Extraction of Nitric Acid from Aqueous Media with OϕD(iB)CMPO-*n*-Dodecane

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A study of the extraction characteristics of nitric acid with octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide [OϕD(iB)CMPO or, simply, CMPO] was conducted. In the experimental program, CMPO was dissolved in n-dodecane to produce the organic extracting medium. The objectives of the project were to infer extraction stoichiometry and to estimate equilibrium constants for the extraction of nitric acid with the CMPO extractant.

Experiments were performed over a limited range of concentrations to avoid conditions favoring formation of a third phase. Aqueous nitric acid concentrations were limited to 0.30 M at 25°C, 1.0 M at 40°C, and 3.0 M at 50°C. The data indicate that CMPO extracts nitric acid with a 1:1 stoichiometry. The value of the equilibrium constant is estimated at 2.66 ± 0.09 at 25°C. The enthalpy of the extraction is estimated to be − 5.46 ± 0.46 kcal/mol.

Introduction

Production operations at many Department of Energy (DOE) sites throughout the United States have resulted in large inventories of stored radioactive wastes. Because disposal costs for transuranium-bearing wastes are exorbitant, it seemed prudent to examine final disposal options involving actinide removal so that the bulk of the waste could be disposed of by less expensive methods. For about a decade, the DOE has sponsored development of the transuranium extraction (TRUEX) process for removing the actinides from the waste. Development of this process and technical data for the process have been described by Horwitz et al. (1982, 1985), Vandegrift et al. (1984), Leonard et al. (1985, 1987), Schulz and Horwitz (1988), and Horwitz and Schulz (1990). Recent tests of the process to demonstrate removal of actinides from waste streams have been reported by Ozawa et al. (1992), Mathur et al. (1993), and Koma et al. (1993).

The TRUEX solvent is a mixture of octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and tri-*n*-butyl phosphate (TBP) in an organic diluent. Both tetravalent and hexavalent actinides are extracted by TBP and CMPO; however, CMPO also extracts trivalent actinides. The primary purpose of TBP in the mixture is to serve as a phase modifier to increase the capacity of the organic phase for nitrate without forming a second, heavy organic phase (i.e., a third phase). Two types of diluent are typically used for the TRUEX solvent: (1) a normal paraffin hydrocarbon (NPH) such as *n*-dodecane, in which the concentrations of CMPO and TBP are typically 0.2 and 1.4 M, respectively; and (2) tetrachloroethylene (TCE), in which the concentrations of CMPO and TBP are typically 0.25 and 0.75 M, respectively. More information is available about the extraction characteristics of the solvent in a TCE diluent; however, to eliminate the addition of chlorine to waste streams, use of NPH diluents is currently favored.

The extraction characteristics of CMPO are not as well understood as those of TBP. Most data reported in the literature are either from studies with the mixed TBP−CMPO solvent, making it necessary to separate the effects of each solvent mathematically, or from studies using a TCE diluent. It is important to understand the extent of extraction of nitric acid because it is present in the aqueous waste-bearing solutions requiring treatment. The extraction of uranyl nitrate and bismuth nitrate will be discussed in future articles.

Literature Review

General extraction equilibria and definitions

For the purposes of discussion, consider the general extraction equilibrium

$$M^{z+}\cdot(\mathrm{H_2O})_h + zX^- + nE \rightleftharpoons MX_z\cdot nE + h\mathrm{H_2O}, \tag{1}$$

where a hydrated salt is extracted by a general extractant, E, as an anhydrous salt with an accompanying release of the waters of hydration. The equilibrium constant may be written as

$$K = \frac{[MX_z\cdot nE]\gamma_{MX_z\cdot nE}(a_w)^h}{\gamma_{MX_z}^{(1+z)}[M^{z+}][X^-]^z[E]^n\gamma_E^n}, \tag{2}$$

where the brackets indicate concentrations and the activity coefficients of both aqueous and organic species are included. Separating the organic-phase activity coefficients from the righthand side of Eq. 2 and lumping them with the equilibrium constant as suggested by Chaiko and Vandegrift (1988) yields

$$K' = \frac{K\gamma_E^n}{\gamma_{MX_z\cdot nE}} = \frac{[MX_z\cdot nE](a_w)^h}{\gamma_{MX_z}^{(1+z)}[M^{z+}][X^-]^z[E]^n}. \tag{3}$$

The equilibrium constant, K', is the quantity calculated under the assumption that the organic phase is ideal. If the organic phase is ideal, then the activity coefficients of the organic species are unity and K' is equal to the true equilibrium constant, K. Otherwise, K' will vary with organic-phase activities, unless the ratio of these coefficients (as shown in Eq. 3) is constant. The equation also shows a strong effect of the waters of hydration. Even in systems where the activity of water deviates little from unity, a large value for the waters of hydration, h, can cause a significant effect on the equilibrium constant.

An important parameter in modeling extraction behavior is the coordination number, which is essentially the stoichiometry indicating the number of extractant molecules associated with the extractable salt in the organic phase (n in Eq. 1). It may also be expressed as the extractant:solute ratio.

Stoichiometry and equilibria constants

Extraction of nitric acid by 0.5 M CMPO in TCE was measured at 25°C and at various acid concentrations by Horwitz et al. (1987). Their data suggested that the stoichiometry was approximately 1:1; thus,

$$\mathrm{H^+_{(aq)}} + \mathrm{NO^-_{3(aq)}} + \mathrm{CMPO_{(org)}} \rightleftharpoons \mathrm{CMPO\cdot HNO_{3(org)}}. \tag{4}$$

Kolarik and Horwitz (1988) assumed that extraction of nitric acid was predominated by a 1:1 solvation of CMPO to permit calculation of the free CMPO concentration in their studies on the extraction of neodymium and the solubility of its CMPO solvate in solutions of dodecane-TBP. Later, Chaiko et al. (1988) made additional measurements on the extraction of nitric acid with 0.25 M CMPO–0.75 M TBP in TCE at 25°C. The effects of TBP on the distribution ratio were removed by separately modeling the extraction of nitric acid with TBP using data from the literature. It was suggested that the equilibrium

$$2\mathrm{H^+_{(aq)}} + 2\mathrm{NO^-_{3(aq)}} + \mathrm{CMPO_{(org)}} \rightleftharpoons \mathrm{CMPO\cdot 2HNO_{3(org)}} \tag{5}$$

should also be used in modeling the extraction when the nitric acid concentration is "moderately high." Further studies by Chaiko et al. (1989) at CMPO concentrations up to 1.0 M in TCE, at a temperature of 25°C, indicated that the extraction constant for Eq. 4, when used as part of the two-parameter model, increased linearly with CMPO concentration, suggesting a dimeric CMPO species. A third equilibrium,

$$\mathrm{H^+_{(aq)}} + \mathrm{NO^-_{3(aq)}} + 2\mathrm{CMPO_{(org)}} \rightleftharpoons \mathrm{(CMPO)_2\cdot HNO_{3(org)}}, \tag{6}$$

was added to the model. Activity coefficients of the aqueous-phase components were calculated using Bromley's method (Bromley, 1972, 1973). All three extraction constants, K', were evaluated by a nonlinear least-squares fit to the data. Extraction constants for CMPO in TCE at 25°C were estimated at 1.60 ± 0.04 for Eq. 4, 0.010 ± 0.001 for Eq. 5, and 1.66 ± 0.06 for Eq. 6. Chaiko et al. (1988) have pointed out that the extraction constants can be reevaluated for other systems, such as CMPO and TBP in dodecane, if the activity coefficients for both organic systems are known. This conclusion was based on the assumption that the true equilibrium constants, K, are independent of diluent type. Marcus (1989) describes the effects of diluents on extraction and the empirical diluent parameter used to quantify these effects as a function of diluent properties.

Extension of Slope-Analysis Method

The coordination number can be inferred from experiments in which the organic-phase extractant concentration is varied. The slope-analysis method, extensive use of which was first reported by Hesford and McKay (1958), is developed in the following way. Define a distribution ratio as the ratio of salt concentration in the organic phase to the concentration in the aqueous phase:

$$D = \frac{[MX_z\cdot nE]}{[M^{z+}]}. \tag{7}$$

Combine this definition with Eq. 2 and rearrange to obtain

$$D = \frac{K\gamma_{MX_z}^{(1+z)}[X^-]^z[E]^n\gamma_E^n}{\gamma_{MX_z\cdot nE}(a_w)^h}, \tag{8}$$

which may be expressed in logarithmic form as

$$\ln D = \ln K + (1+z)\ln \gamma_{MX_z} + z \ln[X^-] + n \ln[E] + n \ln \gamma_E - \ln \gamma_{MX_z \cdot nE} - h \ln a_w. \quad (9)$$

Because the extractant concentration is to be varied experimentally, with all other variables held constant, the effect of changing extractant concentration can be quantified by taking the derivative of each side of Eq. 9 with respect to ln $[E]$ to obtain

$$\frac{\partial \ln D}{\partial \ln[E]} = n. \quad (10)$$

Equation 10 implies that a log-log plot of the distribution ratio vs. the extractant concentration is a straight line whose slope is the coordination number. Noninteger slopes indicate more than one equilibrium or stoichiometry. Experimentally, variations in the distribution ratio necessarily mean the concentration of the extractable salt changes in at least one, and possible both, of the phases. This, together with the assumption that aqueous and organic activities are constant, makes Eq. 10 valid only for the limiting case of very dilute solutions where ideality is approached. Moyer and coworkers (1991) have critically reviewed the slope-analysis technique and have pointed out that the need to restrict concentrations to limiting cases may lead to questions regarding behavior at other conditions. They have also stated that "on the basis of equilibrium data alone, definitive identification of species and determination of equilibrium constants cannot be made without knowledge of organic-phase activity coefficients."

The slope-analysis method can be used to deduce the extraction stoichiometry when both the organic and aqueous phases approximate ideal conditions, or when the experimental conditions are such that the quantities involved are constant. Suppose that the coordination number, n, is known by other means (e.g., spectroscopic analysis) but the slope-analysis method gives different results. Further, suppose that all variables except the activity coefficients of the extractant can be quantified and are shown to be constant, that is, to have no effect on the slope-analysis results. Basically, this is the case where it is suspected that the organic phase is quite nonideal and the activity coefficients of the organic-phase components differ appreciably from unity. A general analysis begins with Eq. 8, which may be rewritten as

$$D' = \frac{D a_w^h}{\gamma_{MX_z}^{(1+z)}} = K[X^-]^z R_\gamma [E]^n, \quad (11)$$

where

$$R_\gamma = \left\{ \frac{\gamma_E^n}{\gamma_{MX_z \cdot nE}} \right\}. \quad (12)$$

Taking the logarithm of both sides of Eq. 11 to obtain

$$\ln D' = \ln K + z \ln[X^-] + \ln R_\gamma + n \ln[E] \quad (13)$$

and then taking the partial derivative with respect to ln [E] yields

$$\frac{\partial \ln D'}{\partial \ln[E]} = \frac{\partial \ln K}{\partial \ln[E]} + z\frac{\partial \ln[X^-]}{\partial \ln[E]} + \frac{\partial \ln R_\gamma}{\partial \ln[E]} + n. \quad (14)$$

By definition, K is constant, and the aqueous-phase anion concentration can be made constant experimentally. Therefore, Eq. 14 reduces to

$$\frac{\partial \ln D'}{\partial \ln[E]} = n + \frac{\partial \ln R_\gamma}{\partial \ln[E]}. \quad (15)$$

By supposition, the ordinary slope-analysis method, defined by Eq. 10, gives a different coordination number than expected. The data correlate strongly with a straight line, but the slope is not equal to the expected coordination number. This condition means that the rightmost term of Eq. 15 is a constant; that is,

$$\frac{\partial \ln R_\gamma}{\partial \ln[E]} = \omega, \quad (16)$$

and Eq. 15 may be written as

$$\frac{\partial \ln D'}{\partial \ln[E]} = n + \omega = n_s. \quad (17)$$

When the slope-analysis method gives a coordination number, n_s, and the true coordination number, n, is known, then the difference, ω, is a measure of the ratio of the organic-phase activity coefficients shown in Eqs. 12 and 16.

Because the slope-analysis method requires the extractant concentration to change, an expression for R_γ in terms of extractant concentration can be derived by integration of Eq. 16,

$$\ln R_\gamma = \omega \ln[E] + \text{constant}. \quad (18)$$

When $[E]$ approaches zero, the activity coefficients approach unity, and R_γ should approach unity. The form of Eq. 18 makes use of these boundary conditions difficult. If the extractant concentration is less than unity, the logarithmic term can be approximated by the Taylor series expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots, \quad (19)$$

which applies for absolute values of x less than 1. Truncating the series to only the first term permits Eq. 18 to be approximated by

$$\ln R_\gamma = \omega([E]-1) + \text{constant}, \quad (20)$$

which, upon substitution of the boundary conditions and rearrangement, yields

$$R_\gamma = e^{\omega[E]}. \quad (21)$$

This equation has the proper limiting value at zero extractant concentration, but is only an approximation. However, the approximation can be improved by selecting a value of ω different from that suggested by Eq. 17. Assuming that the exponential function adequately models the behavior of R_γ when the extractant concentration is low, Eq. 21 can be substituted into Eq. 11 and rearranged to obtain

$$\frac{D'}{K[X^-]^z[E]^n} = R_\gamma = e^{\omega[E]}. \tag{22}$$

Taking the logarithm of both sides of the equation and rearranging yields

$$\ln d \equiv \ln\left\{\frac{D'}{[X^-]^z[E]^n}\right\} = \omega[E] + \ln K. \tag{23}$$

When the coordination number, n, may be parametrically selected or inferred by other means, the term in braces can be evaluated. A semilog plot of the term in braces vs. $[E]$ is a straight line with slope equal to ω and intercept K. Equation 23 together with Eq. 21 provide the means to explore the effect of organic-phase activity coefficients on slope analysis and to obtain an estimate of the true equilibrium constant. This type of analysis does not appear in the literature. It will be convenient to refer to Eq. 23 as the extended slope-analysis method.

Description of Experiments

Apparatus

A laboratory glove box with an internal volume of ~ 0.32 m^3 (11.2 ft^3) was used to prepare atmosphere-sensitive reagents and to maintain a controlled temperature during our extraction tests. Purified CMPO crystals were observed to slowly liquefy on contact with air, presumably due to absorption of moisture. CMPO was weighed in a dry, nitrogen atmosphere maintained in the glove box.

Contact of the aqueous and organic phases, separation of the phases, and sampling of the phases were performed at a controlled temperature in each case. The air contained in the glove box was used as a controlled-temperature bath. The temperature in the glove box was measured by a digital temperature controller using a wire-wound, air-sensing (baffled-shield) platinum resistance-temperature device (RTD). The controller regulated the power fed to wire-wound electric resistance heaters located in the box, in a time-proportioning mode. A small electric fan continuously circulated the air inside the box over the heaters. Control of the temperature to within about 0.1°C was achieved.

Reagents

Reagent-grade chemicals were purchased for use in the extraction tests and in purification of the CMPO extractant. All chemicals except the CMPO were used as received. Ultrapure water was prepared by distillation and demineralization with an ion-exchange resin; it had a measured resistance of ≥ 17.7 MΩ/cm.

CMPO with a purity of 95–97% was purchased from ATOCHEM North America, Philadelphia, PA. The CMPO was purified according to a procedure developed by Gatrone et al. (1987) and Tse and Vandegrift (1989), with modifications supplied by Vandegrift (1993). The essential purification steps included (1) dissolving the CMPO in n-heptane, (2) filtering the resulting solution, (3) vigorously mixing Amberlyst A-26 (Rohm and Haas Company) anionic resin that had been converted from the Cl^- to the OH^- form and Dowex AG MP-50 (Dow Chemical Company) cationic resin with the solution to remove charged particles, (4) filtering the solution to remove the resin particles, (5) washing the organic solution with aqueous sodium carbonate solution, (6) washing the organic again with mild aqueous nitric acid, (7) washing the organic with ultrapure water, (8) drying the organic with anhydrous sodium sulfate, (9) vacuum-evaporating about two-thirds of the n-heptane from the solution, (10) cooling the solution to allow the CMPO to crystallize, (11) grinding the crystals, and (12) drying the crystals under vacuum. The purified CMPO was analyzed using high-performance liquid chromatography (HPLC) with the detector set at an absorbance wavelength of 222 nm, as recommended by Tse and Vandegrift (1989). The purity was greater than 99.4%.

Procedures

Aliquots of organic extractant were preequilibrated with equal (or greater) volumes of aqueous nitric acid having the same concentration as the final aqueous acid for which distributions were to be measured. Three preequilibrations were performed before the final, equal-volume contact. Mixing times from 15 s to 4 min appeared to make no difference in the measured distribution ratios, so 60 s was selected as the standard mixing time. A settling time of 10 min was selected because longer settling times did not affect the results.

Analyses of samples

The nitric acid concentration of each aqueous sample was measured using Environmental Protection Agency (EPA) Acidity (Titrimetric) Method 305.2, which uses a standardized 0.02 N sodium hydroxide solution as the titrant. The end point of the titration, which occurs at pH 8.3, was determined using a pH meter (resolution, ±0.01 pH unit). Measurement of the titrant was within 0.1 mL, and an error of ±5% was estimated from laboratory results.

Acid in the organic phase was measured by using essentially the same technique and the same equipment. A 1-mL aliquot of sample was dissolved in 50 mL of anhydrous methanol. The resulting solution was then titrated with a standardized 0.02 N sodium hydroxide–methanol solution to pH 8.3.

In an attempt to explore the coextraction of water, the water content of the organic phase was determined in accordance with ASTM Method E-1064, coulometric Karl Fischer titration. However, significant scatter in the results, coupled with the small concentrations of extracted salts that might affect water extraction, resulted in a decision to abandon this effort.

Results and Discussion

Equilibrium concentrations of nitric acid distributed between a CMPO–n-dodecane organic phase and a nitric acid aqueous phase were measured primarily at 25°C and 40°C; a few experiments were performed at 50°C. Aqueous concentrations of nitric acid were restricted to low values to prevent formation of a third phase. Higher working temperatures permitted higher concentrations to be used. Most experiments were performed with organic-phase CMPO concentrations of 0.20 M; some experiments, however, were performed at lower CMPO concentrations to provide slope-analysis data. Equilibrium constants were inferred by fitting the data to mathematical models. Activity coefficients for aqueous phase species were calculated using Pitzer's method (Pitzer, 1973, 1991). Densities of aqueous solutions were calculated using tabulated partial molar volumes (see Millero, 1971), and were used to convert activity coefficients between the molal- and molar-scales.

Third-phase formation

The solubility of CMPO-extract complexes in *n*-dodecane is limited and leads to a CMPO-rich third phase when the solvent is sufficiently loaded. Equilibrium concentrations of aqueous nitric acid producing a third phase were bracketed experimentally. Table 1 gives the nitric acid concentration ranges in which a third phase forms as a function of temperature. The lower value of each range represents the highest nitric acid concentration at which no third phase was observed. A third phase was noted at the higher value, the next incremental increase in concentration tested. The third-phase material appeared at the organic-aqueous interface and was slightly yellow in color. At concentrations higher than those listed in Table 1, where greater quantities of third phase formed and could be observed more easily, the third-phase material appeared more viscous and adhered more strongly to the wall of the glass container than either of the other two phases. Formation of the third phase strongly affected phase-separation behavior. When no third phase was formed, the aqeuous and organic phases separated quickly (< 2 min) and were completely clear. Under conditions promoting third-phase formation, the bulk phases separated rapidly; however, the organic phase remained cloudy for an extended period (sometimes > 30 min). The lower limits of the ranges shown in Table 1 were therefore the upper limits of the acid concentrations where distribution ratios were measured free of third-phase effects.

Stoichiometry by slope analysis

Experiments were performed at organic-phase CMPO concentrations of 0.05, 0.10, and 0.20 M to support slope-analysis estimation of the nitric acid extraction stoichiometry. At a temperature of 25°C, a nominal aqueous acid concentration of 0.25 M was used to ensure measurable quantities of acid in the organic phase. At 40°C, the nominal aqueous acid concentration was approximately 0.51 M. These data, along with the calculated distribution ratios, are summarized in Table 2 and plotted in Figure 1 on log-log coordinates as suggested by Eq. 10. Linear regression was used to calculate the slopes of the best straight lines through the data, which are also shown in the figure. At 25°C, the slope of the line is 1.076 ± 0.140 with a correlation coefficient of 0.9990. At 40°C, the slope is 1.065 ± 0.054 with a correlation coefficient of 0.9996.

Table 1. Nitric Acid Concentration Range Wherein a Third Phase Forms

Temp. (°C)	Nitric Acid Conc. (M)
25.0	0.30–0.50
40.0	0.94–1.00
50.0	3.0–4.0

Table 2. Slope-Analysis Data for the Extraction of Nitric Acid

CMPO (M)	Aqueous Phase (M)	Organic Phase (M)	Distribution Ratio O/A*
At 25°C			
0.200	0.252	0.018	0.0714
0.200	0.254	0.017	0.0669
0.100	0.257	0.008	0.0311
0.100	0.257	0.0084	0.0327
0.050	0.256	0.004	0.0156
0.050	0.258	0.004	0.0155
At 40°C			
0.200	0.518	0.044	0.0849
0.200	0.508	0.042	0.0827
0.200	0.522	0.044	0.0843
0.100	0.519	0.021	0.0405
0.100	0.521	0.020	0.0384
0.050	0.518	0.010	0.0193
0.050	0.522	0.010	0.0192

*More significant figures in the distribution ratio are retained than is warranted by the data to prevent round-off from affecting subsequent calculations.

Before these results could be accepted, possible corrections to the slope-analysis method needed to be addressed. The variables under consideration are shown in Eq. 8. In each of the two sets of experiments, the equilibrium constant, aqueous nitric acid concentration, and aqueous nitric acid activity coefficient were constant, either by definition or by experimental conditions and did not need to be considered further. The free CMPO concentration was calculated by subtracting the quantity of CMPO complexed with acid from the initial CMPO concentration. The amount of CMPO complexed with acid is the product of the organic acid concentration and the solvation number. The correction was largest when the solvation number was largest. Assuming the solvation number to be unity, corrections to the free CMPO con-

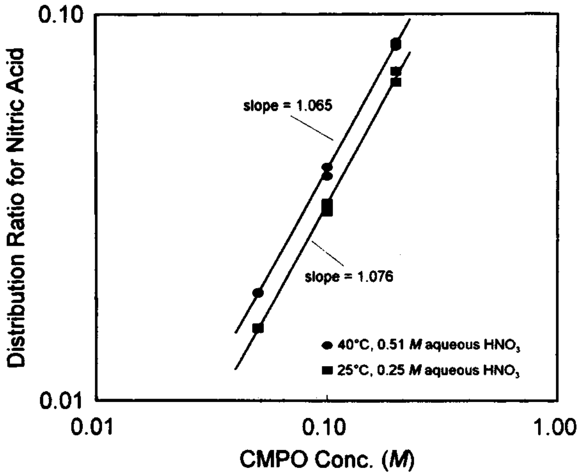

Figure 1. Extraction stoichiometry for the complexation of nitric acid with CMPO.

centration changed the ln D-vs.-ln [CMPO] slopes to 1.082 (correlation coefficient of 0.9988) and 1.081 (correlation coefficient of 0.9992) for data at 25 and 40°C, respectively. This represents essentially no change. If the solvation number were 2, the slopes would become 1.089 (correlation coefficient of 0.9986) and 1.110 (correlation coefficient of 0.9985) at 25 and 40°C, respectively. Again, this represents no appreciable change.

One last term in Eq. 8, the ratio of the activity coefficients of free CMPO and the nitric acid solvate, could affect the slope analysis. No data on activity coefficients are available for the CMPO-n-dodecane system. However, from the work of Diamond et al. (1986), it is known that the activity coefficients for CMPO in toluene are only slightly different for organic phase equilibrated with pure water as compared with organic equilibrated with 0.5 M nitric acid; the activity coefficient is smaller when the organic is equilibrated with acid. This suggests, for a solvation number of unity, little need for correction since the ratio of activity coefficients for organic-phase CMPO species in Eq. 8 is approximately unity. On the other hand, at a solvation number of 2, the stated ratio varied directly with the CMPO concentration. The molar-scale activity coefficients read from the graph in the paper by Diamond et al. are approximately 0.98, 0.96, and 0.92 for CMPO concentrations of 0.05, 0.10, and 0.20 M, respectively. Correcting the distribution ratio by moving the ratio of the activity coefficients of the CMPO species to the lefthand side of Eq. 8 and reanalyzing the data gave slopes of 1.121 (with correlation coefficient of 0.9989) and 1.110 (with correlation coefficient of 0.9998) for data at 25 and 40°C, respectively.

None of the corrections to the slope analysis significantly changed the solvation numbers derived from the raw data. Since the slope is slightly larger than unity, it might be argued that a disolvate is also formed with a relatively small yield. However, the data presented here show that nitric acid forms primarily a unisolvate with CMPO; that is, the 1:1 stoichiometry of Eq. 4 prevails.

Degree of nonideal behavior of organic phase

The extended slope-analysis method was used to investigate the ratio, R_γ, of the activity coefficients of the free CMPO and the CMPO–nitric acid solvate. Because the slope-analysis method strongly suggested a solvation number of 1:1, Eq. 23 could be written as

$$\ln d_{1:1} = \ln\left\{\frac{D'_{1:1}}{[\mathrm{NO_3^-}][\mathrm{CMPO}]}\right\} = \omega[\mathrm{CMPO}] + \ln K_{1:1} \qquad (24)$$

for the extraction of nitric acid. The subscript 1:1 is a reminder of the assumed extraction stoichiometry.

Linear regression was used to compute the best values of the slope and intercept fitting Eq. 24 to the slope-analysis data given in Table 2. These values, along with a correlation coefficient, are recorded in Table 3. The data and the best straight-line fit to the data are illustrated in the semilog plot of Figure 2. The correlation coefficients indicate a moderately good fit. On the other hand, the model does not provide as good a fit as does the usual slope-analysis method to the raw data. This indicates that the activity coefficient ratio, R_γ, is not well modeled by an exponential function and that the estimations of the ratio may be somewhat in error. At a CMPO concentration of 0.20 M, the values of ω in Table 3 give values of R_γ (see Eq. 21) of 1.21 and 1.22 at 25 and 40°C, respectively. Ratios greater than unity imply that the activity coefficient of the CMPO–nitric acid solvate is less than the activity coefficient of the free CMPO. Such results agree with the measurements of Diamond et al. (1986).

Table 3. Extended Slope-Analysis Results for the Extraction of Nitric Acid

Temp. (°C)	ω	$K_{1:1}$	Correlation Coefficient
25.0	0.9554	2.217	0.8830
40.0	1.016	1.642	0.9282

Values of the equilibrium constants given in Table 3 are those associated with infinite dilution of the organic extractant. Equilibrium constants that include the effects of organic-phase nonideality, $K'_{1:1}$, may be evaluated by multiplying $K_{1:1}$ by R_γ, as shown by comparing Eqs. 3 and 12. At a CMPO concentration of 0.02 M, values of $K'_{1:1}$ were 2.68 and 2.01 at 25 and 40°C, respectively. These values compare remarkably well with those calculated by other methods in the following section.

Equilibrium constants for extraction of nitric acid

Equilibrium concentrations for nitric acid partitioned between an aqueous phase and an organic phase consisting of 0.2 M CMPO in n-dodecane were measured at three different temperatures: 25, 40, and 50°C. The resulting data are given in Table 4. Data taken at 25 and 40°C contain some duplicate points from which the estimated standard deviation for measured organic nitric acid concentration was found to be 0.00141 M. (More significant digits are given here than are justified so that the effects of roundoff are reduced.) Only a

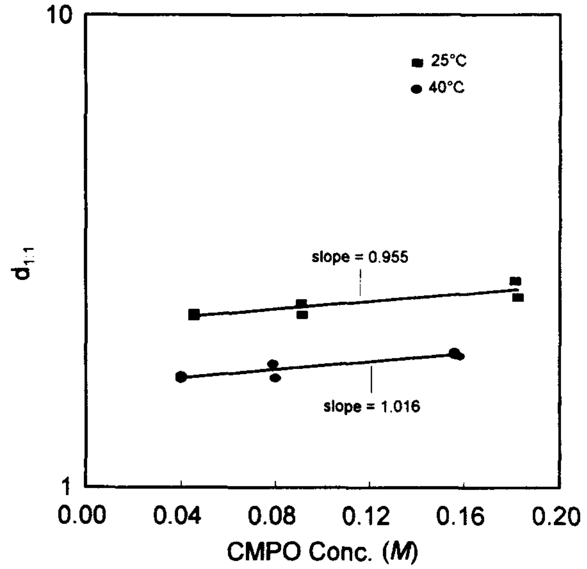

Figure 2. Extended slope-analysis method for the extraction of nitric acid with CMPO-n-dodecane.

Table 4. Equilibrium Concentrations of Nitric Acid with 0.20 M CMPO in *n*-Dodecane from Extraction Experiments

Aqueous Phase (M)	Organic Phase (M)	Distribution Coefficient O/A*
At 25°C		
0.053	0.002	0.0377
0.102	0.002	0.0196
0.104	0.004	0.0385
0.202	0.014	0.0693
0.206	0.012	0.0583
0.252	0.018	0.0714
0.254	0.017	0.0669
0.296	0.024	0.0811
0.302	0.022	0.0728
At 40°C		
0.046	0.001	0.0217
0.116	0.003	0.0259
0.200	0.010	0.0500
0.236	0.010	0.0424
0.508	0.042	0.0827
0.518	0.044	0.0849
0.522	0.044	0.0843
0.756	0.062	0.0820
0.830	0.081	0.0864
0.910	0.086	0.0945
0.938	0.091	0.0970
At 50°C		
1.00	0.054	0.0540
1.85	0.146	0.0789
2.76	0.179	0.0649

*More significant figures in the distribution ratio are retained than is warranted by the data to prevent round-off from affecting subsequent calculations.

few points were taken at 50°C because the test at this temperature was conducted primarily to find the region of third-phase formation.

Nonlinear regression was used to fit the data obtained at 25 and 40°C to mathematical models based on equilibria shown in Eqs. 4, 5, and 6; refer to papers by Chaiko et al. (1988) and Spencer (1994) for the form of such models. The data at 50°C were not treated in this manner because of the small number of data points and because one of those (1.00, 0.054) appears to be in error (organic nitric acid concentration was too low). The parameters of the regression are the equilibrium constants, K', on the molar-concentration scale. Molar-concentration units are used because the chemical analyses of the samples are on that basis and because of a general lack of density data for the multicomponent organic phase with which to convert to other concentration units. The organic-phase densities were measured for six samples and, within the measurement error, were not significantly different from that of pure *n*-dodecane. Density changes caused by extraction of nitric acid were small, probably because of the small amount of material transferred to the organic.

Although the slope-analysis method indicates that the extraction stoichiometry is 1:1, the data were fit to every combination of the three stoichiometries shown in Eqs. 4, 5, and 6. The results of these calculations are presented in Table 5. Each model is identified by the species formed. Values of the equilibrium constant for the species formed are listed directly under it, along with a value for the standard deviation in the equilibrium constant.

It should be noted that some equilibrium constants in Table 5 are negative. These negative values resulted because of our choice to impose no constraint that the parameters should be positive. Negative values can be used as an indicator that a particular stoichiometry adversely affects the model. For each model, two figures of merit are given: the weighted residuals squared, χ^2, and the standard deviation, σ, which are described by Press et al. (1992) and Wadsworth et al. (1990),

Table 5. Comparison of Models Describing the Extraction of Nitric Acid: Model Statistics, Model Parameters and Standard Deviations of Model Parameters

Temp. (°C)	χ^2	σ	K'	$\sigma_{K'}$	K'	$\sigma_{K'}$	K'	$\sigma_{K'}$
			$HNO_3\cdot CMPO$					
25.0	6.561	0.00128	2.660	0.092				
40.0	61.78	0.00350	1.710	0.022				
			$HNO_3\cdot 2CMPO$					
25.0	6.238	0.00124	14.21	0.51				
40.0	346.1	0.00830	6.425	0.029				
			$2HNO_3\cdot CMPO$					
25.0	79.37	0.00444	28.47	0.98				
40.0	1882.	0.01934	1.505	0.016				
			$HNO_3\cdot CMPO$		$HNO_3\cdot 2CMPO$			
25.0	5.881	0.00129	1.521	1.293	7.428	8.791		
40.0	42.85	0.00308	1.574	0.041	2.560	0.659		
			$2HNO_3\cdot CMPO$		$HNO_3\cdot 2CMPO$			
25.0	6.004	0.00131	4.070	3.250	15.68	2.202		
40.0	45.33	0.00316	1.076	0.033	15.79	0.741		
			$HNO_3\cdot CMPO$		$2HNO_3\cdot CMPO$			
25.0	5.820	0.00129	2.960	0.363	−3.462*	4.044		
40.0	48.02	0.00326	1.894	0.055	−0.197*	0.054		
			$HNO_3\cdot CMPO$		$HNO_3\cdot 2CMPO$		$2HNO_3\cdot CMPO$	
25.0	5.793	0.00139	4.984	22.80	−10.31*	117.7	−6.345*	3.859
40.0	38.98	0.00311	0.7850	0.4440	8.384	3.582	0.7585	0.4323

*Negative values are not permitted and indicate "overmodeling" of the data.

respectively. For a "moderately" good fit to the data, χ^2 is equal to the degrees of freedom, $n-p$, with a standard deviation of $[2(n-p)]^{1/2}$. The standard deviation describes the average deviation of measured points from those calculated by the model while accounting for the reduction in the degrees of freedom imposed by model parameters.

A comparison of the results shown in Table 5 for one-parameter models indicates that 1:1 stoichiometry fits the 40°C data best. The model standard deviation, σ, is clearly smallest in this case; however, the data at 25°C are fit by either 1:1 or 2:1 stoichiometry equally well, with standard deviations slightly less than the estimated deviations in the data (~ 0.00141). Wadsworth et al. (1990) show that the F-test statistic computed from the standard deviations may be used to compare models. With the data at 25°C listed in Table 5, $F_{1:1,2:1} = (0.00128/0.00124)^2 = 1.07$, which indicates that the one-parameter models are not statistically different. Equilibrium constants, $K'_{1:1}$, estimated by the extended slope-analysis method are quite close to the values listed in Table 5. That is, 2.68 vs. 2.66 at 25°C and 2.01 vs. 1.71 at 40°C.

The standard deviations of all of the two-parameter models are essentially equal. The best two-parameter model may be selected as the model having the smallest standard deviation at both temperatures. That model includes both 1:1 and 2:1 stoichiometries. However, the standard deviation in the second model parameter, $\sigma_{K'}$, for the data at 25°C is larger than the parameter itself, implying that the parameter is not statistically different from zero. For data at 40°C, the F-test statistic for the best one-parameter vs. that for the best two-parameter model is $(0.00350/0.00308)^2 = 1.29$, which for eight and nine degrees of freedom, respectively, indicates that the two models are not statistically different. The other two-parameter models and the three-parameter model give less favorable results.

In summary, over the range of results obtained in this study, a single stoichiometric representation for the extraction of nitric acid, the 1:1 stoichiometry, adequately fits the data. The model is compared with the data at 25 and 40°C in Figures 3 and 4, respectively. As shown, good agreement is obtained.

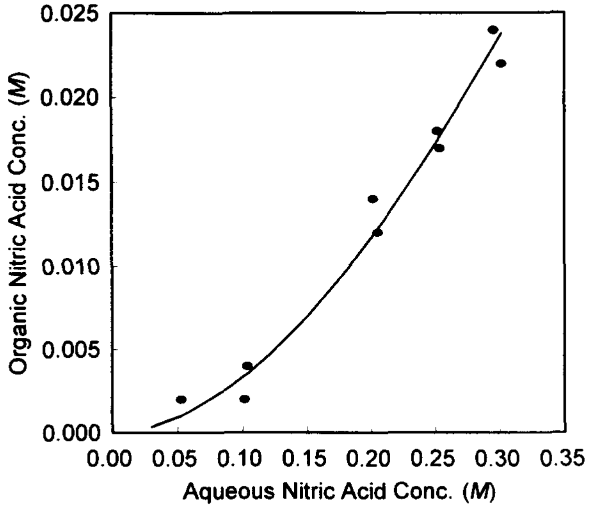

Figure 3. Comparison of the 1:1 stoichiometry-based model for extraction of nitric acid with our experimental data at 25°C.

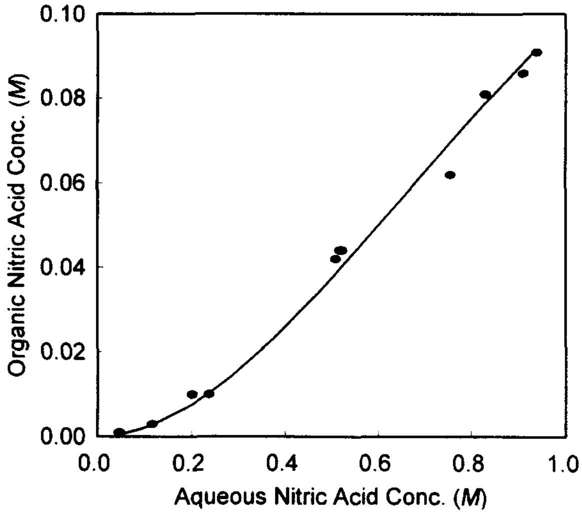

Figure 4. Comparison of the 1:1 stoichiometry-based model for extraction of nitric acid with our experimental data at 40°C.

Enthalpy of extraction

For the study of the extraction of nitric acid presented here, equilibrium constants are available from data collected at 25 and 40°C. Because there are only two points, direct substitution of the values into the van't Hoff equation gives the enthalpy of reaction, ΔH. Errors propagate to the result according to equations given by Holman (1971), assuming that all the errors are in the K-values. The enthalpy of the extraction reaction is calculated as $\Delta H = -5.46 \pm 0.46$ kcal/mol. The reaction is therefore slightly exothermic. At a temperature of 50°C, $K'_{1:1}$ is estimated to be 1.303. Figure 5 compares calculated and measured organic-phase nitric acid concentrations as a function of aqueous nitric acid concentration. The comparison is remarkably favorable, considering

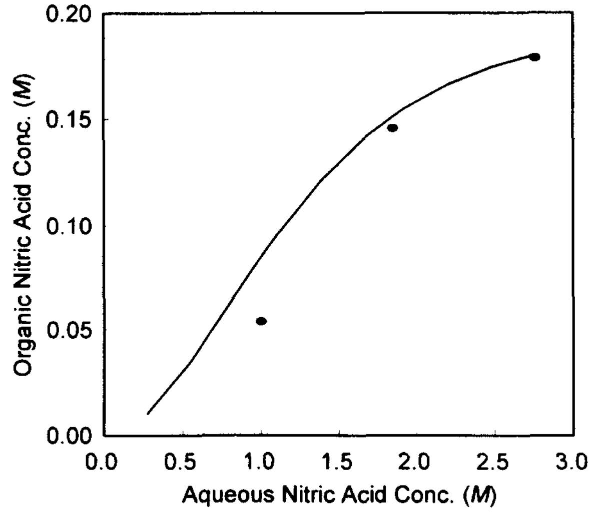

Figure 5. Comparison of the 1:1 stoichiometry-based model for extraction of nitric acid with our experimental data at 50°C, using the extrapolated equilibrium constant.

that the extrapolation is in the dimensions of both temperature and concentration. (The data point at 1.0 M aqueous nitric acid is slightly low, as expected.) This is another indicator that the model is adequate.

Summary

An extended slope-analysis method was developed. When the extraction stoichiometry is estimated by other means, this new method may be used to estimate the true equilibrium constant of the extraction, the equilibrium constant that includes the effects of nonideality of the organic phase, and the ratio of the activity coefficient of the free solvent to that of the complexed solvent. The method works best when the slope-analysis data are obtained over a narrow range of solvent concentrations. Consequently, the method may give better results when the distribution ratios are large.

The extended slope-analysis method was applied to our study of the extraction of nitric acid by CMPO. Analysis of the data indicates that the activity coefficient of the CMPO–nitric acid solvate is ~20% smaller than that of free CMPO in an *n*-dodecane matrix. Unfortunately, a literature search revealed no reported activity data for this system with which to compare our results.

This study of the extraction of nitric acid from an aqueous phase by CMPO into an *n*-dodecane organic phase provides strong evidence that the extraction equilibrium occurs with a 1:1 stoichiometry. Equilibrium data were obtained at more than one temperature, and the equilibrium constants and the enthalpy of reaction were estimated for the 1:1 stoichiometry. It is a bit of a stretch to compare the present work with that of Chaiko et al. (1988). Chaiko et al. concluded that three equilibria, 1:1, 1:2 and 2:1 stoichiometries, describe the extraction of nitric acid with CMPO. In their studies a different diluent was used, the CMPO concentrations were higher, the nitric acid concentration range extended to higher values, and only one temperature was used. Another consideration is the method by which aqueous-phase activity coefficients are calculated. Spencer (1994) has shown that activity coefficients calculated for nitric acid using Pitzer's method (used in this work) more closely reproduce the data in the literature than those coefficients calculated by Bromley's method. In the present study the traditional slope-analysis method indicates a solvation number slightly larger than unity. But the extended slope-analysis method indicates that the variation from unity can be explained by the ratio of the nonideal activity coefficients of the free and complexed extractant in the organic phase. With only one equilibrium constant to describe the organic phase acid concentration, its value must be larger than the analogous constant determined by Chaiko et al.

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Notation

a = activity of a species
d = modified distribution ratio for extended slope-analysis method, Eq. 23
M = a cation
n = the solvation number
R_γ = ratio of activity coefficients of free CMPO and CMPO–nitrate complex, Eq. 12
T = absolute temperature, K (or °C)
X = an anion
x = a general independent variable
z = the charge number of an ion, or the number of anions per formula weight
γ = activity coefficient
Δ = a change in

Superscript and Subscripts

$'$ = indicates parameter modified to include nonideal effects
aq = of, or related to, aqueous phase
i = counter or identifier for reactants or solutes
$n{:}m$ = stoichiometric ratio
org = of, or related to, organic phase
s = value given by slope analysis
w = of, or related to, water

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