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Features of the Thermodynamics of Two-Phase Distribution Reactions of Americium(III) and Europium(III) Nitrates into Solutions of 2,6-Bis[(bis(2-ethylhexyl)phosphino)methyl]pyridine *N*,*P*,*P*′-Trioxide

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New bifunctional and trifunctional organophosphorus ligands, 2-[(bis(2-ethylhexyl)phosphino)methyl]pyridine *N*,*P*-dioxide, DEH(MNOPO), and 2,6-bis[(bis(2-ethylhexyl)phosphino)methyl]pyridine *N*,*P*,*P*′-trioxide, TEH(NOPOPO), have been synthesized. In contrast with previously reported phenyl derivatives, the increased solubility of these ligands in normal paraffinic hydrocarbon solvents make them attractive reagents for actinide partitioning. While the bifunctional reagent DEH(MNOPO) interacts with Eu^{3+} and Am^{3+} comparatively weakly, the trifunctional TEH(NOPOPO) exhibits moderate to high ability to transfer the trisnitrato complexes of these ions into *n*-dodecane from acidic aqueous solutions. We report here the details of TEH(NOPOPO) and DEH(MNOPO) preparation and of their ability to extract HNO_3, $Am(NO_3)_3$, and $Eu(NO_3)_3$ into paraffinic hydrocarbons. The trifunctional TEH(NOPOPO) can extract up to two molecules of HNO_3. The dominant extracted species for both $Am(NO_3)_3$ and $Eu(NO_3)_3$ has two TEH(NOPOPO) ligands associated over the range of temperatures 10–40 °C. From the variation in the equilibrium coefficients for the phase transfer reactions as a function of temperature, we have calculated the enthalpies and entropies for extraction of HNO_3, $Am(NO_3)_3$, and $Eu(NO_3)_3$ into *n*-dodecane. Each metal nitrate is transferred into the organic phase in an exothermic process but opposed by an unfavorable (negative) entropy. The thermodynamic data are interpreted to indicate that the pyridine *N*-oxide is apparently a significantly weaker donor group for these metal ions than the phosphine oxides.

Introduction

Minimization of the volume of high-level wastes from spent nuclear fuels that must be isolated in a geologic repository and of the long-term radiotoxicity of the emplaced wastes can best be accomplished by recovery and transmutation of the transuranic elements. Nuclear incineration of the long-lived transuranium actinides (and selected fission products) can reduce the time during which wastes from spent nuclear fuel are dangerous from more than 10^5 years to less than 10^3 years.[1] The well-known PUREX process efficiently isolates U and Pu from the diverse mixture of fission products but rejects the trivalent actinides.[2] Considerable research and development is underway around the world investigating new methods and reagents for the recovery of the so-called minor actinides (Np, Am, Cm) to enable their incineration in appropriate reactors or through the use of accelerators.[3,4] The primary objective of these efforts is the development of new reagents and processes that ultimately will lead to the most efficient recovery of the target metal ions with minimum generation of secondary wastes.

Several different classes of solvent extraction reagents are being investigated. The Western European program, led by

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France, emphasizes the complete incinerability of extractants with the development of malonamide ligands.[5] In China, the TRPO process, based on trialkylphosphine oxide (TRPO), is the preferred approach to trivalent actinide recovery.[6] In Japan, an actinide partitioning process based on the application of the acidic organophosphorus compound diisodecylphosphoric acid (DIDPA) has been demonstrated through the pilot plant stage.[7] Additional research at the Japan Atomic Energy Research Institute focuses on the development of new diamide extractants[8] and at the Power Reactor and Nuclear Fuel Development Corporation (JNC) on the TRUEX process.[9] This process, developed at Argonne National Laboratory to assist in the cleanup of the nuclear weapons complex, is based on the extraction of electroneutral nitrate complexes into paraffinic hydrocarbons by the bifunctional extractant octyl(phenyl)-*N*,*N*-diisobutyl(carbamoylmethyl)-phosphine oxide (CMPO).[10] This process has also received considerable attention for minor actinide (in this context, Np, Am, and Cm) recovery in India.[11] In Russia, a significant volume of nuclear wastes already has been treated using a modified TRUEX process that relies on a structurally simpler CMPO derivative (diphenyl-*N*,*N*-di-*n*-butyl CMPO) that requires the addition of a fluorinated solvent to maintain adequate solubility.[12] Except for the DIDPA process, each of these phase transfer reagents is of the solvating class, transferring electroneutral metal nitrate salts to the organic phase. The primary drivers for selection of this type of reagent for actinide partitioning are the moderate concentration of nitric acid used for dissolution of spent nuclear fuel prior to reprocessing and the ability to strip the final product into an aqueous medium of comparatively low ionic strength.[2]

Paine and co-workers have investigated the coordination chemistry of lanthanides with phenyl derivatives of phosphinopyridine *N*-oxide ligands[12−17] of the general types illustrated in Figure 1. These earlier studies relied principally on crystallography and spectroscopy for characterization of the coordination complexes formed and demonstrated that the structural version best suited for complexation of lanthanides possess a methylene bridge between the phosphine oxides and the carbon atoms at the 2 and 6 positions of the pyridine *N*-oxide ring. This trifunctional ligand class (NOPOPO's) presents an optimum coordination footprint on Ln(III) ions. The crystallographic studies with the 2,6-bis-[(diphenylphosphino)methyl]pyridine *N*,*P*,*P*′-trioxide, TΦ-(NOPOPO), indicate that the tridentate coordination mode is favored with two ligands found in the inner coordination sphere.[15−20] With chloride as the counterion, three anions are also accommodated in the inner coordination sphere.[19] In nitrate salts, a mix of inner- and outer-sphere (and monodentate and bidentate) nitrate ions is typically seen. Neu et al.[21−23] have recently reported crystal structures of complexes of Pu(IV) with TΦ(NOPOPO) in which the ligand coordinates to Pu(IV) in a tridentate chelate mode.

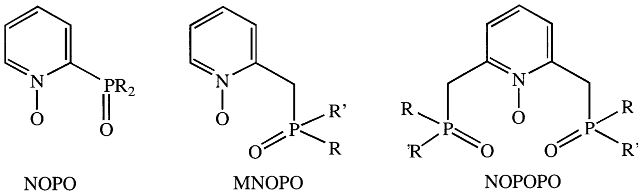

Figure 1. Structural formulas for phosphinopyridine *N*-oxide ligands.

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Though the phenyl derivatives are ideal for crystallography, they are ill-suited for large-scale separations applications, as they tend to be soluble only in polar, volatile solvents such as chloroform. Recent adjustments to the synthesis protocols have enabled the preparation of new derivatives containing normal alkyl chains in place of the phenyl groups.[17] This modification has led to a significant increase in the solubility of the MNOPO and NOPOPO ligands in solvents suitable for possible large-scale applications. The introduction of branched hydrocarbon chains is expected to further improve solubility of the MNOPO and NOPOPO ligands in aliphatic hydrocarbons. In this study, we describe the synthesis of two new (phosphinomethyl)-pyridine *N*-oxide ligands, 2-[(bis(2-ethylhexyl)phosphino)-methyl]pyridine *N*,*P*-dioxide, DEH(MNOPO), and 2,6-bis-[(bis(2-ethylhexyl)phosphino)methyl]pyridine *N*,*P*,*P*′-trioxide, TEH(NOPOPO) ($R = R' =$ 2-ethylhexyl in Figure 1). To gain insight into the coordination chemistry of these ligands in solution, we have investigated the energetics of the phase transfer reaction, focusing on the thermodynamics of the extraction of HNO_3, $Am(NO_3)_3$, and $Eu(NO_3)_3$ by DEH-(MNOPO) and TEH(NOPOPO) into selected aromatic and normal aliphatic solvents.

Experimental Section

The organic reagents used in the syntheses were purchased from Aldrich Chemical Co. Organic solvents were obtained from VWR and dried by standard methods. All ligand synthesis reactions were performed in Schlenk-style glassware under a dry nitrogen gas atmosphere unless noted otherwise. Sodium nitrate, nitric acid, *n*-dodecane, and toluene used in the solvent extraction studies were of reagent grade and used as received. Aqueous solutions were prepared with deionized water. The tracer stock solutions were prepared from the purified radionuclides ^{241}Am and ^{152,154}Eu (ANL stock) and were assayed radiometrically on a Packard Cobra II automatic γ counter.

In a nitrogen-purged flask fitted with a reflux condenser and stir bar, 2-ethyl-1-hexanol (250 g, 1.9 mol) in benzene (150 mL) was added dropwise at 23 °C to a stirred solution of excess thionyl chloride (200 mL) in benzene (150 mL) containing pyridine (1 mL). After the mixture was refluxed (3 h), the benzene and unreacted thionyl chloride were removed by vacuum evaporation. The residue was distilled under vacuum (35−37 °C/2 mTorr) providing a slightly colored liquid (255 g), which was dried over anhydrous Na_2SO_4 and redistilled giving 2-ethyl-1-hexyl chloride: yield 235 g, 82.3%. A 250 mL flask fitted with a reflux condenser was swept with nitrogen and charged with Mg turnings (3.65 g, 0.15 mol) and several pieces of I_2. The solid mixture was heated briefly with a heat gun until purple vapor from the I_2 appeared. A solution of 2-ethyl-1-hexyl chloride (22.3 g, 0.15 mol) in dry diethyl ether (60 mL) was prepared in a nitrogen filled glovebag and transferred to a dropping funnel which was then attached to the reaction flask. An aliquot (10 mL) of solution was added to the Mg turnings, and this mixture was warmed with the heat gun to initiate the reaction. Once started, the additional ether solution was added dropwise at a rate that enabled continuous reflux. After the addition was complete, the mixture was refluxed for an additional 2 h. After cooling of the mixture to room temperature, a solution containing diethylphosphinate (6.08 g, 0.044 mol) in dry diethyl ether (10 mL) and dry benzene (30 mL) was added dropwise. The temperature of the mixture rose during addition, and the final mixture was refluxed (2 h, oil bath temperature 60 °C). A solution of 2,6-bis(chloromethyl)pyridine (3.52 g, 0.02 mol)[24] in dry benzene (30 mL) was prepared, transferred to the addition funnel, and added to the stirred solution containing the Grignard reagent. The resulting mixture was refluxed for an additional 6.5 h. The solvent was then removed under reduced pressure. The resulting orange residue was treated with saturated aqueous NH_4Cl solution (100 mL) and the mixture extracted with $CHCl_3$ (3 × 80 mL). The combined $CHCl_3$ fractions were washed with water (50 mL) and dried with anhydrous Na_2SO_4. Evaporation of the $CHCl_3$, under reduced pressure, gave 2,6-bis-[(bis(2-ethylhexyl)phosphino)methyl]pyridine *P*,*P*′-dioxide, **1**, as a light orange sticky oil: yield 10.5 g, 80.5%. NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ δ 46.2; $^{13}C\{^1H\}$ δ 10.52 (d, $J = 2.4$ Hz), 13.90, 22.71, 26.88 (d of d, $J_1 = 12.0$ Hz, $J_2 = 7.2$ Hz), 28.33 (d, $J = 5.6$ Hz), 33.10 (d, $J = 65.0$ Hz), 33.62, 33.78 (d, $J = 5.0$ Hz), 40.61 (d, $J = 56.9$ Hz), 122.41, 136.90, 153.61 (d, $J = 6.4$ Hz); ^1H δ 0.65−0.90 (m), 1.24−1.83 (m), 3.32 (d, $J = 14.6$ Hz), 7.28 (d, $J = 7.3$ Hz), 7.59 (t, $J = 7.7$ Hz). IR (neat, cm^{-1}): 2958 (s), 2928 (s), 1587 (m), 1456 (m), 1379 (w), 1197 (m), 1167 (s), 1118 (m), 854 (m), 819 (m), 636 (w), 515 (w), 455 (m), 424 (w).

A sample of **1** (10.3 g, 0.016 mol) in $CHCl_3$ (100 mL) was combined with 3-chloroperoxybenzoic acid (5.4 g, 57−86% solution) and the mixture stirred at 23 °C (1 h). The resulting mixture was extracted with saturated aqueous $NaHCO_3/Na_2CO_3$ (5:1) solution (100 mL), and the aqueous phase (pH = 8−9) was washed with CH_2Cl_2 (2 × 50 mL). The $CHCl_3$ and CH_2Cl_2 fractions were combined and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure (23 °C). The product, 2,6-bis-[(bis(2-ethylhexylphosphino)methyl]pyridine *N*,*P*,*P*′-trioxide, **2**, was recovered as a sticky oil by chromatography on silica gel with $CHCl_3$/MeOH (100:2) as the eluant following evaporation of the solvent: yield 9.0 g, 85.3%. NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ δ 47.56; $^{13}C\{^1H\}$ δ 10.20 (d, $J = 4.0$ Hz), 13.96, 22.75, 27.02 (d of d, $J_1 = 7.0$ Hz, $J_2 = 7.0$ Hz), 28.40 (d, $J = 3.4$ Hz), 33.11 (d, $J = 58.4$ Hz), 33.84, 33.95 (d, $J = 7.2$ Hz), 34.09 (d, $J = 65.0$ Hz), 124.69, 125.90, 144.82 (d, $J = 7.5$ Hz); ^1H δ 0.78−0.91 (m), 1.18−1.74 (m), 3.63 (d, $J = 13.4$ Hz), 7.19 (t, $J = 7.8$ Hz), 7.56 (d, $J = 7.8$ Hz). IR (neat, cm^{-1}): 2957 (s), 2926 (s), 1568 (w), 1485 (m), 1462 (s), 1413 (s), 1381 (s), 1240 (s), 1167 (s), 966 (m), 864 (m), 815 (m), 661 (w), 489 (w), 462 (m), 432 (w). Mass spectrum (HR; *m*/*e*): calcd for $C_{39}H_{75}NO_3P_2$ M = 667.5222; found $M^+ = 667.5206$ (5%), 651.5240 ($M - O^+$, 10%), 638.4832 ($M - C_2H_5^+$, 12%), 554.3900 ($M - C_8H_{17}^+$, 20%). Solubility: soluble in $CHCl_3$, C_6H_6, toluene, xylene, heptane, and hexane.

A sample of the phosphino Grignard reagent $(2\text{-EtHx})_2P(O)MgCl$ (0.053 mol) in Et_2O/C_6H_6 solution, prepared as described above, was added with stirring to 2-(chloromethyl)pyridine (6.8 g, 0.053 mol) in dry benzene (30 mL). The mixture was refluxed (6.5 h), and the volatiles were removed by vacuum evaporation. The orange residue was treated with saturated aqueous NH_4Cl (150 mL) and then extracted with $CHCl_3$ (3 × 60 mL). The combined $CHCl_3$ fractions were washed with water (50 mL) and dried over Na_2SO_4. The dried $CHCl_3$ solution was decanted and evaporated and the residue washed with pentane (3 × 40 mL). 2-[(bis(2-ethylhexyl)-phosphino)methyl]pyridine *P*-oxide, **3,** was obtained as a light orange, sticky oil: yield 13.5 g, 83.9%. NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ δ 46.8; $^{13}C\{^1H\}$ δ 10.07 (d, $J = 6.0$ Hz), 13.85, 22.64, 26.87 (d of d, $J_1 = 6.0$ Hz, $J_2 = 6.0$ Hz), 28.26 (d, $J = 6.6$ Hz), 33.06 (d, $J = 64.8$ Hz), 33.57, 33.80 (d, $J = 6.9$ Hz), 40.54 (d, $J = 56.8$ Hz), 121.42, 124.47 (d, $J = 4.3$ Hz), 136.25, 149.07, 153.92 (d, J

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= 6.4 Hz); ^{1}H δ 0.77−0.91 (m), 1.20−1.50 (m), 1.63−1.81 (m), 7.15 (t, J = 6.1 Hz), 7.39 (d, J = 7.9 Hz), 7.63 (t, J = 7.6 Hz), 8.51 (d, J = 4.6 Hz).

A sample of **3** (13.0 g, 0.036 mol) was dissolved in $CHCl_3$ (150 mL) and 3-chloroperoxybenzoic acid (9.6 g, 57−86%) was added with stirring. After 1 h at 23 °C, the mixture was extracted with saturated aqueous $NaHCO_3$/Na_2CO_3 (5:1) (100 mL), and the aqueous phase (pH = 8−9) was washed with CH_2Cl_2 (2 × 50 mL). The combined CH_2Cl_2/$CHCl_3$ solution was dried over Na_2SO_4 and decanted and the solvent removed by vacuum evaporation. The 2-[(bis(2-ethylhexyl)phosphino)methyl]pyridine *N,P*-dioxide, **4**, was isolated as a sticky oil by chromatography on silica gel eluting with $CHCl_3$/MeOH (100:2): yield 11.5 g, 84.8%. NMR spectra ($CDCl_3$): ^{31}P{^{1}H} δ 47.08; ^{13}C{^{1}H} δ 10.08 (d, J = 6.0 Hz), 13.86, 22.64, 26.88 (d of d, J_1 = 7.2 Hz, J_2 = 4.0 Hz), 28.25 (d, J = 4.7 Hz), 32.23 (d, J = 56.8 Hz), 33.72 (d, J = 6.1 Hz), 33.73, 33.97 (d, J = 64.8 Hz), 123.89 (d, J = 1.5 Hz), 125.33, 127.76 (d, J = 3.5 Hz), 139.11, 144.81 (d, J = 7.5 Hz); ^{1}H δ 0.78−0.91 (m), 1.22−1.46 (m), 1.73−1.77 (m), 7.19−7.25 (m), 7.62−7.66 (m), 8.25−8.78 (m). IR (neat, cm^{-1}): 2957 (s), 2926 (s), 2888 (s), 1487 (s), 1460 (s), 1436 (s), 1381 (m), 1236 (s), 1201 (s), 1167 (s), 1130 (sa), 871 (s), 815 (m), 771 (s), 636 (w), 489 (w), 426 (m), 432 (w). Mass spectrum (HR; *m/e*): calcd for $C_{22}H_{40}NO_2P$ M = 381.2797; found M$^+$ 381.2781 (1.3%), 352.2403 (M − $C_2H_5^+$, 25.8%), 268.1452 (M − $C_8H_{17}^+$, 31.2%). Solubility: soluble in $CHCl_3$ benzene, toluene, xylene, heptane, and hexane.

Measurement of the Metal Ion Distribution. Partitioning of the metal ions between the phases was quantified by measuring radiometrically the concentration of Am or Eu in each phase at equilibrium. The metal nitrate distribution ratios (defined as the ratio of the total concentration of metal ions in each phase, $D = [M]_{tot,org}/[M]_{tot,aq}$) were determined by equilibrating the aqueous and organic phases in 13 × 100 mm Pyrex culture tubes in Teflon-lined screw caps. The organic phases were preequilibrated (before introduction of the radiotracer metal ion) three times with equal volumes of fresh $NaNO_3$ or HNO_3 solutions of the appropriate concentration to ensure that the concentration of the aqueous electrolyte did not change during the equilibration with the radiotracer present. A fresh aliquot (0.6 mL) of the aqueous phase containing 5 μL of the ^{241}Am or ^{152,154} Eu tracer was contacted with the equal volume of the preconditioned organic phase. The radiotracers were introduced from stock solutions of 0.01 M HNO_3. For determination of the stoichiometry of the metal complexes in the organic phase, the phases were mixed for 30 min using a vortex mixer at room temperature. We determined that a 15 min contact with vortex mixing was sufficient to reach the biphasic equilibrium. The phases were centrifuged and separated, and duplicate 200 μL aliquots were withdrawn from each phase for the γ radioactivity measurements. Under all conditions, radiotracer mass balance was greater than 95%.

The metal ion distribution experiments as a function of temperature were conducted at 5 deg intervals between 10.0 and 40.0 °C. Chemical equilibrium was attained by vortex mixing of the two phases (3.5 mL of each) for 1 min followed by 10 min for thermal equilibration in a water bath capable of maintaining the temperature constant to within ±0.1 °C. At each temperature the process of vigorous mixing/thermal equilibration was repeated eight times prior to sampling. At this stage, the two-phase sample was centrifuged and duplicate 200 μL aliquots of each phase were taken for radiometric assay. Equal volume samples of both organic and aqueous phases were taken to maintain a constant ratio of the phases throughout data acquisition. The residual solutions then were equilibrated at the next temperature. The distribution data were collected in three independent experiments.

The partitioning of HNO_3 into 0.1 M TEH(NOPOPO) in *n*-dodecane was investigated as a function of $[HNO_3]_{tot}$ at 15, 25, and 40 °C. Aside from its intrinsic interest, this information was needed to determine the free extractant concentration for analysis the stoichiometry of the metal ion phase transfer reactions. The acid concentration in each phase was determined titrimetrically. The aqueous samples were titrated directly with standard NaOH (after phase separation). The concentration of acid in the organic phase was quantified by titration with standard NaOH solution after stripping the acid from the organic phase by repetitive contact with equal volume amounts of deionized water.

Results and Discussion

Ligand Syntheses. Paine and co-workers previously reported[25,26] the results a study of Am(III) distribution between HNO_3 or HCl solutions (0.01−8 M) and 0.05 M TΦ(NOPOPO) solution in $CHCl_3$. These studies showed that

(i) distribution ratios increase significantly as the aqueous acid concentration increases,

(ii) distribution ratios are greater for TΦ(NOPOPO) than CMPO at equivalent acid concentrations,

(iii) extraction kinetics are rapid, and

(iv) back-extraction efficiency is good.

Despite these attributes, TΦ(NOPOPO) is relatively insoluble in practical process solvents. As a result, we turned attention to the preparation of NOPOPO derivatives having alkyl (rather than aryl) substituents on the phosphine oxide donor groups. In a recent report, Paine and co-workers[17] described the syntheses of symmetrical NOPOPO derivatives with R = R′ = Et, Pr, Bu, Pn, Hx, Hp, and Oct and asymmetrical derivatives with R = Ph, R′ = Me, Hx, and Oct. The long, straight-chain symmetrical ligands showed improved solubility in aliphatic solvent, but initial tests revealed a tendency for the organic phase to split into light and heavy fractions, a phenomenon known as third-phase formation, under some conditions. To reduce the impact of this phenomenon, a synthesis for the 2-ethylhexyl derivatives of both the trifunctional ligand, TEH(NOPOPO), and of the bifunctional ligand, DEH(MNOPO), was developed. The details of each synthesis were presented in Schemes 1 and 2. The preparation of the phosphino Grignard reagent followed established procedures for *n*-alkyl derivatives.[17,27] The phosphino Grignard reagent was combined with 2-(chloromethyl)pyridine in benzene in a 1:1 ratio and with 2,6-bis(chloromethyl)pyridine in benzene in a 2:1 ratio to obtain compound **4** or **2,** respectively. The DEH(MNOPO) and TEH(NOPOPO) ligands were characterized by ^{31}P, ^{13}C{^{1}H}, ^{1}H NMR, and IR spectroscopy and high-resolution MS. The data are consistent with expected results and with related

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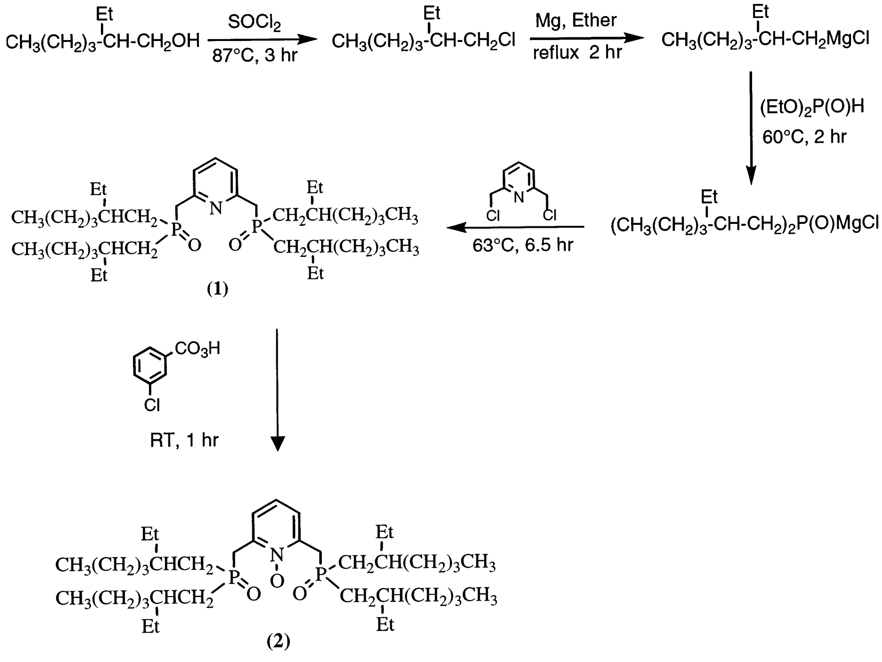
(25) Bond, E. M.; Engelhardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T. The Solvent Extraction of Americium(III) in HNO_3 Solutions by 2,6-Bis[(diphenyl)phosphinomethyl]pyridine *N,P,P′*-Trioxide. *Solvent Extr. Ion Exch.* **1997**, *15*, 381−400.

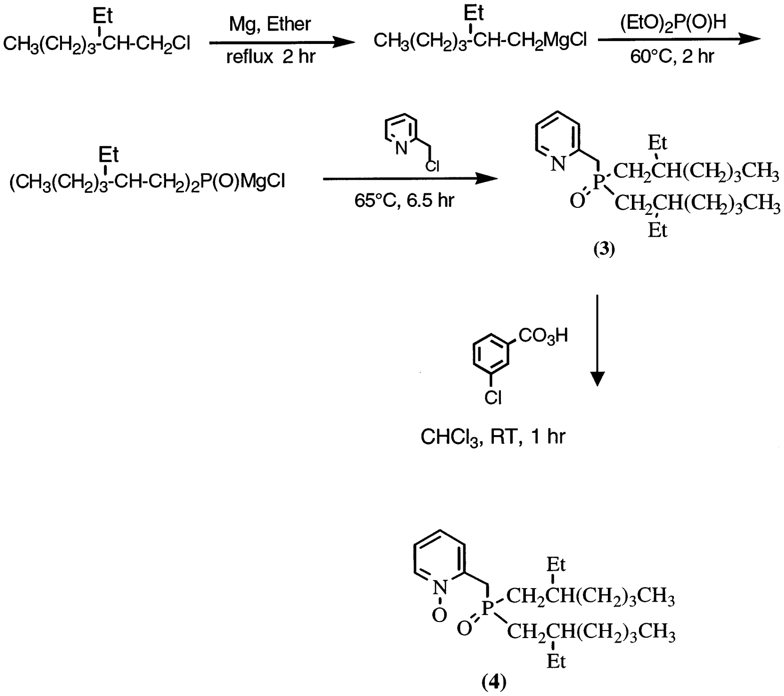
(26) Bond, E. M.; Engelhardt, U.; Deere, T. P.; Rapko, B. M.; Paine, R. T. The Solvent Extraction of Americium(III) in HCl Solutions By 2,6-Bis[(Diphenyl)phosphinomethyl]pyridine *N,P,P′*-Trioxide. *Solvent Extr. Ion Exch.* **1998**, *16*, 967−983.

(27) Williams, R. H.; Hamilton, L. A. Di-*n*-alkylphosphine Oxides. I. Synthesis. *J. Am. Chem. Soc.* **1952**, *74*, 5418−5420.

Scheme 1. Synthesis of TEH(NOPOPO)



Scheme 2. Synthesis of DEH(MNOPO)



n-alkyl substituted derivatives of ligand **2**.[17] As anticipated, both **2** and **4** show good solubility in hexane, heptane, and higher molecular weight aliphatic solvents.

Nitric Acid Partitioning. We learned early in this investigation that (not unexpectedly) TEH(NOPOPO) extracts HNO_3 into *n*-dodecane. To satisfy our objective of fully characterizing the thermodynamics of the Am and Eu nitrate phase transfer reactions, it was therefore necessary to first investigate the thermodynamics of two-phase equilibria describing the interactions of HNO_3 with TEH(NOPOPO). The appropriate equilibrium constants were defined by investigating the partitioning of HNO_3 between aqueous solutions and 0.1 M TEH(NOPOPO) in *n*-dodecane as a function of temperature and of HNO_3 molarity. Isotherms for HNO_3 distribution into 0.1 M TEH(NOPOPO) in *n*-dodecane are shown in Figure 2. At aqueous nitric acid concentrations above 1 M, splitting of the organic phase into the heavy and light fractions was observed; hence, the data are terminated at this concentration. This third phase formation occurs at the approximate 1:1 mole ratio of $[HNO_3]_{org}$ to $[TEH(NOPOPO)]_{total}$.

The best fits of the isotherms were obtained by assuming that both 1:1 (TEH(NOPOPO)·HNO_3) and 1:2 (TEH(NOPOPO)·$2HNO_3$) complexes are present in the *n*-dode-

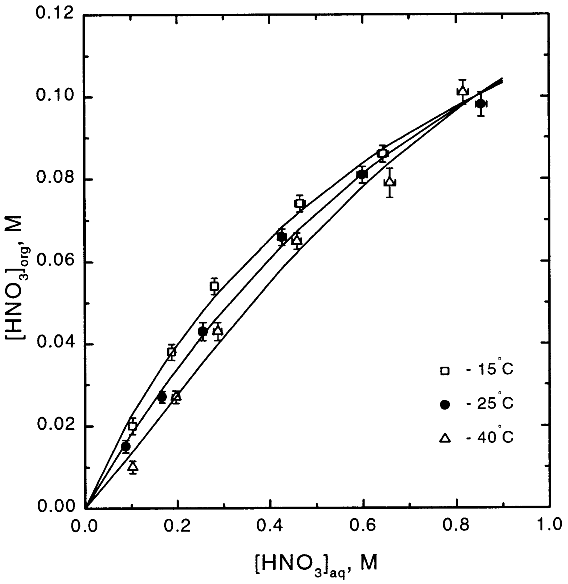


Figure 2. Extraction of HNO_3 into 0.1 M TEH(NOPOPO) in *n*-dodecane at the different temperatures. Lines represent the least-squares fits of the data.

Table 1. Temperature-Dependent Equilibrium Constants and Thermodynamic Parameters for HNO_3 Transfer into *n*-Dodecane by TEH(NOPOPO)

temp, °C	K_1	K_2	% of free TEH(NOPOPO) for 0.5 M HNO_3
15	2.57 ± 0.22	1.45 ± 0.15	42.2
25	1.85 ± 0.20	1.35 ± 0.12	48.3
40	1.24 ± 0.21	1.44 ± 0.12	55.0

equilibrium	Δ*G*, kJ/mol	Δ*H*, kJ/mol	Δ*S*, J/(mol K)
NOPOPO + HNO_3 = NOPOPO·HNO_3	−1.53 ± 0.28	−21.8 ± 0.8	−68 ± 3
NOPOPO + HNO_3 = NOPOPO·2HNO_3	−0.79 ± 0.22	+0.40 ± 2.45	+4 ± 8
NOPOPO·HNO_3 + HNO_3 = NOPOPO·2HNO_3	+0.74 ± 0.34	+22.0 ± 1.4	+71 ± 5

cane phase. The following equation was used to fit the isotherms for nitric acid extraction at each temperature:

$$[HNO_3]_{org} = \frac{[TEH(NOPOPO)]_{total}(K_1[HNO_3]_{aq} + 2K_2[HNO_3]_{aq}^{\ 2})}{1 + K_1[HNO_3]_{aq} + K_2[HNO_3]_{aq}^{\ 2}} \quad (1)$$

Here K_1 (=[TEH(NOPOPO)·HNO_3]/[TEH(NOPOPO)]·[HNO_3]) and K_2 (=[TEH(NOPOPO)·2HNO_3]/[TEH(NOPOPO)][HNO_3]^2) represent respectively the overall equilibrium constants for the extraction of 1 and 2 molecules of HNO_3 by a single TEH(NOPOPO) molecule. The equilibrium constants derived from nonlinear least-squares analysis of the data are presented in Table 1 along with the respective enthalpies and entropies obtained by applying the van't Hoff relationship to the equilibrium constants determined as a function of temperature. To match the conditions of these experiments with those of the metal ion distribution experiments performed at various temperatures from 0.5 M HNO_3, these experiments were necessarily done without control of the ionic strength. Considering this limitation in our experiments, the quality of the fits of the data is acceptable.

The thermodynamic data indicate that extraction of one molecule of HNO_3 is driven by an exothermic enthalpy but opposed by an unfavorable (negative) entropy. In contrast, the stepwise addition of a second HNO_3 molecule to TEH(NOPOPO)·HNO_3 is clearly entropy driven, though opposed by an endothermic enthalpy. FTIR spectra of TEH(NOPOPO) solutions containing stoichiometric ratios of nitric acid molecules appear to indicate association of the HNO_3 molecules only with the P═O groups of the extractants. Vibrational frequency of the pyridine N−O band in the free TEH(NOPOPO) and (TEH(NOPOPO)·1,2HNO_3 solvates was found to be invariant.

Rozen and co-workers previously reported on the thermodynamics of extraction of nitric acid by alkylenediphosphine dioxides ($R_2P(O)(CH_2)_nP(O)R_2$) into dichloroethane.[28] These results differ from the present work in that (1) the bridges between the phosphine oxide groups are normal alkanes (rather than 2,6-dimethylpyridine) and (2) the solvent (dichloroethane) has some tendency to solubilize HNO_3 in the absence of the extractant. From the temperature dependence of the phase transfer reactions, they reported values for Δ*H* of extraction of HNO_3 by *P,P,P′,P′*-tetraoctylmethylenediphosphine dioxide (TOMDPO), *P,P,P′,P′*-tetrabutyl-1,6-hexylenediphosphine dioxide (TBHDPO), and tri-*n*-octylphosphine oxide (TOPO) as a function of [HNO_3]/[extractant]. Rozen and co-workers did not fully resolve the extraction data, preferring to report composite enthalpies that varied with [HNO_3]. At low nitric acid loading, which we assume represents thermodynamic data for a 1:1 complex, their data indicate $\Delta H_{TOMDPO} = -40.0$ kJ/mol, $\Delta H_{TBHDPO} = -48.7$ kJ/mol, and $\Delta H_{TOPO} = -47.0$ kJ/mol with less exothermic values for each of these parameters at higher ratios of [HNO_3]/[extractant]. We interpret the reduced exothermicity at higher ratios to indicate that a second molecule of HNO_3 is extracted in a moderately endothermic process.

Our observations in the TEH(NOPOPO)/*n*-dodecane system produce a pattern similar to that reported by Rozen, though the absolute values for these enthalpies are significantly smaller than those reported by Rozen. This difference is most likely attributable to the combined effects of the different solvating properties of the solvents and of the different basicities of the P═O groups induced by the bridge between the phosphine oxides. The enthalpy change associated with extraction of the first molecule of nitric acid in the present study is actually quite similar to that reported previously for the system HNO_3/CMPO-*n*-dodecane ($\Delta H_{ex} = -22.8$ kJ/mol[29]). Curiously, the free energies (Δ*G*) for the extraction of the first HNO_3 molecule are comparable in all three systems (NOPOPO, CMPO, and DPO).

Since the CMPO investigation and this study were conducted in the same weakly interacting solvent, this result

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(28) Rozen, A. M.; Berkman, Z. A.; Bertina, L. E.; Denisov, D. A.; Zarubin, A. I.; Kossikh, V. G.; Nikolotova, Z. I.; Pisareva, S. A.; Yudina, K. S. Extraction of Nitric Acid with Alkylenediphosphine Dioxides. *Radiokhimiya* **1976**, *18* (4), 493−501.

(29) Spencer, B. B.; Counce, R. M.; Egan, B. Z. Extraction of Nitric Acid from Aqueous Media with OΦD(iB) CMPO−*n*-dodecane. *AIChE J.* **1997**, *43* (2), 555−564.

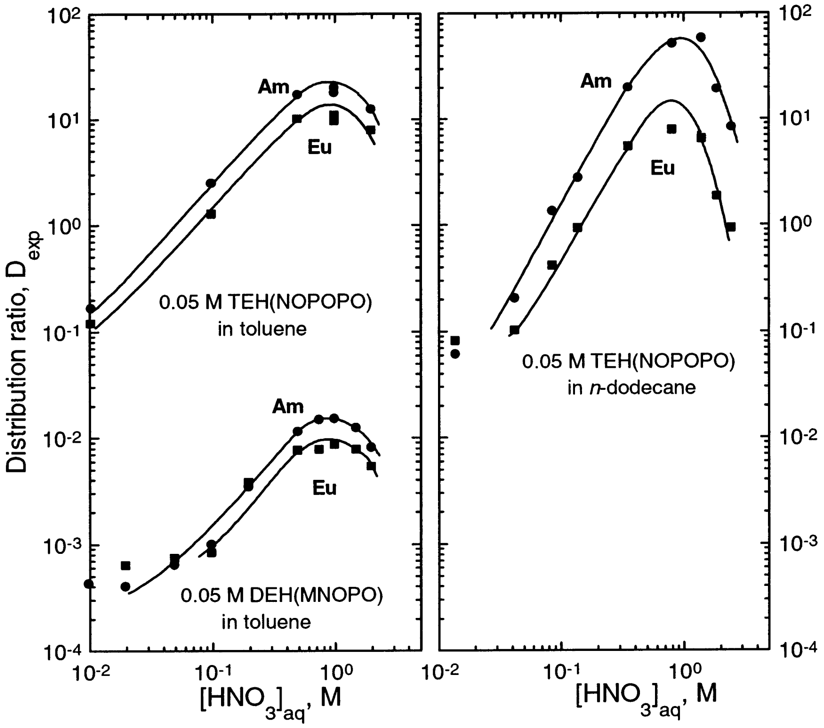

Figure 3. Dependence of the Am and Eu distribution ratios on nitric acid concentrations into TEH(NOPOPO) and DEH(MNOPO) in toluene and *n*-dodecane at 25.0 °C. Solid lines are designed only to assist in demonstrating trends. They are not derived from application of any fitting procedure.

suggests that the basicities of the phosphoryl oxygens in TEH(NOPOPO) and CMPO are comparable. On the basis of the analogy with the Rozen data, the endothermic ΔH observed for addition of the second HNO_3 to TEH(NOPOPO)·HNO_3 appears to be a consistent feature of HNO_3 extraction by bis(phosphine oxides). The origin of the energy penalty implied in this result is not immediately obvious. The intrinsic interaction between the phosphine oxides and the bound HNO_3 molecules is a single hydrogen bond (whether for the first or second HNO_3 bound); steric crowding does not appear to be an issue (at least in the TEH(NOPOPO) system), and there is no obvious reason to expect electrostatic repulsion between the bound HNO_3 molecules. Because a 1:2 complex was implied by the data of Rozen on the *mono*phosphine oxide TOPO, it is possible that the 1:2 solvate in each case may represent the extraction of a dimer of HNO_3.

Extraction of Americium and Europium from Nitric Acid. To assess the relative strength and selectivity of TEH(NOPOPO) and DEH(MNOPO) for trivalent actinides and lanthanides in nitrate medium, distribution ratios of americium and europium were measured as a function of nitric acid concentration. Our first attempts at creating a DEH(MNOPO) solution in n-dodecane resulted in the formation of a third phase upon contact of the organic solution with HNO_3 during preequilibration. The comparison of extraction strength thus was performed for 0.05 M TEH(NOPOPO) and DEH(MNOPO) solutions in toluene. Phase splitting is known to be most problematic in normal alkanes. For comparison, the extraction of both metals into a solution of TEH(NOPOPO) in *n*-dodecane was also examined The results of these experiments are shown in Figure 3. In all systems an increase of the distribution ratio is observed up to ~1 M aqueous nitric acid concentration. The acid dependence is steeper both before and after the maximum distribution ratio (at about 1.0 M HNO_3) in the *n*-dodecane solution than in toluene, though the highest distribution ratios for extraction by TEH(NOPOPO) into *n*-dodecane and toluene are quite similar. The limiting slopes of these plots for the range of HNO_3 concentrations from 0.01 to 1.0 M are about 1.2 in toluene and about 1.9 in *n*-dodecane. The difference in these slopes in the two solvents could indicate lower metal:ligand stoichiometry in the extracted complexes in toluene but is more likely due to differences in the distribution of HNO_3 into *n*-dodecane vs toluene. The decline in the metal ion distribution ratio at $[HNO_3]$ above 1 M is due to increased competitive extraction of HNO_3.

Throughout the range of 0.01 M ≤ $[HNO_3]$ ≤ 2.0 M, the distribution ratios for $Am(NO_3)_3$ and $Eu(NO_3)_3$ into TEH(NOPOPO) remain nearly 10^3 larger than for DEH(MNOPO). In fact, the extraction of these metal nitrates by DEH(MNOPO) is substantially weaker than has been reported for trioctylphosphine oxide (TOPO)[30] or for monocoordinate (P═O bound) CMPO. One interpretation of this result is that the pyridine *N*-oxide group is a comparatively weak donor in these solutions, as one should not expect so large a difference between bidentate and tridentate complexants of similar geometries. It is also apparent that the pyridine *N*-oxide either provides a steric impediment to P═O binding or reduces the basicity of the P═O oxygen (through inductive effects) to reduce its affinity for the metal ions (though the

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(30) Martin, B.; Ockenden, D. W.; Foreman, J. K. The Solvent Extraction of Plutonium and Americium by Tri-*n*-Octylphosphine Oxide. *J. Inorg. Nucl. Chem.* **1961**, *21*, 96−107.

HNO_3 extraction behavior of TEH(NOPOPO) discussed above would appear to argue against the latter explanation). We are presently conducting infrared and NMR spectroscopic investigations of this unexpected observation to develop a clearer understanding of the bonding characteristics of this system. It is also worth noting that $Am(NO_3)_3$ distribution ratios for TEH(NOPOPO) (0.05 M) in $CHCl_3$ continue to increase from 1 to 6 M HNO_3 before they decrease due to H^+ binding competition at higher concentrations of HNO_3. This is a common observation for extractants in hydrogen bonding solvents such as chloroform.

The investigation of the thermodynamics of the extraction of $Am(NO_3)_3$ and $Eu(NO_3)_3$ by TEH(NOPOPO) was conducted only in *n*-dodecane. To learn the stoichiometry of the predominant metal complex in the organic phase and to verify that this stoichiometry is constant over the range of temperatures investigated, experiments were conducted as a function of [TEH(NOPOPO)] at 0.5 M HNO_3 and at 0.5 M $NaNO_3$/0.001 M HNO_3. In principle, the extraction of a trivalent metal cation by a lipophilic complexant that solvates an electroneutral metal salt is described by the following general equation:

$$\log D_c = \log[D_{exp}(1 + \Sigma\beta_i[NO_3^-]^i)] = \log K_{ex} + 3 \log [NO_3^-] + n \log [extr] \quad (2)$$

Here D_{exp} is the experimentally measured value of the distribution ratio and D_c represents the distribution ratio after correction for the existence of aqueous nitrate complexes. If there are no complications in the experiments, distribution ratios measured at a constant extractant concentration should exhibit a slope of 3 in the plot of log D_c vs log $[NO_3^-]$. The correction for the aqueous complexes is typically applied using stability constants from the literature.[31] The best available data support the existence of only the 1:1 complexes $AmNO_3^{2+}$ ($\beta = 2.4$) and $EuNO_3^{2+}$ ($\beta = 2.7$). Higher order complexes are formed in the phase transfer reaction, but they exist only in the organic phase. For systems involving no competing extraction equilibria, a similar plot of log D_c as a function of log $[extr]_{anal}$ (at constant $[NO_3^-]$) should define the stoichiometry of the phase transfer reaction with respect to [extr]. In the present system, both corrections (HNO_3 extraction and aqueous nitrate complexation) must be made to define the stoichiometry of the metal complex in the organic solution.

A test of the validity of the corrections applied in two-phase distribution systems of this type would lie in a comparison of the slopes obtained in parallel experiments run in 0.5 M $NaNO_3$/0.001 M HNO_3 and 0.5 M HNO_3. In the 0.5 M $NaNO_3$/0.001 M HNO_3 experiments corrections for extraction of HNO_3 are unnecessary. The relationship between D_c and the concentration of TEH(NOPOPO) is demonstrated in Figure 4. The extractant dependencies derived from the slope of the log−log plots are 1.94 ± 0.11 for Am^{3+} extraction from 0.5 M $NaNO_3$/0.001 M HNO_3 and 1.89 ± 0.07 from 0.5 M HNO_3 and 1.99 ± 0.17 for Eu^{3+} extraction from 0.5 M $NaNO_3$/0.001 M HNO_3 and 1.78 ± 0.07 from 0.5 M HNO_3. Agreement between the slopes is acceptable and consistent with 1:2 (M:TEH(NOPOPO)) stoichiometry for both Am and Eu in the organic phase. If we apply a correction for extraction of HNO_3 by TEH-(NOPOPO), the plots overlap, as indicated by the dashed line in the figures.

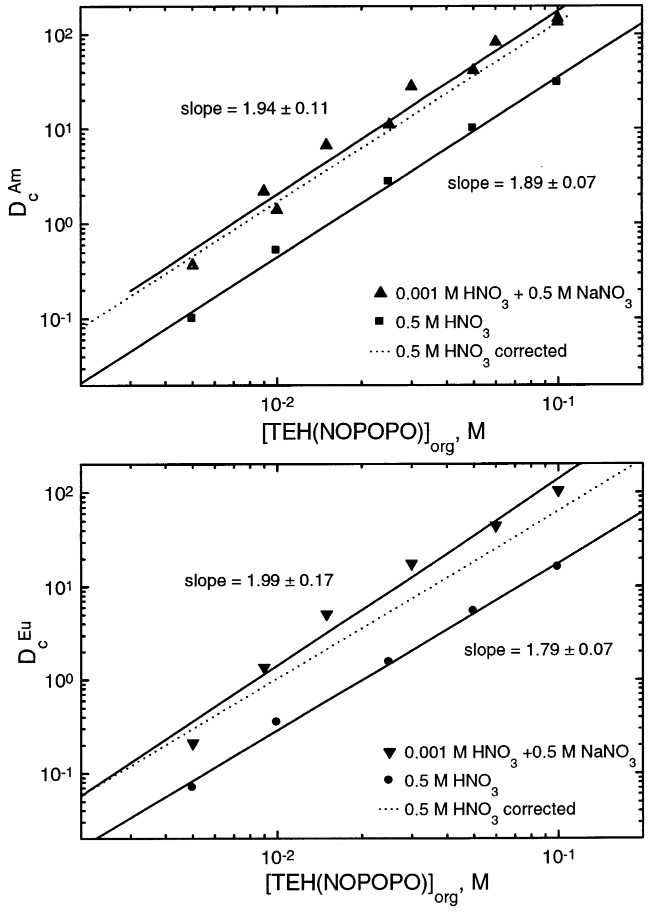

Figure 4. Dependence of the Am and Eu distribution ratios on TEH-(NOPOPO) concentrations in *n*-dodecane from 0.5 M HNO_3 and 0.5 M $NaNO_3$ at 25.0 °C. Lines represent the least-squares fits of the data. Dotted lines represent fits corrected for TEH(NOPOPO) association with HNO_3.

The plots of D_c for extraction of Am and Eu, corrected for the aqueous nitrate complexes and for the HNO_3 in the organic phase ($D_{corr} = D_{exp}(1 + \beta_1[NO_3^-])(1+K_1[HNO_3]_{aq} + K_2[HNO_3]_{aq}^2)^2$), as a function of $[HNO_3]$ are presented in Figure 5. The slopes of these plots are 3.04(±0.07) for Am^{3+} and 2.80(±0.05) for Eu^{3+}. The stoichiometry of the phase transfer reaction of Am(III) and Eu(III) into TEH(NOPOPO)/*n*-dodecane can be represented as follows:

$$M^{3+}_{aq} + 3NO_3^-{}_{aq} + 2TEH(NOPOPO)_{org} \rightleftharpoons (TEH(NOPOPO))_2{\cdot}M(NO_3)_{3\,org} \quad (3)$$

In the temperature variation experiments, electroneutrality of the lipophilic complex was assumed, implying that the nitrate dependence of the equilibrium constant for this reaction remained third power throughout. The dependence of the phase transfer reaction on $[TEH(NOPOPO)]_{cor}$ was

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(31) Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes Database*; NIST Standard Reference Database 46, Version 6.0; NIST: Gaithersburg, MD, 2001.

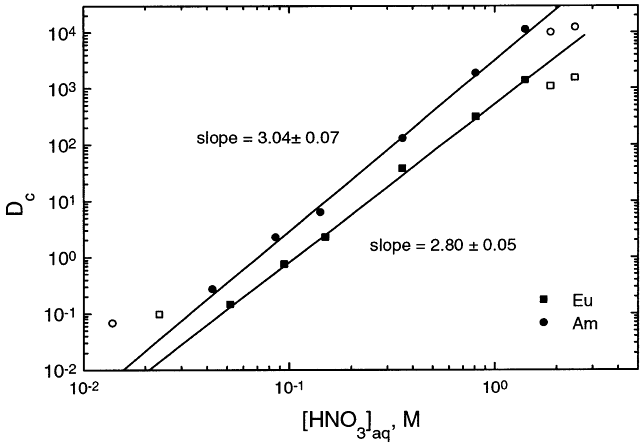

Figure 5. Acid dependence of Am and Eu distribution ratios corrected for TEH(NOPOPO) association with HNO_3 and nitrate ion complexation in the aqueous phase at 25.0 °C. $D_{corr} = D_{exp}(1 + \beta_1[NO_3^-])(1 + K_1[HNO_3]_{aq} + K_2[HNO_3]_{aq}^2)^2$. Lines represent the least-squares fits of the filled points.

determined experimentally at each temperature, after correction for distribution of HNO_3 between the phases using the thermodynamic parameters reported above. The average number of TEH(NOPOPO) molecules in the extracted complex was 1.85 ± 0.12 for Eu and 1.95 ± 0.14 and 1.97 ± 0.12 for Am extracted from 0.5 M HNO_3 and 0.5 M $NaNO_3$/0.001 M HNO_3, respectively. In the range of temperature from 15 to 45 °C the stoichiometry of the extracted species remained constant within these limits of experimental error.

Thermodynamics of Am^{3+} and Eu^{3+} Extraction. To resolve the thermodynamic parameters for the extraction of $Am(NO_3)_3$ and $Eu(NO_3)_3$ by TEH(NOPOPO), equilibrium constants for the phase transfer reaction shown in eq 3 were calculated at each temperature from the combined data sets. In all cases, the distribution data were corrected for the aqueous metal nitrate complexes and, in the 0.5 M HNO_3 experiments, for the extraction of HNO_3. The β_1 values for the NO_3^- complexation of europium(III) at different temperatures were estimated from the literature values[32] at $I = 0.5$ as $\log \beta_1 = 0.44 \pm 0.05$ at 25 °C and reported enthalpy ($\Delta H_1 = -4.6$ kJ/mol). Corresponding literature data for americium do not exist and were estimated according to approach implemented in ref 33. The two-phase equilibrium constants (as defined in eq 3) were calculated at each temperature and for each initial TEH(NOPOPO) concentration according to the following equation:

$$K_{ex} = \frac{D_{exp}(1 + \beta_1[NO_3^-]_{aq})(1 + K_1[HNO_3]_{aq} + K_2[HNO_3]_{aq}^2)^2}{[NO_3^-]_{aq}^3[\text{TEHNOPOPO}]_{org,initial}^2} \quad (4)$$

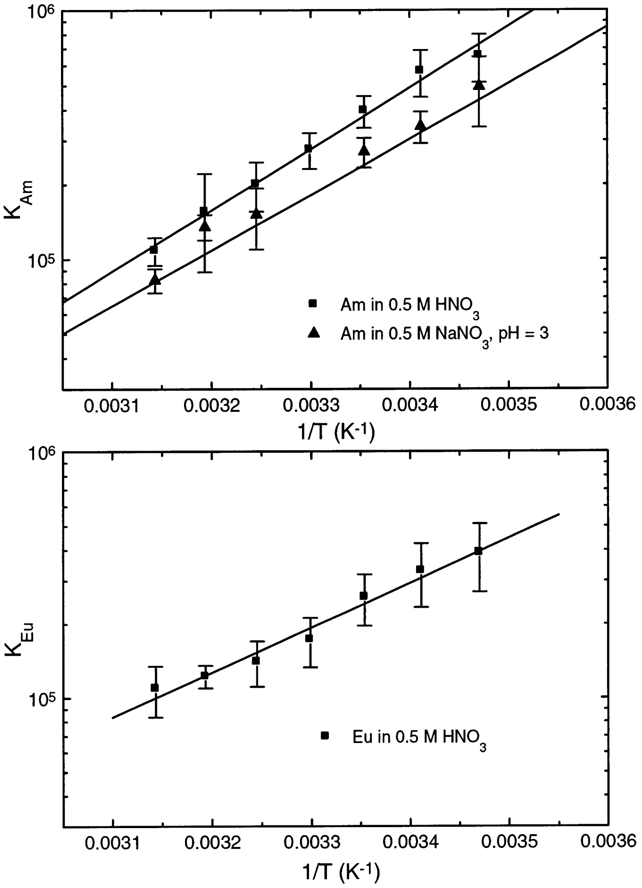

Figure 6. Van't Hoff relationships for Am and Eu extraction into 0.05 M TEH(NOPOPO) in *n*-dodecane.

Table 2. Thermodynamic Parameters for Am^{3+} and Eu^{3+} Extraction from Nitrate Medium by TEH(NOPOPO) in *n*-Dodecane at 25 °C

system	$[HNO_3]_{aq}$	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/(mol K)
$Am(NO_3)_3 \cdot 2TEH(NOPOPO)$	0.001 M	−31.0 ± 0.34	−42.6 ± 2.6	−39 ± 9
$Am(NO_3)_3 \cdot 2TEH(NOPOPO)$	0.5 M	−32.0 ± 0.36	−47.2 ± 2.0	−51 ± 7
$Eu(NO_3)_3 \cdot 2TEH(NOPOPO)$	0.5 M	−30.8 ± 0.60	−35.0 ± 2.4	−14 ± 8
$Am(NO_3)_3 \cdot 3CMPO$[33]	pH = 2.6	−32.18	−49.4	−58
$Eu(NO_3)_3 \cdot 3CMPO$[33]	pH = 2.6	−32.75	−64.5	−106

Here K_1 and K_2 denote the constants defining nitric acid distribution into TEH(NOPOPO) in *n*-dodecane and β_1 denotes the stability constant of metal complexation with nitrate ion in the aqueous phase. Average values for K_{ex} were determined as the mean of the values calculated as a function of [TEH(NOPOPO)] at constant temperature. With application of the van't Hoff relationship to these data (Figure 6), thermodynamic functions for Am(III) and Eu(III) extraction were calculated. The values of the thermodynamic parameters at 25 °C are shown in Table 2 along with the thermodynamic parameters for the extraction of $Am(NO_3)_3$ and $Eu(NO_3)_3$ by CMPO in *n*-dodecane that were reported previously.[33]

The free energies for extraction of $Am(NO_3)_3$ and $Eu(NO_3)$ by TEH(NOPOPO) and CMPO are nearly identical, though the stoichiometries of the dominant complexes in the organic phases differ in the two systems. The exothermic heats for the phase transfer reactions reported here are typical for f-element interactions with solvating extractants.[34] As indicated in eq 3 above, phase transfer reactions of this type result in substantial ordering of the system, despite the waters

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(32) Choppin, G. R.; Strazik, W. F. Complexes of Trivalent Lanthanide Ions. I. Outer-Sphere Ion Pairs. *Inorg. Chem.* **1965**, *4* (9), 1250−1254.

(33) Mathur, J. N.; Nash, K. L. Thermodynamics of Extraction of Am(III) and Eu(III) from Nitrate and Thiocyanate Media with Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine Oxide. *Solvent Extr. Ion Exch.* **1998**, *16* (6), 1341−1356.

of solvation released as the metal ion is transferred to the organic phase. This results in negative entropies, a feature generally consistent with phase transfer reactions of this type. The results for americium extraction in these two systems are nearly identical in all cases. The europium values in contrast show surprising variability. In the TEH(NOPOPO) system, enthalpy for Eu is less exothermic and entropy values are smaller than the corresponding Am values. In the CMPO system the opposite trend is seen.

Reports from the literature indicate that, in the CMPO−nitrate system, the extracted trivalent lanthanide or actinide nitrates contain three bidentate nitrates and three monodentate CMPO's, with the latter coordinated through the P=O group. A similar arrangement of donor groups could be postulated for the TEH(NOPOPO) system in light of the similar thermodynamic parameters. Our investigations of both the DEH(MNOPO) and the TEH(NOPOPO) and conclusions from the IR spectra of extracted nitric acid complexes seem to indicate at best a minor role for the pyridine *N*-oxide in these complexes in the solution phase (though this donor atom is clearly coordinated to the lanthanide ion in the solid state). To maintain an average inner-sphere coordination number of 9 for the trivalent cations in the TEH(NOPOPO) system, we can postulate in the extremes three bidentate nitrates and three donor atoms from the two TEH(NOPOPO) extractants or two tridentate TEH(NOPOPO)'s plus three monodentate nitrates. In the reported crystal structures,[15,17] a tridentate configuration of ligand donor atoms is most typically observed, incorporating one or fewer bidentate or monodentate nitrate counterions in the inner coordination sphere. It is also conceivable, in nonpolar solvents such as *n*-dodecane, that three bidentate nitrate ions and two bidentate TEH(NOPOPO) ligands make up the inner coordination sphere with the pyridine *N*-oxide group not participating in chelation. The thermodynamic data presented herein do not shed light on these fine details of the arrangement of donor atoms in the inner coordination sphere. We can only conclude, on the basis of the more negative entropies observed for the CMPO systems, that the 1:3:3 stoichiometry of the Eu−NO_3^-−CMPO system and the 1:3:2 stoichiometry indicated in the TEH(NOPOPO) systems are probably correct. The indications of this effect are much less clear-cut in the Am−NO_3^-−CMPO system. Perhaps the most telling argument in favor of a multidentate coordination mode for TEH(NOPOPO) is the 10^3 difference we see in the extraction strength of DEH(MNOPO) and TEH(NOPOPO). Overall, the thermodynamic parameters suggest that TEH(NOPOPO) might be expected to perform similarly to CMPO in an appropriate hydrometallurgical extraction scheme.

Molecular mechanics models constructed for the free extractant molecules (TEH(NOPOPO) and octyl(phenyl)-CMPO) appear to indicate that their molecular volumes are quite similar. Similar calculations of $Eu(NO_3)_3$ complexes (with methyl derivatives of the CMPO or NOPOPO employed to reduce the computation time) of the appropriate stoichiometry likewise provide no obvious reason to choose from among the various arrangements of donor atoms that are possible for the two systems. Equally good fits are provided by mono-, bi-, and tridentate tetramethyl derivative of NOPOPO's when accommodations are made to maintain constant coordination numbers by changing nitrate denticity.

Conclusion

Substitution of 2-ethylhexyl groups for phenyl groups on the efficient lanthanide coordination geometry represented by the NOPOPO class of extractant molecules clearly results in a lipophilic reagent with some promise as a possible substitute for CMPO in a TRUEX-like actinide partitioning process. Its ability to extract HNO_3, $Eu(NO_3)_3$, and $Am(NO_3)_3$, and its comparative compatibility with normal paraffinic hydrocarbons are all similar to those exhibited by CMPO. The simplicity of its symmetrical arrangement of ligand donor atoms serve to distinguish it from CMPO. Much like the symmetrical CMPO extractant employed in the Russian TRUEX process, this symmetry could translate into simpler synthesis procedures and ultimately into lower expense for the reagent.

The thermodynamic parameters describing the extraction of $Eu(NO_3)_3$, $Am(NO_3)_3$, and HNO_3 by TEH(NOPOPO) are likewise quite comparable to the corresponding parameters for extraction of these species by CMPO. Unfortunately, the thermodynamic parameters and spectroscopic observations made to date do not allow us to establish with certainty whether TEH(NOPOPO) is coordinated with these metal ions in a mono-, bi-, or tridentate coordination mode in solution. Several aspects of the behavior of TEH(NOPOPO) and DEH(MNOPO) appear to suggest that the N−O oxygen is a weak donor atom, at least for trivalent actinide and lanthanide cations in organic solutions. Overall, we perceive sufficient potential in this system to justify further studies of its applicability as an actinide partitioning reagent. We also are planning additional experiments to investigate the thermodynamics of these systems directly using titration calorimetry.

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