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Thermodynamic Modeling of Solvent Extraction Systems: Successes and Problems

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Abstract

Recent approaches to thermodynamic modeling of solvent extraction systems are applied to nitric acid and Am(III) extraction by dihexyl-*N,N*-diethylcarbamoylmethyl phosphonate in CCl_4. 1:1 and 2:1 complexes were found to form in the organic phase for nitric acid extraction with $\overline{K}_1 = 0.125 \pm 0.00154$ and $\overline{K}_2 = 1.41 \times 10^{-5} \pm (2.60 \times 10^{-7})$. Extraction of nitric acid was also followed by IR spectrophotometry which verified the results obtained. Modeling of Am(III) extraction up to an initial aqueous nitric acid concentration of 4 *M* yielded good results. Extraction constants for species forming in the organic phase were found to be $K_{ex_0} = 38.6 \pm 30.4$ for $[Am(NO_3)_3 \cdot E_3]_o$, $K_{ex_1} = 7.43 \pm 0.572$ for $[Am(NO_3)_3 \cdot E_2 \cdot (E \cdot HNO_3)]_o$ and $K_{ex_2} = 1.04 \pm 0.0281$ for $[Am(NO_3)_3 \cdot E \cdot (E \cdot HNO_3)_2)]_o$. Problems encountered are highlighted and discussed, improvements to modeling approaches are suggested, and results obtained are critically discussed and compared to the literature.

INTRODUCTION

Computer modeling of solvent extraction systems has been particularly apparent in the nuclear industry where complex aqueous solutions are invariably encountered. Programs such as SEPHIS (*1*), which describes the Purex Process, have been indispensable in modeling and thus optimization. Accompanying the recent, ongoing search for novel, selective, actinide extractants has been interest in thermodynamic modeling of extraction systems. Extractants studied in this way include diamides (*2–5*) and the TRUEX solvent, which is a mixture of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and tri-*n*-butyl phosphate (TBP) in an inert diluent (*6–8*).

The extractant dihexyl-*N,N*-diethylcarbamoylmethyl phosphonate (DHDECMP) has already been used in various applications at the Atomic

Energy Corporation (*9*, *10*) and was chosen to assist in the development of modeling techniques which will be applied to novel extractants developed locally. This extractant is similar to CMPO and so is ideal for comparing various problems encountered in thermodynamic modeling with the TRUEX solvent (*7*).

Nitric Acid Extraction

A knowledge of the extraction of nitric acid by new extractants is essential because protons that compete with metal cations for donor groups usually cause depression of the distribution coefficients on increasing acid concentration. Nitric acid is also the most likely acid to be encountered within the nuclear industry. Invaluable information about extraction mechanisms and design may be learned—as in the case of DHDECMP where an intramolecular buffer effect is operative (*11*).

A literature study has revealed a number of problems. These include the following.

Data Acquisition and the Concept of Equilibrium

A major discrepancy lies in the concept of when equilibrium is reached. Some extractants require three to four contacts with an aqueous acid solution of the same concentration before no more acid is extracted. Some authors (*7*) insist that repeated contacts be made, and when no more acid is extracted, then "equilibrium" has been reached. This approach is valid for countercurrent situations, but the same equilibrium equations can be used for a batch situation as well. The question arises as to whether extraction constants should be calculated from distribution data acquired after one contact or several. Examples of data obtained after one contact include work done on TBP (*6*, *12*, *13*), diphosphone oxides (*14–16*), and DBDECP (*17*). Recent studies on bifunctional extractants have all used the multicontact approach (*7*, *8*). Workers investigating the TRUEX solvent (*7*) used the multicontact approach for CMPO but used the data of Davis (*12*) for TBP which were acquired after one contact. In mitigation it should be stated that perhaps there was an underlying assumption that TBP only requires one contact for "equilibrium" to be reached.

Clearly, a more uniform approach is required especially on the concept of when equilibrium is reached. This is important because thermodynamic measurements are taken by definition at equilibrium. We suggest that the one-contact approach is the correct one if equations such as Eqs. (1) and (2) below are to be used. The multicontact approach entails the successive attainment of different equilibria per contact and should not be described in the same way as for the one-contact approach.

Validity of Assumptions

A further problem is the validity of assumptions made. These include assuming negligible formation of complexes at certain initial acid concentrations in order to simplify calculations. Recent developments in statistical computer software have alleviated this problem as nonlinear least squares fitting has become a simple procedure. Nevertheless, valid assumptions often need to be made and should be tested. Even sophisticated programs like ESTA (*18*), which calculates formation constants of species forming in sometimes complex systems, can only give reliable results if the complex is forming to a significant degree. Many recent authors neglect to state assumptions made and how these were tested.

Errors in Quoted Extraction Constants

Another drawback in nonlinear least squares fitting is the high percentage errors obtained when many unknowns are being fitted. Nevertheless, results obtained are usually better than none at all. It has also been surprising to see the number of extraction constants recently published where no errors are quoted.

Use of Nitric Acid Activity

The extraction of nitric acid by DHDECMP has previously been studied by Hugen and coworkers (*19*). Acid extraction constants were incorrectly calculated because aqueous molar acid concentrations were used instead of activities.

Activities used should be for the aqueous equilibrium and not for the initial nitric acid concentrations, as has on occasion been done.

Metal Ion Extraction

A further difference in approach is found in the literature when it comes to metal ion extraction. Some workers first condition organic phases with acid before contacting the same organic phase with an aqueous solution of the same acid concentration containing the metal to be extracted while others do not. Similar confusion for acid extraction as discussed above results.

Chaiko and coworkers extended thermodynamic modeling of extraction systems to Am(III) and $HTcO_4$ extraction by the TRUEX solvent (*7*, *8*). Good comparison was obtained between experimental and calculated values for D_{Am} and D_{HTcO_4}.

In the present study an attempt is made to use Chaiko's approach with modifications to model Am(III) extraction by DHDECMP. Results obtained are critically discussed in the light of their feasibility chemically as well as mathematically. For a model to be reasonable, results must be chemically believable. This has not always been the case in recent literature when results were compared to those obtained by more conventional thermodynamic experiments. Results obtained in the present study are compared to the literature, bearing in mind that fewer data were used here.

EXPERIMENTAL

All chemicals used were reagent grade or better. DHDECMP was obtained from Columbia Chemical Company and was purified by mercury precipitation (*22*).

Nitric Acid Extraction

Various aqueous nitric acid solutions were shaken once for 1 min with different organic phase concentrations of DHDECMP in CCl_4 at 22 ± 2°C. After separation, both phases were analyzed for acid content by pH titration against standardized NaOH.

Am(III) Extraction

Various aqueous nitric acid solutions containing tracer ^{241}Am were shaken once for 1 min with 0.50 *M* DHDECMP in CCl_4 at 22 ± 2°C. After separation, both phases were analyzed for Am using α-spectroscopy. Organic phases were not conditioned with acid prior to Am extraction.

All experiments were carried out in at least duplicate. Statistical modeling was done by using either STATGRAPHICS or GRAPHPAD computer programs.

RESULTS AND DISCUSSION

Nitric Acid Extraction

Distribution isotherms are shown in Fig. 1. Extractant dependency plots of log D_{HNO_3} versus log [DHDECMP] all give slopes close to unity, indicating that only one DHDECMP molecule participates in extracting complexes. The extraction of HNO_3 may be explained by the formation of two complexes in the organic phase—$(E \cdot HNO_3)_o$ and $(E \cdot 2HNO_3)_o$—where

$$H^+ + NO_3^- + (E)_o \overset{K_1}{\rightleftharpoons} (E \cdot HNO_3)_o \tag{1}$$

$$2H^+ + 2NO_3^- + (E)_o \overset{K_2}{\rightleftharpoons} (E \cdot 2HNO_3)_o \tag{2}$$

$$K_1 = \frac{[E \cdot HNO_3]_o}{[E]_o \cdot [H^+] \cdot [NO_3^-]} \frac{\gamma_{(E \cdot HNO_3)_o}}{\gamma_{(E)_o} \cdot \gamma_{H^+} \cdot \gamma_{NO_3^-}} \tag{3}$$

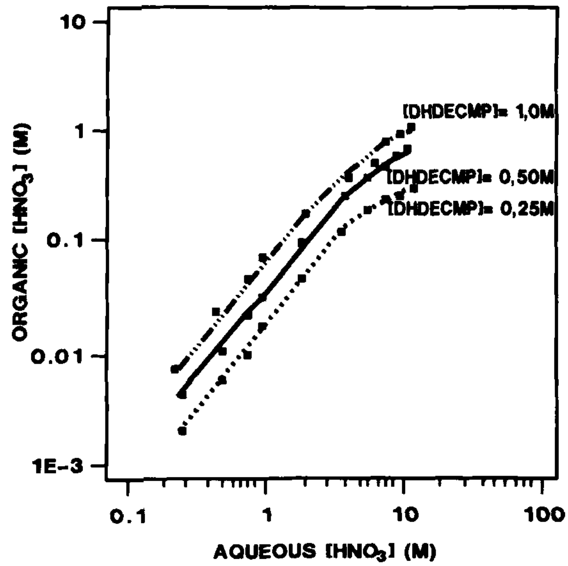

FIG. 1. Distribution isotherms (22 ± 2°C) for nitric acid extraction by DHDECMP in CCl_4.

where γ_{H^+} and $\gamma_{NO_3^-}$ are stoichiometric activity coefficients, i.e., $\gamma_{H^+} = \alpha\gamma_\pm = \gamma_S$, where α = degree of dissociation, $\gamma_\pm$ = mean ionic activity coefficient, and γ_S = stoichiometric activity coefficient. Values for α, $\gamma_\pm$, and γ_S were taken from Davis and de Bruin (*20*).

Using GRAPHPAD, the following equations were fitted to the data. For $[HNO_3] \leq 1\ M$:

$$\gamma_S = 0.0961 \exp(-2.25 \times 10^2[HNO_3]) + 0.176 \times \exp(-10.6[HNO_3]) + 0.731 \qquad (r = 0.998) \qquad (4)$$

where r = correlation coefficient. For $[HNO_3] \geq 1\ M$:

$$\gamma_S = 0.752 - 0.0692[HNO_3] + 0.0706[HNO_3]^2 - (0.511 \times 10^{-2})[HNO_3]^3 + (0.203 \times 10^{-3})[HNO_3]^4 \qquad (r = 0.999) \qquad (5)$$

Now, organic phase activity coefficients have been shown to be constant (*21*). Equation (3) may therefore be written as

$$\overline{K}_1 = \frac{[E \cdot HNO_3]_o}{[E]_o a_{HNO_3}} \qquad (6)$$

where $a_{HNO_3} = \gamma_S^2[H^+]\cdot[NO_3^-]$. γ_S used must be that of the equilibrium $[HNO_3]$ in the aqueous phase. Similarly:

$$\overline{K}_2 = \frac{[E\cdot 2HNO_3]_o}{[E]_o a_{HNO_3}^2} \tag{7}$$

Mass balance equations give

$$[HNO_3]_o = [E\cdot HNO_3]_o + 2[E\cdot 2HNO_3]_o \tag{8}$$

$$[E]_i = [E]_o + [E\cdot HNO_3]_o + [E\cdot 2HNO_3]_o \tag{9}$$

where subscript i = initial.

At low acidity ($[HNO_3]_i \leq 1\ M$), it can be assumed that the formation of $(E\cdot 2HNO_3)_o$ is negligible. Combining Eqs. (6), (7), (8), and (9), we obtain

$$[HNO_3]_o = \overline{K}_1 a_{HNO_3}\{[E]_i - [HNO_3]_o\} \tag{10}$$

Plotting $[HNO_3]_o$ versus $a_{HNO_3}\{[E]_i - [HNO_3]_o\}$ for $[HNO_3] \leq 1\ M$ yields a slope $\overline{K}_1$ (Fig. 2).

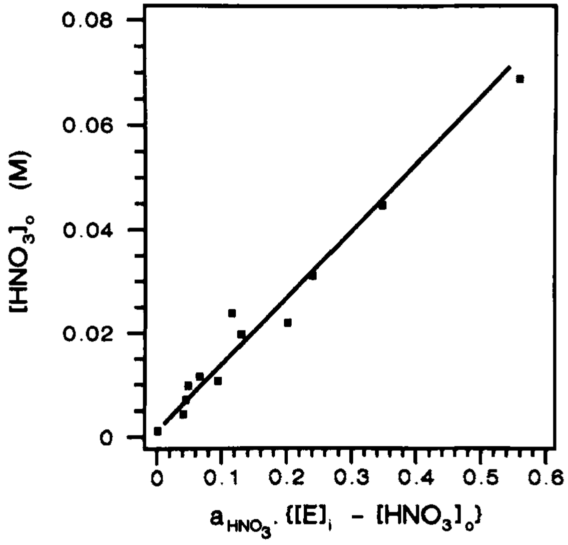

FIG. 2. Plot of Eq. (10). Rejecting outliers, slope $\overline{K}_1$ = 0.125 ± 0.00154. r = 0.999.

At high acid ($[HNO_3]_i \geq 1\ M$), no assumptions can be made. Combining Eqs. (6), (7), (8), and (9), we obtain

$$[HNO_3]_o = \bar{K}_1 a_{HNO_3}\{[E]_i - [HNO_3]_o\} + \bar{K}_2 a^2_{HNO_3}\{2[E]_i - [HNO_3]_o\} \qquad (11)$$

The value of $\bar{K}_1$ used in Eq. (11) was obtained from Eq. (10) and held constant. Plotting $[HNO_3]_o - \bar{K}_1 a_{HNO_3}\{[E]_i - [HNO_3]_o\}$ versus $a^2_{HNO_3}\{2[E]_i - [HNO_3]_o\}$ for $[HNO_3]_i \geq 1\ M$ yields a slope $\bar{K}_2$ (Fig. 3).

Once $\bar{K}_1$ and $\bar{K}_2$ are known, organic phase speciation may be calculated as follows.

$$[E]_o = \frac{[E]_i + [HNO_3]_o}{1 + 2\bar{K}_1 a_{HNO_3} + 3\bar{K}_2 a^2_{HNO_3}} \qquad (12)$$

Other equations for calculating $[E]_o$ may be derived, but experience has shown that both $\bar{K}$'s must be included in the calculation to obtain the most accurate results.

$[E \cdot HNO_3]_o$ and $[E \cdot 2HNO_3]_o$ were calculated using Eqs. (6) and (7) respectively. Speciation for HNO_3 extraction by 0.50 M DHDECMP in CCl_4 is shown in Fig. 4. Organic phases were submitted for IR spectrophotom-

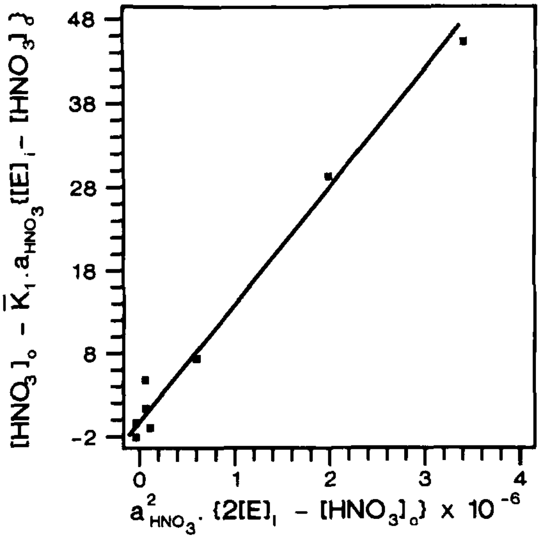

FIG. 3. Plot of Eq. (11). Rejecting outliers, slope $\bar{K}_2 = 1.41 \times 10^{-5} \pm (2.60 \times 10^{-7})$. $r = 0.999$.

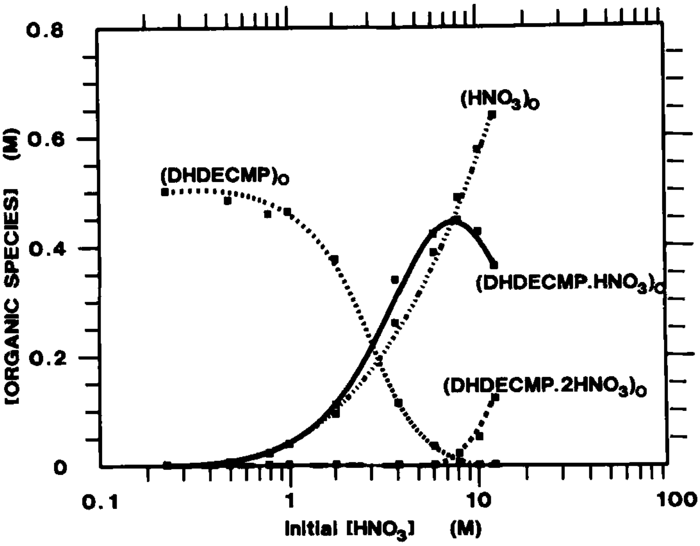

FIG. 4. Organic phase speciation for nitric acid extraction by 0.50 *M* DHDECMP in CCl$_4$.

etry (Figs. 5A and 5B). Plots of relative peak intensities for $\nu_{P=O}$ bound and unbound, $\nu_{C=O}$ bound and unbound, and $\nu_{NO_3^-}$ relative to an adjacent minimum versus $[HNO_3]_i$ are shown in Fig. 6. It can be seen that the curve for $\nu_{P=O}$ mirrors that of $(E \cdot HNO_3)_o$ and the curve for $\nu_{C=O}$ mirrors that of $(E \cdot 2HNO_3)_o$, indicating that protonation occurs first at the phosphoryl and then at the amide center. $\nu_{NO_3^-}$ mirrors $(HNO_3)_o$ as expected.

A comparison of experimental and modeled $[HNO_3]_o$ could now be made for HNO_3 extraction by 0.50 *M* DHDECMP in CCl_4. Results are shown in Table 1. It can be seen that a very good fit is obtained.

Am(III) Extraction

The distribution curve obtained is shown in Fig. 7. Since tracer ^{241}Am was used, it was assumed that activity coefficients for Am were unity and that the contribution of Am–DHDECMP complexes to bound DHDECMP in the organic phase was negligible. Extractant and nitrate dependencies have been shown to be 3, and the extracting complexes do not contain water (*11*, *21*). Using the approach of Chaiko and coworkers, the following equation should explain extraction at low acid:

$$\mathrm{Am(H_2O)_9^{3+} + 3NO_3^- + 3(E)_o \xrightleftharpoons{K_{ex_0}} [Am(NO_3)_3 \cdot E_3]_o + 9H_2O} \qquad (13)$$

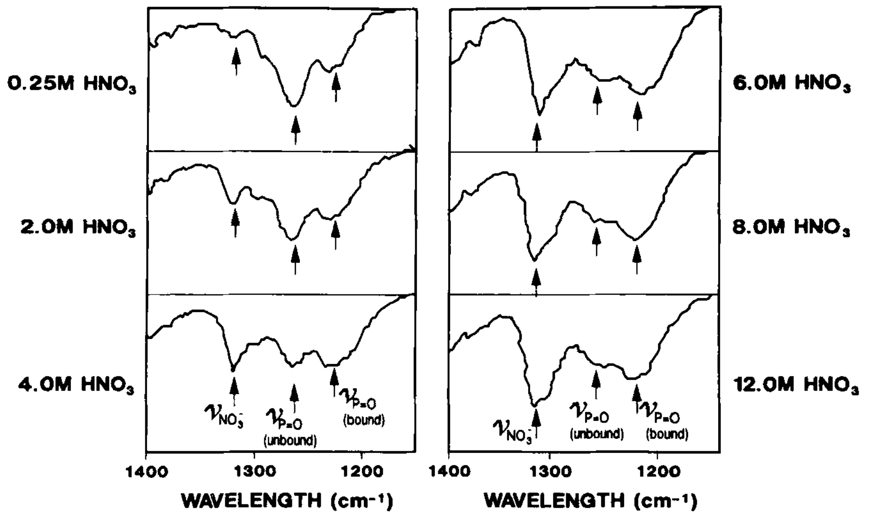

FIG. 5A. IR spectra in the phosphoryl stretching frequency region of various organic phases containing differing amounts of extracted nitric acid. $[DHDECMP]_i = 0.50$ *M* in CCl_4. Quoted $[HNO_3]$'s are initial concentrations.

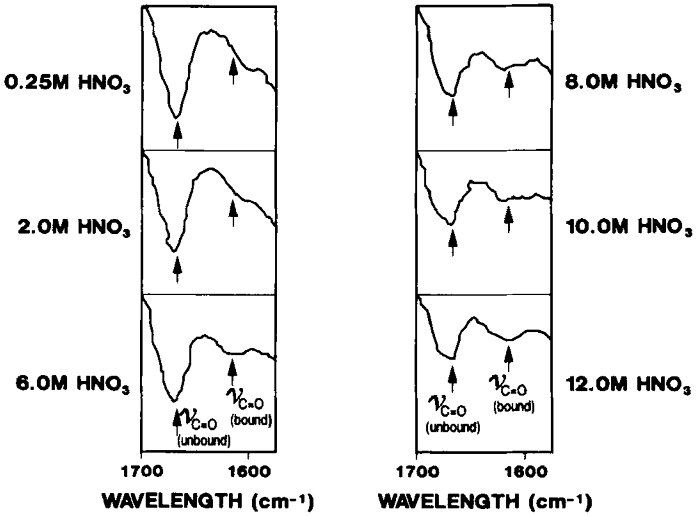

FIG. 5B. IR spectra in the carbonyl stretching frequency region of various organic phases containing differing amounts of extracted nitric acid. $[DHDECMP]_i = 0.50$ *M* in CCl_4. Quoted $[HNO_3]$'s are initial concentrations.

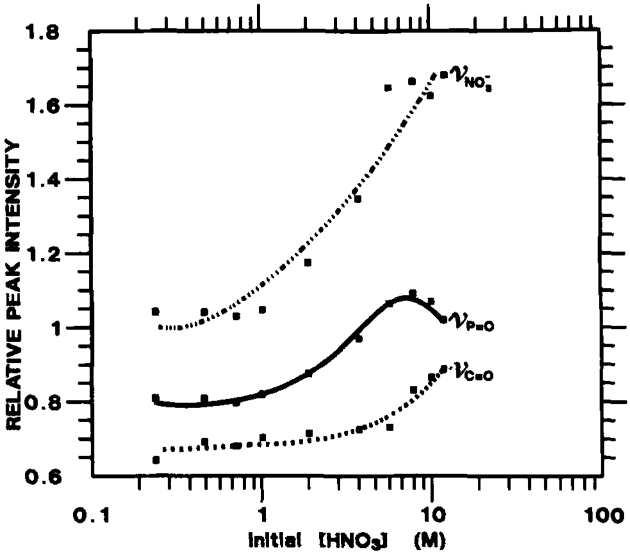

FIG. 6. Extraction of nitric acid by 0.50 *M* DHDECMP in CCl_4 followed by IR spectrophotometry.

Taking into account aqueous nitrate complexation of Am and using Eq. (13), the following quadratic may be derived:

$$\frac{[E]_0^3 \cdot \{NO_3^-\}^3}{D_{Am} \cdot \{H_2O\}^9} = \frac{1}{K_{ex_0}} + \frac{\beta_1}{K_{ex_0}} \frac{\{NO_3^-\}}{\{H_2O\}} + \frac{\beta_2}{K_{ex_0}} \frac{\{NO_3^-\}^2}{\{H_2O\}^2} \tag{14}$$

TABLE 1
Comparison between $[HNO_3]_o$ Obtained by Experiment and Modeling. $[DHDECMP]_i$ = 0.50 *M* in CCl_4

Aqueous $[HNO_3]$ (*M*)	Experimental $[HNO_3]_o$ (*M*)	Modeled $[HNO_3]_o$ (*M*)
0.246	0.004	0.0033
0.486	0.010	0.012
0.743	0.022	0.025
0.956	0.032	0.030
1.88	0.102	0.115
3.81	0.263	0.326
5.70	0.381	0.429
7.68	0.483	0.497
9.60	0.552	0.553
11.65	0.623	0.624

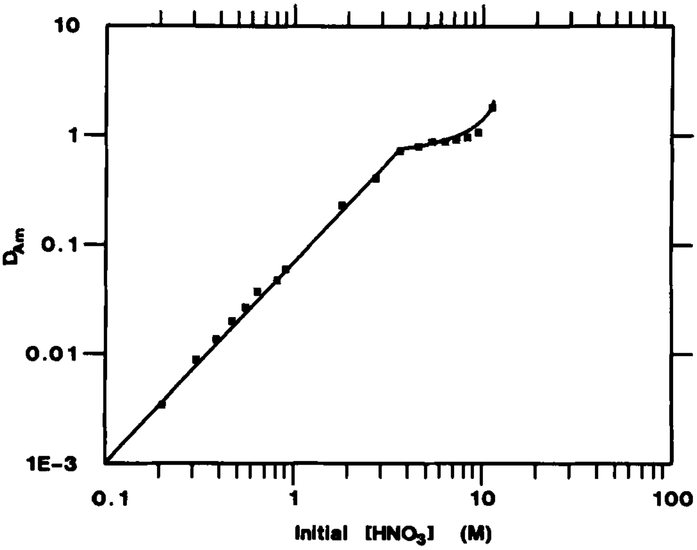

FIG. 7. Distribution curve for Am(III) extraction by 0.50 *M* DHDECMP in CCl_4.

where β_1 and β_2 are the formation constants for the reactions

$$Am^{3+} + NO_3^- \overset{\beta_1}{\rightleftharpoons} Am(NO_3)^{2+} \quad \text{and}$$

$$Am^{3+} + 2NO_3^- \overset{\beta_2}{\rightleftharpoons} Am(NO_3)_2^+$$

[ ] and { } refer to molar concentration and activity, respectively. Data for water activity were obtained from Davis and de Bruin (*20*). Using GRAPHPAD, an equation relating $\{H_2O\}$ to $[HNO_3]$ was fitted to the data:

$$\{H_2O\} = 0.999 \exp(-0.129[HNO_3]) + 0.466[1 - \exp(-0.303[HNO_3])] - 0.0275[HNO_3] \quad (r = 1.000) \quad (15)$$

$[E]_0$ was calculated by using Eq. (12). Plotting the left-hand side of Eq. (14) versus $\{NO_3^-\}/\{H_2O\}$ should give a quadratic-shaped curve. Using data up to 1 *M* $[HNO_3]_i$, this was found to be the case (Fig. 8). Chaiko and coworkers (*8*), in work done on the TRUEX solvent, found that the contribution of the third term on the right-hand side of Eq. (14) was negligible

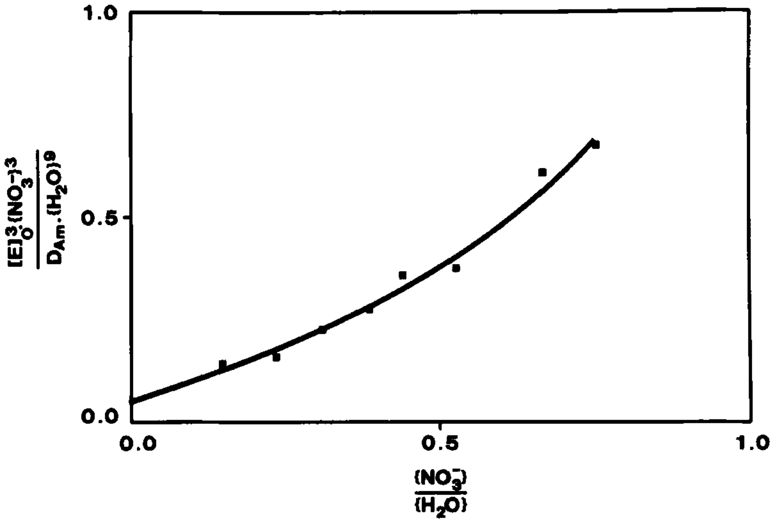

FIG. 8. Plot of Eq. (14). Nonlinear least-squares fitting yields K_{ex_0} = 38.6 ± 30.4, β_1 = 20.4 ± 17.3, and β_2 = 16.7 ± 14.9. r = 0.994.

(i.e., a straight line was obtained). Chemically, this means that the formation of $Am(NO_3)_2^+$ is negligible. This is debatable.

In this study, a quadratic-shaped curve was obtained up to 1 *M* $[HNO_3]_i$. Values for K_{ex_0}, β_1, and β_2 could then be calculated by using nonlinear least squares fitting (Fig. 8). Uncertainties are high due to the number of unknowns needing to be fitted. It is also clear that solvent extraction is not an accurate method for determining nitrate formation constants for Am in this way. Chaiko and coworkers (*7*) found β_1 = 86.5 and β_2 = 63.2 (no uncertainties were quoted). In a later study (*8*), the same workers found β_1 = 28.8. In a far more sophisticated experiment, O'Brien and Bautista found β_1 = 1.89 and β_2 = 0.89 (independent of ionic strength) for Nd^{3+} complexation by nitrate (*23*). Due to the chemical similarities of Nd^{3+} and Am^{3+}, it could be expected that β_1 and β_2 for Am^{3+} would approach those of Nd^{3+}. The situation arising here is that the model fits mathematically but is chemically questionable. This problem needs to be addressed by further research. Attempts were made to use O'Brien and Bautista's data in Eq. (14). β's were made both dependent and independent of ionic strength, but in both cases poor fits were obtained. This is not well understood.

A further problem in nonlinear least squares fitting of a number of unknowns is the great sensitivity of the unknowns to the data used to calculate them. A small change in the data gives rise to large changes in calculated unknowns. For example, K_{ex_0}, β_1, and β_2 were calculated at $[HNO_3]_i$ ranging from 0.2 to 1.0 *M*. If a single point at 0.1 *M* $[HNO_3]_i$ is added, then a quadratic curve is still obtained but the constants become $K_{ex_0} = 11.3$, $\beta_1 = 2.75$, and $\beta_2 = 8.16$ (errors were not calculated here). Although these values fall within the uncertainties quoted above, the sensitivity of the constants to small changes in data is quite clear.

Above 1 *M* $[HNO_3]_i$, the model must be extended to include other equilibria such as

$$Am(H_2O)_9^{3+} + H^+ + 4NO_3^- \xrightleftharpoons{K_{ex_1}} [Am(NO_3)_3 \cdot E_2\cdot(E\cdot HNO_3)]_o + 9H_2O \quad (16)$$

Similarly for the formation of $[Am(NO_3)_3\cdot E\cdot(E\cdot HNO_3)_2]_o$ with constant K_{ex_2} and $[Am(NO_3)_3\cdot(E\cdot HNO_3)_3]_0$ with constant K_{ex_3}.

Up to 4 *M* $[HNO_3]_i$, the following equation was used to fit the data:

$$D_{Am} = \frac{[E]_o^3\cdot\{NO_3^-\}^3\cdot\sum_{n=0}^{2} K_{ex_n}\cdot\{H^+\}^n\{NO_3^-\}^n}{\{H_2O\}^9\cdot\left[1 + \beta_1\frac{\{NO_3^-\}}{\{H_2O\}} + \beta_2\frac{\{NO_3^-\}^2}{\{H_2O\}^2}\right]} \quad (17)$$

K_{ex_0}, β_1, and β_2 were held constant while nonlinear least squares fitting was used to obtain K_{ex_1} and K_{ex_2}. If all the constants were given to the computer programs as unknowns, then very poor fits resulted. Results were $K_{ex_1} = 7.43 \pm 0.572$ and $K_{ex_2} = 1.04 \pm 0.0281$. The smaller uncertainties reflect the fact that only two unknowns needed to be fitted. Table 2 shows the good comparison obtained from experimental and modeled D_{Am}.

Further modeling above 4 *M* $[HNO_3]_i$ was unsuccessful. Both computer programs gave K_{ex_3} as negative, which is chemically impossible, even though good mathematical fits were obtained.

CONCLUSIONS

The modeling of acid extraction using the treatment outlined above yields good results which could be checked by spectrophotometry. Thus the approach is both mathematically and chemically sound.

However, as is the experience of other workers, metal ion extraction modeling using the above treatment is as yet unsatisfactory. More research needs to be done, especially in the area of verifying mathematical models

TABLE 2
Comparison between D_{Am} obtained by Experiment and Modeling.
$[\mathrm{DHDECMP}]_i = 0.50\ M$ in $\mathrm{CCl_4}$

$[\mathrm{HNO_3}]_i$ (M)	Experimental D_{Am}	Modeled D_{Am}
0.2	0.00344	0.00361
0.3	0.00897	0.0842
0.4	0.0147	0.0149
0.5	0.0223	0.0229
0.6	0.0300	0.0325
0.7	0.0437	0.0431
0.9	0.0577	0.0645
1.0	0.0774	0.0843
2.0	0.283	0.273
3.0	0.525	0.528
4.0	0.964	0.965

chemically. This is difficult because complex situations are generally encountered, making interpretation of results obtained from physical techniques such as spectrophotometry complicated. Nevertheless, promising results indicating that the approaches used are indeed useful in building up solvent extraction models have been obtained.

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