THE ANION EXCHANGE BEHAVIOUR OF YTTRIUM, NEODYMIUM AND LANTHANUM IN DILUTE NITRIC ACID SOLUTIONS CONTAINING ETHANOL

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The anion exchange behaviour of the rare earths in nitric acid has been investigated by DANON[1]. These elements were found to be adsorbed to a slight extent by Dowex-1 from concentrated nitric acid solutions, but the small differences between the values of the distribution coefficients did not allow efficient separations. Since replacement of part of the aqueous phase by a non-aqueous component has been shown to enhance anion exchange adsorption and resolution of inorganic ions[2,3], the anion exchange behaviour of some rare earths (Y, Nd and La) in dilute nitric acid solutions containing ethanol has been investigated.

EXPERIMENTAL

Materials and column operation

Resin: Dowex-1, 8X, 50–100 mesh, nitrate form.

Size of resin bed: 22 × 1.9 cm.

Sample: Mixture of specpure rare earth nitrates equivalent to 1 mg each of Y, Nd and La.

Addition of sample to column: Sample was dissolved in 10 ml HNO_3–ethanol solution of the same concentration to be used as eluant and placed in the column head. This solution was allowed to run into the resin bed at a flow rate of 1 ml/min. The resin bed had previously been equilibrated with 300 ml HNO_3–ethanol solution of the same concentration as used for dissolving the rare earth nitrates.

Elution: When the liquid level in the column had almost reached the top of the resin bed, elution was commenced with the appropriate HNO_3–ethanol eluant. Elutions were carried out at room temperature.

The following eluant systems were investigated:

(a) 0.8 *N* HNO_3 and varying concentrations of ethanol (0, 20, 40 and 80%).

(b) 80% ethanol and varying concentrations of HNO_3 (0.16, 0.8 and 1.6 *N*).

Solutions of HNO_3 above 1.6 *N* were not employed since they oxidised the ethanol to acetaldehyde.

Eluant solutions were prepared by diluting the proper volume of concentrated HNO_3 to the mark in a standard flask with the appropriate concentration of ethanol.

The rate of flow of eluant through the column was 1 ml/min and the effluent was collected in 20-ml fractions. These fractions were transferred to 80-ml porcelain evaporating basins and taken to dryness on a "low" hot plate.

Spectrographic monitoring of effluent fractions

The following spectrographic conditions were employed for examining the effluent fractions:

Electrodes: The lower electrode (anode) was a flat top NCC regular grade graphite 3/16 in. diameter rod.

The upper electrode was a pointed Champion "ship" carbon 5-mm diameter rod.

Loading electrodes: Flat topped electrodes were rubbed with a circular downward motion around the bottom and sides of the evaporating dishes.

Spectrograph: Hilger (E492) large quartz and glass; glass optics; wavelength range 3,800–5,300 Å; slit width 0.0025 mm; slit height 3 mm; Hilger F958 quartz lens focussed on slit. Kodak 103-0 plate. Samples were arced to completion at 4.5 A DC. Plates were developed for 4½ min in Kodak D19b developer at 20°.

Construction of semiquantitative elution curves

A semiquantitative measure of the concentration of a rare earth in the effluent fractions was obtained by visually estimating the relative intensity of a suitable spectrum line of the element (Y 4374.94; Nd 4303.57; La 4333.73) using an arbitrary 7-stepped spectrum line as a source of reference. Semiquantitative elution curves were constructed by plotting rare earth relative intensities against effluent volume.

RESULTS AND DISCUSSION

Fig. 1 illustrates the results obtained when a series of ethanol concentrations containing 0.8 *N* HNO_3 were employed as eluants. As the ethanol concentration was increased, rare earths showed increased adsorption by the resin. Nd and La were so firmly adsorbed by Dowex-1 from 80% ethanol containing 0.8 *N* HNO_3 that an eluant in which the adsorbed rare earth "complexes" were no longer stable had to be employed for their removal. Water elution was used for this purpose.

From the elution curves obtained, the volume distribution coefficients (D_v) were evaluated from the familiar relationship

$$D_v = V_{max} - i$$

where V_{max} is the number of column volumes of eluant required to obtain an element in maximum concentration in the effluent and i is the fractional interstitial volume (*ca.* 0.4). D_v values (estimated to within ± 30%) are shown in Table I.

Similar results have been obtained by DANON[4] and MARCUS AND NELSON[5] using acidified nitrate solutions. These workers found the addition of a soluble nitrate such as $LiNO_3$ to a dilute HNO_3 solution resulted in the enhanced adsorption of rare earths

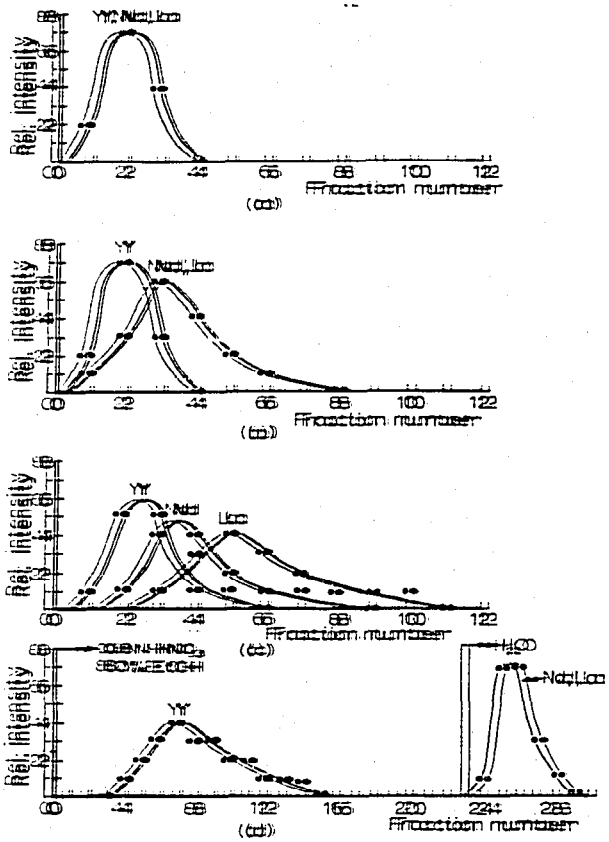

Fig. 21.* The elution of Y, Nd and La from a 22 × 1.9 cm column of Dowex-1, 8X, 50–100 mesh resin with 0.8 *N* HNO_3 containing various concentrations of ethanol. Relative intensity expressed in arbitrary units. (a) 0.8 *N* HNO_3–60% EtOH; (b) 0.8 *N* HNO_3–20% EtOH; (c) 0.8 *N* HNO_3–40% EtOH; (d) 0.8 *N* HNO_3–80% EtOH. Flow rate, 1 ml/min. Volume/fraction, 20 ml.

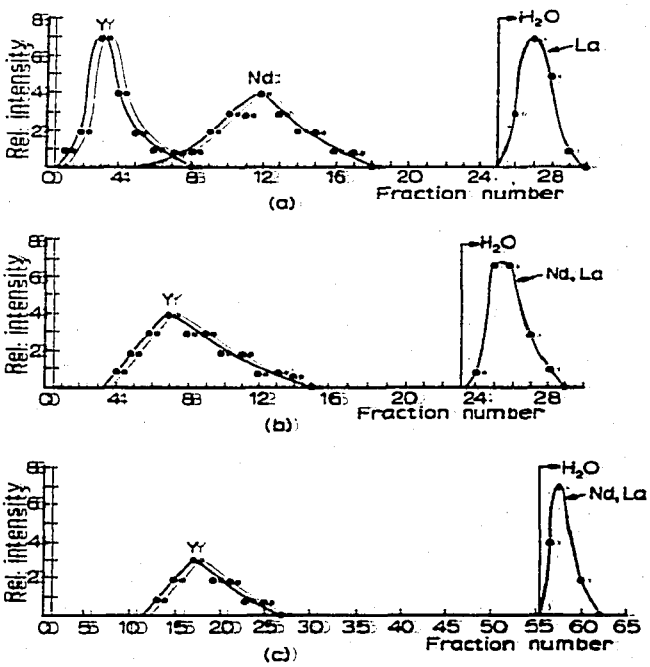

Fig. 22.* The elution of Y, Nd, and La from a 22 × 1.9 cm column of Dowex-1, 8X, 50–100 mesh resin with 80% ethanol containing various concentrations of HNO_3. Relative intensity expressed in arbitrary units. (a) 80% EtOH–0.16 *N* HNO_3; (b) 80% EtOH–0.8 *N* HNO_3; (c) 80% EtOH–1.6 *N* HNO_3. Flow rate, 1 ml/min. Volume/fraction, 20 ml. *Note*: In (a) points have been plotted every 40 ml.

by strong-base anion exchange resins. Adsorbabilities increased with increasing $LiNO_3$ concentration, the lighter rare earths being more strongly adsorbed than the heavier earths.

From Fig. 1 it can also be seen that enhanced resolution of Y, Nd and La occurred with increasing ethanol concentration.

The elution curves obtained using 80% ethanol containing various concentrations of HNO_3 are shown in Fig. 22. Rare earths showed increased adsorption by the resin with increasing HNO_3 concentration. La (in 80% ethanol containing 0.16, 0.8 and 1.6 *N* HNO_3) and Nd (in 80% ethanol containing 0.8 and 1.6 *N* HNO_3) were so firmly adsorbed by Dowex-1 that water elution had to be employed for their removal.

D_f values (estimated to within ± 30%) are given in Table III.

MARCUS AND NELSON[5] found the adsorption of rare earths from $LiNO_3$–HNO_3

* Since overlapping rare earths had very similar relative intensities, their elution has been shown by means of single curves in Figs. 1 and 22.

TABLE I

Eluant	D_v		
	Y	Nd	La
0.8 N HNO_3	0.2	0.2	0.2
0.8 N HNO_3–20% EtOH	0.2	0.5	0.6
0.8 N HNO_3–40% EtOH	0.4	0.7	1.2
0.8 N HNO_3–80% EtOH	1.8	$\geqslant 5$	$\geqslant 5$

TABLE II

Eluant	D_v		
	Y	Nd	La
0.16 N HNO_3–80% EtOH	0.6	3.4	$\geqslant 5$
0.8 N HNO_3–80% EtOH	1.8	$\geqslant 5$	$\geqslant 5$
1.6 N HNO_3–80% EtOH	5.0	$\geqslant 5$	$\geqslant 5$

to be independent of acidity at low acid concentrations (10^{-4}–10^{-2} N). Increasing the acid concentration resulted in decreased adsorption of rare earths.

The rare earth elution sequence obtained with ethanol–HNO_3 systems was according to size

$$Y^{3+} > Nd^{3+} > La^{3+}$$

$$(r = 0.92 \text{ Å}) \; (r = 1.04 \text{ Å}) \; (r = 1.14 \text{ Å})$$

and accorded to that obtained with HNO_3–$LiNO_3$ elution[4,5].

Elution with 0.8 N HNO_3–80% ethanol or 1.6 N HNO_3–80% ethanol would appear admirably suited for preparing "light" and "heavy" concentrates from mixtures of rare earths.

Although the separation of neighbouring rare earths was not investigated, gradient elution techniques would appear to offer possibilities for effecting such separations.

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SUMMARY

The adsorption and resolution of Y, Nd and La by a strong-base anion exchange resin from dilute nitric acid–ethanol solutions was examined.

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