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The Extraction of TcO_4^- and Pd(II) by Dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate from Nitric Acid

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Abstract

The extraction behavior of TcO_4^- and Pd(II) from aqueous HNO_3 was studied using dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate. Distribution ratios were studied as a function of contact time; concentration of solute, acid, and extractant; and extraction temperature. Extraction measurements of TcO_4^- were also made using H_2SO_4 in the aqueous phase. It was found that the extractant dependency for TcO_4^- is third power. Distribution measurements for TcO_4^- as a function of temperature in the range of 0–50°C led to a calculation of the thermodynamic quantity ΔH. A third-power extractant dependency for Pd(II) is suggested but is not strongly corroborated. Interpretation of Pd(II) data was hindered by slow kinetics (approximately 1 h to reach equilibrium and variations in distribution ratios with aqueous Pd(II) concentration.

INTRODUCTION

This laboratory has been involved in two projects associated with actinide partitioning from acidic nuclear waste. The first dealt with HNO_3 waste generated at the Idaho Chemical Processing Plant (ICPP) at the Idaho National Engineering Laboratory (INEL). The nature of the waste and the research leading to the development of a successful solvent extraction flow sheet has been described elsewhere (*1*–*5*). The neutral bifunctional extractant dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP) was shown to be useful in partitioning Am, Cm, Pu, and U from cladding elements, salting agents, and the bulk of fission products present in ICPP wastes. The success of this project led to a coordinated program with the Oak

Ridge National Laboratory (ORNL) on actinide partitioning from nitric acid waste generated during commercial light water reactor (LWR) fuel reprocessing. A flow sheet was developed and demonstrated using DHDECMP as the extractant (*6*).

In the final reports by ORNL on actinide partitioning and transmutation (*7, 8*), the extractant of choice, following the tributylphosphate process, was DHDECMP.

Though flow sheets have been developed for actinide partitioning using DHDECMP, detailed extraction studies of those elements moderately extracted (second-row transition elements Zr through Pd) remained to be done. Recently, papers have appeared on the extrction of transplutonium(III) and lanthanide(III) ions (*9*) and Th(IV) and U(VI) (*10*) by DHDECMP from aqueous nitrate media.

This report is part of a continuing effort to determine the extraction parameters of second-row transition elements from nitric acid media using DHDECMP. Separation of these elements from wastes could be important from either a product value or a waste hazard point of view.

In general, most acidic nuclear wastes of interest are in the range of approximately 3 M HNO_3; however, studies at other acidities and, in the case of Tc, the use of H_2SO_4 as the acid phase have been made to better define extraction mechanisms.

One of the subject elements in this paper, ^{99}Tc, is of particular interest because of its large fission yield (approximately 6%) and long half-life (2×10^5 years). Risk assessment studies of nuclear wastes by ORNL (*11*) concluded that removal or immobilization of ^{99} Tc and ^{129}I might provide more tangible benefits than actinide partitioning and transmutation.

EXPERIMENTAL

Crude (65%) DHDECMP was purchased from Wateree Chemical Co., Lugoff, South Carolina, and purified to approximately 98% by precipitation with $Hg(NO_3)_2$ and regeneration with KCN/Na_2CO_3. The details of this procedure have been described elsewhere (*12*). The major impurities remaining were approximately equal amounts of dihexyl-hexylphosphonate and hexyloctyl-*N,N*-diethylcarbamoylmethylphosphonate (a homologue of DHDECMP). Though diisopropylbenzene (DIPB) was used as a solvent for DHDECMP in earlier flow-sheet studies (*6*), it is believed that a better choice is diethylbenzene (DEB) due to its superior radiation stability compared to other aromatic solvents (*13*). DEB was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, and contained a mixture of *o*-, *m*-, and *p*-isomers. All other chemicals used were Reagent A.C.S. grade.

Tracer ^{99m}Tc and ^{109}Pd were prepared by the neutron irradiation of ^{98}Mo and ^{108}Pd in the Advanced Test Reactor at the INEL. Long-lived ^{99}Tc was purchased from ORNL. Irradiated MoO_2 was dissolved in NH_4OH and excess NH_3 evaporated. The residue was dissolved with 0.1 M HNO_3 and loaded on a 10 cm long by 1 cm diameter column containing 100 to 200 mesh AG 10 Alumina, and ^{99m}Tc was then eluted (or milked) with 0.1 M HNO_3. The eluate containing the Tc was taken to dryness, taking care not to overheat. The residue was picked up with water and, after centrifugation to remove traces of alumina, eluted through a 10 cm long by 0.5 cm diameter column containing 100–200 mesh Dowex 50-X 8 cation exchange resin. The eluate was taken carefully to dryness (no solids were observed at this point) and acid added as dictated by the experiment. The alumina and cation resin were purchased from BIO-RAD Laboratories, Richmond, California.

Irradiated Pd, either as the metal or nitrate, was dissolved in 10 M HNO_3 at 50°C. Generally, 1-h contact was adequate for complete dissolution. Dissolution was carried out in capped bottles to avoid acid loss. Duplicate experiments using tracer prepared from irradiations of metal and nitrate gave the same results within the experimental errors.

Radiometric assays were made using either NaI(Tl) or Ge(Li) gamma-ray spectrometers. Frequently both systems were used on the same samples as a check on their reliability. Results always agreed within the counting accuracies involved. The NaI(Tl) system was used mainly when activity levels were low but only after the purity of the tracer used had been verified on the high-resolution Ge(Li) detector. Liquid sample sizes were kept small (no greater than 1.5 mL) to minimize self-absorption errors due to density differences. In most assays, photopeak areas analyzed contained greater than 10,000 counts. Cumulative counting, geometry, and self-absorption errors are estimated to be less than 10%.

Acidity measurements on aqueous solutions were made by conventional titrations with standard base. Where it was necessary to determine the acidity of an organic phase, the acid was back-extracted with water then titrated with base.

Distribution ratios, K_d's, which were done in duplicate, were determined by contacting equal volumes of organic and aqueous phases in 16 × 100 mm Pyrex culture tubes having Teflon-lined screw caps. All organics, unless otherwise stated, were preequilibrated with nontraced solutions of the same consistency used for the distribution measurement. Excluding Tc and Pd concentration studies, each set of measurements contained the same amount of element being examined. A mechanical wrist shaker was used for phase mixing. Temperature during contact was maintained by a thermostatically controlled water bath to ±0.2°C. With the exception of temperature studies, all extractions were made at 20°C (ambient room temperature). Phases were disengaged by rapid centrifugation, separated using transfer pipettes, and aliquots taken for counting. For temperature dependence studies, phases were allowed to disengage in the water bath and, while still in the bath, separated using transfer pipettes.

RESULTS AND DISCUSSION

HNO_3 Extraction

It has been shown earlier that DHDECMP in DIPB has a considerable affinity for HNO_3 (*6*). Because HNO_3 competes with other solutes for available DHDECMP, it is important that HNO_3 extraction parameters in the DHDECMP–DEB system be measured. Kinetic studies indicated HNO_3 equilibrium between aqueous and organic phases is reached in less than 2 min. All contact times for acid extraction studies were for 5 min. In Fig. 1 are shown the results of HNO_3 extraction between 0.81 *M* DHDECMP in DEB and various aqueous HNO_3 solutions. The organic was not preequilibrated before use. No attempt was made to measure volume changes, only equilibrium HNO_3 molarity. The acid K_d's range from a low of 0.18 to a high of 0.26.

The effect of varying DHDECMP concentration with a constant HNO_3 concentration is shown in Fig. 2 for two different acid concentrations. Organic HNO_3 molarity is plotted versus the DHDECMP molarity. Siddall (*14*) has shown that a slope of 1 indicates that extraction mechanisms studied at that acidity should be meaningful because at a constant aqueous HNO_3 concentration the relative amount of free DHDEMCP available for extraction of a solute is proportional to the initial DHDECMP concentration. A slope of greater than 1 indicates that the extractant is appreciably self-associated and/or the acid is associated with two or more extractant molecules. Freezing point depression measurements using benzene as solvent showed DHDECMP to be monomeric; therefore, at 0.75*M* HNO_3 some HNO_3–DHDECMP complexes contain greater than one DHDECMP molecule. As will be seen later in the Tc extraction section, this interpretation appears to be contradicted where seemingly more meaningful information results from extraction at low acid (0.75 *M* HNO_3). It was also so in Siddall's work on Ce(III) extractions with dihexyl-*N*,*N*-dibutylcarbamoylmethylphosphonate (*14*).

The effect of temperature on HNO_3 extraction from an aqueous 0.75 *M* HNO_3 solution with 0.25 *M* DHDECMP in DEB has been measured from 20 to 50°C. These data are tabulated in Table 1. Assuming 1.3 DHDECMP molecules associated with each HNO_3, only a 5% change in "free" extractant is observed over the temperature range studied. This is important to

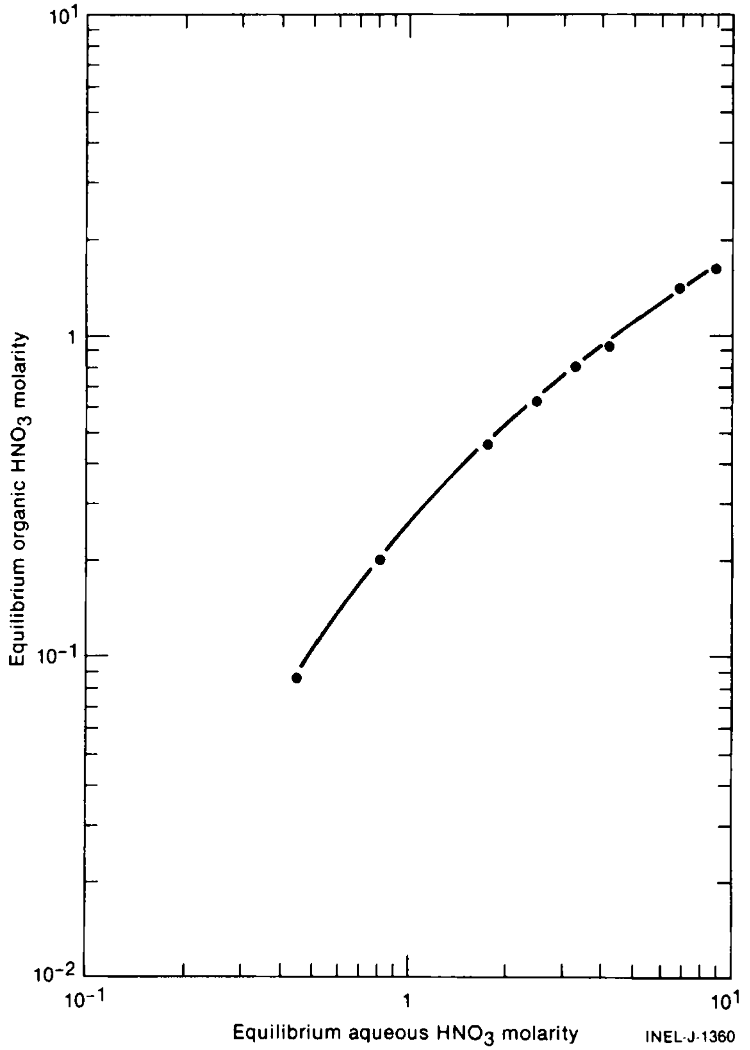

FIG. 1. Equilibrium organic HNO_3 molarity versus aqueous HNO_3 molarity. Organic phase = 0.81 *M* DHDECMP in DEB. $T = 20°C$.

TABLE I

HNO_3 Extraction from 0.75 *M* HNO_3 with 0.25 *M* DHDECMP in DEB

T (°C)	Organic HNO_3 (*M*)
20	0.035
25	0.034
30	0.032
40	0.030
50	0.028

note in the later section when Tc extraction as a function of temperature is discussed.

Tc Distribution

The most common form of Tc in solution is as the pertechnate ion, TcO_4^-, especially in HNO_3 solution or in the presence of oxidizing agents. Most of

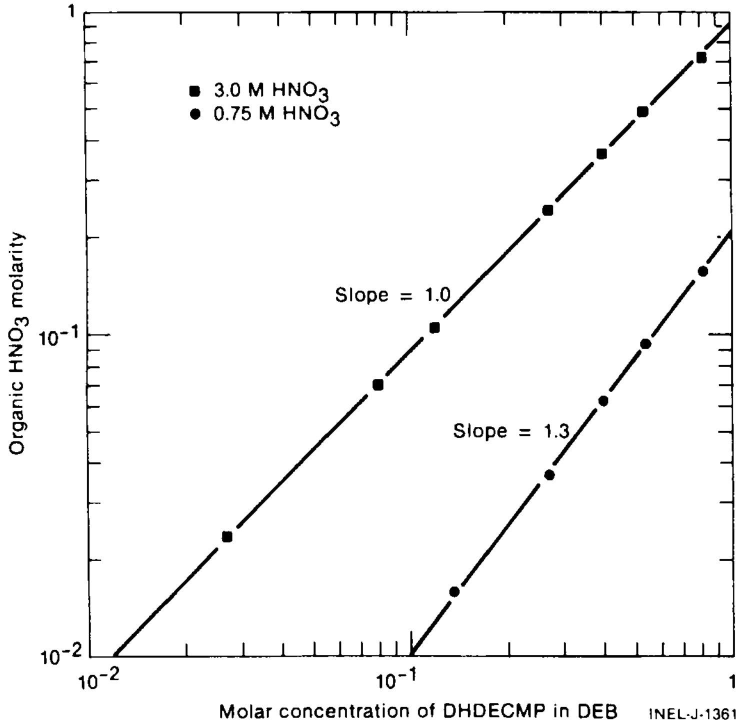

FIG. 2. Equilibrium organic HNO_3 molarity versus molar concentration of DHDECMP in DEB. Aqueous phase = 0.75 and 3.0 *M* HNO_3. $T = 20°C$.

the measurements reported in this paper were from HNO_3 solution. To verify that the TcO_4^- ion was present when using HNO_3, many duplicate runs were made with and without oxidizing agents. No differences were observed. Both H_2O_2 and Cr(VI) were used as holding oxidants. When H_2SO_4 was used in the aqueous media, the Cr(VI) concentration was maintained at 0.002 *M*.

No measurable extraction of Tc was observed by pure DEB, the solvent used for dilution, at any of the acid concentrations used in this work. It was also shown by using differing degrees of purity of DHDECMP that impurities were not significantly involved in Tc extraction.

A kinetic study of Tc extraction between 3*M* HNO_3 and 0.81 *M* DHDECMP in DEB showed equilibrium was reached in less than 2 min. All subsequent extraction measurements were made with contact times of 5 min or longer.

Solutions of 3 *M* HNO_3 varying in Tc concentration from tracer level to 0.2 mg/mL were contacted with 0.81 *M* DHDECMP in DEB. Long-lived ^{99}Tc was used to vary the Tc concentration. Within experimental error, no difference in the K_d's was observed. Experiments with tracer Tc are therefore assumed to be applicable up to the higher (0.2 mg Tc/mL) range, which approximates that occurring in high-level nuclear waste.

The variation of the distribution ratio of Tc from 0.81 *M* DHDECMP in DEB as a function of equilibrium aqueous HNO_3 concentration is shown in Fig. 3. A maximum is observed at about 0.75 *M* HNO_3. The rapid decrease in K_d above this acidity is no doubt caused by the rapid reduction of available DHDECMP by extracted HNO_3.

The variation of distribution ratios of Tc from 0.75 and 3.0 *M* HNO_3 as a function of DHDECMP concentration in DEB is shown in Fig. 4. To better understand the extraction mechanism of Tc, a similar experiment was performed where the aqueous phase was 1.5 *M* H_2SO_4–0.002 *M* Cr(VI). These data are shown in Fig. 5. The extraction of H_2SO_4 into DHDECMP was shown to be negligible; therefore, problems ascribed to acid extraction are minimal. The slopes of the 0.75 *M* HNO_3 and 1.5 *M* H_2SO_4 K_d data are in agreement, suggesting that the extraction stoichiometry for Tc is

$$H_a^+ + TcO_{4\,a}^- + 3CMP_o \rightleftharpoons HTcO_4 \cdot 3CMP_o \qquad (1)$$

where the subscripts *o* and *a* represent the organic and aqueous phases, respectively, and CMP represents the extractant, DHDECMP. To maintain electroneutrality, the extracted specie is assumed to be $HTcO_4$ as shown in Eq. (1). A recent study of TcO_4^- extraction from HCl into TBP has also shown third-order extractant dependency (*15*). With 0.81 *M* DHDECMP in DEB the K_d for Tc from 1.5 *M* H_2SO_4 (having a H^+ concentration of approximately 1.5 *M*) compared to that from 1.5 *M* HNO_3 (see Fig. 3) is about a factor of 10 higher. From Fig. 1 it is seen that the organic phase from

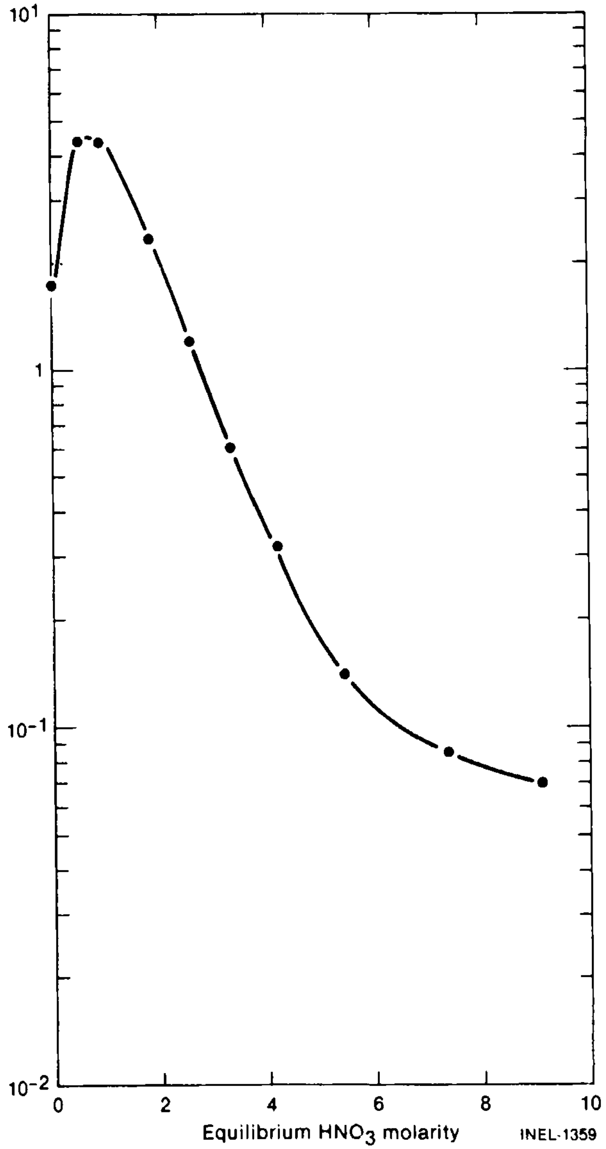

FIG. 3. Distribution ratio of TcO_4^- versus equilibrium aqueous HNO_3 molarity. Organic phase = 0.81 *M* DHDECMP in DEB. *T* = 20°C.

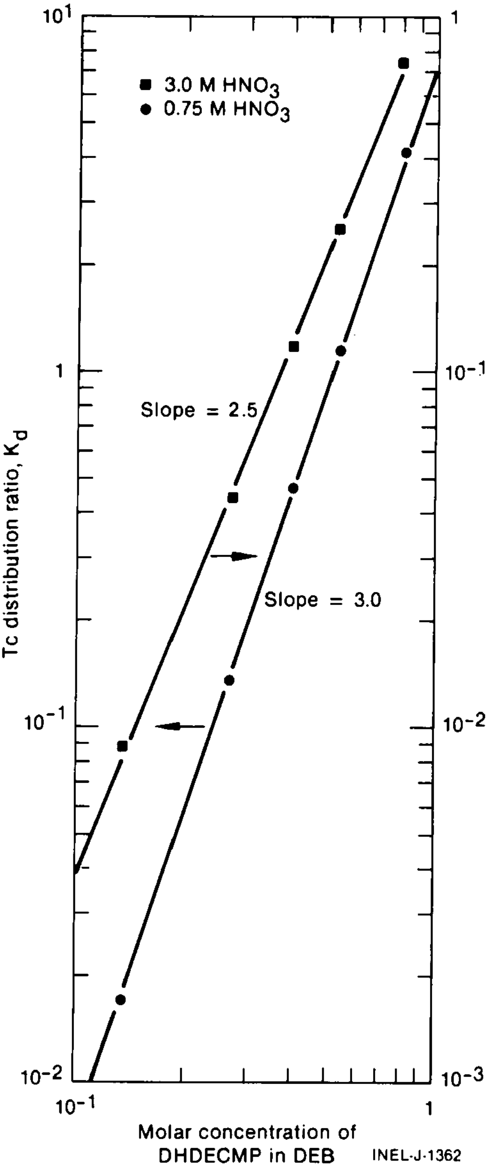

FIG. 4. Distribution ratio of TcO_4^- versus molar concentration of DHDECMP in DEB. Aqueous phases = 0.75 and 3.0 *M* HNO_3. $T = 20°C$.

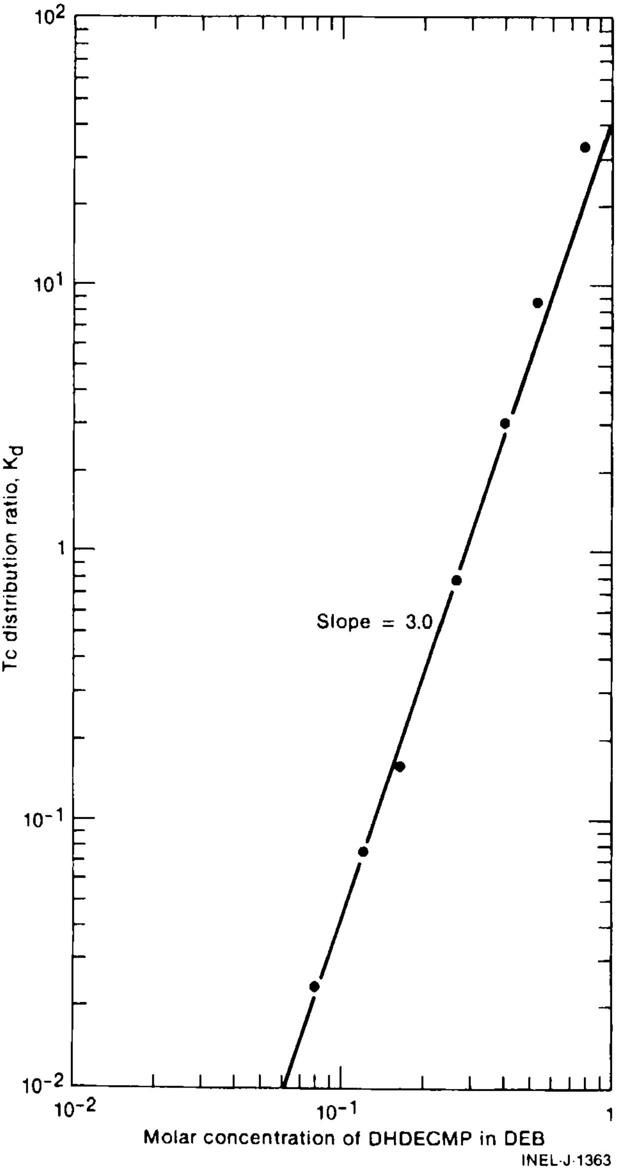

FIG. 5. Distribution ratio of TcO_4^- versus molar concentration of DHDECMP in DEB. Aqueous phase = 1.5 *M* H_2SO_4-0.002 *M* Cr(VI). *T* = 20°C.

the HNO_3 contact is approximately 0.4 *M* in HNO_3. Assuming that approximately one extractant molecule is associated with each molecule of HNO_3, resulting in an effective DHDECMP concentration of approximately 0.4 *M*, the factor of 10 difference is K_d's is reasonable when third-order extractant dependence is considered.

An additional experiment was performed with H_2SO_4 in the aqueous phase. Using a 0.25 *M* DHDECMP in DEB extractant, Tc distribution ratios were measured as a function of the aqueous acid concentration. All aqueous phases were 0.002 *M* Cr(VI). These data are shown in Fig. 6. A value for the second ionization constant of H_2SO_4 of $K_2 = 0.0120$ (*16*) was used in the calculation of acid concentration. The positive slope above 0.5 *M* H^+ supports the acid dependence shown in Eq. (1) and is in marked contrast to the that of Fig. 3. The flat portion of the curve (Fig. 6) at low acidity is not understood but has been observed by another investigator when studying the extraction of TcO_4^- from HNO_3 with cyclohexanol (*17*). Their approach was to subtract the limiting K_d value, which resulted in a log K_d versus log $[H^+]$ plot of slope = 1. A similar treatment of the data in Fig. 6 results in a slope of 1.3. The deviation from unity is most likely due to the increasing ionic strength with increasing acid.

Temperature dependence measurements have been made for the ex-

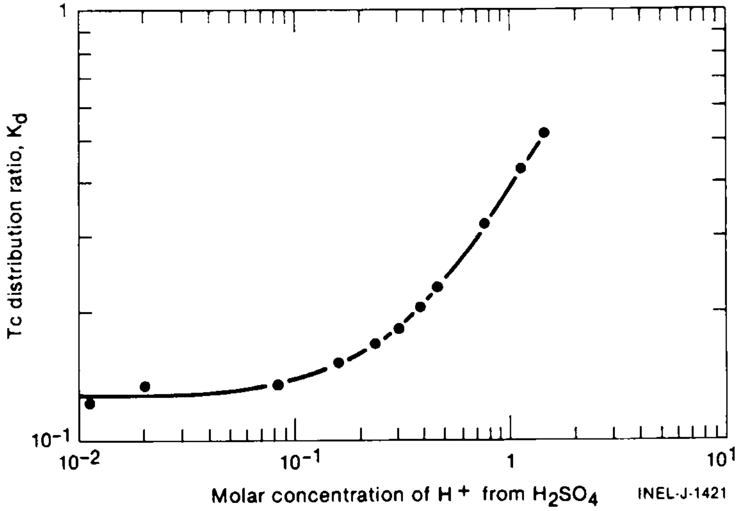

FIG. 6. Distribution ratio of TcO_4^- versus aqueous molar H^+ concentration from H_2SO_4. Oganic phase = 0.25 *M* DHDECMP in DEB. $T = 20°C$. All aqueous phases 0.002 *M* Cr(VI).

traction of Tc between 0.25 *M* DHDECMP in DEB and 0.75 *M* HNO_3. From Eq. (1) the equilibrium constant is defined as

$$K_{eq} = \frac{[HTcO_4 \cdot 3CMP]_o}{[H^+]_a[TcO_4^-]_a[CMP]_o^3} \tag{2}$$

Since

$$K_d = \frac{[HTcO_4 \cdot 3CMP]_o}{[TcO_4^-]_a} \tag{3}$$

$$K_{eq} = \frac{K_d}{[H^+]_a[CMP]_o^3} \tag{4}$$

From the relationship

$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

a plot of $\ln K_{eq}$ versus $1/T$ should yield a straight line with a slope of $-\Delta H/R$. Using experimental K_d values, 0.75 *M* for $[H^+]_a$ and 0.25 *M* for [CMP], corrected for concentration loss due to HNO_3 extraction (see Table 1), the plot shown in Fig. 7 was made. From the slope obtained, $\Delta H = -13$ kcal/mol. Other thermodynamic values were not calculated because of the lack of activity coefficients for the DHDECMP extractant.

An additional set of temperature dependence measurements were made at 0.81 *M* DHDECMP in DEB and 3.0 *M* HNO_3. These results are given in Table 2. Because the extractant dependence plot had a slope of 2.5 at this acid concentration (see Fig. 4), no thermodynamic calculation was considered meaningful.

Using 0.81 *M* DHDECMP in DEB, K_d's greater than 1 for Tc are observed for HNO_3 concentrations less than 2.5 *M*. Careful choice of HNO_3 concentration can improve extraction or lead to stripping. The use of H_2SO_4

TABLE 2

TcO_4^- Extraction as a Function of Temperature

T (°C)	K_d
20	1.20
30	0.74
40	0.46
50	0.29

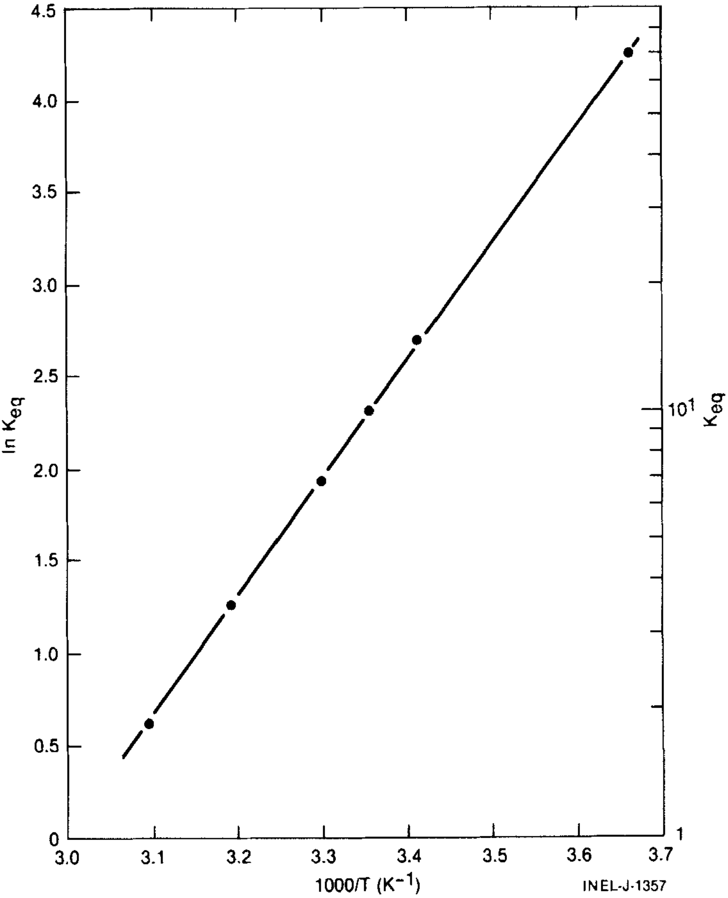

FIG. 7. Effect of temperature on K_{eq} for the extraction of TcO_4^- from 0.25 *M* DHDECMP in DEB from 0.75 *M* HNO_3.

instead of HNO_3 enhances extraction and should be useful in laboratory applications. After extraction with H_2SO_4, HNO_3 could serve as a stripping agent.

Pd Distribution

No measurable extraction of Pd(II) was noted with pure DEB over all HNO_3 acid concentrations used in this work, nor were impurities present in DHDECMP found to play an important role in its extraction.

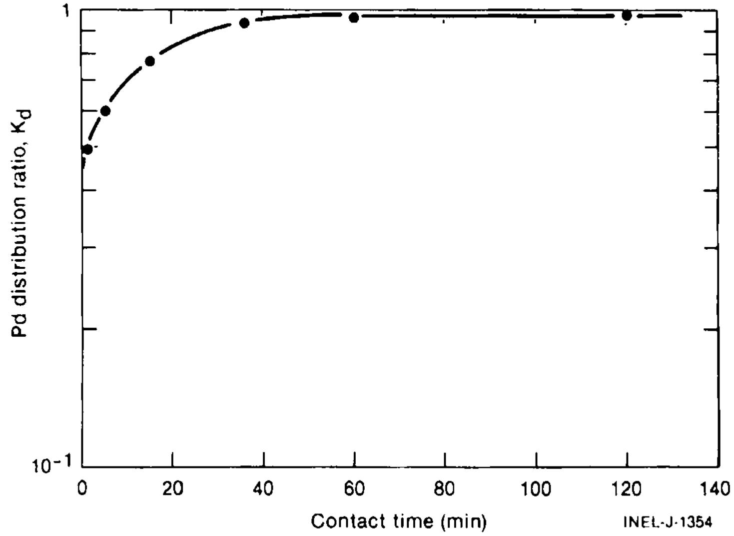

FIG. 8. Distribution ratio of Pd(II) versus contact time. Organic phase = 0.81 *M* DHDECMP in DEB. Aqueous phase = 3.0 *M* HNO_3. $T = 20°C$.

Kinetic measurements on Pd(II) distribution between 3 *M* HNO_3 and 0.81 *M* DHDECMP in DEB are shown in Fig. 8. The initial Pd(II) concentration in the aqueous phase was 4.7×10^{-4} *M*. The extractant was not pretreated with acid before use. A similar run was made using 1.4×10^{-3} *M* Pd(II) which showed lower K_d's but the same time dependency (i.e., 1 h to reach equilibrium). In all subsequent Pd measurements at least 1 h was used for contact time.

Distribution ratio measurements as a function of Pd(II) concentration are shown in Fig. 9. Two acid concentrations (1.0 and 3.0 *M* HNO_3) were used. The extractant, which was not pretreated with acid before use, was 0.81 *M* DHDEMCP in DEB. The highest Pd(II) concentration studied approximates that occurring in high-level nuclear waste. Over the range of Pd(II) concentration studied, K_d's for the lower acid extractions are higher by at least a factor of 2.

The extraction of Pd(II) with 0.81 *M* DHDECMP in DEB as a function of equilibrium aqueous HNO_3 molarity is shown in Fig. 10. All aqueous HNO_3 solutions were initially 4.7×10^{-4} *M* Pd(II). As observed earlier for Tc, increased HNO_3 concentration reduces extraction.

Distribution of Pd(II) from 1.0 and 3.0 *M* HNO_3 as a function of DHDECMP concentration DEB is shown in Fig. 11. All aqueous HNO_3 solutions were initially 4.7×10 ^{4} *M* Pd(II). Only the 1 *M* HNO_3 data

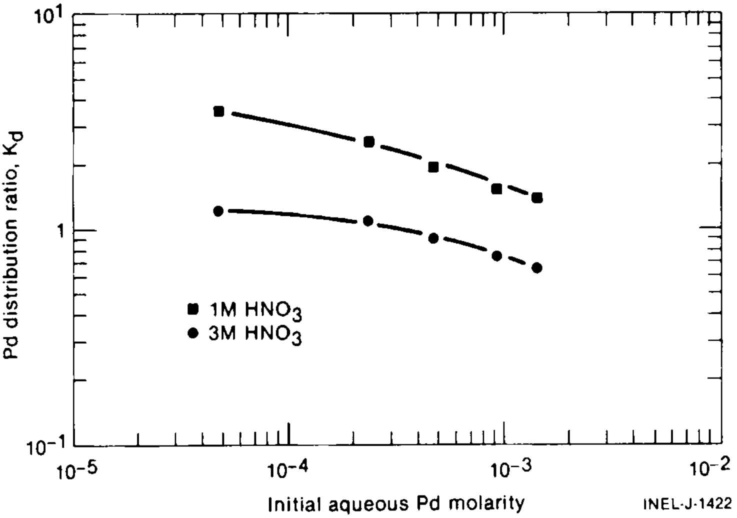

FIG. 9. Distribution ratio of Pd(II) versus initial aqueous Pd(II) molarity. Organic phase = 0.81 *M* DHDECMP in DEB. Aqueous phases = 1.0 and 3.0 *M* HNO_3. $T = 20°C$.

(above 0.2 *M* DHDECMP) produced a meaningful slope, indicating a third-order extractant dependency. The distorted end of both curves is not understood. Due to the low concentration of Pd(II) used, loading does not appear to be the cause.

The extraction stoichiometry suggested by the experimental data for 1 *M* HNO_3 and DHDECMP concentrations above 0.2 *M* is

$$Pd_a^{2+} + 2NO_{3_a}^- + 3CMP_o \rightleftharpoons Pd(NO_3)_2 \cdot 3CMP_o \qquad (6)$$

Slow kinetics and Pd(II) concentration dependence may be an indication of multiple Pd(II) species taking part in the extraction. The two nitrate ions shown in Eq. (6) are added to preserve electroneutrality.

The effect of temperature on the extraction of Pd(II) was measured between 20 and 50°C using 0.81 *M* DHDECMP in DEB. The initial concentration of Pd(II) and HNO_3 in the aqueous phase for all measurements was 4.7×10^{-4} and 3.0 *M*, respectively. These data are tabulated in Table 3. It is felt that a thermodynamic treatment of these data would not be meaningful.

Though not strongly extracted from HNO_3 media with DHDECMP, Pd(II) does exhibit K_d's greater than 1 below 2 *M* HNO_3 with 0.81 *M* DHDEMCP in DEB. Once extracted, Pd(II) can be removed from the extractant with moderately concentrated HNO_3. Slow extraction kinetics

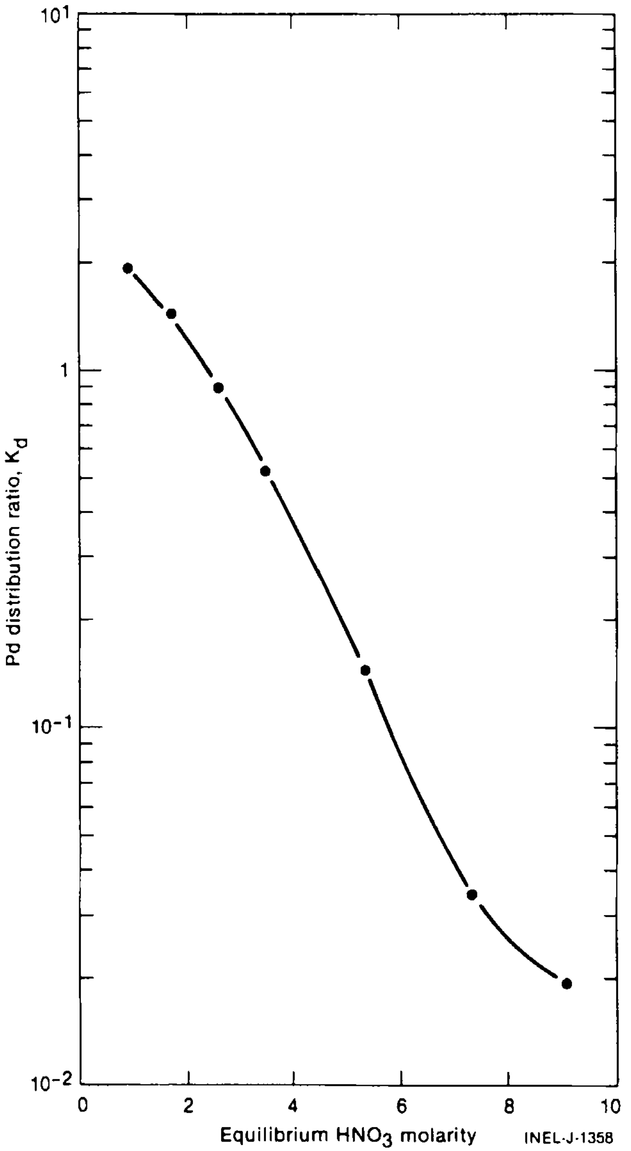

FIG. 10. Distribution ratio of Pd(II) versus equilibrium aqueous HNO_3 molarity. Organic phase = 0.81 *M* DHDECMP in DEB. $T = 20°C$.

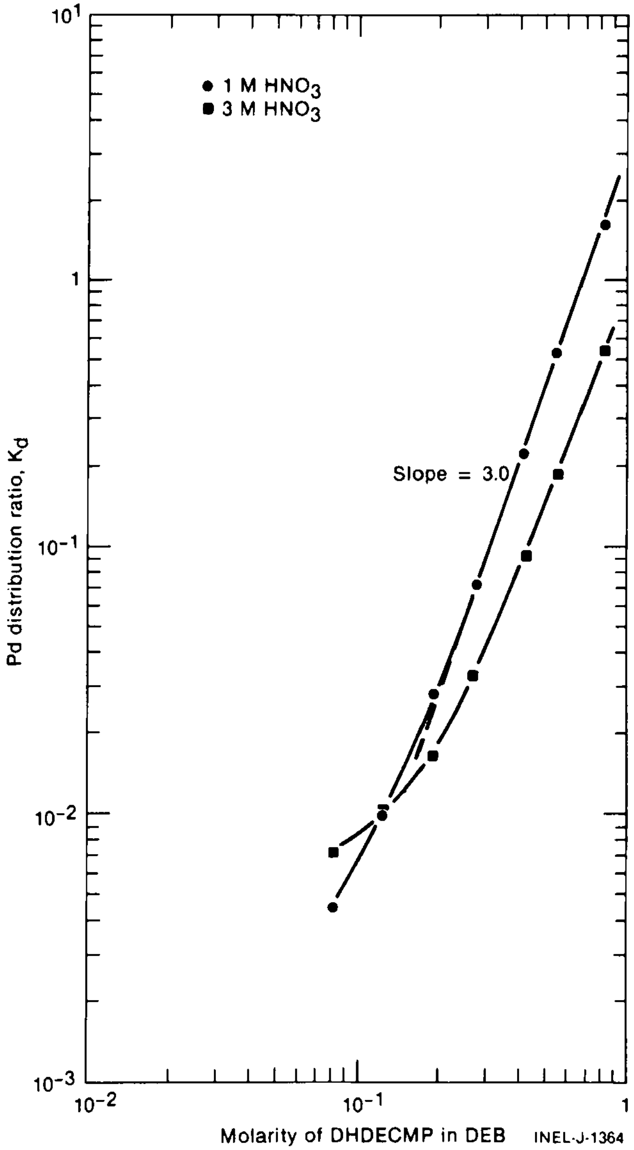

FIG. 11. Distribution ratio of Pd(II) versus molarity of DHDECMP in DEB. Aqueous phases = 1.0 and 3.0 *M* HNO_3. $T = 20°C$.

TABLE 3

Pd(II) Extraction as a Function of Temperature

T (°C)	K_d
20	1.07
30	0.91
40	0.58
50	0.32

could be used to good advantage to minimize the extraction of Pd(II) if short contact periods were used.

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REFERENCES

1. L. D. McIsaac, J. D. Baker, and J. W. Tkachyk, *U.S. ERDA Report ICP-1080*, 1975.
2. W. W. Schulz and L. D. McIsaac, *U.S. ERDA Report ARH-SA-241*, 1975.
3. W. W. Schulz and L. D. McIsaac, *U.S. ERDA Report ARH-263*, 1977.
4. J. D. Baker, L. D. McIsaac, J. F. Krupa, D. H. Meikrantz, and N. C. Schroeder, *U.S. ERDA Report ICP-1182*, 1979.
5. L. D. McIsaac, J. D. Baker, J. F. Krupa, D. H. Meikrantz, and N. C. Schroeder, *Actinide Separations* (ACS Symp. Ser. 117), 1980, p. 395.
6. L. D. McIsaac, J. D. Baker, J. F. Krupa, R. E. LaPointe, D. H. Meiktranz, and N. C. Schroeder, *U.S. ERDA Report ICP-1180*, 1979.
7. A. G. Groff, J. O. Blomeke, and B. C. Finney, *U.S. ERDA Report ORNL-5566*, 1980.
8. D. W. Tedder, B. C. Finney, and J. O. Blomeke, *U.S. ERDA Report ORNL/TM-6982*, 1980.
9. E. P. Horwitz, A. C. Muscatello, D. G. Kalina, and L. Kaplan, *J. Inorg. Nucl. Chem., 16*, 417 (1981).
10. E. P. Horwitz, D. G. Kalina, and A. C. Muscatello, *Sep. Sci. Technol., 16*, 403 (1981).
11. S. E. Logan, R. L. Conarty, H. S. Ng, L. J. Rahal, and C. G. Shirley, *U.S. ERDA Report ORNL/TM-6987*, 1980.
12. N. C. Schroeder, L. D. McIsaac, and J. F. Krupa, *U.S. ERDA Report ENICO-1026*, 1980.
13. C. A. Blake, Jr., and J. M. Schmitt, in *Solvent Extraction Chemistry of Metals* (H. A. C. McKay, T. V. Healy, I. L. Jenkins and A. Naylor, eds.), Macmillan, New York, 1965, p. 161.
14. T. H. Siddall, III, *J. Inorg. Nucl. Chem., 26*, 1991 (1964).
15. D. Pruett, Paper presented at Gatlinburg Symposium on Separation Science and Technology for Energy Application, Gatlinburg, Tennessee, May 5–8, 1981.

16. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1955, p. 376.

17. G. E. Boyd and Q. V. Larson, *J. Phys. Chem., 64*, 988 (1960).

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