

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Ionic liquid as diluent in solvent extraction: First evidence of supramolecular aggregation of a couple of extractant molecules

Received 00th January 20xx,
Accepted 00th January 20xx

T. Sukhbaatar, S. Dourdain, R. Turgis, J. Rey, G. Arrachart and S. Pellet-Rostaing

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ionic liquids have many favorable properties over conventional diluents in solvent extraction. They provide environmentally-benign feature, adjustable polarity and in some cases higher extraction performances, that remain however not predictable. As it may have a major role in extraction mechanisms, we evidence the supramolecular aggregation of HDEHP/TOPO extractant molecules in [OMim][NTf₂] ionic liquid.

Understanding the peculiar mechanisms of ionic liquids based extraction systems is essential to render the use of ILs in solvent extraction more common and reliable. ILs are known to present unique physico-chemical properties: the ability to solubilize a wide range of solutes, low vapor pressure, high thermal stability, structure tailorability, etc...¹ When used as a diluent in solvent extraction, they appear very promising as they prevent economic and ecological problems thanks to higher flash points and lower volatility than conventional organic diluents.² In some cases, they also significantly improve the extraction efficiency compared to conventional organic solvents.³ However, as the underlying mechanisms in such diluents are not fully understood, these higher performances cannot be generalized nor predicted when different systems or experimental parameters are applied.

Metal extraction in ILs occurs through extraction mechanisms which can differ from those observed in molecular solvents.⁴ Among the systems tested, several types of extraction mechanisms have been proposed such as anion⁵ or cation⁶ exchange, solvation⁷ and complexation processes with the extractant molecules as in common organic solvents,⁸ or multiple mechanisms.⁹ Most of the reported studies rely on the characterization of macroscopic data of extraction, proposing for example, complexes' stoichiometry determined from the slope analysis method. Even though very complete studies could explain a posteriori some extraction efficiencies observed in ILs,^{4b} no specific IL property has been evidenced to generalize and predict *a priori*. Moreover, no description of the complexes' and aggregates' microstructure has been investigated in detail to our knowledge. For these reasons, we aim at investigating the supramolecular aggregation of the

extractant molecules in ILs, to evaluate their influence on the key parameters of solvent extraction.

It is now well established that the solvent extraction mechanisms in common diluents are based not only on the molecular chelation properties of the extractant molecules, but also on their ability to form supramolecular reverse aggregates due to their amphiphilic nature.¹⁰ As ILs are widely studied as new media for surfactant self-assembly,¹¹ and as they are known to modify the curvature radii of surfactant reverse microemulsions,¹² it appears essential to evaluate the effect of these diluents having such peculiar polarity and structural properties, on the supra molecular aggregation of the extracting agents. To estimate the influence of ILs on solvent extraction mechanisms, we propose in this paper to compare the results found in an IL based system to those obtained in a common apolar diluent as dodecane, by focusing for the first time on such systems, on the characterization of supramolecular aggregation in ILs. Understanding aggregation phenomenon in detail, will give, in further studies, the opportunity to propose new insight into the influence of ILs as diluents on solvent extraction mechanisms.

We took advantage of previous studies performed on conventional apolar solvents devoted to the extraction mechanisms of hexavalent uranium U(VI) from phosphoric acid by the URPHOS system. In this system, extracting agents consist of a combination of di-(2-ethylhexyl)-phosphoric acid (HDEHP), a cationic exchanger extracting agent and tri-*n*-octyl-phosphine oxide (TOPO), a solvating agent in a 4:1 molar ratio.¹³ We showed in conventional apolar diluents that the synergistic properties of this mixture are related to a favored aggregation,¹⁴ and combined SAXS and SANS measurements revealed a significant influence of the diluent in synergistic mechanisms.¹⁵ Very recently, a study involving the same HDEHP/TOPO system for extraction of U(VI) from a phosphoric acid solution in *n*-octyl substituted imidazolium based ILs, [OMim][NTf₂] and [OMim][PF₆], has indicated that extraction performance is inferior in IL than in *n*-dodecane diluent,¹⁶ but no evidence nor explanation of the mechanism was proposed.

^a ICSM/LTSM, CEA/CNRS/UM2/ENSCM UMR5257, Site de Marcoule, Bat. 426, 30207 Bagnols sur Cèze, France.

Electronic Supplementary Information (ESI) available: [Experimental details: synthesis, extraction, and scattering methods]. See DOI: 10.1039/x0xx00000x

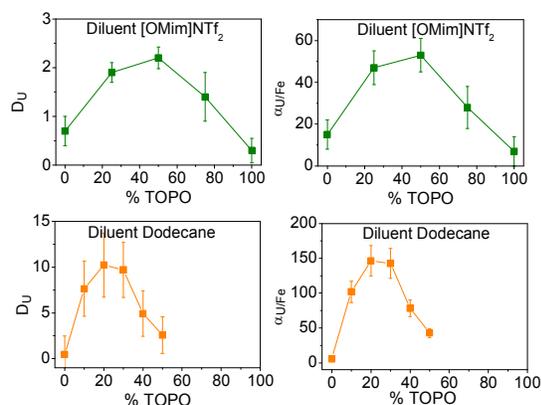


Figure 1 Distribution ratio of uranium and selectivity of uranium toward iron in IL (top part) and in dodecane (bottom) as a function of molar percentage of TOPO in the mixture of extractants, and for total concentration of extractants $[HDEHP]+[TOPO]=0.5M$

In the present study, in order to estimate the $[OMim][NTf_2]$ effects on the aggregation phenomena and on the synergistic extraction by HDEHP/TOPO couple of extractants, different characterization methods were carried out. Extraction of the metals, acid and water were determined by the ICP-AES technique and Karl-Fischer titration. Aggregation of the extractant molecules was characterized from SAXS and SANS measurements. As detailed in the following, this latter point, which is essential to evaluate the presence and the consequence of supramolecular aggregates in solvent extraction, required the specific synthesis of fully deuterated ILs. Organics solutions, containing a total extractant concentration $[HDEHP+TOPO]$ of 0.5M in the IL $[OMim][NTf_2]$ or dodecane, were contacted to 5M phosphoric acid solution containing uranium (VI) and iron (III) at concentrations of 1mmol and 45mmol to be in the similar conditions as in URPHOS process. To look over conditions at and out of the synergism, molar percentages of the extractant molecules were varied from $[TOPO]/[HDEHP+TOPO]=0$ to 100%. Organic and aqueous phases were contacted with a volume ratio 1/1 for 2 hours and separated after 1 hour centrifugation at 4000 rpm.

Variations of the distribution ratio of uranium, D_U , and of the selectivity toward iron in the IL, $\alpha_{U/Fe}$, are plotted in Figure 1 as a function of the TOPO molar percentage in HDEHP/TOPO mixture. They were compared to those conventionally obtained in n-dodecane and to those obtained in the pure IL. A distribution coefficient and selectivity of 0.1 and 6 showed that the pure IL has no extraction performance (see ESI).

Extraction properties of HDEHP/TOPO mixtures appear very different when applied in IL than in dodecane. As already reported,¹⁶ the affinity toward uranium is lower in $[OMim][NTf_2]$. The efficiency to extract U(VI) from phosphoric acid solution remains however significant with more than 66% of uranium selectively extracted with respect to iron ($D_U=2$; $S_{U/Fe}=60$). A striking feature of extraction is also that the maximum synergistic extraction is shifted from 20% of TOPO in dodecane to 40% in the IL.

Although the influence of many parameters (pH, total extractant concentrations or diluents nature...) have been studied for the HDEHP/TOPO system, so far none of them had been shown to modify the synergistic percentage, even when different diluents such as dichloromethane, heptane, or

hexadecane were used.¹⁵ It suggests that the IL influences strongly the synergism mechanisms.

Since the presence of water and acid is very important in the reverse aggregates formation in apolar media,¹⁷ and, in order to characterize fully the extraction properties of HDEHP and TOPO in $[OMim][NTf_2]$, water and acid extraction have been measured and compared to the ones in dodecane (Table 1).

TOPO percentage (%)	0	20	40	50	60	80	100
Extracted H ₂ O in dodecane (mmol/L)	62	89	114	129	*	*	*
Extracted H ₃ PO ₄ in dodecane (mmol/L)	6	25	67	88.5	*	*	*
Extracted H ₂ O in IL (mmol/L)	765	777	748	-	764	647	632
Extracted H ₃ PO ₄ in IL (mmol/L)	23	31	39	-	34.5	24	17

Table 1 Comparison of water and acid extraction in dodecane and IL for various TOPO percentages. (– not measured * TOPO insoluble at these percentages and concentrations)

In contrast to what was measured in dodecane,¹⁴ the increase of TOPO percentage does not gradually enhance the water and acid extraction. Besides, the concentration of acid is much lower in the IL while the extracted water is 6 to 10 times higher. To de-correlate the solubilisation power of the pure IL, water and acid extraction were also characterized without extractant molecules. It appears that pure IL extracts 100 times less acids but solubilises about 600 mmol/L of water (see ESI). This first result is consistent with the formation of reverse aggregates formed by HDEHP and TOPO, which would be able to solubilize about 100 mmol/L of water and 20 to 40 mmol/L of acids in their polar core, as it is often observed with surfactant reverse micelles.

It can also be observed that the concentration of acid in the IL is maximal at 40% of TOPO molar percentage, as for the selectivity of uranium versus iron, while the amount of extracted water is almost constant with the addition of TOPO. These very different features of extraction properties in IL suggest that very different mechanisms are involved in this new class of diluent. This strengthens the need to explore and understand the mechanisms that may be responsible for the different and unpredictable extraction properties in ILs.

As we previously related the synergistic properties of HDEHP/TOPO mixtures in conventional solvents to favored aggregation,¹⁴ and as it has never been characterized in ILs based extraction systems, the aggregation properties of the extractant molecules in $[OMim][NTf_2]$ were characterized by SAXS and SANS.

X ray scattering curves of the extracting organic phases are presented in Figure 2a in the IL and compared to those prepared in dodecane in Figure 2b. First of all, X-ray scattering curves of IL-based extracting solutions show the presence of aggregates, characterized by an increase of intensity at small angles, which is not observed in the pure IL. First of all, X-ray scattering curves of IL-based extracting solutions show the presence of aggregates, characterized by an increase of intensity at small angles, which is not observed in the pure IL. Looking at the signal of the aggregates, it appears that the saturation plateau observed when Q tends to zero, occurs at higher absolute intensities than those in dodecane (c.a. $0.3cm^{-1}$ in IL and $0.1cm^{-1}$ in dodecane), while the beginning of

intensity decrease appears at smaller Q (0.6 to 1nm^{-1} in IL compare to 3 to 4nm^{-1} in dodecane).

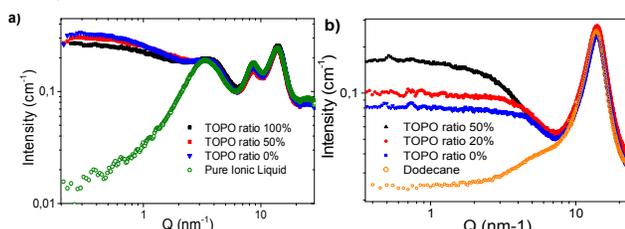
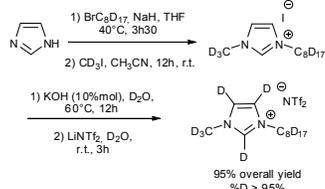


Figure 2 Scattering curves of a) the pure IL [OMim][NTf₂] and IL-based organic phases after extraction; b) pure dodecane and organic phases after extraction at different TOPO percentages. Total extractants concentration is 0.5M

The combination of these two features is in favor of the formation of bigger aggregates in IL than in dodecane. However, the presence of three peaks located at 3.5 , 8.5 , and 13.5nm^{-1} make difficult any further interpretation, such as determination of the aggregates size, shape and microstructure, from a regular fit of the data. These peaks are commonly identified as correlation peaks due to the intrinsic structure of the IL, and are respectively attributed to the anion-anion, anion-cation, carbon-carbon correlation distances.¹⁸ It appears therefore essential to perform complementary measurements by small angle neutron scattering (SANS).

SANS measurements were performed in a deuterated IL. In addition to provide a complementary contrast to characterize aggregates and a decrease of the incoherent signal due to hydrogens, the full deuteration of the IL was also expected to give the possibility of extinguishing the first structural peak of [OMim][NTf₂] (at 3.5nm^{-1} in Figure 2a). As proposed by Hardacre et al. in 2010, a partial to complete deuteration of the IL allows modulation of the intensity of the different peaks, until a complete extinction of the first one for fully deuterated ILs is achieved.¹⁸

We therefore synthesized a fully deuterated [OMim][NTf₂] following the approach described in scheme 1.



Scheme 1 Reactional scheme applied for a synthesis of fully deuterated [OMim][NTf₂]

After the N-alkylation of imidazole by deuterated alkyl chain, the imidazole protons have been exchanged with a deuterium by incubating the imidazole in deuterium oxide (D₂O). The isotope-exchange reaction is followed by NMR and confirmed by mass spectroscopy (see ESI). Finally, the metathesis reaction with lithium bis(trifluoromethylsulfonyl)imide performed in D₂O resulted in a fully deuterated pure IL [OMim][NTf₂].

The scattering curves at different TOPO percentages are presented in Figure 3a and compared to those obtained in dodecane in Figure 3b. Spectra of the pure diluents are also presented to emphasize the signal contribution attributed to the aggregates. As it was observed with X ray scattering, SANS

spectra show clearly that some aggregates are present in the IL extraction phase. An intense saturation plateau at small q values followed by a sharp decrease characterizes a presence of globular particles of about 1 nm in diameter. Moreover, a break in the slope between these two regions is also in favor of slightly bigger aggregates in the IL than in dodecane.

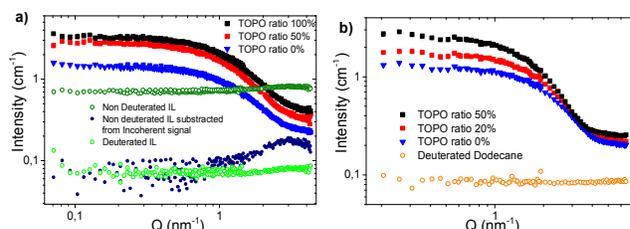


Figure 3 Scattering curves at different TOPO percentages in a) [OMim][NTf₂] and b) dodecane

The IL's deuteration enables full characterization of the aggregates: as shown in Figure 3a when comparing the pure deuterated and not deuterated IL, not only the level of background signals brought by the incoherent signal due to hydrogens decreases; as expected from literature,¹⁸ it participates also to the extinction of the first structural peak appearing at 3nm^{-1} on the signal of the non-deuterated IL subtracted from its incoherent signal.

Aggregates observed by SANS measurements also appear bigger than those observed by X ray. These behaviors are confirmed quantitatively with a guinier estimation of the aggregates radii (Table 2), performed on both SAXS and SANS spectra (Details in ESI).

	in [OMim][NTf ₂]			in dodecane		
TOPO percentage (%)	0	50	100	0	20	50
R _{SAXS} (nm)	1.1	1.0	0.9	0.2	0.3	0.4
R _{SANS} (nm)	1.4	1.5	1.5	0.6	0.7	0.9

Table 2 Estimations of the aggregates radii derived from a guinier analysis (average uncertainty: $\pm 0.2\text{nm}$)

The trend observed with increasing TOPO percentages is similar to the one obtained in deuterated dodecane. Considering a core-shell model as in the common organic diluents, the increase of scattered intensity observed in IL could be interpreted in terms of aggregation number (N_{ag}) and of penetration of the diluent in the apolar shell. This behaviour will be fully quantified in a further study thanks to a complete fit of the data, and related to an estimation of the important thermodynamic driving force of extraction, such as configurational entropy and binding energy of aggregates.¹⁵

While ILs are commonly considered as very promising in solvent extraction, their better efficiency is still not predictable, probably because of a lack of understanding of the main mechanisms in these new kind of diluents, where polarity and structuration properties are very important compared to common solvents. Here, on a system where the extraction mechanisms in IL differ considerably from that in traditional organic diluents, we evidence for the first time the presence of reverse aggregates in the IL based organic phase. Their characterization required a specific deuteration of the ILs, in order to extinguish the strong structural peaks obtained

in these solvents. Thanks to this study, it will be possible to analyze in detail the structure of the aggregates from a full fit of the SAXS and SANS spectra, as well as parameters such as N_{ag} , solvent penetration and critical aggregation concentration (CAC) that appeared to be essential in the understanding of the synergistic mechanisms in common organic diluents.¹⁴⁻¹⁵

Acknowledgement: This work was supported by ANR SILEXE project and NEEDS Resources. We also acknowledge J. Jestin and B. Corso for their help in measuring and T. Zemb and P. Bauduin and D. Turner for fruitful discussions.

References

- (a) Welton, T., Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews* **1999**, *99* (8), 2071-2083; (b) Zhen Ma; Jihong Yu; Dai, S., Preparation of Inorganic Materials Using Ionic Liquids. *Advanced materials* **2010**, *22* (2), 261-285; (c) Lee, S.-g., Functionalized imidazolium salts for task-specific ionic liquids and their applications. *Chem. Commun.* **2006**, *10* 1049-1063.
- (a) Dietz, M. L., Ionic liquids as extraction solvents: Where do we stand? *Sep. Sci. Technol.* **2006**, *41* (10), 2047-2063; (b) Han, X.; Armstrong, D. W., Ionic liquids in separations. *Accounts of Chemical Research* **2007**, *40* (11), 1079-1086; (c) Kunz, W.; Zemb, T.; Harrar, A., Using ionic liquids to formulate microemulsions: Current state of affairs. *Curr. Opin. Colloid Interface Sci.* **2012**, *17* (4), 205-211; (d) Kolarik, Z., Ionic Liquids: How Far Do they Extend the Potential of Solvent Extraction of f-Elements? *Solvent Extr. Ion Exch.* **2013**, *31* (1), 24-60; (e) Billard, I.; Ouadi, A.; Jobin, E.; Champion, J.; Gaillard, C.; Georg, S., Understanding the Extraction Mechanism in Ionic Liquids: UO₂²⁺/HNO₃/TBP/C-4-mimTf(2)N as a Case Study. *Solvent Extr. Ion Exch.* **2011**, *29* (4), 577-601.
- Dai, S.; Ju, Y. H.; Barnes, C. E., Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *Journal of the Chemical Society-Dalton Transactions* **1999**, (8), 1201-1202.
- (a) Dietz, M. L.; Dzielawa, J. A.; Laszak, I.; Young, B. A.; Jensen, M. P., Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. *Green Chemistry* **2003**, *5* (6), 682-685; (b) Billard, I.; Ouadi, A.; Gaillard, C., Is a universal model to describe liquid-liquid extraction of cations by use of ionic liquids in reach? *Dalton Transactions* **2013**, *42* (17), 6203-6212.
- Jensen, M. P.; Neufeind, J.; Beitz, J. V.; Skanthakumar, S.; Soderholm, L., Mechanisms of metal ion transfer into room-temperature ionic liquids: The role of anion exchange. *J. Am. Chem. Soc.* **2003**, *125* (50), 15466-15473.
- Dietz, M. L.; Dzielawa, J. A., 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. *Chemical Communications* **2001**, (20), 2124-2125.
- Sun, X. Q.; Ji, Y.; Guo, L.; Chen, J.; Li, D. Q., A novel ammonium ionic liquid based extraction strategy for separating scandium from yttrium and lanthanides. *Separation and Purification Technology* **2011**, *81* (1), 25-30.
- Cocalia, V. A.; Jensen, M. P.; Holbrey, J. D.; Spear, S. K.; Stepinski, D. C.; Rogers, R. D., Identical extraction behavior and coordination of trivalent or hexavalent f-element cations using ionic liquid and molecular solvents. *Dalton Transactions* **2005**, (11), 1966-1971.
- Dietz, M. L.; Stepinski, D. C., 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* **2005**, *7* (10), 747-750.
- (a) Dejugnat, C.; Dourdain, S.; Dubois, V.; Berthon, L.; Pellet-Rostaing, S.; Dufreche, J.-F.; Zemb, T., Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes. *Physical chemistry chemical physics : PCCP* **2014**, *16* (16), 7339-49; (b) Lefrancois, L.; Delpuech, J. J.; Hebrant, M.; Chrisment, J.; Tondre, C., Aggregation and protonation phenomena in third phase formation: An NMR study of the quaternary malonamide/dodecane/nitric acid/water system. *J. Phys. Chem. B* **2001**, *105* (13), 2551-2564; (c) Ellis, R.J.; Meridiano, Y.; Muller, J.; Berthon, L.; Guilbaud, P.; Zorz, N.; Antonio, M. R.; Demars T.; Zemb, T. *Chem. A Eur. J.* **2014**, *20*, 40, 12796-12807.
- (a) Greaves, T. L.; Drummond, C. J.; *Chem. Soc. Rev.* **2008**, *37*, 1709-1726; (b) Greaves, T. L.; Drummond, C. J., Solvent nanostructure, the solvophobic effect and amphiphile self-assembly in ionic liquids. *Chem. Soc. Rev.* **2013**, *42* (3), 1096-1120; (c) IL-based Surfactant Science" **2015** ISBN 978-1-118-85435-8.
- Liu, L. P.; Bauduin, P.; Zemb, T.; Eastoe, J.; Hao, J. C., Ionic Liquid Tunes Microemulsion Curvature. *Langmuir* **2009**, *25* (4), 2055-2059.
- Hurst, F. J.; Brown, K. B.; Crouse, D. J., Recovery of uranium for wet-process phosphoric acid. *Industrial & Engineering Chemistry Process Design and Development* **1972**, *11* (1), 122-&.
- Dourdain, S.; Hofmeister, I.; Pecheur, O.; Dufreche, J. F.; Turgis, R.; Leydier, A.; Jestin, J.; Testard, F.; Pellet-Rostaing, S.; Zemb, T., Synergism by Coassembly at the Origin of Ion Selectivity in Liquid-Liquid Extraction. *Langmuir* **2012**, *28* (31), 11319-11328.
- Rey, J.; Dourdain, S.; Berthon, L.; Jestin, J.; Pellet-Rostaing, S.; Zemb, T., Synergy in Extraction System Chemistry: Combining Configurational Entropy, Film Bending, and Perturbation of Complexation. *Langmuir* **2015**.
- Mohapatra, P. K.; Raut, D. R.; Sengupta, A., Extraction of uranyl ion from nitric acid medium using solvent containing TOPO and its mixture with D2EHPA in room temperature ionic liquids. *Separation and Purification Technology* **2014**, *133*, 69-75.
- Eicke, H. F.; Christen, H., Is water critical to formation of micelles in apolar media? *Helvetica Chimica Acta* **1978**, *61* (6), 2258-2263.
- (a) Hardacre, C.; Holbrey, J. D.; Mullan, C. L.; Youngs, T. G. A.; Bowron, D. T., Small angle neutron scattering from 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids (C(n)mim PF₆, n=4, 6, and 8). *J. Chem. Phys.* **2010**, *133* (7). (b) Russina, O.; Triolo, A.; Gontrani, L.; Caminiti, R., Mesoscopic Structural Heterogeneities in Room-Temperature Ionic Liquids. *Journal of Physical Chemistry Letters* **2012**, *3* (1), 27-33; (c) Sferrazza, A.; Triolo, A.; Migneco, L. M.; Caminiti, R., Synthesis and Small and Wide Angle X-Ray Scattering Characterization of L-Proline Based Chiral Ionic Liquids. *Current Organic Chemistry* **2015**, *19* (1), 99-104.
- Berthon, L.; Testard, F.; Martinet, L.; Zemb, T.; Madic, C., Influence of the extracted solute on the aggregation of malonamide extractant in organic phases: Consequences for phase stability. *Comptes Rendus Chimie* **2010**, *13* (10), 1326-1334.
- Chatel, G.; Goux-Henry, C.; Mirabaud, A.; Rossi, T.; Kardos, N.; Andrioletti, B.; Draye, M., H₂O₂/NaHCO₃-mediated enantioselective epoxidation of olefins in NTF₂-based ionic liquids and under ultrasound. *Journal of Catalysis* **2012**, *291*, 127-132.