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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Extraction of Oxalic Acid from Solutions of Electrolyte Mixtures

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Abstract—Extraction of oxalic acid with tributyl phosphate and triisoamyl phosphate from solutions of its mixtures with nitric, phosphoric, sulfuric, and hydrochloric acid and with ammonium nitrate and chloride was studied. In the extractability series, oxalic acid occupies the position between nitric and phosphoric acids, with sulfuric and hydrochloric acids acting as strong salting-out agents. Nitric acid salts drastically decrease the distribution ratios of oxalic acid.

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Khibiny apatite concentrate remains the most important potential source of rare-earth elements (REE) in Russia [1]. Their concomitant recovery is possible in the nitric acid procedure for apatite processing into phosphorus fertilizers. However, involvement of this kind of raw materials into production is hampered, among other factors, by certain problems arising in processing of the recovered rare-earth phosphate concentrate. Primary purification to remove phosphorus is mainly performed by oxalate precipitation or extraction [2, 3]. The simplest variant of purification via oxalates is direct conversion into oxalates [4].

Because of high cost of oxalic acid, purification via oxalates should involve the regeneration of oxalic acid incorporated in REE oxalates by their treatment with an alkali [5]. The recovery of excess oxalic acid from mother liquors is not provided, although, along with economic aspects, one should take into account the environmental and economic consequences of the ingress of oxalate ions into production or waste solutions (MPC 2 mg g^{-1}).

In this study we examined the extraction of oxalic acid from solutions of electrolyte mixtures with the aim to evaluate the possibility of its utilization by extraction. For the extraction we used tributyl phosphate (TBP) and triisoamyl phosphate (TiAP), with dodecane as diluent. Preliminary experiments showed that oxalic acid is not noticeably extracted with higher alkanols. Extraction of oxalic acid from its straight aqueous solutions with TBP was studied by Allamuratov et al. [6]. We found no data on extraction in systems containing in the aqueous phase, along with oxalic acid, also mineral acids and their salts. Extraction of oxalic acid with triisoamyl phosphate was not studied either.

EXPERIMENTAL

Extraction was performed in a beaker at room temperature for 3 min with stirring. The phase separation in all the systems was good. Samples were taken after settling for 10 min. The salt composition of the aqueous solution was varied within the limits determined by the conditions of the conversion of phosphates into oxalates. The oxalic acid concentration was determined by titration with potassium permanganate, and the total acidity, by titration with alkali.

Experimental data on the extraction of oxalic acid with TBP and TiAP are given in Figs. 1 and 2. These data show that oxalic acid can be fully recovered with both neat and diluted extractants. The log–log plots of the distribution ratios D on the extractant concentration S (M) are straight lines with a slope close to 2, which suggests formation of the stable extractable complex $H_2C_2O_4 \cdot 2L$ (L = TiAP, TBP). The apparent extraction constant of oxalic acid is

$$K = D/([HC_2O_4^-]_{aq} S_{free}^2),$$

where $[HC_2O_4^-]_{aq}$ is the oxalic acid concentration in the equilibrium aqueous phase (M), and S_{free} is the free extractant concentration (M), which was 2–3 M in our experiments, i.e., it was by an order of mag-

Table 1. Distribution of oxalic acid in extraction of tributyl phosphate containing 20 vol % dodecane

Run no.	Initial solution concentration, M		Equilibrium concentration, M				D
	acid (salt)	$H_2C_2O_4$	$[H^+]_o$	$[H^+]_{aq}$	$[H_2C_2O_4]_o$	$[H_2C_2O_4]_{aq}$	
	HNO_3:						
1	–	0.33	0.31	0.15	0.23	0.1	2.3
2	0.5	0.24	0.41	0.56	0.18	0.06	3.0
3	1.0	0.33	0.61	0.82	0.23	0.1	2.3
4	2.0	0.33	0.97	1.53	0.17	0.16	1.1
5	3.0	0.33	1.37	2.35	0.12	0.22	0.54
	H_3PO_4:						
6*	0.5	0.33	0.76	1.43	0.22	0.11	2.0
7*	1.0	0.33	0.82	1.84	0.22	0.11	2.0
8	2.0	0.38	0.41	1.16	0.27	0.12	2.3
	H_2SO_4:						
9	1.07	0.24	0.41	2.24	0.18	0.06	3.0
10	2.0	0.26	0.46	4.08	0.22	0.04	5.5
	HCl:						
11	1.0	0.24	0.36	1.12	0.18	0.06	3.0
12	1.9	0.24	0.41	2.24	0.2	0.04	5.0
	NH_4NO_3:						
13	1.0	0.38	0.26	0.23	0.19	0.20	0.95
14	2.0	0.38	0.26	0.22	0.15	0.24	0.62
	NH_4Cl:						
15	1	0.38	0.25	0.22	0.25	0.14	1.7
16	2	0.38	0.24	0.21	0.25	0.14	1.7

* In run nos. 6 and 7, the aqueous phase also contained 1 M HNO_3.

nitude higher than that of nitric acid and by several orders of magnitude higher than those of sulfuric, hydrochloric, and phosphoric acids.

Data on extraction of oxalic acid with diluted TBP and TiAP from mixtures of electrolytes are given in Tables 1 and 2. To an oxalic acid solution we added nitric and phosphoric acids, whose presence is predetermined by the conditions of the conversion of REE phosphates into oxalates, and also, for comparison, sulfuric and hydrochloric acids and

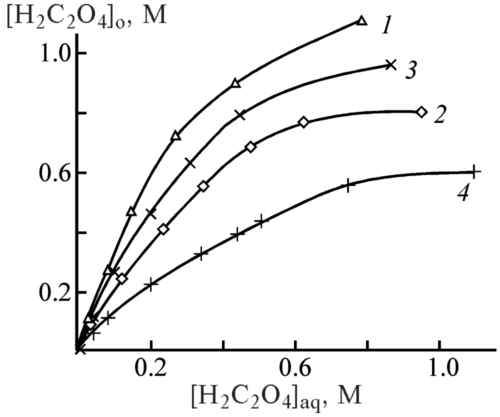

Fig. 1. Isotherms of oxalic acid extraction with (*1*, *2*) tributyl phosphate and (*3*, *4*) triisolamyl phosphate. Extractant content, vol %: (*1*, *3*) 100, (*2*) 80, and (*4*) 70. ($[H_2C_2O_4]_o$, $[H_2C_2O_4]_{aq}$) $H_2C_2O_4$ concentration in the organic and aqueous phases, respectively.

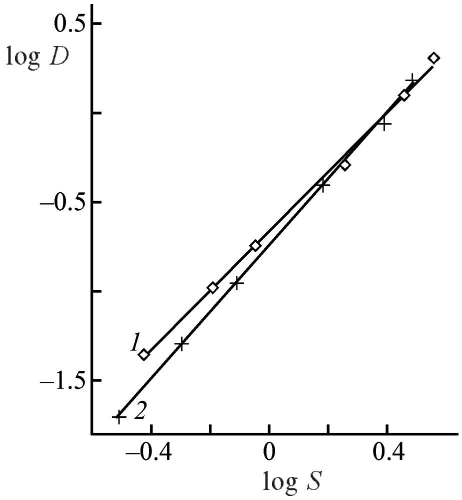

Fig. 2. log–log plot of the distribution ratio of oxalic acid D vs. extractant concentration S. (*1*) TBP and (*2*) TiAP.

Table 2. Distribution of oxalic acid in extraction with triisoamyl phosphate containing 30 vol % dodecane

Run no.	Initial solution concentration, M		Equilibrium concentration, M				*D*
	acid (salt)	$H_2C_2O_4$	$[H^+]_o$	$[H^+]_{aq}$	$[H_2C_2O_4]_o$	$[H_2C_2O_4]_{aq}$	
	HNO_3:						
1	–	0.33	0.2	0.2	0.19	0.14	1.3
2	0.5	0.33	0.35	0.56	0.19	0.14	1.3
3	1.0	0.33	0.46	0.92	0.20	0.13	1.5
4	2.0	0.33	0.71	1.73	0.13	0.2	0.64
5	3.0	0.33	0.97	2.45	0.08	0.25	0.3
	H_3PO_4:						
6*	0.5	0.33	0.48	1.43	0.19	0.14	1.4
7*	1.0	0.33	0.51	1.84	0.19	0.14	1.4
8	2.0	0.38	0.31	1.15	0.25	0.14	1.7
	H_2SO_4:						
9	0.5	0.24	0.20	1.38	0.18	0.06	3.0
10	1.0	0.24	0.2	2.14	0.2	0.04	5.0
	HCl:						
11	1.0	0.24	0.25	1.12	0.16	0.08	2.0
12	2.0	0.24	0.25	2.14	0.18	0.06	3.0
	NH_4NO_3:						
13	1.0	0.59	0.46	0.66	0.16	0.43	0.37
14	2.0	0.59	0.46	0.66	0.14	0.45	0.31
	NH_4Cl:						
15	1	0.38	0.25	0.2	0.19	0.19	1.0
16	2	0.38	0.25	0.2	0.2	0.18	1.2

* In run nos. 6 and 7, the aqueous phase also contained 1 M HNO_3.

ammonium nitrate and chloride. The distribution data are given for the binary mixtures with oxalic acid, except a ternary mixture containing phosphoric acid in a mixture with nitric acid. The extraction was performed at 1 : 1 ratio of the organic and aqueous phases.

As seen from Tables 1 and 2, relationships in the oxalic acid distribution in extraction with TBP and TiAP in the presence of electrolytes are similar. Nitric acid at its concentration of up to 1 M affects the extraction of oxalic acid insignificantly and even acts, to a small extent, as a salting-out agent. However, as the nitric acid concentration is increased, its distribution ratio increases also, and nitric acid starts to displace oxalic acid from the organic phase. Introduction of up to 3 M HNO_3 into the aqueous phase decreases the distribution ratios of oxalic acid by a factor of more than 4. Oxalic acid, on the contrary, exerted no salting-out effect on nitric acid.

Phosphoric acid only slightly affects the extraction, and in the ternary system containing 1 M H_3PO_4 and 1 M HNO_3 the distribution ratios of oxalic acid are relatively high.

Sulfuric and hydrochloric acids are poorly extracted with neutral extractants and therefore act as salting-out agents increasing the activity of oxalic acid. The distribution ratio of oxalic acid in the presence of these acids increases by a factor of more than 2.

Introduction of ammonium nitrate drastically decreases the extraction of oxalic acid because of the exchange decreasing the oxalic acid concentration:

$$2NH_4NO_3 + H_2C_2O_4 \rightleftarrows 2HNO_3 + (NH_4)_2C_2O_4,$$

with simultaneous extraction of the released nitric acid. In the presence of ammonium nitrate, the distribution ratio of nitric acid increases.

In the presence of ammonium chloride, the exchange occurs also and the concentration of oxalic acid decreases. However, the released hydrochloric acid exerts a salting-out effect, and as a result the oxalic acid extraction decreases only slightly.

Thus, oxalic acid recovery from electrolyte solutions by extraction with TBP and TiAP is quite feasible. The extracted oxalic acid can be readily backwashed with an equivalent amount of aqueous ammonia, as ammonium oxalate is only slightly soluble in the extractant.

CONCLUSIONS

(1) The extraction of oxalic acid from a mixture of electrolytes with tributyl phosphate and triisoamyl phosphate was studied. Nitric acid at its concentration in the initial aqueous solution of up to 1 M exerts a weak salting-out effect on the extraction of oxalic acid, and at its higher concentrations nitric acid starts to displace oxalic acid from the organic phase. Phosphoric acid does not noticeably affect the extraction, whereas sulfuric and hydrochloric acids act as strong salting-out agents, increasing the distribution ratios of oxalic acid by a factor of more than 2. Nitric acid salts suppress the extraction of oxalic acid, and hydrochloric acid salts decrease its extraction slightly.

(2) The data on the oxalic acid distribution demonstrate the feasibility of oxalic acid utilization by extraction.

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