



Synergistic separation of copper(II) in sulfate solutions through outer-sphere coordination of dinonylnaphthalene disulfonic acid

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ABSTRACT

Synergistic extraction is a promising strategy to achieve the separation and concentration of metal ions from complex effluents. Herein, the selective extraction behaviors of Cu(II) with 2-ethylhexyl pyridine-4-carboxylate ester (L^{II}) and dinonylnaphthalene disulfonic acid (H_2DNNDS) have been investigated. The extraction of impurity ions including Al(III), Fe(III), Mn(II), Mg(II) and Ca(II) can be effectively depressed at the high molar ratio of the ligand L^{II} and H_2DNNDS , and the separation factors of Cu/Al, Cu/Ca, Cu/Fe, Cu/Mg, and Cu/Mn can reach 840, 1707, 2205, 2241, and 1269, respectively. Moreover, the relationship between the coordination chemistry and the extraction behavior has been demonstrated by X-ray single crystal diffraction, Fourier transform infrared spectroscopy (FT-IR) and electrospray ionization mass spectrometry (ESI-MS). The spectra analyses indicate that the extracted Cu(II) complex would have a similar distorted octahedral coordination environment with the Cu(II) model complex with the corresponding short-chain analogues of the ligand L^{II} and H_2DNNDS . The inner coordination sphere of Cu(II) complex is occupied with three N atoms from pyridine ring of the ligand L^{II} and three O atoms from water molecules, and the deprotonated H_2DNNDS acts as a non-coordinating ion-pairing agent to form an outer-sphere coordination structure. Hence, the extraction efficiency enhancement of Cu(II) with the ligand L^{II} after mixed with H_2DNNDS , can be attributed to the dual contribution of inner- and outer-sphere coordination of synergistic ligands.

1. Introduction

Selective complexation of a specific metal ion by given ligands is an important objective for many applications including catalytic, chromatographic and metal recovery processes. As for base-metal recovery processes, acidic leaching became the mainstream hydrometallurgical technology to deal with resources such as low grade ores and oxidized ores with the depletion of high grade ores. The obtained leachates usually contain impurity metal ions from gangue minerals after leaching. Commonly, solvent extraction is the most convenient technology to achieve the separation and concentration of specific metal ions [1–3]. However, the selectivity continues to be a challenge in the design of extractant systems. Since the formation of coordination assemblies has been recognized in extraction chemistry, attempts have been made to tune the strength and selectivity of new reagents through the interactions in inner-sphere and outer-sphere of metal complexes [4,5]. For instance, the rational design of specific extractant has become possible to achieve the separation and concentration of Co(II), Zn(II) and Pt(II) with the anion recognition [5–9]. During solvent extraction,

pyridinium derivatives could coordinate with the $[MCl_4]^{2-}$ ($M=Co$ and Zn) in chloride media to form a more hydrophobic and transportable complex $[(LH)_2MCl_4]$ through $H\cdots Cl$ hydrogen bonds between the proton on the pyridinium nitrogen and the $[MCl_4]^{2-}$ anion when mixed with each other. Such interactions have also been observed in solid-state structures of chlorometallates [8].

Synergistic effect between two or more extractants can greatly improve the selective separation of metal ions which neither individual extractant achieve [10]. This phenomenon of greatly enhanced extraction due to a mixture of extractants has attracted considerable attention since its discovery in 1958 [11]. In the past three decades, significant extraction selectivities of Cu(II), Ni(II), and Co(II) were revealed with synergistic mixtures [12–14]. Synergistic solvent extraction systems consisting of dinonylnaphthalene sulfonic acid (HDNNS) and various N-donor synergists were explored since a synergistic effect was found for the separation of Cu(II), Ni(II) from Fe(III) and Al(III) in acidic aqueous solutions by the mixture containing HDNNS and LIX63 [15,16]. Lately, this synergistic effect was studied for the extraction of Ni(II) from acidic aqueous solutions by the mixture containing

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dinonylnaphthalene sulfonic acid (HDNNS) and 1-octyl-2-(2'-pyridyl) imidazole [17]. The selectivity of sodium dodecyl benzene sulfonate (SDBS) towards Ni(II) and Cu(II) over Zn(II), Pb(II) and Cd(II) could be extremely enhanced by the addition of synthesized pydazole-based pyridine ligands [18]. Although significant synergistic effect has been noticed in the mentioned extraction systems, the extraction mechanism remains a major challenge. In literatures, the bonding information between metal ions and ligands could be illustrated intuitively by X-ray single crystal diffraction of the metal model complexes with corresponding short chain analogues of active synergistic extractants and using comparative spectroscopic studies between the metal model complexes and the actual extraction systems [19,20]. Not until recently, it has been suggested that the selective extraction of Cu(II) and Ni(II) with the synergistic extractants containing HDNNS and pyridinecarboxylate esters involved the formation of metal complexes with different coordination structures [21,22].

Arylsulfonates is a structural analogy to the phosphonate RPO_3^- , but were not well-explored because sulfonates are weakly coordinating ligands [23,24]. Based upon the library of transition metal sulfonate crystal structures, naphthalenedisulfonate (NDS) was able to generate stable structures with different topologies through π - π and hydrogen-bonding interactions in the presence of other aromatic organic ligands [25]. The coordination behavior of Cu(II) toward arenedisulfonates RSO_3^- could be tailored chemically [26]. An extensive literature survey revealed that there was a dearth of knowledge regarding extraction behavior of arenedisulfonates and the relationship between the extraction behavior and the coordination chemistry, although different coordination modes of arenedisulfonates to Cu(II) has been reported.

A deeper understanding of the chemical binding between Cu(II) and the mixed extractant containing dinonylnaphthalene disulfonic acid (H_2DNNDS) and the ligand L^{II} is therefore needed, with respect to both inner-sphere binding and noncovalent second-sphere interactions. One way to address this problem is by combination of accurate X-ray diffraction data with spectroscopic data. Hence, a Cu(II) model complex was synthesized with n-hexyl pyridine-4-carboxylate ester (L^{I}) and 1,5-naphthalene disulfonic acid (H_2NDS), which were the respective short chain analogues of the ligand L^{II} and H_2DNNDS . The Cu(II) model complex and the extracted Cu(II) complex in the loaded organic phase were characterized using Fourier transform infrared spectroscopy (FT-IR) and electrospray ionization mass spectrometry (ESI-MS).

2. Experimental

2.1. Materials

H_2DNNDS was purchased from Shanghai Jia Chen Chemical Co., Ltd. H_2NDS was purchased from Adamas reagent Co., Ltd. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MgSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ were obtained from Sinopharm Chemical Reagent Co., Ltd. The two types of pyridine-4-carboxylate esters (the ligands L^{I} and L^{II}), whose structures are shown in Fig. 1, were synthesized as the procedure described elsewhere [27]. Sulfonated kerosene was purchased from Shanghai RareEarth Chemical Co, Ltd and used as the diluent without further purification. Other chemicals were of analytical grade (except for specification).

2.2. Solvent extraction

For the solvent extraction experiments, a synthetic leachate containing $2.73 \text{ g} \cdot \text{L}^{-1}$ Cu(II), $5.23 \text{ g} \cdot \text{L}^{-1}$ Mg(II), $0.35 \text{ g} \cdot \text{L}^{-1}$ Ca(II), $1.24 \text{ g} \cdot \text{L}^{-1}$ Al(III), $0.95 \text{ g} \cdot \text{L}^{-1}$ Mn(II), and $0.91 \text{ g} \cdot \text{L}^{-1}$ Fe(III) was prepared. Fresh organic solutions were prepared with sulfonated kerosene as diluent. The extraction behaviors of the individual ligand L^{II} , H_2DNNDS and the mixed extractant containing the ligand L^{I} and H_2DNNDS were compared. The extraction experiments were performed in thermostat vessels at an A/O ratio of 1:1, pH ~ 2 and 25.0 ± 0.1 °C.

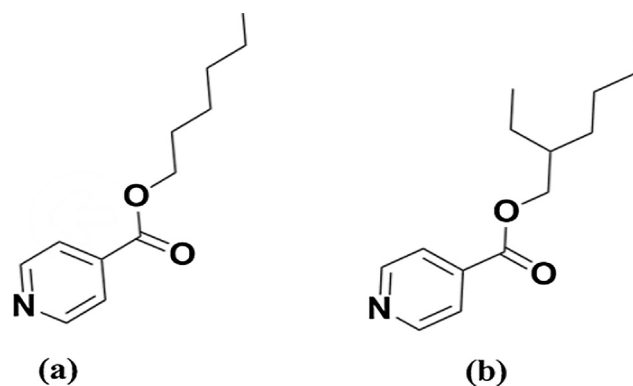


Fig. 1. The structures of the ligand L^{I} , n-hexyl pyridine-4-carboxylate ester (a) and the ligand L^{II} , 2-ethylhexyl pyridine-4-carboxylate ester (b).

The metal concentration in the aqueous phase was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer 5300DV America). The metal concentration in the loaded organic phase was calculated by mass balance.

For further structural characterization, the extracted Cu(II) complex in the loaded organic phase was prepared with the same extraction procedure while sulfonated kerosene was replaced with n-hexane, and the concentrations of the ligand L^{II} and H_2DNNDS were kept at $0.5 \text{ mol} \cdot \text{L}^{-1}$ and $0.25 \text{ mol} \cdot \text{L}^{-1}$, respectively.

2.3. Synthesis of the Cu(II) model complex

Equal volumes (ca. 10 mL) of respective aqueous solutions containing 10 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 10 mmol H_2NDS were mixed and stirred for 30 min at 25 °C to form a precipitate. The precipitate was filtered and washed with acetone for three times. Subsequently, the washed precipitate and a solution (ca. 10 mL) of ethanol and water (20:1, v/v) were added to a conical beaker, and stirred at ambient temperature till the precipitate was dissolved completely. Then a solution of the ligand L^{I} (4.75 g, 23 mmol) in ethanol (ca. 10 mL) was added dropwise to the conical beaker, and stirred for 40 min at 40 °C. After filtration, the filtrate was stood at about 25 °C for several weeks to obtain blue well-shaped single crystals of the Cu(II) model complex by slow evaporation. FT-IR ($\text{KBr}, \nu \text{ cm}^{-1}$): 2957 (s), 2930 (s), 2859 (s), 1729 (m), 1625 (s), 1563 (s), 1503 (s), 1464 (s), 1420 (s), 1386 (s), 1284 (s), 1181 (s), 1027 (s). Anal. Calc. for $\text{C}_{44}\text{H}_{60}\text{CuN}_2\text{O}_{16}\text{S}_2$ (%): C, 53.82; H, 6.14; N, 4.09; S, 6.24; Found (%): C, 54.00; H, 5.54; N, 2.91; S, 6.36.

2.4. Crystal structure determination

Experimental details of the X-ray analyses and crystallographic data were listed in Table 1. All diffraction data were collected at 173 K on a Bruker Smart APEXII diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and a ω scan mode. The structure was refined against with a full-matrix least-squares procedure on F^2 using the program SHELXL (Sheldrick, 2015) and subsequent difference-Fourier map revealed the positions of the remaining atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the organic frameworks were fixed at calculated positions geometrically and refined by using a riding model.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited in the Cambridge Crystallographic Data Center, CCDC 1557255.

2.5. Elemental analysis and spectra studies

Elemental analyses (C, H, N and S) were conducted with Thermo

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