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ORIGINAL PAPER

Cloud point extraction and separation of copper and lanthanoids using Triton X-100 with water-soluble *p*-sulfonatocalix[4]arene as a chelating agent

Yancun Wei · Yanling Li · Xinjun Quan · Wuping Liao

Abstract A method is presented for the cloud-point extraction and separation of copper and lanthanoid ions. A water-soluble calixarene, *p*-sulfonatocalix[4]arene (C4AS), is used as the chelating agent and Triton X-100 is chosen as the surfactant. The factors affecting the extraction efficiency, such as pH, the concentrations of Triton X-100 and C4AS, equilibration time and centrifugation time, were evaluated. The results demonstrate that there are different extraction behaviors for Cu(II) and Ln(III). Cu(II) can be separated from Ln(III) using C4AS as the chelating agent under weakly acidic conditions. The method may be used to remove trace copper from the lanthanoids.

Keywords Cloud point extraction · Copper · Lanthanoids · Triton X-100 · *p*-sulfonatocalix[4]arene

Introduction

The increasing demand of rare earths (REs) including Sc, Y and lanthanoids (Ln) needs the supply of REs not only in big volume but also with high purity. And the purity of REs is not only concerned the other REs but also the non-REs impurity such as copper (for example, when REs were recovered from the spent catalysts of RE phosphates which contain ~0.2% Cu). Recently cloud point extraction (CPE), a

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kind of micelle systems, has attracted considerable attention because it is in agreement with the "green chemistry" principles [1]. For this goal, various ligands have been used in the CPE systems such as quinolinol [2–5], 1-(2-pyridy-lazo)-2-naphthol (PAN) [6–8], 1-(2-thiazolylazo)-2-naphthol (TAN) [9], 5-Br-PADAP [10, 11] and so on [12–16]. Their application in CPE requires both the high coordination ability towards metal ions and high lipophilicity for their dissolving in the micelles. There have been some reports about the CPE procedures for the extraction and preconcentration of Cu(II) [2, 6, 7, 9, 11, 13–15] and RE(III) [3–5, 8, 10, 12, 16]. Calixarenes are also well documented as efficient extractants of metal ions in CPE [17, 18]. For instance, Mustafina et al. [17] used three water-soluble calixarenes, *p*-sulfonatothiacalixarene, tetra-sulfonatomethylated calix[4]resorcinarene, and calix[4]resorcinarene phosphonic acid as chelating agents in CPE with Triton X-100 for the preconcentration of La(III), Gd(III) and Yb(III). Zairov et al. [18] compared the CPE behaviors of La(III) and Gd(III) in a system of *p*-sulfonatocalix[*n*]arenes (*n*=4, 6, 8) as the chelating agents and Triton X-100 as the non-ionic surfactant.

Recently, a series of 3D metal-organic frameworks (MOFs) with some 1D hydrophilic channels has been synthesized in our lab using the lanthanoids, *p*-sulfonatocalix[4]arene and 1,10-phenanthroline. [19] When these MOFs were used to adsorb the copper cations, the frameworks collapsed and a copper compound $Cu_3(phen)_3(C4AS)Cl(H_2O)_{17.6}$ [20] formed, which means C4AS exhibits stronger coordination ability towards the copper cations.

The goal of the present work is to study the extraction behaviors of Cu(II), Ln(III) with a CPE system and the separation of Cu(II) from Ln(III). The extraction of Cu(II) and Ln(III) (La, Gd and Yb) in a CPE system with *p*-sulfonatocalix[4]arene and Triton X-100 was examined in detail and the effect of the factors such as pH, the concen-

trations of Triton X-100 and C4AS, equilibration time and centrifugation time, was evaluated. The recovery of trace copper from the lanthanoid solutions has also been studied.

Experimental

Reagents

High-purity La$_2$O$_3$ (99.99%), Gd$_2$O$_3$ (99.99%) and Yb$_2$O$_3$ (99.99%) were obtained from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China, http://www.ciac.jl.cn). Stock solutions of LnCl$_3$ were prepared from these oxides by dissolving in concentrated hydrochloric acid and diluting with distilled water. CuCl$_2$·2H$_2$O of analytical grade was purchased from Sinapharm Chemical Reagent Beijing Co., Ltd (Beijing, China, http://www.crc-bj.com). The CuCl$_2$ solution was obtained by dissolving an appropriate amount of CuCl$_2$·2H$_2$O in doubly distilled water. Triton X-100 (TX100) purchased from Aldrich (http://www.sigmaaldrich.com) was used without further purification. C4AS was synthesized according to the literature method [21]. All the other chemicals were of analytical reagent grade.

Apparatus

The concentrations of Cu(II) and Ln(III) were determined by molecular absorption spectrophotometry using a 722 N spectrophotometer (Shanghai Precision & Scientific Instrument, China, http://www.jk18.com). A model 720 digital pH meter (Orion Research Inc., USA, http://orionresearchinc.com) was employed for pH measurements. A thermostated bath maintained at the desired temperature was used for cloud point temperature experiments. A model LG10-2.4 centrifuge (Beijing Lab Centrifuge Co., Ltd, China, http://www.bjlabcentrifuge.com) was used to speed up the complete phase separation of turbid solutions above the cloud point temperature.

Typical cloud point extraction procedure

An aqueous solution containing Cu(II)/Ln(III), C4AS and TX100 was placed in a test tube with a glass stopper. The solution was heated for 60 min in a thermostated water bath at 80 °C which is higher than the cloud point of TX100 (about 65 °C [1]). The resulting turbid solution was centrifuged for 3 min to accelerate the phase separation. The upper aqueous phase was removed and the Cu(II) and Ln(III) concentrations were determined by spectrophotometry at 600 nm for Cu(II) using Cuprizone as a complexing agent at pH 9.4 in ammonium chloride-ammonia buffer solution, and 658 nm for Ln(III) using Arsenazo (III) as an indicator at pH 2.8 in chloroactic acid-sodium hydroxide buffer solution.

CPE of Cu(II) and Ln(III) from the micellar solutions was evaluated in terms of extraction efficiency (E), distribution ratio (D), and the selectivity (S) that are defined as follows [5, 12]:

$$E = \frac{C_i V_i - C_f V_f}{C_i V_i} \times 100 \qquad (1)$$

$$D = \frac{C_i - C_f}{C_f} \times \frac{V_i}{V_{srp}} \qquad (2)$$

$$S_{Cu^{2+}/Ln^{3+}} = \frac{D_{Cu^{2+}}}{D_{Ln^{3+}}} \qquad (3)$$

$$V_{srp} = 0.700 \times [TX100]_T + 0.052 \qquad (4)$$

where C_i is the initial concentration of the metal ion in the micellar solution, C_f being the concentration of the metal ion in the aqueous phase after CPE, V_i being the volume of the micellar solution in mL, V_f being the volume of the aqueous phase after CPE in mL, V_{srp} being the volume of the surfactant-rich phase after CPE in mL, and $[TX100]_T$ being the total TX100 concentration (V/V%).

Results and discussion

Effect of equilibration time on the extraction efficiency of Cu(II) and Ln(III)

Theoretically, the optimal equilibration temperature of the extraction occurs when the equilibration temperature is greater than the cloud point temperature of surfactant by 15~20 °C. Therefore, the solution was heated in a thermostated water bath at 80 °C. A series of extraction experiments were processed for different equilibration time to examine the effect of equilibration time on the metal extraction. As shown in Fig. 1, the highest metal extraction was obtained after equilibrating for 60 min. So the optimum equilibration time was fixed to 60 min.

Effect of centrifugation time on the extraction efficiency of Cu(II) and Ln(III)

The effect of centrifugation time on phase separation was studied in the range of 2~10 min at 2,000 rpm. The solution phase could not be completely separated if time is too short or too long. The results revealed that 3 min were enough to get a complete phase separation, and no
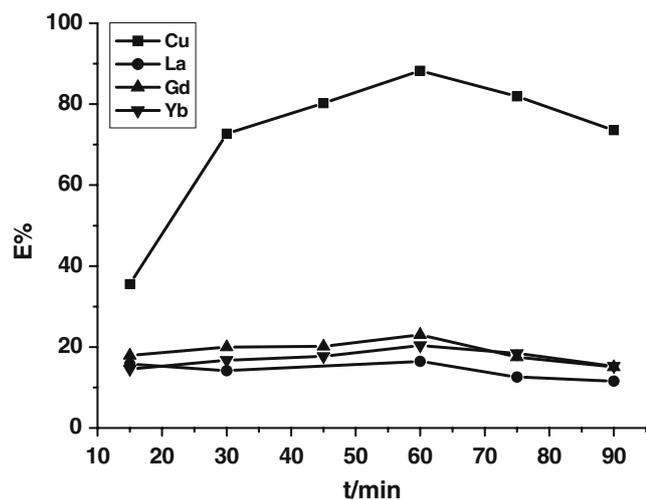
Fig. 1 Effect of the equilibration time on the extraction efficiency of Cu(II) and Ln(III). Fixed parameters: 3.16×10^{-4} mol L^{-1} Cu(II) or Ln (III); pH 6.50; 5% TX100; 3.0×10^{-3} mol L^{-1} C4AS

Fig. 2 Effect of pH on the extraction of Cu(II) and Ln(III). Fixed parameters: 3.16×10^{-4} mol L^{-1} Cu(II) or Ln(III); 3.0×10^{-3} mol L^{-1} C4AS; 5% TX100

considerable improvement was observed for longer periods of time due to cooling down of the CPE system. Therefore, a centrifugation time of 3 min was selected as the optimum.

Effect of pH on the extraction efficiency of Cu(II) and Ln(III)

It is well known that the deprotonation of C4AS depends on the acidity of the solution, which leads to different coordination ability of C4AS toward the metals. So the CPE of copper (II) and lanthanoids (III) with C4AS should be examined in a wide range of pH. As shown in Fig. 2, the extraction of Cu(II) and Ln(III) by the CPE systems with C4AS increases with the increasing pH, exhibiting a similar trend as that in the CPE systems without C4AS [17]. The reasonable explanation might be that more complexes of the metals and C4AS form at higher pH and the hydroxy complexes formed by the hydrolysis of the metals are extracted into micellar pseudo-phase much more efficiently than ionic associates [17]. Importantly, the extraction of Cu (II) is obviously higher than that of the lanthanoids when the pH value is above 6. All the following experiments were carried out at pH 6.50.

Effect of TX100 concentration on the extraction efficiency of Cu(II) and Ln(III)

A successful CPE would be the one that maximizes the extraction efficiency through minimizing the phase volume ratio, thus maximizing the concentration factor. TX100 was chosen as the surfactant due to its commercial availability, low cloud point temperature and high density of the surfactant rich phase. The extraction of the metals with TX100 being in the range of 0.77~1.94% (V/V) was examined (Fig. 3). The
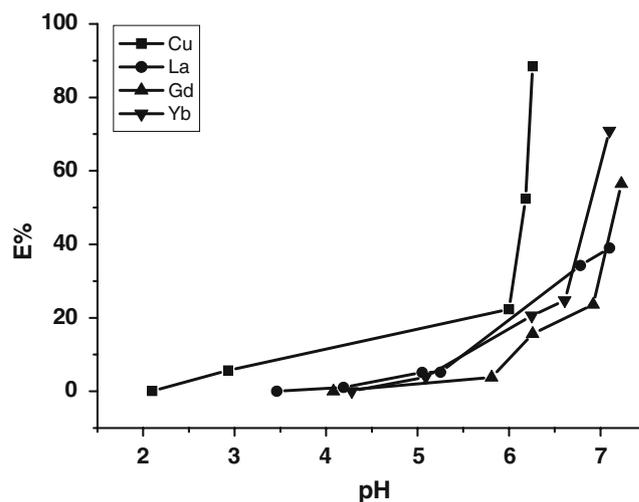
extraction of the metals increases smoothly with the increasing TX100 concentration except an abnormal point at 1.76% (V/V) TX100 concentration, which might be due to the increasing dissolution of C4AS in the surfactant-rich phase. In the following experiments, the TX100 concentration was fixed to 5% (V/V) to avoid the incomplete dissolution of C4AS in the surfactant-rich phase. It is also observed that the extraction of Cu(II) is much higher than that of Ln(III).

Effect of C4AS concentration on the extraction of Cu(II) and Ln(III)

The effect of C4AS concentration on the extraction was studied with C4AS being in the range of $0.30 \times 10^{-3} \sim 3.40 \times 10^{-3}$ mol·L^{-1}. The results are illustrated in Fig. 4. The
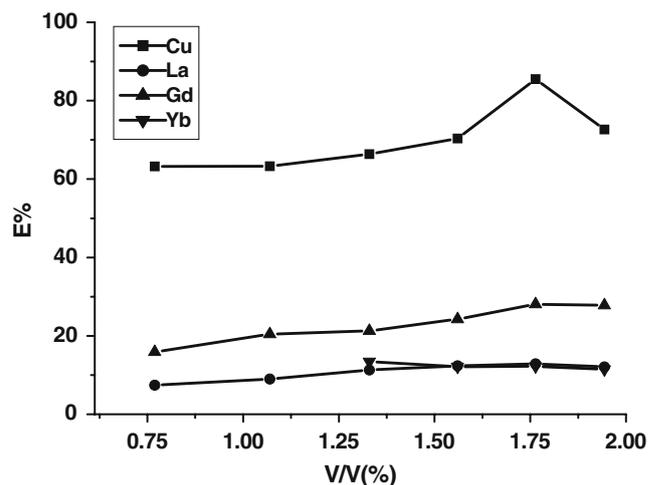

Fig. 3 Effect of TX100 concentration on the extraction of Cu(II) and Ln(III). Fixed parameters: 3.16×10^{-4} mol L^{-1} Cu(II) or Ln(III); pH 6.50; 3.0×10^{-3} mol L^{-1} C4AS
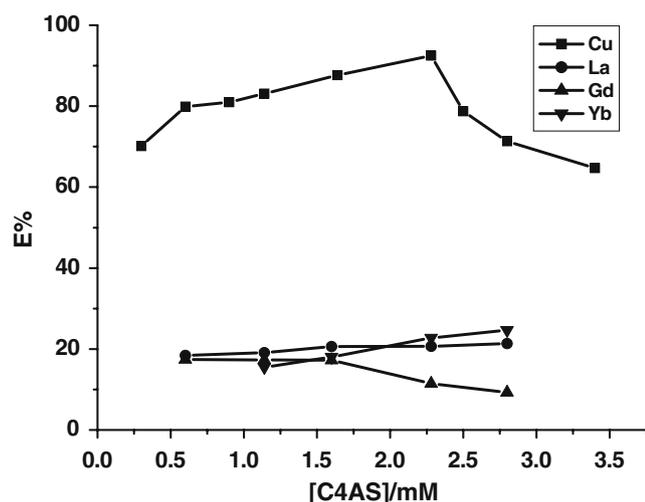
Fig. 4 Effect of C4AS concentration on the extraction of Cu(II) and Ln(III). Fixed parameters: 3.16×10^{-4} mol L^{-1} Cu(II) or Ln(III); pH 6.50; 5% TX100

Fig. 5 Effect of the molar ratio of Ln^{3+}/Cu^{2+} on the selectivity of Cu (II) and Ln(III). Fixed parameters: 3.16×10^{-4} mol L^{-1} Cu(II); pH 6.50; 5% TX100; 3.0×10^{-3} mol L^{-1} C4AS

extraction of Cu(II) increases with the increasing C4AS concentration to a limiting value and then decreases. However, the extraction of La(III) and Yb(III) keeps nearly unchanged while the extraction of Gd(III) keeps unchanged first and then decreases to a half. The decreasing extraction of Cu(II) and Gd(III) with the increasing C4AS concentration might be due to more hydrophilic metal-complexes formed when the C4AS concentration exceeds a value. It is evident that the influence of C4AS concentration on the extraction of Cu(II) is more prominent than that of Ln(III) and C4AS exhibits higher coordination ability to Gd(III) than La(III) and Yb(III).

Selectivity of Cu(II)

Figure 5 shows the effect of different molar ratio of Ln(III)/ Cu(II) on the selectivity. The separation factor (S) increases with the increasing La(III)/Cu(II) or Yb(III)/Cu(II) ratio. For the Gd(III) system, the S value decreases when the Gd (III)/Cu(II) ratio exceeds 4 and then changes little after the Gd(III)/Cu(II) ratio reaches 6. It can be explained by the stronger coordination ability of C4AS to Gd(III) than La (III) and Yb(III) and the fact that the competition of Gd(III) and Cu(II) decreases the extraction of Cu(II). However, the lowest separation factor between Cu(II) and Gd(III) is still above 5. So, in the weakly acidic condition, Cu(II) can be separated from Ln(III) by using C4AS as the chelating agent and TX100 as the surfactant.

Merit for the recovery of Cu(II)

In order to validate the method, recovery experiments were carried out. For this purpose, different amount of copper (II) was added to the simulation solution. The results are
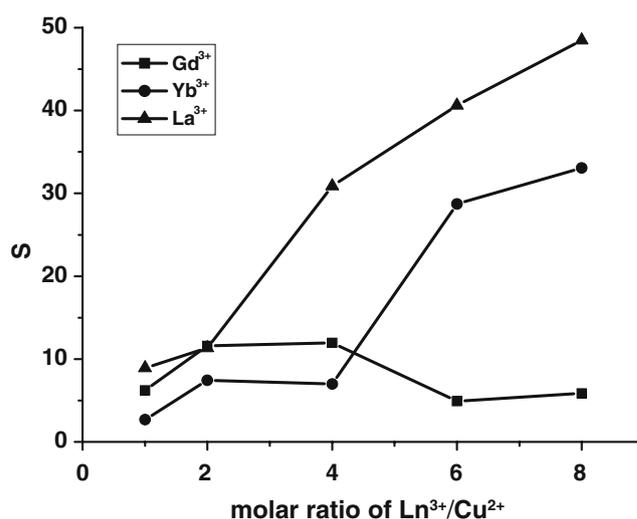
shown in Table 1. The recoveries calculated for the added standards were always higher than 95%, and these results confirm the validity of the method.

Conclusions

The cloud point extraction of copper is more efficient than the lanthanides using *p*-sulfonatocalix[4]arene, which exhibits higher complexability to Cu^{2+} than Ln^{3+}. Various factors affecting the extraction of the metals and the separation factor have been examined. Experimental conditions for the cloud point extraction and separation of Cu(III) and Ln(III) have been optimized. Under the optimum conditions, this cloud point extraction system might be used for the separation of trace copper(II) from the stock lanthanoid solutions.

Table 1 Merit for the recovery of Cu^{2+} from a simulation solution $(n=3)$[a]

No.	Additional Cu added (μg)	Cu found (μg)	RSD (%)	Cu recovery (%)
1[b]		31.45	0.14	
2	18	49.39	0.73	99.67
3	23	55.61	0.94	103.3
4	30	63.05	0.84	99.19
5	36	67.72	0.54	100.8

[a] The test was processed by adding an amount of Cu^{2+} into the simulation solution, extracting Cu^{2+} by CPE and then calculating the amount of Cu^{2+} extracted in the surfactant-rich phase

[b] The simulation solution with unknown Cu^{2+} concentration. The content of Cu^{2+} was obtained by examining the surfactant-rich phase after CPE

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