# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

### 1. Tuning ionic liquids for simultaneous dilution and demulsification of water-in-bitumen emulsions at ambient temperature

By Abdelfatah, Elsayed; Chen, Yining; Berton, Paula; Rogers, Robin D.; Bryant, Steven L.

From SPE Journal (Society of Petroleum Engineers) (2020), 25(2), 759-770. DOI:10.2118/193615-pa

Thermal and flotation processes are widely used to produce bitumen from oil sand in Alberta. However, bitumen contains many surface-active components that tend to form water-in-oil (w/o) emulsion stabilized by fines and/or asphaltenes. Although several demulsifiers have been proposed in the literature to treat such emulsions, these chems. are sometimes not effective. We propose ionic liqs. (ILs) whose compn. has been designed to enable effective treatment of these emulsions. Different ILs were synthesized and tested for their efficiency in treating bitumen emulsion obtained from a field in Alberta. ILs tested are mixts. of org. bases (primary and tertiary amines) with oleic acid. Mixts. of ILs and bitumen emulsion were prepd. at several mass ratios. The two components were mixed under ambient conditions. After mixing, segregation of different components in the mixt. was accelerated by centrifugation for rapid assessment of the degree of emulsion breaking. Optical microscopy, rheol., thermal gravimetric anal., and viscosity measurements were used to assess the effect of ILs on bitumen emulsions. The first set of ILs with primary amine cations of different alkyl chain lengths (N-butylammonium oleate, N-octylammonium oleate) were able to sep. the water from the emulsion. However, these ILs tended to form gels when mixed with water. The IL prepd. from a tertiary amine with short alkyl chain length, triethylammonium oleate, also formed a gel with water. The no. and length of alkyl chains proved crit. for avoiding gel formation. ILs with tertiary amine cations of longer alkyl chain lengths (tri-N-butylammonium oleate and tri-N-octylammonium oleate) were immiscible with the sepd. water and did not gel. These ILs were very efficient in dilg. and demulsifying bitumen emulsion. The emulsion droplet sizes increased upon addn. of the IL. The IL mixes into the bitumen phase released from the emulsion, yielding a viscosity at an ambient temp. close to the pipeline specifications. This work demonstrates that ILs can be tailored to break bitumen emulsions effectively without heat input. The process developed in this paper can replace current practice for the demulsification and diln. of bitumen emulsions, which requires the emulsion to be heated significantly. Hence the IL process reduces the heat requirements and hence greenhouse gas emissions.

### 2. Synthesis of Anhydrous Acetates for the Components of Nuclear Fuel Recycling in Dialkylimidazolium Acetate Ionic Liquids

By Smetana, Volodymyr; Kelley, Steven P.; Titi, Hatem M.; Hou, Xiaomin; Tang, Si-Fu; Mudring, Anja-Verena; Rogers, Robin D.

From Inorganic Chemistry (2020), 59(1), 818-828. DOI:10.1021/acs.inorgchem.9b03077

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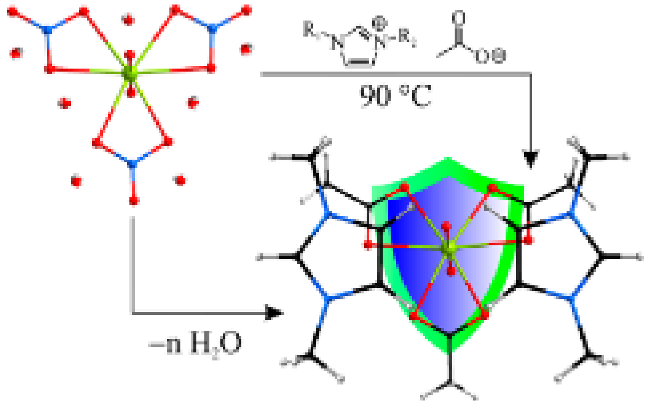
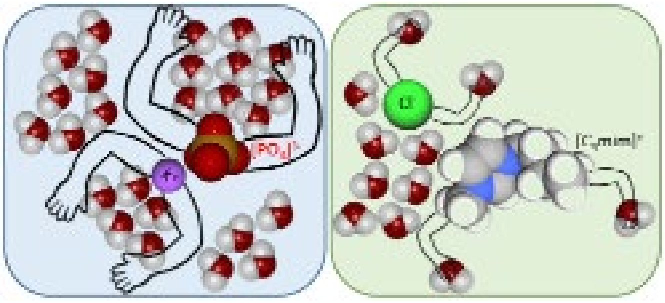


Anhyd. acetate salts with uranium {[$C_2C_1$i.m.][$UO_2(OAc)_3$] (1), [$C_2C_2$i.m.][$UO_2(OAc)_3$] (2), and [$C_4C_1$i.m.][$UO_2(OAc)_3$] (3)}, lanthanides {[$C_2C_2$i.m.]$_2$[$La(OAc)_5$] (4) and [$C_2C_1$i.m.]$_2$[$Nd(OAc)_5$] (5)}, and strontium {[$C_2C_1$i.m.]$_n$[$Sr(OAc)_3$]$_n$ (6)} ($C_2C_1$i.m. = 1-ethyl-3-methylimidazolium, $C_2C_2$i.m. = 1,3-diethylimidazolium, $C_4C_1$i.m. = 1-butyl-3-methylimidazolium, and OAc = acetate) were prepd. and structurally characterized. Both lanthanides and strontium are common components of the nuclear fuel waste, and their sepn. from uranium is an important but still challenging task. A new synthetic approach with dialkylimidazolium acetate ionic liqs. (ILs) as the solvent was developed for the direct synthesis of homoleptic acetates from the corresponding hydrates and, unexpectedly, hardly sol. f-element oxides. Although the group of characterized compds. shows perfect structural variability, all actinide and lanthanide metal ions form monomeric complex anions where the metal cation coordinates to five ligands including two oxygen atoms in the case of uranium, as is commonly obsd. for uranyl compds. Crystallog. analyses revealed that $[UO_2(OAc)_3]^-$ anions possess rather std. $D_{3h}$ symmetry featuring a hexagonal-bipyramidal coordination environment, while the lanthanide anions $[Ln(OAc)_5]^{2-}$ are fully asym. and the $Ln^{3+}$ cations are 10-coordinated as a distorted bicapped tetragonal antiprism. This is the 1st report of lanthanide ions coordinated in this fashion. For $Sr^{2+}$, 9-fold coordination through oxygen atoms as a strongly distorted tricapped trigonal prism is obsd. The crystn. of anhyd., homoleptic, anionic acetate complexes from such a large variety of different metal salts appears to be due to the properties of dialkylimidazolium acetate ILs themselves, including enhanced basicity from the high concn. of free anions and their greater affinity for hydrogen-bonding solutes relative to metal cations. The direct reaction of uranium, selected lanthanides, and strontium salt hydrates with dialkylimidazolium acetate ionic liqs. gives anhyd. metal acetates under ambient conditions. This route allows also direct dissoln. of the corresponding metal oxides and isolation of homoleptic metal complexes in the presence of various competing ligands. The crystal structure analyses reveal unique coordination of the lanthanides in analogy with the uranyl complexes and significantly distinct behavior of $Sr^{2+}$.

### 3. Water in Solutions of Chaotropic and Kosmotropic Salts: A Differential Scanning Calorimetry Investigation

By Berton, Paula; Kelley, Steven P.; Bridges, Nicholas J.; Klingshirn, Marc A.; Huddleston, Jonathan G.; Willauer, Heather D.; Baldwin, Jeffrey W.; Moody, Melanie L.; Rogers, Robin D.

From Journal of Chemical & Engineering Data (2019), 64(11), 4781-4792. DOI:10.1021/acs.jced.9b00222



The use of aq. phase sepns. via aq. biphasic systems (ABS) has been widely explored in the recent decades. For wider and more "intelligent" applications, it is important to look below the surface and study these systems thoroughly at a fundamental level. Two important questions still unsolved are how do polymers and ions of different types organize water (if they in fact they do so) and how does it affect the sepn. of phases. In the present work, differential scanning calorimetry (DSC) was used to relate ABS phase diagrams and the behavior of water in aq. solns. contg. kosmotropic salts ($K_3PO_4$ or $(NH_4)_2SO_4$), a chaotropic ionic liq. ($[C_4mim]Cl$), or a polymer (PEG-2000), all of which are reported components of ABS, and their mixts. Addnl. DSC transitions were obsd. for the two classes of salts which could be assigned based on the fundamental differences between their interactions with water, suggesting that it is the differences in the abilities of kosmotropic and chaotropic salts to interact with water which result in the phase sepn. phenomena obsd. The DSC measurements of solns. of PEG-2000 and $(NH_4)_2SO_4$ indicate that aq. solns. of PEG-2000 supercool and potentially enter a glassy state that exhibits devitrification upon heating. The devitrified state exhibits a clear eutectic with water. Mixts. of the polymer and salt continue to exhibit all the features obsd. for the pure components. These results suggest that the mixts. are phase sepd. and consist of largely sep. concd. solns. of PEG-2000 and $(NH_4)_2SO_4$, indicating an entropy-driven phase sepn. The DSC anal. of these systems further refines the understanding of kosmotropic and chaotropic solutes into more specific phenomena for each compd. This work suggests that DSC can be used to understand the role of each salt/component in ABS.

### 4. Choline-based aqueous biphasic systems: Overview of applications

By Tian, Hongzhe; Berton, Paula; Rogers, Robin D.

From Fluid Phase Equilibria (2019), 502, 112258. DOI:10.1016/j.fluid.2019.112258

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A review. Aq. biphasic systems (ABS) have attracted considerable attention for their unique applications in extn. and purifn. processes. Choline-based ionic liqs. (IL), deep eutectic solvents (DES), or buffers have been studied as replacements to traditional org. solvents because they can be designed to be non-flammable, non-volatile, of low toxicity, and biocompatible. ABS based on the use of choline IL/DES/buffers, thus offer potentially extensive benefits in extn. and sepn. technol. In this review, the development of choline-based ABS and their application to the extn. and purifn. of small org. mols., proteins, and DNA are discussed and the different types of ABS compared and evaluated. The advantages, drawbacks, and further work needed to bring this technol. to fruition are also presented.

**5. Role of separations in sustainability**
By Rogers, Robin D.
From Abstracts of Papers, 257th ACS National Meeting & Exposition, Orlando, FL, United States, Mar. 31-Apr. 4, 2019 (2019), I+EC-0001.

This address will cover a personal journey through the intersection of the worlds of green chem. and ionic liqs. with an emphasis on how the field of sepns. has been crit. to our innovations in both areas. The story starts with roots in undergraduate and graduate research projects on liq. clathrates with Jerry Atwood at The University of Alabama, it grows into research in radiochem. and sepns. with Phil Horwitz at Argonne National Lab., and it continues to pivot with the reemergence of interest in the ionic liqs. phenomenon developed in collaboration with Ken Seddon of Queen's University of Belfast. The constraining or enabling forces of Societal change intersecting with personnel motivation and new insight will provide a backdrop for the lessons learned.

**6. Ionic liquid processes for the extraction of rare earth elements from coal**
By Di Bona, Kristin R.; Hill, Caleb M.; Gurau, Gabriela; Rogers, Robin D.
From Abstracts of Papers, 257th ACS National Meeting & Exposition, Orlando, FL, United States, Mar. 31-Apr. 4, 2019 (2019), I+EC-0069.

Rare earth elements are vital to many modern technologies with applications including renewable energy (wind turbines), consumer products (smartphones), and national security (missile defense). No rare earth ore mines are in currently in operation in the US and the need to develop a domestic supply has become apparent. The recovery of these materials is challenging and costly, with current rare earth sepn. from ore requiring energy intensive, consecutive dissoln. and pptn. steps using strong acids and org. solvents. Coal and coal byproducts are inexpensive alternatives, known to contain elevated levels of rare earth elements (50-350 ppm). Wyonics has designed and demonstrated nonvolatile ionic liq. processes for the dissoln. of coal products and recovery of rare earth elements. The development of Wyonics' ionic liq.-based processes for the sepn. and extn. of these valuable materials directly from coal will be discussed, as well as the future of alternative coal-based products.

### 7. Scaling-up ionic liquid-based technologies: How much do we care about their toxicity? Prima Facie information on 1-ethyl-3-methylimidazolium acetate

By Ostadjoo, Shaghayegh; Berton, Paula; Shamshina, Julia L.; Rogers, Robin D.

From Toxicological Sciences (2018), 161(2), 249-265. DOI:10.1093/toxsci/kfx172

A review. The potential of the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([$C_2$mim][OAc]) to dissolve a variety of biopolymers such as cellulose and chitin, makes it an attractive candidate for scaled-up industrial utilization. In fact, the first steps towards its use at industrial scale have been taken. This increases the urgency to fill the knowledge gaps in its toxicity and environmental impact in order to predict and control its environmental fate. In this mini-review, we discuss the available literature surrounding this key IL. The literature (through the anal. of toxicity of the anion and the cation sep.) suggests that [$C_2$mim][OAc] is a relatively safe choice for industrial applications. However, because the IL should be considered as a compd., with unique properties arising from the interactions between the ions, comprehensive toxicity information for this particular IL is still required. To decide, prima facie, if this IL is toxic or not, evaluation of its influence on human health and ecotoxicity is needed prior to its large scale utilization. We chose in this mini-review to focus on toxicity surrounding this IL and evaluate what is known and what is not. Here with all the information in hand, we hope that the urgent need for [$C_2$mim][OAc] toxicol. assessment before it can be used in numerous technologies is highlighted. In the near future, we expect that the assessment of toxicity and environmental fate and impact can be integrated directly into any research into the industrial utilization of this IL and any others contemplated for industrial application.

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### 8. Efficient dehydration and recovery of ionic liquid after lignocellulosic processing using pervaporation

By Sun, Jian; Shi, Jian; Konda, N. V. S. N. Murthy; Campos, Dan; Liu, Dajiang; Nemser, Stuart; Shamshina, Julia; Dutta, Tanmoy; Berton, Paula; Gurau, Gabriela; et al

From Biotechnology for Biofuels (2017), 10, 154/1-154/14. DOI:10.1186/s13068-017-0842-9

Background: Biomass pretreatment using certain ionic liqs. (ILs) is very efficient, generally producing a substrate that is amenable to saccharification with fermentable sugar yields approaching theor. limits. Although promising, several challenges must be addressed before an IL pretreatment technol. can become com. viable. One of the most significant challenges is the affordable and scalable recovery and recycle of the IL itself. Pervaporation (PV) is a highly selective and scalable membrane sepn. process for quant. recovering volatile solutes or solvents directly from non-volatile solvents that could prove more versatile for IL dehydration. Results: We evaluated a com. available PV system for IL dehydration and recycling as part of an integrated IL pretreatment process using 1-ethyl-3-methylimidazolium acetate ([$C_2C_2$Im][OAc]) that has been proven to be very effective as a biomass pretreatment solvent. Sepn. factors as high as 1500 were obsd. We demonstrate that ≥99.9 wt% [$C_2C_1$Im][OAc] can be recovered from aq. soln. (≤20 wt% IL) and recycled five times. A preliminary technoeconomic anal. validated the promising role of PV in improving overall biorefinery process economics, esp. in the case where other IL recovery technologies might lead to significant losses. Conclusions: These findings establish the foundation for further development of PV as an effective method of recovering and recycling ILs using a com. viable process technol.

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### 9. Ionic Liquids in Pharmaceutical Industry

By Shamshina, Julia L.; Berton, Paula; Wang, Hui; Zhou, Xiaosi; Gurau, Gabriela; Rogers, Robin D.
Edited By:Zhang, Wei; Cue, Berkeley W
From Green Techniques for Organic Synthesis and Medicinal Chemistry (2nd Edition) (2018), 539-577.
DOI:10.1002/9781119288152.ch20

This chapter reviews the roles of ionic liqs. (ILs) in pharmaceutical manufg. processes, including the use of ILs as solvents in the synthesis of drugs or isolation of drug intermediates, the use of ILs in pharmaceutical crystn., in pharmaceutical sepn., for the extn. of drugs from natural products, to deliver drugs, to detect drugs, and even as active pharmaceutical ingredients (APIs). ILs have also been considered as alternatives to org. solvents in the pharmaceutical industry. A large vol. of volatile org. solvents (VOCs) is used in the process of drug extn. from natural products, resulting in serious environmental problems and replacement of conventional solvents by ILs might prevent the emission of VOCs. While ILs have been shown to be efficient vehicles in transdermal drug delivery, until recently they were not studied as transdermal drugs themselves because ionized salts normally diffuse poorly through lipid membranes.

### 10. Deconstruction of oil sand materials using ionic liquids

By Bryant, Steven; Stephenson, Tyler; Rogers, Robin D.; Berton, Paula
From PCT Int. Appl. (2018), WO 2018141067 A1 20180809,

In alternative aspects, the invention provides process for the use of ionic liqs. in the remediation and amelioration of oil sand materials, including treatment of tailings products including but not limited to mature fine tailings (MFT), sepn. of bitumen from oil sand, bitumen transportation, remediation of spilled bitumen and dilbit, treatment (breakage) of steam assisted gravity drainage (SAGD) and heavy oil emulsions, solids removal from oil processing streams, in-situ bitumen recovery, in-situ extn. from mineral reservoirs, prodn. well chems., $CO_2$ sequestration and fracking fluids.

### 11. Coagulation of chitin from ionic liquid solutions using kosmotropic salts

By Rogers, Robin D.; Galpothdeniya, Waduge Indika S.; Shamshina, Julia L.; Zavgorodnya, Oleksandra
From U.S. Pat. Appl. Publ. (2018), US 20180194864 A1 20180712,

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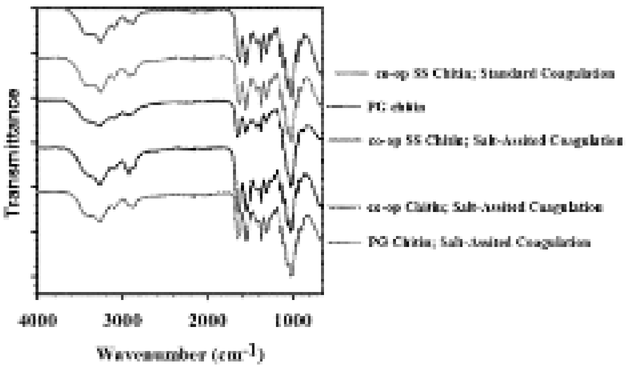

The invention relates to a A method for sepg. chitin from a chitinous biomass, comprising: contacting the mixt. with an aq. soln. of a kosmotropic salt, thereby coagulating the chitin, and forming a biphasic system comprising an ionic liq.-chitin phase, and an aq. kosmotropic salt phase; sepg. the ionic liq.-chitin phase from the aq. kosmotropic salt phase; and collecting the chitin from the sepd. ionic liq.-chitin phase, thereby forming a recycled ionic liq.

### 12. Chitin for the replacement of fluoropolymers in the assembly of electrochemical devices

By King, Catherine; Easton, Max E.; Rogers, Robin D.

From ChemRxiv (2018), 1-10.

Chitin and graphene/chitin composite films were prepd. using ionic liq. processing and tested as separators and electrodes, resp., in a supercapacitor to demonstrate the construction and function of an energy storage device which is constructed solely from bio-based polymer materials. The dry films possessed high thermal (Td = 265 and 246°) and mech. (tensile strength = 5(1) and 1.7(2) MPa) stabilities. Once soaked in an aq. electrolyte (2 M (NH4)$_2$SO$_4$) for use in a supercapacitor test cell, the device reached a peak capacitance value of 2.4 F/g. This work demonstrates a first step towards a scalable method for the prepn. and assembly of biorenewable electrochem. devices, which avoid the use of unsustainable fluoropolymers and solvents, and is poised to be an important part of environmentally-sustainable economies.

### 13. Odd-even effect on the formation of aqueous biphasic systems formed by 1-alkyl-3-methylimidazolium chloride ionic liquids and salts

By Belchior, Diana C. V.; Sintra, Tania E.; Carvalho, Pedro J.; Soromenho, Mario R. C.; Esperanca, Jose M. S. S.; Ventura, Sonia P. M.; Rogers, Robin D.; Coutinho, Joao A. P.; Freire, Mara G.

From Journal of Chemical Physics (2018), 148(19), 193842/1-193842/7. DOI:10.1063/1.5012020

This work provides a comprehensive evaluation of the effect of the cation alkyl side chain length of the 1-alkyl-3-methylimidazolium chloride series ([C$_n$C$_1$i.m.]Cl, n = 2-14) of ionic liqs. (ILs) on their capability to form aq. biphasic systems (ABSs) with salts and self-aggregation derived properties. The liq.-liq. phase behavior of ternary systems composed of [C$_n$C$_1$i.m.]Cl, water, and K$_3$PO$_4$ or K$_2$CO$_3$ and the resp. Setschenow salting-out coeffs. (k$_s$), a quant. measure of the two-phase formation ability, were detd. An odd-even effect in the k$_s$ values along the no. of methylene groups of the longest IL cation alkyl side chain was identified for the ABS formed by $K_2CO_3$, a weaker salting-out agent where the phenomenon is clearly identified. In general, cations with even alkyl side chains, being likely to display higher molar volumes, are more easily salted-out and thus more prone to undergo phase sepn. The odd-even effect in the $k_s$ values is, however, more significant in ILs up to n = 6, where the nanostructuration/nanosegregation of ILs plays a less relevant role. Still, with the $[C_nC_1i.m.]Cl$ (n = 7-14) series of ILs, an odd-even effect was also identified in the ILs' ionization degree, molar cond., and cond. at infinite diln. In summary, it is shown here that the ILs' odd-even effect occurs in IL aq. solns. and not just in neat ILs, an already well-established phenomenon occurring in a series of ILs' properties described as a result of the orientation of the terminal Me groups to the imidazolium ring cation and consequent effect in the ILs' cohesive energy. (c) 2018 American Institute of Physics.

### 14. A Triple Salting-Out Effect is Required for the Formation of Ionic-Liquid-Based Aqueous Multiphase Systems

By Passos, Helena; Costa, Sara H.; Fernandes, Ana M.; Freire, Mara G.; Rogers, Robin D.; Coutinho, Joao A. P.
From Angewandte Chemie, International Edition (2017), 56(47), 15058-15062. DOI:10.1002/anie.201705704

Novel aq. multiphase systems (MuPSs) formed by quaternary mixts. composed of cholinium-based ionic liqs. (ILs), polymers, inorg. salts, and water are reported herein. The influence of several ILs, polymers, and salts was studied, demonstrating that a triple salting-out is a required phenomenon to prep. MuPSs. The resp. phase diagrams and "tie-surfaces" were detd., followed by the evaluation of the effect of temp. Finally, the remarkable ability of IL-based MuPSs to selectively sep. mixts. of textile dyes is shown.

### 15. Separate mechanisms of ion oligomerization tune the physicochemical properties of n-butylammonium acetate: cation-base clusters vs. anion-acid dimers

By Berton, Paula; Kelley, Steven P.; Wang, Hui; Myerson, Allan S.; Rogers, Robin D.
From Physical Chemistry Chemical Physics (2017), 19(37), 25544-25554. DOI:10.1039/C7CP04078D

We investigated the ability of the ions comprising protic ionic liqs. to strongly interact with their neutral acid and base forms through the characterization of n-butylammonium acetate ($[C_4NH_3][OAc]$) in the presence of excess n-butylamine ($C_4NH_2$) or excess acetic acid (HOAc). The conjugate and parent acid or base form new nonstoichiometric, noncovalently bound species (i.e., oligomeric ions) which change the phys. and chem. properties of the resulting liqs., thus offering tunability. The effects of adding $C_4NH_2$ or HOAc to $[C_4NH_3][OAc]$ on the resulting thermal and spectroscopic properties differ and suggest that $C_4NH_2$ interacts primarily with $[C_4NH_3]^+$ to form 3-dimensional polymeric networks likely similar to those in $H_2O/[H_3O]^+$, while HOAc interacts primarily with $[OAc]^-$ to form oligomeric ions (e.g., $[H(OAc)_2]^-$). The densities of the systems increased with the increase of acid content and reached a max. when the acid molar fraction was 0.90, but decreased with increasing amine concn. The viscosities decreased significantly with increasing acid or base concn. The solvent properties of the mixts. were assessed by measuring the solubilities of benzene, Et acetate, di-Et ether, heptane, ibuprofen free acid, and lidocaine free base. The solubilities of the org. solutes and active pharmaceutical ingredients can be tuned with the concn. of acid or amine in the mixts.

In addn., crystn. of the active pharmaceutical ingredients can be induced with the modification of the compn. of the mixts. These observations support the usage of these mixts. for the synthesis and purifn. of acid or basic active pharmaceutical ingredients in the pharmaceutical industry.

**16. Switchable (pH-driven) aqueous biphasic systems formed by ionic liquids as integrated production-separation platforms**

By Ferreira, Ana M.; Claudio, Ana Filipa M.; Valega, Monica; Domingues, Fernando M. J.; Silvestre, Armando J. D.; Rogers, Robin D.; Coutinho, Joao A. P.; Freire, Mara G.

From Green Chemistry (2017), 19(12), 2768-2773. DOI:10.1039/C7GC00157F

The ability to induce reversible transitions between homogeneous solns. and biphasic systems is of paramount relevance in sepn. processes. In this context, pH-triggered aq. biphasic systems composed of ionic liqs. and salts are here disclosed as switchable mono/biphasic systems, and their potential application is further demonstrated through an integrated approach comprising both the prodn. and sepn. of hydroxymethylfurfural from fructose.

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**17. Temperature dependency of aqueous biphasic systems: an alternative approach for exploring the differences between Coulombic-dominated salts and ionic liquids**

By e Silva, Francisca A.; Pereira, Jorge F. B.; Kurnia, Kiki A.; Ventura, Sonia P. M.; Silva, Artur M. S.; Rogers, Robin D.; Coutinho, Joao A. P.; Freire, Mara G.

From Chemical Communications (Cambridge, United Kingdom) (2017), 53(53), 7298-7301. DOI:10.1039/C7CC02294H

Herein we propose an alternative way to distinguish ionic liqs. from Coulombic-dominated salts, based not on their upper limit melting temp. (100 °C), but on the trend of their phase-forming abilities to create aq. biphasic systems as a function of temp., in which a wider plethora of interactions can be appraised.

**18. A critical assessment of the mechanisms governing the formation of aqueous biphasic systems composed of protic ionic liquids and polyethylene glycol**

By Claudio, Ana Filipa M.; Pereira, Jorge F. B.; McCrary, Parker D.; Freire, Mara G.; Coutinho, Joao A. P.; Rogers, Robin D.

From Physical Chemistry Chemical Physics (2016), 18(43), 30009-30019. DOI:10.1039/C6CP06289J

An extensive study on the formation of aq. biphasic systems (ABS) using aq. solns. of protic ionic liqs. (PILs) and polyethylene glycol (PEG) was performed to understand the mechanisms underlying the phase sepn. Aq. solns. of PEG polymers with different mol. wts. (600, 1000, 2000, and 3400 g mol$^{-1}$) and several N-alkyl-, dialkyl-, and trialkyl-ammonium salts of acetate, propanoate, butanoate, hexanoate and octanoate were prepd. and their ability to form ABS at several temps. assessed. The ternary liq.-liq. phase diagrams were detd. at several temps., as well as binary PIL (or salt)-PEG-1000 and salt-water soly. data to better clarify the mechanisms responsible for the phase sepn. All data gathered indicate that the formation of PEG-PIL-based ABS is mainly governed by the PIL-PEG mutual interactions, where PILs with a higher soly. in the polymer exhibit a lower aptitude to form ABS displaying thus a smaller biphasic region, for which a direct correlation was identified. The effects of the mol. wt. and temp. of the polymer were also addressed. The increase of the PEG hydrophobicity or mol. wt. favors the phase sepn., whereas the effect of temp. was more complex and dependent on the nature of the PIL, with an increase or decrease of the biphasic regime with an increase in temp.

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### 19. Double salt ionic liquids of herbicides

By Rogers, Robin Don; Cojocaru, Oana Andreea; Gurau, Gabriela; Shamshina, Julia; Pernak, Juliusz
From PCT Int. Appl. (2016), WO 2016077290 A1 20160519,

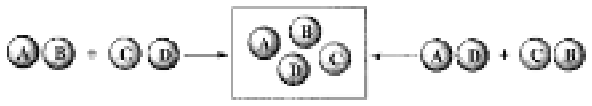


FIGURE 1

Disclosed are compns. and methods of prepg. compns. of active herbicidal ingredients comprising two or more active herbicidal ingredients. Also disclosed are methods of using the compns. described herein to reduce herbicide resistance and minimize off-target movement. The present disclosure relates to compns. of herbicidal ionic liqs. comprising one or more active herbicide ingredients and methods of making and using such ionic liqs. In some aspects, the herbicidal ionic liqs. with multiple active herbicide ingredients can be prepd. as sep. ionic liqs., each with a single active, and later combined.

### 20. Imidazole-2-thiones as liquid sorbents of Hg(0): Thermal behavior, redox chemistry, and loading on solid supports

By Kelley, Steven P.; Rachiero, Giovanni P.; Wang, Jianying; Rogers, Robin D.
From Abstracts of Papers, 251st ACS National Meeting & Exposition, San Diego, CA, United States, March 13-17, 2016 (2016), ENVR-93.

Application of ionic liqs. (ILs) to the extn. of metal ions in aq. media represents an effective methodol. ILs enter the aq. phase to maintain charge balance and enable the extn. of metal ions or charged metal-extractant complexes. However, a general limitation is the transfer of the cations and anions into the aq. phase with the main effects of generating pollutants and loss of the IL. We found that a valid soln. to these issues relies in the development of tailored sulfur-contg. ILs, inspired by the applications proposed for extn. and sepn. of soft metals involving sulfur-contg. extractants. Our interest in sepn. and extn. of heavy metals led us to investigate the ability of specific imidazole-2-thiones in the extn. of $Hg^{2+}$ from aq. media. Imidazole-2-thiones can be derived from dialkylimidazolium ILs and have partially zwitterionic character, placing them in between ILs and neutral mols. in terms of ionicity. However, 1,3-dialkylimidazole-2-thiones have other interesting properties including redox activity and low m.ps. which could make them useful as supported liq. phases for removing Hg(0) vapor from flue gas streams. These mols. may supply sulfur atoms for Hg oxidn. and coordination in a liq. state, thereby overcoming the limitations of solid sorbents such as elemental sulfur. We present our group's recent investigations into two thiones, 1,3-diethylimidazole-2-thione ($C_2C_2$ImT) and 1-ethyl-3-methylimidazole-2-thione ($C_2C_1$ImT), as components of a supported liq. sorbent for Hg(0). Both compds. can be synthesized by simply reacting their resp. imidazolium acetates with elemental sulfur and can be purified through crystn. Their crystal structures, aq. solubilities, m.ps., and mixts. are discussed and compared. Structurally characterized products of thione reactions are shown and discussed in the context of Hg oxidn. The loading of thiones onto silica and its effect on thermal properties such as m.p. and volatility are also investigated.

### 21. Chemical pulping of chitinous biomass for chitin and treatment of biomass composition

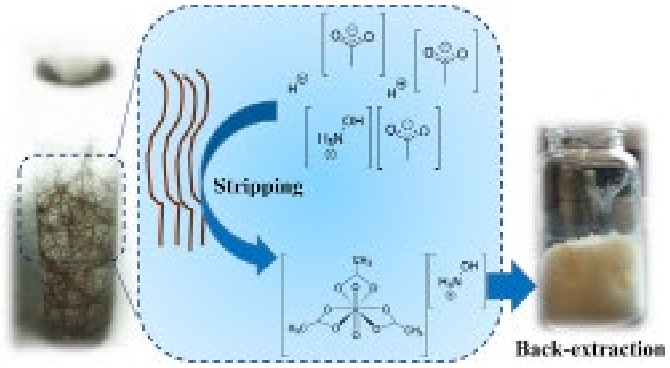
By Barber, Patrick S.; Griggs, Chris S.; Rogers, Robin D.; Gurau, Gabriela; Shamshina, Julia L.
From U.S. Pat. Appl. Publ. (2016), US 20160060363 A1 20160303,

Methods of sepg. chitin from a chitinous biomass that contains chitin and nonchitin material by a chem. pulping process that uses a protic ionic liq. or a compn. comprising acid and base precursor mols. are described. Also methods for purifying chem. pulped chitin resulting in a pure chitin material with a high mol. wt. and a higher degree of acetylation, compared to traditional pulping and ionic liq. extn. based methods are described.

### 22. Stripping Uranium from Seawater-Loaded Sorbents with the Ionic Liquid Hydroxylammonium Acetate in Acetic Acid for Efficient Reuse

By Berton, Paula; Kelley, Steven P.; Rogers, Robin D.
From Industrial & Engineering Chemistry Research (2016), 55(15), 4321-4327. DOI:10.1021/acs.iecr.5b03996

# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids



A new stripping and recovery process was developed to harvest the uranium recovered from seawater with amidoxime-functionalized polyethylene fiber sorbents and allow reuse of the sorbent without loss of capacity and without the need to recondition the sorbent before reuse. Hydroxylammonium acetate ($[NH_3OH][OAc]$)/aq. acetic acid (AcOH) solns. were used as weakly acidic stripping agents and the stripped uranium as a sol. acetate was further immobilized on shrimp shells. These solns. also stripped the vanadium and other metal ions coadsorbed, which reduce capacity through competition with uranium for sorbent binding and can resist stripping even by strong acids. $[NH_3OH][OAc]$/AcOH was found to allow recovery of ≤85% of the uranium although at a substantially longer time than the current 0.5 M HCl-stripping solns., (≤12 h vs 48-72 h, resp.); however, the use of HCl severely compromises the capacity of the sorbent in subsequent reuse (a 50% lost was obsd. on the third reuse of the fiber). Both $[NH_3OH][OAc]$ and the acetic acid were necessary to achieve high uranium recovery without sacrificing the sorbent's capacity on reuse. The ability to reuse the sorbent without pretreatment and with minimal capacity loss could be an important step toward making the extn. of uranium from seawater energy-efficient and economically viable.

### 23. Dual functional chitin based sorbents for coextraction of aqueous copper and uranium

By Kelley, Steven P.; Shamshina, Julia L.; Gurau, Gabriela; Rogers, Robin D.

From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-48.

Chitin-based sorbents have been developed by our group as biodegradable extractants for harvesting uranium from seawater. However, for these materials to be usable, a balance must be obtained between their shorter lifetime in the marine environment and the performance needs for their application. We are investigating the use coextn. of biocidal copper(II) ions naturally present in seawater along with uranium as one possible route to slowing down the biodegrdn. of the sorbent. Native chitin (poly(N-acetylglucosamine)) can be extd. from biomass by dissoln. in ionic liqs. such as 1-ethyl-3-methylimidazolium acetate and formed into usable materials such as fibers and films. Once pptd. from the IL, these materials are insol. in most other solvents and can be exposed to solns. of reactive chems. to selectively functionalize only the exposed surface mols. Deacetylation of chitin by sodium hydroxide gives glucosamine, which has a basic amino group which should show high affinity for early transition metals such as copper. The amino group can also be used as a nucleophile to tether a uranium selective functional group, such as amidoxime, to the chitin backbone. The functional groups can be segregated by joining two sep. functionalized resins or dispersed randomly amongst each other by varying the exposure time of the deacetylated chitin to further treatment.

Here we present the prepn. and characterization of these materials, soln. studies on their affinity for copper(II) and uranyl ions, and the characterization of metals bound to the sorbent surface.

### 24. Double salt ionic liquids with unique chemical environments for separations

By Rogers, Robin D.; Wang, Hui; Kelley, Steven P.

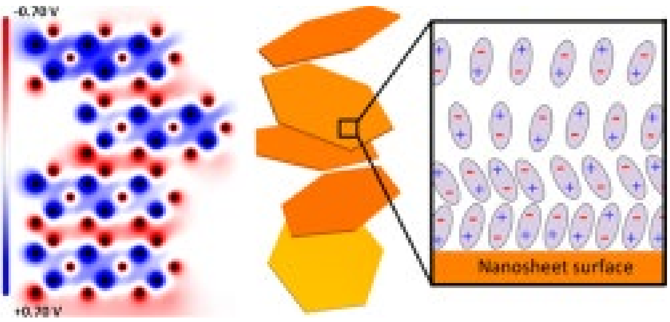
From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-1.

The field of ionic liqs. (ILs) is dominated by binary salts, which are valued for being tunable by changing the ions. However, the tunability of ILs can be further enhanced by combining two ILs or dissolving a solid salt in an IL to give a homogeneous ionic fluid with three or more ions. We have adopted the term Double Salt Ionic Liq. (DSIL) to describe these systems, which are molten analogs of cryst. double salts (salts with three or more ions in a single crystal lattice). While combining molten ILs tends to resemble ideal mixing in some ways, ILs also have a microstructure not commonly found in mol. compds. which would be expected to change upon combination with another ionic compd. Here we present a study of the phys. and spectroscopic properties of DSILs composed of 1-ethyl-3-methylimidazolium ([C$_2$mim]$^+$) cation and two anions, the hydrophilic acetate ([OAc]$^-$) and the hydrophobic bis(trifluoromethane)sulfonimide ([NTf$_2$]$^-$). The high basicity of [OAc]$^-$ allows it to draw [C$_2$mim]$^+$ cations away from the [NTf$_2$]$^-$ anions, creating ionic clusters which are not possible in either of the parent ILs. The soly. of solvent mols. (Et acetate and water) and active pharmaceutical ingredients with different acidities (ibuprofen and diphenhydramine) were found to be finely tunable by varying the ratio of [OAc]$^-$ to [C$_2$mim]$^+$. This study points the possibility that DSILs can provide systems with tunable and unique solubilities which might find use in many new sepn. processes.

### 25. Mechanism of Bismuth Telluride Exfoliation in an Ionic Liquid Solvent

By Ludwig, Thomas; Guo, Lingling; McCrary, Parker; Zhang, Zhongtao; Gordon, Haley; Quan, Haiyu; Stanton, Michael; Frazier, Rachel M.; Rogers, Robin D.; Wang, Hung-Ta; et al

From Langmuir (2015), 31(12), 3644-3652. DOI:10.1021/acs.langmuir.5b00239



Ionic liq. (IL) 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) has been used to exfoliate Bi$_2$Te$_3$ nanoplatelets. In both expts. and in mol. dynamics (MD) simulations, the Bi$_2$Te$_3$ nanoplatelets yielded a stable dispersion of 2D nanosheets in the IL solvent, and the MD simulations provided mol.-level insight into the kinetics and thermodn. of the exfoliation process. An anal. of the dynamics of Bi$_2$Te$_3$ during exfoliation indicates that the relative translation (sliding apart) of adjacent layers caused by IL-induced forces played an important role in the process.

An evaluation of the MD trajectories and electrostatic interactions indicates that the $[C_4mim]^+$ cation was primarily responsible for initiating $Bi_2Te_3$ layer sliding and sepn., while the $Cl^-$ anion is less active.

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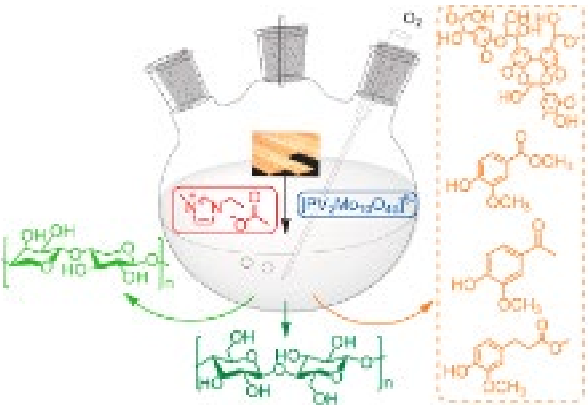
### 26. Pharmaceutically active supported ionic liquids

By Cojocaru, O. Andreea; Siriwardana, Amal; Gurau, Gabriela; Rogers, Robin D.
Edited By:Fehrmann, Rasmus; Riisager, Anders; Haumann, Marco
From Supported Ionic Liquids (2014), 387-405.

A review. This article describes the application of ionic liqs. as solvents in synthesis as well as in crystn. and sepn. of the active pharmaceutical ingredients. The liq. property o f the API-ILs seems to be one soln. to overcome the disadvantages of lim ited soly., low bioavailability, variable polymorphs, and limited membrane transport, but in the same time may also present challenges related to their prepn., handling, and the need for special devices for delivery.

### 27. Oxygen Enhances Polyoxometalate-based Catalytic Dissolution and Delignification of Woody Biomass in Ionic Liquids

By Cheng, Fangchao; Wang, Hui; Rogers, Robin D.
From ACS Sustainable Chemistry & Engineering (2014), 2(12), 2859-2865. DOI:10.1021/sc500614m



Complete dissoln. and over 90% delignification of Southern yellow pine (<0.125 mm) can be achieved in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$) at 110 °C for 6 h by the catalytic action of polyoxometalate in the presence of an appropriate $O_2$ feed. Cellulose-rich materials (CRMs), or pulps, and hemicellulose with a limited lignin content and free lignin were subsequently recovered by adding antisolvents to the IL soln., followed by filtration. Comparison of wood processing in $[C_2mim][OAc]$/POM with or without $O_2$ revealed that the presence of oxygen can greatly facilitate the dissoln., delignification, sepn. of hemicellulose, and oxidn. of lignin. The main products from lignin oxidn. were extd. from the IL using benzene and then THF, and were shown by gas chromatog.-mass spectrometry (GC-MS) to be Me vanillate, acetovanillone, vanillic acid, Me 3-(3-methoxy-4-hydroxyphenyl) propionate, and Me

4-hydroxybenzoate. This study suggests that treating wood with a $[C_2mim][OAc]/POM/O_2$ system could be a viable strategy to sep. wood components with high efficiency and obtain cellulose with high purity for materials or biorefinery applications, particularly those that desire smaller lignin oxidn. fragments for further processing.

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**28. Facile pulping of lignocellulosic biomass using choline acetate**

By Cheng, Fangchao; Wang, Hui; Chatel, Gregory; Gurau, Gabriela; Rogers, Robin D.

From Bioresource Technology (2014), 164, 394-401. DOI:10.1016/j.biortech.2014.05.016

Treating ground bagasse or Southern yellow pine in the biodegradable ionic liq. (IL), choline acetate ([Cho][OAc]), at 100 °C for 24 h led to dissoln. of hemicellulose and lignin, while leaving the cellulose pulp undissolved, with a 54.3% (bagasse) or 34.3% (pine) redn. in lignin content. The IL soln. of the dissolved biopolymers can be sepd. from the undissolved particles either by addn. of water (20 wt% of IL) followed by filtration or by centrifugation. Hemicellulose (19.0 wt% of original bagasse, 10.2 wt% of original pine, contg. 14-18 wt% lignin) and lignin (5.0 wt% of original bagasse, 6.0 wt% of original pine) could be subsequently pptd. The pulp obtained from [Cho][OAc] treatment can be rapidly dissolved in 1-ethyl-3-methylimidazolium acetate (e.g., 17 h for raw bagasse vs. 7 h for pulp), and pptd. as cellulose-rich material (CRM) with a lower lignin content (e.g., 23.6% for raw bagasse vs. 10.6% for CRM).

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**29. Molecular interactions in aqueous biphasic systems composed of polyethylene glycol and crystalline vs. liquid cholinium-based salts**

By Pereira, Jorge F. B.; Kurnia, Kiki A.; Cojocaru, O. Andreea; Gurau, Gabriela; Rebelo, Luis Paulo N.; Rogers, Robin D.; Freire, Mara G.; Coutinho, Joao A. P.

From Physical Chemistry Chemical Physics (2014), 16(12), 5723-5731. DOI:10.1039/c3cp54907k

The relative ability of cholinium-($[Ch]^+$)-based salts, including ionic liqs. (ILs), to form biocompatible aq. biphasic systems (ABS) with polyethylene glycols (PEGs) was deeply scrutinized in this work. Aq. solns. of low mol. wt. PEG polymers (400, 600, and 1000 g $mol^{-1}$) and $[Ch]^+$ salts of chloride, acetate, bicarbonate, glycolate, lactate, dihydrogenphosphate, dihydrogencitrate, and bitartrate can undergo liq.-liq. demixing at certain concns. of the phase-forming components and at several temps. Cholinium butanoate and propanoate were also studied; however, these long alkyl side chain ILs are not able to promote an immiscibility region with PEG aq. solns. The ternary liq.-liq. phase diagrams, binary water activities, PEG-salt and salt-$H_2O$ soly. data, and binary and ternary excess enthalpies estd. by COSMO-RS (COnductor-like Screening MOdel for Realistic Solvation) were used to obtain new insights into the mol.-level mechanisms responsible for phase sepn. Instead of the expected and commonly reported salting-out phenomenon induced by the $[Ch]^+$ salts over the polymer, the formation of PEG-$[Ch]^+$ salt ABS was revealed to be an end result of a more intricate mol. scenario. The multifaceted approach employed here reveals that the ability to promote an ABS is quite different for the higher melting salts vs. the lower melting or liq. ILs. In the latter systems, the ABS formation seems to be controlled by the interplay of the relative strengths of the ion-ion, ion-water, ion-PEG, and water-PEG interactions, with a significant contribution from specific hydrogen-bonding between the IL anion and the PEG hydroxyl groups.

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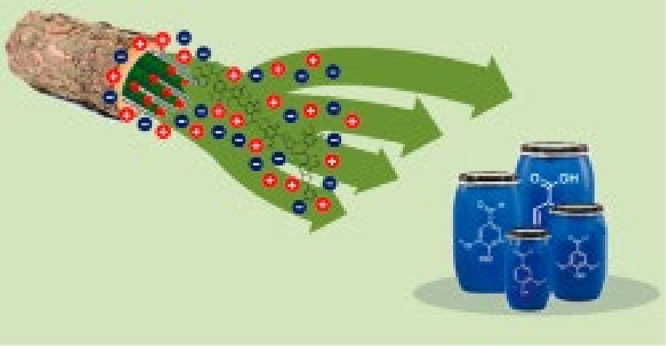
### 30. Review: Oxidation of Lignin Using Ionic Liquids-An Innovative Strategy To Produce Renewable Chemicals

By Chatel, Gregory; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2014), 2(3), 322-339. DOI:10.1021/sc4004086



A review. Lignin, one of the three subcomponents of lignocellulosic biomass (along with cellulose and hemicellulose), represents more than 20% of the total mass of the Earth's biosphere. However, essentially due to its complex structure, this renewable polymer derived from biomass is mainly burned as a source of energy in the pulp and paper industry. Today, the valorization of lignin into the prodn. of chem. feedstocks represents a real challenge in terms of both sustainability and environmental protection. This review first briefly outlines the main points of this challenge and compares the different methods investigated by chemists over the past several decades, pointing out the major difficulties met. Next, the review highlights the recent use of ionic liqs. (ILs) as solvents that have provided some new opportunities to efficiently convert lignin and lignin model compds. into value-added arom. chems. Particular focus is given to these new strategies in terms of selectivity, sepn. and the unique compds. obtained for the oxidn. of lignin using ILs. Finally, an assessment of the challenges that must be resolved in order for ILs to become an eco-friendly way of producing chems. from biomass, including lignin, is proposed.

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### 31. Hydrophobic vs. hydrophilic ionic liquid separations strategies in support of continuous pharmaceutical manufacturing

By Wang, Hui; Gurau, Gabriela; Kelley, Steven P.; Myerson, Allan S.; Rogers, Robin D.

From RSC Advances (2013), 3(25), 10019-10026. DOI:10.1039/c3ra41082j

Taking advantage of the dramatically different solvent properties of hydrophilic ionic liqs. (ILs) when dry vs. when wet allows unique sepns. strategies compared to the use of hydrophobic ionic liqs. This is demonstrated here by comparing the sepn. of a water insol. amide intermediate for aliskiren from its reactants, a water insol. lactone, water sol. 3-amino-2,2-dimethylpropanamide, and the water sol. promoter 2-ethylhexanoic acid, using the hydrophobic ionic liq. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$mim][NTf$_2$]) and the hydrophilic ionic liq. 1-ethyl-3-methylimidazolium acetate ([C$_2$mim][OAc]). Both the water sol. [C$_2$mim][OAc], when dry, and water insol. [C$_2$mim][NTf$_2$] can dissolve the highly hydrophobic and hydrophilic compds. simultaneously, but the two ILs require different strategies to sep. the mixts. of these compds. Using the hydrophobic [C$_2$mim][NTf$_2$], the hydrophobic compds. can be sepd. from the hydrophilic reactants by extn. and pptn. with water, however, the hydrophobic IL is more difficult to completely remove after the sepns. In [C$_2$mim][OAc], the most hydrophobic starting material can be extd. from the IL phase into Et acetate, and then water can be added to ppt. the hydrophobic amide product while at the same time removing the IL from the pharmaceuticals.

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### 32. The role of ionic liquids in the pharmaceutical manufacturing processes

By Wang, Hui; Zhou, Xiaosi; Gurau, Gabriela; Rogers, Robin D.
Edited By:Zhang, Wei; Cue, Berkeley W., Jr
From Green Techniques for Organic Synthesis and Medicinal Chemistry (2012), 469-496. DOI:10.1002/9780470711828.ch17

A review. This article describes about the roles of ionic liqs. in pharmaceutical manufg. processes and products, the synthesis of drugs or drug intermediates, the use of ILs in pharmaceutical crystn., in pharmaceutical sepn., for the extn. of drugs from natural products, to deliver drugs, to detect drugs, and even as APIs.

### 33. Application of unusual metal speciation in ILs to f-element separations

By Kelley, Steven P.; Rogers, Robin D.
From Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), I+EC-105.

Ionic liqs. (ILs) are unique in that they offer a high concn. of free ions at a temp. where many metal complexes and ligands are thermally stable. This has resulted in a no. of reports on unusual metal chem., including the formation of metal-contg. ILs. This also has important implications for liq.-liq. extn. of metals, a leading subfield of IL research. Since the behavior of metals in ILs can be unexpected, research on metal speciation in ILs is needed to design reliable sepns. and take advantage of the new synthetic opportunities of these materials. We have studied the speciation of uranium, thorium, and lanthanides in ILs due to the major relevance of sepg. these metals. Here we present our results in this area including the unusual coordination of f-elements to soft donors and attempts to incorporate f-elements into ILs.

### 34. Amidoxime functionalized materials for the selective extraction of the uranium

By Barber, Patrick S.; Kelley, Steven P.; Griggs, Chris S.; Rogers, Robin D.

From Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), I+EC-54.

The selective extn. of uranium from the environment can lead to a variety of applications from waste remediation to the mining of $UO_2^{2+}$ from seawater. Several studies over the past sixty years has concluded that the amidoxime moiety, $RC(NH_2)=NOH$ is highly selective for the uranyl cation, even under such complex conditions as seawater. Despite these studies, only recently has solid-state structural data been acquired that supports the $\eta^2$ coordination of amidoxime to the uranyl ion. These recent results suggest a higher stability complex and are potentially linked to the selectivity of the amidoxime for the uranyl cation. We have modified both solid (small org. mols. and biopolymers) and liq. (ionic liqs.) materials with this functional group and have applied them towards the sepn. of the uranyl cation. We will discuss the synthesis and modification of these materials and their applied sepns. of uranium.

### 35. Ionic liquids and strategic metals: Challenges and opportunities

By Rogers, Robin D.

From Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), ANYL-189.

The depletion of easily accessible reserves of nonrenewable resources, esp. metals, has forced people to turn to recycling and the use of historically nonviable sources to get these resources. The main hinderance to exploiting these nontraditional resources is the lack of energetically and chem. efficient sepns. methods. Given the need for new solvents that are tunable, robust, and environmentally benign, it is no surprise that sepns. have become one of the chief applications of ionic liqs. (ILs). ILs are salts with low m.ps. that frequently have wide liq. ranges, low volatility, good thermal, chem., and electrochem. stability, and tunable physicochem. properties. This overview will cover the application of ILs to the recovery of resources from nontraditional sources including recovery of uranium from seawater, extn. of rare earth elements and precious metals from spent nuclear fuel, and the processing of metal ores.

### 36. Energetic ionic liquid "Liquid Clathrates"

By Beasley, Preston A.; Cojocaru, O. A.; McCrary, Parker D.; Rogers, Robin D.

From Abstracts of Papers, 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), IEC-8.

Energetic Ionic Liqs. (EILs) provide an interesting set of properties and are being studied for their potential ability to replace current state of the art energetic materials, but may lack key features such as low viscosity and high energy d. Liq. Clathrates, liq. inclusion compds. which form upon the interaction of arom. mols. with certain salt moieties, have long been studied for their bonding features and application into solving sepns. problems. We are incorporating the known property sets of some ILs, including the ability of ILs to form stable liq. clathrates, and the reactive nature of the organoaluminum moieties used to make some of the original liq. clathrates to gain a higher level of understanding of the interaction between the arom. and liq. clathrate and the effect on the energetic properties. This presentation will discuss the novel salts and their 'liq. clathrate' behavior and stability.[p]Research was supported by the Air Force Office of Scientific Research (Grant F49550-10-1-0521).

**37. EDITORIAL - SS&T Special Issue on Ionic Liquids for Separations**

By Chen, Ji; Rodriguez, Hector; Rogers, Robin D.

From Separation Science and Technology (2012), 47(2), 167-168. DOI:10.1080/01496395.2012.639259

**38. Insight into the Interactions That Control the Phase Behaviour of New Aqueous Biphasic Systems Composed of Polyethylene Glycol Polymers and Ionic Liquids**

By Freire, Mara G.; Pereira, Jorge F. B.; Francisco, Maria; Rodriguez, Hector; Rebelo, Luis Paulo N.; Rogers, Robin D.; Coutinho, Joao A. P.

From Chemistry - A European Journal (2012), 18(6), 1831-1839, S1831/1-S1831/6. DOI:10.1002/chem.201101780

New polyethylene glycol (PEG)/ionic liq. aq. biphasic systems (ABS) are presented. Distinct pairs of PEG polymers and ionic liqs. can induce phase sepn. in aq. media when dissolved at appropriate concns. Phase diagrams have been detd. for a large array of systems at 298, 308 and 323 K. A comparison of the binodal curves allowed the anal. of the tunable structural features of the ionic liq. (i.e., anionic nature, cationic core, cationic alkyl side chain length and functionalization, and no. of alkyl substituents in the cation) and the influence of the mol. wt. of the PEG polymer on the ability of these solutes to induce an ABS. It was obsd. that contrary to typical ABS based on ionic liqs. and inorg. salts, in which the phase behavior is dominated by the formation of the hydration complexes of the ions, the interactions between the PEG polymers and ionic liqs. control the phase demixing in the polymer-type ABS studied herein. It is shown that both the ionic liqs. and PEG polymers can act as the salting-out species; i.e., it is an occurrence that is dependent on the structural features of the ionic liq. For the first time, PEG/ionic liq. ABS are reported and insight into the major interactions that govern the polymer/ionic liq. phase behavior in aq. media are provided. The use of two different nonvolatile and tunable species (i.e., ionic liqs. and PEG polymers) to form ABS allows the polarities of the phases to be tailored. Hence, the development of environmentally friendly sepn. processes that make use of these novel systems is envisaged.

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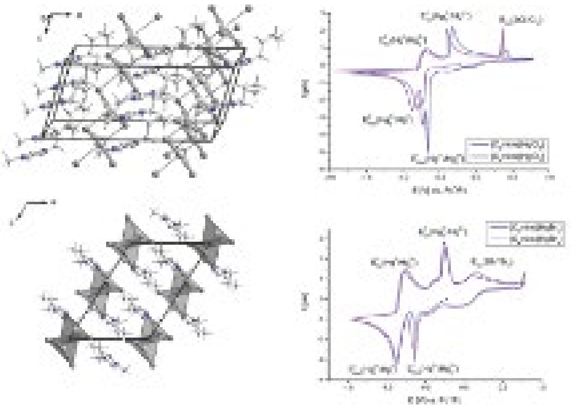
### 39. Mercuric Ionic Liquids: [Cnmim][HgX3], Where n = 3, 4 and X = Cl, Br

By Mallick, Bert; Metlen, Andreas; Nieuwenhuyzen, Mark; Rogers, Robin D.; Mudring, Anja-Verena

From Inorganic Chemistry (2012), 51(1), 193-200. DOI:10.1021/ic201415d



Mercury(II) ionic liqs., [C$_n$mim][HgX$_3$], where [C$_n$mim] = n-alkyl-3-methylimidazolium with n = 3, 4 and X = Cl, Br, were synthesized following two different synthetic approaches, and structurally characterized by single-crystal x-ray structure anal. The crystal parameters are: [C$_3$mim][HgCl$_3$] (1), space group Cc, Z = 4, a 16.831(4), b 10.7496(15), c 7.4661(14) Å, β 105.97(2)° at 298 K; [C$_4$mim][HgCl$_3$] (2), space group Cc, Z = 4, a 17.3178(28), b 10.7410(15), c 7.4706(14) Å, β 105.590(13)° at 170 K; [C$_3$mim][HgBr$_3$] (3), space group P2$_1$/c, Z = 4, a 10.2041(10), b 10.7332(13), c 14.5796(16) Å, β 122.47(2)° at 170 K; [C$_4$mim][HgBr$_3$] (4), space group Cc, Z = 4, a 17.093(3), b 11.0498(14), c 7.8656(12) Å, β 106.953(13)° at 170 K. Compds. 1, 2, and 4 are isostructural and were characterized by strongly elongated trigonal [HgX$_5$] bipyramids, which are connected via common edges in chains. In contrast, 3 contains [Hg$_2$Br$_6$] units formed by two edge-sharing tetrahedra. With m.ps. of 69.3° (1), 93.9° (2), 39.5° (3), and 58.3° (4), all compds. qualify as ionic liqs. Complexes 1, 2, and 4 solidify upon fast cooling as glasses, whereas 3 crystallizes. Cyclic voltammetry shows two sep., quasi-reversible redox processes, which can be assocd. with the 2Hg$^{2+}$/Hg$_2^{2+}$ and Hg$_2^{2+}$/2Hg redox couples.

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### 40. Disruptive technology for biomass processing using ionic liquids

By Daly, Daniel T.; Rogers, Robin D.; Gurau, Gabriela

From Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011 (2011), BMGT-15.

The inevitable depletion of petroleum-based resources and increasing worldwide interest in finding alternative renewable resources combined with the potential to produce multiple products from lignocellulosic biomass offers unique business opportunities if a disruptive technol. which reduces the burden of high transportation cost can be developed. This development will then allow low-vol., but high-value chems. to provide added value to the low-value, but high-vol. liq. transportation fuels being developed. Current biol. and chem. approaches being taken to utilize biomass are limited by the difficulty in processing (particularly pre-treating) lignocellulosic materials and the energy needed for sepn. of the components. Clean sepn. of the three major components of biomass (cellulose, lignin, and hemicellulose,) is the most important challenge for producing reproducible feedstocks for further processing. Ionic liqs. (ILs), defined as salts which melt below 100 °C, have opened a door to effectively explore the carbohydrate economy by direct dissoln. of lignocellulosic biomass and partial sepn. of the major biopolymer constituents (by reconstitution of the dissolved wood using selected solvents), which facilitates enzymic hydrolysis.

### 41. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin

By Li, Weiying; Sun, Ning; Stoner, Breena; Jiang, Xinyu; Lu, Xingmei; Rogers, Robin D.

From Green Chemistry (2011), 13(8), 2038-2047. DOI:10.1039/c1gc15522a

Rapid dissoln. of bagasse and southern yellow pine has been achieved in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([$C_2$mim]OAc) by using a dissoln. temp. above the glass transition of lignin (ca. 150°). When 0.5 g of bagasse or pine is added to 10 g of [$C_2$mim]OAc, complete dissoln. can be obtained in 5-15 min for bagasse at a temp. of 175-195°, compared to 15-16 h at 110°, and over 90% of added pine can be dissolved with heating at 175° for 30 min. Upon regeneration in acetone/water, lignin and carbohydrate can be partially sepd. as lignin and a cellulose-rich material (CRM, pulp). Compared to published methods with lower temps. and longer times (e.g., 110°, 16 h), processing bagasse in [$C_2$mim]OAc at 185° for 10 min results in higher yields of both recovered lignin (31% vs. 26% of the available lignin) and carbohydrate (carbohydrate yield = 66% vs. 63% of the available carbohydrate). In addn., the CRM pulp recovered using the higher temp. method has much lower residual lignin content (6% vs. 20%). Similar results were obtained for pine (lignin content in CRM with higher vs. lower temp. method = 16.1% vs. 23.5%). The IL was recycled and reused although the efficiency decreased and ca. 15% of the IL had degraded after the higher temp. process. These latter results suggest further optimization of the choice of IL and heating conditions might be needed to develop an energy and chem. efficient process.

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### 42. How can we improve the dissolution and recovery of biopolymers from biomass in ionic liquids specifically for biofuels applications?

By Li, Weiying; Sun, Ning; Rogers, Robin D.

From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2010), 55(2), 103.

The dissoln. and sepn. of biopolymers in lignocellulosic biomass using ionic liqs. (ILs) as solvents have been demonstrated. In this presentation, several aspects of this approach which might improve the sepn. and energy efficiency of the process are discussed. Specifically, it examines whether utilizing elevated temps. (above the lignin glass transition temp. of 150°) at shorter times might be more effective than lower temps. at longer times. It also explores potential catalytic routes to help selectively cleave lignin from holocellulose to provide cleaner biopolymers requiring less subsequent processing. Some aspects of IL recycle and reuse are also considered.

### 43. Actinide complexes with N-donors from ionic liquids

By Kelley, Steven P.; Parker, T. Gannon; Rogers, Robin D.

From Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011 (2011), NUCL-57.

Actinide and lanthanide cations are known to be hard Lewis acids, however the actinides have a greater affinity for soft Lewis bases. This is exploited in sepns. of these two otherwise very similar chem. species in nuclear waste. Ionic liqs. (ILs), a class of org. salts with m.ps. below 100 °C, are being investigated as more environmentally friendly alternatives for the volatile org. solvents currently used in nuclear waste sepns. Many of the anions used in ILs, such as azolates and dicyanamide, are or can be exclusively functionalized with nitrogen donors and thus behave as soft Lewis bases. We are investigating the reactivity and complexes of f-elements with ILs incorporating these anions. We will present our research into the reactivity of these ILs with f-elements, including a crystal structure of the first uranyl dicyanamide complex to be synthesized from an ionic liq.

### 44. Award Address (ACS Award in Separations Science and Technology sponsored by Waters Corporation). Ionic liquids from there to here

By Rogers, Robin D.

From Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011 (2011), I+EC-148.

Over the last fifteen years, one aspect of the Rogers' Group research has focused on ionic liqs. (ILs), investigating both the application, and fundamental understanding, of how ILs can be used as sepns. media. This research has included advances in their prepn. and studies on toxicity through applications in reaction and sepns. processes for org. mols., radionuclides, metal cations and complexes and biomols., to the development of IL energetic materials and active pharmaceutical agents. However, the story of this work would not be complete without discussion of its roots in undergraduate and graduate research projects on liq. clathrates with Jerry Atwood at The University of Alabama, its manifestation into liq. sepns. in faculty sabbatical research in radiochem. and sepns. with Phil Horwitz at Argonne National Lab., its re-emergence with the IL phenomenon developed in collaboration with Ken Seddon of Queen's University of Belfast, and the many students and collaborators.

### 45. Biphasic liquid-liquid systems based on ionic liquids and polyethylene glycols

By Francisco, Maria; Rodriguez, Hector; Sun, Ning; Rahman, Mustafizur; Pereira, Jorge F.; Freire, Mara G.; Rebelo, Luis P.; Coutinho, Joao A.; Rogers, Robin D.

From Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011 (2011), I+EC-103.

Some mixts. of ionic liqs. and polyethylene glycols can give rise, at the appropriate compn. and over a broad range of temps., to totally liq., immiscible systems. The two liq. phases formed can be potentially useful in sepn. processes, for example in the combined dissoln. and fractionation of hard-to-dissolve, complex solutes (such as biomass). Ionic liqs. and polyethylene glycols can also be used as co-solutes in an aq. medium to produce aq. biphasic systems at room temp. These systems, in which the two co-existing phases are aq., have potential application in biotechnol. sepns. Phase diagrams will be presented for these two types of liq., biphasic systems, and initial attempts for practical application in sepn. of solutes will also be discussed.

### 46. Ionic liquids for improved liquid-liquid extraction processes

By Rodriguez, Hector; Lago, Sara; Francisco, Maria; Earle, Martyn J.; Holbrey, John D.; Seddon, Kenneth R.; Rogers, Robin D.; Soto, Ana; Arce, Alberto

From Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011 (2011), I+EC-101.

Ionic liqs. exhibit, in general, a very interesting set of properties for their use as solvents. In particular, they look promising in the development of improved liq.-liq. extn. processes. This presentation will show results on the use of several ionic liqs. for diverse applications by solvent extn.: concn. of essential oils of plants, sepn. of arom. and aliph. hydrocarbons, desulfurisation of fuels, and removal of metals from petroleum. These sepn. problems have been modelled by means of ternary systems, and the liq.-liq. equil. data for these systems have been detd. The results allow for an anal. of the suitability of the ionic liqs. as extg. solvents in the applications suggested. Since several ionic liqs. have been tried, an initial identification of desirable ions or structural features in the ionic liq. can also be made, in order to optimize the choice for a practical sepn. process.

### 47. Actinide chemistry in ionic liquids

By Kelley, Steven P.; Parker, T. Gannon; Rogers, Robin D.

From Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011 (2011), I+EC-29.

Ionic liqs. are a class of org. salts with m.ps. below 100 °C. They have been heavily investigated as non-volatile replacements for org. solvents in many processes. One such area of interest is the extn. of actinides in nuclear waste. Fundamental questions about the speciation of actinides in ILs must be answered in order to design better solvents for sepn. and understand the speciation of pollutants that may be leaked into the environment. We are investigating the chem. of actinides in ILs. We will present our research into this area and unique possibilities for sepns., new materials, low melting f-element salt phases, and a better fundamental understanding of the reactivity of actinides and lanthanides. Our results include phase change behavior of f-element salts in the presence of ILs, and crystal structures of f-element salts synthesized from pure ILs.

### 48. Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass?

By Sun, Ning; Rodriguez, Hector; Rahman, Mustafizur; Rogers, Robin D.

From Chemical Communications (Cambridge, United Kingdom) (2011), 47(5), 1405-1421. DOI:10.1039/C0CC03990J

A review. Certain ionic liqs. dissolve cellulose, other biopolymers, and even raw biomass under relatively mild conditions. This particular ability of some ionic liqs., accompanied by concurrent advantages, enables the development of improved processing strategies for the manufg. of a plethora of biopolymer-based advanced materials. The more recent discoveries of dissoln. of lignocellulosic materials (e.g., wood) in ionic liqs., with at least partial sepn. of the major constituent biopolymers, suggest further paths towards the achievement of a truly sustainable chem. and energy economy based on the concept of a biorefinery which provides chems., materials, and energy. Nonetheless, questions remain about the use of ionic liqs. and the advisability of introducing any new process which uses bulk synthetic chems. which have to be made, disposed of, and prevented from entering the environment. The authors discuss their own journey from the discovery of the dissoln. of cellulose in ionic liqs. to the cusp of an enabling technol. for a true biorefinery and some of the key questions which remain are discussed.

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### 49. How can we improve the dissolution and recovery of biopolymers from biomass in ionic liquids specifically for biofuels applications?

By Li, Weiying; Sun, Ning; Rogers, Robin D.

From Abstracts of Papers, 240th ACS National Meeting, Boston, MA, United States, August 22-26, 2010 (2010), FUEL-61.

We and others have demonstrated the dissoln. and sepn. of the biopolymers in lignocellulosic biomass using ionic liqs. (ILs) as solvents. In this presentation, we will discuss several aspects of this approach which might improve the sepn. and energy efficiency of the process. Specifically we will address whether utilizing elevated temps. (above the lignin glass transition temp. of 150 °C) at shorter times might be more effective than lower temps. at longer times. In addn., we will discuss potential catalytic routes to help selectively cleave lignin from holocellulose to provide cleaner biopolymers requiring less subsequent processing. Finally we will discuss some aspects of IL recycle and reuse.

**50. Liquid mixtures of ionic liquids and polymers as solvent systems**
By Rodriguez, Hector; Rogers, Robin D.
From Fluid Phase Equilibria (2010), 294(1-2), 7-14. DOI:10.1016/j.fluid.2009.12.036

A review of the scarce literature on the use of entirely liq. mixts. of ionic liqs. and polymers in a solvent role is presented. These mixts. can present interesting characteristics such as very low volatility, good solvation ability, and tunable phys. and thermal properties, and they can be esp. attractive as solvent systems for carrying out reactions or sepns. The liq. polymer and ionic liq. can be miscible, or can exhibit immiscibility, thus giving rise to totally liq., biphasic systems. Novel systems of the latter kind, constituted by 1-alkyl-3-methylimidazolium chlorides or acetates and poly(alkylene glycol)s such as poly(ethylene glycol) or poly(propylene glycol), are reported herein. Fundamentals of their liq.-liq. equil. are described.

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**51. Crystallization of actinides from ionic liquids**
By Smiglak, Marcin; Gurau, Gabriela; Drab, David M.; Shamshina, Julia L.; Kelley, Steven P.; Cocalia, Violina; Griffin, Scott T.; Mudring, Anja-Verena; Rogers, Robin D.
From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), NUCL-16.

Ionic liqs. (ILs) are being increasingly investigated for applications ranging from electrochem. to energetic materials, and are also rapidly establishing their promise as viable media for synthesis and sepns. operations. Our current projects have demonstrated that actinide ions can be coordinated and extd. from various solns. with ILs using conventional complexants, and that the partitioning mechanisms and modes of coordination can be controlled through selection of an appropriate IL phase. However, fundamental and crit. questions about the role of the IL cation and anion have been raised and we have thus initiated study of the coordination, complexation, and solvation of actinide elements and analogs in IL soln. Here we present a series of crystal structures of uranyl complexes isolated in the presence of imidazolium ILs that were investigated in order to gain a better understanding of the actinide speciation in the presence of imidazolium-based compds.

**52. Wood delignification using polyoxometalates in ionic liquid**
By Sun, Ning; Jiang, Xinyu; Maxim, Mirela L.; Rogers, Robin D.
From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), FUEL-14.

We have recently been exploring the feasibility of using ionic liqs. (ILs) to dissolve, sep., and recover cellulose, hemicellulose, and lignin from lignocellulosic biomass such as wood. We have previously demonstrated total dissoln. and partial sepn. of the biopolymers. Our results suggest that this process could be enhanced with the use of a catalyst or reagent that could selectively cleave lignin-carbohydrate bonds. We have recently begun the exploration of polyoxometalates (POMs) to enhance biomass dissoln. and increase delignification without sacrificing the pulp or holocellulose yield indicating the high selectivity of POM in IL systems. This presentation will overview our current progress in wood delignification with POMs in IL media and suggest how ILs may provide unique routes to new materials and processes which utilize renewable resources.

**53. Dissolution and regeneration of wood in [C2mim]OAc and formation of wood composite fibers**

By Stoner, Breena; Sun, Ning; Rogers, Robin D.

From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), CHED-725.

Currently there is increasing interest in the use of renewable resources such as biomass todecrease society's reliance on fossil fuels. Previous research has shown that bothhardwoods and softwoods can be effectively dissolved by the ionic liq. [C2mim]OAc. However, current dissoln. techniques require 16 h of const. heat and stirring. It is desirable to det. more efficient heating parameters to allow max. dissoln. and regeneration of cellulose materials in min. time. Different temps. and dissoln. times have been attempted for traditional oil bath heating, and microwave heating for different times has also been compared. Mass balance and the ligninholocellulose sepn. efficiency has been evaluated. Wood composite fibers can be prepd. directly from the wood/IL soln. By altering initial treatment of the wood,fiber compn. may be varied, allowing the formation of fibers with differing properties. The biodegradable wood composite fibers are then characterized, and the variation of fiber properties with lignin content and different heating conditions is discussed.

**54. Biphasic liquid mixtures of ionic liquids and polyethylene glycols**

By Rodriguez, Hector; Francisco, Maria; Rahman, Mustafizur; Sun, Ning; Rogers, Robin D.

From Physical Chemistry Chemical Physics (2009), 11(46), 10916-10922. DOI:10.1039/b916990c

We have found that 1-alkyl-3-methylimidazolium chloride ionic liqs. (ILs) can form immiscible liq. mixts. with some polyethylene glycols (PEGs). Binary mixts. of 1-ethyl-3-methylimidazolium chloride with PEG of mol. wt. 1500, 2000, or 3400 g mol$^{-1}$, or of 1-butyl-3-methylimidazolium chloride with PEG of mol. wt. 2000 or 3400 g mol$^{-1}$, have been found to give rise to entirely liq., stable biphasic systems over a significant temp. range (from 333.15 K to 413.15 K), while mixts. of 1-ethyl-3-methylimidazolium chloride with PEG-1000 and 1-butyl-3-methylimidazolium chloride with PEG-1000 and PEG-1500 are miscible. The mutual immiscibility of the IL and the PEG increases as the temp. increases. The evolution of the compn. of the phases in equil. with the mol. wt. of the PEG, or with the variation of the length of the alkyl substituent chain of the imidazolium cation of the IL, has been explored. The trends obsd. are explained through the complexity of interactions present within the binary system. A thermodn. anal. of the liq.-liq. equil. data indicates neg. values for the change of enthalpy and entropy of mixing. The potential application of these biphasic, entirely liq. systems, with low volatility and good solvation properties, for the dissoln. and sepn. of cellulose and lignin at elevated temp. has been preliminarily explored, although only modest results have been achieved to date.

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### 55. Ionic Liquids from Phase Modifier to Solvent for Future Nuclear Fuel Processing

By Bridges, Nicholas J.; Admas, Thad M.; Visser, Ann E.; Williamson, Mark J.; Rogers, Robin D.

From Abstracts, 60th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, United States, November 12-15 (2008), SERM-647.

Ionic liqs. (ILs) have sparked interest in many areas of research as a possible replacement for org. diluents. ILs offer near infinite tunability through the ability to alter an ion independent of the other ion, providing control of the chem. and phys. properties. Here, a survey of work investigating the interactions of ILs in aq. systems to produce an aq. biphasic system, and sep. radiol. stability of ILs in a high gamma field will be presented. ILs are designed to have a depressed m.ps. due to asymmetry in the ions, delocalized charge, and weak hydrogen bond donor and acceptor groups; all of these characteristics are the same as a chaotropic ion. A kosomotropic salt has strong interactions with H2O that can "salt-out" hydrophilic, chaotropic ILs (e.g., 1-butyl-3-methylimidazloium chloride). In order to learn more about the generality and design of such salt/salt ABS, we have investigated phase diagrams of several commonly used ILs and org. salts with known kosmotropic salts. ILs have the potential to be used in replacing high temp. molten salts in pyrochem. processing of spend nuclear fuel, but they have to be radiol. stable to high doses of radiation. We have started investigating gamma irradn. on a range of different classes of ILs, and how the changes in the phys. and chem. affect their likelihood as a replacement solvent.

### 56. Dissolution and Separation of Biomass Utilizing Ionic Liquids

By Sun, Ning; Rahaman, Mustafizur; Qin, Ying; Maxim, Mirela; Rogers, Robin D.

From Abstracts, 60th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, United States, November 12-15 (2008), SERM-250.

With the inevitable depletion of petroleum materials, there has been an increasing interest in finding alternative sources. Wood is a common biomass resource with applications in biofuels, papermaking, and construction. The major components of wood are cellulose, hemicellulose, and lignin. Currently only cellulose and hemicellulose have been utilized in producing paper, fibers, and membranes, while lignin is only burned for energy. The reason of their underutilization comes from the difficulty of dissoln. and the energy needed for sepn. of the different components from wood. The current pulping process involves caustic chems. and generates a large amt. of pollutants. The recent discovery of wood dissoln. in ionic liqs. (ILs) has opened a door to utilize and sep. biomass components more efficiently. In this presentation, we will discuss how ILs can be designed to dissolve and process biomass and how to manipulate soln. properties to process and regenerate biopolymers into a desirable form for specialized applications.

**57. From crystalline salts to ionic liquids and back again: In the hunt for novel separations**
By Rogers, Robin D.
From Abstracts of Papers, 236th ACS National Meeting, Philadelphia, PA, United States, August 17-21, 2008 (2008), IEC-003.

This presentation will review the course of our work in the pages of the ACS journal Industrial & Engineering Chem. Research. It will describe a personal journey from crystallog. of metal salt complexes to the study and utilization of the low melting liq. salts known as ionic liqs. The common theme will be the quest for fundamental knowledge that can be used to develop novel sepns. technologies. Finally, the use of ionic liqs. for sepns. will be placed in context with the overall potential for growth in this exciting field.

**58. Utilization of hydrophilic ionic liquids in separations: Understanding and taming complexity**
By Rogers, Robin D.; Dilip, Meghna; Bridges, Nicholas J.; Smiglak, Marcin; Cordes, David B.; Materna, Katarzyna; Moyna, Guillermo
From Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008 (2008), IEC-078.

Hydrophilic ionic liqs. can be used in aq. phase sepns. via their salting-out and formation of aq. biphasic systems, ABS, (e.g. aq. [C4mim]Cl/K3PO4). For wider and more "intelligent" application, it is important to look below the surface and study these systems thoroughly at a fundamental level. Here we present our work to understand these salt/salt ABS, including phase diagrams (where for example it can be shown that these ionic liq. (IL) solns. generally exhibit upper crit. soln. type soln. behavior) and DSC studies demonstrating the chaotropicity of the ILs studied. Clearly the role of water is crit. to the behavior of these ABS, thus we have also studied IL solns. and inorg. salt solns. sep. in order to isolate ion assocn. and the interactions with water. The results of these studies will be presented.

**59. The Second Evolution of Ionic Liquids: From Solvents and Separations to Advanced Materials-Energetic Examples from the Ionic Liquid Cookbook**
By Smiglak, Marcin; Metlen, Andreas; Rogers, Robin D.
From Accounts of Chemical Research (2007), 40(11), 1182-1192. DOI:10.1021/ar7001304

A review. In this Account of the small portion of the recent research in ionic liqs. (ILs) by the Rogers Group, we fast forward through the first evolution of IL research, where ILs were studied for their unique set of phys. properties and the resulting potential for tunable "green solvents", to the second evolution of ILs, where the tunability of the cation and anion independently offers almost unlimited access to targeted combinations of phys. and chem. properties. This approach is demonstrated here with the field of energetic ionic liqs. (EILs), which utilizes this design flexibility to find safe synthetic routes to ILs with high energy content and targeted phys. properties.

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### 60. Separations, coordination, and solvation of f-elements in ionic liquids

By Rogers, Robin D.; Bridges, Nicholas J.; Cocalia, Violina A.; Gutowski, Keith E.

From Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007 (2007), NUCL-066.

Ionic liqs. (ILs, salts that have m.p. less than 100 °C) have been investigated as potential replacement solvents for liq./liq. sepns. of nuclear waste reprocessing and the complex results have been highly dependent on the specific ILs, ligands, and systems studied. Thus, we have begun to focus more on the fundamental interactions of f-elements with and in IL solvents and we are now gaining more insight into some of the unique aspects of IL solvation. Here we have present the results of our investigations into the coordination and solvation of f-elements utilizing radiochem. techniques, spectroscopic measurements, single-crystal X-ray diffraction, and computational modeling, and put these results in context of previously published data.

### 61. Investigation of aqueous biphasic systems formed from solutions of chaotropic salts with kosmotropic salts (salt-salt ABS)

By Bridges, Nicholas J.; Gutowski, Keith E.; Rogers, Robin D.

From Green Chemistry (2007), 9(2), 177-183. DOI:10.1039/B611628K

A study of salt-salt aq. biphasic systems (ABS) was conducted to increase our understanding of solns. of kosmotropic vs. chaotropic salts, esp. since most ionic liqs. (ILs) fall within the latter class. The salting-out strength of the kosmotropic salts follows the well established Hofmeister series, as obsd. in polymer-salt ABS, and can be directly related to the ions' Gibbs free energies of hydration ($\Delta G_{hyd}$). Most currently studied ILs are designed to have chaotropic cations and are thus salted-out by kosmotropic salts. Here, we describe the phase diagrams for imidazolium-, pyridium-, and quaternary ammonium- and phosphonium-based chloride salts (all chaotropic salts) salted-out by $K_3PO_4$, $K_2HPO_4$, $K_2CO_3$, KOH, and $(NH_4)_2SO_4$ (all kosmotropic salts). The Gibbs free energy of methylene transfer ($\Delta G_{CH2}$) was also detd. for 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$)/$K_3PO_4$, $K_2HPO_4$, and $K_2CO_3$ ABS. The latter results are in the range of an ethanol-water to a chloroform-water system, and can be controlled predominately by the system compn.

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### 62. Separations of metal ions using ionic liquids: the challenges of multiple mechanisms

By Cocalia, Violina A.; Holbrey, John D.; Gutowski, Keith E.; Bridges, Nicholas J.; Rogers, Robin D.

From Tsinghua Science and Technology (2006), 11(2), 188-193. DOI:10.1016/S1007-0214(06)70174-2

A review. The current ionic liq.-based sepn. research for solvent extn. is discussed. The effects of the nature of the solvent ions, ligands, and metal ion species are studied to understand the nature of the challenges in utilizing ionic liqs. for practical metal sepn. applications.

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### 63. The coordination chemistry of actinides in ionic liquids: A review of experiment and simulation

By Cocalia, Violina A.; Gutowski, Keith E.; Rogers, Robin D.

From Coordination Chemistry Reviews (2006), 250(7-8), 755-764. DOI:10.1016/j.ccr.2005.09.019

A review. Ionic liqs. (ILs) found widespread use in biochem., electrochem., catalytic, and synthetic applications, and have recently been applied to important areas of f-element chem. This review highlights the use of ILs in sepn. schemes for the sequestration of actinide ions (including lanthanides, where appropriate, as stand-ins for actinide ions), the solid-state chem. of actinide complexes contg. imidazolium cations, and the spectroscopy and electrochem. of actinide cationic and anionic species. Particular emphasis is placed on the coordination environments that are present under a variety of conditions, such as acidic and basic tetrachloroaluminate melts. Also, this review touches on the recent use of computer simulations to elucidate the microscopic interactions that result in the preferential solvation of actinide ions in ILs.

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### 64. New task-specific ionic liquids incorporating amine groups and their use for reactive capture

By Davis, James H.; Tickell, Morgan; Rogers, Robin D.; Reichert, W. Matthew; Griffin, Scott T.

From Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006 (2006), IEC-280.

The use of ionic liqs. in gas sepn. applications is a topic of considerable current interest. This is esp. true of sepns. involving carbon dioxide. We have investigated the use of functionalized ionic liqs. as materials for such sepns., both as phys. solvents and as agents for reactive carbon dioxide capture. Results involving a first-generation class of amine-contg. trapping agents have been reported (JACS, 2002). Here, we discuss the synthesis and evaluation of new classes of amine-contg. ionic liqs. designed for reactive capture applications. These compds. include not just species in which the amine group is cation tethered, but also materials in which the functional group is anion-bound. Reactions of these compds. with carbon dioxide and other heterocumulenes will be discussed.

### 65. Synthesis, characterization, and application of cross-linked poly(ethylene glycol) networks used for the gelation of ionic liquids

By Klingshirn, Marc A.; Spear, Scott K.; Holbrey, John D.; Huddleston, Jonathan G.; Rogers, Robin D.
From ACS Symposium Series (2005), 913(Ionic Liquids in Polymer Systems), 149-162. DOI:10.1021/bk-2005-0913.ch010

Crosslinking polymn. of functionalized poly(ethylene glycol) (PEG) monomers was found to effectively gel hydrophobic ionic liqs. By coupling a tetra-arm PEG amine with a bifunctional succinimidyl PEG monomer, stable, free-standing gels can be formed. Gelation showed a strong IL anion dependence, whereas changing the IL cations gave little change. The gels showed a shrink-swell response to their solvent environment, while the IL entrained within the gels retains bulk properties of the neat IL. Applications include potential sepns. media and as IL-polymer electrolytes.

### 66. Palladium-catalyzed hydroesterification of styrene derivatives in the presence of ionic liquids

By Klingshirn, Marc A.; Rogers, Robin D.; Shaughnessy, Kevin H.
From Journal of Organometallic Chemistry (2005), 690(15), 3620-3626. DOI:10.1016/j.jorganchem.2005.05.031

The palladium-catalyzed hydroesterification of olefins occurs efficiently in a range of ionic liq. media. Selectivities ranging from 5-7:1 for the linear ester were obtained with styrene in a range of IL solvents. The use of ILs allowed the catalyst to be easily sepd. from the org. product by either extn. or distn. The (Ph$_3$P)$_2$PdCl$_2$ pre-catalyst could be recovered unchanged from the ionic liq. phase. The IL/catalyst phase could be recycled five times with an av. yield of 68%.

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### 67. Ionic liquid technologies for utilization in nuclear-based separations

By Gutowski, Keith E.; Bridges, Nicholas J.; Cocalia, Violina A.; Spear, Scott K.; Visser, Ann E.; Holbrey, John D.; Davis, James H., Jr.; Rogers, Robin D.
From ACS Symposium Series (2005), 902(Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities), 33-48. DOI:10.1021/bk-2005-0902.ch003

A review. The favorable properties of ionic liqs. (ILs) contg. org. cations, such as low m.ps., lack of vapor pressure, wide liquidus ranges, and tunable phys. properties, make this class of liqs. particularly interesting to study as potential replacements for traditional volatile org. solvents (VOCs). While nuclear sepns. are mostly done using non-volatile org. phases such as octanol or dodecane, the potential to use ILs as alternatives is appealing because of the unique solvent environments and solvation properties that are presented for coordination and extn. mechanism studies. Here, the authors show results that illustrate the application of ILs to fundamental problems surrounding nuclear sepns. and waste remediation.

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**68. Ionic Liquids: Fundamental Studies to Technological Applications in Support of Green Chemistry**
By Rogers, Robin D.; Spear, Scott K.; Holbrey, John D.
From Abstracts, 60th Southwest Regional Meeting of the American Chemical Society, Fort Worth, TX, United States, September 29-October 4 (2004), SEPT04-265.

Perhaps as a result of the compelling need for industry to consider the reengineering of entire processes, ionic liqs. (ILs) have begun to receive worldwide academic and industrial attention as VOC replacements in catalysis, synthesis, and sepns. processes, in addn. to their well known role in electrochem. Combined with green chem., a new paradigm in thinking about synthesis in general, ILs provide a unique opportunity for science/engineering/business to work together from the beginning of a field's development and thus lead more quickly to innovative environmentally-and economically-sustainable industrial processes. In the current understanding, ILs contain large, org. cations with a variety of anions and melt at or below about 100 °C (adopted as an arbitrary upper temp. limit for "room temp." ionic liqs.). ILs are usually composed of org. cations such as quaternary ammonium or phosphonium cations, heterocyclic arom. compds., pyrrolidinium cations, and some more esoteric cations. The expectation that real benefits in technol. will arise from IL research and the development of new processes is high, but there is a need for further work in order to demonstrate the credibility of IL-based processes as viable green technol. In particular, comprehensive toxicity studies, phys. and chem. property collation and dissemination, and realistic comparisons to traditional systems are needed. Our treatment and approach to the investigation of IL-based systems in the context of Green Chem. research are based on exploring and gaining a core understanding of their fundamental characteristics and properties, which then leads to the development of new technol. solns., which can then be implemented in process applications. This presentation will briefly define ILs and the motivation behind IL research, discuss the current state of the field, and highlight recent advances from the Center for Green Manufg.

**69. Crystal structures of imidazolium bis(trifluoromethanesulfonyl)imide ionic liquid' salts: the first organic salt with a cis-TFSI anion conformation**
By Holbrey, John D.; Reichert, W. Matthew; Rogers, Robin D.
From Dalton Transactions (2004), (15), 2267-2271. DOI:10.1039/B405901H

Crystal structures of two examples of an important class of ionic liqs., 1,3-dimethylimidazolium and 1,2,3-triethylimidazolium bis(trifluoromethanesulfonyl)imide were characterized by single crystal x-ray diffraction. Crystallog. data are given. The anion in the 1,3-dimethylimidazolium example (m.p. 22°), adopts an unusual cis-geometry constrained by bifurcated cation-anion C-H···O H-bonds from the imidazolium cation to the anion giving fluorous layers within the solid-state structure. In contrast, in the 1,2,3-triethylimidazolium salt (m.p. 57°), the ions are discretely packed with only weak C-H···O contacts between the ions close to the van der Waals sepn. distances, and with the anion adopting the twisted conformation obsd. for all other examples from the limited set of org. bis(trifluoromethanesulfonyl)imide crystal structures. The structures are discussed in terms of the favorable phys. properties that bis(trifluoromethanesulfonyl)imide anions impart in ionic liqs.

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**70. Synthesis, characterization, and application of ionic liquid-poly(ethylene) glycol gel matrices**

By Klingshirn, Marc A.; Spear, Scott K.; Subramanian, Raman; Holbrey, John D.; Rogers, Robin D.

From Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1), 307-308.

The ionic liq. (IL), 1-hexyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([$C_6$mim][$NTf_2$]), can be immobilized to form free standing gels by the in-situ formation of a cross-linked poly(ethylene) glycols (PEG) by the reaction of PEG-succinimate and tetra-amine finctionalized PEG oligomers. The gelled ILs retain the phys. properties of the neat IL, and exhibit shrink-swell responses to solvents consistent with the control PEG hydrogel. Conductive properties of the gels show a small drop in cond. when compared to the neat IL; however, this is consistent with other types of gelled matrixes. Partitioning of linear alcs. from potassium phosphate solns. show the potential viability of the gel as a sepn. medium and suggests that the system hydrophobicity can be altered by modification of the soln. phase.

**71. Synthesis, characterization, and applications of ionic liquid-poly(ethylene) glycol gel matrices**

By Klingshirn, Marc A.; Spear, Scott K.; Subramanian, Raman; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004 (2004), POLY-638.

The ionic liq. (IL), 1-hexyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([$C_6$mim][$NTf_2$]), can be immobilized to form free standing gels by the in-situ formation of a cross-linked poly(ethylene) glycols (PEG) by the reaction of PEG-succinimate and tetra-amine finctionalized PEG oligomers. The gelled ILs retain the phys. properties of the neat IL, and exhibit shrink-swell responses to solvents consistent with the control PEG hydrogel. Conductive properties of the gels show a small drop in cond. when compared to the neat IL; however, this is consistent with other types of gelled matrixes. Partitioning of linear alcs. from potassium phosphate solns. show the potential viability of the gel as a sepn. medium and suggests that the system hydrophobicity can be altered by modification of the soln. phase.

**72. Task specific ionic liquids that incorporate poly (ethylene glycols) functionality for the extraction of metal ions**

# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

By Reichert, W. Matthew; Holbrey, John D.; Griffin, Scott T.; Cocalia, Violina A.; Bridges, Nicholas J.; Chambers, Joe; Rogers, Robin D.
From Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004 (2004), IEC-228.

Ionic Liqs. (ILs) have been used has replacement solvents in the sepn. of metal ions. In order to increase the distribution of the metal ions to the ILs certain extractants must be used. In order to overcome this drawback to ILs the extractant functionality can be incorporated in the ionic liq. forming task specific ionic liqs. In this presentation, task-specific ionic liq. extractants and complexants designed for compatibility with ionic liqs. have been prepd. by appending imidazolium functionalities onto a series of poly (ethylene glycols). The ligands have been characterized by single crystal X-ray crystallog., and the partitioning of cesium, strontium and mercury ion radiotracers have been detd. between aq. and ionic liq. phases contg. the extractants.

### 73. Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: Strategies for actinide or fission product separations

By Rogers, Robin D.; Gutowski, Keith E.; Griffin, Scott T.; Holbrey, John D.
From Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004 (2004), ENVR-033.

Aq. biphasic systems can be formed by salting-out (with kosmotropic, water-structuring salts) water sol. polymers (e.g., polyethylene glycol) or aq. solns. of a wide range of hydrophilic ionic liqs. based on imidazolium, pyridinium, phosphonium and ammonium cations. The use of these novel liq./liq. biphases for sepn. of actinides or other fission products assocd. with nuclear wastes (e.g., pertechnetate salts) has been demonstrated and will be described in this presentation.

### 74. Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: strategies for actinide or fission product separations

By Rogers, Robin D.; Gutowski, Keith E.; Griffin, Scott T.; Holbrey, John D.
From Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2004), 44(1), 403-407.

The group was focusing on the use of both polyethylene glycol (PEG) and Ionic Liqs. (ILs) in sepns. of actinide and fission products using traditional biphasic extns. from acidic media, as well as more challenging extns. from tank radioactive waste conditions. The authors have recently begun to apply this salting-out technol. to the removal of certain fission products, in particular $^{99}TcO_4^-$, from simple kosmotropic salt solns., with the goal of using more complex waste simulants. Partitioning of $^{99}TcO_4^-$ increases with increasing concns. of aq. $K_3PO_4$ solns. without the need for extns. The PEG-based systems also demonstrated the ability to remove actinides from caustic solns. but with the aid of an extractant. For example, the distribution ratios (in 5 and 6 M NaOH) for $^{241}$Am decrease with increasing concn. of the extractant Tiron over the range $10^{-6}$-$10^{-3}$ M (distribution ratios are < 1 in most cases); high distribution ratios are obsd. for the extn. of $^{241}$Am using the extractant, Pyrocatechol Violet, in 3 and 5 M NaOH, with little ligand dependency. Strong ligand dependency is obsd. at 1 M NaOH, with distribution ratios falling off sharply at greater that 104 M PCV.

**75. Polar, non-coordinating ionic liquids as solvents for coordination polymerization of olefins**

By Shaughnessy, Kevin H.; Klingshirn, Marc A.; P'Pool, Steven J.; Holbrey, John D.; Rogers, Robin D.

From ACS Symposium Series (2003), 856(Ionic Liquids as Green Solvents), 300-313. DOI:10.1021/bk-2003-0856.ch025

A review. The use of ionic liqs. (IL)s, e.g., 1-hexylpyridinium bis(trifluoromethanesulfonyl)imide, as solvents in Pd [Bis(acetato)(2,2'-bipyridine)palladium, Bis(acetato)(1,10-Phenanthroline)palladium ] catalyzed polymn. of styrene and carbon monoxide CO and in homopolymn. of ethylene is discussed. Increased polymn. yield was obsd. in the copolymn., compared to that from commonly used mol. solvents using palladium catalysts. Conditions for the copolymns. were optimized and the effect of changes in the cation and anion of the IL solvent were detd. These results suggest that polar, non-coordinating ILs accelerate olefin polymn. catalyzed by electrophilic, charge-sepd. catalyst species.

**76. Selection of ionic liquids for green chemical applications**

By Holbrey, John D.; Turner, Megan B.; Rogers, Robin D.

From ACS Symposium Series (2003), 856(Ionic Liquids as Green Solvents), 2-12. DOI:10.1021/bk-2003-0856.ch001

A review (37 refs.). Ionic liqs. (ILs) are proving to be increasingly promising as viable media for not only potentially "green" synthesis and sepns. operations, but also for novel applications where the unique property set of the IL materials provides new options based upon different chem. and phys. properties. The range and variability in the properties between individual examples within the class of solvents that are known as ILs, however, are both challenges and opportunities for developing new and improved processes. Some of the challenges in understanding IL behavior and in selecting specific IL media for applications is presented in the context of research from The University of Alabama.

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**77. Actinide chemistry in novel solvent media: Room-temperature ionic liquids**

By Visser, Ann E.; Rogers, Robin D.

From Proceedings - Electrochemical Society (2002), 2002-19(Molten Salts XIII), 516-529. DOI:10.1149/200219.0516pv

A review. Recent interest in ionic liqs. (ILs) has focused on their unique properties as alternative solvents in synthesis and sepns. The authors' research with ILs for sepns. is summarized here with an introduction to the use of ILs for actinide sepns. Unique aspects of ionic liq. soln. behavior and their utilization as replacements for org. solvents in liq./liq. actinide sepns. are described.

### 78. Application of ionic liquid technologies to nuclear separations

By Rogers, Robin D.; Holbrey, John D.; Spear, Scott K.; Gutowski, Keith E.; Bridges, Nicholas J.; Cocalia, Violina A.; Swatloski, Richard P.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), NUCL-092.

Room temp. Ionic Liqs. (ILs), org. salts that are liq. at, or close to room temp. have great potential application for uses in liq.-liq. sepns. processes. As a class of liqs., ILs typically have wide liq. ranges, are non-volatile, and have solvent characteristics (hydro- and lipophilicity, hydrogen-bond donor and acceptor ability etc) that can be controlled and modified by suitable changes to either the cation or anionic components of the IL. We have begun the exploration of actinide sepns. using a variety of technologies based upon the use of ILs including, liq./liq. extn. using traditional extractants; incorporating an extractant functionality into an IL; immobilizing IL extractant phases on solid supports; and utilization of the solubilizing power of ILs to prep. cellulose-based materials for f-element sepns. ILs can thus be considered as a new class of materials for nuclear sepns., distinct from mol. solvents and from high temp. molten salts, with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of "green" chem. in various chem. processes.

### 79. Formation of aqueous biphasic systems with hydrophilic ionic liquids via the addition of water-structuring salts: applications to nuclear tank wastes

By Gutowski, Keith E.; Broker, Grant A.; Bridges, Nicholas J.; Huddleston, Jonathan G.; Willauer, Heather D.; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), IEC-131.

The use of Ionic Liqs. (ILs) in aq./IL biphasic sepn. systems is currently limited to examples in which the IL contains anions that are fluorinated, expensive, and environmentally non-benign. However, ILs are very appealing for use in liq.-liq. sepns. due to their very low vapor pressure, wide liquidus range, and tunable phys. properties. We have recently shown that hydrophilic 1-butyl-3-methylimidizolium chloride forms an aq. biphasic systems with $K_3PO_4$, a kosmotropic salt. This salting-out phenomenon occurs with a variety of other such salts providing access to a much wider range of aq. biphase forming systems, leading us to investigate the applicability to partitioning systems using nuclear tank waste simulants for sepn. of fission products and transuranic species. Here we present results which attempt to characterize the phases according to compn. and speciation as well as the partitioning of various org./inorg. solutes between the phases with emphasis on using extractant mols. for metal ion sepns.

**80. CMPO-impregnated cellulosic materials from ionic liquids for f-element separations**
By Rogers, Robin D.; Holbrey, John D.; Spear, Scott K.; Gutowski, Keith E.; Swatloski, Richard P.
From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), IEC-045.

By taking advantage of the soly. of both cellulose and CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide) in the ionic liq. 1-butyl-3-methylimidazolium chloride, we have prepd. CMPO-impregnated cellulosic materials as flocs, beads, rods, and membranes. Americium-241, plutonium-239, and uranium-233 all exhibit significant partitioning from aq. solns. to the cellulose impregnated materials with increasing concns. of nitric acid. In this presentation we will examine the phys. properties of these new materials, as well as their possible application in the sepns. of americium, plutonium, and uranium from acidic aq. solns.

**81. Room temperature ionic liquids as replacements for traditional organic solvents and their applications towards "green chemistry" in separation processes**
By Visser, Ann E.; Swatloski, Richard P.; Reichert, W. Matthew; Willauer, Heather D.; Huddleston, Jonathan G.; Rogers, Robin D.
From NATO Science Series, II: Mathematics, Physics and Chemistry (2003), 92(Green Industrial Applications of Ionic Liquids), 137-156.

A review. The use of room temp. ionic liqs. (RTIL) as solvent alternatives in liq./liq. sepns. is discussed. The partitioning of benzene derivs. and ionizable solutes in liq./liq. extn. systems is outlined and use of metal ion extractants in RTIL-based liq./liq. sepns. is discussed. The utilization of RTIL for liq./liq. extn. and in chromatog., supercrit. fluid extn. is also discussed. The prospects for use of RTILs in industrial processes as true green chem. alternatives are also discussed.

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**82. Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations**
By Gutowski, Keith E.; Broker, Grant A.; Willauer, Heather D.; Huddleston, Jonathan G.; Swatloski, Richard P.; Holbrey, John D.; Rogers, Robin D.

# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

From Journal of the American Chemical Society (2003), 125(22), 6632-6633. DOI:10.1021/ja0351802

Hydrophilic ionic liqs. can be salted-out and concd. from aq. soln. upon addn. of salts forming aq. biphasic systems as illustrated by the phase behavior of mixts. of 1-butyl-3-methylimidazolium chloride and $K_3PO_4$.

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**83. Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry**
By Visser, Ann E.; Rogers, Robin D.
From Journal of Solid State Chemistry (2003), 171(1-2), 109-113. DOI:10.1016/S0022-4596(02)00193-7

A concise review on ionic liqs. as solvents for metal extn. precedes the expts. with actinide ions. (ILs) are composed of org. cations and either org. or inorg. anions that remain liq. over a wide temp. range, including room temp. IL characteristics can be dramatically adjusted (e.g., hydrophobic vs. hydrophilic) by changing the anion type, or subtly altered by changing the length or no. of alkyl groups appended to the cation. Changing alkyl chain lengths in the 1-alkyl-3-methylimidazolium cation, in combination with $PF^-_6$ or $N(SO_2CF_3)^-_2$ anions, produces hydrophobic ILs with rheol. properties suitable for their use in liq./liq. sepns. Actinides exhibit significant partitioning to these ILs from aq. solns. with the addn. of an extractant (e.g., octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide) to the IL. Ionic liqs. can, thus, be considered for actinide chem. as a new class of materials with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of "green" chem. in various chem. processes. Here we highlight the unique phys. properties of some ILs and their use in liq./liq. sepns.

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**84. Characterization of hydrophilic and hydrophobic ionic liquids: Alternatives to volatile organic compounds for liquid-liquid separations**
By Visser, Ann E.; Reichert, W. Matthew; Swatloski, Richard P.; Willauer, Heather D.; Huddleston, Jonathan G.; Rogers, Robin D.
From ACS Symposium Series (2002), 818(Ionic Liquids), 289-308. DOI:10.1021/bk-2002-0818.ch023

A review, combining the authors' published current results. The review describes the phys. and chem. properties for several Ionic Liqs. (ILs) comprised of the 1-alkyl-3-methylimidazolium cation with the $Cl^-$, $Br^-$, $I^-$, $BF_4^-$, or $PF_6^-$ anions. Liq.-liq. sepns. with the $PF_6^-$ ILs are highlighted to illustrate their use in "Green Chem.," as alternatives to traditional org. solvents in sepns. The partitioning of org. mols., combined with IL characterization, has facilitated successful metal ion extn. with both anionic and mol. extractants. This report discusses the authors' results in the characterization of ILs, their use in liq.-liq. extn., new concepts for metal ion sepns., and solid-state analyses.

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# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

**85. Supported ionic liquid membranes and facilitated ionic liquid membranes**

By Scovazzo, Paul; Visser, Ann E.; Davis, James H., Jr.; Rogers, Robin D.; Koval, Carl A.; DuBois, Dan L.; Noble, Richard D.

From ACS Symposium Series (2002), 818(Ionic Liquids), 69-87. DOI:10.1021/bk-2002-0818.ch006

A review. Supported liq. membranes (SLMs) use porous supports impregnated with a solvent. In SLMs, solute mols. dissolve into the membrane at the feed/membrane interface. The dissolved species diffuse through the membrane and desorb at the opposite membrane surface. The addn. of a third mobile chem. or carrier to the solvent that can reversibly bind to the dissolved species enhances the selectivity of the membrane (facilitated transport). Supported ionic liq. membranes (SILMs) have an advantage over SLMs due to the negligible loss through vaporization of room temp. ionic liqs. (RTILs) and the ability to selectively modify the properties of the membrane solvent. The review presents the proof-of-concept of SILMs, the basic principles of facilitated ionic liq. membrane (FILM) development, and discusses future needs for continued development of SILMs and FILMs. The authors also review their publications focused on the $CO_2$ sepn. from $N_2$ using RTILs with and without ionic and neutral doping compds. The SILM used in those published papers had a $CO_2$ permeability of $4.6 \times 10^{-11}$ mol/(cm$^2$ kPa s) with a selectivity over air of 29; these values are competitive with existing membrane materials. The FILMs had a 1.8 improvement in $CO_2$ permeability with a driving force of 4.6 kPa of $CO_2$.

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**86. Green chemistry and ionic liquids: Synergies and ironies**

By Holbrey, John D.; Rogers, Robin D.

From ACS Symposium Series (2002), 818(Ionic Liquids), 2-14. DOI:10.1021/bk-2002-0818.ch001

A review. Ionic liqs. are often portrayed as Green Solvents, however, "Greenness" can only be measured in the context of the overall process. Possible applications of ionic liqs. are considered to Green Chem., which focuses on the characteristics of ionic liqs. and their contributions to Green Synthesis and Sepns. processes.

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**87. Liquid-liquid extraction from ionic liquids using renewable plant-based soybean oil methyl ester as alternatives to organic solvents**

By Spear, Scott K.; Reichert, W. Matthew; Rogers, Robin D.

From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-091.

Several liq.-phase extn. technologies employing environmentally benign solvents have the potential to replace volatile org.

compds. (VOCs) in classical solvent extn. technologies. One such class of solvents emerging as novel solvent replacement for VOCs are ionic liqs. Another class of solvents made from renewable resources under investigation are transesterifed vegetable oils. Solvents made from transesterified soybean oil are suitable for the sepn. of small org. mols. in industrial and environmental applications. We report on the partitioning of several org. species between ionic liqs. and vegetable oil Me esters. The partitioning behavior of several biomols. and substituted benzenes were studied. PH dependent partitioning in these solvents is also reported.

### 88. Investigation of actinide and fission product extraction in room-temperature ionic liquids: Liquid/liquid separations and in situ solution analysis

By Visser, Ann E.; Jensen, Mark P.; Nash, Kenneth L.; Rogers, Robin D.

From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-088.

In liq./liq. sepns. systems incorporating [1-alkyl-3-methylimidazolium][$PF_6$] IL with crown ethers or octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) in the IL phase, we have successfully demonstrated an increase in distribution ratios for actinides, $Sr^{2+}$, and $Cs^{+}$ from acid solns. Early results indicate that the extractability of $Sr^{2+}$, $Cs^{+}$, and actinides in their most representative oxidn. states is different from that obsd. in conventional diluents with these extractants. EXAFS expts. have been used to gain insight into the coordination environment for $UO_2^{2+}$, $Y^{3+}$, and $Th^{4+}$ extd. with CMPO in liq./liq. systems with IL/aq. and, for comparison, dodecane/aq. systems. This presentation will highlight successful partitioning of actinides and fission products and present data to elucidate the coordination environment for the selected metal ions in IL.

### 89. Insight into the solvent properties of ionic liquids: A comparative study of solute partitioning in organic/ionic liquid biphasic systems

By Reichert, W. Matthew; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-087.

Sepn. of reaction products, starting materials, or even contaminants from ionic liq. (IL) solvents is currently complicated by a lack of data on the partitioning of solutes between an IL and an immiscible second liq. phase. In this presentation, the partitioning of org. solutes between an org. phase (e.g., hexane, TBK, and toluene) and several different ILs (hydrophobic and hydrophilic imidazolium and pyridinium salts) will be discussed. The org./IL systems will be compared to both currently used aq./org. systems and previously studied aq./IL systems.

## 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

**90. Hydrophobic n-alkyl-isoquinolinium ionic liquids: Characterization, solvent properties, and use in separations**
By Visser, Ann E.; Huddleston, Jonathan G.; Holbrey, John D.; Rogers, Robin D.
From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-021.

The broad appeal and interest in Ionic Liqs. (IL) stems from the unique properties exhibited by the liqs. and the ease in which many of their properties can be modified. Here, we have synthesized a series of IL comprised of n-alkyl-isoquinolinium cations and $PF_6^-$, $N(SO_2CF_3)_2^-$, and $N(SO_2CF_2CF_3)_2^-$ anions resulting in hydrophobic IL that have been used in liq./liq. sepns. of org. solutes. In addn. to the liq./liq. sepn. results, the phys. and chem. properties of these new IL will be discussed. A linear solvent energy relationship (LSER) and $\Delta G_{transfer}$ will be presented to illuminate the mol. interactions underlying partitioning in selected n-alkyl-isoquinolinium/water systems.

**91. Room temperature ionic liquids as alternatives to traditional organic solvents in solvents extraction**
By Visser, Ann E.; Holbrey, John D.; Rogers, Robin D.
From International Solvent Extraction Conference, Cape Town, South Africa, Mar. 17-21, 2002 (2002), 474-480.

A review with refs. on a new class of solvents comprised of low melting salts known as room temp. ionic liqs. Recent interest has focused on their unique properties as alternative solvents in synthesis and sepns. The properties of both hydrophobic and hydrophilic ionic liqs. reveal how water content, d., viscosity, surface tension, m.p., and thermal stability are affected by changes in the nature of both cation and anion. Applications for ionic liqs., with particular attention to their solvating ability and utilization as replacements for org. solvents in liq./liq. sepns., are described.

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**92. Production, refining and recycling of lightweight and reactive metals in ionic liquids**
By Wu, Banqiu; Reddy, Ramana G.; Rogers, Robin D.
From U.S. Pat. Appl. Publ. (2002), US 20020070122 A1 20020613,

Lightwt. and reactive metals can be produced from ore, refined from alloy, and recycled from metal matrix composites using electrolysis in electrolytes including an ionic liq. contg. a metal chloride at or near room temp. Low elec. energy consumption and pollutant emission, easy operation and low prodn. costs are achieved.

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### 93. On the solubilization of water with ethanol in hydrophobic hexafluorophosphate ionic liquids

By Swatloski, Richard P.; Visser, Ann E.; Reichert, W. Matthew; Broker, Grant A.; Farina, Lindsy M.; Holbrey, John D.; Rogers, Robin D.

From Green Chemistry (2002), 4(2), 81-87. DOI:10.1039/b108905f

The soly. of water in the hydrophobic 1-alkyl-3-methylimidazolium hexafluorophosphate [alkyl = Bu (I), hexyl(II), and octyl(III)] ionic liqs., can be significantly increased in the presence of ethanol as a co-solute. 1-Hexyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate are completely miscible with ethanol, and immiscible with water, whereas 1-butyl-3-methylimidazolium hexafluorophosphate is totally miscible with aq. ethanol only between 0.5-0.9 mol. fraction ethanol at 25°. At higher and lower mole fraction of ethanol, the aq. and IL components are only partially miscible and a biphasic system is obtained upon mixing equal vols. of the IL and aq. ethanol. The observation of a large range of total miscibility between water and the IL in the three-component system has important implications for purifications and sepns. from IL.

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### 94. Actinides in room temperature ionic liquids; old elements - new solvents

By Swatloski, Richard P.; Visser, Ann E.; Davis, James H., Jr.; Rogers, Robin D.

From Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002 (2002), NUCL-132.

Ionic Liqs. (ILs) are solvents composed of org. cations with either org. or inorg. anions, which typical have m.ps. less than 150-C. The ability to fine-tune an IL can provide one with an extremely efficient Task Specific IL (TSIL), suitable for a wide range of tasks, including selective sepns. of metal ions. We have successfully demonstrated this concept by the incorporation of traditional extractant mols. that function to dehydrate metal ions and increase their affinity for the extg. phase. We have employed a well-known actinide extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), to produce a TSIL that ext. $UO_2^{2+}$, $Pu^{4+}$, and $Am^{3+}$ from aq. solns. In this presentation, we will discuss the overlap of the more mature chem. of the actinides with the fledgling field of ionic liqs.

### 95. Hydrophobic ionic liquids incorporating N-alkylisoquinolinium cations and their utilization in liquid-liquid separations

By Visser, Ann E.; Holbrey, John D.; Rogers, Robin D.

From Chemical Communications (Cambridge, United Kingdom) (2001), (23), 2484-2485. DOI:10.1039/b109340c

The first examples of Room Temp. Ionic Liqs. (RTIL) contg. fused polycyclic N-alkylisoquinolinium cations ([$C_n$isoq]$^+$) in combination with the bis(perfluoroethylsulfonyl)imide anion ([BETI]$^-$) have been synthesized, characterized, and utilized in liq.-liq. partitioning from water; these salts have unexpectedly low m.ps. and give high distribution ratios for arom. solutes, esp.

chlorobenzenes, between the RTIL and water.

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**96. Non-sugar products from sugarcane for the new millennium: green pathways to a carbohydrate-economy?**

By Rogers, Robin D.; Spear, Scott K.; Swatloski, Richard P.; Reichert, W. Matthew; Godshall, Mary An; Johnson, Tere Pi; Moens, Luc

From Publication of Technical Papers and Proceedings of the Annual Meeting of Sugar Industry Technologists (2001), 60, 291-301.

A review. Green Chem. focuses on interdisciplinary activities related to waste minimization, the development of green manufg. processes, and the minimization of environmental and manufg. costs. Increasingly, new technologies, new laws, and public awareness are ushering in plant matter as the new material base for the new millennium, the so-called "carbohydrate economy.". Carbohydrates can be converted into chems., energy, textiles, building materials, paper, and many other industrial products, but a major barrier to utilization is the availability of cost effective, clean sepn. and processing technologies. The nascent field of ionic liqs. as solvents offers a unique opportunity to investigate such new technologies from several perspectives having the same overall objectives.

**97. Solvation of 1-butyl-3-methylimidazolium hexafluorophosphate in aqueous ethanol-a green solution for dissolving 'hydrophobic' ionic liquids**

By Swatloski, Richard P.; Visser, Ann E.; Reichert, W. Matthew; Broker, Grant A.; Farina, Lindsy M.; Holbrey, John D.; Rogers, Robin D.

From Chemical Communications (Cambridge, United Kingdom) (2001), (20), 2070-2071. DOI:10.1039/b106601n

The relatively hydrophobic ionic liq. 1-butyl-3-methylimidazolium hexafluorophosphate has been found to be totally miscible with aq. ethanol between 0.5 and 0.9 mol fraction ethanol, whereas the ionic liq. is only partially miscible with either pure water or abs. ethanol. The ability to dissolve 1-butyl-3-methylimidazolium hexafluorophosphate in a 'green' aq. solvent system has important implications for cleaning, purifn., and sepns. using ionic liqs.

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**98. Anionic extractants for metal ion partitioning in room temperature ionic liquids**

By Visser, Ann E.; Swatloski, Richard P.; Reichert, W. Matthew; Rogers, Robin D.

From Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), IEC-026.

# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

We have used [1-alkyl-3-methylimidazolium][$PF_6$] Room Temp. Ionic Liqs. (RTIL) as alternatives to traditional org. solvents in liq./liq. sepns. of metal ions. In the absence of extractants, most metal ions remain in the aq. phase, testament to their highly hydrated nature. Org. metal ion extractants have often been employed to rearrange the hydration sphere of the metal ions and perform well in IL, but here we will demonstrate the effect of complexing anions (e.g., halides and pseudohalides) on the partitioning of metal ions in RTIL-based liq./liq. systems.

### 99. Derivatization of chitin in room temperature ionic liquids

By Reichert, W. Matthew; Visser, Ann E.; Swatloski, Richard P.; Spear, Scott K.; Rogers, Robin D.

From Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), IEC-025.

Biorenewables are gaining attention as replacements for petroleum-based products, due to their favorable properties and natural abundance. Efficient processing and sepns. are usually the key steps preventing economic processing of biomass. Chitin is the world's second most abundant biopolymer, behind cellulose, and in this presentation, we will demonstrate the use of room temp. ionic liqs. as solvents in the chem. modification of chitin. In addn., the use of ionic liqs. for value added processing (e.g., decolorization of chitin) will be discussed.

### 100. Solubility determination of organic and inorganic compounds in hydrophobic and hydrophilic room temperature ionic liquids

By Rogers, Robin D.; Broker, Grant A.; Klingshirn, Marc A.; Holbrey, John D.

From Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), IEC-023.

Room Temp. Ionic Liqs. (RTIL) are receiving much attention recently due to their potential applications in sepn. science and their ability to replace many different solvents in chem. syntheses. One potential factor that may influence their use as solvents is their ability to solvate both org. and inorg. compds. Such properties are important in many areas of chem. including inorg. and org. synthesis as well as in the area of coordination chem. Here we present a method that utilizes ion chromatog. to det. the soly. limits of various org. and inorg. compds. in both hydrophilic and hydrophobic ionic liqs. The methodol. and soly. limits for several solutes in various ionic liqs. will be discussed.

### 101. Synthesis and characterization of 1-alkyl-3-methylimidazolium bromide ionic liquids

By Rogers, Robin D.; Betts, Herbert A.; Swatloski, Richard P.; Visser, Ann E.; Reichert, W. Matthew
From Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), IEC-020.

Ionic Liqs. (IL) have been gaining considerable attention for their potential use as green solvents. In our labs., we have utilized IL as VOC replacements in liq./liq. and solid/liq. sepns. A barrier assocd. with IL is the lack of phys. property data. Several [1-R-3-methylimidazolium]$^+$[Br]$^-$ (where R=n-alkyl $C_4$-$C_{10}$) ionic liqs. have been prepd. and characterized in our labs. Results from structural studies, as well as important phys. properties will be discussed. This research is sponsored by the U.S. Environmental Protection Agency, Technologies for a Sustainable Environment Program.

### 102. Liquid/liquid extraction of metal ions in room temperature ionic liquids

By Visser, Ann E.; Swatloski, Richard P.; Griffin, Scott T.; Hartman, Deborah H.; Rogers, Robin D.
From Separation Science and Technology (2001), 36(5 & 6), 785-804. DOI:10.1081/SS-100103620

The search for more environmentally-friendly reaction media has prompted the development of a wide array of alternative systems that will sustain biphasic sepns. with aq. solns. without the use of volatile org. compds. (VOCs). We have begun to employ Room Temp. Ionic Liqs. (RTIL), specifically 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim][$PF_6$]), as VOC replacements in liq./liq. sepns. of metal ions from aq. solns. Here we show that the partitioning of metal ions in these novel biphasic systems is consistent with traditional liq./liq. sepns.: the metal ion affinity for the hydrophobic phase necessitates the presence of an extractant. In this report we explore the application of well-known extractants, i.e. 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolylazo)-2-naphthol (TAN) and inorg. modifiers, namely $CN^-$, $OCN^-$, $SCN^-$, and halides for partitioning a variety of metal cations between [$C_4$mim][$PF_6$] or [$C_6$mim][$PF_6$] and an aq. phase. PAN and TAN show pH dependent extn. of $Cd^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Fe^{3+}$ where their partitioning to the RTIL increases at least 2 orders of magnitude from pH 1 to 13. The effect of the halides on the partitioning of $Hg^{2+}$ complexes increases $F^- < Cl^- < Br^- < I^-$. Pseudohalides, esp. $SCN^-$, had the greatest effect on enhancing the partitioning of $Hg^{2+}$ to the RTIL, whereas $CN^-$ and $OCN^-$ provided little benefit for the extn. of any of the metal ions examd.

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### 103. Ionic liquids as benign solvents for extraction of astaxanthin and solubilization of chitin

By Spear, Scott K.; Reichert, W. Matthew; Swatloski, Richard P.; Rogers, Robin D.
From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-412.

Research priorities laid out in the Vision 2020 Technol. Roadmap for Renewable Resources include biosepns. The sepn. processing of biomass into a series of distinct chems. poses many challenges because of the high diversity of chem. components present in living materials. Ionic liqs. are an interesting new class of solvents exhibiting solvating abilities of biol. materials and biomoecules. This presentation will focus on our exploratory progress to study ionic liqs. as novel solvent systems for the extn.

of astaxanthin and solubilization of chitin from decalcinated shrimp shells.

**104. Green chemistry, the carbohydrate economy, and ionic liquids: Compatible goals, compatible chemistries?**
By Rogers, Robin D.; Godshall, Mary An; Johnson, Tere Pi; Moens, Luc; Spear, Scott K.
From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-347.

Green Chem. focuses on interdisciplinary activities related to waste minimization, the development of green manufg. processes, and the minimization of environmental and manufg. costs. Increasingly, new technologies, new laws, and public awareness are ushering in plant matter as the new material base for the new millennium, the so-called "carbohydrate economy." Carbohydrates can be converted into chems., energy, textiles, building materials, paper, and many other industrial products, but a major barrier to utilization is the availability of cost effective, clean sepn. and processing technologies. The nascent field of ionic liqs. as solvents offers a unique opportunity to investigate such new technologies from several perspectives having the same overall objectives. This presentation will discuss our new efforts to apply ionic liqs. to the development of new products from sugar cane.

**105. Applications of room temperature ionic liquids: Actinide separations**
By Rogers, Robin D.; Visser, Ann E.; Swatloski, Richard P.; Griffin, Scott T.; Reichert, W. Matthew
From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-192.

Room Temp. Ionic Liqs. (RTIL) are liqs. composed of org. cations and either org. or inorg. anions that remain liq. at room temp. Of the anions that can be incorporated to produce water immiscible RTIL, we have used $PF_6^-$ and $N(CF_3SO_2)_2^-$ in combination with various [1-alkyl-3-methylimidazolium] cations to replace traditional org. solvents in liq./liq. extn. of actinides. Since the highly hydrated $UO_2^{2+}$, $Pu^{4+}$, and $Am^{3+}$ remain in the aq. phase, well-known metal ion extractants such as CMPO can be incorporated to increase the affinity of the metal ions for the RTIL phase. This presentation will explore the effect of various metal ion extractants, as well as different ionic liq. systems on actinide extn.

**106. Supported ionic liquid membranes and facilitated ionic liquid membranes**
By Scovazzo, Paul; Visser, Ann E.; Davis, James H., Jr.; Rogers, Robin D.; Koval, Carl; Noble, Richard D.
From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-054.

Supported Liq. Membranes (SLM's) use porous supports whose pores are impregnated with a solvent. In SLM's, solute mols.

dissolve into the membrane at the feed/membrane interface. The dissolved species diffuse through the membrane and desorb at the opposite membrane surface. The addn. of a third mobile chem. or carrier to the solvent that can reversibly bind to the dissolved species enhances the selectivity of the membrane (facilitated transport). The disadvantages of SLM's are the loss of solvent via volatilization and the loading limits (soly.) on complexing agents in the solvent that limits the obtainable flux rate. Unlike the solvents currently used in SLM's, Room Temp. Ionic Liq. (RTIL) properties may be adjusted via chem. alteration of the ions to produce "designer solvents" for a specific membrane application. The potential exists for complexing agents to be one of the ions giving a mole fraction loading of a complexing agent in the solvent of one, much greater than the loadings in std. systems. Supported Ionic Liq. Membranes (SILM) also have an advantage over SLM's due to the RTIL's negligible loss through vaporization. Our initial research focus is on the $CO_2$ sepn. from $N_2$ using RTIL's with and without ionic and non-ionic doping compds. We have proven the concept of SILM's. In addn., we are detg. the basic principles for developing working Facilitated Ionic Liq. Membranes (FILM's). Our paper presents the proof-of-concept of SILM's, the basic principles of FILM development, and discusses future needs for continued development of SILM's and FILM's.

**107. Supported ionic liquid membranes and facilitated ionic liquid membranes**

By Scovazzo, Paul; Visser, Ann E.; Davis, James H., Jr.; Rogers, Robin D.; Noble, Richard D.; Koval, Carl

From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-028.

Supported Liq. Membranes (SLM's) use porous supports whose pores are impregnated with a solvent. In SLM's, solute mols. dissolve into the membrane at the feed/membrane interface. The dissolved species diffuse through the membrane and desorb at the opposite membrane surface. The addn. of a third mobile chem. or carrier to the solvent that can reversibly bind to the dissolved species enhances the selectivity of the membrane (facilitated transport). The disadvantages of SLM's are the loss of solvent via volatilization and the loading limits (soly.) on complexing agents in the solvent that limits the obtainable flux rate. Unlike the solvents currently used in SLM's, Room Temp. Ionic Liq. (RTIL) properties may be adjusted via chem. alteration of the ions to produce "designer solvents" for a specific membrane application. The potential exists for complexing agents to be one of the ions giving a mole fraction loading of a complexing agent in the solvent of one, much greater than the loadings in std. systems. Supported Ionic Liq. Membranes (SILM) also have an advantage over SLM's due to the RTIL's negligible loss through vaporization. Our initial research focus is on the CO2 sepn. from N2 using RTIL's with and without ionic and non-ionic doping compds. We have proven the concept of SILM's. In addn. we are detg. the basic principles for developing working Facilitated Ionic Liq. Membranes (FILM's). Our paper presents the proof-of-concept of SILM's, the basic principles of FILM development, and discusses future needs for continued development of SILM's and FILM's.

**108. Green chemistry and ionic liquids: Synergies and ironies**

By Rogers, Robin D.

From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-001.

One of Society's biggest challenges as we enter the new millennium, is the elimination of industrial pollution. Perhaps as a result of the compelling need for industry to consider the reengineering of entire processes, ionic liqs. have begun to receive worldwide academic and industrial attention as VOC replacements in catalysis, synthesis, and sepns. processes, in addn. to their well known role in electrochem. Combined with green chem., a new paradigm in thinking about synthesis in general, ionic liqs. provide a unique opportunity for science/engineering/business to work together from the beginning of a field's development and thus lead more quickly to innovative environmentally- and economically-sustainable industrial processes. This presentation will discuss the role of green chem. in the ionic liq. research agenda.

### 109. Green separation science and technology: replacement of volatile organic compounds in industrial scale liquid-liquid or chromatographic separations

By Spear, Scott K.; Visser, Ann E.; Willauer, Heather D.; Swatloski, Richard P.; Griffin, Scott T.; Huddleston, Jonathan G.; Rogers, Robin D.

From ACS Symposium Series (2001), 766(Green Engineering), 206-221. DOI:10.1021/bk-2001-0766.ch016

One area of opportunity for new chem. science and engineering technol. which will help meet the goals of the U.S. Chem. Industry's Technol. Vision 2020 is the development of new sepns. technologies that eliminate the use of flammable, toxic VOCs as industrial solvents. Alternative technologies currently under investigation in the labs. include those based on the use of water sol. polyethylene glycol polymers in either liq./liq. (aq. biphasic systems - ABS) or chromatog. (aq. biphasic extn. chromatog. resins - ABEC) sepns., and those based on air and moisture stable, water immiscible room temp. ionic liqs. (RTIL). The ABS and ABEC applications are highlighted with two patented technologies for pertechnetate sepn. including: (a) applications in radiopharmacy where the use of cleaner neutron-irradiated isotopes rather than fission-produced isotopes is possible, and (b) applications in nuclear waste remediation where redn. of secondary waste streams produced by conventional technologies are anticipated. The potential and challenges for using the much less studied RTIL in novel sepns. are also discussed. Within a new paradigm of pollution prevention and with industry participation, it is anticipated that a tool-box approach to green sepn. science & technol. leads to new technologies which do not utilize VOCs.

### 110. Crystallographic characterization of solid-state analogs of room temperature ionic liquid solvents.

By Swatloski, Richard P.; Visser, Ann E.; Reichert, W. Matthew; Rogers, Robin D.

From Abstracts of Papers, 220th ACS National Meeting, Washington, DC, United States, August 20-24, 2000 (2000), IEC-041.

Room Temp. Ionic Liqs. (RTIL) have been gaining considerable attention for their potential use as green solvents. In our labs., we have utilized both RTIL and low melting analogs as VOC replacements in liq./liq. and solid/liq. sepns. We are currently investigating the solid-state structures of low melting analogs to gain insight into the weak intermol. forces responsible for their unique behavior, and to be able to predict their phys. properties. Several [1-R-3-methylimidazolium]$^+$[X]$^-$ (where R=n-alkyl and X=PF$_6^-$ or BF$_4^-$) ionic liqs. have been prepd. and crystallog. characterized in our labs. Results from the structural studies, as well as important phys. properties and partitioning data will be discussed. This research is sponsored by the U.S. Environmental Protection Agency, Technologies for a Sustainable Environment Program.

**111. Traditional Extractants in Nontraditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids**

By Visser, Ann E.; Swatloski, Richard P.; Reichert, W. Matthew; Griffin, Scott T.; Rogers, Robin D.

From Industrial & Engineering Chemistry Research (2000), 39(10), 3596-3604. DOI:10.1021/ie000426m

The crown ethers - 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DCH18C6), 4,4'-(5')-di-(tert-butylcyclohexano)-18-crown-6 (Dtb18C6) - were dissolved in 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim][$PF_6$], n = 4, 6, 8) room-temp. ionic liqs. (RTILs) and studied for the extn. of $Na^+$, $Cs^+$, and $Sr^{2+}$ from aq. solns. In the absence of extractant, the distribution ratios for the metal ions indicate a strong preference for the aq. phase. With the crown ethers as extractants in RTIL-based liq./liq. sepns., the resulting metal ion partitioning depends on the hydrophobicity of the crown ether and also on the compn. of the aq. phase (e.g., concn. of $HNO_3$ vs $Al(NO_3)_3$). Aq. solns. of HCl, $Na_3$ citrate, $NaNO_3$, and $HNO_3$ (the latter at low concns.) decrease the metal ion distribution ratios and also decrease the water content of the RTIL phase. High concns. of $HNO_3$ decomp. $PF_6^-$ and increase both the water content and the water soly. of the RTIL phase. Highly hydrated salts such as $Al(NO_3)_3$ and $LiNO_3$ salt out both the RTIL ions and the crown ethers; thus, when the aq. phase contains $Al(NO_3)_3$, the trend more closely resembles traditional solvent extn. behavior where $D_{Sr} > D_{Cs}$ and the most hydrophobic extg. phase produces the highest partitioning. When [$C_8$mim][$PF_6$] is used as the extg. phase, the metal ions can be loaded from $Al(NO_3)_3$ and stripped using water. Dtb18C6 forms 1:1 complexes with $Cs^+$ and $Sr^{2+}$ and also yields the highest distribution ratios out of the three crowns examd. In comparison to traditional solvent extn. behavior, the metal ion partitioning in these systems exhibits exceptional behavior and, in certain instances, suggests a complicated partitioning mechanism, which necessitates a more thorough understanding of RTILs as solvents before interpretation of the results.

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**112. Crown ethers as extractants for group I and II metal ions in room-temperature ionic liquids.**

By Rogers, Robin D.; Visser, Ann E.; Swatloski, Richard P.; Griffin, Scott T.

From Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), IEC-086.

The partitioning of crown ethers and their assocd. behavior as metal ion extractants has been studied in Room Temp. Ionic Liqs. (RTIL). Removal of alkali and alk. earth metals, esp. $Sr^{2+}$ and $Cs^+$, from aq. solns. has focused on crown ethers as metal ion complexants in traditional liq./liq. sepns. employing VOCs as the extg. phase. In liq./liq. extn., RTIL have demonstrated their utility as novel solvent alternatives to VOCs, yet are hydrophobic and require metal ion extractants to increase the partitioning of metal ions to that phase. We will discuss the behavior of crown ethers in the RTIL systems and their effect on the partitioning of hard metal ions.

**113. Investigation of room-temperature ionic liquids via X-ray crystallographic characterization of low-melting analogs.**
By Rogers, Robin D.; Visser, Ann E.; Reichert, W. Mathew; Swatloski, Richard P.
From Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), IEC-084.

Room Temp. Ionic Liqs. (RTIL) have been gaining considerable attention for their potential use as green solvents. In our labs., we have utilized both RTIL and low melting analogs as VOC replacements in liq./liq. and solid/liq. extns. Investigation of the solid state structure for low melting salts reveals some interesting clues to their behavior as solvents in liq. form. Several [1-R-3-methylimidazolium]$^+$[X]$^-$ (where R=n-alkyl and X=$PF_6^-$ or $BF_4^-$) ionic liqs. have been prepd. and crystallog. characterized in our labs. Results from the structural studies, as well as liq./liq. extn. data at elevated temps., and other sepn. strategies will be discussed.

**114. Green chemistry and engineering in separations science.**
By Rogers, Robin D.; Visser, Ann E.; Huddleston, Jonathan G.; Swatloski, Richard P.; Broker, Grant A.; Willauer, Heather D.
From Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), IEC-025.

Green Chem. & Engineering aims to eliminate industrial pollution by the design of new products or processes which are inherently non-polluting. One area of opportunity for new chem. science and engineering technol. which will help meet this goal is the development of new sepns. technologies that eliminate the use of flammable, toxic VOCs as solvents. Used in conjunction with, or instead of appropriate current manufg. processes, such technologies would help to prevent pollution and increase safety. This presentation will discuss the role of green chem. in the development of sustainable industrial development and the relationship of this approach with new sepns. technologies such as the use of room temp. ionic liqs., wholly aq.-based sepns., and crystal engineering of porous solids.

**115. Room-temperature ionic liquids as alternatives to volatile organic solvents in liquid/liquid extraction.**
By Rogers, Robin D.; Visser, Ann E.; Swatloski, Richard P.; Hartman, Deborah H.
From Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000), IEC-003.

The use of Room Temp. Ionic Liqs. (RTIL) as alternatives to VOCs in liq./liq. sepns. has encouraged research into methods to control changes in their solvent properties. For example, we have shown that increasing the length of the alkyl chain from Bu to decyl in [1-alkyl-3-methylimidazolium][PF6] changes the hydrophobicity and also increases the m.p. sufficiently such that the decyl analog is a solid that melts just above room temp. Conversely, using Bu derivs. of various alkylpyridine cations in conjunction with the PF6 anion produces RTIL with different phys. properties while maintaining the characteristics necessary to function in liq./liq. sepns. This presentation will discuss the characteristics of various RTIL as a function of structural changes in both cation and anion, and the partitioning of org. and inorg. solutes in those systems.

**116. pH-Dependent partitioning in room temperature ionic liquids**

By Visser, Ann E.; Swatloski, Richard P.; Rogers, Robin D.

From Green Chemistry (2000), 2(1), 1-4. DOI:10.1039/a908888a

Room temp. ionic liqs. (RTILs) are emerging as novel solvent replacement for volatile org. compds. (VOCs) traditionally used in liq.-liq. sepns., however, the basic science involved with fully characterizing these systems (phys. properties, solubilities, partitioning of solutes, water miscibilities, etc.) may be artificially holding back utilization of the green solvents. By demonstrating the compatibility of RTILs with fundamental principles used in solvent extn., sepn. scientists may use the considerable expertise developed in solvent extn. techniques for the sepn. of RTILs. Here, by using a simple indicator dye, thymol blue, reversible pH-dependent liq.-liq. partitioning, the use of $CO_2$ and $NH_3$ to activate the proton switching of phase preference, utilization of structural variation in the RTILs ions to fine-tune partitioning behavior, and possibility of solid-liq. sepns. with low melting ionic liqs. are demonstrated.

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**117. Metal ion separations in room temperature ionic liquids: potential replacements for volatile organic diluents**

By Rogers, Robin D.; Visser, Ann E.; Swatloski, Richard P.; Hartman, Deborah H.

Edited By:Liddell, KNona C

From Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing, Proceedings of a Symposium, Kahuku, Hawaii, June 13-18, 1999 (1999), 139-147.

Room temp. ionic liqs. (RTIL) can replace certain traditional org. solvents in liq./liq. extn. of metal ions from aq. systems. The very low vapor pressure and non-flammable nature of RTIL warrant consideration of these neoteric solvents for new processing technologies which will reduce pollution, increase safety, and lower costs. Metal ion sepns. in RTIL, however, will typically require the use of an extractant and research is needed to identify suitable selective extractants which have appreciable soly. in the RTIL and low soly. in the aq. phase. Choice of extractant should also take into account the toxicity, expense, and disposal of the ligand.

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# 525 Solutions, Inc. Publications Related to Separations with Ionic Liquids

**118. Environmentally benign liquid/liquid extraction media for metal ion separations: Aqueous biphasic systems and room temperature ionic liquids**

By Rogers, Robin D.; Visser, Ann E.; Swatloski, Richard P.; Hartman, Deborah H.; Griffin, Scott. T.

From Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21-25 (1999), I&EC-109.

We are currently investigating the utility of liq./liq. systems for sepns. which do not use volatile org. compds. as diluents. Aq. biphasic systems (ABS) are formed when water sol. polymers and certain inorg. salts are mixed in specific concns. and together form the components of two immiscible aq. layers. (Immobilizing the polymer on a solid support allows similar chromatog. (aq. biphasic extn. chromatog. or ABEC) sepns. Room temp. ionic liqs. (RTIL) are hydrophobic liqs. composed entirely of ions and resemble the ionic melts produced by heating metallic salts to high temps. This presentation will discuss current results on partitioning of pertechnetate, perrhenate, iodide, and metal cations. Properties of suitable metal extractants for these systems will also be discussed.

**119. Room temperature ionic liquids for liquid/liquid extraction of dyes from aqueous media**

By Visser, Ann E.; Hartman, Deborah H.; Huddleston, Jonathan G.; Rogers, Robin D.

From Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21-25 (1999), I&EC-041.

Room temp. ionic liqs. (RTIL), composed entirely of ions and thus closely resembling ionic melts produced by heating metallic salts to high temps., have been demonstrated to be effective in liq./liq. sepns. of arom. mols. from aq. solns. An important characteristic of RTIL is their ability to solvate a large amt. of org. material with minimal water uptake. Common environmental issues facing the textile or pigment industries include effluents from manufg. processes which inevitably contain some raw material or product. Pursuing alternative sepn. processes, such as RTIL, may provide both insight to the general behavior of these novel systems and also new liq./liq. sepns. technologies which eliminate the use of VOCs.

**120. Odd-even effect on the formation of aqueous biphasic systems formed by 1-alkyl-3-methylimidazolium chloride ionic liquids and salts**

By Belchior Diana C V; Sintra Tania E; Carvalho Pedro J; Ventura Sonia P M; Coutinho Joao A P; Freire Mara G; Soromenho Mario R C; Esperanca Jose M S S; Rogers Robin D; Rogers Robin D

From The Journal of chemical physics (2018), 148(19).

This work provides a comprehensive evaluation of the effect of the cation alkyl side chain length of the 1-alkyl-3-methylimidazolium chloride series ([C n C1im]Cl, n = 2-14) of ionic liquids (ILs) on their capability to form aqueous biphasic systems (ABSs) with salts and self-aggregation derived properties. The liquid-liquid phase behavior of ternary systems composed of [C n C1im]Cl, water, and K3PO4 or K2CO3 and the respective Setschenow salting-out coefficients (ks ), a quantitative measure of the two-phase formation ability, were determined. An odd-even effect in the ks values along the number of methylene groups of the longest IL cation alkyl side chain was identified for the ABS formed by K2CO3, a weaker salting-out agent where the phenomenon is clearly identified. In general, cations with even alkyl side chains, being likely to display higher molar volumes, are more easily salted-out and thus more prone to undergo phase separation. The odd-even effect in the ks values is, however, more significant in ILs up to n = 6, where the nanostructuration/nanosegregation of ILs plays a less relevant role. Still, with the [C n C1im]Cl (n = 7-14) series of ILs, an odd-even effect was also identified in the ILs' ionization degree, molar conductivity, and conductivity at infinite dilution. In summary, it is shown here that the ILs' odd-even effect occurs in IL aqueous solutions and not just in neat ILs, an already well-established phenomenon occurring in a series of ILs' properties described as a result of the orientation of the terminal methyl groups to the imidazolium ring cation and consequent effect in the ILs' cohesive energy.

### 121. Efficient dehydration and recovery of ionic liquid after lignocellulosic processing using pervaporation

By Sun Jian; Shi Jian; Murthy Konda N V S N; Liu Dajiang; Dutta Tanmoy; Simmons Blake A; Singh Seema; Sun Jian; Shi Jian; Liu Dajiang; et al

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BACKGROUND: Biomass pretreatment using certain ionic liquids (ILs) is very efficient, generally producing a substrate that is amenable to saccharification with fermentable sugar yields approaching theoretical limits. Although promising, several challenges must be addressed before an IL pretreatment technology can become commercially viable. One of the most significant challenges is the affordable and scalable recovery and recycle of the IL itself. Pervaporation (PV) is a highly selective and scalable membrane separation process for quantitatively recovering volatile solutes or solvents directly from non-volatile solvents that could prove more versatile for IL dehydration. RESULTS: We evaluated a commercially available PV system for IL dehydration and recycling as part of an integrated IL pretreatment process using 1-ethyl-3-methylimidazolium acetate ([C2C1Im][OAc]) that has been proven to be very effective as a biomass pretreatment solvent. Separation factors as high as 1500 were observed. We demonstrate that >99.9 wt% [C2C1Im][OAc] can be recovered from aqueous solution (≤20 wt% IL) and recycled five times. A preliminary technoeconomic analysis validated the promising role of PV in improving overall biorefinery process economics, especially in the case where other IL recovery technologies might lead to significant losses. CONCLUSIONS: These findings establish the foundation for further development of PV as an effective method of recovering and recycling ILs using a commercially viable process technology.