

Notes

Anion exchange behaviour of some rare earths in dilute sulphuric acid solutions containing ethanol

Although rare earths are not appreciably adsorbed by strong base anion exchangers from hydrochloric^{1,2}, nitric^{1,2} and sulphuric^{2,3} acid solutions, adsorption from dilute nitric acid-ethanol and dilute hydrochloric acid-ethanol solutions has been reported⁴. The differences between the distribution coefficients of Y, Nd and La in the nitric acid-ethanol media were sufficient to permit satisfactory separations. These findings prompted the author to investigate the anion exchange behaviour of some rare earths (Y, Nd, Pr and La) in dilute sulphuric acid solutions containing ethanol.

Experimental

Materials. Air dried Amberlite IRA-400 8 ×, 100–200 mesh in the SO₄ form. Specpure Y, Nd, Pr and La oxides; A.R. H₂SO₄ (s.g. 1.84) and C. P. ethanol (96 %).

Distribution coefficient measurements. Adsorbabilities were determined at room temperature (23 to 25°) by the batch equilibrium method. 0.25 g of resin was shaken with 20 ml of the appropriate sulphuric acid-ethanol solutions containing 20 μg Y, Nd, Pr or La in a stoppered 100 ml erlenmeyer flask for 16 h. The following H₂SO₄-ethanol solutions were investigated:

(a) 80% ethanol containing varying concentrations of H₂SO₄ (0.1, 0.01 and 0.001 N).

(b) 0.01 N H₂SO₄ containing varying concentrations of ethanol (0, 20, 50 and 80 %).

From analyses of the solution phase before and after equilibration, distribution coefficients K_D ($\frac{\text{concentration of rare earth /g resin}}{\text{concentration of rare earth /ml solution}}$) were computed. Rare earths were determined spectrophotometrically with bromopyrogallol red⁵.

Blank runs showed no significant adsorption by the container walls, all equilibrations were carried out in triplicate and the average of the triplicate results is reported. The average spread of the triplicate determinations was 10 %.

Results and discussion

The distribution coefficients of Y, Nd, Pr and La in 80% ethanol containing various concentrations of H₂SO₄ are shown in Fig. 1.

For a given rare earth, the adsorbability decreases with increasing sulphuric acid concentration. The adsorption of yttrium by a strong base anion exchanger from dilute ammonium sulphate solutions was found to decrease with increasing ammonium sulphate concentration⁶.

At constant N H_2SO_4 , the adsorbability of the rare earths increases in the order:

$$Nd < Pr < Y < La.$$

With the exception of Y, this sequence is also the order of increasing ionic radii in the rare earth series (Y^{3+} (0.92 Å); Nd^{3+} (1.04 Å); Pr^{3+} (1.06 Å) and La^{3+} (1.14 Å)).

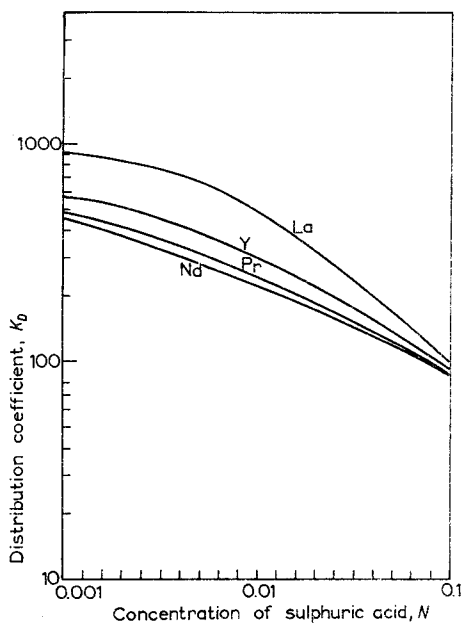


Fig. 1. Adsorption of Y, Nd, Pr and La by Amberlite IRA-400 from dilute sulphuric acid solutions containing 80% ethanol.

The distribution coefficients obtained for Y, Nd and La in 0.01 N H_2SO_4 solutions containing 0, 20, 50 and 80% ethanol are given in Table I.

TABLE I

Solution	K_D		
	Y	Nd	La
0.01 N H_2SO_4	< 1	< 1	< 1
0.01 N H_2SO_4 -20% EtOH	32	24	34
0.01 N H_2SO_4 -50% EtOH	166	160	176
0.01 N H_2SO_4 -80% EtOH	303	220	491

From Table I it is seen that as the percentage non-aqueous component of the solution was increased, rare earths showed increased adsorption by the resin.

For satisfactory column separations, separation factors (ratio of distribution coefficients) as different as possible from unity are desirable. Suitable eluant concentrations to use for some rare earth separations are indicated in Table II.

TABLE II

Separation	Separation factor	H ₂ SO ₄ -EtOH concentrations
Nd-La	1.9	0.01-0.001 N H ₂ SO ₄ -80% EtOH
Y-La	1.6	0.01-0.001 N H ₂ SO ₄ -80% EtOH
Nd-Y	1.8	0.01 N H ₂ SO ₄ -80% EtOH
Pr-Y	1.2	0.01 N H ₂ SO ₄ -80% EtOH

Separations would be expected to be slow because of the strong adsorption of rare earths by the anion exchanger.

The distribution coefficient data plotted in Fig. 1 offer little prospect for an effective anion exchange separation of the neighbouring rare earths Nd and Pr.

Dilute sulphuric acid-ethanol eluants are unsuitable for the separation of macro amounts of rare earths owing to the limited solubility of rare earth sulphates in these media.

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A fog precipitator for gas chromatography

The flow of hot carrier gas from a gas chromatography column usually results in the sample emerging as a fog. Flow rates commonly used make efficient collection using conventional cold traps almost impossible, yields often being as low as 60%. The apparatus described below makes possible recoveries of over 98%.

In this laboratory, eluting material is collected from columns of between 1/4 and 1 in. diameter, with nitrogen flow rates of between 20 ml/min and 2 l/min, and temperatures from 20 to 220°.

The apparatus consists of a glass cold trap and a metal precipitator containing an electric field supplied from a source of constant current sufficient to develop a field strength of from 5,000 to 12,000 direct volts.

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