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THE SOLVENT EXTRACTION OF HEPTAVALENT TECHNETIUM BY TRIBUTYL PHOSPHATE

D. J. Pruett

Consolidated Fuel Reprocessing Program
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

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D. J. Pruett
Chemical Technology Division

Consolidated Fuel Reprocessing Program
Oak Ridge National Laboratory
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ABSTRACT

The solvent extraction of heptavalent technetium from aqueous nitric or hydrochloric acid by tributyl phosphate in n-dodecane (TBP-NDD) has been studied over a wide range of TBP and acid concentrations at 25, 50, and 60°C. The extraction was found to proceed according to the reaction $3TBP + H^+ + TcO_4^- \rightarrow (HTCl_4 \cdot 3TBP)$. A discussion of possible reaction mechanisms is presented, along with values for ΔG, ΔH, ΔS and the equilibrium constant for the extraction reaction. Finally, evidence for the coextraction of technetium by uranyl ions is presented.

INTRODUCTION

Tc-99 is a high yield (6.06% from thermal neutron fission of ^{235}U (13), long liver ($T_{1/2} = 2.12 \times 10^5 y$) fission product that, along with ^{129}I, makes up a dominant portion of the nuclides remaining in radioactive wastes after decay periods of 200 to 1000y. A knowledge of the solvent extraction behavior of the element may suggest ways to isolate it and perhaps simplify the waste problem. The solvent extraction chemistry of technetium has been studied under a variety of conditions (1-5), but relatively little work has been done in systems like those used in treating nuclear waste. In one investigation, carried out under conditions similar to those used in the Purex process (6), tributyl phosphate (TBP) was used to extract technetium from an aqueous UO_2^{2+}-TcO_4^--HNO_3 solution. However, only a limited range of conditions were studied. There are a few other reported instances where TBP has been used as an extractant for technetium (e.g., ref. 2), but there has been no comprehensive study of this system.

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The present work was undertaken to examine the use of tributyl phosphate in n-dodecane (TBP-NDD) as an extractant for aqueous, heptavalent technetium under a wide range of conditions. Distribution coefficients as a function of temperature and the concentrations of TBP, HNO_3, HCl, and $UO_2(NO_3)_2$ were determined and analyzed. These data were used to determine a probable stoichiometry for the extraction equilibrium reaction, and to calculate certain approximate thermodynamic properties of the solvent extraction process.

EXPERIMENTAL

Technetium - Tc-99 was obtained as solid NH_4TcO_4 from the Isotopes Division, Oak Ridge National Laboratory. The salt was purified and converted to the potassium salt by dissolution in warm, ammoniacal H_2O_2, followed by the addition of KOH and heating to drive off NH_3 and precipitate $KTcO_4$. The solution was chilled in an ice bath, and the fine white crystalline precipitate was filtered and washed with cold absolute ethanol. Finally, the product was vacuum dried at 80°C in an Abderhalden drying apparatus.

Tributyl phosphate - Solutions of TBP-NDD were prepared as described previously (7). All TBP-NDD solutions were saturated with water during their preparation, and remained so during their analysis and use.

Distribution Measurements - Nitric acid solutions of $KTcO_4$ were prepared by diluting 2.00 ml of 0.0495 M $KTcO_4$, along with an aliquot of 10.0 M HNO_3 sufficient to produce the desired final acid concentration, to exactly 25 ml with distilled water. Exactly 20 ml of these solutions were emulsified with an equal volume of TBP-NDD that had been preequilibrated with nitric acid of the same concentration, but containing no technetium. Note that when the water-saturated TBP-NDD solution was equilibrated with an aqueous solution of nitric acid, a small change in the volume of the TBP phase occurred as HNO_3 was transferred into and H_2O was transferred out of the organic phase. At high TBP and HNO_3 concentrations, this effect can produce a substantial change in the volume of the organic phase, and hence in the TBP concentration. However, under the conditions of the experiments reported here, a maximum volume change of about 5% (usually much less) occurs. These small changes were neglected, and all TBP concentrations cited refer to the initial, water-saturated TBP-NDD solution before it was equilibrated with HNO_3 and $KTcO_4$. If desired, the final concentration of TBP in the organic phase may be calculated using the data of Davis (8-10).

Equilibrations were carried out in a water bath at 25, 40, and 60 ± 0.5°C for 20 min to ensure thermal and chemical equilibrium. Preliminary experiments had shown that identical results were obtained for samples withdrawn any time after 10 min. In those experiments containing uranyl nitrate, aliquots of a stock solution prepared by dissolving reagent grade $UO_2(NO_3)_2 \cdot 6H_2O$ (Alfa-Ventren) in distilled water were added to the volumetric flask before dilution.

Studies of the $KTcO_4$-HCl-H_2O-TBP system were carried out as described above, except that HCl was substituted for HNO_3. It was necessary to dilute the stock solution of HCl to a concentration of less than 6 M before adding $KTcO_4$ to prevent reduction of the pertechnetate ion.

Analyses — TBP was analyzed by a modification of the dielectric constant method originally developed by Kelly et al. (11). Samples were washed once with 0.01 M Na_2CO_3, followed by two washings with distilled water. The dielectric constant of the sample was then measured and the

TBP concentration determined by comparison with a calibration curve prepared by measuring the dielectric constants of a series of standard TBP-NDD solutions and fitting the data to a quadratic equation. The estimated error of the method is ±0.1 v/o TBP.

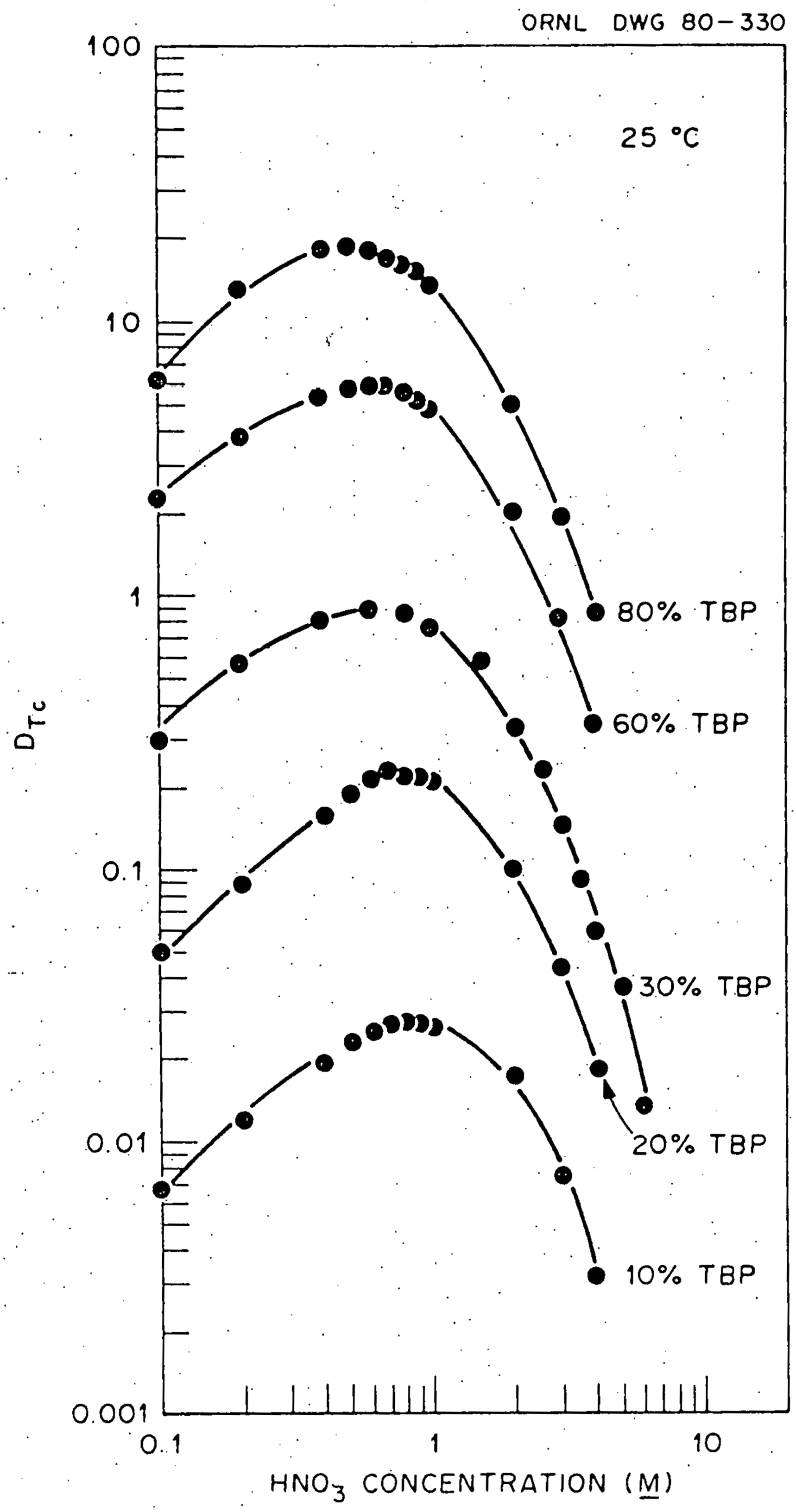
Technetium concentrations in aqueous and organic solutions were determined by beta counting using a Packard Model 2425 liquid scintillation spectrometer. Counting efficiency was greater than 80%. Most solutions required a dilution prior to beta counting; acid solutions were diluted with water, and organic solutions were diluted with 30% TBP-dodecane. Quenching was minimized by counting small aliquots of the dilution. The liquid scintillation medium was Packard Instagel.

Uranium was determined by Neutron Activation Analysis.

RESULTS AND DISCUSSIONS

Effect of Nitric Acid Concentration

Figures 1-3 show plots of D_{Tc} [i.e., $(Tc)_{organic}/(Tc)_{aqueous}$] as a function of nitric acid concentration at 25, 50, and 60°C. For any given TBP concentration, the distribution coefficient increases rapidly with increasing acidity until a maximum is reached between 0.6 and 1.0 $\underline{M}$ HNO_3. Above 1.0 $\underline{M}$ HNO_3, D_{Tc} falls off rapidly as competition from the significant amounts of nitric acid present in the organic phase reduces the amount of free TBP available to extract technetium. The maximum seems to occur at slightly lower acidities as the TBP concentration increases, and at slightly higher acidities as the temperatures increases. These trends, while not very pronounced, follow the qualitative changes in the distribution coefficient of nitric acid and hence the concentration of free TBP.


ORNL DWG 80-330
25 °C
D_{Tc}
100
10
1
0.1
0.01
0.001
0.1
1
10
HNO$_3$ CONCENTRATION (M)
80% TBP
60% TBP
30% TBP
20% TBP
10% TBP

g. 1
J. PRUETT

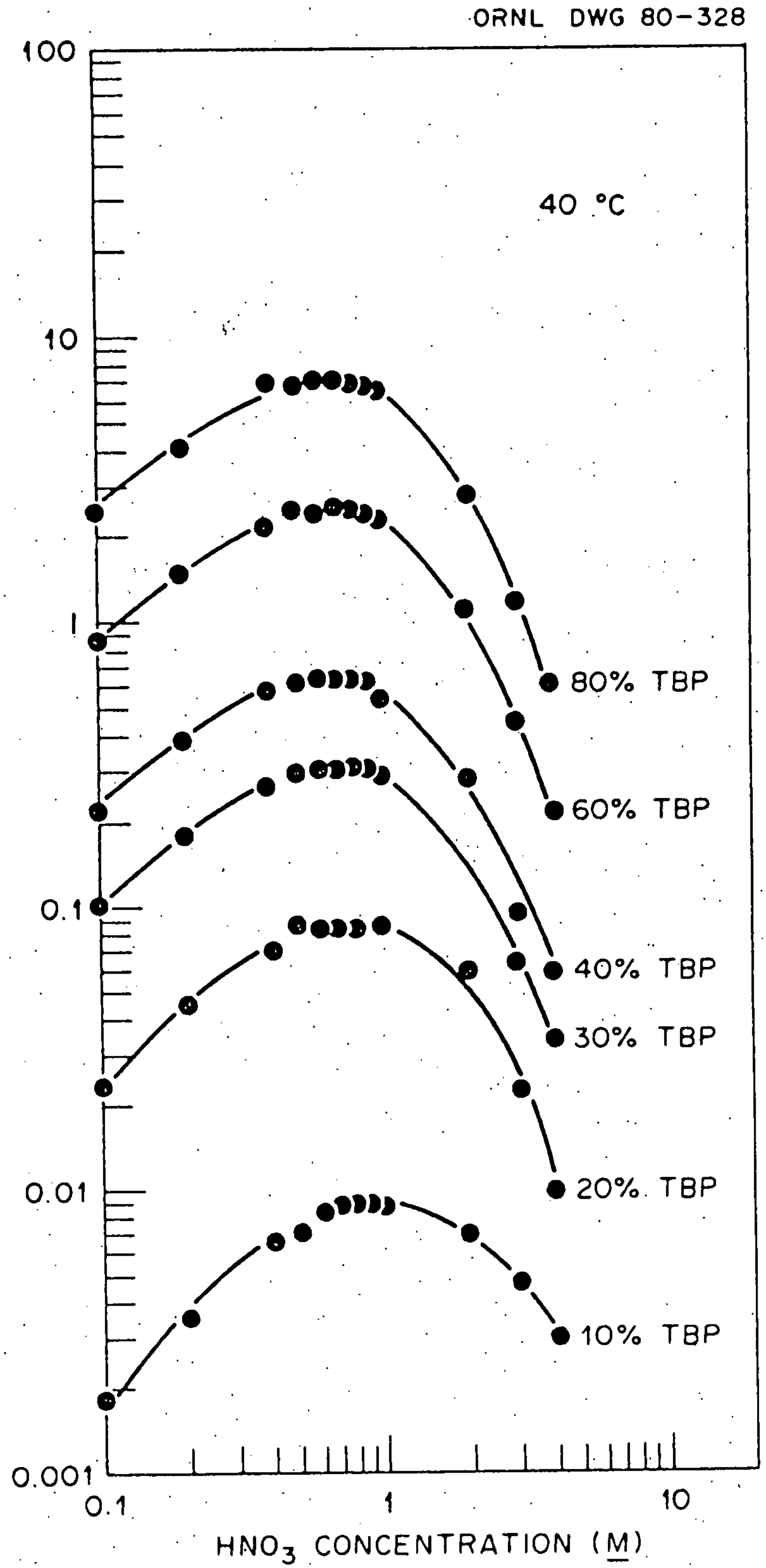


Fig. 2.
D. J. PRUETT

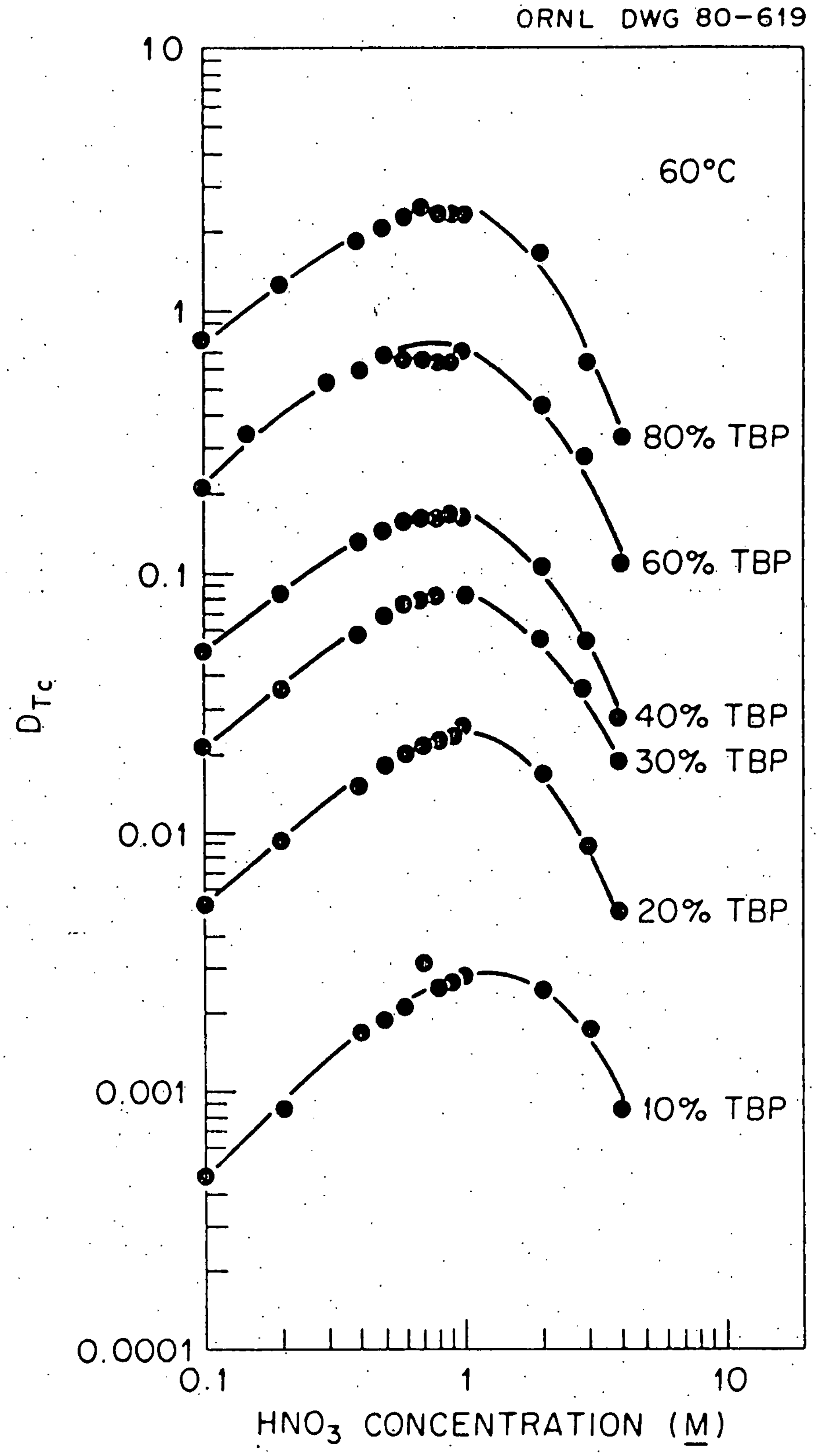


Fig. 3
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Effect of Hydrochloric Acid Concentration

In contrast, figures 4-6 show the distribution behavior of technetium when hydrochloric acid is substituted for nitric acid under the same conditions of temperature and TBP concentrations. The distribution coefficient increases smoothly as the HCl or TBP concentration is increased. The differences in the distribution behavior between the two systems can be largely attributed to the relatively large amounts of nitric acid that can be extracted by TBP, which reduce the amount of uncomplexed or "free" TBP available to extract pertechnetate. Hydrochloric acid is much less extractable, so corrections for the amount of TBP complexed by the mineral acid are small or negligible over the range of conditions studied.

Figure 7 shows that plotting D_{Tc} as a function of the mean molar activity of hydrochloric acid (4) at 25° yields linear curves with a slope of one under all conditions studied. This suggests that a single proton is involved in the extraction reaction and that, under these conditions, competition between $HTcO_4$ and HCl for TBP is negligible. Implicit in this treatment is the assumption that the activity coefficients of the aqueous and organic technetium species are constant (and probably near unity) in these dilute (0 to 500 μg/ml) solutions. The activity coefficient of TBP at a given concentration is also assumed to be unchanged by the extraction of small amounts of technetium and HCl.

Effect of TBP Concentration

Typical plots of D_{Tc} as a function of TBP concentration in the nitric acid system are shown in Fig. 8. The slopes of these and similar lines that may be constructed from the data in Figs. 1-3 have an average value of 3.1 ± 0.2, suggesting that three TBP molecules are involved in the extraction of pertechnetate. Similar results have been found previously

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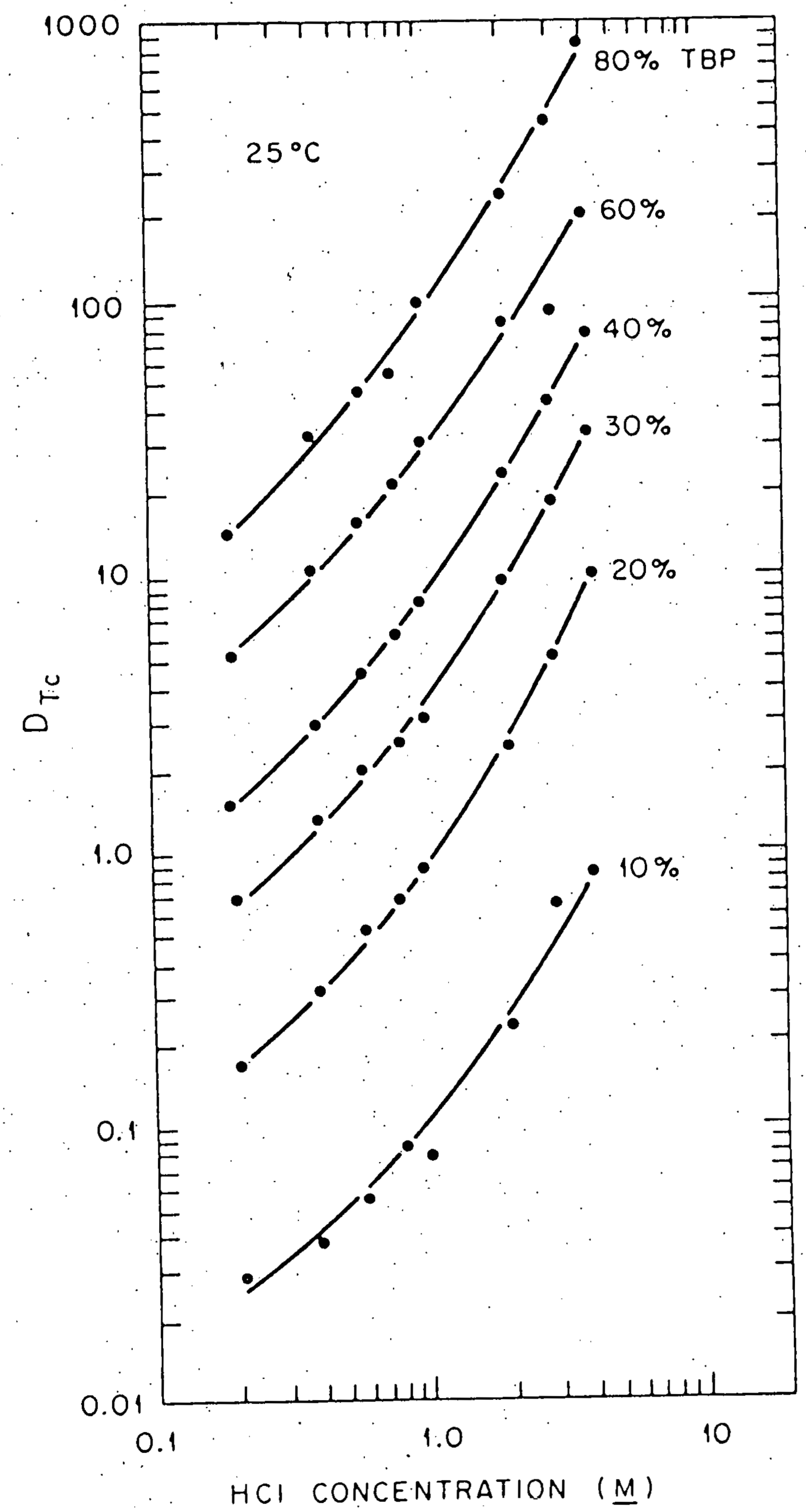

FIG. 4
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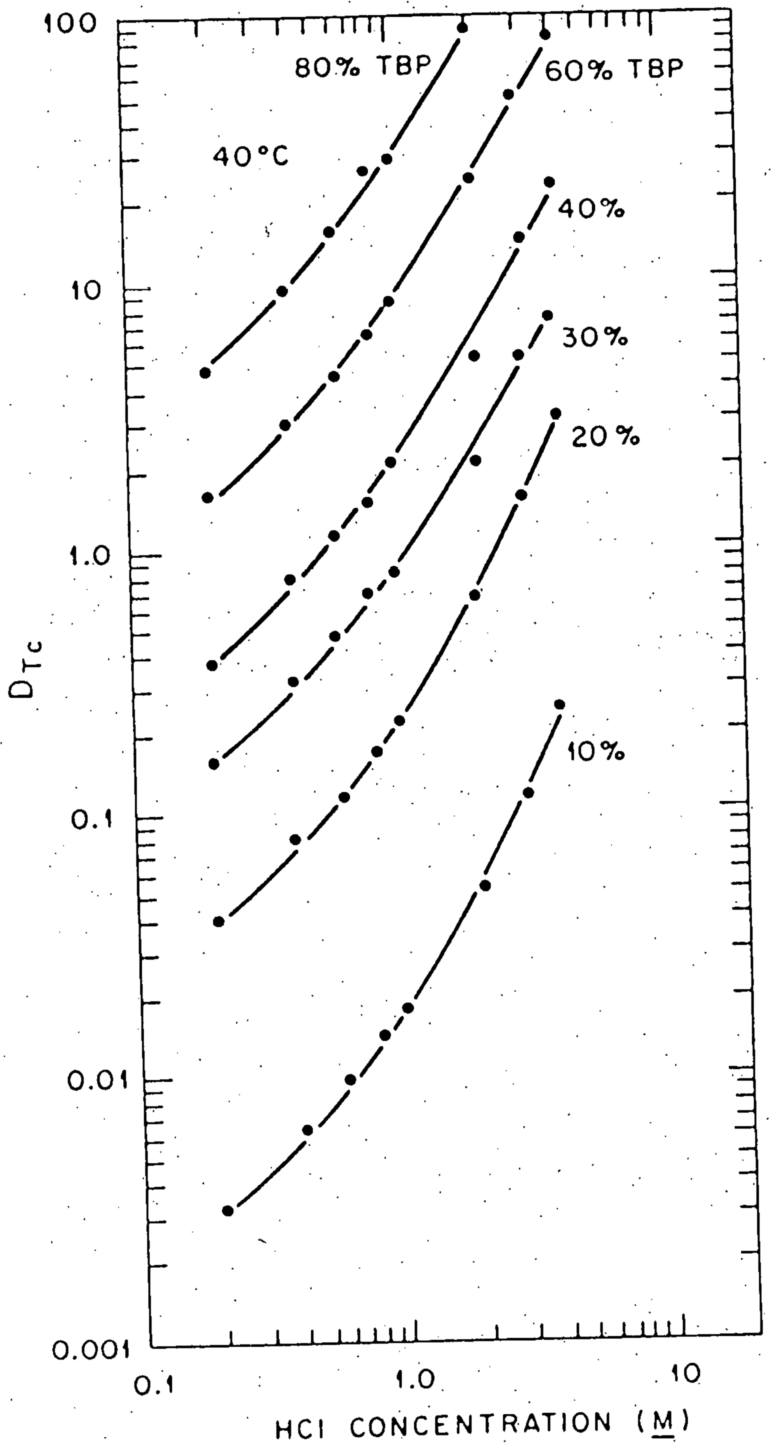

FIG. 5
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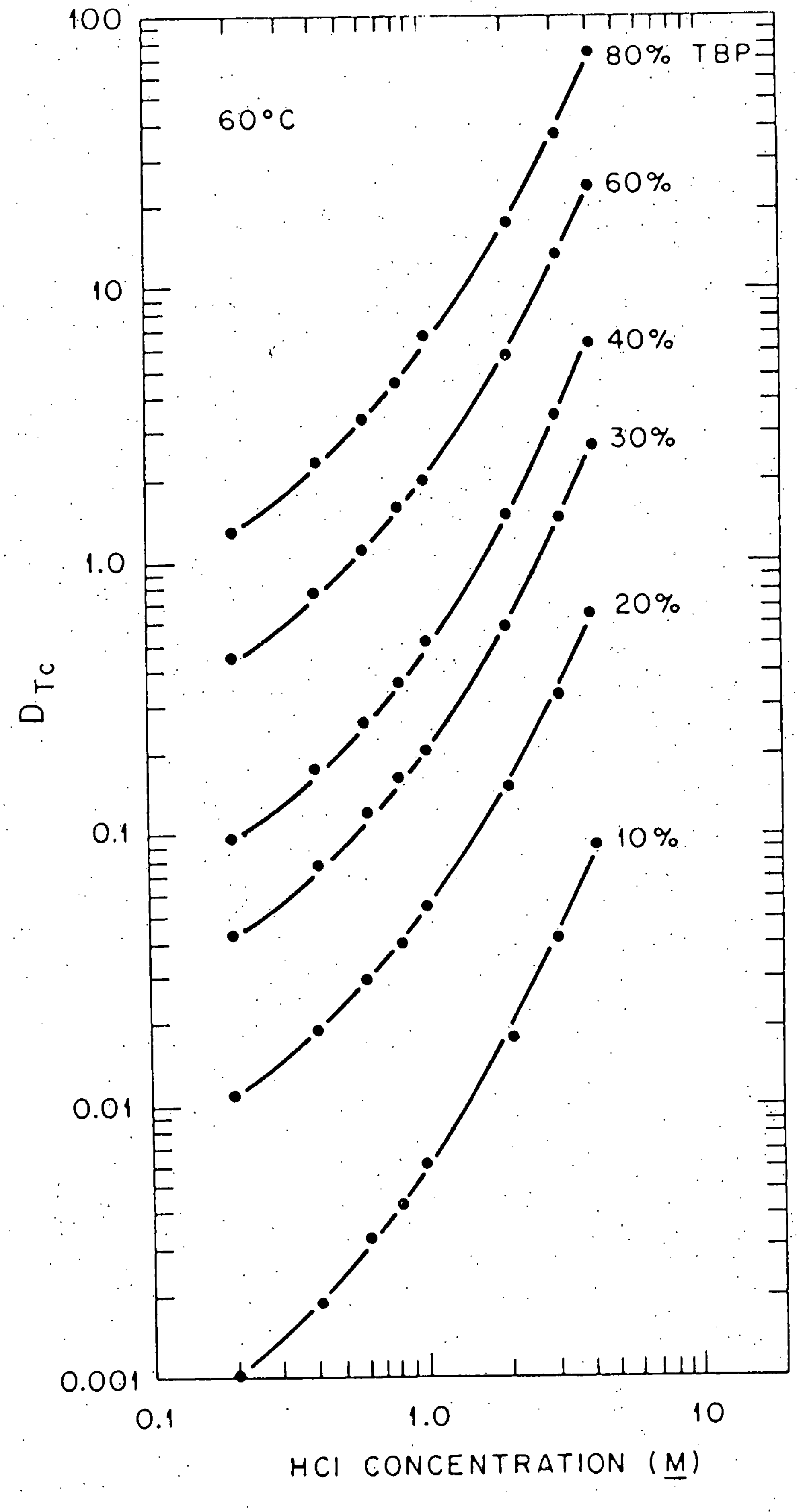

FIG. 6
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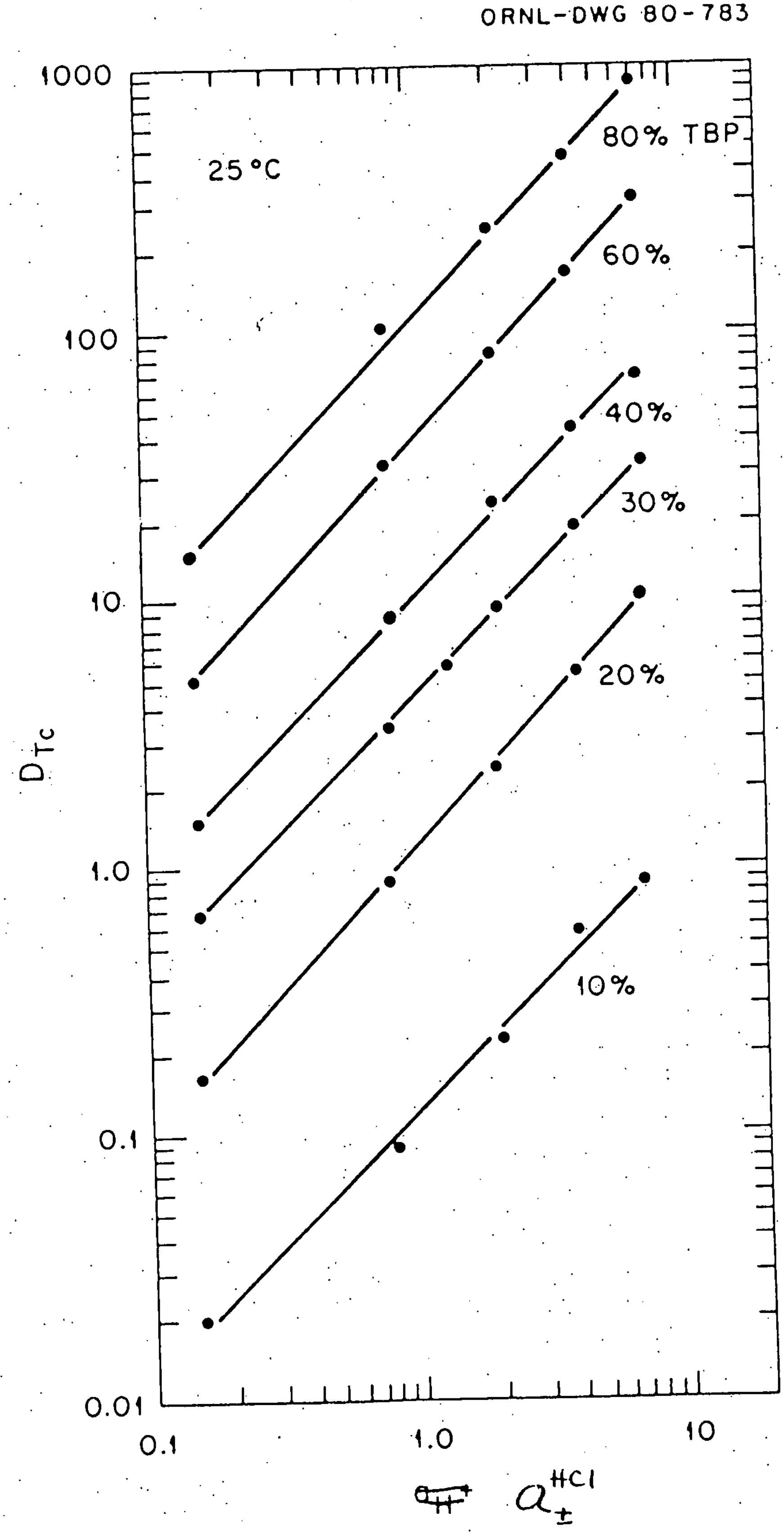

FIG. ~~6~~ 7
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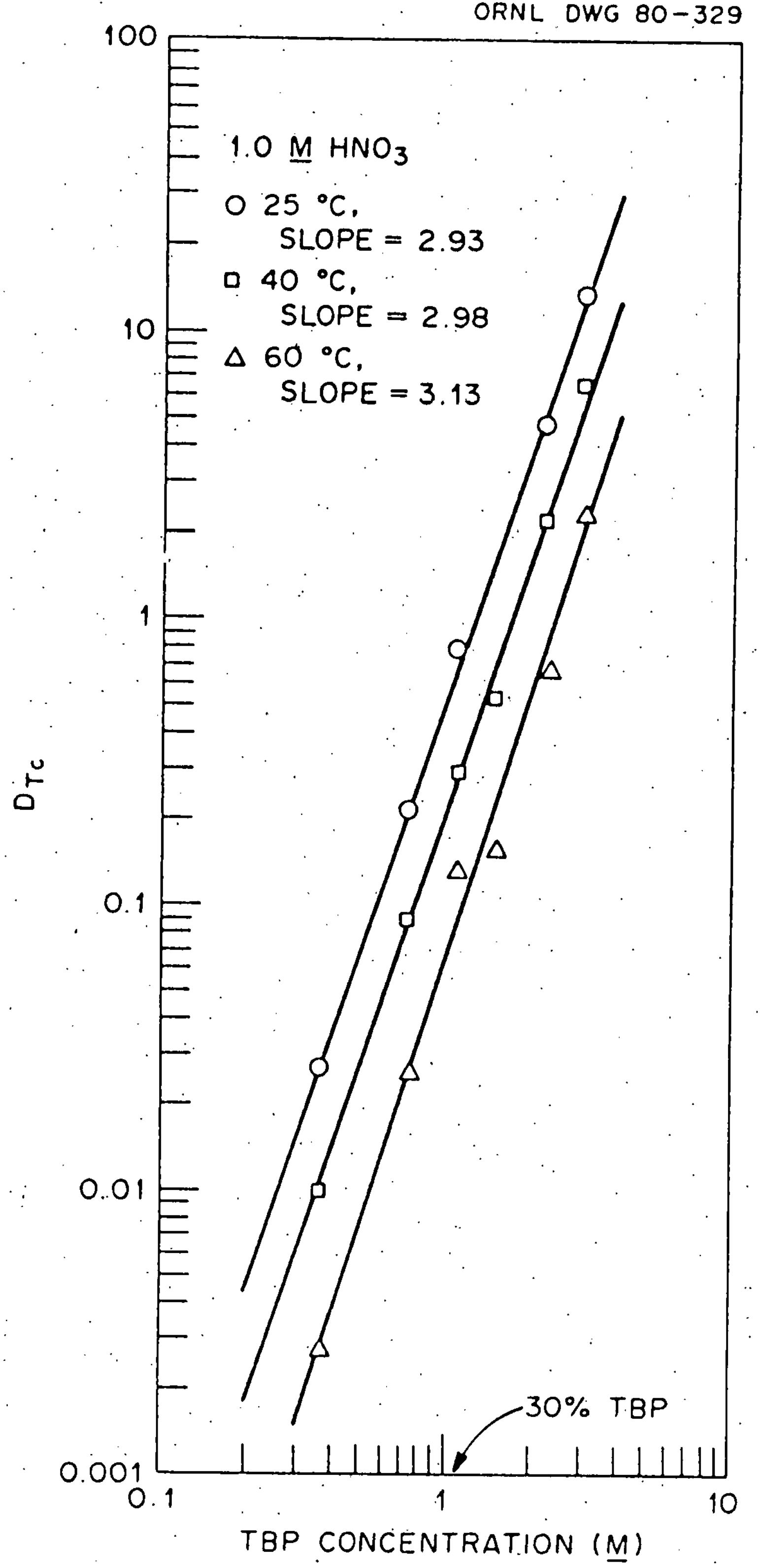


Fig. 8
D. J. PRUETT

for both pertechnetate (6) and perrhenate (which behaves similarly) (11), though over a much smaller range of conditions. If the distribution data for the hydrochloric acid system (Fig. 4-6) is treated in the same way, a similar family of curves is generated with an average slope of 3.2 ± 0.1.

Figure 9 compares plots of $D°_{Tc}$ as a function of mean molar activity in the HNO_3 and HCl systems. $D°_{Tc}$ is obtained by dividing D_{Tc} by the concentration of free TBP to the third power $[(TBP)_{free} = (TBP)_{organic} - n(HX \cdot nTBP)_{organic}]$. This normalizes the distribution coefficient to a constant 1 M concentration of free TBP [see refs. (7) and (12)]. A straight line with a slope of one is obtained for the HCl system; however, the curve for the HNO_3 system is nonlinear. The initial portion of the HNO_3 curve has a slope near one and lies close to the HCL curve. However, as the acid concentration in increased, the HNO_3 data begin to curve, and consistently lower values of $D°_{Tc}$ are obtained. The HNO_3-TBP-H_2O system is known to be quite complicated (13), and it would appear that the empirical method used to correct for free TBP in this system is not adequate to account for the rapidly increasing concentration of nitric acid and subsequent activity coefficient changes in the organic phase. In the HCl system, much less acid is extracted, and these corrections are not so critical. It is also possible that a second species may be extracted in the HNO_3 system, but this has not yet been established.

Extraction Reaction Stoichiometry

These data presented above suggest that the following equilibrium predominates in the extraction of pertechnetate ion from acid solution by TBP:

$$H^+ + TcO_4^- + 3TBP \rightarrow (HTcO_4 \cdot 3TBP)_{organic} \quad . \qquad (1)$$

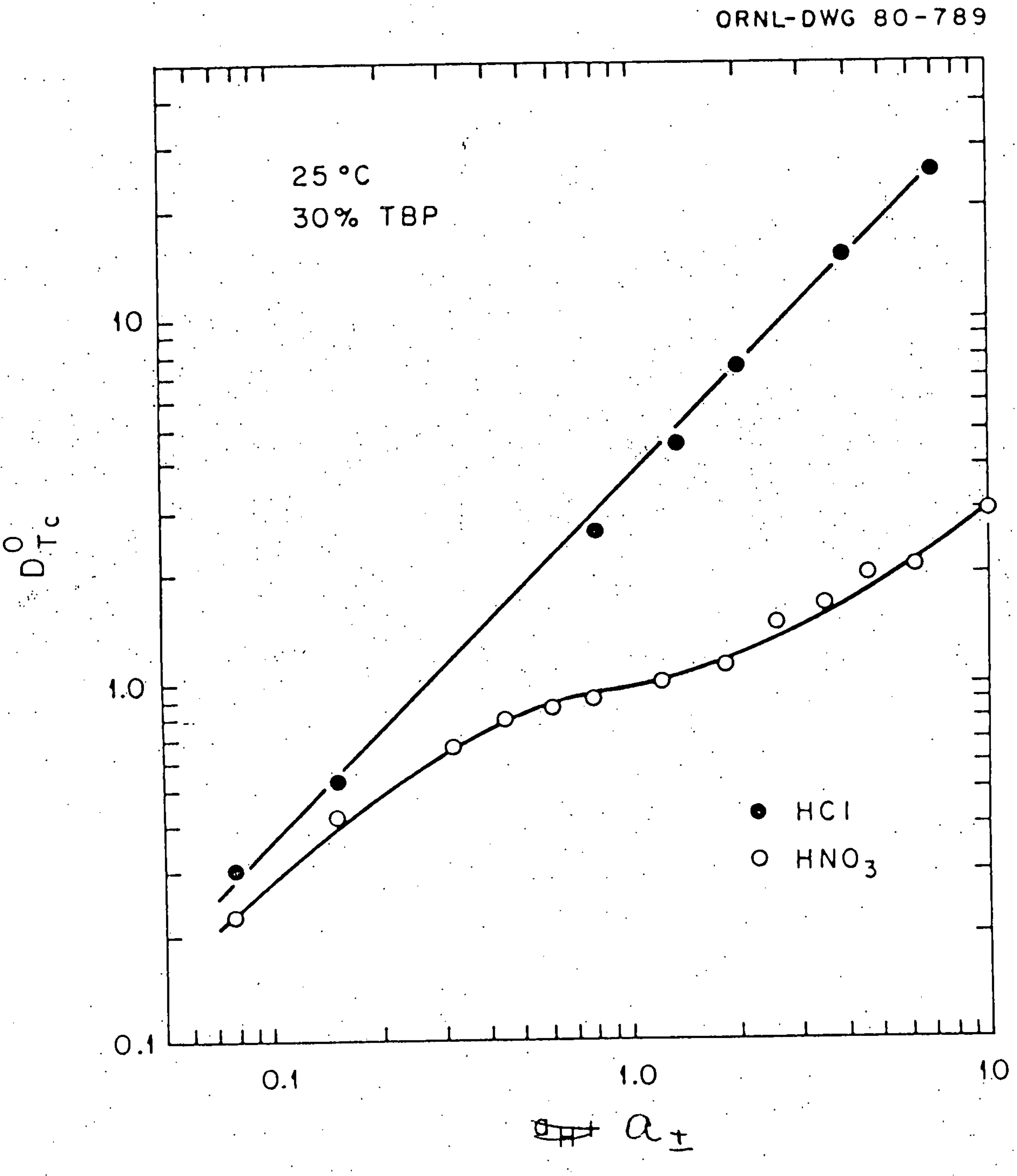


FIG. [illegible]

Pruett

This stoichiometry has been suggested for both pertechnetate (6) and perrhenate (11), although Kertes and Beck (14) report a fourth-order dependence on TBP. Each species in Eq. (1) would also be hydrated to an undetermined degree.

Since $HTcO_4$ is a strong acid (15), it might be expected to behave like other strong acids, especially strong oxy-acids, when interacting with TBP. However, while there is evidence for 1:2 and 2:1 TBP:HA complexes containing varying numbers of H_2O molecules (13, 16), most of the acids that have been studied form 1:1 complexes with TBP under most conditions. A solvation number of three appears to be most unusual. $HClO_4$ has been reported to form complexes containing 1, 2, or 4 TBP molecules and from 2.5 to 10 water molecules, depending on the total $HClO_4$ concentration (17).

On the basis of extensive physicochemical data, the following interaction between TBP monohydrate and tetrahydrated perchloric acid was proposed in dilute (up to 2 M $HClO_4$) solution:

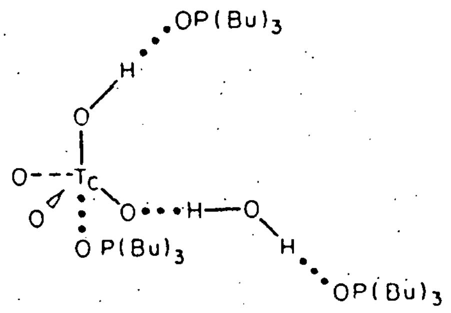
$$4(TBP \cdot H_2O)_{(org)} + H_9O_4^{+}(aq) + ClO_4^{-}(aq) \rightarrow$$

$$[TBP_4 \cdot HClO_4 \cdot (H_2O)_8]_{(org)} \ . \qquad (2)$$

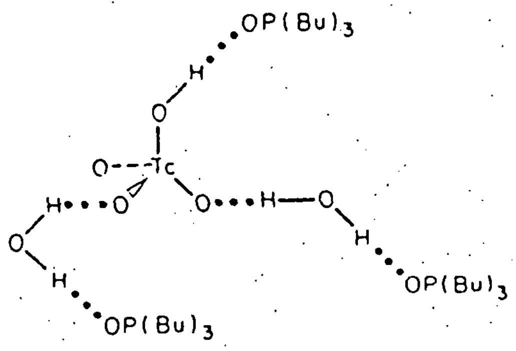
The TBP monohydrate molecules may be hydrogen bonded to either the ClO_4^- oxygen atoms or the tetrahydrate proton, since $HClO_4$ is extensively dissociated in TBP (16). In the former case, the perchlorate ion may be considered as the species being extracted, with a hydrated proton providing for electroneutrality. In the latter case, a hydrated proton is extracted, and the anion serves to balance electrical charge. Intermediate cases, where both the perchlorate ion and the hydrated proton are hydrogen bonded to one or more $TBP \cdot H_2O$ complexes, are also possible.

$HClO_4$ is unique in that it is the only mineral acid that is strong in TBP, even though its ionization is suppressed when a diluent is added to the organic phase. It is unlikely that $HTcO_4$ behaves as a strong acid in an organic TBP-NDD-HNO_3-H_2O phase. Hence, mechanism involving the exclusive solvation of a hydrated proton by TBP are unlikely. These mechanisms are further excluded by the experimental results presented here. If TBP were actively solvating only protons and not the TcO_4^- ions, the TBP-H^+-H_2O complex would carry essentially only NO_3^- ions into the organic phase to maintain electroneutrality since they are far more available (0.1 to 4.0 M̲) than TcO_4^- ions (0.004 M̲), and no appreciable distribution of technetium into the organic phase would be observed.

A more likely bonding scheme might involve TBP molecules hydrogen bonded to a $HTcO_4$ molecule. In the organic phase, both TBP and TBP monohydrate are available to form coordination complexes. At the aqueous-organic interface, TBP·H_2O is probably the predominant species. Consideration of these facts and an examination of molecular scale models lead to two possible structures of the TBP-$HTcO_4$ complex, represented by I and II, below.



I



II

Structure I is the less satisfying of the two, as it involves three different types of $HTcO_4$-to-TBP bonds, is highly unsymmetrical, and is slightly more crowded sterically than is the second model. Structure II involves bonding only through the oxygen atoms of the pertechnetate ion and no direct TBP–Tc bonds. Such a complex could form in two steps. Two TBP monohydrate molecules on the interface could coordinate to the oxygen atoms of the pertechnic acid molecule. This complex could move into the organic phase, where a free TBP molecule could then hydrogen bond to the pertechnic acid proton.

The fourth oxygen atom of $HTcO_4$ is also available to coordinate to a TBP monohydrate complex. This site is somewhat obscured in the tri-TBP complex, but it can be reached and the resulting $HTcO_4 \cdot TBP \cdot (TBP \cdot H_2O)_3$ complex, while somewhat more crowded, does not appear to be impossible. Indeed, the existance of this higher TBP solvate may account for the fact that plots of D_{Tc} versus TBP concentration in the HCl system produce lines whose slopes are constantly slightly greater than 3.0 (3.08 to 3.48). Similar complexes may account for the reported $HReO_4 \cdot 4TBP$ and $HClO_4 \cdot 4TBP$ (14) complexes.

Methods are available to determine if these or some other structures actually exist. For example, a study of the interphase transfer kinetics of pertechnetate could be used to determine the order of the aqueous-to-organic and organic-to-aqueous rate equations with respect to the concentration of TBP. If the two-step mechanism leading to the formation of the tri-solvated species in the organic phase is correct, the aqueous-to-organic rate expression will have a second-order dependence on TBP concentration, and the organic-to-aqueous rate expression will have a negative first-order dependence on the TBP concentration. Obviously, if this mechanism is incorrect, other results are possible that may suggest other mechanisms and structures. Infrared or Raman spectral studies may also prove helpful in identifying these complexes. Attempts to isolate crystalline compounds are also being made.

Calculation of Equilibrium Quotients

The concentration equilibrium quotient expression for Eq. (1) may be written as:

$$K_c = \frac{[HTcO_4 \cdot 3TBP]}{[TcO_4^-][TBP]^3[H^+]} , \qquad (3)$$

where $[HTcO_4 \cdot 3TBP]$ is equated with the measured concentration of technetium in the organic phase. Unfortunately, the available activity coefficient data for the components of this system, needed to calculate a true, thermodynamic equilibrium constant, are quite limited, especially at temperatures other than 25°C. Nonetheless, a reasonably constant value for K_c can be obtained by inserting the known stoichiometric concentrations of each species into Eq. (3). Further, by taking advantage of the known activity coefficients of nitric acid and hydrochloric acid, an improved expression can be developed.

In the nitric acid system at 25°C, Eq. (3) can be modified to take into account the degree of dissociation (α) of nitric acid (18) and to correct for free TBP effects (12):

$$K_c^{\alpha} = \frac{[HTcO_4 \cdot 3TBP]}{[TcO_4^-][TBP]^3_{free}\ \alpha\ [HNO_3]} \qquad (4)$$

Table 1 shows some typical values of K_c^{α} calculated from Eq. (4). For a given TBP concentration, the values of K are somewhat higher at low acid concentration, pass through a minimum near 2.0 <u>M</u>, then rise again slightly. For the data shown in Table 1, the average value of K is 0.94 ± 0.15.

Table 1. Calculated values of K_c^α for the extraction of $HTcO_4$ from nitric acid (10 v/o TBP, 25°C)

(HNO_3)	0.1	0.2	0.4	0.5	0.6	0.7	0.8	0.9	1.0	2.0	3.0	4.0
K_c^α	1.27	1.16	1.02	0.97	0.95	0.91	0.89	0.86	0.82	0.77	0.81	0.89

If all the data in Fig. 1 are used, the average value of K is found to be 0.97 ± 0.45. Large deviations from this value occur at high TBP concentrations and low acid concentrations, resulting in a large standard deviation on the value for K. For example, in 0.2 M HNO_3 using 80 v/o TBP, a value of 2.51 is obtained for K. Similar deviations were observed in a study of the ReO_4^- system (14) and are apparently due to changes in the activity coefficients of the various components of the system.

Unfortunately, no data are available to correct for the concentration of free TBP or the degree of dissociation of HNO_3 at elevated temperatures. However, such corrections should be small at nitric acid concentrations below 0.8 M, and using uncorrected values for [TBP] and $[H^+]$ in Eq. (3) under these conditions yields values of 0.42 ± 0.16 and 0.11 ± 0.05 for K_c at 40 and 60°C.

In the HCl system, free TBP corrections are negligible, and values of K_c can be calculated directly from Eq. (3) by equating $[H^+]$ with the stoichiometric hydrochloric acid concentration. K_c has an average value of 3.4 ± 1.8 at 25°C, 0.89 ± 0.49 at 40° and 0.23 ± 0.14 at 60°. As in the nitric acid system, large deviations from the average values occur at high acid and TBP concentrations.

For those HCl concentrations where activity data are available, a mixed concentration-activity equilibrium constant, K_c', may be calculated by substituting the mean molar hydrochloric acid activity for the stoichiometric hydrochloric acid concentration in Eq. (3). The average value of K_c' obtained in this way is 3.4 ± 0.8 at 25°C. Apparently, the variation in the values of K_c that lead to the large standard deviation is due mainly to activity effects, since using even a limited amount of activity data in Eq. (3) results in the much more constant value of K_c'. Since the technetium concentrations are so low (10^{-3} M or less), most of the remaining variance in the value of the equilibrium constant is probably due to the changing activities of TBP over the wide range of conditions studied. A typical set of values for K_c and K_c' is shown in Table 2 for 30% TBP at 25°C.

Similar results are obtained when K_c and K_c' are calculated at 40 and 60°C. These values are summarized in Table 3, along with average values of ΔG obtained from the relationship $\Delta G_c = -RT \ln K_c$ (or $\Delta G_c' = -RT \ln K_c'$).

From the general relationship $\ln K = -(\Delta H/RT) + C$, it can be easily shown that when [TBP] and $[H^+]$ are held constant, $\ln D_{Tc} = -(\Delta H/RT) + C'$, and semilogarithmic plots of $\log D_{Tc}$ versus $1/T$ such as those shown in Fig. 10 should be linear with slope $-(\Delta H/2.3\ R)$. The data in Figs. 4–6 may be used to construct 48 such plots, which yield an average ΔH value of -62.3 ± 4.2 kJ/mole. Using this average value of ΔH, ΔS_c (or $\Delta S_c'$) may be calculated from the relationship $\Delta S_c = (\Delta H/T) + R \ln K_c$ [or $\Delta S_c' = (\Delta H/T + R \ln K_c')$]. The average values of ΔS_c and $\Delta S_c'$ calculated in this way are shown in Table 3.

It should be noted that use of the average value of K_c or K_c' to calculate ΔG_c or $\Delta G_c'$ (and subsequently ΔS_c and $\Delta S_c'$) gives slightly different values for the free energy and entropy changes than are shown in Table 2. This difference arises because taking the logarithm of each calculated value of K and then averaging is not mathematically equivalent to taking the logarithm of an average value for K. In an ideal data set, this difference would not occur.

It should also be noted that the average values of the various parameters are essentially the same when calculated with or without the use of the available activity coefficient data. However, the scatter in the values, as measured by the standard deviation of the average, is substantially reduced when the activity coefficients are used.

Table 2. Calculated values of K_c and K_c' for the extraction of $HTcO_4$ from aqueous HCl (30% TBP, 25°C)

HCl (M)	K_c	K_c'
0.2	2.67	3.49
0.4	2.51	--
0.6	2.57	--
0.8	2.54	--
1.0	2.61	3.23
2.0	3.72	3.69
3.0	4.99	3.79
4.0	6.54	3.71

Table 3. Average values of K_c, K'_c, ΔG_c, $\Delta G'_c$, ΔS_c, and ΔS_c for the extraction of $HTcO_4$ from aqueous HCl

T (°C)	K_c	ΔG_c (kJ/mole)	ΔS_c (J/mole K)	K'_c	$\Delta G'_c$ (kJ/mole)	$\Delta S'_c$ (J/mole K)
25	3.4 ± 1.8	-0.66 ± 0.24	-47.8 ± 0.8	3.4 ± 0.8	-0.68 ± 0.17	-47.6 ± 0.5
40	0.89 ± 0.49	0.17 ± 0.34	-48.1 ± 1.0	0.87 ± 0.32	0.13 ± 0.23	-48.0 ± 0.7
60	0.23 0.14	1.1 ± 0.34	-47.9 ± 1.0	0.23 ± 0.07	1.0 ± 0.20	-47.8 ± 0.6

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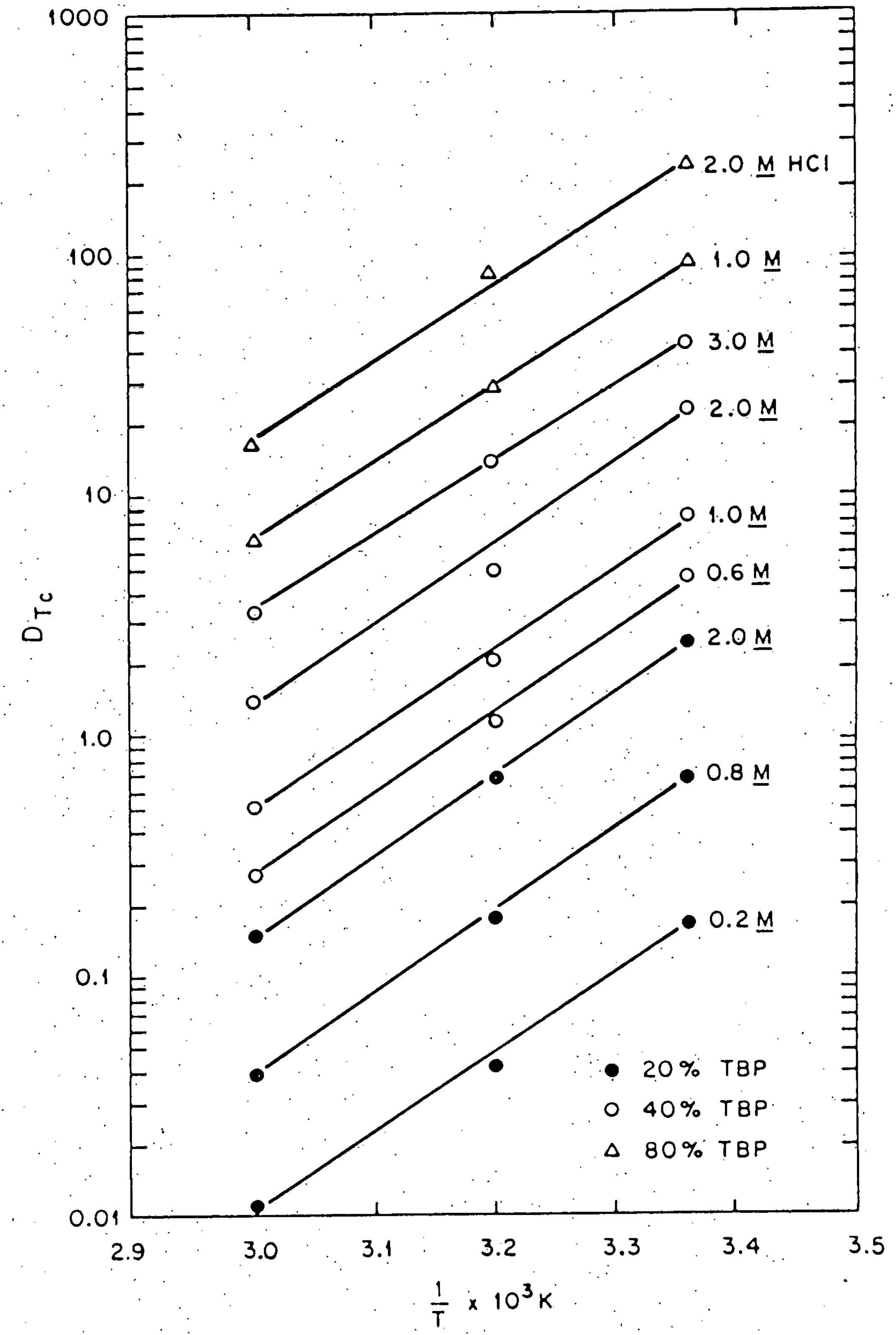

FIG. 10
D. J. Pruett

A similar treatment of the data from the nitric acid system (Fig. 1-3) can be carried out, but is hampered by a lack of activity data and data to correct for the concentration of free TBP at elevated temperatures. Nonetheless, an approximate value for ΔH can be obtained in the same way as in the hydrochloric acid system. Linear plots of D_{Tc} versus 1/T, such as those shown in Fig. 11, are obtained for nitric acid concentrations up to 1.0 M and TBP concentrations up to 60 v/o (2.2 M). If all the data presented in Figs. 1-3 is analyzed in this way, an average value for ΔH of −58.2 ± 3.1 kJ/mole is obtained. Using the average value of 0.97 for K_c^{α} at 25°C, a value of 75 ± 800 J/mole is obtained for ΔG and ΔS is calculated to be −197 ± 25 J/mole°K. The large, negative entropy term obtained in both acid systems is consistent with the large amounts of ordering that must occur as the five molecules and ions on the left hand side of Eq. (1) condense into a single complex species and as the structure-breaking oxyanions are removed from the aqueous phase and allow the structure of the solvent to reform. Table 4 summarizes the values of the various parameters calculated for the HNO_3 system.

Ideally, of course, the true thermodynamic equilibrium constant for Eq. (1) could be calculated using Eq. (3) along with the appropriate activity coefficients. This constant would be independent of the type of acid used to supply the protons for the reaction. This is clearly not the case for the "constants" calculated here, as a comparison of the values in Tables 3 and 4 will show. However, this treatment does have some predictive value, especially for the less complicated HCl system. Substituting D_{Tc} for $[HTcO_4 \cdot 3TBP]/[HTcO_4]$ in Eq. (3) and taking logrithms, it is easily shown that

$$\ln D_{Tc} = \ln K_c + \ln [H^+] + 3 \ln [TBP] . \qquad (4)$$

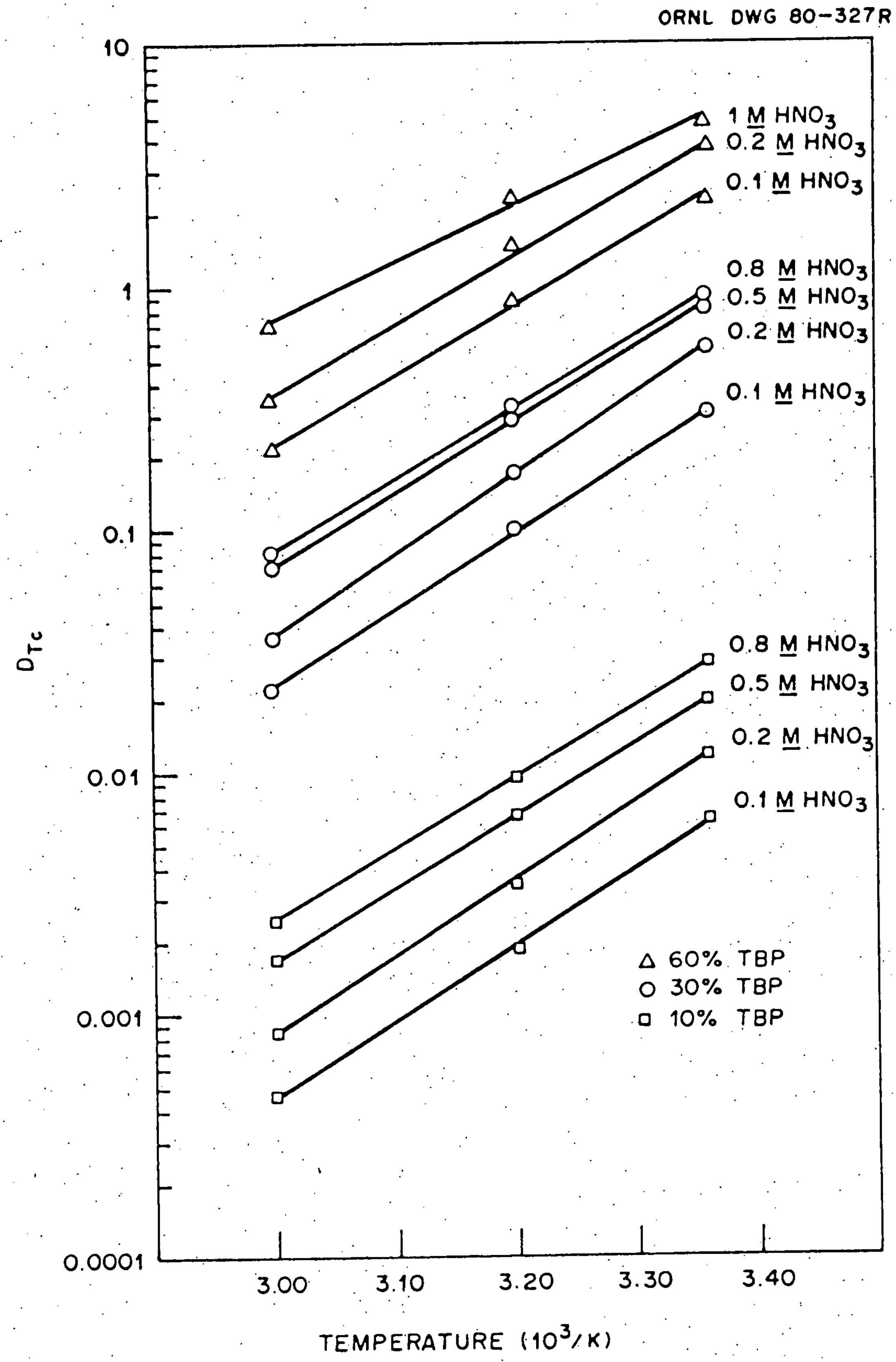

Fig. 11
D. J. PRUETT

Table 4.

T (°C)	K_c	ΔG_c (kJ/mole)	ΔS (J/mole K)
25	0.97 ± 0.45[a]	0.075 ± 0.8	-197 ± 25
40	0.42 ± 0.16[b]	2.3 ± 1.4	193 ± 13
60	0.11 ± 0.05[b]	6.1 ± 1.7	193 ± 14

[a] K_c from Eq. (4).

[b] K_c from Eq. (3).

But since $\Delta G = -RT\ln K = \Delta H - T\Delta S$, then $\ln K = (\Delta S/R) - (\Delta H/RT)$ and using the calculated values of ΔS and ΔH,

$$\ln D_{Tc} = -24.1 + 7500/T + \ln [H^{+}] + 3 \ln [TBP] \qquad (5)$$

This equation can then be used to calculate an approximate value for D_{Tc} at any given temperature, acid concentration and TBP concentration <u>in the hydrochloric acid system</u>. However, an improved equation can be obtained by allowing ΔS, ΔH, and the power dependences of $[H^{+}]$ and [TBP] in Eq. (3) to act as parameters in the general equation

$$\ln D_{Tc} = a + b/T + c\ln [H^{+}] + d \ln [TBP] \; . \qquad (6)$$

The multiple linear regression program in the statistics package of a Hewlett-Packard 41C calculator was used to fit this equation to the experimental values for D_{Tc}, TBP concentration and the mean molar activity of hydrochloric acid, yielding equation (7)

$$\ln D_{Tc} = -23.0 + (7160/T) + 1.05 \ln a_{\pm}^{HCl} + 3.37 \ln [TBP] \; . \qquad (7)$$

The values of a, b, c, and d are not drastically different from their "ideal" values in Eq. (5), but generally yield values of D_{Tc} much closer to the experimentally determined values. As shown by the examples in Table 5, the calculated values are often quite close to the experimental values, but can be substantially different at high acid or TBP concentrations. In extreme cases, the calculated value of D_{Tc} may be in error by as much as 60%, bur more typically it will be within 5-15% of the experimental value.

Attempts to correlate the data from the nitric acid system were unsatisfactory except over very narrow ranges of conditions.

<u>Effects of Adding Uranyl Nitrate</u>

The final parameter affecting technetium extraction by TBP that was included in this study was the addition of uranyl nitrate to the aqueous

Table 5. Selected calculated and experimental values for D_{Tc} in the HCl system

(HCl) ($\underline{M}$)	(TBP) ($\underline{M}$)	T (K)	$D_{expt.}$	$D_{calc.}$	Difference (%)
1.0	0.366	298	0.230	0.199	-10
3.0	0.366	298	0.401	0.403	+1
0.8	2.20	298	22.4	24.1	+8
0.2	2.93	298	14.9	6.8	-54
0.2	0.732	313	0.223	0.243	+9
2.0	2.20	313	24.6	25.1	+2
0.2	2.93	313	4.75	4.60	-3
1.0	1.47	333	0.521	0.615	+18
0.2	2.93	333	1.31	1.15	-12

Average of all data: -4.8.

phase. Figure 12 shows some values of D_{Tc} at various nitric acid concentrations when 0.1 M $UO_2(NO_3)_2$ is added to the aqueous phase compared to those with no uranium in the system. Under most conditions, D_{Tc} is substantially increased. Apparently, a pertechnetate anion is substituted for a nitrate anion in the extraction of the uranyl in (6):

$$UO_2^{2+} + NO_3^- + TcO_4^- + 2TBP \rightarrow UO_2(NO_3)(TcO_4)\cdot 2TBP \qquad (8)$$

Efforts are currently being made to quantify and explain this effect.

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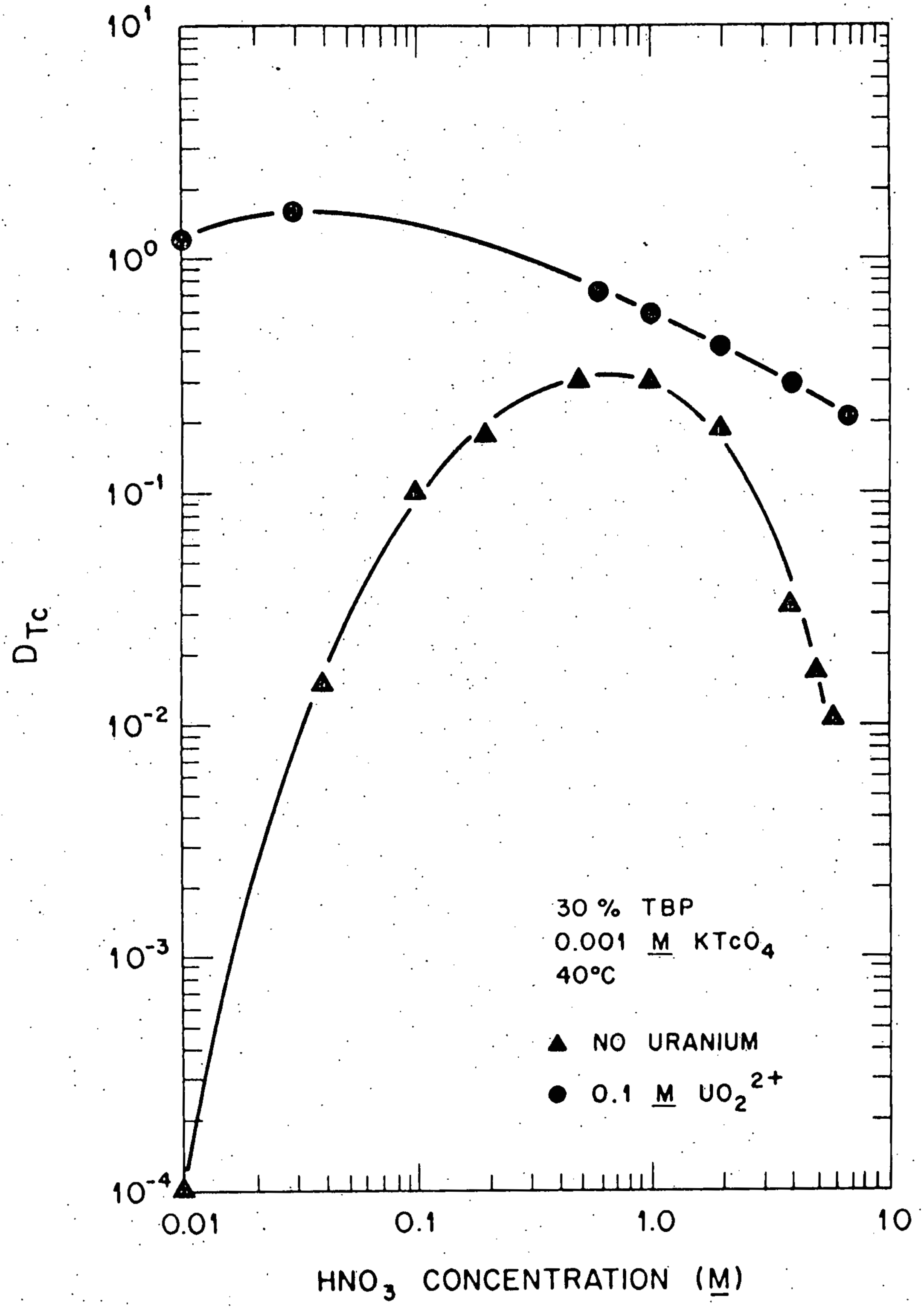
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
D_{Tc}
0.01
0.1
1.0
10
HNO_3 CONCENTRATION (M)
30 % TBP
0.001 M $KTcO_4$
40°C
▲ NO URANIUM
● 0.1 M UO_2^{2+}

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