Extraction of copper with p-tert-butyl-calixarenes

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The extraction of copper with calixarenes was researched by comparing the results from calix[4]-, calix[6]- and calix[8]-arenes. The extraction ability increased as the order: calix [4]- > calix[8]- > calix[6]-arenes, with the binding ratio being 1:1. The extraction mechanism was also discussed, and its equation $Cu(NH_3)_4^{2+} + H_2L_{(0)} \xrightarrow{K_{ex}} Cu(NH_3)_4L_{(0)} + 2H^+$ and the extraction equilibrium constants (K_{ex}) for calix[6]- and calix[8]-arenes were obtained respectively.

Keywords   Calixarenes, copper, extraction equation, equilibrium constants

Introduction

Calixarenes, cyclo-oligomers of formaldehyde and p-substituted phenol, display an extraordinary versatility as metal binding agents.[1] The typical parent p-tert-butyl-calixarenes are tetramer (1a), hexamer (2a), and octamer (3a) (showed in following Chart).
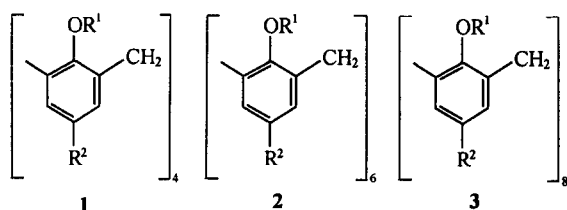
a: R^1=H, R^2=Bu'
b: R^1=CH₂CO₂Me, R^2=Bu'
c: R^1=CH₂CO₂Et, CH₃, or P(O)(OC₂H₅)₂,
   R^2=SO₃⁻M⁺, CH₃,C₆H₅ or F

The unsubstituted p-tert-butyl-calixarene has been found to form neutral complexes with copper(II) cations, in which copper(II) ion sits as a guest into the cone of the calixarenes. As a new category of macrocyclic compound, calixarenes contain cavities with sufficient diameter and depth to form host-guest complexes.

In the paper, the extraction ability of calixarenes, the extraction mechanism and the equilibrium constant were researched. Many significant experimental results concerning the coordination chemistry of calixarenes were gained. So far, few theoretical studies on coordination chemistry of calixarenes have been reported.[2,8]

Experimental

Analytical procedures

The melting point (mp) was measured with a Thiele tube, using sealed capillaries. The Cu^{2+} concentration in the aqua phase was measured by 722 spectrophotometer at 580 nm with xylenol as solvent.

Preparation of calixarenes

Calix[4]-, calix[6]- and calix[8]-arenes were prepared according to the literatures.[3,4] The pure products were gained by recrystallization with chloroform at mp 343—345℃, 380—381℃ and 409—411℃ respectively.

Liquid-Liquid extraction

The organic solutions were freshly prepared by dissolving an amount of the calixarenes in the organic solvent with 1/3 ratio of CH_2Cl_2 to CCl_4(analytical grade). Copper nitrate and sodium nitrate (analytical grade), that were used as received without further purification, were dissolved in de-ionized water as stock solutions. In these systems, the pH values of the aqueous solution were adjusted to the desired values using either the acid corresponding to the anion (nitric) or the base of the cation (KOH, and ammonia). The extraction experiments were conducted in the closed glass tube at $30 \pm 1\,^{\circ}C$, in which 2 mL of organic and 2 mL of stock solution were contained. The tubes were shaken for more than 1 h to reach equilibrium, then were centrifuged. The phases were separated and the final pH was measured. The distribution ratio of the copper cation was calculated by the ratio of the concentrations, C, measured from each phase, as:

$$D_M = [M^+]_{org}/[M^+]_{aq} = C_{org}/C_{aq}$$

What we are interested in is how the copper cations were extracted by calixarenes under conditions an initial of concentration of calixarenes far lower than that of copper cations ($[calix] < 100[copper(II)]$). The equilibrium concentration of calixarenes could be calculated by the difference between initial concentrations of calixarenes and final concentrations of extraction compounds in organic phase.

Results and discussions

Extraction of picric acid (HPi) with p-tert-butyl calix[8]arene

The crown ester is often used in extracting metal ion by forming $MCr^+ Pi^-$ ion-pairs. But for calixarene, it is not sure which ion-pairs are responsible for the extracting of metal ion. In order to study the ion-pairs formed, the extraction of picric acid with calixarene is conducted first.

The extraction experiments were carried out by using an initial working volume of 4 L, with a pH value of 1, at $30 \pm 1\,^{\circ}C$. The medium of aqua phase is HNO_3 (0.1 mol/L), calix[8]arene concentrations in organic

phase are $0 \sim 10 \times 10^{-4}$ mol/L. The results from the extraction of picric acid show that the distribution ratio D_{HPi} of picric acid does not vary with calix[8]arene concentration, and keeps at 0.730. This suggests that distribution of picric acid between organic and aqua phase depend on physical distribution. The distribution constant K_d and the distribution ratio of picric acid D_{HPi} can be given by:[5,6]

$$D_{HPi} = [HPi]_{(0)}/([HPi] + [Pi])$$
$$= K_d\beta_1[H]/(\beta_1[H] + 1)$$

$$K_d = D_{HPi}(\beta_1[H] + 1)/\beta_1[H]$$
$$= 0.730(1.34 \times 0.1 + 1)/1.34 \times 0.1$$
$$= 6.3$$

A comparison between extraction experiments was carried out under the condition of pH = 1, calix[6]arene concentration 2×10^{-3} mol/L, picric acid concentration $0 \sim 4.2 \times 10^{-3}$ mol/L and temperature being $30 \pm 1\,^{\circ}C$. The results from the extraction of copper(II) with picric acid also show that D_{HPi} kept at 0.760, and did not vary obviously as variety of picric acid concentration.

Extraction of copper with three kinds of calixarenes

Having only phenolic hydroxyl groups, these three kinds of calixarenes fail to show any ionophoric activity for alkali metal cations, so that cannot extract alkali metal into organic phase in the form of $M(H_2L)^+ Pi^-$, and cannot extract alkali earth metal ion either. But they can extract transitional metal ion in absence of picric acid. So extraction of copper with these three calixarenes was first studied.

There is obvious difference on extraction ability to copper for these three kinds of calixarenes. Among them, extraction ability for copper(II) increases in order of calix[4]-, calix[8]- and calix[6]-arene. It was considered that the extractability exhibited by the present calixarene is dependent upon ion size, which is similar to that exhibited by the typical crown ether-type ionophores. This can be explained by that the octamer is conformationally more flexible than hexamer resulting in that copper(II) ion fits into calix[8]arene more difficultly than calix[6]arene. The calix[4]arene has smaller size than calix[6]arene and calix[8]arene, so the copper(II) ion fits into calix[4]arene hardly.

Extraction of copper with p-tert-butyl-calix[6]arene

The mechanism of extraction with calixarene was studied first by adopting the method of Martell Laboratory. On the assumption that $p[H] = -lg[H^+]$, $p[H]$ was taken instead of pH, in order to avoid correction of activity.

Keeping the $p[H]$ constant, the distribution ratio D was determined at various concentrations of $[H_2L]_{(0)}$. In the case, NH_3, NH_4Cl or KOH was added to keep $p[H]$ constant. The experimental condition is, for system a: $C_{NH_3} = 1$ mol/L, $C_{NH_4Cl} = 0.003$ mol/L, relation coefficient $\gamma = 0.992$; and for system b: $C_{NH_3} = 1$ mol/L, $C_{KOH} = 0.0043$ mol/L, relation coefficient $\gamma = 0.971$.

The relation of $\log D$ versus $\log [H_2L]_{(0)}$ was showed in Fig. 1. It can be seen approximately that two straight lines respectively were presented with slope of 1, which suggests that a copper(II) form isolated extraction compound with a calix[6]arene.

As a comparison, the distribution ratio D was determined at various $p[H]$. The experimental conditions were as follows: $C_{Cu}^{0}{}^{2+} = 8.00 \times 10^{-5}$ mol/L, $C_{NH_4Cl} = 1.5$—6.5×10^{-5} mol/L, $C_{NH_3} = 1$ mol/L. When $p[H]$ is varied as C_{NH_4Cl} varies, $[H_2L]_{(0)}$ concentrations cannot keep constant due to a minor initial calix[6]-arene concentration so as to variation for coordination of calix[6]arene with copper(II). Therefore D' was taken
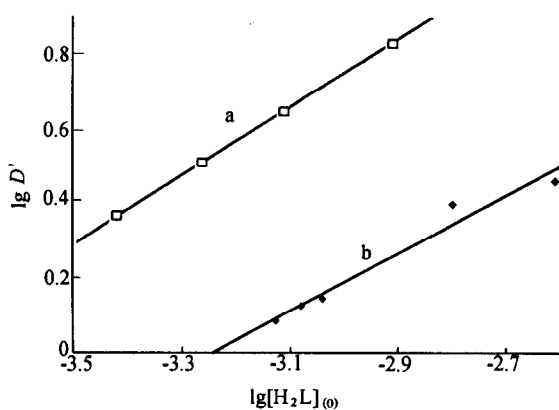

Fig. 1 Effect of calix[6]arene concentration on distribution ratio D. (Ion strength $I = 0.1$; $T = 30\,^{\circ}\text{C}$; $C_{Cu}^{0}{}^{2+} = 8.00 \times 10^{-5}$ mol/L. a: $C_{NH_3} = 1$ mol/L, $C_{KOH} = 0.0043$ mol/L, $\gamma = 0.971$; b: $C_{NH_3} = 1$ mol/L, $C_{NH_4Cl} = 0.003$ mol/L, $\gamma = 0.992$).

instead of D, and its correction equation was:

$$D' = D \times C_{H_2I}^0 / [\, C_{H_2L}^0 - D \times C_{Cu}^0/(D+1)\,]$$

The $\log D'$ as a function of $p[H]$ is showed in Fig. 2, which presents approximately a straight line with a slope of 2.

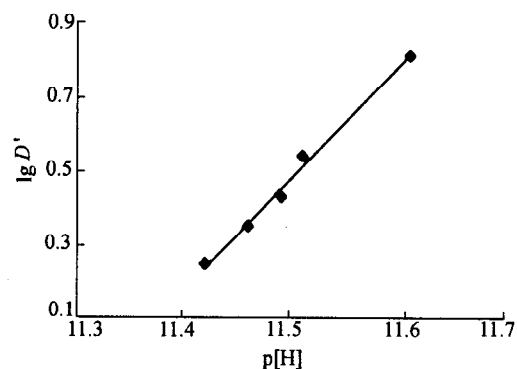

Fig. 2 Effect of $p[H]$ variation ($I = 0.1$, $T = 30\,^{\circ}\text{C}$, C_{H_2L} $= 1 \times 10^{-3}$ mol/L, $\gamma = 0.985$).

Extraction of copper with p-tert-butyl-calix[8]arene

The extraction property of copper(II) with calix[8]arene was researched by changing ammonia concentration in the extraction systems. The experiment conditions are: a: $C_{NH_3} = 0.1$ mol/L, $C_{KOH} = 0.1$ mol/L, $\gamma = 0.976$, and b: $C_{NH_3} = 1$ mol/L, $C_{KOH} = 0.1$ mol/L, $\gamma = 0.974$.

As can be seen from Fig. 3, the copper(II) ion can be extracted from aqua ammonia. The distribution ratio of copper(II) ion between the organic and the aqua phase increases linearly as increase of initial concentration of calix[8]arene in the organic phase similarly, which suggests that the binding ratio of calix[8]arene with copper(II) be 1:1, the same as the results of calix[6]arene. As a result, a calixarene must form isolated extraction compound with a copper(II) in the extraction.

Fig. 3 also shows that extractability of copper(II) with calix[8]arene in 1 mol/L aqua ammonia solution is higher than that in 0.1 mol/L aqua ammonia solution, which suggests that higher aqua ammonia concentration should result in higher extractability of calixarene. When calixarene is used to extract copper(II) in aqua ammonia

solution, increasing aqua ammonia concentration can easily promote the coordination of calixarene with copper (II) and is in favor of the extraction.
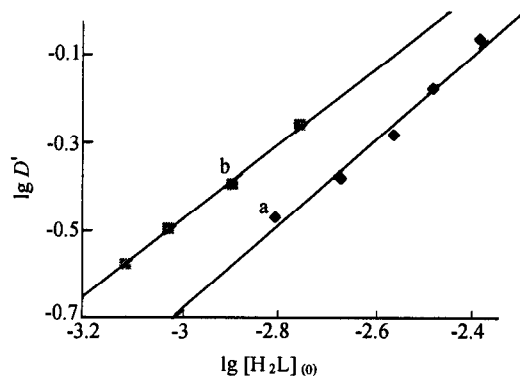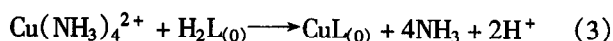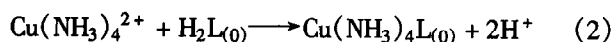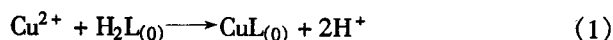

Fig. 3 Extraction results of copper with calix[8]arene ($C_{calix[8]} = 1 \times 10^{-3}$ mol/L, $T = 30\,°C$, $C_{Cu^{2+}}^0 = 8.00 \times 10^{-5}$ mol/L. a: $C_{KOH} = 0.1$ mol/L, $C_{NH_3} = 0.1$ mol/L, $\gamma = 0.976$; b: $C_{KOH} = 0.1$ mol/L, $C_{NH_3} = 1.0$ mol/L, $\gamma = 0.974$).

Discussion of reaction mechanism for extraction of copper with calixarene

As shown from above-mentioned results, the extraction mechanism of metal ion with calixarene is more complex than that with crown ester. Alkali metal is usually extracted with crown ester in the form of ion-pairs with extraction compound being $(MCr^+)Pi.^7$ However, calix[4]-, calix[6]-, and calix[8]-arene are difficult to form ion pairs with alkali metal ion. Only are alkyl acetate groups attached to the phenolic groups of calixarene in **1a**, **2a**, and **3a** to give the methyl ester of calixarene **1b**, **2b**, **3b**, and all these three calixarene ester series are found, analogous to the crown ester, to have phase-transfer affinity for alkali metal cations and easily form typical ion-pairs.

In another aspect, 2M protons from OH of calixarene was released when complex of copper(II) ion with calixarene was extracted into organic phase, which is similar to ion exchange. It can be seen that the mechanism for extraction of metal ion with calixarene is more complex than with crown ester. The metal ion can be extracted with calixarene both in the form of cation exchange and ion-pairs, which result in complex extraction properties of calixarene.

According to slopes of line in Fig. 1—3, equation of extraction reaction is probable as follows:

$$Cu^{2+} + H_2L_{(0)} \longrightarrow CuL_{(0)} + 2H^+ \qquad (1)$$

$$Cu(NH_3)_4^{2+} + H_2L_{(0)} \longrightarrow Cu(NH_3)_4L_{(0)} + 2H^+ \qquad (2)$$

$$Cu(NH_3)_4^{2+} + H_2L_{(0)} \longrightarrow CuL_{(0)} + 4NH_3 + 2H^+ \qquad (3)$$

It can be seen in Fig. 3 that, because of the extractability of copper(II) with calixarene increases as increases of aqua ammonia concentration, Eq. (3) is untenable, nor is Eq. (1), so extraction equation might be considered as Eq. (2).

Acquisition of $\lg K'_{ex}$ value

According to Fig. 1—3, K'_{ex} could be obtained and the results were listed in Table 1.

Table 1 Values of extraction equilibrium constants ($T = 30\,°C$, $I = 0.1$)

Calixarene	Calix[6]arene	Calix[8]arene	Calix[8]arene
C^0 (mol/L)	1	0.1	1
$\lg K'_{ex}$	-19.45^a	-22.83	-22.68

^{a}From Fig. 1 and Fig. 2, $\lg K'_{ex}$ of calix[6]arene was acquired as -19.50, -19.40 respectively, average value -19.45.

As seen from Table 1, equilibrium constant in 0.1 mol/L aqua ammonia was less than that in 1 mol/L aqua ammonia for calix[8]arene, and the difference between their $\lg K'_{ex}$ was 0.15. According to Eq. (2), when $\alpha = [Cu(NH_3)_3]_4^{2+}]/C_{Cu} = 0.99$ when $C = 0.1$ mol/L, and $\alpha = 0.90$ when $C = 1$ mol/L, the difference of $\lg \alpha$ was 0.05, but the difference of $\lg K_{ex}$ was 0.15 acquired from experiments. The latter was apparently within the range of experimental error.

Reference

1. Zhang, P.M.; Guo F.; Huang, Z.T., *Acta Chim. Sin.*, **47**, 731(1989).
2. Robert, P., *Top. Inclusion Sci.*, **3**, 235(1991).
3. Gutsch, C.D., *J. Org. Chem.*, **51**, 742(1986).
4. Gutsch, C.D., *J. Am. Chem. Soc.*, **103**, 3782(1981).
5. Wang, W.J.; Chen, B.Z., *J. Nucl. Radi. Chem.* (in Chinese), **2**, 153(1980).
6. Smith, R.M.; Martell, A.E., *Critical Stability Constants*, Vol. 5, Plenum, N.Y., 1982.
7. Chen, Y.D., *The Chemistry of Uranium, Thanium, Plutonium Nuclear Fuel*, Atomic Energy Pub., Beijing, 1985.
8. Ferguson, G., *J. Chem. Soc., Chem. Commun.*, 584 (1987).