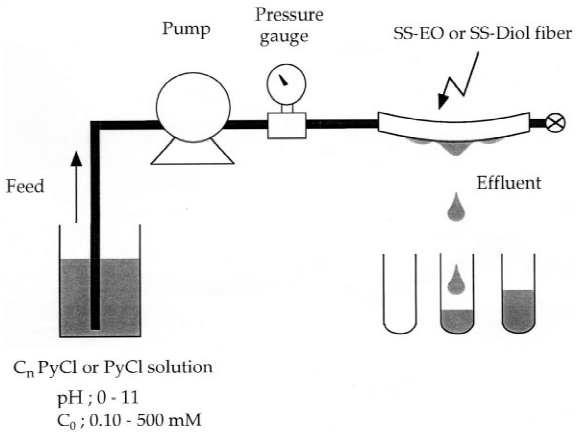

Fig. 2. Experimental apparatus for determination of equilibrium binding capacity of ionic surfactants on charged polymer brush.

and its surfactant content was determined by measuring UV absorbance (259 nm). The permeation experiment was carried out at ambient temperature.

Equilibrium binding capacity (EBC), i.e. the amount of C_{12}PyCl bound to the charged polymer brush in equilibrium with the feed concentration, was evaluated as follows:

$$\mathrm{EBC} = \int_0^{V_e} (C_0 - C)\, \mathrm{d}V/W \quad (2)$$

where C_0 and C are the feed and effluent concentrations of the surfactant, respectively. V, V_e, and W are the effluent volume, the effluent volume where C reached C_0, and the mass of the SS-EO fiber, respectively. After equilibration, i.e. the effluent concentration reached the feed concentration, deionized water was permeated to wash the pores and subsequently, 1 *M* HCl was fed to elute the adsorbed surfactant. Here, elution percentage is defined as

Elution percentage
= 100(amount eluted)/[(amount adsorbed)
− (amount washed)] (3)

For comparison, a similar permeation experiment was carried out for a cetylpyridinium chloride (C_{16}PyCl), butylpyridinium chloride (C_4PyCl), or pyridinium chloride (PyCl) solution.

After the binding of C_{12}PyCl onto the SS-EO fiber in equilibrium with the feed concentrations of 0.50 and 15 m*M*, the IR profile across the fiber thickness was determined using a micro-FT-IR spectrophotometer (Perkin-Elmer, Spectrum One Auto Image System) in the attenuated total reflectance mode to determine the distribution of C_{12}PyCl in the SS-EO fiber. The aperture size was $100 \times 100\ \mu m^2$, and the measurement region was scanned in 100-μm steps.

3. Results and discussion

3.1. Increase in liquid permeability by ionic crosslinking

The degree of GMA grafting, i.e. the percentage of weight increase in the poly-GMA brush relative to

Table 2
Properties of porous hollow-fiber membrane immobilizing SO_3H-group-containing polymer brush (SS-EO fiber)

	SS-EO fiber	SS-Diol fiber
dg (%)	140	140
Conversion (%)	30	30
Inner diameter (mm)	2.2	2.6
Outer diameter (mm)	3.7	4.1
Pure water flux[a] (m/h)	0.092	0.15

[a] $\Delta P = 0.2$ MPa, temp. = 297 K.

the trunk polymer, of 140% and subsequent 30% molar conversion of the epoxy group to the sulfonic acid group resulted in a sulfonic acid group density of 0.99 mol per kg of the SS-EO fiber. Properties of the SS-EO fiber are summarized in Table 2.

A much lower water permeability of the SS-EO fiber was observed, compared to that of the trunk polymer, because the charged polymer brush extends from the pore surface to the pore interior due to

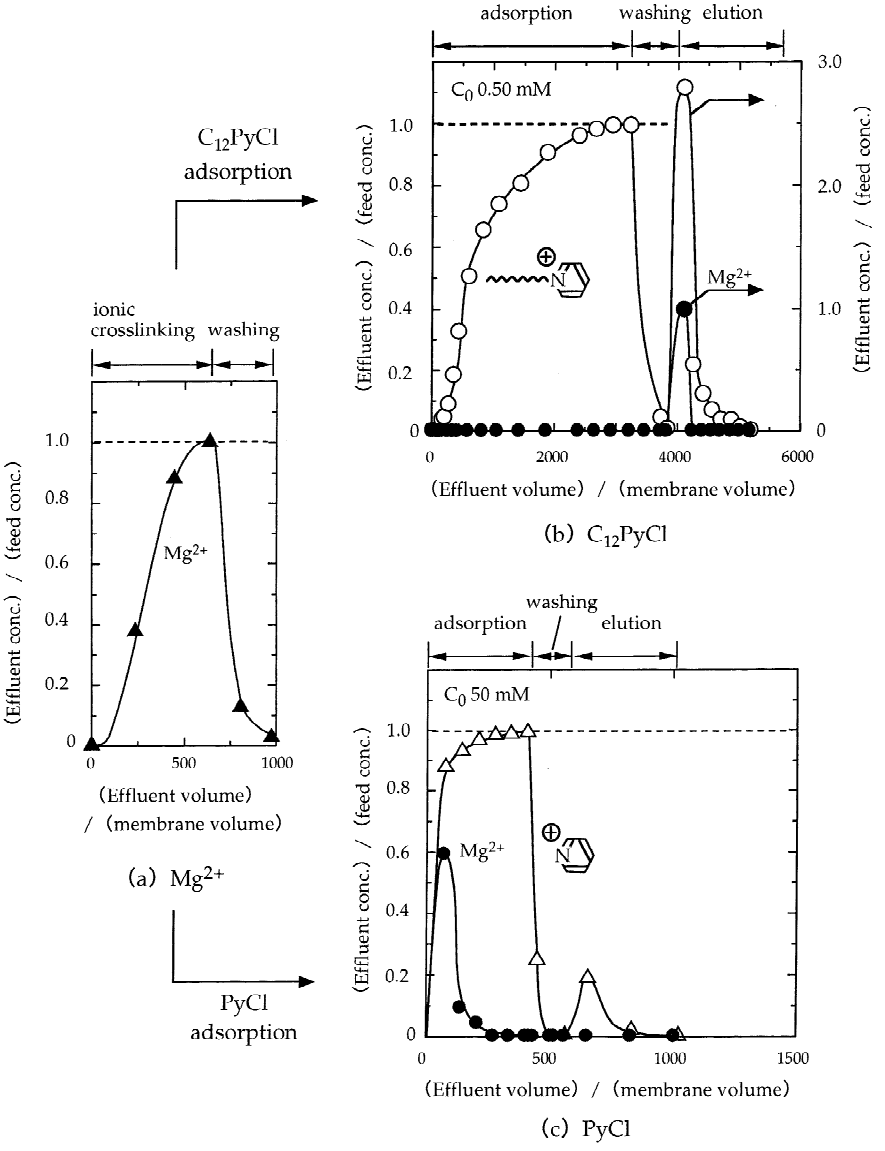

Fig. 3. Breakthrough and elution curves for the SO_3H-group-containing polymer brush in the permeation mode. (a) Mg^{2+}; (b) $C_{12}PyCl$; (c) PyCl.

electrostatic repulsion, which reduces the effective pore size; however, the permeation of a magnesium chloride solution across the SS-EO fiber allowed the charged polymer brush to contract via ionic crosslinking of the sulfonic acid groups. The degree of ionic crosslinking via magnesium ion was calculated as 54% by Eq. (1) from the breakthrough curve of magnesium ion (Fig. 3(a)). The water permeability of the SS-EO fiber was recovered up to 48% of that of the trunk polymer (Fig. 4(a)).

3.2. Binding of N-alkylpyridinium chloride to charged polymer brush

A breakthrough curve, i.e. the change in the effluent concentration of C_{12}PyCl as a function of the effluent volume during the permeation of the C_{12}PyCl solution through the pore of the SS-EO fiber, is shown in Fig. 3(b) along with an elution curve. The abscissa is a dimensionless effluent volume (DEV) defined by dividing the effluent

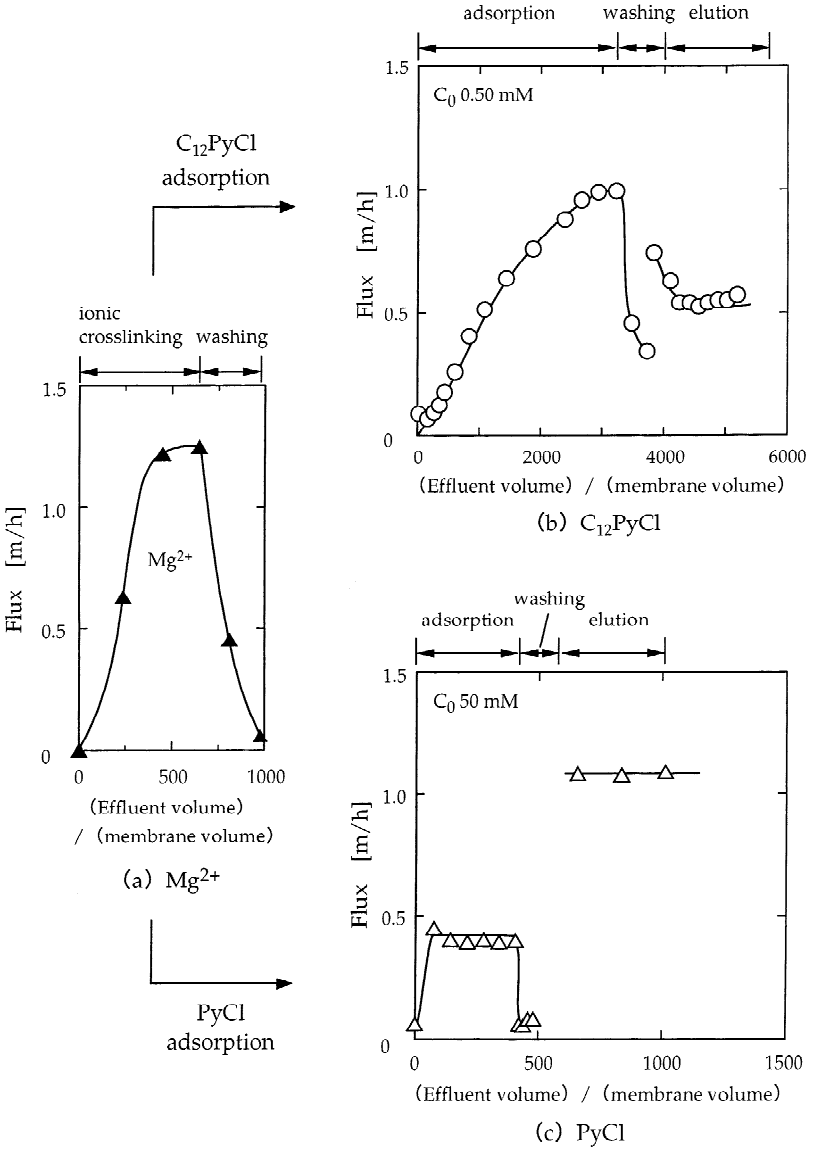

Fig. 4. Permeation flux of the SS-EO fiber during binding and elution of C_{12}PyCl and PyCl. (a) Mg^{2+}; (b) C_{12}PyCl; (c) PyCl.

volume by the membrane volume excluding the lumen part; the ordinate is the ratio of the effluent concentration to the feed concentration of the surfactant. Below DEV=270, all of the surfactant was captured by the charged polymer brush grafted onto the porous hollow-fiber membrane; the effluent concentration of C_{12}PyCl was zero. At DEV=about 270, the surfactant started to appear in the effluent. Subsequently, the effluent concentration increased and finally attained an equilibrium at DEV=3300.

The magnesium concentration changes during the process of adsorption, washing, and elution are also shown in Fig. 3(b). Magnesium ion was not released into the effluent during the binding of C_{12}PyCl to the charged polymer brush which had been ionically crosslinked with magnesium ion. In contrast, during the permeation of the PyCl solution, PyCl expelled the magnesium ion from the charged polymer brush (Fig. 3(c)). This sharp contrast demonstrates that the selectivity of the charged polymer brush to C_{12}PyCl is lower than that to PyCl; the order of selectivity was $C_{12}Py^+ < Mg^{2+} < Py^+$.

A flux change reflects the extension or contraction of the charged polymer brush. The flux changes during the adsorption, washing, and elution of C_{12}PyCl and PyCl are shown in Fig. 4(b) and (c), respectively. The progression of C_{12}PyCl binding caused a gradual increase in the flux of 1.0 m/h. Whereas, the flux increased to 0.4 m/h due to PyCl binding during magnesium ion release (Fig. 3(c)).

3.3. Effects of pH and concentration on equilibrium binding capacity

The surfactant solutions with various pH values were permeated through the SS-EO fiber to determine the equilibrium binding capacity (EBC). The EBC of the SS-EO fiber for C_{12}PyCl at a feed concentration of 0.50 m*M* in the permeation mode exhibited a maximum of 0.55 mol per kg of the SS-EO fiber at pH 5 (Fig. 5).

Binding isotherms, i.e. EBCs of C_nPyCl (n=4, 12, and 16) and PyCl versus respective equilibrium concentrations ranging from 0.10 to 500 m*M*, are shown in Fig. 6. The EBC at pH 5.4–5.8 for C_{12}PyCl exhibited a peak at an equilibrium concentration of 5.0 m*M* which was equivalent to 67% lower than the critical micelle concentration (15 m*M*

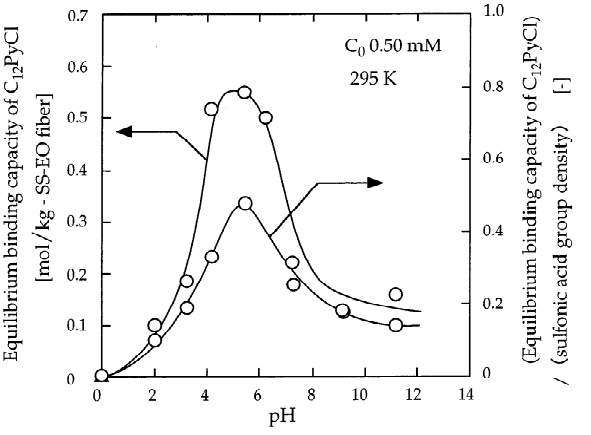

Fig. 5. Equilibrium binding capacity of C_{12}PyCl on the SS-EO fiber as a function of pH.

[19] at 298 K). Similarly, the peak of EBC for C_{16}PyCl shifted to 40% of its critical micelle concentration (2.5 m*M* at 298 K). In contrast, the EBCs for PyCl and C_4PyCl which have no critical micelle concentration increased with increasing equilibrium concentration and levelled off above 50 m*M*. Potentials of micelle formation are related to the existence of the EBC peak in binding isotherms. As

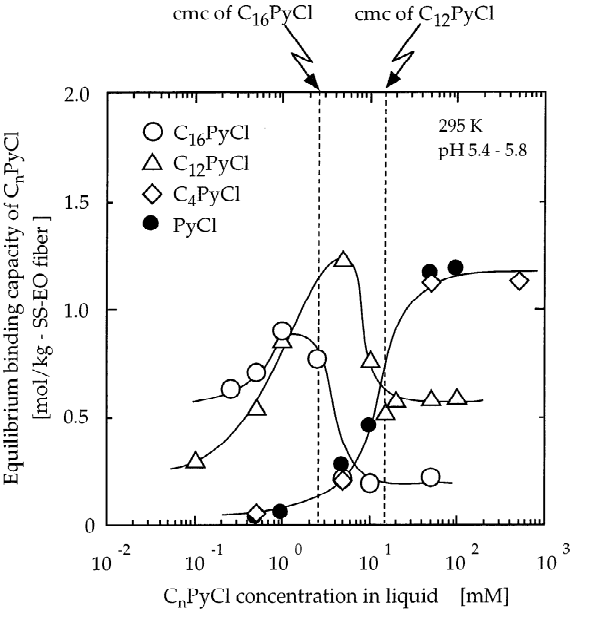

Fig. 6. Binding isotherms of C_nPyCl and PyCl on the charged polymer brush.

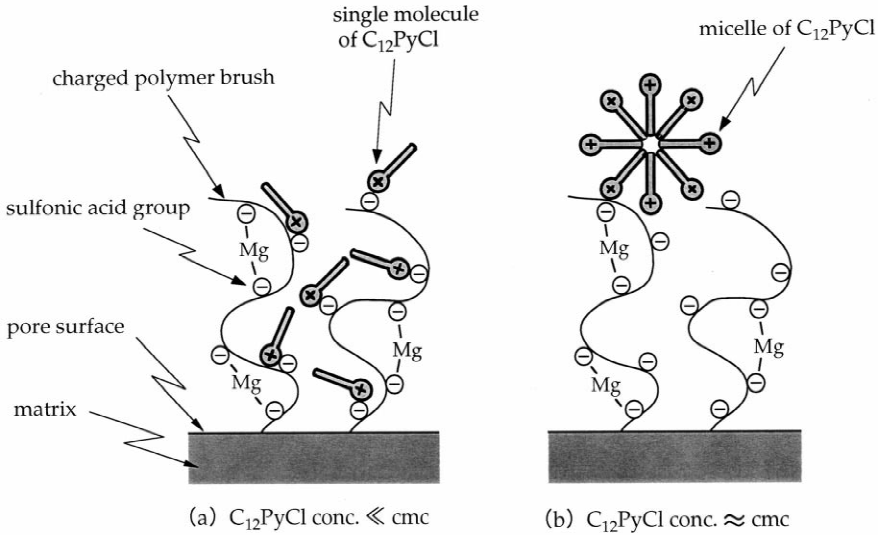

Fig. 7. Schematic illustration of binding of ionic surfactants with critical micelle concentration onto the charged polymer brush. (a) C_{12}PyCl conc. ≪ cmc; (b) C_{12}PyCl conc. ≈ cmc.

illustrated in Fig. 7, this difference can be explained by the formation of micelles by the ionic surfactants C_{12}PyCl and C_{16}PyCl when their concentrations approach the critical micelle concentration; lower accessibility of a micelle to the charged polymer brush than a single molecule diminishes the EBC. In contrast, PyCl and C_4PyCl which have no critical micelle concentration values can invade the charged polymer brush and electrostatically interact with the sulfonic acid group of the polymer brush while expelling the magnesium ion.

The ratios of the micro-FT-IR intensity fiber at 750 cm^{-1} assigned to the pyridium ring of C_{12}PyCl to that at 2917 cm^{-1} assigned to the methylene group of polyethylene, across the thickness of the SS-EO fiber, are shown in Fig. 8. The uniform profile of the ratios indicates the uniform binding of C_{12}PyCl throughout the fiber thickness in the permeation mode.

3.4. Comparison of coexisting groups with charged group on polymer brush

The epoxy and diol groups coexisting with the sulfonic acid group of the charged polymer brush are compared regarding the EBC (Fig. 9(a)) and elution percentage (Fig. 9(b)) as a function of equilibrium concentration. In the vicinity of the concentration corresponding to an EBC peak, the EBC of C_{12}PyCl for the SS-EO fiber exceeded that for the SS-Diol fiber by 41%, and in addition, the C_{12}PyCl was not quantitatively eluted with 1 *M* hydrochloric acid. Almost all of the C_{12}PyCl bound to the SS-EO fiber

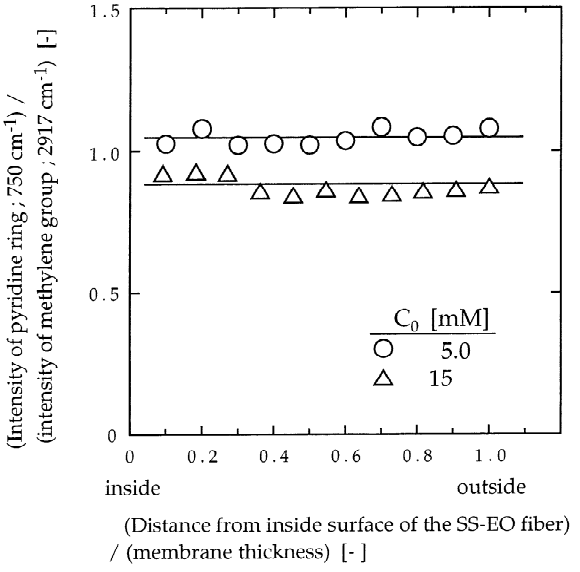

Fig. 8. Micro-FT-IR profiles of C_{12}PyCl bound to the SS-EO fiber across the membrane thickness.

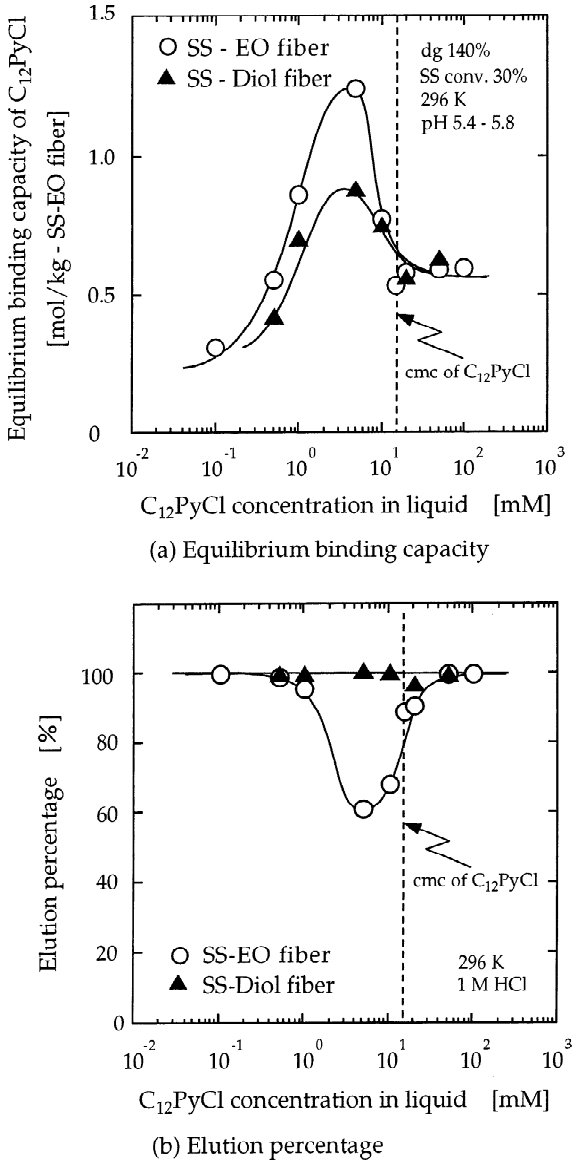

Fig. 9. Comparison of EBC and elution percentage of C_{12}PyCl between the SS-EO and SS-Diol fibers. (a) Equilibrium binding capacity; (b) Elution percentage.

was eluted with 1 *M* hydrochloric acid above the critical micelle concentration. In contrast, the SS-Diol fiber exhibited a lower EBC with a quantitative elution above this equilibrium concentration range. This is because, for the SS-EO fiber, the hydrophobic interaction of the epoxy group coexisting with the sulfonic acid group of the polymer brush with the alkyl group of C_{12}PyCl as a single molecule will lead to both an increase in EBC and a decrease in elution percentage, and the hydrophilic surface of the C_{12}PyCl micelle cannot distinguish between the epoxy group and the diol group.

4. Conclusions

The binding behavior of ionic surfactants to the charged polymer brushes was investigated in the permeation mode using the charged-polymer-brush-immobilized substrate of a porous hollow-fiber form. Poly-glycidyl methacrylate brushes were appended onto an electron-beam-irradiated porous hollow-fiber membrane uniformly across the membrane thickness; subsequently, some of the epoxy group was converted to a sulfonic acid group. The resultant charged polymer brush was ionically crosslinked with a bivalent ion. *N*-Alkylpyridinium chloride (C_{16}PyCl, C_{12}PyCl, and C_4PyCl) and PyCl solutions of various concentrations were fed to the charged polymer brush. Binding of the surfactants (C_{16}PyCl and C_{12}PyCl) to the charged polymer brush was retarded when their concentrations approached the critical micelle concentration. The equilibrium binding capacity of C_{16}PyCl and C_{12}PyCl exhibited a peak before the critical micelle concentration. In contrast, the equilibrium binding capacity of C_4PyCl and PyCl without micelle formation increased monotonically with increasing concentration. The epoxy and diol groups coexisting with the charged group did not affect the equilibrium binding capacity of the C_{12}PyCl micelle, whereas below the critical micelle concentration, the epoxy group interacted with the alkyl group of the surfactant in a hydrophobic manner.

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