

Halogen-Free Water-Immiscible Ionic Liquids Based on Tetraoctylammonium Cation and Dodecylsulfate and Dodecylbenzenesulfonate Anions, and Their Application as Chelate Extraction Solvent

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The tetraoctylammonium cation forms water-immiscible room temperature ionic liquids with dodecylsulfate and dodecylbenzenesulfonate anions. The ionic liquids are halogen-free and can be considered environmentally friendly solvents. At 25°C, the solubilities of water in tetraoctylammonium dodecylsulfate and tetraoctylammonium dodecylbenzenesulfonate were 2.8 and 4.0%, respectively, and the densities were 0.92 and 0.93 g cm⁻³. The ionic liquids formed stable interfaces with water at 25°C. The possible use of tetraoctylammonium dodecylsulfate as chelate extraction solvent was evaluated by using 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione as extractant. Tetraoctylammonium dodecylsulfate showed high extraction performance for divalent transition metal cations.

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Introduction

Much attention has been devoted to room-temperature ionic liquids (RTILs) owing to their potentiality as alternatives of conventional organic solvents. Recently, the applications of water-immiscible RTILs in extractive separation as solvents have been the subjects of research interest by several authors.¹⁻⁵ These researches have been developed with the use of RTILs based on alkylimidazolium (Rmim⁺) cations and hexafluorophosphate (PF₆⁻), tetrafluoroborate and bis-(trifluoromethylsulfonyl)imide (TFSI⁻) anions. These RTILs include fluorine atoms for their acquisition of hydrophobicity and, therefore, pose some severe environmental risks.

We found that tetraoctylammonium (TOctA⁺) cation forms RTILs with dodecylsulfate (DS⁻) and dodecylbenzenesulfonate (DBS⁻) anions. In this communication, we describe the preparation and the physical properties of tetraoctylammonium dodecylsulfate (TOctADS) and dodecylbenzenesulfonate (TOctADBS). The RTILs are immiscible and form stable interfaces with water. Chelate extraction behavior of divalent transition metal cations from water to the RTILs containing 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) as an extractant was studied. We report herein the first example of the application of halogen-free RTIL as extraction solvent.

Experimental

Reagents and apparatus

Tetraoctylammonium bromide (TOctABr, 98%) was obtained from Fluka. Sodium dodecylsulfate (NaDS) and sodium dodecylbenzenesulfonate (NaDBS), standard reference materials, were obtained from Wako Pure Chemicals Industries Ltd. Other chemicals were reagent-grade materials and were used without further purification. Distilled deionized water was used throughout.

A Hitachi Model Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous solution.

Chelate extraction of metal ions

In a centrifuge tube, an aliquot of RTIL (1 cm³) containing 1 × 10⁻² mol dm⁻³ of Htta and 5 cm³ of an aqueous phase containing 1 × 10⁻⁵ - 1 × 10⁻⁴ mol dm⁻³ of M²⁺ (M = Mn, Co, Ni, Cu, Zn, Cd or Pb), 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 30 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 extract RTIL phase was calculated from that in the aqueous phase.

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Results and Discussion

Preparation of TOctADS and TOctADBS

The TOctADS and TOctADBS RTILs were prepared as follows: Equimolar (usually 100 mmol dm⁻³) TOctABr and NaDS or NaDBS were mixed in 1:1 water + acetone. The mixture was kept at room temperature for a few days under atmospheric pressure until acetone evaporated completely. The mixture was then separated into an oily substance and an aqueous phase. The mixture was transferred to a separating funnel, and the aqueous phase was removed. The resultant crude RTIL was purified by shaking with water several times. The RTIL was dried at 80°C under 40 mmHg for 3 h and freed of water. The yield was 95% for both RTILs.

¹H NMR (CDCl₃, 90 MHz, ppm) TOctADS: 4.01 (t, 2H), 3.26 (t, 8H), 1.53 (m, 68H), 0.88 (t, 15H); TOctADBS: 7.81 (d, 2H), 7.05 (d, 2H), 3.27 (t, 8H), 1.53 (m, 70H), 0.88 (t, 15H).

Properties of TOctADS and TOctADBS

The melting points of TOctADS and TOctADBS were 20 and -10°C, respectively. When the RTILs contained water to some extent, the depression of the melting point was observed. Thermo-gravimetric analysis (performed by a Shimadzu TG-50 at 10°C/min heating rate, under nitrogen flow of 50 ml/min) showed good thermal properties. TOctADS and TOctADBS exhibited thermal stability up to 254 and 244°C, respectively.

The viscosity values of TOctADS and TOctADBS were determined to be 1010 and 1720 mPa s, respectively, at 25°C, which are higher than those of Rmim⁺-based RTILs¹ but on the order of those of tetraalkylammonium⁺-TFSI⁻ RTILs.⁶ The conductivity was determined to be 27 and 6.5 μS cm⁻¹, which are smaller than those of Rmim⁺-based RTILs¹ and tetraalkylammonium⁺-TFSI⁻ RTILs.⁶

The solubilities of water in TOctADS and TOctADBS were 2.8 and 4.0%, respectively, which can be compared with those of Rmim⁺-based RTILs.¹ The density of TOctADS and TOctADBS were determined to be 0.92 and 0.93 g cm⁻³, respectively, at 25°C. The TOctADS and TOctADBS RTILs formed stable interfaces with water at 25°C, so that the RTILs can be used as the extraction solvent as mentioned below.

Recently, it has been shown that the interface between RTIL and water can be studied electrochemically.⁷⁻⁹ Ion-transfer voltammetric study was performed with the interface between TOctADS and 0.05 M Li₂SO₄ aqueous solution, but no available polarizable potential range was observed, indicating that the interface has a non-polarized character.⁷

Chelate extraction behavior of divalent metal ions into TOctADS

As blank test, extraction experiment using Htta-free RTILs was performed at several aqueous phase pH conditions. The TOctADS system showed negligible extractability (less than 3% for all M²⁺), whereas the TOctADBS system showed higher value (ca. 5–50%). This result seems to originate from the hydrophobicity of DBS⁻ being higher than that of DS⁻. It was found that neither TOctA⁺ cation nor DS⁻ anion act as strong extractant, thus the TOctADS system was used in further study.

The extracted ratios (%E) of M²⁺ into TOctADS extract phase with Htta are plotted as a function of the aqueous phase pH in Fig. 1. The obtained extraction selectivity order was Cu ≫ Ni ≈

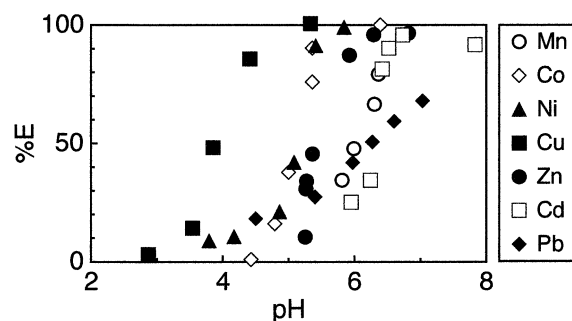


Fig. 1 Plots of the extracted ratios (%E) for some divalent metals as a function of the aqueous phase pH equilibrated with TOctADS phase in Htta system. Initial Htta concentration in extraction phase was 1 × 10⁻² mol dm⁻³.

Co > Zn > Cd ≈ Mn (Pb showed inexplicable extraction behavior). The order is similar to that in Rmim⁺-PF₆⁻ RTIL systems,¹ although the extractability is somewhat lower than that for Rmim⁺-PF₆⁻ systems.¹ The extracted species are estimated as M(tta)₂ for M = Cu, Zn and Mn and M(tta)₃⁻ for M = Ni, Co and Cd, although further structural study is indispensable. The TOctADS RTIL showed much higher extraction ability than nitrobenzene, chloroform and toluene, except for M = Cu and Pb.¹ Namely, it was found that the TOctADS can be used as chelate extraction solvent.

One hundred millimolar tetrabutylammonium (TBuA⁺) bromide or tetradodecylammonium (TDodecA⁺) bromide and equimolar NaDS were mixed in 1:1 water + acetone, and the acetone was evaporated. The mixture of TBuA⁺ cation and DS⁻ anion was a homogeneous aqueous solution, suggesting that the TBuA⁺-DS⁻ salt is miscible with water. From the mixture of TDodecA⁺ cation and DS⁻ anion, a white precipitate was produced at 25°C, suggesting that the TDodecA⁺-DS⁻ salt is solid at room temperature. Now studies concerned with the salts of other hydrophobic cations with DS⁻ and DBS⁻ anions are in progress.

References

1. J.-F. Liu, J. Å. Jönsson, and G.-B. Jiang, *Tre. Anal. Chem.*, **2005**, 20, 24, and references herein.
2. N. Hirayama, M. Deguchi, H. Kawasumi, and T. Honjo, *Talanta*, **2005**, 65, 225.
3. K. Nakashima, F. Kubota, T. Maruyama, and M. Goto, *Ind. Eng. Chem. Res.*, **2005**, 44, 4368.
4. D. C. Stepinski, M. P. Jensen, J. A. Dzielawa, and M. L. Dietz, *Green Chem.*, **2005**, 7, 151.
5. V. A. Cocalia, M. P. Jensen, J. D. Holbrey, S. K. Spear, D. C. Stepinski, and R. D. Rogers, *Dalton Trans.*, **2005**, 1966.
6. H. Matsumoto, H. Kageyama, and Y. Miyazaki, *Chem. Lett.*, **2001**, 182.
7. T. Kakiuchi, N. Tsujioka, S. Kurita, and Y. Iwami, *Electrochem. Commun.*, **2003**, 5, 159.
8. T. Kakiuchi and N. Tsujioka, *Electrochem. Commun.*, **2003**, 5, 253.
9. H. Katano and H. Tatsumi, *Anal. Sci.*, **2003**, 19, 651.