

Ionic Liquids as Liquid Materials for Analytical Chemistry

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Ionic liquids (ILs) are attracting liquid media for analytical chemistry due to their several fascinating characteristics, such as negligible vapor pressure, chemical and electrochemical stability, and a unique ionic solvation environment. ILs have been studied in a vast area of analytical chemistry research fields^{1,2} such as chromatography,³⁻⁵ extraction,⁵⁻¹¹ optical^{12,13} and electrochemical¹⁴⁻¹⁷ sensing, and interfacial^{18,19} and bulk liquid^{20,21} analysis.

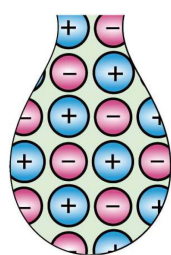
The usage of ILs as extracting liquid media in liquid-liquid extraction is an attractive strategy to enhance the extraction ability and selectivity. Eguchi *et al.* reported on the extraction of group-13 metals from aqueous solutions to ILs using 8-quinolinol as a chelating agent. They used three ILs, 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C_nmim][TFSA], *n* = 2, 4, 8), whose cations have different alkyl chain lengths, and therefore different hydrophobicity.⁹ The extractability of the metal cations increased with increasing the hydrophobicity. Yoshida *et al.* used [C₈mim][TFSA] in a supported liquid membrane to selectively separate Pt(IV) from Pd(II) from a feeding solution to a receiving solution.¹⁰ They found that a 0.1 M NaClO₄ solution showed the best performance as the receiving solution among the solutions and the concentrations they investigated, where 93% of Pt(IV) was transported while most of the Pd(II) remained in the feeding solution. Hamamoto and Katsuta developed an *in-situ* solvent formation microextraction technique for the preconcentration of paraquat in water into an IL for HPLC determination.⁵ The IL that they used, [C₂mim][NNf₂] (NNf₂: bis(nonafluorobutanesulfonyl)amide), was composed of a hydrophilic cation and a hydrophobic anion, which was suitable for the extraction of dicationic paraquat *via* the cation exchange mechanism. The paraquat concentrated in the IL was successfully determined by HILIC with good detection limits and linearity ranges. Toita *et al.* found the formation of the third phase in their IL-water

two-phase system containing trioctylphosphine oxide (TOPO).⁸ Among the ILs they investigated, [C_nmim][TFSA] with *n* = 2, 4, 6, 8, the third phase appeared only for more hydrophilic ones with *n* = 2, 4. The third phase was found to be mainly composed of TOPO and its protonated form, and showed an extraction concentration ability for the Fe(III)-thiocyanato complex. Atanassova *et al.* studied the extraction behavior of three lanthanoid ions (La³⁺, Eu³⁺, and Lu³⁺) with 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) in the two-phase system of water and [C₄mim][TFSA].⁷ The extraction performance was enhanced compared with the case of using chloroform instead of IL.

Sensing using ILs has been extensively studied as well. Aiming at the development of an electrochemical sensing of xylazine hydrochloride in human serum samples, El-Shal and Hendawy fabricated a carbon-paste electrode with a multi-walled carbon nanotube, sodium dodecyl sulfate, and an IL, 1-butyl-3-methylpyridinium hexafluorophosphate, although the IL is solid at room temperature.¹⁷ For optical sensing applications, Mizuta *et al.* developed a method to immobilize a IL-containing PVC membrane on a convex-shaped PDMS substrate.¹³ Their ILs were based on dye dianions combined with trihexyltetradecylphosphonium, a hydrophobic monocation. The ILs play dual roles for a plasticizer and an optode. Such ILs enabled them to make the dye density high in a thin PVC film for an optical sensor.

Since air-stable and water-stable classes of ILs were re-discovered in 1992, ILs have been applied in analytical chemistry. Some recent interesting applications can also be found in the studies introduced in this Highlights section, such as ILs as liquid materials made of functional ions themselves at super-high concentration and ILs in multi-phase (more than two) liquid systems.

Keywords Molten salts, electroanalytical chemistry, optode, HPLC, solvent extraction



Application of Ionic liquids to analytical chemistry

- Separation
 - Extraction
 - Chromatography
- Sensing
 - Optical sensor
 - Electrochemical sensor

Liquid drop full of ions whose shape is derived using the Bashforth-Adams equation.

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