J. Chem. Eng. Data **2010,** *55,* 3391–3394 **3391**

Extraction of Sodium Chloride from Water and Solubility of Water in Hydrophobic Trialkylammonium Alkanoate-Based Ionic Liquids

Camiel H. C. Janssen,[†,‡] Maaike C. Kroon,[†] Sybrand J. Metz,[‡] Jaap van Spronsen,[†] and Geert-Jan Witkamp*[,†]

Process Equipment Department of Process & Energy, Faculty of Mechanical Maritime & Materials Engineering, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands, and Wetsus Centre of Excellence for Sustainable Water Technology, Agora 1, 8900 CC, Leeuwarden, The Netherlands

The sodium chloride extraction from aqueous solutions by using hydrophobic trialkylammonium alkanoate ionic liquids (ILs) is studied experimentally. The water solubility in these ILs is also determined. It is found that trialkylammonium alkanoate ILs show sodium chloride extraction efficiencies up to 0.101 g NaCl extracted/g NaCl start. This efficiency cannot be explained by the low water uptake (up to 0.02 g_{water}/g_{IL}) in the IL. Instead, the sodium chloride extraction must be attributed to other factors, such as steric hindrance considerations. Steric hindrance considerations also explain the dependence of sodium chloride extraction efficiency on the IL structure. Kinetic experiments were performed to ensure a state of chemical equilibrium.

Introduction

Ionic liquids (ILs) have been described as environmentally benign replacements for traditional volatile organic solvents due to their negligible vapor pressure at room temperature.[1] ILs are molten salts that are liquid at temperatures below 373 K. Their characteristics include excellent solubility properties, a wide liquid temperature range, and a wide electrochemical window. Because it is possible to tune the physical and chemical properties of ILs by varying the nature of the anions and cations, they can be task-specifically designed for a certain application. ILs have successfully been applied as solvents in chemical synthesis, catalysis, and separation technology.[1,2]

An interesting application of ILs is their usage as extraction media. For example, hydrophobic ILs have been used to extract organics from aqueous media.[3,4] However, even the most hydrophobic ILs still show some mutual asymmetric solubility with water.[5−8] These mutual solubilities of ILs and water are not symmetric. Generally, a much higher mole fraction of water is present in the IL phase than IL in the water phase at the same temperature.[5,7,9−13] The upper critical solution temperature (UCST) is thus found at very low mole fractions of the IL.[14]

When an IL is used as a solvent to extract solutes from water, the dissolution of the IL in the aqueous phase could represent a wastewater treatment challenge,[7] especially since many ILs present toxicity toward micro-organisms.[1] It was recently found that the mutual solubilities between IL and water could be decreased by an addition of an inorganic salt, a so-called salting-out effect.[15−18] Therefore, if an IL is used to extract a salt from a water phase, the cross-contamination problems could be designed to be less severe.

The extraction of salts from water by using ILs is not commonly studied, because of problems with cross contamination mentioned before and because the solubility of salts in the conventionally used imidazolium-based ILs is generally very low (less than 1 %).[1] Salt solubilities in ILs can be increased (i) by changing the IL structure[19−23] or (ii) by the addition of ligands.[24−27] The first option involves the development of task-specific ILs with both hydrophilic and metal ion-ligating functional groups. An example is the use of urea-, thiourea-, and thioether-substituted imidazolium hexafluorophosphate ILs for the extraction of Hg^{2+} and Cd^{2+} from water.[20] It was also found that imidazolium-based ILs with iodide and bromide anions show higher IL/water partitioning for Hg^{2+} than imidazolium-based ILs with chloride, fluoride, or cyanide anions.[20] However, a correlation between the chain length of the alkyl group on the cation and the Hg^{+} extraction efficiency was absent.[23] The second option involves enhanced solubility of the metal ions using ligands. Especially the solvation of crown ether complexes in ILs has been studied to increase metal salt solubilities in ILs.[24−27]

In this article a new type of hydrophobic ILs based on trialkylammonium alkanoate is described as a salt extraction medium from aqueous solutions. To the best of our knowledge, this type of ILs has never been investigated before as an extracting solvent. The focus of this research is to determine the sodium chloride (NaCl) extraction efficiency from aqueous solutions by using trialkylammonium alkanoate ILs. The water uptake by these ILs will also be measured.

Experimental Section

A NaCl solution was prepared by mixing 3.4 g of NaCl with 100 mL of water. A mixture of 2.5 g of the prepared NaCl solution and 2.5 g of IL were put into an Erlenmeyer flask at the start of the experiment. The samples were weighed on a balance and had an uncertainty of 0.0001 g. After shaking the mixture vigorously for 10 min on a vortex mixer, the phases were put into a centrifuge tube. The tube was put into a centrifuge (Beckman Coulter Allegra X-12R and centrifuged for 5 min at 3750 rpm. The phases were then separated by using syringes. All experiments were performed at room temperature (295 K).

The Na^{+} content in the water phase after extraction was analyzed twice using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Perkin-Elmer Optima 5300DV)

---

* Corresponding author. Tel.: +31-15-2783602. Fax: +31-15-2786975. E-mail address: geertjanwitkamp@me.com.
[†] Delft University of Technology.
[‡] Wetsus Centre of Excellence for Sustainable Water Technology.

10.1021/je100062b

Table 1. Trialkylammonium Alkanoate ILs with Given Numbers Used in This Research, Indicating the Specific R_1 and R_2 Groups from Figure 1 for Each IL

IL	no.	R_1	R_2
trioctylammonium acetate	1	octyl	methyl
trioctylammonium butyrate	2	octyl	propyl
trioctylammonium *trans*-2-hexenoate	3	octyl	1-pentenyl
trioctylammonium heptanoate	4	octyl	hexyl
trioctylammonium octanoate	5	octyl	heptyl
trioctylammonium decanoate	6	octyl	nonyl
trioctylammonium (±) 2-butyloctanoate	7	octyl	1-butylheptyl
triisobutylammonium hexanoate	8	isobutyl	pentyl
triisobutylammonium heptanoate	9	isobutyl	hexyl
triisobutylammonium octanoate	10	isobutyl	heptyl
triisobutylammonium decanoate	11	isobutyl	nonyl

with an uncertainty of 1 %. The ICP-AES had a detection limit of 0.05 $\text{mg}\cdot\text{L}^{-1}$ and a measuring range of (0 to 10) $\text{mg}\cdot\text{L}^{-1}$. The water content in the IL phase was measured by a Karl Fischer coulometer (Metrohm KF 756 coulometer) and had an uncertainty of 1 $\text{mg}\cdot\text{L}^{-1}$.

The ILs used for these experiments can be found in Table 1 and were purchased from Bioniqs. The purity of the ILs was > 98 % with a water content of less than 0.13 % and an anion purity of > 99.4 %. The NaCl was supplied by Bohm and was of technical grade. The purity was 99.5 % and contained traces of calcium (0.002 %), copper (0.0001 %), magnesium (0.0001 %), iron (0.0001 %), and sulfate (0.15 %).

To validate the measurements and to ensure a state of chemical equilibria after 10 min, kinetic experiments using the ILs triisobutylammonium octanoate and trioctylammonium octanoate were carried out as well. For the kinetic experiments a mixture of 2.0 g of NaCl solution and 2.0 g of IL were put into a centrifuge tube and shaken vigorously using a Heidolph Multi Reax for (1, 2, 5, 10, 15, or 300) min with an uncertainty of 0.05 min. The tubes shaken for (5, 10, 15, and 300) min were then put into a centrifuge (Beckman Coulter Allegra X-12R) for 5 min at 3750 rpm. The kinetic experiments with durations of 1 and 2 min had a centrifuge time of 2 min at 3750 rpm. The phases were separated by using syringes. The Na^+ content in the water phase after extraction was measured by ICP-AES.

Results and Discussion

The trialkylammonium alkanoate ILs studied in this research can be found in Table 1. The general structure of these ILs is shown in Figure 1. For all ILs from Table 1 the NaCl extraction efficiency was measured. To be able to ensure a state of chemical equilibrium, first, kinetic experiments were carried out using the ILs triisobutylammonium octanoate and trioctylammonium octanoate. Figure 2 clearly shows that equilibrium has been reached after 10 min for triisobutylammonium octanoate.

Next, for all ILs from Table 1 the NaCl extraction efficiency from a 34 g NaCl/L H_2O aqueous solution (ratio NaCl solution/IL = 1:1) at room temperature (295 K) was measured. The extraction efficiencies are defined as the amount of NaCl that has been transferred from the water phase to the IL phase over the initial amount of NaCl present in the aqueous phase. The results are shown in Table 2. It can be seen that the NaCl extraction efficiencies vary from (0.0180 to 0.101) g NaCl extracted/g NaCl start, depending on the IL used. The same data have also been expressed in Table 2 as partition coefficient P $((\text{mol}_{\text{NaCl}}\cdot\text{L}^{-1})_{\text{IL}}/(\text{mol}_{\text{NaCl}}\cdot\text{L}^{-1})_{\text{water}})$. A plot of the extraction efficiency versus the number of carbon atoms in the anion of the IL is shown in Figure 3. The error bars were obtained from propagation of error calculations from duplicate analyses.

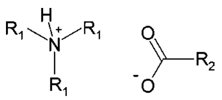

Figure 1. Generic structure of trialkylammonium alkanoate ILs.

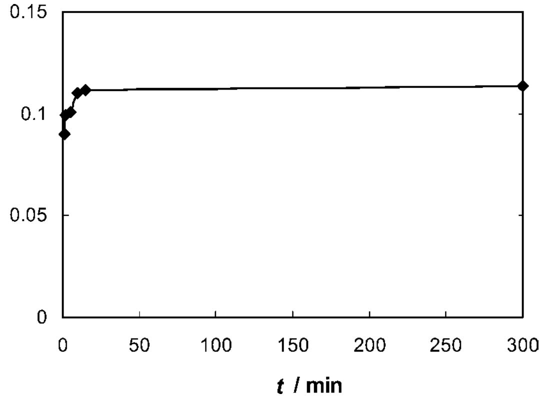

Figure 2. NaCl extraction efficiency, η, of the IL triisobutylammonium octanoate as a function of the extraction time, t. A state of equilibrium is reached after 10 min.

Table 2. NaCl Extraction Efficiencies, η, in g NaCl Extracted/g NaCl Start Solution, as Measured in This Work, from a NaCl Solution (34 $\text{g}\cdot\text{L}^{-1}$) by Using Trialkylammonium Alkanoate ILs (Ratio of NaCl Solution/IL = 1:1), the Partition Coefficients, P, in $(\text{mol}_{\text{NaCl}}/\text{L})_{\text{IL}}/(\text{mol}_{\text{NaCl}}/\text{L})_{\text{water}}$, and the Number of Carbon Atoms in the Cation, n_c, and in the Anion, n_a, for Each IL[a]

IL	n_c	n_a	η	P
1	24	2	0.079	0.25
2	24	4	0.090	0.29
3	24	6	0.047	0.14
4	24	7	0.036	0.11
5	24	8	0.065	0.20
6	24	10	0.054	0.17
7	24	12	0.065	0.21
8	12	6	0.058	0.19
9	12	7	0.018	0.06
10	12	8	0.10	0.34
11	12	10	0.058	0.19

[a] All experiments were conducted at room temperature.

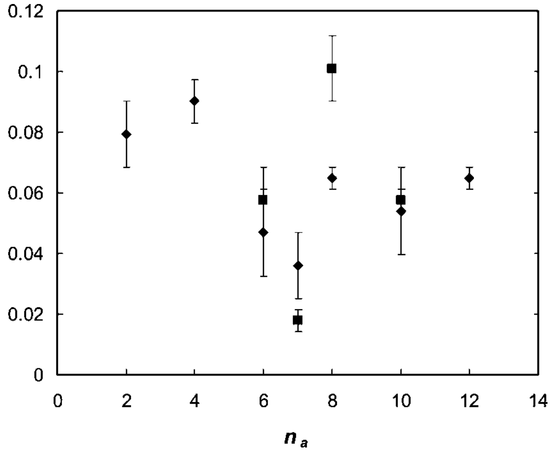

Figure 3. NaCl extraction efficiencies, η, versus the number of carbon-atoms in the anion of the IL, C_{anion}. The square points (■) represent the results for triisobutylammonium-based ILs, and the trioctylammonium-based ILs are represented by the diamond points (♦).

From Figure 3 it can be noticed that the extraction efficiency is dependent on the IL structure. If a trioctylammonium-based IL is used in combination with a small anion, the extraction efficiency is relatively high. The small anions can easily travel

Table 3. Ratio Water Uptake and NaCl Extraction, w_{H_2O}/w_{NaCl}, Calculated from the Water Uptake in the IL, w_{H2O}, in g_{water}/g_{IL}, and the Fraction of NaCl in the IL, w_{NaCl}, in g_{NaCl}/g_{IL}

IL	w_{H_2O}	w_{NaCl}	w_{H_2O}/w_{NaCl}
1	0.0185	0.00270	6.85
2	0.0156	0.00310	5.08
3	0.0167	0.00160	10.5
4	0.00980	0.00120	8.04
5	0.00900	0.00220	4.08
6	0.0143	0.00180	7.80
7	0.00420	0.00220	1.89
8	0.0204	0.00200	10.4
9	0.00790	0.000600	13.0
10	0.0144	0.00340	4.18
11	0.00190	0.00200	0.97

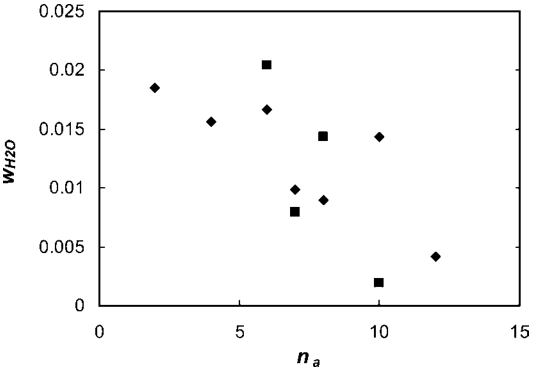

Figure 4. Mass fraction of water uptake, w_{H_2O}, by each IL as function of the number of carbon-atoms in the anion, C_{anion}. The square points (■) represent the results for triisobutylammonium-based ILs, and the trioctylammonium-based ILs are represented by the diamond points (♦).

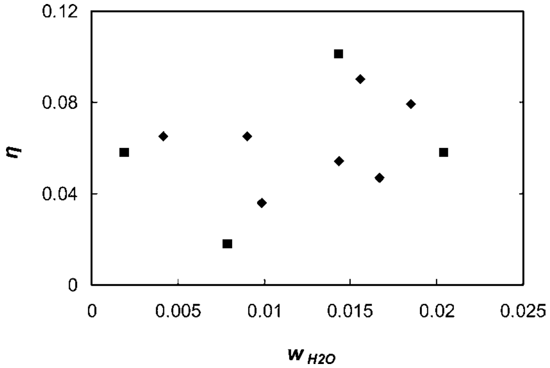

Figure 5. NaCl extraction efficiency, η, versus the mass fraction of water uptake, w_{H_2O}. The square points (■) represent the results for triisobutylammonium-based ILs, and the trioctylammonium-based ILs are represented by the diamond points (♦).

through the liquid and can achieve a high level of coordination with the large cation. The NaCl can be easily coordinated in between the cation and the anion, hence explaining the relatively high extraction efficiency compared to most commonly known ILs, such as imidazolium- and pyridinium-based ILs with hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions.[1] If the anion is much larger (ILs 5, 6, 7), less coordination is possible. If the anion has an octyl chain, it will fit quite well in between the alkyl chains of the cation. This will give an increased coordination over ILs 3 and 4. If the alkyl chain of the anion has 10 or 12 carbon atoms, then the coordination is also better. This can perhaps be explained by the fact that if larger anions are being used they need to have an even number of carbon atoms on the alkyl chain. Apparently these give better coordination and thus better NaCl extraction. This of course has to be further investigated, that is, by testing anions with alkyl chain lengths of an odd number of carbon atoms.

The extraction efficiencies for the triisobutylammonium-based ILs do not show a clear trend. Since the cation undergoes strong steric hindrance, the anion must make a good fit to be able to coordinate and extract Na^+ and Cl^- ions. It appears that if the alkyl chain of the anion contains eight carbon atoms, the extraction efficiency increases significantly. No specific reason can be found why the extraction efficiency is much lower if the alkyl chain length of the anion only contains seven carbon atoms. Perhaps this could be explained once more by the odd number of carbon atoms. However, this should be further investigated before definitive conclusions can be drawn.

Relating to Figure 3, the molar amounts of IL follow the opposite trend compared to the number of carbons in the anion. Therefore, it can be said that the molar amount of IL does not dictate the extraction efficiency either.

The water uptake by the ILs during NaCl extraction was also measured and can be found in Table 3. Figure 4 shows the water uptake graphically as a function of the number of anions in the IL. The error bars are small, and they fall within the symbols representing the data points. It is interesting to notice that only a small correlation can be found between the water uptake and the length of the alkyl chains of the cation and anion. It is expected that ILs with longer alkyl chains are more hydrophobic and therefore show less water uptake. However this trend is less pronounced than expected. The absence of a correlation between the chain length of the alkyl group on the cation and the water uptake has been previously observed in Hg^+ extraction experiments in ILs.[17]

It could also be expected that a higher water uptake by the IL results in a higher NaCl extraction efficiency because of coordination considerations. The NaCl extracted to the IL can also be extracted as a crystal coordinated by water which has been taken up by the IL. However, Figure 5 depicts that the extraction efficiency does not show any trend with the water uptake. Therefore, the coordination of the Na^+ and Cl^- ion by the IL does not dictate the extraction efficiency. For example, the 0.101 g NaCl extracted/g NaCl start extraction efficiency of triisobutylammonium octanoate cannot be fully explained by a water uptake of only 0.014 g_{water}/g_{IL}. This means that the NaCl extraction efficiency of the IL has to be attributed to other factors, such as the steric hindrance considerations described in the previous paragraphs. It is important to address the fact that in some cases the water uptake is sufficient for NaCl coordination by water. A NaCl molecule can be coordinated by up to six H_2O molecules. Table 3 shows that the ratio between the water uptake and the NaCl uptake by the IL varies from (0.97 to 13.0). High ratios are generally observed when the NaCl extraction efficiency is low. Lower ratios are however observed with higher NaCl extraction efficiencies.

Conclusions

The extraction efficiencies of NaCl into a new type of hydrophobic trialkylammonium alkanoate-based ILs were measured. Some correlation can be found between the IL structure and the water uptake, but this is not of significant value. There is also not a one-to-one relationship between the water uptake and the extraction efficiency. Furthermore, from these experiments its seems that the coordination of the Na^+ and Cl^- ion by the IL does not dictate the extraction efficiency. It appears that steric hindrance considerations play the greatest role in extracting NaCl from aqueous phases by using ILs.

Acknowledgment

The authors thank Jan Schouten and Jan Michels for their expertise and Jelmer Dijkstra and Petra Maarsingh for their help with the analyses. The authors also thank the participants of the Wetsus “Salt” theme for the fruitful discussions.

Literature Cited

(1) Wasserscheid, P.; Welton, T., Eds. *Ionic Liquids in Synthesis*; Wiley-VHC Verlag: Weinheim, 2003.

(2) Brennecke, J. F.; Maginn, E. J. Ionic Liquids; Innovative Fluids for Chemical Processing. *AIChE J.* **2001**, *47*, 2384–2389.

(3) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for Clean Liquid-Liquid Extraction. *Chem. Commun.* **1998**, 1765–1766.

(4) McFarlane, J.; Ridenour, W. B.; Luo, H.; Hunt, R. D.; DePaoli, D. W.; Ren, R. X. Room Temperature Ionic Liquids for Separating Organics form Produced Water. *Sep. Sci. Technol.* **2005**, *40*, 1245–1265.

(5) Freire, M. G.; Santos, L. M. N. B. F.; Fernandes, A. M.; Coutinho, J. A. P.; Marrucho, I. M. An Overview of the Mutual Solubilities of Water-Imidazolium-Based Ionic Liquids Systems. *Fluid Phase Equilib.* **2007**, *261*, 449–454.

(6) Kakiuchi, T. Mutual Solubility of Hydrophobic Ionic Liquids and Water in Liquid-Liquid Two-Phase Systems for Analytical Chemistry. *Anal. Sci.* **2008**, *24*, 1221–1230.

(7) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. *J. Phys. Chem. B* **2001**, *105*, 10942–10949.

(8) Domańska, U.; Rękawek, A.; Marciniak, A. Solubility of 1-Alkyl-3-ethylimidazolium-Based Ionic Liquids in Water and 1-Octanol. *J. Chem. Eng. Data* **2008**, *53*, 1126–1132.

(9) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydlowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romaní, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. A detailed thermodynamic analysis of [C(4)mim][BF4] plus water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.

(10) Domańska, U. Thermophysical properties and thermodynamic phase behavior of ionic liquids. *Thermochim. Acta* **2006**, *448*, 19–30.

(11) Domańska, U.; Marciniak, A. Phase behavior of 1-hexyloxymethyl-3-methyl-imidazolium and 1,3-dihexyloxymethyl-imidazolium based ionic liquids with alcohols, water, ketones and hydrocarbons: The effect of cation and anion on solubility;. *Fluid Phase Equilib.* **2007**, *260*, 9–18.

(12) Chapeaux, A.; Simoni, L. D.; Stadtherr, M. A.; Brennecke, J. F. Liquid phase behavior of ionic liquids with water and 1-octanol and modeling of 1-octanol/water partition coefficients. *J. Chem. Eng. Data* **2007**, *52*, 2462–2467.

(13) Wagner, M.; Stanga, O.; Schröer, W. Corresponding states analysis of the critical points in binary solutions of room temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3943–3950.

(14) Domańska, U.; Rękawek, A.; Marciniak, A. Solubility of 1-Alkyl-3-ethylimidazolium-Based Ionic Liquids in Water and 1-Octanol. *J. Chem. Eng. Data* **2008**, *53*, 1126–1132.

(15) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. 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.* **2003**, *125*, 6632–6633.

(16) Freire, M. G.; Carvalho, P. J.; Silva, A. M. S.; Santos, L. M. N. B. F.; Rebelo, L. P. N.; Marrucho, I. M.; Coutinho, J. A. P. Ion Specific Effects on the Mutual Solubility of Water and Hydrophobic Ionic Liquids. *J. Phys. Chem. B* **2009**, *113*, 202–211.

(17) Tomé, L. I. N.; Varanda, F. R.; Freire, M. G.; Marrucho, I. M.; Coutinho, J. A. P. Towards an Understanding of the Mutual Solubilities of Water and Hydrophobic Ionic Liquids in the Presence of Salts; The Anion Effect. *J. Phys. Chem. B* **2009**, *113*, 2815–2825.

(18) Najdanovic-Visak, V.; Lopes, J. N.; Visak, Z. P.; Trindade, J.; Rebelo, L. P. Salting-Out in Aqueous Solutions of Ionic Liquids and K_3PO_4: Aqueous Biphasic Systems and Salt Precipitation. *Int. J. Mol. Sci.* **2007**, *8*, 736–748.

(19) Davis, J. H., Jr. Task-Specific Ionic Liquids. *Chem. Lett.* **2004**, *33*, 1072–1077.

(20) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H., Jr.; Rogers, R. D. Task-Specific Ionic Liquids Incorporating Novel Cations for the Coordination and Extraction of Hg^{2+} and Cd^{2+}: Synthesis, Characterization, and Extraction Studies. *Environ. Sci. Technol.* **2002**, *36*, 2523–2529.

(21) Ouadi, A.; Gadenne, B.; Hesemann, P.; Moreau, J. J. E.; Billard, I.; Gaillard, C.; Mekki, S.; Moutiers, G. Task-Specific Ionic Liquids Bearing 2-Hydroxybenzylamine Units: Synthesis and Americium-Extraction Studies. *Chem.—Eur. J.* **2006**, *12*, 3074–3081.

(22) Lee, S. Functionalized Imidazolium Salts for Task-Specific Ionic Liquids and Their Applications. *Chem. Commun.* **2006**, 1049–1063.

(23) Germani, R.; Mancini, M. V.; Savelli, G.; Spreti, N. Mercury Extraction by Ionic Liquids; Temperature and Alkyl Chain Length Effect. *Tetrahedron Lett.* **2007**, *48*, 1767–1769.

(24) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. Traditional Extractants in Non-traditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596–3604.

(25) Dai, S.; Ju, Y. H.; Barnes, C. E. Solvent Extraction of Strontium Nitrate by a Crown Ether using Room-Temperature Ionic Liquids. *J. Chem. Soc., Dalton Trans.* **1999**, *8*, 1201–1202.

(26) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. Influence of Structural Variation in Room-Temperature Ionic Liquids on the Selectivity and Efficiency of Competitive Alkali Metal Salt Extraction by a Crown Ether. *Anal. Chem.* **2001**, *73*, 3737–3741.

(27) Wei, G.-T.; Yang, Z.; Chen, C.-J. Room Temperature Ionic Liquid as a Novel Medium for Liquid/Liquid Extraction of Metal Ions. *Anal. Chim. Acta* **2003**, *488*, 183–192.

Received for review February 8, 2010. Accepted June 9, 2010. This work was performed in the TTIW-cooperation framework of Wetsus. Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the Province of Fryslân, the City of Leeuwarden, and the EZ/Kompas program of the “Samenwerkingsverband Noord-Nederland”. The authors are indebted to the participants of the Wetsus “Salt” theme for their financial support.

JE100062B