Effect of Water Content of Hydrophilic Amidoxime Polymer on Adsorption Rate of Uranium from Seawater

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Synopsis

Amidoxime polymers crosslinked with tetraethylene glycol dimethacrylate (40 wt%) and with differing water contents were prepared by poly(acrylonitrile) treatment in various quantities of toluene with hydroxylamine. Adsorption rates of uranium on the amidoxime polymers from seawater were examined in relation to their porosity. The amidoxime polymer prepared from poly(acrylonitrile) in an increasing quantity of toluene exhibits a significantly increasing water content. On the basis of mercury intrusion measurements, the increasing water content was revealed to be predominantly owing to the enhancement of porosity. The adsorption rate of uranium from seawater increased steadily with an increase of porosity, suggesting the dependence of the adsorption rate on a diffusion process of uranium into the pore domain.

INTRODUCTION

It has already been reported that an amidoxime polymer crosslinked with hydrophilic tetraethylene glycol dimethacrylate (4EGDM) of 40 wt% exhibits a much higher adsorption rate of uranium from seawater than that crosslinked with divinylbenzene (DVB).[1] The adsorption rate of uranium is primarily governed not by a diffusion process of uranium into a domain of pores with pore radii larger than the ionic dimension of tricarbonatouranate(VI) ion $[UO_2(CO_3)_3]^{4-}$, the assumed species of uranium in seawater,[2] but by diffusion of uranium into a polymeric network. The enhancement of adsorption rate of uranium by the use of a hydrophilic crosslinking agent is presumed to be due to an increasing hydrophilicity of polymer matrix. Undoubtedly the proton-binding nature of amidoxime ligands allows their existence as neutral species in seawater (pH: 8.1–8.3);[3–5] this situation is significantly different from the case of ordinary ion-exchange resins possessing the ligands of ionic species. Therefore, crosslinking with a hydrophilic agent is essential for the enhancement of hydrophilicity of amidoxime polymer and therefore the adsorption rate or uranium from seawater.[1]

The enhancement of hydrophilicity of amidoxime polymers permits the migration of $[UO_2(CO_3)_3]^{4-}$ into the polymeric network, because of the higher

swelling by uptake of a larger amount of water and, therefore, makes very feasible the uranium diffusion into a polymeric network compared with the case of amidoxime polymers crosslinked with DVB. These findings stimulate our interest in the effect of porosity of amidoxime polymer upon the adsorption rate of uranium from seawater. Accordingly, in the present study, amidoxime polymers with different water contents crosslinked with 4EGDM of 40 wt% were prepared, and the adsorption rates of uranium on these polymers from seawater were measured and discussed in relation to their porosity.

EXPERIMENTAL

Materials

A solution containing acrylonitrile (AN) (60 wt%), and tetraethylene glycol dimethacrylate (4EGDM) (40 wt%), in a prescribed quantity of toluene as a diluent was dispersed and polymerized with vigorous stirring into an aqueous solution saturated with the monomers, at 80°C for 8 h by the method of suspension polymerization to afford particles of poly(acrylonitrile).[6,7] In this polymerization, gelatin and calcium carbonate were employed as a suspension stabilizer. The yield of the particles was 90.9–93.7%. These polymer particles were treated with hydroxylamine in methanol at 60°C for 8 h to give polymers with amidoxime groups. The infrared spectra of the resultant polymer revealed negligible attack of hydroxylamine on the ester groups in the crosslinker. Significant infrared bands (KBr): 3400 [ν (N—H)], 1735 [ν (C=O)], 1650 [ν (C=N)], and 930 cm^{-1}[ν (N—O)].

The polymer particles were sieved in water and a fraction of 32–60 mesh was employed in the subsequent experiments.

Adsorptive Capacity for Cu(II)

An adsorptive capacity of amidoxime polymer for Cu(II) was obtained by the batch method as follows. A 0.05 mol dm^{-3} copper(II) dichloride solution was adjusted at a pH of 4.5 with an acetic acid–sodium acetate buffer solution. Next, 25 cm^3 of the Cu(II) solution was added to 0.1 g of the amidoxime polymer in a 50 cm^3 vessel. The vessel was sealed and maintained at 25°C for 48 h with shaking. After filtration, the concentration of Cu(II) in the filtrate was determined. The adsorptive capacity was evaluated from the difference between the initial and the final concentrations in the solution phase.

Mercury Intrusion Measurements

Mercury intrusion measurements of amidoxime polymers were carried out with a Carlo Erba model series 200 porosimeter. It was found that the polymers were contracted by air-drying; this contraction was more remarkable for the polymer with a larger water content. Accordingly, the following freeze-drying technique was employed to examine a pore structure of amidoxime polymer as identical as possible with that immersed in water. The polymers immersed fully in water were frozen instantaneously at −196°C and dried at room temperature in vacuo for 5 days.

Next, 0.1–0.2 g of the dried polymer in a cell with a capillary (inner diameter, 3 mm; height, 9 cm) was evacuated at 1.0 Pa for 5 h, and was installed in the porosimeter after introduction of mercury into the evacuated cell. The mercury intrusion into the polymer specimen was controlled automatically up to 1.1×10^8 Pa in almost the cases, and the mercury height in the capillary was read out as a function of pressure with a digital read-out unit. According to the Washburn equation[8] using the values of a contact angle $= 141.3°$ and a surface tension $= 0.480$ N m^{-1}, the pore radius was calculated as a function of pressure. Thus, the cumulative pore volume was plotted out as a function of pore radius. The surface area was calculated by assuming all the pores to be cylindrical.

Water Contents

An amidoxime polymer immersed fully in water was wrapped with a spongy filter and weighed (W_w) after removal of only the water adhering to outer surfaces of polymer particles with a centrifuge. Then the wetted polymer was dried at 40°C in vacuo for 24 h and the weight was determined (W_d). The water content of amidoxime polymer was defined as $(W_w - W_d)/W_w \times 100$ (%) or $(W_w - W_d)/W_d$(g − H$_2$O g^{-1}).

On the other hand, an adsorption isotherm of water on amidoxime polymer was obtained as follows: 0.2 g of amidoxime polymer freeze-dried as mentioned above was stored at 25°C in a weighing bottle in a desiccator, which relative humidity was maintained at a given value with an aqueous H$_2$SO$_4$ solution. After attaining the adsorption equilibrium, the weight of the polymer was determined, and the water content of the polymer was calculated.

Microcalorimetric Equilibrium Measurements

Microcalorimetric equilibrium measurements of the heat of immersion of amidoxime polymers with water were carried out at 30°C by the method reported in a preceding paper[1] using an LKB model 2107 microcalorimeter system. The polymer samples were freeze-dried before the measurements by the same method as mentioned above.

Uptake of Uranium from Seawater

Amidoxime polymer 5 g was loaded in a glass column (inner diameter: 2.5 cm, height: 20 cm). Seawater was passed upward through the column at $25 \pm 2°C$ and at a flow rate of 100 ± 10 cm^3 min^{-1}. This flow rate was determined for the polymer to exhibit the highest adsorption rate. After a prescribed time, approximately 50 mg of the polymer was collected and then washed well with distilled water. Uranium adsorbed on the polymer was eluted with a 1 mol dm^{-3} HCl solution with reflux. The concentration of uranium in the filtrate was measured to determine the amount of uranium adsorbed.

Quantitative Determinations of Metal Ions

The concentration of uranium was determined by fluorimetry with an Aloka model FMT-3B fluorimeter, and that of Cu(II) was determined by

TABLE I
Water Content and Adsorptive Capacities for Cu(II) of Amidoxime Polymers

Polymer	Toluene[a] (wt%)	Water content		Water adsorbed[b] $(g - H_2O \ g^{-1})$	Content of amidoxime groups[c] $(mmol \ g^{-1})$	Adsorptive capacity for Cu(II) $(mmol \ g^{-1})$
		(wt%)	$(g - H_2O \ g^{-1})$			
1	0	22.4	0.29	0.295	0.19	0.14
2	50	46.8	0.88	0.364	1.93	1.87
3	75	57.2	1.34	0.338	1.91	1.87
4	100	60.5	1.53	0.310	2.12	2.09
5	150	69.4	2.27	0.289	2.20	2.15

[a]The values are quantities of toluene as a diluent added in preparation of the relevant poly(acrylonitrile)s, and expressed in units per the total weight of monomers, AN and 4EGDM.
[b]The values are the amounts of water adsorbed at a relative humidity of 1.
[c]The values were obtained by the same method as in a previous paper (Ref 1).

atomic absorption spectroscopy with a Perkin-Elmer model 403 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Amidoxime Polymers with Widely Different Water Contents

Poly(acrylonitrile)s in this research were prepared through a radical polymerization of AN (60 wt%) and 4EGDM (40 wt%) in various quantities of toluene (0–150 wt% of monomers) as a diluent in order to significantly change the water content of the relevant amidoxime polymers. Toluene is considered to act as a precipitant for poly(acrylonitrile) crosslinked with 4EGDM, because it was used as a precipitant for poly(acrylonitrile) crosslinked with DVB.[9] Amidoxime polymers were obtained by treatment of these poly(acrylonitrile)s with hydroxylamine. Water content of the resulting amidoxime polymers are listed in Table I. Of interest, the amidoxime polymers from poly(acrylonitrile) prepared in a larger quantity of toluene exhibit a significantly higher water content, whereas they possess an approximately equal adsorptive amount of water at a relative humidity of 1. It could be presumed that the latter values refer primarily to those of bound water on the polymers. Polymer 1 was translucent in water, while polymers 2, 3, 4, and 5 were opaque. Polymers 2, 3, 4, and 5 highly contract on air-drying. These observations imply that polymer 1 is a gel-type resin while the others are porous.[10] The morphological characteristics are elucidated satisfactorily on the basis of porous properties obtained by the mercury intrusion method mentioned below.

From these results, it was clear that the water content of amidoxime polymer can be varied successfully by a quantity of toluene as diluent added to the preparation of prepolymer poly(acrylonitrile). This would be due to the action of toluene as a precipitant for poly(acrylonitrile).

Adsorptive Capacities for Cu(II)

The adsorptive capacities for Cu(II) of amidoxime polymers prepared in this research are listed together with the contents of amidoxime groups in

Table I. The former values considerably agree with the latter ones in every case; thus the adsorptive capacities for Cu(II) can be assumed to refer to the effective contents of amidoxime ligands, as noted in a previous paper.[1] The adsorptive capacity for Cu(II) changes widely, although all the polymers possess the same degree of crosslinking of 40 wt% 4EGDM. It is obvious from Table I that the polymer with the larger water content exhibits the higher adsorptive capacity for Cu (II). Porous-type polymers 2–5 exhibit higher adsorptive capacities of Cu(II) than the gel-type polymer 1; the values of the former four polymers are larger than those of amidoxime polymers crosslinked with DVB.[1] This suggests the more ready penetration of hydroxylamine into the polymer matrix with pore phases and accordingly the more extensive conversion of nitrile groups to amidoxime ones.

Porous Properties

From the dependence of water content upon the amount of amidoxime ligands as described in a preceding paper,[1] the amidoxime polymers with the exception of polymer 1 are supposed to take up large quantities of free water as well as bound water. This implies that these polymers swollen in water possess pore phases together with the ordinary gel phase inherent to a polymeric network crosslinked with 40 wt% 4EGDM.[11] Some information on porous properties of amidoxime polymers are necessary for examination on the diffusion process of uranium into the polymer matrix from seawater.[1] Accordingly, in this study the pore structures of amidoxime polymers were estimated from the mercury intrusion measurements on the polymer samples swollen in water and dried by the two different methods.

The results on amidoxime polymers air-dried are shown in Figure 1 and Table II. The value of cumulative pore volume on polymer 1 was zero within an error in measurements at the values of pore radius down to 7 nm. Unexpectedly, the values of pore volume, V_p, are scarcely related to those of water content shown in Table I; in particular, the V_p value of polymer 5 is too smaller than expected from the water content. This is probably due to the significant contraction of amidoxime polymers on air-drying. Excessively large ratios of porogen/monomer can lead to resin morphologies which lie outside the macroporous domain.

On the other hand, the results on the polymers freeze-dried as described in the Experimental section are shown in Figure 2 and Table II. As evident from comparison with Figure 1, the shapes of pore radius distribution in the case of freeze-drying are similar to those in the case of air-drying, although the positions of frequent pore radii shift considerably. It is, therefore, safely assumed that the morphological structures of polymer matrices are hardly destroyed by the rapid freezing at $-196°C$. This is a reasonable assumption from the experimental results on the amidoxime polymers crosslinked with DVB, which hardly contract on air-drying, that the pore spectra obtained by the mercury intrusion method were identical regardless of the two different drying methods.

Plots of water content are shown against pore volume in Figure 3. In the case of freeze-drying, a linear relationship is well satisfied between these values and expressed by a straight line with a slope = 1.32 and an intercept = 0.24, while any linear relationship does not appear in the case of air-drying. A
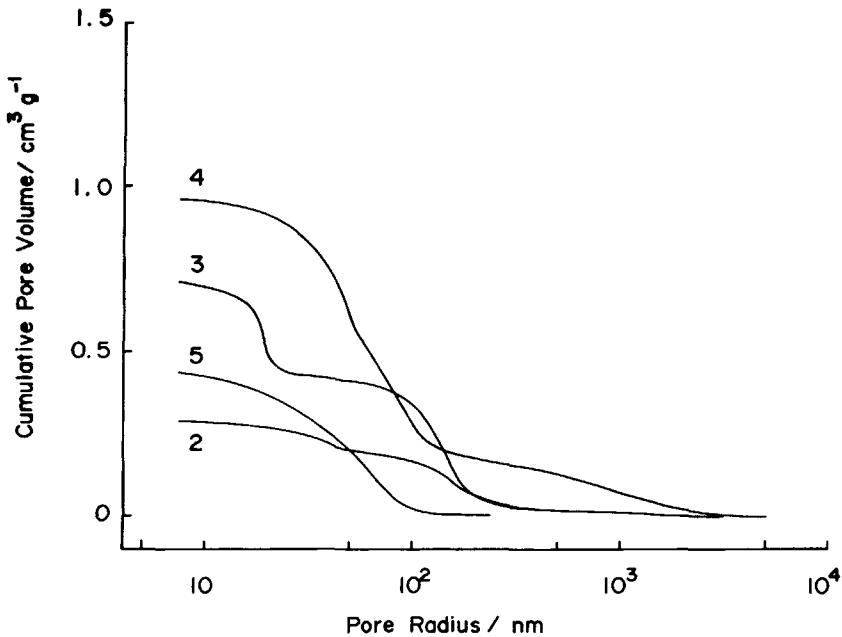
Fig. 1.   Pore radius distribution spectra of amidoxime polymers air-dried. The numbers specify polymer samples (Table I).

value of the intercept is close to that of the uptaken amount of water at the relative humidity of 1, which is assumed to be the amount of water bound on the polymer predominantly on the gel phase. It is, therefore, assumed from the result in Figure 3 that the pore structure of amidoxime polymer swollen in water could be satisfactorily estimated by the mercury intrusion measurements on the freeze-dried polymer. Provided that this assumption is reasonable, these results on the water content and porous properties confirm that, except for polymer 1, consisting predominantly only of gel phase, the polymers consist of pore phase and gel phase.

From the results on amount of water adsorbed shown in Table I, the gel phase is thought to be constructed via a similar polymeric network regardless of a quantity of toluene added as a diluent in the preparation of poly(acrylonitrile). On the other hand, the pore structure of amidoxime

TABLE II
Porous Properties of Amidoxime Polymers Freeze-Dried

Polymer	Pore volume[a] $(cm^3 \ g^{-1})$	Surface area[a] $(m^2 \ g^{-1})$	Average pore radius[b](nm)
1	0.052(—)	3.71(—)	28.0
2	0.376(0.294)	31.20(8.9)	24.1
3	0.963(0.720)	46.12(46.6)	41.8
4	1.04(0.961)	46.30(45.1)	44.9
5	1.431(0.437)	36.16(22.2)	79.1

[a] The values of amidoxime polymers air-dried are shown in parentheses.
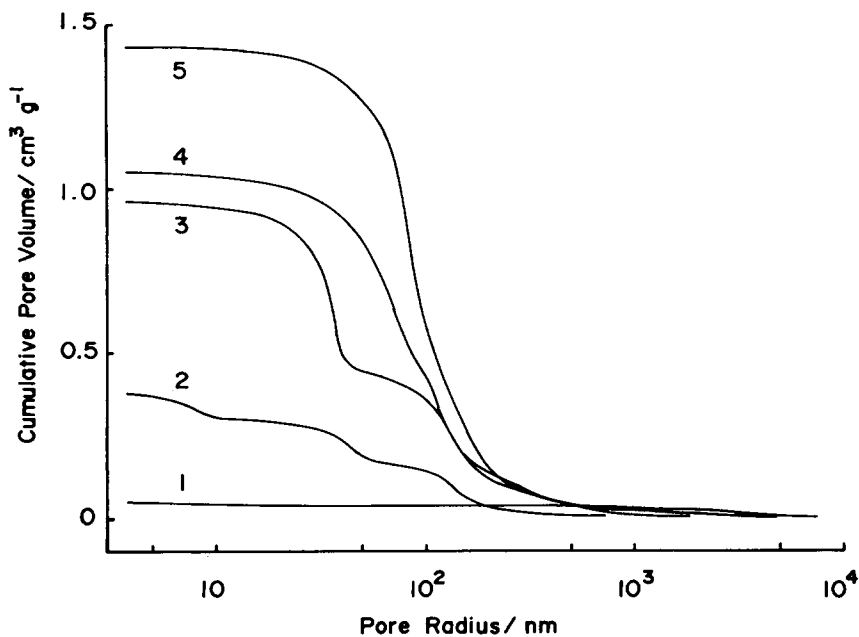[b] The average pore radius is defined as $2V_p/S_p$.

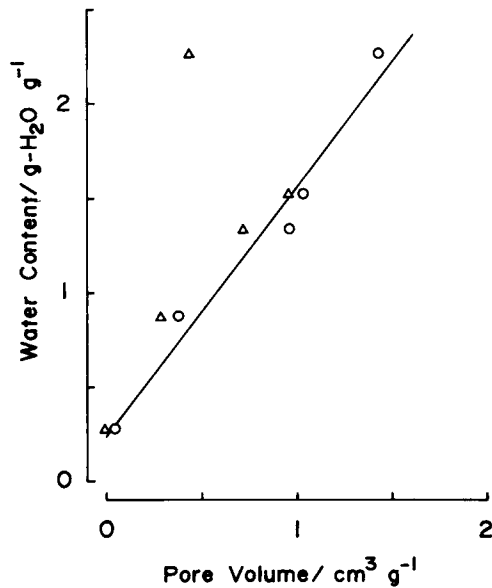Fig. 2. Pore radius distribution spectra of amidoxime polymers freeze-dried. The numbers specify polymer samples.

Fig. 3. Plots of water content against V_p in the cases of freeze-drying (○) and air-drying (△). The straight line represents a least-squares fitting line in the case of freeze-drying.

polymer depends significantly on the quantity of toluene as shown in Figure 2. As the quantity of toluene increases, the average pore radius, $\bar{r}_p$, and the pore volume, V_p, increase; that is, the polymer exhibits a higher porosity. A maximal value of surface area, S_p, appears in polymers 3 and 4. When toluene is not added, the polymer does not exhibit any porosity; this results that polymer 1 is of gel type. These results reveal the action of toluene as a precipitant on poly(acrylonitrile). Similar phenomena have been reported on macroporous polystyrenes crosslinked with DVB which were prepared with 2,2-dimethylpropanol and hexane as precipitants.[12, 13]

From the above results, it was confirmed that the amidoxime polymers of widely differing porosities could be prepared by the present method. These polymers possess many pores with the pore radius much larger than the ionic dimension of $[UO_2(CO_3)_3]^{4-}$ of ca. 1 nm,[14, 15] and are favorable for examining the effect of porosity on uranium diffusion into polymer matrix.

Heats of Immersion in Water

Heats of immersion of amidoxime polymers in water, $-\Delta H_w$, were determined by the microcalorimetric measurements in order to estimate a hydrophilicity of amidoxime polymer. The sample polymers were freeze-dried by the same method as mentioned before in order to exclude the effect of swelling in water. As already reported on the amidoxime polymers crosslinked with 40 wt% 4EGDM, the heat of immersion in water depends primarily on the content of amidoxime ligands.[1] Hence the heats of immersion in water are drawn against the effective content of amidoxime ligands, C_L, in Figure 4. The polymers (except polymer 1) exhibit much larger values of $-\Delta H_w$ than amidoxime polymers crosslinked with DVB.[1] A straight line represents the
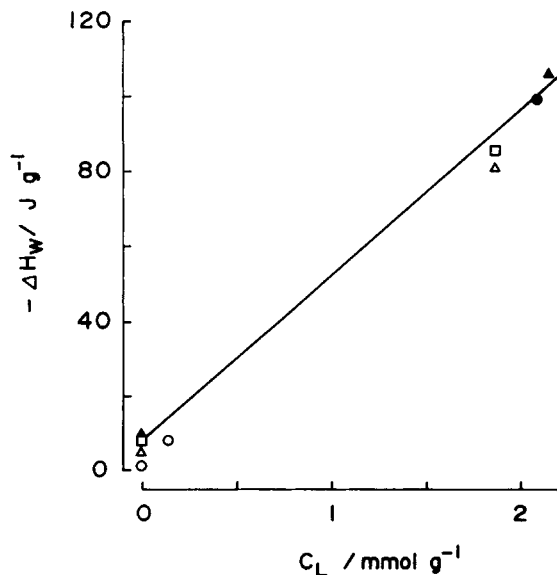

Fig. 4. Heats of immersion in water of amidoxime polymers at 30°C. The straight line is represented by the equation, $-\Delta H_w = 8.97 + 43.63\ C_L$. Polymers: 1(○), 2(△), 3(□), 4(●), and 5(▲). The $-\Delta H_w$ values at $C_L = 0$ are those of the corresponding poly(acrylonitrile)s.
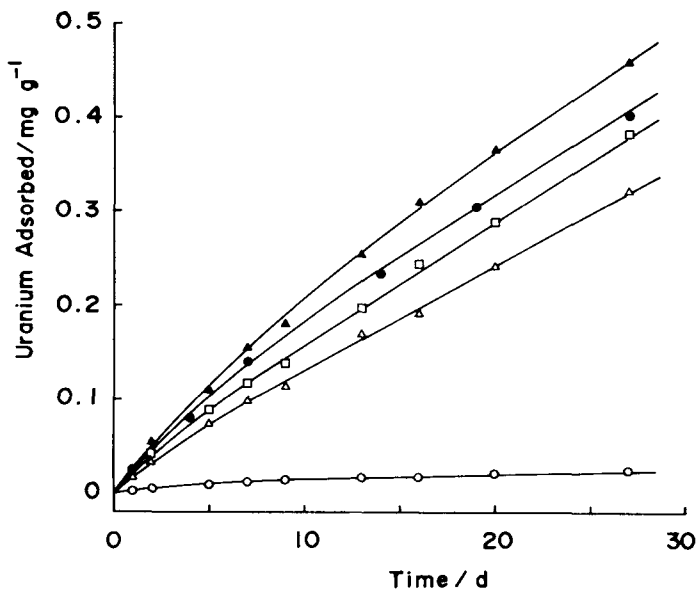
Fig. 5.   Uptakes of uranium on amidoxime polymers from seawater at 25°C. Polymers: 1(○), 2(△), 3(□), 4(●), and 5(▲).

equation, $-\Delta H_w = 8.97 + 43.63 \, C_L$. This equation holds for a series of polymers 4 prepared from poly(acrylonitrile) prepared in 100 wt% toluene as reported in a preceding paper.[1] The values of $-\Delta H_w$ at $C_L = 0$ are those of the relevant poly(acrylonitrile)s. If the heats of immersion of the prepolymers are taken into account, $-\Delta H_w$ values of the corresponding amidoxime polymers can be satisfactorily estimated by this equation. This result means that the heat of immersion in water and, therefore, the hydrophilicity of the amidoxime polymer are determined primarily by the content of amidoxime ligands. Furthermore, it is shown in Figure 4 that the heat of immersion of amidoxime polymer is not so much dependent on the water content. It is, therefore, suggested that the amidoxime polymer possessing pore phases takes up a large quantity of free water in the pore domain, which does not largely contribute to the heat of immersion.

Influence of Water Content on Adsorption Rate of Uranium from Seawater

The amount of uranium adsorbed on amidoxime polymer from seawater is plotted against the immersion time in Figure 5. The adsorption rate of uranium on polymer 1, which is of gel type and possesses the low content of amidoxime groups, is much lower than those on the other polymers having pore phases. The adsorption rate is apparently dependent on the amount of amidoxime groups, and furthermore, from the difference between polymers 2 and 3 the adsorption rate of uranium is also affected by the water content.

In the present study, the flow rate of seawater was set so that all the polymers exhibit the highest adsorption rates of uranium; therefore, the results in Figure 5 might be discussed in particular from the standpoint of
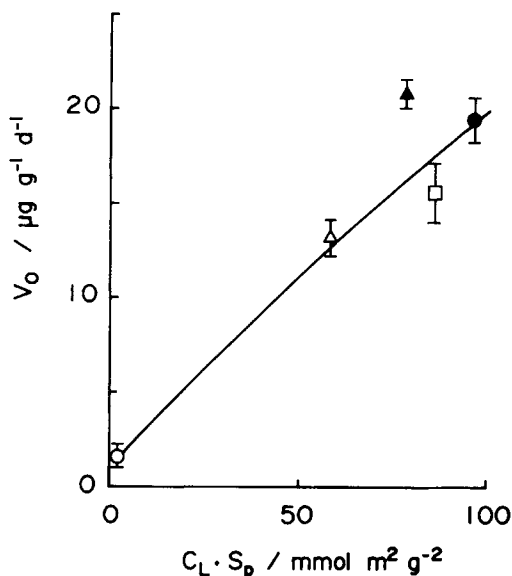
Fig. 6.   A plot of V_0 against $C_L \times S_p$. Polymers as in Figure 5.

diffusion of uranium into the polymer.[1] Figure 6 shows the dependence of the initial adsorption rate, V_0, on the value of $C_L \times S_p$. V_0 depends rather extensively on $C_L \times S_p$; it is, therefore, suggested that the adsorption rate of uranium from seawater is determined primarily by a diffusion process of uranium into the polymer network rather than that into the pore domain.[1] This explains satisfactorily the extremely low adsorption rate of uranium on the gel type polymer 1 and the difference of adsorption rate of uranium between polymers 2 and 3 having the same content of amidoxime groups but different pore structures. However, the V_0 value of polymer 5 seems to be a little higher. This unexpected deviation stimulates an interest in dependence of the adsorption rate of uranium on the morphology, in particular the porosity.

The present polymers differ in the contents of amidoxime ligands; therefore, the corrected initial adsorption rate, V_0^c, is defined as follows, $V_0^c = V_0 \times C_L^{-1}$. A plot of V_0^c against V_p is shown in Figure 7. V_0^c increases steadily with an increasing value of V_p, although the experimental point of polymer 1 deviates significantly from the other polymers. This implies that the adsorption rate of uranium is also affected by a porosity of the polymer crosslinked with 4EGDM.

In the case of amidoxime polymers crosslinked with DVB, the adsorption rate of uranium from seawater is determined predominantly not by a diffusion process of uranium into pore phases, but by diffusion into the hydrophobic polymeric network.[1] This is probably due to the significant interference of the migration of bulky $[UO_2(CO_3)_3]^{4-}$ ions into a hydrophobic and tightly cross-linked polymer network but hardly into pores with the pore radius much larger than the ionic radius of this uranyl(VI) species. It was shown in the previous article that the adsorption rate of uranium increases by the enhancement of hydrophilicity of polymer.[1] This means that enhanced hydrophilicity
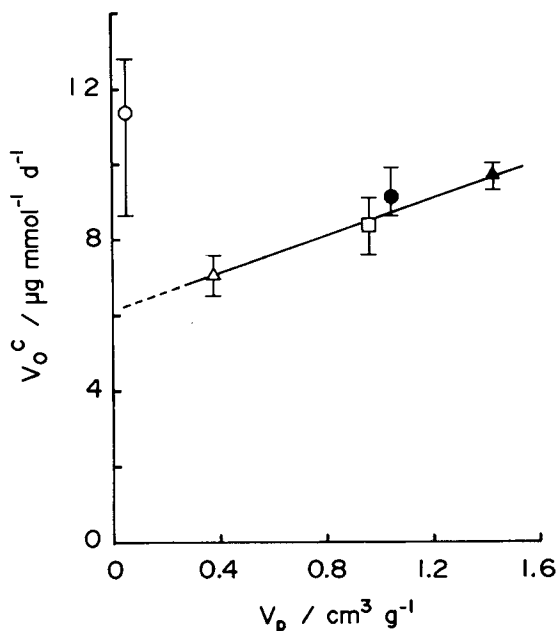
Fig. 7.   A plot of V_0^c against V_p. Polymers as in Figure 5.

of the polymer matrix induces the uptake of a larger quantity of water by the polymeric network and accordingly the more feasible penetration of $[UO_2(CO_3)_3]^{4-}$ into the polymer matrix. When the diffusion of $[UO_2(CO_3)_3]^{4-}$ into a hydrophilic polymeric network becomes comparable to the diffusion into the portion of pores, a steady dependence is expected between the adsorption rate of uranium and the porosity as shown in Figure 7. The unexpected high V_0^c value of polymer 1 would be owing to a higher distribution of amidoxime ligands near the outer surface.

In the present study, the amidoxime polymers with different water contents were obtained from the prepolymer, poly(acrylonitrile)s crosslinked with 4EGDM polymerized in the presence of various quantities of toluene as a diluent. The difference in water content is due to the difference in the porosity. The porosity of the amidoxime polymer enhanced the adsorption rate of uranium from seawater. In conclusion, the porosity of hydrophilic amidoxime polymer is one of the essential factors for developing the adsorbents for a promising uptake of uranium from seawater.

References

1. T. Hirotsu, S. Katoh, K. Sugasaka, N. Takai, M. Senō, and T. Itagaki, *Ind. Eng. Chem. Res.*, **26**, 1970 (1987).

2. N. Ogata, N. Inoue, and H. Kakihana, *Nippon Genshiryoku Gakkaishi*, **13**, 560 (1971).

3. T. Hirotsu, S. Katoh, K. Sugasaka, M. Senō, and T. Itagaki, *J. Chem. Soc., Dalton Trans.*, 1986, 1609.

4. T. Hirotsu, S. Katoh, K. Sugasaka, M. Senō, and T. Itagaki, *J. Chem. Soc., Dalton Trans.*, 1986, 1983.

5. T. Hirotsu, S. Katoh, K. Sugasaka, M. Senō, and T. Itagaki, *Sep. Sci. Technol.*, **21**, 1101 (1986).

6. H. Takahashi, N. Takai, T. Hirotsu, S. Katoh, K. Sugasaka, and Y. Umezawa, Japan Pat. 126 445, 1981; *Chem. Abstr.*, **96**, 72439 (1982).

7. P. Hodge and D. C. Sherrington, Eds., *Polymer-Supported Reactions in Organic Synthesis*, Wiley, New York, 1980, p. 469.

8. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London, 1982, p. 173.

9. H. Egawa, H. Harada, and T. Nonaka, *Nippon Kagaku Kaishi*, 1767 (1980).

10. D. C. Sherrington, in *Polymer-Supported Reactions in Organic Synthesis* edited by H. Hodge and D. C. Sherrington, Wiley, New York, 1980, Chap. 1, p. 16.

11. K. Kun and R. Kunin, *J. Polym. Sci. C*, **16**, 1457 (1967).

12. K. Kun and R. Kunin, *J. Polym. Sci. A-1*, **6**, 2689 (1968).

13. W. L. Sederel and G. J. De Jong, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).

14. A. Anderson, C. Chieh, D. E. Irish, and J. P. K. Tong, *Can. J. Chem.*, **58**, 1651 (1980).

15. R. Graziani, G. Bombieri, and E. Forsellini, *J. Chem. Soc., Dalton Trans.*, 1972, 2059.