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SEPARATION OF MOLYBDENUM(VI) AND VANADIUM(V) BY USE OF POLYSTYRENE RESINS WITH A FUNCTIONAL GROUP HAVING BIS(2-HYDROXYETHYL)AMINO AND BIS(PHOSPHONOMETHYL)AMINO MOIETY

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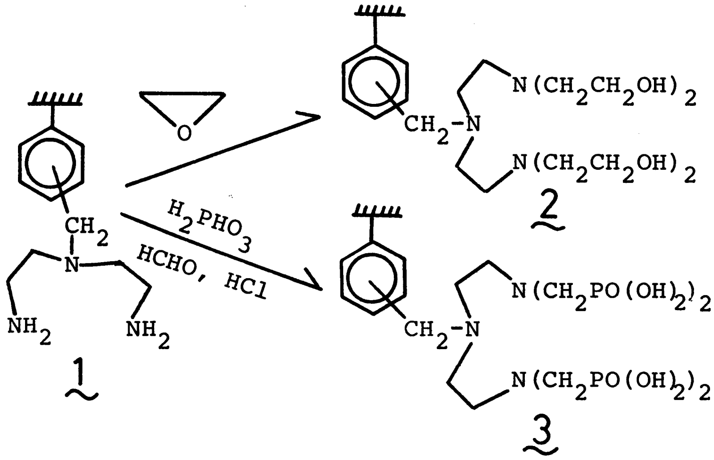
Styrene-divinylbenzene copolymers containing bis(2-hydroxyethyl)-amino and bis(phosphonomethyl)amino moiety have been synthesized and applied to the recovery of molybdenum(VI) and/or vanadium(V) from aqueous solution. The former resin is particularly effective for the separation of molybdenum(VI) and vanadium(V) by the column method owing to its high adsorption capacity and rapid exchange.

Waste catalysts used in desulfurization of petroleum contain appreciable amounts of molybdenum and vanadium.1) In order to recover these important metals from the leaching solution, we have been searching for highly selective chelating resins useful for the recovery of the metal ions.2) Here we report the preparation of styrene-2%-divinylbenzene copolymer resins with pendant multidentate ligands and their application to the column chromatographic separation of $\mathrm{Mo}^{\mathrm{VI}}$ and V^{V}.



The chelating resin 2 was prepared by treating resin 1 3) (11 g, 200-400 mesh) with aqueous ethyleneoxide solution (9.6 g in 100 cm^3) for 10 h at room temperature. Yield: 19.5 g. Resin 3 was obtained by refluxing a mixture of resin 1 (15 g), 6 M HCl (80 cm^3), H_2PHO_3 (33 g), and 37% aqueous formaldehyde solution (64 cm^3) for 3 h. Yield: 25.3 g. Both kind of resin were washed with water, dioxane and diethylether, and dried in vacuo at 50 °C. Nitrogen contents of the resins 2 and 3 are 7.3 and 6.5%, respectively; the amounts of functional group on the polymer are approximately 1.7 and 1.6 mmol per gram of dry resin, respectively.

The adsorption capacity of a resin for metal ions was determined as a function of pH by the batch procedure (Fig. 1). A typical procedure was as follows: 100 mg of the resin was shaken with 500 ppm metal ion solution (100 cm^3) for 20 h. The concentration of the remaining metal ions in the solution was then analyzed by atomic absorption spectrometry. The maximum capacities of the resins 2 and 3 for $\mathrm{Mo}^{\mathrm{VI}}$ and V^{V} uptake are around 3 mmol per gram resin, which are nearly twice as much as the content of the functional group. An evidence of complex formation between

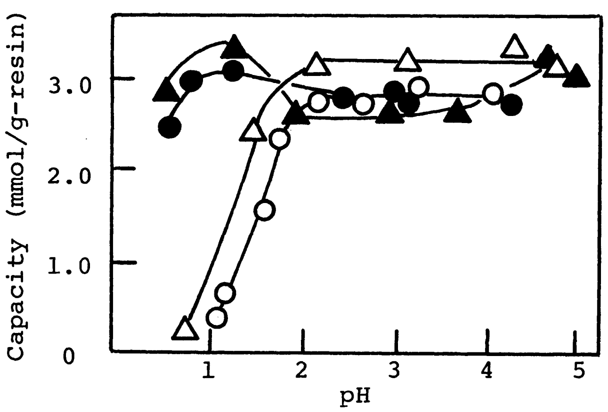


Fig. 1. Adsorption capacity vs. pH plots for resin **2** (● : Mo^{VI}, ○ : V^{V}), and resin **3** (▲ : Mo^{VI}, △ : V^{V}).

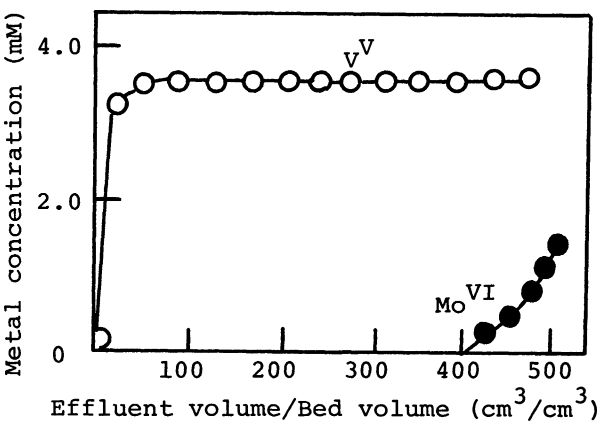


Fig. 2. Breakthrough curves of Mo^{VI} and V^{V} mixture using resin **2**.

the functional group of resin **2** and Mo^{VI} was obtained by ^{13}C-NMR study.[4)]

Below pH 1.5 the capacity for V^{V} is remarkably lower than that of Mo^{VI}. This result suggests the possibility of separating the two metal ions. When an aqueous solution (pH 1.0, HCl) containing equimolar Mo^{VI} and V^{V} (4 mM, M = mol dm^{-1}) was passed through the column of resin **2** (5 g, ϕ1.3 cm x 10 cm) at a rate of 1.5 cm^3 min^{-1}, Mo^{VI} was quantitatively adsorbed on the resin while V^{V} was found in the eluate (Fig. 2). The adsorbed Mo^{VI} is eluted with 4 M sodium hydroxide solution. The adsorption capacity of the resin **2** was reproducible after three adsorption-regeneration cycles. Both Mo^{VI} and V^{V}, however, leaked out of a similar column of resin **3** regardless of the pH of initial solution. The time-course experiment revealed that resin **2** can adsorb Mo^{VI} and V^{V} almost completely within 3 min at the optimum pH region, whereas resin **3** requires more than 10 h to attain equilibrium. Such slow adsorption on the resin **3** may be explained by considering that the adsorption of anions on the resin **3** may be retarded by the charge repulsion between the oxo-metal anion and phosphonate groups. On the contrary, the functional group of the resin **2** is expected to be positively charged in the acidic medium due to the protonation of the tertiary amine, and the migration of the oxo-metal anions into polymer matrix can be facilitated. The resin **2** must be a promising agent for the selective recovery of Mo^{VI} and V^{V} from the leaching solution of waste catalysts.

References

1) "Proceeding of the Climax Third International Conference on the Chemistry and Uses of Molybdenum," ed by H. F. Barry and P. C. H. Mitchell, Climax Molybdenum Company, Ann Arbor, Michigan, (1979), pp. 73-113.
2) T. Yokoyama, A. Kikuchi, T. Kimura, and T. M. Suzuki, Nippon Kagaku Kaishi, 1983, 363.
3) T. M. Suzuki and T. Yokoyama, Polyhedron, 2, 127 (1983); The resin **1** contains 3 mmol of ligand per gram resin which corresponds approximately 62% of the available benzene rings are occupied by diethylenetriamine branches.
4) Seven peaks were observed at 52.7, 55.4, 57.5, 59.7, 59.9, 63.0, and 73.9 ppm relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ in the D_2O solution (pH 5.0) containing N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine and K_2MoO_4 in 1 : 2 molar ratio. The signals of the free ligand were appeared at 50.5, 57.9, and 58.4 ppm.

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