

Organoindate Room Temperature Ionic Liquid: Synthesis, Physicochemical Properties and Application

Brenno A. da Silveira Neto,^a Gunter Ebeling,^a Reinaldo S. Gonçalves,^a Fabio C. Gozzo,^b Marcos N. Eberlin,^{*b} Jairton Dupont^{*a}

^a Laboratory of Molecular Catalysis, Institute of Chemistry – UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre, 91501-970 RS Brazil
Fax +55(51)33167304; E-mail: dupont@iq.ufrgs.br

^b Thomson Mass Spectrometry Laboratory – Institute of Chemistry, State University of Campinas – UNICAMP, 13083-970 Campinas, SP Brazil

Received 29 December 2003; revised 19 February 2004

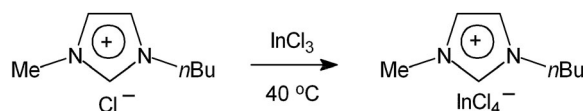
Abstract: The combination of equimolar amounts of solid 1-*n*-butyl-3-methylimidazolium chloride (BMI-Cl) with solid indium trichloride affords the new room temperature and air stable ionic liquid BMI-InCl₄ (mp -6 °C). The major physicochemical properties (density, viscosity, electrical conductivity and electrochemical window) of BMI-InCl₄ are complementary to those of classical tetrafluoroborate or hexafluorophosphate analogues. However, this liquid possesses similar Lewis acidity properties to those of organoaluminate melts and can be used as recyclable media, as demonstrated here for the tetrahydropyranlation of alcohols.

Key words: organoindate, ionic liquid, physicochemical properties, Lewis acid catalysis, tetrahydropyranlation, electrospray ionization mass spectrometry

Organoaluminate melts are among the most investigated class of so-called room temperature ionic liquids (molten salts).¹ Simple mixing of quaternary ammonium salts, especially *N*-alkylpyridinium and 1,3-dialkylimidazolium halides, with AlCl₃, leads to the facile preparation of these compounds.² For example, the combination of 1,3-dialkylimidazolium chloride with aluminum trichloride produces ionic liquids whose physicochemical properties depend mainly upon the molar fraction of the aluminum compound.³ Inasmuch organoaluminate melts have donor and acceptor patterns, the Lewis acidity can also be modulated by the relative amount of the aluminum compound and super acids may be formed by addition of Brønsted acids.⁴ These properties have been extensively explored in organic synthesis and organometallic catalysis.⁵ However, these compounds are reactive towards air and water, difficult to handle and several organic substrates and organometallic compounds are not chemically inert in these media, limiting their application as recyclable media compared with those of fluorine-containing anions such as BF₄⁻ and PF₆⁻.¹ It is therefore of great interest to develop new ionic liquids that possess similar physical-chemical properties to those of organoaluminate melts without being reactive towards air, water and organic molecules. We wish to report herein that the combination of 1-*n*-butyl-3-methylimidazolium chloride with indium trichloride affords the air sta-

ble room temperature ionic liquid BMI-InCl₄ that can be used as an alternative to organoaluminate melts.

The mixing of equimolar amounts of solid 1-*n*-butyl-3-methylimidazolium chloride⁶ with solid indium trichloride at 40 °C affords after 1.5 hours a colorless liquid (Scheme 1).⁷



Scheme 1 Syntheses of organoindate ionic liquid.

This new ionic liquid (BMI-InCl₄) was fully characterized and its main physicochemical properties are summarized in Table 1.

Table 1 Comparison of the Physicochemical Properties of Some Room Temperature Ionic Liquids

Ionic Liquid	Mp (°C)	ν_{30} ^a (mPa.s)	d_{30} ^b (g mL ⁻¹)	k_{50} ^c 10 ³ (S cm ⁻¹)	Ref.
BMI-AlCl ₄	-88	294	1.23	19.66	- ²
BMI-InCl ₄	-6	26	1.55	9.37	- ^d
BMI-BF ₄	-81 ^e	233	1.15	6.03	- ⁸
BMI-PF ₆	10	312	1.37	4.58	- ⁸

^a Viscosity at 30 °C.

^b Density at 30 °C.

^c Conductivity at 50 °C.

^d This work.

^e Transition-glass temperature.

BMI-InCl₄ is almost insoluble in light alkanes and diethyl ether and soluble in polar solvents such as dichloromethane, acetone and acetonitrile. Interestingly, benzene has a relatively high solubility in the BMI-InCl₄ ionic liquid (37 wt% at r.t.), similar to that reported for BMI-PF₆.⁹ The solubility of water in BMI-InCl₄ is around 15% wt% at room temperature.

BMI-InCl₄ melts at -6 °C, that is a temperature far higher than that reported for its organoaluminate analogue.²

SYNTHESIS 2004, No. 8, pp 1155–1158

Advanced online publication: 10.05.2004

DOI: 10.1055/s-2004-822372; Art ID: M10103SS

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We may note that the density of BMI-InCl₄ is relatively higher than that of the majority of imidazolium ionic liquids whereas its viscosity is much lower. These properties may facilitate the stirring and product separation when using BMI-InCl₄ as a recyclable reaction medium.

The IR spectra (neat) of BMI-InCl₄ shows the characteristic aromatic C–H stretching¹⁰ between 3100 and 3200 cm⁻¹ that is generally attributable to C–H---X hydrogen bonds interactions.¹¹ These values (3150 and 3116 cm⁻¹) are around 15 cm⁻¹ lower than those observed in the IR spectra of the analogous¹² BMI-PF₆ and BMI-BF₄ and 25 cm⁻¹ higher than that reported for BMI-AlCl₄.^{10a} Therefore it can be qualitatively assumed that the strength of the hydrogen bonds between the cation and the anions increases in the order: BMI·AlCl₄ < BMI·InCl₄ < BMI·BF₄ < BMI·PF₆. This order has been further corroborated by tandem mass spectrometric experiments (ESI-MS/MS).

Electrospray ionization mass spectrometry (ESI-MS) is characterized by the gentleness by which gaseous ions are formed, with allows handling of loosely bonded, supramolecular ionic species.¹³ ESI-MS of acetonitrile solutions of BMI·InCl₄ provide very simple spectra and shows as far the main ions InCl₄⁻ (negative ion mode) of *m/z* 257 (*m/z* are reported for the most abundant isotopomer) and BMI⁺ (positive ion mode) of *m/z* 139. The supramolecules [(BMI)(InCl₄)₂]⁻ of *m/z* 653 and [(BMI)₂(InCl₄)⁺ of *m/z* 535 together with InCl₂⁺ of *m/z* 185 are also detected as minor ions.

These results are in sharp contrast to those reported for other imidazolium ionic liquids such as BMI·BF₄ in that the ESI-MS in both the positive and negative ion modes is found to transfer, gently and efficiently, small to large ionic liquid supramolecules to the gas phase.^{13d} An equimolar acetonitrile solution of BMI·InCl₄, BMI·PF₆ and BMI·BF₄ was also prepared and its ESI(-)-MS spectrum acquired. The mixed-anion (A_n) supramolecules [A₁---BMI---A₂]⁻ were formed, gently transferred to the gas phase, and thus they were clearly observed in the mass spectrum.

Mass selection of the gaseous [A₁---BMI---A₂]⁻ supramolecules followed by low-energy collision-induced dissociation in ESI-MS/MS experiments allow us to determine the intrinsic solvent-free relative strengths of their hydrogen bonds. Figure 1 shows, for instance, that [BF₄---BMI---InCl₄]⁻ dissociates exclusively to InCl₄⁻ of *m/z* 257, which shows that BF₄⁻ binds much more strongly to BMI⁺ than InCl₄⁻. From the complete set of ESI-MS/MS data, the order of intrinsic hydrogen bond strength to the 1-*n*-butyl-3-methylimidazolium ion (BMI⁺) is: PF₆⁻ > BF₄⁻ > InCl₄⁻. This order is the same estimated in the condensed phase by IR spectroscopy (see above).

Also of note is that the conductivity of BMI·InCl₄ is higher than BMI·BF₄ but less than that of its tetrachloroaluminate analogue (Table 1). These data strongly suggest that the BMI·InCl₄ ionic liquid is less associated through a hydrogen bond structure than other imidazolium ionic liq-

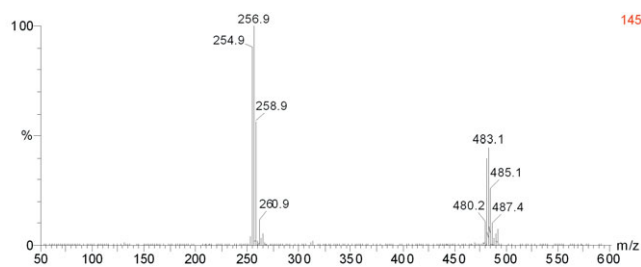


Figure 1 ESI(-)MS/MS product ion mass spectrum of [BF₄---BMI---InCl₄]⁻ of *m/z* 483. Note that InCl₄⁻ of *m/z* 257 is the exclusive fragment, which shows that BF₄⁻ binds much more strongly to BMI⁺ than InCl₄⁻.

uids containing fluorinated anions, which form polymeric supramolecular structures in the liquid phase.¹

The electrochemical windows of the organoindate ionic liquid have been determined for two working electrode materials. The voltammograms were characteristic for each electrode and are shown in Figures 2 and 3 in air and in deaerated conditions. The cathodic limit should occur at the onset reductions processes of the imidazolium ion or In(III) to In(I)¹⁵ at -0.75 V (PQRE) on vitreous carbon in aerated and deaerated ionic liquid, and at -0.5 V (PQRE) on a platinum electrode in both conditions.

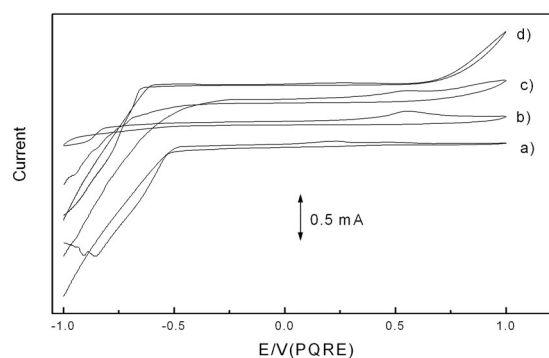


Figure 2 Cyclic voltammograms of working electrodes with 0.13 cm² of surface in aerated BMI·InCl₄: a) Pt at 1000 rpm; b) CV at 1000 rpm; c) Pt static; and d) CV static, recorded at 0.10 Vs⁻¹ and r.t.

On the other side the anodic limit is influenced by electrode rotation and oxygen concentration. On platinum electrode this value is 0.75 V (PQRE) under static condition and around 2.0 V (PQRE) at 1000 rpm in aerated and deaerated ionic liquid. Vitreous carbon electrode shows the anodic limit around 0.75 V (PQRE) in aerated and 1.0 V (PQRE) in deaerated ionic liquid.

On the other hand, the anodic limit is influenced by electrode rotation. On platinum electrode this value is 0.75 V (PQRE) under static conditions and around 2.0 V (PQRE) at 1000 rpm. This process is most probably related to the electrooxidation of adsorbed species or to the electrochemical decomposition of the ionic liquid. The same anodic limit around 0.25 V (PQRE) was obtained using vitreous carbon electrode. These anodic and cathodic lim-

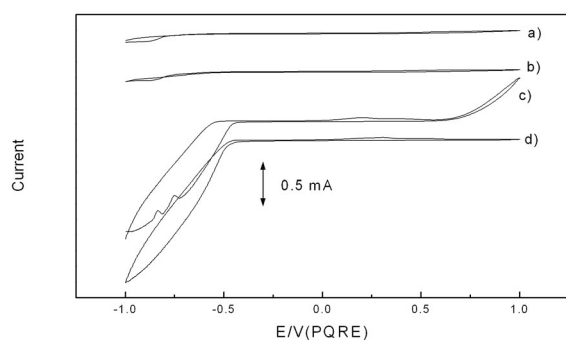


Figure 3 Cyclic voltammograms of working electrodes in deaerated BMI-InCl₄ recorded at 0.10 V s⁻¹: a) CV static; b) CV at 1000 rpm; c) Pt static; and d) Pt at 1000 rpm.

its (electrochemical windows) are inferior to those observed for BMI·BF₄, BMI·PF₆¹⁶ (up to 7V) and the tetrachloroaluminate analogue (up to 3V).¹⁷

The properties of the ionic liquid as media for organic transformations involving Lewis acid catalysis have been tested in the tetrahydropyranlation of alcohols (Scheme 2).¹⁸



Scheme 2 Tetrahydropyranlation of alcohols in BMI-InCl₄.

An equimolar mixture of 1.0 mL (10.94 mmol) of tetrahydropyran and the alcohols in 0.5 mL of BMI-InCl₄ containing 5 mol% of InCl₃ (relative to the tetrahydropyran) affords a clear solution. Stirring at room temperature for 18–24 hours yields a two-phase system (Figure 4) from which the organic phase is separated by simple decanting, weighed and analyzed by GC, ¹H and ¹³C NMR spectra. The *O*-protected alcohols were obtained in very good yields (see Table 2) and the recovered ionic liquid phase could be reused at least 4 times.

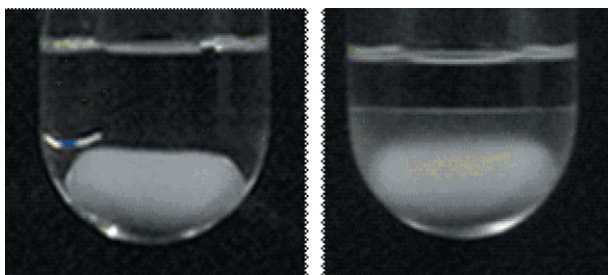


Figure 4 Pentan-1-ol protection in BMI-InCl₄ with 3,4-dihydro-2H-pyran. Before (left) and after catalysis (right).

In summary the combination of indium chloride with 1-*n*-butyl-3-methylimidazolium chloride yields a new air stable ionic liquid that is much less viscous but denser than classical imidazolium ionic liquids. In opposition to the

Table 2 BMI-InCl₄ Promoted Protection of Alcohols as THP

Entry	Alcohol	Enol Ether (equiv)	InCl ₃ (mol%)	Time (h)	Yield (%)
1	pentan-1-ol	1.0	-	72	54
2	pentan-1-ol	1.0	5	24	88
3	pentan-1-ol	1.0	5 ^a	24	89
4	pentan-1-ol	1.0	5 ^b	24	94
5	pentan-1-ol	1.0	5 ^c	24	96
6	pentan-1-ol	1.0	5 ^d	48	89
7	ethylene glycol	1.0	5	24	78 ^e
8	ethylene glycol	2.1	5	24	89
9	(±)-menthol	1.0	5	24	81

^a Recharge from entry 2.

^b Recharge from entry 3.

^c Recharge from entry 4.

^d Recharge from entry 5.

^e Mixture of mono- and diprotected in 80:20 favoring the monoprotected compound.

imidazolium ionic liquids associated with fluorinated anions that possess a quasi-molecular structure (a polymeric supramolecular structure resulting from the association of cations and anions through hydrogen bonds) the organoindate apparently displays a greater degree of ionic structure in the condensed phase. The air stable organoindate ionic liquid can be used as an alternative to organoaluminate analogues that are air and water sensitive and difficult to handle.

All reactions were carried out under argon or N₂ in oven-dried Schlenk tubes. 1-*n*-Butyl-3-methylimidazolium chloride was prepared according to known procedures.⁶ Solvents were dried with suitable drying agents and distilled under argon prior to use. All the other chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. Elemental analyses were performed by the Analytical Central Service of IQ-USP (Brazil). NMR spectra were recorded on a Varian Inova 300 spectrometer. IR spectra were performed on a Bomem B-102 spectrometer. Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70eV). Gas chromatography analyses were performed with a Hewlett-Packard-5890 Gas Chromatograph with a FID and 30-meter capillary column with a dimethylpolysiloxane stationary phase.

ESI mass and tandem mass spectra in both the negative and positive ion modes were acquired using a Micromass (Manchester – UK) QToF instrument of ESI-QqToF configuration with 7.000 mass resolving power in the TOF mass analyzer. The following typical operating conditions were used: 3kV capillary voltage, 40 V cone voltage, desolvation gas temperature of 100 °C. Tandem ESI-MS/MS spectra were collected after 5 eV collision induced dissociation (CID) of mass-selected ions with argon. Mass-selection was performed by Q1 using a unitary *m/z* window, and collisions were performed in the rf-only quadrupole collision cell, followed by mass analysis of product ions by the orthogonal-reflectron TOF analyzer.

Cyclic voltammograms were recorded with a Potentiostat Autolab PGSTAT30. RDE rotation was performed using an analytical rotator (EG & G Rotor mode 616). Working electrodes were both rotating disc electrode (RDE) either platinum or vitreous carbon with a surface area of 0.13 cm². The RDE were polished to a mirror-like surface, cleaned with pure water, degreased with acetone and dried. Reference and counter electrodes were platinum wire.

1-*n*-Butyl-3-methylimidazolium Tetrachloroindate

InCl₃ (6.64 g, 30.0 mmol) was added under argon to a Schlenk tube containing 1-*n*-butyl-3-methylimidazolium chloride (5.24 g, 30.0 mmol) and a magnetic stirring bar. The Schlenk tube was placed under reduced pressure (2–5 mm Hg) and heated with stirring at 40 °C. The mixture melted and after 1.5 h, the liquid thus formed was filtered under argon using a sintered glass Schlenk filter, furnishing a colorless liquid in nearly quantitative yield; n_D^{20} 1.5117.

IR (film): 3150 and 3116 (C–H imidazolium), 2962, 2938 and 2875 (C–H aliphatic), 1590 and 1564 cm⁻¹ (C=C).

¹H NMR (CDCl₃): δ = 8.55 (br s, 1 H, CH imidazolium), 7.41 (br s, 2 H, CH imidazolium), 4.20 (br s, 2 H, NCH₂), 3.95 (br s, 3 H, NCH₃), 1.85 (br s, 2 H, CH₂), 1.33 (br s, 2 H, CH₂), 0.88 (br s, 3 H, CH₃).

¹³C{¹H} NMR (CDCl₃): δ = 135.2, 123.9 and 122.7 (CH imidazolium), 50.1 (NCH₂), 37.1 (NCH₃), 31.9 and 19.5 (CH₂), 13.7 (CH₃).

Protection of Alcohols Using BMI-InCl₄ as Catalyst; General Procedure

In a Schlenk tube the 3,4-dihydro-2*H*-pyran (10.9 mmol) was added to a solution of BMI-InCl₄ (0.5 mL) and the corresponding alcohol (10.9 mmol), followed by the addition of InCl₃ (5 mol%). The Schlenk tube was closed and the solution stirred for 24 h at r.t. In the case of the formation of a two-phase system, simple decanting separated the organic phase. Otherwise the mixture was extracted with Et₂O and the organic layer was separated and the Et₂O evaporated affording the protected alcohol.

Acknowledgment

We thank FAPERGS, FAPESP and CNPq (Brazil) for partial financial support and C. S. Consorti for helpful suggestions.

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