# Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, A. A. KOLESNIKOV

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## Abstract

## Full Text

Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, A. A. KOLESNIKOV

# THE EXTRACTION SYSTEM $La(NO_3)_3 - HNO_3 - H_2O - (C_4H_9O)_3PO$ AT 25°

The separation of rare-earth elements by extraction can be carried out in the system: rare-earth nitrates—nitric acid—tributyl phosphate (TBP) ($^{1-6}$). Studies of separation conditions are usually carried out with microconcentrations of metals and diluted TBP. Meanwhile, it is precisely the study of the distribution of rare-earth elements over all concentration regions of the extraction system, with determination of the distribution coefficients ($D$) of all components of the aqueous phase, that makes it possible to reveal more fully the regularities governing extraction processes.

A study of this type was carried out for the extraction system $La(NO_3)_3 - HNO_3 - H_2O - (C_4H_9O)_3PO$.

The experiments were conducted under isothermal conditions at $25 \pm 0.1°$. Lanthanum was determined complexometrically ($^7$), the water content in the organic phase by the Fischer method ($^8$), and nitric acid by titration with alkali using methyl red as indicator. The distribution coefficient of a component of the system was determined as the ratio of its analytical concentrations, in weight percent, in the organic phase to that in the aqueous phase.

Table 1 presents data from the study of the extraction system $La(NO_3)_3 - HNO_3 - H_2O - (C_4H_9O)_3PO$, and in Fig. 1 this system is depicted by the method described by us earlier ($^9$).

The basis of the extraction diagram (Fig. 1) is the solubility isotherm of the system $La(NO_3)_3 - HNO_3 - H_2O$.*

The extraction rays, denoted in the figure by Roman numerals ($I$-$X$), have no point of intersection; consequently, both lanthanum and nitric acid are extracted, and their ratio in the organic phase depends on the composition of the aqueous phase. The course of the rays is determined by the distribution coefficients of the components and by their mutual influence in both the aqueous and the organic phases. The extraction of nitric acid is several times greater than that of lanthanum nitrate; therefore, over a large portion of the diagram the rays run with a small inclination to the abscissa axis, changing it in the concentration region of 15 wt.% $> HNO_3 > 65 \div 70$ wt.%, i.e., when the extraction of lanthanum increases.

The course of the isolines of the distribution coefficients of the system $La(NO_3)_3$

$-HNO_3-H_2O-(C_4H_9O)_3PO$ (Fig. 1) has a definite pattern and reflects the extraction mechanism of each of its components. Common to each series of isolines is the presence of minima.

For the isolines $D_{La(NO_3)_3}$ and $D_{H_2O}$, the character of the arrangement of the minima is practically identical, with a slight shift ($5 \div 10$ wt.%) in $HNO_3$. A slight minimum is observed for the isolines $D_{HNO_3}$, since in this region the extraction of $HNO_3$ does not exert a large influence on the content of lanthanum nitrate in the aqueous phase.

The distribution coefficient of lanthanum, depending on the ratio of components in the equilibrium aqueous phases, varies from 0.01 to 1.0 and higher. The region of low extraction is located at the origin of the coordinates (Fig. 1), i.e., it is the region where a large number of extraction stages is required for complete extraction of lanthanum. One can enter the region of low extraction if sequential extraction is carried out from any point

* According to data of L. A. Khripin.

**Table 1**

| Ray No. | Ratio of volumes of initial phases, $V_{org}/V_{aq}$ | $d_4^{25}$, organic phase | $d_4^{25}$, aqueous phase | Organic phase: $La(NO_3)_3$ | Organic phase: $HNO_3$ | Organic phase: $H_2O$ | Aqueous phase: $La(NO_3)_3$ | Aqueous phase: $HNO_3$ | $D_{La(NO_3)_3}$ | $D_{HNO_3}$ | $D_{H_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | – | 1,2532 | 1,4887 | 4,12 | 51,74 | 5,48 | 3,58 | 78,99 | 1,510 | 0,655 | 0,306 |
| I | 0,5 | 1,1878 | 1,4726 | 2,46 | 44,24 | 3,93 | 2,74 | 74,95 | 0,898 | 0,590 | 0,176 |
| I | 1,0 | 1,1290 | 1,4412 | 0,98 | 35,11 | 3,25 | 2,76 | 67,42 | 0,356 | 0,521 | 0,109 |
| I | 1,0 | 1,0934 | 1,4040 | 0,48 | 28,35 | 2,81 | 3,38 | 57,71 | 0,142 | 0,491 | 0,072 |
| I | 2,0 | 1,0569 | 1,2893 | 0,37 | 20,01 | 1,88 | 4,71 | 37,58 | 0,079 | 0,532 | 0,033 |
| II | 0,2 | 1,0701 | 1,3812 | 0,56 | 24,42 | 2,45 | 5,97 | 49,21 | 0,094 | 0,496 | 0,055 |
| II | 1,0 | 1,0532 | 1,3248 | 0,54 | 20,37 | 1,92 | 6,56 | 38,18 | 0,082 | 0,533 | 0,035 |
| II | 1,0 | 1,0500 | 1,2623 | 0,73 | 17,54 | 1,75 | 7,56 | 28,39 | 0,097 | 0,618 | 0,027 |
| II | 1,0 | 1,0383 | 1,1998 | 1,07 | 14,01 | 3,27 | 7,90 | 19,55 | 0,135 | 0,717 | 0,045 |
| II | 2,0 | 1,0224 | 1,1125 | 1,38 | 7,34 | 5,1 | 6,88 | 7,36 | 0,201 | 0,997 | 0,059 |
| II | – | 0,9991 | 1,0735 | 1,07 | 2,63 | 5,90 | 5,13 | 2,39 | 0,209 | 1,100 | 0,064 |
| III | – | 1,2718 | 1,5392 | 6,69 | 50,68 | 5,66 | 10,31 | 72,46 | 0,649 | 0,699 | 0,328 |
| III | 0,5 | 1,2106 | 1,5292 | 6,66 | 42,30 | 3,92 | 8,62 | 70,78 | 0,773 | 0,598 | 0,190 |
| IV | 0,2 | 1,0771 | 1,4467 | 1,72 | 23,92 | 2,40 | 14,21 | 43,22 | 0,121 | 0,553 | 0,056 |
| IV | 1,0 | 1,0594 | 1,3988 | 1,56 | 20,04 | 1,93 | 16,71 | 32,17 | 0,093 | 0,623 | 0,038 |
| IV | 1,0 | 1,0527 | 1,3392 | 2,03 | 16,60 | 2,23 | 18,10 | 21,82 | 0,112 | 0,761 | 0,037 |
| IV | 2,0 | 1,0419 | 1,2199 | 3,66 | 9,55 | 3,93 | 16,72 | 8,21 | 0,219 | 1,163 | 0,052 |

| Ray No. | Ratio of volumes of initial phases, $V_{org}/V_{aq}$ | $d_4^{25}$, organic phase | $d_4^{25}$, aqueous phase | Organic phase: $La(NO_3)_3$ | Organic phase: $HNO_3$ | Organic phase: $H_2O$ | Aqueous phase: $La(NO_3)_3$ | Aqueous phase: $HNO_3$ | $D_{La(NO_3)_3}$ | $D_{HNO_3}$ | $D_{H_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IV | 3,0 | 1,0146 | 1,1530 | 3,20 | 2,84 | 5,31 | 11,72 | 0,8 | 0,273 | 3,55 | 0,061 |
| V | 0,17 | 1,2095 | 1,5424 | 7,11 | 39,49 | 3,56 | 11,64 | 67,7 | 0,611 | 0,589 | 0,172 |
| V | 1,0 | 1,1435 | 1,5146 | 3,91 | 32,58 | 3,02 | 12,62 | 58,20 | 0,310 | 0,560 | 0,103 |
| V | 1,0 | 1,1029 | 1,4816 | 2,39 | 25,90 | 2,57 | 14,86 | 48,62 | 0,161 | 0,533 | 0,070 |
| V | 1,0 | 1,0753 | 1,4420 | 1,61 | 21,58 | 2,26 | 17,08 | 37,20 | 0,094 | 0,580 | 0,049 |
| V | 0,5 | 1,1708 | 1,5776 | 7,42 | 32,88 | 2,94 | 17,89 | 54,95 | 0,415 | 0,598 | 0,108 |
| V | – | 1,1446 | 1,5609 | 5,70 | 29,47 | 2,71 | 18,59 | 51,57 | 0,302 | 0,571 | 0,091 |
| VI | 0,5 | 1,1708 | 1,5776 | 7,42 | 32,88 | 2,94 | 17,89 | 54,95 | 0,415 | 0,598 | 0,108 |
| VI | – | 1,1446 | 1,5609 | 5,70 | 29,47 | 2,71 | 18,59 | 51,57 | 0,302 | 0,571 | 0,091 |
| VII | 0,17 | 1,0925 | 1,5100 | 2,37 | 23,62 | – | 19,55 | 40,24 | 0,121 | 0,590 | – |
| VII | 0,46 | 1,0752 | 1,4859 | 2,42 | 21,12 | 2,01 | 20,43 | 35,71 | 0,118 | 0,591 | 0,046 |
| VII | 1,0 | 1,0605 | 1,4358 | 2,39 | 17,21 | 1,93 | 23,68 | 25,22 | 0,101 | 0,682 | 0,038 |
| VII | – | 1,0791 | 1,3762 | 4,12 | 14,26 | 2,56 | 24,97 | 15,05 | 0,165 | 0,947 | 0,043 |
| VII | 0,33 | 1,0701 | 1,3812 | 4,51 | 4,67 | 4,89 | 21,33 | 2,92 | 0,211 | 1,599 | 0,064 |
| VIII | – | 1,0926 | 1,5819 | 4,39 | 23,47 | 2,18 | 29,08 | 33,08 | 0,151 | 0,706 | 0,058 |
| VIII | 1,0 | 1,0738 | 1,5456 | 4,40 | 19,36 | 1,84 | 32,89 | 22,89 | 0,134 | 0,858 | 0,042 |
| VIII | 2,0 | 1,0330 | 1,4700 | 7,47 | 10,41 | 2,65 | 31,50 | 8,02 | 0,237 | 1,298 | 0,044 |
| IX | – | 1,1385 | 1,6432 | 6,15 | 15,68 | 1,84 | 41,93 | 12,99 | 0,147 | 1,207 | 0,041 |
| IX | 0,5 | 1,1320 | 1,6301 | 7,01 | 13,69 | 1,83 | 43,72 | 9,65 | 0,160 | 1,419 | 0,039 |
| IX | 1,0 | 1,1184 | 1,5522 | 12,24 | 8,09 | 2,07 | 42,87 | 4,18 | 0,285 | 1,935 | 0,039 |
| X | 0,5 | 1,1962 | 1,6867 | 9,16 | 13,76 | 1,50 | 48,64 | 8,24 | 0,188 | 1,670 | 0,035 |
| X | 1,0 | 1,1600 | 1,6469 | 10,34 | 5,66 | 4,04 | 47,35 | 5,29 | 0,218 | 1,070 | 0,085 |

**Separate points**

Fig. 1. Extraction system $La(NO_3)_3$—$HNO_3$—$H_2O$—$(C_4H_9O)_3PO$

Figure 1: Fig. 1. Extraction system $La(NO_3)_3$—$HNO_3$—$H_2O$—$(C_4H_9O)_3PO$

| Ray No. | Ratio of volumes of initial phases, $V_{org}/V_{aq}$ | $d_4^{25}$, organic phase | $d_4^{25}$, aqueous phase | Organic phase: $La(NO_3)_3$ | Organic phase: $HNO_3$ | Organic phase: $H_2O$ | Aqueous phase: $La(NO_3)_3$ | Aqueous phase: $HNO_3$ | $D_{La(NO_3)_3}$ | $D_{HNO_3}$ | $D_{H_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| – | – | 1,1215 | 1,4832 | 2,86 | 29,98 | 2,79 | 11,40 | 55,51 | 0,251 | 0,540 | 0,084 |
| – | 2,0 | 1,1043 | 1,2957 | 13,73 | 2,03 | 3,14 | 27,12 | 0,85 | 0,506 | 2,388 | 0,044 |
| – | 2,0 | 1,1033 | 1,4699 | 9,31 | 7,33 | 3,04 | 39,80 | 10,30 | 0,234 | 0,712 | 0,061 |
| – | 0,5 | 1,0926 | 1,6377 | 6,20 | 14,28 | 1,85 | 43,38 | 9,36 | 0,143 | 1,526 | 0,039 |
| – | – | 1,0913 | 1,6322 | 5,75 | 16,92 | 1,62 | 41,53 | 16,45 | 0,138 | 1,018 | 0,038 |
| – | – | 1,1314 | 1,608 | 6,19 | 26,93 | 2,70 | 26,35 | 45,48 | 0,235 | 0,634 | 0,087 |
| – | – | 1,0251 | 1,1251 | 1,81 | 6,38 | 4,68 | 9,74 | 5,56 | 0,186 | 1,149 | 0,055 |
| – | – | 1,0327 | 1,1728 | 1,73 | 10,74 | 4,29 | 10,42 | 11,69 | 0,166 | 0,919 | 0,055 |
| – | – | 1,0425 | 1,2174 | 1,18 | 14,13 | 3,31 | 9,97 | 18,41 | 0,118 | 0,767 | 0,046 |
| – | – | 1,0470 | 1,2818 | 0,70 | 17,42 | 2,16 | 10,55 | 26,50 | 0,066 | 0,657 | 0,034 |
| – | – | 1,0827 | 1,4240 | 0,95 | 26,12 | 2,45 | 9,85 | 49,20 | 0,096 | 0,531 | 0,060 |
| – | – | 1,1164 | 1,4836 | 2,44 | 29,71 | 2,74 | 10,23 | 56,20 | 0,240 | 0,530 | 0,082 |
| – | – | 1,1327 | 1,4991 | 3,39 | 32,60 | 3,08 | 10,42 | 59,25 | 0,325 | 0,550 | 0,101 |
| – | – | 1,1721 | 1,5123 | 5,23 | 37,14 | 3,35 | 10,0 | 66,53 | 0,523 | 0,558 | 0,143 |
| – | – | 1,1924 | 1,5260 | 6,37 | 41,65 | 3,37 | 9,65 | 70,30 | 0,660 | 0,592 | 0,168 |

diagrams with a content of $La(NO_3)_3 \leqslant 8$ wt.%, as is evident from the course of the extraction rays and the isolines of $D_{La(NO_3)_3}$ (Fig. 1). The maximum value of $D_{La(NO_3)_3}$ in the system is observed in the region of high concentrations of $HNO_3$ (1-1.5) and $La(NO_3)_3$ (0.5-0.6).

The distribution coefficients $D_{HNO_3}$ vary from 0.45 to 3 and higher. The high coefficients are due to the salting-out action of lanthanum nitrate.

The values of $D_{H_2O}$ in the system vary from 0.025 to 0.15 and higher. The region of low extraction is located in the upper left corner of the diagram, and that of maximum extraction in the lower right corner. In the organic phase, the water content varies depending on the concentration of $HNO_3$ in it. A minimum is observed at 20 wt.% $HNO_3$, and with a further increase in the acid concentration the water content increases.

Fig. 1. Extraction system $La(NO_3)_3$—$HNO_3$—$H_2O$—$(C_4H_9O)_3PO$: *a*—extrac-

tion rays, *b*—isolines of the distribution coefficients of $La(NO_3)_3$, *v*—the same for $HNO_3$, *g*—the same for $H_2O$.

Thus, study of the extraction system $La(NO_3)_3$—$HNO_3$—$H_2O$—$(C_4H_9O)_3PO$ made it possible to determine the distribution coefficients of the three components $La(NO_3)_3$, $HNO_3$, and $H_2O$ in all concentration regions.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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*Note: Figure translations are in progress. See original paper for figures.*