VDOVENKO, V.M.; LIPOVSKIY, A.A.; KUZINA, M.G.

Formation of the complex compound neptunyl trinitrate. Radiokhimiia 2 no.3:312-314 '60. (MIRA 13:10)
(Neptunyl compounds)

20650

S/186/60/002/005/003/017
A051/A130

21.3100

AUTHORS: Vdovenko, V. M.; Krivokhatskiy, A. S.; Gusyev, Yu. K.

TITLE: The extraction of various metal nitrates with mixed solvents

PERIODICAL: Radiokhimiya, v. 2, no. 5, 1960, 531 - 536

TEXT: The present article offers the results obtained in a study of the extraction of micro-quantities of metal nitrates of various valency: cerium, zirconium, niobium and ruthenium. The study was carried out on the extraction of trivalent cerium nitrates, and the other metal nitrates using mixtures of simple oxygen-containing solvents, and on the phenomenon of non-addivity, i.e., the extraction of the nitrates exceeding that of the computed value of extraction, estimated from the assumption of independence of the extraction by each component of the mixture with respect to the presence of the other. The following preparations were used in the experiments: Ce^{144}, Zr^{95}, Nb^{95}, Ru^{106}, of the "non-carrier" grading. Two mixtures were used as the extracting agents, which were extreme with respect to the extraction of the nitric acid and uranyl nitrate, i.e., ex-

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tracting these better than pure solvents individually, dibutyl ether-ββ'--dichlorodiethyl ether, (chlorex) and diethyl ether-acetophenone. Figures 1 - 7 show the results of the experiments, indicating that the investigated mixtures are really non-additive with respect to the extraction of all the mentioned elements, and the values of deviation from the addivity become rather high. The extremeness, however, is only present for the solvent mixtures which extract the given nitrate in the pure form, to about an equal extent. The data showed that the non-addivity (formation of mixed solvates) is characteristic not only for the extraction of the given element by the mixtures of various oxygen-containing solvents (Ref. 1: V. M. Vdovenko, A. S. Krivokhatskiy, ZhNKh, 5, 494, 1960), but also for the extracting of various elements by one mixture, proving the generality of the phenomenon. The possibility of increasing the degree of separation of the elements by selection of the corresponding composition of the extracting agent, as a result of the difference in the shapes of the curves of extraction of the various elements is shown. There are 1 table and 7 figures, 3 references: 2 Soviet-bloc, 1 non-Soviet-bloc, The English language publication reads as follows: (Ref. 2) H. A. C. McKay, Chemistry a. Industry, 51, 154, 1954.

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S/186/60/002/006/008/026
A051/A129

AUTHORS: Vdovenko, V. M.; Yefimova, K. I.; Chaykhorskiy, A. A.

TITLE: An investigation of the complex-formation in non-aqueous solutions
II. The system water-butylacetate-benzene.

PERIODICAL: Radiokhimiya, v. 2, no. 6., 1960, 675 - 681

TEXT: The authors deal with the method for determining the hydration number of the extracted substance in the organic and water phase on the example of the water-butylacetate-benzene system. The possibility is shown by using the general distribution equation in a slightly different form for this purpose. The experimental investigation of the interaction of n-butylacetate with water in an aqueous solution and organic medium within the range of the butylacetate concentration of up to 0.2 M (0.4 %) proves that butylacetate forms with water molecules associates of the BA · H_2O composition at an equilibrium constant equal to 0.99 ± 5 % in benzene and aqueous solution within the given range. The experimental results were treated by the general distribution equation:

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$$a_0 = \frac{C_0}{C_W^n} \qquad (1)$$ and changed to $$a_0 = \frac{C_0^p f_0^p}{C_W^q f_W^q} \qquad (2)$$

where C_0 and C_W are the concentrations of the distributed substance in the organic and water phases, f_0 and f_W the corresponding activity coefficients, p and q the degrees of polymerization of the distributed substance in the organic and water phases. It is assumed that if water forms compounds in both phases with butylacetate, then their compositions would be: in the organic phase: BA $\cdot$ $(H_2O)_x$, in the aqueous phase BA $\cdot$ $(H_2O)_y$. The activity of water in salt solutions was also calculated from table data of osmotic coefficients (Ref. 4: R. A. Robinson, R. H. Stokes. Trans Farad. Soc., 45, 7, 612, 1949 and Ref. 5: R. H. Stokes, Trans. Farad. Soc. 44, 5, 295, 1948). The activity coefficients in the organic phase was calculated from the formula:

$$f_0 = \frac{a_0 a_{(H_2O)_W}}{[H_2O]_0} \qquad (5)$$

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where f_0 is the average activity coefficient of water in the organic phase, $a_{(H_2O)_W}$ the water activity in the aqueous solution, $[H_2O]_0$ the water concentration in the organic phase, a_c the coefficient of (thermodynamic) distribution of water between benzene and water equal to $5.3 \cdot 10^{-4}$. The activity of water in benzene solutions containing 0.216, 0.360, 0.504 and 0.720 M butylacetate was determined in a similar manner. The degree of polymerization of water in the aqueous and benzene phases is the same. These data led to the conclusion that water forms a compound with butylacetate containing one water molecule: in the organic phase $(BA)_x \cdot H_2O$, in the water phase $(BA)_y \cdot H_2O$. Since this conclusion is considered only qualitative, an investigation of the chemical equilibrium taking place in the water and organic phases was made. Assuming that the increase in the water solubility in benzene with an increase of the butylacetate concentration is associated with the formation of the compound $(BA)_n(H_2O)_m$, the following equation is derived:

$$K_0 = \frac{\frac{1}{m}\left(\Sigma H_2O - [H_2O]_0\right)}{[H_2O]_0^n \left[\Sigma BA - \frac{n}{m}\left(\Sigma H_2O - [H_2O]_0\right)\right]^n} \qquad (6)$$

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where ΣH_2O and $[H_2O]_0$ are the general and equilibrium concentrations of water in the organic phase, ΣBA is the general concentration of butylacetate in the organic phase, n and m is the number of molecules of the components, constituting part of the complex. After transformation and taking the logarithm of (6) for the value of n:

$$\lg (\Sigma H_2O - [H_2O]_0) = \lg \Sigma BA + \lg \frac{m K_0 [H_2O]_0^m}{1 + K_0 [H_2O]_0^m} \qquad (7)$$

from where the function is derived:

$$\varphi = \frac{\Sigma H_2O - [H_2O]_0}{\Sigma BA} = \frac{m K_0 [H_2O]_0^m}{1 + K_0 [H_2O]^m} = \text{const.} \qquad (8).$$

At n = 1 the function is a constant value. A method is derived for determining the number of hydration of the organic component in the organic phase for the

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case, when the value of the product $K[H_2O]_0^m \ll 1$: $\varphi_1 = mK_0[H_2O]_{01}^m$, $\varphi_2 = mK_0[H_2O]_{02}^m$. Dividing φ_2 by φ_1 and transforming to logarithms the following equation is derived:

$$m = \frac{\lg \varphi_2 - \lg \varphi_1}{\lg[H_2O]_{02} - \lg[H_2O]_{01}} \qquad (9),$$

where $[H_2O]_{01}$ and $[H_2O]_{02}$ are the equilibrium water concentration in the organic phase for various series of experiments. A similar principle is used to prove the formation of the BA · H_2O compound in an aqueous solution. Using the relation

$$a_{H_2O} = \frac{a(H_2O)_0}{a(H_2O)_W},$$

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$$\alpha_{BA \cdot H_2O} = \frac{a(BA \cdot H_2O)_0}{a(BA \cdot H_2O)_W},$$

$$\alpha_{BA} = \frac{a(BA)_0}{a(BA)_W}$$

where a_{H_2O}, $a_{BA \cdot H_2O}$ and a_{BA} are the distribution coefficient of the corresponding components, the following equation is derived:

$$\frac{\alpha_{BA \cdot H_2O}}{\alpha^m_{H_2O} \cdot \alpha^n_{BA}} K_B = \frac{a(BA \cdot H_2O)_0}{(H_2O)^m_0 (BA)^n_0} \qquad (10),$$

where K_B is the equilibrium constant of $BA \cdot H_2O$ in the aqueous solution. If

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n = 1 and m = 1 as established above, it is concluded that a BA · H_2O compound is formed in the aqueous solution, proven previously from the analysis of the general distribution equation (4). Combining (6) and (10):

$$K_B = K_0 \frac{a_{H_2O} a_{BA}}{a_{BA \cdot H_2O}} \quad (11)$$ or by another method: $$K_B = \frac{\frac{(\Sigma BA)_W}{[BA]_0} \alpha_{BA} - 1}{55.51} \quad (12)$$

and also

$$K_B = \frac{1}{55.51 \frac{(\Sigma BA)_W}{[BA \cdot H_2O]_0}} \quad (13)$$

If a_{BA} or $a_{BA \cdot H_2O}$ are known, K_B can be calculated. There are 2 tables, 4 figures and 5 references: 2 Soviet-bloc and 3 non-Soviet-bloc. The references to the English language publications read as follows: Katzin, L; J. Sullivan,

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S/186/60/002/006/008/026
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An investigation of the complex-formation ...

J. Phys. collid chem., 55, 3, 346, 1951; R. A. Robinson a. R. H. Stokes, Trans. Farad. Soc., 45, 7, 612, 1949; R. H. Stokes Tans. Farad.Soc., 44, 5, 295, 1948.

SUBMITTED: January 20, 1960.

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VDOVENKO, V.M.; KRIVOKHATSKIY, A.S.

Extraction capacity of mixed solvents. Zhur.neorg.khim. 5 no.2: 494-497 F '60. (MIRA 13:6)
(Extraction(Chemistry))

VDOVENKO, V.M.; KRIVOKHATSKIY, A.S.

Extraction of ferric chloride with diisobutyl sulfide. Zhur.neorg. khim. 5 no.3:745-746 Mr '60. (MIRA 14:6)
(Iron chloride)
(Sulfide)

VDOVENKO, V.M., LIPOVSKIY, A.A., NIKITINA, S.A.

Extraction of uranium from HCl solutions by means of tributyl phosphate. Zhur neorg. khim. 5 no.4:935-940 Ap '60. (MIRA 13:7)

(Uranium) (Butyl phosphate)

VDOVENKO, V.M.; KRIVOKHATSKIY, A.S.; CHIZHOV, A.V.

Extraction of chlorides with mixed solvents. Zhur. neorg. khim. 5 no.10:2363-2365 O '60. (MIRA 13:10)
(Chlorides)

VDOVENKO, V.M.; SUGLOBOV, D.N. (Leningrad)

Study of solutions of uranyl salts in organic solvents by means of infrared absorption spectra. Zhur.fiz.khim. 34 no.1:51-56 Ja '60. (MIRA 13:5)
(Uranyl nitrate--Spectra)

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B004/B060

11.1190

AUTHORS: Vdovenko, V. M., Corresponding Member of the AS USSR, Legin, Ye. K., Slebunov, O. B., and Shcherbakov, V. A.

TITLE: Relaxation of Protons in Hydrogen Peroxide Solutions Irradiated With Ultraviolet Light

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3, pp. 645 - 647

TEXT: The present paper deals with the problem of reducing the relaxation time T_1 of protons in aqueous solutions by the effect of ionizing radiation. As a special case, they report on their measurements of T_1 in H_2O_2, where chain reactions take place under the action of ultraviolet light. Initial 30% H_2O_2 was concentrated at 15 - 20 mm Hg. Tests were conducted in quartz ampoules at room temperature. The radiation source was a ПРК-2 (PRK-2) lamp. Fig.1 shows the ratio between relaxation signal A in irradiated H_2O_2 of varying concentration and signal A_0 in non-irradiated H_2O_2

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Relaxation of Protons in Hydrogen Peroxide Solutions Irradiated With Ultraviolet Light

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as a function of time (min). The curves tend toward saturation. The effect of paramagnetism of free radicals should vanish because of their short lifetime, immediately after illumination is stopped. The authors, however, observed an effect persisting for hours. Thus, the effect is caused, not by free radicals, but by products formed under their action. Stirring of irradiated H_2O_2 led to a decrease of signals proportional to the intensity of mechanical action, under the evolution of oxygen. The authors conclude therefrom that the effect observed is caused by dissolved oxygen. The curves in Fig. 1 would then correspond to the degree of O_2 oversaturation at the given H_2O_2 concentration. The authors mention L.L. Dekabrun and A.P. Purmal', and thank Yu. V. Gurikov for a discussion. There are 3 figures and 6 references: 4 Soviet and 2 US.

ASSOCIATION: Radiyevyy institut im. V. G. Khlopina Akademii nauk SSSR (Radium Institute imeni V. G. Khlopin of the Academy of Sciences USSR)

SUBMITTED: June 23, 1960

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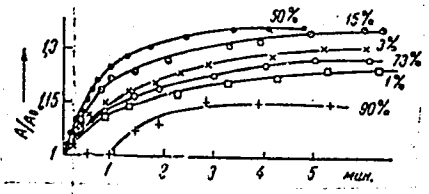

Fig.1

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S/192/61/002/001/005/006
B107/B218

AUTHORS: Vdovenko, V. M., Stebunov, O. B., and Shcherbakov, V. A.

TITLE: Proton relaxation in aqueous solutions of diamagnetic salts

PERIODICAL: Zhurnal strukturnoy khimii, v. 2, no. 1, 1961, 64-65

TEXT: It is of special interest to study solutions of uranyl salts, which the authors have already previously described (Ref. 1: V. M. Vdovenko, V. A. Shcherbakov. Zh. strukt. khimii, 1, no. 1, 28, (1960)). Such a study is of importance not only to gather information on the nature of this ion and its hydrates but also with respect to another question the authors have been dealing with earlier. The method of the present work hardly differs from the one they have described in the first communication of this series. UO_4 was prepared by precipitating it in the cold with hydrogen peroxide from aqueous solutions of uranyl nitrite. After that, UO_4 was dissolved in the corresponding solution. By working with a certain excess of acid, hydrolysis was excluded (the pH of the solution was about 0). The concentration was controlled manganometrically. Only in the case of hydrochloric solutions, the

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gravimetric method was applied. The experimental results are given in the Figure and in the Table. The ratios τ_c^i/τ_c^o were calculated by a method described in communication II. As may be seen from the Figure, the influence of the uranyl ion upon the time of proton relaxation $(1/T_1)$ depends on the nature of the anion. This dependence is confirmed by the values of the molar relaxation shift ΔM, and above all, by the values for τ_c^i/τ_c^o (Table). The latter values are about the same for hydrochloric and nitric solutions, but are much higher for perchloric and sulfuric solutions. The correlation between shift and ratio τ_c^i/τ_c^o for the uranyl ion on one hand and the ionic radii on the other, is of special interest (cf. Table). The most important conclusion drawn by the authors is that the degree of covalence of the bond U - OH_2 does not remain constant, but depends on the nature of the anion in the solution. If one considers the anion capability of complex formation with uranyl then the explanation of the above effect as being due to the formation of covalent bonds ion-anion is rather unconvincing, especially, since the stability of the complexes increases in the order $ClO_4^- < Cl^-$, $NO_3^- \ll SO_4^{2-}$ (Ref. 2: Sammelband "Aktiniden". Redaktion G. Seaborg

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und J. Katz. Izd-vo inostr. lit., M. 1955. Ref. 3: I. I. Lipilina. Uranil i yego soyedineniya (uranyl and its compounds). Izd-vo AN SSSR, M., 1959). The only anion that may possibly enter into a covalent bond with uranyl is sulfate, but not perchlorate. The increase of the molar shift ΔM and of the ratio τ_c^i/τ_c^o for the anions with longer ionic radii leads to the assumption that two competing processes take place in the present case: hydration of uranyl, and its complex formation. It is probable that in these reactions it is not the capability of complex formation with uranyl of the one or the other anion that manifests itself in the measured quantities but the degree of deformation of the hydrate shell of the central ion. This assumption, however, needs a further experimental proof. The authors also point out another important characteristic of the above effect: the probable competition in the reaction of uranyl with water and the anion strongly influences the value τ_c^i/τ_c^o for the respective anion, which means that, even if these quantities can be determined with sufficient accuracy for alkali metals and halide ions, this determination is much more difficult for ions that enter into a covalent reaction with water. Uranyl forms many covalent bindings with water, which greatly influences its values τ_c^i/τ_c^o. There are 1 figure, 1 table, and 3 Soviet-bloc references. [Abstracter's note: This is a full transla-

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Proton relaxation ....

tion from the original.]

ASSOCIATION: Radiyevyy institut AN SSSR im. V. G. Khlopina, Leningrad
(Radium Institute, AS USSR imeni V. G. Khlopin, Leningrad)

SUBMITTED: January 7, 1960

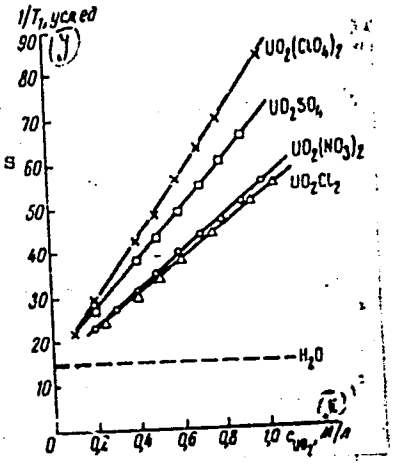

Figure: Change of the time of proton relaxation in solutions of uranyl salts. The signal of a solution of Mn^{2+} (concentration of $4.02 \cdot 10^{-4}$ M/l) is taken to be 100.0. (x) c_{UO_2} in M/l (y) $1/T_1$, arbitrary units

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Legend to the Table: 1) salt; 2) $\Delta M(\pm 0.5)$, arbitrary units; 3) radius of the anion, A.

(1) Соль	(2) Δ_M ($\pm$0.5), усл. ед.	(3) Радиус аниона, А	τ_c^i/τ_c^0
$UO_2(ClO_4)_2$	68,0	2,36	42,2
UO_2SO_4	56,0	2,06	34,5
$UO_2(NO_3)_2$	40,0	1,89	25,1
UO_2Cl_2	38,5	1,81	25,2

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2369

S/186/61/003/001/001/020
A051/A129

AUTHORS: Vdovenko, V.M., Koval'skaya, M.P., Shirvinskiy, Ye.V.

TITLE: Thorium extraction from sulfate solutions using octylamine

PERIODICAL: Radiokhimiya, v 3, no. 1, 1961, 3-6

TEXT: The use of amine-salts as extracting agents is more advantageous than ion-exchanging resins. The purpose of the authors' investigations was to determine the possibility of extracting thorium from acidic sulfate solutions using primary amines, and to investigate the composition of the extracted compound. During the extraction the neutralization of the amine by sulfuric acid takes place according to the equation: $2RNH_2+H_2SO_4 \rightarrow (RNH_3)_2SO_4$ and its salt is distributed between the water and organic phases. Table 1 shows the results of experiments on the relationship of this distribution to the concentration of the sulfuric acid in the water phase. It is seen that with an increase in the concentration, there is a certain tendency toward an increase in the solubility of the amine-salt. The effect of concentration of

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the sulfuric acid and the nature of the solvent on the extraction of micro-quantities of thorium from aqueous solutions with a primary amine was further investigated and the results are shown in Fig.1. It is noted that the distribution coefficient of UX_1 decreases with an increase in the sulfuric acid concentration, and the nature of this relationship is maintained for all three diluents investigated (chloroform, carbon tetrachloride, benzene). The highest extraction of UX_1 is observed when using chloroform. The extraction of thorium from sulfuric acid solutions is expressed by the following formula: $Th^{4+}_{aqu.} + 2SO_{4\,aqu.}^{2-} + n(RNH_3)_2SO_{4\,aqu.} \rightleftarrows n(RNH_3)_2SO_4 \cdot Th(SO_4)_2$ (3), where n is the number of amine sulfate moles bound with one molecule of thorium sulfate, thus,

$$K = \frac{[n(RNH_3)_2SO_4 \cdot Th(SO_4)_2]}{[Th^{4+}] \cdot [SO_4^{2-}]^2 \cdot [(RNH_3)_2SO_4]^n} \quad (4).$$

$$Q = \frac{[n(RNH_3)_2SO_4 \cdot Th(SO_4)_2]}{[Th^{4+}]} \quad (5), \text{ then}$$

replacing Q in equation (4),

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$$K = \alpha \frac{1}{[(RNH_3)_2SO_4]^n \, SO_4^{2-}]^2} \qquad (6),$$

and $\alpha = K_1[(RNH_3)_2SO_4]^n$. If the log of equation (6) is taken, then $\lg \alpha \simeq n\lg[(RNH_3)_2SO_4]$; $n \simeq \frac{\lg}{\lg[(RNH_3)_2SO_4]}$. The experimental data on the study of the effect of the amine concentration on the distribution coefficient of thorium revealed the value of n graphically (i.e., the number of moles of the amine-salt to 1 mole of thorium) for the case of macro- and microquantities extractions of thorium (Figs.2,3). Table 2 shows the experimental data obtained. From these data it is seen that with a change in the concentration of the amine, the ratio between the thorium and sulfate ion in the organic phase actually remains constant and equal to 1:4. The authors draw the following conclusions: 1) it is shown that octylamine sulfate can hardly be extracted with chloroform; 2) it is established that an increase in the sulfuric acid concentration in the aqueous phase brings about a sharp

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Thorium extraction from sulfate solutions...

drop in the thorium distribution coefficient; 3) the existence of a proportionality between the thorium distribution coefficient and amine concentration in the organic phase is proven; two molecules of amine sulfate pass into the organic phase with one molecule of thorium sulfate; 4) a determination is made of the shape of the extracted complex compound $(C_8H_{17}NH_3)_4Th(SO_4)_4$. There are 2 tables, 3 graphs and 8 references: 3 Soviet-bloc, 5 non-Soviet-bloc.

Table 1:

$C_{H_2SO_4}$ (in M)	Content of amine salt in chloroform (in %)
0.11	0.01
0.22	0.01
0.68	0.01
1.20	0.01
1.83	0.02
3.20	0.03
4.45	0.05

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21.3100

AUTHORS: Vdovenko, V.M., Stroganov, Ye.V., Sokolov, A.P.

TITLE: The structural investigation of trihydrate and dihydrate uranyl-nitrate crystals

PERIODICAL: Radiokhimiya, v 3, no. 1, 1961, 19-23

TEXT: The authors have developed a method for taking roentgenograms of the single crystals of hygroscopic substances and have produced $UO_2(NO_3)_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 2H_2O$ crystals. The main characteristics of the uranylnitrate trihydrate and dihydrate lattice have been established. The present article deals with the first half of a study of the aqua-complex compounds of uranyl through the structural investigation of trihydrate and dihydrate of uranylnitrate. The authors prove that uranylnitrate dihydrate belongs to the monoclinic syngony rather than to the rhombic syngony assumed by Vasil'yev (Ref. 5). The $UO_2(NO_3)_2 \cdot 3H_2O$ single crystals were produced according to Colani's method (Ref. 6) by evaporating and cooling uranylnitrate solutions

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containing nitric acid from 36 to 53%. $UO_2(NO_3)_2 \cdot 2H_2O$ single crystals were produced by dissolving finely-crystalline uranylnitrate dihydrate in 98% HNO_3 while heating slightly. Fig 1 is a diagram of the apparatus used for photographing the crystals. Lauegrams and roentgenograms of oscillations were taken using the KPOH-2 (KRON-2), PKB (RKV), PKOП (RKOP) and C-25(S-25) type chambers. Dejongograms were obtained on a roentgenogoniometer according to De Jong. Weissenbergograms were taken on [illegible]K-1 (RGIK-1) and S-55 roentgenogoniometers. Roentgenograms of all types were taken on tubes with copper anticathodes, excepting certain lauegrams taken on silver emission. The computation of the α- and β-angles for the trihydrate of uranylnitrate was conducted by using the dejongograms according to Burger's method (Ref 7) of the "displacement" of planes. Angle γ was computed according to the formula: $\cos\gamma = \cos\alpha \cdot \cos\beta - \sin\alpha \cdot \sin\beta \cdot \cos\gamma$, obtained by studying the elementary triclinal cell and the plane of the reverse lattice normal to the side c. Burger's formula (Ref 7) is said to be more complex. The crystallographic investigations of the dihydrate of uranylnitrate were conducted on a bi-annullar goniometer (Federov). The obtained coordinates of the planes and the corresponding hkl indices are given in table 1. The dimensions of the

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elementary cell $UO_2(NO_3)_2 \cdot 2H_2O$ were obtained from the oscillation roentgenograms. The obtained values characterizing the elementary cells of both investigated crystals are given in table 2. The complete solution of the structures of the two crystals based on the analysis of the reflex intensities using the calculations of Patterson's functions and the electronic density are to be published in a later issue. There are 7 figures, 2 tables and 8 references: 4 Soviet-bloc, 4 non-Soviet-bloc.

Table 1:

Crystallographic symbols and coordinates of the faces of uranylnitrate dihydrate.

hkl	ρ	ϕ
(100)	90°	90°
(1$\bar{1}$0)	30°	90°
($\bar{1}$10)	330°	90°
($\bar{1}$00)	270°	90°
($\bar{1}$10)	210°	90°
(110)	150°	90°
(201)	90°	134°30'
(001)	90°	199°
(2$\bar{2}$3)	9°	143°
(223)	171°	143°

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S/186/61/003/002/008/018
E111/E452

21.3200

AUTHORS: Vdovenko, V.M., Suglobov, D.N. and Mashirov, L.G.

TITLE: Vapour pressure over ethereal solutions of uranyl nitrate

PERIODICAL: Radiokhimiya, 1961, Vol.3, No.2, pp.173-180

TEXT: In view of the wide use of extraction methods in uranium chemistry, considerable interest has recently been shown in the thermodynamic properties of organic solutions of uranyl salts, but few investigations have been carried out. In the present work the vapour pressure of uranyl nitrate dihydrate over the ethereal solution in concentrations up to saturation was determined at 0.3, 15, 20 and 30°C. This salt was chosen since its solution in ether can be regarded as a simple two-component system. Vapour pressure was measured by a static method in the apparatus previously described by V.M.Vdovenko and A.P.Sokolov (Ref.12: Radiokhimiya, 1, 2, 117 (1959)), a glass membrane being used as the null-instrument. Sensitivity was 0.2 to 0.3 mm Hg per mm of scale length. The apparatus was checked with water, acetone and ether. For a measurement, 10 to 15 ml of solution was placed in the apparatus, whose working space was then thoroughly degassed. The membrane

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Vapour pressure ...

vessel was then placed in a thermostat with temperature maintained constant to an accuracy of up to 0.02°C. After equilibrium had been reached, the membrane was brought accurately back to zero position by external pressure, the pressure being measured with a mercury manometer. After the measurement the uranyl nitrate dihydrate concentration in the test liquid was determined by ordinary gravimetric analysis for uranium content. The dihydrate was obtained by drying finely ground hexahydrate over concentrated sulphuric acid. Ether was purified by a standard procedure, dried and distilled. The experimental results are shown by continuous curves in Fig.1 as plots of pressure (mm Hg) against concentration of the dihydrate (mol fraction), curves 1 to 4 relating to temperatures of 30, 20, 15 and 0.3°C, respectively. The straight lines give the ideal (Raoult-law) relationships . Activities were calculated with the normal standard states. The activity coefficient of $UO_2(NO_3)_2.2H_2O$ was found by graphical integration of the Gibbs-Duhem equation and is shown in Fig.2 by continuous curves as functions of concentration (mols per kg of solvent). Curves 1 to 4 relate to 0, 15, 20 and 30°C respectively. Values found by H.A.C.McKay and others were used to plot the

interrupted curve. The curves indicate considerable bonding with ether. The average number of molecules of ether bound to one of the dihydrate n was found from the deviations from the Raoult law. Generally, n increases with increasing concentration and falls with increasing temperature, the highest value of 3.8 being obtained at 0.3°C and 2.0 mols/kg of solvent. These results are not in line with simple solution and indicate that the system is subject to the action of factors not allowed for in the solvation treatment. The authors consider the possibilities of polymerization, an effect which has been reported (Ref.16: A.E.Comyns, B.N.Gathehouse, E.Wait, J.Chem.Soc., 4655 (1958)). Accepting a proposed structure (Ref.15: V.M.Vdovenko, I.G.Suglobova, D.N.Suglobov, Radiokhimiya, 1, 6, 637 (1959)) for the dihydrate, the probable mechanism of polymerization is

$$2\{[UO_2(NO_3)_2 \cdot 2H_2O] \cdot 4(C_2H_5)_2O\} \rightleftarrows \{[UO_2(NO_3)_2 \cdot 2H_2O]_2 \cdot 7(C_2H_5)_2O\} + (C_2H_5)_2O, \quad (2)$$

On the basis of the equilibrium constant K thus obtained, the

Vapour pressure . . .

authors derive an equation for Raoult's law in terms of the equilibrium concentration of the dimer and the dihydrate concentration: the pressure values calculated from this equation are shown by the interrupted curve in Fig.1, the deviation from experimental values above concentrations of 2.5 being due to formation of higher polymers. Better agreement could be obtained if both this further polymerization and also dissociation of solvates were to be allowed for. Other possible dimerization equations result in poorer agreement. For Eq.(2), K rises with rising temperature and the reaction is endothermic, occurring on account of entropy increase. There are 2 figures, 3 tables and 18 references: 10 Soviet-bloc and 8 non-Soviet-bloc. The four most recent references to English language publications read as follows: A.W.Gardner, H.A.C.Mckay, Trans.Farad.Soc., 48, 12, 1099 (1952); H.A.C.Mckay, Chem.Ind., 51, 1549 (1954); T.H.Siddall, J.Am.Chem.Soc., 81, 16, 4176 (1959); A.E.Comyns, B.N.Gathehouse, E.Wait, J.Chem.Soc., 4655 (1958).

SUBMITTED: March 1, 1960

Card 4/5

S/186/61/003/003/008/018
E071/E435

AUTHORS: Chaykhorskiy, A.A., Vdovenko, V.M., Yefimova, K.I. and Belov, L.M.

TITLE: On the Investigation of the Formation of Complexes in Non-Aqueous Solutions. III. The Determination of Thermodynamic Characteristics of Systems: Water-Tributylphosphate-Benzene and Water-Butylacetate-Benzene

PERIODICAL: Radiokhimiya, 1961, Vol.3, No.3, pp.295-301

TEXT: The mechanism of the distribution of water between aqueous and organic phases in the above systems was investigated previously (Ref.6: V.M.Vdovenko, L.M.Belov, A.A.Chaykhorskiy, Radiokhimiya, 1, 4, 439 (1959); and Ref.7: V.M.Vdovenko, K.I.Yefimova and Chaykhorskiy, Radiokhimiya, 2,6,675 (1960)). It was then found that in aqueous and organic phases of the above system, in the range of concentration of the organic component of up to 10%, molecular compounds of the composition TBPh·H_2O and BA·H_2O (TBPh-tributylphosphate; BA - butylacetate) are formed. On the basis of data on the distribution of water between the phases, the equilibrium constants for the above compounds in the organic phase at 20°C were calculated. In the present paper the

On the Investigation of ... S/186/61/003/003/008/018
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results of an investigation of the chemical equilibrium in the organic phase of the above system at 6, 13 and 20°C are reported and, on the basis of these data, complete thermodynamic characteristics of the reaction of formation of $TBPh \cdot H_2O$ and $BA \cdot H_2O$ as well as of the process of distribution of water between water and benzene were calculated. The results obtained indicated that the process of formation of complexes TBPh and BA with water are exothermic, the values of enthalpies are practically equal ($\Delta H^\circ = -3.84 \pm 4\%$ and $-3.13 \pm 6\%$ k cal/mole for $TBPh \cdot H_2O$ and $BA \cdot H_2O$ respectively) while the isobar potentials differ by one order (ΔZ_T - 1.41 ± 2% and 0.0546 ± 3% kcal/mole, respectively) which indicated that the stability of $TBPh \cdot H_2O$ is higher than that of $BA \cdot H_2O$. The process of solution of benzene in water is endothermic ($\Delta H^\circ = 5.19 \pm 6\%$ kcal/mole). The numerical value of the heat of the solution of benzene in water is higher than the heat effect of the reaction of the above complexes. Thus, despite the reaction of formation of complexes being exothermic, the overall process of the solution of water in a benzene solution of TBPh or BA remains endothermic. There are 5 figures, 5 tables and 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc. The four references to

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On the Investigation of ...

S/186/61/003/003/008/018
E071/E435

English publications read as follows: E.Gluecauf, H.A.C.McKay and A.R.Mathieson, Trans.Farad.Soc., 47, 5, 437 (1951);
A.W.Gardner and H.A.C.McKay, Trans.Farad.Soc., 48,12,1099 (1952);
H.A.C.McKay, Trans.Farad.Soc., 47,12,1103 (1952);
T.H.Siddell, J.Am.Chem.Soc., 81,16,4176 (1959).

SUBMITTED: May 16, 1960

Card 3/3

22493
S/186/61/003/003/017/018
E071/E435

21,3200

AUTHORS: Vdovenko, V.M., Lipovskiy, A.A. and Kuzina, M.G.

TITLE: On the Adsorption of Uranyl Nitrate From Organic Solvents With Anion-Exchange Resins

PERIODICAL: Radiokhimiya, 1961, Vol.3, No.3, pp.365-371

TEXT: Strongly basic anion-exchange resins are widely used for separation of simple and complex anions from aqueous solutions. High molecular aliphatic amines are also used for this purpose. At present extraction with amines is considered as an ionic exchange on a liquid anionite. Also, for the extraction it is considered necessary that the element under separation from its aqueous solution is in the state of a complex anion. It is also possible to describe the extraction (and adsorption on a resin) starting from the formation of a non-charged complex, forming with an amine salt, the extractable complex compound. In both cases, after the extraction the same compound is found in the organic phase. An experimental proof of the mechanism of separation related to the formation of a complex compound can be obtained by investigating the separation with anion-exchange resins from solutions which do not contain an excess of anions and in which the

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element under separation is known to exist in the form of a neutral complex. For this purpose, the authors investigated the separation of uranyl nitrate from a number of organic solvents on an anion-exchange resin AM, the capacity of which in respect of NO_3^- ion was 2.9 mg-equiv. per 1 g of resin. A weighed sample of the resin (1 g) in NO_3^- form was shaken with 10 ml of a solution of uranyl nitrate dihydrate for 20 to 25 hours. Previously it was established that this time is sufficient to attain equilibrium. Uranium was washed out from the resin with 0.1 N nitric acid and analysed colorimetrically. The analysis of the equilibrium liquid phase was also carried out. In experiments on the separation of uranium from organic extracts, air dried resin was used, in all other cases it was dried at 70°C. The coefficients of distribution of uranium between resin and organic solvents were calculated from the formula: K_p(mg U/g resin) / (mg U/ml solution). Data on the adsorption of uranium from 16 different solvents by dried resin were obtained. The results indicate that adsorption of uranylnitrate depends on the nature of the solvent. As the stability of uranyl trinitrate complex depends on the content of water in the organic phase, the influence of the latter on the

On the Adsorption of Uranyl ...

separation process was also investigated. It appears that the change in the dielectric constant of the solution due to an addition of water cannot explain the difference in the degree of adsorption and some change in the resin phase should be assumed. The presence of maximum on the adsorption curves at a certain content of water in the solution could be explained by the fact that at a certain water concentration, its presence leads to dissociation of the formed uranyl trinitrate complex. The influence of the concentration of the uranium in solution on its adsorption on the resin was also investigated. It was found that the coefficient of distribution (K_p) is inversely proportional to the uranium concentration. Thus at low concentrations, uranium can be particularly well separated from organic solvents. From the resin, uranium can be easily extracted with 0.1 N nitric acid, the desorption can also be done with tributylphosphate. On the basis of the results obtained, it is concluded that adsorption of uranylnitrate on resin can be related to the formation of complexes with the resin. There are 2 figures, 2 tables and 11 references: 2 Soviet-bloc and 9 non-Soviet-bloc. The four

most recent references to English language publications read as follows: L.Kaplan, R.A.Hildebrandt, M.Ader, J.Inorg.Nucl.Chem., 2,153 (1956); J.Kennedy, R.V.Davies, J.Inorg.Nucl.Chem., 12,193 (1959); W.Gerrard, E.D.Macklen, Chem.Rev., 59,1105 (1959); C.W.Davies, B.D.R.Owen, J.Chem.Soc., 1676 (1956).

SUBMITTED: July 5, 1960

26602
S/186/61/003/004/001/007
E141/E164

21.4200

AUTHORS: Vdovenko, V.M., Lipovskiy, A.A., and Nikitina, S.A.

TITLE: On the mechanism of the extraction of tetravalent plutonium with primary alkylamine from H_2SO_4 solutions

PERIODICAL: Radiokhimiya, 1961, Vol.3, No.4, pp. 396-402

TEXT: Extraction with high molecular weight aliphatic amines has recently found wide application. C.F. Coleman, K.B. Brown, J.G. Moore and K.A. Allen (Ref.1: Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy,) have described the extraction of U^{IV}, Th^{IV}, Ce^{IV} and Zr^{IV} from H_2SO_4 solutions, but they do not give any data on the mechanism of the reaction. The authors investigated this reaction mechanism. The authors used a mixture of primary aliphatic amines consisting of C_7 - C_9 atoms (d = 0.7846), the amount not exceeding 0.5%; chloroform was used as organic solvent. The Pu^{IV} content in the aqueous and the organic phase was determined by measuring the α-activity of aliquot samples on a standard device type D. Pu^{IV} was re-extracted from the organic phase into a 1.5N HNO_3 solution. Preliminary experiments showed that equilibrium was attained in not

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more than five minutes. The concentration of the amine in the starting solutions was determined by titrating with acid in an alcoholic solution whilst using bromophenolblue as indicator. After extraction the amine content in the aqueous and organic phase can be determined with alkalized solutions when the amine is converted into the base. The concentration of nitrate-ions in the organic phase was determined after re-extraction by titrating with indigo-red (Ref.6: J. Ungar, J. Appl. Chem., Vol.6, 2, 245 (1956)). The sulphate-ion was determined gravimetrically as $BaSO_4$ and in some cases after β-irradiation with S^{35} whilst using tagged H_2SO_4. When determining the distribution of the amine between the chloroform and the aqueous H_2SO_4 solution, the sulphate was found mainly in the aqueous solution. The coefficients of distribution of plutonium (α) increase with increasing concentration of the amine and of H_2SO_4 in the aqueous solution. This is possibly due to the formation of complex sulphate compounds of Pu^{IV} containing the amine. The composition of the separated compound was determined by investigating the dependence of $\alpha_{Pu(IV)}$ on the concentration of the amine at constant concentration of Pu^{IV} and H_2SO_4. It was found that two moles of amine nitrate

associate with one mole of the metal nitrate, forming the compound $(R_3NH)_2\ Me\ (NO_3)_6$, where R = alkyl radical. The amine sulphate is not extracted by chloroform. The composition of the complex compounds extracted from H_2SO_4 solutions and from nitrate-sulphate solutions was confirmed by extraction and with the aid of absorption spectra. On the basis of concept on the anion-exchange character of extraction processes, carried out with amines, the separation of Pu^{IV} from H_2SO_4 solutions can be envisaged as a sulphate-ion exchange on an anion complex of Pu^{IV} which is formed in the aqueous phase:

$$Pu^{4+} + 3SO_4^{2-} \rightleftarrows Pu(SO_4)_3^{2-} ,$$

$$2(RNH_3)_2SO_4 + Pu(SO_4)_3^{2-} \rightleftarrows (RNH_3)_4Pu(SO_4)_4 + SO_4^{2-} \qquad (1)$$

The extraction can also be described by the formation of neutral plutonium sulphate which is formed from the amine sulphate of the extracted complex compound:

$$Pu^{4+} + 2SO_4^{2-} \rightleftarrows Pu(SO_4)_2 \quad ;$$

$$2(RNH_3)_2SO_4 + Pu(SO_4)_2 \rightleftarrows (RNH_3)_4Pu(SO_4)_4 \qquad (2)$$

Pu^{IV} is known to form complex sulphate compounds even when a considerable excess of nitrate-ions is present in the solution (Ref.5: A.A. Lipovskiy, N.B. Chernyavskaya, ZhNKh, Vol.4, 10, 2244 (1959)). Experiments were therefore carried out on the extraction of plutonium from a mixture of HNO_3 and H_2SO_4 solutions. At low concentrations of the amine the nitrate is hardly extracted by chloroform but with increasing concentration polymeric amine aggregates are formed which are extracted by the organic solvent. An increase in the concentration of HNO_3 in the aqueous solution at constant concentration of the amine leads to an increased content of the amine nitrate in the organic phase. Colloidal solutions of amine nitrate in chloroform show a different behaviour on extraction with respect to ions which are present in the aqueous solution and experiments were carried out to investigate the behaviour of the sulphate-ion during extraction from nitrate-sulphate solutions. When the concentration of HNO_3, and therefore

also of the amine nitrate in the solution was small, the amine sulphate was not extracted into the chloroform. Deposits were formed at the phase boundary as well as during extraction from pure H_2SO_4 solutions. At concentrations of approximately 0.15N HNO_3 the deposits disappear and the concentration of the sulphate-ion in the organic phase increases sharply. A gradual substitution of the sulphate-ions and nitrate-ions takes place during the later stages. It is also suggested that the amine sulphate is separated from the nitrate-sulphate solutions because a finely dispersed phase is present in the chloroform, the dispersion being formed by the amine nitrate. Acknowledgments are expressed to L.N. Lazarev for his cooperation.

There are 5 figures, 2 tables and 7 references: 2 Soviet and 5 non-Soviet. The 4 English language references read as follows:

Ref.1: as in text above.
Ref.3: A.S. Wilson. Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy.
Ref.6: As in text above.
Ref.4: D.J. Carswell, J.J. Laurenset. J.Inorg.Nucl.Chem., V.11, 1, 69 (1959)

Card 5/5. SUBMITTED July 5, 1960.

VINOGRADOV, V.M.; KOVALENKO, P.N.; FILIPOVA, Ye.I.

Extraction of nitric acid and uranyl nitrate with tri-n-nonylamine and tri-n-octylamine from aqueous solutions.
Radiokhimiia 3 no.4:403-410 '61. (MIRA 14:7)
(Nitric acid)
(Uranyl nitrate)
(Amines)

VIKOVENKO, V.I.; [illegible]

Study of complexing in nonaqueous solutions. Part 5: Ionization of triethylamine nitrate in benzene. Radiokhimiia 3 no.4:447-454 '61. (MIRA 14:7)
(Complex compounds)
(Amines)

31669
S/186/61/003/005/007/022
E071/E485

21.4200

AUTHORS: Vdovenko, V.M., Lipovskiy, A.A., Kuzina, M.G.

TITLE: The extraction of uranium (VI) with solutions of trioctylamine nitrate

PERIODICAL: Radiokhimiya, v.3, no.5, 1961, 555-566

TEXT: The extraction of uranium (VI) with solutions of trioctylamine (TOA) in various diluents (carbon tetrachloride, benzene, trichloroethylene, chloroform, chlorobenzene, bromobenzene, tetrachloroethane, dichloroethane, butylbromide and nitro-benzene) and the dependence of the separation of uranium with an anion exchange resin AM on the composition of the aqueous solution were investigated. Equal volumes of the phases were used for the extraction. The coefficient of distribution was calculated from $\alpha_u = C_o/C_w$ where C_o and C_w - equilibrium concentrations of uranium in organic and aqueous phases. The re-extraction of uranium was done with a soda solution which was subsequently used for the colorimetric determination of uranium. In experiments on the separation of uranium with a resin, a strongly basic resin AM was used, its capacity in respect of NO_3^- was 2.9 mg/equiv per 1 g of air-dried resin. The coefficients of distribution were

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calculated from

$$k_p = \frac{\text{g U/g resin}}{\text{g U/ml of solution}}$$

The composition of extracted compounds was determined by the absorption spectra. It was shown that the lack of correspondence in data obtained by various methods on the determination of the composition of uranium compounds in the organic phase is due to changes in the nature of the association of amine nitrate caused by the extraction of excess nitric acid. In all the cases investigated the extraction of uranium with TOA nitrate is related to the formation of a complex compound of uranyltrinitrate. The dependence of the coefficients of distribution of uranium on the composition of aqueous solution indicates that the formation of uranylnitrate molecules is necessary for the extraction of uranium. The extraction of uranium with TOA solutions in various diluents can be represented as a process of complex formation between neutral molecules of uranylnitrate and molecules of aminenitrate. The sorption of uranium with anion exchange resins can be described similarly. The analogy between the extraction of uranium with amines and its extraction with oxygen containing solvents from

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X

nitric acid solutions as well as from solutions containing salting-out agents was pointed out. Changes in the extracting properties of TOA nitrate in various diluents is related to the polar properties of the diluents used and interactions in the system extracting agents-diluent. There are 4 figures, 3 tables and 20 references: 12 Soviet-bloc, 2 Russian translations of non-Soviet publications and 6 non-Soviet-bloc. The four most recent references to English language publications read as follows: Ref.4: W.E.Keder, J.C.Sheppard, A.S.Wilson, J. Inorg. Nucl. Chem., 12, 314, 327 (1960); Ref.6: D.J.Carswell, J.J.Lawrence, J. Inorg. Nucl. Chem., v.111, 69 (1959); Ref.17: J.K.Foreman, J.R.McGowen, T.D.Swith, J.Chem. Soc., 738 (1959); Ref.18: A.G.Gobbe, A.G.Maddock, J. Inorg. Nucl. Chem., v.7, 2, 94 (1958).

SUBMITTED: October 27, 1960

X

31894
S/186/61/003/005/018/022
E111/E185

21.4300

AUTHORS: Vdovenko, V.M., Sugobov, D.N., Artem'yev, V.I., and Suglobova, I.G.

TITLE: Reaction of uranyl nitrate with amines

PERIODICAL: Radiokhimiya, v.3, no.5, 1961, 636-637

TEXT: Amines are used for extraction of uranium salts from acid solution . Extraction conditions have been studied sufficiently thoroughly, but not the reaction of amines with pure uranium salts. The authors give a brief account of their experiments on the reaction of hydrated uranyl nitrate with mono-, di- and tri-octyl amine in chloroform, benzene and ethyl ether. Chemical analyses as well as infrared and visible spectra indicate that when adding uranyl nitrate to a solution of tri-octyl amine in chloroform the following reaction occurs:

$$nUO_2(NO_3)_2 \cdot 2H_2O_S + m(C_8H_{17})_3N_{solution} = m(C_8H_{17})_2NH\left[UO_2(NO_3)_3\right]_{sol.}^{+}$$
$$+ \left[(UO_2)_{n-m} \cdot (NO_3)_{2n-3m} \cdot (OH)_m \cdot (H_2O)_{2n-m}\right]_S$$

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3189h
S/186/61/003/005/018/022
E111/E185

Reaction of uranyl nitrate with amines

Treating $UO_2(NO_3)_2 \cdot 2H_2O$ with an excess of amine solution a precipitate with an uranium content on drying slightly less than that corresponding to $UO_2(OH)_2$ is obtained, perhaps through formation of $(C_8H_{17})NH^+$ cation. Reactions with mono- and di-amines in chloroform and all the amines in benzene are similar, a peculiarity of the latter being the easy appearance of two layers at the slightest reduction in temperature. Mixing of ethereal solutions of uranyl nitrate and the mono-octyl amine gives almost complete separation of uranium. Chemical analysis of the precipitate and supernatant liquid indicated that the nitrate in ethereal solution is in the form of mono-octyl ammonium nitrate, the reaction being

$$UO_2(NO_3)_2 \cdot 2H_2O_{solution} + 2(C_8H_{17})NH_2 \text{ solution} =$$

$$= C_8H_{17}NH_3NO_3 \text{ solution} + UO_2 \cdot NO_3 \cdot C_8H_{17}NH \cdot 2H_2O_s$$

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S/186/61/003/005/018/022
E111/E185

Reaction of uranyl nitrate with amines.

The mixed uranyl mono-octyl amide-nitrate is a new compound. Variations in its composition are attributable to impurities. The vibration spectrum of uranyl amidonitrate indicated that the nitrate group of this compound is coordinated to uranium. The reaction with the tri-octyl amine fails to give a precipitate but gives increased coloration which, since this amine has no active proton, indirectly confirms the above mechanism.
There are 3 references: 2 Soviet-bloc and 1 Russian translation of non-Soviet publication.

SUBMITTED: July 5, 1961

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X

VDOVENKO, Viktor Mikhaylovich; MATVEYEVA, A.V., red.; POPOVA, S.M., tekhn.red.

[Scientific studies of Academician V.G.Khlopin]Akademik V.G. Khlopin; nauchnaia deiatel'nost'. Moskva, Gosatomizdat, 1962. 126 p. (MIRA 16:1)

1. Chlen-korrespondent Akademii nauk SSSR (for Vdovenko).
(Khlopin, Vitalii Grigor'evich, 1890-1950)

VDOVENKO, V.M.; PAVLOVA, L.L.; SHCHERBAKOV, V.A.

Relaxation of F^{19} in paramagnetic solutions. Zhur.strukt.khim. 3 no.6:707-709 '62. (MIRA 15:12)

1. Radiyevyy institut imeni V.G.Khlopina AN SSSR.
(Fluorine—Isotopes)
(Paramagnetic resonance and relaxation)

34623
S/186/62/004/001/002/008
E075/E436

21.4200

AUTHORS: Vdovenko, V.M., Kovaleva, T.V., Potapov, V.G.

TITLE: Salting-out action of nitrates of the metals in the second group of the periodic system of elements during extraction of uranyl nitrate with diethylether

PERIODICAL: Radiokhimiya, v.4, no.1, 1962, 34-39

TEXT: The authors determined distribution coefficients for uranyl nitrate between diethylether and aqueous solutions containing metal nitrates to obtain more accurate data than those available at present. Experiments were carried out at 0, 15 and 25°C. Concentration of uranyl nitrate was 0.0254 g equiv per 100 g of solution. The results obtained show that the values of distribution coefficients for the solutions containing Zn, Cd and Sr nitrates differ considerably from those published previously by V.M.Vdovenko and T.V. Kovaleva (Ref.6 and 7). This is explained by the use of a more satisfactory method of analysis and also by the fact that in the previous determinations, with Zn, Cd and Sr nitrates as salting-out agents, the water of crystallization in these compounds was not taken into account. For Ca and Mn

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Salting-out action of nitrates ...

nitrates the distribution coefficients obtained in the present work were similar to those determined previously (Ref.6 and 7) with the exception of the values at high concentration regions of the salts. The disagreement in the latter case is, however, within the experimental error. The distribution coefficients for the solutions containing Li, Na, K, NH_4, Fe and Al nitrates agree with those published previously (Ref.6 and 7). It was shown that at the different temperatures the effectiveness of the salting out action of the nitrates decreases in the following order:

$$Mg(NO_3)_2 > Zn(NO_3)_2 > Cd(NO_3)_2 > Ca(NO_3)_2 > Sr(NO_3)_2 > Ba(NO_3)_2$$

The radii of the cations in the above salts increase in the same order. It was shown that for the metals in the major and minor sub-groups of the second group in the periodic system the distribution coefficients depend on the radius of the cation of a salting-out compound. The distribution coefficients for the solutions containing Zn and Cd nitrates were checked at 0 C for the molar fractions of the salts of 0.04. The results obtained agree well with those extrapolated from the curves relating

Salting-out action of nitrates . . .

distribution coefficients to concentration of salting out agents. The dependence of the distribution coefficient on the cation radii indicated that the salting-out effectiveness of the metal nitrates in the Zn sub-group is greater than that for the metals in the major sub-group. There are 6 figures and 2 tables.

SUBMITTED: July 22, 1961

Card 3/3

VDOVENKO, V.M.; STROGANOV, Ye.V.; SOKOLOV, A.P.; LUNGU, G.

Structure of uranyl nitrate dihydrate. Radiokhimia 4 no.1:59-66 '62. (MIRA 15:4)

(Uranyl nitrate)

VDOVENKO, V.M.; SUGLOBOVA, I.G.; MEZEI, M.

Mutual solubility in the system uranyl nitrate - water - isopropyl ether. Radiokhimia 4 no.4:388-392 '62. (MIRA 15:11)

(Uranyl nitrate) (Isopropyl ether) (Solubility)

S/186/62/004/005/007/009
E075/E135

AUTHORS: Vdovenko, V.M., Kovaleva, T.V., and Ryazanov, M.A.

TITLE: The formation of a second organic phase during extraction of uranyl nitrate with trioctylamine solutions in carbon tetrachloride

PERIODICAL: Radiokhimiya, v.4, no.5, 1962, 609-610

TEXT: The authors observed the formation of two organic phases during extraction of uranyl nitrate from 1 N HNO_3 with 0.185 M trioctylamine (TOA) in CCl_4 at 25 °C. The phenomenon occurred only for uranyl nitrate concentrations > 1.5 M in the equilibrium aqueous phase. With increasing concentration of $UO_2(NO_3)_2$, the concentrations of U and the amine increase in the second organic phase and decrease correspondingly in the first phase. At the same time the ratio $C_{TOA}/C_{UO_2(NO_3)_2}$ decreases in the second phase, indicating an enrichment in the U content. Thus the formation of two organic phases is not connected only with a limited solubility of the solvate forming during the

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extraction, but is a more complex process. Study of this phenomenon continues.
There is 1 table.

SUBMITTED: April 2, 1962

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S/186/62/004/005/008/009
E075/E135

AUTHORS: Vdovenko, V.M., Koval'skaya, M.P., and Smirnova, Ye.A.

TITLE: Extraction of hydrofluoric acid and uranium fluoride with tri-n-nonylamine solution in benzene

PERIODICAL: Radiokhimiya, v.4, no.5, 1962, 610-611

TEXT: The distribution of HF and UF_6 between aqueous solutions and tri-n-nonylamine (TNA) in benzene was studied. This follows the authors' previous work (Radiokhimiya, v.3, no.4, 1961, 403) on the extraction of mineral acids and U salts with TNA and tri-n-decylamine in benzene. The content of HF in the organic phase decreases markedly with its increasing concentration in the aqueous phase. On extraction of HF from 16-24 M solutions the organic phase contains 4 moles of the acid per mole of the amine. The transfer of water to the organic phase together with HF indicates that the amine salt is hydrated. The distribution coefficient of $U^{(VI)}$ decreases with a negligible increase of the acid concentration in the aqueous phase. On extraction from 10 M acid with 0.3 M amine the distribution coefficient decreases with the increasing concentration of $U^{(VI)}$ in the original solution,

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Extraction of hydrofluoric acid and ... S/186/62/004/005/008/009
E075/E135

due to a lowered concentration of the free amine.
There are 4 tables.

SUBMITTED: April 9, 1962

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S/186/62/004/006/001/009
E075/E433

AUTHORS: Vdovenko, V.M., Lipovskiy, A.A., Nikitina, S.A.

TITLE: On the mechanism of extraction of $U^{(VI)}$ with solutions of tridecylamine fluoride

PERIODICAL: Radiokhimiya, v.4, no.6, 1962, 625-632

TEXT: In order to elucidate the mechanism of the extraction process, some relationships in the extraction of $U^{(VI)}$ from solutions in HF and NaF with tridecylamine fluoride (TDA) were studied. Using a spectrographic method it was shown that in organic solutions complex compounds $TDAHUO_2F_3$ and $(TDAH)_2UO_2F_4$ are formed. The composition of the complex compounds was also determined from the results of the analysis of equilibrium organic solutions and construction of the dependence $\lg \alpha_U$ on $\lg C_{TDA \cdot HF}$ (where α_U - the coefficient of distribution of uranium). It was shown that complex compounds with the ratio $F/U > 4$ were not formed. The investigation of the extraction of uranyl fluoride from aqueous solutions with tridecylamine fluoride indicated that the extraction takes place due to the formation of complexes of UO_2F_2 with one or two molecules of TDA·HF. The

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On the mechanism ...

S/186/62/004/006/001/009
E075/E433

best removal of $U^{(VI)}$ with amine fluoride is obtained on extraction from solutions of UO_2F_2 not containing an excess of fluorine ions. There are 5 figures and 7 tables.

SUBMITTED: August 26, 1961

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VDOVENKO, V.M.; SUGLOBOV, D.N.; ROMANOV, G.A.

Structure of $UO_2(NO_3)_2 \cdot 2NO_2$. Dokl. AN SSSR 146 no.5:1078-1080 O '62. (MIRA 15:10)

1. Chlen-korrespondent AN SSSR (for Vdovenko)
(Uranyl nitrate) (Nitrogen oxide)

S/186/63/005/001/006/013
E075/E436

AUTHORS: Vdovenko, V.M., Mashirov, L.G., Blokhina, V.K., Suglobova, I.G., Suglobov, D.N.

TITLE: Mutual solubility in the systems uranyl perchlorate-water-diethyl ether and uranyl perchlorate-water-di-n-butyl ether at 25°C

PERIODICAL: Radiokhimiya, v.5, no.1, 1963, 80-89

TEXT: The work was carried out in view of insufficient knowledge on the solubilities in organic solvents of U salts other than $UO_2(NO_3)_2$. Different hydrates of $UO_2(ClO_4)_2$ and the anhydrous salt were prepared by dissolving pure UO_3 in $HClO_4$ and drying. In the system $UO_2(ClO_4)_2$-H_2O-diethyl ether the critical point on the layer separation curve occurs at 25% $UO_2(ClO_4)_2$ and 5% H_2O. The aqueous and ethereal branches of the distribution curve merge. The effect of hydration on the solubility of the salt is negligible and the solubility of the anhydrous salt in ethyl ether is 35%. The salt begins to dissolve in aqueous ethereal solutions only when their H_2O content is less than 15% and the ether content of H_2O is more than 50%. The salt dissolves in H_2O -ether in the form of hydrates. Ethyl ether is

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highly soluble in concentrated aqueous $UO_2(ClO_4)_2$ solutions, the solubility increasing sharply at about 43% salt content. In n-butyl ether the concentration of $UO_2(ClO_4)_2$ in contact with its saturated H_2O solution is 0.6%. The maximum solubility in the ether is 50.5%. The solubility of the anhydrous salt in ether is 3.7%. The degree of hydration of $UO_2(ClO_4)_2$ at the point of separation of layers is 4.7 and 4.8 in ethyl- and butyl-ether respectively. This suggests that the coordination number of U in the solutions is 5. The value is supported also by the composition of crystallo-solvates and the composition of the $UO_2(ClO_4)_2$ antipyrene complex obtained by E. Wilke-Dorfurt and O. Shliephake (Z. anorg. allgem. Chem., v.170, 1-2, 1928, 129). The following solid phases were identified in the system perchlorate - water - diethyl ether: $UO_2(ClO_4)_2$ with 7, 5 and 3 molecules of H_2O, $UO_2(ClO_4)_2 \cdot H_2O \cdot 4(C_2H_5)_2O$, $UO_2(ClO_4)_2 \cdot 3(C_2H_5)_2O$. In the system with dibutyl ether the solid phases were: $UO_2(ClO_4)_2$ with 7, 5 and 3 molecules of H_2O and $UO_2(ClO_4)_2 \cdot 2(C_4H_9)_2O$. There are 4 figures and 2 tables.

SUBMITTED: November 2, 1961
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VDOVENKO, V.M.; STROGANOV, Ye.V.; SOKOLOV, A.P.

Structure of uranyl nitrate trihydrate. Radiokhimiia 5 no.1:97-103 '63. (MIRA 16:2)
(Uranyl nitrate crystals)

VDOVENKO, V.M.; ROMANOV, G.A.; SHCHERBAKOV, V.A.

Hydrolysis of a $U^{(IV)}$ ion. Radiokhimiia 5 no.1:137-138 '63. (MIRA 16:2)

(Uranium compounds)
(Hydrolysis)

S/186/63/005/001/011/013
E075/E436

AUTHORS: Vdovenko, V.M., Lipovskiy, A.A., Nikitina, S.A.

TITLE: Investigation of the solvation of uranyl chloride with the molecules of tri-n-butyl phosphate

PERIODICAL: Radiokhimiya, v.5, no.1, 1963, 139-141

TEXT: Spectroscopic methods were used to investigate the nature of UO_2Cl_2 added to a solution of tri-n-butylphosphate (TBP) in CCl_4. In the original solution (saturated solution of anhydrous UO_2Cl_2 in TBP dissolved in CCl_4) the solute had the composition of $UO_2Cl_2 \cdot 2TBP$. As the proportion of TBP increased (100% TBP), the UV spectra of the solutions changed and indicated that UO_2Cl_2 coordinates with 3 molecules of TBP. The equilibrium constant for the formation of $UO_2Cl_2 \cdot 3TBP$ is 3.1 ± 0.2. The interaction of P = O groups with the U atom was shown in infrared spectra to be less strong in $UO_2Cl_2 \cdot 3TBP$ than in $UO_2Cl_2 \cdot 2TBP$. The complex with 4 molecules of TBP did not form, presumably due to steric hindrance. There are 3 figures and 1 table.

SUBMITTED: October 31, 1962

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L 17579-63 EWP(q)/EWT(m)/BDS AFFTC/ASD/ESD-3 RM/JD/JW/ES/JG

ACCESSION NR: AP3005230 S/0089/63/015/002/0168/0169

AUTHORS: Vdovenko, V. M.; Romanov, G. A.

TITLE: Stability of fluoro-complexes of tetravalent uranium

SOURCE: Atomnaya energiya, V. 15, no. 2, 1963, 168-169

TOPIC TAGS: uranium, fluorine, aluminum, fluorine-uranium complex

ABSTRACT: The authors investigated the relationship between the inverse of the relaxation time T_1 of aqueous solutions of U(IV) in 2N $HClO_4$, and the concentration of fluorine ion in the presence of an aluminum ion. At a low concentration of fluorine ion, there is an interaction between fluorine and U(IV), i.e., $1/T_1$ is increasing. When all uranium(IV) is in the form UF^{3+}, the complex AlF^{2+} begins to form; $1/T_1$ remains constant, as the magnetic properties of the solution do not change. When all Al^{3+} is in the form AlF^{2+}, UF_2^{2+} starts to form, and $1/T_1$ decreases. Authors conclude that the instability constants of the fluorine complexes U(IV) and Al(III) can be ordered in the following series

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$$K_{UF^{3+}} < K_{AlF^{2+}} < K_{UF_2^{2+}} < K_{AlF_2^{+}}$$

$$7\times10^{-8} \quad 7.4\times10^{-7} \quad 5.5\times10^{-6} \quad 9.5\times10^{-6}$$

These results are in agreement with the published data. Orig. art. has: 1 fig.

ASSOCIATION: none

SUBMITTED: 14Nov62 DATE ACQ: 06Sep63 ENCL: 00

SUB CODE: PH NO REF SOV: 000 OTHER: 000

Card 2/2

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)

1. Radiyevyy institut im. V.G. Khlopina i Voyenno-meditsinskaya akademiya im. S.M. Kirova. 2. Chlen-korrespondent AN SSSR. (for Vdovenko).

VDOVENKO, V.M.; LIPOVSKIY, A.A.; NIKITINA, S.A.; YAKOVLEVA, N.Ye.

Extraction of $U^{(IV)}$ and $U^{(VI)}$ from hydrochloric solutions by means of tri-n-butyl phosphate. Radiokhimiia 7 no.5:509-516 '65.
(MIRA 18:10)

VDOVENKO, V.M.; RYAZANOV, M.A.

Activity coefficients in multicomponent systems. Part 3: Calculation of the activity coefficients of uranyl nitrate in aqueous solutions of magnesium, calcium, strontium, and zinc nitrates. Radiokhimiia 7 no.5:545-553 '65. (MIRA 18:10)

L 14698-66

ACC NR: AP6008247 SOURCE CODE: UR/0089/65/019/005/0433/0437

AUTHOR: Vdovenko, V. M.; Gurikov, Yu. V.; Legin, Ye. K.

63
13

ORG: none

TITLE: Cation hydration in heavy water

SOURCE: Atomnaya energiya, v. 19, no. 5, 1965, 433-437

TOPIC TAGS: heavy water, hydration, cation, enthalpy, aqueous solution, alkali metal, halide, free energy, chemical kinetics

ABSTRACT: An account is given of the use of the molecular-kinetic description of the two-layer model of hydration for the analysis of the isotopic differences of the free energy and enthalpy of solution in water and heavy-water solutions of alkali metal halides. The lifetime and distribution density of water molecules in the layer of secondary hydration are examined. It is shown that in heavy-water solutions dehydration of the ions occurs. It is established that the difference of free energy and enthalpy of solution in light and heavy water should increase with an increase of the cation radius, i.e., from Li^+ to Cs^+. The results obtained agree with experimental data. [NA]

SUB CODE: 07, 18, 20 / SUBM DATE: 28Jan65 / ORIG REF: 009 / OTH REF: 008

BVK

UDC: 542.934:546.212.02

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VDOVENKO, V.M.; BULYANITSA, L.S.

Distribution of alkali metal halides between aqueous solutions and organic solutions of iodine. Part 3: Distribution of alkali metal iodides between aqueous solutions and iodine solutions in mixtures of nitrobenzene and nitromethane with low polar diluents. Radiokhimiia 6 no.6:666-676 '64.

(MIRA 18:2)

VDOVENKO, V.M.; KOVAL'SKAYA, M.P.; SMIRNOVA, Ye.A.

Extraction of uranium from HF - HNO_3 by tertiary amine solutions in benzene. Radiokhimiia 7 no.1:7-14 '65.

(MIRA 18:6)

VIOVENKO, V.M.; RYAZANOV, M.A.

Activity coefficients in multicomponent systems. Part 1.
Radiokhimiia 7 no.1:39-45 '65. (MIRA 18:6)

VDOVENKO, V.M.; LAZAREV, L.N.; SHIRVINSKIY, Ye.V.

Study of thermodynamic characteristics of the system HF - HNO_3 - H_2O. Part 1: Measurement of vapor pressure of components of systems HF - H_2O and HF - HNO_3 - H_2O. Radiokhimiia 7 no.1:46-48 '65. (MIRA 18:6)

VDOVENKO, V.M.; BULYANITSA, L.S.

Distribution of the alkali metal halides between aqueous solutions and organic solutions of iodine. Part 4: Distribution of cesium chloride between aqueous and organic solutions of iodine. Radiokhimiia 7 no.1:104-107 '65. (MIRA 18:6)

VDOVENKO, V.M.; KOVALEVA, T.V.; RYAZANOV, M.A.

Effect of the nature of a diluent on the distribution coefficients.
Radiokhimiia 7 no.2:133-139 '65. (MIRA 18:6)

[redacted], V.E.; [redacted], L.E.; [redacted], Ye.V.; [redacted], N.I.

Thermodynamic characteristics of the system HF - HNO_3 - [redacted]. Part 2: Calculation of activity of components in the system HF - HNO_3 - H_2O. Radiokhimiia 7 no.2:151-159 '65.

(MIRA 18.[redacted])

VDOVENKO, V.M.; DUBASOV, Yu.V.

Physicochemical study of some radium compounds. Part 1: Ionic refraction of radium. Radiokhimiia 7 no.2:214-220 '65. (MIRA 18:6)

VDOVENKO, V.M.; LAZAREV, L.N.; KHVOROSTIN, Ya.S.

Solutions of $Ru^{(IV)}$ in perchloric and sulfuric acids. Radiokhimiia 7 no.2:232-240 '65. (MIRA 18:6)

VDOVENKO, V.M.; RYAZANOV, M.A.

Activity coefficients in multicomponent systems. Part 2: Importance of Zdanovskii's rule for estimating the thermodynamic properties of mixed solutions. Radiokhimiia 7 no.4:442-449 '65. (MIRA 18:8)

VDOVENKO, V.M.; MASHIROV, L.G.; SUGLOBOV, D.N.

Uranyl perchlorate complexes with neutral ligands. Dokl. AN SSSR 163 no.1:100-102 Jl '65. (MIRA 18:7)

1. Chlen-korrespondent AN SSSR (for Vdovenko).

VDOVENKO, V.M.; MASHIROV, L.G.; SUGLOBOV, D.N.

Infrared spectra of uranyl perchlorate and its crystal hydrates. Coordination of a perchlorate ion. Radiokhimiia 6 no.3:299-305 '64. (MIRA 18:3)

VDOVENKO, V.M.; BULYANITSA, L.S.

Distribution of alkali metal halides between aqueous solutions and organic solutions of iodine. Part 1: Distribution of the iodides of cesium and some other alkaline metals between aqueous solutions and organic solutions of iodine. Radiokhimiia 6 no.4:385-[illegible].

Distribution of alkali metal halides between aqueous solutions and organic solutions of iodine. Part 2: Distribution of cesium iodide between aqueous solutions and solutions of iodine in tributyl phosphate. Ibid.:399-411 (MIRA 18:4)

VDOVENKO, V.M.; SKOBLO, A.I.; SUGLOBOV, D.N.

Anion perchlorate complexes of uranyl. Radiokhimiia 6 no.6: 677-682 '64. (MIRA 18:2)

L 55078-65 EWT(m)/EPF(c)/EPR/EWP(j)/T/EWP(t)/EWP(b) Pc-4/Pr-4/Ps-4 IJP(c)
JD/JW

ACCESSION NR: AP5018001 UR/0186/64/006/006/0724/0732

AUTHOR: Vdovenko, V. M.; Lazarev, L. N.; Khvorostin, Ya. S.

TITLE: Investigation of nitrosoruthenium complexes in solutions

SOURCE: Radiokhimiya, v. 6, no. 6, 1964, 724-732

TOPIC TAGS: ruthenium, nitrate, ruthenium compound, solution property

Abstract: A spectrophotometric method was used to investigate nitrosonitrates of ruthenium, and to study the processes of replacement of coordinated nitrate ions by other ligands. The absorption spectra of ruthenium nitrosonitrates and their distribution between aqueous and organic solvents were studied, utilizing [illegible] nitric acid and [illegible] nitrates [illegible] ruthenium [illegible] tions of alkyl ammonium nitrates is due to the presence of the so-called RuD form in the aqueous phase. In the organic phase, ruthenium exists in the form of the pentanitrate complex of nitrosoruthenium. It was shown that chromatographic separation of nitrosoruthenium complexes on paper can be widely used as a method of checking on the chemical state of ruthenium in solutions, using methyl isopropyl ketone as the organic solvent. In nitric

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ACCESSION NR: AP5018001

acid solutions, ruthenium nitrosonitrates react with thiourea, sulfate and chloride ions. Fluoride compounds are not formed by nitrosoruthenium under these conditions. The reaction of the nitrosonitrates with Cl^- leads to the formation of a number of nitrate-chloride complexes of nitrosoruthenium. Data were obtained on the compositions of some of these compounds and on their stability. Orig. art. has 6 formulas, 4 graphs, and 5 tables.

ASSOCIATION: none

SUBMITTED: 20Nov63 ENCL: 00 SUB CODE: IC, GC

NO REF SOV: 004 OTHER: 007 JPRS

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VDOVENKO, V.M. (Leningrad); [illegible]OVSKIY, A.A. (Leningrad); KUZINA, M.G. (Leningrad); DEM'YANOVA, T.A. (Leningrad); NIKITINA, S.A. (Leningrad)

Hydrogen bonds in alkyl ammonium salts. Ukr. fiz. zhur. 9 no.4:453-457 Ap '64. (MIRA 17:8)

VDOVENKO, V.M.; SUGLOBOVA, I.G.; SUGLOBOV, D.N.

Solubility of uranyl perchlorate trihydrate in mixed solvents.
Radiokhimiia 6 no.5:539-542 '64. (MIRA 18:1)

VDOVENKO, V.M.; VASIL'YEV, Ya.V.; DUBASOV, Yu.V.

Magnetic susceptibility of radium chloride and radium bromide.
Dokl. AN SSSR 159 no.3:536-538 N '64 (MIRA 18:1)

1. Chlen-korrespondent AN SSSR (for Vdovenko).

L 44275-65

ACCESSION NR: AP5008001 S/0186/65/007/001/0007/0014

solutions of tertiary amines

SOURCE: Radiokhimiya, v. 7, no. 1, 1965, 7-14

TOPIC TAGS: uranyl radical, extracting agent, hydrofluoric acid, nitric acid, nonylamine, decylamine

the extraction of uranium from an HF-HNO_3 mixture the extraction of the acids themselves from their mixtures was studied. Solutions of tri-n-nonylamine and tri-n--decylamine in benzene were used as extractants. During the extraction of HNO_3 and

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