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

Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors

Joseph F. Birdwell Jr.[a]; Joanna McFarlane[a]; Rodney D. Hunt[a]; Huimin Luo[a]; David W. DePaoli[a]; Denise L. Schuh[b]; Sheng Dai[c]
[a] Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA [b] Nuclear Engineering Department, University of Wisconsin, Madison, Wisconsin, USA [c] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

To cite this Article Birdwell Jr., Joseph F. , McFarlane, Joanna , Hunt, Rodney D. , Luo, Huimin , DePaoli, David W. , Schuh, Denise L. and Dai, Sheng(2006) 'Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors', Separation Science and Technology, 41: 10, 2205 — 2223

To link to this Article: DOI: 10.1080/01496390600745719

URL: http://dx.doi.org/10.1080/01496390600745719

Separation Science and Technology, 41: 2205–2223, 2006
This document is not subject to US Copyright Law
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600745719

Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors

Joseph F. Birdwell, Jr., Joanna McFarlane, Rodney D. Hunt, Huimin Luo, and David W. DePaoli
Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Denise L. Schuh
Nuclear Engineering Department, University of Wisconsin, Madison, Wisconsin, USA

Sheng Dai
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Abstract: Separations of dispersions formed by mixing immiscible organic room-temperature ionic liquids (IL)/hydrocarbon/and aqueous systems using a centrifugal solvent-extraction contactor have been successfully demonstrated in proof-of-concept testing. This accomplishment is significant in that physical property factors that are typical of ionic liquid systems (e.g., similar densities of the bulk phases, low interfacial tensions, and high viscosities) are typically unfavorable for dispersion separation, particularly in continuous processes. Efficient separation of dispersions containing ionic liquid solvents is essential for utilization of these compounds in liquid-liquid extraction applications to maximize both solute transfer efficiency and solvent recovery. Efficient solvent recovery is of particular concern in IL applications because of the high cost of most IL solvents.

This paper presents the results of initial experiments with three hydrophobic ionic liquids to determine how their physical properties affect phase mixing and phase disengagement in contact with an aqueous solution using a centrifugal contactor. While the results of the reported work are promising, additional work is needed to optimize

Received 23 October 2005, Accepted 23 March 2006

Address correspondence to Joseph F. Birdwell, Jr., Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6181, USA. E-mail: birdwelljfjr@ornl.gov

existing mathematical models of contactor hydraulics to address special considerations involved in IL-based processes and to optimize the equipment itself for IL applications.

Keywords: Ionic liquid, liquid-liquid extraction, solvent extraction, centrifugal contactor

INTRODUCTION

Several recent studies and reviews e.g. (1) have indicated that ionic liquids have promise for use in liquid-liquid extraction processes for a variety of energy-related separations, ranging from desulfurization of diesel fuel (2) to extraction of hydrocarbons from oil shales (3) and asphaltenes from petroleum (4). Applications related to both energy and environmental issues have been investigated since the late 1990s, with work done at the University of Alabama on metal ion extraction (5). This work has developed into the removal of Cs^{+} and Sr^{+2} fission products from waste generated in the nuclear fuel cycle (6–8), and the mechanisms of extraction are now beginning to be understood (9). Hydrophobic ionic liquids have been investigated for use in removal of water-soluble organics from water generated during oil and gas production (10). Ionic liquids have also been identified as being able to promote specific chemical reactions; acting as carriers of metal catalysts (11). Separations of bio-based materials have been demonstrated using ionic liquids (12), which may help solve one of the most important concerns with these feedstocks that are being considered to replace or enhance petrochemical supplies.

Ionic liquids are organic salts that are liquids at room temperature with low vapor pressures, suggesting that they may be safer to use and have lower losses than other organic solvents in particular applications (13). Their chemical and physical properties, such as solvent behavior, hydrophobicity, and viscosity are determined by the choice of the anion and cation, allowing the possibility for them to be tailor-made for a particular application (14, 15). Although many are expensive to synthesize in the laboratory, ionic liquids may be recycled using electrochemical or pH cycling techniques to improve their cost effectiveness (16).

Certain characteristics of ionic liquids make them especially attractive for use as extraction solvents. The ability to tailor a liquid by the choice of the anion allows optimization of solvent selectivity and solute extractability (17). Extraction characteristics may be tuned by varying the anion concentration, which facilitates optimization of the solute distribution coefficient within a process cascade. Extremely high extraction coefficients can be obtained in the extraction section of a cascade, while very low coefficients can be established in the stripping (or back-extraction) section of the process, thereby minimizing the number of total stages of mass transfer required to achieve specific solute recovery and purification targets (18).

To accelerate the use of ionic liquids in industrial applications, there is need for development and demonstration of process technologies that efficiently employ ionic liquids (18). A better understanding of chemical reactivity and stability; phase behavior and physical properties; and the means to reduce costs must be achieved. Although various aspects have to be addressed before implementation, we expect centrifugal solvent extraction contactors to provide significant advantages over conventional technologies for extraction processes performed using ionic liquids. In particular, minimal solvent hold-ups required for centrifugal contactor operation minimizes ionic liquid inventory requirements, and highly efficient phase separations obtained using these devices mitigate solvent losses due to entrainment. Consequently, ionic liquid costs (which can be significant enough to preclude their use in production-scale operations) are greatly reduced.

The primary objective of this experimental program was to evaluate the separation of immiscible fluids that have potential use in aqueous/organic separations. These included dispersions of $NaCl_{(aq)}$ and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($Bmim \cdot NTf_2$) or Terrasail®, 1,1′-oxybis(2,1-ethanediyloxy)butane (commonly dibutyl-carbitol)/aqueous nitric acid, cyclohexane, water and 1-butyl-3-methylimidazolium bis(perfluoroethanesulfonyl)imide (Bmim · BETI) using a commercially available centrifugal contactor/separator. The ionic liquids were selected because they have low water solubility (and are less susceptible to loss in the contacting aqueous phase), and because they are among the more commonly used and studied RTIL's. Demonstration of thermo-mechanical suitability is important to the application of ionic liquids in extraction applications, because knowledge of phase behavior will assist development of models to predict optimized mass transfer efficiency and process economics (reducing the need for solvent replacement).

EXPERIMENTAL PROCEDURE

Equipment

The centrifugal contactor used in testing was procured from Costner Industries Texas (formerly Costner Industries Nevada Company), and is the vendor's standard V-2 model. As indicated by the model designation, the rotor in the test apparatus has a 2-inch (5 cm) diameter. The selected contactor is designed for use of interchangeable heavy-phase weirs. This capability allows the operator to optimize phase separation performance both by fine tuning the total liquid holdup (and residence time within the rotor) and by altering the relative volumes of the inlet phases within the rotor. The contactor is equipped with a variable speed motor capable of operating at speeds up to 6000 rpm. The contactor was installed in a closed loop configuration as indicated in the photograph in Fig. 1. All wetted components of the

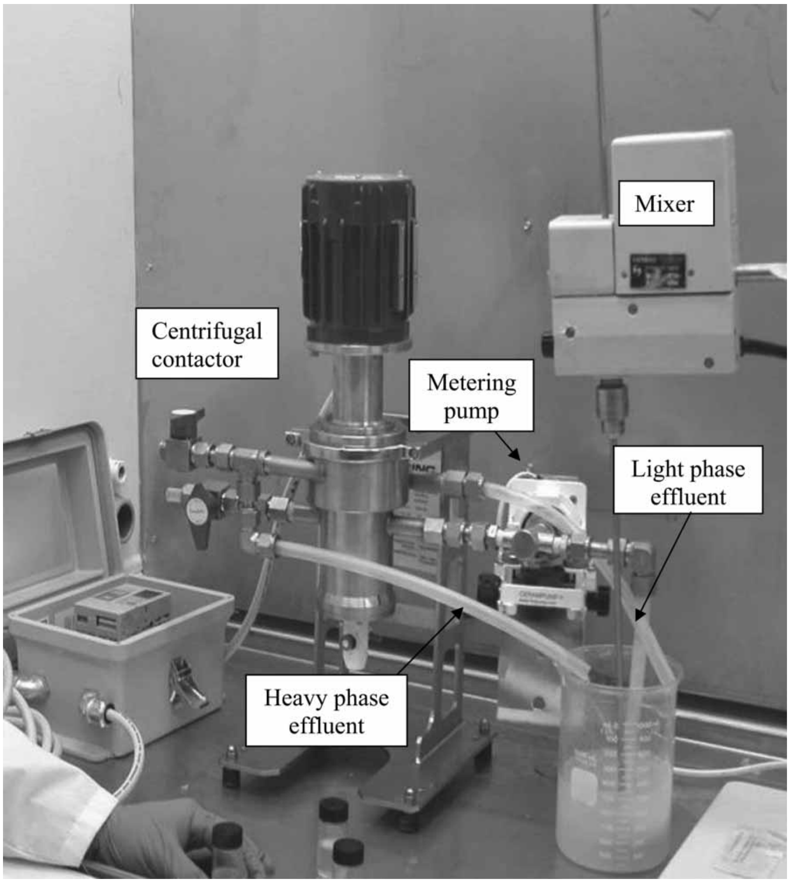

Figure 1. Photograph of centrifugal contactor closed loop configuration.

contactor test loop were fabricated from corrosion-resistant materials: 300 series stainless steels, TFA Teflon®, and Viton®.

As shown in Fig. 1, the phases to be separated were mixed prior to being introduced into the contactor. This arrangement differs from the conventional contactor configuration (Fig. 2) in which the phases are introduced separately into the apparatus, are dispersed in the annulus between the rotor and housing as a result of Couette mixing, and are subsequently separated inside the contactor's rotor. The separated phases are directed by internal channels to discharge ports at different elevations along the rotor. As shown in Fig. 2, the two phases are removed from the rotor into collection troughs that have been machined into stationary housing, and flow from these troughs is directed into outlet nozzles.

The unconventional arrangement used in the subject effort was dictated by the limited volumes of ionic liquids available for testing. Specifically,

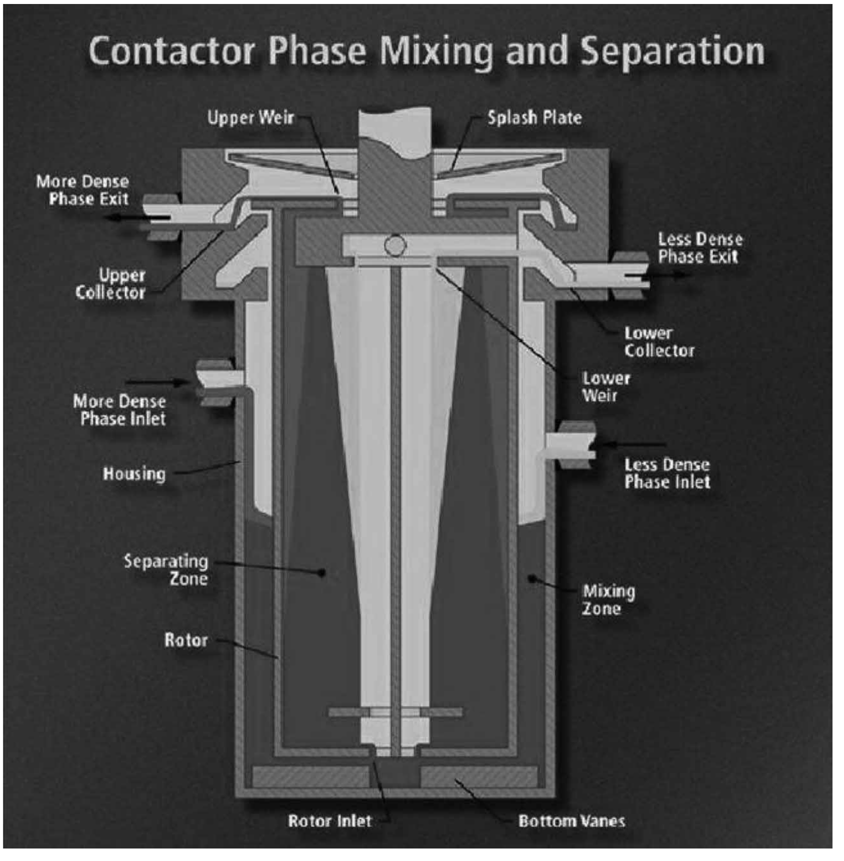

Figure 2. Cutaway schematic of contactor internal flows. The least dense phase is the light-color shade closest to the centerline of the rotor. The most dense phase is medium-grey closest to the wall of the rotor. The dispersed phase is the darkest shade in between the other two phases in the rotor and is the only phase present in the mixing zone.

the inventories of ionic liquids available (500 mL Terrasail®, 250 mL Bmim · NTf_2, and 700 mL Bmim · BETI) were not adequate to fill the contactor, a feed pump, ionic-liquid–phase feed and discharge lines, and provide a minimal surge volume. By combining the feed solutions outside the contactor, one complete feed system (feed vessel, pump, and feed line) was eliminated, resulting in a significant reduction in the volume of ionic liquid required for operation. The feed method used allowed the feed stream phase ratio to be determined by the relative starting volumes of the phases in the feed vessel, as measured. This was confirmed by periodic collection and centrifugation of feed-stream samples. Final, thorough mixing of the feed stream was accomplished in the contractor's mixing zone, per standard contactor operating practice.

The feed solutions were mixed in an unbaffled tank using a turbine impeller (IKA Works Inc., model T25 B S1) driven by a variable-speed stirrer (Carframo Model RFR2000). The impeller speed was varied during testing from 150 to 252 rpm, depending on the solutions being mixed and the total solution volume. Feed was delivered to the contactor by a FMI Model Q, piston-type metering pump.

Effluent samples were collected at each set of contactor operating conditions; samples were collected in volumes proportional to the phase ratio to avoid feed ratio upsets. Centrifugal samples were collected batchwise and examined visually for cross-phase contamination. Whenever an upset condition was encountered the system was returned to operating parameters that were known to provide stable operation, all liquids that had been withdrawn as samples were returned to the test loop, and the system was operated for an extended period to re-establish steady state at the desired phase ratio.

Physical and chemical property determinations were performed to evaluate the effects of interphase contact (e.g., ion transfer) and the effectiveness of phase separation. These data will also be used for calculations in the future design of an optimized contactor. Analyses included determinations of viscosity, surface tension and interfacial tensions, chloride ion concentration, H_2O content in the ionic liquids, ionic liquid content in the aqueous solution after contact, differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The DTA and TGA analysis were performed using a Harrop Differential Thermal Analyzer 760, heating rate of $30^\circ C \cdot h^{-1}$, and an inert atmosphere over the samples, 99.97% N_2 at $100\,mL \cdot min^{-1}$ or 100% Ar at $73\,mL \cdot min^{-1}$. Raman spectroscopy was carried out on ionic liquid and cyclohexane samples before and after contact to check for purity and phase carryover, using a Nicolet Magma IR 560 Spectrometer with an FT-Raman module.

Viscosities of the ionic liquids as functions of temperature were determined using a Brookfield Model DV-III Rheometer. Interfacial and surface tensions were measured using a Central Scientific Company DuNoűy tensiometer (PN#70535), and a Cole Palmer Surface Tensiomat 21. The Pt-Ir rings for the tensiometers (0.955725 cm ring radius, 0.017766 wire radius) were rinsed in isopropanol and acetone between measurements and flame-purified. Measurements were also carried out using a Tantec contact angle meter. Chloride ion transfer to $Bmim \cdot NTf_2$ was determined by measuring the conductivity of the NaCl solution before and after contact using an Orion Model 520A ohmmeter.

The extent of Bmim cation transfer into the 1 *M* NaCl solution was determined from the imidazolium cation maximum absorbance at 211 nm using a Varian Cary 50000 UV-Vis-NIR spectrophotometer. Transfer of water into two of the ionic liquids used in testing was evaluated using a Karl-Fisher titrator (Brinkman 652 KF-Coulometer). Differential thermal analyses and thermogravimetric analyses were performed using a Harrop model ST-736

DTA/TGA device, to investigate the thermal stability of the ionic liquids as well as carryover into the ionic liquid phase after treatment in the contactor.

Materials

Terrasail® was obtained from SACHEM, Inc., and was used as received. Bmim · NTf_2 and Bmim · BETI were synthesized at ORNL according to procedures published by Luo et al. (7). The final salts were rinsed several times with distilled-deionized water to remove inorganic impurities (e.g., LiBr). Reaction product purity was checked using nuclear magnetic resonance spectroscopy for organics (NMR), DTA/TGA, and Karl-Fischer titration for H_2O. Cyclohexane (EM Science, 0.02% H_2O, 0.002% evaporation residue) and 1,1′-oxybis(2,1-ethanediyloxy)butane (Aldrich Chemical Co., Inc, 99 + %) were used without further purification. The NaCl solution was prepared by dissolving 1 mol of the ACS reagent grade compound in water that had been purified using a Barnstead Nanopure treatment system and diluting to a final volume of 1L in a volumetric flask. Concentrations of HNO_3 (0.1 and 0.5 *M*) were obtained by diluting aliquots of concentrated HNO_3 (EM, 68–70%, impurities <5 ppm) in distilled de-ionized water. Densities, viscosities, and surface tensions of the pure liquids and solutions used in testing are presented in Table 1.

RESULTS

Gravity Settling Evaluations

To predict phase separation performance based on residence time, gravity settling experiments were performed on the dispersion pairs under consideration: 1 *M* NaCl and Bmim · NTf_2, 1 *M* NaCl and Terrasail®, Bmim · BETI and H_2O, Bmim · BETI and cyclohexane, and HNO_3 and 1,1′-oxybis(2,1-ethanediyloxy)butane. Gravity settling tests for the 1*M* NaCl/Bmim · NTf_2 pair were performed at organic-to-aqueous phase ratios of 0.5, 1.0, and 2.0. Gravity settling examination of the 1 *M* NaCl/Terrasail® system was performed at a single organic-to-aqueous volume ratio of 1.0, and for Bmim · BETI systems at volumetric ratios of 1 : 1 and 2 : 1 ionic liquid/immiscible phase. Under all test conditions the two phases were placed separately into a 100 mL graduated cylinder. The location of the interface was observed and recorded, as was the total height of liquid in the column, following the method of Leonard and coworkers (19). A stopper was placed in the cylinder and the cylinder was agitated for 20 s, followed by a 10 s hold period and a second agitation period of 20 s. Timing of the phase separation process was initiated immediately upon completion of the second period of agitation.

Table 1. Densities, viscosities, and surface tensions of test soloutions

Component	Density, $g \cdot mL^{-1}$	Viscosity, m Pa s	Surface tension, $mN \cdot m^{-1}$
Terrasail®	0.98	970 (23°C) 82.0, 93.6 (50°C) 22.3 (80°C)	Not measured
Bmim · NTf_2	1.42	52 (23°C) 21.7, 22.0 (50°C) 10.7 (80°C)	Not measured
Bmim · BETI	1.46 [12] 1.49402 (24.5°C)	119.7 ±0.8 (25°C) 39.66 ± 0.05 (50.2°C)	30.2 ± 0.2
1 *M* $NaCl_{(aq)}$	1.04	1.10	Not measured
1 *M* $HNO_{3(aq)}$	1.03 (25°C)	Not measured	Not measured
cyclohexane	0.7781 (20°C) 0.76918 (24.5°C)	0.66 (20°C) 0.894 (25°C)	25.5 (20°C) 24.65 (25°C)
1,1′-oxybis(2,1-ethanediyloxy) butane	0.88214 (24.5°C)	2.39 (20°C)	29.9 ± 0.2
Deionized-distilled water	0.99692 (24.5°C)	Not measured	75.8 ± 0.1

The results of gravity settling tests for the immiscible liquid pairs are presented in Table 2. Values in the rightmost column in Table 2 are the dispersion numbers, N_{Di}, which describe phase separation as a dimensionless value according to the expression (19)

$$N_{Di} = \frac{1}{t_b}\sqrt{\frac{z}{g_c}}$$

in which t_b is the breaktime in seconds, z is the dispersion band height in m, and g_c is the gravitational constant ($9.806\,m/s^2$ at ORNL).

Dispersion numbers obtained for the $NaCl_{(aq)}$/Bmim · NTf_2 system, Table 2, are similar to those that have been obtained for conventional solution pairs used in metal extraction operations that have been performed successfully in a system of centrifugal contactors. Therefore, the results of the gravity settling experiment predict successful phase separation using a centrifugal contactor. The dispersion number for Bmim · BETI/H_2O is lower, but as will be discussed later, the separation of the 2 phases was possible in the centrifugal contactor. The separation of Bmim · BETI and cyclohexane occurred very rapidly—within a few seconds—allowing only an estimate of the dispersion band height. The estimated dispersion number is three orders of magnitude higher than the Bmim · BETI/H_2O system. The 1, 1′-oxybis(2,1-ethanediyloxy)butane/$HNO_{3(aq)}$ system has been studied extensively in the past and served as a control. The measured

Table 2. Gravity settling results for systems of immiscible fluids

Mixture	Phase[a] ratio	Separation time (s)	Dispersion band height (m)	N_{Di}
$1M$ $NaCl_{(aq)}$/ Bmim · NTf_2	0.5	50	0.165	2.6×10^{-3}
	1	35	0.114	3.1×10^{-3}
	2	28 ± 2	0.165	$(4.7 \pm 0.4) \times 10^{-3}$
H_2O/Bmim · BETI	1	$>18 \times 10^4$		
	2	3420	0.114	3.2×10^{-5}
Cyclohexane/ Bmim · BETI	1	6 ± 1	Separated too quickly to measure	$>10^{-2}$
	2	9.7 ± 0.6		
Cyclohexane/ Deionized H_2O	1	45 ± 2	0.146	$(2.35 \pm 0.1) \times 10^{-3}$
	2	33 ± 2	0.110	$(3.20 \pm 0.2) \times 10^{-3}$
1,1′-oxybis (2,1-ethanediyloxy) butane +				
a) Deionized H_2O	0.5	$>3.6 \times 10^4$		
	1	80.3 ± 0.6	0.108	$(1.31 \pm 0.01) \times 10^{-3}$
	2	90.7 ± 0.6	0.163	$(1.42 \pm 0.01) \times 10^{-3}$
b) $0.5\,M$ HNO_3	1	79 ± 1	0.054	$(1.32 \pm 0.02) \times 10^{-3}$
c) $1\,M$ HNO_3	0.5	154 ± 3	0.162	$(8.3 \pm 0.1) \times 10^{-4}$
	1	170	0.108	$(6.2 \pm 0.1) \times 10^{-4}$
	2	214 ± 4	0.162	$(6.0 \pm 0.1) \times 10^{-4}$

[a] For the ionic liquid and aqueous contacts, the volumetric ratio refers to IL:aqueous phases. For the cyclohexane/Bmim ·BETI, the phase ratio is for IL:cyclohexane. For all other systems the ratio is defined as organic volume:aqueous volume.

dispersion numbers, which were found to be highly dependent on the concentration of the acid, are similar to what has been reported elsewhere for tri-n-butyl phosphate, validating the test method used in this study.

A meaningful dispersion number for the $NaCl_{(aq)}$/Terrasail® system could not be measured; while some discernable separation occurred within a few minutes after agitation, both the less dense Terrasail® and more dense aqueous phases exhibited considerable opposite phase entrainment that remained in both phases after several hours of gravity settling. Significant opposing phase entrainment remained in both phases of the $NaCl_{(aq)}$/Terrasail® system after several hours of gravity settling. Poor phase separation by gravity settling, as shown by the turbidity of the two phases, suggested that this ionic liquid may not be suitable for removal of organics from aqueous systems. However, testing using this system in a centrifugal contactor was performed as an example of a limiting case. The potential limitations posed by this system included a small density difference, high organic phase viscosity, and apparently unfavorable interfacial properties.

Centrifugal Contactor Separation Results

Contactor separations of $NaCl_{(aq)}/Bmim \cdot NTf_2$ dispersions were performed at an organic (ionic liquid):aqueous volume ratio of 0.5 (with an aqueous continuous phase), due to the minimal supply of the ionic liquid. Separations were performed at a single rotor speed of 3600 rpm. A heavy-phase weir having a relatively large opening (27.94 mm dia) was selected for use in $NaCl_{(aq)}/Bmim \cdot NTf_2$ separations to shift the interface within the rotor outward toward the rotor wall. This resulted in reducing the volume of the heavier phase (in this case, the ionic liquid) within the rotor relative to the lighter phase, and was done to minimize the $Bmim \cdot NTf_2$ holdup in the contactor.

The total (combined phases) flow rate to the contactor was set initially at $100\,mL \cdot min^{-1}$. As satisfactory phase separation was verified at a particular feed rate, the feed rate was increased incrementally to a maximum throughput of $1300\,mL \cdot min^{-1}$ (the maximum capacity of the pump). Subsequent testing was performed at higher and lower contactor speeds (4400 and 3300 rpm) to determine if separation performance was enhanced or degraded.

At each flow rate condition the centrifugal contactor provided excellent phase separation.

Separations of a $NaCl_{(aq)}$/Terrasail® dispersion (having an aqueous continuous phase, as determined by observation of samples removed from the mixing zone of an operating ccontactor) with a phase ratio of 1.0 were performed at feed rates ranging from 100 to $1000\,mL \cdot min^{-1}$. Unlike the gravity settling experiments, phase separation of $NaCl_{(aq)}$/Terrasail® dispersions were relatively good, i.e., while only minor cross-phase contamination was observed the effluent levels of contamination were greater than those observed in $NaCl_{(aq)}/Bmim \cdot NTf_2$ samples. Since the solutions exiting the contactor remained quite turbid, samples were processed in a batch centrifuge and re-examined for cross-phase carryover. Batch centrifugation did not increase the apparent volume of carryover observed in the effluent samples but did reduce the turbidity. This result indicates that

(a) the turbidity was due to minor cross-phase contamination, or
(b) may be due, at least in part, to air entrainment.

Air entrainment in centrifugal contactor effluents is not unusual, since the design of these devices results in generation of a slight suction pressure within the rotor, causing air to flow through the apparatus. However, a relatively small bubble of aqueous solution was observed in the bottom of the Terrasail® sample after batch centrifugation suggesting that cross contamination occurred. This was corroborated by Karl-Fischer titration as will be discussed later. Similarly, the turbidity in the effluent NaCl solution was probably due to entrainment of Terrasail®, though there was no visible indication of the presence of Terrasail® after batch centrifugation.

The entrainment in the effluent streams did not change significantly in response to increases in feed rate, which indicates that residence time was not a limiting factor in contactor performance. Attempts to improve performance by increasing the rotor speed resulted in reduced aqueous carryover in the ionic liquid effluent, but increased ionic liquid carryover in the aqueous discharge. This result indicates that the interface was near the heavy phase underflow (in this case, the aqueous flow path), since increased rotor speed causes the interface within the rotor to shift outward. The amount of ionic liquid carryover in the aqueous phase was reduced by reducing the diameter of the heavy phase weir, which shifted the interface toward the centerline of the rotor, away from the heavy phase flow path.

To evaluate the purity of the ionic liquids, DTA and TGA were performed both before and after centrifugal contact. Figure 3 gives three traces for heating of separate Bmim · BETI samples,

(a) before contact or as-synthesized,
(b) after contact with cyclohexane, and
(c) after subsequent aeration to remove cyclohexane.

These traces were taken to 140°C, well above the normal boiling point of cyclohexane, 80.7°C. Negligible mass loss was observed in the as-synthesized Bmim · BETI, 0.1%, but 2.3 mass% was lost from the contacted ionic liquid. This was promptly removed by aeration, vigorous stirring in air for a few minutes. In the last trace very little mass was lost as the system was heated to 140°C, $<1\%$. These results were confirmed using Raman spectroscopy, by examining a strong cyclohexane absorption at a shift of $\sim 800\,\mathrm{cm}^{-1}$ from the Raleigh line. The cyclohexane peak is well separated from any ionic liquid absorption, the closest peak being at a shift of $\sim 745\,\mathrm{cm}^{-1}$, and well resolved at the $2\,\mathrm{cm}^{-1}$ setting of the spectrometer. A small residual peak was observed in the contacted Bmim · BETI, but it disappeared after aeration. Because a separate phase was not observed in the Bmim · BETI after being removed from the contactor, it is possible that the cyclohexane is slightly soluble in this ionic liquid.

Little or no entrainment was apparent in the H_2O/Bmim · BETI system from DTA/TGA analyses. Under conditions of $200\,\mathrm{mL \cdot min^{-1}}$, 4400 rpm, no entrainment was observed. A DTA/TGA analysis was carried out on the Bmim · BETI/H_2O system after contact at $300\,\mathrm{mL \cdot min^{-1}}$, 3300 rpm, shown in Fig. 4. In this case, the upper trace is for H_2O after contact. Most of the sample evaporates below 100°C, suggesting little ionic liquid is present; but a slight transfer of ionic liquid into the aqueous phase was observed, Fig. 3a, leaving a trace $<0.2\%$ by mass. The second graph in Fig. 4 is for Bmim · BETI after contact with H_2O. There was negligible mass loss from Bmim · BETI when heated to 140°C, Fig. 4b, suggesting no significant transfer of water into the ionic liquid occurred during contact

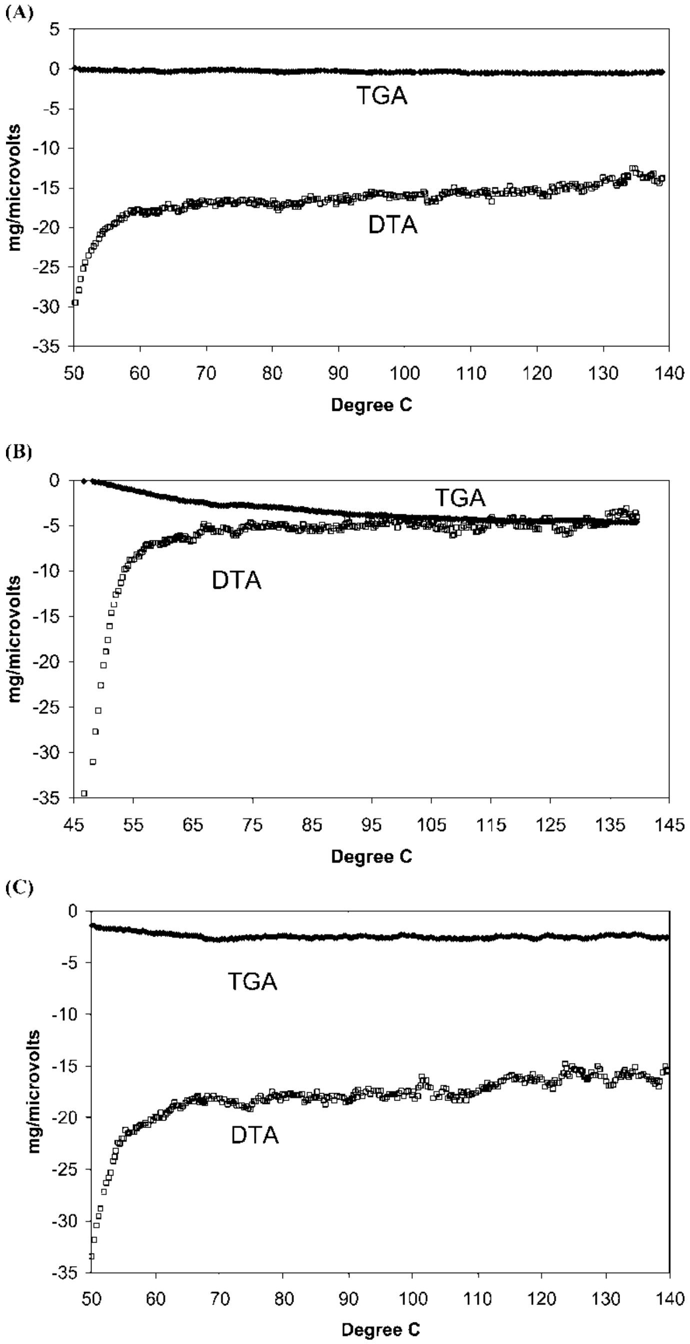

Figure 3. DTA/TGA analyses of Bmim · BETI, (A) as synthesized, (B) after contact with cyclohexane, and (C) after aeration to remove the cyclohexane.

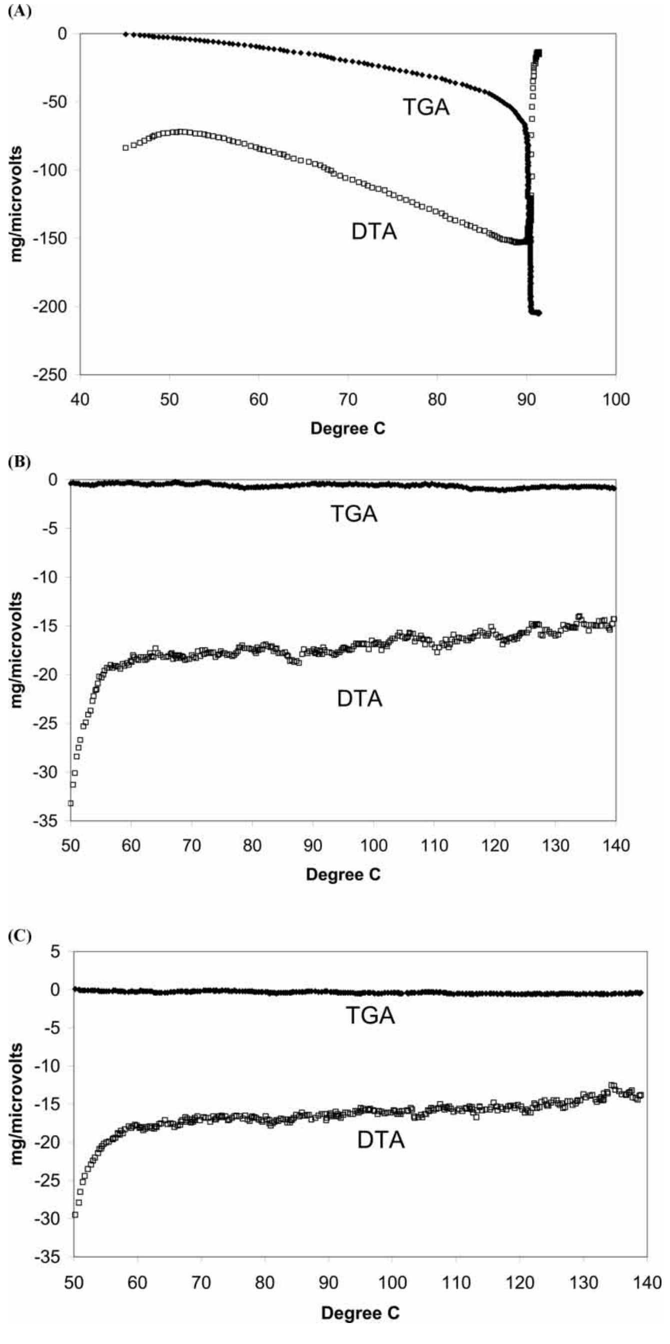

Figure 4. DTA/TGA analysis of (A) H_2O after contact with Bmim · BETI, (B) Bmim · BETI after contact with H_2O, and (C) as-synthesized Bmim · BETI for contrast, showing the negligible carryover of phases in the contactor.

and that good phase separation was obtained for the Bmim · BETI/H_2O system. The last graph, Fig. 4c, is for as-synthesized Bmim · BETI.

Physical and Chemical Analyses

Viscosity determinations as a function of temperature were made for the ionic liquids used in the reported work, Table 2. Fluidic properties such as viscosity and interfacial tension, Table 3, are required for modeling contactor hydraulics to optimize design and operating parameters for specific ionic liquids.

Viscosities were determined at ambient conditions, 23°C. Measurements were then made after heating first to 50°C, then to 80°C because viscosity for these fluids is a strong function of temperature. An additional determination was made after cooling each ionic liquid to 50°C to determine if the rheology was changed by heating. The viscosity of Bmim · NTf_2 determined at 50°C after cooling from 80°C was unchanged from the previous 50°C determination, within experimental error. The viscosity of the Terrasail® at 50°C after cooling from 80°C (93.6 mN · m^{-1}) was higher than the value determined before heating to the higher temperature (82 mN · m^{-1}). Changes in appearance were also noted after the heating cycle, suggesting some physical change at higher temperatures although breakdown was not shown in DTA/TGA results as will be discussed later.

The conductivity of the NaCl solution before and after contact with Bmim · NTf_2 was measured to determine the extent of chloride ion transfer, if any, into the ionic liquid. The results of the determinations are presented in Table 4. The results of the conductivity measurements indicate no significant transfer of chloride ions into Bmim · NTf_2 as a result of contact with the 1 *M* NaCl solution.

An aqueous effluent sample from contactor separation of the $NaCl_{(aq)}$/Bmim · NTf_2 dispersion was spectrophotometrically analyzed to determine the extent of Bmim cation transfer into the aqueous solution. The results indicate an after-contact concentration of 0.016 ± 0.01 *M* Bmim cation in the aqueous salt solution, which is an order of magnitude greater than the

Table 3. Interfacial tension measurements for equilibrated immiscible ionic liquid systems (24.5°C)

System	Interfacial tension (mN · m^{-1})
H_2O/air	75.8
Bmim · BETI/H_2O	17.6 ± 0.4
Bmim · BETI/cyclohexane	8.87 ± 0.06
1,1′-oxybis(2,1-ethanediyloxy) butane/0.5 M HNO_3	40.9

Table 4. Results of chloride extraction analysis for NaCl(aq)/ Bmin · NTf$_2$ system

Sample description	Cl^- concentration(g · mL^{-1})
1 *M* NaCl solution before IL contact	0.030 ± 0.001
1 *M* NaCl solution after IL contact	0.031 ± 0.001

solubility of Bmim · BETI in 1 *M* NaCl (aq), 0.0027 ± 0.0001 *M* (20) suggesting some physical entrainment occurred in the contactor.

Karl-Fischer titrations of samples of Bmim · NTf$_2$ and Terrasail® effluents from contactor testing were performed to evaluate water transfer into the ionic liquids. The results of these analyses indicate the presence of H_2O in the Bmim · NTf$_2$ effluent at 0.013 g · mL^{-1}, and 0.086 g · mL^{-1} H_2O in the Terrasail® effluent. The water content of the Bmim · NTf$_2$ was close to the saturation water content reported as 0.014 g · mL^{-1} (10). Because larger than expected amounts of water were not observed in the ionic liquid phase, this confirmed that good phase separation had occurred.

To evaluate the thermal behavior as well as purity of the ionic liquids, DTA and TGA were performed up to temperatures above 300°C, the point at which most organic ionic liquids decompose. Figure 5 shows the heating of Terrasail®, with initial and final weights of 0.1695 and 0.0024 g, respectively. Phase transitions/reactions occurred at 85° and 230°C. In Fig. 6, the initial and final weights of Bmim · NTf$_2$ were 0.1988 and 0.1299 g. Results presented in Fig. 6 indicate weak phase transitions/reactions that were observed at 200° and 300°C. Note that the DTA for as-synthesized Bmim · BETI is available in Fig. 3c for comparison, and this work and work done elsewhere, e.g., (20), indicate that the Bmim · BETI ionic liquid is also stable to 300°C.

DISCUSSION AND CONCLUSIONS

Dispersion number results along with measured densities and viscosities were used to predict contactor throughput as a function of rotor speed for the NaCl$_{(aq)}$/Bmim · NTf$_2$ and H_2O/Bmim · BETI systems. Contactor performance was predicted following methods developed earlier (e.g., 21, 22), shown in Figs. 5a and b, and is consistent with the results of phase separation demonstrations, up to 1300 mL · min^{-1}. The configuration of the feed inlets in the particular contactor model used in the reported work has resulted in poor phase separation at rotor speeds exceeding 4000 rpm in previous unrelated testing, as entry of feeds normal (perpendicular) to the rotor results in impingement. This can lead to excessive splashing and entrainment of feed solutions in the vapor space above the contactor mixing zone at higher operating speeds,

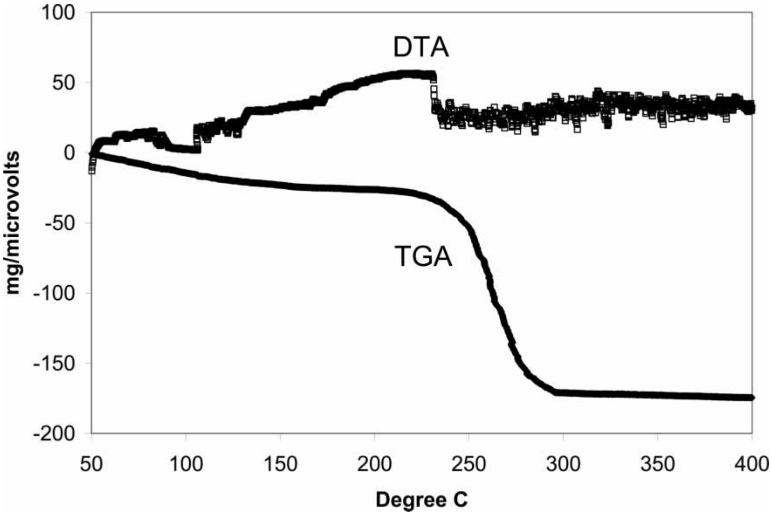

Figure 5. DTA/TGA results from Terrasail® analysis, showing stability up to 230°C.

which may extend upward into the product collection channels. Given the good agreement between predicted and actual results at lower speeds, it is expected that increased throughput could be achieved using a modified contactor having a different inlet nozzle configuration which would facilitate generation of increased separation force without this artifact. Carryover of the

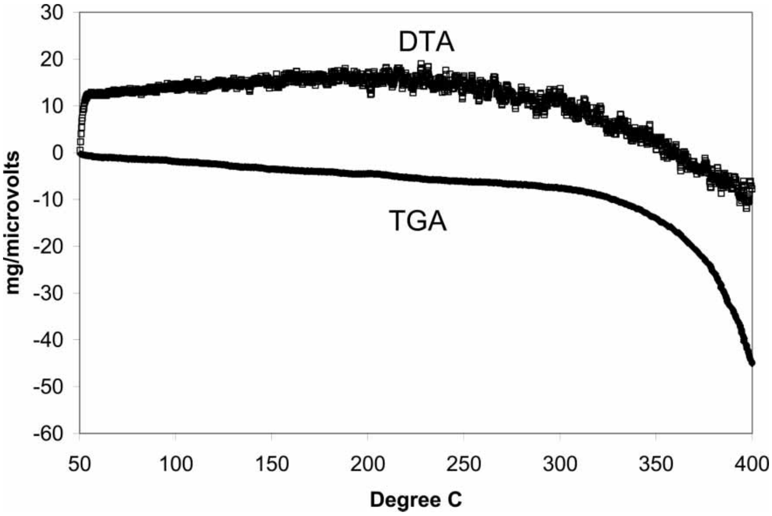

Figure 6. DTA/TGA results from Bmim · NTf_2 analysis, showing stability to over 300°C.

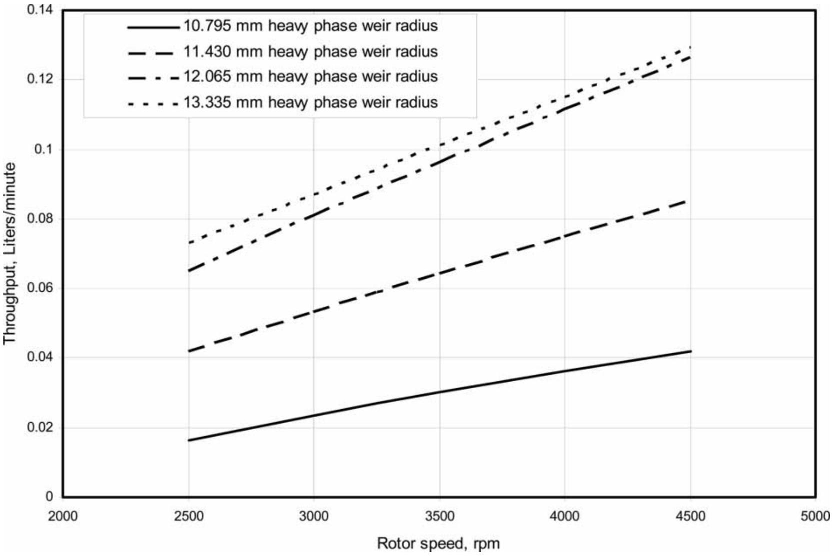

Figure 7. Predicted 5-cm contactor performance for the $H_2O/Bmim \cdot BETI$ system at a 1 : 2 phase ratio.

ionic liquid, or heavy phase, can be minimized by adjustment of the diameter of the heavy phase weir. This indicates that the versatility of the centrifugal contactor design meshes well with the varied properties of the ionic-liquid systems considered for industrial processing.

Because of the inability to determine a meaningful dispersion number for the $NaCl_{(aq)}$/Terrasail® system, no attempt was made to predict contactor performance for this system. Phase separation using the contactor was good, but effluents from contactor exhibited significant turbidity, which was reduced after extended processing in a batch centrifuge. The primary source of turbidity in the Terrasail® effluent was probably aqueous phase contamination, as indicated by the water content determined by Karl-Fischer titration. Given the promising preliminary contactor separation results for the $NaCl_{(aq)}$/Terrasail® system, it is expected that improved separation could be achieved by modifying the separator for higher speed operation and increased separator residence time, and by operating the system at increased temperature in order to reduce the viscosity of the Terrasail® phase.

Chloride analysis of the 1 *M* NaCl solution before and after contact with $Bmim \cdot NTf_2$ indicated no significant transfer of chloride ions from the aqueous solution. While not significant in terms of phase separation performance, this result indicates that this particular ionic liquid can be used for the treatment of saline waste water without accumulating chloride ions that would impair removal of target organic contaminants, primarily polar molecules such as phenols and aromatics (10).

Separation of the Bmim · BETI/cyclohexane dispersion was very effective, both with gravity settling and in the centrifugal contactor. The separation was enhanced by the large density difference in the two fluids. Some entrainment of the organic phase in the molten salt was observed, but was easily removed by aeration at room temperature.

In summary, a number of different dispersions of immiscible fluids were examined in this work, most involving ionic liquids, and benchmarked by the 1,1′-oxybis(2,1-ethanediyloxy)butane/$HNO_{3(aq)}$ system. Separations were possible on all of the systems, even when densities were very similar, e.g., Terrasail®/1 *M* NaCl(aq). Rapid separations were achieved when interfacial tensions were low, viscosities were low, and density differences large. Some systems did not separate well under conditions of gravity settling. However, employment of the centrifugal contactor technology allowed all of the systems to be separated. Hence, the use of centrifugal contactor technology not only minimizes the amount of solvent used in the separation, allowing more cost effective use of ionic liquids, but will facilitate separations where physical properties of the fluids in the dispersion would otherwise make separations very difficult.

ACKNOWLEDGMENTS

The authors received funding for the work from the US Department of Energy (DOE), Natural Gas and Oil Technology Partnership, and support from industrial partners representative of the Petroleum Energy Research Forum. Oak Ridge National Laboratory is operated by UT-Battelle under contract to the DOE#AB05483OR41. One of us, D.L. Schuh, was sponsored by the DOE Student Undergraduate Laboratory Internship (SULI) program.

REFERENCES

1. Davis, J.H. (2003) From curiosities to commodities, ionic liquids begin the transition. *Chemical Communications*, 11: 1209–1212.
2. Boesmann, A., Datsevich, L., Jess, A., Lauter, A., Schmitz, C., and Wasserscheid, P. (2001) Deep desulfurization of diesel fuel by extraction with ionic liquids. *Chemical Communications*, 23: 2494–2495.
3. Koel, M., Ljovin, S., Hollis, K., and Rubin, J. (2001) Using neoteric solvents in oil shale studies. *Pure Appl. Chem.*, 73 (1): 153–159.
4. Liu, Y.S., Hu, Y.F., Wang, H.B., Xu, C.M., Ji, D.J., Sun, Y., and Guo, T.M. (2005) Ionic liquids: novel solvents for petroleum asphaltenes. *Chinese Journal of Chemical Engineering*, 13 (4): 564–567.
5. Rogers, R.D., Visser, A.E., Swatloski, R.P., and Hartman, D.H. (1999) metal ion separations in room-temperature ionic liquids: potential replacements for volatile organic diluents. In *Metal Separation Technologies Beyond 2000*; Liddell, K.C. and Chaiko, D.J. (eds.), The Minerals, Metals and Materials Society: Warrendale, PA, 139–147.

6. Chen, P.Y. and Hussey, C.L. (2005) Electrochemistry of ionophore-coordinated Cs and Sr ions in the tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide ionic liquid. *Electrochimica Acta*, 50 (12): 2533–2540.
7. Luo, H., Dai, S., and Bonneson, P.V. (2004) Solvent extraction of Sr^{+2} and Cs^{+} based on room temperature ionic liquids containing monoaza-substituted crown ethers. *Anal. Chem.*, 76 (10): 2773–2779.
8. Luo, H., Dai, S., and Bonneson, P.V. (2004) Extraction of cesium ions from aqueous solutions using calix[4]arene-bis(*tert*-octylbenzo-crown-6) in ionic liquids, *Anal. Chem.*, 76 (11): 3078–3083.
9. Dietz, M.L. and Stepinski, D.C. (2005) A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): implications for the “greenness” of RTILs as extraction solvents. *Green Chemistry*, 7 (10): 747–750.
10. McFarlane, J., Ridenour, W., 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.
11. Zhao, H., Xia, S.Q., and Ma, P.S. (2005) Use of ionic liquids as ‘Green’ solvents for extractions. *Journal of Chemical Technology and Biotechnology*, 80 (10): 1089–1096.
12. Swatloski, R.P., Spear, S.K., Holbrey, J.D., and Rogers, R.D. (2002) Dissolution of cellulose with ionic liquids. *Journal of the Americal Chemical Society*, 124 (18): 4974–4975.
13. 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.
14. 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 Chemistry*, 3 (4): 156–164.
15. Davis, J.H. (2004) Task specific ionic liquids. *Chemistry Letters*, 33 (9): 1072–1077.
16. Chen, P.Y. and Hussey, C.L. (2004) Electrodeposition of cesium at mercury electrodes in the tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide room-temperature ionic liquid. *Electrochimica Acta*, 49 (28): 5125–5138.
17. Luo, H.M., Dai, S., Bonnesen, P.B., Haverlock, T.J., Moyer, B.A., and Buchanan, A.C. (2006) A striking effect of ionic liquid anions on the separation of Sr^{2+} and Cs^{+} by dicyclohexano-18-crown-6. *Solvent Extraction and Ion Exchange*, 24 (1): 19–31.
18. Vision 2020 Partnership (2004) *Accelerating Ionic Liquid Commercialization*; BCS Inc.
19. Leonard, R.A.J. and Ziegler, A.A.H. (1980) Annular centrifugal contractors for solvent-extraction. *Separation Science and Technology*, 15 (4): 925–943.
20. Toh, S.L.I., McFarlane, J., Tsouris, C., DePaoli, D.W., Luo, H., and Dai, S. (2005) Room-temperature ionic liquids in liquid–liquid extraction: effects of solubility in aqueous solutions on surface properties. *Solvent Extraction and Ion Exchange*, 24 (1): 33–56.
21. Leonard, R.A. (1988) Recent advances in centrifugal contactor design. *Sep. Sci. Technol.*, 28 (1–3): 177–200.
22. Leonard, R.A., Wygmans, D.G., McElwee, M.J., Wasserman, M.O., and Vandegrift, G.F. (1993) The centrifugal contactor as a concentrator in solvent extraction processes. *Sep. Sci. Technol.*, 28 (1–3): 177–200.