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Bifunctional Cation Exchange Resin Having Both Phosphonate and Sulfonate Groups Derived from Macroreticular Poly(ω -bromobutylstyrene-co-divinylbenzene)

Kenji OKADA, Naomi JO, and Akinori JYO

Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

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Abstract

A bifunctional cation exchange resin (R4PS) having both phosphonate and sulfonate groups was derived from macroreticular poly(ω -bromobutylstyrene-co-divinylbenzene). Phosphorus and sulfur contents of R4PS were 2.2 and 2.5 mmol/g, respectively, and its acid capacity was 6.6 meq/g. R4PS exhibits the characteristic metal ion selectivity, which is different from that of each monofunctional resin containing phosphonate or sulfonate group alone. In the strongly acidic region below pH 2, R4PS has higher capacities for uptake of Fe(III) than does a corresponding monofunctional phosphonate resin. In column-mode uptake of Fe(III) from strongly acidic feeds, R4PS exhibited excellent kinetic performances because of its high swelling in the wide pH range.

1 Introduction

Phosphonate resins exhibit the high selectivity to hard Lewis acid cations, such as, Fe(III), U(VI) and Zr(IV).[1] Since these high valence metal ions tend to precipitate as hydroxides, their adsorption operation by phosphonate resins must be conducted under strongly acidic media, which are not suitable for high swelling of resins having weakly acidic sites like oxy-acid groups of phosphorus. Incomplete swelling of resins leads to poor kinetics and low capacities in uptake of metal ions. To overcome this difficulty in phosphonate resins, Alexandratos *et al.* have proposed bifunctional resins having both phosphonate and sulfonate groups.[2-4] In almost the same period, Tomoi *et al.* [5] reported thermally stable anion exchange resins derived from poly(ω -bromobutylstyrene-co-divinylbenzene) (R4). This spacer chain type copolymer R4 is attractive as a new type of the precursor for preparation of various bifunctional resins, since one kind of functional group can be introduced into the terminal of n-butyl chains and the other to phenyl group of R4. This paper describes preparation and characterization of a bifunctional resin having both phosphonate and sulfonate groups (R4PS). Properties of R4SP were also compared with those of the monofunctional phosphonate resin R4P.

2 Experimental

2.1 Materials

The monomers, ω -bromobutylstyrene (BBS) and divinylbenzene (DVB) (81 %), were kindly provided by Mitsubishi Chemical Co. (Tokyo, Japan). To remove inhibitors, BBS was passed through a silica-gel (Waco-gel C 200) column, and DVB was shaken with 1 M ($M = \text{mol dm}^{-3}$) NaOH and then washed with water. DVB thus treated was dried on anhydrous sodium sulfate before use. Other reagents were of guaranteed grade, unless otherwise specified.

2.2 Preparation of resins

BBS and DVB were polymerized in the presence of the porogen *n*-heptane according to a conventional suspension polymerization technique. The degree of the crosslinking was 10 mol% of DVB, and volume ratio of the porogen to the monomer mixture was 0.80. The resulting copolymer beads (R4) with diameter of 246–496 μm were collected by meshing, and used in further study. Its BET specific surface area and bromine content were 25 m^2/g and 2.8 mmol/g, respectively. The bifunctional resin (R4SP) and monofunctional one (R4P) were prepared according to a method almost the same as one reported by Alexandratos *et al.* [2] The resulting R4PS and R4P were further treated with refluxed aqueous NaOH (1 M) for 24 h and again with refluxed conc. hydrochloric acid for 24 h for the purpose of complete hydrolysis and conditioning as well. After washing with water, they were air-dried and then dried in vacuum at 40 $^{\circ}\text{C}$ for more than 24 h. Both resins were used in the H^+ form, unless otherwise noted, and their phosphorus contents and acid capacities were measured as described.[6] Sulfur content of R4PS was measured by ion chromatography after the combustion of a R4PS sample as described.[7]

2.3 Studies on uptake of metal ions

Distribution ratios (*D*) of metal ions and capacities for uptake of metal ions were measured by batchwise methods as reported in detail elsewhere.[6] Behavior of both resins in column mode adsorption and elution of Fe(III) was examined according to the reported method.[6] Detailed experimental conditions will be given with results in later sections.

3 Results and discussion

3.1 Properties of resins.

Table 1 shows results of chemical analyses, acid capacities, and dry and wet volumes of R4PS and R4P. Acid capacities of both resins are nearly equal to or slightly less than ones calculated from their analytical data. Wet volumes of R4PS equilibrated with water and 1 M HCl are larger than those of R4P, indicating that R4PS highly swells even in strongly acidic media as anticipated. Equilibration with 1 M NaOH converts both resins into the Na^+ form, resulting in a marked increase in their wet volumes. The difference in wet volumes of R4PS between Na^+ and H^+ forms is less than that of R4P. This is also one of advantages of R4SP, since the resin with small change in wet volumes in wide pH range is preferable in column-mode use.

3.2 Distribution of metal ions

The distribution study was conducted to evaluate the metal ion selectivity sequences of R4PS and

Resin	Phosphorus content (mmol/g)	Sulfur content (mmol/g)	Acid capacity (meq/g)	Volume (cm^3/g)			
				dry	1M NaOH	water	1 M HCl
R4PS	2.2	2.5	6.6	1.92	3.55	3.14	3.10
R4P	2.7	-	5.3	2.40	3.83	2.72	2.71

R4P by keeping the equivalence ratio E_M/E_H is much less than unity; here, E_H and E_M are an initial equivalences of hydrogen ion as counterion in each resin (0.04 g) and that of the metal ion in solutions (0.0001 M, 25 mL), respectively. Since E_H is much greater than E_M , E_H can be regarded as constant, the following equation (i) holds so long as the distribution of metal ions occurs by the ion exchange mechanism:[1]

$$\log D = \text{Constant} + n \cdot \text{pH} \quad (\text{i})$$

Here, n means a formal charge number of a given metal ion. For 12 kinds of metal ions, the equation (i) holds, and observed slopes were nearly equal to n in the case of R4PS, whereas those were somewhat lower than n in the case of R4P. From these linear relations, values of a half extraction pH ($\text{pH}_{1/2}$) were calculated, and they are shown in Fig.1 along with values of sulfonate resin Diaion PK216 for comparison.[8] The bifunctional R4SP clearly exhibits the characteristic metal ion selectivity sequence different from those for both R4P and Diaion PK 216; the metal ion selectivity sequence of R4SP seems to be the convolution of those of sulfonate and phosphonate resins.

Fig. 1 Half extraction pH values of metal ions for three cation exchangers. Values for Diaion PK 216 were quoted from Ref. [8]. Experimental conditions: resin 0.04 g, metal ion solution 0.0001 M (25 cm³). The pH of aqueous phases was adjusted with nitric acid. Roman and italic symbols mean divalent and trivalent cations, respectively.

In the distribution of Fe(III) from nitric acid media into R4PS and R4P, $\log D$ vs. pH plots describe curves with minimum at pH *ca.* -0.6. This indicates that Fe(III) is distributed into the both resins through normal cation exchange and solvation extraction mechanisms as reported.[1] These results indicate that R4PS and R4P have the highest affinity to Fe(III) among the tested 13 kinds of metal ions different from the sulfonate resin Diaion PK216.[8]

3.3 Capacities for uptake of metal ions

Capacities for uptake of Fe(III) and Pb(II) as a function of pH were measured under conditions that the equivalence ratio E_M/E_H is greater than unity opposed to the case of the distribution study. Figure 2 shows the results. The bifunctional R4PS takes up much more amount of both Pb(II) and Fe(III) than does the monofunctional R4P. These results suggest that sulfonate groups in R4PS assist the complexation of phosphonate groups giving enough free space for complexation of phosphate groups as a result of the higher swelling of R4PS. On the contrary, the majority of phosphonate groups in R4P can not work well under acidic conditions because of its lower swelling, in particular, in the pH region less than 2. Iron(III) tends to form bulky multinuclear species under conditions that analytical

Fig. 2 Uptake of Fe(III) and Pb(II) as a function of pH. R4PS: ○ Pb(II), △ Fe(III). R4P: ● Pb(II), ▲ Fe(III). Amount of resin 0.1g. Metal ion solutions 0.01 M (45 cm³). The pH was adjusted with nitric acid, acetic acid, and/or sodium acetate.

concentrations of Fe(III) are greater than $10^{-3.7}$ M at pH 1 ~ 2.[9] Thus, the effect of the low swelling becomes more marked in the adsorption of Fe(III). Indeed, uptake of Fe(III) by R4P between pH 0 and 2 does not so markedly increase with an increase in pH.

3.4 Column-mode Adsorption and Elution of Fe(III)

Figure 3 illustratively shows breakthrough profiles of Fe(III) during the column-mode adsorption of Fe(III), and numerical data are summarized in Table 2. As judged from Fig. 3 and Table 2, R4PS is also superior to R4P in performances of the column-mode adsorption of Fe(III); breakthrough and column capacities of R4PS for Fe(III) are much greater than those of R4P. The adsorbed Fe(III) was quantitatively eluted with aqueous 6 M HCl, and their repeated use was possible. As judged from Table 2, column capacity of R4PS for Fe(III) corresponds to more than 90 percents of its acid capacity, whereas that of R4P is less than a half the acid capacity of R4P.

As demonstrated in this work, macroreticular poly(ω -bromobutylstyrene-co-divinylbenzene) is a promising precursor for various kinds of bifunctional chelating resins, which have high performances in uptake of metal ions from strongly acidic solutions.

Fig. 3 Breakthrough profiles of Fe(III) in the column-mode adsorption of Fe(III). ○ R4PS (run1) and ● R4P (run 1). Column (i.d. 6 mm): 1 cm³ of each wet resin in hydrogen ion form. Feed: ca. 0.01 M ferric nitrate in 0.1 M nitric acid, flow rate, 10 h⁻¹ in SV. Refer to Table 2 for other conditions.

Table 2 Column mode adsorption and elution of Fe(III)

Resin	Run	Conditions for feed ^{a)}			Breakthrough point ^{b)} (Bed volumes)	Breakthrough capacity ^{b)} (mmol/cm ³ -R) ^{a)}	Column capacity (mmol/cm ³ -R)	Amount ^{a)} eluted (mmol/cm ³ -R)
		C ₀ (mM)	pH	Volume (Bed volumes)				
R4PS	1	9.0	1.04	183	33	0.30(0.94) ^{c)}	0.62(1.9)	0.63(2.0)
	2	11	1.05	188	29	0.30(0.94)	0.72(2.2)	0.68(2.1)
R4P	1	10	1.05	195	11	0.11(0.30)	0.26(0.71)	0.28(0.76)
	2	9.5	1.04	191	12	0.11(0.30)	0.26(0.71)	0.27(0.73)

^{a)} Flow rates of feeds and eluent (6 M HCl) were 10 h⁻¹ in space velocity. ^{b)} 5 % breakthrough point and capacity. ^{c)} Figures in parentheses are quantities in mmol/g-dry resin. Refer to Fig. 3 for other conditions.

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