CHEMISTRY LETTERS, pp. 1535-1538, 1989.

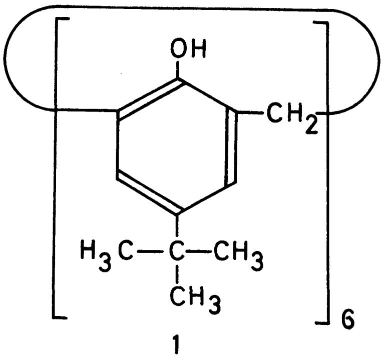
Solvent Extraction of Copper(II) Ion with p-t-Butylcalix[6]arene from the Ammonia Alkaline Solution

Isao YOSHIDA,* Shigehiro FUJII, Keihei UENO, Seiji SHINKAI,† and Tsutomu MATSUDA†
Department of Industrial Chemistry, Kumamoto Institute of Technology,
4-22-1, Ikeda, Kumamoto 860
†Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Higashi-ku, Fukuoka 812

It was found that p-t-butylcalix[6]arene(tb-calix[6], H_2L) in the organic solvents such as chloroform or benzene can extract copper(II) ion from the ammonia alkaline solution. The results from extraction study suggested the formation of the 1:1 copper(II) to tb-calix[6] complex as the extracted species.

It has been known that calix[n]arenes are the oligo-phenols in which n moles of phenols are connected by n moles of methylene groups to form cyclic compounds.1-7) This structure suggests the use of calix[n]arenes as an extraction reagent for metal ions. However, no report has been published on the use of calix[n]arenes as the extraction reagent for heavy metal ions. In this study, one of the calix[n]arenes, p-t-butylcalix[6]arene(1) has been investigated as a solvent extraction reagent for copper(II) ion from the ammonia alkaline solution.

The extraction reagent 1 was synthesized according to Gutsche et al.5) and obtained as a 1:1 chloroform adduct. This was characterized by elemental analyses, ir and nmr spectra. A typical extraction procedure was as follows: Ten cm^3 of the organic solution containing 1 was mixed with 20 cm^3 of the aqueous ammonia containig copper(II) nitrate in a 50 cm^3 glass-stoppered tube. The initial concentration of 1 was usually 10.0×10^{-4} M(1M=1 mol dm^{-3}) in chloroform or 3.68×10^{-4} M in benzene and that for copper(II) nitrate was 1.00×10^{-4} M in the aqueous phase. After shaking the tube for 2 h with benzene or 20 h with chloroform at room temperature, it was centrifuged at 3600 rpm for 2 min, and then both phases were separated. An aliquot of the aqueous phase was transferred into a volumetric flask, and diluted to 25 cm^3 with 0.1 M hydrochloric acid. The concentration of copper(II) ion in the solution was determined by an atomic absorption method using a Hitachi 180-30 AA spectrophotometer. On the other hand, 5 cm^3 of the organic phase was transferred into another glass-stoppered tube containing 10 cm^3


1

of 2 M hydrochloric acid. Then the tube was shaken for 30 min, followed by the centrifugation for 2 min at 3600 rpm. After phase separation, an aliquot of the aqueous phase was diluted to 25 cm^3 with water. The concentration of copper(II) ion in the solution was determined by the AA method. The pH of the aqueous phase was also measured with a Toa HM-7B pH meter.

As **1** was soluble in chloroform up to 5.0 x 10^{-3} M and up to 1.84 x 10^{-3} M in benzene at room temperature(ca. 20 °C), the saturated solutions were used as the stock solutions. The white-blue precipitate was formed in benzene after the extraction of copper(II) with **1** at 3 x 10^{-4} M level, while no precipitate was observed in chloroform at the 10 x 10^{-4} M level. However, in the extraction with the higher concentration of **1**, the precipitate was also formed in chloroform. These results indicate poor solubility of the copper(II) complex with **1** in the organic solutions. Thus, the concentration of copper(II) in the benzene phase was estimated from the difference of its initial and final concentrations in the aqueous phase.

Figure 1 shows the rate of extraction of copper(II) ion with **1** from the aqueous ammonia into the chloroform or benzene phases at pH 11.6. While the extraction equilibrium was attained within 40 min-shaking with benzene, the extraction into chloroform reached equilibrium with 20 h-shaking. Therefore, the shaking time was fixed at 2 h for benzene and at 20 h for chloroform. An addition of chloroform to benzene decreased the rate of extraction, but, the extent of copper(II) extraction at the equilibrium point seemed to be nearly same as that in the pure benzene system. Figure 2 illustrates the effect of pH on the extraction of copper(II) ion, where pH of the aqueous phase was adjusted with ammonia and ammonium chloride, total ammonia concentration being kept at 1 M. It is shown that copper(II) ion can be extracted from aqueous ammonia at pH higher than 10. The log distribution ratio, log D, of copper(II) ion between the organic and the aqueous phases increases linearly with an increase of pH, from 11.3 to 11.8 showing a slope 2. Figure 3 indicates the effect of the initial concentration of **1** in the organic phase on the extraction of copper(II) ion from the aqueous ammonia at pH 11.6. The log D

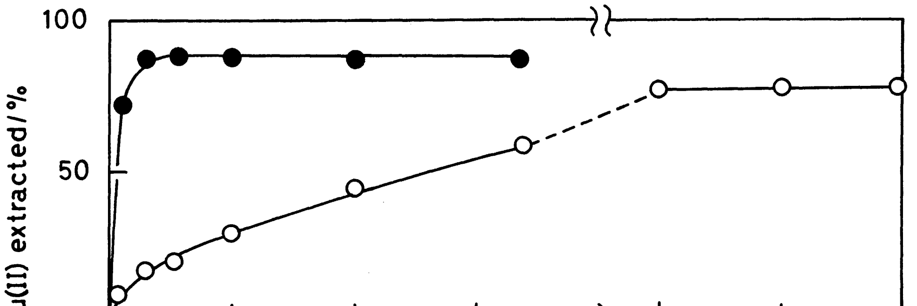


Fig. 1. Relations between shaking-time and copper(II) ion extracted at pH 11.6 and at room temperature.
(○) CHCl$_3$, (●) Benzene

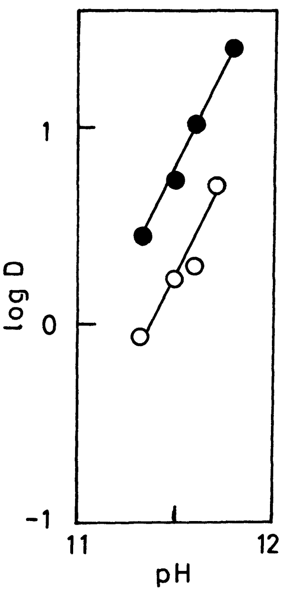


Fig. 2. Relations between pH and log D.
(○) $CHCl_3$
(●) benzene

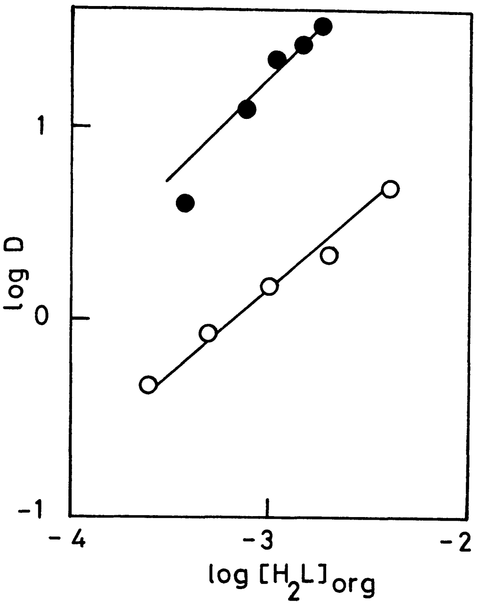


Fig. 3. Relations between log$[H_2L]_{org}$ and log D.
(○) $CHCl_3$
(●) benzene

values increase linearly with an increase of initial concentration of **1** in the organic phase showing a slope of unity. The continuous variation method was applied to the chloroform-water system to estimate the binding ratio of the extracted species. The concentration of copper(II) ion in chloroform after the extraction at pH 11.6 was the maximum at $T_{Cu}/(T_{Cu} + T_{\mathbf{1}})=0.5$, again showing the binding ratio of **1** with copper(II) ion to be 1:1. T_{Cu} and $T_{\mathbf{1}}$ represent the total amounts of copper(II) ion and **1** in the extraction system, respectively.

In these extraction studies, the concentrations of **1** in organic phases were not in large excess compared with that of copper(II) ion in the aqueous phase. However, the results in Figs. 2 and 3 suggest that the 1:1 complex of copper(II) ion with **1** was extracted into the organic phase releasing 2 moles of protons from one mole of **1**.

Thus, the extraction reaction of the present systems can be expressed as Eq. 1.

$$Cu(NH_3)_n{}^{2+}{}_{(aq)} + H_2L_{(org)} = CuL_{(org)} + 2H^+{}_{(aq)} + nNH_{3(aq)} \qquad (1)$$

Then, the extraction constant can be defined as below.

$$Kex = [CuL]_{org}\ [H^+]_{aq}{}^2\ [NH_3]_{aq}{}^n\ [Cu(NH_3)_n{}^{2+}]_{aq}{}^{-1}\ [H_2L]_{org}{}^{-1} \qquad (2)$$

In Eqs. 1 and 2, org and aq represent organic and aqueous phases, and the concentration of ammonia is in large excess and can be considered to be constant in the narrow pH range of the alkaline solution compared with other species. Then Eq. 2 can be simplified as Eqs. 3 and 4. In these equations, Kex and Kex' are the con-

$$Kex' = D\,[H^+]_{aq}^{\;2}\,[H_2L]_{org}^{\;-1} \tag{3}$$

$$\log D = \log Kex' + \log[H_2L]_{org} + 2pH \tag{4}$$

ditional constants under the given conditions in this study.

According to Eq. 4, the values for log Kex' were evaluated to be -19.5 (chloroform) and -18.6(benzene), respectively. As stated previously, the extraction reagent **1** has been obtained as the one-mole chloroform adduct, **1**·$CHCl_3$. From the adduct, chloroform could not be removed even after 3-days-heating at 130 °C under reduced pressure. This suggests that chloroform was tightly encapsulated within the hole of calixarene. This may be the reason for the rather slow rate of extraction with **1** in chloroform solution.

References

1) H. Kammerer, G. Happel, and F. Caeser, Makromol. Chem., **162**, 179 (1972).
2) G. Happel, B. Mathiasch, and H. Kammerer, Makromol. Chem., **176**, 3317 (1975).
3) C. D. Gutsche, Acc. Chem. Res., **16**, 161 (1983).
4) S. Shinkai and O. Manabe, Nippon Kagaku Kaishi, **1988**, 1917.
5) C. D. Gutsche, B. Dhawan, K. H. No, and R. Muthukrishnan, J. Am. Chem. Soc., **103**, 3782 (1981).
6) G. D. Andreetti, R. Ungaro, and A. Pochini, J. Chem. Soc., Chem. Commun., **1979**, 1005.
7) C. D. Gutsche and R. Muthukrishnan, J. Org. Chem., **43**, 4905 (1978).

(Received May 15, 1989)