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Extraction of Mineral Acids and Lanthanum Salts  
with Binary Extractants

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**Abstract**—Extraction of mineral acids with methyltrioctylammonium dialkylphosphinate was studied, and the extraction ability of acids was shown to decrease in the series  $\text{HNO}_3 \gg \text{HBr} > \text{HCl}$ , which corresponds to anion-exchange series for the initial salts of quaternary ammonium bases (QAB). Extraction of lanthanum bromide with methyltrioctylammonium dialkylphosphinate was studied, the composition of extracted compounds was established, and extraction constants were calculated. The extraction ability of dinonylnaphthalenesulfonate was found to be considerably lower than that of QAB dialkylphosphinate because of a larger value of acid dissociation constant for dinonylnaphthalenesulfonic acid. It was shown that lanthanum in systems with binary extractants can be back extracted from organic phase with dilute solutions of mineral acids.

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The features of substance extraction with binary extractants (the salts of organic bases with organic acids) are fundamentally different from the features of extraction with cation-exchange, anion-exchange, and neutral extractants [1–6]. Binary extraction is characterized by exchange chemical reaction: both products are distributed into organic phase, cations and anions transfer between phases in stoichiometric ratio.

Interfacial distribution of  $m$ -basic acid  $\text{H}_m\text{B}$  in the systems with binary extractants, salts of quaternary ammonium bases (QAB) with organic anions, is described by the equation [6]:



where  $\text{A}^-$  is organic acid anion, indices (a) and (o) designate aqueous and organic phase, respectively.

Extraction constant has the following view:

$$K_{\text{H}_m\text{B}} = \frac{C_{(\text{R}_4\text{N})_m\text{B}_{(o)}} C_{\text{HA}_{(o)}}^m \gamma_{(\text{R}_4\text{N})_m\text{B}_{(o)}} \gamma_{\text{HA}_{(o)}}^m}{C_{\text{H}_{(a)}^+}^m C_{\text{B}_{(a)}^{m-}} C_{\text{R}_4\text{NA}_{(o)}}^m \gamma_{\text{H}_{(a)}^+}^m \gamma_{\text{B}_{(a)}^{m-}} \gamma_{\text{R}_4\text{NA}_{(o)}}^m}. \quad (2)$$

Under stoichiometry conditions for protons and anions of mineral acid in aqueous and organic phases (the lack of salting-out agents) at constant activity coefficients for the components in organic phase, the isotherm of acid distribution according to equation 2 is described by the equation [6]:

$$C_{\text{H}_m\text{B}_{(o)}} = \bar{K}_{\text{H}_m\text{B}}^{1/(m+1)} C_{\text{R}_4\text{NA}_{(o)}}^{m/(m+1)} C_{\text{H}_m\text{B}_{(a)}} \gamma^{\pm}, \quad (3)$$

where concentration-based constant

$$\bar{K}_{\text{H}_m\text{B}} = K_{\text{H}_m\text{B}} \frac{\gamma_{\text{R}_4\text{NA}_{(o)}}^m}{\gamma_{\text{R}_4\text{NA}_{(o)}} \gamma_{\text{HA}_{(o)}}^m}. \quad (4)$$

It follows from equation (3) that isotherm of binary extraction of mineral acids at constant equilibrium concentration of binary extractant has a straight shape irrespective of the basicity of extracted acids, distribution ratio  $D_{\text{H}_m\text{B}}$  of acid is independent of  $\text{H}_m\text{B}$  concentration in aqueous phase in contrast to extraction with neutral extractants.

The constant of binary extraction of acid is associated with the constants of simpler processes by equation [1, 6]:

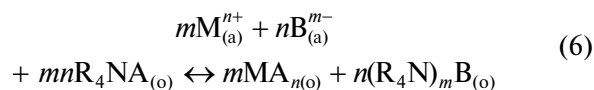
$$K_{\text{H}_m\text{B}} = \frac{K_{\text{HA}}^m K_{\text{B-OH}}}{K_{\alpha}^m K_{\text{A-OH}}}, \quad (5)$$

where  $K_{\text{HA}}$  and  $K_{\alpha}$  are the distribution and dissociation constants of organic acid, respectively,  $K_{\text{B-OH}}$  and  $K_{\text{A-OH}}$  are the constants of anion exchange with hydroxide ion for mineral and organic acids in the systems with QAB salts.

The analysis of equation (5) shows that extraction constant  $K_{\text{H}_m\text{B}}$  on extraction of mineral acids  $\text{H}_m\text{B}$  with the same binary extractant is determined by the magnitude of  $K_{\text{B-OH}}$ , i.e., the order of acid extractability should correspond qualitatively to anion-exchange series for initial systems with QAB salts. For example, on the extraction of mineral acids with QAB dinonylnaphthalenesulfonate, the extractability of acids decreases in the series of hydrohalic acids  $\text{HI} > \text{HBr} >$

HCl > HF, which corresponds to the anion-exchange series of initial QAB salts [7].

The processes of binary extraction of  $M_mB_n$  salts are described by equation [5]:



with isotherm of binary extraction for salts under conditions of stoichiometric ratio of cations and anions concentration in aqueous and organic phases [5]:

$$C_{M_mB_n(o)} = \bar{K}_{M_mB_n}^{1/n+m} C_{R_4NA(o)}^{nm/n+m} C_{M_mB_n(a)} \gamma_{\pm}^{\pm}, \quad (7)$$

where  $K_{M_mB_n}$  is binary extraction constant for salt.

It follows from equation (7) that binary extraction isotherm for salts have linear character irrespective of cation and anion charges. The obtained relationships indicate the efficiency of binary extraction of salts in the regions of their low concentrations where distribution ratios for neutral extractants considerably decrease.

Binary extraction constant for salt is expressed through the constants of simpler processes by equations [1, 5]:

$$K_{M_mB_n} = \frac{K_{HA}^{mn} K_{M-H}^m K_{B-OH}^n}{K_a^{mn} K_{A-OH}^{mn}}. \quad (8)$$

It should be noted that the quantitative description of component interactions in organic phase in complex systems with binary extractants is very difficult. Activity coefficients for extracted compounds  $\gamma_{(R_4N)_mB(o)}$ ,  $\gamma_{HA(o)}$ , and for extractant  $\gamma_{R_4NA(o)}$  can be considered to be constant at their low concentrations, which we took into account to calculate extraction constants for acids and lanthanum salts. Activity coefficients for acids and metal salts in aqueous solutions vary considerably with their concentrations. The values of mean ionic activity coefficients  $\gamma_{\pm}$  obtained by different authors are given in reference books.

Previously, we studied the extraction of lanthanides from chloride and nitrate solutions with binary extractants based on QAB and dialkylphosphinic acid derivatives [8–11]. We revealed the relationships of salt distribution and compositions of extracted compounds and showed that complexes of composition  $LnA_3$  form in organic phase upon extraction of lanthanide chlorides with QAB dialkylphosphinates, while more complex compounds are extracted from nitrate solutions. Extraction of lanthanide bromides was not examined previously, therefore we studied lanthanum bromide extraction in comparison with extraction of  $LaCl_3$ . We also obtained new data on the relationships of interfacial distribution of mineral acids HCl, HBr, and  $HNO_3$  in a system with methyltrioctylammonium bis(2,4,4-trimethylpentyl)phosphinate.

## EXPERIMENTAL

Solutions of hydrochloric, hydrobromic, and nitric acids used in the work were prepared by the dissolution of concentrated HCl and HBr acids of reagent grade and  $HNO_3$  of analytical grade in distilled water to necessary concentrations.

Initial lanthanum chloride solutions were obtained by the dissolution of a weighed sample of  $LaCl_3$  (reagent grade) in distilled water. Solutions of  $LaBr_3$  were prepared by the dissolution of lanthanum(III) oxide (reagent grade) in concentrated HBr followed by the evaporation of the resultant solution on a water bath until neutral medium. Initial aqueous solutions of lanthanum salts were diluted with distilled water to necessary metal concentrations. In certain experiments, aqueous solutions of lanthanum chlorides and bromides were used with NaCl or NaBr (reagent grade) additives, respectively.

The processes of lanthanum back extraction from organic phase were studied with the use of a 0.05 M sulfuric acid solution.

The binary extractants ( $R_4NA$ ) were obtained by the dissolution of equimolar amounts of methyltrioctylammonium chloride ( $R_4NCl$ ) and the corresponding organic acid (HA) in toluene followed by agitation of the organic solution with equal volume of 1 M NaOH solution for 10 min and subsequent washing of the organic phase with water. Toluene of analytical grade was used as a solvent. Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and dinonylnaphthalenesulfonic acid were used as organic acids.

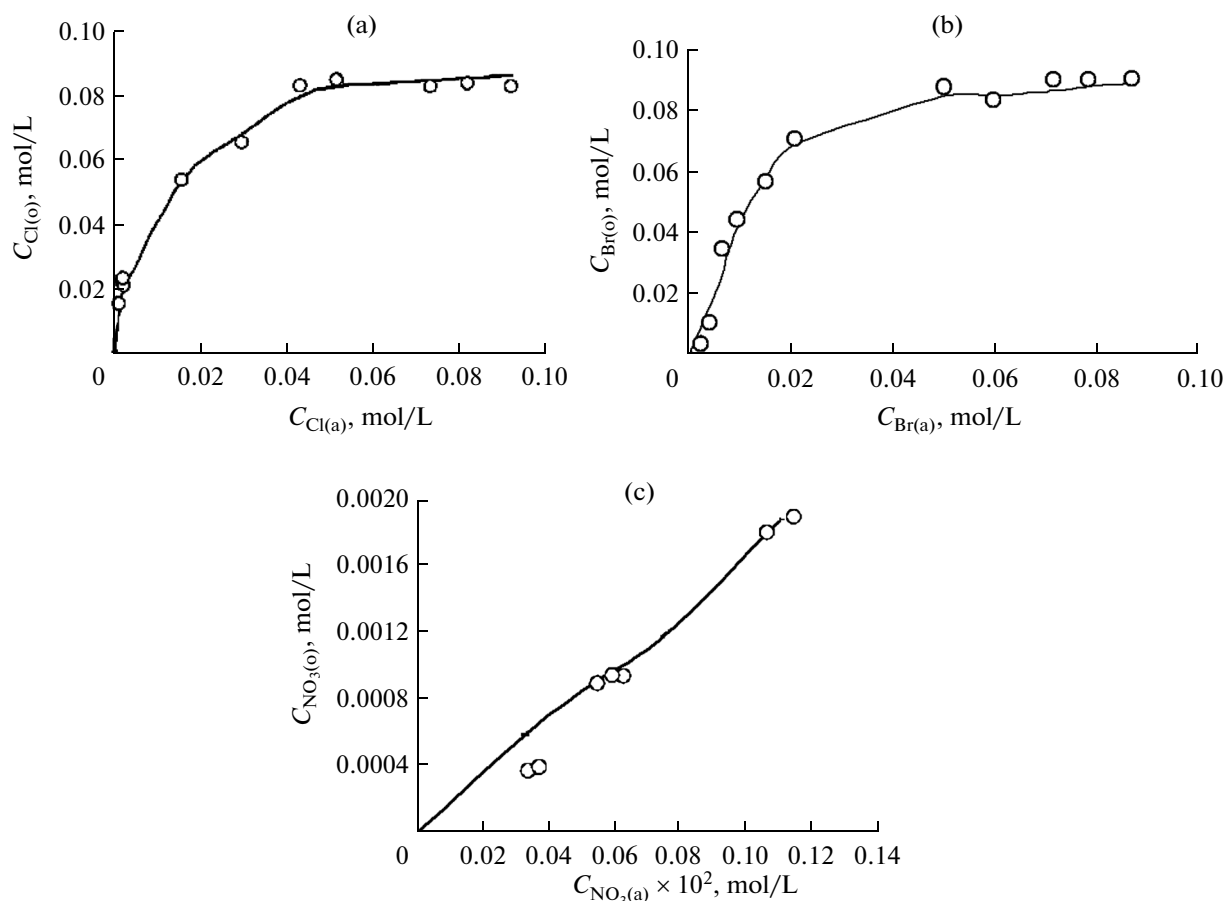
Extraction was carried out at 20°C in test tubes with ground-glass stoppers at equal volumes of aqueous and organic phases. Phase stirring time was 15 min that provided extraction equilibrium.

Mineral acid concentrations in initial solutions and aqueous phases after extraction were determined by volumetric acid–base titration. Acid concentration in organic phases was determined from the difference between the concentrations in initial solution and in aqueous phase after extraction.

Lanthanum concentration in initial solutions and aqueous phases after extraction was determined by trilonometric titration with Xylenol Orange as an indicator or spectrophotometric method with Arsenazo III. Lanthanum concentration in organic phases was determined from the difference between the concentrations in initial solution and aqueous phase after extraction. In certain cases, quantitative back extraction of the metal from organic phase was conducted using 0.1 M sulfuric acid solution followed by determination of lanthanum concentration in back extracts.

## RESULTS AND DISCUSSION

The obtained experimental values of isotherms for hydrochloric, hydrobromic, and nitric acids extraction with methyltrioctylammonium bis(2,4,4-trime-



**Fig. 1.** Theoretical (solid curves) and experimental (dots) isotherms for extraction of hydrochloric (a), hydrobromic (b), and nitric (c) acids with solutions of methyltrioctylammonium dialkylphosphinate in toluene.  $C_{\text{ex}}$ , mol/L: 0.1 (a, b), 0.01 (c).

thylpentyl)phosphinate presented in Fig. 1 (marked with dots) show that the isotherms in initial concentration range have a straight character with slopes close to 1, which corresponds to the relationships of binary extraction of mineral acids.

Since the studied mineral acids are monobasic, the ratio of initial concentration of binary extractant to concentration of mineral acid anions in organic phase should be 1 : 1 according to equation (1), which was confirmed by supplementary studies on organic phase saturation. Using equation (2), we calculated the efficient constants of mineral acids extraction with methyltrioctylammonium bis(2,4,4-trimethylpentyl)phosphinate ( $\bar{K}_{\text{H}_m\text{B}}$ ) presented in Table 1. The values of mean ionic activity coefficients for acids  $\gamma_{\pm}$  were taken from the reference book [12]. The data of Table 1 indicates that the extraction ability of mineral acids in the system with methyltrioctylammonium dialkylphosphinate decreases in the series  $\text{HNO}_3 \gg \text{HBr} > \text{HCl}$ .

The obtained values of constants of mineral acids extraction with the binary extractant (Table 1) were used for constructing calculated extraction isotherms

(Fig. 1, solid curves), which showed good agreement between calculated and experimental data.

The reaction reverse to the binary extraction of mineral acid (equation (1)) may be considered as a reaction of binary extractant formation. Formation constant for methyltrioctylammonium dialkylphosphinate is reversibly proportional to the constant of binary extraction of the corresponding mineral acids and can be calculated by the equation:

$$\bar{K}_{\text{R}_4\text{NA}} = \frac{\alpha_{\text{H}^+(\text{a})}^m C_{\text{B}^{m-}(\text{a})} C_{\text{R}_4\text{NA}(\text{o})} \gamma_{\text{B}^{m-}(\text{a})}}{C_{(\text{R}_4\text{N})_m\text{B}(\text{o})} C_{\text{HA}(\text{o})}^m}. \quad (9)$$

**Table 1.** Constants of mineral acids extraction with methyltrioctylammonium dialkylphosphinate in toluene ( $P = 0.95$ )

Acid	$\bar{K}_{\text{H}_m\text{B}}$	$\log \bar{K}_{\text{H}_m\text{B}}$
$\text{HNO}_3$ ( $n = 9$ )	$(3.85 \pm 0.13) \times 10^6$	$6.56 \pm 0.12$
$\text{HBr}$ ( $n = 8$ )	$(1.87 \pm 0.32) \times 10^2$	$2.25 \pm 0.08$
$\text{HCl}$ ( $n = 5$ )	$(1.40 \pm 0.51) \times 10^2$	$2.10 \pm 0.17$

**Table 2.** Formation constants of methyltrioctylammonium dialkylphosphinate in different media ( $P = 0.95$ )

Acid	$\bar{K}_{R_4NA}$	$\log \bar{K}_{R_4NA}$
HNO <sub>3</sub> ( $n = 9$ )	$(2.94 \pm 0.13) \times 10^{-7}$	$-6.56 \pm 0.12$
HBr ( $n = 8$ )	$(5.86 \pm 0.32) \times 10^{-3}$	$-2.25 \pm 0.08$
HCl ( $n = 5$ )	$(7.93 \pm 0.51) \times 10^{-3}$	$-2.10 \pm 0.17$

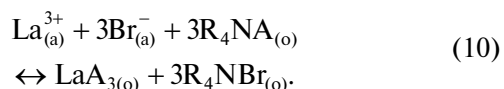
The values of formation constants for methyltrioctylammonium dialkylphosphinate in solutions in hydrochloric, hydrobromic, and nitric acids are presented in Table 2, which indicates that the worst formation of methyltrioctylammonium dialkylphosphinate occurs in nitrate solutions, i.e., the binary extractant in nitric acid solutions is less stable than in HCl and HBr solutions.

Extraction of lanthanum bromide from 2 M NaBr solutions with 0.05 M solution of methyltrioctylammonium dialkylphosphinate in toluene was studied. Extraction isotherms for LaBr<sub>3</sub> and LaCl<sub>3</sub> are compared in Fig. 2. Solution ionic strength was maintained by addition of 2 M NaBr and 2 M NaCl, respectively. The data given in Fig. 2 display that the ratio of lanthanum concentration in organic phase to the initial concentration of binary extractant on saturation is close to 1 : 3, which indicates the formation of extractable compounds of composition LaA<sub>3</sub> upon extraction of both bromide and chloride.

To establish the composition of extracted lanthanum bromide complexes, we also conducted experiments on organic phase saturation and revealed the

ratio of lanthanum concentration in organic phase to initial binary extractant concentration to be 1 : 3.

The data given in Fig. 2 and the results obtained on organic phase saturation allow us to assume that the distribution of lanthanum bromide and chloride [10, 11] in the system with methyltrioctylammonium dialkylphosphinate in general view without regard for the possible interactions of the components in organic phase is described by the equation:



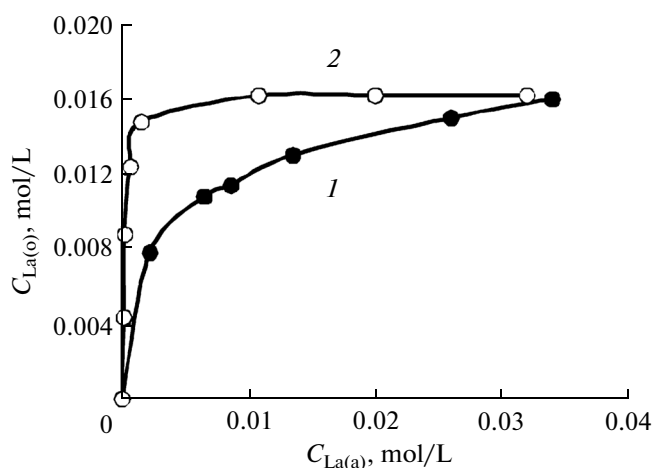
In accordance with equation (10), the expression for efficient constant of binary extraction of lanthanum bromide has the following view:

$$\bar{K}_{\text{LnBr}_3} = \frac{C_{\text{Ln}(o)} C_{\text{R}_4\text{NBr}(o)}^3}{C_{\text{Ln}(a)} C_{\text{Br}(a)}^3 C_{\text{R}_4\text{NA}(o)}^3 \gamma_{\pm(a)}^4} \quad (11)$$

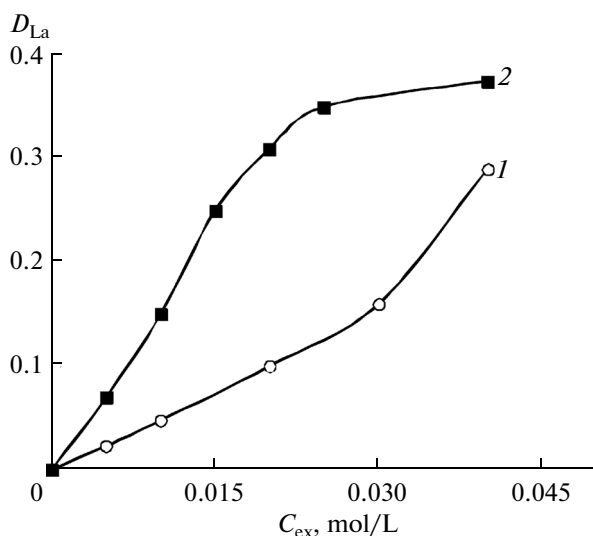
The constant of binary extraction of lanthanum bromide was calculated using equation (11):  $\ln \bar{K}_{\text{LnBr}_3} = -1.47 \pm 0.34$  ( $P = 0.95$ ,  $n = 7$ ). It was assumed that  $C_{\text{R}_4\text{NBr}(o)} = 3C_{\text{Ln}(o)}$ , while  $C_{\text{R}_4\text{NA}(o)} = C_{\text{R}_4\text{NA}(\text{initial})} - 3C_{\text{Ln}(o)}$ . The activity coefficients for bromide and lanthanum ions were taken from the reference book [13].

According to equation (8), extraction ability in the binary extraction of salts of the same metal with different anions is determined by the values of exchange constant of mineral acid anions with hydroxide ion ( $K_{B-OH}$ ). The extraction isotherms of lanthanum salts given in Fig. 2 show considerable growth of lanthanum distribution ratios on passing from chloride to bromide ions, which corresponds to anion-exchange extraction series for the initial QAB salts [14].

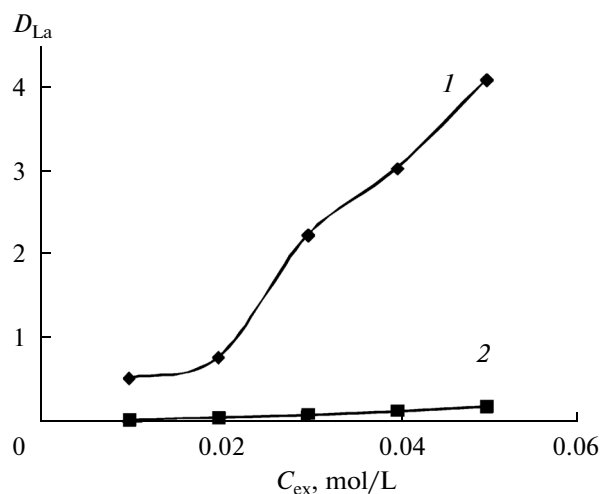
On the binary extraction of metal salts with binary extractants with the same organic cations and different organic anions according to equation (8), the extraction ability of binary extractant will be determined by the value of acid dissociation constant of organic acid comprising the binary extractant ( $K_a$ ). Figures 3 and 4 show the data on lanthanum chloride extraction with solutions of methyltrioctylammonium dialkylphosphinate and dinonylnaphthalenesulfonate in toluene in comparison with extraction with the initial organic acids. On extraction with dialkylphosphinic acid (Fig. 3, curve 1), acetate buffer was added to aqueous solutions to maintain constant pH value (pH ~ 4). The obtained results (Fig. 3) indicate that the extraction of lanthanum with QAB dialkylphosphinate proceeds more efficiently than that with initial dialkylphosphinic acid, whereas lanthanum distribution ratios in the system with dinonylnaphthalenesulfonic acid (Fig. 4, curve 1) are much higher than in extraction with methyltrioctylammonium dinonylnaphthalenesulfonate (curve 2). Moreover, the extraction ability of dinonylnaphthalenesulfonate is considerably lower than that



**Fig. 2.** Isotherms of lanthanum chloride (1) and bromide (2) extraction with 0.05 M solution of methyltrioctylammonium dialkylphosphinate in toluene.  $C_{\text{NaCl}} = 2$  mol/L (1),  $C_{\text{NaBr}} = 2$  mol/L (2).



**Fig. 3.** Dependence of lanthanum chloride extraction on the concentration of dialkylphosphinic acid (1) and methyltriocetylammmonium dialkylphosphinate (2). Toluene as a solvent.  $C_{La} = 0.055$  mol/L,  $C_{NaCl} = 2$  mol/L. pH  $\sim 4.0$  (1).



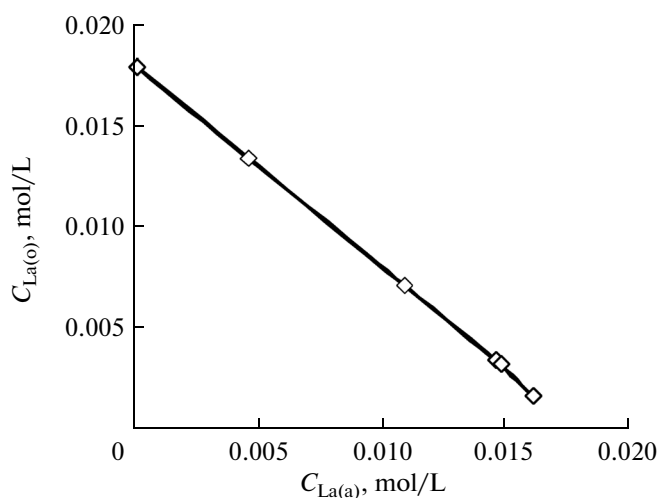
**Fig. 4.** Dependence of lanthanum chloride extraction on the concentration of dinonylnaphthalenesulfonic acid (1) and methyltriocetylammmonium dinonylnaphthalenesulfonate (2). Toluene as a solvent.  $C_{La} = 0.02$  mol/L.

of QAB dialkylphosphinate. For example, on the use of 0.02 M solutions of binary extractants,  $D_{La}$  values equal to 0.31 and 0.037 for methyltriocetylammmonium dialkylphosphinate and dinonylnaphthalenesulfonate, respectively. This is caused by the larger value of acid dissociation constant of dinonylnaphthalenesulfonic acid ( $pK_a \sim 1$ ) as compared with bis(2,4,4-trimethylpentyl)phosphinic acid ( $pK_a \sim 3.5$  [15]). The high thermodynamic stability of the binary extractant based on dinonylnaphthalenesulfonic acid causes also its low extraction ability as compared with the initial organic acid (Fig. 4).

One of considerable advantages of binary extractant systems is the simpler process of metal back extraction from organic phase on account of formation of thermodynamically stable binary extractants [1–3]. We obtained the isotherm of lanthanum chloride back extraction (Fig. 5) with 0.05 M solution of sulfuric acid in the system with methyltriocetylammmonium dialkylphosphinate in toluene. The experimental data presented in Fig. 5 display the possibility of efficient back extraction of metal with dilute solutions of mineral acids. It should be noted that the back extraction isotherm like lanthanum chloride extraction isotherm (Fig. 1a) is a straight line with a slope close to 1.

We studied the back extraction of lanthanum chloride and bromide in the system with 0.05 M solution of methyltriocetylammmonium dialkylphosphinate with the use of dilute sulfuric acid solutions at equal ratio of aqueous and organic phases. Back extraction efficiency was found to be 85–95% of initial metal concentration in organic phase ( $C_{La(o)} = 0.015$  mol/L) over one contact.

Thus, we showed that the extraction ability of mineral acids in the system with methyltriocetylammmonium



**Fig. 5.** Isotherm of lanthanum chloride back extraction with 0.05 M solution of  $H_2SO_4$  from 0.05 M solution of methyltriocetylammmonium dialkylphosphinate in toluene.

dialkylphosphinate decreases in the order  $HNO_3 \gg HBr > HCl$ , which corresponds to anion-exchange series for the initial QAB salts. The stoichiometry of lanthanum bromide extraction was established and extraction constants were calculated. It was shown that lanthanum can be back extracted from organic phase with dilute solutions of mineral acids.

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