Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Metal Ion Selectivity of a Macroreticular Styrene-Divinylbenzene Copolymer-Based Methylenephosphonic Acid Resin

Akinori Jyo[a]; Kazunori Yamabe[a]; Hiroaki Egawa[b]
[a] DEPARTMENT OF APPLIED CHEMISTRY AND BIOCHEMISTRY, KUMAMOTO UNIVERSITY, KUMAMOTO, JAPAN [b] KUMAMOTO INSTITUTE OF TECHNOLOGY, KUMAMOTO, JAPAN

To cite this Article Jyo, Akinori , Yamabe, Kazunori and Egawa, Hiroaki(1997) 'Metal Ion Selectivity of a Macroreticular Styrene-Divinylbenzene Copolymer-Based Methylenephosphonic Acid Resin', Separation Science and Technology, 32: 6, 1099 — 1105

To link to this Article: DOI: 10.1080/01496399708000948

URL: http://dx.doi.org/10.1080/01496399708000948

SEPARATION SCIENCE AND TECHNOLOGY, 32(6), pp. 1099–1105, 1997

Metal Ion Selectivity of a Macroreticular Styrene–Divinylbenzene Copolymer-Based Methylenephosphonic Acid Resin

AKINORI JYO* and KAZUNORI YAMABE
DEPARTMENT OF APPLIED CHEMISTRY AND BIOCHEMISTRY
KUMAMOTO UNIVERSITY
KUMAMOTO 860, JAPAN

HIROAKI EGAWA
KUMAMOTO INSTITUTE OF TECHNOLOGY
KUMAMOTO 860, JAPAN

ABSTRACT

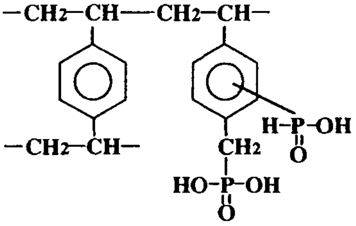
The selectivity of a macroreticular styrene–divinylbenzene copolymer-based methylenephosphonic acid resin (RCSP) toward 17 kinds of metal ions was evaluated in nitric acid media by means of distribution ratio measurements; the order of decreasing affinity was found to be Fe(III) $\sim$ U(VI) $\sim$ Mo(VI) $>$ Bi(III) $>$ Al(III) $>$ Gd(III) $>$ La(III) $\sim$ V(V) $>$ Pb(II) $>$ Cd(II) $>$ Cu(II) $\sim$ Ca(II) $\sim$ Ba(II) $\sim$ Zn(II) $>$ Mg(II) $\sim$ Co(II) $\sim$ Ni(II). Among the tested metal ions, Fe(III), Mo(VI), and U(VI) were highly distributed into RCSP even from 6 M nitric acid as in the case of solvent extraction with organophosphorous acids and esters. However, RCSP did not exhibit as high an affinity with these metal ions in 6 M hydrochloric acid.

INTRODUCTION

As early as the 1950s, Kennedy and Davies (1) reported that styrene–divinylbenzene copolymer-based methylenephosphonic acid resins exhibit the following decreasing order of metal-ion selectivity: U(VI) $\sim$ Fe(III) $>$ rare earths(III) $>$ Cu(II) $\sim$ Co(II) $\sim$ Ba(II) $>$ Na(I). Later, Alexandratos's

---

* To whom correspondence should be addressed.



SCHEME 1 Structure of the macroreticular methylenephosphonic acid resin RCSP. For detailed properties, refer to Ref. 7.

group (2, 3) and Egawa et al. (4–6) also studied the properties and utilities of resins of these kinds. More recently, we found that a macroreticular methylenephosphonic acid resin (RCSP, Scheme 1) exhibits a characteristic selectivity toward Mo(VI) which is adsorbed from acidic regions but not from neutral and alkaline ones (7) as opposed to the pH effect in the adsorption of the usual metal ions. This finding led us to investigate the more detailed aspects of the metal-ion selectivity of RCSP in order to further develop its utility as well as to estimate its limits in separation technology.

The present work was an attempt to clarify the metal-ion selectivity sequence of RCSP toward 17 kinds of metal ions: Mo(VI), U(VI), V(V), Al(III), Bi(III), Fe(III), La(III), Gd(III), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), Mg(II), Ni(II), Pb(II), Zn(II). The distribution of these metal ions from nitric acid media was studied, and then the distribution behavior of several metal ions [Al(III), Fe(III), Mo(VI), Ni(II), U(VI)] from hydrochloric acid media was also examined to clarify the effect of acid species. An interesting phenomenon was observed in the effect of acid species on the distribution of Fe(III), Mo(VI), and U(VI).

EXPERIMENTAL

Materials

Preparation of RCSP and its properties are reported elsewhere (7). The resin was used as the hydrogen ion form throughout. Stock solutions of Mo(VI), U(VI), and V(V) were prepared from sodium molybdate, uranyl nitrate, and ammonium metavanadate, respectively, and those of the other metal ions were prepared by dissolving the nitrate salt of each metal ion in water.

Distribution Ratio Measurement

The resin RCSP (0.04 g) and a test solution (0.0001 M solution of each metal ion, 25 mL) were taken in a 50-mL Erlenmeyer flask. After sealing the flask with a Parafilm, it was shaken for 24 hours at 30°C and then the metal ion concentration in the supernatant was determined by means of inductively coupled plasma atomic emission spectrometry. To adjust the pH of the test solutions, nitric acid or hydrochloric acid was used. Adsorption percentages and distribution ratios (*D*) were calculated from the decrease in the metal concentration in the supernatant. Here, *D* is defined as follows:

$$D = \frac{\text{amount of metal ion in resin at equilibrium (mmol/g)}}{\text{amount of metal ion in solution at equilibrium (mmol/mL)}}$$

RESULTS AND DISCUSSION

Distribution from Nitric Acid Media

Figure 1 illustrates the adsorption percentages of metal ions as a function of pH. For the sake of simplicity, a negative logarithm of the acid concentration has been adopted for pH at the high acid concentration levels where pH is less than unity. Except for Fe(III), Mo(VI), and U(VI), plots of adsorption percentages against pH are sigmoid curves. Under the

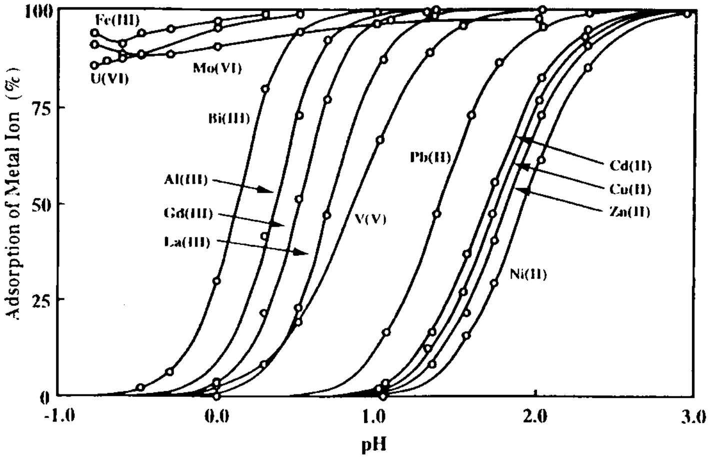


FIG. 1 Adsorption percents vs pH. Results for Ba(II), Ca(II), Co(II), and Mg(II) are omitted to avoid superpositions in this figure.

present experimental conditions, the total amount of a metal ion (0.0025 mmol) is much less than that of the functional group (0.16 mmol). This means that the amount of the metal ion-free ion-exchange sites (RPO_3H_2) can be approximated to be constant. Therefore, as long as a metal ion (M^{n+}) is adsorbed through ion exchange with a proton as follows:

$$n\mathrm{RPO_3H_2} + \mathrm{M}^{n+} \rightleftarrows (\mathrm{RPO_3H^-})_n\mathrm{M} + n\mathrm{H}^+$$

or

$$(n/2)\mathrm{RPO_3H_2} + \mathrm{M}^{n+} \rightleftarrows (\mathrm{RPO_3^{2-}})_{n/2}\mathrm{M} + n\mathrm{H}^+$$

the following equation can be derived:

$$\log D = \text{constant} + n\mathrm{pH}$$

Figure 2 shows plots of log D vs pH. Except for Fe(III), Mo(VI), and U(VI), linear relationships are observed. Table 1 lists the metal ion species having the linear relationship, along with the slopes of the plots and the pH values at half adsorption [except for V(V)]. The slopes for the respective metal ions are nearly equal to their positive charge numbers (n), indicating that these metal ions are adsorbed through ion exchange with a proton. In the case of V(V), however, the real meanings of the slope

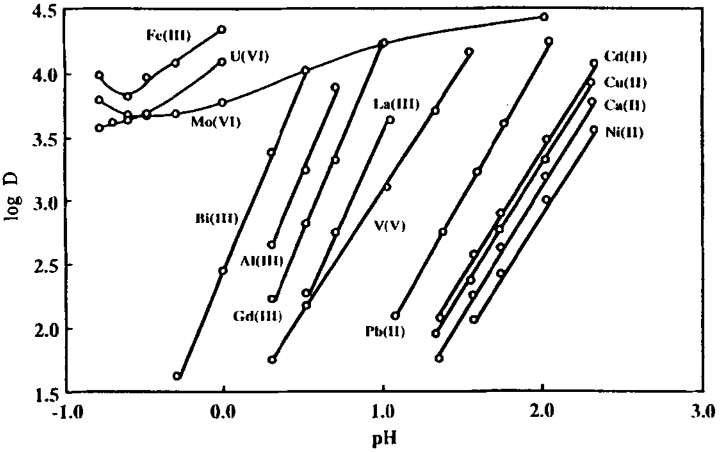


FIG. 2 Log D vs pH. Refer to Table 1 for Ba(II), Co(II), Mg(II), and Zn(II) because these are omitted to avoid superposition.

TABLE 1
pH at a Half Adsorption ($pH_{1/2}$) and Slopes ($\partial \log D/\partial pH$) for the Ions Giving a Linear Relationship between log *D* and pH

Metal ion	$pH_{1/2}$	$\partial \log D/\partial pH$
Bi(III)	0.1_1	2.9_5
Al(III)	0.3_6	3.0_8
Gd(III)	0.5_1	2.8_6
La(III)	0.7_2	2.5_8
V(V)	0.8_5	1.9_4
Pb(II)	1.4_0	2.2_4
Cd(II)	1.7_0	2.0_5
Cu(II)	1.7_5	2.0_3
Ca(II)	1.8_3	2.0_9
Ba(II)	1.8_4	2.0_5
Zn(II)	1.8_4	2.1_2
Mg(II)	1.9_0	2.0_2
Co(II)	1.9_1	1.9_8
Ni(II)	1.9_3	2.0_0

(ca. 2) are difficult to interpret since V(V) tends to condense, resulting in a polymerized species (8).

Of particular interest is the distribution behavior of Fe(III), Mo(VI), and U(VI). For them, a simple linear relationship is not observed between log *D* and pH, and a high distribution is observed even from 6 M nitric acid. These results suggest that the distribution of these ions at high concentration levels of nitric acid cannot be explained by ion exchange with a proton. A detailed discussion of this phenomenon is given in the next section.

From the results mentioned above, it can be concluded that the decreasing order of metal ion affinity with RCSP in nitric acid media (pH 2.3 to -0.8, HNO_3) is Fe(III) ~ U(VI) ~ Mo(VI) > Bi(III) > Al(III) > Gd(III) > La(III) ~ V(V) > Pb(II) > Cd(II) > Cu(II) ~ Ca(II) ~ Ba(II) ~ Zn(II) > Mg(II) ~ Co(II) ~ Ni(II). This sequence means that RCSP exhibits a metal ion selectivity sequence quite different from that of strong-acid resins containing sulfonic acid groups (9). For example, although strong-acid resins prefer Ba(II) to Pb(II) (9), RCSP exhibits the highest selectivity toward Pb(II) among the divalent metal ions tested, indicating that RCSP is more suitable for the elimination of Pb(II) in the presence of alkaline earth metal ions than the strong-acid resins (10). In addition, the relatively high selectivity of RCSP for V(V) is also attractive for the recovery of vanadium.

Distribution from Hydrochloric Acid Media

Since Fe(III), Mo(VI), and U(VI) are highly distributed into RCSP even from 6 M nitric acid, of particular importance is whether similar high distributions of these metal ions can be achieved from other mineral acid solutions or not. Therefore, their distribution from hydrochloric acid media was examined. Two metal ions, Al(III) and Ni(II), were also added to this test as examples of ions adsorbed through ion exchange (refer to Table 1).

Figure 3 compares the results for hydrochloric acid media with those for nitric acid. Marked difference cannot be seen in the distribution of Al(III) and Ni(II) between the two acid media. On the other hand, the distribution of Fe(III), Mo(VI), and U(VI) is significantly lowered at high concentration levels of hydrochloric acid. As is well known, these metal ions form chloro complexes in concentrated hydrochloric acid media (11–15). Therefore, the present results indicate that no specific interaction occurs between the functional groups and the chloro complexes of these metal ions. On the other hand, the high distribution of Fe(III), Mo(VI), and U(VI) at high concentration levels of nitric acid clearly means that some specific interaction exists between the functional groups and nitrato complexes of these metal ions, as in the case of solvent extraction of these metal ions from concentrated nitric acid media with organophosphorous acids and esters (8, 16). In this connection we point out that Alexandratos's group has also observed similar effects of acid species on the distribution of actinide ions and Fe(III) into a similar but somewhat different phosphonic acid resin (Diphonix) (17–19).

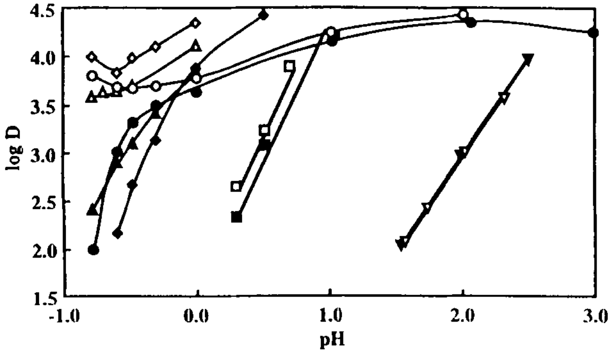


FIG. 3 Effect of acid species on distribution of metal ions. Open and filled symbols represent hydrochloric and nitric acids, respectively. (○, ●) Mo(VI); (△, ▲) U(VI); (□, ■); Al(III); (◇, ◆) Fe(III); (▽, ▼) Ni(II).

REFERENCES

1. J. Kennedy and R. V. Davies, *Chem. Ind.*, p. 378 (1956).
2. S. D. Alexandratos, D. R. Quillen, and M. E. Bates, *Macromolecules*, *20*, 1191 (1987).
3. S. D. Alexandratos, D. W. Crick, and D. R. Quillen, *Ind. Eng. Chem. Res.*, *30*, 772 (1991).
4. H. Egawa, T. Nonaka, and M. Ikari, *J. Appl. Polym. Sci.*, *29*, 2045 (1984).
5. H. Egawa, T. Nonaka, and M. Nakayama, *Ind. Eng. Chem. Res.*, *29*, 2273 (1990).
6. H. Egawa, K. Yamabe, and A. Jyo, *J. Appl. Polym. Sci.*, *52*, 1153 (1994).
7. A. Jyo, K. Yamabe, and H. Egawa, *Sep. Sci. Technol.*, *31*, 513 (1996).
8. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes* (Special Publication 25), The Chemical Society, London, 1971, p. 36.
9. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, NY, 1962, p. 168.
10. A. Jyo, K. Yamabe, and H. Egawa, *Proceedings of International Conference on Chemistry for the Protection of the Environment*, September 1995, Lublin, Poland, In Press.
11. E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, *64*, 335 (1942).
12. J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, *64*, 870 (1960).
13. G. W. Brady, M. B. Robin, and J. Varimbi, *Inorg. Chem.*, *3*, 1168 (1964).
14. H. M. Neumann and N. C. Cook, *J. Am. Chem. Soc.*, *79*, 3026 (1957).
15. W. P. Griffith and T. D. Wickins, *J. Chem. Soc. (A)*, p. 675 (1967).
16. A. V. Gorelova, L. M. Sukova, T. I. Romantseva, M. A. Kolenkovva, and O. P. Chernova, *Zh. Neorg. Khim.*, *31*, 2065 (1986); *Chem. Abstr.*, *105*, 197980k (1986).
17. E. P. Horwitz, R. Chiarizia, H. Diamond, R. C. Gatrone, S. D. Alexandratos, A. Q. Trochimczuk, and D. W. Crick, *Solv. Extr. Ion Exch.*, *11*, 943 (1993).
18. E. P. Horwitz, R. Chiarizia, and S. D. Alexandratos, *Ibid.*, *12*, 831 (1994).
19. R. Chiarizia, E. P. Horwitz, R. C. Gatrone, S. D. Alexandratos, A. Q. Trochimczuk, and D. W. Crick, *Ibid.*, *11*, 967 (1993).

Received by editor May 10, 1996