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CHEMICALLY BASED MODELS TO PREDICT DISTRIBUTION COEFFICIENTS IN THE Pu(IV) and Np(IV) NITRATE-TBP SYSTEMS

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ABSTRACT

Chemically based thermodynamic models to predict the distribution coefficients have been developed for the Pu(IV) and Np(IV) Nitrate - TBP systems. The predictive model equation makes use of the aqueous actinide nitrate complex stoichiometric stability constant expressed as its degree of formation, their extraction mechanism and the equilibrium constant for the extraction reaction. Sets of Laximinarayanan's (1964) and Moskvin's (1970) equilibrium data on plutonium (IV) and neptunium (IV) nitrate systems respectively were used to apply to the model equations. Good agreements were obtained between the reported experimental data and the predictive values.

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INTRODUCTION

Liquid-liquid extraction is one of the most important techniques for the quantitative separation of actinides since they are very similar in their chemical properties. The use of liquid-liquid extraction to separate plutonium and neptunium, is of major importance in the processing and reprocessing of nuclear materials.[1-5]

In this work, thermodynamic models have been developed and applied to describe the liquid-liquid extraction of plutonium (IV) and neptunium (IV) nitrate from aqueous HNO_3 solutions by tri-n-butyl phosphate (TBP) using the equilibrium data from literature. In addition, these models developed using very few experimental data may be used to predict the extraction trends and distribution coefficients of plutonium and neptunium in the same systems.

MODEL DEVELOPMENT

Healy and McKay[6] reported that tetravalent actinide nitrates dissolve in tri-n-butyl phosphate to form the complexes of $M(NO_3)_4 \cdot 2TBP$, where M represent the plutonium (IV) and neptunium (IV) ionic species. They also proposed that the extraction of plutonium (IV) and neptunium (IV) into TBP can be represented by the reaction

$$M^{+4}|_A + 4NO_3^-|_A + 2TBP|_O \rightleftarrows M(NO_3)_4 \cdot 2TBP|_O \qquad (1)$$

and the equilibrium constant, K_e, by

$$K_e = \frac{[M(NO_3)_4 \cdot 2TBP]_O}{[M^{+4}]_A [NO_3^-]_A^4 [TBP]_O^2} \qquad (2)$$

where the brackets represent the activities and the subscripts A and O denote the aqueous and organic phases respectively. By using the relation

between the activity and activity coefficient, Equation 2 can be written as

$$K_e = \frac{(M(NO_3)_4 \cdot 2TBP)_0 \, \gamma^*_{M(NO_3)_4 \cdot 2TBP}}{(M^{+4})_A \, (NO_3^-)_A^4 \, (TBP)_0^2 \, \gamma_{M^{+4}} \, \gamma_{NO_3^-}^4 \, \gamma_{TBP}^{*2}} \tag{3}$$

where the parenthesis are the concentrations and γ and γ^* are the activity coefficients in the aqueous and organic phases respectively.

The total metal ion concentration in the organic phase can be written as:

$$(M^{+4})_0^T = K_e \cdot (M^{+4})_A \, (NO_3^-)_A^4 \, (TBP)_0^2 \, \frac{\gamma_{M^{+4}} \, \gamma_{NO_3^-}^4 \, \gamma_{TBP}^{*2}}{\gamma^*_{M(NO_3)_4 \cdot 2TBP}} . \tag{4}$$

Fomin and Maiorva[7], Moskvin[8] and Laxminarayanan, et al.[9] proposed the following complex formation reactions for the tetravalent actinides.

$$M^{+4} + NO_3^- \leftrightarrows MNO_3^{+3} \tag{5}$$

$$M^{+4} + 2NO_3^- \leftrightarrows M(NO_3)_2^{+2} \tag{6}$$

$$M^{+4} + 3NO_3^- \leftrightarrows M(NO_3)_3^{+1} \tag{7}$$

$$M^{+4} + 4NO_3^- \leftrightarrows M(NO_3)_4 . \tag{8}$$

The stoichiometric over-all stability constants for the above reactions are as follows:

$$\beta_1 = \frac{(MNO^{+3})}{(M^{+4})(NO_3^-)} \tag{9}$$

$$\beta_2 = \frac{(M(NO_3)_2^{+2})}{(M^{+4})(NO_3^-)^2} \tag{10}$$

$$\beta_3 = \frac{(M(NO_3)_3^{+1})}{(M^{+4})(NO_3^-)^3} \tag{11}$$

$$\beta_4 = \frac{(M(NO_3)_4)}{(M^{+4})(NO_3^-)^4} \tag{12}$$

The total metal ion concentration in the aqueous phase is given by:

$$(M^{+4})_A^T = (M^{+4}) + (MNO_3^{+3}) + (M(NO_3)_2^{+2}) + (M(NO_3)_3^{+1}) + (M(NO_3)_4). \quad (13)$$

Substitution of Equations 9, 10, 11 and 12 into Equation 13 gives:

$$\begin{aligned}(M^{+4})_A^T &= (M^{+4})[1 + \beta_1(NO_3^-) + \beta_2(NO_3^-)^2 + \beta_3(NO_3^-)^3 + \beta_2(NO_3^-)^4] \\ &= (M^{+4})[1 + \sum_i \beta_i (NO_3^-)^i]\end{aligned} \quad (14)$$

The distribution coefficient K_d is defined for a single metal component system by the ratio of the total concentration of the actinide species in the organic phase to the total concentration of the actinide species in the aqueous phase

$$K_d = \frac{(M)_O^T}{(M)_A^T} \quad (15)$$

Substitution of equations 4 and 14 into Equation 15 y elds

$$K_d = (NO_3^-)_A^4 (TBP)_0^2 \frac{K_e}{[1 + \sum_i \beta_i (NO_3^-)^i]} \cdot \frac{\gamma_{M^{+4}} \gamma_{NO_3^-}^4 \gamma_{TBP}^{*2}}{\gamma^*_{M(NO_3)_4 \cdot 2TBP}} \quad (16)$$

The degree of formation α_i of a complex AB_i was defined by Bjerrum in 1915 (as cited by reference 10) as follows

$$\alpha_i = \frac{(AB_i)}{(A)_T} = \frac{(AB_i)}{(A) + (AB) + (AB_2) \ldots + (AB_i) + \ldots + (AB_m)} \quad (17)$$

where A and B are the central group and the ligand respectively. In the present case, $A = M^{+4}$ and $B = NO_3^-$.

Substitution of Equation 14 into Equation 17 gives

$$\alpha_i = \frac{\beta_i (B)^i}{1 + \sum_i \beta_i (B)^i} \quad (18)$$

Therefore, we can have

$$\alpha_0 = \frac{1}{1 + \sum_i \beta_i (NO_3^-)^i} \tag{19}$$

At this point, the assumption is made that the ratio of the activity coefficients of the molecules obtained in Equation 16 varies slightly with concentration. Should this assumption hold, then the quotient of activity coefficients in Equation 16 can be represented as a constant value given by:

$$K_\gamma = \frac{\gamma_{M(NO_3)_4 \cdot 2TBP}}{\gamma_{M^{+4}} \ \gamma^4_{NO_3^-} \ \gamma^2_{TBP}} \tag{20}$$

Combining this activity coefficient ratio constant with the liquid-liquid extraction equilibrium constant, that is

$$k_1 = \frac{K_e}{K_\gamma} \tag{21}$$

gives a value for an effective equilibrium constant k_1 for the extraction equilibria. Substitution of Equations 19, 20 and 21 into Equation 16 gives

$$K_d = k_1 \alpha_o (NO_3^-)^4_A (TBP)^2_O \tag{22}$$

where α_o is the degree of formation.

Healy and McKay[6] reported that nitric acid will dissolve in TBP forming the complex ($HNO_3 \cdot TBP$). Alcock, et al.[11] and Fomin and Maiorova[7] proposed that the reaction between nitric acid and TBP is given by the equation

$$[H^+]_A + [NO_3^-]_A + [TBP]_O \rightleftarrows [HNO_3 \cdot TBP]_O \quad (23)$$

and the equilibrium constant by the equation

$$K_e = \frac{(HNO_3 \cdot TBP)_O}{(H^+)_A (NO_3^-)_A (TBP)_O}. \quad (24)$$

Fomin and Maiorova[7] reported that the equilibrium constant of the reaction represented by Equation 23 and 24 is equal to 0.22 $\pm$ 0.02 when the initial nitric acid concentration does not exceed 4 M. Since it was difficult to determine the free TBP concentration, it was desirable to determine the concentration of $HNO_3 \cdot TBP$ by estimating the concentration of nitric acid in the organic phase. Equation 24 can be rewritten as:

$$(TBP)_O = \frac{(HNO_3 \cdot TBP)_O}{(H^+)_A (NO_3^-)_A K_e}. \quad (25)$$

Substitution of Equation 25 into Equation 22 gives:

$$K_d = k_1' \alpha_O (HNO_3 \cdot TBP)_O^2 \frac{(NO_3^-)_A^2}{(H^+)_A^2}. \quad (26)$$

where

$$k_1' = \frac{k_1}{K_e^3}. \quad (27)$$

APPLICATION OF THE MODEL

The system of $Np(NO_3)_4$ - HNO_3 - H_2O - TBP - Benzene

Moskvin[8] studied the complex formation of trace amount of neptunium nitrate by using the liquid-liquid extraction method at ionic strength I = 2 M. The stoichiometric stability constants of the nitrato-complexes of Np (IV) were reported as $\beta_1 = 6.8$, $\beta_2 = 20.6$, $\beta_3 = 35.3$ and $\beta_4 = 34.3$. The equilibrium data are given in Table 1. The degree of formation were calculated from the equilibrium data according to Equation 19.

$$\alpha_0 = \frac{1}{1 + \sum_i \beta_i (NO_3)^i} \tag{19}$$

When the degrees of formation and the equilibrium data are available, the effective equilibrium constant k_1 in each set of data can be calculated by the model Equation 22.

$$K_d = k_1 \alpha_0 (NO_3^{-4})(TBP)_0^2 \tag{22}$$

or

$$k_1 = \frac{K_d}{\alpha_0 (NO_3^{-4})_A (TBP)_0^2} . \tag{28}$$

Figure 1 is the plot of the degree of formation α_0 versus the nitrate ion concentrations at ionic strength I = 2 M. The plot shows the degree of formation decreases sharply as the nitrate ion concentration increases from 0 to 0.6 M. The value of effective equilibrium constant k_1 was found by linear regression analysis of the available data and is equal to 126.34 ± 2.43. Table 2 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value

of the effective equilibrium constant, the model Equation 22 can now be written as

$$K_d = 126.3357\ \alpha_0 (NO_3)_A^{-4} (TBP)_0^2 \qquad (29)$$

The distribution coefficients can be calculated at different nitrate ion and TBP concentrations using this model equation. Table 2 also shows the comparison between the calculated K_d values obtained by Equation 29 and the experimental K_d data reported by Moskvin[8]. Figure 2 is the plot for K_d(model) vs. K_d(data) with a correlation coefficient $R^2 = 0.996$. It shows that the model equation 22 gives good predictive distribution coefficients within the experimental conditions and at ionic strenth I = 2 M.

The system $Pu(NO_3)_4$ - HNO_3 - H_2O - TBP - Toluene

Laxminarayanan, et al.[9] determined the stability constants for nitrato complexes of trace amount of plutonium by a solvent extraction method using TBP as the solvent and toluene as the diluent. Table 3 shows the stability constants for plutonium nitrate complexes at different ionic strengths. Table 4 gives the equilibrium data for this system which was reported by Laxminarayanan, et al.[9] The equilibrium hydrogen ion concentration in the aqueous phase was not reported. However, the hydrogen ion concentrations in the sample solutions were reported in detail. It can be assumed that the changes of the hydrogen ion concentrations before and after the equilibration varied very slightly since the neutral organophosphorus compound only extract the neutral species from the aqueous phase. No hydrogen ion is liberated from the organic phase to the aqueous phase. Should this assumption hold, their equilibrium data can be used to test the accuracy and consistency of the developed thermodynamic model.

The degree of formation can be calculated by using Equation 19 and the equilibrium data as well as the stability constants of the plutonium nitrate complexes. The effective equilibrium constants k_1' can then be calculated according to the model given by Equation 26.

$$K_d = k_1' \alpha_o (HNO_3 \cdot TBP)_0^2 \frac{(NO_3^-)_A^2}{(H^+)_A^2} \tag{26}$$

The calculated degrees of formation and the effective equilibrium constants are presented in Table 5. Figure 3 gives the plot of degree of formation vs. the nitrate ion concentrations at ionic strength I = 1.02. The dotted lines represent the extrapolation to the regions of low nitrate ion concentration. Table 5 shows that the fluctuation of k_1' values was not so large within each ionic strength range and no particular trend could be observed in each case. These are good indications that support the assumption of a constant activity ratio.

A linear regression analysis technique was applied to estimate the effective equilibrium constant k_1' in the model Equation 26. The calculated effective equilibrium constants were 2891.0, 2659.08 and 889898.65 at ionic strengths of 1.01, 1.9 and 4.7 M respectively. From the regressed value k_1' ($k_1' = k_1/K_e^3$), the model was solved for the predicted distribution coeeficients at each specific ionic strength using Laxminarayanan's, et al[9]. data given in Table 4. The results are shown in Table 6 and Figure 4. Good results were obtained by using the predictive thermodynamic model equation at constant ionic strength.

Comparison of the results obtained from the above two different single component systems and the other reported results [12-16] indicate that better predictive distribution coefficients are obtained at constant

ionic strength. The activity coefficients at constant ionic strength are assumed to be independent of the concentrations of the reacting species and dependent only on the nature and concentration of the bulk electrolyte. Therefore, the quotient of activity coefficients is a constant. This gives a good representative effective equilibrium constant for each of the cases examined. The effective equilibrium constant is defined by the equation

$$k_1 = \frac{K_e}{K_\gamma} \tag{30}$$

where K_γ is the activity coefficient ratio. From this relation it can be concluded that the effective equilibrium constant is still a constant at the condition of constant ionic strength. In other words, if the quotient of activity coefficients is not constant, the effective equilibrium constant also varies with the changing K_γ. In this case k_1 is no longer a constant. As a result, this will give an inaccurate predictive distribution coefficients when using the model equations 22 and 26.

SUMMARY AND CONCLUSION

Chemically based thermodynamic models to predict the distribution coefficients for the liquid-liquid extraction of actinides-organophosphorus compounds have been developed by assuming that the quotient of the activity coefficients of each species varies slightly with its concentrations, by using the aqueous actinide complexes stoichiometric stability constants expressed as its degrees of formation, by making use of the extraction mechanism and the equilibrium constant for the extraction reaction.

For a single metal component system, the thermodynamic model equation which predict the distribution coefficients is dependent on the free organic concentration, the equilibrated ligand concentrations, the degree of formation, and on the extraction mechanism.

The procedures for the development of a model equation for application to a liquid-liquid extraction system are as follows: (1) Calculate the degree of formation by Equation 19. (2) Estimate the effective equilibrium constant by a linear regression technique. (3) The predicted distribution coefficients can be obtained by using the equilibrium data as well as the suitable thermodynamic model equation.

When using the developed model equations in this work, the following informations should be available: (1) the stability constants, (2) the equilibrated ligand concentrations in the aqueous phase, (3) the equilibrated organic concentration and (4) the distribution coefficients.

The developed thermodynamic model equations can be used with a few data points to predict extraction trends which would otherwise be difficult to determine experimentally.

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NOTATIONS

A : a central group of a complex

B : a ligand

I : ionic strength

k_1 : K_e/K_3

k_1' : k_1/K_e

K_d : distribution coefficient

K_e : equilibrium constant

K_γ : a quotient of activity coefficients

M : a metallic ion

ϕ : organic concentration/aqueous acidity

Subscripts

A : aqueous phase

O : organic phase

Superscripts

T : total

Greek Letters

α_i : degree of formation

β_i : stability constant

γ_i : activity coefficient in the aqueous phase

γ_i^* : activity coefficient in the organic phase

Table 1. Equilibrium data for the system neptunium nitrate -nitric acid-water-TBP-benzene[1]

$(NO_3^-)_A$, M	K_d
0.0	0.00503
0.1	0.00775
0.2	0.06845
0.4	0.354
0.6	0.776
0.8	1.10
1.0	1.40
1.2	1.62
1.4	1.67
1.6	1.82
1.8	1.91
2.0	2.23

[1]Experimental conditions:

Ionic Strength I = 2.0 M

(TBP) = 1.0 M

T = $25^o \pm 1^o$ C.

Equilibrium data were reported by Moskvin[8].

Table 2. The calculated degree of formation and the effective equilibrium constant for the system neptunium nitrate-nitric acid-water-TBP-benzene

$(NO_3^-)_A$, M	α_o	k_1	K_d(data)[1]	K_d(model)
0.1	0.5196	149.160	0.0078	0.0063
0.2	0.2840	150.530	0.0685	0.0568
0.4	0.0985	140.400	0.3540	0.3184
0.6	0.0407	147.093	0.7760	0.6671
0.8	0.0193	138.968	1.1000	1.0005
1.0	0.0102	137.199	1.4000	1.2880
1.2	0.0059	133.552	1.6200	1.5325
1.4	0.0036	121.514	1.6700	1.7359
1.6	0.0023	120.524	1.8200	1.9077
1.8	0.0016	117.523	1.9100	2.0529
2.0	0.0011	129.368	2.2300	2.1780

[1]Data were reported by Moskvin[8].

Table 3. Stability constants for plutonium nitrate complexes[1]

Ionic strength I,(M)	Stability Constants			
	β_1	β_2	β_3	β_4
1.02	5.3	9.2	4.0	---
1.90	4.0	7.5	4.0	1.2
4.70	4.6	14.8	10.8	2.0

[1]Data were reported by Laxminarayana, et al.[9].

Table 4. Equilibrium data for the system plutonium nitrate-nitric acid-water-TBP-toluene[1]

$(NO_3^-)_A$ M	K_d	$(HNO_3 \cdot TBP)$ M	I M	(H^+) M
0.22	0.13	0.049	1.02	1.02
0.42	0.49	0.070	1.02	1.02
0.62	1.04	0.089	1.02	1.02
0.82	1.65	0.104	1.02	1.02
1.02	2.19	0.128	1.02	1.02
0.26	0.46	0.049	1.90	0.6
0.51	1.68	0.070	1.90	0.6
0.61	2.25	0.075	1.90	0.6
0.75	2.43	0.078	1.90	0.6
0.91	3.17	0.087	1.90	0.6
1.16	4.55	0.105	1.90	0.6
1.40	5.66	0.127	1.90	0.6
1.70	5.20	0.129	1.90	0.6
1.90	7.34	0.131	1.90	0.6
0.30	8.12	0.123	4.70	0.7
0.50	20.61	0.139	4.70	0.7
0.72	24.60	0.139	4.70	0.7
0.92	33.86	0.172	4.70	0.7
1.12	44.18	0.184	4.70	0.7
1.32	53.70	0.214	4.70	0.7
1.52	69.52	0.239	4.70	0.7

[1]Equilibrium data were reported by Laxminarayanan, et al.[9].

Table 5. The calculated degree of formation and the effective equilibrium constant for the system plutonium nitrate-nitric acid-water-TBP-toluene

$(NO_3^-)_A$, M	k_1'	α_o	α_1	α_2	α_3	α_4	I M
0.22	3088.77	0.3768	0.4394	0.1678	0.0161	0.000	1.02
0.42	3034.64	0.1944	0.4326	0.6154	0.0576	0.000	1.02
0.62	3118.58	0.1139	0.3744	0.4030	0.1086	0.000	1.02
0.82	3242.65	0.0728	0.3164	0.4503	0.1605	0.000	1.02
1.02	2703.08	0.0494	0.2673	0.4733	0.2099	0.000	1.02
0.26	2674.99	0.3813	0.3966	0.1933	0.0268	0.0021	1.90
0.51	2658.64	0.1785	0.3641	0.3490	0.0947	0.0145	1.90
0.61	2826.92	0.1369	0.3340	0.3820	0.1243	0.0228	1.90
0.75	2629.31	0.0972	0.2917	0.4102	0.1641	0.0370	1.90
0.91	2674.25	0.0681	0.2478	0.4229	0.2052	0.0560	1.90
1.16	2666.29	0.0414	0.1922	0.4179	0.2586	0.0899	1.90
1.70	2302.39	0.0169	0.1150	0.3644	0.3322	0.1694	1.90
1.90	3358.90	0.0127	0.0965	0.3438	0.3484	0.1986	1.90
0.30	529545.60	0.2488	0.3433	0.3314	0.0725	0.0040	4.70
0.50	798810.40	0.1180	0.2714	0.4366	0.1593	0.0148	4.70
0.72	898068.80	0.0604	0.2001	0.4635	0.2435	0.0325	4.70
0.92	824479.80	0.0362	0.1533	0.4538	0.3047	0.0519	4.70
1.12	988997.60	0.0232	0.1197	0.4314	0.3526	0.0731	4.70
1.32	948022.00	0.0157	0.0952	0.4044	0.3895	0.0952	4.70
1.52	1056470.00	0.0110	0.0770	0.3766	0.4178	0.1176	4.70

Table 6. Model predictions for the system plutonium nitrate-nitric acid-water-TBP-toluene

$(NO_3^-)_A$, M	I, M	K_d(data)[1]	K_d(model)
0.22	1.02	0.130	0.116
0.42	1.02	0.490	0.463
0.62	1.02	1.040	0.954
0.82	1.02	1.650	1.474
1.02	1.02	2.190	2.341
0.26	1.90	0.460	0.452
0.51	1.90	1.680	1.675
0.61	1.90	2.250	2.127
0.75	1.90	2.430	2.450
0.91	1.90	3.170	3.164
1.16	1.90	4.550	4.547
1.40	1.90	5.660	5.328
1.70	1.90	5.200	6.009
1.90	1.90	7.340	5.823
0.30	4.70	8.120	17.790
0.50	4.70	20.610	24.700
0.72	4.70	24.600	26.700
0.92	4.70	23.860	35.590
1.12	4.70	44.196	44.690
1.32	4.70	53.706	53.400
1.52	4.70	69.526	62.290

[1]Data were reported by Laxminarayanan, et al.[9].

FIGURE CAPTIONS

Figure 1. Degree of formation α_0 for neptunium nitrate in the aqueous phase.

Figure 2. The comparison between the K_d (model) in this work and the K_d (data) obtained experimentally by Moskvin[8] for the system $Np(NO_3)_4$-HNO_3-H_2O-TBP-Benzene.

Figure 3. Degree of formation α_i for plutonium nitrate in the aqueous phase at ionic strength I = 1.02 M.

Figure 4. The comparison between the K_d (model) in this work and the K_d (data) obtained experimentally by Laxminarayanan et al.[9] for the system $Pu(NO_3)_4$-HNO_3-H_2O-TBP-Toluene.

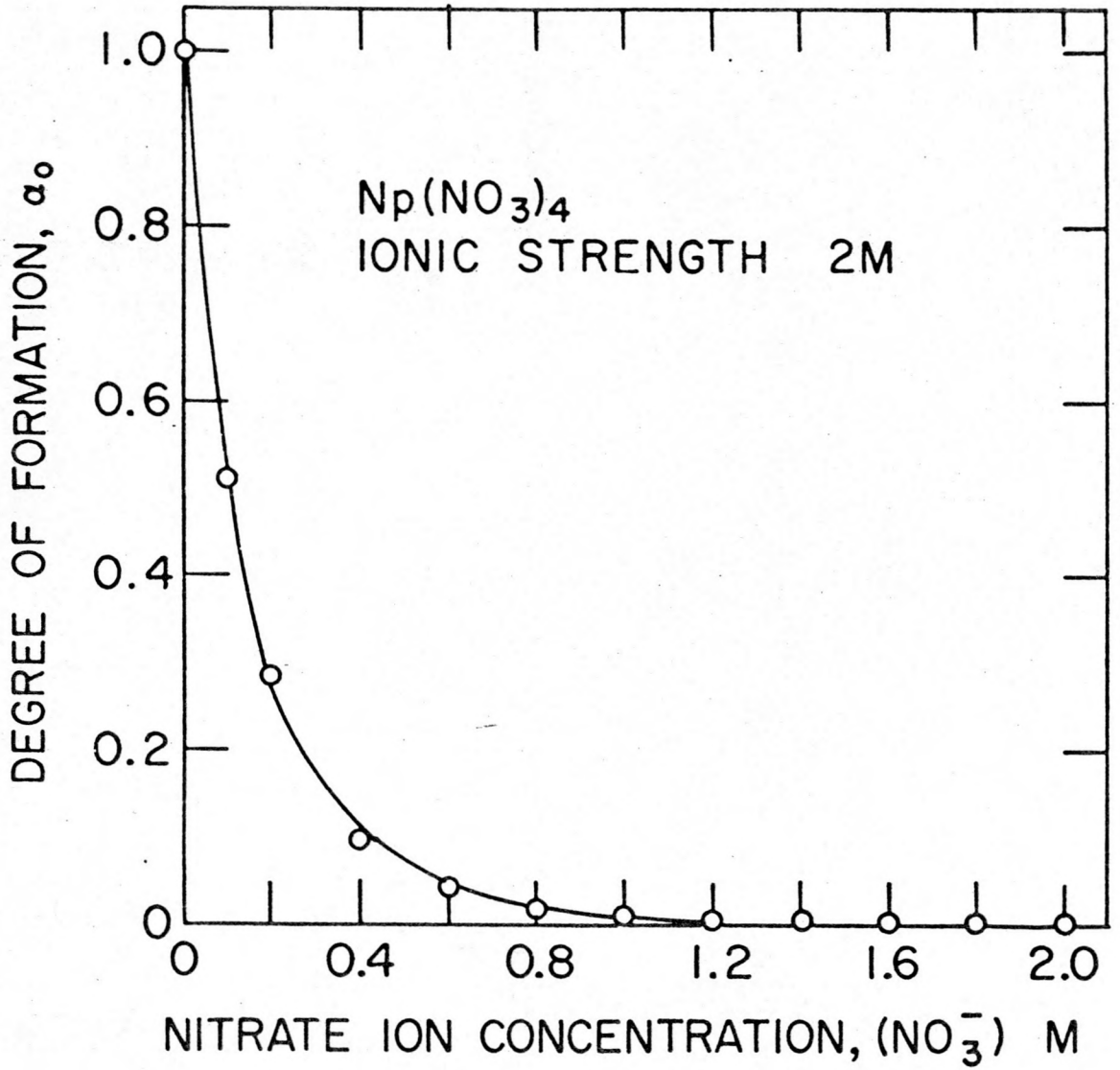

Figure 1. Degree of formation α_0 for neptunium nitrate in the aqueous phase.

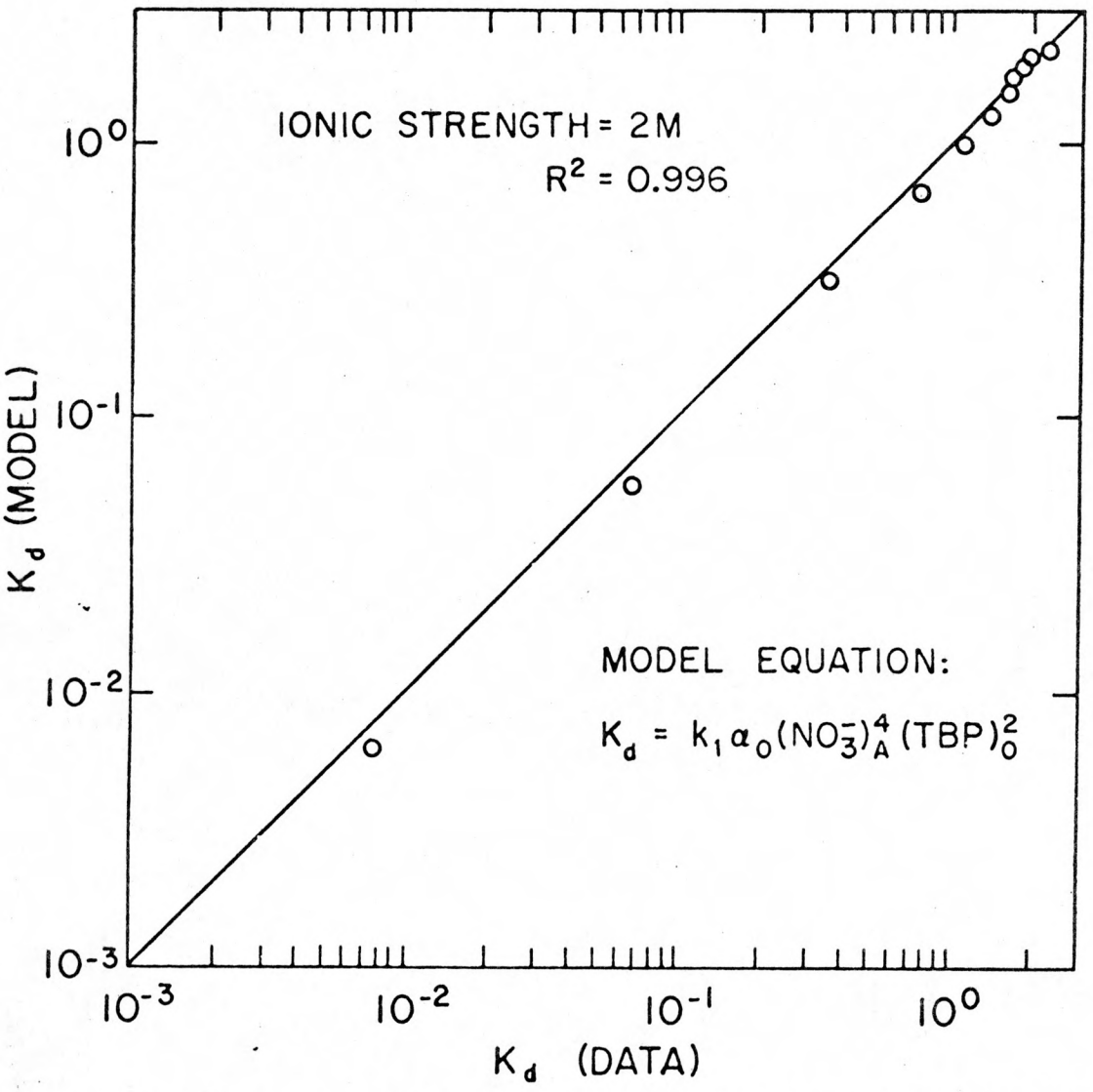

Figure 2. The comparison between the K_d (model) in this work and the K_d (data) obtained experimentally by Moskvin[8] for the system $Np(NO_3)_4$-HNO_3 -H_2O-TBP-Benzene.

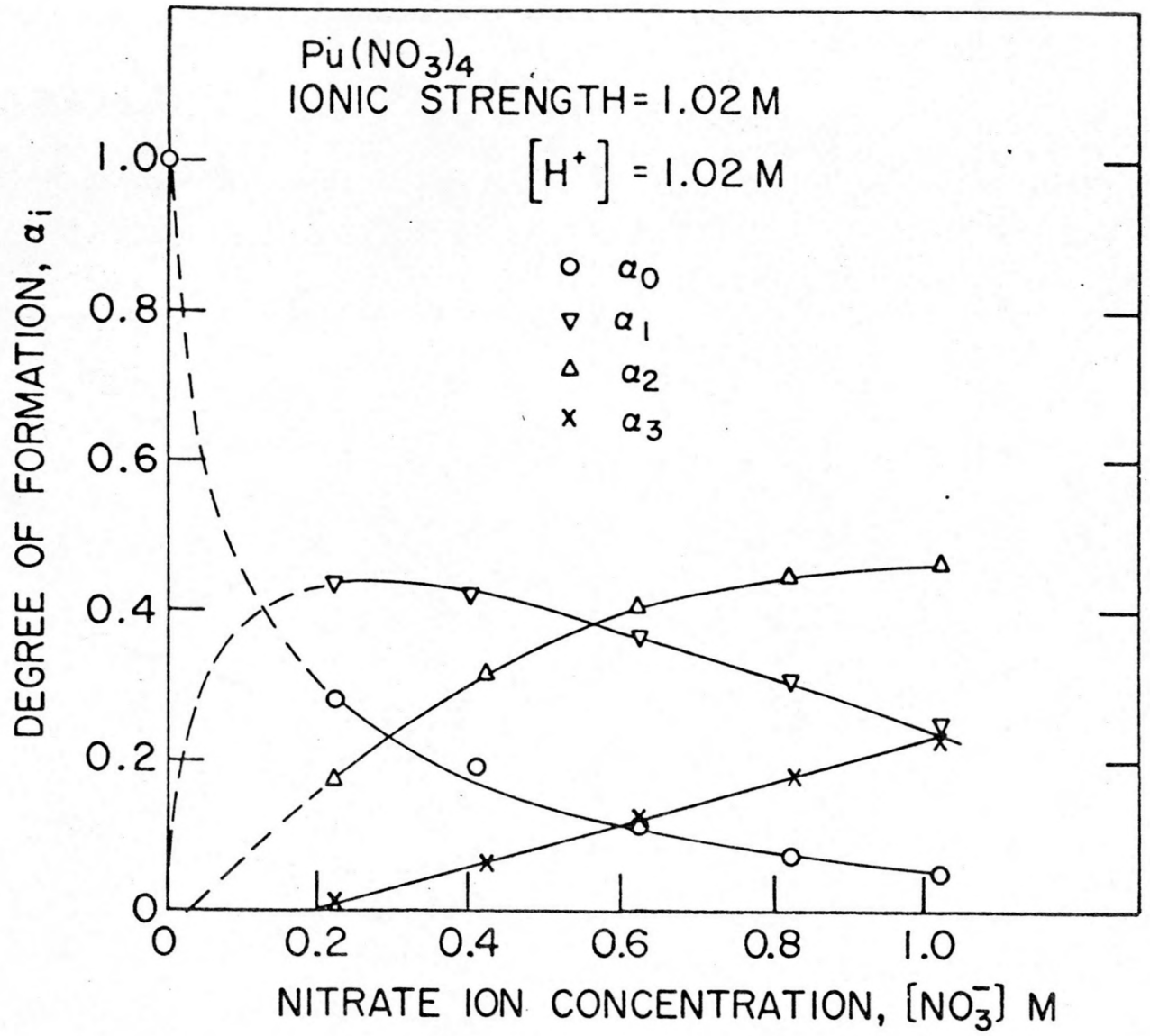

Figure 3. Degree of formation α_i for plutonium nitrate in the aqueous phase at ionic strength I = 1.02 M.

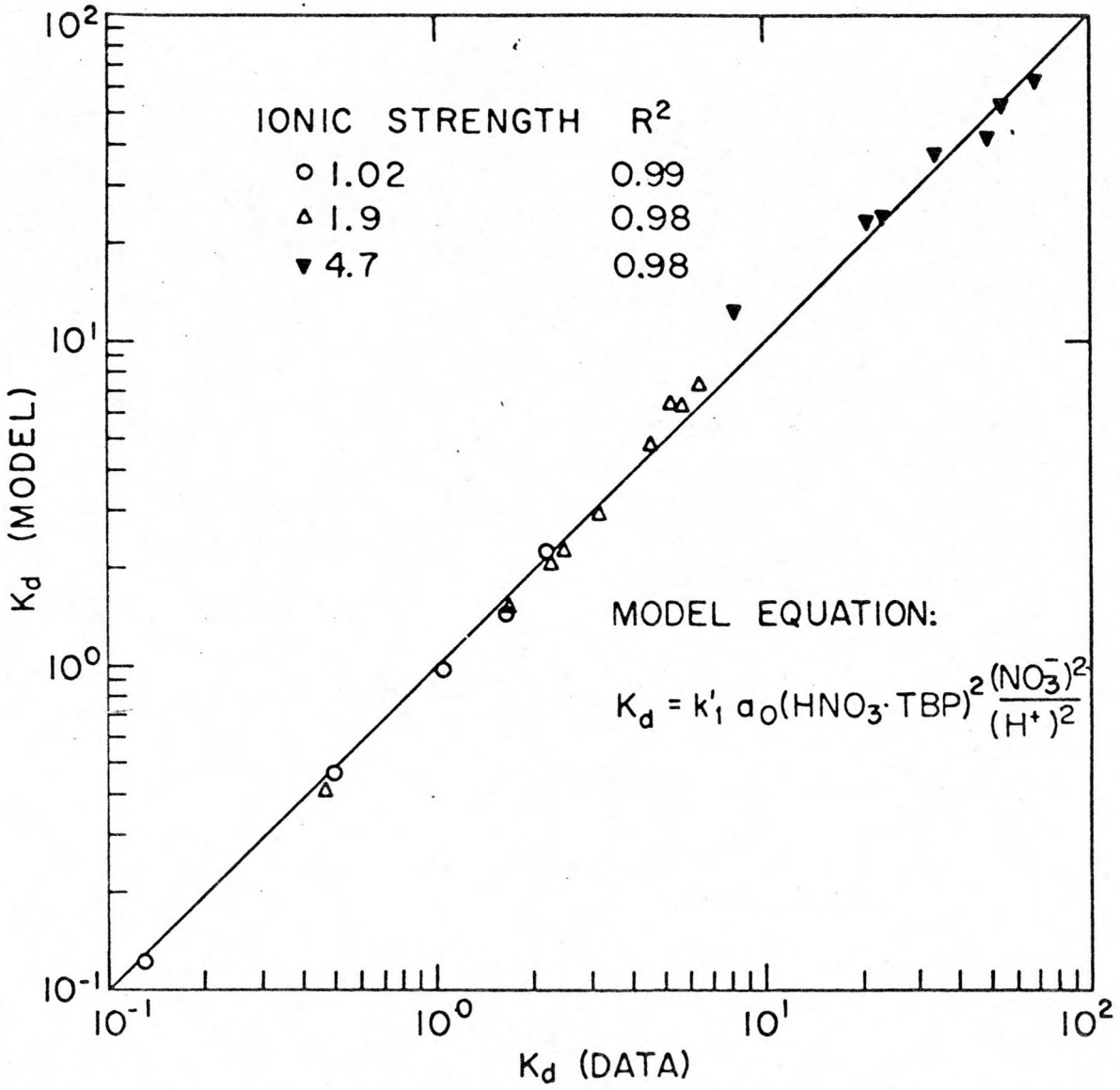

Figure 4. The comparison between the K_d (model) in this work and the K_d (data) obtained experimentally by Laxminarayanan et al.[9] for the system $Pu(NO_3)_4$-HNO_3-H_2O-TBP-Toluene.