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A MATHEMATICAL MODEL FOR THE SOLVENT EXTRACTION OF URANYL NITRATE AND NITRIC ACID

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ABSTRACT

A generalized least squares technique can be used to calculate equilibrium constants in solvent extraction equilibria by minimizing the difference between observed and calculated distribution ratios. The method has been successfully applied to the extraction of uranyl nitrate and nitric acid by TBP dissolved in an inert diluent.

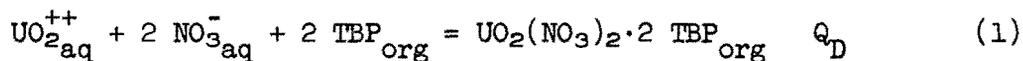
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A series of computer programs is being written in an attempt to calculate distribution ratios in successively more complicated solvent extraction equilibria. The general procedure involves setting up equilibrium expressions and determining the parameters by a generalized least squares technique. The present paper describes calculations on the distribution of $\text{UO}_2(\text{NO}_3)_2$ and HNO_3 between an aqueous phase and an organic phase consisting of tributyl phosphate (TBP) dissolved in an inert diluent (Amsco 125-90W). Since it is desired to keep the model simple the assumed equilibria do not necessarily involve all species which may have been shown to exist in the solutions in question. Also when equilibria involving additional species were incorporated into the model, mathematical convergence difficulties were encountered, presumably because the data were not sufficiently precise to enable unique determination of additional parameters.

The $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ System

In considering the equilibration of the aqueous $\text{UO}_2(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$ system with TBP-diluent the following equilibrium was assumed:



where

$$Q_D = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}]_{\text{org}}}{[\text{UO}_2^{++}]_{\text{aq}} [\text{NO}_3^-]_{\text{aq}}^2 [\text{TBP}]_{\text{org}}^2} \quad (2)$$

$$[\text{NO}_3^-] = 2 [\text{UO}_2^{++}] + m_s$$

$$m_s = \text{molarity of } \text{NH}_4\text{NO}_3$$

$$[\text{TBP}] = T_0 - 2 [\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}]$$

$$T_0 = \text{initial molarity of TBP.}$$

The equation for conservation of total uranium with equal volumes in the two phases is

$$[\text{UO}_2^{++}]_{\text{aq}} + [\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}]_{\text{org}} = \text{UTOT} \quad (3)$$

where UTOT is the sum of the initial concentrations in both phases. Hence equations (2) and (3) represent two equations in the two unknowns $[\text{UO}_2^{++}]$ and $[\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}]$ which may be solved for any particular value of Q_D. It was assumed that the ionic strength dependence of the logarithm of the distribution quotient can be expressed by

$$\ln Q_D = \ln K_D - \frac{6 \mathcal{S} \sqrt{I}}{1 + A \sqrt{I}} + BI \quad (4)$$

where K_D is the distribution constant, ℒ is the Debye-Hückel limiting slope for a singly charged ion, A and B are adjustable parameters, and I is the ionic strength of the solution given by

$$I = m_s + 3 [\text{UO}_2^{++}] \quad (5)$$

Equation (4) was used without the Debye-Hückel term in all cases where a salting agent was present and the ionic strength was fairly high, and without the linear term in the absence of a salting agent. This procedure is consistent with theory since the Debye-Hückel (DH) term varies considerably with ionic strength at low electrolyte concentrations where the linear term is relatively unimportant; at high values of ionic strength the linear term becomes much more important while the DH term approaches a limiting value of $-6 \mathcal{S} / A$. Attempts were made to evaluate both A and B of equation (4) and to include an equilibrium involving the undissociated species $\text{UO}_2(\text{NO}_3)_2$ in the aqueous phase. However, in these cases convergence difficulties were encountered in the least squares procedure, very likely because the data were not sufficiently precise to evaluate

additional parameters. For this reason and because the authors wished to use a minimum number of parameters, only one of the two terms mentioned was allowed to have an adjustable value; hence equation (4) will be written in two alternative forms:

$$\ln Q_D = \ln K_D - \frac{6 \mathcal{L} \sqrt{I}}{1 + A \sqrt{I}} \quad (4a)$$

$$\ln Q_D = \ln K'_D + BI \quad (4b)$$

where $\ln K'_D$ may be considered to be approximately equal to the high concentration limit of (4a), i.e., $\ln K'_D = \ln K_D - \frac{6 \mathcal{L}}{A}$. Thus the overall problem involved the evaluation of $\ln K_D$ and A or $\ln K'_D$ and B by a non-linear least squares procedure subject to the restrictions represented by equation (2), (3), and (5).

The criterion adopted in solving the above set of equations was that $\sum_i (D_{obs} - D_{calc})^2$ be a minimum, where the distribution coefficient D is defined as the ratio $[\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}]_{org} / [\text{UO}_2^{++}]_{aq}$ and the summation is taken over all the data points. Accordingly a series expansion of D was made in terms of the partial derivatives with respect to the adjustable parameters, either K_D and A or K'_D and B , as

$$D_{obs} = D_{calc} + \frac{\partial D}{\partial \ln K_D} \Delta \ln K_D + \frac{\partial D}{\partial A} \Delta A \quad (6a)$$

or

$$D_{obs} = D_{calc} + \frac{\partial D}{\partial \ln K'_D} \Delta \ln K'_D + \frac{\partial D}{\partial B} \Delta B \quad (6b)$$

in which D_{calc} and the partial derivatives are computed for approximate values of the parameters. The increments $\Delta \ln K_D$ and ΔA or $\Delta \ln K'_D$ and ΔB then give approximate corrections to these parameters.

The procedure used to evaluate $\ln K_D$ and A or $\ln K'_D$ and B was as

follows:

(a) At each data point a preliminary value of \underline{I} was computed (equation 5) from the experimental values of m_s and $[UO_2^{++}]$. (In subsequent iterations the calculated value of $[UO_2^{++}]$ was used in computing \underline{I}).

(b) The preliminary value of \underline{I} was substituted into equation (4a) or (4b) along with initial guesses of the parameters. With the value of \underline{Q}_D so obtained equations (2) and (3) were solved simultaneously by the Newton-Raphson method (2).

(c) After the converged values of $[UO_2^{++}]$ and $[UO_2(NO_3)_2 \cdot 2 \text{ TBP}]$ had been obtained D_{calc} was computed for each data point and approximate values for the partial derivatives in equation (6a) (or (6b)) were computed by incrementing the current estimate of the parameters by 1% and assuming that

$$\frac{D(\ln K_D + \delta) - D(\ln K_D)}{\delta (\ln K_D)} \approx \frac{\partial D}{\partial \ln K_D}$$

$$\frac{D(B + \delta) - D(B)}{\delta B} \approx \frac{\partial D}{\partial B}$$

$$\frac{D(A + \delta) - D(A)}{\delta A} \approx \frac{\partial D}{\partial A}$$

where the values of δ for the different parameters are not necessarily the same.

(d) The values of the partial derivatives for each data point were then used in the standard least squares technique (3) to compute $\Delta \ln K'_D$ and $\Delta \underline{B}$ or $\Delta \ln K'_D$ and $\Delta \underline{A}$, the corrections for modifying the initial estimates. Steps (a) through (d) were repeated with the new values of the parameters until two successive values of each differed by less than

0.1%.

Calculations were performed on two different sets of data; the first set was taken from IDO-14501 (4). In Table I are shown the observed and calculated distribution-ratios for $\text{UO}_2(\text{NO}_3)_2$ between aqueous NH_4NO_3 and TBP-diluent phases as well as the $\ln K'_D$ and linear term B as a function of TBP concentration.

Calculations were also performed on a set of data that included much higher concentrations of $\text{UO}_2(\text{NO}_3)_2$ (5). In Figure 1 are shown the observed and calculated concentrations of uranium in the organic and aqueous phases for the extraction of $\text{UO}_2(\text{NO}_3)_2$ with 5.39% TBP in Amsco as a function of NH_4NO_3 concentration. The results for 10.3 and 20.1% TBP were equally good.

The values of $\ln K'_D$ computed by the method outlined above varied slightly with the concentration of salting agent, the concentration of uranium, and the concentration of TBP used. Hence all the individual values were grouped together and used to determine the coefficients of equation (7) by the method of least squares.

$$\ln K'_D = \ln K^O + B_1 I_{\text{NH}_4\text{NO}_3} + B_2 I_{\text{UO}_2(\text{NO}_3)_2(\text{aq})} + B_3 (\text{vol } \% \text{ TBP}) \quad (7)$$

The coefficients of equation (7) describing the two sets of data are given in Table II.

The calculations so far described all involved the use of a salting agent. In all cases the ionic strength of the aqueous phase was high, and no Debye-Hückel activity coefficient term was used. However, the calculations converged equally well at lower concentrations of uranium in the absence of a salting agent and with a Debye-Hückel activity

Table I

Observed and Calculated Distribution Ratios D (Organic/Aqueous) for
 $\text{UO}_2(\text{NO}_3)_2$ between Aqueous NH_4NO_3 and TBP-Diluent Phases

Vol. % TBP	M NH_4NO_3	Initial M $\text{UO}_2(\text{NO}_3)_2$	$D(o/a)_{\text{obs.}}$	$D(o/a)_{\text{calc.}}$
5	.68	.0098	.18	.13
	1.37	.0102	.68	.53
	2.00	.0112	1.22	1.13
	2.74	.0109	2.17	2.20
	3.42	.0111	3.50	3.58
	4.70	.0158	6.83	6.80
$\ln K_D' = 2.17 \quad B = .111$				
10	.68	.0107	.68	.54
	1.37	.0102	1.98	2.21
	1.97	.0270	4.85	4.08
	2.00	.0099	4.88	4.97
	2.74	.0106	9.54	9.96
	3.42	.0108	16.2	16.6
	3.42	.0114	17.1	16.5
$\ln K_D' = 2.22 \quad B = .115$				
20	.68	.0101	2.58	2.27
	1.37	.0141	12.95	9.38
	2.00	.0134	28.1	21.2
	2.74	.0105	44.7	43.3
	3.42	.0094	60.8	72.5
	3.94	.0273	97.4	90.7
$\ln K_D' = 2.30 \quad B = .0964$				

Table II

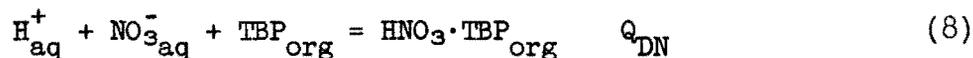
Coefficients of Equation 7

	IDO-data (4)	ORNL-data (5)
$\ln K^0$	2.14	2.57
B_1	.110	- .116
B_2	- .174	.468
B_3	.0083	- .0440

coefficient term. In this case the parameters of the fit were $\ln K_D$ and A (as defined above) and the linear term was not used. In Table III is shown a comparison of D_{obs} and D_{calc} for the distribution of uranium between TBP-Amsco in the absence of a salting agent. The best agreement between observed and calculated distribution coefficients was obtained with A taken as 2.0 at both 5 and 10% TBP in Amsco. Also, if the limiting value for the DH term (-3.5) is added to $\ln K_D$ (about 5.55), a value of about 2.05 is obtained for $\ln K_D'$, which compares favorably with the values shown in Table I.

The HNO₃ System

In considering the equilibration of aqueous HNO₃ with TBP-diluent the following equilibrium was assumed:



where

$$Q_{\text{DN}} = \frac{[HNO_3 \cdot TBP]_{\text{org}}}{[H^+]_{\text{aq}} [NO_3^-]_{\text{aq}} [TBP]_{\text{org}}} \quad (9)$$

and

$$[H^+] = [NO_3^-]$$

$$[TBP] = T_0 - [HNO_3 \cdot TBP]$$

$$T_0 = \text{initial molarity of TBP}$$

The equation for conservation of HNO₃ (on the assumption of equal volumes in the two phases) is

$$[H^+] + [HNO_3 \cdot TBP] = HNO \quad (10)$$

where HNO is the sum of the original concentrations in both phases.

Thus equations (9) and (10) represent two equations in the two unknowns $[H^+]$ and $[HNO_3 \cdot TBP]$ which may be solved for any particular value of Q_{DN} .

Table III

Distribution of Uranium between TBP-Amsco and Water in the
Absence of a Salting Agent

<u>Vol. % TBP</u>	<u>U-feed conc. (M)</u>	<u>A</u>	<u>D_{obs.} (6)</u>	<u>D_{calc.}</u>	<u>lnK_D</u>
5	.0417	2.0	.012	.012	5.5731
	.0837		.029	.033	
	.2058		.089	.087	
	.2376		.10	.095	
10	.0412	2.0	.033	.043	5.5292
	.0824		.091	.11	
	.1172		.15	.16	
	.1566		.20	.20	
	.2021		.24	.24	
	.2381		.26	.26	
	.2978		.29	.28	
	.3475		.31	.28	

Again it was assumed that the ionic strength dependence of the logarithm of the distribution quotient can be expressed by

$$\ln Q_{DN} = \ln K_{DN} - \frac{2 \int \sqrt{I}}{1 + A \sqrt{I}} \quad (11)$$

where K_{DN} is the distribution constant, \int and A have the same significance as before, and the ionic strength of the aqueous solution is given by $[H^+]$. The Debye-Hückel term should correct for the variation in activity coefficient of the HNO_3 in the aqueous phase.

The calculation itself was carried out as described previously for the $UO_2(NO_3)_2$ system and the results are summarized in Table IV. The value of 2.0 for the A -parameter at the lower TBP concentrations does indeed correct (to a reasonably good approximation) for the variation in activity coefficient of the aqueous HNO_3 to nearly 1.0 M, as can be verified by comparing values of the above term with those of known activity coefficients. At higher concentrations of TBP, however, the best agreement between observed and calculated distribution coefficients was obtained with smaller values of the A -parameter. Since the A -parameter as used should correct for ionic strength effects in the aqueous phase only, there is no obvious reason why it should vary with the percentage of TBP. If one considers the Debye-Hückel term merely as an empirical expression, it evidently does correct for effects in the non-aqueous phase as well. The values of $\ln K_{DN}$ do not vary linearly with TBP concentration throughout the entire range, but appear to be quadratic, at least at the higher percentages of TBP. However, if only the three lowest TBP concentrations are considered, then one can compute a linear coefficient, such as B_3 in equation (7), with a value of about

Table IV

Distribution of HNO₃ between TBP-Amsco and Water

Vol. % TBP	HNO ₃ Conc. (M)	A	D _{obs.}	D _{calc.}	lnK _{DN}	lnK _{DN} *
5	.1991	2.0	.0054	.0055	-1.2682	-1.330
	.4084		.0085	.0099		
	.5989		.0134	.0134		
	.8062		.0167	.0167		
	1.0035		.0209	.0194		
10	.1990	2.0	.0152	.0151	- .9322	-1.023
	.4088		.0271	.0271		
	.6004		.0352	.0362		
	.8070		.0426	.0445		
	1.0042		.0482	.0510		
15	.1001	1.0	.0214	.0184	- .4464	- .646
	.1997		.0291	.0308		
	.4090		.0486	.0502		
	.6073		.0654	.0638		
	.8216		.0754	.0750		
1.0163	.0812	.0829				
30	.4041	1.0	.126	.128	- .1344	- .342
	.6042		.169	.161		
	.8110		.184	.187		
	1.0140		.203	.205		
65	.1004	0.8	.131	.133	.1715	.051
	.2071		.206	.215		
	.4135		.332	.320		
	.5670		.414	.376		
	.8005		.459	.439		
	.9845		.459	.476		
1.5305	.502	.543				
100	.1002	0.5	.253	.261	.5396	.405
	.2045		.401	.399		
	.4080		.588	.566		
	.6050		.681	.670		
	.8160		.786	.748		
	1.0180		.824	.802		
	1.5480		.850	.884		
	1.9840		.854	.910		

* W. Davis, Jr., private communication

.08.

Davis (7) treated the same HNO_3 data by correcting with literature values for the aqueous HNO_3 activity coefficients, assuming that the logarithm of the ratio of the activity coefficients of $\text{HNO}_3 \cdot \text{TBP}_{\text{org}}$ to TBP_{org} was a linear function of the concentration of HNO_3 in the organic phase, and evaluating $\ln K_{\text{DN}}$ by extrapolating to zero HNO_3 concentration in that phase. His values are given in the last column of Table IV.

Distribution of Uranium between HNO_3 Solutions and TBP-Amsco

In describing the solvent extraction of uranium from HNO_3 solution it is necessary to consider simultaneously the equilibrium quotients given by equations (2) and (9) and observe that

$$[\text{NO}_3^-] = m_s + 2 [\text{UO}_2^{++}] + [\text{H}^+]$$

and

$$[\text{TBP}] = T_o - 2 [\text{U}\phi] - [\text{HN}\phi] .$$

where

$\text{U}\phi$ = molarity of uranium in the organic phase

$\text{HN}\phi$ = molarity of HNO_3 in the organic phase

In these equations m_s and T_o have the same significance as before. In addition to the two equilibrium quotients, equation (3) for conservation of total uranium and equation (10) for the conservation of HNO_3 are needed to permit the evaluation of the unknowns $[\text{H}^+]$, $[\text{UO}_2^{++}]$, $[\text{U}\phi]$, and $[\text{HN}\phi]$. In actual practice the conservation equations were used to express $[\text{U}\phi]$ and $[\text{HN}\phi]$ in terms of $[\text{H}^+]$ and $[\text{UO}_2^{++}]$ and hence it was necessary to solve only equations (2) and (9) by the Newton-Raphson method.

In carrying out the calculation an attempt was first made to

determine the four parameters $\ln K_{\underline{DH}}$, $\ln K_{\underline{DU}}$, B_1 , and B_2 as defined in equations 12 and 12a:

$$\ln Q_{\underline{DU}} = \ln K_{\underline{DU}} + B_1 I \quad (12)$$

$$\ln Q_{\underline{DH}} = \ln K_{\underline{DH}} + B_2 I \quad (12a)$$

where the K values represent distribution constants and

$$I = m_s + [H^+] + 3 [UO_2^{++}] \quad (13)$$

However, mathematical difficulties were encountered in the evaluation of $\frac{\partial D}{\partial B_1}$ and $\frac{\partial D}{\partial B_2}$ (undoubtedly because the data were not sufficiently precise to determine unique values of the B parameters) and hence only two parameters, the $\ln K$ values in equations (12) and (12a), were used.

In Table V is shown a comparison of observed (4) and calculated distribution coefficients for the $UO_2(NO_3)_2 - HNO_3$ system at two different NH_4NO_3 and two different TBP concentrations. It is interesting to compare the values of $\ln K_{\underline{D}}$ and $\ln K_{\underline{DN}}$ (really $\ln Q_{\underline{D}}$ and $\ln Q_{\underline{DN}}$, since no linear term was used) shown in Table V with the corresponding values given in Tables I and IV, where each was determined separately. In the case of 5% TBP $\ln K'_{\underline{D}} = 2.17$ and $B = .111$ (Table I). Hence $\ln Q_{\underline{D}} = 2.61$ in 3.94 M NH_4NO_3 and 2.95 in 6.89 M NH_4NO_3 . These values are to be compared with 3.09 as shown in Table V. In the case of 10% TBP values of 2.68 for $\ln Q'_{\underline{D}}$ in 3.94 M NH_4NO_3 and 3.02 for $\ln Q'_{\underline{D}}$ in 6.89 M NH_4NO_3 are to be compared with 2.98 as shown in Table V. Similarly, average $\ln Q_{\underline{DN}}$ values of -2.24 and -1.90 computed for 5% and 10% TBP from the parameters given in Table IV are to be compared with the corresponding values of -2.16 and -2.24 shown in Table V. Hence the parameters calculated for the combined $UO_2(NO_3)_2 - HNO_3$ system are consistent with those obtained in each system separately.

Table V

Observed and Calculated Distribution Ratios D (Organic/Aqueous)
for $UO_2(NO_3)_2$ between Aqueous NH_4NO_3 - HNO_3 and TBP-Diluent Phases

5 vol % TBP

<u>D_{obs}</u>	<u>D_{calc}</u>	<u>M_{NH₄NO₃}</u>	<u>M_{HNO₃}</u>	<u>M_H⁺</u>	<u>10³ x M_{UO₂⁺⁺}</u>
4.82	4.57	3.94	1.04	.98	3.02
4.55	3.72	3.94	1.55	1.48	3.49
3.65	3.00	3.94	2.07	1.99	4.19
3.16	2.51	3.94	2.59	2.49	4.45
11.2	11.6	6.89	.52	.48	1.44
7.81	7.23	6.89	1.04	.97	2.41
4.44	5.05	6.89	1.55	1.47	3.32
2.83	3.87	6.89	2.07	1.97	3.77
2.97	3.10	6.89	2.59	2.48	3.95

$$\ln K_D (\text{uranium}) = 3.09$$

$$\ln K_{DN} (\text{nitric acid}) = -2.16$$

10 vol % TBP

<u>D_{obs}</u>	<u>D_{calc}</u>	<u>M_{NH₄NO₃}</u>	<u>M_{HNO₃}</u>	<u>M_H⁺</u>	<u>10⁴ x M_{UO₂⁺⁺}</u>
22.6	24.3	3.94	.517	.46	7.35
22.1	22.0	3.94	1.04	.93	4.85
21.1	16.9	3.94	1.55	1.41	9.14
19.7	13.5	3.94	2.07	1.90	12.4
15.2	11.3	3.94	2.59	2.40	13.1
35.2	38.1	6.89	1.04	.90	4.00
33.0	28.4	6.89	1.55	1.37	3.83
17.0	19.1	6.89	2.07	1.87	8.90
7.5	16.1	6.89	2.59	2.36	5.92

$$\ln K_D (\text{uranium}) = 2.98$$

$$\ln K_{DN} (\text{nitric acid}) = -2.24$$

Calculations were also performed on the $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-TBP}$ system in the absence of a salting agent (6); the values of the parameters $\ln K_{\underline{D}}$ (for uranium) and $\ln K_{\underline{DN}}$ (for nitric acid) are given in Table VI. In carrying out the calculations an attempt was first made to consider each acid concentration separately. However, except in the case of 0.5 M HNO_3 and 10% TBP convergence difficulties were experienced unless all the data were considered simultaneously. Hence it was necessary with the 15% TBP system to calculate single values of $\ln K_{\underline{D}}$ and $\ln K_{\underline{DN}}$ determined by all the data; as expected, the values of D_{obs} and D_{calc} showed much greater discrepancies at 0.5 M HNO_3 than the values calculated separately for the 10% TBP system at the same acid concentration. (See Appendix).

The values of $\ln Q_{\underline{D}}$ for this system can also be calculated in two different ways: using either the parameters in Table I or those in Table III along with an average ionic strength value (and the assumption that the Q values vary with ionic strength alone, i.e., are independent of the medium). A comparison of the values calculated in these two ways with those shown in Table VI is given in Table VII.

Since the values calculated using the Table III parameters agree more closely with the observed values than do those calculated using the Table I parameters it seems that the activity coefficients of $\text{UO}_2(\text{NO}_3)_2$ in HNO_3 media more closely resemble those in pure aqueous $\text{UO}_2(\text{NO}_3)_2$ solution than those in the presence of NH_4NO_3 .

A comparison of the $\ln Q_{\underline{DN}}$ values shows reasonably good agreement at 0.5 M HNO_3 . In the higher concentration regions all that can be said is that the calculated values are qualitatively in the right direction. The parameters given in Table IV were obtained in the concentration

Table VI

Values of the Distribution Constants for the System
 $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-TBP-Diluent}$ in the Absence of
a Salting Agent

<u>% TBP</u>	<u>M_{HNO₃}</u>	<u>lnK_D (uranium)</u>	<u>lnK_{DN} (nitric acid)</u>
10	0.5	3.27	-1.94
	2.0-4.0	2.72	-3.48
15	0.5-4.0	2.47	-3.47

Table VII

Comparison of Observed and Calculated Equilibrium
Quotients (10% TBP)

M_{HNO_3}	$\ln Q_D$ (calc)		$\ln Q_D$ (obs)
	Using Table I Parameters	Using Table II Parameters	
0.5	2.28	3.43	3.27
2.0-4.0	2.57	2.80	2.72
	$\ln Q_{DN}$ (calc)		
	Using Table IV Parameters		
0.5	-1.63		-1.94
2.0-4.0	-1.8		-3.5
0.5-4.0*	-1.9		-3.5

* 15% TBP

range 0-1 M; the poor agreement in the 2-4 M range in the mixed system indicates that a Debye-Hückel activity coefficient term is not sufficient and that a linear term is needed. Actually this is known to be the case: the activity coefficient of HNO_3 increases with ionic strength above about 1 M.

Hence a relatively simple mathematical model may be used to describe solvent extraction equilibria over wide ranges of concentration of material being extracted, of salting agent, and of extractant. In principle there is no reason why the model cannot be extended to much more elaborate systems. It appears, however, that as the number of parameters increases the likelihood of encountering mathematical convergence difficulties also increases. Part of the difficulty probably results from the fact that the data may not be sufficiently precise to determine unique values for as many parameters as may be desired. Part of the difficulty is also related to the fact that in non-linear problems solved by successive approximations (e.g. the solution of a set of non-linear equations by the Newton-Raphson method or the evaluation of non-linear parameters by the method of least squares) very close initial guesses may be required in order that the values obtained by continued iterations converge.

It is therefore recommended that in any extension of the work described here:

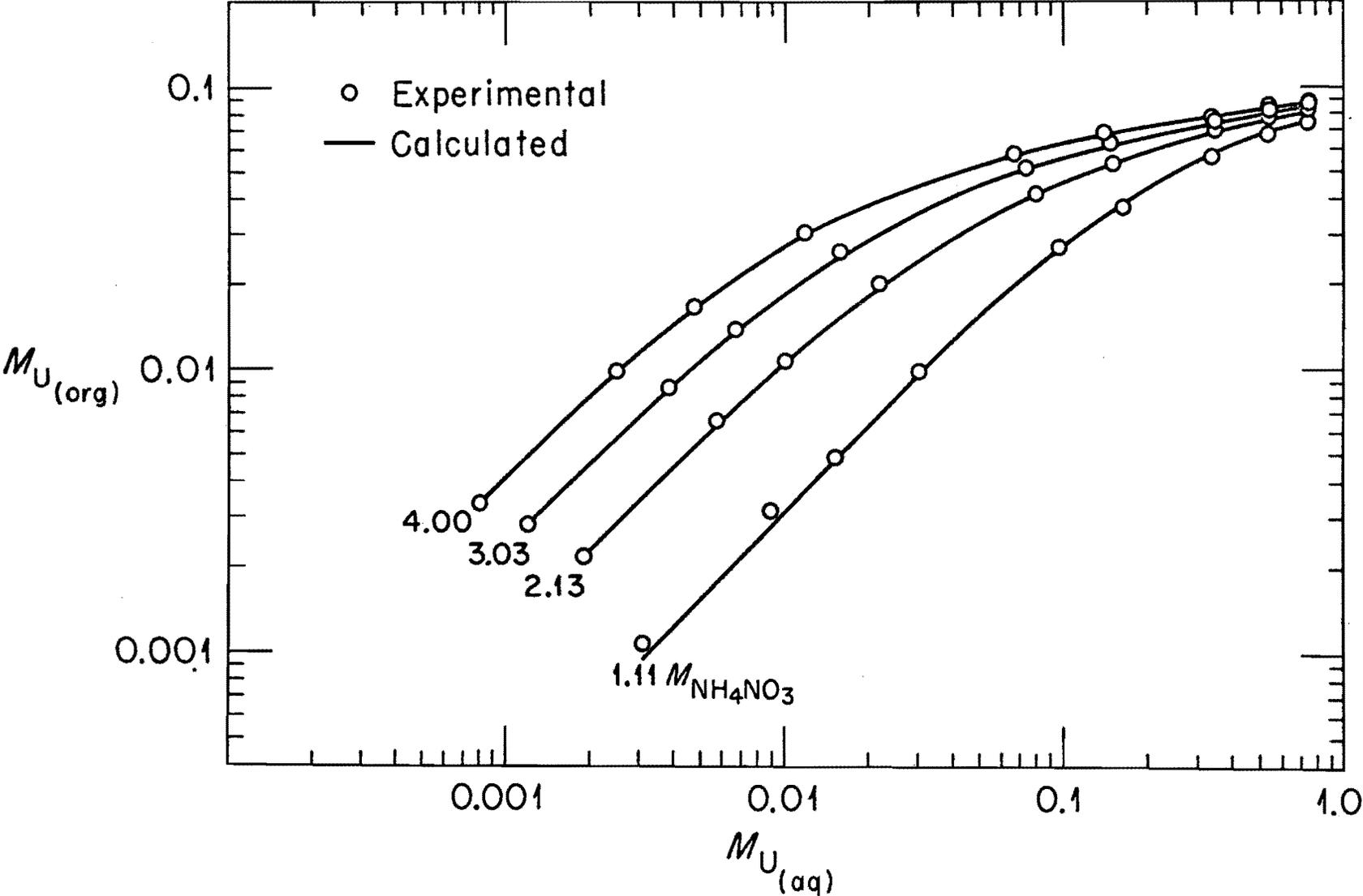
- (1) the number of parameters be kept to a minimum, and
- (2) the development of new methods for forcing convergence (as well as using known ones) be considered an integral part of the problem.

One method of complying with (1) above without necessarily losing accuracy is to permute over a range of fixed values of one (or more) of

the parameters while evaluating the other(s). As far as (2) is concerned, methods in use include (a) replacing a parameter by the square of another in order to keep it positive (if desired); (b) setting the value of a known positive parameter to some arbitrary positive value if it goes negative during an iteration; (c) preventing a parameter from varying by more than some arbitrary amount (e.g., 10%) in any one iteration; and (d) altering the Newton-Raphson procedure to use the squares of functions of the first derivatives of the variables rather than the first powers.

Figure 1

Observed and Calculated Concentrations of Uranium
in the Organic and Aqueous Phases for the
Extraction of $\text{UO}_2(\text{NO}_3)_2$ with 5.39% TBP in Amsco



REFERENCES

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- (2) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry", D. Van Nostrand Co., Inc., New York, N. Y., p. 475 (1943).
- (3) M. H. Lietzke and R. W. Stoughton, J. Phys. Chem. 65, 2247 (1961).
- (4) R. A. Kent and K. L. Ronde, IDO-14501, Table 3 (July 1960).
- (5) TM-177, Chemical Technology Division Chemical Development Section B, Quarterly Progress Report, Oct. through Dec. 1961.
- (6) CF-60-7-76, Chemical Technology Division, Chemical Development Section B, Monthly Progress Report, June-July 1960.
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Appendix

Calculation of Distribution Coefficients for $\text{UO}_2(\text{NO}_3)_2$
between Aqueous $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ and TBP-Diluent Phases

Some of the data from ref. (6) involved the extraction of $\text{UO}_2(\text{NO}_3)_2$ from aqueous $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ into a TBP-organic diluent phase. The initial organic phase contained 10 or 15 volume % TBP. The initial concentration of HNO_3 in the aqueous phase was 0.5, 2.0, 3.0 or 4.0 M while the $\text{UO}_2(\text{NO}_3)_2$ was a few hundredths to a few tenths molar. An attempt was made to evaluate the four parameters $\ln K_{\text{DU}}$, $\ln K_{\text{DH}}$, B_1 and B_2 in equations (12) and (12a),

$$\ln Q_{\text{DU}} = \ln K_{\text{DU}} + B_1 I \quad (12)$$

$$\ln Q_{\text{DH}} = \ln K_{\text{DH}} + B_2 I \quad (12a)$$

by the method described in the paper. Convergence difficulties were encountered. Hence B_1 and B_2 were set equal to zero and an attempt was made to evaluate $\ln K_{\text{DU}}$ and $\ln K_{\text{DH}}$ (actually $\ln Q_{\text{DU}}$ and $\ln Q_{\text{DH}}$) at each HNO_3 concentration, so that the B values could be obtained from the variation of the $\ln K$ (actually $\ln Q$) values with stoichiometric ionic strength. However, only in the case of 10% TBP and 0.5 M HNO_3 could extraction quotients be calculated; these are shown in Table VIA. The data for 2.0, 3.0 and 4.0 M HNO_3 and 10% TBP were then combined as were all the data at 15% TBP. With the data combined into the two indicated sets, converged values for the $\ln K$'s (actually $\ln Q$'s) were obtained (with the B 's set equal to zero); these values are shown in Table VIA. The numbers in the columns of Table VIA from left to right are the observed and calculated distribution ratios, the initial molarity of HNO_3 , and the final molarities

of HNO_3 and $\text{UO}_2(\text{NO}_3)_2$ in the aqueous phase.

Table VIA

Observed and Calculated Distribution Coefficients D (o/a) for $\text{UO}_2(\text{NO}_3)_2$ between Aqueous $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ and TBP-Diluent Phases in the Absence of a Salting Agent

10% TBP

D_{obs}	D_{calc}	M_{HNO_3}	M_{H^+}	$10^2 \times M_{\text{UO}_2^{++}}$
.69	.69	0.5	.489	1.24
.69	.69	0.5	.489	1.26
.69	.68	0.5	.489	2.52
.66	.68	0.5	.489	2.49
.52	.53	0.5	.490	13.7
.45	.44	0.5	.490	22.1
.38	.37	0.5	.492	30.1

$$\ln K_D (\text{uranium}) = 3.27$$

$$\ln K_{\text{DN}} (\text{nitric acid}) = -1.94$$

D_{obs}	D_{calc}	M_{HNO_3}	M_{H^+}	$10^2 \times M_{\text{UO}_2^{++}}$
4.54	4.56	2.0	1.97	0.36
4.46	4.51	2.0	1.97	0.38
4.39	3.70	2.0	1.97	0.89
3.84	3.71	2.0	1.97	0.87
2.89	2.47	2.0	1.98	2.43
1.19	1.01	2.0	1.98	10.5
0.72	0.64	2.0	1.99	18.9
0.53	0.47	2.0	1.99	28.3
7.43	7.76	3.0	2.94	0.23
6.98	7.70	3.0	2.94	0.24
6.48	6.11	3.0	2.94	0.59
6.06	6.11	3.0	2.94	0.58
4.00	3.78	3.0	2.95	1.74
1.45	1.20	3.0	2.97	9.52
0.81	0.71	3.0	2.98	18.2
0.55	0.49	3.0	2.98	28.2
10.3	9.99	4.0	3.90	0.19
9.17	10.12	4.0	3.90	0.18
8.79	7.86	4.0	3.91	0.47
7.97	7.93	4.0	3.91	0.46
5.74	4.67	4.0	3.93	1.46
1.52	1.34	4.0	3.96	8.77
0.81	0.74	4.0	3.97	17.8
0.56	0.51	4.0	3.98	27.7

$$\ln K_D (\text{uranium}) = 2.72$$

$$\ln K_{\text{DN}} (\text{nitric acid}) = -3.48$$

Distribution

1. M. H. Lietzke
2. R. W. Stoughton
- 3-302. R. H. Rainey
- 303-304. Central Research Library
- 305-306. Laboratory Records
307. ORNL RC
308. Document Reference Section
- 309-323. DTIC, AEC
324. H. M. Roth, Division of
Research and Development, ORO