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L. Nuñez[a]; M. Kaminski[a]; G. F. Vandegrift[a]
[a] Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois

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APPLICATION OF SINGLE-ION ACTIVITY COEFFICIENTS TO DETERMINE THE SOLVENT EXTRACTION MECHANISM FOR COMPONENTS OF HIGH-LEVEL NUCLEAR WASTE

by

L. Nuñez, M. Kaminski, and G. F. Vandegrift
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

ABSTRACT

The TRUEX solvent extraction process is being developed to remove and concentrate transuranic (TRU) elements from high-level and TRU radioactive wastes that are currently stored at U.S. Department of Energy sites. Phosphoric acid is one of the chemical species of concern in the application of solvent extraction processes for removal of actinides, for instance at the Hanford site, where bismuth phosphate was used to recover plutonium.

The mechanism of phosphoric acid extraction with TRUEX-NPH solvent at 25°C was determined from phosphoric acid distribution ratios, which were measured by using a phosphoric acid radiotracer and a variety of aqueous phases containing different concentrations of nitric acid and nitrate. A model was developed for predicting phosphoric acid distribution ratios as a function of the thermodynamic activities of nitrate ion, and hydrogen ion. The Generic TRUEX Model (GTM) was used to calculate these activities based on the Bromley method. The derived model supports extraction by CMPO and TBP in TRUEX-NPH solvent of a phosphoric acid-nitric acid complex and a CMPO-phosphoric acid complex.

Keywords: CMPO, TRUEX-NPH, phosphoric acid, solvent extraction

INTRODUCTION

One of the current interests of the U.S. Department of Energy is the treatment of the waste stored in Hanford single-shell tanks. We are focusing on chemical species never considered before with the TRUEX solvent extraction process.[1] One chemical component that is found in the tanks and was excluded from the model is phosphoric acid, which originated from the $BiPO_4$

process that was used to recover plutonium from irradiated uranium.[2] The anhydrous form of the acid has been used in conjunction with high concentrations of HNO_3 for maintaining adequate decontamination of Zr and Nb in the PUREX process.[3] Thus understanding the chemistry of phosphoric acid extractions is important in nuclear waste treatment.[3] The current study attempts to elucidate the chemistry and mechanism of phosphoric acid extraction by TRUEX-NPH solvent [1.4M tributyl phosphate (TBP) and 0.2M octyl(phenyl)-diisobutylcarbamoylmethylphosphine oxide (CMPO) in normal paraffinic hydrocarbon]. In nitrate solutions of high ionic strength the extraction behavior of phosphoric acid will simulate that expected after dissolution of actual tank waste.

The extraction of mineral acids with TBP is well documented.[4,5] The order of extractability ($HF>HNO_3>H_3PO_4>HCl>H_2SO_4$) is independent of acidity, oxygen donor and other chemical features of the acids. By contrast, the order of extractability for selected acids with the combination of CMPO and TBP is $HNO_3>H_2SO_4>HCl>HF$.[6] There is only a limited amount of data on extraction of mineral acids by the mixed TRUEX-NPH system.[7] In TBP studies in which phosphoric acid was mixed with nitrate salts, there appeared to be an increase in the phosphoric acid extractability. The studies of mixed HNO_3/H_3PO_4 systems with TBP showed that partitioning of HNO_3 increases with increased H_3PO_4 concentration, while phosphoric acid distribution ratios decrease with increased nitric acid concentration.[8] The HNO_3/H_3PO_4 combination has not been studied extensively with the TRUEX solvent.

This report describes the experimental measurements made with ^{32}P-labeled H_3PO_4 to obtain a thermodynamic model for the extraction of H_3PO_4 in TRUEX-NPH solvent. The combination of existing activity values for water, nitric acid,[9,10] and the amount of free organic species (i.e., TBP and CMPO)[8] was used to derive a thermodynamic model.

EXPERIMENTAL

Extraction of $H_3{}^{32}PO_4$ as a Function of the Concentrations of HNO_3 and $HNO_3/NaNO_3$ Mixtures

The TRUEX solvent was prepared with recrystallized[11] CMPO and TBP (Gold Label Aldrich Chem. Co.) in normal paraffinic hydrocarbon (NPH, C_{12}-C_{14}, Conoco Chemicals) solvent with an average carbon chain length of 13.4. The purity of the constituents was confirmed by measuring forward and reverse ^{241}Am extractions at high and low nitric acid concentrations. The $H_3{}^{32}PO_4$ was purchased carrier-free from Amersham.

Mixtures of $NaNO_3$ and HNO_3 were prepared with nitric acid concentrations between 0.01 and 4M and sodium nitrate concentrations between 0.01 and 8M. These solutions were spiked with $H_3{}^{32}PO_4$ radiotracer and contacted with TRUEX solvent. The aqueous HNO_3 solutions (0.01-4M HNO_3) were also spiked with tracer, then contacted with preequilibrated TRUEX solvent that had been repetitively contacted with fresh HNO_3 solution prior to the radiotracer extractions. The phases were separated and counted as previously described.[12] Distribution ratios were calculated for phosphoric acid. The distribution ratio is defined as $D_p = [P]_{org}/[P]_{aq}$, where [P] is the concentration of $H_3{}^{32}PO_4$.

RESULTS AND DISCUSSION

Extraction of $H_3{}^{32}PO_4$ as a Function of HNO_3 Concentrations

The phosphoric acid distribution (D_p) ratio showed an initial linear increase as a function of increasing nitric acid concentrations (Fig. 1), then slowly dropped at HNO_3 between concentrations of 0.5 and 1.0M. Distribution ratios for phosphoric acid as a function of HNO_3 concentration were also measured at various (constant) concentrations of sodium nitrate. The concentrations of aqueous phase nitric acid were calculated from the initial concentration of nitric acid in the aqueous phase and the organic to aqueous volume ratio using the Generic TRUEX Model.[13] Data for $NaNO_3$ concentrations between 0.1 and 2.7M and between 3.18 and 8M are shown in Figs. 2 and 3, respectively. Again, D_p initially increased, then dropped at HNO_3 concentration's higher than 0.5M.

The decrease in D_p values above 1.0M nitric acid (Figs. 1, 2 and 3) is suggestive of nitric acid competition with the phosphoric acid for CMPO complexation in the TRUEX-NPH solvent. The nitric acid complexation equilibria with both CMPO and TBP are accounted for by the GTM model. The D_p values in the presence of 4.4M $NaNO_3$ were lower than expected, but followed the same trend as was observed at other sodium nitrate concentrations.

Previous reports showed that the extraction of nitric acid in TBP is enhanced by phosphoric acid.[8] The addition of nitrate salts, such as $Ca(NO_3)_2$, increased nitric acid distribution ratios while decreasing phosphoric acid distribution ratios.[8] In the case of high nitrate salt and nitric acid concentrations, increased distribution ratios for nitric acid were explained by the precipitation of the phosphoric acid as an alkaline diphosphoric acid species and were not attributed to common ion effects.[8]

H_3PO_4 Equilibria

Based on vapor pressure, pH, and conductance measurements[14] the equilibria that describes the phosphoric acid system at concentrations from 0.1 to 10 molal are:

$$H_3PO_4 \xleftrightarrow{K_1} H^+ + H_2PO_4^- \qquad (1)$$

$$H_3PO_4 + H_2PO_4^- \xleftrightarrow{K_2} H_5P_2O_8^- \qquad (2)$$

$$H_6P_2O_8 \xleftrightarrow{K_3} H^+ + H_5P_2O_8^- \qquad (3)$$

Development of an extraction mechanism for phosphoric acid in TRUEX-NPH requires concentrations of the aqueous species to be expressed in terms of individual activities. For the nitric acid and salt concentrations, it is possible to determine the activities using the GTM. The GTM calculates (1) the activities of water, hydrogen ion, and nitrate ion (i.e., $\{H_2O\}$, $\{H^+\}$, and $\{NO_3^-\}$) based on the Bromley method,[15-16] and (2) the concentrations of free CMPO and TBP (i.e., the concentration of those extractants not bound to nitric acid in the organic phase).

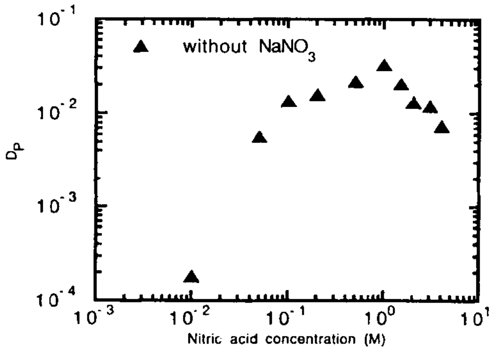

FIGURE 1. Distribution Ratios for Phosphoric Acid as a Function of Aqueous Nitric Acid Concentration

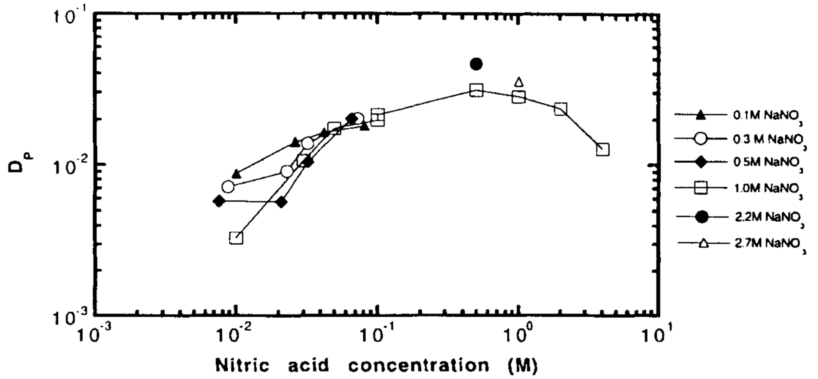

FIGURE 2. Distribution Ratios for Phosphoric Acid as a Function of Aqueous Nitric Acid Concentration at Constant Sodium Nitrate Concentrations (0.1-2.7<u>M</u> $NaNO_3$)

The stoichiometric activity coefficients for a pure solution of electrolytes, (ij), is expressed by $\gamma^0{}_{ij}$ in the Bromley equation (Eq. 4) at the ionic strength for the mixed electrolyte solution at 25°C. The odd subscripts (1, 3, 5, ..., i) in Eq. 4 represent cationic species, while even subscripts (2, 4, ..., j) represent the anionic species. The $\gamma^0{}_{ij}$ values were obtained from the literature and fitted with the following equation:

$$\log \gamma^0_{ij} = \frac{-A\, Z_i\, Z_j \sqrt{I}}{1 + B\sqrt{I}} + \beta I + C I^2 + D I^3 + E I^4 + \ldots\ldots \qquad (4)$$

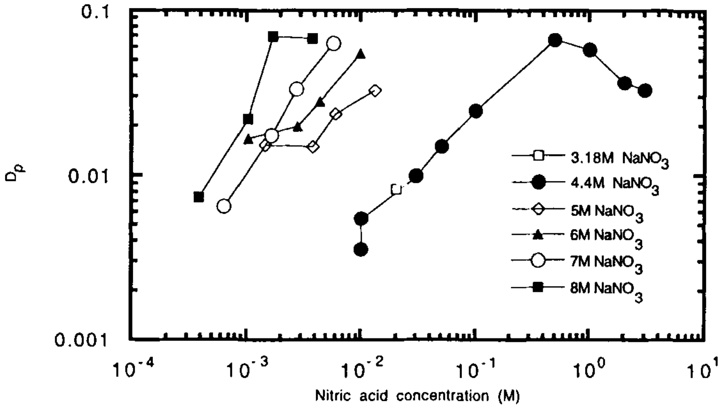

FIGURE 3 Distribution Ratios for Phosphoric Acid as a Function of Nitric Acid Concentration at Constant Sodium Nitrate Concentrations (3.18-8M $NaNO_3$)

where A is the Debye-Hückel constant, 0.5108 $kg^{1/2}\ mol^{-1/2}$ at 25°C
I is I_m (ionic strength, molal)
Z_i, Z_j are absolute values of ionic charge
B, β, C, D, and E are constants
The ionic strength, I, assumes complete dissociation.[17]

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

$$\log \gamma_i = \frac{-A Z_i^2 \sqrt{I}}{1+\sqrt{I}} + F_i \tag{5}$$

$$\log \gamma_j = \frac{-A Z_j^2 \sqrt{I}}{1+\sqrt{I}} + F_j \tag{6}$$

The F terms are defined as the following:

$$\begin{aligned} F_1 &= \left(Y_{12} \log \gamma_{12}^0 + Y_{14} \log \gamma_{14}^0 + \ldots + Y_{1j} \log \gamma_{1j}^0\right) \\ &+ \frac{A\sqrt{I}}{1+\sqrt{I}}\left(Z_1 Z_2 Y_{12} + Z_1 Z_4 Y_{14} + \ldots + Z_1 Z_j Y_{1j}\right) \end{aligned} \tag{7}$$

and

$$\begin{aligned} F_2 &= \left(X_{12} \log \gamma_{12}^0 + X_{32} \log \gamma_{32}^0 + \ldots + X_{i2} \log \gamma_{i2}^0\right) \\ &+ \frac{A\sqrt{I}}{1+\sqrt{I}}\left(Z_1 Z_2 X_{12} + Z_3 Z_2 Y_{32} + \ldots + Z_i Z_2 Y_{i2}\right) \end{aligned} \tag{8}$$

Where

$$Y_{1j} = \left(\frac{Z_1 + Z_j}{2}\right)^2 \left(\frac{m_j}{I}\right) \tag{9}$$

$$Y_{i2} = \left(\frac{Z_i + Z_2}{2}\right)^2 \left(\frac{m_j}{I}\right) \tag{10}$$

The osmotic coefficients, or (Φ), of single component electrolyte solutions were fitted with the following (Eq. 7):

$$\Phi = 1 - 2.3025\left[\frac{AZ_iZ_j}{BI_3}\right]\left[1 + BI^{1/2} - 4.605\log\left(1 + BI^{1/2}\right) - \frac{1}{1 + BI^{1/2}}\right] - \beta\frac{I}{2} + \frac{2}{3}CI^2 - \frac{3}{4}DI^3 + \ldots \tag{11}$$

and the water activity, a_w°, can be determined by Eq. 8.

$$\log a_w^\circ = \frac{-2\Phi I}{55.510 * 2.303 Z_i Z_j} \tag{12}$$

The GTM calculated equilibrated concentrations of the nitric acid after taking into account the acid complexation with CMPO and TBP, and the activities $\{H_2O\}$, $\{H^+\}$, and $\{NO_3^-\}$ (Table 1a and 1b).

TBP and CMPO Solvent Chemical Equilibria

Based on previous knowledge of the extraction of phosphoric acid species by CMPO and TBP, the experimentally determined distribution ratio measurements were modeled according to the following chemical equilibria for phosphoric acid in the organic phase (Eqs. 13 through 15).

Organic Phase

$$H_3PO_4 + \overline{CMPO} \xleftrightarrow{K_1} \overline{H_3PO_4 \bullet CMPO} \tag{13}$$

$$H_3PO_4 + HNO_3 + \overline{CMPO} \xleftrightarrow{K_2} \overline{H_3PO_4 \bullet HNO_3 \bullet CMPO} + H_2O \tag{14}$$

$$H_3PO_4 + HNO_3 + \overline{TBP} \xleftrightarrow{K_3} \overline{H_3PO_4 \bullet HNO_3 \bullet TBP} + H_2O \tag{15}$$

In the nitric acid solutions, phosphoric acid was assumed to be present as the monomer since tracer concentrations were used in the experiments. The presence of monomeric phosphoric acid was later confirmed through speciation modeling.

The distribution ratio for phosphorus was modeled according to:

$$D_{H_3PO_4} = \frac{[\overline{H_3PO_4 \bullet CMPO}] + [\overline{H_3PO_4 \bullet HNO_3 \bullet CMPO}] + [\overline{H_3PO_4 \bullet HNO_3 \bullet TBP}]}{\{H_3PO_4\}_{total}} \tag{16}$$

Substituting K_1, K_2 and K_3 equilibrium constants relationships, Eq. 16 takes the form.

$$D_{H_3PO_4} = \frac{\{H_3PO_4\}\left([\overline{CMPO}]\left(K_1 + K_2\ \{H^+\}\{NO_3^-\}\right) + K_3\,[\overline{TBP}]\{H^+\}\{NO_3^-\}\right)}{\{H_3PO_4\}_{total}} \tag{17}$$

TABLE 1a. GTM-CALCULATED ACTIVITIES OF (H_2O), (H^+), and (NO_3^-) AND FREE CMPO AND TBP CONCENTRATIONS IN TRACER H_3PO_4 EXPERIMENTS

$NaNO_3$[a] M	HNO_3[a] M	CMPO[b]	TBP[b]	(H_2O)[c]	(NO_3^-)[c]	(H^+)[c]	(HNO_3)[c]	D_{H3P04}[d]
0	1.00E-02	2.00E-01	1.40E+00	1.00E+00	9.40E-03	9.04E-03	8.19E-05	8.40E-04
0	5.00E-02	1.98E-01	1.40E+00	9.98E-01	4.12E-02	4.12E-02	1.70E-03	7.60E-03
0	1.00E-01	1.93E-01	1.39E+00	9.97E-01	7.85E-02	7.85E-02	6.17E-03	1.64E-02
0	2.00E-01	1.77E-01	1.36E+00	9.93E-01	1.50E-01	1.50E-01	2.25E-02	1.88E-02
0	5.00E-01	1.20E-01	1.20E+00	9.83E-01	3.62E-01	3.62E-01	1.32E-01	2.04E-02
0	1.00E+00	6.03E-02	9.13E-01	9.64E-01	7.54E-01	7.54E-01	5.70E-01	2.07E-02
0	1.50E+00	3.27E-02	6.76E-01	9.42E-01	1.22E+00	1.22E+00	1.49E+ 00	1.96E-02
0	2.00E+00	1.87AE-02	5.00E-01	9.19E-01	1.78E+00	1.78E+00	3.17E+00	1.50E-02
0	3.00E+00	6.40E-03	2.76E-01	8.68E-01	3.23E+00	3.23E+00	1.05E+01	1.14E-02
0	4.00E+00	2.11E-03	1.53E-01	8.11E-01	5.25E+00	5.25E+00	2.76E+01	7.71E-03
1.000E-02	0.000E+00	1.999E-01	1.400E+00	9.997E-01	9.038E-03	9.038E-03	8.192E-05	5.120E-04
5.000E-02	0.000E+00	1.979E-01	1.396E+00	9.983E-01	4.123E-02	4.123E-02	1.705E-03	6.640E-03
1.000E-01	0.000E+00	1.928E-01	1.387E+00	9.966E-01	7.846E-02	7.846E-02	6.174E-03	1.504E-02
1.000E-01	1.000E-02	1.935E-01	1.389E+00	9.966E-01	7.780E-02	7.015E-02	5.474E-03	8.820E-03
1.000E-01	3.000E-02	1.927E-01	1.387E+00	9.960E-01	9.077E-02	6.821E-02	6.209E-03	1.415E-02
1.000E-01	5.000E-02	1.919E-01	1.386E+00	9.954E-01	1.035E-01	6.650E-02	6.904E-03	1.639E-02
1.000E-01	1.000E-01	1.902E-01	1.382E+00	9.939E-01	1.346E-01	6.296E-02	8.499E-03	1.810E-02
2.000E-01	0.000E+00	1.767E-01	1.356E+00	9.933E-01	1.496E-01	1.496E-01	2.245E-02	1.735E-02
3.000E-01	1.000E-02	1.677E-01	1.336E+00	9.915E-01	1.860E-01	1.792E-01	3.343E-02	7.130E-03
3.000E-01	3.000E-02	1.665E-01	1.334E+00	9.909E-01	1.973E-01	1.768E-01	3.499E-02	9.050E-03
3.000E-01	5.000E-02	1.653E-01	1.331E+00	9.903E-01	2.085E-01	1.747E-01	3.653E-02	1.389E-02
3.000E-01	1.000E-01	1.627E-01	1.325E+00	9.889E-01	2.362E-01	1.698E-01	4.021E-02	2.035E-02
5.000E-01	0.000E+00	1.197E-01	1.203E+00	9.828E+00	3.621E-01	3.621E-01	1.315E-01	2.104E-02
5.000E-01	1.000E-02	1.400E-01	1.266E+00	9.866E-01	2.849E-01	2.784E-01	7.953E-02	5.770E-03
5.000E-01	3.000E-02	1.389E-01	1.263E+00	9.860E-01	2.956E-01	2.763E-01	8.189E-02	5.730E-03
5.000E-01	5.000E-02	1.378E-01	1.260E+00	9.855E-01	3.062E-01	2.742E-01	8.422E-02	1.052E-02
5.000E-01	1.000E-01	1.352E-01	1.253E+00	9.840E-01	3.325E-01	2.695E-01	8.989E-02	2.024E-02
1.000E+00	0.000E+00	6.031E-02	9.128E-01	9.637E-01	7.541E-01	7.541E-01	5.702E-01	2.689E-02
1.000E+00	1.000E-02	8.673E-02	1.067E+00	9.741E-01	5.372E-01	5.314E-01	2.863E-01	3.310E-03
1.000E+00	3.000E-02	8.604E-02	1.063E+00	9.735E-01	5.475E-01	5.302E-01	2.911E-01	6.739E-02
1.000E+00	5.000E-02	8.536E-02	1.060E+00	9.730E-01	5.578E-01	5.291E-01	2.960E-01	1.740E-02
1.000E+00	1.000E-01	8.371E-02	1.052E+00	9.715E-01	5.836E-01	5.265E-01	3.082E-01	2.171E-02
1.000E+00	1.000E-01	8.371E-02	1.052E+00	9.715E-01	5.836E-01	5.265E-01	3.082E-01	1.982E-02
1.000E+00	5.000E-01	7.299E-02	9.931E-01	9.598E-01	7.812E-01	5.151E-01	4.036E-01	3.142E-02

TABLE 1b. GTM-CALCULATED ACTIVITIES OF (H_2O), (H^+), AND (NO_3^-) AND FREE CMPO AND TBP CONCENTRATIONS IN TRACER H_3PO_4 EXPERIMENTS

$NaNO_3$[a] <u>M</u>	HNO_3[a] <u>M</u>	CMPO[b]	TBP[b]	(H_2O)[c]	(NO_3^-)[c]	(H^+)[c]	(HNO_3)[c]	^{D}H3P04[d]
1.000E+00	1.000E+00	6.334E-02	9.333E-01	9.452E-01	1.013E+00	5.151E-01	5.232E-01	2.845E-02
1.000E+00	2.000E+00	5.024E-02	8.381E-01	9.160E-01	1.440E+00	5.366E-01	7.748E-01	2.385E-02
1.000E+00	4.000E+00	3.491E-02	6.991E-01	8.578E-01	2.210E+00	6.115E-01	1.355E+00	1.288E-02
1.500E+00	0.000E+00	3.267E-02	6.756E-01	9.425E-01	1.219E+00	1.219E+00	1.491E+00	2.014E-02
2.000E+00	0.000E+00	1.865E-02	4.995E-01	9.193E-01	1.777E+00	1.777E+00	3.166E+00	1.405E-02
2.200E+00	1.000E+00	2.139E-02	5.386E-01	9.068E-01	1.833E+00	1.445E+00	2.657E+00	3.589E-02
2.700E+00	5.000E-01	1.643E-02	4.657E-01	9.046E-01	2.014E+00	1.834E+00	3.704E+00	4.643E-02
3.000E+00	0.000E+00	6.398E-03	2.757E-01	8.678E-01	3.231E+00	3.231E+00	1.047E+01	1.168E-02
3.180E+00	2.000E-02	1.299E-02	4.086E-01	9.023E-01	2.214E+00	2.207E+00	4.902E+00	8.270E-03
4.000E+00	0.000E+00	2.113E-03	1.526E-01	8.108E-01	5.248E+00	5.248E+00	2.762E+01	7.550E-03
4.400E+00	1.000E-02	4.652E-03	2.317E-01	8.513E-01	3.761E+00	3.760E+00	1.418E+01	4.485E-03
4.400E+00	3.000E-02	4.618E-03	2.308E-01	8.506E-01	3.775E+00	3.772E+00	1.428E+01	9.900E-03
4.400E+00	5.000E-02	4.585E-03	2.299E-01	8.498E-01	3.789E+00	3.783E+00	1.438E+01	1.489E-02
4.400E+00	1.000E-01	4.502E-03	2.276E-01	8.480E-01	3.824E+00	3.812E+00	1.462E+01	2.446E-02
4.400E+00	5.000E-01	3.900E-03	2.107E-01	8.335E-01	4.091E+00	4.052E+00	1.663E+01	6.610E-02
4.400E+00	1.000E+00	3.271E-03	1.919E-01	8.156E-01	4.411E+00	4.376E+00	1.936E+01	5.790E-02
4.400E+00	2.000E+00	2.321E-03	1.602E-01	7.800E-01	5.024E+00	5.093E+00	2.566E+01	3.631E-02
4.400E+00	3.000E+00	1.631E-03	1.335E-01	7.421E-01	5.697E+00	5.886E+00	3.363E+01	3.275E-02
5/000E+00	1.000E-02	2.730E-03	1.744E-01	8.238E-01	4.738E+00	4.739E+00	2.252E+01	1.527E-02
5.000E+00	3.000E-02	2.709E-03	1.737E-01	8.231E-01	4.753E+00	4.753E+00	2.266E+01	1.483E-02
5.000E+00	5.000E-02	2.688E-03	1.730E-01	8.223E-01	4.768E+00	4.768E+00	2.280E+01	2.352E-02
5.000E+00	1.000E-01	2.638E-03	1.713E-01	8.204E-01	4.804E+00	4.806E+00	2.316E+01	3.252E-02
6.000E+00	1.000E-02	1.062E-03	1.072E-01	7.753E-01	6.750E+00	6.753E+00	4.571E+01	1.670E-02
6.000E+00	3.000E-02	1.054E-03	1.068E-01	7.745E-01	6.766E+00	6.774E+00	4.597E+01	1.969E-02
6.000E+00	5.000E-02	1.045E-03	1.063E-01	7.737E-01	6.782E+00	6.796E+00	4.622E+01	2.797E-02
6.000E+00	1.000E-01	1.024E-03	1.053E-01	7.718E-01	6.821E+00	6.851E+00	4.687E+01	5.468E-03
7.000E+00	1.000E-02	3.898E-04	6.458E-02	7.239E-01	9.336E+00	9.342E+00	8.747E+01	6.470E-03
7.000E+00	3.000E-02	3.865E-04	6.431E-02	7.231E-01	9.354E+00	9.372E+00	8.792E+01	1.741E-02
7.000E+00	5.000E-02	3.834E-04	6.404E-02	7.223E-01	9.371E+00	9.402E+00	8.836E+01	3.317E-02
7.000E+00	1.000E-01	3.755E-04	6.337E-02	7.204E-01	9.415E+00	9.477E+00	8.948E+01	6.285E-02
8.000E+00	1.000E-02	1.400E-04	3.812E-02	6.708E-01	1.260E+01	1.261E+01	1.593E+02	7.340E-03
8.000E+00	3.000E-02	1.388E-04	3.796E-02	6.700E-01	1.262E+01	1.265E+01	1.600E+02	2.199E-02
8.000E+00	5.000E-02	1.377E-04	3.779E-02	6.692E-01	1.264E+01	1.268E+01	1.608E+02	6.970E-02
8.000E+00	1.000E-01	1.349E-04	3.738E-02	6.672E-01	1.269E+01	1.278E+01	1.626E+02	6.739E-02

[a] Initial organic phase/aqueous phase concentration.

[b] Equilibrated organic phase concentration calculated by the GTM.

[c] Activity calculated in the molar mode.

[D] Experimental values obtained by using $H_3{}^{32}PO_4$.

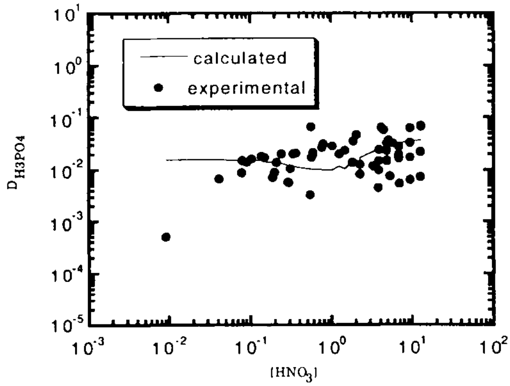

FIGURE 4. Phosphoric Acid Distribution Ratios Determined Experimentally and Calculated by the GTM.

This converts to a simpler form of Eq. 17.

$$D_{H_3PO_4} = \left([CMPO]\left(K_1 + K_2 \{H^+\}\{NO_3^-\}\right) + K_3 [TBP]\{H^+\}\{NO_3^-\}\right) \tag{18}$$

Various chemical equation scenarios were analyzed, which gave least square fits significantly inferior to those obtained using Eqs. 13-15. Equation 19 is the thermodynamic model that best fits the experimental and calculated results.

$$D_{H_3PO_4} = [CMPO]\left(\left(0.110 + 0.067 \{H^+\}\{NO_3^-\}\right) + 0.059\, TBP \{H^+\}\{NO_3^-\}\right) \tag{19}$$

Figure 4 shows the difference between experimental and calculated distribution ratios as a function of nitrate activities. However, at low phosphoric acid concentration the distribution ratios are hard to measure and increases the scatter in the data shown in Figure 4. The resulting mechanism is similar to those obtained in experiments with bulk phosphoric acid and TRUEX-NPH solvent,[17] where a dimer of phosphoric acid extracted with CMPO and TBP, and a monomer as a CMPO-phosphoric acid complex. During this study, one of the dimer phosphoric acid molecules was substituted for a nitric acid molecule (higher extractability in TRUEX-NPH solvent). There was also a H_3PO_4•CMPO molecule present with $K_1 = 0.110$, a similar value to that obtained in the bulk phosphoric acid study with the TRUEX-NPH solvent (K = 0.190).

The speciation for the organic phase species in the TRUEX solvent is illustrated in Fig. 5.

Figure 5 clearly demonstrates the dominance of extraction of the monomer phosphoric acid-CMPO complex as the nitric acid activity approached 1<u>M</u>. At higher nitric acid activities, the two mixed phosphoric-nitric acid species of CMPO and TBP dominated the extraction chemistry, and as in to the bulk phosphoric acid study,[17] the TBP complexes began to dominate the overall

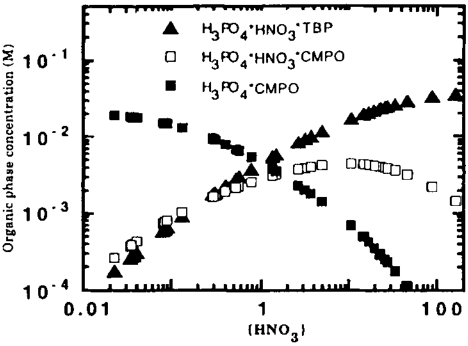

FIGURE 5. Organic Phase Speciation as a Function of Nitric Acid Activity

extraction chemistry. The decrease in the CMPO species can be attributed to the loading of extractant with HNO_3 and H_3PO_4.

Conclusions

A thermodynamic model for phosphoric acid was derived, based on $H_3{}^{32}PO_4$ tracer experiments performed in high concentrations of nitrate. The tracer phosphorous distribution ratios support the extraction of $CMPO \bullet H_3PO_4 \bullet HNO_3$, $CMPO \bullet H_3PO_4$, and $TBP \bullet H_3PO_4 \bullet HNO_3$ as organic complexes in TRUEX-NPH solvent. At low concentrations of phosphoric acid the data does not allow to validate the fine structure of the model due to the scatter, however, the model does predict the results as accurately as the experimental data allows. At high nitrate concentrations, CMPO and TBP extract a $H_3PO_4 \bullet HNO_3$ complex which is analogous to the H_3PO_4 dimer, which is extracted in the absence of nitric acid.[17]

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