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THERMODYNAMIC MODELING OF CHEMICAL EQUILIBRIA IN METAL EXTRACTION*

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ABSTRACT

Models of equilibrium extraction data are being developed for use in computer simulations of metal extraction processes. The correlations are based on chemical mass action principles in which the effects of metal complexation and aqueous phase activity coefficients are considered. Activity coefficients in mixed electrolyte solutions at high ionic strengths are calculated using methods available in the literature. This modeling approach is demonstrated for HNO_3 extraction with both the PUREX and TRUEX solvents and for Am^{3+} extraction by octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide, which is the primary extractant in the TRUEX solvent.

INTRODUCTION

Present trends are toward an ever increasing reliance on the use of mathematical models for process design and control in hydrometallurgical operations. When coupled with an optimization algorithm, process simulation models can be used to obtain an optimum flowsheet design or to determine the best operating conditions (1). An early attempt in this direction was the

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computer program developed by Robinson and Paynter (2). Their program included a process simulator to which the design and operating parameters were systematically varied until arriving at a minimum in the projected capital costs while maintaining an optimum balance between production rate and operating costs. Program output included details such as specifications for the organic phase extractant concentration, the total number of stages required, and the flow ratio of organic solvent to aqueous solution. In addition to flowsheet design and optimization, current interests in the use of computer simulation models also extend to the area of nuclear safeguards and materials control (3). In this application, mathematical models of complex chemical processes are being developed to aid in estimating physical inventories within fuel reprocessing facilities.

The computer simulation of metal extraction processes requires an ability to predict distribution equilibria. Empirical correlations are often used for this purpose, but they cannot be considered reliable under conditions that are outside the experimental data base that was used to validate the model. For process design work being carried out in this laboratory, an equilibria-based approach to the modeling of solvent extraction data has been taken in order to improve the confidence in model predictions. The effects of aqueous phase metal complexation and aqueous phase activity coefficients have been included in models that are based on chemical mass action equilibria. This paper presents results on the thermodynamic modeling of extraction equilibria between complex aqueous solutions and both the PUREX and TRUEX solvents. The PUREX process is used throughout the world for the recovery and purification of uranium and plutonium from dissolved, irradiated fuels. The TRUEX process is a new solvent extraction process designed for actinide removal from acidic nuclear waste solutions (4, 5).

Extraction data for this effort were either measured in our laboratory or obtained from the literature. Activity coefficients for mixed electrolyte solutions at high ionic strengths were calculated using the method of Bromley (6). The extraction models which are presented here are intended for incorporation in algorithms designed for flowsheet simulation of countercurrent solvent extraction processes (5).

CALCULATION OF ACTIVITY COEFFICIENTS

In the modeling of hydrometallurgical processes, a common difficulty has been the treatment of activity coefficients. However, considerable advances have been made in the techniques for calculating aqueous activity coefficients since the 1970s. While the extended Debye-Hückel equation can be used to an ionic strength of about 0.1 molal (7), the methods developed by Bromley (6), Meissner et al. (8), and Pitzer et al. (9) often work well for both single and multicomponent electrolyte solutions at ionic strengths (I) commonly encountered in hydrometallurgical systems (i.e., $I \geq 6$ molal).

Meissner and colleagues (8) used an empirical equation with a single adjustable parameter to relate the reduced activity coefficient to ionic strength. At the other end of the spectrum is the model developed by Pitzer et al. in which the Guggenheim equation was extended by adding a third viral coefficient to account for triple ion interactions. The Pitzer model (9) has been expanded by Beutier and Renon (10) and also by Chen et al. (11) to include ion-molecule and molecule-molecule interactions, which are important for weak electrolytes.

For the modeling work described in this paper, the stoichiometric mean activity coefficients for nitric acid in $HNO_3/NaNO_3$ solutions were calculated using Bromley's method (6):

$$\log \gamma_{12} = \frac{-A\, Z_1 Z_2 \sqrt{I}}{1 + \sqrt{I}} + \frac{\nu_1 F_1 + \nu_2 F_2}{\nu_1 + \nu_2} \qquad (1)$$

with A = Debye-Huckel constant, 0.5108 $kg^{1/2}\ mol^{-1/2}$ at 25°C
I = $0.5\ \Sigma\ mZ^2$ (complete electrolyte dissociation assumed)
ν_i, ν_j = stoichiometric coefficient (e.g., for $Fe_2(SO_4)_3$ $\nu_i = 2$ and $\nu_j = 3$)
Z_i, Z_j = absolute value of ionic charge
γ_{12} = mean activity coefficient, molal concentration scale

Odd subscripts (1,3,5,..i) represent cationic species; even subscripts (2,4,6,..j) represent anionic species.

The terms F_1 and F_2 are defined as follows:

$$F_1 = (Y_{12} \log \gamma^{\circ}_{12} + Y_{14} \log \gamma^{\circ}_{14} + \ldots Y_{1j} \log \gamma^{\circ}_{1j}) + \frac{A\sqrt{I}}{1 + \sqrt{I}} (Z_1 Z_2 Y_{12} + Z_1 Z_4 Y_{14} + \ldots Z_1 Z_j Y_{1j}) \qquad (2)$$

$$F_2 = (X_{12} \log \gamma^{\circ}_{12} + X_{32} \log \gamma^{\circ}_{32} + \ldots X_{i2} \log \gamma^{\circ}_{i2}) + \frac{A\sqrt{I}}{1 + \sqrt{I}} (Z_1 Z_1 X_{12} + Z_3 Z_2 X_{32} + \ldots Z_i Z_2 X_{i2}) \qquad (3)$$

where

$$Y_{1j} = \left(\frac{Z_1 + Z_j}{2}\right)^2 \left(\frac{m_j}{I}\right) \qquad (4)$$

$$X_{i2} = \left(\frac{Z_i + Z_2}{2}\right)^2 \left(\frac{m_i}{I}\right) \tag{5}$$

The symbols m_j and m_i are the molal concentrations of anion j and cation i, respectively. The γ°_{ij} values in Eqs. 2 and 3 refer to the molal activity coefficients of single electrolyte solutions at the total ionic strength of the mixed electrolyte solution. They were calculated from:

$$\log \gamma^\circ_{ij} = \frac{-A \; Z_i Z_j \sqrt{I}}{1 + \sqrt{I}} + \frac{(0.06 + 0.6B)\; Z_i Z_j \; I}{\left(1 + \frac{1.5I}{Z_i Z_j}\right)^2} + BI \tag{6}$$

where B is an ionic interaction parameter (6). For HNO_3 and $NaNO_3$, the B values are 0.0776 and -0.0128 (6), which are valid up to an ionic strength of 6 molal. Above this ionic strength, the activity coefficients of HNO_3 (γ°_{12}) were obtained from the data of Davis and De Bruin (12). Converting their activity coefficients from the molar to the molal scale required the densities of nitric acid, which were obtained from the International Critical Tables (13). The activity coefficients of $NaNO_3$ (γ°_{32}) at ionic strengths greater than 6 molal were obtained from the data compiled by Hamer and Wu (14). Nitrate activity coefficients in mixed electrolyte solutions were calculated from (6):

$$\log \gamma_2 = \frac{-A \; Z_1 Z_2 \sqrt{I}}{1 + \sqrt{I}} + F_2 \tag{7}$$

Water activities in $HNO_3/NaNO_3$ mixtures were calculated using Meissner's method (8). For HNO_3 only solutions, water activities were obtained from the literature (12).

EXPERIMENTAL

Reagents

The primary metal extractant in the TRUEX solvent is n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). This extractant is combined with TBP and a diluent that is either a normal paraffinic hydrocarbon (NPH) or tetrachloroethylene (TCE). The TRUEX-NPH solvent contains 0.2M CMPO and 1.4M TBP in Conoco C_{12}-C_{14}, an NPH diluent mixture with an average carbon chain length of 13.4. The composition of the TRUEX-TCE solvent is 0.25M CMPO and 0.75M TBP in TCE. The TBP (Aldrich, Gold Label), TCE (Aldrich HPLC grade), and the Conoco-NPH were used as-received. The purity of the CMPO (M&T Chemical Inc.) was estimated to be ~98%.

Acid Distribution Measurements

The organic phase was equilibrated by contacting it repeatedly with a fresh aqueous phase at an organic/aqueous volume ratio of one. Based on the measured distribution ratios, the aqueous phase HNO_3 concentration remained unchanged from its initial value by the fourth and final contact. The organic phase HNO_3 concentration was determined by back extraction into distilled water and subsequent titration of the aqueous solution with standardized NaOH solution.

Am Distribution Measurements

Before extraction, the TCE solution of 0.25$\underline{M}$ CMPO was pre-equilibrated with the requisite nitric acid solution. Forward and reverse distribution ratios of ^{241}Am at 25°C were measured using the 60 KeV gamma ray activity in each phase.

RESULTS AND DISCUSSION

HNO_3 Extraction by TBP

In the TRUEX solvent, nitric acid is extracted by both TBP and CMPO. Consequently, it was necessary to model acid extraction by TBP and CMPO alone before attempting to model the extraction behavior of the TRUEX solvent. In both the PUREX and TRUEX processes, nitric acid, as a source of nitrate ion, enhances the extraction of metal ions as their neutral nitrate species, but it also competes for extractant molecules by its own extraction.

The extraction of HNO_3 by TBP was modeled according to the following reaction equilibria (15):

$$H^+ + NO_3^- + \overline{TBP} \rightleftharpoons \overline{TBP \bullet HNO_3} \tag{8}$$

$$H^+ + NO_3^- + 2\,\overline{TBP} \rightleftharpoons \overline{(TBP)_2 \bullet HNO_3} \tag{9}$$

where the bar represents an organic phase species.

The equilibrium constants for Eqs. 8 and 9, considering activity coefficients, are:

$$KT1 = \frac{[\overline{TBP \bullet HNO_3}]}{[\overline{TBP}]\ [H^+][NO_3^-]\ y_{12}^2} \tag{10}$$

$$KT2 = \frac{[\overline{(TBP)_2 \bullet HNO_3}]}{[\overline{TBP}]^2 [H^+][NO_3^-]\ y_{12}^2} \tag{11}$$

where y_{12} refers to the stoichiometric mean activity coefficient of nitric acid. Organic phase activity coefficients of TBP, $TBP \bullet HNO_3$, and $(TBP)_2 \bullet HNO_3$ are included in the equilibrium constants KT1 and KT2. These parameters, therefore, are a function of TBP concentration and choice of diluent.

The total organic phase HNO_3 concentration $[\overline{HNO_3}]_t$ is given by

$$[\overline{HNO_3}]_t = KT1\ [\overline{TBP}]_f\ [H^+][NO_3^-]y_{12}^2 + KT2\ [\overline{TBP}]_f^2\ [H^+][NO_3^-]y_{12}^2 \quad (12)$$

The free TBP concentration is defined by

$$[\overline{TBP}]_f = [\overline{TBP}]_t - [\overline{TBP \bullet HNO_3}] - 2[\overline{(TBP)_2 \bullet HNO_3}] \quad (13)$$

When the extraction of nitric acid is from aqueous solutions having a stoichiometric $[HNO_3]$ greater than approximately 6<u>M</u>, the formation of the 1:2 species, $TBP \bullet 2HNO_3$, must be considered. This modification to the extraction model is discussed in detail elsewhere (15).

The parameters KT1 and KT2 were obtained from a least-squares fit to the extraction data of Davis (16) for TBP concentrations of 5, 15, and 30 vol % TBP in Amsco 125-85. The constants KT1 and KT2 are affected by TBP concentration, but only to a small extent. For all practical purposes, they may be considered independent of TBP concentration. Excellent agreement was obtained between the calculated and experimental extraction isotherms (see Fig. 1) using values of KT1 = 0.185 ± 0.003 and KT2 = 0.444 ± 0.009 $\underline{M}^{-1}$ (obtained by curve fitting all the data for 5, 15, and 30% TBP simultaneously).

The present model also fits HNO_3 extraction data for solutions of 5 to 100% TBP and is able to predict the extraction of nitric acid from mixed nitrate salt solutions (15).

HNO_3 Extraction by CMPO

Acid loading studies have shown that HNO_3 extraction by CMPO yields a HNO_3 stoichiometry greater than one at moderately high aqueous HNO_3 concentrations (17). The extraction of nitric acid by CMPO was, therefore, modeled according to the following chemical equilibria:

$$H^+ + NO_3^- + \overline{CMPO} \overset{KC1}{\rightleftharpoons} \overline{CMPO \bullet HNO_3} \quad (14)$$

$$2H^+ + 2NO_3^- + \overline{CMPO} \overset{KC2}{\rightleftharpoons} \overline{CMPO \bullet 2HNO_3} \quad (15)$$

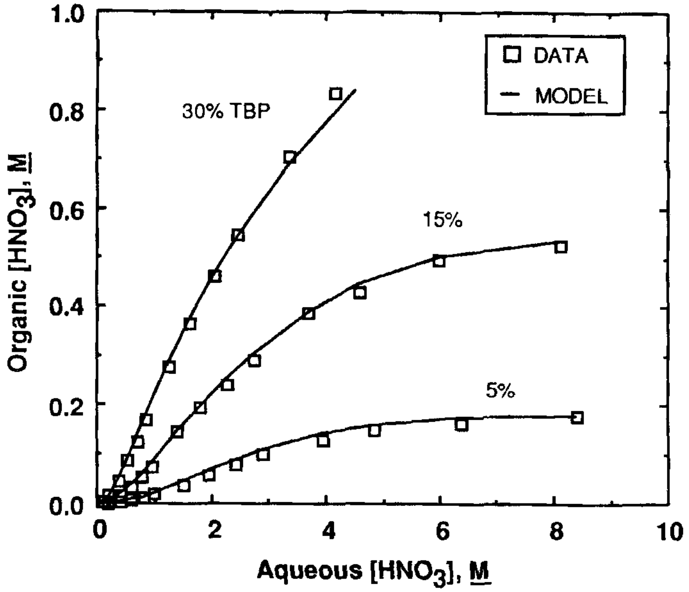

Fig. 1. Measured and Calculated Nitric Acid Extraction by TBP in Amsco 125-82 at 25°C. Data are from Davis (16).

Based on Eqs. 14 and 15, the total organic phase HNO_3 concentration is given by

$$[\overline{HNO_3}]_t = KC1 \bullet [\overline{CMPO}]_f [H^+][NO_3^-] y_{12}^2$$

$$+ 2 \bullet KC2 [\overline{CMPO}]_f [H^+]^2 [NO_3^-]^2 y_{12}^4 \qquad (16)$$

From a nonlinear least-squares analysis of the extraction data, the values of KC1 and KC2 were found to be 1.9 ± 0.1 and 0.009 ± 0.004$\underline{M}^{-1}$, respectively, for 0.25$\underline{M}$ CMPO. This agrees with the value of 2.0 ± 0.3 reported by Horwitz et al. (18). In that study, however, only the formation of the $CMPO \bullet HNO_3$ species was considered. From extraction data for 0.5$\underline{M}$ CMPO (17), the constants were KC1 = 2.21 ± 0.07 and KC2 = 0.014 ± 0.004$\underline{M}^{-1}$. As shown in Fig. 2, the calculated extraction isotherms agree quite well with the experimental data, even at high solvent loading levels.

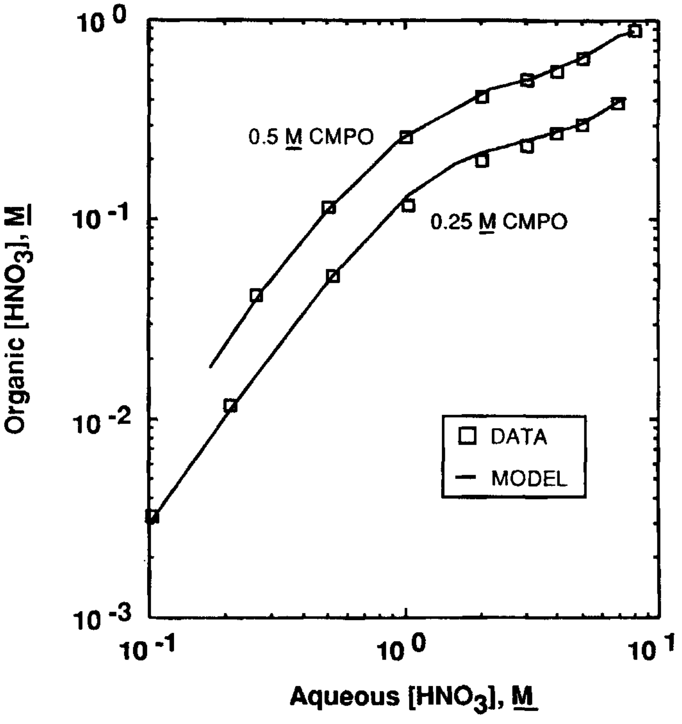

Fig. 2. Measured and Calculated HNO_3 Extraction Isotherms for 0.25M and 0.5M CMPO in TCE. The 0.5M CMPO data were obtained from (17).

The fact that solvent loading has essentially no influence on the values of KC1 and KC2 suggests that the ratios for the organic phase activity coefficients, $y(CMPO \bullet HNO_3)/y(CMPO)$ and $y(CMPO \bullet 2HNO_3)/y(CMPO)$, remain constant. This is consistent with the activity coefficients of CMPO reported by Diamond et al. (19). Their data showed that the activity of 0.25M CMPO in toluene changed only slightly (~0.75%) between organic solutions that were equilibrated with water and those that were equilibrated with 0.5M HNO_3. At 0.5M CMPO this difference increased to about 1.5%.

Nitric Acid Extraction by the TRUEX Solvents

As a first approximation, it was assumed that no specific interactions occurred between CMPO and TBP in both the TRUEX-TCE

Table I. Nitric Acid Extraction Constants for the TRUEX-TCE and TRUEX-NPH Solvents, 25°C

Equilibrium Constant	Value
TRUEX-TCE	
KT1	0.07 ± 0.03
KT2	0.23 ± 0.08
KC1	3.7 ± 0.6
KC2	0.02 ± 0.02
TRUEX-NPH	
KT1	0.16 ± 0.01
KT2	0.24 ± 0.01
KC1	6.4 ± 0.4
KC2	0.02 ± 0.02

and TRUEX-NPH solvents. The extraction of nitric acid by the TRUEX solvent is, therefore, simply a combination of the separate equilibria for the extraction of nitric acid by CMPO and TBP as described above (see Eqs. 12 and 16). Since organic phase activity coefficients are combined with the extraction constants (KC1, KC2, KT1, and KT2), these constants must be reevaluated for both the TRUEX-TCE and TRUEX-NPH solvents. The extraction constants were influenced mostly by the choice of diluent and, to a lesser extent, by extractant concentration. The equilibrium constants that were obtained from a least-squares fit of the extraction data are listed in Table I, and in Fig. 3 the experimental nitric acid data are plotted together with the calculated extraction isotherms.

An excellent agreement was obtained between the experimental and calculated nitric acid extraction profiles, except at low acid concentrations. It is believed that the extraction mechanism in this region (i.e., aqueous [HNO_3] <0.03<u>M</u>) changes, possibly due to the presence of impurities in the organic phase. It should be pointed out, however, that the discrepancies in concentrations for the organic phase nitric acid at these small values will not influence process conditions. Therefore, the differences between the calculated and measured isotherms are of little consequence.

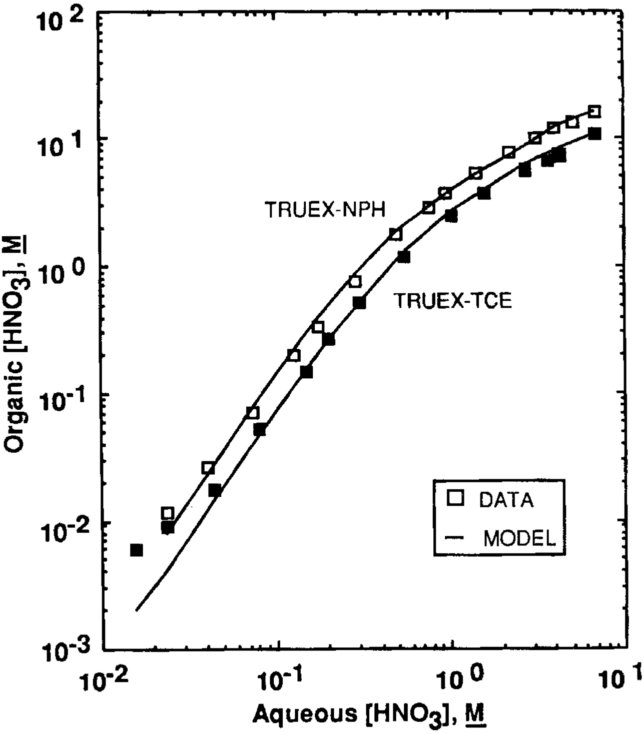

Fig. 3. Measured and Calculated Nitric Acid Extraction by the TRUEX Solvents.

Salt Effects

The salting out of nitric acid by inextractable nitrate salts can be viewed as a result of both the common ion effect and changes in the water activity brought about by the addition of highly hydrated cations such as Al^{3+}. In mixed electrolyte solutions, both of these effects are accounted for by the activity coefficients of nitric acid, which were calculated from Eq. 1.

Salting-out effects for the CMPO-only and TBP-only systems will be presented elsewhere (15, 20). Some results for HNO_3 extraction by the TRUEX-NPH solvent from $HNO_3/NaNO_3$ solutions are given in Table II; agreement between measured and calculated organic HNO_3 concentrations is reasonably good. Similar agreements between experimental and calculated results were obtained for the TRUEX-TCE solvent and also for aqueous solutions containing $HNO_3/NaNO_3/Al(NO_3)_3$ mixtures (20).

Table II. Effect of $NaNO_3$ on the Extraction of HNO_3 by the TRUEX-NPH Solvent, 25°C

$[HNO_3]$, M	$[NaNO_3]$, M	$[NO_3^-]$, M	Organic $[HNO_3]$, M	
			Measured	Calculated
1	4	5	0.82	0.81
2	3	5	1.04	1.08
3	2	5	1.19	1.23
4	1	5	1.27	1.35

Am^{3+} Extraction by CMPO

From Karl-Fisher titration data, it appears that americium is extracted by CMPO as an anhydrous complex (4). Also, slope analysis studies on the extraction of Am(III) from nitric acid solutions by CMPO-type extractants have shown a third order dependency on extractant concentration (21). Accordingly, Am^{3+} extraction by CMPO can be described by

$$Am(H_2O)_9^{3+} + 3NO_3^- + 3\overline{CMPO} \overset{K_0}{\rightleftharpoons} \overline{Am(NO_3)_3(CMPO)_3} + 9H_2O \qquad (17)$$

If the distribution ratio of Am is defined as $D_{Am}=[\overline{Am}]/[Am]_{total}$, and the activity coefficients of all aqueous Am species are assumed to be constant, D_{Am} (based on Eq. 17 and aqueous phase complexing of Am^{3+} by one or two nitrate ions) is given by

$$D_{Am} = \frac{K_0\,[\overline{CMPO}]_f^3\,\{NO_3^-\}^3}{\left(1 + \beta_1 \frac{\{NO_3^-\}}{\{H_2O\}} + \beta_2 \left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^2\right)\{H_2O\}^9} \qquad (18)$$

The symbols { } and [ ] refer to activity and molar concentration, respectively. The concentration of the free CMPO, $[\overline{CMPO}]_f$, can be calculated from Eq. 16. The denominator of Eq. 18 takes into account the aqueous phase complexation of Am^{3+} by NO_3^-, which forms an inner sphere complex (22) assumed to be monodentate. Equation 18 can be rearranged to the form of a polynomial to give

$$\frac{[\overline{CMPO}]_f^3\,\{NO_3^-\}^3}{D_{Am}\,\{H_2O\}^9} = \frac{1}{K_0} + \frac{\beta_1}{K_0}\,\frac{\{NO_3^-\}}{\{H_2O\}} + \frac{\beta_2}{K_0}\left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^2 \qquad (19)$$

The constants K_O, β_1, and β_2 were obtained by a least-squares fit with the extraction data for $[HNO_3] \lesssim 0.5\underline{M}$. The values of K_O, β_1, and β_2 were found to be 1.6×10^6, 86.5, and 63.2, respectively. Since K_O, β_1, and β_2 are based on activities, they are assumed to be independent of ionic strength.

The complexation constants (β_1 and β_2) reported here differ considerably from those obtained by O'Brien and Bautista (23) for Nd(III), which were $\beta_1 = 1.89$ and $\beta_2 = 0.89$. Given the similarity of ionic radii between Am(III) and Nd(III), their nitrate complexation constants are expected to be similar. Studies using our CMPO data and literature data for other extractants are under way in an attempt to explain this discrepancy.

Equation 18 gives a good fit to the extraction data up to about $1\underline{M}$ HNO_3 (see Fig. 4, curve A). For aqueous acid concentrations of $1\underline{M}$ or greater, Eq. 18 must be modified to include the participation of the CMPO•HNO_3 species in Am^{3+} extraction. In using Nd(III) as a substitute for Am(III), infrared spectroscopy studies have shown that nitric acid is associated with the metal-CMPO complex through hydrogen bonding to the carbonyl group (24). Chemical analysis of CMPO-TCE solutions containing macroconcentrations of Nd(III) have confirmed that at high acid concentrations, the metal-CMPO complex contains the CMPO•HNO_3 species (17). In principle, each of the three CMPO molecules in the Am-CMPO complexes is available for association with nitric acid.

Remaining consistent with the form of Eq. 17, the extraction equilibria involving CMPO•HNO_3 are written in terms of the free CMPO species:

$$Am(H_2O)_9^{3+} + H^+ + 4NO_3^- + 3\overline{CMPO} \overset{K_1}{\rightleftharpoons} \overline{Am(NO_3)_3(CMPO)_2(CMPO{\bullet}HNO_3)} + 9H_2O \quad (20)$$

$$Am(H_2O)_9^{3+} + 2H^+ + 5NO_3^- + 3\overline{CMPO} \overset{K_2}{\rightleftharpoons} \overline{Am(NO_3)_3(CMPO)(CMPO{\bullet}HNO_3)_2} + 9H_2O \quad (21)$$

$$Am(H_2O)_9^{3+} + 3H^+ + 6NO_3^- + 3\overline{CMPO} \overset{K_3}{\rightleftharpoons} \overline{Am(NO_3)_3(CMPO{\bullet}HNO_3)_3} + 9H_2O \quad (22)$$

When the equilibria of Eqs. 20-22 are incorporated into Eq. 18, the expression for D_{Am} becomes

$$D_{Am} = \frac{[\overline{CMPO}]_f^3 \{NO_3^-\}^3 \left(K_O + K_1\{H^+\}\{NO_3^-\} + K_2\{H^+\}^2\{NO_3^-\}^2 + K_3\{H^+\}^3\{NO_3^-\}^3\right)}{\left(1 + \beta_1 \frac{\{NO_3^-\}}{\{H_2O\}} + \beta_2\left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^2\right)\{H_2O\}^9} \quad (23)$$

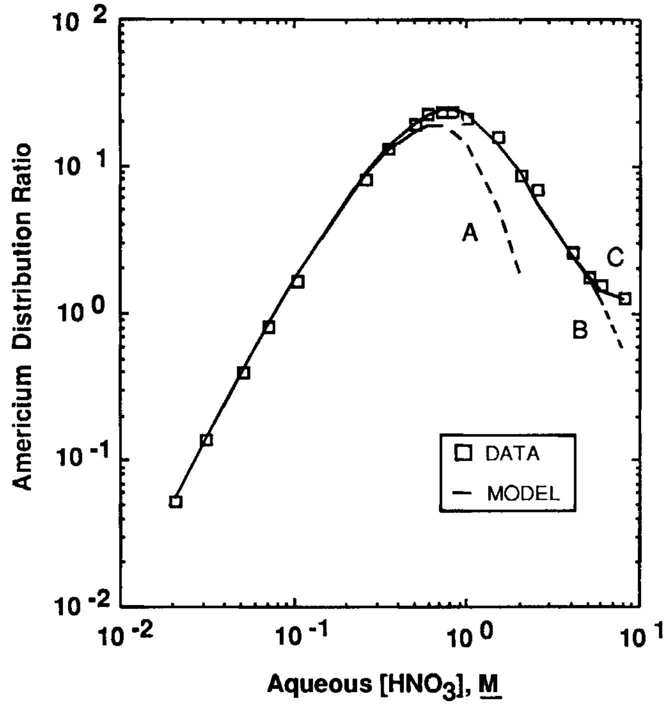

Fig. 4. Measured and Calculated Americium Extraction by 0.25M CMPO in TCE at 25°C. Curve A was calculated from Eq. 18; Curve B was calculated from Eq. 23; Curve C was generated from the complete extraction model. Some of the data were obtained from Ref. (18).

The addition of the terms containing K_1, K_2, and K_3 extends the range of the model up to 5M HNO_3 (Fig. 4, curve B). To model the remainder of the data (Fig. 4, curve C), it was necessary to include an additional term (K_4 $\{H^+\}^4\{NO_3\}^4$) in Eq. 23, which results from the following extraction equilibrium

$$Am(H_2O)_9^{3+} + 4H^+ + 7NO_3^- + 3\overline{CMPO} \overset{K_4}{\rightleftharpoons} \overline{Am(NO_3)_3(CMPO \bullet HNO_3)_2(CMPO \bullet 2HNO_3)} + 9H_2O \qquad (24)$$

The values of the extraction constants, obtained by curve fitting, are given in Table III.

Table III. Americium Extraction Constants for 0.25M CMPO in TCE, 25°C

Equilibrium Constant	Value[a]
K_0	1.6×10^6
K_1	1.4×10^6
K_2	1.17×10^5
K_3	4.25×10^2
K_4	1.96

[a] Values are reported without error estimates since the statistical package, SYSTAT, does not calculate standard deviations with the SIMPLEX routine.

Table IV. Americium Extraction by 0.25M CMPO in TCE from $HNO_3/NaNO_3$ Solutions, 25°C

		D_{Am}	
$[HNO_3]$, M	$[NaNO_3]$, M	Measured	Calculated
0.5	1	63.3	63.7
1.0	1	30.1	30.5
2.0	1	8.6	9.7
4.0	1	2.2	2.9

Preliminary data show that the model does a good job of predicting the effects of inextractable nitrate salts (i.e., $NaNO_3$) on Am extraction. The calculated and experimental D_{Am} values are given in Table IV for the extraction of Am^{3+} from $HNO_3/NaNO_3$ solutions.

General Extraction Behavior

In this paper, we have presented the methodology that we are currently using to model the extraction equilibria of species important to the TRUEX process. The extraction models are based on chemical mass action equations and are written in terms of the activities of the aqueous phase species. This approach is an advancement over other extraction models such as the SEPHIS code, which is used in the design and testing of PUREX flowsheets (25). In that model, empirical correlations are used to relate the nonthermodynamic extraction constants with ionic strength.

The extraction models described above are based on the minimum number of chemical equilibria necessary to fit the data. This work is not intended to be a fundamental study of reaction pathways in the TRUEX solvent extraction process. Because of the complexity of systems like the TRUEX process, there are, undoubtedly, existing organic phase species which have not been included in the HNO_3 and Am^{3+} extraction models. Future data may show that under certain conditions new extraction equilibria must be added to the TRUEX model. Nevertheless, this approach has allowed us to develop models having extraction constants which are independent of the aqueous feed composition.

A number of methods are described in the literature (26) for calculating activity coefficients in mixed electrolyte solutions at high ionic strengths (6<u>M</u> or greater) and at high temperatures (50 to 150°C). We have found these techniques to be quite useful. Modeling of HNO_3 extraction by the PUREX and TRUEX solvents showed the extraction constants to be independent of ionic strength and unaffected by the presence of inextractable cations such as Na^+, K^+, Li^+, and Al^{3+} (15, 20). This same approach has also been successful in describing the influence of Na^+, K^+, Ca^{2+}, and Mg^{2+} on Pu(IV) extraction by TBP from chloride media (27).

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