Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Extraction Theory and Form of the Extraction Complex of Terbium, Erbium, Ytterbium, and Lutecium in the Synergistic System Kerosene/HTTA/TBP/Dilute HNO_3

Irene H. Gerow[a]; J. G. Hayden[a]; K. Gaggar[a]; M. W. Davis Jr.[a]
[a] COLLEGE OF ENGINEERING UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA

To cite this Article Gerow, Irene H. , Hayden, J. G. , Gaggar, K. and Davis Jr., M. W.(1977) 'Extraction Theory and Form of the Extraction Complex of Terbium, Erbium, Ytterbium, and Lutecium in the Synergistic System Kerosene/HTTA/TBP/Dilute HNO_3', Separation Science and Technology, 12: 5, 511 — 527
To link to this Article: DOI: 10.1080/00372367708068464
URL: http://dx.doi.org/10.1080/00372367708068464

SEPARATION SCIENCE, 12(5), pp. 511–527, 1977

Extraction Theory and Form of the Extraction Complex of Terbium, Erbium, Ytterbium, and Lutecium in the Synergistic System Kerosene/HTTA/TBP/Dilute HNO_3

IRENE H. GEROW, J. G. HAYDEN, K. GAGGAR, and M. W. DAVIS, JR.*

COLLEGE OF ENGINEERING
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SOUTH CAROLINA 29208

Abstract

Analysis of extensive distribution data taken in the synergistic system kerosene/HTTA/TBP/dilute HNO_3 indicates that the rare earths terbium, erbium, ytterbium, and lutecium are extracted into the organic phase as $M(NO_3)(TTA)_2(TBP)_2$. The thermodynamic stability constants for the four metals in the two-phase system have been calculated to be 41±10, 26±10, 19±10, and 14±10%, respectively.

INTRODUCTION

The last three papers published in this series (*1–3*) have developed the theory which allows the determination of the form of the extracted metal complex in the two-phase system kerosene/thenoyltrifluoroacetone (HTTA)/tributyl phosphate (TBP)/dilute HNO_3. The equation for the mixed phase equilibria is written in general form as

$$[M(NO_3)_p{}^{+(Z-p)}]_{aq} + n(HTTA)_o + m(TBP)_o \overset{K_e}{\rightleftarrows} [M(NO_3)_{Z-n}(TTA)_n(TBP)_m]_o + n(H^+)_{aq} + (p-1)(NO_3{}^{-1})_{aq} \qquad (1)$$

*To whom correspondence should be sent.

The most recent paper by Hayden, Gerow, and Davis (*3*) concludes that the rare earths are present in the aqueous phase as a nitrate complex $M(NO_3)_2^{+1}$ if the form of the extracted complex is taken to be $M(NO_3)(TTA)_2(TBP)_2$ for the trivalent rare earths and curium. This paper tests the theory on four more rare earths, terbium, erbium, ytterbium, and lutecium, and calculates the thermodynamic stability constant, K_e, for each of them from the distribution data obtained over a wide range of conditions.

$$K_e = \frac{q\ \mathrm{o/a}[H^+]_{aq}^n[NO_3^{-1}]_{aq}^{p-1}}{[HTTA]_o^n[TBP]_o^m} \tag{2}$$

where q o/a = measured distribution coefficient

$$= \frac{[M(NO_3)_{Z-n}(TTA)_n(TBP)_m]_o}{[M(NO_3)_p^{Z-p}]}$$

$[HTTA]_o$ = free HTTA in the organic phase
$[TBP]_o$ = free TBP in the organic phase

Equation (2) may also be rearranged to the form of

$$q\ \mathrm{o/a} = \frac{K_e[HTTA]_o^n[TBP]_o^m}{[H^+]_{aq}^n[NO_3^{-1}]_{aq}^{p-1}} \tag{3}$$

EXPERIMENTAL

Rare earths were obtained from Research Chemicals Division of Nuclear Corporation of America, Phoenix, Arizona, as the hydrates, based on individual lot assays

$Tb(NO_3)_3 \cdot 5.9H_2O$

$Er(NO_3)_3 \cdot 5.9H_2O$

$Yb(NO_3)_3 \cdot 5.9H_2O$

$Lu(NO_3)_3 \cdot 5.9H_2O$

Stock solutions were prepared by dissolving weighed amounts of the salts in previously prepared nitric acid solutions.

The remaining reagents and experimental apparatus have been described previously by Cox and Davis (*2*), as have the procedures used in determining the metal distribution ratios.

Total HTTA concentrations were 0.10, 0.15, and 0.20 *M* with total TBP concentrations varying between 0.0073 and 0.73 *M*. The metal concentrations were all 0.001 *M*.

THEORY

The theory used for the calculation of free HTTA and TBP concentration in the organic phase was that first proposed by Cox and Davis (*2*) and extended by Hayden, Gerow, and Davis (*3*). The relevant equations are

$$[\mathrm{TBP}]_{\mathrm{free}} = \frac{[\mathrm{TBP}]_{\mathrm{total}}}{1 + \dfrac{aK_1K_2q_1[\mathrm{TBP}]_{\mathrm{total}}[\mathrm{HTTA}]_{\mathrm{total}}}{q_2 + 1}} \tag{4}$$

and

$$[\mathrm{HTTA}]_{\mathrm{free}} = \frac{q_1[\mathrm{HTTA}]_{\mathrm{total}}}{q_2 + 1} \tag{5}$$

where q_1 = distribution ratio of HTTA with no TBP in the system, Fig. 1

q_2 = distribution ratio of HTTA with TBP in the system, Fig. 2

$[\mathrm{TBP}]_{\mathrm{total}}$ = total concentration of TBP, molar units

$[\mathrm{HTTA}]_{\mathrm{total}}$ = total concentration of HTTA, molar units

a = the H_2O brought into the organic phase due to the TBP = 0.33

K_1 = equilibrium constant for HTTA with no TBP in the system = 14.0

K_2 = equilibrium constant for HTTA with TBP in the system = 3.45

ANALYSIS OF DATA

Log q o/a plotted as a function of log $[\mathrm{TBP}_{\mathrm{total}}]_o$ for the metals Tb, Er, Yb, and Lu at each concentration of total HTTA and HNO_3 is shown in Figs. 3 and 4.

Using Eq. (4) and Figs. 1 and 2 to find the free TBP concentrations, Figs. 5 and 6 show log q o/a for all four metals plotted as a function of the log $[\mathrm{TBP}]_{\mathrm{free}}$.

Using Eq. (5) to find the free HTTA concentrations and Fig. 7 to find γ (HTTA activity coefficient), the log q o/a for all four metals is plotted as

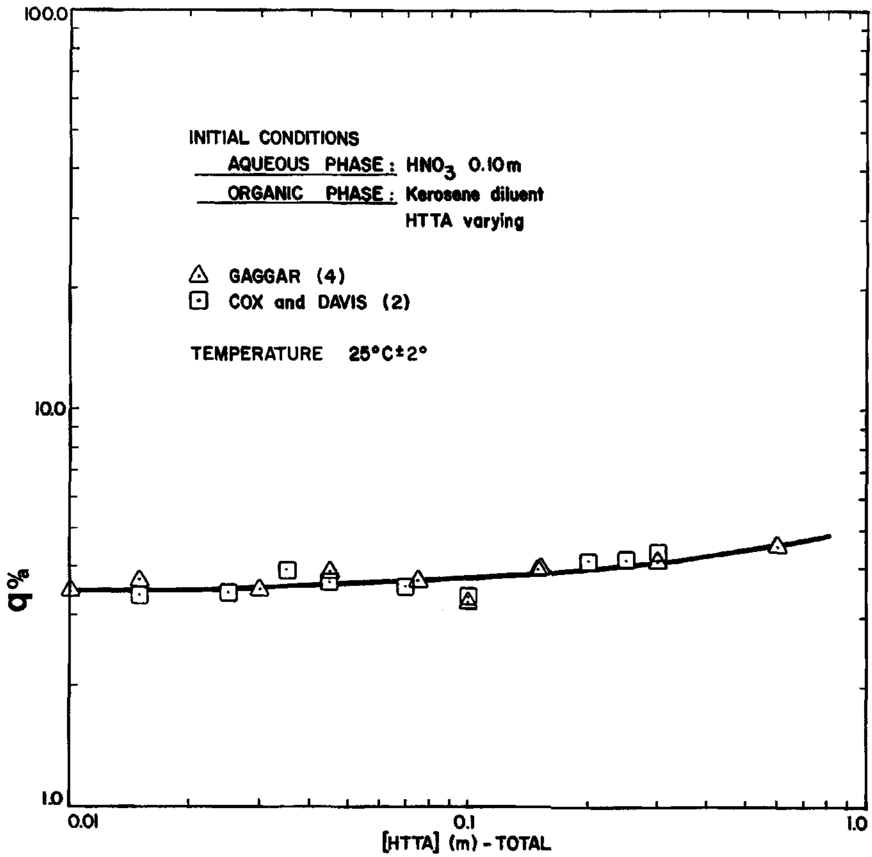

FIG. 1. Distribution ratio of HTTA as a function of the total HTTA concentration with no TBP in the system.

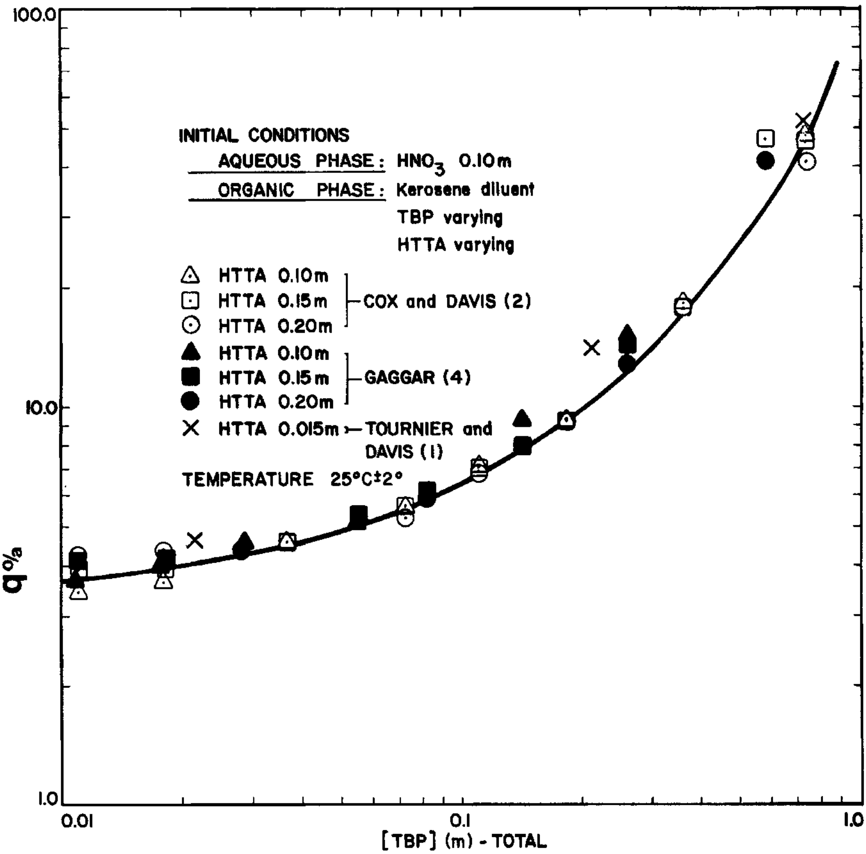

FIG. 2. Distribution of HTTA as a function of the total HTTA and TBP concentrations.

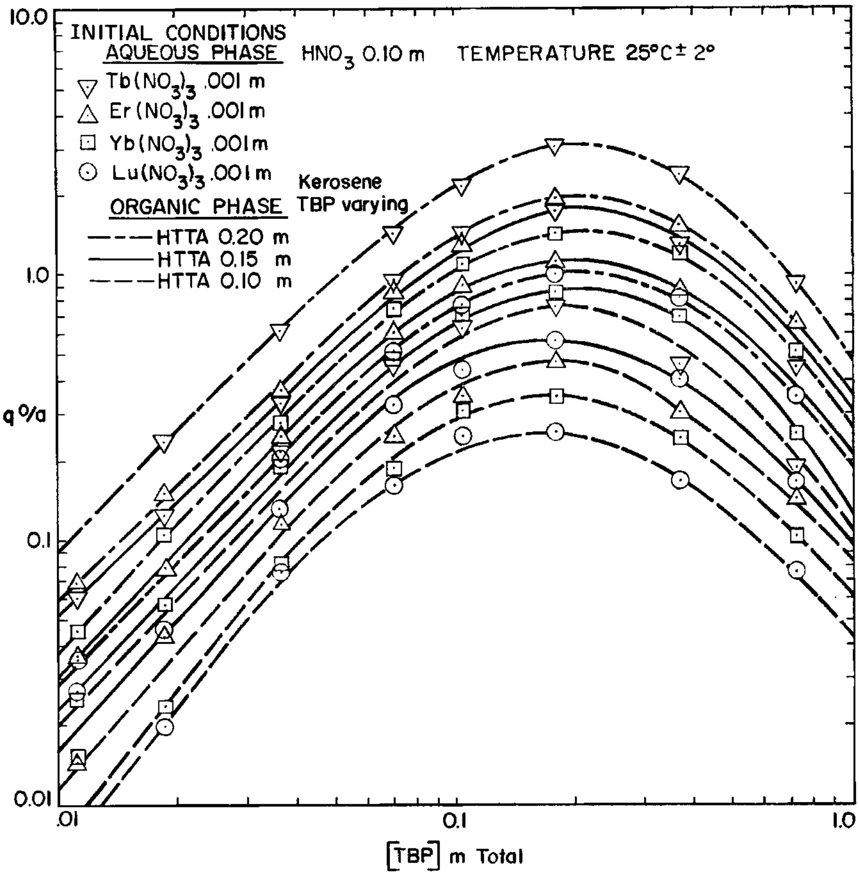

FIG. 3. Distribution ratios of Tb, Er, Yb, and Lu at 0.10 M HNO_3 and varying total HTTA concentrations as a function of total TBP concentrations.

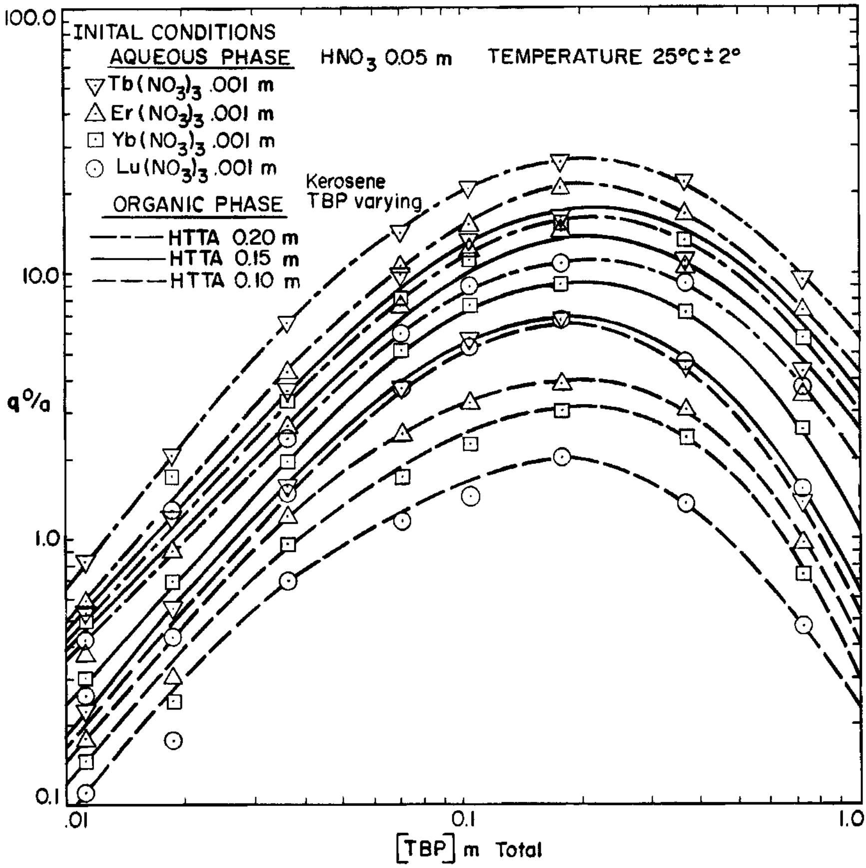

FIG. 4. Distribution ratios of Tb, Er, Yb, and Lu at 0.05 M HNO_3 and varying total HTTA concentrations as a function of total TBP concentrations.

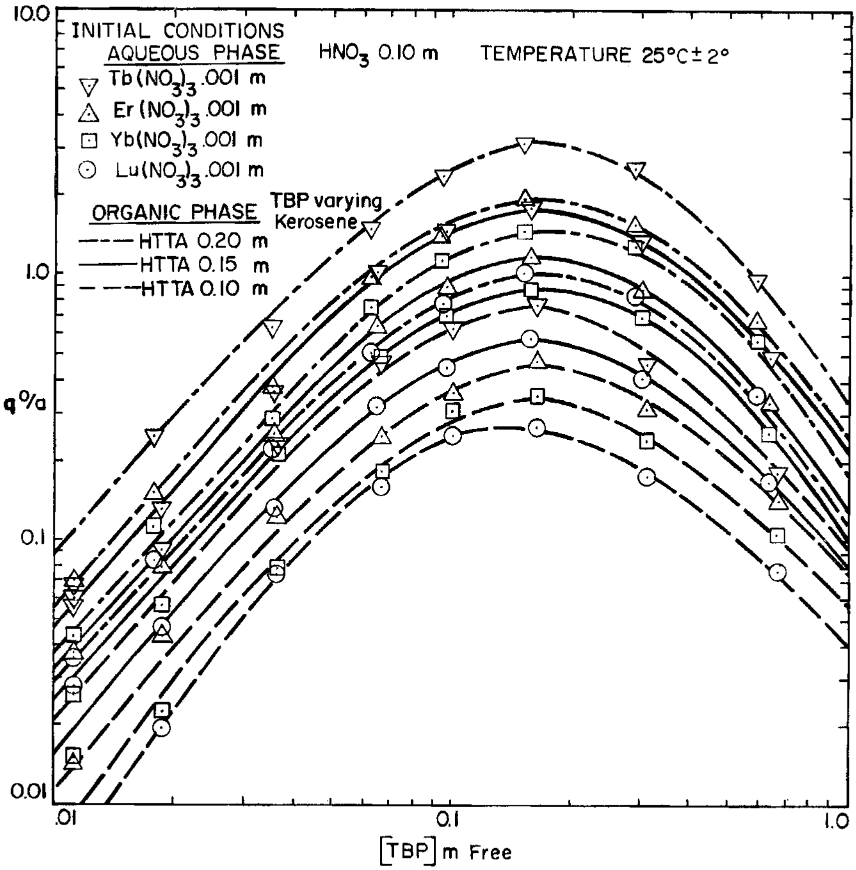

FIG. 5. Distribution ratios of Tb, Er, Yb, and Lu at 0.10 *M* HNO_3 and varying total HTTA concentrations as a function of free TBP concentrations.

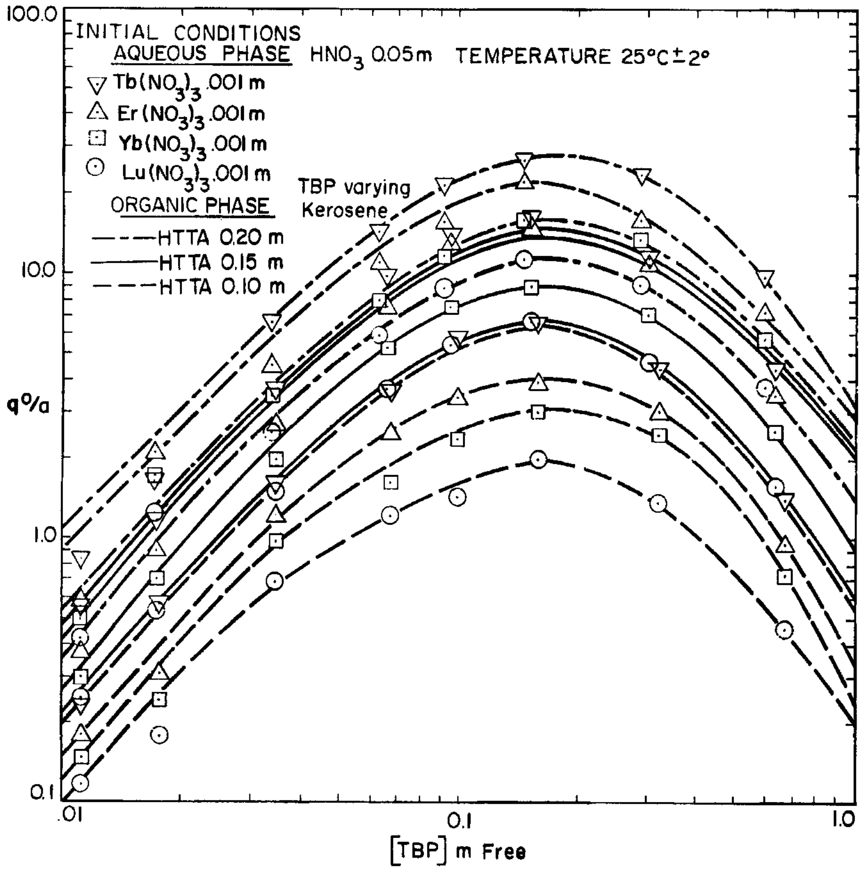

FIG. 6. Distribution ratios of Tb, Er, Yb, and Lu at 0.05 M HNO_3 and varying total HTTA concentrations as a function of free TBP concentrations.

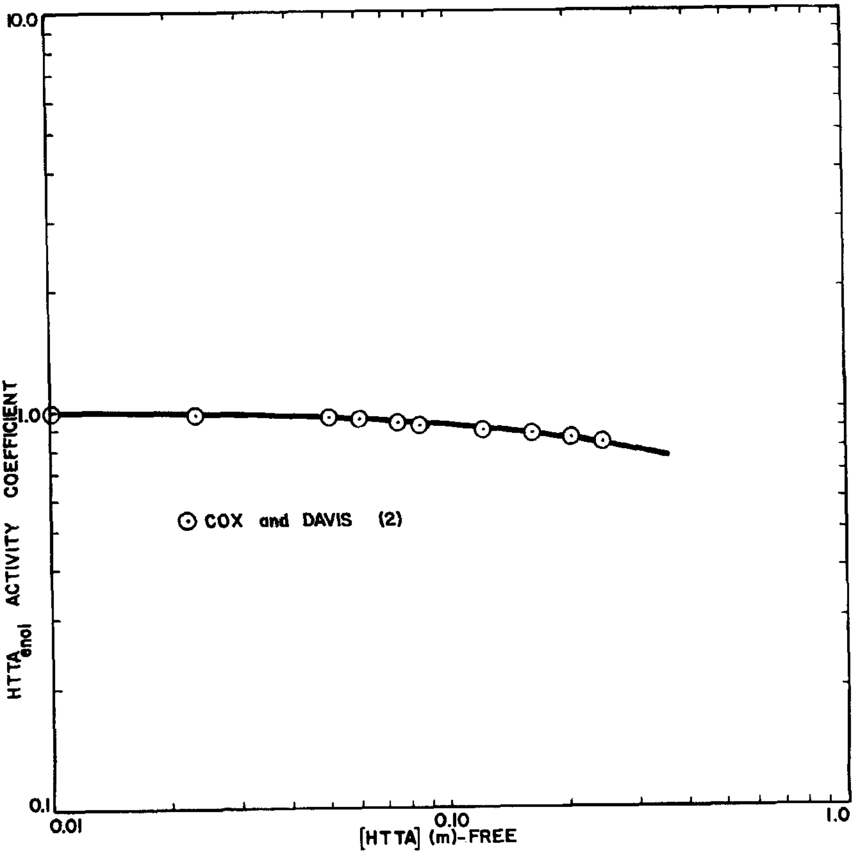

FIG. 7. Activity coefficients of $HTTA_{enol}$ as a function of the free HTTA concentration.

a function of log [HTTA] free activity in Figs. 8 and 9 with $[TBP]_{free}$ concentration as a parameter. The average slopes of the lines are 2.27 for Tb, 2.21 for Er, and 2.25 for Yb and Lu, indicating that two molecules of HTTA are involved in the metal complex.

Similarly, the log q o/a plotted as a function of log $[TBP]_{free}$ with free HTTA activity as a parameter, Figs. 10 and 11, gives average slopes of 1.63 for Tb, 1.75 for Er, 1.78 for Yb, and 1.70 for Lu. This indicates that the metal complexes contain two molecules of TBP and confirms the results of Cox and Davis (*2*).

Also, to determine the number of NO_3^- molecules in the complex, log q o/a was plotted as a function of the log NO_3^- concentration from Eq. (3) free TBP concentration and free HTTA activity as parameters. However, the H^+ concentration was not held constant either, so from Eq. (3) for the mixed equilibrium constant

$$\log q \text{ o/a} = -(p-1)\log [NO_3^-]_{aq} - n \log [H^+] + \log K_e[HTTA]^n[TBP]^n \quad (6)$$

The last term is constant. Then, since the contribution of NO_3^- from the metal salt is negligible compared to the amount contributed by the acid, $[NO_3^-]_{aq} = [H^+]_{aq}$.

Therefore, we have

$$\log q \text{ o/a} = -(p-1+n)\log [NO_3^-]_{aq} + C \quad (7)$$

Then, by setting $n = 2$ and $p = 2$, it can easily be seen that the slope of the graph should be -3. These plots are shown in Fig. 12. The average slopes of the lines are -3.12 for Tb, -3.32 for Er, -3.33 for Yb, and -3.11 for Lu. This is exactly as predicted, indicating that Eq. (7) is correct as proposed by Hayden, Gerow, and Davis [3].

DISCUSSION OF RESULTS AND CONCLUSIONS

By using the method of Cox and Davis (*2*) to calculate free HTTA activities, free TBP concentrations, and the nitrate dependency established by Hayden, Gerow, and Davis (*3*), the analysis of the metal distribution ratios indicates that the extracted complex is of the form $M(NO_3)(TTA)_2(TBP)_2$. This confirms the results of Cox and Davis (*2*) and supports the modification of the HTTA distribution theory of Tournier and Davis (*1*).

From the data presented here, the stability constants for the four metals are as follows:

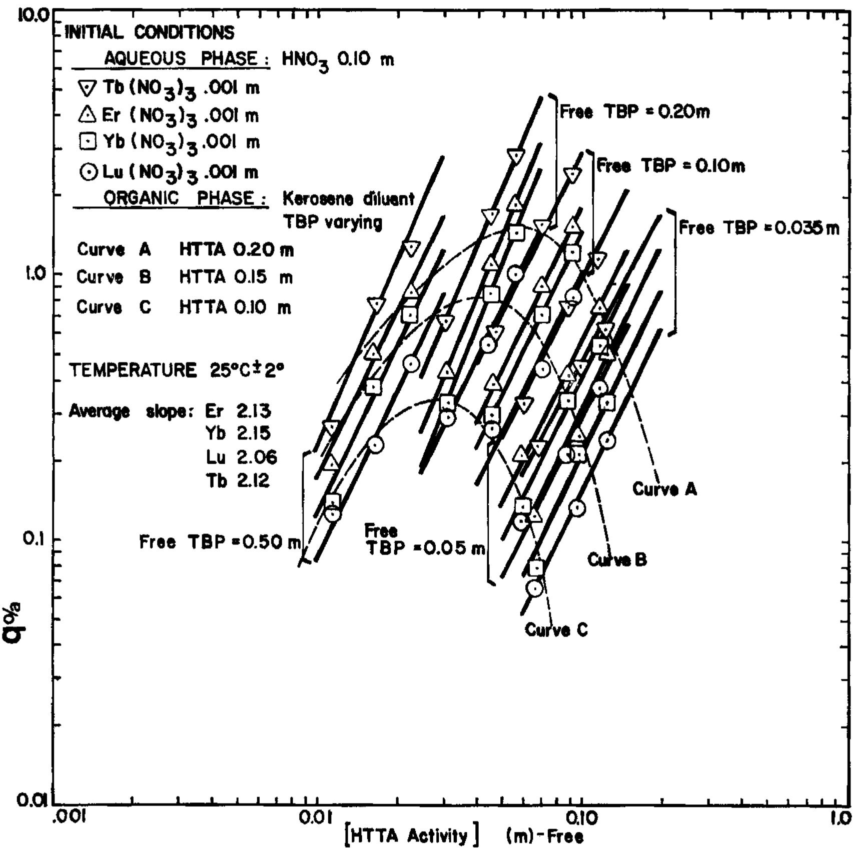

FIG. 8. Distribution ratios of Tb, Er, Yb, and Lu at 0.10 M HNO_3 as a function of free HTTA activity and free TBP concentration.

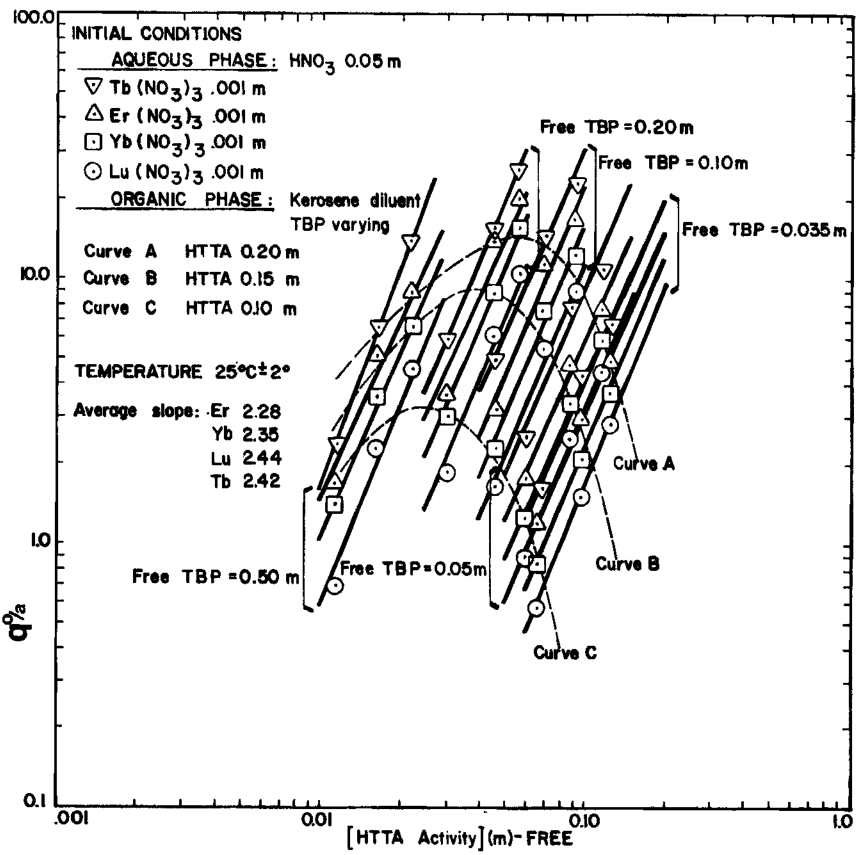

FIG. 9. Distribution ratios of Tb, Er, Yb, and Lu at 0.05 M HNO_3 as a function of free HTTA activity and free TBP concentration.

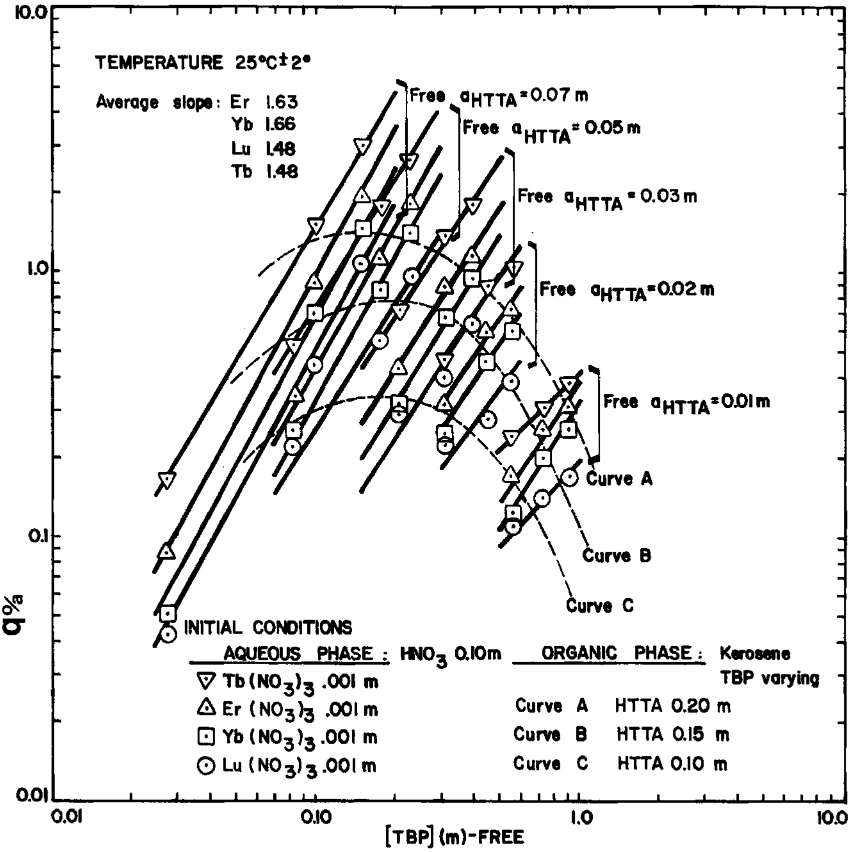

FIG. 10. Distribution ratios of Tb, Er, Yb, and Lu at 0.10 M HNO_3 as a function of free TBP concentration and free HTTA activity.

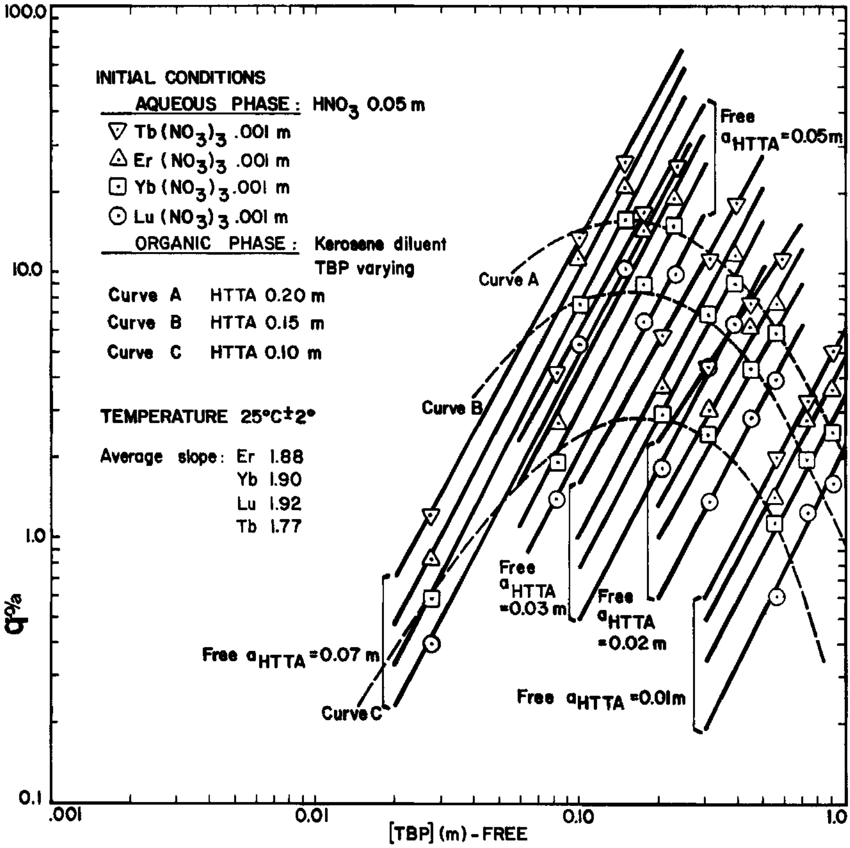

FIG. 11. Distribution ratios of Tb, Er, Yb, and Lu at 0.05 M HNO_3 as a function of free TBP concentration and free HTTA activity.

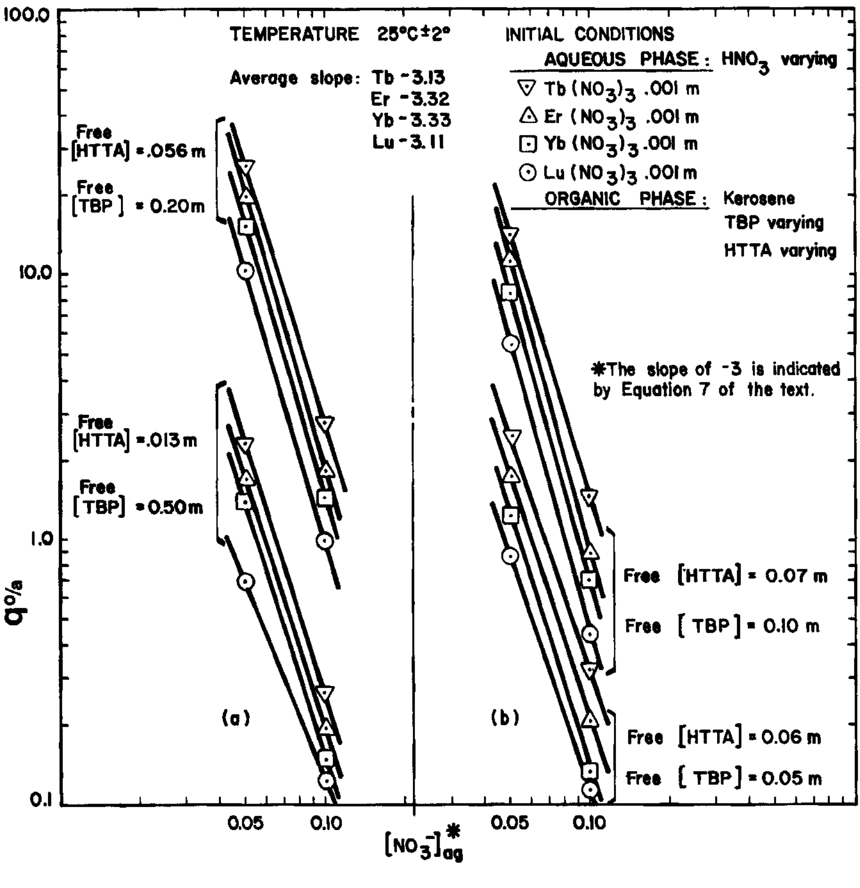

FIG. 12. Distribution ratios of Tb, Er, Yb, and Lu as a function of free HTTA activity, free TBP, and acid concentration.

Metal	K_e
Tb	41 ± 10%
Er	26 ± 10%
Yb	19 ± 10%
Lu	14 ± 10%

Acknowledgment

This research was sponsored by the Savannah River Office of Atomic Energy Commission under Contract AT(38–1)–763.

REFERENCES

1. R. A. Tournier and M. W. Davis, Jr., *Sep. Sci.*, *7*, 159 (1972).
2. E. C. Cox, Jr. and M. W. Davis, Jr., *Ibid.*, *8*, 205 (1973).
3. J. G. Hayden, I. H. Gerow, and M. W. Davis, Jr., *Ibid.*, *9*, 337 (1974).
4. K. Gaggar, "Synergistic Extraction of the Rare Earth Metals Erbium, Ytterbium, and Lutecium the System Kerosene/HTTA/TBP/Dilute HNO_3," Thesis Submitted for the Degree of Master of Science in the College of Engineering, University of South Carolina.

Received by editor December 16, 1976