

EXTRACTION OF HEXAVALENT URANIUM FROM CITRATE MEDIUM BY THE TOLUENE SOLUTION OF TRILAURYLAMINE

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Complexes of the type $(\text{UO}_2\text{HA})_p(\text{TLA})_q(\text{H}_3\text{A})_r$ are formed in the extraction of uranyl by the toluene solutions of trilaurylamine (TLA) from the isomolar aqueous phase formed by $1\text{M}-(\text{H},\text{Na},(\text{UO}_2)_{0.5})_3\text{A}$, where H_3A is citric acid. The extraction was studied at pH 1.62 with the equilibrium concentration of uranium in the aqueous phase in the range $10^{-4}-10^{-1}\text{ mol l}^{-1}$ and with TLA concentration in the organic phase ranging from 0.0305 to 0.308 mol l^{-1} . Complexes with $q = 5$ and $p + r = 3$ predominate in the extraction by TLA solutions of lower concentrations ($c(\text{TLA}) = 0.0305\text{ mol l}^{-1}$). The fraction of more associated complexes ($q = 8-9$, $q - (p + r) = 0-2$) increase with the increase of TLA concentration.

Carboxylic acids can participate in the extraction of metals by aliphatic amines in various ways. In the presence of mineral acids the anions of which form with the alkylammonium cation more strongly associated ion pairs than the anions of carboxylic acids, the metal is extracted into the organic phase in the form of an anion complex with the mineral ligand, whereas the carboxylic acid — forming an associate with the alkylammonium salt — can decrease the distribution ratio of the metal. Koehly and coworkers¹ found that U(VI) extraction by trilaurylamine (TLA) from HNO_3 medium decreases in the presence of capric acid (HA) due to the decrease of the free trilaurylammonium nitrate concentration in the organic phase caused by the formation of $\text{TLA}.\text{HNO}_3.(\text{HA})_2$ associate.

In the U(VI) extraction by trioctylamine from the solutions containing oxalic acid (H_2A) and HNO_3 either the complexes with NO_3^- ligands or mixed complexes containing both nitrate and oxalate ligands are extracted depending on the ratio of H_2A and HNO_3 concentrations. At the highest concentrations of H_2A the extraction of U(VI) decreases again due to the formation of a mixed salt². Only in the case of very low mineral acid concentrations in comparison with the concentration of amine (or in the complete absence of the mineral acid) the ion pair formation of alkylammonium cation with carboxylic anion or with the anionic metal complex with organic ligands becomes the most important equilibrium in the system.

Uranium ion forms strong complexes with various ligands derived from carboxylic acids and these complexes are easily extracted by tertiary aliphatic amines³. The extraction from the citrate medium is analytically exploited^{4,5} but so far little atten-

tion has been paid to the stoichiometry of extraction in this system. Patil and co-workers⁶ found that the absorption spectra (in the region 360–500 nm) of U(VI) extracts from citric and acetic acids are similar so that it can be assumed that the structure of the complex extracted from the citrate medium is similar to the structure of the complex $(R_3NH)_2UO_2Ac_4$ extracted from the acetic acid (HAc) medium⁷.

The extraction of uranyl from citric acid (H_3A) by tetradecylammonium salts was studied in detail⁸. The extraction and saturation measurements as well as the infrared spectra of the organic phase revealed that with the decrease of acidity the extracted complexes of the composition $(R_4N)UO_2A$ are transformed into a trimer $(R_4N)_4 \cdot (UO_2)_3A_2(OH)_4$ (at pH > 6). From the infrared spectra of the benzene extract the authors deduce that the same complexes are extracted even with trioctylamine as the extractant^{8,9}.

In this paper the composition of complexes in the organic phase during the extraction of uranyl citrate by TLA solution was determined. Similarly as in our previous study on the Fe(III)-citrate extraction¹⁰ the composition of complexes is determined on the basis of the equilibrium distribution of uranium in the system TLA–toluene– $1M-(H,Na,(UO_2)_{0.5})_3A$. The previously acquired information on the citric acid extraction by TLA (ref.¹¹) and on the formation of uranyl complexes in $1M-(H,Na,(UO_2)_{0.5})_3A$ solutions¹² were considered in the analysis of this system. The extraction was carried out at a constant pH value of the aqueous phase (1.62 ± 0.04) chosen on the basis of preliminary experiments in the region of the highest values of the distribution ratios of uranium. The interpretation of results is thus much easier. A similar approach was used by Österberg and Sjöberg in their study of Cu(II) complexes with glycyl-L-histidylglycine¹³.

EXPERIMENTAL

Reagents and solutions. Trilaurylamine ("pureté nucléaire", Rhône-Poulenc) (henceforth TLA), toluene, citric acid, and sodium citrate were the same as in our previous studies^{10–12}. Uranium trioxide (analytical grade, Lachema) was gravimetrically analyzed for the uranium content after calcination to U_3O_8 .

Stock solutions of citric acid (2M), sodium citrate (1M), and toluene solutions of TLA (2, 5, and 20% (v/v), i.e. 0.0308, 0.0771, and 0.308 mol l⁻¹, respectively) were prepared and analyzed similarly as in the citric acid extractions¹¹. The stock solution of uranyl citrate in 0.667M citric acid was prepared by dissolving 15.142 g of UO_3 and 21.014 g of H_3A in 70–80 ml of water and adjusting to 100 ml by addition of water. After filtration the content of uranium was determined spectrophotometrically using the thiocyanate method in aqueous–acetone medium according to Crouthamel and Johnson¹⁴. The solutions used in extraction were prepared by dilution of these stock solutions.

Experimental procedure. The distribution measurements were carried out similarly as in the extraction of citric acid. The contact time of both phases was prolonged to 24 h which is sufficient for the establishment of equilibrium as proved by preliminary experiments. After the separation of phases the content of uranium in the aqueous phase was determined according to Crouthamel

and Johnson¹⁴. Citric acid was then selectively reextracted from 5 ml of the organic phase using 8M-HCl. To samples with higher content of uranium in the organic phase pure TLA had to be added so that no more than 1% of uranium was transferred into the aqueous phase. After the reextraction of citric acid the uranium concentration in the organic phase was determined spectrophotometrically using the alcohol-pyridine solution of dibenzoylmethane¹⁵. The deviation from the mass balance of uranium in both phases was maximum 9% (for 2 experimental points) and in most cases better than 2%. The concentration of citrate anion reextracted from the organic phase into 8M-HCl was determined — after neutralization with concentrated NaOH solution — by titration with ferric chloride according to Šucha and Volka¹⁶. The results were corrected for the reextraction efficiency (95–98%) and for the volume increase of the aqueous phase during reextraction (<3%).

The aqueous phase acidity after extraction was measured with a combined electrode (glass-AgCl) Metrohm EA-120 U using the potentiometer Compensator E-388 (Metrohm, Switzerland). The pH values measured with the combined electrode differed from the values calculated on the basis of citric acid dissociation constants¹¹ by as much as 0.05 pH units, evidently due to the difference in the liquid-junction potentials in both measuring systems (combined electrode glass-AgCl and the glass electrode connected with the reference AgCl electrode by a salt bridge). The measured pH values were therefore corrected for the differences in the junction potentials.

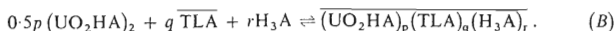
RESULTS

Extraction of uranium and citrates from 1M-(H,Na₃(UO₂)_{0.5})₃ A was followed by the measurement of the dependence of the UO₂ equilibrium concentration in the aqueous phase ($c_{\text{UO}_2,\text{aq}}$) at the constant concentration of TLA (c_{TLA}). In all measurements the acidity of the equilibrium aqueous phase was kept at the approximately constant pH value of 1.62 ± 0.04 .

The results expressed in the form $Z_{\text{UO}_2} = c_{\text{UO}_2,\text{org}}/c_{\text{TLA}}$ and $Z_{\text{A}} = c_{\text{A,org}}/c_{\text{TLA}}$ are listed as sets of values ($c_{\text{UO}_2,\text{aq}}$, pH, Z_{UO_2} , Z_{A}) c_{TLA} in Table I and presented in Fig. 1 in the form of functions $Z_{\text{UO}_2} = f(c_{\text{UO}_2,\text{aq}})$ and $Z_{\text{A}} = f(c_{\text{UO}_2,\text{aq}})$. The pH values in Table I are already corrected for the effect of the liquid-junction potential.

Treatment of Experimental Data

Because a non-polar diluent (toluene) was used it can be assumed on the basis of general concepts for the amine extraction systems that only uncharged complexes can pass into the organic phase. From our previous work¹² it follows that two uncharged complexes exist in the aqueous phase, namely the monomer UO₂HA and the dimer (UO₂HA)₂. The extraction equilibrium can then be expressed by the equations:



The components in the organic phase are denoted by a bar.

As the ratio of UO_2HA and $(\text{UO}_2\text{HA})_2$ concentrations in the aqueous phase is given by the dimerization constant

$$K_d = [(\text{UO}_2\text{HA})_2]_{\text{aq}} / [\text{UO}_2\text{HA}]_{\text{aq}}^2 = \beta_d / \beta_m^2, \quad (1)$$

where β_d and β_m are the stability constants of $(\text{UO}_2\text{HA})_2$ and UO_2HA complexes, respectively¹², both Eqs (A) and (B) can be used for the description of the extraction equilibrium.

Using Eq. (A) and assuming constant activity coefficients of all components (this problem is discussed in¹¹ in connection with H_3A extraction) the equilibrium

TABLE I

Extraction of uranyl by toluene solutions of TLA from $1\text{M}-(\text{H},\text{Na}_4(\text{UO}_2)_{0.5})_3\text{A}$ solutions at the approximately constant pH of the equilibrium aqueous phase. The following values are given for each point: $\log c_{\text{UO}_2,\text{aq}}$, pH, Z_{UO_2} and Z_{A}

$$c(\text{TLA}) = 0.03045 \text{ mol l}^{-1}$$

-3.928, 1.626, 0.00316, 0.426;	-3.633, 1.628, 0.00575, 0.433;
-3.455, 1.627, 0.0140, 0.466;	-3.182, 1.621, 0.0374, 0.447;
-2.870, 1.619, 0.0880, 0.470;	-2.530, 1.608, 0.163, 0.529;
-2.321, 1.624, 0.237, 0.532;	-2.119, 1.621, 0.283, 0.545;
-1.967, 1.612, 0.312, 0.571;	-1.550, 1.606, 0.404, 0.571;
-1.345, 1.621, 0.447, 0.578;	-1.059, 1.618, 0.466, 0.578;
-0.985, 1.624, 0.473, 0.588;	

$$c(\text{TLA}) = 0.07713 \text{ mol l}^{-1}$$

-3.717, 1.618, 0.0110, 0.596;	-3.542, 1.613, 0.0240, 0.577;
-3.316, 1.620, 0.0456, 0.602;	-3.253, 1.629, 0.0583, 0.590;
-3.184, 1.620, 0.0688, 0.605;	-3.000, 1.624, 0.1159, 0.622;
-2.597, 1.609, 0.215, 0.642;	-2.231, 1.625, 0.296, 0.647;
-1.987, 1.632, 0.371, 0.642;	-1.595, 1.647, 0.463, 0.640;
-1.208, 1.647, 0.500, 0.643;	-1.001, 1.621, 0.515, 0.644;

$$c(\text{TLA}) = 0.3082 \text{ mol l}^{-1}$$

-3.767, 1.615, 0.0125, 0.759;	-3.611, 1.616, 0.0254, 0.782;
-3.407, 1.634, 0.0496, 0.788;	-3.349, 1.630, 0.0620, 0.775;
-3.289, 1.627, 0.0766, 0.779;	-3.111, 1.617, 0.1282, 0.772;
-2.883, 1.617, 0.1937, 0.772;	-2.660, 1.628, 0.257, 0.782;
-2.670, 1.645, 0.260, 0.795;	-2.446, 1.643, 0.315, 0.785;
-1.951, 1.667, 0.409, 0.795;	-1.345, 1.663, 0.490, 0.798;
-1.141, 1.656, 0.516, 0.785;	-0.879, 1.632, 0.535, 0.805.

constants of Eq. (A), *i.e.*, the stability constants of the extracted complexes, are expressed by

$$\beta_{p,q,r} = [(UO_2HA)_p(TLA)_q(H_3A)_r]_{org}/[UO_2HA]^p[TLA]_{org}^q[H_3A]^r \quad (2)$$

For the treatment of the experimental data the procedure described previously in the paper¹⁰ was adopted, *i.e.*, first the relations between the coefficients p , q , and r and the types of complexes in the organic phase were determined using the computational program MESAK (ref.¹⁷) and then for this set of all possible complexes the most probable set of complexes was chosen by a statistical treatment of this data using the program LETAGROP (refs¹⁸⁻²⁰).

Determination of p , q , and r Values

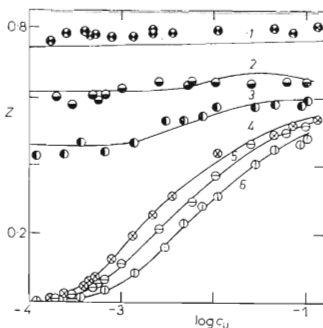
Using the method of the program MESAK the average values of coefficients can be calculated only for two-component complexes. However, in our previous work a possibility is shown of using this method even for systems with three components, consisting of the determination of a pair of coefficients for a set of data with a constant concentration of the free third component.

The computation with the program MESAK requires data for the determination of the integration constant. A constant value of the distribution ratios of UO_2HA (D_m) and $(UO_2HA)_2$ (D_d) in systems with a constant TLA concentration and with low concentrations of uranium was therefore assumed using this reasoning:

The distribution ratio of uranium D_{UO_2} can be expressed by the equation:

$$D_{UO_2} = c_{UO_2,org}/c_{UO_2,aq} = ([UO_2HA]_{org} + 2[(UO_2HA)_2]_{org})/c_{UO_2,aq} \quad (3)$$

FIG. 1
The dependences of Z_{UO_2} and Z_A on $\log \cdot c_{UO_2,aq}$ for the extraction of uranyl by toluene solutions of TLA from the aqueous phase formed by $1M-(Na,H_2(UO_2)_0.5)_3A$ at $pH \approx 1.62$. The dependence of Z_{UO_2} for $c(TLA)/mol\ l^{-1}$: 6 0.0305, 5 0.0771, 4 0.308. The dependence of Z_A for $c(TLA)/mol\ l^{-1}$: 3 0.0305, 2 0.0771, 1 0.308. Solid curves were calculated for the following set of complexes: (1,5,2), (2,5,1), (3,5,0), (2,8,5), (3,8,5), and (5,9,4) using the extraction constants given in the text



Assuming constant distribution ratios of both complexes in the region $Z_{\text{UO}_2} \ll 1$, i.e.,

$$K_{\text{D}_1} = [\text{UO}_2\text{HA}]_{\text{org}}/[\text{UO}_2\text{HA}]_{\text{aq}} = \text{const.} \quad \text{and} \quad (4)$$

$$K_{\text{D}_2} = [(\text{UO}_2\text{HA})_2]_{\text{org}}/[(\text{UO}_2\text{HA})_2]_{\text{aq}} = \text{const.}$$

Eq. (3) can be transformed to

$$D_{\text{UO}_2} = (K_{\text{D}_1}[\text{UO}_2\text{HA}] + 2K_{\text{D}_2}[(\text{UO}_2\text{HA})_2])/c_{\text{UO}_2, \text{aq}}. \quad (5)$$

Introducing the dimerization constant of the complex UO_2HA ($K_d = 18.2$, cf. ref.¹²) we obtain

$$D_{\text{UO}_2} = (K_{\text{D}_1}[\text{UO}_2\text{HA}] + 2K_{\text{D}_2}K_d[\text{UO}_2\text{HA}]^2)/c_{\text{UO}_2, \text{aq}} \quad (6)$$

which can be rewritten in the form

$$c_{\text{UO}_2, \text{org}}/[\text{UO}_2\text{HA}] = K_{\text{D}_1} + 2K_{\text{D}_2}K_d[\text{UO}_2\text{HA}]. \quad (7)$$

From Eq. (7) it follows that in the region $Z_{\text{UO}_2} \ll 1$ the dependence of $c_{\text{UO}_2, \text{org}}/[\text{UO}_2\text{HA}]$ on $[\text{UO}_2\text{HA}]$ is a straight line with the slope $2K_{\text{D}_2}K_d$ and with the ordinate K_{D_1} .

$[\text{UO}_2\text{HA}]$ was calculated using the stability constants of this complex determined in our previous work¹². It was found that the function $c_{\text{UO}_2, \text{org}}/[\text{UO}_2\text{HA}] = f([\text{UO}_2\text{HA}])$ is indeed a straight line (a certain deviation from the straight line was observed for 5% TLA) and the parameters of these straight lines are as follows: for 2% TLA: $a = 1.584$, $s_a = 0.495$, $b = 2.21 \cdot 10^4$, $s_b = 4.28 \cdot 10^3$, $r = 0.96$ (from four points); for 5% TLA: $a = 13.7$, $s_a = 3.1$, $b = 7.92 \cdot 10^4$, $s_b = 2.29 \cdot 10^4$, $r = 0.89$ (from five points); for 20% TLA: $a = 48.4$, $s_a = 10$, $b = 6.96 \cdot 10^5$, $s_b = 8.86 \cdot 10^4$, $r = 0.98$ (from five points), where a is the ordinate on the y axis, b is the slope, s_a and s_b are the standard deviations of a and b , respectively, and r is the correlation coefficient. The values of K_{D_1} and K_{D_2} can be therefore assumed to be constant for the given TLA concentration and for $c_{\text{UO}_2, \text{aq}} < 7 \cdot 10^{-4} \text{ mol l}^{-1}$.

$K_{\text{D}_2} \approx 200K_{\text{D}_1}$, which is probably caused by a lower hydration degree of the dimer so that its transfer into the organic phase is easier.

On the basis of the obtained values of K_{D_1} and K_{D_2} the value of the integration constant for the evaluation of coefficients according to the program MESAK was calculated for the region between $Z_{\text{UO}_2} = 0$ and the lowest measured value of Z_{UO_2} . Moreover, a correction for complexes with $p = 0$ (i.e., complexes of H_3A with TLA) was introduced so that the values \bar{p} and \bar{q} in the output of the program MESAK are the average values of p and q only for uranyl-containing complexes. The average

number of H_3A molecules, *i.e.* \bar{r} , is obtained from the relation

$$\bar{r} + \bar{p} = \bar{p} \{ Z_A - (\sum r \beta b^q c^r)_{p=0} / B \} / Z_{UO_2} \quad (8)$$

where β 's are the extraction constants of H_3A (ref.¹¹), b is the free concentration of TLA obtained during the execution of the program MESAK, B is the total concentration of TLA in the organic phase, and c is the free concentration of H_3A in the aqueous phase. The obtained dependences of \bar{q} on \bar{p} and of $(\bar{p} + \bar{r})$ on \bar{q} are given in Figs 2 and 3.

From Fig. 2 it is evident that \bar{q} , *i.e.* the average number of TLA molecules in the complex, depends on the total concentration of amine in the organic phase while it practically does not change with the increase of \bar{p} . For \bar{r} we have $\bar{p} + \bar{r} = \bar{q} - x$ (Fig. 3), where the value of x increases with the decrease of B from $x = 1$ for 20% amine to nearly 2 for 2% amine. On the basis of these dependences a list of complexes was chosen, the values p , q , and r of which lie in Figs 2 and 3 in the region of the highest density of points and in the regions extrapolated to higher values of \bar{q} . Hence-

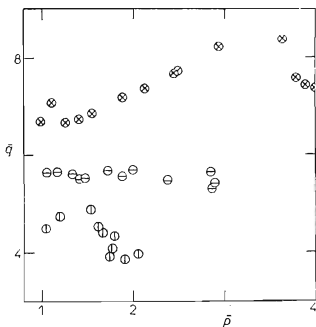


FIG. 2

The dependence of \bar{q} on \bar{p} in $(UO_2HA)_p \cdot (TLA)_q (H_3A)_r$ complexes formed in the organic phase during the extraction in the system 1M-(H,Na, $(UO_2)_{0.5}$)₃A-TLA-toluene at pH \approx 1.62. $c(TLA)/mol\ l^{-1}$: \circ 0.0305, \square 0.0771, \diamond 0.308.

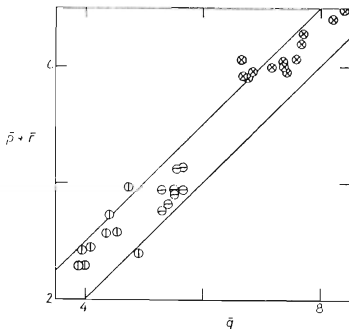


FIG. 3

The dependence of $(\bar{p} + \bar{r})$ on \bar{q} in the $(UO_2HA)_p (TLA)_q (H_3A)_r$ complexes formed in the organic phase during the extraction in the system 1M-(H,Na, $(UO_2)_{0.5}$)₃A-TLA-toluene at pH \approx 1.62. $c(TLA)/mol\ l^{-1}$: \circ 0.0305, \square 0.0771, \diamond 0.308. Solid curves give the relations $\bar{p} + \bar{r} = \bar{q} - 2$ and $\bar{p} + \bar{r} = \bar{q} - 1$

forth the complexes $(\text{UO}_2\text{HA})_p(\text{TLA})_q(\text{H}_3\text{A})_r$, will be – for the sake of simplicity – expressed by the symbol (p, q, r) . Several sets chosen from the following list of complexes were tested: (1,5,2), (2,5,1), (3,5,0), (3,5,1), (2,6,2), (1,7,5), (2,8,5), (3,8,4), (3,8,5), (4,8,2), (4,8,3), (5,9,3), (5,9,4), and (6,10,3).

The computation was done using the program LETAGROP (ref.^{18,19}) in which complexes from the given list were chosen using a selector of complexes²⁰, their equilibrium constants were calculated, and then it was decided whether their addition to the hitherto chosen set of complexes increased the agreement between the calculated and experimental dependences $Z_{\text{UO}_2} = f(\log [\text{UO}_2\text{HA}]_{\text{aq}})$ and $Z_{\text{A}} = f(\log [\text{H}_3\text{A}]_{\text{aq}})$. The sum of squares of relative errors expressed by

$$U = \sum(a + b)^2, \quad (9)$$

where $a = |Z_{\text{UO}_2, \text{exp}} - Z_{\text{UO}_2, \text{calc}}| / Z_{\text{UO}_2, \text{calc}}$

$$b = |Z_{\text{A}, \text{exp}} - Z_{\text{UO}_2, \text{exp}} - Z_{\text{A}, \text{calc}} + Z_{\text{UO}_2, \text{calc}}| / |Z_{\text{A}, \text{calc}} - Z_{\text{UO}_2, \text{calc}}|$$

was used as a measure of the agreement. This approach gives a true picture of the effect of the complex composition changes on the organic phase composition in the entire concentration range under study.

The set of complexes (1,5,2), (2,5,1), (3,5,0), (2,8,5), (3,8,5), and (5,9,4) with the equilibrium constants $\log \beta_{1,5,2} = 10.04 \pm 0.10$, $\log \beta_{2,5,1} = 13.65 \pm 0.13$, $\log \beta_{3,5,0} = 15.67 \pm 0.16$, $\log \beta_{2,8,5} = 18.88$ max 19.26, $\log \beta_{3,8,5} = 22.26$ max 22.62 and $\log \beta_{5,9,4} = 28.86$ max 29.10 was found to be the best. Similarly as in our previous work¹⁰, the precision of calculated constants is given by $\pm 3s_\beta$, where s_β is the standard deviation of the arithmetic mean. The confidence interval of the constant $\beta \pm 3s_\beta$ is transformed into the logarithmic scale using the approximate relation¹⁹ $\log \beta \pm (\log(\beta + 1.5s_\beta) - \log(\beta - 1.5s_\beta))$. This relation cannot be used for $s_\beta > 0.2$ and in this case only the upper value of the deviation is given, i.e., $\log(\beta + 3s_\beta)$, in the form β max $(\beta + 3s_\beta)$.

For the given set of complexes and equilibrium constants calculated from 39 experimental points the value of $U = 0.804$ was found. Solid lines in Fig. 1 were calculated for this set of complexes. A good agreement was found for $\log Z_{\text{UO}_2} = f(\log c_{\text{UO}_2})$ and also for $\log Z_{\text{A}} = f(\log c_{\text{UO}_2})$ in the region of low c_{TLA} . A systematic deviation of curves (Fig. 1) for high TLA concentrations and low uranyl concentrations is probably caused (similarly as in the extraction of Fe(III) (ref.¹⁰)) by the change of the citric acid extraction constants if going from the 1M-(H₃, Na₃)A medium to 1M-(H, Na, (UO₂)_{0.5})₃A.

DISCUSSION

The experimental data presented in this paper and the computational procedure allowed to determine the ratio $\text{TLA} : \text{UO}_2^{2+} : \text{A}^{3-}$ in the extracted complexes. The

concentration of the UO_2HA complex in the aqueous phase was chosen as the main variable for the computation of the equilibrium constants of complexes because it is the simplest electroneutral complex of uranyl ion in the aqueous phase used. This choice does not mean that the given stoichiometric composition of $(\text{UO}_2\text{HA})_p \cdot (\text{TLA})_q (\text{H}_3\text{A})_r$ also implies that the complex is composed only of the species UO_2HA , TLA, and H_3A and not, *e.g.*, of UO_2^{2+} , UO_2A^- , H_2A^- , TLAH^+ , *etc.*

Figs 4 and 5 present the relative participation of individual complexes in the dependence on the uranyl concentration in the equilibrium aqueous phase, both for the extraction with solutions of the lowest (Fig. 4) and highest (Fig. 5) concentrations of TLA. According to the relative participation of individual complexes in the TLA solution of the concentration of $0.0305 \text{ mol l}^{-1}$ (Fig. 4) these complexes can be divided into two groups. Complexes (1,5,2), (2,5,1), and (3,5,0) constitute the first group — each of them is a predominant component in a certain region of c_{UO_2} .

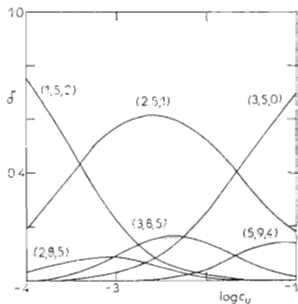


FIG. 4

Distribution coefficients of individual complexes in the organic phase (δ) as a function of the equilibrium concentration of uranyl in the aqueous phase in the extraction of toluene solution of TLA ($c(\text{TLA}) = 0.0305 \text{ mol l}^{-1}$) from $1\text{M} \cdot (\text{H.Na}, (\text{UO}_2)_{0.5})_3\text{A}$ at $\text{pH} \approx 1.62$. Complexes $(\text{UO}_2\text{HA})_p(\text{TLA})_q(\text{H}_3\text{A})_r$ are represented by the symbol (p, q, r) . The curves were calculated using the stability constants of complexes given in the text

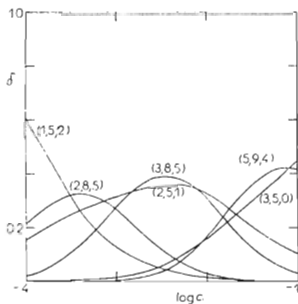


FIG. 5

The same functions as in Fig. 4 for the extraction by the toluene solution of TLA ($c(\text{TLA}) = 0.308 \text{ mol l}^{-1}$)

These complexes are also better defined than the remaining complexes as can be deduced from the values of standard deviations. Complexes (1,5,2), (2,5,1), and (3,5,0) form a continuous series in which H_3A molecules are gradually substituted by UO_2HA species. The remaining complexes, *i.e.*, (2,5,8), (3,8,5), and (5,9,4) belong to the second group. They can be assumed to be either real species (or rather representatives of real polymeric species of approximately double relative molecular weight than the complex series ($p,5,3-p$)), or as artefacts introduced during the computation to compensate the deviations of the system from the ideal one assumed in the computation according to Eq. (2) as already discussed in our previous work¹⁰.

In the extraction system with Fe(III) it was possible to derive several complexes formed by the substitution of H_3A in $(TLA)_q(H_3A)_r$ by the FeA species. The same relation between p , q , and r ($p + r = q - 1$) is true both for the complexes containing Fe and for the ammonium salts containing only H_3A (ref.¹¹).

In the system under study the individual members of the series ($p,5,3-p$) can also be derived by the substitution of H_3A by UO_2HA , but the relation between the coefficients is $p + r = q - 2$ so that it does not link up with the series of H_3A complexes with TLA. This discrepancy can be perhaps explained by higher steric requirements of UO_2HA in comparison with FeA.

The participation of higher associated complexes also increases with the increase of TLA concentration — the value of x in the relation $p + r = q - x$ decreases with the association degree from $x = 2$ to $x = 0$. In comparison with a similar extraction system with Fe(III) (ref.¹⁰) the complexes are more associated because the acidity of the aqueous phase is higher in the system with UO_2 .

The composition of complexes described in this study differs from the complex $TOA.UO_2HA$ observed by Vdovenko and coworkers⁸ in the extraction by trioctylamine (TOA) at the acidity of the equilibrium aqueous phase about pH 2–3. The experimental methods used made possible the determination of the ratio $TOA : UO_2 : H_3A$ but on their basis the polymerization degree cannot be deduced. The value of x in the relation $p + r = q - x$ is equal to zero, which corresponds to the most associated complexes found in this study that would be the predominant component in the organic phase at the concentrations of TLA and UO_2 higher than those used in this study. Vdovenko and coworkers give the conditions of the formation of $TOA.UO_2HA$ only partly ($c_{TOA} = 0.1 \text{ mol l}^{-1}$ in benzene, $c_{H_3A} = 0.3 \text{ mol l}^{-1}$) and its existence is deduced from the comparison of the absorption spectra of the extract in TOA with the absorption spectra of the extract in tetra-*n*-decylammonium citrate⁹. In the extraction system with the quaternary ammonium salt $R_4N.UO_2HA$ was found under the following concentrations of the reactants: $c_{R_4N} = 0.27-0.3 \text{ mol l}^{-1}$, $c_{UO_2} = 0.06-0.22 \text{ mol l}^{-1}$, and $c_{H_3A} = 0.06-0.26 \text{ mol l}^{-1}$. It can be therefore stated that the complex assumed by Vdovenko and coworkers⁸ is not in contradiction with the extraction model proposed in this work.

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