Thermodynamics of Extraction Equilibria. Part 7.* Solvent Extraction of Thorium Nitrate with Tri-n-butyl Phosphate

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A previous method for the determination of equilibrium constants of extraction processes has been simplified without decreasing the accuracy of the determination. The method has been applied to the extraction of thorium nitrate with tri-n-butyl phosphate. Formation of a 1 : 3 adduct of thorium nitrate with the phosphate has been established and the formation constant, log K = 3.43, determined. The influence of diluents on this constant is considered.

For the separation of thorium from uranium in the reprocessing of spent thorium-based nuclear fuel the Thorex process has been invented. The chemical flowsheet of this process is based upon the solvent extraction of thorium nitrate with tri-n-butyl phosphate. The extraction chemistry of thorium nitrate has been reviewed.[1-4] It reacts with tri-n-butyl phosphate to form a solvate of the type $Th(NO_3)_4{\cdot}nPO(OBu^n)_3$. However, the solvation number, n, has not been definitely established and the formation of 1:2,[5-7] 1:3,[3,8-10] and 1:4[11] adducts has been proposed. Due to the unclear stoicheiometry, the thermodynamics of solvent extraction of thorium nitrate with $PO(OBu^n)_3$ has not been elucidated.

The tri-n-butyl phosphate solvate of thorium nitrate has a limited solubility in organic diluents and it is separated at high thorium nitrate loading in the organic phase as the second organic phase.[2,3,5,12-14] The influence of the diluent[10,15,16] and salting out[17,18] on extraction equilibria, as well as the i.r. spectra[10,19] and solubility of thorium nitrate in $PO(OBu^n)_3$,[20] have been investigated.

The aim of this work was to clarify the stoicheiometry of thorium nitrate extraction with $PO(OBu^n)_3$ and to determine the thermodynamic equilibrium constant of the extraction process. Therefore, experiments were performed on the thorium nitrate distribution within a wide range of concentrations in the organic phase. The equilibrium constant has been calculated from distribution data by means of the method developed previously.[21]

Theoretical

A method for determination of thermodynamic extraction constants was presented previously.[21] It is based on the use of distribution data for species within the range corresponding to the middle part of the extraction isotherm, and does not demand any extrapolation of the apparent equilibrium constants to infinite dilution. However, the calculation of the constants as described is a little complicated and a shorter method has been sought, without loss of accuracy.

As detailed previously,[21] the solvent extraction equilibrium can be represented by equation (1). For simplicity, designation

$$M + nS \rightleftharpoons M{\cdot}nS \qquad (1)$$

of the species existing in the aqueous or in the organic phase has been avoided; M is always related to the aqueous phase and S and M·nS to the organic phase. The equilibrium constant expression (2) can be rearranged to the form (3). All notations and thermodynamic definitions have been given previously.[21]

$$K = a_{MS}/a_M a_S^n \qquad (2)$$

$$-\log a_M = y = \log K + \log (a_S^n/a_{MS}) \qquad (3)$$

The expression dln a_S/da_{MS} in equation (4) can be evaluated *via* the Gibbs–Duhem equation (5), now applied to a binary

$$2.303\frac{dy}{da_{MS}} = n\frac{d\ln a_S}{da_{MS}} - \frac{1}{a_{MS}} \qquad (4)$$

$$c_S d\ln a_S + c_{MS} d\ln a_{MS} = 0 \qquad (5)$$

mixture of M·nS and S species existing in the organic phase. The very small concentration of free thorium nitrate that may occur in the organic phase may be neglected. Equations (4) and (5) lead to (6), taking into account the mass-balance equation $c_{S(tot)} = c_S + nc_{MS}$. Here c is the stoicheiometric concentration of the species denoted by the corresponding subscript. Further differentiation of equation (6) gives (7). When it is set to zero, in

$$2.303\, dy/da_{MS} = -c_{S(tot)}/a_{MS}c_S \qquad (6)$$

$$2.303\frac{d^2y}{da_{MS}^2} = \frac{c_{S(tot)}}{a_{MS}c_S}\left(\frac{1}{a_{MS}} + \frac{1}{c_S}\cdot\frac{dc_S}{da_{MS}}\right) \qquad (7)$$

order to fulfil the condition for the inflection point, and rearranged, one obtains equation (8). Following the same pattern as in equations (3)—(8), but differentiating equation (3) with respect to a_S, one obtains equation (9).

$$d\ln a_{MS} = -d\ln c_S \qquad (8)$$

$$d\ln a_S = -d\ln c_{MS} \qquad (9)$$

After integrating equations (8) and (9) and dividing the solutions obtained, in order to get the quotient a_S^n/a_{MS} in equation (3), we obtain equation (10) where P is an integration

$$a_S^n/a_{MS} = (c_S/c_{MS}^n)P \qquad (10)$$

constant. Evaluation of the integration constant, carried out as in Part 6, leads to $P = [c_{S(tot)}^2 n^{\frac{1}{2}}/n(1 + n^{\frac{1}{2}})^2]^{n-1}$. When this value for P is introduced into equation (10) we finally obtain equation (11), where $c_{S(tot)}$ = constant. It must be stressed that

$$\frac{a_S^n}{a_{MS}} = \frac{c_S}{c_{MS}^n}\left[\frac{c_{S(tot)}^2 n^{\frac{1}{2}}}{n(1 + n^{\frac{1}{2}})^2}\right]^{n-1} \qquad (11)$$

equations (8)—(11) are valid only at the inflection point.

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* Part 6 is ref. 21.

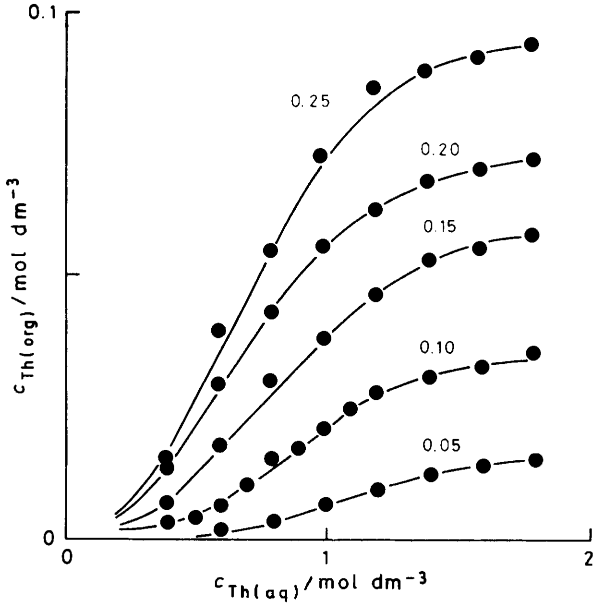

Figure 1. Distribution data for thorium nitrate at different total molar concentrations (numbers beside the curves) of $PO(OBu^n)_3$ in n-hexane at about 295 K and 0.1 mol dm^{-3} nitric acid

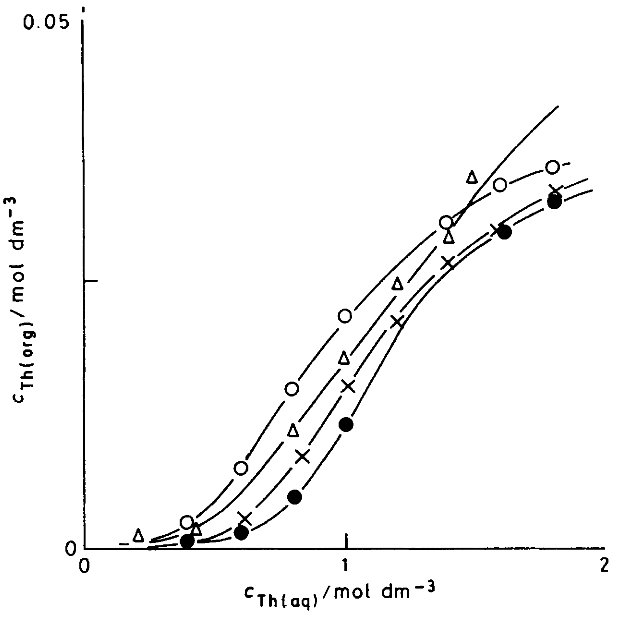

Figure 2. Distribution of thorium nitrate at 0.1 mol dm^{-3} $PO(OBu^n)_3$ in carbon tetrachloride (●), benzene (×), cyclohexane (○), and chloroform (△) at 295 K and 0.1 mol dm^{-3} nitric acid

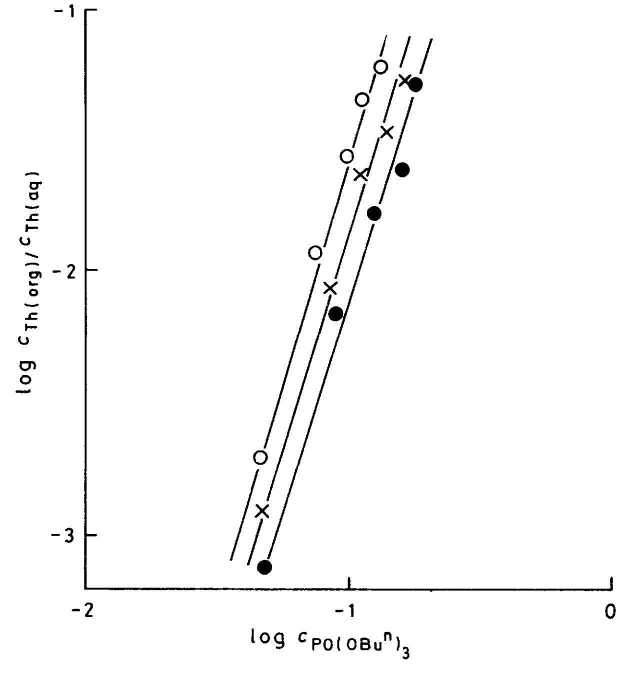

Figure 3. Slope analysis of distribution data for constant equilibrium concentrations of aqueous thorium nitrate of 0.4 (●), 0.5 (×), and 0.6 (○) mol dm^{-3} and for different concentrations of free $PO(OBu^n)_3$ in n-hexane

In practice, the extraction constant is calculated by plotting experimental data as $y = f(c_{MS})$, keeping the total concentration of extractant constant. The y values are obtained from the activity of M in the aqueous phase according to equation (3). The assumption in presenting experimental data as $y = f(c_{MS})$, instead of $y = f(a_{MS})$, has been explained in Part 6. Values of c_{MS} are obtained as the abscissa of the inflection point, while those of c_S are calculated by means of the mass-balance equation. The values of c_{MS} and c_S at the inflection point are introduced into equation (11) in order to calculate the corresponding value of $a_S{}^n/a_{MS}$. Therefore, once the value for y (the ordinate of the inflection point) and $a_S{}^n/a_{MS}$ [calculated by means of equation (11)] are obtained, one can calculate K according to equation (3).

The simplified method presented in this work has been tested with experimental results published previously.[21-23] The value of K was calculated by means of the formula (18), given in Part 6, and of equation (11), given in this paper. The values obtained were identical. That confirms that the simplification performed in this paper is justified. A further illustration of the validity of equation (11) was provided by study of the extraction of thorium nitrate with $PO(OBu^n)_3$.

Extraction of Thorium.—The distribution of thorium nitrate was investigated by changing the total concentration of $PO(OBu^n)_3$ with n-hexane as the diluent, and by changing the type of diluent but, at the same time, keeping the total concentration of $PO(OBu^n)_3$ constant. The experimental data, covering a wide range of thorium concentration in the organic phase, are shown in Figures 1 and 2. Formation of a third phase was not expected, since the total concentrations of $PO(OBu^n)_3$ were $\leqslant 0.25$ mol dm^{-3}, while the initial acidity of the aqueous phase was rather low (0.1 mol dm^{-3}). This low (nitric acid) concentration was added to avoid hydrolysis of thorium nitrate.

Considering the maximum loading of the organic phase (Figure 1), one can deduce that the solvation number, n, is about 2.5. This value is not reasonable. The solvation number is probably three at lower loadings of the organic phase, and, as the thorium extraction is increased, changes from three to two. Slope analysis of the thorium nitrate distribution data has been used to determine the solvation number. The total concentration of $PO(OBu^n)_3$ in hexane was varied, whereas the concentration of thorium nitrate in the aqueous phase was kept constant. Values of $c_{Th(org)}$ were taken from the smoothed isotherms for constant aqueous thorium nitrate concentrations of 0.4, 0.5, and 0.6 mol dm^{-3}. Plotting of the logarithm of the thorium nitrate distribution values *versus* the logarithm of the concentrations of

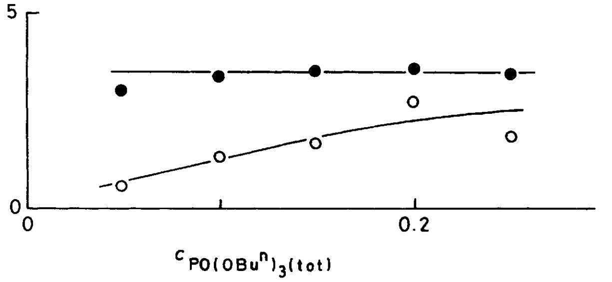

Figure 4. Equilibrium constant values, defined by equation (2), when $n = 2$ (○) or 3 (●)

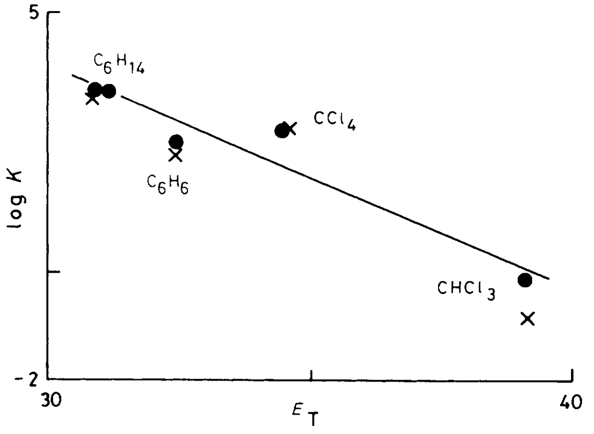

Figure 5. The effect of diluents on the extraction constants interpreted by means of the polarity factor E_T[26] (●). The results of Torgov *et al.*[10] are also included (×)

free $PO(OBu^n)_3$ gave straight lines (Figure 3), of slope 3.0 ± 0.1. The concentrations of free $PO(OBu^n)_3$ were calculated assuming that the 1:3 adduct was formed. The points in Figure 3 were fitted by a linear least-squares procedure. The extraction equilibrium (12) and corresponding equilibrium constant in equation (13) were obtained as a result of the slope analysis.

$$Th^{4+} + 4NO_3^- + 3PO(OBu^n)_3 \rightleftharpoons Th(NO_3)_4 \cdot 3PO(OBu^n)_3 \quad (12)$$

$$K = a_{adduct}/a_{Th}a_{NO_3}{}^4 a_{PO(OBu^n)_3}{}^3 \quad (13)$$

The equilibrium constant has been determined by means of the method explained in the Theoretical section. The K values, calculated for different total concentrations of $PO(OBu^n)_3$, initially for $n = 2$ and then for $n = 3$, are shown in Figure 4. The demonstration of the stoicheiometry with $n = 3$ is obvious, and log $K = 3.43$ arises from the upper line as the value common to all concentrations of $PO(OBu^n)_3$ used. The advantage of this method for determination of thermodynamic equilibrium constants is that it differentiates a correct from an incorrect stoicheiometry. The present result is in very good agreement with log $K = 3.23$, obtained by Torgov *et al.*[10] for solutions of $PO(OBu^n)_3$ in n-heptane. The small difference can be ascribed to the use of n-heptane (dielectric constant 1.924) instead of n-hexane (dielectric constant 1.890).

The activity coefficients for thorium nitrate have been taken from Robinson and Stokes[24] and recalculated on the molarity scale using density data for thorium nitrate aqueous solutions.[25] It seems that the isotherm for $c_{PO(OBu^n)_3(tot)} = 0.5$ mol dm^{-3}, in comparison with the others (Figure 1), has been determined with less accuracy due to the rather small total concentration of $PO(OBu^n)_3$ and the experimental difficulties encountered. The deviation of the corresponding point from the straight line in Figure 4 (for $n = 3$) may, perhaps, be the consequence of this inaccuracy. On the other hand, it cannot be excluded that this deviation should be ascribed to a change in the stoicheiometry.

The variation in the extraction constant for reaction (12) with the type of diluent has been correlated by means of the empirical polarity factor,[26] E_T, of the diluent in which the extraction was performed. Figure 5 illustrates the linear dependence between the logarithm of the extraction constant and E_T. The results of Torgov *et al.*[10] have been included, and show very good agreement with the present values.

Experimental

Thorium nitrate and the diluents (all BDH) were used without further purification. Tri-n-butyl phosphate (BDH) was distilled by means of a Karl Zeiss molecular distillation apparatus. Distribution equilibria of thorium nitrate were achieved by mixing phases in a Griffin flask shaker at a room temperature of about 20 ± 2 °C, within 1 h. The aqueous phase always contained 0.1 mol dm^{-3} of nitric acid to prevent thorium hydrolysis. The emulsion formed was centrifuged and an aliquot was taken from the aqueous phase, treated with concentrated hydrochloric acid, and evaporated to transform thorium nitrate into thorium chloride. The thorium in the aqueous phase (as chloride) was analysed with thoron[27] (BDH). The nitrate was avoided because of its oxidative influence on thoron. The concentration of thorium in the organic phase was calculated from the difference between the total and equilibrium concentration of thorium in the aqueous phase.

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References

1 Y. Sze and D. P. Archambault, *Solvent Extr. Ion Exch.*, 1985, **3**, 785.
2 T. Nakashima, E. Zimmer, and E. Merz, *Solvent Extr. Ion Exch.*, 1984, **2**, 635.
3 D. G. Kalina, G. W. Mason, and E. P. Horwitz, *J. Inorg. Nucl. Chem.*, 1981, **43**, 159.
4 T. Tanabe and Y. Kondo, *Trans. Jpn. Inst. Met.*, 1976, **17**, 360, 426.
5 E. Hesford, H. A. C. McKay, and D. Scargill, *J. Inorg. Nucl. Chem.*, 1957, **4**, 321.
6 B. Marin, J. Y. Sellier, and D. Gourisse, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1377.
7 G. A. Yagodin, V. V. Sergievski, L. V. Evdokimova, L. M. Babenko, *Dokl. Akad. Nauk SSSR*, 1981, **258**, 695.
8 D. C. Madigan and R. W. Cuttrall, *J. Inorg. Nucl. Chem.*, 1961, **21**, 334.
9 A. Apelblat and A. Hornik, *Isr. J. Chem.*, 1969, **7**, 45.
10 V. G. Torgov, M. K. Drozdova, Z. A. Larionova, and G. A. Mardezhova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, **1**, 81.
11 S. Tataru and Gh. Filip, *Rev. Roum. Chim.*, 1966, **11**, 733.
12 T. V. Healy and H. A. C. McKay, *Trans. Faraday Soc.*, 1956, **52**, 633.
13 A. L. Mills and W. R. Logan, 'Solvent Extraction Chemistry,' eds. D. Dyrsen, J. O. Liljenzin, and J. Rydberg, North-Holland, Amsterdam, 1967, p. 322.
14 T. Nakashima and Z. Kolarik, *Solvent Extr. Ion Exch.*, 1983, **1**, 497.
15 S. Siekerski, *J. Inorg. Nucl. Chem.*, 1962, **24**, 205.
16 A. Saleh, *Z. Anorg. Allg. Chem.*, 1969, **371**, 106.
17 V. I. Tikhomirov and V. P. Popov, *Radiokhimiya*, 1967, **9**, 419, 427, 431.

18 Z. Kolarik and K. Grudpan, *Solvent Extr. Ion Exch.*, 1985, **3**, 61.
19 T. Sato, *J. Appl. Chem.*, 1965, **15**, 489.
20 L. J. Katzin, J. R. Ferraro, W. W. Wendlandt, and R. L. McBeth, *J. Am. Chem. Soc.*, 1956, **78**, 5139.
21 Dj. M. Petković, *J. Chem. Soc., Dalton Trans.*, 1983, 591.
22 Dj. M. Petković, S V. Ribnikar, and I. D. Pokidisheva, *Bull. Soc. Chim. Beograd*, 1984, **49**, 97.
23 M. M. Kopečni and Dj. M. Petković, *Solvent Extr. Ion Exch.*, 1986, **4**, 435.
24 R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1969, p. 503.
25 A. Apelblat, *J. Chem. Soc., Faraday Trans. 1*, 1973, 1618.
26 Ch. Reinchardt, 'Lösungsmittel-Effekte in der Organischen Chemie,' Verlag Chemie, Weinheim, 1969, p. 136; see also A. Koppel and V. A. Palm, in 'Advances in Linear Free Energy Relationships,' Plenum, London, 1972, p. 211.
27 C. V. Banks and C. H. Byrd, *Anal. Chem.*, 1953, **25**, 416.

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