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Studies on Separation of Samarium(III) Nitrate Complexes from Neodymium(III) on Strongly Basic Anion Exchangers

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ABSTRACT

With the development of new branches of industry like optoelectronics, power metallurgy, and modern techniques of raw material or plastics admixture, there is greater demand for rare earth elements of high purity. This paper presents the selective separation of neodymium(III) microquantities from samarium(III) macroquantities in the 90% v/v polar organic solvent–10% v/v 1 or 7 M HNO₃ system on strongly basic anion exchangers of various types. Weight and bed distribution coefficients as well as the number of theoretical plates were determined. It is shown that the neodymium(III) content in purified samarium(III) decreases to a value below 10^{−3}% under optimal conditions.

INTRODUCTION

Industrial demand for rare earth metals has increased lately due to their new possibilities for such applications as, e.g., supermagnets of the Nd-Fe-B type and ceramic high-temperature superconductors. At the same time the application of rare earth elements in metallurgy, catalysis, ceramics, etc. is still of significant importance (1–3).

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Synthesis of compounds of the SmCo_5 type started an era of magnetic lanthanide materials. It seemed that using compounds of the $\text{Sm}_2\text{Co}_{17}$ type could give even better materials. However, these expectations were not fulfilled due to the unfavorable anisotropy of the cobalt lattice in these compounds. Compounds based on multicomponent materials of the $\text{Sm}(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr})_7$ or $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Ti})_7$ type were a compromise between high magnetization of saturation for $\text{Sm}_2\text{Co}_{17}$ and great magnetic hardness of SmCo_5 . Their preparation required accurate, multistage thermal treatment of the alloy, which resulted in superimposition of the two basic substructures SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ (4, 5). Both components of such a material are relatively expensive, which makes their common application difficult. Samarium was used as the addition to polycrystalline sintered products, characterized by heat resistance and large cross section for thermal neutrons. The sintered products are used as control elements in nuclear reactors and neutron absorbers. Samarium is characterized by a forced emission of a +2 degree of oxidation. In lasers and luminophores it is a component of matrices and an activator (4). Magnetic properties of rare earth elements are used in the preparation of computer memory elements. The basic components of memory are nonmagnetic crystal of rare earth garnets and magnetic garnets, most frequently yttrium-iron ones. Depending on the application, garnet magnetic layers superimposed in the epitaxy way can include Y, Sm, Eu, Er, Lu, and Gd (4) as well as ceramics based on α -Sialon (6). Sm_2O_3 can also be used as a potential addition for stabilization of the ZrO_2 structure (4). A small addition of samarium to ceramics of pure aluminum oxide modifies the sintered products microstructure and improves the application properties of aluminum ceramics (4). Samarium reduces the volume changes during melting of Al_2O_3 (4), which is important in the production of melted refractory materials. Samarium fluoride also improves the thermomechanical and electrical properties of ceramics made of aluminum nitride (7). Samarium chlorides or oxides are used in the production of ceramic semiconductor condensers (4, 8). The addition of samarium oxide including La_2O_3 and Nd_2O_3 with a small amount of Sm_2O_3 to glazes increases their thermal resistance. The property of glasses used in technology is luminescence caused by the presence of rare earth elements. Samarium ions with +2 and +3 degrees of oxidation show luminescence in yellow, orange, and red ranges of radiation. Samarium was used to activate CaSO_4 in thermoluminescence dosimetry, characterized by unique sensitivity, in long-term measurements at increased temperatures (4). Thermoluminescence enamels were applied also in dosimetry. They are composed of thermoluminophores including, e.g., Sm-Pb, Sm-As, and Sm-V.

High purity is required in most applications of samarium in modern technology. One method used to prepare high purity samarium is ion exchange. In-



teresting results were obtained by using solid or liquid anion exchangers for the separation of rare earth elements(III) complexes with organic and inorganic ligands. The literature includes much data about the separation of micro- or milligram amounts of rare earth elements on anion exchangers by means of frontal analysis. Solutions of nitric acid, lithium, aluminum, magnesium, calcium, and ammonium nitrates in aqueous-organic solvents (9, 10) were used as the eluants.

New possibilities for anion-exchange separation of rare earth elements(III), and in particular the preparation of high purity yttrium(III) on the macroscale, are provided by the $\text{Ln}(\text{NO}_3)_3\text{--HNO}_3$ –polar organic solvent system by frontal analysis (11, 12).

The aim of this paper is to study possibilities of selective purification of macroquantities of samarium(III) nitrate complexes from neodymium(III) microquantities in the water–organic solvent system on anion exchangers of various types.

EXPERIMENTAL

Separation of nitrate complexes of samarium(III) from neodymium(III) (about 1 and 0.1%) on various types of anion exchangers in the polar organic solvent– H_2O – HNO_3 system was investigated. The anion exchangers Wofatit SBW \times 4% (25.90 g), Wofatit SBW \times 6% (16.50 g)—microporous type 1, Wofatit SBK \times 7% (26.90 g)—microporous type 2, and Lewatit MP 5080 (16.15 g)—macroporous type 1 were used in their nitrate forms. The grain sizes of the applied anion exchangers were as follows: Wofatit SBW \times 4, SBW \times 6, and Lewatit MP 5080 (100–200 mesh) and Wofatit SBK \times 7 (50–100 mesh). The anion exchangers in their nitrate forms were placed in a beaker with the corresponding solutions of HNO_3 –polar organic solvent for about 24 hours. Separation by frontal analysis was carried out in glass columns of 2 cm diameter filled with the anion exchanger (50 cm^3) at 22°C . The solutions of rare earth elements were prepared by dissolving the oxide in a stoichiometric quantity of HNO_3 (1–2% excess) while heating. The nitrates of rare earth elements were next dissolved in the following mixtures: 90% v/v CH_3OH –10% v/v 1 M HNO_3 , 90% v/v CH_3OH –10% v/v 7 M HNO_3 , 90% v/v CH_3COCH_3 –10% v/v 1 M HNO_3 , 90% v/v CH_3COCH_3 –10% v/v 7 M HNO_3 . Rare earth elements nitrate solutions with concentrations of about 5.23 and 1.75 g $\text{Ln}_2\text{O}_3/\text{dm}^3$ in the above-mentioned systems were passed through the columns continuously at a flow rate of about $0.2\text{ cm}^3/\text{cm}^2\cdot\text{min}$. The effluent was collected in fractions of about 100 cm^3 volume from which the oxalates were precipitated and converted to oxides.



TABLE 1

The Results of Purification of Samarium(III) from 1% (*0.1%) Neodymium(III) (concentrations: 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$ and 1.748 g Ln_2O_3 in 90% v/v CH_3OH –7 M HNO_3 system on Wofatit SBW \times 6% DVB) in the 90% v/v CH_3OH –1 or 7 M HNO_3 System on Various Types of Anion Exchangers^a

Anion exchangers	Concentration of HNO_3							
	1 M HNO_3				7 M HNO_3			
	m (g)	K_d	K'_d	N	m (g)	K_d	K'_d	N
Wofatit SBW \times 4%	1.46	76.22	39.48	6	1.47	55.95	28.98	13
Wofatit SBW \times 6%	5.19	146.91	48.48	15	5.79	422.67	139.48	24
Wofatit SBK \times 7%	2.05	63.12	33.98	8	2.44	88.19	47.48	3
Lewatit MP 5080	11.89	201.98	65.28	354	12.32	190.22	61.48	763
Wofatit SBK \times 7%					*3.62	57.73	31.08	54

^a m (g) = amount of $\text{Sm}_2\text{O}_3 < 10^{-3}\%$ Nd_2O_3 purified on 50 cm^3 of anion exchangers. K_d = weight distribution coefficients (Nd(III)). K'_d = bed distribution coefficients (Nd(III)). N = number of theoretical plates.

The percentage of neodymium in samarium was determined by means of spectrophotometric analysis using a spectrophotometer Specord M 40 produced by Zeiss, Germany. The determinations were made by means of a direct method using the neodymium absorption maximum for $\lambda = 794.3$ nm.

TABLE 2

The Results of Purification of Samarium(III) from 1% (*0.1%) neodymium(III) (concentration 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$) in the 90% v/v CH_3COCH_3 –1 or 7 M HNO_3 System on Various Types of Anion Exchangers^a

Anion exchangers	Concentration of HNO_3							
	1 M HNO_3				7 M HNO_3			
	m (g)	K_d	K'_d	N	m (g)	K_d	K'_d	N
Wofatit SBW \times 4%	1.31	69.46	35.98	6	1.41	63.67	32.98	6
Wofatit SBW \times 6%	4.99	101.45	33.48	116	9.05	164.48	54.28	74
Wofatit SBK \times 7%	1.62	54.76	29.48	10	1.90	103.05	55.48	4
Lewatit MP 5080					12.90	202.05	67.08	298
Wofatit SBK \times 7%					*3.46	52.90	28.48	194

^a m (g) = amount of $\text{Sm}_2\text{O}_3 < 10^{-3}\%$ Nd_2O_3 purified on 50 cm^3 of anion exchangers. K_d = weight distribution coefficients (Nd(III)). K'_d = bed distribution coefficients (Nd(III)). N = number of theoretical plates.



The solutions of rare earth element chlorides were found to have a concentration of about 0.5 g Ln_2O_3 in 10 cm^3 of 2 M hydrochloric acid solution. The detection limit of neodymium(III) in samarium(III) under these conditions was 0.001%.

RESULTS AND DISCUSSION

The results of purification of samarium(III) from neodymium(III) in the aqueous-polar organic solvent medium of nitric acid on various types of anion exchangers are presented in Tables 1 and 2. The concentrations of neodymium as a microcomponent in the effluent are shown graphically in Figs. 1–8.

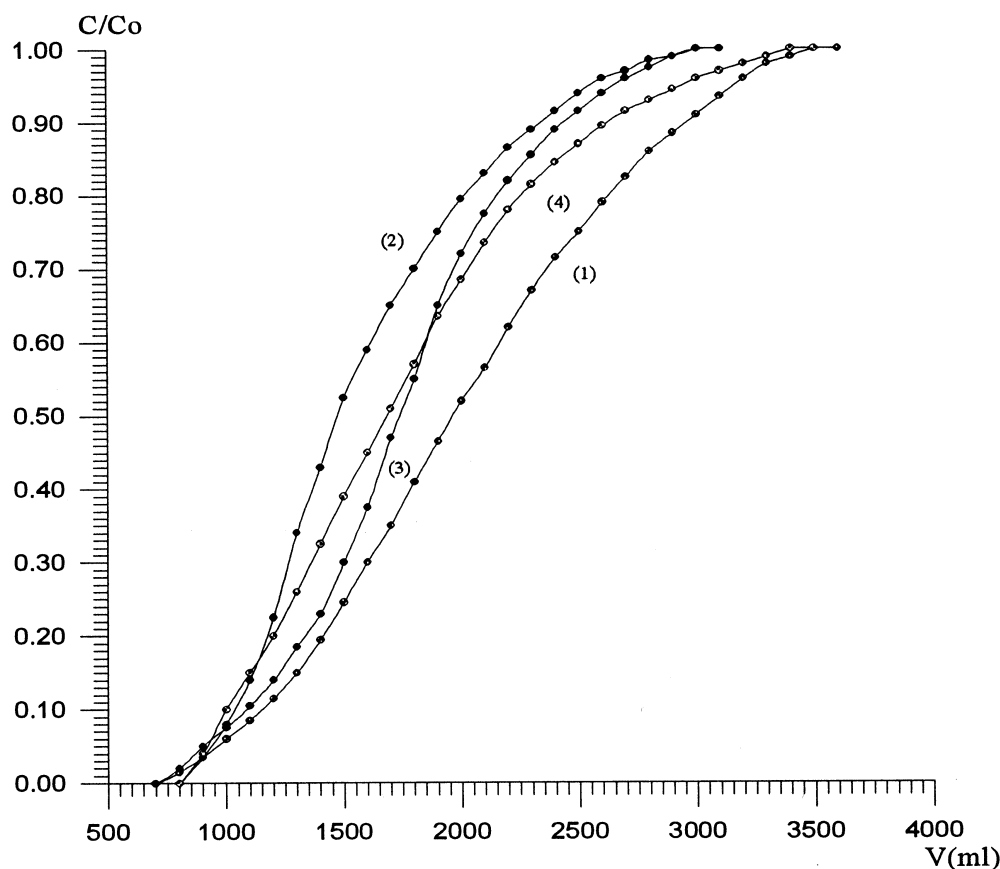


FIG. 1 Breakthrough curves for neodymium(III) on Wofatit SBW \times 4% DVB in the systems (1) 90% v/v CH_3OH –10% v/v 1 M HNO_3 , (2) 90% v/v CH_3OH –10% v/v 7 M HNO_3 , (3) 90% v/v CH_3COCH_3 –10% v/v 1 M HNO_3 , and (4) 90% v/v CH_3COCH_3 –10% v/v 7 M HNO_3 with 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$ in all systems.



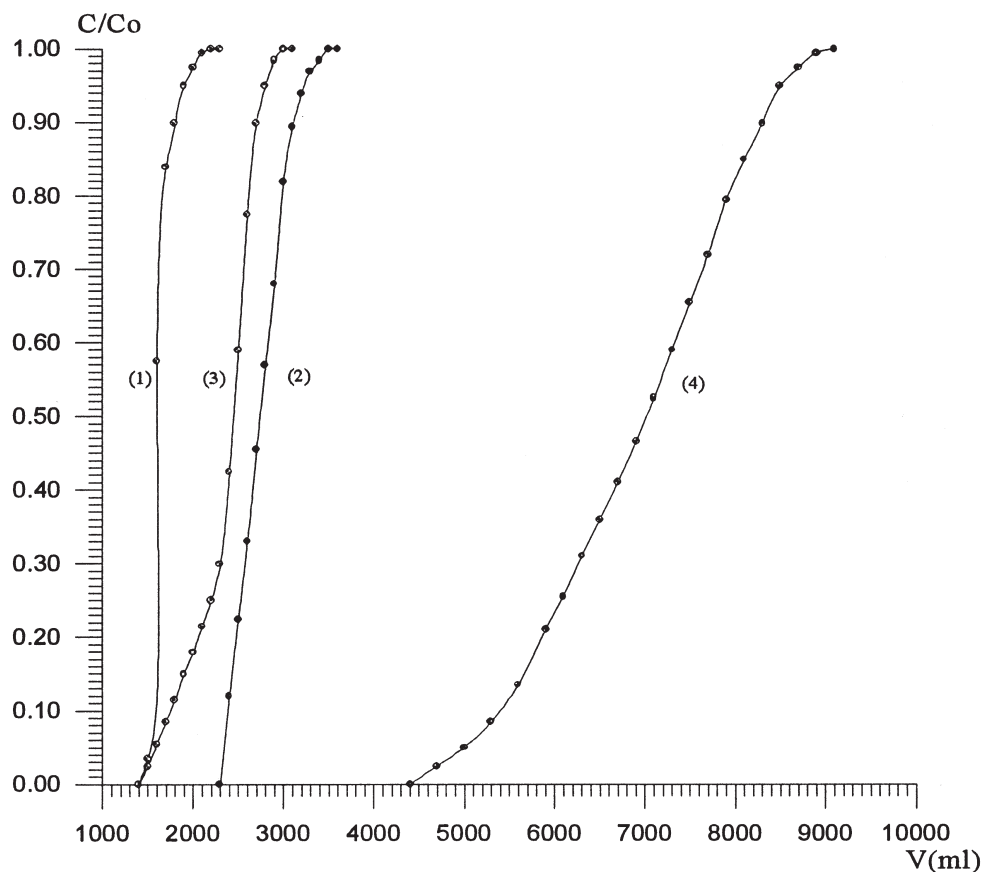


FIG. 2 Breakthrough curves for neodymium(III) on Wofatit SBW \times 6% DVB in the systems (1) 90% v/v CH_3COCH_3 –10% v/v 1 M HNO_3 –5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$, (2) 90% v/v CH_3COCH_3 –10% v/v 7 M HNO_3 –5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$, (3) 90% v/v CH_3OH –10% v/v 1 M HNO_3 –5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$, and (4) 90% v/v CH_3OH –10% v/v 7 M HNO_3 –1.748 g $\text{Ln}_2\text{O}_3/\text{dm}^3$.

The curves make it possible to calculate the weight distribution coefficients (K_d) for the microcomponent ion (13):

$$K_d = \frac{(\bar{U} - U_0 - V)}{m_j}$$

The bed K'_d distribution coefficients is

$$K'_d = K_d d_z$$

The number of theoretical plates N can be calculated from

$$N = \frac{(\bar{U} - U_0)(U' - U_0)}{(U - U')^2}$$



where K_d = weight distribution coefficients
 K'_d = bed distribution coefficients
 N = number of theoretical plates
 \bar{U} = the effluent volume (cm^3) at $c = c_0/2$ (determined graphically)
 U_0 = the dead volume (cm^3) in the column (6 cm^3)
 V = the void (interpartide) resin bed volume (cm^3) which amounts to ca. 0.4 of the resin bed volume
 m_j = the dry resin weight (g)
 d_z = the bed density (Wofatit SBW $\times 4\% = 0.518 \text{ g/cm}^3$, Wofatit SBW $\times 6\% \text{ DVB} = 0.330 \text{ g/cm}^3$, Wofatit SBK $\times 7\% = 0.538 \text{ g/cm}^3$, Lewatit MP5080 $= 0.323 \text{ g/cm}^3$)
 U' = the effluent volume at $c = 0.159c_0$ (determined graphically)

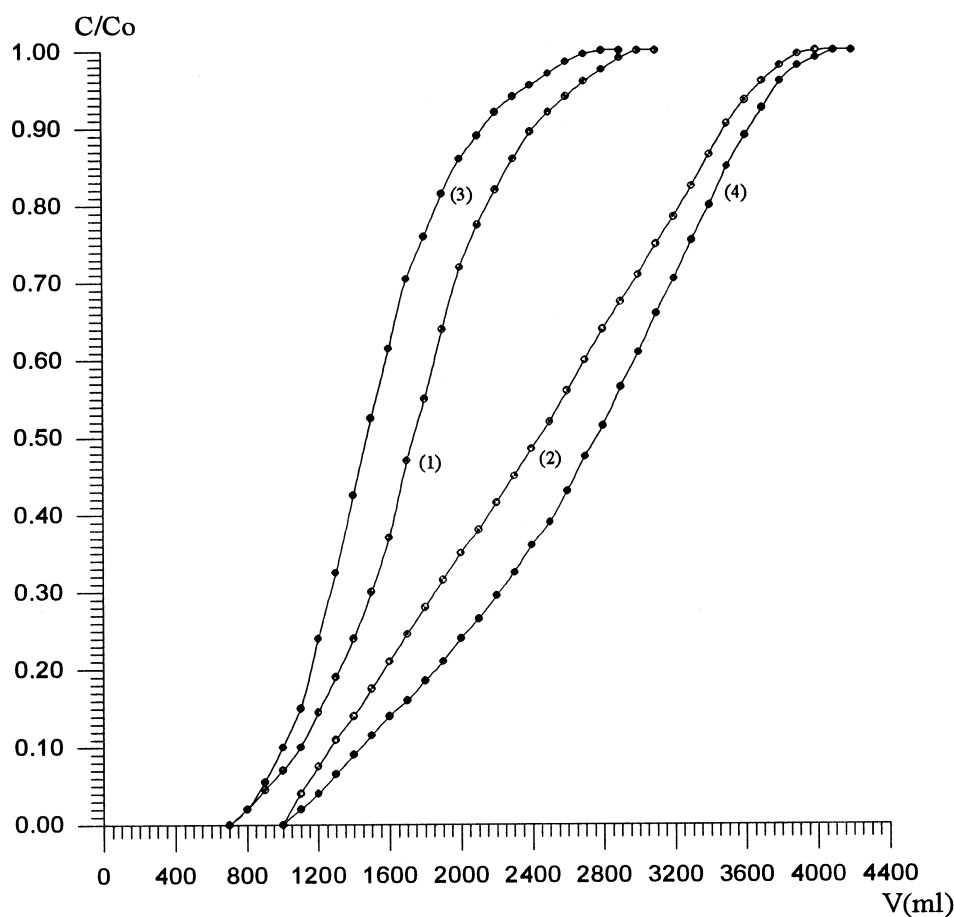


FIG. 3 Breakthrough curves for neodymium(III) on Wofatit SBK $\times 7\% \text{ DVB}$ in the systems (1) 90% v/v CH_3OH –10% v/v 1 M HNO_3 , (2) 90% v/v CH_3OH –10% v/v 7 M HNO_3 , (3) 90% v/v CH_3COCH_3 –10% v/v 1 M HNO_3 , and (4) 90% v/v CH_3COCH_3 –10% v/v 7 M HNO_3 with $5.231 \text{ g Ln}_2\text{O}_3/\text{dm}^3$ in all systems.

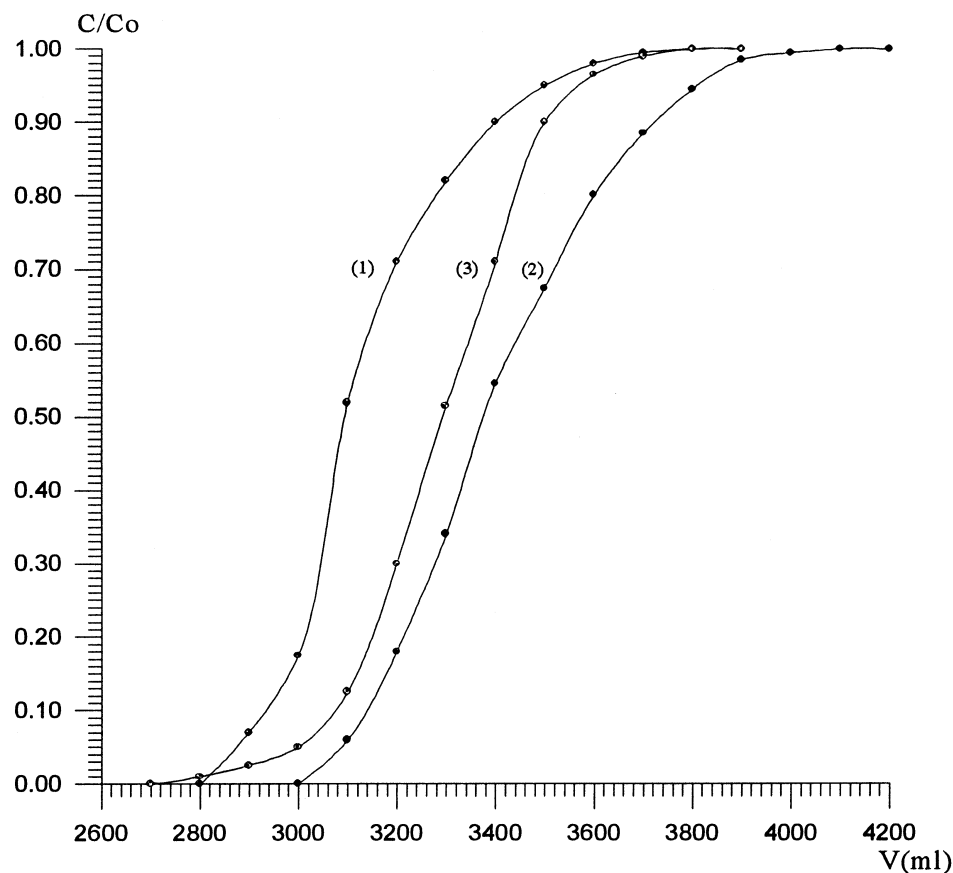


FIG. 4 Breakthrough curves for neodymium(III) on Lewatit MP 5080 in the systems (1) 90% v/v CH_3OH –10% v/v 7 M HNO_3 , (2) 90% v/v CH_3COCH_3 –10% v/v 7 M HNO_3 , and (3) 90% v/v CH_3OH –10% v/v 1 M HNO_3 with $5.231 \text{ g Ln}_2\text{O}_3/\text{dm}^3$ in all systems.

Based on the affinity series determined earlier (14) as well as the literature data concerning the separation of microquantities of samarium and neodymium by the elution technique (15, 16), the possibilities of the purification of several gram quantities of samarium(III) from 1% neodymium(III) admixture on strongly basic anion exchangers of various types were studied.

The microporous and macroporous skeleton anion exchangers examined for their applicability in the purification of macroquantities of samarium(III) from neodymium(III) can be arranged as follows (Tables 1 and 2):

Lewatit MP 5080 > Wofatit SBW \times 6%

> Wofatit SBK \times 7% > Wofatit SBW \times 4%

The strongly basic anion exchanger Merck MP 5080 of the macroporous skeleton structure proved to be the most effective. On a 50 cm^3 bed of Lewatit



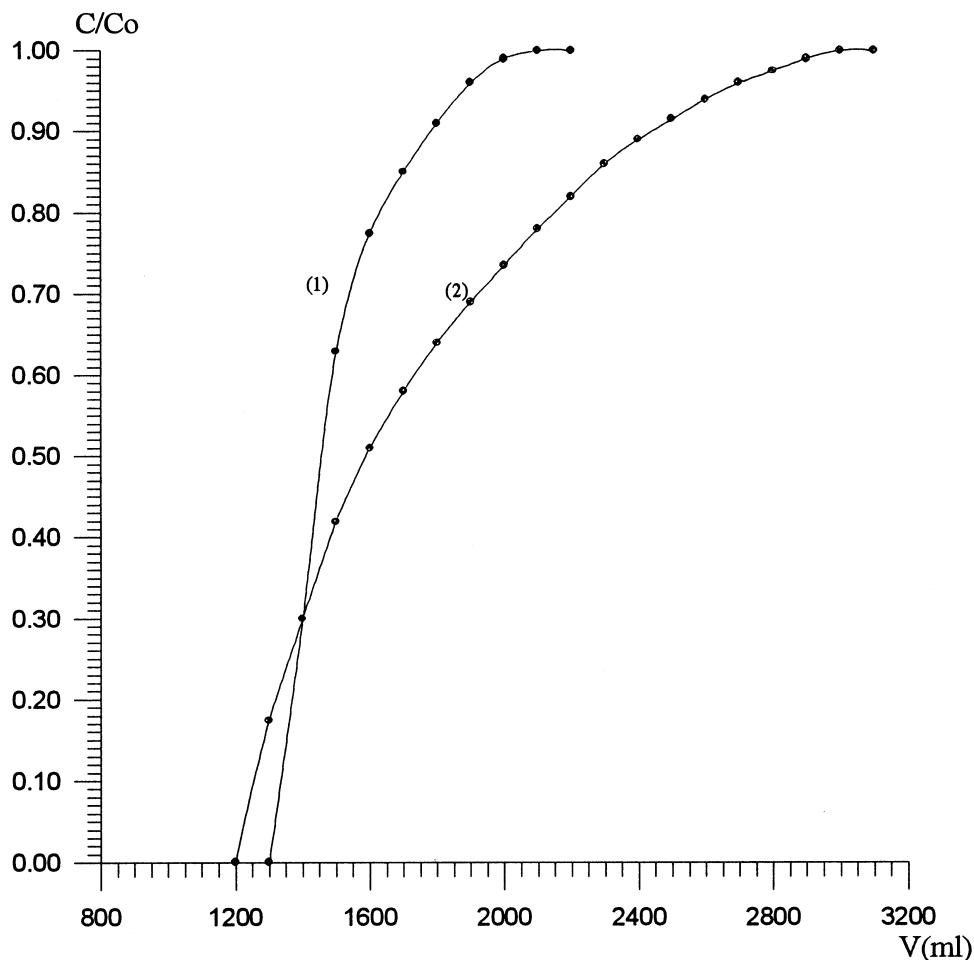


FIG. 5 Breakthrough curves for neodymium(III) (0.1% Nd_2O_3) Wofatit SBK \times 7% DVB in the systems (1) 90% v/v CH_3COCH_3 -10% v/v 7 M HNO_3 , and (2) 90% v/v CH_3OH -10% v/v 7 M HNO_3 with 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$ in all systems.

MP 5080 in nitrate form it is possible to obtain about 12 g Sm_2O_3 by decreasing the Nd_2O_3 content from 1% to a value below 0.001%.

The much smaller yield of Sm(III) from Nd(III) purification compared with that of Y(III) from Nd(III) [on Lewatit MP 5080 in the 90% v/v CH_3COCH_3 -10% v/v 7 M HNO_3 system, 114.22 g $\text{Y}_2\text{O}_3/50 \text{ cm}^3$ ion exchanger were purified (17) and in the 90% v/v CH_3OH -10% v/v 7 M HNO_3 system, 94.16 g $\text{Y}_2\text{O}_3/50 \text{ cm}^3$ anion exchanger were purified (18)] is caused by a smaller difference between the distribution coefficients of Sm(III)-Nd(III) compared with Y(III)-Nd(III).

The different affinities of neodymium(III) and samarium(III) nitrate complexes in the systems $\text{Ln}(\text{NO}_3)_3$ -90% v/v CH_3OH -10% 1 or 7 M HNO_3 as



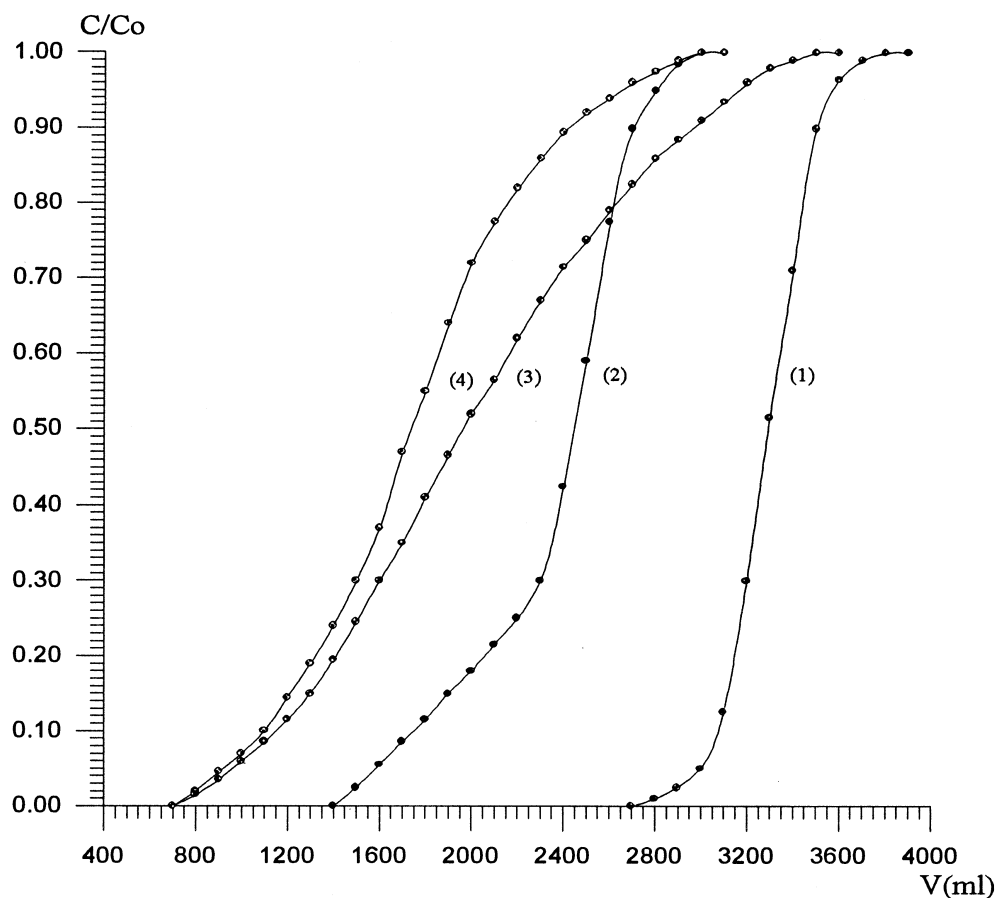


FIG. 6 Breakthrough curves for neodymium(III) in the 90% v/v CH_3OH -10% v/v 1 M HNO_3 system on (1) Lewatit MP 5080, (2) Wofatit SBW \times 6%, (3) Wofatit SBW \times 4%, and (4) Wofatit SBK \times 7% with $5.231 \text{ g Ln}_2\text{O}_3/\text{dm}^3$ in all systems.

well as in $\text{Ln}(\text{NO}_3)_3$ -90% v/v CH_3COCH_3 -10% 1 or 7 M HNO_3 are probably caused by the formation of neodymium nitrate complexes with a higher negative charge (e.g., $[\text{Nd}(\text{NO}_3)_5]^{2-}$) than that of samarium(III) complexes (e.g., $[\text{Sm}(\text{NO}_3)_4]^-$) or by their different structures (possibly by the differences in the degree of solvation) and the kinetics of formation of neodymium(III) and samarium(III) anionic nitrate complexes. The results obtained are confirmed by the weight and bed distribution coefficient values determined from the breakthrough curves.

FIG. 8 Breakthrough curves for neodymium(III) in the 90% v/v CH_3COCH_3 -10% v/v 7 M HNO_3 system on (1) Lewatit MP 5080, (2) Wofatit SBK \times 7%, (3) Wofatit SBW \times 6%, and (4) Wofatit SBW \times 4% with $5.231 \text{ g Ln}_2\text{O}_3/\text{dm}^3$ in all systems.

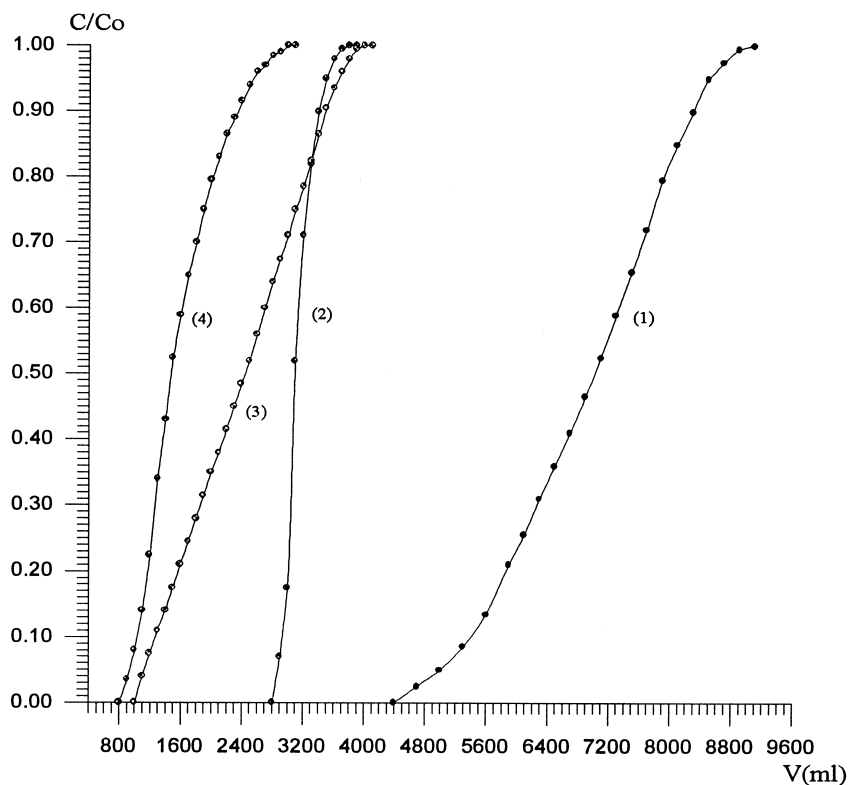
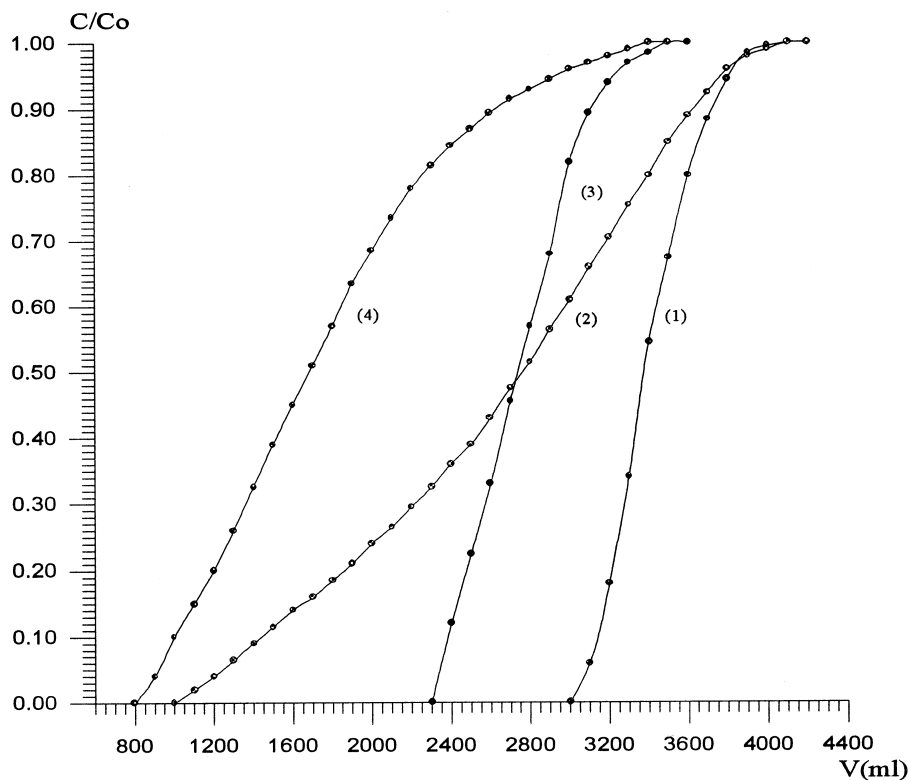


FIG. 7 Breakthrough curves for neodymium(III) in the 90% v/v CH_3OH –10% v/v 7 M HNO_3 system on (1) Wofatit SBW \times 6%–1.748 g $\text{Ln}_2\text{O}_3/\text{dm}^3$, and on (2) Lewatit MP 5080, (3) Wofatit SBK \times 7%, and (4) Wofatit SBW \times 4% with 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$ in systems (2), (3), and (4).



CONCLUSION

The strongly basic macroporous anion exchanger Lewatit MP 5080 can be regenerated with water in the amount of 2–4 bed volumes after the purification process of samarium(III) from neodymium(III).

The relatively high yield of samarium(III) from neodymium(III) purification, the low costs and the simple and cheap regeneration of the anion-exchanger bed when the purification process is over, as well as the possibility of methanol recovery from the eluate by using the distillation method suggest the possibility of using this process in technologies for high purity samarium production.

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