October, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 3003—3006 (1986) 3003

Synergistic Extraction of Copper(II) and Zinc(II) with Tributyl Phosphate and Crown Ether

Yuko HASEGAWA,* Hirofumi MIYATA, and Satoshi YOSHIDA
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received March 29, 1986)

The solvent extraction of copper(II) and zinc(II) with 12-crown-4 (12C4) or 15-crown-5 (15C5) as picrates into chloroform containing tributyl phosphate (TBP) has been studied. The following conclusions have been reached. i) Even in the presence of TBP which is more basic than crown ether, either copper(II) or zinc(II) is extracted in association with 2 moles of 12C4 or 15C5. ii) The crown ether complex of either copper(II) or zinc(II) forms 1 : 1 : 1 (metal(II) : crown ether : TBP) stoichiometric adducts in chloroform. iii) The 12C4 complex of either copper(II) or zinc(II) forms more stable adducts with TBP than the 15C5 complex. iv) The extraction of the metal (II) with 15C5 and TBP is better than that of 12C4 and TBP. v) The copper(II) complex with 12C4 or 15C5 forms more stable TBP adducts than those from zinc(II) complex.

It has been previously reported[1] that the extraction of zinc(II) with crown ether and picrate ion is not very different from that of copper(II), while the extraction of zinc(II) with β-diketones such as acetylacetone is remarkably poorer than that of copper(II).[2] The different behavior of the ion pair extraction of zinc(II) from the chelate extraction has been explained in terms of the difference in coordination structure of the extracted metal(II) species. This leads to the idea that the adduct formation or the solvation of zinc(II) complexes in organic phase may be different between the ion pair and the chelate.

In the present work, the adduct formation constants between the crown ether–picrate ion pair of zinc(II) or copper(II) and tributylphosphate (TBP) in chloroform have been determined by the solvent extraction method to compare with those of the chelates.

Experimental

All reagents employed were of analytical grade. Tributylphosphate ex. Tokyo Kasei Inc. was purified by washing with water, 0.1 M (M=mol dm^{-3}) sodium hydroxide solution, and 0.1 M perchloric acid.

Copper(II) or zinc(II) nitrate (2.5×10^{-2}M), lithium picrate, and a crown ether were agitated in a stoppered glass tube by a mechanical shaker for an hour with same volume of chloroform containing TBP of various concentrations. The metal(II) in organic phase was then back-extracted with 0.1 M perchloric acid and its concentration was measured by means of atomic absorption spectrometer. Detailed procedures have been described previously.[1]

The distribution ratio D was defined as

$$D=\frac{[\mathrm{M(II)}]_{\mathrm{o,total}}}{[\mathrm{M(II)}]_{\mathrm{a,total}}},$$

where the subscripts "o" and "a" denote the organic and aqueous phases, respectively.

Results and Discussion

When zinc(II) and copper(II) were extracted from lithium picrate solution containing a given amount of 12C4 or 15C5 into chloroform in the presence of 0.1 M TBP, the distribution ratio increased in proportion to the square of the anion concentration. This result indicates that one mole of the metal ions are extracted with two moles of picrate ions, in the similar manner to the extraction of the metal(II)–crown ether–picrate into chloroform reported earlier.[1]

The distribution ratio of the metal(II) between lithium picrate solution and TBP–chloroform is plotted against the concentration of TBP in Fig. 1 (symbols are triangles). The log-log plots give straight lines with inclination of 2, although the plots deviate from the straight line in a higher concentration region. It indicates that the ion pair between the metal(II) and picrate ion is accompanied by 2 moles of TBP. From the slope analysis, the extraction constants ($K\mathrm{ex}_{02}$= $D[\mathrm{A}^-]_{\mathrm{a}}^{-2}[\mathrm{TBP}]_{\mathrm{o}}^{-2}$) of copper(II) and zinc(II) from lithium picrate solution into TBP–chloroform were determined to be 1.3 and 0.4 as log $K\mathrm{ex}_{02}$, respectively.

In the higher concentration region these metal ions seem to be extracted with more than 2 moles of TBP. Hence, the data obtained in the TBP region lower than 0.3M were employed to the data analysis in the present study.

It has been reported[1] that the ion pair between the metal(II) and picrate ion is accompanied by 1 or 2 moles of crown ethers when extracted. Therefore, when the ion pair including a crown ether forms adducts with TBP, the distribution ratio can be represented as

$$D=\frac{\sum[\mathrm{ME}_l\mathrm{A}_2]_{\mathrm{o}}+[\mathrm{MT}_2\mathrm{A}_2]_{\mathrm{o}}+\sum[\mathrm{ME}_m\mathrm{T}_n\mathrm{A}_2]_{\mathrm{o}}}{[\mathrm{M}^{2+}]_{\mathrm{a}}}, \tag{1}$$

where M, E, A, and T denote the metal(II), crown ether, picrate ion, and TBP, successively, *l*, *m*, and *n* being the integer 1 or 2.

Equation 1 can be rewritten by introducing the extraction constants as follows:

$$D=\{(K\mathrm{ex}_{10}[\mathrm{E}]_{\mathrm{a}}+K\mathrm{ex}_{20}[\mathrm{E}]_{\mathrm{a}}^2)+K\mathrm{ex}_{02}[\mathrm{T}]_{\mathrm{o}}^2 + \sum K\mathrm{ex}_{mn}[\mathrm{E}]_{\mathrm{a}}^m[\mathrm{T}]_{\mathrm{o}}^n\}[\mathrm{A}^-]_{\mathrm{a}}^2 \tag{2}$$

Figure 1 also shows the relationship between distribution ratio and TBP concentration in the case of metal(II) extraction from an aqueous solution contain-

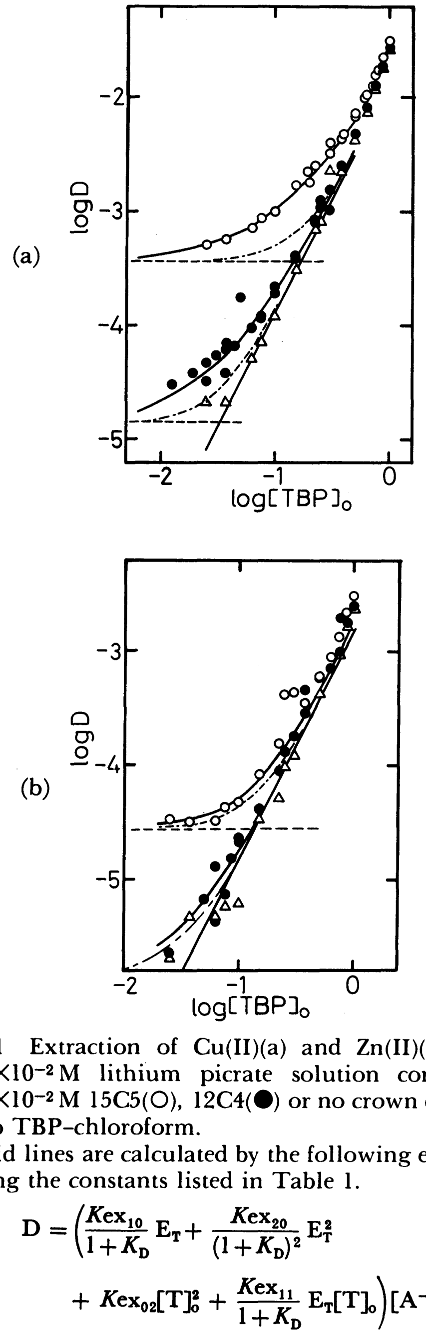

Fig. 1 Extraction of Cu(II)(a) and Zn(II)(b) from 2.5×10^{-2} M lithium picrate solution containing 2.5×10^{-2} M 15C5(○), 12C4(●) or no crown ether(△) into TBP–chloroform.
Solid lines are calculated by the following equation using the constants listed in Table 1.

$$\mathrm{D}=\left(\frac{K\mathrm{ex}_{10}}{1+K_\mathrm{D}}\mathrm{E_T}+\frac{K\mathrm{ex}_{20}}{(1+K_\mathrm{D})^2}\mathrm{E_T^2}+K\mathrm{ex}_{02}[\mathrm{T}]_\mathrm{o}^2+\frac{K\mathrm{ex}_{11}}{1+K_\mathrm{D}}\mathrm{E_T}[\mathrm{T}]_\mathrm{o}\right)[\mathrm{A}^-]^2$$

Chain lines are calculated using only the first three terms in the equation, i.e. ignoring adduct formation.

Table 1. Summary of Equilibrium Constants When the Metal(II) is Extracted as Picrates with Crown Ethers and/or TBP into Chloroform

	Cu(II)		Zn(II)	
	12C4	15C5	12C4	15C5
$\log K\mathrm{ex}_{10}$ [1)]	0.6_4	2.0_9	-0.1_5	1.0_1
$\log K\mathrm{ex}_{20}$ [1)]	3.0_7	4.4_4	1.8_0	3.2_8
$\log K\mathrm{ex}_{11}$	2.5_4	3.4_9	1.2_5	1.6_9
$\log K\mathrm{ex}_{02}$	1.3_0		0.3_6	
$\log\bar{\beta}_{11}$	1.9_0	1.4_0	1.4_0	0.6_8

$$K\mathrm{ex}_{mn}=\frac{[\mathrm{ME}_m\mathrm{T}_n\mathrm{A}_2]_\mathrm{o}}{[\mathrm{M}^{2+}]_\mathrm{a}[\mathrm{E}]_\mathrm{a}^m[\mathrm{T}]_\mathrm{o}^n[\mathrm{A}^-]_\mathrm{a}^2}$$

m and n = 0, 1, or 2

$$\bar{\beta}_{11}=\frac{[\mathrm{MEA_2T}]_\mathrm{o}}{[\mathrm{MEA_2}]_\mathrm{o}[\mathrm{T}]_\mathrm{o}}$$

ing lithium picrate and crown ether into TBP–chloroform. The chain curves in Fig. 1 are obtained by combining the extraction with crown ether $\{(K\mathrm{ex}_{10}[\mathrm{E}]_\mathrm{a}+K\mathrm{ex}_{20}[\mathrm{E}]_\mathrm{a}^2)[\mathrm{A}^-]^2\}$ with the extraction with TBP $(K\mathrm{ex}_{02}[\mathrm{T}]_\mathrm{o}^2[\mathrm{A}^-]^2)$. The observed distribution ratio is higher than the calculated value given by the chain line. The difference will be ascribed to the adduct formation represented by the third term of the numerator in Eq. 1. Then the extraction constants of the mixed complex or the complex solvated with TBP can be determined as

$$\begin{aligned}\mathrm{D}/[\mathrm{A}^-]_\mathrm{a}^2-K\mathrm{ex}_{02}[\mathrm{T}]_\mathrm{o}^2&=K\mathrm{ex}_{10}[\mathrm{E}]_\mathrm{a}+K\mathrm{ex}_{20}[\mathrm{E}]_\mathrm{a}^2\\&\quad+(K\mathrm{ex}_{11}[\mathrm{E}]_\mathrm{a}+K\mathrm{ex}_{21}[\mathrm{E}]_\mathrm{a}^2)[\mathrm{T}]_\mathrm{o}\\&\quad+(K\mathrm{ex}_{12}[\mathrm{E}]_\mathrm{a}+K\mathrm{ex}_{22}[\mathrm{E}]_\mathrm{a}^2)[\mathrm{T}]_\mathrm{o}^2+\cdots\end{aligned}\tag{3}$$

When the left side of Eq. 3 was plotted against $[\mathrm{T}]_\mathrm{o}$, straight lines were obtained for the data in Fig. 1. It indicates that the dominant species extracted is accompanied by one mole of TBP in these systems. The slope is $(K\mathrm{ex}_{11}[\mathrm{E}]_\mathrm{a}+K\mathrm{ex}_{21}[\mathrm{E}]_\mathrm{a}^2)$. Since the data in Fig. 1 were obtained at a constant crown ether concentration, $K\mathrm{ex}_{11}[\mathrm{E}]_\mathrm{a}$ and $K\mathrm{ex}_{21}[\mathrm{E}]_\mathrm{a}^2$ can not be calculated separately. As the first approximation, $K\mathrm{ex}_{21}$ was ignored and only $K\mathrm{ex}_{11}$ was determined. The constants obtained are listed in Table 1.

To check the validity of $K\mathrm{ex}_{11}$, the distribution ratio of the metal(II) between an aqueous solution containing crown ether and lithium picrate (2.5×10^{-2} M) and 0.1 M TBP–chloroform has been measured. Figure 2 shows the plot of the distribution ratio against the total concentration of crown ether. The chain curves were obtained by combining the metal(II) extraction from an aqueous solution containing lithium picrate of constant concentration without crown ether into chloroform containing 0.1 M TBP (flat lines given by broken lines in Fig. 2) with the extraction from lithium picrate solution with crown ethers into chloroform containing no TBP (another broken line in Fig. 2). The observed distribution ratio is higher than the calculated one due to the adduct formation. The situation is thus similar to that in Fig. 1.

The solid curves in Figs. 1 and 2 calculated using the constants fit well with the observed distribution ratios.

The validity of $K\mathrm{ex}_{11}$ was also confirmed by measuring the distribution ratio at a higher concentration, 0.1 M, of crown ether, because the relationship between the distribution ratio and concentrations of crown ether and TBP in Eq. 3 applies to all concentrations. Figure 3 gives the plot of the distribution ratio against TBP concentration in the logarithmic units.

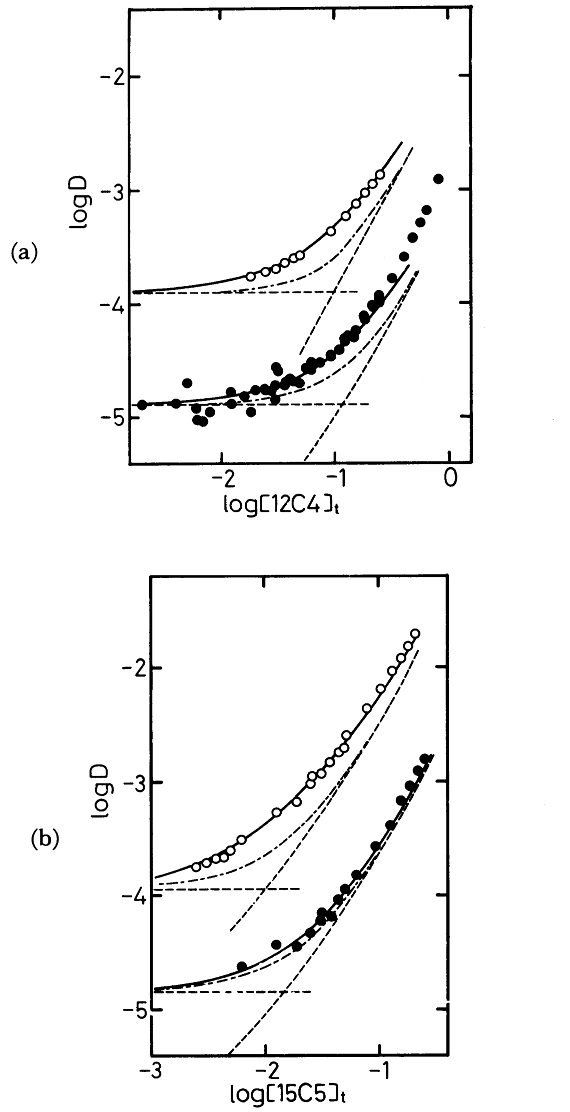

Fig. 2. Distribution ratio of Cu(II)(○) and Zn(II)(●) between 2.5×10^{-2} M lithium picrate solution contaning 12C4(a) and 15C5(b) and 0.1M TBP chloroform as a function of crown ether concentration.

Broken lines shows the extraction with TBP (flat lines) or a crown ether as picrates. Chain lines are obtained by combining the two lines above mentioned.

Solid lines are calculated by the equations denoted in Fig. 1 using the constants in Table 1.

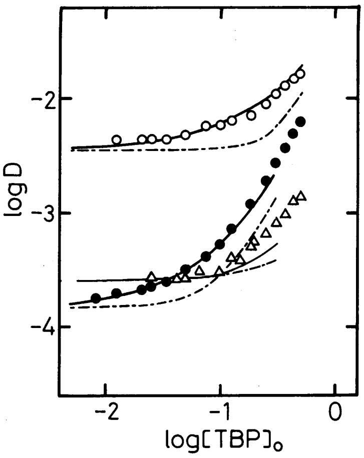

Fig. 3. Extraction of copper(II) with 0.1M 15C5(○) and 12C4(●) or of zinc(II) with 15C5(△) from 2.5×10^{-2} M lithium picrate solution into TBP–chloroform.

Solid lines are calculated by the equation in Fig. 1 using the constants in Table 1.

Chain lines are calculated on assuming no adduct formation.

The calculated values by using the constants in Table 1 are shown by solid line in Fig. 3. The calculated values fit well the experimental data for copper(II). However, the fitness does not appear for zinc(II) in the higher TBP concentration range, although the constants explain well the data in Figs. 1 and 2. The result may suggest that in the extraction with such a high concentration of crown ether, TBP could form adducts with bis-crown ether complex, ZnE_2A_2 as well as the mono-complex, $ZnEA_2$.

The present study reveals that the crown ether complex of either copper(II) or zinc(II) forms 1:1:1 (metal(II): crown ether: TBP) stoichiometric adducts similar to those formed between neutral ligands and metal(I)–crown ether complexes.[3,4] Since TBP seems to be more basic than crown ether, crown ether in the complexes could be replaced by TBP, although the metal(II) can be extracted in association with two moles of crown ether in the absence of TBP. However, Fig. 2 shows that the limiting slope of the plot between crown ether concentration and the distribution ratio is two, indicating that the complex with 2 moles of crown ether may be extracted even in the presence of TBP.

The formation constant of the adducts can be represented as

$$MEA_{2(o)} + T_{(o)} \rightleftharpoons MEA_2T_{(o)}$$

$$\bar{\beta}_{11} = \frac{[MEA_2T]_o}{[MEA_2]_o[T]_o} \tag{4}$$

and $\bar{\beta}_{11}$ can be obtained from the relation

$$\bar{\beta}_{11} = Kex_{11}/Kex_{10}. \tag{5}$$

The formation constants of the adducts are listed in Table 1. As seen in Table 1, the complex of either copper(II) or zinc(II) with 12C4 will form more stable adducts with TBP than the metal complex with 15C5, of which cavity size being larger than 12C4. However, the increase of the extraction with the adduct formation is more remarkable in 15C5 complexes than in 12C4 complexes as seen in Fig. 1. The larger enhancement in the extraction with 15C5 in spite of smaller formation constant of the adduct can be explained as follows: the extractability of the adduct (Kex_{11}) depends on the extractability of the parent crown ether complex as well as on the property of adduct formed in the organic solvent ($\bar{\beta}_{11}$), i.e., the 12C4 complex forms more stable adducts than the 15C5 complex, while the 15C5 complex as picrate is extracted better than the 12C4 complex. Consequently, the enhancement in the extraction is more remarkable with 15C5–TBP than with 12C4–TBP.

Table 1 also shows that the adducts from copper(II) complexes with crown ether are more stable than those from zinc(II) complexes. The tendency seems to be opposite to the chelate extraction system. For example, Sekine and Ihara reported[2] that the first formation constant of the adduct between TBP and (trifluoroacetylacetonato)copper(II) is 2.16 in logarithmic unit, whereas that of the zinc(II) chelates is 4.29, that is, zinc(II) chelate forms more stable adduct with TBP than copper(II) chelate. They further suggested,[2] as a general tendency of adduct formation of metal chelates, that the chelate easily extractable forms less stable adducts. For example, the extraction of tfa–zinc(II) (tfa means trifluoroacetylacetonato) was much poorer than that of tfa–copper(II) under the same conditions. They explained the difference between the extractability of copper(II) and zinc(II) with chelating agents and the difference of adduct stability between copper(II) and zinc(II) in terms of the different coordination structures; when zinc(II) is extracted with β-diketones, zinc(II) takes the coordination number of 6, so that the zinc(II) chelate with β-diketone may hydrate with water molecules. Therefore, the extraction of (β-diketonato)zinc(II) is poorer than that of (β-diketonato)copper(II). Furthermore, since the hydrated water molecules may be replaced with neutral ligands such as TBP, the adduct from zinc(II) chelate is more stable than that from copper(II) chelate. On the other hand, since zinc(II) takes the coordination number of four when the metal(II) is extracted as the ion pair,[1,5] zinc(II) does hardly have a room to accept extra ligand. The different electronic structure of zinc(II) and copper(II) will be one of the reasons why the adduct formation is different between their chelates and their ion pairs.

When the adduct formation of the crown ether complex in the present study is compared with the adduct formation in chelates, the behavior of adduct formation of ion pair or cationic complex in organic phase seems to be very different from that of metal chelates.

References

1) Y. Hasegawa, H. Tanabe, and S. Yoshida, *Bull. Chem. Soc. Jpn.*, **58**, 3649 (1985).

2) T. Sekine and N. Ihara, *Bull. Chem. Soc. Jpn.*, **44**, 2942 (1971).

3) Y. Hasegawa, K. Suzuki, and T. Sekine, *Chem. Lett.*, **1981**, 1075.

4) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **54**, 526 (1981).

5) H. Moriya and T. Sekine, *Bull. Chem. Soc. Jpn.*, **45**, 1626 (1972).