

SOME REGULARITIES OF EXTRACTION OF RARE EARTH ELEMENTS
BY ORGANOPHOSPHORIC ACIDS

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At present organophosphoric acids (OPA) are widely used for separation of rare earth elements (REE). The main industrial representative of OPA is D2EHP. In saturated hydrocarbonates D2EHP is dimerized and when extracting REE it forms compositions of a chelate type which are characterized by the highest selectivity. At the same time high dimerization constants of D2EHP under certain conditions lead to formation of undesired polymeric sediments. Less selective solvatic mechanism of extraction does not practically manifest itself in chloride media in contrast to nitrate and perchlorate media (Fig. 1). This is the reason why the greatest attention was paid to chloride media, as the most selective though less technological.

This paper presents the results of investigation of extraction of the REE macroquantity out of nitrate solutions by the OPA examples synthesized on the basis of the ramificated alcohol 2- isopropyl 5-methylhexanol D-2 isopropyl 5 methylhexylphosphoric acid (D2iP5MHPA) and 2 isopropyl 5 methylhexylphosphonic acid (2iP5MHMPA). The dimerization constants of these acids are significantly lower than D2 EHP and show less tendency to form sediments [1]. D2iP5MHPA has 10-12 times less extraction capability and thus re-extraction of heavy REE is of no difficulty (Fig. 2).

As it is known the extraction of REE by organophosphoric acids is defined by the following four processes: extraction accordingly to cation-exchange mechanism, extraction by neutral solvates, extraction by acid solvates, concurrence extraction of a mineral acid. The three latter processes are most characteristic for neutral organophosphoric compounds (NPC) and define the form the dependence curves between distribution coefficient value and the composition of the aqueous phase. For OPA all the four processes must operate but the first process will be a defining one since the REE extraction accordingly the solvating mechanism is less distinct at OPA than at NPC. At the extraction of HNO_3 by 1 M solution of D2EHP and T1OP (Fig. 3) the isotherms for the neutral extractant are typical and their form is defined by the formation of two solvates, i.e. 1:1 and 1:2. In case of D2EHP a noticeable the extraction of HNO_3 is observed only at HNO_3 concentration of 3-4 M. It is defined by the fact that the extracted solvate is formed by a dimerized molecule of OPA, moreover the extractant remains in the

dimerization form up to the concentration of HNO_3 equaled to 10-12M. At Sm extraction by D2EHP and TiOP in dodecane the solvating mechanism for D2EHP starts to manifest itself only when the concentration of samarium nitrate is more than 1 M or NO_3^- 4M (it is correlated with the extraction of HNO_3). It is indirectly confirmed by the fact that the extraction isotherms of individual REE are described rather exactly by a simple equation within the limits of 0.1-1.0 M concentration. This equation corresponds to the ionexchange mechanism of the formation of the extracted compounds with the help of the concentration constants:
$$Y = \frac{k \cdot x [\text{H}_2\text{R}_2]^p}{[\text{H}^+]^2} \quad (\text{Fig. 5}).$$

The form of the curves of dependences of the change between the distribution coefficients of REE and HNO_3 concentra-

$[\text{HNO}_3]$	K
0.43	14.02±0.25
0.63	9.26±0.34
0.86	6.93±0.69

tion at their extraction by the 1M solutions of D2EHP and TiOP, as well as the location and the width of the minimum change with the increase of the atomic number of the lanthanide; moreover the range of HNO_3 concentration in aqueous phase, where the suppression of the cation-exchange mechanism occurs, is shifted towards the larger side and it becomes narrower with the growth of the atomic number of the lanthanide. It is quite natural since the growth of the number of the lanthanide causes the increase of the value of the extraction constant accordingly the cation-exchange mechanism (Fig. 6). At the same time the sensitivity for the concurrent extraction of HNO_3 itself becomes lower. The region of HNO_3 concentration where the change of the extraction mechanism for NPC and OPA takes place is the same and is situated within the range of formation of acid solvates (Fig. 7). The depth of the minimum in the curves of NPC grows with the decrease of the atomic number and the concentration of the extractant. D_{Ln} becomes lower to the third power and D_{HNO_3} - to the first power (Fig. 8).

When investigating the selectivity of REE extraction in nitrate media the following system was adopted as the basic one: the extractant is 1M solution of D2EHP in dodecane (the limited loading accordingly 1:6 stoichiometry is 0.15 M REE or 20-30 g/l; the aqueous phase is REE nitrates - HNO_3 . REE concentration does not exceed 0.5-0.6M or 100 g/l by the oxides of REE, i.e. the condition when the solvating mechanism of extraction does not manifest itself. The lower concentration of HNO_3 is defined by the absence of polymeric sediments in the chosen system (Nd-0.3 M, Sm-0.4 M, Eu-0.5 M, Gd-0.6, Tb-1.2 M, Dy -1.5M $t=20^\circ\text{C}$). The growth of the acidity of aqueous phase decreases the selectivity and loading of OPA (Fig. 9). The selectivity is usually higher at the background of macroquantity of a poorly

extracted component (Fig. 10) but sometimes a reverse case happens. This phenomenon can be caused by the changes of the value of the activity coefficients of cations on the system, by the fall of the coordination number with the growth of Z, by structural changes of extracted forms (it is often observed at the edges of Sm-Nd and Gd-Tb tetrads), by decrease of hydration degree by deformation of the crystalline structure of REE nitrates etc. The substitution of the diluent for a more polar one which monomerizes OPA (the worst case is when the diluent itself extracts REE after the solvating mechanism under reverse procedure of the change of D_{Ln} from Z respective to OPA) leads to the loss of selectivity (Fig. 11, 12 and Table 1). But in small quantities (0.2-0.5 M) polar diluents (modifiers) ensures stability of the system for formation of sediments. A number of modifiers (ethers, ketones, alcohols, carboxylic acids) changes the selectivity within the accepted limits. Such modifiers monomerize OPA but do not extract REE themselves.

Table 1. Effects of the modifiers on loading and separation coefficients

Modifier 0.5M	[Eu] g/l	[Gd] g/l	β Gd - Eu
Dodecane	20.0	20.0	1.8-1.7
MiBK	19.0	21.0	1.5-1.6
Naphthenic acid	17.0	18.0	1.5-1.6
isodecanol	13.5	14.5	1.5-1.4
alkylphenol	11.5	12.5	1.6-1.5
TBP	30.0	36.0	1.3-1.25
TAA	24.0	27.0	1.2-1.1

The application of TBP is an exception. The decrease of selectivity for a number of REE (Sm-Nd, Tb-Gd) is compensated by the increase of loading and, respectively, the growth of productivity. The optimal sphere of D2EHP application is separation of the group of the middle lanthanides from Nd to Y.

The analogues of D2EHP on the basis of ramificated alcohol C_{10} , with selectivity comparable with D2EHP, has certain advantages. Both samples of OPA provide extraction process under lower concentration of HNO_3 without risk of sediments formation of extracted compounds in the organic phase.

Table 2. Separation coefficients of REE of the middle group and D2EHP loading (g/l)

Ln	[HNO ₃] M	Modifier 0.33 M							
		Dodecane		Isodecanol		TBP		Versatic	
		β	[Ln] _o	β	[Ln] _o	β	[Ln] _o	β	[Ln] _o
Nd	0.4	-	20.0	3	15	-	27	-	-
Sm	0.4	5.2-5.0	22	3.0-3.5	16	2.7-2.3	35	-	-
Eu	0.6	2.0-2.2	24	1.8-1.6	18	1.3-1.2	35	1.6-1.7	20
Gd	0.8	1.8-1.7	20.5	1.5-1.4	17	1.4-1.3	35	1.6-1.7	19
Tb	1.2	4.6-4.1	25	3.9-3.5	20	3.1-2.4	38	-	-
Dy	1.5	2.8-2.6	30	2.6-2.3	25	2.3-1.8	40	-	-

The phosphone acid in dodecane is less selective but may be successfully used for separation of a number of lanthanide pairs (Fig.13, Table 3). The analogue of D2EHP has considerable advantage at separation of yttrium REE. The selectivity is rather high at 0.8M, sediments of extracted compounds are absent and loading is two times higher than for D2EHP (Fig.15, Table 4).

Table 3. Separation coefficients and 1M 2iP5MHPA loading in dodecane, g/l

$\text{Ln}_I\text{-Ln}_{II}$	$[\text{HNO}_3], \text{M}$	β	$[\text{Ln}_I]_0$	$[\text{Ln}_{II}]_0$
Ce-La	0.2	3.0-2.4	30.0	24.0
Sm-Nd	0.2	3.3-2.5	50.0	30.0
Tb-Gd	0.8	4.5-2.1	55.0	30.0

Table 4

Separation coefficients and 1M 2iP5MHPA loading in dodecane, g/l

Ln	$[\text{HNO}_3], \text{M}$	$\beta_{\text{LnII/LnI}}$	$[\text{Ln}]_0$	Ln	$[\text{HNO}_3], \text{M}$	$\beta_{\text{LnII/LnI}}$	$[\text{Ln}]_0$
La	0.2	1.0	8.5	Gd	0.8	1.0	11.0
Ce	-	3.3-3.1	13.8	Tb	-	4.3-4.7	21.6
Pr	-	1.6-1.4	15.5	Dy	-	2.7-2.65	27.0
Nd	-	1.5-1.4	28.5	Ho	-	1.9-1.5	29.0
Sm	-	4.0-4.7	28.5	Er	-	2.8-3.45	33.0
Sm	0.4	1.0	17.0	Tm	-	2.6-1.8	43.0
Eu	-	1.7-1.5	21.0	Yb	-	2.3-2.0	46.0
Gd	-	1.5-1.6	21.5	Lu	0.8	1.4-1.35	47.0

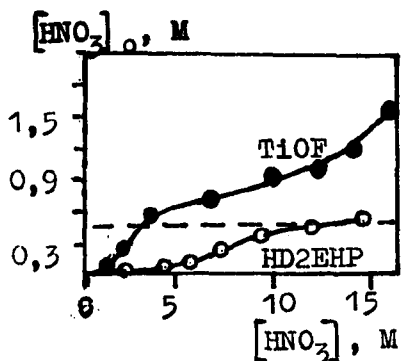


Fig. 1. 0.5 M HD2EHP

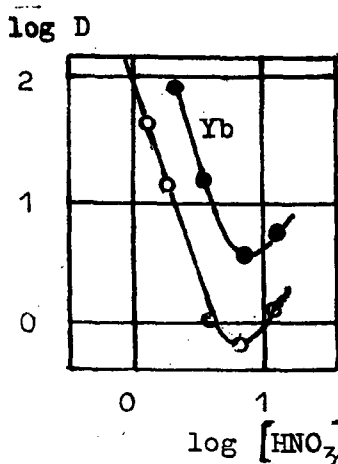


Fig. 2. 1 - 1 M HD2EHP
2 - 1 M HD2iP5MHMP

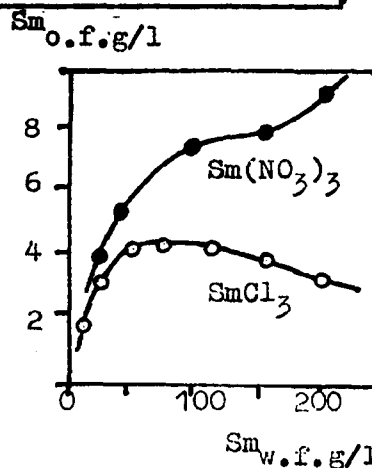


Fig. 3. 1 M in dodecane

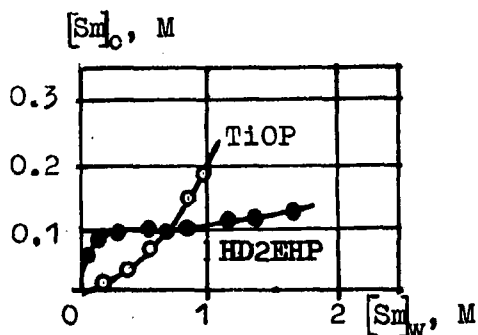


Fig. 4. 1M in dodecane

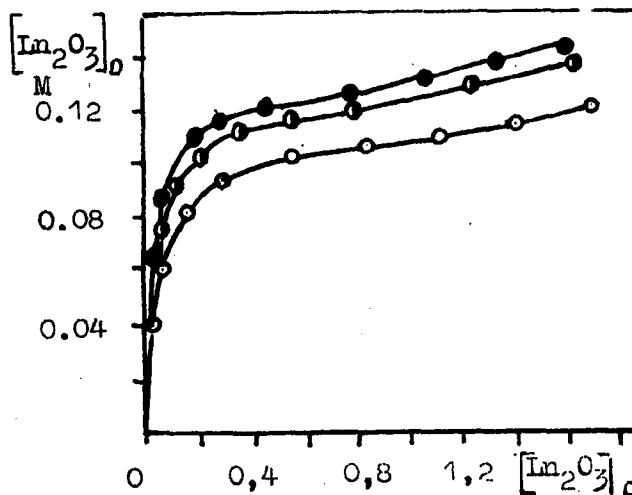


Fig. 5. 1M HD2EHP in dodecane

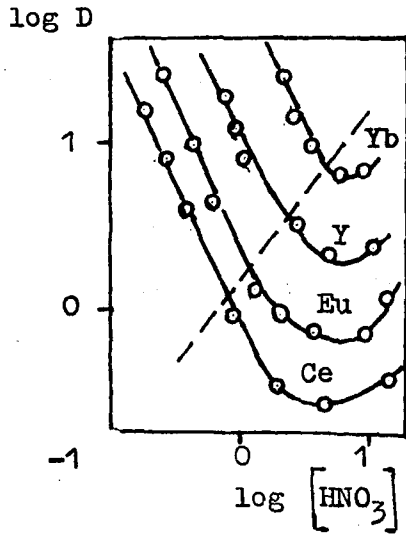


Fig. 6. 1M HD2IP5MHMP

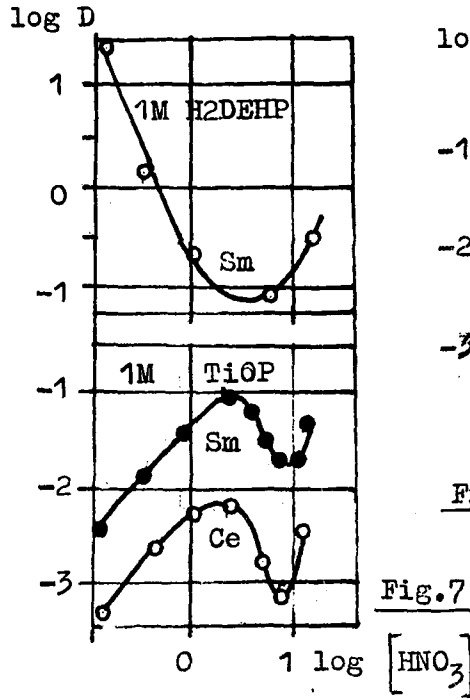


Fig. 7

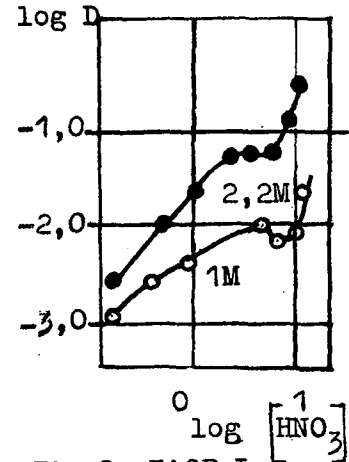


Fig. 8. TiOP-Lu

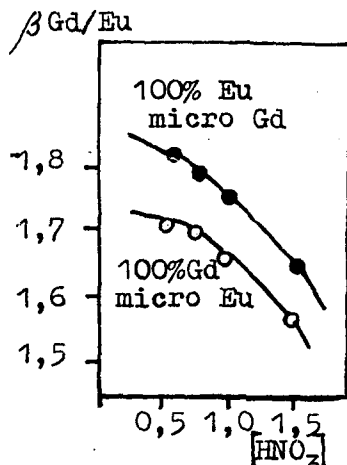


Fig. 9. 1M HD2EHP

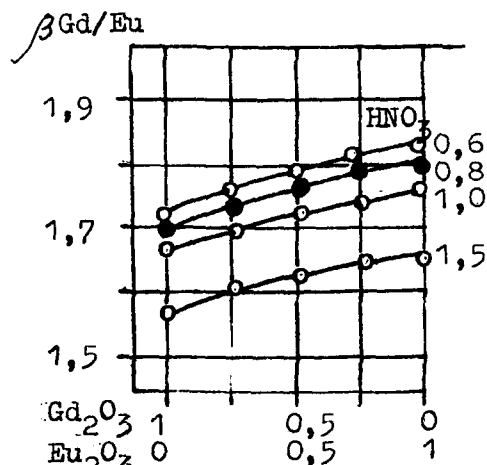


Fig. 10. 1M HD2EHP

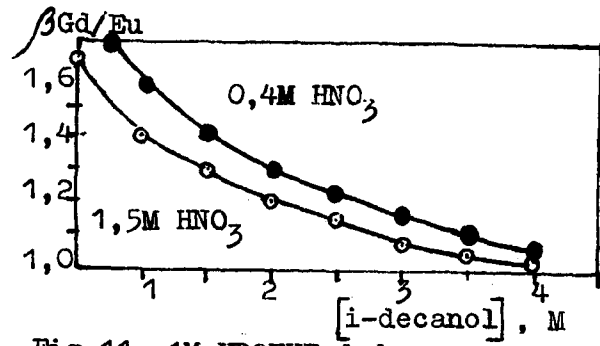


Fig. 11. 1M HD2EHP+dodecane+
+ i-decanol

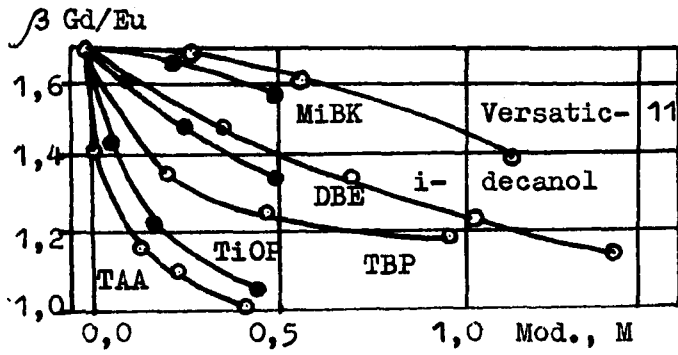


Fig. 12. 0,8M HNO₃ - 1M HD2iP5MHP

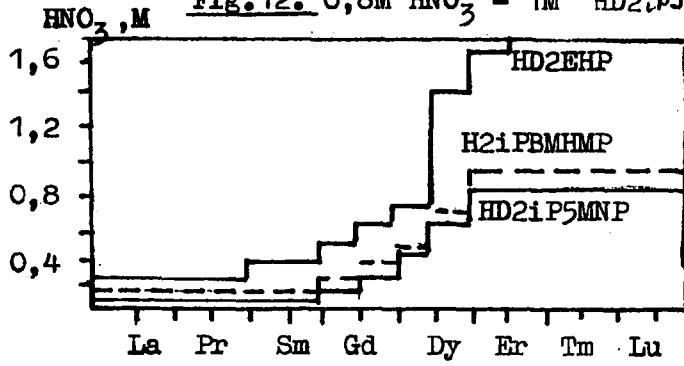


Fig. 13. 1M Phosphororg.acids in dodec

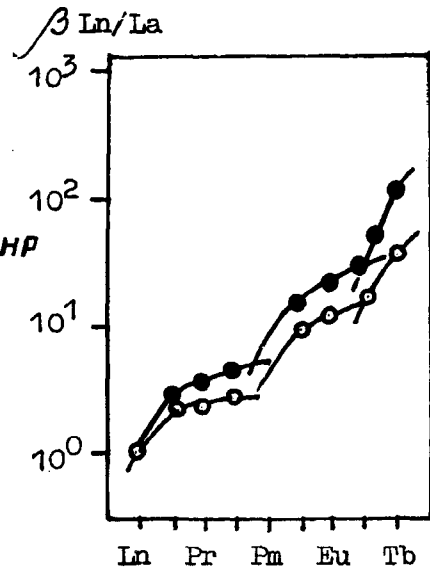


Fig. 14. 1M H2iP5MHMP

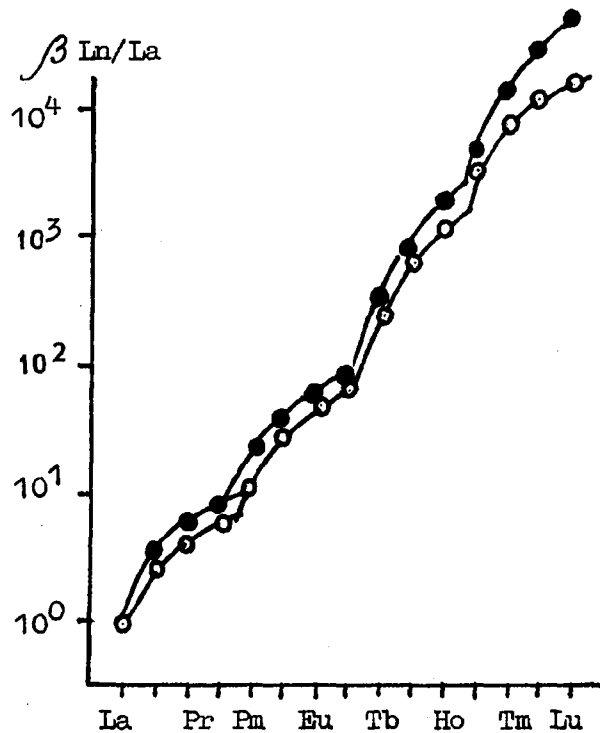


Fig. 15. 1 M HD2iP5MHP

Fig.1-15. Main regularities of REE extraction by organophosphorus acids

Reference.

1. Djumamuradov B.D., Korpusev G.V., Danilov N.A.//Zhurn.fiz. khimii. 1984. V.58, N 12.