Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Room Temperature Ionic Liquids for Separating Organics from Produced Water

J. McFarlane[a]; W. B. Ridenour[a]; H. Luo[a]; R. D. Hunt[a]; D. W. DePaoli[a]; R. X. Ren[b]
[a] Separations and Materials Research Group, Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA [b] Department of Chemistry, Wesleyan University, Middletown, CT, USA

To cite this Article McFarlane, J. , Ridenour, W. B. , Luo, H. , Hunt, R. D. , DePaoli, D. W. and Ren, R. X.(2005) 'Room Temperature Ionic Liquids for Separating Organics from Produced Water', Separation Science and Technology, 40: 6, 1245 — 1265
To link to this Article: DOI: 10.1081/SS-200052807
URL: http://dx.doi.org/10.1081/SS-200052807

Separation Science and Technology, 40: 1245–1265, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200052807

Room Temperature Ionic Liquids for Separating Organics from Produced Water

J. McFarlane, W. B. Ridenour, H. Luo, R. D. Hunt, and D. W. DePaoli
Separations and Materials Research Group, Nuclear Science and
Technology Division, Oak Ridge National Laboratory,
Oak Ridge, TN, USA

R. X. Ren
Department of Chemistry, Wesleyan University, Middletown, CT, USA

Abstract: The distribution of polar organic compounds typical of water contaminants (organic acids, alcohols, and aromatic compounds) associated with oil and gas production was measured between water and nine hydrophobic, room-temperature ionic liquids. The ionic liquids used in this study were 1-butyl-3-methylimidazolium bistrifluoromethanesulfonylimide, 1-hexyl-3-methylimidazolium bistrifluoromethanesulfonylimide, 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide, 1-butyl-3-methylimidazolium hexafluorophosphate, trihexyltetradecylphosphonium bistrifluoromethanesulfonylimide, 1-butyl-1-methyl-pyrrolidinium bistrifluoromethanesulfonylimide, trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecylphosphonium methanesulfonate. Sensitivity of the distribution coefficients to salinity, temperature, concentration, and pH was investigated. Partitioning into the ionic liquid varied considerably. Acetic acid did not significantly partition into the ionic liquid phase, except for the sulfonate-anion ionic liquids. The solubility of hexanoic acid in the ionic liquids was significant, where uptake of the protonated form from aqueous solution was observed for all of the ionic liquids studied. Other organics also showed high distribution coefficients, up to several hundred in the case of toluene and 1-nonanol. The distribution coefficients for toluene, 1-nonanol, cyclohexanone, and hexanoic acid were independent of ionic liquid-to-water ratio over the range

Received 20 September 2004, Accepted 9 January 2005

Address correspondence to J. McFarlane, Separations and Materials Research Group, Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181, USA. Fax: 865-241-4829; E-mail: mcfarlanej@ornl.gov

from 0.02 to 1.0. The ionic liquids showed a large capacity for some organics, with solubilities measured above $100\,\mathrm{g \cdot L^{-1}}$. Regeneration of the ionic liquids by rinsing and heating was studied, with mixed success. These experiments show that certain hydrophobic ionic liquids do have an affinity for organic contaminants in aqueous solution. However, practical application of the ionic liquids tested for detection or removal of selected water-soluble organics from the aqueous waste streams appears to be limited by the small, but significant, solubility of the ionic liquids in the aqueous phase and by difficulty in solvent regeneration. Further work aimed at determination of ionic liquids that dissolve target compounds and are nonhazardous and less soluble in aqueous solutions is recommended.

Keywords: Produced water, ionic liquids, liquid phase separation, water-soluble organics

INTRODUCTION

Oil and gas production usually involves pumping of large amounts of contaminated water along with the hydrocarbon phase, termed "produced water" by the industry (1). This high-volume waste stream, on the order of a trillion gallons of water a year, is subject to National Pollution Discharge Elimination System (NPDES) permits. For Gulf of Mexico wells, the Environmental Protection Agency (EPA) limit on oil and grease content in produced water discharged in the ocean is a daily maximum of $42\,\mathrm{mg \cdot L^{-1}}$ and a monthly average of no more than $29\,\mathrm{mg \cdot L^{-1}}$ (2). Wastewater is analyzed for total petroleum hydrocarbon content, an analysis that not only measures the less-soluble paraffinic hydrocarbons, but also soluble polar molecules: phenols and organic acids (3). There is a variety of methods for removal of trace amounts of hydrocarbon, but physical methods (i.e., filtration) are subject to fouling, and chemical methods (i.e., acidification) can be defeated by the chemistry of the oil (4). It would be desirable to have improved treatment as well as on-line sampling of water-soluble organics in produced water so that a problem with separation of the organics could be detected quickly, should it arise, thus lessening any impact to the environment. This work investigates the potential of room temperature ionic liquids for application in the analysis of organics and remediation of produced water.

Ionic liquids that are hydrophobic and are stable in the presence of air and water are possible candidate solvents for liquid-liquid extraction (5). Most work has been aimed at extraction of metal ions, with the ionic liquid replacing conventional organic diluents. For instance, Wei and coworkers (6) investigated the extraction of metal ions from aqueous solution—including measurement of the aqueous solubility of $[\mathrm{C_4mim}][\mathrm{PF_6}]$ (1 to $8\,\mathrm{mg \cdot mL^{-1}}$). The partitioning of metal ions from aqueous solution into ionic liquids containing extractants [e.g., crown ethers, calixarenes, or 1-(pyridylazo)-2-napthol] far exceeds that obtainable with any conventional solvent (7–10). The ultimate separating agent, a task-specific solvent, can be formed by incorporating a metal ion–ligating functional group into one of the ions of an ionic liquid, such that it functions as both a hydrophobic solvent and an extracting agent (11–13). Hydrophobic ionic liquids have also been used to extract organic compounds from aqueous solution (14, 15), and have been evaluated for use as the stationary phase in chromatographic analysis (16). The pH-dependent distribution of certain solutes (e.g., organic acids) may provide a route for reverse extraction (8, 14, 17).

After well-head separation of the aqueous phase from the hydrocarbon phase, produced water is expected to contain a low concentration of organics (18), and, hence, a sensitive method of analysis is required for online monitoring. One such technique may be provided by uptake on a quartz crystal microbalance (19–22). A quartz oscillator is covered with a film onto which the analyte can dissolve, and a change in frequency corresponds to the mass of the substance that is taken up onto the microbalance. Classes of solvents that promise to have good properties for film formation include ionic liquids because of their unique physical and chemical properties (5), which are determined by the choice of the anion and cation, allowing them, in principle, to be optimized for a particular application (15, 23). For instance, the ionic liquids studied here have high viscosities, which is an advantage in this research, as they are more likely to form a stable film on the quartz crystal microbalance (24). Although currently expensive to synthesize, ionic liquids may be recycled and used repeatedly in a cost-effective process.

In spite of their high cost, the promise of ionic liquids means that their use is being actively investigated for many industrial and environmental applications. In addition to waste remediation (25), other applications of ionic liquids in oil production have been explored elsewhere, such as in the extraction of hydrocarbons from oil shales (26).

The experiment described in this paper tested the effectiveness of nine different ionic liquids in removing organics from the aqueous phase as a function of temperature, salinity, and pH. The organic compounds selected were representative of various classes of water-soluble organics that have been shown to contaminate produced water. Saturation behavior and regeneration were also investigated. The effect on organic removal by addition of a diluent to the ionic liquid phase was also examined, as this has been shown to enhance organic acid uptake in studies with amine/aqueous systems (27).

Demonstration of organic solubility in selected ionic liquids is the first step into the development of treatment systems and online sensors for produced water contamination. The results of the current experiments were compared to octanol-water coefficients available in the literature (28), to assist with prediction of the uptake of organics from water into an immiscible ionic liquid phase.

EXPERIMENTAL

The uptake of organics into the ionic liquid from the aqueous phase was measured using liquid-liquid contact experiments. Nine different ionic liquids were selected for investigation: 1-butyl-3-methylimidazolium bistrifluoromethanesulfonylimide–[C_4mim][NTf_2], 1-hexyl-3-methylimidazolium bistrifluoromethanesulfonylimide–[C_6mim][NTf_2], 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide–[C_8mim][NTf_2], and 1-butyl-3-methylimidazolium hexafluorophosphate–[C_4mim][PF_6], were synthesized at Oak Ridge National Laboratory (ORNL) (29). Trihexyltetradecylphosphonium bistrifluoromethanesulfonylimide–[$P_{666,14}$][NTf_2] and 1-butyl-1-methylpyrrolidinium bistrifluoromethanesulfonylimide–[C_4mPm][NTf_2] were purchased from Merck. Trihexyltetradecylphosphonium dodecylbenzenesulfonate–[$P_{666,14}$][LABS], tributyltetradecylphosphonium dodecylbenzenesulfonate–[$P_{444,14}$][LABS], and trihexyltetradecylphosphonium methanesulfonate–[$P_{666,14}$][OMS] were synthesized by Rex Ren (Wesleyan University, Connecticut) (30, 31). The affinity to water was checked for most of these ionic liquids following a 60-min contact between 1 mL of ionic liquid and 10 mL of deionized H_2O in a vibrating mixer. Karl-Fischer titration (Brinkman 652 KF-Coulometer) was used to determine the water solubility in the ionic liquid, and ultra violet (UV) spectroscopy (on a Varian Cary 5000 UV-Vis-NIR spectrophotometer) was used to determine the ionic liquid solubility in deionized water. These tests were done under ambient conditions in the laboratory, with temperatures ranging from 20 to 24°C. Differential thermal analysis (DTA) and thermogravimetric analyses (TGA) were also performed on some of the ionic liquids, using a Harrop model ST-736 DTA/TGA apparatus ($30^\circ C \cdot h^{-1}$, $100\,cm^3 \cdot min^{-1}$ N_2 or O_2). Viscosities were recorded using a Brookfield Model DV-III Rheometer.

Contact experiments typically used 50 or 100 μL of ionic liquid and 1 to 2 mL of aqueous solution shaken together in a small vial. For some experiments as little as 20 μL or as much as 1 mL of ionic liquid was used. Aqueous solutions of representative organics (0.1 to $10\,g \cdot L^{-1}$): hexanoic acid (Sigma 99–100%), glacial acetic acid (J.T. Baker), 1-nonanol (Aldrich 98%), toluene (Aldrich 99%), cyclohexanone (Spectrum Quality Products 97%), and octane (MCB Manufacturing 98%) were used without further purification.

Contacts took place over a range of conditions: in temperature (22 ± 2°C, 37°C, 75°C), in salinity (distilled-deionized water, 0.2*M* NaCl, 1.8*M* NaCl), in pH (<2 to 12), in ionic liquid-to-water volumetric ratio (0.02 to 1.0), and in organic concentration (0.1 to $10\,g \cdot L^{-1}$). A diluent, 1-nonanol, was added to some of the ionic liquids, [C_4mim][PF_6], [$P_{666,14}$][LABS], [$P_{444,14}$][LABS], and [$P_{666,14}$][OMS]. In the case of the [C_4mim][PF_6], the tests were carried out to compare results on organic acid extraction with and without a diluent. Ratios of ionic liquid to diluent ranged from 0.2 to 2. The sulfonate ionic liquids were extremely viscous, and a 1:1 volumetric dilution ratio was required to be able to test extraction in the laboratory. The 1-nonanol was chosen as the diluent because of its high solubility in the ionic liquids.

The two-phase systems were prepared, shaken for two minutes, centrifuged, and then allowed to settle for a few days. The aqueous phases were analyzed on a Waters high performance liquid chromatograph (HPLC) (refractive index detector 2410, auto sampler 717 Plus) or acidified and extracted with methylene chloride and measured on a Hewlett Packard 5890 gas chromatograph (GC) using a flame ionization detector (FID). To simplify the analysis, separate extraction experiments were carried out for mixtures of the organic acids followed by HPLC analysis. Aqueous solutions of toluene, 1-nonanol, and cyclohexanone, were treated separately and analyzed by GC. Hexanoic acid could be analyzed using both methods. Results were compared to controls, consisting of similarly treated aqueous solutions without addition of ionic liquid. The effect of equilibration time was investigated, with samples taken from mixtures that had been in contact from periods of a few minutes, a few hours, a day, or up to a week. The results showed no significant change in mixtures that had been contacted for at least for one day. In addition to organic concentration, pH and Cl^- concentrations of the aqueous solutions were recorded before and after contact using an Orion Model 520A ohmmeter.

Regeneration studies were carried out on a series of three replicate samples, of 100 μL $[C_4mim][PF_6]$ in contact with 2 mL of a solution of hexanoic acid, toluene, and 1-nonanol in deionized water (all $1\,g \cdot L^{-1}$ in concentration), which were subjected to a number of washing steps: deionized water, pH10, pH10, pH2, pH10, pH10. At each step, the rinse solutions were analyzed for the three organics of interest, until concentrations of the organics in the rinse solution were negligible. One sample of ionic liquid was then heated to 120°C to drive off the toluene, and the other two samples were reused in contact experiments to measure the change, if any, in distribution coefficient after the cycle of rinses. A similar procedure was carried out for contacts with $[C_4mim][NTf_2]$.

RESULTS

The physical properties measured for the ionic liquids under study are listed in Table 1: mutual solubility with water, thermal stability, and viscosity. Some of the information in the table was taken from the literature (16, 32, 33), with good agreement, such as in the saturation water content of $[C_4mim][NTf_2]$. The dynamic viscosity of $[C_4mim][NTf_2]$ measured here was close to the literature value of 52 cp at 20°C. The decomposition of the ionic liquid was taken as the point at which the TGA sample showed significant weight loss, to within ± 10°C. Phase transitions were not apparent in the DTA traces.

Table 1. Physical properties of ionic liquids

Ionic liquid	Solubility in water (mM)	Saturation water content (ppm wt.)	Viscosity (cp, $mPa \cdot s^{-1}$)	Decomposition temperature ($\pm 10°C$)	Source of data
$[C_4mim][NTf_2]$	16	14,000	52 (23°C) 22 (50°C) 11 (80°C) 50 (cooled to 22°C) 52 (20°C) (33)	300 (99.97% N_2) 290 (100% O_2)	ORNL (33)
$[C_6mim][NTf_2]$	7.6	11,000	C	280 (100% O_2)	ORNL
$[C_8mim][NTf_2]$	4.7	8,100	C	290 (100% O_2)	ORNL
$[C_4mim][PF_6]$	63	23,000	310 (25°C)	180 (99.97% N_2)	(16, 32)
$[P_{666,14}][NTf_2]$	A	C	C	270 (100% O_2)	ORNL
$[C_4mPm][NTf_2]$	A	15,000	C	300 (100% O_2)	(32)
$[P_{666,14}][LABS]$–1-nonanol (1:1)	A	B	50 (25°C) 20 (50°C)	320°C (99.97% N_2)	ORNL
$[P_{444,14}][LABS]$–1-nonanol(1:1)	A	B	76 (25°C) 28 (50°C)	350°C (99.97% N_2)	ORNL
$[P_{666,14}][OMS]$–1-nonanol (1:1)	A	B	74 (25°C) 27 (50°C)	360°C (99.97% N_2)	ORNL

Notes:

A. Not measured because spectrometer calibrated for imidazolium cation, absorption at 210 nm.

B. Not measured because water content will be affected by 1-nonanol diluent.

C. Insufficient sample to perform measurement.

Table 2. Distribution coefficients for organic compounds between 1-butyl-3- methylimidazolium bistrifluoromethanesulfonylimide and aqueous solution

$[C_4mim][NTf_2]$	Hexanoic acid	Acetic acid	1-Nonanol	Toluene
pH, @22°C, in deionized water				
1.8 ± 0.2	8 ± 7	<3	260 ± 40	140 ± 20
3.5 ± 0.5	11 ± 5	<3	80 ± 40	200 ± 100
6 ± 1	< 0.5	<3	50 ± 40	110 ± 20
Temperature (°C) @pH3, in deionized water				
22	12 ± 7	<3	70 ± 50	110 ± 50
37	12 ± 3	<3	70 ± 40	—
Salinity @pH3, 22°C				
Deionized water	11 ± 7	<3	80 ± 50	170 ± 70
0.2 M NaCl	10 ± 2	<3	80 ± 60	—
1.8 M NaCl	17 ± 3	<3	80 ± 10	130 ± 20

Tabulated results are given for each of the ionic liquids (Tables 2 through 10) giving the distribution coefficient, K_D, or the concentration ratio of water-soluble organics, designated "*i*," between the ionic liquid and aqueous phases:

$$K_D = \frac{[i]_{IL}}{[i]_{aq}} = \frac{v_{H_2O}}{v_{IL}} \cdot \frac{(S_{control} - S_{contact})}{S_{contact}} \tag{1}$$

where v_{H2O} and v_{IL} refer to the volumes of fluids used in the contact tests. The peak areas from the chromatographic analyses for each analyte are given as *S*, for the contact and control tests respectively. The tabulated results include measurements taken under various conditions for each ionic liquid, as given in the left-hand column, and many data are averaged over repeated measurements to give a mean and standard deviation. As mentioned earlier, two separate experiments were conducted using GC or HPLC methods of analysis. The organics not studied in any particular set of runs are displayed as the blank entries in the tables. Of course, measurement of the partitioning of 1-nonanol into the mixtures of sulfonate ionic liquids diluted with 1-nonanol was not possible and has been denoted "not applicable in the table.".

Because the ionic liquid could not be analyzed directly using the methods available to us, the concentrations were derived by a mass balance from the water analyses; the concentrations in the contact solutions were compared to the concentrations in uncontacted controls. The uncertainty in the HPLC analyses was calculated as ± 4% and that of the GC analyses ±11% by repeated measurements. In most cases, three replicate contacts were performed under each set of conditions, and each of these was injected twice into the GC. These efforts were made to minimize the scatter in the calculated distribution coefficients, which were determined through difference

Table 3. distribution coefficients for organic compounds between 1-hexyl-3-methylimidazolium bistrifluoromethanesulfonylimide and aqueous solution

$[C_6mim][NTf_2]$ @22°C	Hexanoic acid	Cyclohexanone	1-Nonanol
pH in deionized water			
2.5 ± 0.5	11 ± 3	12.2 ± 0.4	—
5 ± 1	2.0 ± 0.6	—	230 ± 60
10.5 ± 0.5	<1	15 ± 1	—
Salinity @pH4.5			
Deionized water	—	—	180 ± 60
0.2 M NaCl	—	—	200 ± 200

calculations, as shown in the previous equation. When the difference in concentration was less than the detection limit before and after contact, this is indicated with a less than sign in Tables 2 through 10. In some cases, hexanoic acid was completely extracted, with the amount remaining in the aqueous phase below the detection limit of the analysis. In such cases, the distribution coefficient could not be calculated, and so a greater than sign is used in the table. Even though the uncertainties are large in some cases, they have been included in Tables 2 through 10 to illustrate the performance of gas chromatography, a standard for the analysis of produced water organics (3).

The measured distribution coefficients covered a broad range, from essentially no extraction to complete extraction from the aqueous phase into the ionic liquid. The organics that were best extracted were toluene and 1-nonanol. Other organics, such as cyclohexanone and hexanoic acid, transferred into the ionic liquid phase only under certain conditions. Still others, such as acetic acid, were not taken up into the ionic liquid in measurable amounts in most of the ionic liquids tested. For instance, the extraction of hexanoic acid was sensitive to pH, as indicated by results from $[C_4mim][NTf_2]$ where the protonated form better partitioned into the ionic liquid than the nonprotonated form. Yet removal of acetic acid with the sulfonate ionic liquids did not demonstrate such a pH dependence. In the

Table 4. Distribution coefficients for organic compounds between 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide and aqueous solution

$[C_8mim][NTf_2]$ @22°C, in deionized water	Hexanoic acid	Acetic acid	1-Nonanol	Toluene
pH 3.5 ± 0.5	20 ± 3	<1	410 ± 60	500 ± 200
No dilution with 50% nonanol	120	2	Not applicable	—

Table 5. Distribution coefficients for organic compounds between 1-butyl-3-methylimidazolium hexafluorophosphate and aqueous solution

$[C_4mim][PF_6]$	Hexanoic acid	Acetic acid	1-Nonanol	Toluene
pH @22°C in deionized water				
1.8 ± 0.2	6 ± 1	<2	9 ± 8	80 ± 20
3.5 ± 0.5	4 ± 2	<0.1	—	—
6 ± 1	—	<2	6 ± 5	100 ± 20
12 ± 0.5	4	<2	16 ± 6	60 ± 20
Temperature (°C) @pH3, in deionized water				
25	4 ± 2	<1	9 ± 8	80 ± 20
75	3 ± 3	—	A	A
Salinity @pH3, 22°C				
Deionized water	6 ± 4	<1	5 ± 6	68 ± 9
0.2 M NaCl	2 ± 2	<1	17	106

A: sample lost through volatilization.

case of hexanoic acid, the pH sensitivity suggested a mechanism for recycling the ionic liquid by rinses with controlled pH. Rinsing with a high-pH aqueous solution will deprotonate the hexanoic acid and, thus, reduce its solubility in the ionic liquid. The possibility of using pH control to enhance separation and to clean up the ionic liquid solvent has been suggested by the work of other groups: Visser and coworkers (34) using an indicator dye, Cull and colleagues (35), who observed a pH sensitivity in the removal of erythromycin from water by $[C_4mim][PF_6]$, and Rogers et al. (13) and Carda-Broch et al. (17) on the pH-dependent extraction of a variety of organics by $[C_4mim][PF_6]$.

The performance of the ionic liquid as solvent was investigated under conditions of changing solute concentration, from $0.1\,g \cdot L^{-1}$ up to $10\,g \cdot L^{-1}$, Fig. 1. In the cases of hexanoic acid, toluene, and 1-nonanol in

Table 6. Distribution coefficients for organic compounds between trihexyltetradecylphosphonium bistrifluoromethanesulfonylimide and aqueous solution

$[P_{666,14}][NTf_2]$ @22°C	Hexanoic acid	Cyclohexanone	1-Nonanol
pH in deionized water			
2.5 ± 0.5	25 ± 2	15 ± 2	—
5 ± 1	6.4 ± 0.4	—	—
10.5 ± 0.5	1.0 ± 0.2	10 ± 2	—
Salinity @pH4.5			
Deionized water	—	—	170 ± 60
0.2 M NaCl	—	—	200 ± 200

Table 7. Distribution coefficients for organic compounds between 1-butyl-3-methylpyrrolidinium bistrifluoromethanesulfonylimide and aqueous solution

$[C_4mPm][NTf_2]$ @22°C	Hexanoic acid	Cyclohexanone	1-Nonanol
pH in deionized water			
2.5 ± 0.5	9 ± 3	10 ± 1	—
5 ± 1	1.6 ± 0.6	—	200 ± 30
10.5 ± 0.5	< 1	11.5 ± 0.7	—
Salinity @pH4.5			
Deionized water	—	—	180 ± 50
0.2 M NaCl	—	—	200 ± 100

$[C_4mim][PF_6]$, the solubility limits in the ionic liquid were not reached. Results for $[C_4mim][NTf_2]$ were similar. However, the sulfonate ionic liquids showed a slight decrease in distribution coefficient at the highest concentration of the organics. Saturation of the ionic liquid was also investigated as a function of volume ratio, ionic liquid-to-H_2O, Fig. 2. The solvent did not appear to lose its ability to extract organics as the ratio was changed from 0.02 to 1.

For the ionic liquids where several ionic liquid-to-aqueous phase ratios were studied, organic solubility in ionic liquid was estimated from the amount of organic transferred into the ionic liquid divided by the volume of ionic liquid used in the contact, Table 11. Using published values of activity (36) and of octanol-water partition (37) coefficients, the activity coefficients of the organics in $[C_4mim][PF_6]$ were calculated: γ_{IL} (toluene) = 3.8, γ_{IL} (hexanoic acid) = 3.9, and γ_{IL} (cyclohexanone) >3.5. The value for toluene compares reasonably well with the infinite dilution values measured by Krummen and coworkers (45), γ_{IL} (olefins) of 10–20 and γ_{IL}

Table 8. Distribution coefficients for organic compounds between Trihexyltetradecylphophonium dodecylbenzenesulfonate-1-nonanol (1 : 1) and aqueous solution

$[P_{666,14}][LABS]$– 1-nonanol (1:1) @22°C	Hexanoic acid	Acetic acid	Cyclohexanone	Toluene
pH in deionized water				
3.2	>10000	0.6	—	140 ± 20
4.3	>185	—	3.9 ± 0.3	200 ± 100
10.7	10 ± 1	—	4.20 ± 0.02	110 ± 20
11.1	3.2 ± 0.3	1.9 ± 0.2	—	—
Salinity @pH4.3				
Deionized water	>185	—	3.9 ± 0.3	200 ± 100
0.2 M NaCl	300 ± 100	—	6 ± 2	—

Table 9. Distribution coefficients for organic compounds between tributyltetradecylphophonium dodecylbenzenesulfonate-1-nonanol (1:1) and aqueous solution

$[P_{444,14}][LABS]$–1-nonanol (1:1) @22°C	Hexanoic acid	Acetic acid	Cyclohexanone	Toluene
pH in deionized water				
3.2	>119	1.9 ± 0.8	—	—
4.3	>146	—	4.9 ± 0.7	60 ± 5
10.7	17 ± 4	—	7.12 ± 0.08	—
11.1	2.4 ± 0.6	1.3 ± 0.9	—	—
Salinity @pH4.3				
Deionized water	>146	—	4.9 ± 0.7	60 ± 5
0.2 M NaCl	180 ± 80	—	5.6 ± 0.3	—

(benzene)$\sim$2 for imidazolium $[NTf_2]$ ionic liquids. It must be noted that the values measured in the current work are estimates and do not represent ideal solution behavior.

The salinity of the brine, Tables 2–10, did not appear to change the solubility of the organic in the ionic liquid. Nor did the $[C_4mim][NTf_2]$ affect the salinity of the brine, from chloride ion measurements of the aqueous phase, so significant ion exchange was not observed. Similar results have been reported elsewhere in contacts with solutions of chlorophenols (25). However, Bekou and coworkers did find that ionic strength does affect ionic liquid solubility in water, in agreement with recent Oak Ridge National Laboratory results that will be reported elsewhere, where the solubility of the ionic liquid was found to be inversely related to the ionic strength in solutions with salt concentration up to 3 M (60).

Table 10. Distribution coefficients for organic compounds between trihexyltetradecylphosphonium methanesulfonate-1-nonanol (1:1) and aqueous solution

$[P_{666,14}][OMS]$–1-nonanol (1:1) @22°C	Hexanoic acid	Acetic acid	Cyclohexanone	Toluene
pH in deionized water				
3.2	>183	0.8 ± 0.4	4 ± 1	57 ± 4
4.3	481	—	3.2 ± 0.7	12.8 ± 0.1
10.9 ± 0.2	58 ± 1	6.3 ± 0.4	—	—
Salinity @pH4.3				
Deionized water	481	—	4 ± 1	60 ± 5
0.2 M NaCl	300 ± 50	—	8 ± 1	—

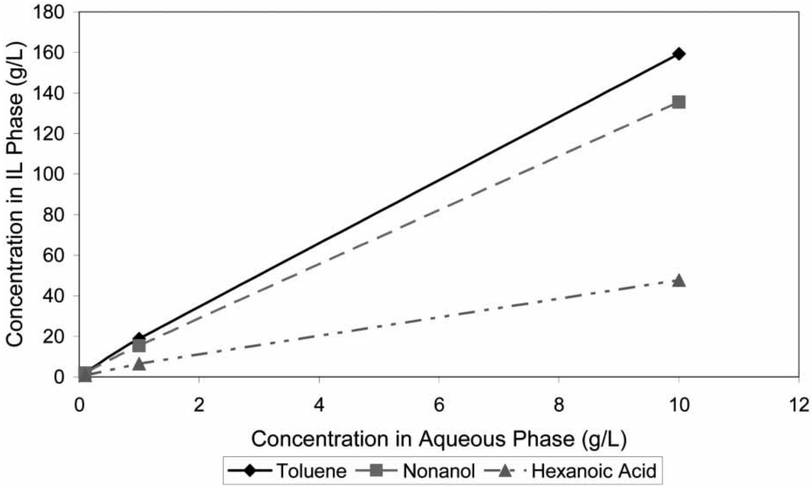

Figure 1. Concentration of organic compounds in $[C_4mim][PF_6]$ ionic liquid as a function of aqueous concentration with other factors held constant: temperature (25°C), ambient pressure, ratio of ionic liquid to aqueous phase 1:10.

Temperature effects were complicated by the enhanced solubility of the ionic liquid in the aqueous phase and losses through volatilization. Hence, the effect of temperature on organic solubility was not quantified.

Because of its apparent affinity for ionic liquids, 1-nonanol was also used as a diluent of the ionic liquid, with the objective being an enhancement of the

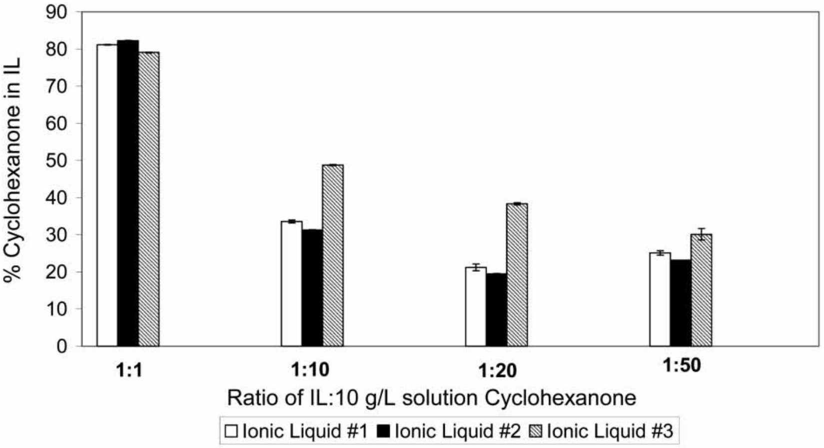

Figure 2. Percentage of cyclohexanone taken up into the sulfonate ionic liquids as a function of phase ratio: #1 $[P_{666,14}][OMS]$, #2 $[P_{666,14}][LABS]$, #3 $[P_{444,14}][LABS]$.

Table 11. Estimates of solubility using ratio experiments

Organic	Organic solubility ($g \cdot L^{-1}$) in ionic liquid			
	$[C_4mim]$ $[PF_6]$	$[P_{666,14}]$[LABS]− 1-nonanol (1:1)	$[P_{444,14}]$[LABS]− 1-nonanol (1:1)	$[P_{666,14}]$[OMS]− 1-nonanol (1:1)
Toluene	200 ± 40	230	213	339
1-nonanol	20 ± 10	Miscible	Miscible	Miscible
Hexanoic acid	20 ± 10	430	576	865
Cyclohexanone	—	47	111	53

uptake of other organic molecules into the ionic liquid phase. Diluents have been used to increase the ability of amine solvents to remove organic acids from aqueous solution through more efficient mass transfer (27). As can be seen with the results for $[C_8mim][NTf_2]$, Table 4, the 1-nonanol diluent assisted with the uptake of organic acids into the ionic liquid. All of the data on the sulfonate ionic liquid was taken with 50% (v/v) mixtures of 1-nonanol and ionic liquid, because the neat ionic liquid was too viscous to allow for reliable sampling.

The results of the regeneration experiments, Fig. 3, showed that the remediation of $[C_4mim][PF_6]$ through rinsing was successful in the case of

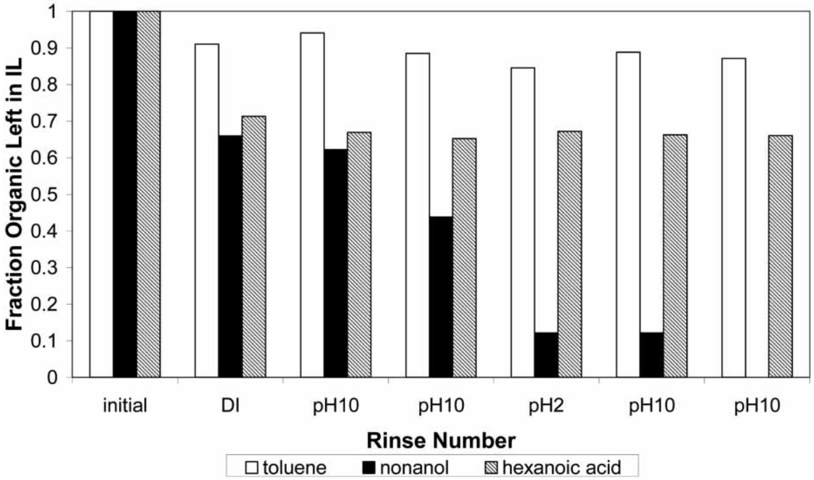

Figure 3. Fraction of organic remaining in $[C_4mim][PF_6]$ after treatment. The initial amount of organic transferred into the ionic liquid from the aqueous phase was normalized to one. Note that all of the 1-nonanol was removed from the ionic liquid following the final rinse.

1-nonanol, but less so for hexanoic acid, and not at all for toluene. After heating at 120°C for several hours, the response to toluene and 1-nonanol returned for $[C_4mim][NTf_2]$, Fig. 4, but not for hexanoic acid. This finding was borne out by nuclear magnetic resonance (NMR) studies on the regenerated ionic liquid which showed small peaks from impurities in the spectra. Heating $[C_4mim][PF_6]$ to remove the toluene was not successful because it induced decomposition of the $[C_4mim][PF_6]$, as observed in NMR spectra taken after heating.

DISCUSSION

The focus of these experiments was to investigate the interaction between ionic liquids and organics, and some background information will assist in the interpretation of the current results. Elsewhere, it has been reported that the affinity between an ionic liquid and an organic is related to the existence of polarizable electrons in the solute (38). Indeed, polar organics appear to show an affinity for ionic liquids of most types, in contrast to aliphatic hydrocarbons (16). The existence of polarizable π electrons present in aromatic compounds has a positive effect on solubility in ionic

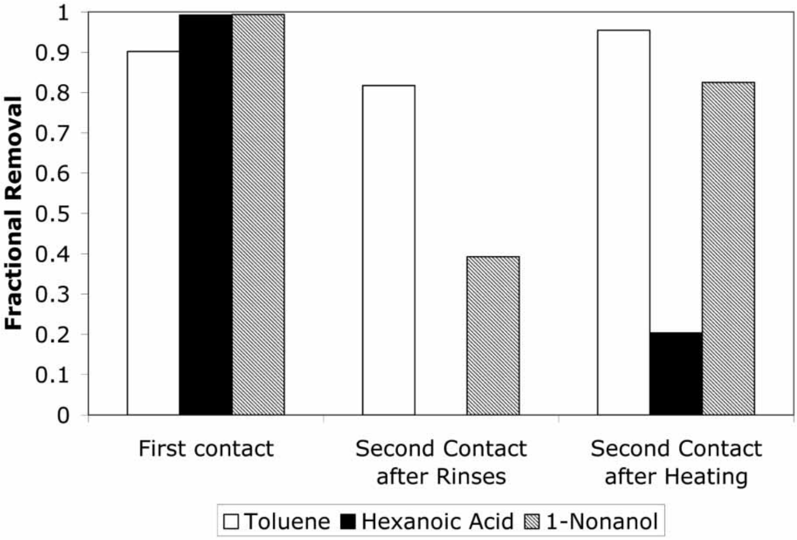

Figure 4. Fractional removal of various organics for aqueous contacts with fresh ionic liquid $[C_4mim][NTf_2]$ (cycle 1), rinsed ionic liquid (cycle 2), and ionic liquid both rinsed and heated (cycle 3). Note that the removal of hexanoic acid was negligible after the aqueous rinses.

liquids, in some cases it gives rise to exothermic heats of solution (39). On the basis of this type of analysis, however, it is surprising that the interaction of organic acids with ionic liquids is so complex. Highly polar organics, such as acetic acid, are not strongly absorbed from water into ionic liquids. However, longer chain aliphatic acids, such as hexanoic acid, do partition into the ionic liquid in the protonated form, when the pH is less than the pKa of the acid.

One explanation for the behavior of acids in ionic liquids relates to the relative basicities of the conjugate bases of the ionic liquid anion and the deprotonated acid (40). For instance, the ionic liquids that have the [NTf_2] and the [PF_6] anions, are very weakly basic, and the anion is a weaker Lewis base (or electron donor) than water. In this case, an acid dissolved in such an ionic liquid would be expected to be less dissociated than it is in water. For hexanoic acid, this is indeed the case, where the solubility of the acid in any of the ionic liquids tested was much higher at low than at neutral or high pH.

Such behavior was not observed for acetic acid; therefore, this may be related to the possibility of forming an ionic liquid with the acetate anion through anion exchange. Ionic liquids with the acetate anion are more basic than water, and would behave as Lewis bases to deprotonate the organic acid. If the organic acid anion, such as acetate, has a high solubility in water, it will, therefore, not be extracted from aqueous solution. The observed small uptake of acetic acid into the sulfonate ionic liquids likely arose because of the presence of the 1-nonanol diluent, rather than the effect of the ionic liquid itself. Methanesulfonate will be approximately the same, or even less basic than H_2O (the pKas of methanesulfonic acid and the hydronium ion being about -2 and -1.74 respectively).

Octanol-water coefficients (41, 42), K_{ow} values, for various organic species studied are listed in Table 12, along with the range of distribution coefficients observed in the ionic liquids in this work. Arguments have been presented in the literature that the K_{ow} values correlate with the uptake into ionic liquids (25, 43). Although such a trend does appear to describe the data when considering one ionic liquid and a series of similar organics,

Table 12. Distribution coefficients and activity coefficients for organics in ionic liquids

Organic	K_{ow} (ref.)	$K_{IL/W}$ range
Toluene	2.73 (41)	13–200
1-nonanol	3.77 (42)	5–410
Acetic acid	-0.17 (41)	Not extracted–6
Hexanoic acid	1.92 (41)	Not extracted–25
Cyclohexanone	0.81 (41)	3–15

such as chloroalkanes (43), it is apparent that one distribution coefficient does not predict the behavior over the range of ionic liquids studied here, even though the ionic liquids that were selected for this study could all be classified as nonreacting, weakly basic ionic liquids. Activity coefficients at infinite dilution have been measured for toluene and other hydrocarbons compounds in [C_4mim][NTf_2], [C_6mim][NTf_2], and [C_4mim][PF_6] (43–45). These are not only dependent on the ionic liquid, but also on physical conditions such as temperature. Chemical interactions such as acid-base phenomena (46), and the interactions between charged and noncharged molecules in both the aqueous and ionic liquid phases (47) must be considered in understanding the behavior of multiphase systems involving ionic liquids. Quantum mechanical calculations have been used to predict thermodynamic properties of mixtures, and they have proved particularly successful for the prediction of gas solubility in ionic liquids (e.g., 48). Alternatively, an empirical approach has been used, that includes solvent polarizability and acidity as variables in the analysis (17, 49).

A number of factors must be considered in the choice of an ionic liquid that would perform the best for a particular application. If extraction from an aqueous solution is required, solubility of the ionic liquid must be negligible to minimize losses (50–52). The ionic liquid must be thermally stable and have the correct physical properties, i.e., liquidity, viscosity, and low vapor pressure, under field conditions. The ionic liquid must have a high affinity to the organic of interest in comparison to water, but yet be regenerable. Many of these factors have been examined in this series of experiments. Toxicity, another key concern has not, although it is being investigated elsewhere (53).

All of the ionic liquids tested, were of course, liquid at ambient temperatures. Most were stable to temperatures well above 200°C, higher than a petroleum extraction operation; (54) although, [C_4mim][PF_6] was observed to degrade at a slightly lower temperature, 180°C. In addition, the reactivity of [C_4mim][PF_6] in water resulting in the release of HF (hydrogen fluoride) precludes its use in most applications (23). The viscosity of the sulfonate ionic liquids would render them difficult to use in bulk chemical processing under ambient conditions; however, they may be employed as stable film materials on membrane substrates (55). Also, because the viscosity of ionic liquids drops rapidly with temperature, the sulfonate-based materials may be useful for processes at elevated temperatures.

The aqueous solubilities of the ionic liquids varied considerably, and are not negligible even for "hydrophobic" ionic liquids. Although not measured here, one would also expect aqueous solubility to change in a ternary system involving hydrophilic organics, such as alcohols and acids. The phase behavior of ionic liquids will affect the practicality of processing and sensor applications. In processing, the treated water will contain ionic liquids at concentrations approaching their solubility, which poses two issues: 1) environmental acceptability of the effluent, and 2) operating cost for makeup of lost ionic liquids. In the first case, the liquid extraction process could be seen as trading one type of organic contamination for another. In the case of $[C_8mim][NTf_2]$ solubility is approximately $2.2\,g \cdot L^{-1}$, far greater than the $29\,mg \cdot L^{-1}$ NPDES limit. The focus of industrial applications must be either to find much less soluble ionic liquids or to develop processes for their recovery from the aqueous phase, such as use of supercritical phase splitting (56) or by water-structuring salts (57). Losses have an economic impact as well as a potential environmental effect, since ionic liquids are currently significantly more costly than are conventional solvents. Losses would also limit sensor lifetime and contribute to a constantly changing baseline. The advantages of ionic liquids may be best suited for closed systems, where recovery can be carefully controlled. In summary, the criteria for minimal solubility in water become much more stringent when ionic liquid systems are taken from the laboratory bench and applied to an industrial process.

CONCLUSIONS

In this study, the use of nine different ionic liquids in produced water remediation was investigated. As a first step, the distribution coefficients of prototypical organic contaminants between water and ionic liquids were measured. The organic contaminants studied to date were hexanoic acid, 1-nonanol, toluene, acetic acid, and cyclohexanone. Measured distribution coefficients (concentration in the ionic liquid divided by concentration in the aqueous phase after equilibration) ranged from negligible to several hundred. The uptake of acetic acid was marginal in the ionic liquids tested, which may pose a problem for use in produced water remediation because acetic acid is the most important organic constituent (58). The distribution coefficient for hexanoic acid was pH-sensitive; higher for the hexanoic acid at low pH. This pH sensitivity may assist in regenerating the ionic liquid. High organic concentrations in ionic liquids were determined for many species that showed significant partitioning from the aqueous into the ionic liquid phase.

The results of the experiment showed that ionic liquids may be very effective in the selective removal of particular contaminants in produced water, and yet will be fairly blind to other constituents such as paraffinic organic compounds. Although this would present difficulties in across-the-board remediation, it may prove advantageous in sampling for a particular priority pollutant (59). Chemical selectivity is one of many considerations for the use of ionic liquids in environmental applications. Other factors include losses by dissolution into the aqueous phase, degradation over time from uptake of contaminants, regeneration, fluid properties such as viscosity, and toxicity, all of which merit further investigation.

ACKNOWLEDGMENTS

The authors would like to thank the U.S. Department of Energy Natural Gas and Oil Technology Partnership Office for funding under contract AC10151000, and our industrial partners, the DOE Community College Initiative, and the DOE Higher Education Research Experience program.

REFERENCES

1. Ray, J.P. and Engelhardt, F.R. Eds. (1992) *Produced Water, Technological/Environmental Issues and Solutions*; Environmental Science Research, 46, Plenum Press: New York.
2. USEPA. *Notice of Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico* (GMG290000), FRL-7119-5, Federal Register, 66 (243), Tuesday, December 18, 2001, notices, 65209; Environmental Protection Agency.
3. USEPA. *Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-Polar Material) by Extraction and Gravimetry*, EPA-821-R-98-002; Environmental Protection Agency.
4. Wills, J.A. (2000) *Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping*; M.Inst.Pet. for Ekologicheskaya Vahkta Sakhalina (Sakhalin Environment Watch).
5. Marsh, K.N., Deev, A., Wu, A.C.-T., Tran, E., and Klamt, A. (2002) Room temperature ionic liquids as replacements for conventional solvents—A review. *Korean J. Chem. Eng.*, 19 (3): 357–362.
6. Wei, G.-T., Yang, Z., and Chen, C.-J. (2003) Room temperature ionic liquid as novel medium for liquid/Liquid extraction of metal ions. *Anal. Chim. Acta*, 488: 183–192.
7. Dai, S., Ju, Y.H., and Barnes, C.E. (1999) Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *Journal of the Chemical Society-Dalton Transactions*, 8: 1201–1202.
8. Visser, A.E., Swatloski, R.P., Peichert, W.M., Griffin, S.T., and Rogers, R.D. (2000) Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. *Ind. Eng. Chem. Res.*, 39 (10): 3596–3604.
9. Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davis, J.H., and Rogers, R.D. (2001) Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. *Chem. Commun.*, 1: 135–136.
10. Bartsch, R.A., Chun, S., and Dzyuba, S.V. (2002) Ionic liquids as novel diluents for solvent extraction of metal salts by crown ethers. *In Ionic Liquids*; Am. Chem. Soc. Symp. Ser., 818, 58–68.
11. Visser, A.E., Holbrey, J.D., and Rogers, R.D. (2001) Hydrophobic ionic liquids incorporating N-alkylisoquinolium cations and their utilization in liquid-liquid separations. *Chem. Commun.*, 23: 2484–2485.

12. Visser, A.E., Reichert, W.M., Swatloski, R.P., Willauer, H.D., Huddleston, J.G., and Rogers, R.D. (2002) Characterization of hydrophilic and hydrophobic ionic liquids: alternatives to volatile organic compounds for liquid-liquid separations. In *Ionic Liquids*; Am. Chem. Soc. Symp. Ser., 818289–308.
13. Holbrey, J.D. and Rogers, R.D. (2002) Green industrial applications of ionic liquids: Technology review. In *Ionic Liquids*; Am. Chem. Soc. Symp. Ser., 818, 446–458.
14. Huddleston, J.G., Willauer, H.D., Swatloski, R.P., Visser, A.E., and Rogers, R.D. (1998) Room temperature ionic liquids as novel media for Clean Liquid-Liquid Extraction. *Chem. Commun.*, 16: 1765–1766.
15. Poole, C.F. (2004) Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *J. Chromatogr. A*, 1037: 49–82.
16. Berthod, A. and Carda-Broch, S. (2003) A new class of solvents for CCC: The room temperature ionic liquids. *J. of Liquid Chromatography and Related Technologies*, 26 (9,10): 1493–1508.
17. Carda-Broch, S., Berthod, A., and Armstrong, D.W. (2003) Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal. Bioanal. Chem.*, 375: 191–199.
18. Bostick, D.T., Luo, H., and Hindmarsh, B. (2002) *Characterization of Soluble Organics in Produced Water*; Oak Ridge National Laboratory: Oak Ridge, TN, ORNL/TM-2001/78.
19. Culbertson, B. (2003) *CO_2 Separation and Fuel Desulfurization Involving Room Temperature Ionic Liquids*; University of Tennessee: Knoxville, TN, USA, M. Eng. Thesis.
20. Applebee, M.B., Geissler, J.D., Schellinger, A.P., Haeger, R.J., and Pierce, D.T. (2004) Field screening of waterborne petroleum hydrocarbons by thickness shear-mode resonator measurements. *Environ. Sci. Technol.*, 38: 234–239.
21. Zhou, X.C., Ng, S.C., Chan, H.S.O., and Li, S.F.Y. (1997) Detection of organic amines in liquid with chemically coated quartz crystal microbalance devices. *Sensors and Actuators B*, 42: 137–144.
22. Rosler, S., Lucklum, R., Borngraber, R., Hartmann, J., and Hauptmann, P. (1998) Sensor system for the detection of organic pollutants in water by thickness shear mode resonators. *Sensors and Actuators B*, 48: 415–424.
23. Huddleston, J.G., Visser, A.E., Riechert, W.M., Willauer, H.D., Broker, G.A., and Rogers, R.D. (2001) Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.*, 3 (4): 156–164.
24. Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H., and DePaoli, D.W. (2004) Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance. *J. Phys. Chem. B*, 108: 721–727.
25. Bekou, E., Dionysiou, D.D., Qian, R.Y., and Botsaris, G.D. (2003) Extraction of chlorophenols from water using room temperature ionic liquids. In *Ionic Liquids as Green Solvents: Progress and Prospects*; Am. Chem. Soc. Symp. Ser., 856, 544–560.
26. Koel, M., Ljovin, S., Hollis, K., and Rubin, J. (2001) Using neoteric solvents in oil shale studies. *Pure Appl. Chem.*, 73 (1): 153–159.
27. Morales, A.F., Albet, J., Kyuchoukov, G., Malmary, G., and Molinier, J. (2003) Influence of extractant (TBP and TOA), diluent, and modifier on extraction equilibrium of monocarboxylic acids. *J. Chem. Eng. Data*, 48 (4): 874–886.

28. Rogers, R.D. (2004) Room Temperature Ionic Liquids, http://uva1vm.ua.edu/~rdrogers/webdocs/ionicliquids.html.
29. Makote, R.D., Luo, H.M., and Dai, S. (2002) Synthesis of ionic liquid and silica composites doped with dicyclohexyl-18-crown-6 for sequestration of metal ions. In *Clean Solvents*; Am. Chem. Soc. Symp. Ser., 819, 26–33.
30. Ren, R.X. (2003) Green Synthesis of Ionic Liquids for Green Chemistry. In *Ionic Liquids as Green Solvents: Progress and Propects*; Am. Chem. Soc. Symp. Ser., 865, 70–81.
31. Ren, R.X. and Robertson, A.J. (2003) *Preparation of Ionic Liquids*; WO 0351894.
32. Merck, KGaA. Darmstadt, Germany http://www.ionicliquids-merck.de/servlet/PB/menu/1302610/index.html, Last update 26.02.2004.
33. Bonhôte, P., Dias, A.-P., Papageorgiou, N., Kalyanasundaram, K., and Grätzel, M. (1996) Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.*, 35: 1168–1178.
34. Visser, A.E., Swatloski, R.P., and Rogers, R.D. (2000) pH-dependent partitioning in room temperature ionic liquids provides a link to traditional solvent extraction behavior. *Green Chem.*, 2 (1): 1–4.
35. Cull, S.G., Holbrey, J.D., Vargas-Mora, V., Seddon, K.R., and Lye, G.J. (2000) Room-temperature ionic liquids as replacements for organic solvents in multiphase bioprocess operations. *Biotechnol. and Bioengin.*, 69 (2): 228–233.
36. Belousov, V.P. and Panov, M.Yu. (1994) *Thermodynamic Properties of Aqueous Solutions of Organic Substances*; CRC Press: Boca Raton, Vol. 115–120, 331–334.
37. Verschuenen, K. (2001) *Handbook of Environmental Data on Organic Chemicals*; Wiley-Interscience: New York; Vol. I, 422–423, 621–623, Vol. 2, 1657, 2005–2012.
38. Anthony, J.L., Maginn, E.J., and Brennecke, J.F. (2002) Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B*, 106: 7315–7320.
39. Heintz, A., Lehmann, J.K., and Verevkin, S.P. (2003) Thermodynamic properties of liquid mixtures containing ionic liquids. In *Ionic Liquids as Green Solvents*; Rogers, R.D. and Seddon, K.R., Eds.; Am. Chem. Soc. Symp. Ser., 856, 134–150.
40. MacFarlane, D.R. and Forsyth, S.A. (2003) Acids and bases in ionic liquids. In *Ionic Liquids as Green Solvents*; Rogers, R.D. and Seddon, K.R., Eds.; Am. Chem. Soc. Symp. Ser., 856, 264–276.
41. Hansch, C., Hoekman, D., Leo, A., Zhang, L.T., and Li, P. (1995) The expanding role of quantitative structure-activity-relationships (QSAR) in toxicology. *Toxicology Letters*, 79: 45–53.
42. Tewari, T.B., Miller, M.M., Wasik, S.P., and Martire, D.E. (1982) Aqueous solubility and octanol water partition-coefficients of organic-compounds at 25.0°C. *J. Chem. Eng. Data*, 27 (4): 451–454.
43. Dupont, J., Consorti, C.S., and Spencer, J. (2000) Room temperature molten salts: neoteric "green" solvents for chemical reactions and processes. *J. Braz. Chem. Soc.*, 11: 337–344.
44. Letcher, T.M., Soko, B., Ramjugernath, D., Deenadayalu, N., Nevines, A., and Naicker, P.K. (2003) Activity coefficients at infinite dilution of organic solutes in 1-hexyl-3-methylimidazolium hexafluorophosphate from gas-liquid chromatography. *J. Chem. Eng. Data*, 48: 708–711.

45. Krummen, M., Wasserscheid, P., and Gmehling, J. (2002) Measurement of activity coefficients at infinite dilution in ionic liquids using the dilutor technique. *J. Chem. Eng. Data*, 47: 1411–1417.
46. Yoshizawa, M., Xu, W., and Angell, C.A. (2003) Ionic liquids by proton transfer: vapor pressure, conductivity, and the relevance of ΔpKa from aqueous solutions. *J. Am. Chem. Soc.*, 125: 15411–15419.
47. Rafal, M., Berthold, J.W., Scrivner, N.C., and Grise, S.L. (1994) Models for electrolyte solutions. In *Models for Thermodynamic and Phase Equilibria Calculations*; Sander, S.I., Ed.; Marcel Dekker, 601–670.
48. Marsh, K.N., Boxall, J.A., and Lichtenthaler, R. (2004) Room temperature ionic liquids and their mixtures—A review. *Fluid Phase Equilbria*, 219: 93–98.
49. Abraham, M.H., Zissimos, A.M., Huddleston, J.G., Willauer, H.D., Rogers, R.D., and Acree, W.E., Jr. (2003) Some novel liquid partitioning systems: Water-ionic liquids and aqueous biphase systems. *Ind. Eng. Chem. Res.*, 43: 413–418.
50. Anthony, J.L., Maginn, E.J., and Brennecke, J.F. (2001) Solution thermodynamics of imidazolium-based ionic liquids and water. *J. Phys. Chem. B*, 105: 10942–10949.
51. Dietz, M.L. and Dzielawa, J.A. (2001) Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for the “Greenness” of ionic liquids as diluents in liquid-liquid extraction. *Chem. Commun.*, 20: 2124–2125.
52. Jensen, M.P., Dzielawa, J.A., Rickert, P., and Dietz, M.L. (2002) EXAFS investigations of the mechanism of facilitated ion transfer into a room-temperature ionic liquid. *J. Am. Chem. Soc.*, 124 (36): 10664–10665.
53. Swatloski, R.P., Holbrey, J.D., and Rogers, R.D. (2003) Ionic liquids are not always green: Hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.*, 5: 261–363.
54. Jacobs, R.P.W.M., Grant, R.O.H., Kwant, J., Marquenie, J.M., and Mentzer, E. (1992) The composition of produced water from shell operated oil and gas production in the North sea. In *Produced Water*; Ray, J.P. and Engelhart, F.R., Eds.; Plenum Press: New York, 13–21.
55. Anderson, J.L. and Armstrong, D.W. (2003) High-stability ionic liquids. A new class of stationary phases for gas chromatography. *Anal. Chem.*, 75: 4851–4858.
56. Scurto, A.M., Aki, S.N.V.K., and Brennecke, J.F. (2003) Carbon dioxide induced separation of ionic liquids and water. *Chem. Commun.*, 5: 572–573.
57. Gutowski, K.E., Broker, G.A., Willauer, H.D., Huddleston, J.G., Swatloski, R.P., Holbrey, J.D., and Rogers, R.D. (2003) Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations. *J. Am. Chem. Soc.*, 125 (22): 6632–6633.
58. Kharaka, Y.K. and Hanor, J.S. (2003) Deep fluids in the continents: I. Sedimentary basins. In *Treatise on Geochemistry*; Holland, H.D. and Turekian, K.K., Eds.; Elsevier Pergamon: Amsterdam; Vol. 5, 499–540.
59. Material Safety Data Sheet, Petroleum Crude Oil, #1582. National Institute of Standards and Technology, September 1994.
60. Toh, I. (2004) Private communication.