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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Recovery and Separation of Ce^{3+} and Y^{3+} Ions from Aqueous Solutions by Ion Flotation

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Abstract—Experimental dependences of the distribution coefficients of cerium(III) and yttrium(III) dodecyl sulfates on the pH value of the equilibrium aqueous phase in the course of ion flotation are reported. Conditions for separation of cerium(III) and yttrium(III) are discussed. A value of the dissociation constant found from experimental results of potentiometric titration of dodecylsulfuric acid with sodium hydroxide is presented.

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The ion flotation is a method for recovery of inactive, as a rule, inorganic ions with the use of surfactants. Surfactants are molecules containing a hydrophobic and a hydrophilic parts, commonly represented by an ionogenic group and an organic radical with a large number of carbon atoms. In the course of flotation, the surfactant interacts with the inorganic ion and can be removed from the solution together with the foam.

The goal of this study was to examine the distribution of rare-earth metal (REM) ions in the system constituted by an aqueous phase and a foam phase, formed by model solutions of Ce^{3+} and Y^{3+} nitrates and sodium dodecyl sulfate, and to find the dissociation constant of dodecylsulfuric acid, for which published data are rather contradictory.

EXPERIMENTAL

The dependence of the distribution coefficient of rare-earth metals among the aqueous and organic phases on the solution pH was studied to find conditions for the most complete recovery of REM and determine whether cerium(III) and yttrium(III) can be separated. As model solutions were used 0.001 M aqueous solutions of cerium(III) and yttrium(III) nitrates; as a surfactant served sodium dodecyl sulfate (SDS) whose concentration corresponded to the stoichiometry of the reaction

$$M^{3+} + 3DS^- = M\{DS\}_3$$

i.e., it was 0.003 mol kg^{-1}, which constitutes 0.864 g kg^{-1} (DS^- is the dodecyl sulfate ion).

The volume of the aqueous phase was varied from 100 to 200 ml, and the pH value, from 0 to 11 with a step of 0.5 by addition of a nitric acid or sodium hydroxide solution.

The ion flotation was performed during 10 min on a 137 V-FL flotation machine of the mechanical type, with a chamber volume of 1.0 dm^3.

In solution, REM ions form strong complexes with surfactants, and these complexes pass into the foam phase because of the hydrophobicity of alkyl radicals. The sampled foam was disintegrated by addition of 30 ml of a 1 mol kg^{-1} sulfuric acid solution. The resulting solution (foam product) and the solution remaining in the cuvette on performing the flotation (chamber residue) were analyzed for the content of a rare-earth element by the procedure described in [1]: to an aliquot amount of a solution under study (20 ml) were successively added 20 ml of a 5% solution of ascorbic acid, 5 drops of α-dinitrophenol indicator, a solution of sodium hydroxide or nitric acid until the solution pH became about 4.5 (which was judged from appearance of a yellow coloration), 5 ml of an acetate buffer solution, 50 ml of distilled water, and 5 drops of Arsenazo-III indicator. The solution was titrated with Trilon-B with a concentration of 0.05 mol kg^{-1}. The

Table 1. Experimental data of REM flotation at various pH vales

PH	$[Y^{3+}]$, mol kg^{-1}		K	$[Ce^{3+}]$, mol kg^{-1}		K
	in foam	in chamber residue		in foam	in chamber residue	
1.0	0.00012	0.00088	0.136	0.00039	0.00061	0.639
1.5	0.00012	0.00088	0.136	0.00039	0.00061	0.639
2.0	0.00012	0.00088	0.136	0.00045	0.00055	0.818
2.5	0.00013	0.00087	0.154	0.00036	0.00064	0.562
3.0	0.00016	0.00084	0.190	0.0004	0.0006	0.666
3.5	0.00018	0.00082	0.219	0.0004	0.0006	0.666
4.0	0.0003	0.0007	0.428	0.00035	0.00065	0.538
4.5	0.0008	0.0002	4.000	0.00035	0.00065	0.538
5.0	0.001	0.00001	100	0.0007	0.0003	2.333
5.5	0.001	0.00001	100	0.00075	0.00025	3.000
6.0	0.001	0.00001	100	0.001	0.00001	100
6.5	0.001	0.00001	100	0.001	0.00001	100
7.0	0.001	0.00001	100	0.001	0.00001	100
7.5	0.001	0.00001	100	0.001	0.00001	100
8.0	0.001	0.00001	100	0.001	0.00001	100
8.5	0.001	0.00001	100	0.001	0.00001	100
9.0	0.001	0.00001	100	0.001	0.00001	100
9.5	0.001	0.00001	100	0.001	0.00001	100
10	0.001	0.00001	100	0.001	0.00001	100
10.5	0.001	0.00001	100	0.001	0.00001	100
11	0.001	0.00001	100	0.001	0.00001	100

results of this experiment are listed in Table 1.

The distribution coefficient K of the ion being recovered among the aqueous and organic phases was calculated as the ratio between the concentration $[M^{3+}]$ (Ce^{3+} or Y^{3+}) in the foam to the concentration $[M^{3+}]$ in the chamber residue:

$$K = [M^{3+}]_{org}/[M^{3+}]_{aq}$$

The results of the experiment are shown in Figs. 1a, 1b.

The content of sodium dodecyl sulfate in the chamber residue and in the foam was determined by potentiometric titration with the use of an ion-selective electrode fabricated at the Chair of physical chemistry, St. Petersburg State University. A 0.002 mol kg^{-1} solution of cetyltrimethylammonium chloride served as a titrant.

The experimental dependences of the REM distribution coefficient on the pH value indicate that Y^{3+} starts to be recovered at pH 5, and Ce^{3+}, at pH 6. Thus, a conclusion

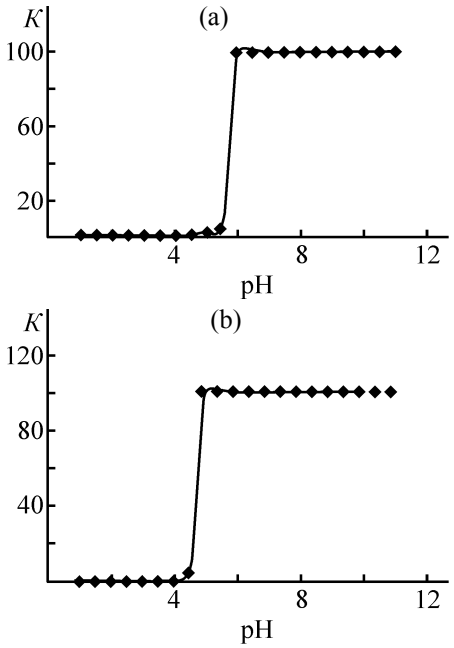

Fig. 1. Distribution coefficient K of (a) Ce^{3+} and (b) Y^{3+} vs. the solution pH.

Table 2. Experimental results of a potentiometric titration of solutions

Run no.	State of the system	V, ml	pH	I, mol kg^{-1}	γ±	C, mol kg^{-1}	pK_a
1	1st pH jump	5.5	4.1			0.0024	5.60
	Buffer region	6.1	6.1	0.061	0.81	0.0023	6.19
	2nd pH jump	6.8	8.5	0.068	0.80	0.0022	5.85
2	1st pH jump	4.6	4.3			0.0024	5.98
	Buffer region	4.8	6.0	0.053	0.82	0.0024	5.91
	2nd pH jump	5.1	8.4	0.056	0.81	0.0024	5.60
3	2nd pH jump	193	8.0	0.0045	0.93	0.0003	5.58

can be made that certain selectivity in recovery of the REMs under study can be obtained by varying the pH value.

At pH values lower than the pH of hydrate formation (range of pH values in which hydroxo complexes are formed) cerium and yttrium dodecyl sulfates, rather than hydroxides, are floated. The REM flotation in the form of dodecyl sulfates is confirmed by analysis of the chamber and foam products, in which the balance between the amount of REM and dodecyl sulfate ions in the equilibrium aqueous phase and in the foam is verified.

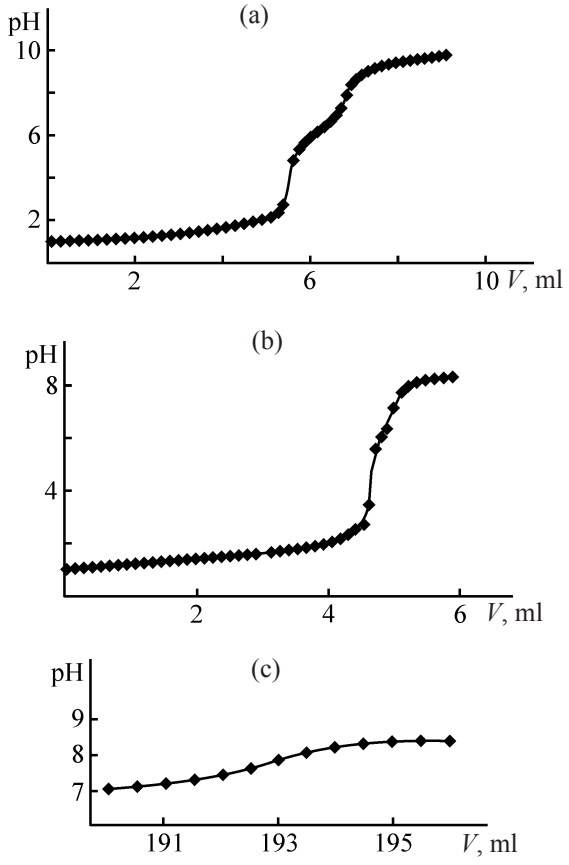

Fig. 2. Titration curve of SDS with a NaOH solution. (V) NaOH volume. NaOH solution concentration (M): (a, b) 0.263 and (c) 0.00325. Run no.: (a) 1, (b) 2, and (c) 3.

The next stage of the study consisted in determining the dissociation constant K_a of dodecylsulfuric acid. For this purpose, a number of experiments on potentiometric titration with a sodium hydroxide solution of a 0.001 mol kg^{-1} solution of sodium dodecyl sulfate, acidified with nitric acid to pH 1. The titration curves obtained are shown in Figs. 2a, 2b.

The data in Table 1 demonstrate that the recovery of both rare-earth elements begins at a certain pH value: at pH ≥ 5 for yttrium(III) cations and at pH ≥ 6 for cerium(III). In all probability, this is due to dissociation of the flotation agent, because it reacts with REM cations in the anionic form at pH ≥ pK_a ≈ 1, as shown in [2]. However, the published value of the dissociation constant $K_a = 3 \times 10^{-2}$ [3], contradicts the results of the present study.

The value reported in [3] nearly coincides with the second-stage dissociation constant of sulfuric acid; at the same time, the value obtained in the present study well accounts for the maximum degree of Ce^{3+} and Y^{3+} recovery at pH ≥ 5–6.

Two pH jumps were observed in the titration curves (Figs. 2a, 2b). The first jump at pH 4.1 corresponds to the equivalence point of titration of the strong nitric acid with the alkali. At this point, a weak dodecylsufuric acid and sodium nitrate were present in the solution. The dissociation constant pK_a of dodecylsulfuric acid was

calculated by the formula

$$pK_a = 2pH + \log c, \quad (1)$$

where c is the concentration of dodecylsulfuric acid, calculated with the dilution in the course of titration taken into account.

The second jump at pH = 8.5 corresponds to the equivalence point of titration of the weak dodecylsulfuric acid with the alkali. At this equivalence point, a mixture of a hydrolyzable salt, sodium dodecyl sulfate, and sodium nitrate was present in the solution. The activity of the hydrolysis products (OH–) was described by the formula

$$\alpha_{OH^-} = \gamma_{\pm} \sqrt{K_h c}. \quad (2)$$

where K_h is the hydrolysis constant, and c, concentration of sodium dodecyl sulfate.

The ionic strength was calculated from the concentration of sodium salt, with the dilution in the course of titration taken into account. The dissociation constant was calculated by the formula

$$pK_a = 14 - 2pOH - \log C - 2\log \gamma_{\pm}, \quad (3)$$

were $\gamma_{\pm}$ is the ion-average activity coefficient of sodium nitrate in solution, taken from the reference book [4].

Between the pH jumps in the titration curve, there is a region of a buffer solution composed of dodecylsulfuric acid and sodium dodecyl sulfate. In the middle of this region, at equal concentrations of a weak acid and its salt,

$$pK_a = pH + \log \gamma_{\pm}, \quad (4)$$

Thus, pK_a values can be found from the titration curves obtained.

The curve of titration (run no. 3) with an alkali solution diluted to 0.00325 N, the first pH jump was not observed, and, therefore, Figs. 2a and 2b show only the region corresponding to the second pH jump.

The calculated values of pK_a are listed in Table 2. The initial concentration of dodecylsulfuric acid was 10^{-3} mol kg^{-1} in all experiments; the volume of the aliquots was 20 ml in run nos. 1 and 2 and 10 ml in run no.3. The NaOH concentration was 0.263 N in run nos.1 and 2, 0.0065 N in run no. 3 at an alkali added in amounts of up to 100 ml, and 0.00325 N at amounts exceeding 100 ml.

The error d was calculated by the formula [5]:

$$d = t \sqrt{(\overline{x} - x_i)^2/n(n-1)},$$

where n is the number of measurements; $\overline{x}$ and x_i, average and running values of the calculated quantity; t, Student's coefficient equal to 2.8 at $n = 7$ and confidence probability of 0.95.

A calculated value $K_a = (1.7 \pm 0.8) \times 10^{-6}$ was obtained. According to the data of [3], the K_a of dodecylsulfuric acid is 10^{-2}, which certainly contradicts the data obtained in flotation, because the recovery pH is 5.0 for Y^{3+} cations and 6.0 for Ce^{3+}. Consequently, the value found in this study, $pK_a = 5.82$, which corresponds to the pH of a 50% transition of dodecylsulfuric acid to the anionic form, is in a better agreement with the experimental data on REM flotation.

Thus, a conclusion can be made that, at pH values in the range from 4.5 to 6.0, cerium(III) and yittrium (III) can be separated from solutions of their salts.

CONCLUSIONS

(1) It was found that, in ion flotation from solutions of rare-earth metals at pH 4.5–6.0, cerium(III) and yttrium(III) can be separated from solutions of their salts with sodium dodecyl sulfate used as a surfactant.

(2) A calculated value of the dissociation constant of dodecylsulfuric acid was obtained from experimental potentiometric titration curves of the solutions: $K_a = (1.7 \pm 0.8) \times 10^{-6}$.

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