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Effect of the Structure of Alkyl Salicylaldoxime on Extraction of Copper(II)

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Abstract: Four kinds of alkyl salicylaldoxime (AS) were investigated to probe the effect of molecular structure on the extraction of Cu(II). With the augment of R groups, *tert*-octylsalicylaldoxime and nonylsalicylaldoxime have much stronger extraction ability for Cu(II) than salicylaldoxime and *tert*-butylsalicylaldoxime, which is consistent with the rise of hydrophobicity (Log P) of the extractants. The umbrella structure of the R group can endow *tert*-octylsalicylaldoxime with stronger steric-hindrance effect than nonylsalicylaldoxime, which results in the better separation efficiency of Cu(II) from Fe(III) for *tert*-octylsalicylaldoxime. The extraction ability of the extractants for Cu(II) is related to the hydrophobicity and molecular size, as predicted from quantum chemistry calculation.

Keywords: alkyl salicylaldoxime; Copper(II) ion; molecular structure; extraction efficiency; separation

1. Introduction

With increased demand for copper, rich copper deposits are rapidly decreasing, and people are now focusing attention on copper recovery from low-grade copper ore or/and secondary copper resources [1,2]. The hydrometallurgical technique involving crushing, leaching, solvent extraction (SX), and electrowinning is being applied to recover copper from these low-grade copper resources [3,4]. SX is one key unit operation in the hydrometallurgical process because it determines the copper separation from the leaching solutions and also has great influence on the following electrowinning efficiency [5]. Thus, it is vital to find or synthesize effective extraction reagents for copper recovery and production.

Alkyl salicylaldoximes (AS)—the N–O type chelating organic agents—are widely-used extractants which present excellent extraction efficiency for Cu(II) [6,7]. AS are comprised of a benzene ring, phenolic hydroxyl, ortho-directing oximido, and para-directing alkyl (i.e., R group). In this group of chemical compounds, the para-directing R group has great impact on their charge distribution, steric-hindrance effect, and so on, which determines their extraction ability for Cu(II) [8,9]. At present, AS are produced by bio-extraction and artificial synthesis, with the artificial synthesis route being the dominant technique for the production of AS [10,11]. It was reported that many types of AS with different R groups (e.g., nonyl, decyl, and dodecyl) have been synthesized in the laboratory [12–16]. Some researchers investigated the extraction ability of AS with more than 12 carbon atoms in the R group for Cu(II). It was shown that these AS presented bad fluidity and phase separation during SX, which resulted in the unsatisfactory extraction ability for Cu(II) [11]. Therefore, one of the most widely used AS is 5-nonylsalicylaldoxime (or nonylsalicylaldoxime) where the R group is a straight chain containing nine carbon atoms. It has good fluidity and steric-hindrance effect, and has been widely

used to extract Cu(II) as the main effective component in the common commercial extractants LIX984, LIX984N, P50, and so on. However, there is little information in the literature about the performance of AS with the carbon atoms less than nine and/or non-straight chains in the R groups on the extraction of Cu(II).

In this study, two kinds of AS with non-straight R groups—one being *tert*-butylsalicylaldoxime with four carbon atoms in the R group and the other *tert*-octylsalicylaldoxime with eight carbon atoms in the R group—were synthesized in laboratory. We compared their extraction ability for Cu(II) with two other commercial salicylaldoxime-based extractants: salicylaldoxime without the R group and nonylsalicylaldoxime. Besides, the effect of the R group on the structure of the four kinds of reagents and the Cu(II) extraction were also discussed. This study not only provides useful guidance for the design and development of salicylaldoxime-based extractants for Cu(II) extraction, but also has significance for the exploitation and utilization of complex copper resources.

2. Experimental

2.1. Materials

tert-Butylsalicylaldoxime and *tert*-octylsalicylaldoxime were synthesized by using para-*tert*-butyl phenol (purity > 95%) and para-*tert*-octyl phenol (purity > 97%) as raw materials, respectively, and the mixture of methanol (purity > 99%) and methylbenzene (purity > 99%) as solvent through sequential salt forming reaction, acylation reaction, oximation reaction, and acidification reaction. The detailed synthesis procedures can be seen in [17]. The purity of the synthesized chemical reagents is no less than 95% according to the liquid chromatographic analysis (LC-8A, Shimadzu, Kyoto, Japan). Salicylaldoxime (analytical grade) and nonylsalicylaldoxime (analytical grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China); Kerosene (analytical grade) was purchased from Shanghai Rare-Earth Chemical Co., Ltd. (Shanghai, China), was washed with concentrated H_2SO_4 twice to eliminate the influence of unsaturated hydrocarbon, and was then washed to neutrality with deionized water before use. The Cu(II) sulfate, Fe(III) sulfate, and sulfuric acid obtained from Tianjin Kaitong Chemical Co., Ltd. (Tianjin, China) were also of analytical grade.

2.2. Methods

2.2.1. Extraction of Cu(II) and Fe(III)

The organic phases with different concentrations of extractants were prepared by dissolving the corresponding reagents in the pretreated kerosene. The Cu(II) solution and Fe(III) solution were prepared by dissolving Cu(II) sulfate and Fe(II) sulfate in diluted sulfuric acid, respectively. The extraction of Cu(II) by the four kinds of extractants was carried out at room temperature and atmospheric pressure. The separation factors of the extractants for Cu(II) and Fe(III) ($\beta_{Cu/Fe}$) were evaluated by

$$\beta_{Cu/Fe} = \frac{C_{Cu(O)} \cdot C_{Fe(A)}}{C_{Cu(A)} \cdot C_{Fe(O)}} \tag{1}$$

where $C_{Cu(O)}$ and $C_{Cu(A)}$ indicate the concentration of Cu(II) in organic phase and aqueous phase (g/L), respectively, and $C_{Fe(O)}$ and $C_{Fe(A)}$ indicate the concentration of Fe(III) in organic phase and aqueous phase (g/L), respectively. The concentration of metal ions—including Cu(II) and Fe(III)—in the organic phase ($C_{metal(O)}$) can be obtained by

$$C_{metal(O)} = \frac{(C^0_{metal(A)} - C^1_{meta(A)}) \cdot V_{(A)}}{V_{(O)}} \tag{2}$$

where $C^0_{metal(A)}$ and $C^1_{metal(A)}$ are the metal concentrations in aqueous solutions before and after extraction (g/L), respectively. $V_{(A)}$ is the volume of aqueous phase (L) and $V_{(O)}$ is the volume

of organic phase (L). The concentration of Cu(II) and Fe(III) in aqueous solution was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.2.2. The Structure Properties of Reagents

The molecular structures of the four organic reagents were first drawn by Chemoffice 2010, then the molecular sizes of the extractants were calculated by Connolly Solvent-Excluded Volume method in Chemoffice 2010 [18], and their hydrophobicity (Log P) was also calculated by Chemoffice 2010. The optimum 3-D structures of the extractants were obtained based on the optimization using HF/3–21 G (d) basis set in Gaussian.

3. Results and Discussion

3.1. The Structures of the Extractants

The calculated molecular structures of the four salicylaldoxime-based extractants are shown in Figure 1, which can be verified by nuclear magnetic resonance and mass spectrograph. It can be clearly seen that the four extractants have similar molecular structures, except for the R groups linked to the benzene rings (Figure 1). Thus, their different extraction ability for metals may be due to the molecular structures which are influenced by the R groups.

3.2. The Extraction of Cu(II)

Under the conditions of the initial Cu(II) concentration of 1.92 g·L^{-1}, 15% (*v/v*) of extractants and the phase ratio (aqueous phase to organic phase) of 1, the single-stage extraction efficiency for Cu(II) after 3 min at different initial pH is shown in Figure 2.

It is observed that nonylsalicylaldoxime and *tert*-octylsalicylaldoxime present a similar trend for Cu(II) extraction with pH (see Figure 2). The Cu(II) extraction efficiency initially increased with pH and then decreased after pH 3–4. Although salicylaldoxime and *tert*-butylsalicylaldoxime showed by far the weaker extraction capacity for Cu(II) than nonylsalicylaldoxime and *tert*-octylsalicylaldoxime, their extraction efficiencies for Cu(II) were also slightly higher at pH of 3–4 than at other pH values (Figure 2). Salicylaldoxime-based extractants are acid organics, and they chelate Cu(II) in a 2:1 ratio, as shown in Figure 3 [19].

With the rise of pH, the above extraction reaction shifts towards the right and the metal extraction efficiency also increases, which is why the Cu(II) extraction efficiency initially increased with pH and reached a plateau at pH 3–4. The extraction efficiency declined after the pH exceeds 4, because Cu(II) presents solid or colloidal particle forms in high pH solutions, which may interfere with its extraction [19].

At pH = 4, salicylaldoxime, *tert*-butylsalicylaldoxime, *tert*-octylsalicylaldoxime, and nonylsalicylaldoxime could extract 5.15%, 9.25%, 91.53%, and 92.11% of Cu(II) from the solutions, respectively (Figure 2), indicating that their extraction ability for Cu(II) is enhanced with the increase of carbon chain length in the R groups linked to the benzene rings. As the carbon atom number in the R group increases to eight, *tert*-octylsalicylaldoxime presents a similar extraction capacity to nonylsalicylaldoxime, with nine carbon atoms in the R group.
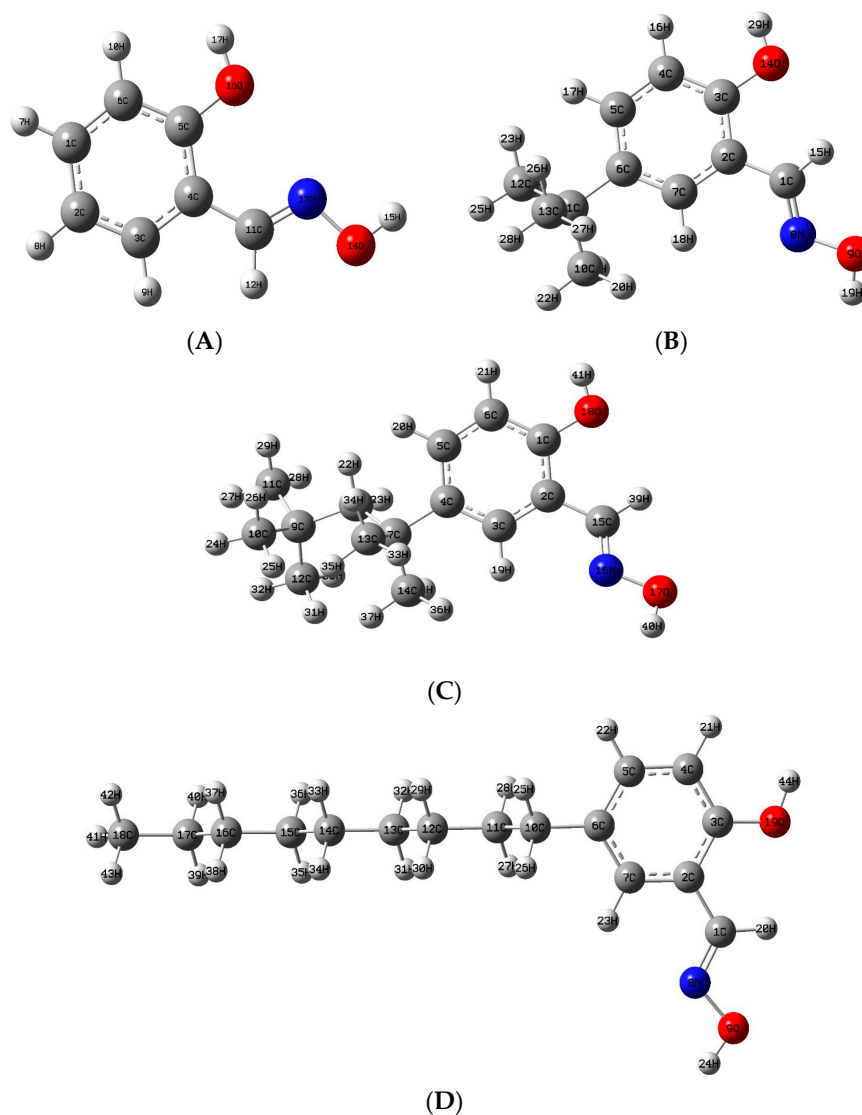
Figure 1. The optimum structures of four kinds of extractants: (**A**) salicylaldoxime; (**B**) *tert*-butylsalicylaldoxime; (**C**) *tert*-octylsalicylaldoxime; (**D**) nonylsalicylaldoxime.
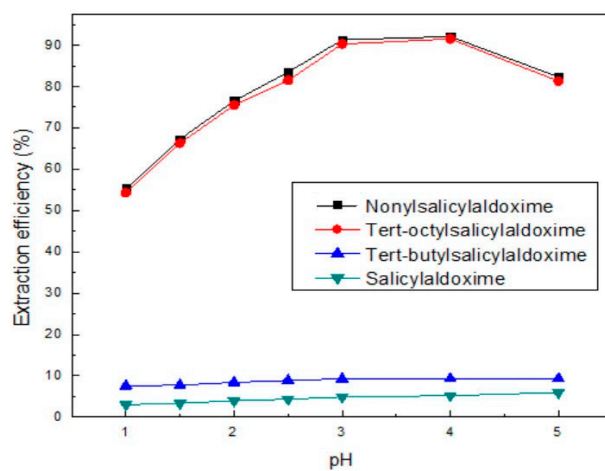

Figure 2. Effect of initial pH of aqueous phases on the extraction efficiency of Cu(II).
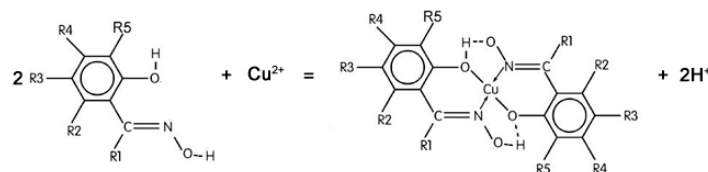
Figure 3. The reaction between salicylaldoxime-based extractants and Cu(II).

3.3. Separation of Cu(II) and Fe(III)

The main raw ores for copper extraction are refractory complex copper sulfides and copper oxide ores, including chalcopyrite ($CuFeS_2$), chalmersite ($CuFe_2S_3$), and bornite (Cu_5FeS_4). Cu(II) and Fe(III) will be leached from these ores by acid in the hydrometallurgical process, so Fe(III) is a common impurity ion in the copper leaching solutions, and it is also one significant ion interfering with the Cu(II) extraction. Thus, the separation factor for Cu(II) and Fe(III) ($\beta_{Cu/Fe}$) is a key evaluation index for the extractants.

In order to investigate the separation factor in the wide pH range, the initial concentrations of Cu(II) and Fe(III) were set at 1.92 mg/L and 1.12 mg/L, respectively, to prevent their precipitation at relatively high pH. Other extraction conditions were the same as those in Section 3.2. The effect of pH on $\beta_{Cu/Fe}$ is illustrated in Figure 4.
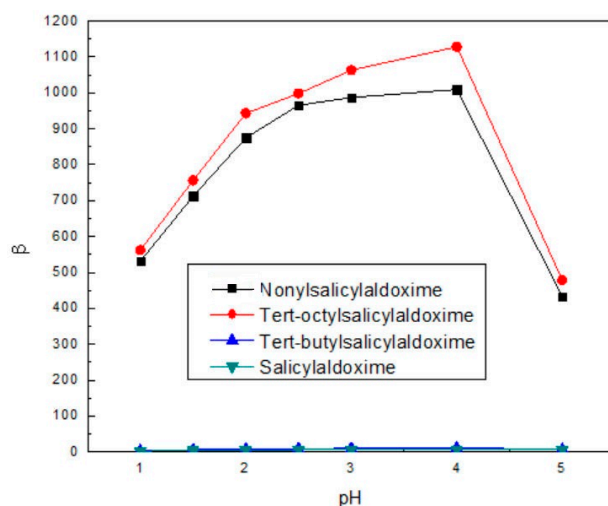

Figure 4. Effect of initial pH of aqueous phase on the $\beta_{Cu/Fe}$.

$\beta_{Cu/Fe}$ increased with the rise of pH and reached a peak of 1128 and 1009 at pH = 4 for nonylsalicylaldoxime and *tert*-octylsalicylaldoxime, respectively, which is consistent with the trend of Cu(II) extraction efficiency; salicylaldoxime and *tert*-butylsalicylaldoxime showed much lower $\beta_{Cu/Fe}$ at the pH range studied due to their poor extraction ability for Cu(II) (Figure 3). *tert*-Octylsalicylaldoxime showed better $\beta_{Cu/Fe}$ than nonylsalicylaldoxime, and this may be caused by the different R group structures in their molecules. The umbrella structure of the R group in *tert*-octylsalicylaldoxime can provide a stronger steric-hindrance effect than the linear chain structure of the R group in nonylsalicylaldoxime, which presumably endows the former with stronger selectivity for Cu(II). The steric-hindrance effect was also used to explain the selective extraction ability for tertiary amines of the Alamine type [20] and β-diketone extractants [21].

3.4. Hydrophobicity (Log P) and Molecular Sizes

It can be seen from Table 1 that the R groups have significant impact on the hydrophobicity (Log P) of the extractants. With the increase of carbon atoms in the R groups, the values of Log P

increase and the chemical reagents become more hydrophobic. Generally, the extractants should have relatively strong hydrophobicity to effectively extract metals [22–24]. It is known that there is no R group in salicylaldoxime, and the para-directing R group is tertiary butyl with four carbon atoms in *tert*-butylsalicylaldoxime (Figure 1), which results in the weaker hydrophobicity than *tert*-octylsalicylaldoxime and nonylsalicylaldoxime with eight and nine carbon atoms in the R groups, respectively (Table 1). Thus, the latter two reagents present remarkably higher Cu(II) extraction ability than salicylaldoxime and *tert*-butylsalicylaldoxime under the same conditions. As the atoms in the R groups increase to eight and nine, the extractants have similar hydrophobicity (Table 1) and they also present similar extraction ability for Cu(II) (Figure 2). The calculated molecular sizes of the four extractants increase with the augment of the R groups, and this can also be observed from their molecular structures (Figure 1).

Table 1. Hydrophobicity (Log P) and molecular sizes of the extractants.

Items	Log P	Molecular Sizes (nm^3)
Salicylaldoxime	1.78	100.15
tert-Butylsalicylaldoxime	3.48	170.50
tert-Octylsalicylaldoxime	5.12	241.27
Nonylsalicylaldoxime	5.61	254.12

4. Conclusions

The structure of the para-directing R group linked to the benzene ring determines the Cu(II) extraction ability of salicylaldoxime-based extractants to a large extent. The extractants with 0–4 carbon atoms in the R group are not suitable for Cu(II) extraction, but *tert*-octylsalicylaldoxime and nonylsalicylaldoxime with eight and nine carbon atoms in the R group, respectively, possess excellent extraction ability for Cu(II). Moreover, *tert*-octylsalicylaldoxime and nonylsalicylaldoxime also present satisfactory separation effect for Cu(II) and Fe(III), but the former's performance is better than that of the latter due to the special umbrella structure of its R group, which may provide a stronger steric-hindrance effect for the separation of Cu(II) and Fe(III).

The quantum chemical calculation indicates that the hydrophobicity of the extractants is enhanced gradually with the augment of the R groups, which is consistent with the trend of extraction ability of the extractants for Cu(II). The Cu(II) extraction ability of the extractants can be speculated according to the quantum chemical calculation.

Author Contributions: Liqing Li conceived and designed the experiments; Yi Wang and Wenjuan An performed the experiments; Liqing Li and Shenxu Bao analyzed the data; Liqing Li contributed materials; Shenxu Bao and Liqing Li wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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