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Figure 1: Fig. 1. Extraction system $La(NO_3)_3$—NH_4NO_3—H_2O—$(C_4H_9O)_3PO$

Abstract

Full Text

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EXTRACTION SYSTEM $La(NO_3)_3$—NH_4NO_3—H_2O—$(C_4H_9O)_3PO$

The distribution coefficient (D) of rare-earth elements varies within wide limits depending on the conditions under which extraction is carried out ($^{1-5}$). Thus, in the system $La(NO_3)_3$—HNO_3—H_2O—TBF, $D_{La(NO_3)_3}$ changes its value from 0.01 to 1.2 (^{1,6,7}). With successive replacement of HNO_3 by $NaNO_3$, while maintaining their total concentration at 2 mol/l, D_{Cl} changes from 0.03 to 17.6 (^{8}). The form in which lanthanum exists in TBF has been established as the trisolvate $La(NO_3)_3 \cdot 3TBF$ (^{9}); the dependence of D on the atomic number of the rare-earth elements has been found (^{7}); and the condition for separation of rare-earth elements with TBF has been established (^{2,10}).

Fig. 1. Extraction system $La(NO_3)_3$—NH_4NO_3—H_2O—$(C_4H_9O)_3PO$

However, investigation of phase equilibria not only in individual regions of extraction systems, but over the entire range of their concentrations, is of practical and theoretical interest. The system $La(NO_3)_3$—NH_4NO_3—H_2O—TBF was studied under isothermal conditions at $25 \pm 0.1°$. The extraction-ray method (^{11}) was used, together with the equilibrium-analysis method for individual points. Lanthanum was determined complexometrically (^{12}), and at microconcentrations (down to $5.22 \cdot 10^{-6}$ mol/l) the radioactive isotope La^{140} was used. Water was determined by the Fischer method (^{13}), and the ammonium ion by the method of distillation of ammonia. The distribution coefficient was calculated for concentrations in weight percent.

Numerical data on the investigation of phase equilibria in the region of stratification of the system $La(NO_3)_3$—NH_4NO_3—H_2O—TBF at 25° are given in

Tables 1 and 2. In Fig. 1, in the field of unsaturated solutions of the solubility diagram of the system $La(NO_3)_3$—NH_4NO_3—H_2O, extraction rays and isolines of the distribution coefficients of lanthanum nitrate and water are plotted.

The distribution coefficients of lanthanum nitrate vary from 0.1 to 70 and higher, depending on the component ratio in the equilibrium state of the system. The isolines of the distribution coefficients (in Fig. 1 indicated by thin lines) have a definite pattern and to some extent resemble the course of isolines in the system $UO_2(NO_3)_2$—NH_4NO_3—H_2O—$(C_2H_5)_2O$ ([11]).

Table 1

Beam no.	Point no.	Ratio of phase volumes org./aq.	Density d_4^{25}, organic phase	Density d_4^{25}, aqueous phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, organic phase	Equilibrium concentration, wt. %, H_2O, organic phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, aqueous phase	Equilibrium concentration, wt. %, NH_4NO_3, aqueous phase	Distribution coefficient D, $La(NO_3)_3$	Distribution coefficient D, H_2O
I	1	–	–	–	8,85	–	14,50	4,10	0,60	–
I	2	–	–	–	8,44	–	14,31	4,91	0,59	–
I	3	–	–	–	2,92	–	6,61	5,17	0,44	–
I	4	–	–	–	1,29	–	3,23	5,54	0,40	–
I	5	–	–	–	0,58	–	1,56	6,54	0,38	–
II	6	0,4	1,2125	1,6627	22,5	1,07	40,12	4,12	0,56	0,019
II	7	1,0	1,1948	1,5567	20,77	1,51	34,61	5,21	0,60	0,024
II	8	1,0	1,1670	1,4421	18,2	2,0	29,27	5,49	0,62	0,031
II	9	2,0	1,1149	1,2875	13,0	2,95	20,45	7,11	0,63	0,041
II	10	3,0	1,0493	1,1520	6,9	4,19	10,76	7,98	0,64	0,052
II	11	3,0	1,0025	1,0481	2,77	5,35	4,80	8,07	0,58	0,061
III	12	–	1,1759	1,5467	19,80	1,48	31,86	9,75	0,62	0,025
III	13	–	1,1448	1,3899	15,63	2,31	23,19	14,91	0,67	0,037
III	14	–	1,1073	1,2559	12,50	3,01	14,38	17,13	0,87	0,044
III	15	–	1,0687	1,1643	8,79	3,78	7,27	18,49	1,21	0,051
III	16	–	1,0237	1,1152	4,86	4,7	2,82	20,77	1,72	0,062
III	17	–	0,9948	1,0990	1,74	5,70	0,57	23,42	3,05	0,075
IV	18	–	1,2384	1,7601	24,85	0,58	45,40	17,12	0,55	0,015
IV	19	–	1,2149	1,5853	23,10	0,73	34,83	21,00	0,66	0,017
IV	20	–	1,1761	1,3448	19,16	1,68	20,28	26,99	0,94	0,032
IV	21	–	1,1135	1,1813	13,26	2,80	7,50	28,46	1,77	0,044
IV	22	–	1,0363	1,1163	5,95	4,53	1,1	31,6	5,41	0,067
V	23	0,5	1,1154	1,3048	13,03	2,80	3,68	54,36	3,55	0,067

Beam no.	Point no.	Ratio of phase volumes org./aq.	Density d_4^{25}, organic phase	Density d_4^{25}, aqueous phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, organic phase	Equilibrium concentration, wt. %, H_2O, organic phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, aqueous phase	Equilibrium concentration, wt. %, NH_4NO_3, aqueous phase	Distribution coefficient D, $La(NO_3)_3$	Distribution coefficient D, H_2O
V	24	0,5	1,0650	1,2705	8,35	3,92	0,54	57,51	15,46	0,093

Separate points

Beam no.	Point no.	Ratio of phase volumes org./aq.	Density d_4^{25}, organic phase	Density d_4^{25}, aqueous phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, organic phase	Equilibrium concentration, wt. %, H_2O, organic phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, aqueous phase	Equilibrium concentration, wt. %, NH_4NO_3, aqueous phase	Distribution coefficient D, $La(NO_3)_3$	Distribution coefficient D, H_2O
–	25	–	1,2354	2,2010	24,5	0,88	57,31	–	0,43	0,021
–	26	–	–	2,000	24,0	0,82	55,05	–	0,44	0,018
–	27	1,0	1,2073	1,6506	21,15	1,39	39,75	–	0,54	0,023
–	28	1,0	1,1901	1,5901	20,44	1,48	37,26	–	0,55	0,024
–	29	1,0	1,1537	1,4410	17,30	2,17	30,07	–	0,57	0,030
–	30	1,0	1,1136	1,3072	13,09	2,89	22,70	–	0,58	0,037
–	31	1,0	1,0696	1,2025	8,8	3,75	16,05	–	0,55	0,045
–	32	1,0	1,0264	1,1410	5,23	4,70	11,65	–	0,45	0,053
–	33	1,0	0,9982	1,0875	1,83	5,39	7,81	–	0,23	0,058
–	34	1,0	0,9784	1,0470	0,32	5,98	4,34	–	0,07	0,062
–	35	0,5	0,9776	1,0469	0,29	5,93	4,28	–	0,068	0,062
–	36	–	–	–	27,63	0,38	59,18	8,69	0,47	0,012
–	37	–	–	–	27,39	0,4	55,98	9,56	0,49	0,012
–	38	–	–	–	28,18	0,35	54,71	8,95	0,51	0,010
–	39	–	–	–	27,10	0,49	33,46	34,98	0,81	0,016
–	40	–	–	–	25,38	0,65	27,09	45,64	0,93	0,024
–	41	–	–	–	22,80	0,95	15,20	53,80	1,50	0,031
–	42	–	–	–	22,68	1,16	12,29	55,0	1,85	0,035

Beam no.	Point no.	Ratio of phase volumes org./aq.	Density d_4^{25}, organic phase	Density d_4^{25}, aqueous phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, organic phase	Equilibrium concentration, wt. %, H_2O, organic phase	Equilibrium concentration, wt. %, $La(NO_3)_3$, aqueous phase	Equilibrium concentration, wt. %, NH_4NO_3, aqueous phase	Distribution coefficient *D*, $La(NO_3)_3$	Distribution coefficient *D*, H_2O
–	43	–	–	–	20,92	1,30	8,00	59,86	2,62	0,040
–	44	1,0	0,9780	1,3098	0,23	5,97	–	67,96	–	0,19
–	45	1,0	1,0329	1,3082	5,03	4,76	0,16	64,30	31,44	0,13
–	46	0,5	1,0280	1,1792	5,15	4,75	0,16	38,64	4,44	0,079
–	47	1,1	0,9778	1,1804	1,08	5,73	0,078	39,88	13,85	0,095
–	48	0,6	1,1251	1,3713	14,85	2,52	19,09	39,1	0,78	0,049
–	49	–	1,1915	1,7418	20,15	1,42	40,30	12,46	0,50	0,030
–	50	–	1,1941	1,4480	20,65	1,57	33,85	13,57	0,55	0,030
–	51	–	–	–	17,86	1,90	26,07	15,68	0,68	0,033
–	52	–	–	–	16,35	2,22	20,11	17,49	0,80	0,035
–	53	–	–	–	12,21	3,07	13,20	19,6	1,02	0,046
–	54	–	–	–	11,48	3,24	9,68	20,8	1,19	0,047
–	55	–	1,0190	1,0750	6,32	2,23	3,76	22,37	1,68	0,035
–	56	–	1,2009	1,4069	21,27	1,24	32,26	8,50	0,59	0,021
–	57	–	1,1944	1,3371	19,32	1,63	30,73	8,49	0,63	0,026
–	58	–	1,0319	1,0050	5,87	4,55	9,49	8,16	0,62	0,056
–	59	–	1,0751	1,2090	8,80	3,74	14,55	2,39	0,60	0,045

Table 2

Equilibrium concentrations: La^{140}, imp/g × 100 sec (organic phase)	Equilibrium concentrations: NH_4NO_3, wt. % (aqueous phase)	Equilibrium concentrations: La^{140}, imp/g × 100 sec (aqueous phase)	$D_{La(NO_3)_3}$	Equilibrium concentrations: La^{140}, imp/g × 100 sec (organic phase)	Equilibrium concentrations: NH_4NO_3, wt. % (aqueous phase)	Equilibrium concentrations: La^{140}, imp/g × 100 sec (aqueous phase)	$D_{La(NO_3)_3}$
94	0.0	2767	0.034	3748	11.45	4279	0.876
1372	2.85	23442	0.054	4913	18.74	2314	2.13

Fig. 2. Quaternary system $La(NO_3)_3$–NH_4NO_3–H_2O–$(C_4H_9O)_3PO$ in the region of stratification

Figure 2: Fig. 2. Quaternary system $La(NO_3)_3$–NH_4NO_3–H_2O–$(C_4H_9O)_3PO$ in the region of stratification

Equilibrium concentrations: La^{140}, imp/g × 100 sec (organic phase)	Equilibrium concentrations: NH_4NO_3, wt. % (aqueous phase)	Equilibrium concentrations: La^{140}, imp/g × 100 sec (aqueous phase)	$D_{La(NO_3)_3}$	Equilibrium concentrations: La^{140}, imp/g × 100 sec (organic phase)	Equilibrium concentrations: NH_4NO_3, wt. % (aqueous phase)	Equilibrium concentrations: La^{140}, imp/g × 100 sec (aqueous phase)	$D_{La(NO_3)_3}$
637	3.91	5736	0.110	16994	29.31	2673	6.36
1241	6.73	4808	0.258	6763	45.20	94	71.95

The isolines run fanwise and converge on the ordinate axis. Near the point of 10 wt. % NH_4NO_3 they deviate in the composition field in different directions. Therefore, for the isolines of $D_{La(NO_3)_3}$ the entire diagram is, as it were, divided into two parts by the isoconcentrate at 10 wt. % NH_4NO_3. In the upper part (more than 10%) of the diagram, the extraction of lanthanum increases smoothly with increasing concentration of the salting-out agent NH_4NO_3 and with decreasing content of lanthanum nitrate. Near the NH_4NO_3 saturation region, the distribution coefficients rise sharply and reach values of 70 and higher (region of maximum extraction). The sharpest rise in $D_{La(NO_3)_3}$ is observed at microconcentrations of lanthanum (Table 2), i.e., near the ordinate axis. In the lower part of the diagram, bounded on one side by the abscissa axis and on the other by the isoconcentrate of 10 wt. % NH_4NO_3, a region of low extraction of lanthanum is located at the origin; it disappears as the contents of both lanthanum and ammonium nitrates increase. In this part of the diagram there is a maximum in the region of 30 wt. % $La(NO_3)_3$, where $D_{La(NO_3)_3} = 0.6$–0.65. With a further increase in the concentration of lanthanum, its extraction falls, and in the region of saturation with lanthanum nitrate $D_{La(NO_3)_3} = 0.43$.

Fig. 2. Quaternary system $La(NO_3)_3$–NH_4NO_3–H_2O–$(C_4H_9O)_3PO$ in the region of stratification.

The distribution coefficient of water D_{H_2O} in the system varies from 0.01 to 0.19. The isolines of D_{H_2O}, indicated in Fig. 1 by thin dashed lines, at low lanthanum concentrations run almost parallel to the ordinate axis. Their slope increases with increasing lanthanum concentration, and in the region of high concentrations they form an obtuse angle with the abscissa axis. The maximum value $D_{H_2O} = 0.07$—0.19 is located near the ordinate axis and does not depend on the concentration of NH_4NO_3, while the minimum $D_{H_2O} = 0.015$ is located in the region of the eutonic point (double salt and solid solutions). As can be seen, the distribution of water between tributyl phosphate and the aqueous solution of ammonium and lanthanum nitrates is mainly affected by lanthanum nitrate.*

The extraction rays, indicated in Fig. 1 by Roman numerals, for larg-

* It is capable of displacing water from tributyl phosphate.

···over a greater extent are rectilinear and have an extraction pole corresponding to 100% $La(NO_3)_3$, i.e., anhydrous lanthanum nitrate is extracted into the organic phase. The figurative point of the composition moves along the ray toward the ordinate axis and, at a concentration of the salting-out agent NH_4NO_3 of less than 10%, may enter the region of low extraction, where a very large number of extraction stages is required for complete extraction, since D decreases in the region of low concentrations; when the NH_4NO_3 content is more than 10 wt.%, the ray leads to a region where D increases as extraction proceeds, which ensures complete extraction. The upward curvature of the rays in the concentration region $< 5\%$ $La(NO_3)_3$ is associated with extraction of water, owing to which the concentration of the salting-out agent in the aqueous phase increases.

Extraction of lanthanum by tributyl phosphate with the salting-out agent NH_4NO_3 must be carried out with these features taken into account; for example, it must begin with a definite initial concentration of salting-out agent and lanthanum. In Fig. 2 the system $La(NO_3)_3$—NH_4NO_3—H_2O—TBP is represented in the form of a tetrahedron. In constructing the diagram, the solubility of TBP in the aqueous phase and of NH_4NO_3 in the organic phase were neglected because of their small values. Thus, the content of NH_4NO_3 in TBP at equilibrium with a saturated solution is 1% (14), and the solubility of TBP in a saturated solution of NH_4NO_3 approaches zero, as special investigations have shown.

The vertices of the tetrahedron correspond to the pure components. The plane of the base corresponds to the aqueous phases of the system, and the compositions of the organic phases in equilibrium with them are represented by the line connecting the points $(C_4H_9O)_3PO \cdot H_2O$ and $La(NO_3)_3 \cdot 3(C_4H_9O)_3PO$, which lies entirely on the edge H_2O—$(C_4H_9O)_3PO$—$La(NO_3)_3$. The thin lines (tie lines) connect the equilibrium compositions in the aqueous and organic parts of the system. The volume enclosed between the conjugate elements of the compositions of the organic phases and the surface of the compositions of the aqueous phases represents the region of stratification of two-phase liquid mixtures. A complete study of the system and the use of the tetrahedron for representation confirm the previously expressed opinion concerning the form in which the compounds exist in the organic phase. It is probable that in the organic phase there exists the compound $La(NO_3)_3 \cdot 3TBP$ (Fig. 2). It is interesting that all compositions of the organic phases are, as it were, mixtures of this compound and the compound $TBP \cdot H_2O$ (a saturated solution of water in TBP). As the concentration of lanthanum in the system increases, water is displaced to an ever greater extent from the organic phase by lanthanum and, finally, $La(NO_3)_3$ almost completely replaces it; for example, at the concentration of the components in the system corresponding to the point of the equilibrium aqueous phase where $D_{La(NO_3)_3} = 0.49$. The quantitative ratios of the compound formed, as well as of all components of the system, can be determined by the usual methods of phase diagrams.

Since each ray in the aqueous phase corresponds to a conjugate ray in the organic phase (15), it is possible to determine quantitatively the principal parameters of the process: the number of extraction stages, the minimum (relative) solvent consumption, and the compositions of the aqueous and organic phases.

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REFERENCES CITED

1. A. V. Nikolaev, A. A. Kolesnikov, *Dokl. Akad. Nauk SSSR*, **154**, 1395 (1964).
2. A. V. Nikolaev, A. A. Sorokina, *Dokl. Akad. Nauk SSSR*, **129**, 341 (1959).
3. N. E. Brezhneva, V. I. Lenindr., II Conference on the Peaceful Uses of Atomic Energy, Report 2295, Moscow, 1959.
4. *The Rare Earths*, New York–London, 1961, p. 42.
5. K. K. Kriss, Z. A. Sheka, *Zh. Neorg. Khim.*, **5**, 12, 2819 (1960).
6. A. V. Nikolaev, Proceedings of the Commission on Analytical Chemistry, **14**, 31 (1963).
7. D. F. Peppard et al., *J. Inorg. and Nucl. Chem.*, **5/6**, 326 (1957).
8. I. I. Scargö et al., *J. Inorg. and Nucl. Chem.*, **5/6**, 304 (1957).
9. E. Hesford, C. E. Jackson, H. A. C. McKay, *J. Inorg. and Nucl. Chem.*, **9**, 279 (1959).
10. D. F. Peppard et al., *J. Phys. Chem.*, **57**, 294 (1953).

11. A. V. Nikolaev, A. G. Kurnakova, *Zh. Neorg. Khim.*, **3**, 1037 (1958).

12. J. Körbe, *Chemist-Analyst*, **45**, 4, 102 (1956).

13. J. Mitchell, D. Smith, *Aquametry*, 1962, Moscow—Leningrad, p. 68.

14. I. I. Yakovlev, R. I. Opalovskaya, *Izv. SO AN SSSR*, No. 12, 62 (1962).

15. A. V. Nikolaev, I. I. Yakovlev, *Dokl. Akad. Nauk SSSR*, **145**, No. 5, 1064 (1962).

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