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Cation-Exchange Separation of Scandium from the Rare-Earth Elements*

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Summary

From certain organic solvents containing organic phosphorus compounds such as trioctylphosphine oxide (TOPO), bis(2-ethylhexyl)orthophosphoric acid (HDEHP), or tri-*n*-butylphosphate (TBP) and hydrochloric acid, scandium is much less retained on the strongly acidic cation-exchange resin Dowex 50 than are all other members of the rare-earth group. Thus on this resin in a medium which is 95% tetrahydrofuran, 5% 6 *M* hydrochloric acid, and 0.1 *M* TOPO, the separation factor for scandium–rare earths is greater than 4×10^3 (corresponding to distribution coefficients of < 1 for scandium and $> 4 \times 10^3$ for all the other rare-earth elements). By the use of this system a complete and highly effective separation of tracer and macro quantities of scandium from the rare earths can be achieved on a column of this exchanger. Among the organic solvents investigated, tetrahydrofuran gives the best results. The effectiveness of the organic extractants increases in the order TBP < HDEHP < TOPO

INTRODUCTION

All rare earths including scandium and yttrium are strongly adsorbed on strong acid cation-exchange resins from pure aqueous hydrochloric acid solutions with normalities ranging from 0.1–~0.5 (distribution coefficients $> 10^3$) (*1–3*). At these acidities as well as at higher hydrochloric acid concentrations, the affinities of the rare

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earths and scandium for cation exchangers are very similar. Consequently, pure hydrochloric acid systems can neither be employed for the separation of adjacent rare earths nor for separating scandium from the other members of this group (*4*,*5*).

Similar conditions exist if hydrochloric acid solutions are used which contain water-miscible organic solvents. From such media the rare-earth elements are as a rule more strongly adsorbed on cation-exchange resins, e.g., Dowex 50, than from pure aqueous solutions of comparable acidity (*6*). However, as in the pure aqueous systems, no separation of scandium from the rare earths can be achieved.

It has been shown (*7*) that scandium is much more extractable than the other rare earths from hydrochloric acid solutions using as extractants organic phosphorus compounds such as TOPO, HDEHP, and TBP dissolved in heptane, toluene, or other water-immiscible organic solvents. Because these extractants are also readily miscible with aqueous hydrochloric acid of various concentrations in the presence of a large excess of water-miscible organic solvents, these systems can also be employed as eluents in ion exchange, making use of the principle of combined ion exchange–solvent extraction (CIESE) earlier described (*8*).

The results presented in this article make possible a complete and simple separation of scandium from all rare earths on Dowex 50. Under favorable conditions, separation factors for scandium and the rare earths are obtained which are higher by orders of magnitude than those obtained on strong acid cation-exchange resins in media containing other complexing agents [e.g., sulfuric acid (*9–14*)]. Also with respect to separations of scandium from the rare earths on strong base anion-exchange resins in hydrochloric acid (*15–17*), sulfuric acid (*18*), and thiocyanate media (*19–24*), the present method shows decided advantages. In saturated hydrochloric acid solutions the resin capacity for scandium is very low and in sulfuric acid media its solubility as well as that of the rare-earth sulfates is low so that macro quantities of the elements cannot be separated. Thiocyanate media are relatively unstable.

EXPERIMENTAL

Apparatus

For the ion-exchange separations, ion-exchange columns 0.5 cm in diameter and 25 cm in length have been employed.

Reagents and Solutions

Ion-Exchange Resin. Air-dried Dowex AG 50W-X8 (100–200 mesh; hydrogen form) was used for the column separations and for the batch experiments.

Organic Phosphorus Compounds. Trioctylphosphine oxide (TOPO) (Eastman Organic Chemicals, Rochester, New York), bis(2-ethylhexyl)orthophosphoric acid (HDEHP) (laboratory stock), and tri-*n*-butylphosphate (TBP) (laboratory stock; unpurified).

Organic Solvents. The following reagent-grade solvents were employed: tetrahydrofuran (THF), methyl isobutyl ketone (hexone), acetone, methyl glycol (monomethyl ether of ethylene glycol), methanol, and glacial acetic acid.

Eluent Solution. 0.1 *M* TOPO in 95% THF/5% 6 *M* HCl (v/v). This solution is prepared by mixing 19 parts of THF with 1 part of 6 *M* HCl in the presence of the required amount of TOPO (e.g., 3.86 g of TOPO are dissolved in 50 ml of THF, 5 ml of 6 *M* hydrochloric acid is added, and the mixture is diluted with THF to 100 ml) (molecular weight of TOPO = 386.65).

Tracers. Hydrochloric acid solutions of many radioactive tracers were used. These included: ^{46}Sc, ^{169}Yb, ^{152,154}Eu, ^{144}Ce, ^{85}Sr, ^{22}Na, and ^{137}Cs.

The radioactive measurements were performed by using standard counting techniques.

Determination of Distribution Coefficients

The batch distribution coefficients (K_D values) of scandium, rare earths, and the other investigated elements were determined by using the same technique as has earlier been described (25).

Working Procedure (separation of scandium from the rare earths and other elements)

Step 1: Pretreatment of Resin Bed. One gram of the resin is soaked for about 5 min in a few milliliters of the eluent solution and the slurry is then transferred to the ion-exchange column. The resulting resin bed is supported by a pad of glass or quartz wool and is subsequently washed with about 5–10 ml of the eluent solution. The column is now ready for the subsequent step 2.

Step 2: Sorption and Elution. 0.5 milliliters of 6 *M* hydrochloric acid containing up to 150 mg of scandium and the elements to be separated from it is mixed with 9.5 ml of THF containing 386 mg of

TOPO, and, after cooling to room temperature, this solution is passed through the pretreated resin bed at a flow rate corresponding to the back-pressure of the resin column (~0.5 ml/min). Under these conditions the rare earths, alkali metals, alkaline-earth metals, and several other elements are strongly retained by the resin while scandium passes into the effluent. Its complete elution is effected by passing, at the same flow rate as above, 50–150 ml of the eluent solution; in the eluate scandium is determined radiometrically. If scandium is present on the tracer level (millicurie quantities), 50 ml of the eluent solution are sufficient to effect its quantitative elution. Larger amounts of scandium (up to 150 mg) can be removed completely only by passing 100 or 150 ml of the eluent, whereby 98 or 100%, respectively, of the scandium is eluted.

RESULTS AND DISCUSSION

Batch Studies

Determinations of the batch distribution coefficients on Dowex 50 of scandium and ytterbium in organic solvent media which were 5 vol. % in concentrated hydrochloric acid and 0.1 *M* in TOPO or HDEHP or TBP gave the results recorded in Table 1.

Ytterbium has been selected as a representative of the whole group of the lanthanides because this element as well as other members of the very heavy rare earths are better extracted with these organic phosphorus compounds from hydrochloric acid solu-

TABLE 1

Distribution Coefficients of Scandium and Ytterbium on Dowex 50 in 95% Organic Solvent/5% Concentrated Hydrochloric Acid Media which are 0.1 *M* in TOPO or HDEHP or TBP

	TOPO		HDEHP		TBP	
Organic solvent	Sc	Yb	Sc	Yb	Sc	Yb
Tetrahydrofuran	<1	460	3.7	2,253	74	4,200
Hexone	5.7	7,660	11	8,636	305	75,000
Acetone	8.3	3,220	13	5,374	360	20,000
Methyl glycol	15	10,206	200	100,000	8,450	450,000
Methanol	105	17,960	1043	83,000	17,700	100,000
Acetic acid	251	11,045	265	9,080	651	11,880

TABLE 2

Distribution Coefficients of Scandium and Ytterbium on Dowex 50 in Media which are 0.1 *M* in TOPO (or HDEHP or TBP), 95% in Tetrahydrofuran, and 5% in Hydrochloric Acid of Varied Molarity

Molarity of HCl	TOPO		HDEHP		TBP	
	Sc	Yb	Sc	Yb	Sc	Yb
12	<1	460	3.7	2,253	74	4,200
6	<1[a]	4,000[a]	14	9,447	1,800	9,000
6	4	212,250	35	54,670	5,720	46,546
1	150	421,000	62	74,275	105,150	75,000

[a] In the absence of TOPO the K_D values of scandium and ytterbium are 3355 and 58,000, respectively.

tions than are the light rare earths (7). Therefore determinations of the distribution coefficients of ytterbium are of special importance in connection with the separation of scandium from the rare earths because all the other rare earths of lower atomic weight will be stronger adsorbed on the resin and hence their separation factors in relation to scandium will even be higher than that for scandium–ytterbium.

From the data shown in Table 1 it is seen that in all cases (except for ytterbium in acetic acid) TOPO is a stronger extractant than HDEHP, which in turn is more effective than TBP. In other words, in the presence of these extractants the adsorption of scandium and ytterbium on the resin increases in the order TOPO < HDEHP < TBP, the adsorption of scandium being much lower than that of ytterbium. Consequently, ready separations of these two elements are feasible in many of the media, especially in those in which the distribution coefficient of scandium is in the range of < 1 to 15.

From an analytical point of view the THF–TOPO mixture is the most suitable because with this solution scandium ($K_D = < 1$) is readily eluted from a column of Dowex 50, while ytterbium is still strongly retained ($K_D = 460$). This separation condition is considerably improved when the acidity is lowered to 6 *M*, which corresponds to an overall acidity of the mixtures of 0.3 *M*. This effect of acidity is shown in Table 2.

From the distribution data shown in Table 2 it is seen that in the TOPO systems containing 6 and 3 *M* hydrochloric acid, separation factors for scandium–ytterbium (separation factor = K_D Yb/K_D Sc) of $> 4 \times 10^3$ and $\sim 5.3 \times 10^4$, respectively, are obtained. Consequently, very effective separations of scandium from ytterbium and the other rare earths (e.g., in the presence of 6 *M* hydrochloric acid the distribution coefficients of europium and cerium are 50,000 and 750,000, respectively) can be effected.

The TOPO–THF system containing 6 *M* hydrochloric acid is most suitable and hence was used as eluent in the working procedure described above.

The other mixtures shown in Table 2 which contain HDEHP or TBP are much less advantageous for effective separations of scandium from the rare earths because in most of these the distribution coefficient of scandium is too high to allow its rapid elution.

At acid concentrations below 6 *M* the distribution coefficients of both scandium and ytterbium increase considerably (Table 2). The same effect is observed when decreasing the percentage of tetrahydrofuran at constant concentrations of hydrochloric acid and TOPO. On the other hand, a simultaneous decrease of the concentration of the organic solvent and an increase of the hydrochloric acid concentration causes a decrease in the distribution coefficients of these elements.

When the concentration of the organic phosphorus compounds is increased, all other conditions being kept constant, the general

TABLE 3

Distribution Coefficients of Scandium, Ytterbium, and Cerium On Dowex 50 in 95% THF/5% Concentrated Hydrochloric Acid Media Containing Varying Molarities of TOPO, HDEHP, and TBP

	Molarities						
	TOPO		HDEHP			TBP	
Metal ion	0.1	0.5[a]	0.1	1.0	2.0	0.1	1.0
Sc	<1	<1	3.7	<1	1.0	74	7.8
Yb	460	26	2,253	25	1.7	4,200	837
Ce	21,600	55,515	44,450	13,443	7,244	30,710	45,400

[a] In this medium the distribution coefficient of europium has a value of 4130.

TABLE 4

Distribution Coefficients of Scandium, Ytterbium, and Cerium on Dowex 50 in Media which Are 1 *M* in HDEHP, 95% in THF, and 5% in Hydrochloric Acid of Varied Molarity

Molarity of HCl	Sc	Yb	Ce
12	<1	25	13,443
6	<1	31	5,114
3	<1	58	6,360

trend is a reduced adsorption of scandium and ytterbium. These conditions are illustrated by the data presented in Table 3.

From Table 3 it is seen that the adsorption of ytterbium is very much reduced at high concentrations of both TOPO and HDEHP so that separation factors for ytterbium–cerium of $> 10^3$ are obtained in the media containing 0.5 *M* TOPO and 2 *M* HDEHP. However, these media are less suitable for the separation of scandium from rare earths than the system which is 0.1 *M* in TOPO.

When the concentration of hydrochloric acid is varied in the tetrahydrofuran media which are 1 *M* in HDEHP, the results recorded in Table 4 are obtained.

These data indicate the same general trend of increasing adsorption of ytterbium with a decrease of the acid concentration, as has also been observed in the TOPO–hydrochloric acid media (see Table 2). The behavior of cerium is irregular, showing a minimum of adsorption in the presence of 6 *M* hydrochloric acid and a maximum when the acidity is raised to 12 *M*.

All these media are, however, not very well suited for effective separations of scandium from the rare earths because of the relatively low distribution coefficients that are obtained for ytterbium (see Table 4).

If acetone is used in place of tetrahydrofuran, results very similar to those shown in Tables 2–4 are obtained. Since, however, the extraction effect of the organic phosphorus compounds is less pronounced in this solvent (i.e., scandium is stronger retained on Dowex 50 from acetone media; see Table 1), its efficiency for separating scandium from the rare earths is less than when using tetrahydrofuran as the solvent.

Separations

The working procedure described in the experimental section of this article has been amply tested using millicurie and milligram amounts of scandium and rare earths. In all cases absolutely complete separations of scandium from the rare earths were obtained.

Other elements which are strongly retained ($K_D > 10^3$–10^4) by the resin from the eluent solution (see working procedure) include yttrium, lanthanum, alkali metals, magnesium, alkaline-earth metals, aluminum, chromium(III), nickel, and trivalent transplutonium elements. These elements also are readily separated from scandium. All other elements investigated show the same behavior as scandium. These include Zr(IV), Hf(IV), Mn(II), Ga(III), In(III), Cu(II), Fe(III), Co(II), Au(III), UO_2(II), Zn(II), Cd(II), Hg(II), Bi(III), Sn(II), Sn(IV), Pb(II), Ge(IV), V(V), Mo(VI), and the platinum metals. All these metal ions have distribution coefficients which are < 1 except maganese(II), for which a coefficient of 19 was measured. Consequently, if scandium has to be separated from one or a mixture of the above ions, these have to be removed, e.g., by anion exchange in pure aqueous hydrochloric acid media of suitable acidities (*26–35*). Another possibility to separate scandium from these metal ions is by using cation exchange in tetrahydrofuran (*36*) or acetone (*37*) media containing hydrochloric acid but no TOPO. From such systems scandium is strongly retained on a column of Dowex 50 together with the rare earths, while most of the other metal ions pass into the effluent. Subsequently, the scandium plus rare earths and other coadsorbed elements can be eluted with pure aqueous 6 *M* hydrochloric acid and the separation of scandium from the coeluted elements is effected in a second cation-exchange step by using the working procedure described in this article. The direct elution of the adsorbed scandium by means of the TOPO–THF–eluent is also possible, but in this case a very large volume of this eluent solution is required so that the two-step procedure mentioned above is to be preferred.

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