Amidoxime Resins Based on Poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) and Their Behavior in Uptake of Uranium from Sea Water

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SYNOPSIS

Amidoxime resins were derived from poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) beads, which were prepared by suspension polymerization of the ternary monomeric mixtures in the presence of 4-methyl-2-pentanone (MIBK) or 1,2-dichloroethane (DCE) as the diluent (porogen), in order to clarify the effect of copolymerized vinylidene chloride on properties of the resulting amidoxime resins. Pore structure analyses of the copolymers as well as of their amidoximated derivatives clarified that MIBK yields larger pores than does DCE and then the latter gives larger specific surface areas than does the former. On the other hand, chemical properties of the amidoximated resins, such as anion-exchange capacities and uranyl ion uptake, were not essentially affected by the diluent species, indicating that both MIBK and DCE as the porogen lead to the amidoxime resins with almost the same ability in recovery of uranium from sea water. The uranium recovery decreased with increase in the vinylidene chloride content, but the decrease in the recovery was minor up to the 10 mol % of vinylidene chloride. It was also clarified that the uranium recovery by the amidoxime resins containing vinylidene chloride is greatly enhanced by the alkali treatment. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A wide range of adsorbents with amidoxime groups has been described in the literature[1-13] and recently reviewed.[14] It has been clarified that amidoxime resins derived from binary copolymers poly-(acrylonitrile-co-divinylbenzene) are one of the most promising candidates in the recovery of uranium from sea water,[14] but problems to be resolved still remain. For example, a low density of amidoxime resins is not suitable for stable fluidization under high linear velocities of sea water.[15,16] On the basis of binary copolymers consisting of acrylonitrile and a cross-linking comonomer, the introduction of new functions to amidoxime resins is difficult to achieve. This difficulty will be overcome by the amidoxi-mation of ternary copolymers consisting of acrylonitrile, a cross-linking comonomer, and a third comonomer for the new additive functions. Unfortunately, studies on amidoxime resins based on ternary copolymers are very rare.[7-9,17]

In a previous article, we preliminarily reported the preparation and characterization of amidoxime resins derived from lightly cross-linked poly-(acrylonitrile-co-vinylidene chloride-co-divinylbenzene).[17] This article describes the further results on the preparation and characterization of amidoxime resins based on poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene). In this work, 4-methyl-2-pentanone as the solvating diluent was also adopted in addition to 1,2-dichloroethane in the preparation of the precursory copolymers, and the columnar adsorption of uranium from sea water by the resulting resins was studied in order to clarify the effect of copolymerized vinylidene chloride on the uranium uptake.

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EXPERIMENTAL

Resin Preparation

Acrylonitrile, divinylbenzene (DVB), and azobisisobutylonitrile (AIBN) were purified as described.[6,11] Vinylidene chloride (VC) was provided by Asahi Chemical Co. (Nobeoka, Japan) and used as received. As the diluent (porogen), 1,2-dichloroethane (DCE) and 4-methyl-2-pentanone (MIBK) of reagent grade were used without purification. Poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene) beads were synthesized by suspension polymerization in the presence of the diluent (DCE or MIBK) using AIBN (180 mmol/L of a monomeric mixture) as the polymerization initiator according to the described method.[17] The copolymer beads with a diameter of 32–60 mesh were selected, and the selected beads were amidoximated by the reaction with 3 wt % hydroxylamine in methanol at 80°C for 2 h. Aliquots of the amidoximated resins were treated with $1 M$ NaOH at 30°C for 72 h (alkali treatment).

In this article, the ternary copolymers are designated as RN(DVB-X,VC-Y,DCE-Z) or RN(DVB-X,VC-Y,MIBK-Z), where the figures X and Y represent mol % of DVB and VC in monomeric mixtures, respectively, and where the figure Z means volume ratio (%) of DCE or MIBK to the monomeric mixtures. The amidoximated derivatives of RN(DVB-X,VC-Y,DCE-Z) and RN(DVB-X,VC-Y,MIBK-Z) are denoted by the symbols RNH(DVB-X,VC-Y,DCE-Z) and RNH(DVB-X,VC-Y,MIBK-Z), respectively.

Physical Properties

The specific surface areas were measured by means of a BET method using a Shimadzu Flowsorb II 2300 apparatus, and pore structures were analyzed by a mercury penetration method using a Carlo Erba porosimeter. Volumes of wet resins were measured according to the method described elsewhere.[7]

Chemical Properties

Both anion-exchange and cation-exchange capacities were determined according to the reported methods.[6] The capacities for uncomplexed uranyl ion were evaluated by shaking 0.125 g of a resin with 50 mL of $0.01 M$ uranyl nitrate solution. The adsorption of uranium from sea water was carried out at 30°C as follows: To a column (inner diameter 1 cm, length 30 cm) packed with 0.5 g of a resin, 20 L of natural sea water was upflow delivered at a flow rate of 900 mL/h using a peristaltic pump. The elution and analysis of the adsorbed uranyl were conducted as described.[6]

RESULTS AND DISCUSSION

Properties of Ternary Copolymers Cross-linked with 5 Mol % DVB

In the preceding work, it was clarified that DCE as the porogen results in highly porous amidoxime resins based on lightly cross-linked poly(acrylonitrile-co-vinylidene chloride-co-divinylbenzene).[17] In this work, six ternary copolymers containing nominal 5 mol % DVB were synthesized using MIBK or DCE as the diluent. The effect of the diluents on chemical and physical properties of the resulting copolymers is summarized in Table I. The analytical data of the copolymers indicate that the diluents do not affect the chemical compositions of the resulting copolymers. However, their pore structures depend on the diluent species; pore volumes and average pore radii of the copolymers prepared in the presence of MIBK are greater than those of the copolymers obtained in the presence of DCE, and DCE yields greater specific surface areas than does MIBK. With increasing the amount of VC, a clear difference in the effect of the diluent species on the pore structures can be seen between the two diluents. In the case of MIBK, parameters concerning the pore structures are not greatly dependent on Y. In the case of DCE, on the other hand, the parameters decrease markedly with an increase in Y, especially the pore volumes. However, the effect of the diluent species on the pore structures is not easily explainable, since the situation is much more complex in the ternary systems than that in the binary ones.[11]

Properties of Amidoxime Resins Based on Ternary Copolymers Cross-linked with 5 Mol % DVB

In Table II, properties of the amidoxime resins are summarized. Clearly, the amidoximation reduces the pore volumes but increases the average pore radii, resulting in the decrease in specific surface areas of the amidoximated resins. However, the amidoximation does not cause drastic changes in the pore structures, since it seems that characteristic pore structures of the both precursors RN(DVB-5,VC-Y,DCE100) and RN(DVB-5,VC-Y,MIBK100) are still maintained to some extent in those of the respective amidoximated resins RNH(DVB-5,VC-Y,DCE100) and RNH(DVB-5,VC-Y,MIBK100).

Table I Analytical Data and Pore Structures of Ternary Copolymers

Copolymer[a]	Analytical Data				Pore Structure		
	H (%)	C (%)	N (%)	Cl (%)	SSA[b] (m^2/g)	PV[c] (cm^3/g)	APR[d] (Å)
RN(DVB-5, VC-0, MIBK-100)	6.26	71.79	21.44	—	44.4	0.917	378
RN(DVB-5, VC-0, DCE-100)	6.16	71.79	21.62	—	68.7	0.650	204
RN(DVB-5, VC-5, MIBK-100)	5.82	68.40	19.05	6.40	53.6	0.855	367
RN(DVB-5, VC-5, DCE-100)	5.88	68.65	19.45	5.90	67.5	0.595	192
RN(DVB-5, VC-10, MIBK-100)	5.61	65.35	17.43	11.24	48.5	0.833	335
RN(DVB-5, VC-10, DCE-100)	5.62	65.30	17.67	11.20	49.5	0.459	183
RN(DVB-5, VC-20, MIBK-100)	5.09	59.98	14.12	20.63	43.6	0.831	310
RN(DVB-5, VC-20, DCE-100)	5.14	59.79	14.26	20.60	47.7	0.263	111

[a] For notations, refer to the Experimental section.
[b] Specific surface area.
[c] Pore volume.
[d] Average pore radius.

A pair of the resins RNH(DVB-5,VC-Y,DCE100) and RNH(DVB-5,VC-Y,MIBK100) with the same Y value have almost the same anion-exchange capacities, indicating that yields of the amidoximation of the both precursors are nearly equal. This means that the difference in the pore structures between RN(DVB-5,VC-Y,DCE100) and RN(DVB-5,VC-Y,MIBK100) does not have a significant meaning in the amidoximation reaction. Naturally, the anion-exchange capacities decrease with an increase in Y, since nitrile groups in the precursors decrease with increasing Y (Table I).

As summarized in Table II, physical and chemical properties of the amidoximated resins are greatly affected by the mol % of vinylidene chloride (Y).

Thus, the uranium uptake from sea water cannot be simply related to Y. In this article, however, the uranium uptake is plotted against Y in order to estimate the overall effects of the copolymerized vinylidene chloride on uranium uptake from sea water. Figure 1(A) shows the uranium uptake from sea water by the untreated resins. As uranium uptake per unit volume of a wet resin will be mentioned in the last section, the uranium uptake described in this and the next sections is represented on the basis of unit weight of the dry resins. The uranium uptake almost linearly decreases with an increase in Y. As shown in Figure 1(B), the alkali treatment markedly enhances the uranium uptake; surprisingly, the uptake does not decrease up to Y = 5, whereas it

Table II Properties of Untreated Amidoxime Resins Derived from Ternary Copolymers Given in Table I

Resin[a]	SSA[b] (m^2/g)	PV[c] (cm^3/g)	APR[d] (Å)	Ca[e] (meq/g)	V[f] (mL/g)
RNH(DVB-5, VC-0, MIBK-100)	19.6	0.596	568	3.81	3.0(4.8)[g]
RNH(DVB-5, VC-0, DCE-100)	29.1	0.307	216	4.03	2.8(4.6)
RNH(DVB-5, VC-5, MIBK-100)	18.4	0.614	623	3.31	3.0(4.5)
RNH(DVB-5, VC-5, DCE-100)	26.6	0.325	260	3.84	2.6(4.2)
RNH(DVB-5, VC-10, MIBK-100)	18.7	0.606	608	2.99	2.8(4.8)
RNH(DVB-5, VC-10, DCE-100)	23.8	0.248	243	3.38	2.4(4.2)
RNH(DVB-5, VC-20, MIBK-100)	15.0	0.589	591	1.76	2.8(4.3)
RNH(DVB-5, VC-20, DCE-100)	19.6	0.231	208	2.03	2.2(3.6)

[a] For notations, refer to the Experimental section.
[b] Specific surface area.
[c] Pore volume.
[d] Average pore radius.
[e] Anion-exchange capacity.
[f] Volume of resins in 3% NaCl solution.
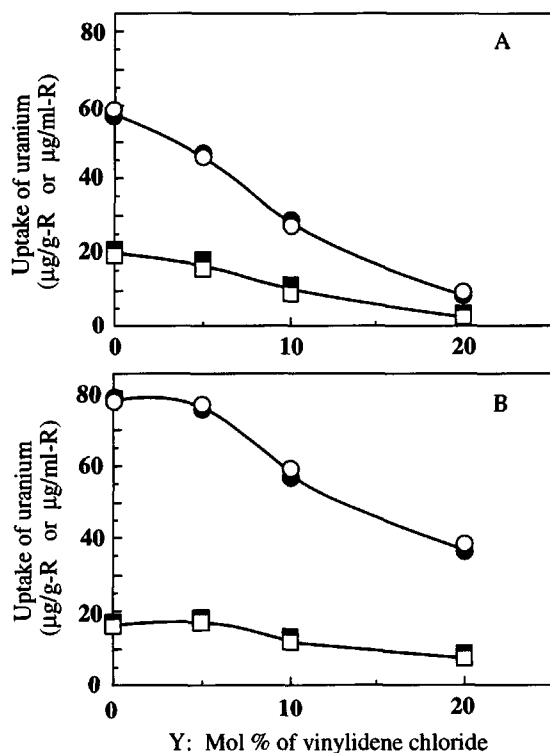[g] Figures in parentheses are volumes of the alkali-treated resins.

Figure 1 Uptake of uranium from sea water by the amidoxime resins cross-linked with 5 mol % DVB. (A) Untreated resins: (O) RNH(DVB-5,VC-Y,MIBK-100) in μg/g-R; ($\bullet$) RNH(DVB-5,VC-Y,DCE-100) in μg/g-R; ($\square$) RNH(DVB-5,VC-Y,MIBK-100) in μg/mL-R; ($\blacksquare$) RNH(DVB-5,VC-Y,DCE-100) in μg/mL-R. (B) Alkali-treated resins: (O) RNH(DVB-5,VC-Y,MIBK-100) in μg/g-R; ($\bullet$) RNH(DVB-5,VC-Y,DCE-100) in μg/g-R; ($\square$) RNH(DVB-5,VC-Y,MIBK-100) in μg/mL-R; ($\blacksquare$) RNH(DVB-5,VC-Y,DCE-100) in μg/mL-R.

decreases with a further increase in Y. The relative increase in the uranium uptake caused by the alkaline treatment becomes much greater with in-

creasing Y. The increase of Y enhances the hydrophobicity of the untreated resins as judged from their wet volumes, but it decreases the amount of the introduced amidoxime groups (Table II). Because of these facts, it seems that the uranium uptake by the untreated resins drastically decreases with the increase of Y. As judged from the wet volumes of the alkali-treated resins (Table II), on the other hand, the alkaline treatment greatly enhances their hydrophilicity, and, hence, a greater amount of amidoxime groups in the alkali-treated resins will be able to participate in the uptake of uranium from sea water.

Properties of Amidoxime Resins Based on Ternary Copolymer Cross-linked with 10 Mol % DVB

In general, wet volumes of lightly cross-linked resins greatly change with surrounding conditions, and the large change in the resin volumes frequently causes serious problems in column operations. Then, more highly cross-linked amidoxime resins were derived from a series of the ternary copolymers that were prepared by fixing the amount of DVB at 10 mol % but by changing mol % of VC in the presence of the porogen MIBK. Physical properties of the amidoximated resins are summarized in Table III. Pore volumes of RNH(DVB-10,VC-Y,MIBK-100) are greater than those of the corresponding RNH(DVB-5,VC-Y,MIBK-100), but average pore radii of the former are much less than those of the latter. Consequently, specific surface areas of RNH(DVB-10,VC-Y,MIBK-100) become much greater than those of RNH(DVB-5,VC-Y,MIBK-100). The wet volumes of RNH(DVB-10,VC-Y,MIBK-100) are not markedly increased by the alkali treatment because of the high cross-linking.

Table III Physical Properties of Untreated Amidoxime Resins Containing 10 Mol % DVB

Resin[a]	SSA[b] (m^2/g)	PV[c] (cm^3/g)	APR[d] (Å)	V[e] (mL/g)
RNH(DVB-10, VC-0, MIBK-100)	36.9	0.664	303	2.8(3.0)[f]
RNH(DVB-10, VC-5, MIBK-100)	38.1	0.743	338	2.8(2.8)
RNH(DVB-10, VC-10, MIBK-100)	33.5	0.631	298	2.6(2.8)
RNH(DVB-10, VC-20, MIBK-100)	47.7	0.807	239	2.8(3.0)
RNH(DVB-10, VC-30, MIBK-100)	68.9	0.782	196	3.0(3.0)

[a] For notations, refer to the Experimental section.
[b] Specific surface area.
[c] Pore volume.
[d] Average pore radius.
[e] Volume of resins in 3% NaCl solution.
[f] Figures in parentheses are values for the alkali-treated resins.

Table IV   Chemical Properties of Amidoxime Resins Containing 10 Mol % DVB

Resin	Untreated			Alkali-treated		
	Ca^a (meq/g)	Cc^b (meq/g)	UO_2^{2+} Uptake[c] (mmol/g)	Ca^a (meq/g)	Cc^b (meq/g)	UO_2^{2+} Uptake[c] (mmol/g)
RNH(DVB-10, VC-0, MIBK-100)	2.56	1.03	0.71	2.52	1.66	0.73
RNH(DVB-10, VC-5, MIBK-100)	2.15	0.85	0.58	2.00	1.27	0.63
RNH(DVB-10, VC-10, MIBK-100)	1.66	0.72	0.49	1.54	1.07	0.54
RNH(DVB-10, VC-20, MIBK-100)	1.03	0.43	0.29	0.91	0.83	0.37
RNH(DVB-10, VC-30, MIBK-100)	0.73	0.35	0.17	0.48	0.78	0.27

[a] Anion-exchange capacity.
[b] Cation-exchange capacity.
[c] Uncomplexed uranyl ion.

Table IV summarizes chemical properties of RNH(DVB-10,VC-Y,MIBK-100). Anion-exchange capacities (amount of amidoxime groups) decrease with an increase in Y, as is anticipated. The alkali treatment slightly reduces the anion-exchange capacities but greatly increases the cation-exchange capacities. The increase in the cation-exchange capacities can be ascribed to the formation of the acidic sites by hydrolysis of amidoxime groups and/or remaining nitrile groups during the alkali treatment.[11]

As clarified in previous works,[9,11] the uptake of the uncomplexed uranyl ion is essentially governed by the amount of amidoxime groups. Thus, the uptake of the uncomplexed uranyl ion by RNH(DVB-10,VC-Y,MIBK-100) decreases with an increase in Y, and both the untreated and alkali-treated RNH(DVB-10,VC-Y,MIBK-100) have nearly equal capacities for the uncomplexed uranyl ion, whereas there is a tendency that the discrepancy in the capacities between the alkaline-treated and untreated resins becomes marked with an increase in Y.

The uranyl ion in sea water exists as the stable complexed form of $UO_2(CO_3)_3^{4-}$.[4] For the adsorption of uranium from sea water, then, resins should allow fast diffusion of the bulky complexed uranium and also have the complexing power strong enough to substitute the coordinated carbonates; in other words, well-swollen micropores as the space for the reaction of the bulky $UO_2(CO_3)_3^{4-}$ with amidoxime groups will be necessarily required in addition to the macropores. The micropore formation by the alkali treatment was already proved experimentally by means of a gel permeation chromatographic approach.[11] As shown in Figure 2, which shows the overall effects of the copolymerized VC on the uranium uptake from sea water, the alkali-treated RNH(DVB-10,VC-Y,MIBK-100) more effectively and rapidly take up uranium from sea water than

do the untreated ones. Naturally, the uranium uptake by the untreated and alkali-treated RNH-(DVB-10,VC-Y,MIBK-100) decreases with an increase in Y. However, it is noteworthy that the decrease in the uptake from Y = 0 to Y = 10 is not so remarkable.

Uranium Uptake from Sea Water Represented by the Unit Volume of the Wet Resin

In practical large-scale operations, uranium uptake per unit volume of a wet resin is much more important than the uptake per unit weight of a dry resin. The uptake per unit volume of RNH(DVB-10,VC-Y,MIBK-100) is nearly equal to or slightly higher than that of the corresponding RNH(DVB-5,VC-Y,MIBK-100), since the wet volumes of the resins
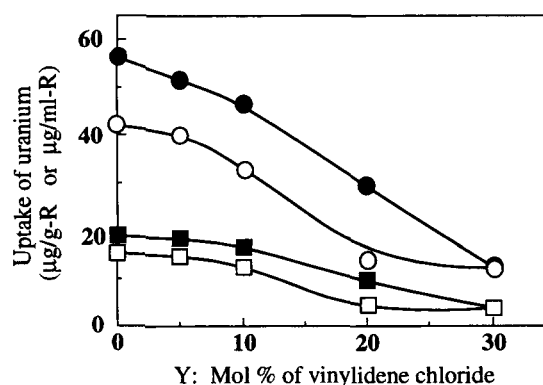

Figure 2   Uptake of uranium from sea water by the amidoxime resins cross-linked with 10 mol % DVB: (○) Untreated RNH(DVB-10,VC-Y,MIBK-100) in μg/g-R; (●) alkali-treated RNH(DVB-10,VC-Y,MIBK-100) in μg/g-R; (□) untreated RNH(DVB-10,VC-Y,MIBK-100) in μg/mL-R; (■) alkali-treated RNH(DVB-10,VC-Y,MIBK-100) in μg/mL-R.

increase with decreasing cross-linking. When Y is less than 10, the uptake per unit volume of the alkaline-treated RNH(DVB-10,VC-Y,MIBK-100) and RNH(DVB-5,VC-Y,MIBK-100) is not markedly influenced by the copolymerized VC (Figs. 1 and 2). Thus, amidoxime resins based on the ternary copolymers become meaningful if the third comonomer could give new functions, e.g., high densities. On the basis of this concept, the study on the preparation of amidoxime resins with high sedimentation rates in sea water is now in progress.

REFERENCES

1. H. Egawa and H. Harada, *Nippon Kagaku Kaishi*, 958 (1979).
2. H. Egawa, H. Harada, and T. Nonaka, *Nippon Kagaku Kaishi*, 1767 (1980).
3. H. Egawa, H. Harada, and T. Shuto, *Nippon Kagaku Kaishi*, 1773 (1980).
4. H. J. Schenk, L. Astheimer, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **17**, 1293 (1982).
5. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **18**, 307 (1983).
6. H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Appl. Polym. Sci.*, **33**, 1993 (1987).
7. H. Egawa, M. Nakayama, T. Nonaka, H. Yamamoto, and K. Uemura, *J. Appl. Polym. Sci.*, **34**, 1557 (1987).
8. M. Nakayama, K. Uemura, T. Nonaka, and H. Egawa, *J. Appl. Polym. Sci.*, **36**, 1617 (1988).
9. H. Egawa, N. Kabay, S. Saigo, T. Nonaka, and T. Shuto, *Bull. Soc. Seawater Sci. Jpn.*, **45**, 324 (1991).
10. H. Egawa, T. Nonaka, S. Abe, and M. Nakayama, *J. Appl. Polym. Sci.*, **45**, 837 (1992).
11. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *J. Appl. Polym. Sci.*, **46**, 129 (1992).
12. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ind. Eng. Chem. Res.*, **32**, 540 (1993).
13. H. Egawa, N. Kabay, T. Shuto, and A. Jyo, *Ind. Eng. Chem. Res.*, **32**, 709 (1993).
14. N. Kabay and H. Egawa, *Sep. Sci. Technol.*, to appear.
15. Y. Ito, S. Nakamura, M. Shirakashi, and M. Kanno, *Research Report 1990 on "Energy Conversion and Utilization with High Efficiency,"* The Ministry of Education of Japan, Tokyo, 1990, p. 313.
16. Y. Ito, S. Nakamura, and M. Shirakashi, *Research Report 1993 on "Energy Conversion and Utilization with High Efficiency,"* The Ministry of Education of Japan, Tokyo, 1993, p. 243.
17. N. Kabay and H. Egawa, *J. Appl. Polym. Sci.*, **51**, 381 (1994).