

Use of 8-sulfonamidoquinoline derivatives as chelate extraction reagents in ionic liquid extraction system

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Abstract

Possible use of 8-sulfonamidoquinoline derivatives as chelate extraction reagents for solvent extraction of several divalent metal cations using an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) as extraction phase was investigated as fundamental approach to develop novel extraction reagents for ionic liquid extraction system. The studied reagents were able to be used as extractants for the metal cations in the [bmim][PF₆] extraction system. Furthermore, their extractability in the [bmim][PF₆] system was superior to that in chloroform system. Most of the extracted species were (hydrated) neutral complexes, whereas, in use of the derivative having trifluoromethyl group, Cd²⁺ was extracted as anionic complex accompanied with anion-exchange process.

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1. Introduction

Ionic liquids (strictly speaking, room temperature ionic liquids) have attracted much interest as novel solvents [1–11]. They are salts with low melting points (ca. <100 °C) and hydrolytically stable. Furthermore, several ionic liquids are water-immiscible and, therefore, can be used as solvent (extraction phase) for liquid–liquid extraction.

Use of ionic liquids as extraction phase in solvent extraction of organic materials was reported by Huddleston et al. first in 1998 [12] and that of metal cations was reported by Dai et al. first in 1999 [13], provided that studies on similar extraction systems were reported more previously [14,15]. Many researchers have studied the ionic liquid extraction system and several reviews concerning the system have been reported [16–18].

In use of ionic liquids for metal extraction, extraction of charged complexes with neutral extractants by ion-exchange processes with the ionic liquid ions, reported by Dietz and Dzielawa first in 2001 [19], has been given attention. In the extraction system, however, recovery of the extracted metals is a serious problem because of negligible volatility of the ionic liquids. On the contrary, use of anionic chelating agents such as dithizone [20], 8-hydroxyquinoline derivatives [21] and β-diketones [22,23] or neutral ligands having protonatable N-donor [24–26] as extraction reagents and back-extraction of the extracted metals into aqueous acid solution seem to be effective for the achievement of the recovery. Furthermore, in use of the anionic chelate extraction reagents, possible extracted species into the ionic liquid extraction phase are not only conventional neutral chelates but also anionic (or cationic) ones. Namely, in the ionic liquid chelate extraction system, various kinds of extraction mechanism can be constructed. However, traditional chelate extraction reagents were optimized for use of organic solvents as extraction phase and, therefore, are not always suitable for use of ionic liquids. In other words, it is necessary to

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develop novel extraction reagents for the ionic liquid chelate extraction system.

8-Sulfonamidoquinoline derivatives (HRsq), which are sulfonamide-type analogs of 8-hydroxyquinoline, can act as N,N^- -bidentate anionic chelate extraction reagents [27–37] since sulfonamide group has acidity comparable to that of phenolic-OH [38–40]. Furthermore, other sulfonamide-type ligands were researched as anionic chelate extraction reagents [41–47]. Since the HRsq derivatives are generally synthesized by reaction between 8-aminoquinoline and respective sulfonyl halides (RSO_2X , $X=F$, Cl or Br), it is very easy to introduce various substituents (R) onto 8-sulfonamidoquinoline structure. Namely, use of the HRsq derivatives in the ionic liquid chelate extraction system is an effective approach to develop novel chelate extraction reagents optimized for the system. Furthermore, the HRsq derivatives as well as 8-hydroxyquinoline exist as hydrophobic neutral forms at wide pH region [39]. From these viewpoints, we performed a fundamental study concerning possible use of several HRsq derivatives, such as 8-(*p*-toluenesulfonamido)quinoline [4-methyl-*N*-(8-quinolyl)benzenesulfonamide, $H(C_7H_7)sq$], 8-(methanesulfonamido)quinoline [8-quinolylaminosulfonylmethane, $H(CH_3)sq$] and 8-(trifluoromethanesulfonamido)quinoline [trifluoro(8-quinolylaminosulfonyl)methane, $H(CF_3)sq$] (see Fig. 1), as chelate extraction reagents for extraction of several divalent metal cations in ionic liquid chelate extraction system using 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]).

2. Experimental

2.1. Reagents

The synthesis of $H(C_7H_7)sq$ was performed from 8-aminoquinoline and *p*-toluenesulfonyl chloride according to the reported procedure [48]. Other ligands such as $H(CH_3)sq$ and $H(CF_3)sq$ were prepared in a similar manner to $H(C_7H_7)sq$ from 8-aminoquinoline and methanesulfonyl chloride or trifluoromethanesulfonyl fluoride. The structures were identified by ¹H-NMR spectra and elemental analysis [39,48].

The ionic liquid [bmim][PF₆] was synthesized from 1-chlorobutane, 1-methylimidazole and hexafluorophosphoric acid according to the reported procedure [12]. Other chem-

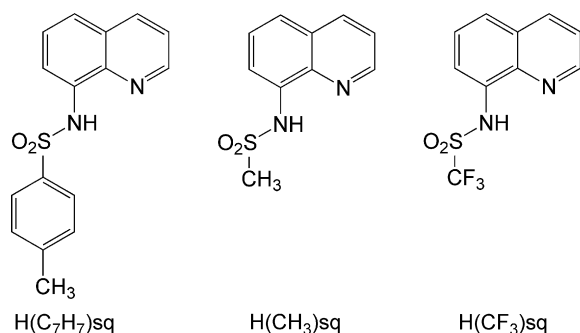


Fig. 1. Chemical structures of 8-sulfonamidoquinoline derivatives used in this study.

icals were reagent-grade materials and were used without further purification. Distilled deionized water was used throughout.

2.2. Apparatus

A Hitachi model Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous phase. A Horiba model F-12 pH meter equipped with a Horiba 9510-10D combined glass electrode was used to determine the pH values.

2.3. Distribution of the metals

In a centrifuge tube, an aliquot (1 cm³) of [bmim][PF₆] containing 1×10^{-3} mol dm⁻³ of an HRsq and 5 cm³ of an aqueous phase 1×10^{-5} to 1×10^{-4} mol dm⁻³ of M^{2+} ($M = Co$, Cu , Zn or Cd), 1×10^{-1} mol dm⁻³ of potassium nitrate and 1×10^{-2} mol dm⁻³ of buffer (chloroacetic acid, acetic acid or 2-(*N*-morpholino)ethanesulfonic acid) were shaken at 25 ± 1 °C for 45 min. After the two phases were separated by centrifugation, the pH and the metal concentration in the aqueous phase were determined and the measured pH was used as equilibrated pH. The metal concentration in the extraction phase was determined after back-extraction into 10-fold volume of 1 mol dm⁻³ nitric acid.

3. Results and discussion

3.1. $H(C_7H_7)sq$ system

The extracted ratios (%*E*) of M^{2+} into [bmim][PF₆] extraction phase with $H(C_7H_7)sq$ were plotted as a function of aqueous phase pH. The results are shown in Fig. 2 with the plots using chloroform as extraction phase. The use of [bmim][PF₆] extraction phase resulted in higher extractability for all of M^{2+} compared with the use of chloroform. In addition, Mn^{2+} was not extracted in the examined extraction conditions and extraction of Ni^{2+} needed long time for equilibration as reported previously for chloroform system [34]. The extraction selectivity order in the $H[(C_7H_7)sq]$ -[bmim][PF₆] system was $Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Co^{2+} (\gg Mn^{2+})$, which was almost the same as that in use of chloroform extraction phase, $Cu^{2+} > Zn^{2+} > Co^{2+} \geq Cd^{2+} (\gg Mn^{2+})$.

As reported previously [34], $H(C_7H_7)sq$ extracts M^{2+} as neutral $M[(C_7H_7)sq]_2$ complex (probably hydrated $M[(C_7H_7)sq]_2(H_2O)_n$ complex) in use of an organic solvent as extraction phase. In this case, the extraction equilibrium and the extraction constant (K_{ex}) can be expressed as follows:



$$K_{ex} = \frac{[M[(C_7H_7)sq]_{2(e)}][H^+]^2}{[M^{2+}][H(C_7H_7)sq]_{(e)}^2} \quad (2)$$

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