SovietRxiv

Soviet-era science, translated into English

Chemistry

N. V. SHAKHOVA, Corresponding Member of the Academy of Sciences of the USSR I. P. ALIMARIN,

1963

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196301.33637

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Chemistry

N. V. SHAKHOVA, Corresponding Member of the Academy of Sciences of the USSR I. P. ALIMARIN,
Yu. A. ZOLOTOV

COEXTRACTION OF CALCIUM AND STRONTIUM WITH OXINATES OF CERTAIN ELEMENTS

Several cases of coextraction have been described in the literature; a review of the known facts and an attempt at their systematization were made earlier ([1]). In the present work it is shown that, in a weakly alkaline medium, calcium and strontium are coextracted with the 8-oxinolates of scandium, neodymium, thorium, and aluminum.

Aqueous solutions of chlorides were used as starting materials; the concentration of the elements was established by the usual methods. Radioactive isotopes Ca^{45}, Sr^{90}, freed daily from Y^{90}, Sc^{46}, Nd^{147}, and Fe^{59} were used. Reversible buffer solutions were employed to regulate pH. Oxine, purified by sublimation, was dissolved in distilled benzene; the concentration of the working oxine solution was 0.138 mol/l (2% by weight). This solution was renewed periodically.

To an aqueous solution containing one or two elements, buffer solutions were added to a total volume of 5 ml (with manual shaking) or 10 ml (with mechanical shaking), together with an equal volume of the benzene solution of oxine. The phases were mixed at room temperature ($\sim 22^{\circ}$) in separatory funnels by hand for 3 min, or mechanically in conical flasks with ground-glass stoppers for 15 or 30 min. The time required to establish equilibrium with one or the other method of shaking was found in separate experiments.

Fig. 1. Extraction of strontium with a 0.138 M benzene solution of 8-oxine from borate buffer solutions. 1—only strontium is present in the initial aqueous solution; 2—strontium in the presence of thorium; 3—strontium in the presence of neodymium; 4—strontium in the presence of scandium

After phase separation, 5 ml of the organic phase was taken, dried, and the radioactivity was determined with an end-window counter. Because of the rather high salt content in the aqueous phases, the activity of the latter was not mea-

SovietRxiv

Fig. 2

Figure 2: Fig. 2

sured. The degree of extraction was determined by comparing the activity of the organic phase with the standard activity of the initial aqueous solution. The data obtained were used to calculate the percent extraction E and the distribution coefficient D; the latter was determined as the ratio of the concentrations in the organic and aqueous phases. The hydrogen-ion concentration in the equilibrium aqueous phases was measured with a glass electrode.

Data on the extraction of strontium in the presence of scandium, thorium, and neodymium as a function of pH are given in Fig. 1. The same figure gives the curve characterizing the extraction of strontium in the absence of other elements. The concentration of strontium in all cases was $9.1 \cdot 10^{-5}$, and the concentration of the other elements was $2.73 \cdot 10^{-4}$ mol/l. As is evident from Fig. 1, strontium is coextracted with the oxinolates of scandium and other elements. With aluminum oxinolate, coextraction is manifested more weakly.

The results of experiments on the extraction of calcium in the absence and in the presence of other elements are presented in Fig. 2 (the preliminary data given in (1) were refined). Calcium is extracted rather weakly in the form of its oxinate if other elements are absent (the calcium concentration in the initial aqueous phase was $1.51 \cdot 10^{-4}$ mole/l). In the presence of neodymium, thorium, and scandium it is extracted considerably better (the concentration of these elements was 3-6 times higher than the calcium concentration). With aluminum, calcium is coextracted to a lesser extent; with iron it is not coextracted. The oxinates of scandium, neodymium, thorium, aluminum, and iron themselves are extracted fairly well in the pH region studied.

Fig. 2. Extraction of calcium with a 0.138 M solution of 8-hydroxyquinoline in benzene from borate buffer solutions. 1—only calcium is present in the initial aqueous solution; 2—calcium in the presence of neodymium; 3—calcium in the presence of thorium; 4—calcium in the presence of scandium.

To elucidate the possible mechanism of calcium coextraction with strontium, the extraction of calcium in the presence of scandium was studied in more detail.

The distribution coefficients of calcium in the presence of scandium were measured at pH 9.2 by the direct and back-extraction methods. The concentrations of calcium and scandium in the initial aqueous phases were, respectively, $9.1 \cdot 10^{-5}$ and $2.77 \cdot 10^{-4}$ mole/l. The aqueous phases were contacted with the extractant and then discarded. Part of the organic phases (from a series of parallel experiments) was left for determination of the distribution coefficients in direct extraction; the other part was brought into contact with aqueous phases of the same composition as in the direct extraction, but not containing calcium and scandium. After phase separation, the activity of the organic phases was measured. It was shown that the distribution coefficients in direct extraction

SovietRxiv

Fig. 3

Figure 3: Fig. 3

and in back extraction are practically identical.

The influence of the concentration of scandium in the aqueous phase on the extraction of calcium was investigated. The calcium concentration was kept constant and equal to $6.0 \cdot 10^{-5}$ mole/l, and the pH of the initial buffer solution was 9.2. The extraction of calcium increases with increasing scandium concentration, but only up to a certain limit. At a scandium-to-calcium ratio of approximately $3 : 1$, optimal conditions for calcium extraction are attained.

The dependence of the extraction of calcium on the initial concentration of oxine in the aqueous phase was also studied. The calcium concentration was $6.0 \cdot 10^{-5}$ mole/l, the pH of the initial solution was 9.2, and the $Sc : Ca$ ratio in the aqueous phase was $3 : 1$. The results obtained are shown in Fig. 3. The extraction of calcium increases with increasing oxine concentration.

Fig. 3. Extraction of calcium in the presence of scandium (initial ratio $Sc : Ca = 3$) as a function of the concentration of 8-hydroxyquinoline in benzene.

Absorption spectra were recorded for scandium extracts containing and not containing calcium. The optical densities of the organic solutions were measured on an SF-4 spectrophotometer (10-ml cuvettes; reference solution—a benzene solution of oxine). The concentration of calcium in the aqueous phase

before extraction was $3.0 \cdot 10^{-5}$, that of scandium $9.3 \cdot 10^{-5}$ mol/l. The shaking time was 15 min. The spectra were recorded immediately after separation of the phases.

The optical densities of extracts containing calcium were lower than the optical density of extracts obtained in its absence. Since scandium itself is extracted in both cases practically completely, the decrease in optical density is associated with the effect of calcium. Calcium oxinate has an absorption maximum approximately coinciding in position with the absorption maximum of scandium oxinate. If calcium were extracted in the form of a simple oxinate, the optical density should increase in comparison with the optical density of extracts containing only scandium. The observed decrease in optical density indicates that calcium is not extracted in the form of a simple oxinate. Apparently a mixed compound is formed, containing calcium and scandium.

Table 1

Results of experiments on electrophoresis of scandium extracts

SovietRxiv

Composition of the aqueous phase from which extraction was carried out	Composition of the organic phase before electrophoresis	Duration of experiment, h	Scandium transferred, % to the anode	Scandium transferred, % to the cathode
Sc + Ca	Benzene	5	0.4	0.2
Sc + Ca	Benzene + dichlorodiethyl ether (10 : 1)	5	2.5	1.6
Sc + Ca	Benzene + nitrobenzene (1 : 1)	5	3.3	8.8
Sc + Ca	Benzene + nitrobenzene (1 : 1)	10	4.8	49
Sc	Benzene + nitrobenzene (1 : 1)	10	0	48

One may also note another fact observed by us. The spectra of benzene solutions (extracts) of scandium oxinate change substantially with time—the optical density decreases, even to the disappearance of the maximum; however, the presence of calcium in these extracts slows the decrease in optical density.

Experiments were carried out on electrophoresis of the organic phases in order to determine the sign of the charge of those forms in which calcium and scandium exist in the organic phase. The experiments were performed in a U-shaped vessel for 5–10 h at a voltage of 2200 V. To increase the dielectric constant of the organic phases, β,β'-dichlorodiethyl ether or nitrobenzene was added to them before electrophoresis. Scandium was labeled with a radioisotope. For comparison, electrophoresis of extracts containing only scandium was carried out under the same conditions.

The results obtained are given in Table 1. A significant part of the scandium is transferred to the cathode both in the presence of calcium and without it, i.e., scandium oxinate is apparently destroyed. However, if calcium is present in the extract, part of the scandium is transferred to the anode, which is not observed in the case of extracts not containing calcium. These data make it possible to

SovietRxiv

suppose that the mixed compound contains calcium in the cationic part, and scandium in the anionic part.

To determine the ratio in which calcium and scandium may react in the presumed mixed compound, the method of isomolar series was used. In this case, the radioactivity of the extractable compound, due to the presence in it of Ca^{45} (the total radioactivity of the entire organic phase), was used as the measured property. The total concentration of the components in one phase was $6.16 \cdot 10^{-4}$ and $3.08 \cdot 10^{-4}$ mol/l. The data obtained were poorly reproducible, and it was impossible to draw an unambiguous conclusion from them; however, there is evidently more scandium than calcium in the compound.

Thus, the results obtained indicate that calcium is extracted not in the form of a simple oxine complex; that in the mixed compound scandium is in the anionic part and calcium in the cationic part; and that the scandium : calcium ratio in the compound is apparently greater than unity. These data are to some extent consistent with the formula $Ca(ScOx_4)_2$. If the coordination number of scandium in this compound is six, then it must be assumed that two oxine molecules occupy two coordination positions each, and the other two one each, with the formation of valence bonds. The formula, of course, requires verification.

The facts established in this work concerning the coextraction of calcium and strontium with oxine complexes of certain tri- and tetravalent elements, as well as other known cases of coextraction ([1]), suggest that greater attention should be paid to the study of the phenomenon of coextraction. The possibility of coextraction should be taken into account in the development and application of extraction methods for separation and concentration.

The authors are grateful to L. A. Izosenkova for assistance in the experiment.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky
Academy of Sciences of the USSR

Received
12 VII 1963

CITED LITERATURE

[1] I. P. Alimarin, Yu. A. Zolotov, N. V. Shakhova, *Transactions of the Commission on Analytical Chemistry*, **14**; *Extraction Methods in Analytical Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1963, p. 24.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.