DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 18, No. 4, 1974
Printed in Republic of Korea

질산유로퓸을 TBP로 추출할때 TBP와 유로퓸착물의 활동도계수간의 관계

姜 益 均
경희대학교 문리과대학 화학과
(1974. 4. 2 접수)

The Activity Coefficients of Tri-*n*-butylphosphate and Europium Complex in the Extraction of Europium by Tri-*n*-butylphosphate in Nitric Acid Solution

Ick Kyun Kang
Department of Chemistry, College of Liberal Arts and Sciences, Kyung Hee University, Seoul, Korea
(Received April 2, 1974)

요 약. 분배계수와 용매의 용해도 파라미터 도표상의 추출포물선을 검토하여 질산산성에서 유로퓸을 TBP로 추출할때 유로퓸착물과 TBP의 활동도계수간의 관계를 알 수 있었고 이에따라 TBP의 용해도 파라미터를 결정하는 가능성을 제시하였다.

용매로서는 cyclohexane, 벤젠, 톨루엔, chlorobenzene을 사용하였고 TBP의 농도를 용적백분율로 5에서 50까지 변화시켰다.

Abstract. A relationship between the activity coefficients of tri-*n*-butylphosphate(TBP) and europium complex was studied in the extraction of europium by TBP in nitric acid solution. Diluents chosen are cyclohexane, toluene, benzene and chlorobenzene. Concentrations of TBP were varied from 5 to 50 by volume per cent and the composition of inorganic layer was kept constant. A method of estimating the solubility parameter of TBP is suggested.

Introduction

In case that the process of the extraction of an innert molecule of a metal complex can be described by the following equation:

$$Me^{m+}_{aq} + mR^{-}_{aq} + nE_{org} = MeR_mE_{n,\,org} \qquad (1)$$

the distribution coefficient of metal complex is represented by the following equation provided that the composition of inorganic layer and the temperature are kept constant.[1]

$$\log Kd = \frac{V_c - nV_e}{2.3RT} d_D^2 + \frac{2(V_c d_c - nV_e d_e)}{2.3RT} d_D + C_1 \qquad (2)$$

The Symbols of the Above Two Eqations are:

Me^{m+} : metal
R^- : anion
E : extractant
m, n : stoichiometry coefficients
aq : aqueous phase
org : organic phase

d : solubility parameter
e : extractant
c : complex
D : diluent
K_d : distribution coefficient
V : molar volume
R : gas constant
T : temperature
C_1 : constant

A linearre lationship was reported to hold between the logarithms of the activity coefficients of TBP and Eu-complexin the extraction of Eu with TBP in nitric acid solution.[2] Expressing this relationship as:

$$\log y_c = u \operatorname{Log} y_e + C_2 \qquad (3)$$

the distribution coefficient of the eq. (2) can be simplified as follows:

$$\log K_d = -\frac{(n-u)}{2.3RT}\varphi_D^2(d_D-d_e)^2 + C_3 \qquad (4)$$

where y_c and y_e denote the activity coefficients of complex and TBP respectively and u is a constant; reportedly the stoichiometry constant n is 3 in this extraction system[2] and C_2 is a constant for all the systems, C_3 is constant for a given concentration of TBP and φ_D is the volume fraction of diluent. The constant u can be determined through the distribution coefficients of Eu-complex using the following eqations:[2]

$$\ln a_e = \ln \varphi_e + \varphi_D\left(1-\frac{V_e}{V_D}\right) + V_e\varphi_D^2(d_e-d_D)^2/RT \qquad (5)$$

$$K_d = k_{100}\times\frac{a_e^3}{y_c} \qquad (6)$$

where φ_e is the volume fraction of the extractant, k_{100} and a_e are the distribution coefficient of the complex in pure TBP and activity of TBP respectively.

The shapes of extraction Parabolas seem to be related to $(n-u)$ of the eq. (4) if there exist a relationship between the activity coefficients as represented by the eq. (3). Thus in the extraction of TTA by alcoholes[3] and by esters[4] there appeared the maximal extraction indicating that the extraction parabolas will be convexed if they followed the ideal condition. In the extraction of GeX (X=Cl, Br, and I) by innert solvents the regularity was clearly revealed and the extraction parabola appeared to be convexed.[5] In those cases, since there are no additional extractant, the stoichiometry coefficient n of the eq. (4) is zero and naturally the convexed parabola results. In the extraction of zinc by TTA and TBP the maximal extraction appeared by TTA alone while minimal extraction resulted in the synergic extraction by TTA and TBP[6]. In the present work the value of u and the solubility parameter of TBP were simultaneously determined.

Experimental

The TBP was purified by the standard method[7]. $NaNO_3$ and HNO_3 were analar grade. Inorganic layer was kept 0.06 M and 4 M with respect to HNO_3 and $NaNO_3$ respectively. Solvents of analar grade were used without further purification. $^{152,154}Eu$ tracer was used. The distribution coefficient for Eu was determined by measuring the y activities of both phase with a liquid counter. Three independent equilibrations were caried out for each composition of organic phase agitaling three different period of time namely 5, 10 and 15 minutes. Temperatue was kept at 12±1°C.

Results and Discussion

1. The Dependence of the Distribution Coefficient of Europium Complex on the Molar Concentration of TBP. The distribution coefficients of europium complex were measured

Table 1. Distribution coefficients of europuim complex

No.	Diluents	C_{TBP}(v/o)	log K_d
1	Cyclohexane	5	−1.77
2		10	−0.886
3		20	−1.20
4		50	0.799
5	Benzene	5	−2.51
6		10	−1.51
7		20	−0.585
8		50	0.623
9	Toluene	5	−2.42
10		10	−1.48
11		20	−0.523
12		50	0.644
13	Chlorobenzene	5	−2.51
14		10	−1.54
15		20	−0.62
16		50	0.62
17		100	30

aq. phase; 4 *M* $NaNO_3$ and 0.06 *M* HNO_3

at 5, 10, 20 and 50 volume percent of TBP in four different diluents: cyclohexane, benzene, toluene and chlorobenzene. The results are shown in *Table* 1. In *Fig.* 1 is shown the dependence of Log K_d's on the molar concentration of TBP. The third power dependence of the distribution coefficients on the molarities of TBP appeared to hold clearly for the diluents of higher solubility parameter: for benzene, toluene and chlorobenzene. This relationship appeared to be slightly violated at the higher concentration of TBP for cyclohexane.

Neglecting this slight violence the reported value of the stoichiometry coefficient m as 3 for the dilute solution of TBP seems to hold through out this extraction system.

2. The Relaion between the Activity Coefficients of TBP and the Complex. Quoting the value of the solubility parameter of TBP as 10.6 the activity coefficients of TBP were calculated by the eq. (5) and (6) for each extraction system and the results are shown in *Fig.* 2. From *Fig.* 2 it can be shown that the

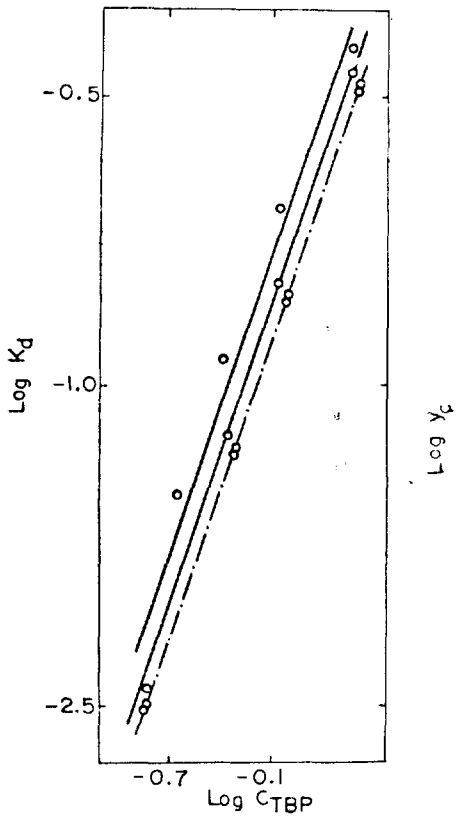

Fig. 1. The dependence of the distribution coefficients on the molar concentrations of TBP. Marks for the experimental points: upper circle; for cyclohexane, lower circle for toluene; combined circle for benzene and chlorobenzen.

value of u should be 2. Then the slope of straight line connecting two points corresponding two log K_d values can be calculated from the following equation:

$$\text{Slope}=-\frac{(3-2)\,V_e}{2.3RT}-\varphi_D^2(d_1+d_2-2d_e) \qquad (7)$$

where the subscripts 1 and 2 denote two diluents of different kind. The values of slopes calculated by the eq. (7) are compared with those deterimined experimentally and results are shown in *Table* 2.

3. The Extrapolation of the Parabola to $d_D=0$. The intersects of the Parabola (4)

with $d_D=0$ were calculated and results are shown in *Table* 3. Taking the mean value of the intersects as one of the two points of log K_d's of the straight lines on the parabolas the slopes of straight lines for each diluents of different systems were calculated by the eq. (7) letting d_1 to be zero and results are compared with those determined through the measured distribution coefficients. They are shown in *Table* 4. It can be seen that two values, calculated and determined, agree very closely. From this fact it may be suggested that the intersect, which corresponds to the distribution coefficient of the complex in the hypothetical diluent whose solubility parameter is zero, log K_d°, provides an effective mean in tracing the extraction behavior.

4. The Solubility Parameter of TBP. A

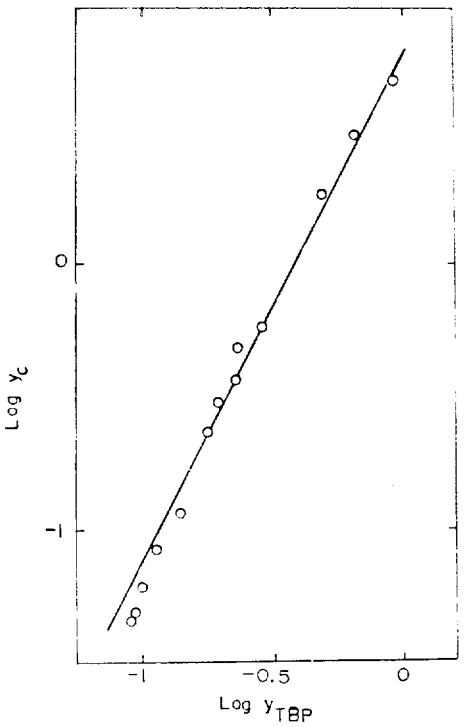

Fig. 2. Relation between log y_{TBP} and log Y_c ($\mu=2$ and $d_c=10.6$)

Table 2. Slopes of straight lines on the parabola of eq. (4)

Lines	Slopes (1) calculated	Slopes (2) determined	Ratio: (2)/(1)
1~2	−0.778	−0.779	1.07
1~3	−0.851	−0.929	1.09
1~4	−0.662	−0.569	0.86
1~2	−0.654	−0.656	1.00
1~3	−0.764	−0.850	1.12
1~4	−0.594	−0.502	0.85
1~2	−0.517	−0.489	0.95
1~3	−0.603	−0.576	0.96
1~4	−0.469	−0.385	0.82
1~2	−0.202	−0.185	0.92
1~3	−0.236	−0.221	0.94
1~4	−0.183	−0.152	0.83

1, 2, 3 and 4 represent log K_d's in cyclohexane, benzene, toluene and chlorobenzens, respectively

Table 3. The interesects of the extraction parabolas with $d_D=0$ (Log K_d)

Diluents	C_{TBP} =5v/o	C_{TBP} =10v/o	C_{TBP} =20v/o	C_{TBP} =50v/o
Cyclohexane	18.4	17.2	14.2	6.4
Benzene	18.3	17.2	14.2	6.4
Toluene	18.3	17.1	14.2	6.4
Chlorobenzene	18.5	17.3	14.3	6.4

Table 4. Slopes determined through log K_d°

No.	Diluents	C_{TBP} (v/o)	Calculated	Determined
1	Cyclohexane	5	−2.46	−2.46
2		10	−2.21	−2.21
3		20	−1.74	−1.75
4		50	−0.68	−0.68
5	Benzene	5	−2.29	−2.29
6		10	−2.06	−2.04
7		20	−1.63	−1.62
8		50	−0.63	−0.63
9	Toluene	5	−2.33	−2.34
10		10	−2.01	−2.10
11		20	−1.65	−1.65
12		50	−0.64	−0.64
13	Chlorobenzene	5	−2.21	−2.20
14		10	−1.98	−1.97
15		20	−1.57	−1.56
16		50	−0.61	−0.60

Table 5. The solubility parameter of TBP (calculated)

No.	Diluents	C_{TBP} (v/o)	Log K_d^o	d_{TBP}
1	Cyclohexane	5	18.7	10.7
2		10	17.4	10.7
3		20	13.9	10.5
4		50	6.3	10.5
5	Benzene	5	18.7	10.7
6		10	17.4	10.7
7		20	13.9	10.5
8		50	6.3	10.4
9	Toluene	5	18.7	10.7
10		10	17.4	10.7
11		20	13.9	10.5
12		50	6.3	10.4
13	Chlorobenzene	5	18.7	10.7
14		10	17.4	10.6
15		20	13.9	10.6
16		50	6.3	10.5

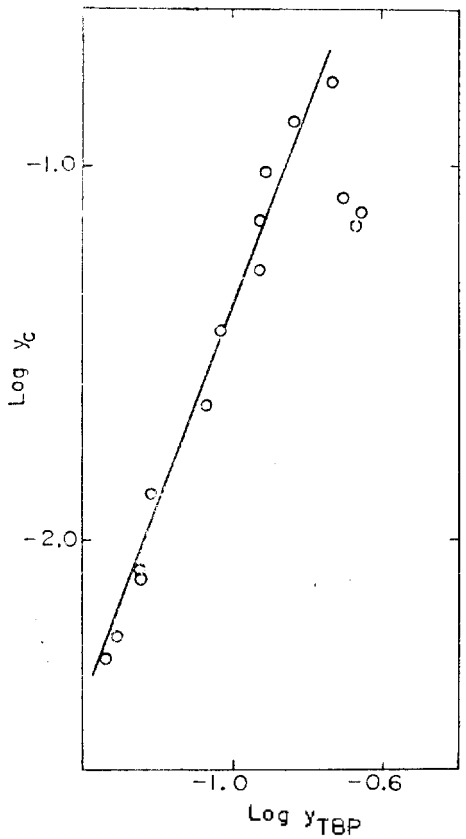

Fig. 3. Relation between log y_{TBP} and log y_c. (n=1 and d_e=9.7)

relationship between the intersect (log K_d^o) and u can be derived by cancelling out d_e from two slopes.

$$\frac{\log K_{d1}-\log K_d^o}{d_1}=\frac{\log K_{d2}-\log K_d^o}{d_2}$$

$$=\frac{(3-u)V_e\varphi_D^2}{2.3RT}(d_1-d_2) \quad (8)$$

Then d_e can be estimated by:

$$\frac{\log K_{d1}-\log K_d^o}{d_1}=\frac{V_e\varphi_D^2}{2.3RT}(d_1-2d_e) \quad (9)$$

Thus if the values of u were assumed then the solubility parameter of TBP can be calculated by the eq. (8) and (9). There are no reasons for assuming the values of u to be integer, but as a first step only positive integers were assumed. In general the slope of the extraction parabola of an extractant is influenced by a metal complex.[1] So that the value of u to be zero seems to be impractical. It is clear that the value of u to be 3 is also impractical because the distribution coefficient is influenced by solvnts of different solubility parameter.

So that the calculations were carried out for u=2 and u=1. Results are: d_e=10.6 and 9.7 for u=2 and u=1 respectively. In the case of u=2 and d_e=10.6, the relation between log y_c and log y_e calculated by the measured distribution coefficients shows the linear relationship of slope 2 as in *Fig.* 2 proving the assumption of u=2 to be reasonable. But when u=1 and d_e=9.7 the relation between log y_c and log y_e does not satisty the condition of the assumption as shown in *Fig.* 3. Follwing the same procedure the solubility parameter of TBP for each 16 different cases were calculated and results are shown in *Table* 5.

References

1. J. Narbutt, "Role of the Organic Phase in Extraction Processes", P. 1~9, INR Report, Institute

of Nuclear Research, Warsaw, Poland, 1972.
2. S. Siekierski, *J. Inorg. Nucl. Chem.* **24**, 205(1962).
3. N. Suzuki, K. Akiba T. Kanno and T. Wakahayasi, *J. Inorg. Nucl. Chem.*, **30**, 2521(1968).
4. N. Suzuki, L. Akiba and T. Kanno, *Anal, Chim. Acta.*, **43**, 311(1968).
5. S. Siekierski and R. Olszer, *J. Inorg. Nucl. Chem.*, **25**, 1351(1963).
6. K. Akiba, N. Suzuki and T. Kanno, *Bulletin of the Chem. Soc. of Japan*, **42**, 2537(1969).
7. C. J. Hardy and D. Seargill, *J. Inorg. Nucl. Chem.* **13**, 215(1956).