

AUSTRALIAN JOURNAL OF CHEMISTRY

The cover shows how the molecular design of ionic liquids can provide very specific properties, such as melting point and solvation, as reviewed by Forsyth et al. (p. 113).

Guest Editorial

Ionic Liquids Symposium

Douglas R. MacFarlane

Aust. J. Chem. 2004, 57, 111-112.



This special issue presents a selection of papers presented at the Ionic Liquids Symposium, held in Melbourne in May 2003, selected to reflect research achievements and current challenges in the field.

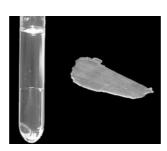
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Review

Ionic Liquids—An Overview

Stewart A. Forsyth, Jennifer M. Pringle, Douglas R. MacFarlane

Aust. J. Chem. 2004, 57, 113-119.



More than just a simple replacement for conventional organic solvents, ionic liquids (ILs) find an increasingly wide range of applications, on account of their design and selection. Some of these liquids can be hydrophobic and thus immiscible with water. Core to the design are the nature and interaction of the ionic components, as surveyed in this manuscript. The graphic shows two ILs, on the left a water-immiscible one, liquid at room temperature; on the right one that melts just about room temperature.

Rapid Communications

Ionic Liquids Based on Imidazolium and Pyrrolidinium Salts of the Tricyanomethanide Anion

Stewart A. Forsyth, Stuart R. Batten, Qing Dai, Douglas R. MacFarlane

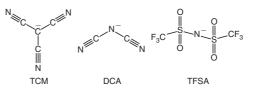
Aust. J. Chem. 2004, 57, 121-124.

Manganese Dioxide Allylic and Benzylic Oxidation Reactions in Ionic Liquids

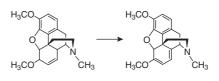
Ivan Hemeon, Neil W. Barnett, Nicholas Gathergood, Peter J. Scammells, Robert D. Singer

Aust. J. Chem. 2004, 57, 125-128.

Dicyanamide-based ionic liquids are known to afford low melting, low viscosity materials. A related anion, tricyanomethanide, was therefore used to prepare ionic liquids. The properties of these novel ionic liquids are similar, including possessing an electrochemical window, over 3 V, but usefully less hygroscopic.



The use of the ionic liquids $[bmIm][BF_4]$ and $[bmIm][PF_6]$ as reaction media for allylic and benzyllic oxidation reactions using manganese dioxide was investigated. For codiene methyl ether (shown) oxidation with MnO_4 produces a yield a few percent better than using the radical TEMPO, a reagent seven times more costly. Procedures for recycling the ionic liquids used in these oxidation reactions were also developed.

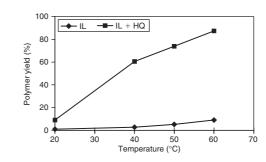


Charge Transfer Polymerization in Ionic Liquids

Ranganathan Vijayaraghavan, Douglas R. MacFarlane

Aust. J. Chem. 2004, 57, 129-133.

The reaction rate for the polymerization of methyl methacrylate may be enhanced by running the reaction in an ionic liquid. The effect of various reaction conditions including concentration of electron donor, ionic liquid (IL), temperature, and promoter (in this case hydroquinone, HQ) have been studied; the graphic shows how the promoter dramatically aids the reaction.



Indium-mediated addition of 4-bromocrotonic acid to a variety of aldehydes

and ketones provides, in a simple one-pot procedure, exclusively α -addition

100

 $\overset{O}{\underset{R}{\overset{}}}\overset{I. \text{ In } (0), \overset{Br}{\underset{2. H_2O}{\overset{}}}\overset{I. \text{ In } (0), \overset{I. \{In } (0),$

Indium-Mediated Addition of 4-Bromocrotonic Acid to Aldehydes and Ketones—A Simple, High Yielding Route to α-Allyl-β-Hydroxy Carboxylic Acids

Michael C. Bowyer, Charles M. Gordon, Sarah K. Leitch, Adam McCluskey, Craig Ritchie

Aust. J. Chem. 2004, 57, 135-137.

Design of Ionic Liquids for Electrochemical Applications

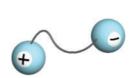
Masahiro Yoshizawa, Asako Narita, Hiroyuki Ohno

Aust. J. Chem. 2004, 57, 139-144.

Thermal Degradation of Ionic Liquids at Elevated Temperatures

Krisztian J. Baranyai, Glen B. Deacon, Douglas R. MacFarlane, Jennifer M. Pringle, Janet L. Scott

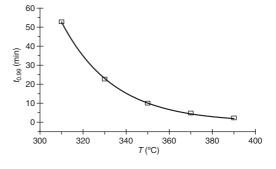
Aust. J. Chem. 2004, 57, 145-147.



products in good yield.

Zwitterionic liquids composed of a tethered cation and anion, as shown schematically, were synthesized. Their thermal properties and the ionic conductivity were investigated with reference to electrochemical applications.

Ionic liquids based on the imidazolium cation degrade on heating, yielding volatile products. The temperatures at which degradation begins to occur are significantly lower than that previously reported. A parameter $T_{z/x}$ is described to more appropriately estimate thermal stability. The graph shows the relationship of time taken to effect 1% decomposition and temperature.

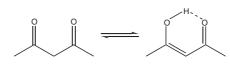


Keto-Enol Tautomerism as a Polarity Indicator in Ionic Liquids

Martyn J. Earle, Brian S. Engel, Kenneth R. Seddon

Aust. J. Chem. 2004, 57, 149-150.

Ionic liquid polarity has been previously estimated to lie between that of methanol and ethanenitrile, based on excited-state investigations with solvatochromatic dyes. Here, by employing keto–enol tautomeric equilibria (see scheme) the ground-state polarities were explored for several imidazolium-based ionic liquids, suggesting higher apparent polarities than those previously reported.

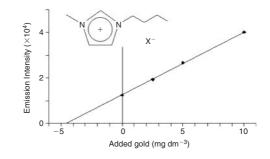


Analysis of Gold in Solutions Containing Ionic Liquids by Inductively Coupled Plasma Atomic Emission Spectrometry

Jacqueline A. Whitehead, Geoffrey A. Lawrance, Adam McCluskey

Aust. J. Chem. 2004, 57, 151–155.

For the analysis of gold in aqueous solutions by ICP-AES in the presence of high concentrations of ionic liquids (an example of the linear increase in signal with gold concentration is shown), both surface tension and viscosity influence signal intensity, and hence apparent concentration. The graph indicates the linear increase with signal with added gold with the standard addition method described herein.



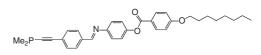
Full Papers

A Long-Chain Phosphine Designed as a Metallomesogen Generator—Synthesis and Coordination Properties

Daravong Soulivong, Dominique Matt, Jack Harrowfield, Loïc Toupet

Aust. J. Chem. 2004, 57, 157–160.

The platinum(II) complex *cis*-[PtCl₂L₂] containing the long-chain phosphine $Me_2PC \equiv C-(p-C_6H_4CHNR^{C8})$ [L; $R^{C8} = p-C_6H_4OC(O)(p-C_6H_4OC_8H_{17})$ as shown] has been obtained in three steps from 4-ethynylbenzaldehyde. The crystal structure of the intermediate $HC \equiv C-(p-C_6H_4CHNR^{C8})$ has been determined by an X-ray diffraction study and analysis of this structure provides a basis for understanding the liquid crystalline character of the intermediate and its absence in *cis*-[PtCl₂L₂].



Metal-Ion Recognition—Selective Bulk Membrane Transport of Silver(1) Using Thioether Donor Macrocycles as Ionophores, and X-Ray Structure of the Silver Complex of an S₄-Donor Ring

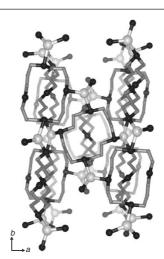
Marina Fainerman-Melnikova, Leonard F. Lindoy, Show-Yee Liou, John C. McMurtrie, Noel P. Green, Azizollah Nezhadali, Gholamhossin Rounaghi, William N. Setzer

Aust. J. Chem. 2004, 57, 161–166.

An Evaluation of Some Hindered Diamines as Chiral Modifiers of Metal-Promoted Reactions

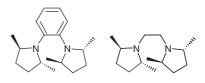
Jayamini Illesinghe, Richard Ebeling, Brett Ferguson, Jim Patel, Eva M. Campi, W. Roy Jackson, Andrea J. Robinson

Aust. J. Chem. 2004, 57, 167–176.



Competitive seven-metal bulk membranetransport experiments have been carried out using a range of thiacrown macrocycles as ionophores. Sole transport selectivity for silver(I) was demonstrated for individual systems. The X-ray structure of the silver complex of an S₄-donor ring shows *exo*coordination to the silver ion to yield a three-dimensional network.

Chiral diamines have been shown to be effective ligands in a wide range of metal-modified reactions. The authors here explore the effectiveness of the diamino compounds shown in potentially enantioselective reactions. NMR experiments showed that these ligands were too bulky to coordinate to osmium in the osmium tetraoxide dihydroxylation of stilbene.



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