Thermodynamics of Extraction Equilibria. Part II.[1] Extraction of Uranyl Nitrate and Chloride with Trioctylphosphine Oxide

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Thermodynamic equilibrium constants of extraction of nitric ($K = 6{\cdot}0 \pm 0{\cdot}6$) and hydrochloric acid [$K = (2{\cdot}5 \pm 0{\cdot}2) \times 10^{-3}$] and uranyl nitrate [$K = (1{\cdot}0 \pm 0{\cdot}1) \times 10^{5}$] and chloride [$K = (6{\cdot}0 \pm 0{\cdot}6) \times 10^{2}$] with trioctylphosphine oxide in carbon tetrachloride have been determined.

THE mechanism of the extraction of nitric acid

$$H^+ + NO_3^- + TOPO_{org} \rightleftharpoons HNO_3,TOPO_{org} \quad (1)$$

and uranyl nitrate

$$UO_2^{2+} + 2NO_3^- + 2TOPO_{org} \rightleftharpoons UO_2(NO_3)_2,2TOPO_{org} \quad (2)$$

was found to be the same as in the extraction with tributyl phosphate[1-8] (where TOPO is trioctylphosphine oxide). Papers dealing with the extraction of hydrochloric acid and uranyl chloride are less numerous. Among the others, the equimolar complex formation

$$H^+ + Cl^- + TOPO_{org} \rightleftharpoons HCl,TOPO_{org} \quad (3)$$

was found to predominate in the process of extraction.[9-11] However, there are some differences in opinion about the stoicheiometry and stability of other existing complexes. At any rate, the isotherm of the extraction

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of hydrochloric acid with 0·25M-TOPO[9] shows that the maximum concentration of hydrochloric acid in the organic phase does not exceed the analytical concentration of the extractant, up to 5M-hydrochloric acid in the aqueous phase at equilibrium. The mechanism of the extraction of uranyl chloride was established by Watanabe[12,13] and Laskorin[11,14] as in equation (4).

$$\mathrm{UO_2}^{2+} + 2\mathrm{Cl}^- + 2\mathrm{TOPO}_{\mathrm{org}} \rightleftharpoons \mathrm{UO_2Cl_2{,}2TOPO}_{\mathrm{org}} \qquad (4)$$

This paper deals with the determination of thermodynamic equilibrium constants of the processes presented by equations (1)—(4), by the new method reported in Part I.[1] Since the stoicheiometry of hydrates of extracted species is not sufficiently well established, the composition of extracted species was not considered in view of the coextraction of water. The low and constant concentration of TOPO enabled us also to avoid the use of diluent activity. Therefore, the thermodynamic equilibrium constants obtained in this work should be regarded as overall equilibrium constants.

EXPERIMENTAL

Nitric acid and hydrochloric acid were Merck, while uranyl nitrate and chloride were B.D.H. products.

Tri-n-octylphosphine oxide, Eastman Kodak, and carbon tetrachloride, B.D.H. were used without further purification.

Distribution measurements of inorganic acids and uranyl salts were carried out by agitating the two phases in a Griffin flask shaker for 1 h in a thermostated room at 20 ± 1 °C, and the aliquots for analyses were taken from both phases. The equilibrium was reached in the systems investigated since the concentrations of distributing species in both phases were not changed after 30 min equilibration. Uranium was determined spectrophotometrically[15] and the acids by titration with the standard solution of sodium hydroxide. Determination of uranium in organic phase was done by its re-extraction and of acids by direct titration.

List of Symbols.—a, Thermodynamic activity, molar scale; A, Anion; C, equilibrium concentration, molar scale; H, H^+; HCT, HCl,TOPO; HNT, $\mathrm{HNO_3}$,TOPO; K, thermodynamic equilibrium constant, molar scale; M, cation; MAS, $\mathrm{MA}_z,n\mathrm{S}$; n, number of extractant molecules; S, extractant; T, TOPO; TOPO, Tri-n-octylphosphine oxide; U, $\mathrm{UO_2}^{++}$; UCT, $\mathrm{UO_2Cl_2}$,2TOPO; UNT, $\mathrm{UO_2(NO_3)_2}$,2TOPO; x, equilibrium concentration, mole fraction scale; y, activity coefficient, molar scale; z, ion charge; subscript org denotes the organic phase. For the aqueous phase a subscript is omitted. Subscript tot denotes the total concentration of a component.

THEORETICAL

The simple graphical method for the determination of thermodynamic equilibrium constants, originally created for ion-exchange processes,[16] was extended to solvent extraction processes.[1] Here the method is mathematically developed and some efforts to obtain more precise results are made.

For an extraction equilibrium

$$\mathrm{M}^{z+} + z\mathrm{A}^- + n\mathrm{S}_{\mathrm{org}} \rightleftharpoons \mathrm{MA}_z,n\mathrm{S}_{\mathrm{org}} \qquad (5)$$

the thermodynamic equilibrium constant equation

$$K = \frac{a_{\mathrm{MAS(org)}}}{a_{\mathrm{M}}a_{\mathrm{A}}{}^{z}a_{\mathrm{S}}{}^{n}{}_{\mathrm{(org)}}} \qquad (6)$$

is transformed into the following form

$$\log\frac{1}{a_{\mathrm{M}}a_{\mathrm{A}}{}^{z}} = \log K + \log\frac{a_{\mathrm{S}}{}^{n}{}_{\mathrm{(org)}}}{a_{\mathrm{MAS(org)}}} \qquad (7)$$

When

$$a_{\mathrm{S}}{}^{n}{}_{\mathrm{(org)}} = a_{\mathrm{MAS(org)}} \qquad (8)$$

then equation (7) becomes

$$\log\frac{1}{a_{\mathrm{M}}a_{\mathrm{A}}{}^{z}} = \log K. \qquad (9)$$

The same condition, given by equation (8), also locates an inflexion point in the plot of equation (7) since

$$\frac{\mathrm{d}a_{\mathrm{S(org)}}}{\mathrm{d}a_{\mathrm{MAS(org)}}} = \frac{1}{n}a_{\mathrm{MAS(org)}}^{(1/n)-1} \qquad (10)$$

$$\frac{\mathrm{d}^2a_{\mathrm{S(org)}}}{\mathrm{d}a^2{}_{\mathrm{MAS(org)}}} = \frac{1}{n}\left(\frac{1}{n} - 1\right)a_{\mathrm{MAS(org)}}^{(1/n)-2} \qquad (11)$$

When these values are inserted in the right hand side of the second derivative of equation (7)

$$\frac{\mathrm{d}^2\left(\log\dfrac{1}{a_{\mathrm{M}}a_{\mathrm{A}}{}^{z}}\right)}{\mathrm{d}a^2{}_{\mathrm{MAS(org)}}} = \frac{2{\cdot}303n}{a_{\mathrm{S(org)}}} \times \frac{\mathrm{d}^2a_{\mathrm{S(org)}}}{\mathrm{d}a^2{}_{\mathrm{MAS(org)}}} - \frac{2{\cdot}303n}{a^2{}_{\mathrm{S(org)}}}\left(\frac{\mathrm{d}a_{\mathrm{S(org)}}}{\mathrm{d}a_{\mathrm{MAS(org)}}}\right)^2 + \frac{2{\cdot}303}{a_{\mathrm{MAS(org)}}} \qquad (12)$$

the second derivative becomes zero, thus providing a sufficient condition for an inflexion. The third derivation of equation (7) is not equal to zero for the condition given by equation (8).

The same results can be obtained if the following relations

$$a_{\mathrm{S(org)}} = y_{\mathrm{S}}C_{\mathrm{S(org)}} \qquad (13)$$

$$a_{\mathrm{MAS(org)}} = y_{\mathrm{MAS}}C_{\mathrm{MAS(org)}} \qquad (14)$$

$$C_{\mathrm{S(tot)}} = C_{\mathrm{S(org)}} + nC_{\mathrm{MAS(org)}} \qquad (15)$$

are introduced in equation (7). Provided the total concentration of extractant, $C_{\mathrm{S(tot)}}$, is maintained constant throughout, $C_{\mathrm{S(org)}}$ is a function of $C_{\mathrm{MAS(org)}}$ and $a_{\mathrm{S(org)}}$ is also a function of $a_{\mathrm{MAS(org)}}$. It is therefore convenient to replace the variable $\log a_{\mathrm{S}}{}^{n}{}_{\mathrm{(org)}}/a_{\mathrm{MAS(org)}}$ by the more immediately accessible $f[C_{\mathrm{MAS(org)}}]$, and to plot equation (7) as

$$\log\frac{1}{a_{\mathrm{M}}a_{\mathrm{A}}{}^{z}} = f[C_{\mathrm{MAS(org)}}]. \qquad (16)$$

This function has an inflexion point where equation (8) holds and the equilibrium constant is determined by equation (9).

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There are difficulties to locate exactly the inflexion point. To improve the location of such a point, the results from smoothed out isotherms, $C_{\mathrm{M(org)}} = f(C_{\mathrm{M}})$, can be used. Furthermore, we also made a graphical differentiation of the plot obtained by function (16) which yielded a parabola. The abscissa of its minimum corresponded to the abscissa of the inflexion point. In this manner the error in the graphical location of the inflexion point does not exceed 10% of the K value. On the other hand the abscissa of the inflexion point is usually found in the vicinity of 50% of the maximal saturation of organic phase by extracting species. As a system is approaching the ideal state the inflexion point abscissa displaces to the value corresponding to 50% of the saturation of organic phase. Therefore, the taking of ordinate value of the point on function (16), where abscissa is equal to the half of the capacity of organic phase, for the value of log K is often a good approximation. In the systems we investigated (Figures 2 and 5) the K values obtained by a such approximation are within the errors of judging of the inflexion point. The same conclusions were drawn from a number of ion exchange systems.[16]

The suggestion for the location of inflexion point, given previously [1,16] as an intersection of two straight lines, is not mathematically justified and we gave it up. The work on development of a computer programme for evaluation of the inflexion point co-ordinates, based on a third order polynomial, is in progress in our Laboratory.

The successful application of the simple graphical method to ion exchange [16] and solvent extraction processes [1] is extended in our Laboratory to the determination of dissociation constants of weak organic acids in homogeneous systems. The results obtained will be published soon. Therefore, the application of the method to different systems leads to the acception of it as a general method for the determination of thermodynamic equilibrium constants.

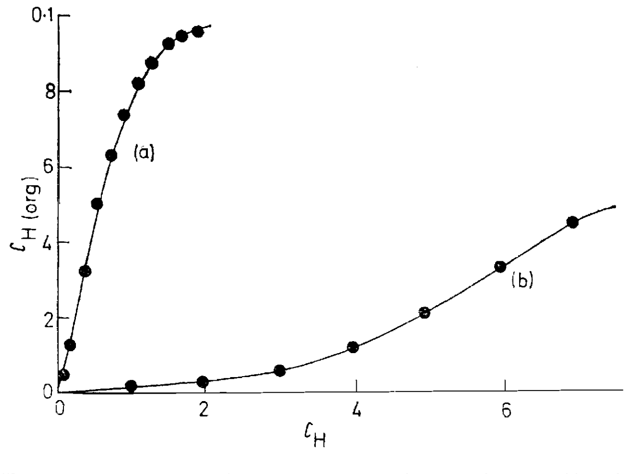

FIGURE 1 The experimental data of (a) HNO_3–0·1M-TOPO–carbon tetrachloride, and (b) HCl–0·05M-TOPO–carbon tetrachloride systems at 20 ± 1 °C

Extraction of Nitric and Hydrochloric Acid.—The isotherms of the extraction of nitric and hydrochloric acid with the solutions of TOPO in carbon tetrachloride are shown in Figure 1, and the equilibrium constants of reactions (1) and (3), taken from the literature,[5,6,17] are given in Table 1. Thermodynamic equilibrium constants of reactions (1) and (3) were determined using the data from smoothed out isotherms (Figure 1) and plotting them by function (16) (Figure 2). The activities of ions in the aqueous phase were taken from the literature.[18] The concentrations of the inorganic acid–TOPO complex in the organic phase, $C_{\mathrm{HAS(org)}}$, were approximated by the total acid concentrations, $C_{\mathrm{H(org)}}$, in the organic phase. One can see from Figure 2 that the complex formation constants of HNO_3,TOPO and HCl,-TOPO are $K_{\mathrm{HNT}} = 6{\cdot}0 \pm 0{\cdot}6$ and $K_{\mathrm{HCT}} = (2{\cdot}5 \pm 0{\cdot}2) \times 10^{-3}$, respectively.

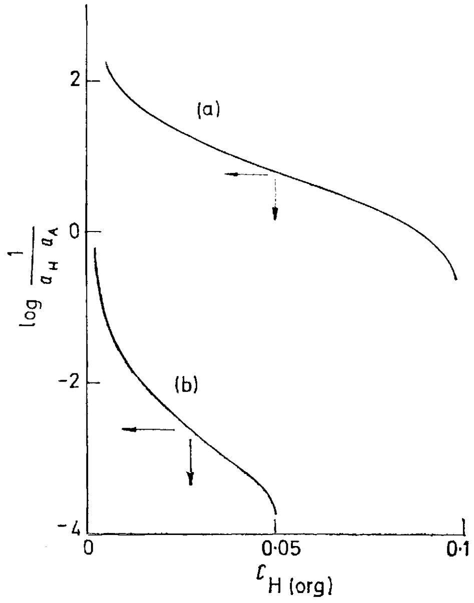

FIGURE 2 The data from the smoothed out isotherms presented by function (16); (a) up to 2M-HNO_3–0·1M-TOPO–carbon tetrachloride and (b) up to 7M-HCl–0·05M-TOPO–carbon tetrachloride

In order to prove that the ordinate of the inflexion point of function (16) gives the thermodynamic equilibrium constant, a graphical integration of the same systems, based on the Gibbs–Duhem equation, to obtain the activity coefficients of the species present in the organic phase, was carried out as suggested by Högfeldt [19] and explained in Part I.[1] The calculated activities of the species present in the organic phase are shown in Figure 3(a). The intersection of the curves, referring to the activities of the free

TABLE 1

Equilibrium constants of reactions (1) and (3), where K is given in $(\mathrm{l/mol})^2$ units

System	t/°C	K	Ref.
1M-HNO_3–TOPO–1,2-dichlorobenzene	25	10·2	17
0·0075M-HNO_3–0·04M-TOPO–cyclohexane	20	17·7	5
Up to 1M-HNO_3–0·1M-TOPO-benzene	25	15·2	6
Up to 2M-HNO_3–0·1M-TOPO–carbon tetrachloride	20	6·0 ± 0·6	This work
Up to 7M-HCl–0·05M-TOPO-carbon tetrachloride	20	(2·5 ± 0·2) × 10^{-3}	This work

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TOPO and inorganic acid–TOPO complex, has the value of abscissa which corresponds to the inflexion point abscissa in Figure 2. This is another proof that the inflexion point exists where $a_{S^n(org)} = a_{MAS(org)}$. The values of thermodynamic equilibrium constants, obtained from these activities over whole range of concentrations, are in very good agreement with the constants determined by our method.

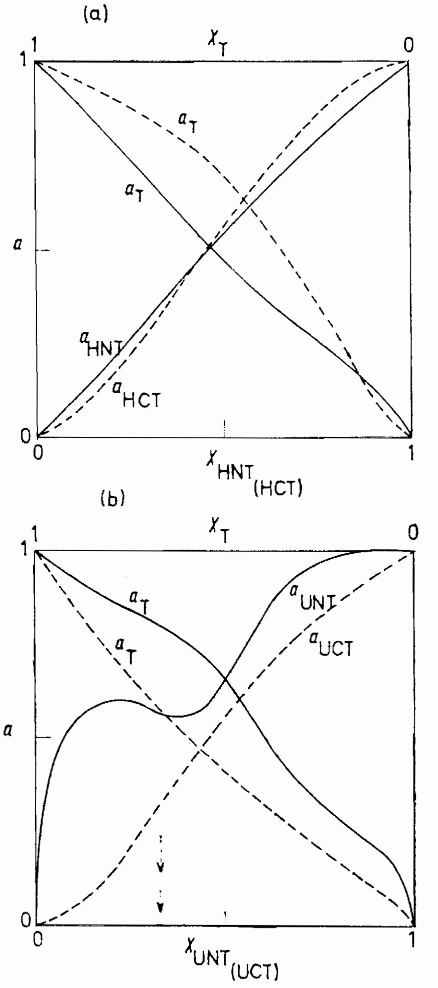

FIGURE 3 Activities of the species present in the organic phase in the extraction of nitric and hydrochloric acid (a) and uranyl nitrate and chloride (b) with TOPO in carbon tetrachloride. Solid lines denote nitrate and dashed lines denote chloride systems. The arrows show $x_{UNT(UCT)}$ values where $a_{T^2(org)} = a_{UNT(UCT)org}$

TABLE 2

Equilibrium constants of reactions (2) and (4), where K is given in $(l/mol)^4$ units

System	t/°C	K	Ref.
Up to 0·03M-$UO_2(NO_3)_2$–1M-HNO_3–0·1M-TOPO–dichlorobenzene	25	$9{\cdot}1 \times 10^4$	17
3×10^{-4}M-$UO_2(NO_3)_2$–0·02M-HNO_3–0·025M-TOPO–cyclohexane	20	3×10^8	5
Up to 0·05M-$UO_2(NO_3)_2$–0·5M-HNO_3–0·05M-TOPO–carbon tetrachloride	20	$(1{\cdot}0 \pm 0{\cdot}1) \times 10^5$	This work
Up to 0·05M-UO_2Cl_2–1·0M-HCl–0·05M-TOPO–carbon tetrachloride	20	$(6{\cdot}0 \pm 0{\cdot}6) \times 10^2$	This work

Extraction of Uranyl Nitrate and Chloride.—Experimental data of the extraction of uranyl nitrate and chloride with TOPO–carbon tetrachloride solutions are presented in Figure 4. The equilibrium constants of reaction (**2**), taken from the literature,[5,17] are given in Table 2. The equilibrium constant of the extraction of uranyl chloride with TOPO was not found in the literature.

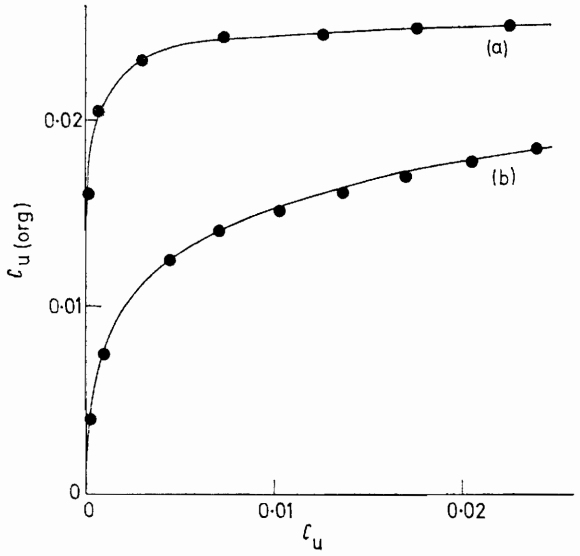

FIGURE 4 The experimental data of (a) $UO_2(NO_3)_2$–0·5M-HNO_3–0·05M-TOPO–carbon tetrachloride, and (b) UO_2Cl_2–1·0M-HCl–0·05M-TOPO–carbon tetrachloride systems, at 20 ± 1 °C

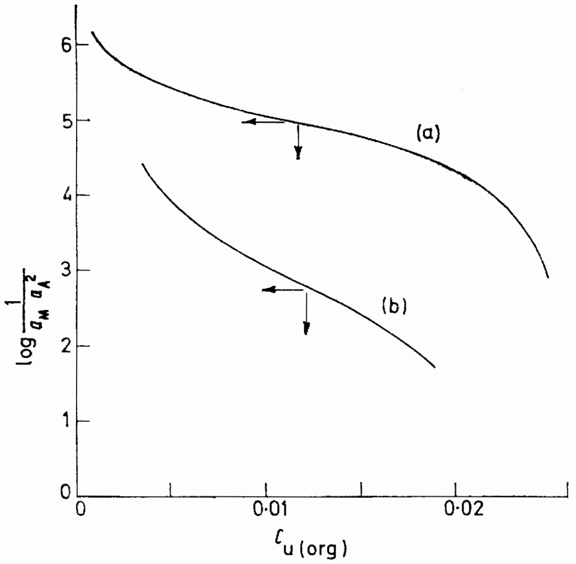

FIGURE 5 The data from the smoothed out isotherms presented by function (16); (a) $UO_2(NO_3)_2$–0·05-HNO_3–0·05M-TOPO–carbon tetrachloride, and (b) UO_2Cl_2–1·0M-HCl–0·05M-TOPO–carbon tetrachloride

The thermodynamic equilibrium constants of reactions (2) and (4) were determined using the data from smoothed out isotherms (Figure 4) and applying function (16) (Figure 5). The activity coefficients of hydrogen and uranyl ions were taken from the literature,[18,20] and recalculated for mutual influence according to Glueckauf.[21] The concentrations of uranyl salt–TOPO complexes in the organic phase, $C_{MAS(org)}$, were approximated by the total concentrations, $C_{U(org)}$, in the organic phase. As seen from Figure 5, the formation constants of $UO_2(NO_3)_2$,2TOPO and UO_2Cl_2,2TOPO are $K_{UNT} = (1{\cdot}0 \pm 0{\cdot}1) \times 10^5$ and $K_{UCT} = (6{\cdot}0 \pm 0{\cdot}6) \times 10^2$, respectively.

The activities of the species present in the organic phase, calculated by graphical integration of the same systems, as in the case of mineral acids extraction, are shown in Figure 3(b). One can see that $a_{S}{}^{2}{}_{(org)} = a_{MAS(org)}$ at the value of $x_{MAS(org)}$ which corresponds to the abscissa of the inflexion point in Figure 5.

The values of the equilibrium constants, given in Tables 1 and 2, are difficult to compare due to the various diluents used and various approaches to the evaluation of equilibrium constants.

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