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The Nitrate Dependence of the Dysprosium Distribution Coefficient at Constant Ionic Strength in the Synergistic System Kerosene/HTTA/TBP/Dilute HNO_3

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Abstract

Analysis of dysprosium distribution data determined at varying nitrate concentration but constant ionic strength indicates that the dysprosium exists in the aqueous phase as $Dy(NO_3)_2^{+1}$. The corresponding complex which is extracted into the organic phase is taken to be $Dy(NO_3)(TTA)_2(TBP)_2$.

INTRODUCTION

The last two papers published in this series (*1*, *2*) have developed the theory which allows the determination of the form of the extracted metal complex in the two-phase system kerosene/thenoyltrifluoroacetone (HTTA)/tributylphosphate (TBP)/dilute HNO_3. The most recent one by Cox and Davis (*1*) concludes that the form of the extracted metal complex is $M(NO_3)(TTA)_2(TBP)_2$ for the trivalent lanthanides and curium. The presence of the nitrate group was inferred since only two (TTA^-) molecules were found to satisfy the +3 valence requirements of the rare earths, and HTTA cannot act as a bidentate molecule satisfying two valence positions. This conclusion was at variance with essentially all previous authors who have generally reported the form of the extracted rare earth complex to be

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$M(TTA)_3(TBP)_2$. It was therefore felt that it was necessary to devise an experimental technique which would allow the determination of the amount of nitrate in the complex directly. This paper deals with these experiments.

EXPERIMENTAL

In order to determine the amount of nitrate in the extracted complex directly, measurements were made of the dysprosium distribution coefficient at constant ionic strength but varying nitrate concentration. This was done by using the nitrates of Al^{+3}, Ca^{+2}, and Na^{+} in combination and separately to give varying nitrate but constant ionic strength. All other variables, such as pH, TBP concentration, HTTA concentration, and metal concentration, were held constant. It had been previously determined that Al^{+3}, Ca^{+2}, and Na^{+} do not complex appreciably in this system.

The rare earth used in this experiment was obtained from Research Chemicals Division of Nuclear Corporation of America, Phoenix, Arizona, and was of the form $Dy(NO_3)_3 \cdot 5.9\ H_2O$ based on individual lot assay. A stock solution of the metal was prepared by dissolving a weighed amount of the salt in a 0.10-*M* HNO_3 solution. Stock solutions of $NaNO_3$, $Ca(NO_3)_2$, and $Al(NO_3)_3$ were prepared in a similar fashion. The $NaNO_3$ was obtained from General Chemicals Division of Allied Chemical, New York, New York; $Ca(NO_3)_2 \cdot 4\ H_2O$ from J. T. Baker Chemical Company, Phillipsburg, New Jersey; and $Al(NO_3)_3 \cdot 9\ H_2O$ from Matheson Coleman and Bell, Norwood, Ohio. Sample solutions were prepared by combining portions of the stock solutions so that the nitrate concentration varied while the ionic strength remained constant.

Sources and preparation of tri-*n*-butyl phosphate, thenoyltrifluoroacetone, and kerosene have been described previously by Cox and Davis (*1*).

All chemicals were reagent grade or better.

Metal distribution ratios were determined by contacting 25 ml portions of aqueous and organic phases in a 125-ml glass-stoppered iodine flask. Samples were shaken at 330 oscillations/min for 1 hr on a wrist-action shaker manufactured by Burrell Corporation, Pittsburgh, Pennsylvania. Shaking was followed by centrifugation after which the aqueous phases were isolated for analysis. Temperature was held at 25 ± 2°C.

The concentration of Dy in the aqueous phase was determined by using a Jarrell Ash Model 530 Atomic Absorption Spectrophotometer. To enhance the absorption signal, samples and standards alike were diluted with an equal portion of a stock solution of 10,000 ppm KCl and 50% isopropanol in water. The Dy line source was a Jarrell Ash-type 45595 hollow cathode tube operated at 9 mA. The wavelength for analysis was 421.2 nm.

After the aqueous Dy concentrations were determined, the organic concentrations were found by material balance.

THEORY

In the paper by Cox and Davis (*1*) it was deduced that the extracted metal complex probably had the form $M(NO_3)(TTA)_2(TBP)_2$. It was reasoned that data taken under conditions of constant ionic strength and varying nitrate content with other variables being held constant should allow confirmation of the nitrate group in the complex. If a single nitrate group is attached to the metal complex and the metal (rare earth) is present as the fully ionized +3 species in the aqueous phase, the mixed equilibrium constant would be written as follows:

$$(M^{+3})_{aq} + 2(HTTA)_o + 2(TBP)_o + (NO_3^-)_{aq} \overset{K_e'}{\rightleftarrows} [M(NO_3)(TTA)_2(TBP)_2]_o + 2(H^+)_{aq} \tag{1}$$

$$K_e' = \frac{[M(NO_3)(TTA)_2(TBP)_2]_o[H^+]_{aq}^2}{[M^{+3}]_{aq}[TBP]_o^2[HTTA]_o^2[NO_3^-]_{aq}} \tag{2}$$

If q o/a $= [M(NO_3)(TTA)_2(TBP)_2]/[M^{+3}]$ is defined as the distribution coefficient, then

$$q\ \mathrm{o/a} = \frac{K_e'(TBP)_o^2(HTTA)_o^2(NO_3^-)_{aq}}{(H^+)_{aq}^2} \tag{3}$$

or at constant ionic strength, pH, TBP, and HTTA

$$q\ \mathrm{o/a} = C(NO_3^-)_{aq} \tag{4}$$

Then

$$\log(q\ \mathrm{o/a}) = \log(NO_3^-)_{aq} + \log C \tag{5}$$

Therefore, a plot of log q o/a vs $\log(NO_3^-)_{aq}$ should give a line whose slope is +1. However, if the rare earth exists in the aqueous phase as an equilibrium mixture of nitrates M^{+3}, $M(NO_3)_2^{+2}$, $M(NO_3)^+$, and $M(NO_3)_3$, then four equilibria are involved, and the slope of the log q o/a vs $\log(NO_3^-)_{aq}$ will reflect the form and concentration of the nitrate complexes in the aqueous phase as well as the number of nitrates associated with the complex in the organic phase.

In the derivation that follows, only one complex is assumed to be present in the organic phase, that having the form $M(NO_3)(TTA)_2(TBP)_2$:

$$(M^{+3})_{aq} + 2(HTTA)_o + 2(TBP)_o + (NO_3^-)_{aq} \overset{K_6}{\rightleftarrows} [M(NO_3)(TTA)_2(TBP)_2]_o + 2(H^+)_{aq} \tag{6}$$

$$(MNO_3^{+2})_{aq} + 2(HTTA)_o + 2(TBP)_o \overset{K_7}{\rightleftarrows} [M(NO_3)(TTA)_2(TBP)_2]_o + 2(H^+)_{aq} \tag{7}$$

$$[M(NO_3)_2^{+}]_{aq} + 2(HTTA)_o + 2(TBP)_o \overset{K_8}{\rightleftarrows} [M(NO_3)(TTA)_2(TBP)_2]_o + 2(H^+)_{aq} + (NO_3^-)_{aq} \tag{8}$$

$$[M(NO_3)_3]_{aq} + 2(HTTA)_o + 2(TBP)_o \overset{K_9}{\rightleftarrows} [M(NO_3)(TTA)_2(TBP)_2]_o + 2(H^+)_{aq} + 2(NO_3^-)_{aq} \tag{9}$$

To shorten some of the algebraic expressions to follow, use the following nomenclature:

a_{ij} = activity of component i in phase j
$i = 1, 2, \ldots, 9$
j = aq, o
γ_{ij} = activity coefficient of component i in phase j
c_{ij} = concentration of component i in phase j

Number the components

1	M^{+3}
2	$M(NO_3)^{+2}$
3	$M(NO_3)_2^{+}$
4	$M(NO_3)_3$
5	H^+
6	NO_3^-
7	$[M(NO_3)(TTA)_2(TBP)_2]$
8	HTTA
9	TBP

Define the activity in molar units

$$a_{ij} = \gamma_{ij} c_{ij}$$

with the standard state referred to infinite dilution for all components. Now assume that all $\gamma_{ij} = 1$. The metal distribution ratio becomes in this notation

$$q\ \mathrm{o/a} = \frac{c_{7o}}{c_{1aq} + c_{2aq} + c_{3aq} + c_{4aq}} \tag{10}$$

Now write the equilibrium relations for the four reactions and rearrange each one in terms of an inverse metal distribution ratio for use later.

$$K_6 = \frac{c_{7o}c_{5aq}^2}{c_{1aq}c_{8o}^2c_{9o}c_{6aq}} \tag{11a}$$

$$\frac{c_{1aq}}{c_{7o}} = \frac{c_{5aq}^2}{K_6c_{8o}^2c_{9o}^2c_{6aq}} \tag{11b}$$

$$K_7 = \frac{c_{7o}c_{5aq}^2}{c_{2aq}c_{8o}^2c_{9o}^2} \tag{12a}$$

$$\frac{c_{2aq}}{c_{7o}} = \frac{c_{5aq}^2}{K_7c_{8o}^2c_{9o}^2} \tag{12b}$$

$$K_8 = \frac{c_{7o}c_{5aq}^2c_{6aq}}{c_{3aq}c_{8o}^2c_{9o}^2} \tag{13a}$$

$$\frac{c_{3aq}}{c_{7o}} = \frac{c_{5aq}^2c_{6aq}}{K_8c_{8o}^2c_{9o}^2} \tag{13b}$$

$$K_9 = \frac{c_{7o}c_{5aq}^2c_{6aq}^2}{c_{4aq}c_{8o}^2c_{9o}^2} \tag{14a}$$

$$\frac{c_{4aq}}{c_{7o}} = \frac{c_{5aq}^2c_{6aq}^2}{K_9c_{8o}^2c_{9o}^2} \tag{14b}$$

Now rewrite Eq. (10) as reciprocal q o/a

$$\frac{1}{q\ \mathrm{o/a}} = \frac{c_{1aq}}{c_{7o}} + \frac{c_{2aq}}{c_{7o}} + \frac{c_{3aq}}{c_{7o}} + \frac{c_{4aq}}{c_{7o}} \tag{15}$$

and substitute Eq. (11b), (12b), (13b), and (14b) into Eq. (15):

$$\frac{1}{q\ \mathrm{o/a}} = \frac{c_{5aq}^2}{K_6c_{8o}^2c_{9o}^2c_{6aq}} + \frac{c_{5aq}^2}{K_7c_{8o}^2c_{9o}^2} + \frac{c_{5aq}^2c_{6aq}}{K_8c_{8o}^2c_{9o}^2} + \frac{c_{5aq}^2c_{6aq}^2}{K_9c_{8o}^2c_{9o}^2} \tag{16}$$

For a run made at constant ionic strength and at constant concentrations of H^+, HTTA, and TBP, Eq. (16) is of the form

$$(q\ \mathrm{o/a})^{-1} = \alpha c_{6aq}^{-1} + \beta + \gamma c_{6aq} + \delta c_{6aq}^2 \tag{17}$$

where

$$\alpha = \frac{c_{5\mathrm{aq}}^2}{K_6 c_{8\mathrm{o}}^2 c_{9\mathrm{o}}^2}$$

$$\beta = \frac{c_{5\mathrm{aq}}^2}{K_7 c_{8\mathrm{o}}^2 c_{9\mathrm{o}}^2}$$

$$\gamma = \frac{c_{5\mathrm{aq}}^2}{K_8 c_{8\mathrm{o}}^2 c_{9\mathrm{o}}^2}$$

$$\delta = \frac{c_{5\mathrm{aq}}^2}{K_9 c_{8\mathrm{o}}^2 c_{9\mathrm{o}}^2}$$

The fit of experimental data to Eq. (17) should then allow us to tell something about any nitrate complex that may be formed by the metal in the aqueous phase.

ANALYSIS OF DATA

Measurements have been made of the dysprosium distribution coefficient as a function of nitrate concentration at constant ionic strength. A plot of log[q o/a(Dy)] vs log[NO_3^-] at a constant ionic strength of 1.0 is shown in Fig. 1. As can be seen from the plot, when these points are connected they give a slope of -1 rather than a slope of $+1$, which was expected if a single NO_3^- group is attached to the extracted complex and the metal exists as the $+3$ ion in solution. These new data are interpreted as indicating that under the present experimental conditions the metal ion exists in aqueous solution largely as $Dy(NO_3)_2^+$. The conclusion that the rare earths form nitrate complexes of considerable stability has been confirmed by a variety of references (*3–5*).

In order to confirm the importance of the rare earth nitrate complexes, a second set of data was obtained at constant nitrate content and varying ionic strength using $NaClO_4$ as the salt for varying the ionic strength. The ClO_4^- ion does not complex metal ions readily and therefore should not affect the metal distribution coefficient. These data are shown in Fig. 2. It can be seen that over the small range of ionic strengths studied, the distribution coefficient for dysprosium is almost constant with a slight decrease noted as the ionic strength increases. This confirms the fact that nitrate has an effect on the distribution coefficient independent of its effect on the ionic strength. It appears likely that an equilibrium distribution of nitrate complexes of each rare earth will be present in aqueous nitrate

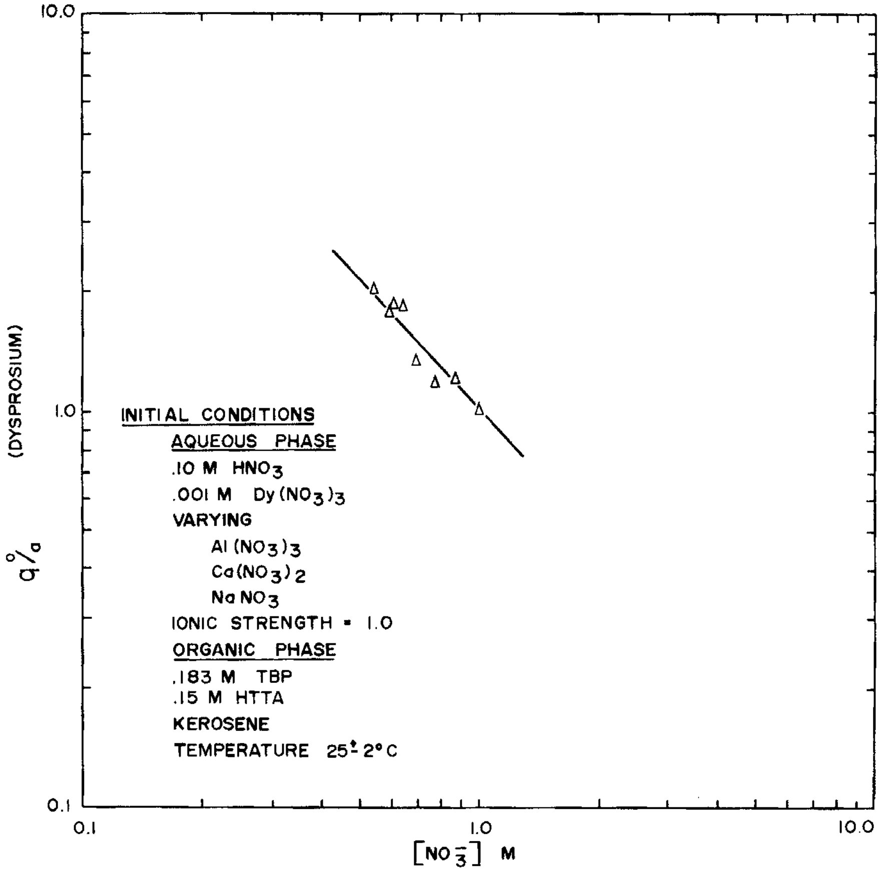

FIG. 1. The nitrate dependence of the dysprosium distribution coefficient at constant ionic strength.

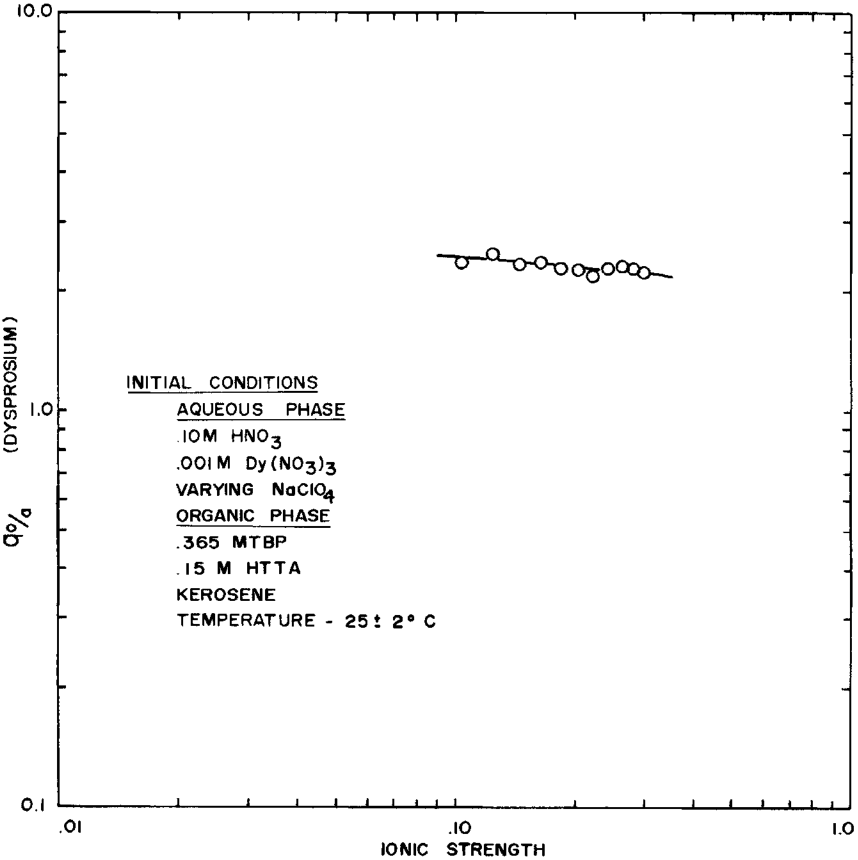

FIG. 2. The dysprosium distribution coefficient as a function of ionic strength at constant nitrate.

solutions with the abundance of each a function of the nitrate concentration in solution.

A plot of q o/a^{-1} vs NO_3^- concentration ($c_{6_{aq}}$) at an ionic strength of 1.0 shows that the experimental data are nearly linear, indicating that the third term of Eq. (17) predominates. A rough fit of equation (17) to the data gives

$$\alpha = 0.01$$

$$\beta = 0.01$$

$$\gamma = 0.85$$

$$\delta = 0.13$$

Both the experimental data and Eq. (17) are shown in Fig. 3.

It should be noted here that the degree of ionization of dysprosium required to fit the data is determined by the assumed form of the extracted complex. In the present case the major part of the dysprosium must be $Dy(NO_3)_2^+$ to conform with the extracted complex $Dy(NO_3)(TTA)_2(TBP)_2$ which has been deduced by Cox and Davis (*1*).

The values of the various K's may be calculated using the values for α, β, γ, δ, and those for $(H^+)_{aq}$, $(HTTA)_o$, and $(TBP)_o$. The initial conditions for the run were:

0.10 *M*	HNO_3
0.15 *M*	HTTA
0.183 *M*	TBP
0.001 *M*	$Dy(NO_3)_3$

It is inappropriate to use total concentrations of TBP and HTTA to find values for the K's due to the formation of the ketohydrate of HTTA ($HTTA \cdot H_2O$) and of its complex with TBP ($HTTA \cdot H_2O \cdot TBP$). These species, which cannot form a chelate, are effectively removed from the system as complexing agents; hence, free concentrations of HTTA and TBP should be used. Cox and Davis (*1*) have given in detail the method for calculating these free concentrations. The relevant equations are

$$C_{8_o} = \frac{q_1[\mathrm{HTTA}]_{\mathrm{total}}}{q_2 + 1} \tag{18}$$

$$C_{9_o} = \frac{[\mathrm{TBP}]_{\mathrm{total}}}{1 + \left(\dfrac{aK_1K_2q_1[\mathrm{TBP}]_{\mathrm{total}}[\mathrm{HTTA}]_{\mathrm{total}}}{q_2 + 1}\right)} \tag{19}$$

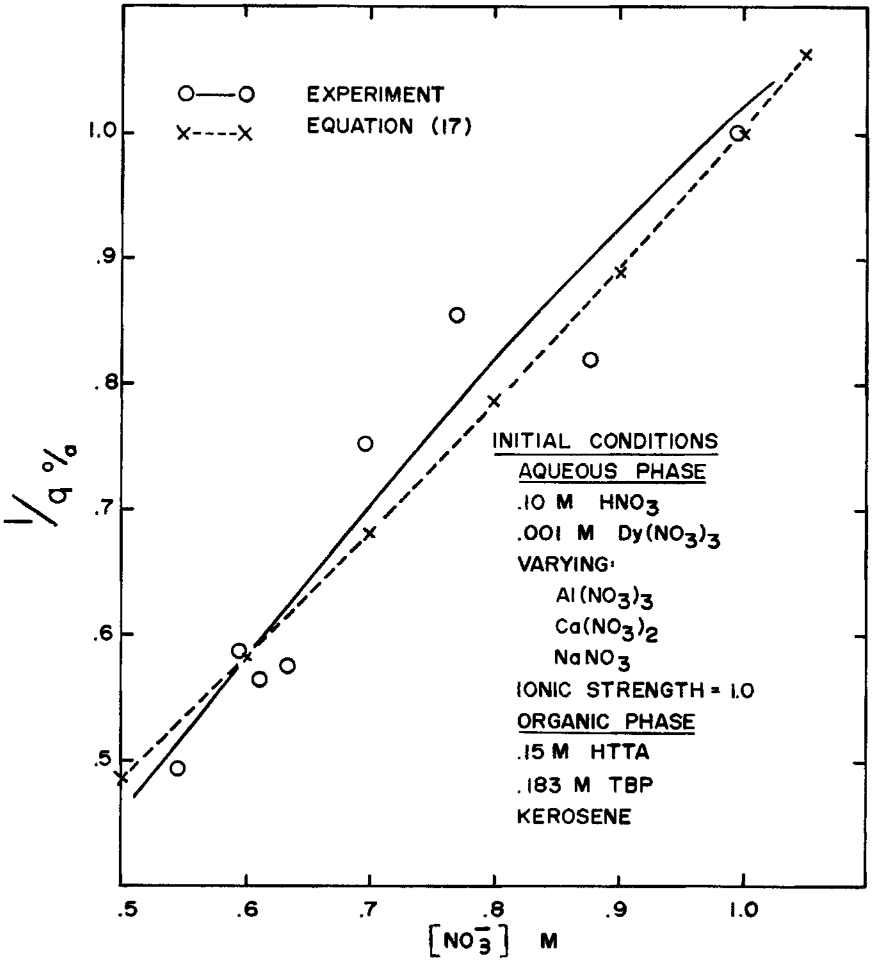

FIG. 3. Fit of dysprosium distribution data to a model of the aqueous phase ionization of $Dy(NO_3)_3$.

where

q_1 = distribution ratio of HTTA with no TBP in system, given in Fig. 4
q_2 = distribution ratio of HTTA with TBP in system, given in Fig. 5
$[\mathrm{TBP}]_{\mathrm{total}}$ = total concentration of TBP, molar units
$[\mathrm{HTTA}]_{\mathrm{total}}$ = total concentration of HTTA, molar units
a = constant = 0.33
K_1 = constant = 14.0
K_2 = constant = 3.45

By using Eqs. (18) and (19), with $q_1 = 3.9$ from Fig. 4 and $q_2 = 9.2$ from Fig. 5, the free concentrations of HTTA and TBP are

$$C_{8_o} = 0.057$$

$$C_{9_o} = 0.157$$

Also

$$C_{5_{aq}} = 0.10$$

since the acid is essentially completely disassociated. Then

$$\begin{aligned} K_6 &= \frac{c_{5_{aq}}{}^2}{\alpha c_{8_o}{}^2 c_{9_o}{}^2} \\ &= \frac{(0.10)^2}{(0.01)(0.057)^2(0.157)^2} \\ &= 1.25 \times 10^4 \end{aligned}$$

Similarly $K_7 = 1.25 \times 10^4$, $K_8 = 147$, and $K_9 = 960$. These K values are only approximate due to the scatter of the experimental data.

Equation (17), which was derived by assuming that four equilibria are involved in the extraction process and that the metal complex in the organic phase has only one form containing a single nitrate, fits the data reasonably well. These results do not show conclusively that there is a single nitrate in the extracted complex. This investigation does show, however, that for the experimental conditions studied, $Dy(NO_3)_3$ in the aqueous phase is only partially dissociated, with $Dy(NO_3)_2{}^+$ being the principal species provided that the extracted complex contains a nitrate group. Further experiments must be devised to determine the degree of ionization of $Dy(NO_3)_3$ in the aqueous phase at an ionic strength of 1.0.

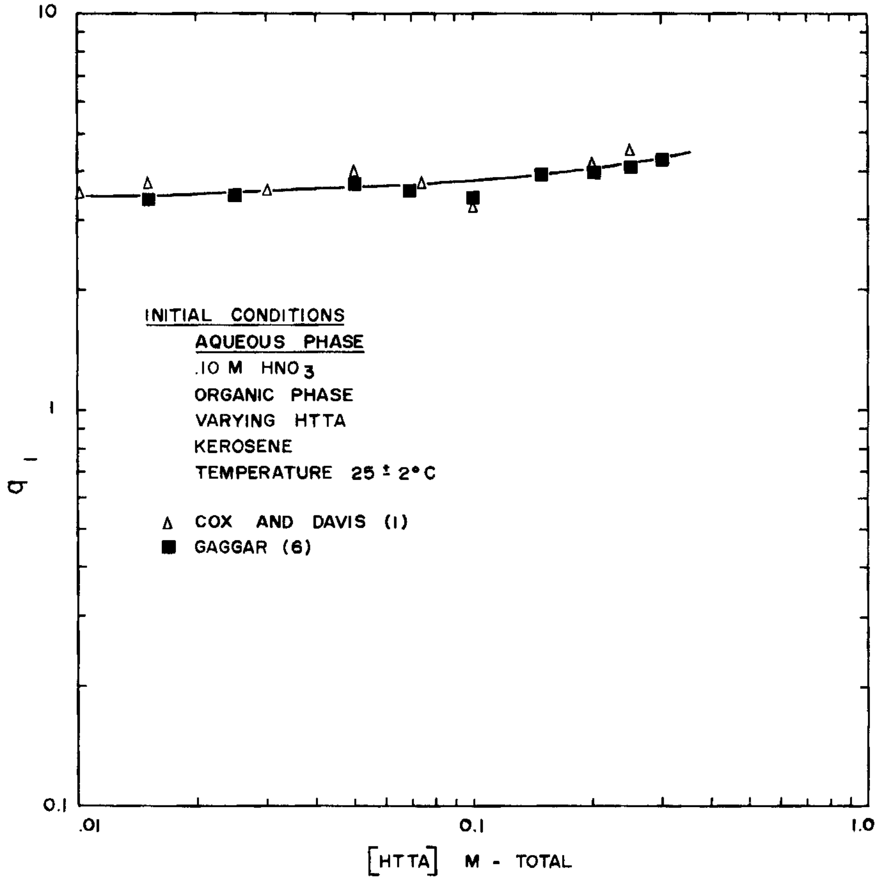

FIG. 4. Distribution ratios of HTTA as a function of the total HTTA concentration with no TBP in the system.

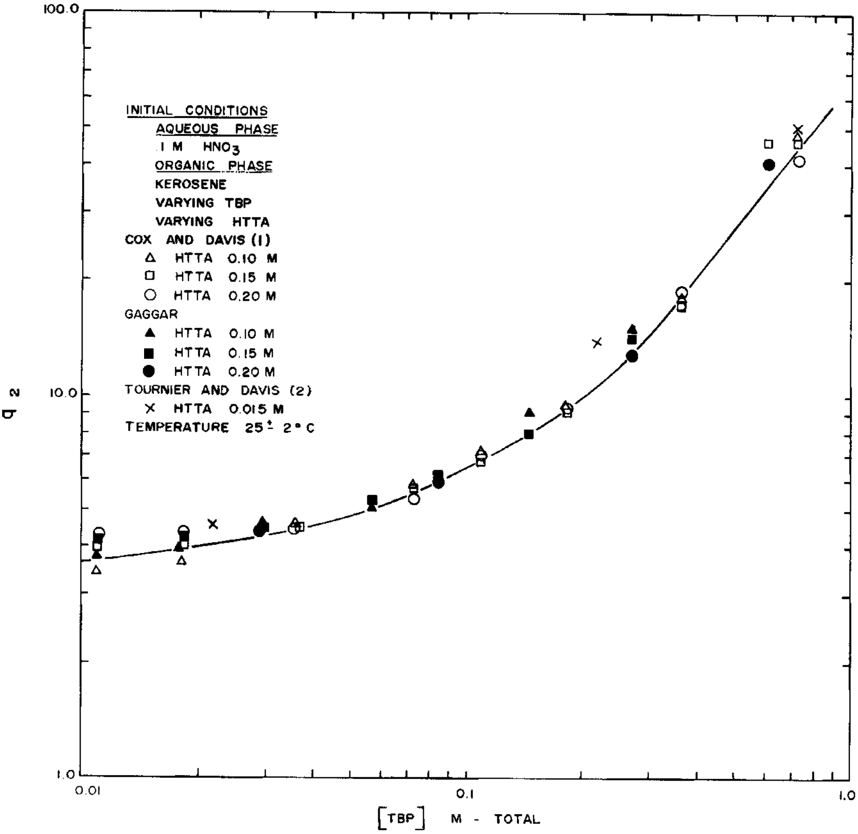

FIG. 5. Distribution ratios of HTTA as a function of the total HTTA and TBP concentrations.

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