

A comprehensive extraction study using a mono-alkylated diglycolamic acid extractant: Comparison between a secondary amide group and a tertiary amide group

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Liquid-liquid extraction is an effective separation method for the purification of valuable metals, removal of toxic metals, and recovery of fission products. The efficiency of metal separation with liquid-liquid extraction depends on the extractant. To date, numerous extractants, which have superior extraction and separation ability, have been developed. Most novel extractants, however, are expensive for large-scale applications because of laborious and elaborate synthetic processes, and are unsuitable for industrial extraction processes.

Recently, we developed *N,N*-dioctyldiglycolamic acid (DODGAA, Fig. 1), which is a carboxylic acid-type extractant with an amide group and an ether oxygen donor [1, 2]. The extractant can be synthesized simply and readily in a single step, which helps to reduce its production cost. Although DODGAA is a carboxylic acid-type extractant and has a simple molecular structure consisting only of C, H, O, and N atoms, the compound provides an excellent extraction ability for a variety of metal ions compared with commercial carboxylic acid-type extractants.

In this study, we comprehensively investigated the extraction of 56 metal ions using *N*-dodecyldiglycolamic acid (C₁₂DGAA, Fig. 1). The obtained extraction data for C₁₂DGAA were compared with those for DODGAA to evaluate the effect of the amide group on the extractability and selectivity of DGAA-type extractants. In addition, selective removal of toxic metal ions from a metal ion mixture was carried out using C₁₂DGAA.

In a preliminary experiment, we examined the distribution of C₁₆DGAA, C₁₂DGAA, and C₈DGAA (Fig. 1) between the organic and aqueous phases. Although alkane solvents such as isooctane or dodecane are acceptable in industrial extraction processes, the DGAA-type extractants with a linear alkyl chain were poorly soluble in isooctane. In contrast, the extractants were readily soluble in 1-octanol. Thus, isooctane containing a small amount of 1-octanol (5 vol%) was employed as an extracting solvent in this study. As a result, C₁₆DGAA was not dissolved in isooctane containing 5 vol% 1-octanol. C₁₂DGAA and C₈DGAA were soluble in the organic solution, but C₈DGAA slightly distributed into the aqueous phase. Therefore, C₁₂DGAA was selected as the extractant.

To evaluate the effect of amide group in DGAA-type extractant on the extraction ability, extraction behavior for various metal ions were compared between C₁₂DGAA and DODGAA. Based on the extraction data, the metal ions are divided into the following two groups, depending on whether C₁₂DGAA provides a higher or lower extraction ability for the metal ions than DODGAA:

- C₁₂DGAA > DODGAA
 Mg(II), Al(III), Sc(III), Ti(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Ga(III), Pd(II), Hf(IV), Hg(II)
- C₁₂DGAA < DODGAA
 Ca(II), Sr(II), Y(III), Zr(IV), Ru(III), In(III), Ba(II), Au(III), Pb(II), Lanthanides

In addition, we investigated here the selective separation of Hg(II) from aqueous solutions containing various divalent metal ions (Hg(II), Pb(II), Cu(II), Cd(II), Zn(II), Mn(II), Co(II), and

Ni(II)) for the purpose of demonstrate the usefulness of C₁₂DGAA in removing toxic metal ions. As shown in Fig. 2, C₁₂DGAA provided the highest selectivity for Hg(II) among 8 divalent metal ions, which permits the selective removal of Hg(II) from the metal mixture. In contrast, DODGAA can remove Hg(II) and Pd(II) from the other metal ions, but mutual separation between Hg(II) and Pb(II) is less efficient than with C₁₂DGAA.

The DGAA framework with a tertiary amide group (DODGAA) has a relatively rigid molecular geometry because of the partial double-bond character of the C-N bond of the amide group, which leads to a stronger basicity of the amide oxygen atom. In contrast, the DGAA framework with a secondary amide group (C₁₂DGAA) makes the basicity of the amide oxygen atom weaker. Therefore, it is obvious that DODGAA offers high coordination ability for metal ions compared with C₁₂DGAA. However, C₁₂DGAA tended to provide better extraction for relatively small-sized metal ions compared to DODGAA, with a few exceptions. Although the reason for this difference is unclear at this stage, we postulate that the steric hinderance of the alkyl chain of the extractants is involved in the extraction of small-sized metal ions.

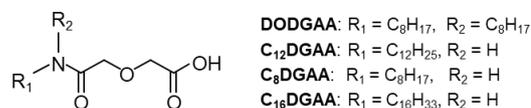


Fig. 1 Molecular structures and abbreviations of extractants.

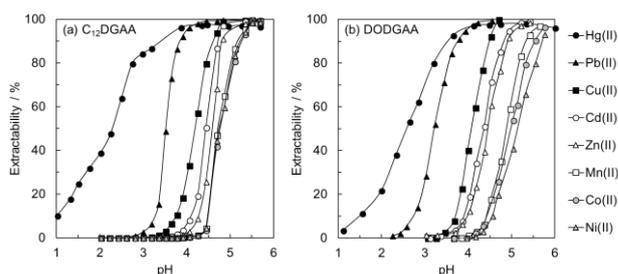


Fig. 2 Extraction removal of the toxic metal Hg(II) from various divalent metal ions with (a) C₁₂DGAA and (b) DODGAA.

References

- [1] H. Naganawa *et al.*, *Solvent Extr. Res. Dev., Jpn.* **14**, 151 (2007).
 [2] K. Shimojo *et al.*, *Anal. Sci.* **30**, 513 (2014).