

Synthesis of Thiosalicylate based Hydrophobic Ionic Liquids and their Applications in Metal Extraction from aqueous solutions

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Summary: Two new hydrophobic ionic liquids were synthesized through ion exchange metathesis and characterized through spectral data and thermogravimetric analysis. These include 1,3-dibutylimidazolium thiosalicylate [BBIM][TS] (**1**) and 1,3-dihexylimidazolium thiosalicylate [HHIM][TS] (**2**). The application of these ILs in extraction of seven transition metal ions (Cr, Mn, Fe, Co, Ni, Cu and Zn) from aqueous solution has been investigated. High extraction efficiencies were observed. Extraction occurs rapidly at room temperature, no heating is required unlike previous reports. [HHIM][TS] (**2**) Showed higher extraction efficiency in almost all metal ions tested as compare to [BBIM][TS] (**1**).

Keywords: Ionic liquid, Hydrophobic, Room temperature, Imidazolium, Thiosalicylate, Metal extraction.

Introduction

Ionic liquids (ILs) are organic salts with very low melting points (around or below 100 °C) as compare to classical salts like sodium chloride showing high melting points (usually greater than 500 °C). These unique materials comprise only cation and anion like salts but due to bulky size and unsymmetrical organic cation and weakly coordinating anion they exhibit low melting points and majority exist as liquid at room temperature [1-3]. The significance of ionic liquids is due to the unique features of ILs including low melting points, negligible vapor pressure, high ionic conductivity and low inflammability [4-9]. Another reason for rapid growth in ionic liquids synthesis is, vast applications of these materials encompassing material science to organic laboratory applications including catalysis, organic and polymer chemistry, electrochemistry, analytical chemistry, energy, nanotechnology and biotechnology. Furthermore, physical and chemical properties of ionic liquids can be modified as per requirement by altering the combination of cation and anion. Ionic liquids designed to acquire desired applications are termed as Task Specific ionic liquids [10-17].

Metal ions extraction from aqueous solutions is one of the many applications of ILs. The extraction of metal ions from aqueous solutions using ILs not only presents environmentally benign technology but exhibits excellent extraction potential beside very good chemical and thermal stability [18-21].

A large number of articles are reported on the use of ILs as metal extracting agents [22-27]. However; many of these ionic liquids require heating for metal extraction from aqueous solutions. In addition, at least one hour is required for maximum removal of metal ions from water. In many cases IL is used in excess (in a ratio of 1:200; Metal-to-IL) [28].

In this paper, we are presenting synthesis of hydrophobic task-specific ionic liquids composed of imidazolium and thiosalicylate ions and extraction of seven transition metal ions (Cr, Mn, Fe, Co, Ni, Cu and Zn) from aqueous media using these ILs. Selection of imidazolium moieties is based on their characteristic features like lower viscosity and higher thermal stability [29], likewise choice of thiosalicylate based on chelation ability of sulfur for a number of metals.

Experimental

General

All reagents were purchased from Sigma-Aldrich and Merck and were used without further purification. Only 1,3-dibutylimidazolium bromide and 1,3-dihexylimidazolium bromide were synthesized according to the literature [34]. Deionized water is used at all stages. Technical grade solvents were used for chromatography and distilled prior to use. Thin layer chromatography was performed on M-N ALUGRAM (registered, Precoated aluminium plates, Kieselgel 60, F 254,

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0.25mm; Merck Germany) Silica gel/ UV 254 sheets, and detection of spots was made by UV light (254 nm) and/or iodine vapors.

NMR spectra were recorded at room temperature on Bruker AM instrument operating at 400 and 500 MHz. Residual solvent signals are internally referenced. Chemical shifts δ is referred in terms of ppm, coupling constants J are given in Hz. Following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad signal. Infrared spectra were recorded on a Shimadzu system and reported in cm^{-1} . Samples were prepared in thin film technique. Mass spectra were done using QSTAR® XL Hybrid LC/MS/MS System by Applied Biosystems, USA. Atomic absorption studies were carried out at Analyst 700, Atomic Absorption Spectrometer by PerkinElmer, USA.

Synthesis of 1,3-dibutylimidazolium thiosalicylate (1)

In a round bottomed flask containing 5 mmol solution of dialkylimidazolium bromide, 15 ml of 1.1 eq. sodium thiosalicylate solution in water was added. The reaction mixture was stirred for 15 minutes at room temperature. Lower green coloured layer was extracted with ethyl acetate. Ethyl acetate layer was washed with water, dried over anhydrous sodium sulfate and evaporated in vacuo. % yield 95. Green coloured gummy product. IR (KBr) v/cm^{-1} 3508, 3327, 3220, 2957, 2927, 2857, 2604, 1740, 1604, 1461, 1382, 1261, 1089, 1026, 801, 593. MS (ESI^- , m/z) 151.9 [thiosalicylate]. MS (ESI^+ , m/z) 181.1 [BBIM]. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (s, 2H, CH x 2), 6.99-6.85 (m, 4H, CH x 4), 3.87 (t, 4H, J 7.0, CH_2 x 2), 1.70 (quin, 4H; J 7.5, CH_2 x 2), 1.28 (sextet, 4H, J 7.5, CH_2 x 2), 0.89 (t, 6H; J 7.0, CH_3 x 2).

Synthesis of 1,3-dihexylimidazolium thiosalicylate (2)

2 was prepared following same procedure as in **1** taking 1,3-dihexylimidazolium as cation. % yield 96. Green coloured viscous product. IR (KBr) v/cm^{-1} 3135, 2956, 2929, 2859, 2450, 1935, 1718, 1690, 1637, 1604, 1567, 1524, 1460, 1378, 1259, 1166, 1107, 1021, 799, 760. MS (ESI^- , m/z) 151.9 [thiosalicylate]. MS (ESI^+ , m/z) 237.2 [HHIM]. ^1H NMR (400 MHz, CDCl_3) δ 10.33 (s, 1H, CH), 7.95 (d, 1H, J 2.0, 1.5, CH), 7.54 (d, 1H, J 2.0, 1.5, CH), 7.55 (m, 4H, CH x 4), 6.86 (s, 1H, CH), 4.18 (t, 4H, J 2.5, CH_2 x 2), 1.74 (q, 4H, J 10.0, CH_2 x 2), 1.16 (m, 12H; J 5.0, CH_2 x 6), 0.77 (t, 6H; J 6.5, CH_3 x 2).

Extraction and Stripping of Metals

0.16 mM ionic liquid solution was prepared in ethyl acetate (Solution A). 2.0 ml of 0.16 mM aqueous solution of transition metal (Solution B) was taken in a test tube followed by introduction of solution A. Mixture of solution was shaken well. Aqueous layer was separated. 1.0 ml of 1.0 M nitric acid was added to aqueous layer and centrifuged for 5 minutes at 5000 rpm. Solid particles were removed by filtration and aqueous filtrate collected for atomic absorption spectroscopy. Following formula has been used for percent extraction;

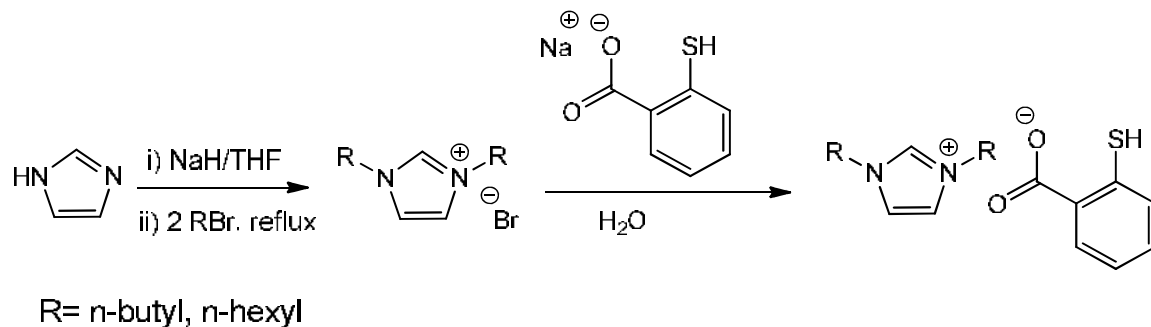
$$\text{Percent extraction (\%)} = \frac{\text{Initial conc.} - \text{Final conc.}}{\text{Initial conc.}} \times 100\%$$

TGA/DTA: To determine the decomposition/sublimation temperature, TGA/DTA was performed using TA Instrument set at heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere from room temperature to 350°C .

Results and Discussion

The present work describes synthesis of hydrophobic ionic liquids based on organic cations and anions for metal extraction from aqueous solutions. Furthermore, dialkyl imidazolium ions have been chosen as majority of 3-methyl-1-alkyl imidazolium ionic liquids are reported to have water miscibility. Since, longer side chains provide less viscous ionic liquids, therefore, butyl and hexyl groups incorporated as side chains to cation. Thiosalicylate ion opted as anion because ionic liquids with fluoride containing anions like PF_6 are poor at extracting metal cations from solvent. In addition, these anions decompose on contact with water and produce a very toxic, hazardous by-product HF [24, 25]. In addition, published literature shows that thiosalicylate based ILs enable high extraction efficiencies [24, 26].

The synthesis of ionic liquids is depicted in Scheme 1, showing preparation of cation with halide followed by replacement of halide *via* ion exchange metathesis with anion of the choice (thiosalicylate ion) [27]. For specific purpose, functionality is created at either of the ions to make it task-specific ionic liquid [28]. Thiosalicylate ion has been used as anion in ionic liquids to extract metals with ammonium, phosphonium and pyridinium based cations [24, 26]. The mode of chelation of thiosalicylate ion with different metals has been described earlier [29-30]. Furthermore, being non-halogenated, these are non-hazardous and non-toxic and have low solubility in water. These properties make them safer for human and environment.



Scheme-1: Synthesis of dialkyl imidazolium thiosalicylate ionic liquids.

Both 1,3-diethyl imidazolium thiosalicylate **(1)** [HHIM][TS] and 1,3-dibutyl imidazolium thiosalicylate **(2)** [BBIM][TS] obtained as dark green highly viscous semi solid material. Structures and purity of ionic liquids were confirmed using spectroscopic techniques including NMR experiments, FTIR analysis and electrospray ionization mass spectrometry (ESI-MS). Signals for N-butyl groups appeared demonstrating the attachment of butyl group to imidazole. The ^1H NMR displayed imidazolic hydrogens at δ 10.33 as singlet for one proton and δ 7.95 and 7.54 as two doublets or two singlets for the two protons. Sometimes the most deshielded proton disappears due to deuterated exchange [31-32]. Both ionic liquids are immiscible with water and soluble in organic solvent. Due to immiscibility with water impurities (NaBr) were removed easily.

The TGA results of [HHIM][TS] **(2)** and [BBIM][TS] **(1)** are shown in **Figure 1** which clearly indicates the difference in the thermal stability of the both systems. Before the onset of decomposition, [HHIM][TS] shows better thermal stability than [BBIM][TS]. [HHIM][TS] undergoes one stage of decomposition in which the decomposition occurs between 150 °C and 375 °C and the weight loss of the sample is up to 96 wt% in this temperature range. However, [BBIM][TS] shows three stages of decompositions in which the first, second and third stages occur in the temperature range of 100 °C to 190 °C, 195 °C to 380 °C and 382 °C to 485 °C, respectively. The weight losses of [BBIM][TS] in the first, second and third decomposition stages are 10 wt%, 75 wt% and 5 wt%, respectively. The weight loss of [BBIM][TS] in the second stage of decomposition is much more rapid than in the first or third stages of decomposition. After the decomposition, the remaining residue in [HHIM][TS] is higher than [BBIM][TS].

The evaluation of the Cr (II), Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) extraction from aqueous solutions of salts of these metal ions using ILs was carried out at room temperature (around 298 K), presented in Table-1 (*vide experimental*). Excellent extracting properties were discovered unlike previously reported literature on transition metal ions extraction efficiency of imidazolium based ion liquids [22]. The enhanced extracting efficiency can be attributed to introduction of thiosalicylate ion containing sulfur moiety, as sulfur is known to strongly interact with different transition metal ions. Another factor responsible for improved extracting efficiency is low solubility (hydrophobic character) of ILs.

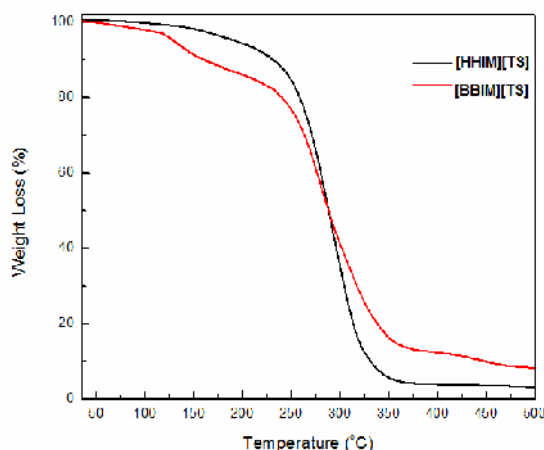


Fig. 1: TGA analysis of [HHIM][TS] and [BBIM][TS].

A graphical comparison of percentage extraction efficiency is shown in Fig. 2. Although, extracting properties of both ILs are high, it can be seen that in almost all cases percent efficiency of [HHIM][TS] is higher than [BBIM][TS]. This can be attributed to distribution coefficient of longer side chain in organic phase.

Table-1: Percent extraction efficiencies of transition metal ions from aqueous solution with [HHIM][TS] and [BBIM][TS].

Ionic Liquid	S. No.	Salt of Metal	Metal Ion	Initial Concentration (ppm)	Final Concentration (ppm)	Extraction Efficiency (%)
[BBIM][TS] (1)	1.	CrCl ₃ .6H ₂ O	Cr ³⁺	19.9500	4.5190	77
	2.	MnCl ₂ .4H ₂ O	Mn ²⁺	15.0400	3.2800	78
	3.	FeSO ₄ .7H ₂ O	Fe ²⁺	10.8700	3.2000	71
	4.	Co(OAc) ₂	Co ²⁺	0.0536	0.0123	77
	5.	NiSO ₄ .6H ₂ O	Ni ²⁺	0.0314	0.0212	32
	6.	CuSO ₄ .5H ₂ O	Cu ²⁺	15.4150	5.4460	65
	7.	Zn(OAc) ₂ .2H ₂ O	Zn ²⁺	19.3800	7.7000	60
[HHIM][TS] (2)	8.	CrCl ₃ .6H ₂ O	Cr ³⁺	19.9500	3.8590	81
	9.	MnCl ₂ .4H ₂ O	Mn ²⁺	15.0400	1.0960	93
	10.	FeSO ₄ .7H ₂ O	Fe ²⁺	10.8700	1.2300	89
	11.	Co(OAc) ₂	Co ²⁺	0.0536	0.0227	58
	12.	NiSO ₄ .6H ₂ O	Ni ²⁺	0.0314	0.0123	61
	13.	CuSO ₄ .5H ₂ O	Cu ²⁺	15.4150	0.5910	96
	14.	Zn(OAc) ₂ .2H ₂ O	Zn ²⁺	19.3800	0.1470	99

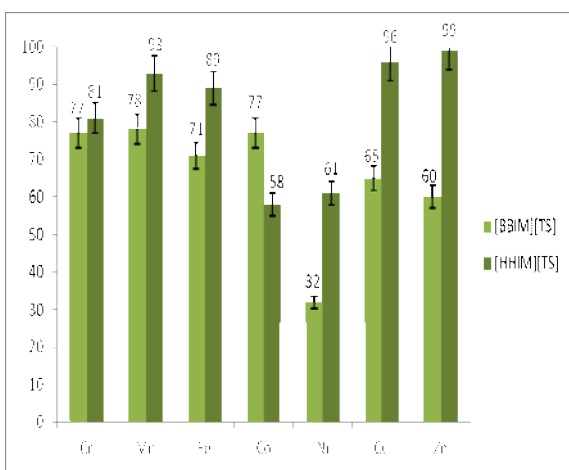


Fig. 2: Percent Extraction Efficiencies of the Metal Ions (Analysis performed in triplicate).

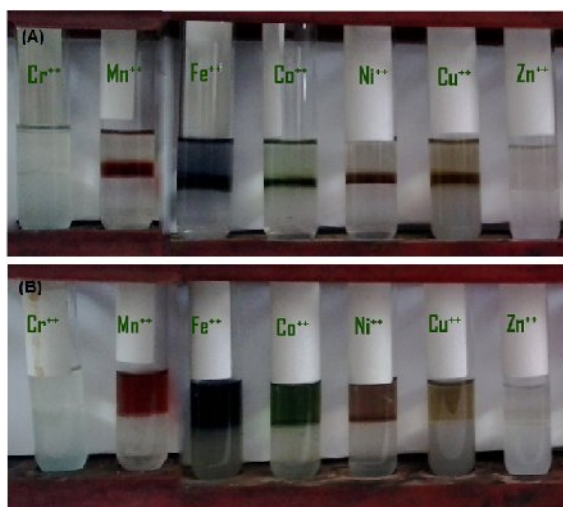


Fig. 3: (A) Ionic Liquid Solution on addition to metal ion solution; B) After shaking; upper layer Ionic liquid and lower layer aqueous.

Aqueous solution of each transition metal salt is taken in a test tube. Ionic liquid in ethyl acetate is added to each test tube. Metal ion-Ionic Liquid ratio in all cases was maintained as 1:10. On shaking, color of the organic phase changes as seen in Fig. 3. Extraction took place at room temperature unlike previous reports employing heating [33-34]. As it can be seen in Fig. 3A that extraction process starts on contact of ionic liquid solution with metal ion aqueous solution. The extraction process is completed within a minute after shaking Fig. 3B. Literatures on metal extraction using ionic liquids show that it takes several minutes.

Conclusions

Two thiosalicylate based hydrophobic ionic liquids were synthesized and characterized. The extraction of seven metal ions from aqueous solutions was investigated. The influence of length of side chain of cation on extraction efficiency was observed. Longer side chain enhanced extraction efficiency of transition metal ions from aqueous solutions especially for Zn²⁺, Cu²⁺ and Mn²⁺ (more than 90 %). Extraction carried out at room temperature and completes within a few minutes.

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