BOBROVA, V. N.

AUTHORS: Grebenshchikova, V. I., Bobrova, V. N. 78-1-9/43

TITLE: Co-Precipitation of Lanthanium, Cerium and Americium With Potassium Sulfate (Soosazhdeniye lantana, tseriya i ameritsiya s sernokislym kaliyem).

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1958, Vol. 3, Nr 1, pp. 40-45 (USSR)

ABSTRACT: The common crystallization of salts with a formation of anomalous mixed crystals and the cases of the co-precipitation with formation of compounds of internal adsorption (vnutrenne-adsorptsionnye soeyedineniya Pl.) are insufficiently investigated. In the case of the precipitation mentioned in the title the authors assumed (ref. 1,2), based on their work, that the elements mentioned will form compounds of internal adsorption with K_2SO_4. Momentum quantities (impul'snyye kolichestva) of La^{3+}, Ce^{3+} and Am^{3+} are not only captured by the K_2SO_4-deposit forming in the presence of microcomponents but also by coarse-crystalline deposits (table 1). Therefore adsorption and common crystallization were investigated separately. The specific surface of the adsorbent was

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was calculated from the adsorption of the isotope ion K^{42}. The authors found that its magnitude with an adsorbent which is precipitated by quick mixing from a strictly determined supersaturated solution, remains the same and varies within the limits of ± 5 % (table 2). This is proved by the straight dependence of the extent of the adsorption of K42 on the weight of the adsorbent (fig. 1). The elements mentioned form, as we know, with K_2SO_4 difficultly soluble double salts. Their solubility in the K_2SO_4 solution was unknown. The authors isolated them and also determined their composition in addition to their solubility (table 3). Experiments with the adsorption of Ce^{2+} and La^{3+} showed that the absolute quantity of adsorbed ions increases with the concentrations of the elements in the solutions. As is seen from fig. 3 and 4 the percentage of adsorbed Ce^{3+} and La^{3+} is not changed in the concentrations of microcomponents investigated. This proves that the operation is carried out on the straight part of the curve where the adsorption is far off the saturation

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of the surface with the adsorbed ion. Because of the small solubility of the double salt of the microcomponent K_2SO_4 the whole curve cannot be obtained. From table 4 is seen that this phenomenon must not be attributed to a secondary exchange adsorption through the influence of foreign ions. Tables 5-7 give the results of the co-crystallization of the salts mentioned in the title according to Khlopin (ref. 4), namely through the isothermal removal of supersaturation. In order to explain the mechanism of capturing the crystallisation coefficients were calculated according to:

$$D = \frac{x(b-y)}{y(a-x)} \quad \text{and} \quad \ln \frac{x}{a-x} = \lambda \ln \frac{b}{b-y}, \text{ where}$$

D= the distribution coefficient from Khlopin's theorem; a, b correspond to the micro- and macro-components' structure in the solution into crystallization; x, y - are corresponding quantities of micro- and macro-components in the deposit; a-x, b-x = the corresponding concentrations of the latter

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in the solution after the crystallization and λ-the distribution coefficient in the lograithmic formula of Derner-Goskins (Doerner-Hoskins). From the results it appears that La^{3+}, Ce^{3+} and Am^{3+} are taken along into the interior of the K_2SO_4-crystal and there distribute according to a constant crystallization coefficient. The values

$$\lambda_{Ce} = 15, \lambda_{La} = 17 \text{ and } \lambda_{Am} = 42$$

remain constant, independent from the quantity of the solid phase separated. The value of the crystallization coefficient of the microcomponents remains constant between the concentrations $1,6.10^{-6}$ and 3.10^{-10} (fig. 3,4). Each of the three micro-components distributes between the K_2SO_4-deposit and its concentrated solution according to its own and constant distribution coefficient (tables 6,7). According to Khlopin this speaks in favor of a formation of mixed crystals (ref. 4). The dependence of the crystallization

GREBENSHCHIKOVA, V.I.; BRYZGALOVA, R.V.; CHERNYAVSKAYA, N.B.; BOBROVA, V.N.

Cocrystallization of small quantities of substances with crystalline precipitates. Radiokhimiia 1 no.1:11-21 '59. (MIRA 12:4)
(Crystallization)

S/186/60/002/002/017/022
E071/E433

AUTHOR: Bobrova, V.N.

TITLE: On the problem of the existence of double potassium and barium sulphate

PERIODICAL: Radiokhimiya, 1960, Vol.2, No.2, pp.243-245

TEXT: It is well known that alkali metals coprecipitate with barium sulphate, but the views of various investigators on the nature of the coprecipitation differ. In order to investigate the mechanism of the coprecipitation of potassium with barium sulphate it was necessary to establish the possibility of the formation of a double potassium and barium sulphate in saturated solutions of potassium sulphate and to determine its solubility under these conditions. The experimental procedure consisted of adding a solution of barium nitrate to a solution of potassium sulphate. The salt obtained was washed with a saturated potassium sulphate solution in 0.5 N nitric acid. The analysis of the salt obtained was done by two methods: extraction of potassium sulphate from the ignited salt (at 900°C) with hot distilled water and by a wet method in which the content of barium sulphate was determined by a blank experiment and the content of potassium sulphate by

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determining its content in the mother liquor. It was found that the precipitated barium sulphate contained between 5.5 to 6.7% potassium sulphate which cannot be washed out with water. It is assumed that the formation of mixed crystals of $BaSO_4$ and K_2SO_4 takes place. The assistance of V.I.Grebenshchikova is acknowledged. There are 3 tables and 5 references: 2 Soviet-bloc and 3 non-Soviet-bloc. The reference to an English language publication reads as follows:
G.Walton and G.H.Walden, J.Amer.Chem.Soc., 68, 9, 1742 (1946).

SUBMITTED: July 3, 1959

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BOBROVA, V.N.

Determination of the solubility of zirconium and plutonium double sulfates in saturated potassium sulfate solutions by means of radioactive indicators. Radiokhimiia 2 no.3:364-368 '60. (MIRA 13:10)
(Potassium plutonium sulfate) (Potassium zirconium sulfate)

BOBROVA, V.N.

Determination of the solubility of double sulfates of cerium and lanthanum in saturated solutions of potassium sulfate by the use of radioactive tracers. Radiokhimiia 2 no.4:500-504 '60.
(MIRA 13:9)

(Potassium cerium sulfate)
(Potassium lanthanum sulfate)

BOBROVA, V.N.

Concerning the existence of a double sulfate of potassium and barium. Radiokhimiia 2 no.6:243-245 '60. (MIRA 14:4)
(Potassium barium sulfate)

GREBENSHCHIKOVA, V.I.; BOBROVA, V.N.

Coprecipitation of yttrium, zirconium, and barium with potassium sulfate. Radiokhimiia 3 no.4:384-390 '61.

(MIRA 14:7)

(Yttrium compounds)
(Zirconium compounds)
(Barium compounds)
(Potassium sulfate)

GREBENSHCHIKOVA, V.I.; BOBROVA, V.N.

Coprecipitation of cerium and lanthanum with potassium sulfate.
Radiokhimia 3 no.5:377-383 '61. (MIRA 14:7)
(Cerium compounds)
(Lanthanum compounds)
(Potassium sulfate)

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21.4200

AUTHORS: Grebenshchikova, V.I., Bobrova, V.N.

TITLE: Coprecipitation of plutonium and americium with potassium sulphate

PERIODICAL: Radiokhimiya, v.3, no.5, 1961, 544-550

TEXT: A study of the coprecipitation of transuranium elements plutonium$^{(IV)}$ and americium$^{(III)}$ with potassium sulphate is described. Radioactive Pu^{239} and Am^{421} and chemically pure and twice recrystallized potassium sulphate were used for the experiments which were carried out at 20 ± 0.1°C. The study consisted in the determination of the crystallization coefficients of plutonium and americium and their dependence on: 1) rate of crystallization of the solid phase; 2) presence in the solution of other ions (Fe^{3+} and Bi^{3+}); 3) simultaneous presence in the solution of ions of Pu^{4+} and Am^{3+}; 4) concentration of microcomponents within 10^{-5} M - 10^{-9} M for plutonium and 10^{-7} - 10^{-9} M for americium. Two experimental methods were used: isothermal desaturation and partial recrystallization. The relationships obtained, namely the independence of the crystallization coefficients on the proportion of solid and liquid

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phases, rate of crystallization of the solid phase, the presence of other ions and the concentration of the two microcomponents within the investigated range, lead to the conclusion that $Pu^{(IV)}$ and $Am^{(III)}$ form with potassium sulphate anomalous mixed crystals and that there is no lower limit of miscibility during the formation of mixed crystals. It was established that plutonium adsorbed by the precipitated potassium sulphate strongly decreases the rate of its recrystallization (the rate of recrystallization of precipitated potassium sulphate was found by adding radioactive sulphur to the solution). The high values of the crystallization coefficients of plutonium ($\lambda = 30$) and americium ($\lambda = 42$) on their coprecipitation with potassium sulphate makes the use of the latter as a carrier for trans-uranium elements possible. There are 2 figures, 10 tables and 8 references: 7 Soviet-bloc and 1 non-Soviet-bloc. The reference to an English language publication reads as follows: Ref.5: H.Doerner, W.Hoskins, J. Am. Chem. Soc., v.47, 2, 662 (1925).

SUBMITTED: June 12, 1960

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S/186/61/003/005/006/022
E071/E485

AUTHORS: Grebenshchikova, V.I., Bobrova, V.N.

TITLE: On the nature of distribution of $Ce^{(III)}$ between the precipitate and solution of potassium sulphate

PERIODICAL: Radiokhimiya, v.3, no.5, 1961, 551-554

TEXT: It was shown in earlier works (Ref.3: ZhNKh, v.3, 1, 21 (1958)) that on the determination of the crystallization coefficient of cerium by isothermal desaturation, the concentration of cerium in mixed crystals depends on the concentration of acid. In the present paper, some experimental results are reported which confirm that the nature of the distribution of $Ce^{(III)}$ between the precipitate and the solution of potassium sulphate during isothermal desaturation depends on the ability of the solid phase to recrystallize. For this purpose the distribution of $Ce^{(III)}$ (radioactive isotope Ce^{144}, containing less than 1% of active impurities) between the solid and liquid phases was determined at various acid concentrations by isothermal desaturation, partial recrystallization of the solid phase and attainment of equilibrium from "below". By comparing the obtained results of the crystallization coefficients of $Ce^{(III)}$ in 0.5, 1

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and 1.5 N HNO_3 with the data on the velocity of isotopic exchange of K^{42} between the precipitate (mixed crystals, obtained from supersaturated solutions of K_2SO_4, containing $Ce^{(III)}$) and solution (saturated solution of K_2SO_4 in 0.5 N HNO_3) it was established that the ability of the mixed crystals formed to recrystallize governs the nature of distribution of $Ce^{(III)}$. If during the time of precipitation of the mixed crystals the latter can recrystallize, then a homogeneous distribution of cerium takes place; if the precipitate can recrystallize only partially, the logarithmic distribution with lower values of the coefficient of distribution (λ) takes place and if practically no recrystallization of the precipitated crystals occurs, then a non-homogeneous distribution of the microcomponent in the solid phase with a maximum value of λ takes place. It was also established that the value of the coefficient of distribution of $Ce^{(III)}$ between the precipitate and solution of potassium sulphate in 0.1, 1 and 1.5 N nitric acid is independent of the acid concentration ($\lambda = D = 15$). It follows from the data obtained that with the same macrocomponent, the nature of its distribution in a system during isothermal desaturation will depend on the nature of the microcomponent, as the
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recrystallization degree of the precipitate will depend on the solubility of the chemical compounds of microcomponents formed on the surface of the crystals. There are 5 tables and 6 references: 5 Soviet-bloc and 1 non-Soviet-bloc. The reference to an English language publication reads as follows: Ref.4: H.Doerner, W.Hoskins, J. Am. Chem. Soc., v.47, 675 (1925).

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S/186/61/003/006/001/010
E040/E185

AUTHORS: Grebenshchikova, V.I., and Bobrova, V.N.

TITLE: On the form of cerium and lanthanum penetration into the crystals of potassium sulphate.

PERIODICAL: Radiokhimiya, v.3, no.6, 1961, 645-649

TEXT: Results are reported of an investigation designed to prove that double salts with the compositions of $K_5La(SO_4)_4$ and $K_5Ce(SO_4)_4$ are formed during adsorption of Ce^{3+} and La^{3+} ions on the surface of growing K_2SO_4 crystals. For this purpose, the crystallisation coefficients of Ce^{3+} and La^{3+} were determined in the systems of:

$K_5La(SO_4)_4 - Ce^{3+} - K_2SO_4 - 0.5N\ HNO_3$ and $K_5Ce(SO_4)_4 - La^{3+} - K_2SO_4 - 0.5N\ HNO_3$. The method of partial recrystallisation employed in the investigation was described previously (Ref.3: V.I. Grebenshchikova, R.V. Bryzgalova, ZhNKh, v.3, no.1, 36, 1958). Use was made of La^{140} and Ce^{144} radioisotopes. Determination was also made of the distribution coefficients of Ce^{3+} and La^{3+}

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adsorbed on the surface of K_2SO_4 crystals. The proof of the double salt formation is based on the equality between the crystallisation coefficients of cerium, or lanthanum, of the respective double salts and their distribution coefficients on the surface of potassium sulphate crystals. From the experimental results obtained it is concluded that mixed crystals are, in fact, formed by Ce^{3+} and La^{3+} ions with K_2SO_4 and are co-precipitated in the form of double salts of $K_5La(SO_4)_4$ and $K_5Ce(SO_4)_4$ with K_2SO_4.

The method used in the investigation can be used for determining the form of adsorbed compounds in all cases when the chemical compound formed on the surface has a composition different from that of the adsorbent.

There are 7 tables and 4 Soviet-bloc references.

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GREBENSHCHIKOVA, V.I.; BOBROVA, V.N.

Effect of the composition of a complex ion on the value of the coefficient of crystallization. Radiokhimiia 5 no.1:3-8 '63. (MIRA 16:2)

(Complex compounds)
(Crystallization)

GREBENSHCHIKOVA, V.I.; BOBROVA, V.N.

Problem of the coprecipitation of plutonium with potassium sulfate. Radiokhimiia 5 no.1:9-11 '63. (MIRA 16:2)
(Plutonium crystals) (Potassium sulfate)

VDOVENKO, V.M.; IVANOV, I.I.; BOBROVA, V.N.; GAVRILENKO, I.S.; IVANOV, A.I.;
SOLOV'YEV, A.L.; RUMYANTSEVA, L.N.

Possibility of applying 3-(3,4-dihydroxyphenyl)alanine (DOPHA) as a mediator introducing radioisotopes into melanoma. Dokl. AN SSSR 164 no.1:95-98 S '65. (MIRA 18:9)

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