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Thermodynamic Modeling of the Extraction of Cadmium Nitrate by the TRUEX-NPH Solvent

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ABSTRACT

The TRUEX solvent extraction process is being developed to remove low concentrations of transuranic (TRU) elements from high-level and TRU wastes currently stored at US Department of Energy sites. Cadmium is an important constituent of some of these wastes, especially at the Idaho Chemical Processing Plant. Cadmium distribution ratios were measured by using a radioactive Cd tracer under a variety of aqueous-phase compositions to elucidate the mechanism of cadmium extraction by TRUEX-NPH solvent at 25°C. A model for predicting cadmium distribution ratios was developed as a function of the thermodynamic activities of water and nitrate ion. The Generic TRUEX Model (GTM) was used to calculate these activities. The GTMs calculation of activity coefficients is based on a Bromley method.

Key Words. CMPO; TRUEX-NPH; Cadmium nitrate; Stability constant; Activity coefficients; Solvent extraction

INTRODUCTION

The TRUEX (TRansUranic EXtraction) process is used to separate transuranic (TRU) elements from nuclear waste solutions (1–4). The TRUEX program at Argonne National Laboratory has focused on understanding the TRUEX extraction chemistry (5, 6, 15–17) of waste streams at various US Department of Energy (DOE) sites. An important tool in this research is the Generic TRUEX Model (GTM), a thermodynamically

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based model that is used to design TRUEX flow sheets for a variety of waste streams (7, 8).

One of the DOE waste streams needing remediation is generated at Idaho National Engineering Laboratory (INEL) during the reprocessing of nuclear submarine fuel. This waste stream has a high ionic strength and high concentrations of cadmium and boron (both added as neutron poisons during fuel dissolution), as well as fluoride and zirconium.

The high concentration of Cd^{2+} in the INEL waste stream could reduce solvent performance: solvent consumed in extracting cadmium is not available to extract TRU. Therefore, it is important that we understand the cadmium extraction mechanism so we can accurately predict the effects of solvent loading and design the TRUEX flow sheets accordingly (9). In this report we describe how the GTM has been used to derive a thermodynamically accurate extraction mechanism for a cadmium nitrate species $Cd(NO_3)_2 \cdot 2CMPO$ in the TRUEX-NPH solvent.

The TRUEX solvent is composed of 1.4 M tributyl phosphate (TBP) and 2.0 M octyl(phenyl)-diisobutylcarbamoylmethyl phosphine oxide (CMPO) in normal paraffinic hydrocarbons (NPH). The TBP in the solvent acts generally as a phase modifier to greatly reduce the propensity of the solvent to form a third phase. It also acts in many cases as a secondary extractant.

The behavior of cadmium in organic solvents is understood to some extent. The fluoride, chloride, and bromide salts of cadmium are generally nonextractable. The solvent extraction of cadmium into an organic solvent involves the solvation of a complexed anion, cation, or neutral salt into a water-immiscible phase by ion association, chelation, or solvation. In organophosphates (e.g., di-*n*-butyl phosphoric acid), however, the extraction of cadmium is nonselective and is usually driven by ion association (10, 11). In TBP systems, the extractability of cadmium fluoride is low (12), but chloride and iodide cadmium salts have produced ion-associated and chelated species such as $CdCl_2 \cdot 2TBP$, $CdI_2 \cdot 2TBP$, $H_2CdCl_4 \cdot 2TBP$, $HCdCl_3 \cdot 3TBP$, and many other species (13–17). In CMPO, little is known about cadmium extraction. In particular, extraction of cadmium nitrate with CMPO has not been reported. For nitrate species that are highly extractable, such as those containing Am^{3+}, Pu^{4+}, Np^{4+}, and UO_2^{2+}, there are well-established thermodynamic models based on the chemical equilibria of CMPO, TBP, and mixed CMPO–TBP complexes (2, 6). However, for nitrate species with low extractability in the TRUEX solvent, such as cadmium nitrate, thermodynamic models have not been adequately investigated.

A mathematical model for the extraction of cadmium nitrate by the TRUEX-NPH solvent requires the collection of distribution ratios under a variety of aqueous-phase conditions and the determination of the activity

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coefficient of water, hydrogen ion, and nitrate ion in high-ionic-strength solutions. The calculation of activity coefficients at high ionic strengths has been a major research interest for several years. The extended Debye–Huckel equation for activity coefficients is only useful for ionic strengths less than 0.1 molal, which makes it impractical for our research, which involves ionic strengths greater than 1 molal. Pitzer (18), Meissner (19), and others (20) have developed methods to determine activity coefficients for pure and multicomponent systems by accounting for triple-ion interactions and other ion-neutral interactions. Pitzer's method is difficult to use for practical applications because many fitting parameters are required and the availability of data is limited. A somewhat simpler approach to determining activity coefficients for high ionic strengths is based on the Meissner (19) and on the Bromley (21) methods, which have large existing databases (19).

Distribution ratios and activity coefficients can be calculated by using built-in features of the GTM. This model uses activity coefficient values from the literature in a form to which the Bromley method can be applied. This model calculates the activities of $\{H^+\}$, $\{NO_3^-\}$, and $\{H_2O\}$ (where the braces, { }, symbolize activities). The GTM also calculates aqueous-phase speciation, extractant mass balance, concentration, and organic phase CMPO/TBP/HNO_3 speciation using solution thermodynamic properties.

Thermodynamically correct modeling based on chemical equilibria for nitrate species with low extractability in the TRUEX solvent has not been adequately investigated. Modeling based on the chemical equilibria of CMPO, TBP, and mixed CMPO–TBP complexes of highly extractable nitrate species such as Am^{3+}, Pu^{4+}, Np^{4+}, and UO_2^{2+} are well understood (2, 6). Thermodynamic modeling for nitrate species containing Cd and Zr (cladding component) in the TRUEX solvent has only recently been investigated.

The TRUEX technology-base-development program at Argonne National Laboratory has focused on understanding TRUEX extraction chemistry (15–17) of waste streams at various DOE sites. In this report, we describe how thermodynamic modeling has been used to derive an extraction mechanism for a $Cd(NO_3)_2 \cdot 2CMPO$ species in the TRUEX solvent.

EXPERIMENTAL

Extraction of Cadmium as a Function of HNO_3 Concentrations

The TRUEX solvent was prepared in normal paraffinic hydrocarbon solvent with a carbon average length of 13.4 (NPH, C_{12}–C_{14}, Conoco Chemicals) using CMPO that had been recrystallized (8) and TBP (Aldrich Chemical Company, Gold Label). The purity of the constituents was confirmed by forward and reverse ^{241}Am extractions at high and low nitric acid concentrations. The ^{241}Am concentration was measured by counting the 59 keV gamma ray with a sodium iodide detector. The distri-

TABLE 1

Cadmium Distribution Ratios and Initial Aqueous Concentrations of $NaNO_3$ and HNO_3

$NaNO_3$ (*M*)	HNO_3 (*M*)	D_{Cd}
0	9.00E-03	1.64E-05
0	4.95E-02	8.28E-05
0	9.80E-02	6.97E-05
0	1.95E-01	2.90E-04
0	3.20E-01	7.90E-04
0	9.85E-01	3.33E-03
0	1.49E+00	4.40E-03
0	1.98E+00	6.41E-03
0	3.01E+00	6.86E-02
0	3.75E+00	1.18E-01
2.00E-02	3.18E+00	3.14E-01
1.00E-01	9.69E-02	2.83E-03
1.00E-01	4.92E-02	2.28E-03
1.00E-01	3.02E-02	2.35E-03
1.00E-01	1.13E-02	1.51E-03
3.00E-01	9.80E-02	9.16E-03
3.00E-01	4.24E-02	1.04E-02
3.00E-01	3.01E-02	7.80E-03
3.00R-01	1.14E-02	8.45E-03
5.00E-01	2.70E+00	7.52E-02
5.00E-01	9.79E-02	1.61E-02
5.00E-01	4.76E-02	1.47E-02
5.00E-01	3.07E-02	1.59E-02
5.00E-01	1.11E-02	1.70E-02
1.00E+00	4.00E+00	1.81E-02
1.00E+00	5.00E-01	2.45E-02
1.00E+00	1.00E+00	2.12E-02
1.00E+00	2.00E+00	1.78E-02
1.00E+00	1.00E-01	3.43E-02
1.00E+00	1.00E-01	3.38E-02
1.00E+00	1.00E-02	3.83E-02
1.00E+00	5.00E-02	3.42E-02
1.00E+00	3.00E-02	3.64E-02
2.20E+00	1.00E+00	3.49E-02
4.40E+00	3.00E+00	3.07E-02
4.40E+00	2.00E+00	4.14E-02
4.40E+00	1.00E+00	7.62E-02
4.40E+00	5.00E-01	1.61E-02
4.40E+00	1.00E-02	9.41E-01
4.40E+00	1.00E-01	4.95E-01
4.40E+00	5.00E-02	4.64E-01
4.40E+00	3.00E-02	4.91E-01
4.40E+00	1.00E-02	3.94E-01
5.00E+00	8.82E-02	9.44E-01
5.00E+00	4.35E-02	9.76E-01
5.00E+00	2.85E-02	9.65E-01
5.00E+00	1.13E-02	9.44E-01
6.00E+00	9.04E-02	1.57E+00
6.00E+00	4.48E-02	1.97E+00
6.00E+00	2.94E-02	2.07E+00
6.00E+00	1.12E-02	2.23E+00
7.00E+00	8.06E-02	2.34E+00
7.00E+00	4.18E-02	2.74E+00
7.00E+00	2.61E-02	4.48E+00
7.00E+00	1.04E-02	4.27E+00
8.00E+00	9.26E-02	2.36E+00
8.00E+00	4.67E-02	2.90E+00
8.00E+00	2.93E-02	3.12E+00
8.00E+00	1.13E-02	3.62E+00

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bution ratios ($D_{Am} = [Am]_{org}/[Am]_{aq}$) at both acidities were compared with those obtained for a TRUEX solvent previously studied.

A series of 10 nitric acid solutions with concentrations ranging from 0.009 to 3.94 M was pre-equilibrated with TRUEX-NPH (first 10 entries in Table 1). The pre-equilibration involves triplicate contact of the TRUEX solvent with fresh aqueous (acid) solution in a 1:3 organic to aqueous volume ratio. After pre-equilibration, the aqueous acid solutions were spiked with a ^{109}Cd stock solution. The organic and aqueous solutions were mixed, placed in a thermostat-controlled bath at 25°C until equilibrated, removed, mixed again, and returned to the bath. This procedure was repeated twice. The organic and aqueous phases were separated and gamma counted on a Packard NaI crystal detector (Minaxi γ Autogamma 5000 Series) to determine the cadmium activity. The distribution ratios ($D_{Cd} = [Cd]_{org}/[Cd]_{aq}$) were calculated.

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Extraction of Cadmium as a Function of HNO₃ and NaNO₃ Concentrations

The cadmium distribution ratios were also measured for given HNO_3/$NaNO_3$ mixtures (Table 1). Acid solutions were prepared with salt concentrations between 0.01 and 8 M $NaNO_3$. All solutions were spiked with a ^{109}Cd stock solution by using the procedure previously described, except without initial pre-equilibration of the organic solvent.

All nitric acid concentrations were determined by potentiometric titration of standardized NaOH using a Brinkman Titroprocessor 670.

RESULTS AND DISCUSSION

Extraction of Cadmium as a Function of HNO₃ Concentration

The cadmium distribution ratios showed a linear increase as a function of nitric acid concentration in a log-log plot (Fig. 1). The least-squares fit converges to a power nitrate dependency, $[NO_3^-]^n$, where $n = 1.64$. The difference between 1.64 and the value of 2 expected for the extraction of a neutral cadmium nitrate species can be attributed to the nitrate activity. The distribution ratios ranged from 1.64×10^{-5} for 0.009 M HNO_3 to 0.12 for 3.99 M HNO_3. These results can be compared with those obtained in a partitioning study (22) of cadmium in mixed fluoride and nitrate solution from a synthetic INEL waste stream with 0.1 M CMPO and 1.4 M TBP. Within the acid region of 0.1 to 10 M HNO_3, D_{Cd} values of ≤ 0.002 were obtained: no significant cadmium extraction was observed. This result can be attributed to the high concentrations of fluoride and extractable metals.

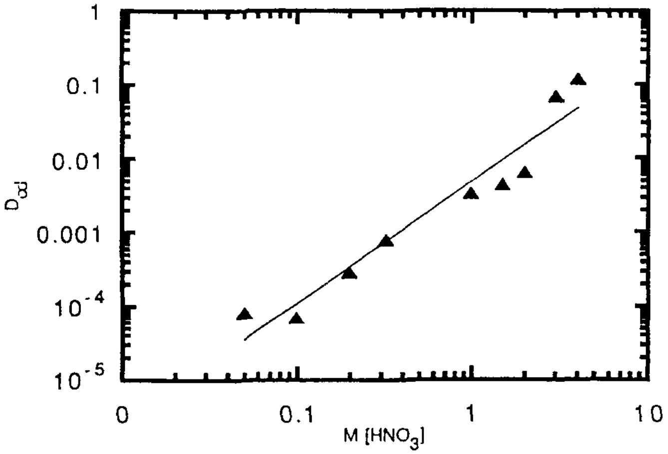

FIG. 1 Cadmium distribution ratio as a function of nitric acid concentration for pre-equilibrated TRUEX-NPH and ^{109}Cd at 25°C.

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Extraction of Cadmium as a Function of HNO$_3$ and NaNO$_3$ Concentrations

The addition of a nonextractable salt such as sodium nitrate results in a salting-out effect. Increasing the aqueous-phase concentration of the salt has two important effects: 1) it decreases water activity and 2) it provides a common-ion effect to promote the extraction of $Cd(NO_3)_2$, changing the $\{NO_3^-\}$ while having only a minimal effect on the $\{H^+\}$. The GTM accounts for most of the principal nonaqueous acid complexes (HNO_3, CMPO, TBP). The effect of nitric acid addition is shown in Figs. 2 and 3, in which the nitric acid concentration is given as the aqueous-phase concentration before contact with the TRUEX solvent (0–1 M in Fig. 2; 4.4–8 M in Fig. 3).

The cadmium distribution ratio increases with increasing nitrate ion concentration. For $NaNO_3$ concentrations greater than 1 M (Fig. 3), the distribution ratios decrease slightly with increasing nitric acid concentration. For $NaNO_3$ concentrations greater than 5 M, the distribution ratios are greater than 1.

Both the acid and the salt concentration were varied in three data points to maintain the total nitrate ion concentration at 3.14 M. These data points show significant changes in distribution values as a function of acid concentration.

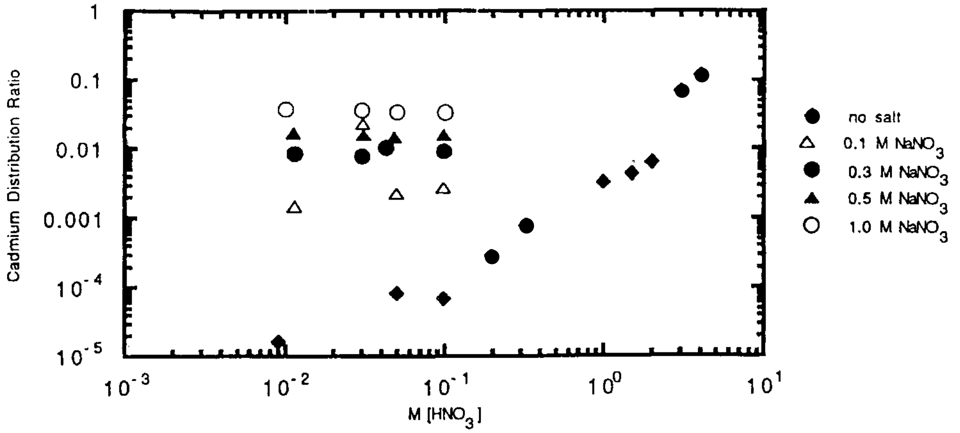

FIG. 2 Cadmium distribution ratio at 25°C as a function of nitric acid concentration and sodium nitrate concentrations from 0 to 1 M.

Determining Stability Constant and TRUEX-NPH Chemical Equilibria

The first step in developing an extraction mechanism for cadmium nitrate in TRUEX-NPH is normalizing the D_{Cd} values by expressing the

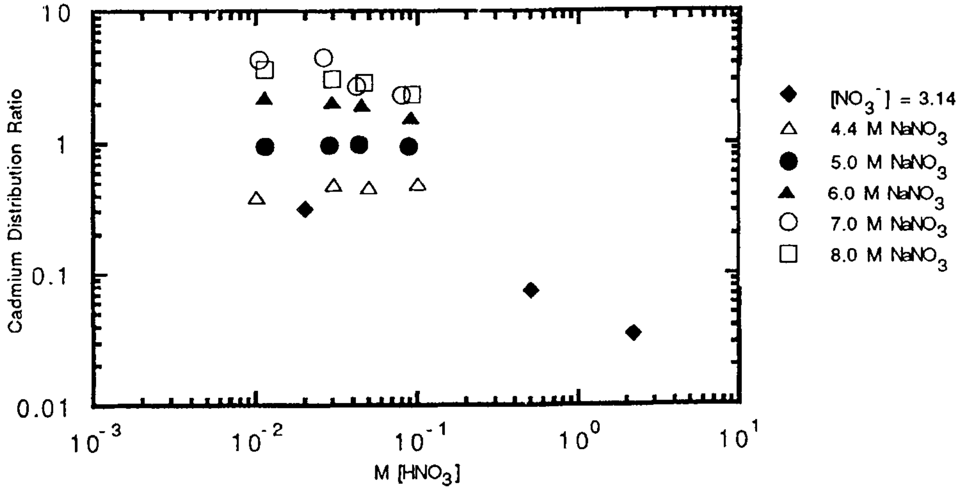

FIG. 3 Distribution constants of cadmium at 25°C as a function of nitric acid concentration and sodium nitrate concentrations from 4.4 to 8 M.

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concentrations of the aqueous species in terms of individual activities. For the nitric acid and salt concentrations, it is possible to determine the activities at 25°C by using the GTM activity coefficient feature, which is based on the Bromley method (21) as described below.

Bromley's equation for multiple and single ion activity in a mixed electrolyte solution is expanded below (variables are identified after Eq. 5):

$$\log \gamma_{12} = \frac{-AZ_1Z_2\sqrt{I}}{1 + \sqrt{I}} + \frac{\nu_1F_1 + \nu_2F_2}{\nu_1 + \nu_2} \tag{1}$$

The F terms are defined as the following:

$$\begin{aligned} F_1 = {} & (Y_{12}\log\gamma_{12}^0 + Y_{14}\log\gamma_{14}^0 + \cdots + Y_{1j}\log\gamma_{1j}^0) \\ & + \frac{A\sqrt{I}}{1 + \sqrt{I}}(Z_1Z_2Y_{12} + Z_1Z_4Y_{14} + \cdots + Z_1Z_jY_{1j}) \end{aligned} \tag{2}$$

and

$$\begin{aligned} F_2 = {} & (X_{12}\log\gamma_{12}^0 + X_{32}\log\gamma_{32}^0 + \cdots + X_{i2}\log\gamma_{i2}^0) \\ & + \frac{A\sqrt{I}}{1 + \sqrt{I}}(Z_1Z_2X_{12} + Z_3Z_2Y_{32} + \cdots + Z_iZ_2Y_{i2}) \end{aligned} \tag{3}$$

where

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

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

and A = Debye–Hückel constant, 0.5108 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ at 25°C
$I = I_m$ (ionic strength)
γ_{12}, γ_{ij} = activity coefficient, molality scale
ν_1, ν_2 = stochiometric coefficients
Z_i, Z_j = absolute value of ionic charge
m_i, m_j = molality
$i = (1, 3, 5, \ldots)$; cationic species
$j = (2, 4, \ldots)$; anionic species

The γ_{ij}^0 terms in Eqs. (2) and (3) refer to the stochiometric activity coefficients of the pure solution of the electrolyte ij at the ionic strength of the mixed solution at 25°C. The γ_{ij}^0 values were obtained from literature and

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fitted with the following equation:

$$\log \gamma_{ij}^{0} = \frac{-AZ_iZ_j\sqrt{I}}{1 + B\sqrt{I}} + \beta I + CI^2 + DI^3 + EI^4 + \cdots \tag{6}$$

where B, β, C, D, and E are constants, and the ionic strength, I, assumes complete dissociation (5).

The activity coefficient of a single-component electrolyte solution was determined as follows:

$$\log \gamma_i = \frac{-AZ_i^2\sqrt{I}}{1 + \sqrt{I}} + F_i \tag{7}$$

$$\log \gamma_j = \frac{-AZ_j^2\sqrt{I}}{1 + \sqrt{I}} + F_j \tag{8}$$

The water activity of a single-component electrolyte solution (a_w^0) was calculated from the component's osmotic coefficients (ϕ) as shown in Eq. (9) (similar expressions can be derived for multicomponent solutions):

$$\log a_w^0 = \frac{-2\phi I}{55.510(2.303Z_iZ_j)} \tag{9}$$

where the osmotic coefficient of the single-component electrolyte solution was fitted with the following equation:

$$\begin{aligned}\phi = 1 - 2.3025\left[\frac{AZ_iZ_j}{B^3I}\right]\left[1 + BI^{1/2} - 4.605\log(1 + BI^{1/2}) - \frac{1}{1 + BI^{1/2}}\right]\\ - \beta\frac{I}{2} + \frac{2}{3}CI^2 - \frac{3}{4}DI^3 + \frac{4}{5}EI^4 + \cdots\end{aligned} \tag{10}$$

By using the method presented above, the GTM calculates individual activities. In the present case, the GTM used the initial aqueous acid and salt concentrations and the measured values of D_{Cd}, and calculated the equilibrium concentrations of the nitric acid (after taking into account the acid complexation with TBP and CMPO), amount of CMPO and TBP available, and activities of H_2O, and NO_3^-. These results (Table 2) were used to derive the extraction equilibria, as described below.

The next step in deriving the extraction mechanism was determining the power nitrate dependency. In Fig. 4 the distribution ratios are plotted as a function of nitrate activities. Only the sodium nitrate concentrations from 0.1 to 8 M were included in Fig. 4. High nitric acid concentrations were excluded because the $\{H^+\}$ for high acid concentrations were not

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TABLE 2
Activities and Concentrations Determined by the GTM

	Aqueous phase (pre-equilibrated)				Organic phase (pre-equilibrated)	
Measured D_{Cd}	$[NaNO_3]$ (M)	$[HNO_3]$ (M)	$\{NO_3^-\}$	$\{H_2O\}$	$CMPO_{free}$	TBP_{free}
1.64E-05	0	9.000E-03	8.706E-04	1.000E+00	2.000E-01	1.400E+00
8.28E-05	0	4.950E-02	4.084E-02	9.983E-01	1.980E-01	1.396E+00
6.97E-05	0	9.800E-02	7.701E-02	9.967E-01	1.930E-01	1.388E+00
2.90E-04	0	1.954E-01	1.464E-01	9.934E-01	1.775E-01	1.358E+00
7.90E-04	0	3.202E-01	2.691E-01	9.874E-01	1.434E-01	1.276E+00
3.33E-03	0	9.850E-01	7.405E-01	9.643E-01	6.158E-02	9.215E-01
4.40E-03	0	1.487E+00	1.206E+00	9.431E-01	3.317E-02	6.809E-01
6.41E-03	0	1.984E+00	1.757E+00	9.201E-01	1.898E-02	5.043E-01
6.86E-02	0	3.008E+00	3.245E+00	8.673E-01	6.343E-03	2.744E-01
1.18E-01	0	3.994E+00	5.234E+00	8.111E-01	2.128E-03	1.531E-01
2.83E-03	9.980E-02	7.851E-03	8.199E-02	9.964E-01	1.994E-01	1.399E+00
2.28E-03	9.980E-02	2.293E-02	9.256E-02	9.959E-01	1.980E-01	1.397E+00
2.35E-03	9.980E-02	3.728E-02	1.026E-01	9.954E-01	1.965E-01	1.394E+00
1.51E-03	9.980E-02	7.072E-02	1.256E-01	9.943E-01	1.921E-01	1.386E+00
9.16E-03	2.994E-01	5.900E-03	2.061E-01	9.901E-01	1.989E-01	1.398E+00
1.04E-02	2.994E-01	1.747E-02	2.135E-01	9.898E-01	1.967E-01	1.394E+00
7.80E-03	2.994E-01	2.877E-02	2.208E-01	9.894E-01	1.945E-01	1.390E+00
8.45E-03	2.994E-01	5.602E-02	2.384E-01	9.885E-01	1.889E-01	1.380E+00
1.61E-02	4.990E-01	4.697E-03	3.175E-01	9.840E-01	1.987E-01	1.398E+00
1.47E-02	4.990E-01	1.402E-02	3.233E-01	9.837E-01	1.960E-01	1.393E+00
1.59E-02	4.990E-01	2.326E-02	3.291E-01	9.834E-01	1.934E-01	1.388E+00
1.70E-02	4.990E-01	4.603E-02	3.436E-01	9.826E-01	1.871E-01	1.376E+00
9.44E-01	9.980E-01	2.915E-03	5.680E-01	9.688E-01	1.985E-01	1.397E+00
9.76E-01	9.980E-01	8.815E-03	5.718E-01	9.686E-01	1.954E-01	1.392E+00
9.65E-01	9.980E-01	1.481E-02	5.756E-01	9.684E-01	1.925E-01	1.387E+00
9.44E-01	9.980E-01	3.015E-02	5.855E-01	9.679E-01	1.852E-01	1.373E+00
3.49E-02	2.196E+00	2.481E-01	1.282E+00	9.228E-01	8.390E-02	1.052E+00
7.52E-02	2.695E+00	7.097E-02	1.353E+00	9.152E-01	1.316E-01	1.242E+00
3.14E-01	3.174E+00	1.116E-03	1.489E+00	9.039E-01	1.978E-01	1.396E+00
9.41E-01	4.391E+00	2.410E-04	1.959E+00	8.672E-01	1.992E-01	1.399E+00
4.91E-01	4.391E+00	7.546E-04	1.959E+00	8.672E-01	1.975E-01	1.396E+00
1.62E-02	4.391E+00	1.311E-03	1.960E+00	8.671E-01	1.957E-01	1.392E+00
1.62E-02	4.391E+00	2.903E-03	1.961E+00	8.670E-01	1.907E-01	1.383E+00
7.62E-02	4.391E+00	1.136E-01	2.063E+00	8.615E-01	8.016E-02	1.033E+00
4.14E-02	4.391E+00	4.754E-01	2.426E+00	8.426E-01	2.889E-02	6.333E-01
3.07E-02	4.391E+00	9.946E-01	3.042E+00	8.133E-01	1.249E-02	3.997E-01
9.44E-01	4.990E+00	1.630E-04	2.198E+00	8.480E-01	1.993E-01	1.399E+00
9.76E-01	4.990E+00	5.112E-04	2.198E+00	8.480E-01	1.978E-01	1.396E+00
9.65E-01	4.990E+00	8.904E-04	2.198E+00	8.480E-01	1.963E-01	1.394E+00
9.44E-01	4.990E+00	1.985E-03	2.199E+00	8.479E-01	1.920E-01	1.386E+00

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TABLE 2. Continued

	Aqueous phase (pre-equilibrated)				Organic phase (pre-equilibrated)	
Measured D_{Cd}	$[NaNO_3]$ (M)	$[HNO_3]$ (M)	$\{NO_3^-\}$	$\{H_2O\}$	$CMPO_{free}$	TBP_{free}
1.57E+00	5.988E+00	8.281E−05	2.682E+00	8.094E−01	1.995E−01	1.399E+00
1.97E+00	5.988E+00	2.605E−04	2.682E+00	8.094E−01	1.984E−01	1.397E+00
2.07E+00	5.988E+00	4.551E−04	2.682E+00	8.094E−01	1.972E−01	1.395E+00
2.23E+00	5.988E+00	1.021E−03	2.683E+00	8.093E−01	1.939E−01	1.389E+00
2.34E+00	6.986E+00	3.658E−05	3.519E+00	7.485E−01	1.996E−01	1.399E+00
2.74E+00	6.986E+00	1.153E−04	3.519E+00	7.485E−01	1.989E−01	1.398E+00
4.48E+00	6.986E+00	2.020E−04	3.519E+00	7.485E−01	1.981E−01	1.397E+00
4.27E+00	6.986E+00	4.559E−04	3.520E+00	7.485E−01	1.957E−01	1.392E+00
2.36E+00	7.984E+00	1.112E−05	5.608E+00	6.377E−01	1.998E−01	1.400E+00
2.90E+00	7.984E+00	3.514E−05	5.608E+00	6.377E−01	1.994E−01	1.399E+00
3.12E+00	7.984E+00	6.163E−05	5.608E+00	6.377E−01	1.989E−01	1.398E+00
3.62E+00	7.984E+00	1.401E−04	5.608E+00	6.377E−01	1.975E−01	1.396E+00

accounted for in the extraction model. Two general features can be observed in this plot of the distribution ratios. 1) The best least-square power fit of $\{NO_3^-\}^n$ was $n = 1.98$ ($R = 0.78$). Even with the large scattering, this value is close to the expected value of 2 for extracting a neutral cadmium nitrate species. 2) All of the distribution ratios generally converged onto one curve because the activity coefficients were independent of the ionic strength.

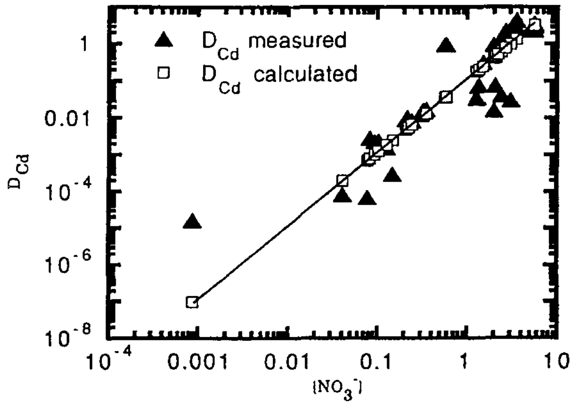

FIG. 4 Relationship of cadmium distribution ratio to nitrate activity.

Next, we determined the contribution of CMPO, TBP, and $\{H_2O\}$ to the thermodynamic model. The measured distribution ratios (Table 1) were fitted to the following chemical equilibria for cadmium nitrate in the organic and aqueous phases.

Aqueous phase:

$$Cd^{2+}(H_2O)_{4(aq)} + NO_3^- \overset{\beta_1}{\Leftrightarrow} Cd(NO_3)^+ \tag{11}$$

Organic phase:

$$Cd^{2+}(H_2O)_{4(aq)} + 2NO_3^- + 2CMPO \overset{K_1}{\Leftrightarrow} Cd(NO_3)_2{\cdot}2CMPO + 4H_2O \tag{12}$$

where K_1 and β_1 are equilibrium constants relationship shown in Eqs. (11) and (12).

The waters of hydration for cadmium can vary from 1 to 6 in inorganic salts (23). For the hydrous cadmium nitrate salt, the hydration number is 4, which agrees with the number of water molecules in the organic phase determined in the thermodynamic model. Chelation excludes inner-sphere water molecule coordination by stabilization from the strong extractant (CMPO). Commonly known TBP cadmium complexes are formed at high ionic strength by ion association or outer-sphere coordination and complexation of neutral hydrated species (13, 14), while our data support a dehydrated cadmium nitrate complex with two CMPO molecules. Experimentally, it has been found that neutral extraction from nitric acid by TRUEX involves one, two, or three CMPO molecules (24, 25).

In our graphical analysis (using an Excel-solver and KaleidaGraph package), we evaluated many possible chemical equilibria scenarios with H_2O, CMPO, or TBP, or mixtures of each, in the organic phase. However, none of these analyses gave a better least-square fit than the simple $Cd(NO_3)_2{\cdot}2CMPO$ complex and the cadmium nitrate cation species.

For the chemical equilibria in Eqs. (11) and (12), the distribution ratio for cadmium nitrate is defined by

$$D_{Cd} = \frac{K_1\{NO_3^-\}^2[CMPO]^2}{\{H_2O\}^4(1 + \beta_1\{NO_3^-\})} \tag{13}$$

By using Eq. (13) the equilibrium constant for the cadmium nitrate CMPO complex and the cation stability constant cadmium nitrate can be determined simultaneously. A plot of D_{Cd} versus $\{NO_3^-\}$ (Fig. 4) to determine the least-square fit of this function gave the values of $K_1 = 3.31$ and $\beta_1 = 0.59$.

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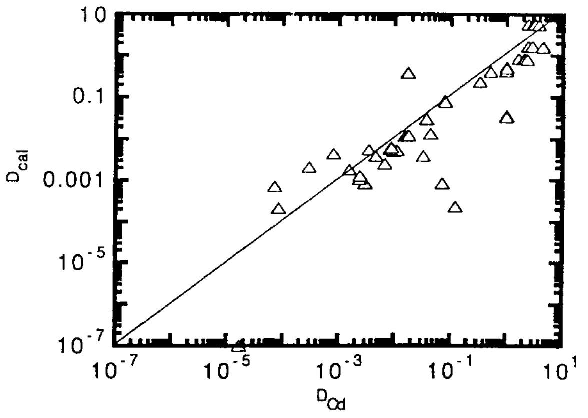

FIG. 5 Comparison of the calculated and measured cadmium distribution ratios.

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Thus Eq. (13) takes the form

$$D_{Cd} = \frac{3.31\{NO_3^-\}^2[CMPO]^2}{\{H_2O\}^4(1 + 0.59\{NO_3^-\})} \tag{14}$$

Distribution ratios calculated from Eq. (14) (D_{Cd}-calc) are compared to the measured values in Fig. 5. The plot shows a fair correlation at both high and low distribution ratios. The points with some scatter are for low nitrate concentrations. Despite this scatter, the general trend of the data points is followed. These data give β_1 values within the range of values found in determinations. These previous determinations of β_1 were obtained by conductivity (26), polarography (27), and other methods (28, 29), and gave values between 0.62 and 1.29.

CONCLUSIONS

The distribution ratio measurements of cadmium radioactive tracer with $HNO_3/NaNO_3$ mixtures allowed the determination of the TRUEX solvent extraction mechanism for a cadmium nitrate complex with two CMPO molecules. In addition, the β_1 for a cadmium nitrate cation was determined and found to be in reasonable agreement with the values of β_1 obtained by other experimenters. The incorporation of this cadmium extraction mechanism into the GTM permits the design of flow sheets for INEL waste streams. Similar techniques of thermodynamic modeling can be applied to enhance the GTM database for dealing with other real waste solutions.

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REFERENCES

1. E. P. Horwitz and W. W. Schulz, "The TRUEX Process: A Vital Tool for Disposal of U.S. Defense Nuclear Waste," in *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications* (L. Cecille, M. Casarci, and L. Pietrelli, Eds.), Elsevier Applied Science, London, 1991, pp. 21–29.
2. G. F. Vandegrift, R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. T. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, *Transuranic Decontamination of Nitric Acid Solution by the TRUEX Solvent Extraction Process—Preliminary Development Studies*, Argonne National Laboratory Report ANL-84/45, 1984.
3. L. E. Trevorrow and G. F. Vandegrift, *Alternatives for Disposal of Raffinate from the TRUEX Process*, Argonne National Laboratory Report ANL-89/27, 1989.
4. E. P. Horwitz, K. A. Martin, H. Diamond, and L. Kaplan, "Extraction of Am from Nitric Acid by Carbamoyl-Phosphoryl Extractants: The Influence of Substituents on the Selectivity of Am over Fe and Selected Fission Products," *Solv. Extr. Ion Exch.*, *4*, 1009 (1986).
5. D. B. Chamberlain, R. A. Leonard, J. C. Hoh, E. C. Gay, D. G. Kalina, and G. F. Vandegrift, *TRUEX Hot Demonstration: Final Report*, Argonne National Laboratory Report ANL-89/37, 1989.
6. G. F. Vandegrift, D. B. Chamberlain, C. Conner, J. M. Copple, J. A. Dow, L. Everson, J. C. Hutter, and R. A. Leonard, L. Nuñez, M. C. Regalbuto, J. Sedlet, B. Srinivasan, S. Weber, and D. G. Wygmans, "Development and Demonstration of the TRUEX Solvent Extraction Process," in *Proceedings of WM Symposia*, Tucson, Arizona, February 28–March 4, 1993.
7. B. A. Buchholz, L. Nuñez, and G. F. Vandegrift, "Effect of Alpha-Radiolysis on TRUEX-NPH Solvent," in *Proceedings for Symposium on Characterization and Treatment of High-Level Wastes*, 208th American Chemical Society National Meeting Washington, D.C., August 21–26, 1994.
8. D. C. Chaiko, P. K. Tse, and G. F. Vandegrift, "Modeling of the Aqueous and Organic Phase Speciation for Solvent Extraction Systems," *Miner. Mater. Soc.*, *2*, 246 (1988).
9. R. A. Leonard, "Use of Electronic Worksheet for Calculation of Stagewise Solvent Extraction Processes," *Sep. Sci. Technol.*, *22*(2&3), 535 (1987).
10. E. M. Scadden and N. E. Ballou, "Solvent Extraction Chemistry of Zirconium and Niobium," *Anal. Chem.*, *25*, 1602 (1953).
11. T. E. Moore, N. G. Rhode and R. E. Williams, "Extraction of Inorganic Salts by 2-Octanol. III. Zinc and Cadimium Chlorides Aqueous Phase Activities," *J. Phys. Chem.*, *62*, 372 (1958).
12. R. Back and M. Herrerman, "Die Verteilung Anorganischer Fluoride Zwischen Wabrigen HF-Losungen und Organischen Losungsmitteln," *Z. Anorg. Chem.*, *284*, 288 (1956).
13. J. Korkisch, J. D. Navratil, and W. W. Schulz, "Analytical Applications: A Review,"

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in *CRC Science and Technology of Tributyl Phosphate*, Vol. IIb (W. W. Schulz and J. D. Navratil, Eds.), CRC Press, Boca Raton, Florida, 1984.

14. P. P. Kish and I. S. Balog, "Extraction of Cadmium Halide and Thiocyanate Complexes by Tributyl Phosphate from Sulfuric Acid Solutions," *J. Anal. Chem. USSR*, *32*, 557 (1977).
15. S. Kalyanaramn and S. M. Khopkar, "Diluted Tributyl Phosphate as an Extractant for Cadmium," *J. Indian Chem. Soc.*, *56*(2), 203 (1979).
16. S. T. Takezhanoc, S. L. Getskin, and G. L. Pashkov, "Mechanism of Extractant of Cadmium by Tributyl Phosphate," *Sb. Nauch. Tr. Vses. Nauchno-Issled. Gorno-Met. Inst. Tsvet. Metal.*, (12), 15 (1968).
17. V. M. P. Forrest, D. Scargill, and D. R. Spickernell, "The Extraction of Zinc and Cadmium by Tri-*n*-butyl Phosphate from Aqueous Chloride Solutions," *J. Inorg. Nucl. Chem.*, *31*, 187 (1969).
18. K. S. Pitzer, "Theory: Ion Interaction Approach," in *Activity Coefficients in Electrolyte Solutions* (R. M. Pytkowicz, Ed.), CRC Press, Boca Raton, Florida, 1978, pp. 157–208.
19. H. P. Meissner, "Prediction of Activity Coefficients of Strong Electrlolyte in Aqueous Systems," in *Thermodynamics of Aqueous Systems with Industrial Application*, ed. (ACS Symposium Series 133, S. A. Newman, Ed.), Washington D.C., 1980, p. 495.
20. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Academic Press, New York, 1959.
21. L. A. Bromley, "Thermodynamic Properties of Strong Electrolytes in Aqueous Solution," *AIChE*, *19*, 313 (1973).
22. J. D. Baker, B. J. Mincher, and D. H. Meikrantz, "Partitioning Studies to Separate Actinides from ICPP HLW," *Solv. Extr. Ion Exch.*, *6*, 1049 (1988).
23. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry—A Comprehensive Text*, Wiley-Interscience, 3rd ed., New York, 1972, p. 503.
24. D. J. Chaiko, D. R. Fredrickson, L. Reichley-Yinger, and G. F. Vandegrift, "Thermodynamic Modeling of Chemical Equilibria in Metal Extraction," *Sep. Sci. Technol.*, *23*(12&13), 1435 (1988).
25. D. J. Chaiko and G. F. Vandegrift, "A Thermodynamic Modeling of Nitric Acid Extraction by Tri-*n*-Butyl Phosphate," *Nucl. Technol.*, *82*, 52 (1988).
26. L. G. Sillen, *Chem. Soc. Spec. Publ.* No. 25, London, 1971.
27. L. G. Sillen and A. E. Martell, *Ibid.*, No. 17, London, 1964.
28. I. Leden, "Einige Potentiometrische Messunggen zur Bestimmung der Komplexionen in Cadmiumsalzlosungen," *Z. Phys. Chem.*, *A188*, 160 (1941).
29. W. L. Masterton and L. H. Berka, "Evaluation of Ion-Pair Dissociation Constants from Osmotic Coefficients," *J. Phys. Chem.*, *70*, 1924 (1966).

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