A Chemical Model of the Solvent Extraction System: Water–Uranyl Nitrate–Nitric Acid–Tri-*n*-butyl Phosphate–Diluent

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A chemical model founded on the equilibrium constant expression for a solvent-extraction reaction has been proposed for the extraction of uranyl nitrate with tri-*n*-butyl phosphate. The model utilizes the chemical activities of the extraction species in the aqueous phase. Introduction of self-association of the extractant on the coextraction of nitric acid compensates to some extent for the neglect of the corresponding activity coefficients in the organic phase. The model fits well the distribution results over the whole concentration range of the extraction isotherm. Extraction and dimerization constants obtained by means of the model are in agreement with literature data.

Determination of solvent-extraction equilibrium constants has been a prevailing interest of our research team, with particular attention to the reprocessing of spent nuclear fuel. A new approach for the evaluation of thermodynamic extraction constants based on the use of distribution data within the medial part of the extraction isotherm has been published by us.[1,2] The method does not require any doubtful extrapolation of the apparent constants to infinite dilution.

The equations which relate the concentration of uranyl salts in an organic phase with that in an aqueous phase are of prime importance in the control of a large-scale reprocessing operation. Since the apparent equilibrium constants cannot give a valid characterization of the distribution equilibria, the thermodynamic equilibrium constants have to be used as the basis of any mathematical model of distribution equilibria.

The aim of this work is to propose a chemical model based on the chemical reaction where a neutral extractant interacts with an inorganic salt present in the aqueous phase to form an uncharged complex which is extracted into the organic phase. As starting data, the chemical activities of the aqueous ionic species and the concentrations of the solvate and free extractant in the organic phase are employed. Thermodynamic extraction constants determined in our previous papers are compared with the estimates calculated by the model proposed here.

A comprehensive survey on the mathematical description of solvent extraction of uranyl salts with extractants containing phosphorus-bonded oxygen-donor atoms has been published by Kolarik.[3] The use of electronic computer programs in the interpretation of solvent-extraction data has been reviewed by Baes and co-workers[4–6] and Meloun *et al.*[7] Drawbacks of the published distribution models have been discussed by Kolarik and Petrich.[8] As Kolarik[3] emphasizes, a complete thermodynamic description of distribution equilibria is hardly possible at the moment due to the lack of activity coefficients for the components in the aqueous phase over broad concentration ranges and for the components present in the organic phase. The consideration of apparent concentration equilibrium constants or distribution ratios of different concentration variables is the only practicable approach. The large number of empirical equations suggested in the literature have been reviewed by Kolarik.[3]

A Chemical Model of Solvent Extraction Equilibria

The principle of the chemical model we propose is illustrated by the extraction of a metal salt $MA_{z/b}$ with a neutral extractant S. The solvent-extraction process is represented by equation (1). The thermodynamic equilibrium constant for reaction (1) is defined by equation (2). Here, a is the chemical activity of the species which is denoted by an appropriate subscript and defined on the mol dm^{-3} scale. To simplify the chemical reaction formulae, an extra notation to specify the species in the organic phase has been omitted; M^{z+} and A^{b-} refer to the aqueous phase, while S and $MA_{z/b}\cdot nS$ (abbreviated as MAS) always refer to the organic phase components. The standard state for the activities is the infinite dilution of the species either in water or in the water-saturated organic diluent.

$$M^{z+} + \frac{z}{b}A^{b-} + nS \rightleftharpoons MA_{z/b}\cdot nS \qquad (1)$$

$$K = a_{MAS}/a_M a_A{}^{z/b} a_S{}^n \qquad (2)$$

The availability of the activity coefficients (γ) of the species in the organic phase is limited and equation (2) has therefore to be rearranged to (3). Here, c denotes the analytical concentration of the various species defined on the mol dm^{-3} scale. The concentration of the extractable complex, c_{MAS}, is equated to that of the metal salt in the organic phase. The concentration of the free extractant in the organic phase at equilibrium, c_S, has been calculated by subtracting the concentration of the extractant bound in the solvate from the total concentration of the extractant, $c_S{}^{tot}$. Unfortunately, this difference can be very small, at low and high loading of the organic phase, so magnifying the uncertainties in the curve fitting of the experimental data in these regions. The mean activity coefficients ($\gamma_\pm$) for the species in the aqueous phase, defined on the mol dm^{-3} scale, are available in the literature.[9] Using equation (3) and the experimental data on c_M, $\gamma_\pm$ and $c_S{}^{tot}$ = constant, one can compute c_{MAS} in the organic phase for the best-fit Q value. Equation (3), applied to the extraction of uranyl nitrate with tri-*n*-butyl phosphate, when

$$Q = K\gamma_S{}^n/\gamma_{MAS} = c_{MAS}/a_M a_A{}^{z/b} c_S{}^n \qquad (3)$$

$z = 2$, $b = 1$ and $n = 2$, can be rearranged in explicit form for c_{UAS} leading to equation (4).

$$c_{UAS} = [B - \sqrt{B^2 - 16(c_S{}^{tot})^2}]/8 \quad (4)$$

$$B = 4c_S{}^{tot} + (1/Q4c_U{}^3\gamma_\pm{}^3) \quad (5)$$

The Q values obtained for the various sets of distribution data (diverse isotherms), distinguished by different $c_S{}^{tot}$ values, have to be unchanged. Usually, this is not the case so that an additional chemical reaction has to be introduced. To compensate for the lack of activity coefficients for the species in the organic phase, the self-association of the extractant in the organic phase has been included [equation (6)] and equation (7)

$$2S \rightleftharpoons S_2 \quad (6)$$

$$K_2 = c_{S(D)}/c_S{}^2 \quad (7)$$

defines the corresponding equilibrium constant. Here, $c_{S(D)}$ denotes the concentration of the extractant in the dimeric form. Taking into account equation (8), which expresses the presence

$$c_S{}^{tot} = c_S + 2c_{S(D)} + nc_{MAS} \quad (8)$$

of the dimer in the organic phase, together with (3) and (7), one obtains the final form (9). It enables one to calculate $a_Ma_A{}^{z/b}$,

$$a_Ma_A{}^{z/b} = \frac{c_{MAS}}{Q}\left[\frac{4K_2}{-1 + \sqrt{1 - 8K_2(nc_{MAS} - c_S{}^{tot})}}\right]^n \quad (9)$$

that is c_M, for the best-fit values of Q and K_2. The use of equation (9) for the system $[UO_2(NO_3)_2]$–$PO(OBu^n)_3$–diluent is enabled when $z = 2$, $b = 1$ and $n = 2$.

A SIMPLEX based non-linear least-squares computer procedure has been applied to equation (9) to fit the experimental data of c_{UAS} and $a_Ua_A{}^2$ for constant $c_S{}^{tot}$. For this purpose equation (9) is expressed in logarithmic form and parameters Q and K_2 were adjusted. The difference between the experimental $a_Ma_A{}^{z/b}$ value and that obtained by equation (9) is computed.

To obtain c_U from the values of $a_Ua_N{}^2$ calculated by equation (9) we used relationship (10) based on literature $\gamma_\pm$ data.[9]

$$c_U = A_0 + A_1\log a_Ua_N{}^2 + A_2(\log a_Ua_N{}^2)^2 + A_3(\log a_Ua_N{}^2)^3 \quad (10)$$

The A_i coefficients, range of uranyl nitrate concentration (c_{UN}) in the aqueous solutions and the standard error of the fit are reported in Table 1. Unfortunately, one cannot calculate c_U directly from $a_Ua_N{}^2$ obtained by means of equation (9) since the $\gamma_\pm$ value corresponding to the unknown c_U value is not known.

Application of the Model to Experimental Data

Modelling of solvent-extraction data, according to equation (9), is illustrated with data on the extraction of uranyl nitrate with $PO(OBu^n)_3$ published elsewhere.[10] Fig. 1 shows the use of equation (9) to fit to the experimental data. The lines represent the solution of equation (9) for log $Q = 2.35$ and $K_2 = 0.41 \pm 0.24$ dm^3 mol^{-1} for $c_P{}^{tot}$ from 0.15 to 1.00 mol dm^{-3}. The fitting of the experimental data with equation (4) resulted in inconsistent Q values. On the contrary, equation (9) led to a pair of invariable Q and K_2 values with appropriate match to the experimental points.

The numerical procedure exemplified above was shown to be valid using data of Davis *et al.*,[11] with $PO(OBu^n)_3$ and Amsco 125–82 as an inert diluent. The lines fitting the experimental points, Fig. 2, have been calculated by use of equation (9) with log $Q = 2.20$ and $K_2 = 0.76 \pm 0.23$ dm^3 mol^{-1}. The K_2 values have rather high errors as a consequence of the low self-association of the extractant in comparison with the uranyl nitrate extraction process. Nevertheless, these K_2 values are in agreement with the literature data as shown later.

Table 1 Coefficients A_i of equation (10) for given c_{UN} ranges in the aqueous solutions and the corresponding standard error (S) of the fit

c_{UN}	A_0	A_1	A_2	A_3	S
0.01–0.10	0.788 24	0.388 28	0.068 88	0.003 92	0.000 16
0.10–1.00	0.874 35	0.415 07	0.051 12	−0.000 93	0.001 86

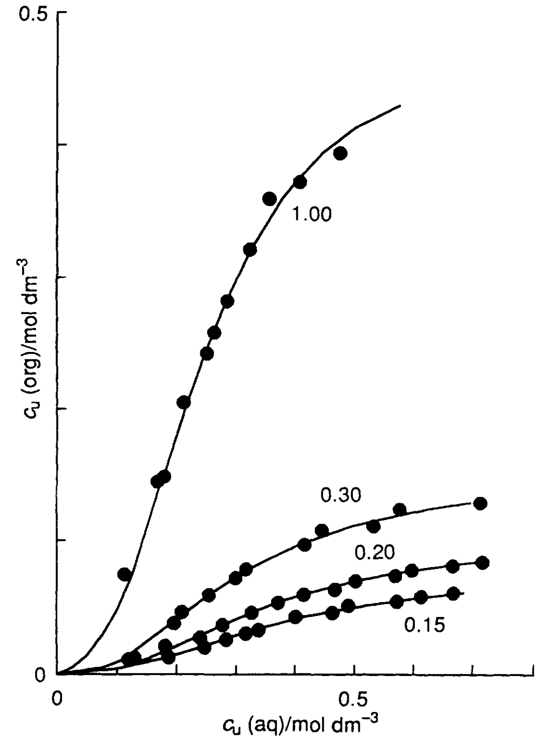

Fig. 1 Experimental data[10] on uranyl nitrate extraction with $PO(OBu^n)_3$ in hexane fitted by use of equation (9) with $K = 224$ dm^6 mol^{-2} and $K_2 = 0.41$ dm^3 mol^{-1}. The total phosphate concentrations (mol dm^{-3}) are shown beside the isotherms

Figs. 1 and 2 demonstrate a good agreement between the actual distribution data $c_{UN\cdot 2S}(c_{UN})$ and the lines representing the proposed model. The calculated values of log $Q = 2.35$ and 2.20 for hexane and Amsco, respectively, are in agreement with the log K value of 2.25, critically evaluated by Marcus[12] and log $K = 2.23$ obtained by our method.[1,2] The proposed model shows that one extraction constant value can mathematically describe equilibria over a broad concentration range of the extractant and within the whole isotherm up to the maximum loading of the organic phase.

The dimerization constants for $PO(OBu^n)_3$, $K_2 = 0.41$ dm^3 mol^{-1} in hexane and 0.76 dm^3 mol^{-1} in Amsco as diluent, have been calculated in this work for systems where water was present. They are four to seven times less than the K_2 value of 2.9 dm^3 mol^{-1} we obtained for the dry $PO(OBu^n)_3$–hexane system.[13,14] Poczynailo *et al.*,[15] reported $K_2 = 1.24$ dm^3 mol^{-1}, which is in better agreement with the result we report here. To obtain it those authors used vapour-pressure data for the system $PO(OBu^n)_3$–hexane–uranyl nitrate–water. The hydration of $PO(OBu^n)_3$ has been discussed in more detail elsewhere.[16]

Our consideration of the solvent extraction of uranyl nitrate with $PO(OBu^n)_3$ has been extended to the case where nitric acid is present. The coextraction of nitric acid has then to be taken into account as shown by equation (11) and the corresponding

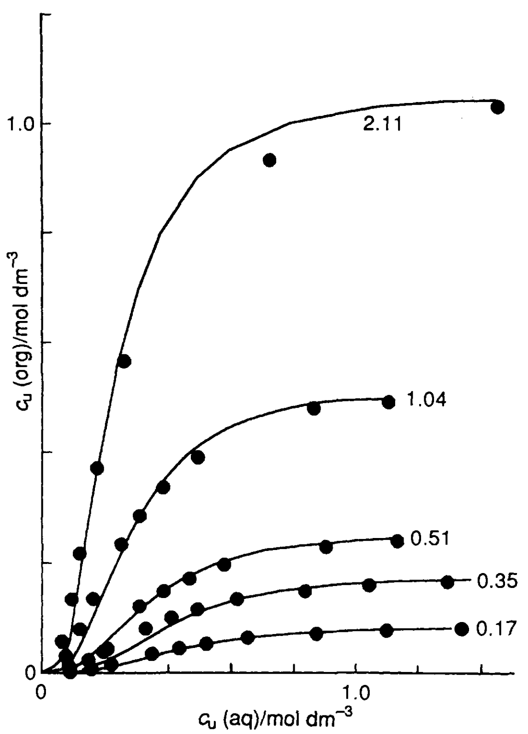

Fig. 2 Experimental data[11] on uranyl nitrate extraction with $PO(OBu^n)_3$ in Amsco fitted by use of equation (9) with $K = 158$ dm^6 mol^{-2} and $K_2 = 0.76$ dm^3 mol^{-1}. The total phosphate concentrations (mol dm^{-3}) are indicated beside the isotherms

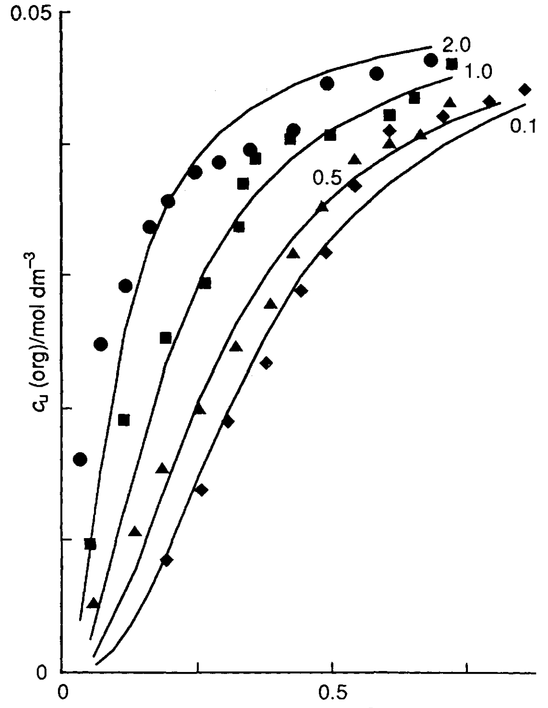

Fig. 3 Experimental data[10] on the extraction of uranyl nitrate with 0.1 mol dm^{-3} $PO(OBu^n)_3$ in hexane for different concentrations (mol dm^{-3}) of nitric acid (shown beside the curves), fitted by use of equation (4) with $K = 630$ dm^6 mol^{-2}

equilibrium constant (12). Owing to the coextraction of nitric

$$H^+ + NO_3^- + S \rightleftharpoons HNO_3{\cdot}S \qquad (11)$$

$$K_{HNS} = a_{HNS}/a_H a_A a_S \qquad (12)$$

acid the dimerization of $PO(OBu^n)_3$ can be neglected and reaction (13) has to be introduced. Equation (14) represents the equilibrium constant for reaction (13). Now the extraction constant defined by equation (2) is an overall constant including reactions (11) and (13), as summed in equation (15).

$$UO_2^{2+} + 2HNO_3{\cdot}S \rightleftharpoons UO_2(NO_3)_2{\cdot}S + 2H^+ \qquad (13)$$

$$K_{UHNS} = a_{UHNS}a_H^2/a_U a_{HNS}^2 \qquad (14)$$

$$K = K_{HNS}^2 K_{UHNS} \qquad (15)$$

Fig. 3 illustrates the application of equation (4) to the experimental data[10] on the system uranyl nitrate–nitric acid–0.1 mol dm^{-3} $PO(OBu^n)_3$–hexane. The use of equation (4) is enabled due to the decrease in dimerization of $PO(OBu^n)_3$ as a consequence of the formation of another extractable species, $HNO_3{\cdot}S$, in the organic phase. As one can see from Fig. 3 the isotherms are different for the same phosphate concentration, depending on the aqueous phase nitric acid concentration. This is known as the acidity effect on the solvent-extraction equilibria. As it has been suggested[1] our experimentally determined activities[17] of uranyl nitrate in nitric acid aqueous solution are used in equation (4). The described non-linear least-squares fit procedure has been applied to the experimental data,[10] so that the Q values were adjusted according to equation (4). For all the isotherms shown in Fig. 3, where $c_P^{tot} = 0.1$ mol dm^{-3} and the nitric acid concentration varied from 0.5 to 2.0 mol dm^{-3}, the best fit gave $Q = 630 \pm 176$. Since the value $Q = 224$ has been determined by means of equation (9) for the extraction of uranyl nitrate with $PO(OBu^n)_3$ when nitric acid is absent, one can presume that $Q = 630 \approx K_{UHNS}$ and $Q = 224 \approx K$. Then, using equation (15), one calculates $K_{HNS} = 0.60$. This value is about three times greater than our value published earlier,[18] but close to that of 0.4 critically evaluated by Marcus.[12]

The chemical model proposed in this paper is not based on empirical equations. It is founded on the true equilibrium constant expressions for the chemical reactions involved in the solvent-extraction processes. A successful description of different extraction equilibria by means of equation (4) or (9) has been established by the use of the chemical activities of the extracting species in the aqueous phase, corrected if nitric acid is present, or when dimerization of the extractant occurs in the organic phase. Neglect of the activity coefficients of the species in the organic phase is compensated by introducing self-association of the extractant or competitive extraction of nitric acid. The model fits well the experimental data over the whole extraction isotherm concentration range, within the experimental errors. The errors are greater at the end of the extraction isotherms, *i.e.* at low and high loadings of the organic phase, where the analytical procedure is more susceptible to experimental errors. As a consequence, the distribution data have to be critically selected with regard to the conditions of the analytical determinations of the species in both phases.[8] The proposed model may describe mathematically the distribution equilibria of any solute extracted by a solvation mechanism. Its extension to other types of solvent extraction equilibria will be the subject of further studies.

References

1 D. M. Petković, M. M. Kopečni and P. M. Janićijević, *J. Serb. Chem. Soc.*, 1991, **56**, 479.
2 D. M. Petković, *J. Chem. Soc., Dalton Trans.*, 1988, 1813; M. A. Hughes and H. Sungshon, *J. Chem. Eng. Data*, 1986, **31**, 4.
3 Z. Kolarik, in *Gmelin Handbook of Inorganic Chemistry, Uranium*, 8th edn., Springer, New York, 1982, no. 55, Suppl. vol. D2, p. 108.
4 C. F. Baes, jun., W. J. McDowell and S. A. Bryan, *Solv. Extr. Ion Exch.*, 1987, **5**, 1.

5 C. F. Baes, jun., B. A. Moyer, G. N. Case and F. Case, *Sep. Sci. Technol.*, 1990, **25**, 13.

6 B. A. Moyer, W. J. McDowell, C. F. Baes, jun., G. N. Case and F. I. Case, *Solv. Extr. Ion Exch.*, 1991, **9**, 833.

7 M. Meloun, J. Havel and E. Högfeldt, *Computation of Solution Equilibria: A Guide to Methods in Potentiometry, Extraction and Spectrophotometry*, Ellis Horwood, Chichester, 1988.

8 Z. Kolarik and G. Petrich, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 1110.

9 I. Marcus and S. A. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, London, 1969.

10 D. M. Petković, *Bull. Soc. Chim. Beograd*, 1980, **45**, 281.

11 W. Davis, jun., J. Mrochek and R. R. Judkins, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1689.

12 I. Marcus, *Critical Evaluation of Some Equilibrium Constants involving Organophosphorous Extractants*, Butterworths, London, 1974.

13 D. M. Petković, in *Solvent Extraction Chemistry*, eds. D. Dyrssen, J. O. Ljiljenzin and J. Rydberg, North-Holland, Amsterdam, 1967, p. 305; D. M. Petković, *J. Inorg. Nucl. Chem.*, 1968, **30**, 603.

14 M. M. Kopečni, Z. E. Ilić and S. K. Milonjić, *J. Chromatogr. Sci.*, 1979, **17**, 253.

15 A. Poczynailo, P. R. Danesi and G. Scibona, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3249.

16 D. M. Petković and Z. B. Maksimović, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2031.

17 W. Davis, jun., P. S. Lawson, H. J. deBruin and J. Mrochek, *J. Phys. Chem.*, 1965, **69**, 1904.

18 D. M. Petković, *Bull. Soc. Chim. Beograd*, 1978, **43**, 529.

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