

SEPARATION OF SCANDIUM AND RARE EARTHS BY ANION EXCHANGE IN ACETIC ACID-HCl MIXTURES

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INTRODUCTION

Studies on the ion exchange behavior of scandium in mineral acid-organic solvent systems are rather scarce. Information has been presented concerning ion exchange behavior of scandium in mixtures of hydrochloric acid and oxalic acid¹; hydrochloric acid and several alcohols²; hydrochloric acid and ethanol³; nitric acid and ethanol⁴, and thiocyanate and ethanol/or acetone⁵. Other information about the behavior and separation of scandium in different media has been reviewed in various papers⁶⁻¹⁴. In order to obtain a more extensive understanding of the anion exchange adsorption characteristics of scandium in mixed solvent systems, the present work was undertaken with mixtures of hydrochloric acid and acetic acid. The system afforded a method for a good separation of scandium and the rare earths including yttrium on a short column.

EXPERIMENTAL

Reagents and apparatus

0.5 N hydrochloric acid solutions of scandium, yttrium, rare earths and thorium were prepared as stock solutions. The concentration of the solutions was standardized by titration with a standard EDTA solution using xylenol orange as indicator. A strong base type anion exchange resin, Dowex I, X-8, Cl-form, 100 to 200 mesh in particle size, was used. Conventional ion exchange columns of 1.05 cm I.D. and 18 cm high, pulled to a tip and plugged with glass wool at the outlet of the column were generally used. Six grams of the resin dried under a constant humidity over saturated potassium bromide solution were taken, slurried with water and packed into the column. The resulting bed was usually 13 cm long. The sample solution was introduced into the column through a separatory funnel of appropriate capacity whose stem was attached to the top of the column.

All metal ions concerned were determined by titration with EDTA using xylenol orange as the indicator.

Procedure

Measurement of distribution coefficients. The weight distribution coefficient data were obtained by a batch equilibrium method¹⁵. An aliquot of the stock solution, which contained less than 0.05 mequiv. of metal ion concerned, was taken, evaporated

just to dryness and taken up in 20 ml of a hydrochloric acid-acetic acid mixture of varying composition (in vol. %). 0.5 grams of the dried resin was then added to this solution which was mechanically shaken for 24 h to ensure complete equilibrium at room temperature.

Column separation of scandium. Prior to loading a sample solution onto the column, 100 ml of a mixture of glacial acetic acid and 3 *N* hydrochloric acid (9:1) is passed through the column. Approximately 5 ml of the sample solution, adjusted to the same composition of acetic acid-HCl as above, is then introduced to the free volume of the column, and allowed to pass down the column.

The rare earths and yttrium are first removed from the column by passing 90% glacial acetic acid-10% 3 *N* hydrochloric acid through the column at a flow rate of 0.2 ml per min. Depending upon the atomic number of the rare earths the volume of effluent will extend over 90 to 160 ml. Lighter rare earths can be recovered within 90 ml of the effluent, while yttrium and lutetium tend to extend to approximately 160 ml for complete elution. Scandium, which remains adsorbed on the column, is easily stripped in a sharp band by elution with 1 *N* hydrochloric acid.

RESULTS AND DISCUSSION

Fig. 1 shows the distribution coefficients of scandium, thorium and the rare earths plotted as a function of the volume per cent of acetic acid in the mixed solvent. The concentration of hydrochloric acid was kept constant at 3 *N* throughout.

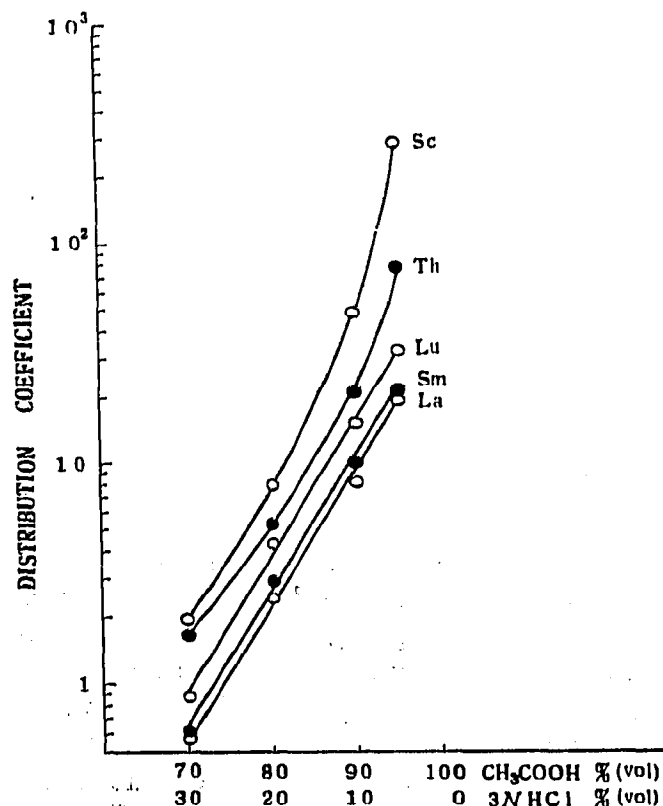


Fig. 1. Distribution coefficients of scandium, thorium and the rare earths on Dowex I anion exchange resin in acetic acid-hydrochloric acid media.

Lanthanum, samarium and lutetium were selected here as representatives of the rare earths. The results show that the adsorption increases regularly with increasing concentration of acetic acid. Quantitative uptake of scandium may be obtained in the range of more than 90 % acetic acid.

The effect of hydrochloric acid concentration on the adsorption of scandium, thorium and samarium is illustrated in Fig. 2. No sign of variation of the adsorption with increasing concentration is observed over the hydrochloric acid concentration tested for these elements. Therefore it is the concentration of acetic acid that has a pronounced effect on the adsorption of these elements in this media.

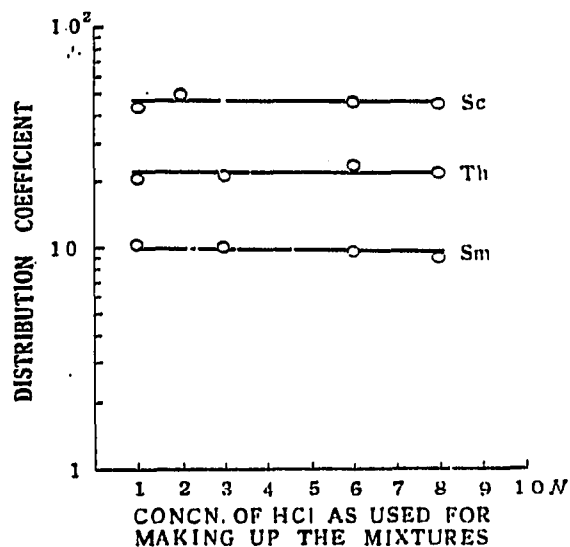


Fig. 2. Variation of distribution coefficient with the concentration of hydrochloric acid. Concentration of acetic acid kept constant at 90 % (by vol.).

KORKISCH AND HAZAN¹⁶ have recently investigated the anion exchange behavior of uranium, thorium, the rare earths and several other ions in 12 different organic solvents containing hydrochloric acid. Values for the distribution coefficient of lanthanum, cerium, praseodymium, samarium, gadolinium and ytterbium on Dowex I, X-8 were all the same (only 0.1) in 90 % acetic acid-10 % 6 *N* hydrochloric acid and in 95 % acetic acid-5 % 12 *N* hydrochloric acid media. These values are markedly lower than those given in Figs. 1 and 2. No results were reported for the distribution coefficient of scandium in their work. Our values for the rare earths were further confirmed through elution experiments involving the separation of the rare earths and scandium.

Working capacities of the resin for scandium were obtained by measuring the distribution coefficients in mixtures of 90 % glacial acetic acid and 10 % 3 *N* hydrochloric acid, which contain 0.7 to 20 mg of scandium, using 0.5 g of the resin. The distribution coefficients of scandium, as a function of varying amounts of scandium in 20 ml of the mixed solution, are: 50 (0.73), 40 (1.86), 33 (4.97), 31 (10.3), and 23 (20.6), where values in parentheses indicate the weight in mg of scandium used. There are no regions in which the distribution coefficient remains constant. For the other elements which have a lower distribution coefficient than scandium, the effect of loading on the working capacities may be expected to be greater.

Typical results of the separation of scandium from the rare earths and yttrium are quoted in Table I. Several elution profile curves are also shown in Fig. 3. The separation of scandium from these elements can easily be achieved using the shorter column of 13 cm, because the separation factor involved, defined as K_{dA}/K_{dB} , is

TABLE I

SEPARATION OF SCANDIUM AND THE RARE EARTHS (OR YTTRIUM)

Sc (mg)		Foreign ions (mg)	
Added	Found	Added	Found
1.09	1.09	La	17.0 16.5
1.10	1.11	Sm	1.26 1.24
1.08	1.06	Sm	11.3 11.4
1.09	1.11	Lu	1.02 1.06
1.09	1.05	Lu	10.2 10.1
1.00	0.975	Y	4.83 4.79
1.09	1.08	Y	24.7 24.5

5 for scandium(A) and lanthanum(B); 4.5 for scandium(A) and samarium(B); and 3 for scandium(A) and lutetium(B), respectively, in 90% glacial acetic acid-10% 3 N hydrochloric acid medium. A somewhat longer column must be employed for a good separation of scandium and thorium, as the separation factor concerned, $K_{d(Sc)}/K_{d(Th)}$, is 2.3 in the same medium.

In general, the method described above is well suited for the quantitative separation of mg amounts of scandium from at least 10 to 20 times more of the rare earths/or yttrium. Use of larger amounts of scandium should be avoided because of the rather marked decrease of the distribution coefficient with increasing amounts

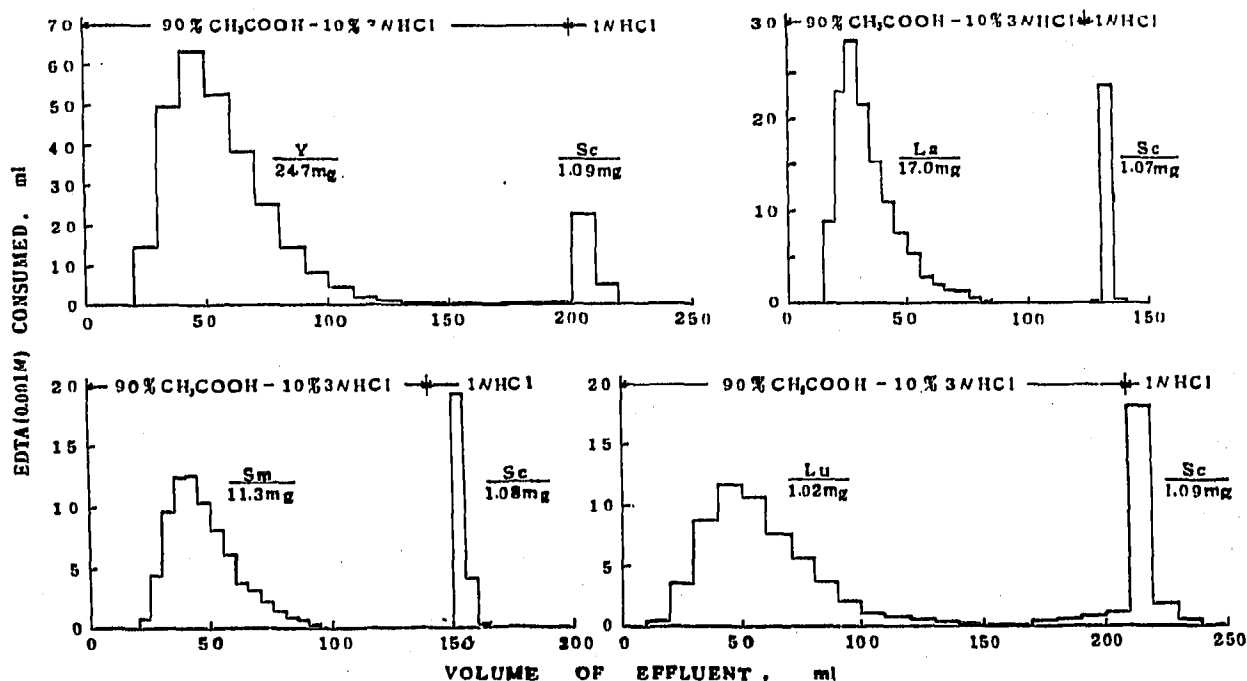


Fig. 3. Typical separations of scandium and the rare earths (or yttrium).

of scandium. For example, 20 mg of scandium can only be partially separated from 1 mg of lanthanum because of early breakthrough of the former. It is of interest to see here whether or not the use of a mineral acid other than hydrochloric acid alters the adsorption characteristics of the rare earths and scandium on Dowex I anion exchanger. KORKISCH AND ARRHENIUS¹⁷ found that pronounced adsorption of the rare earths occurred in 90 % glacial acetic acid–10 % 5 *N* nitric acid, while the adsorption of scandium occurred to a less marked extent. The distribution coefficients on Dowex I, X-8 decreased with increasing atomic number of the rare earths, ranging from 1400 for lanthanum to 100 for lutetium (scandium showed a value of only 21 in the same medium), whereas the higher rare earths are most strongly held by the same resin in hydrochloric acid–acetic acid media, as can be seen in Fig. 1. This may be regarded as a characteristic feature of the present anion exchange system.

TABLE II

DISTRIBUTION COEFFICIENTS OF LANTHANUM AND SCANDIUM IN ACETIC ACID AND PERCHLORIC ACID MIXTURES ON DOWEX I, X-8

	70 % CH_3COOH – 30 % 3 <i>N</i> $HClO_4$	80 % CH_3COOH – 20 % 3 <i>N</i> $HClO_4$	90 % CH_3COOH – 10 % 3 <i>N</i> $HClO_4$
La	No adsorption	0.54	1.66
Sc	No adsorption	No adsorption	1.00

The adsorption of scandium and lanthanum on Dowex I, X-8 was briefly investigated in acetic acid–perchloric acid media. The results are listed in Table II. The distribution coefficient of both metals tends to increase with increasing concentration of acetic acid. No further investigation was attempted because acetic acid–perchloric acid system seems to offer little prospect for an effective anion exchange separation of scandium and the rare earths. Scandium and the rare earths are not easily soluble in mixtures of acetic acid and sulfuric acid, so that reliable results have not been obtainable regarding the distribution coefficient of these elements in this medium.

SUMMARY

The anion exchange behavior of scandium, the rare earths and thorium has been investigated in mixtures of acetic acid and hydrochloric acid. These elements do not adsorb to any great extent on a strong base type anion exchange resin from hydrochloric acid, but their adsorption characteristics are greatly improved by introducing acetic acid into the system. The elements concerned thus become moderately adsorbed on the resin from a medium consisting of 90 % glacial acetic acid and 10 % 3 *N* hydrochloric acid. Differences in the distribution coefficients are large enough to permit a sharp separation of scandium and the rare earths (or yttrium) in this medium. The rare earths (or yttrium) are eluted first, and then scandium can easily be removed from the column by elution with dilute hydrochloric acid.

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