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Modeling of Aqueous and Organic Phase Speciation for Solvent Extraction Systems

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MODELING OF AQUEOUS AND ORGANIC PHASE SPECIATION FOR

SOLVENT EXTRACTION SYSTEMS[*]

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Abstract

The TRUEX (TRansUranic EXtraction) solvent extraction process has the ability to remove, separate, and recover transuranic (TRU) elements from acidic nuclear waste solutions. A computer model of the TRUEX process is currently being developed for use in flowsheet design and process optimization. The correlations that are to be used in the model for generating extraction distribution ratios are based on chemical mass action principles and require calculation of aqueous and organic phase speciation. Aqueous phase activity coefficients are calculated using methods available in the literature, while the organic phase species are treated in terms of ideal associated solution theory. This approach is demonstrated for the extraction of HNO_3, $HTcO_4$, and americium nitrate by n-octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) - the primary metal extractant in the TRUEX solvent.

Computer programs for simulating solvent extraction processes are useful tools that can aid in the design and testing of process flowsheets and can form the basis of an expert system with applications in optimization and control, operator training, and system analysis during process upset. The degree of confidence with which such simulations can be performed depends to a great extent on an ability to model distribution data. This can be a formidable challenge in complex chemical systems in which a number of competitive reactions may be taking place, and depending on the physico-chemical properties of the system, the distribution data may contain a kinetic component that must also be addressed.

Liquid-liquid extraction equilibria are often modeled using empirical or semi-empirical expressions. One particular extraction model of importance in the nuclear industry, pertaining to the processing of dissolved, irradiated fuel, is the SEPHIS code (1). In the original version of SEPHIS, the distribution of uranium, plutonium, and nitric acid between an organic solvent containing tributyl phosphate (TBP) and aqueous nitrate solutions was expressed as a polynomial function of the total aqueous nitrate concentration. More inclusive descriptions of extraction equilibria are possible if details of chemical speciation in the aqueous and organic phases are available. In later efforts (2,3), the distribution data correlations used in the SEPHIS code have been improved upon by including reaction equilibria. However, the equilibrium constants remain concentration dependent and are expressed as polynomial functions of aqueous nitrate concentration.

The TRUEX process is designed to remove transuranic elements from acidic solutions of mixed nitrate salts (4-6). The process uses a modified Purex solvent that contains n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in addition to TBP and an organic diluent such as tetrachloroethylene (TCE) or a normal paraffinic hydrocarbon (NPH). As part of the TRUEX-Technology-Base Development effort, a mathematical model is being developed for flowsheet design, process optimization, and cost estimation. In this paper, we present modeling examples for the extraction of nitric acid, pertechnetic acid, and americium nitrate by CMPO. The mass action equations were written in terms of the concentrations of organic phase species and the activities of major aqueous phase species. Aqueous metal species at the tracer level were assumed to have constant activity coefficients.

Background

Aqueous Phase Speciation

Candidate waste streams for TRUEX processing are characteristically of high ionic strength (I>1 molar). The predominant anion is nitrate, whose concentration can be as high as 8M. Aqueous phase complexants such as fluoride, sulfate, and oxalate may also be present.

The activity coefficients of nitric-acid-only solutions were obtained from Davis and De Bruin (7). In mixed electrolyte solutions, the stoichiometric activity coefficients of H^+ and NO_3^- were calculated by the method of Bromley (8). The details of these calculations are presented elsewhere (9). The dissociation equilibrium of nitric acid was taken into account through the use of stoichiometric activity coefficients (y_i):

$$y_i = \alpha \, y_{\pm}$$ (1)

where α is the degree of dissociation, and y is the mean ionic activity coefficient. Water activities in multicomponent electrolyte solutions (aw) were calculated by the method of Kusik and Meissner (10):

$$\log\left(a_w\right) = \sum_i \sum_j X_i Y_j \log\left(a_w^\circ\right)$$ (2)

where a_w° is the water activity of an individual component in the mixture at the ionic strength and temperature of the mixture; X and Y are the cationic fraction and anionic fraction respectively (10); and the subscripts i, j refer to cationic and anionic species respectively. While Eq. 2 does not rigorously satisfy the Gibbs-Duhem equation for multicomponent systems containing ions of unequal charge (e.g., $HNO_3 + Al(NO_3)_3$) it does, nevertheless, fit the available data for most multicomponent systems (10).

Aqueous phase metal complexation can have a dramatic influence on extraction behavior. To include complexation effects in the extraction models, the mass balance equations for aqueous phase metal ions were written in terms of a pseudo-thermodynamic complexation constant (β):

$$[M]_{total} = [M(H_2O)_h^{Z+}] \left(1 + \sum_i \sum_j \beta_{i,j} \frac{\{A_j\}^i}{\{H_2O\}^{n*i}} \right)$$ (3)

where the symbols [] and {} refer to concentrations and activities respectively, h represents the hydration number of the cation, and n refers to the number of waters of hydration lost during complexation. No distinction is made between inner and outer sphere coordination. In the case of highly concentrated electrolytes, the hydration number is undoubtedly a function of ionic strength. This occurs when the water to electrolyte concentration ratio becomes less than the hydration number. For the sake of simplicity, it is assumed that a single hydration number is sufficient to adequately describe the extraction behavior of metals. In Eq. 3 all the waters of hydration have been assigned to the cation but it can be shown that the mass balance expression would reduce to the form presented above regardless of where the hydration waters were placed. It is worth noting that the activity coefficients reported in the literature almost always refer to the unhydrated electrolyte. By defining the association constants (β_i) as in Eq. 3, we have attempted to take into account hydration effects on metal extraction behavior. This becomes very important when modeling metal extraction at high ionic strengths.

Organic Phase Speciation

In attempting to include extractant speciation terms in a solvent extraction model, one quickly faces the difficulty of estimating activity coefficients of nonelectrolytes in the organic phase. Aside from the thermodynamic issues, simply identifying the major organic phase species can be a challenge.

Slope analysis and continuous variation are standard techniques used to evaluate the stoichiometry of the principal extraction products. Such studies are often done at fixed ionic strength in order to maintain a constant ionic interaction contribution to the aqueous phase activity coefficients. For the

organic phase, the best that can be done is to work at low extractant concentrations and under low solvent loading conditions. Unfortunately, these restrictions do not realistically reflect actual process conditions.

Only a few attempts at direct calculation of organic phase activity coefficients in metal solvent extraction systems have been reported (11-13). These were based on the Scatchard-Hildebrand model. The difficulty with this approach, however, lies in the potentially large number of molecular interaction terms necessary to calculate activity coefficients - all of which must be obtained by curve-fitting extraction equilibrium data. For example, a total of 10 organic phase interaction parameters were required in modeling metal extration from Cu/Co sulfate mixtures by bis(2-ethylhexyl)phosphonic acid (12).

Our approach to modeling organic phase speciation is loosely based on ideal associated solution theory (14,15). The ideal approximation assumes that all species behave ideally and that complex formation can explain any solution deviations from ideality. Physical interactions are assumed to be negligible in comparison with the chemical contributions to nonideality. This is a rather simplistic approach and has been criticized on a number of points, but it does appear to be consistent with the thermodynamic properties of a number of organic systems in which strong complex formation occurs (14,15).

Experimental

Reagents

Solvent-extraction grade n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) was purchased from M&T Chemical Company and was purified to >98% by a modified, mixed-ion-exchange, crystallization procedure. The modification included sequential contacts, at room temperature, of two hours between a heptane solution of CMPO and the ion exchange resins. The original procedure recommended a 1/2-hour contact at 50°C (16). HPLC grade tetrachloroethylene (TCE) was used as-received.

Procedures

All extraction equilibrium measurements were performed at 25°C. All organic phase CMPO solutions were preequilibrated with the appropriate aqueous solution by repeated contact with a fresh aqueous phase until the aqueous phase HNO_3 concentration remained unchanged from its initial value. The details of the nitric acid and the americium distribution ratio measurements are presented elsewhere (9). Distribution ratio measurements for ^{99}Tc were obtained between aqueous nitric acid solutions and CMPO dissolved in TCE. Organic phases preequilibrated with HNO_3 were contacted with nitric acid solutions at the appropriate nitric acid concentrations and $2 \times 10^{-4}M$ $HTcO_4$. Both forward and reverse distribution ratios were measured using the beta activity in each phase. In duplicate experiments, the distribution ratios agreed to within ±5%.

Nitric Acid Extraction

An important consideration in modeling metal extraction is the speciation of the extractant. CMPO is capable of extracting considerable amounts of nitric acid and, therefore, other extractable species will be in competition for free CMPO. The extraction of nitric acid by CMPO was previously described by a two-parameter model (9). The extraction equilibria were defined accordingly:

$$H^+ + NO_3^- + \overline{CMPO} \; \underset{\longleftarrow}{\overset{KC_1}{\longrightarrow}} \; \overline{CMPO \cdot HNO_3} \tag{4}$$

$$2H^+ + 2NO_3^- + \overline{CMPO} \; \underset{\longleftarrow}{\overset{KC_2}{\longrightarrow}} \; \overline{CMPO \cdot 2HNO_3} \tag{5}$$

Equations 4 and 5 agree with the extraction data in Fig. 1 that show an organic phase acid stoichiometry of [HNO3] to [CMPO] of greater than one at moderately high HNO3 concentrations. However, extraction data with 0.25, 0.5M, and 1M CMPO indicated that the extraction constant KC_1 increased
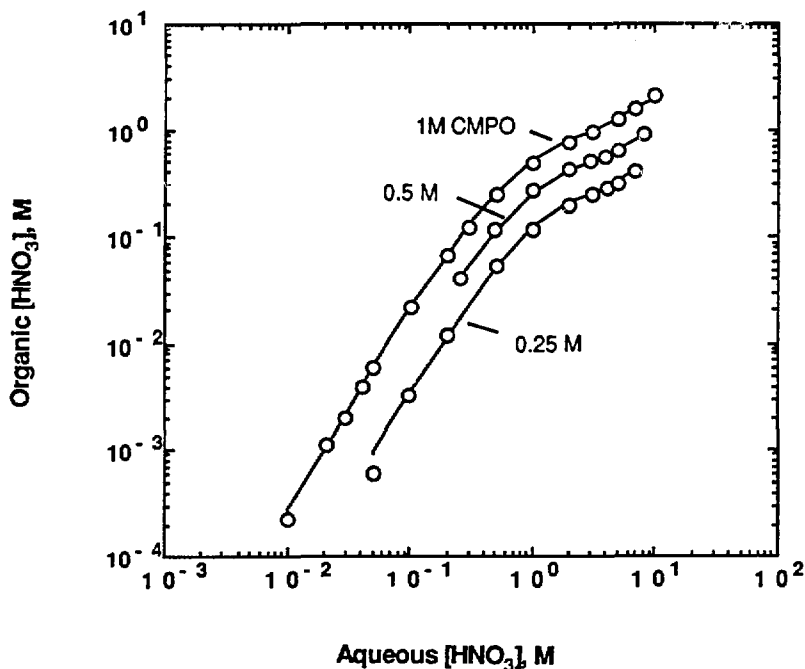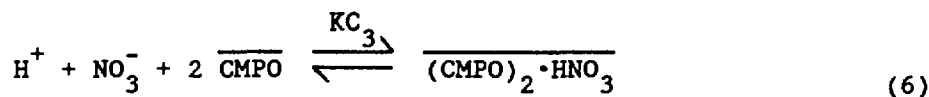

Figure 1. Extraction of HNO3 by CMPO-TCE. The Data at 0.5M CMPO were obtained from Ref. 18. Continuous Line Calculated from Eq. 7.

linearly with CMPO concentration. This is suggestive of the presence of a dimeric CMPO species. Thus, a third extraction equation can be added to the model:

$$H^+ + NO_3^- + 2\,\overline{CMPO} \; \underset{\longleftarrow}{\overset{KC_3}{\longrightarrow}} \; \overline{(CMPO)_2 \cdot HNO_3} \tag{6}$$

The organic phase nitric acid concentration is then given by:

$$[\overline{HNO_3}]_{total} = KC_1 \cdot [\overline{CMPO}]_{free}\{H^+\}\{NO_3^-\}y_{HNO_3}^2$$

$$+ 2 \cdot KC_2[\overline{CMPO}]_{free}\{H^+\}^2\{NO_3^-\}^2 y_{HNO_3}^4$$

$$+ KC_3 \cdot [\overline{CMPO}]_{free}^2\{H^+\}\{NO_3^-\}y_{HNO_3}^2 \qquad (7)$$

The concentration of free CMPO is obtained by a simultaneous solution of Eq. 7 and the appropriate mass balance equation for CMPO.
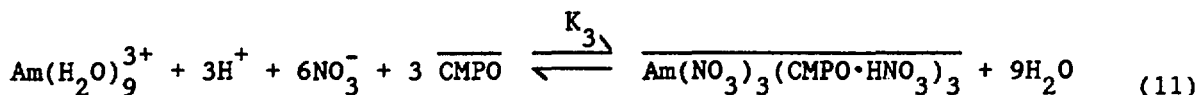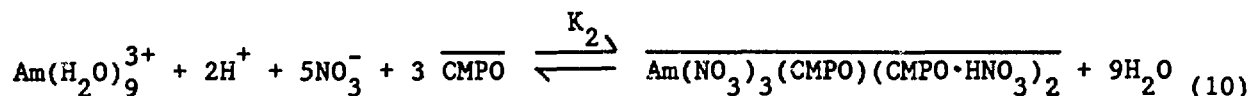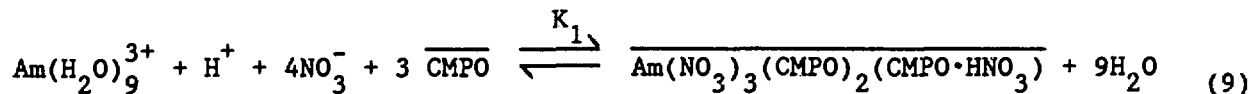
Estimates for KC_1, KC_2, and KC_3 were obtained by a nonlinear fit of the extraction data in Fig. 1. The calculated extraction isotherms were produced with a single set of extraction constants. These values were: $KC_1 = 1.60 \pm 0.04$, $KC_2 = 0.010 \pm 0.001$, and $KC_3 = 1.66 \pm 0.06$. As demonstrated below, the extraction of nitric acid by CMPO plays a pivotal role in determining metal extraction behavior.

Americium Extraction

Earlier work has shown that americium extraction by CMPO has a third order dependence on extractant concentration and that americium is extracted as an anhydrous complex (17). At low acid concentrations, the predominant extractant species is the free CMPO molecule. Consequently, Am^{3+} extraction from nitric acid solutions can be described by:

$$Am(H_2O)_9^{3+} + 3NO_3^- + 3\overline{CMPO} \xrightleftharpoons{K_o} \overline{Am(NO_3)_3(CMPO)_3} + 9H_2O \qquad (8)$$
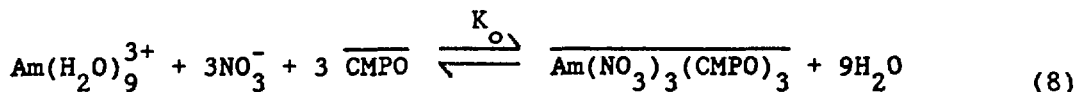
Because of the bifunctional structure of CMPO, the carbonyl group is free to extract HNO_3 while the phosphoryl group participates in metal complexation. This intramolecular buffering phenomenon is responsible for CMPO's ability to extract metals at high acid concentrations (18). This means that each of the three carbonyl groups present in the $Am(NO_3)_3(CMPO)_3$ complex is available for extracting nitric acid. An alternative view is to consider both CMPO and CMPO·HNO_3 as being capable of metal extraction. At high nitric acid concentrations, the following extraction equilibria become important:

$$Am(H_2O)_9^{3+} + H^+ + 4NO_3^- + 3\overline{CMPO} \xrightleftharpoons{K_1} \overline{Am(NO_3)_3(CMPO)_2(CMPO \cdot HNO_3)} + 9H_2O \qquad (9)$$

$$Am(H_2O)_9^{3+} + 2H^+ + 5NO_3^- + 3\overline{CMPO} \xrightleftharpoons{K_2} \overline{Am(NO_3)_3(CMPO)(CMPO \cdot HNO_3)_2} + 9H_2O \qquad (10)$$

$$Am(H_2O)_9^{3+} + 3H^+ + 6NO_3^- + 3\overline{CMPO} \xrightleftharpoons{K_3} \overline{Am(NO_3)_3(CMPO \cdot HNO_3)_3} + 9H_2O \qquad (11)$$

By including the speciation of americium in aqueous nitric acid solutions, the mass balance equation for Am is:

$$[Am]_{total} = [Am(H_2O)_9^{3+}]\left(1 + \sum_i \beta_i \left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^i\right)$$

(12)

In the above equation, it is assumed that one water of hydration is lost for each nitrate complexed to americium. While this is a highly simplistic view, it does seem to adequately fit the extraction data under high salt concentrations as shown below. An expression for the distribution ratio of Am at low nitric acid concentrations can be obtained by combining Eqs. 8 and 12 to give:

$$D_{(Am)} = \frac{K_o \, \overline{[CMPO]}_{free}^3 \, \{NO_3^-\}^3}{\left(1 + \sum_i \beta_i \left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^i\right)\{H_2O\}^9}$$

(13)

Equation 13 can be rearranged to the form of a polynomial expression that can be used to evaluate K_o and the complexation constants (β_i):

$$\frac{\overline{[CMPO]}_{free}^3 \, \{NO_3^-\}^3}{D_{(Am)} \, \{H_2O\}^9} = \frac{1}{K_o} + \frac{\beta_1}{K_o}\left(\frac{\{NO_3^-\}}{\{H_2O\}}\right) + \frac{\beta_2}{K_o}\left(\frac{\{NO_3^-\}}{\{H_2O\}}\right)^2 + \ldots$$

(14)

This equation is plotted in Fig. 2 using data for americium extraction by 0.25M CMPO-TCE from HNO_3-only and HNO_3/$NaNO_3$ solutions. The straight line fit indicates that at the nitrate concentrations studied ($\geq$ 5M), the terms beyond β_1 are not significant. From the slope and intercept of the plot in Fig. 2, the values of K_o and β_1 were found to be 5.6 x 10^5 and 28.8, respectively.
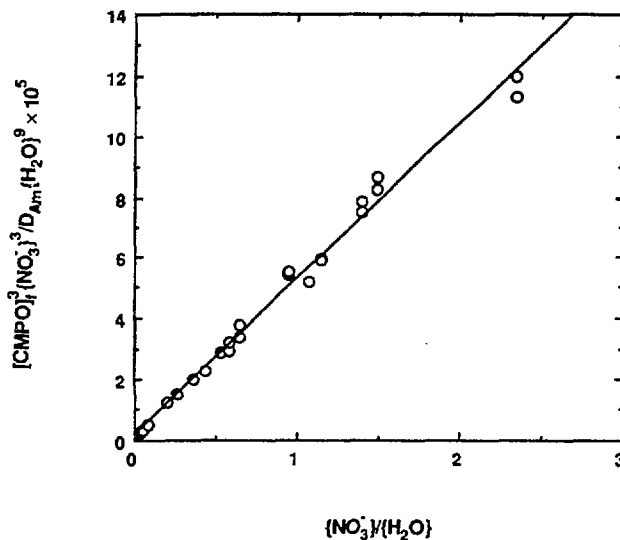

Figure 2. Plot of Eq. 14 Using Am Extraction Data
From HNO_3 Only and HNO_3/$NaNO_3$ Solutions.

Equation 13 gives a good fit to the extraction data up to about 1M aqueous nitric acid. At higher acid concentrations, the model must be expanded to include extraction of the species $Am(NO_3)_3 \cdot 3CMPO \cdot nHNO_3$ (where $n = 1$ to 3). The complete Am extraction model is therefore:

$$D_{(Am)} = \frac{[CMPO]_{free}^3 \{NO_3^-\}^3 \left(K_o + K_1\{H^+\}\{NO_3^-\} + K_2\{H^+\}^2\{NO_3^-\}^2 + K_3\{H^+\}^3\{NO_3^-\}^3\right)}{1 + \beta_1\left(\dfrac{\{NO_3^-\}}{\{H_2O\}}\right) \{H_2O\}^9}$$

(15)

Figure 3 shows the fit of Eq. 15 to the extraction data for 0.25M CMPO-TCE. The values of K_1, K_2, and K_3 were 7.2×10^5, 2×10^3, and 9, respectively. The distribution ratio at 0.01M HNO_3 was determined with pretreatment of the organic phase using diazomethane (19). This was done in order to methylate any acidic impurities which would be capable of extracting Am^{3+} to a greater extent than CMPO.
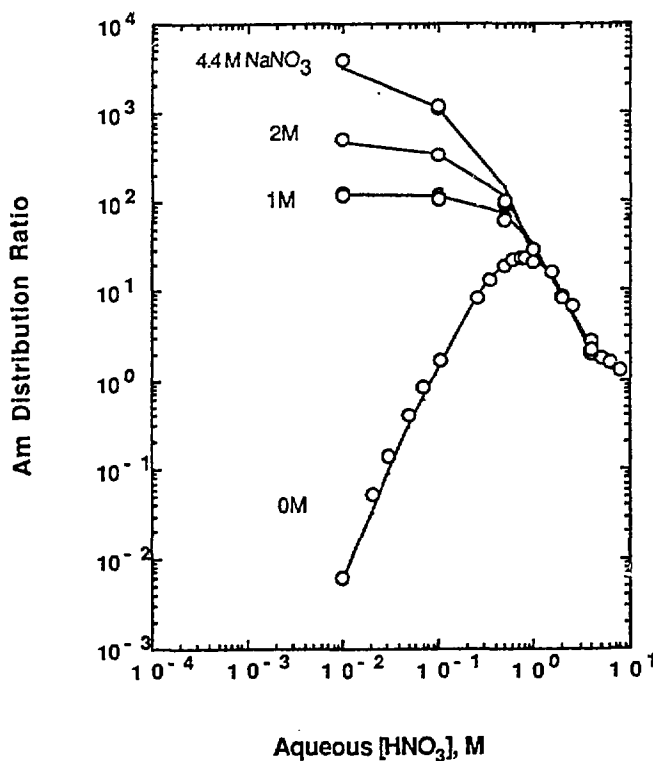

Figure 3. Americium Extraction From $HNO_3/NaNO_3$ Solution by 0.25M CMPO-TCE. Continuous Line Calculated from Eq. 15.

The model depicted in Eq. 15 is also capable of describing Am extraction from $HNO_3/NaNO_3$ solutions using the same set of constants listed above. The fit between the model and the data is shown in Fig. 3. To model the salting-out of Am by $NaNO_3$ as well as the extraction at high HNO_3 concentrations, it was necessary to include the hydration terms in Eq. 15.

The extraction dependency of $HTcO_4$ on organic-phase CMPO concentration was determined at aqueous phase equilibrium concentrations of 1.0 and 6.0M HNO_3 as shown in Fig. 4. The slopes of the two curves in Fig. 4 are in close agreement and suggest the following extraction stoichiometry:

$$H^+ + TcO_4^- + 2\ \overline{CMPO} \rightleftharpoons \overline{HTcO_4 \cdot 2CMPO}$$

(16)
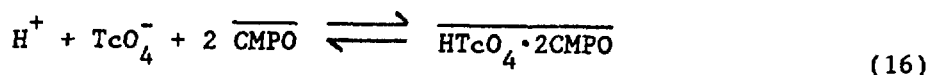
The extractant dependency of CMPO differs from that reported in recent studies of the extraction of technetium by TBP (20) and dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) (21). For both TBP and DHDECMP a third-order extractant dependency was observed in the extraction of $HTcO_4$ from nitric acid solutions (20,21). This difference in extractant dependency between CMPO and that of TBP and DHDECMP is probably due to the difficulty of accommodating more than two of the more rigid and larger CMPO molecules in the organic-phase $HTcO_4$ complex.
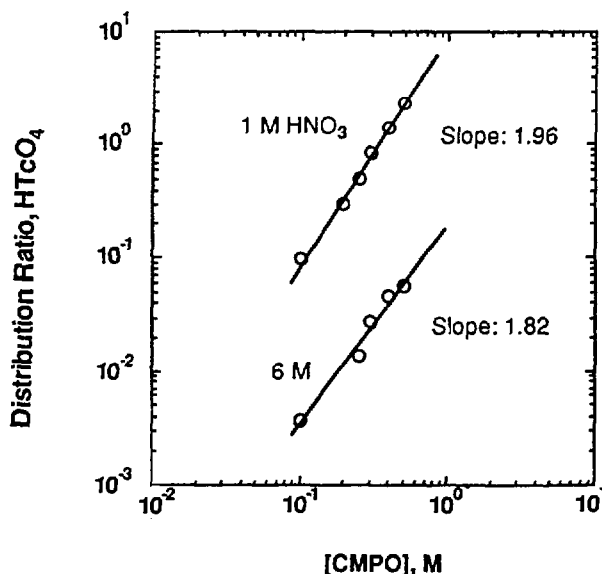

Figure 4.   Dependency of $HTcO_4$ Extraction on CMPO Concentration.

The distribution ratios of $HTcO_4$ between 0.25M CMPO in TCE and aqueous nitric acid solutions are shown in Fig. 5. The appearance of a maximum value of D_{Tc} as a function of HNO_3 concentration is a result of (1) the competition between HNO_3 and $HTcO_4$ for uncomplexed CMPO and (2) the acid association equilibrium of $HTcO_4$.

In attempting to explain the extraction behavior of Tc, it is important to consider its aqueous phase speciation. An acid dissociation constant for $HTcO_4$ has been reported by Rulfs et al. (22) to be 0.5 ($K_a = 2$). This number was determined by potentiometric titration, but in a later UV spectroscopic study (23), $HTcO_4$ was determined to be a strong acid having a dissociation constant $> 10^8$. If $HTcO_4$ is as strong an acid as they indicated in their later publication, pertechnetic acid would be completely dissociated in all aqueous solutions. Our extraction data however, indicate that the acid association equilibrium is important in the range of HNO_3 concentrations used in the present study.
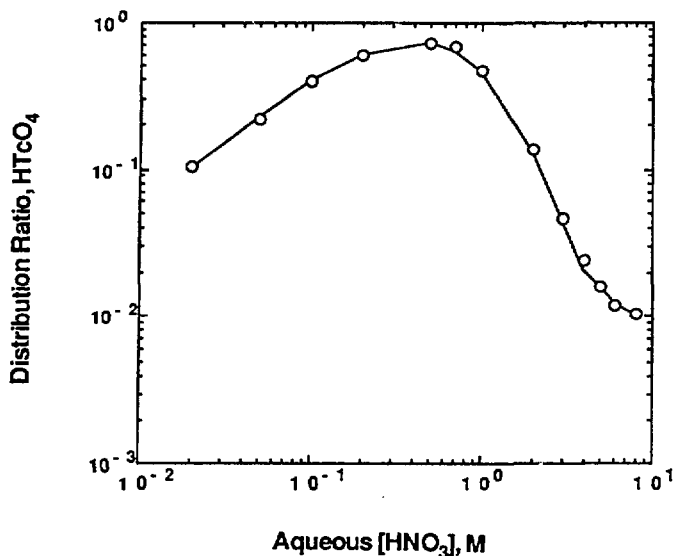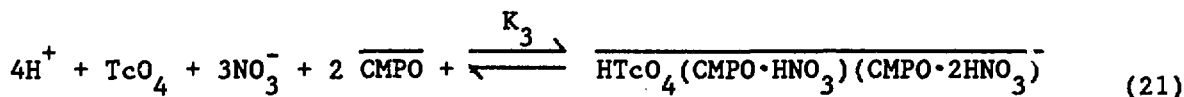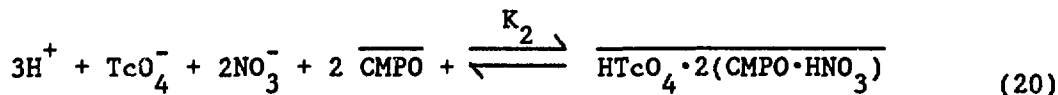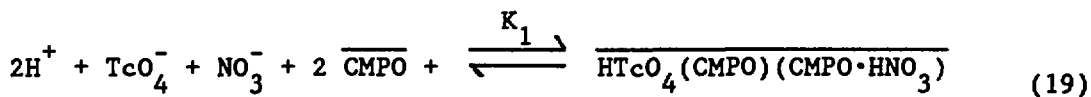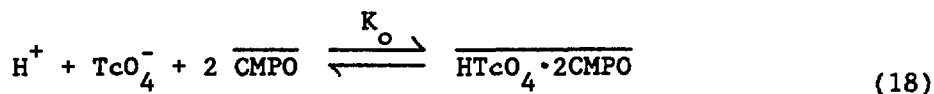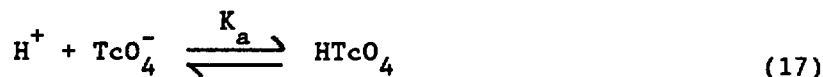
Figure 5. Extraction of HTcO$_4$ by 0.25M CMPO-TCE as a Function
of the Equilibrium HNO$_3$ Concentration. Continuous
Line Calculated from Eq. 22.

Figures 4 and 5 indicate that at low HNO$_3$ concentrations (i.e., <0.5M),
the predominant organic phase technetium species is HTcO$_4 \cdot$2CMPO. However, as
the concentration of nitric acid increases, the species HTcO$_4 \cdot$2CMPO$\cdot$nHNO$_3$
(where n = 1 or 2) become increasingly important. The extraction model of Tc
therefore, is based on the following equilibria:

$$H^+ + TcO_4^- \xrightleftharpoons{K_a} HTcO_4 \tag{17}$$

$$H^+ + TcO_4^- + 2\,\overline{CMPO} \xrightleftharpoons{K_o} \overline{HTcO_4 \cdot 2CMPO} \tag{18}$$

$$2H^+ + TcO_4^- + NO_3^- + 2\,\overline{CMPO} + \xrightleftharpoons{K_1} \overline{HTcO_4(CMPO)(CMPO \cdot HNO_3)} \tag{19}$$

$$3H^+ + TcO_4^- + 2NO_3^- + 2\,\overline{CMPO} + \xrightleftharpoons{K_2} \overline{HTcO_4 \cdot 2(CMPO \cdot HNO_3)} \tag{20}$$

$$4H^+ + TcO_4 + 3NO_3^- + 2\,\overline{CMPO} + \xrightleftharpoons{K_3} \overline{HTcO_4(CMPO \cdot HNO_3)(CMPO \cdot 2HNO_3)}^- \tag{21}$$

Based on Eqs. 17-21, the distribution of HTcO$_4$ between CMPO-TCE and aque-
ous HNO$_3$-HTcO$_4$ solutions can be estimated by:

$$D_{Tc} = \frac{[\overline{CMPO}]_{free}^2 \, \{H^+\}\left(K_o + K_1\{H^+\}\{NO_3^-\} + K_2\{H^+\}^2\{NO_3^-\}^2 + K_3\{H^+\}^3\{NO_3^-\}^3\right)}{\left(1 + K_a\,\{H^+\}\right)} \tag{22}$$

The D_{Tc} values calculated from Eq. 22 show good agreement with the measured values in Fig. 5 where $K_a = 2.54$, $K_o = 96.58$, $K_1 = 47.3$, $K_2 = 0.53$, and $K_3 = 0.035$. When K_a is taken as zero, Eq. 22 gives a poor fit to the extraction data. Thus, our extraction data suggest that $HTcO_4$ is a weak acid. Other, unpublished data on the extraction of Tc by the TRUEX-TCE and TRUEX-NPH solvents have also suggested a K_a value of 2.5.

Conclusions

Extraction models based on organic and aqueous phase speciation have proved successful in describing extraction data for the CMPO-TCE system. The assumption that the activity coefficients for all organic phase species are constant appears to be reasonable. This is supported by the fact that the extraction equilibrium constants were independent of organic-phase CMPO concentration and of aqueous-phase ionic strength. In the case of nitric acid extraction by CMPO, the extraction constants were independent of organic phase nitric acid concentration even at very high levels of solvent loading.

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