

CHROM. 7730

SELECTIVE PROPERTIES AND ANALYTICAL USE OF AN ION-EXCHANGE RESIN BASED ON α -PHENYLVINYLPHOSPHONIC ACID

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SUMMARY

The selective properties of a resin based on a copolymer of α -phenylvinylphosphonic acid with acrylic acid were investigated. The selectivity of the resin decreases in the order $\text{Th(IV)} > \text{Sc(III)} > \text{Fe(III)} > \text{U(VI)} > \text{divalent elements}$. Several interesting separations using the selectivity of this resin are discussed.

INTRODUCTION

Several papers have been published dealing with the synthesis and properties of various selective ion-exchange resins. For the synthesis of these resins, miscellaneous polymeric materials were used on which suitable ionogenic groups were fixed by additional reactions. Styrene-divinylbenzene copolymer has been the most commonly used carrier for these groups.

However, little interest has been shown in the preparation of resins obtained by polymerization or copolymerization of monomers containing suitable ionogenic groups, probably because of the difficulties involved in obtaining suitable monomers or the problems that occur during the polymerization of the monomers. Fortunately, these disadvantages are usually compensated by the fact that monofunctional resins with homogeneous structures are obtained.

For the preparation of selective ion-exchange resins containing phosphinic, phosphonic or phosphoric ionogenic groups by polymerization of suitable monomers, attention was focused particularly on various dichloroanhydrides of butadiene- or styrene-phosphonic acids¹⁻³, dialkyl esters of vinylphosphonic acids⁴, and diallylphosphates^{5,6}. Resins or membranes with good chemical and physical properties were obtained by copolymerization of α -phenylvinylphosphonic acid with divinylbenzene, acrylic acid or acrylonitrile⁷⁻⁹. The radiation copolymerization of vinylphosphonic acid with different compounds has also been carried out¹⁰.

EXPERIMENTAL

The ion-exchange resin was prepared by the suspension copolymerization of α -phenylvinylphosphonic acid and acrylic acid^{7,8}. The molar ratio of phosphonic acid to acrylic acid was 0.40:0.60, which gave copolymers with good chemical and mechanical properties. The resin obtained was washed with water, a 5% solution of ammonium acetate and 5% hydrochloric acid. After washing with water, the resin was dried in air.

The titration curve of the exchanger was measured in a 2 *M* potassium chloride–0.10 *M* potassium hydroxide mixture at constant ionic strength ($I = 2.0$). The phosphorus content and swelling properties of the resin were determined by the method described earlier¹¹.

Distribution studies

A 0.120-g amount of air-dried resin in the H^+ form was brought into equilibrium with 50.0 ml of a solution of nitric acid containing 0.50 mequiv. of the studied ion (as nitrate). This system was shaken mechanically for 180 h and then the concentration of the ion under investigation was determined in the aqueous phase.

The results are expressed as weight distribution coefficients, D_n , where

$$D_n = \frac{\text{mequiv. metal/g of dry resin}}{\text{mequiv. metal/ml of solution}}$$

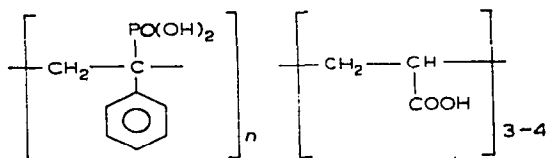
Breakthrough curves

A 1.780-g amount of air-dried exchanger in the H^+ form (sieve fraction 0.10–0.20 mm) previously swollen in water was packed in a glass or plastic column (180 \times 10 mm). After pre-treatment of the resin bed with 0.10 or 0.50 *M* nitric acid, 250 ml or more of a solution containing 20 mequiv./l of the element studied in 0.10 or 0.50 *M* nitric acid, respectively, was passed through the column at a flow-rate of 0.3 ml/min. The flow-rate was kept constant by using an Elutionspumpe H (Serva, Heidelberg, G.F.R.). Fractions of about 2.5 ml of the eluate were analysed. In some instances, ⁵⁹Fe or ⁶⁰Co were used as radioactive tracers.

Standard compleximetric or colorimetric procedures were employed for the determination of the elements. Radioactivity measurements were carried out with a Tesla NZQ 612 counter using an NaI(Tl) scintillator.

RESULTS AND DISCUSSION

From the IR spectra, phosphorus content and titration curve, the structure of the ion-exchange resin used could be written as^{7,8}



The phosphorus content in the resin was 8.88% (exchange capacity 5.7 mequiv./g,

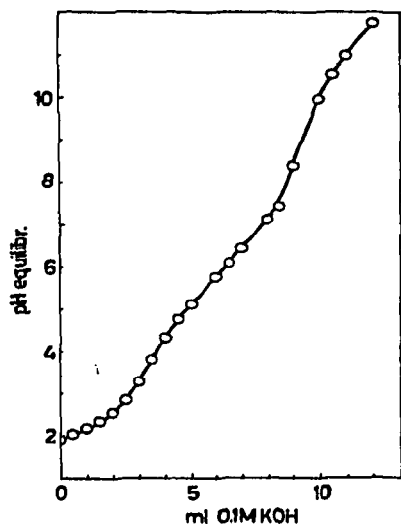


Fig. 1. Titration curve of the resin in 2.0 M KCl-0.10 M KOH.

based on phosphorus content). From the titration curve in Fig. 1, it can be seen that the resin has an overall potassium-hydrogen exchange capacity of 6.91 mequiv./g. The actual exchange capacities based on the phosphorus content are 2.54 mequiv./g and 4.73 mequiv./g, respectively. The remaining exchange is due to carboxylic groups.

The swelling properties of the exchanger in various media are summarized in Table I.

TABLE I
SWELLING PROPERTIES OF THE RESIN IN WATER AND NITRIC ACID

<i>Ionic form</i>	<i>Swelling medium</i>	<i>Resin volume (ml/g)</i>
NH ₄ ⁺	Water	2.24
H ⁺	Water	1.32
H ⁺	0.10 M HNO ₃	0.93
H ⁺	0.50 M HNO ₃	0.74
H ⁺	1.00 M HNO ₃	0.67

Results showing the variation of distribution coefficients with the concentration of nitric acid are summarized in Fig. 2. The D_a values generally decrease with increasing nitric acid concentration. The selectivity of the exchanger decreases in the order Th(IV) > Sc(III) > Fe(III) > U(VI) > M(II). A higher selectivity for Fe(III) than for U(VI) was observed compared with results on various exchangers containing the -PO(OH)₂ group directly on the benzene ring, where the order of selectivity U(VI) > Fe(III) was reported^{5,6}.

A strong dependence of the sorption of all the elements mentioned on the acidity of the solution was observed using 0.10-1.0 M nitric acid. With further increase in the acid concentration, the sorption of Th, Sc, Fe and U decreases only slowly.

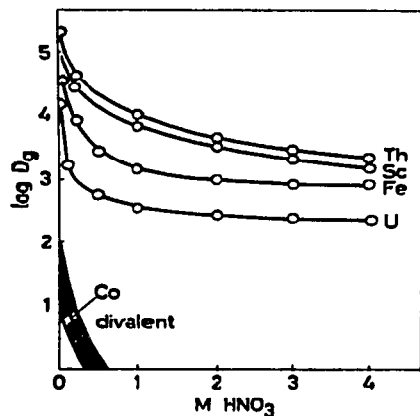


Fig. 2. D_o values of Th(IV), Sc(III), Fe(III), U(VI) and some divalent elements as a function of nitric acid concentration.

The adsorbability of the divalent elements (Ca, Mg, Sr, Co, Ni, Cd, Cu and Pb) is strongly affected by the concentration of the acid. It decreases to zero using nitric acid above 0.40 M for Pb and using nitric acid above 0.20–0.30 M for the other divalent elements.

The results of the column experiments, in the form of breakthrough curves in 0.10 and 0.50 M nitric acid, are given in Figs. 3 and 4. The results confirm the selectivity of the resin as derived from the batch experiments. All divalent elements

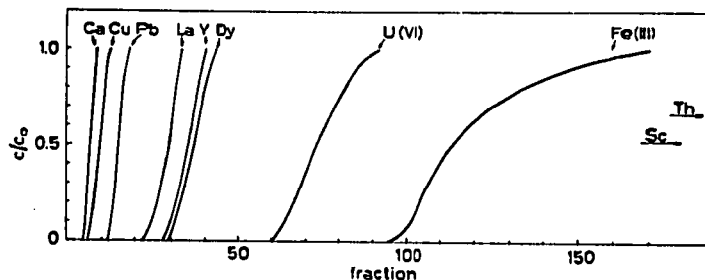


Fig. 3. Breakthrough curves of various elements in 0.10 M nitric acid. c = Actual concentration of the element; c_0 = initial concentration of the element.

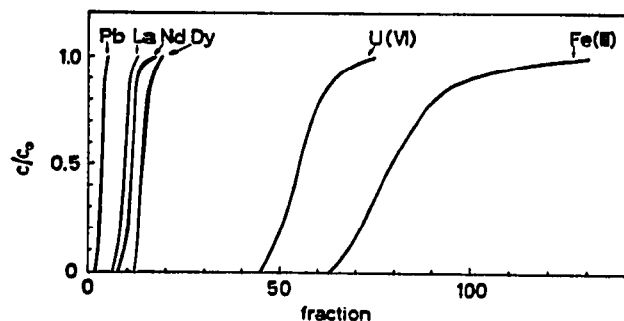


Fig. 4. Breakthrough curves of various elements in 0.50 M nitric acid.

penetrated through the resin bed in the first fractions when 0.50 *M* nitric acid was used. The selectivity of the resin for Y and lanthanides increases with increasing atomic number of the element sorbed. The sorbabilities of some lanthanides differ to such an extent that it could serve as a basis for separation without using complex-forming eluting agents.

The elution experiments show that the divalent elements are easily desorbed from the resin using nitric acid above 0.40 *M*; Y and lanthanides are quickly and quantitatively desorbed with nitric acid above 3.0 *M*. If Th, Sc, Fe or U was to be eluted, difficulties occurred because of high affinity of the resin for these elements. Fe(III) and U(VI) could be eluted effectively with the mixture 5.0 *M* nitric acid–1.0 *M* ammonium fluoride. No elution of Th and Sc was observed in 5.0 *M* nitric acid or 6–12 *M* hydrochloric acid and only a slow desorption was obtained by using 0.05 *M* EDTA solution at pH 2.5. After washing the resin with 0.5 *M* ammonium acetate solution, Th or U could be eluted with ammonium carbonate solution. Scandium was eluted very slowly with 1.0 *M* sulphuric acid.

From the D_0 values and breakthrough curves, it is obvious that Th, Sc, Fe or U can be effectively separated from elements that have lower D_0 values, *i.e.*, from Y, lanthanides and the divalent elements. Table II presents results showing the separation

TABLE II
SELECTIVE SEPARATIONS OF Fe, Sc, Th AND U FROM VARIOUS MIXTURES

<i>Metal</i>	<i>Taken (mg)</i>	<i>Found (mg)</i>	<i>Sorption or elution conditions</i>
Fe Co	1.860 5 780.000	1.866 5 779.910	Sorption from 0.3 <i>M</i> HNO ₃
Fe Co	34.646 1.462	34.708 1.473	Sorption from 0.3 <i>M</i> HNO ₃
Fe Co	9.300 0.0070	9.260 0.0078	Sorption from 0.3 <i>M</i> HNO ₃
Fe Ni	20.000 0.0070	20.000 0.0075	Sorption from 0.3 <i>M</i> HNO ₃
Zn, Cd, Cu U	Σ 100.000 1.556	Σ 100.000 1.552	Sorption from 0.3 <i>M</i> HNO ₃
Cu, Cd, Zn La, Pr, Nd, Sm	Σ 150.000 Σ 2.864	Σ 150.000 Σ 2.860	Sorption from 0.15 <i>M</i> HNO ₃
La, Pr, Nd Sm, Gd, Eu Sc	Σ 4.600 2.015	Σ 4.590 —	Sorption from 1.0 <i>M</i> HNO ₃
La, Pr, Nd, Sm, Gd, Eu Th	Σ 15.900 2.867	Σ 15.910 —	Sorption from 2.0 <i>M</i> HNO ₃
La, Pr, Nd, Sm, Gd, Eu Th, Sc in 1000 ml of 1.5 <i>M</i> HNO ₃	Σ 2.864 Σ 125.000	Σ 2.860 —	Rinsing with 2.0 <i>M</i> HNO ₃

of grams down to a few micrograms of the elements mentioned, taken as representative of the use of the selectivity of the resin.

Analysis by means of this method offers the possibility of the rapid and easy determination of some impurities in thorium, scandium, iron or uranium nitrates. Rapid separation of the pairs Fe-Co and Fe-Ni suggest the possibility of using this resin in metallurgical laboratories also.

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