APPLICATION OF^{OSU} SINGLE ION ACTIVITY COEFFICIENTS TO DETERMINE SOLVENT EXTRACTION MECHANISM FOR COMPONENTS OF HIGH LEVEL NUCLEAR WASTE

by

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ABSTRACT

The TRUEX solvent extraction process is being developed to remove and concentrate transuranic (TRU) elements from high-level and TRU radioactive wastes currently stored at U.S. Department of Energy sites. Phosphoric acid is one of the chemical species of concern 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 by phosphoric acid distribution ratios, which were measured by using phosphoric acid radiotracer and a variety of aqueous phases containing different concentrations of nitric acid and nitrate ions. 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 CMPO and TBP extraction of a phosphoric acid-nitric acid complex and a CMPO-phosphoric acid complex in TRUEX-NPH solvent.

INTRODUCTION

One of the current clean-up 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. One chemical component found in the tanks and excluded from the Generic TRUEX Model (GTM) is phosphoric acid, which originated from the BiPO_4 process to recover plutonium from irradiated uranium.

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.

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Thus, understanding the phosphoric acid extraction chemistry is important in nuclear waste treatment applications. The current study attempts to elucidate the extraction chemistry and mechanism for phosphoric acid by TRUEX-NPH solvent (1.4M TBP and 0.2M CMPO, octyl(phenyl)-diisobutylcarbamoylmethyl phosphine oxide in normal paraffinic hydrocarbon). In nitrate solutions of high ionic strength the extraction behavior of phosphoric acid will simulate that expected after dissolution of tanks sludge. The extraction of mineral acids with TBP is well documented. The order of extraction ($\text{HF} > \text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{HCl} > \text{H}_2\text{SO}_4$) 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 $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HF}$. There is only a limited amount of data on extraction of mineral acids with the mixed TRUEX-NPH system. 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 $\text{HNO}_3/\text{H}_3\text{PO}_4$ 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. The $\text{HNO}_3/\text{H}_3\text{PO}_4$ combination has not been studied extensively with the TRUEX solvent. This report describes the experimental measurements of (phosphorus-32) 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, and the amount of free organic species (e.g., TBP and CMPO) was used to derive a thermodynamic model.

EXPERIMENTATION

The TRUEX solvent was prepared with recrystallized 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 $\text{H}_3^{32}\text{PO}_4$ 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 the $\text{H}_3^{32}\text{PO}_4$ radiotracer and contacted with TRUEX solvent. The aqueous HNO_3 acid solutions (0.01-4M HNO_3) were spiked with the tracer, then contacted with preequilibrated TRUEX solvent (which was repetitively contacted with fresh HNO_3 solution prior to the radiotracer extractions) separated and counted.

CONCLUSIONS

A thermodynamic model for phosphoric acid was derived based on $\text{H}_3^{32}\text{PO}_4$ radiotracer experiments in high nitrate concentrations. The results from the tracer phosphorous distribution ratios support the extraction of $\text{CMPO} \cdot \text{H}_3\text{PO}_4 \cdot \text{HNO}_3$, $\text{CMPO} \cdot \text{H}_3\text{PO}_4$, and $\text{TBP} \cdot \text{H}_3\text{PO}_4 \cdot \text{HNO}_3$ as organic complexes in TRUEX-NPH solvent. In high nitrate solutions, CMPO and TBP extract a $\text{H}_3\text{PO}_4 \cdot \text{HNO}_3$ complex analogous to the H_3PO_4 dimer extracted as a function of H_3PO_4 concentration in the absence of nitric acid.

Fig. 1. Distribution Ratios for Phosphoric Acid as a Function of Nitric Acid

Fig. 2. Distribution Ratios for Phosphoric Acid as a Function of Nitric Acid Concentration at Constant Sodium Nitrate Concentrations (0.1-2.7M $NaNO_3$)

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

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

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

BROMLEY EQUATION

$$\log \gamma_{ij}^0 = \frac{-A Z_i Z_j \sqrt{I}}{1 + B \sqrt{I}} + \beta I + C I^2 + D I^3 + E I^4 + \dots$$

where

A is the Debye-Hückel constant,

$0.5108 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ 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.

SINGLE COMPONENT ELECTROLYTE

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

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

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

The F terms are defined as the following:

$$F_1 = \left(Y_{12} \log \gamma_{12}^0 + Y_{14} \log \gamma_{14}^0 + \dots + Y_{1j} \log \gamma_{1j}^0 \right) + \frac{A \sqrt{I}}{1 + \sqrt{I}} (Z_1 Z_2 Y_{12} + Z_1 Z_4 Y_{14} + \dots + Z_1 Z_j Y_{1j})$$

and

$$F_2 = \left(X_{12} \log \gamma_{12}^0 + X_{32} \log \gamma_{32}^0 + \dots + X_{i2} \log \gamma_{i2}^0 \right) + \frac{A \sqrt{I}}{1 + \sqrt{I}} (Z_1 Z_2 X_{12} + Z_3 Z_2 Y_{32} + \dots + Z_i Z_2 Y_{i2})$$

Where

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

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

OSMOTIC COEFFICIENT

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

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

EQUILIBRIA

Aqueous

Organic

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