REPORT DOCUMENTATION PAGE		Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 15 December 04	3. REPORT TYPE AND DATES COVERED Final Report 15 July 03 - 14 November 04
4. TITLE AND SUBTITLE Ionic Liquids as Solvent, Catalyst Support: Chemical Agent Decontamination and Detoxification		5. FUNDING NUMBERS DAAD19-03-1-0212
6. AUTHOR(S) William M. Nelson		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Illinois-Urbana-Champaign 109 Coble Hall, 801 S. Wright Street Champaign, IL 61820-6242		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 45571.1-CH
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.		
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Ionic Liquids as Solvent, Catalyst Support: Chemical Agent Decontamination and Detoxification
William M. Nelson

The final results indicate that ionic liquids (ILs) hold promise for the decontamination and detoxification of chemical agents. The results from this project provide the information and outline for development of a novel decon/detox cleaning formulation. The emphasis during the one-year's funding was to establish the chemistry surrounding the oxidative decontamination/detoxification of surrogates for mustard and phosphorus nerve agents. Surrogates were shown to react rapidly and nearly quantitatively in laboratory tests. Work was expended in developing a literature survey, which complemented the preliminary laboratory work. The goals beyond the project should be to use the initial results and perform further tests on the phosphorus surrogates, in order to develop a better mechanistic understanding of the reactions in ILs. This final report includes a complete literature presentation and a detailed outline of future work.

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT **UNCLASSIFIED**	18. SECURITY CLASSIFICATION ON THIS PAGE **UNCLASSIFIED**	19. SECURITY CLASSIFICATION OF ABSTRACT **UNCLASSIFIED**	20. LIMITATION OF ABSTRACT **UL**

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Catalysis in ionic liquid-surfactants
(Work up to July 31, 2004)

As the results after one year will indicate, this project will provide the information and outline for development of a novel decon/detox cleaning formulation. The emphasis during this year has been on the oxidative decontamination/detoxification of surrogates for mustard and phosphorous nerve agents. More work was expended in developing a literature survey, because the ability to do laboratory work was restricted by competing projects. The intent was to resume in the fall, but the second year's funding was cut. Therefore, this final report will be a complete literature presentation and a detailed outline of future work.

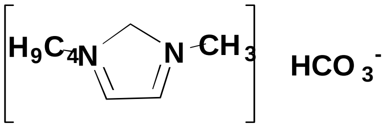
1.0 Background

We established our goal to develop formulations of superior cleaning agents that catalyze chemical reactions. In order to accomplish this we reasoned that the ability of room temperature ionic liquids (ILs) dissolved in aqueous ethanol (aq EtOH) to solubilize and promote the oxidation of three chemical agent surrogates was feasible. Such a series of cleaning agents, we believe, would have immediate use in chemical detoxification and decontamination of a wide range of contaminants of importance to the Department of Defense (DoD).

The ILs, as will be seen, bear strong chemical resemblance to surfactants.[1] This has important ramifications for the direction of this project. First, it suggests that ILs can become constitutive elements of the cleaning formulations and thereby provide necessary catalytic character to the formulations.[2] Equally important, chemical knowledge learned about the behavior of surfactants in micelles and microemulsions can be applied to the ILs.

Previously we reported the application of ionic liquids in surfactants **1** to the decontamination of mustard simulant **2**. Many chemical agents have only limited solubility with the typical water based solutions used (oil and water). Environmental as well as cost concerns preclude the mass use of organic solvents as the base for many applications (e.g., decontamination solutions). Surfactants have been successfully used in formulations to aide solubility and to facilitate cleanup.[3-6] We have taken the next step: By incorporating an ionic liquid (IL) into the backbone of the surfactant molecule we felt that we could accomplish three goals: enhanced solubility, improved kinetics and chemoselectivity.[7,8]

Initially, we wished to compare organic transformation in organic solvents with results gained by using IL-surfactants. After that, we would test these new IL-surfactants in the catalyzed transformation of surrogates of sulfide and phosphorous nerve agents in designer microemulsions. By demonstrating the results of oxidation reactions in these novel ionic liquid surfactants we would lay the groundwork for the future work to be done in the area of decontamination-detoxification of chemical warfare agents.



[BMim] HCO_3^-

1

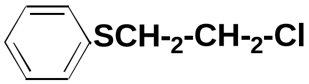


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Figure 1: Task-specific ionic liquid and mustard simulant

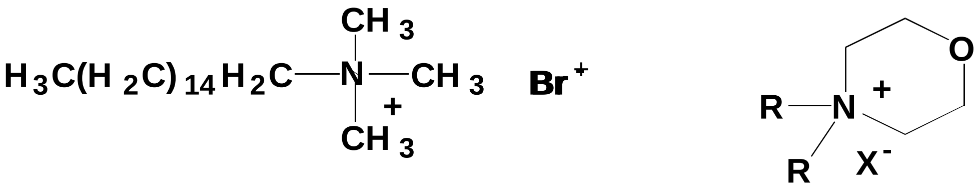
The Waste Management and Research Center (WMRC) of the Illinois Department of Natural Resources (DNR) has been independently researching aspects of surfactant technology and ionic liquid catalysis. There emerged immediately a synergism that has become the major thrust of our research during the first year of the project. In this progress report, we describe an expanded effort to elucidate the practical application of ionic liquids in the development of designer microemulsions toward the decontamination and detoxification of chemical agents. The cumulative effect of our work, will highlight the best attributes of the catalytic qualities of room temperature ionic liquids (IL) incorporated into microemulsions and directed toward contaminant solubility and detoxification for the US Army. The use of ionic liquids can be employed, using three different strategies. First, an ionic liquid can be used as an environmentally friendly solvent to replace less desirable solvents. Second, the ionic liquid can be used to stabilize or act as a catalyst. Finally, the ionic liquid can be used in conjunction with other components of a solution. This is the strategy we intend to explore.[7,9-11]

2.0 Surfactants

A key component to our investigations on this project was to develop a decon/detox system that would be effective, safe, and non-toxic, but relatively inexpensive, as well. While water fits the role as a green solvent, it is not usually the solvent of choice in which to carry our chemical transformations. As we pursued the efforts in the area of microemulsions, we found that a deeper understanding of some of the key features involved in the role of water in promoting chemical reactions involved large molecular assemblies including micelles and microemulsions.[12] The special properties of the liquid give rise to intra- and intermolecular non-covalent interactions leading to novel solvation behavior and interesting reaction enhancement.[13]

From our work in cleaning technologies we know that cationic surfactants have structures that are potentially highly compatible with many of the common ionic solvents. The chemical structures and descriptions of the physical qualities of cationic surfactants may be found in most surfactant texts.[14-16] Cationic surfactants were first recognized for their general biocidal activity and have since become incorporated in many cosmetics, soaps, and general cleaners. This fact will be discussed later, when we address the issue of biodegradable ionic liquids. Since the ability of the positive charge to collect at negatively charged surfaces, cationic polymers have not been used in many detergent formulations since most dirt or grime tends to be negatively charged. Only zwiterionic (carboxylated) amines have seen much play in detergents and alkaline cleanser products because of their ability to retain negative charge in highly alkaline environments.

Cationic surfactants are typically salts of substituted amines, which reminded us of the basic structure of ILs. One of the most studied cationic surfactants is CTAB (cetyltrimethylammonium bromide). Another example is the class of surfactants made from N-alkylpyridinium halides. The morpholinium salts are common non-aromatic substituted rings.



CTAB (cetyltrimethylammonium bromide)

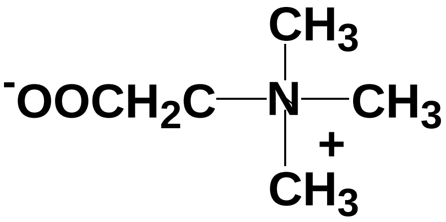
morpholinium salts

N-alkylpyridinium halides

salts of
alkyl-substituted
pyridines

Figure 2: Examples of common cationic surfactants

Natural betaine (Figure 3) is a quaternized ammonium compound that exhibits bactericidal properties. The parent compound may be altered by replacement of the methyl groups with longer aliphatic moieties. This class of compounds (derivatives of amino acids) has the advantage that they are zwitterionic at nearly all pH ranges. There are a vast number of similar zwitterionic compounds that can be developed from substitution of an alkyl group for a carboxylated group. As previously mentioned, the zwitterionic surfactants have been utilized in alkali cleanser formulations because of their ability to retain the negative charge under high pH.



$^{-}OOCH_2C-N^{+}(CH_3)_3$

Figure 3: Trimethyl-aminoacetate, betaine

Another class of potentially compatible surfactants is the imidazoline derivatives. The surfactant may be tailored by choosing R and the pendant group on the secondary amine. The first step in the production, shown in Figure 5 produces a product whose structure is similar to the cationic portion of the ionic liquids we are studying.

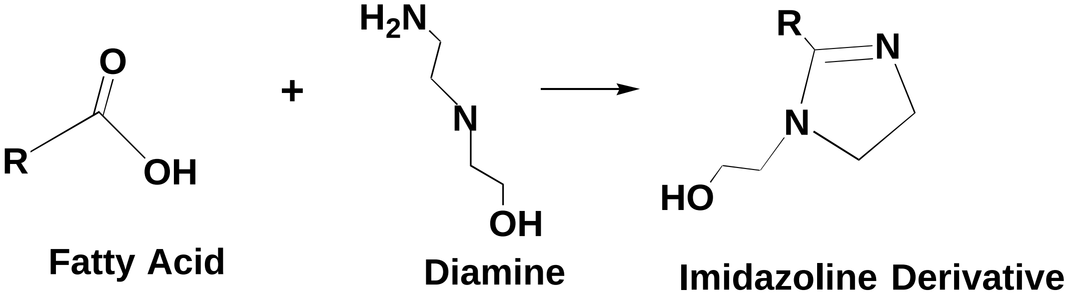


Figure 4: The first step in production of imidazoline amphoteric surfactants

We read early in the work that the presence of a very lipophilic amphiphilic additive may improve substantially the solubilization in microemulsions.[5] This substance is called a lipophilic linker because its preferential orientation in the oil layers next to the interface might provide some ordering of the oil molecules as well as an additional link with the surfactant. We wanted to take advantage of this phenomenon in our work.

As a final concern with the microemulsion formulation, we needed to ensure that the solubility was high for contaminants. Work by Graciaa et al.[17] has shown that the longer the chain of the alcohol, the lesser it adsorbs at the interface. As a consequence, long chain alcohols (above C8**)** enhance the solubilization in optimum surfactant-oil-water systems. In some of our preliminary measurements this proved to be very advantageous. The linker-based formulation of surfactant microemulsion systems has great potential mainly because of the flexibility it offers in tailoring the surfactant and linkers according to the needs of the specific application.[18] The main disadvantage of linker formulations is that not all the linker participates or segregates near the interface, but instead some partitions between the different phases.[18]

3.0 Ionic liquids and cationic surfactants

In general, ionic liquids are salts formed by large asymmetric organic cations and large inorganic anions. A characteristic of these compounds is a low melting temperature (less than 50 ^{0}C), extremely low volatility, and stability at high temperatures (300 ^{0}C).[19] The first materials studied were the salts of aluminum trichloride, which are highly reactive in the presence of water. Wilkes and Zaworotko introduced air and moisture stable, ambient temperature ionic liquids.[20] This work opened an extended range of possible solvent formulations. Newer moisture stable chemistries are based on tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) anions. Room temperature ionic solvents have been reported for polymerization, hydrogenation, and as catalysts for Diels-Alter and Friedel-Crafts reactions.[21-23]

One of the most frequently studied ionic solvent systems is 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6).[24] From this beginning it is possible to design an ionic liquid based upon desired qualities. .

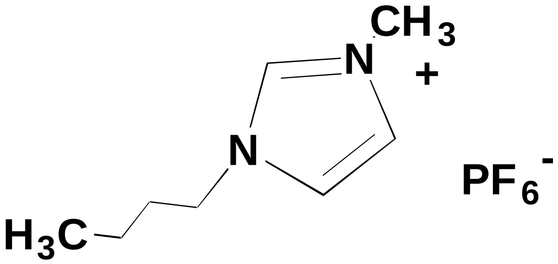
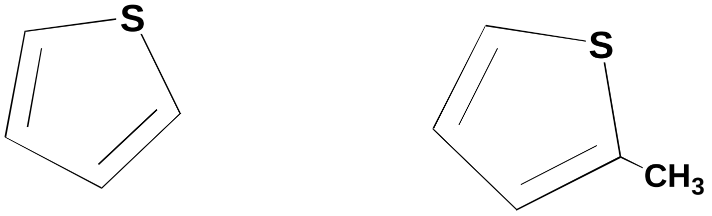


Figure 5: 1-butyl-3-methylimidazonium hexafluorophosphate

In another recent publication, Wasserscheid et al.[25] successfully created an ionic liquid from $BMIM^+$ coupled with the octyl-sulfate ion ($CH_3(CH_2)_6CH_2SO_4^-$, with the claim that the sulfate anions are “more green” than other common ionic liquids because they do not contain halides. This reference is significant to the present discussion because it points-out the inherent stability of two compounds (the anion and the cation) that, otherwise, are considered surfactants. Furthermore, as we design functionality into the microemulsion, we will incorporate the principles of green chemistry into the design.[26]

3.1 Potential Utility of the Mixed, Surfactant and Ionic Solvent Systems

Zhang and Zhang[27] described one recent application of the ionic solvents for environmental control. The thiophene and methyl thiophene are removed from gasoline. These stable heterocyclic sulfur compounds are extremely difficult to remove from fuel components below 50 ppm sulfur. These authors studied the absorption capacity of $EMIM^+BF_4^-$, $BMIM^+PF_6^-$, and $BMIM^+BF_4^-$. These compounds are stable in the presence of moisture, insoluble in petroleum, and are liquids at room temperature. The three ionic liquids showed little absorption of paraffin and olefins, with a high degree of selectivity of thiophenes (Figure 6) over aromatics. Mustard is a sulfide, so this preferential selectivity for sulfur compounds was reassuring. Ionic solvents were cleaned by distillation.



thiophene **2-methylthiophene**

Figure 6: Heterocyclic sulfur compounds

More recently, Lo et al.[28] have investigated removing sulfur-containing compounds from light oils by a combination of both chemical oxidation and solvent extraction using the room temperature ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]$^{+}$PF6$^{-)}$ and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]$^{+}$BF4^{-}). In a one-pot operation, which we envision as similar to that occurring within a microemulsion, the sulfur-containing compounds in the light oils were extracted into ILs and then S-oxidized (H_2O_2-acetic acid) to form the corresponding sulfones. The advantage of performing both extraction and oxidation of sulfur compounds from light oil simultaneously in ILs is that this process increases the desulfurization yield by about an order of magnitude relative to that of merely extracting with ILs. It also mimics perfectly the necessary steps in decon/detox. The room temperature ionic liquids can be recycled after workup and reused without any loss of activity. (Figure 7[28])

Lo et al.[28] oxidized the sulfur compound all the way to the sulfone. As workers have shown[29] the desired decon/detox level for mustard is the sulfoxide. Under conditions we have tested, we can stop at that level.

Much like the potential of microemulsions to orient the reactants and direct the production of specific isomers, ionic liquids also are known to perform this task. Sethi and Welton[30] report on the isomer ratio production in the Diels-Alder addition of methyl acrylate to cyclopentadiene. The key component is the hypothesis that the hydrogen bonding potential of the ionic solvent controls the production of the endo and exo isomers. In our system we are taking advantage of the microemulsion to orient the rectants. Sethi and Welton report on how this proper orientation can result in higher selectivity. The stronger the hydrogen bonding within the solvent, the larger the production of the endo form. Importantly, these authors also demonstrate the counter ion to BMIM^{+} may also be ClO_4^- or $CH_3SO_3^-$.

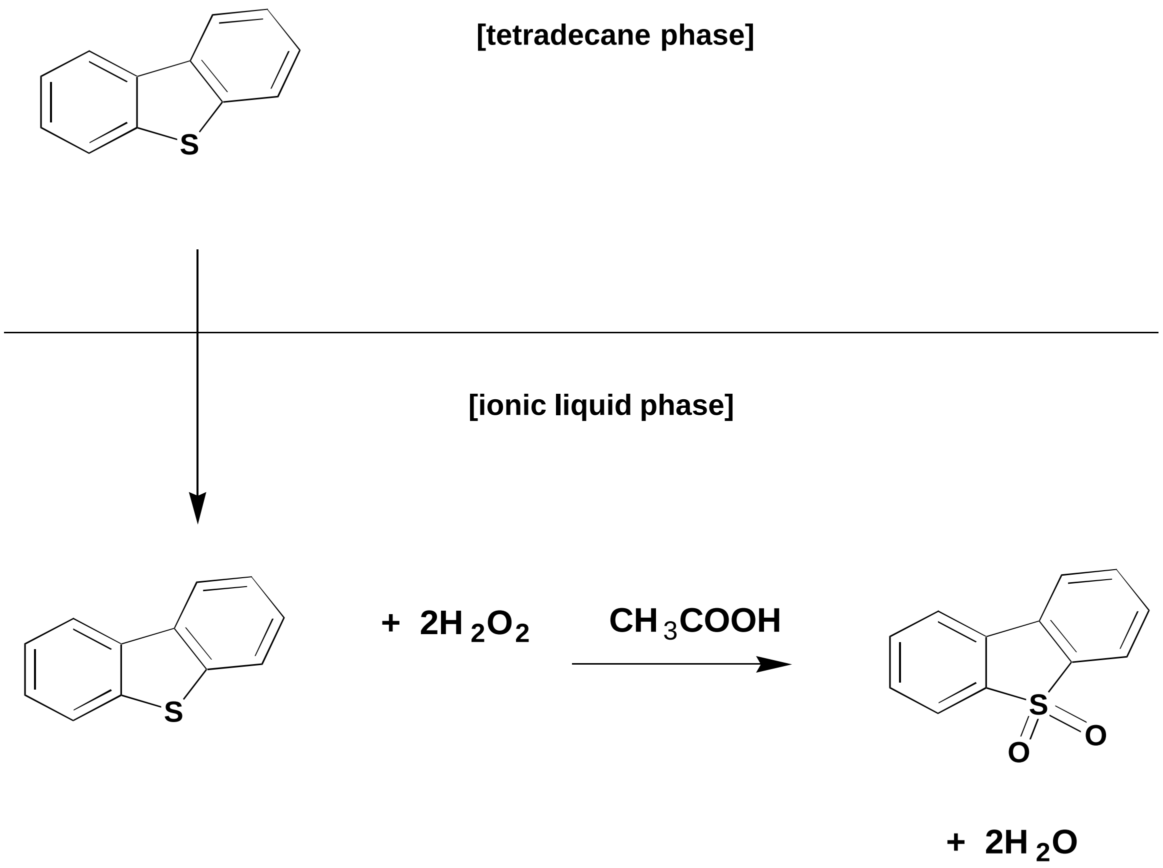


Figure 7: Representative oxidation reaction of DBT using H_2O_2 and AcOH as the oxidizing agent in an oil–ionic liquid system.[28]

Ionic liquids are also capable of catalytic oxidation of organic compounds using manganese catalysts and hydrogen peroxide.[31] The authors studied the kinetics and thermodynamics of the reaction of methyltrioxorhenium (MTO) with hydrogen peroxide in ambient temperature ionic liquids. The values of the rate constants are highly dependent on the concentration of water in the solvent. These results indicate that the ionic liquids can behave like organic solvents and aqueous solutions of high salt concentrations. However, we would like to avoid the use of any metal catalysts or other substances that would lead to undesired waste streams.[32]

The above cited results led us to conclude that the range of chemistries performed with the various forms systems formulated using ionic liquids is limited only by the imagination. It should also seem clear that oxidation-type chemistries may be enhanced in surfactant micellular systems. Some of the chemicals that are potentially ammenable to destruction in such tailored solvent systems are the various classes of chemical agents.

3.2 Reactions in surfactant systems

Currie studied the reaction between 3-bromo-1-propanol and phenol and a series of phenols carrying substituents in 4-position in micellar media and in microemulsions based on either a cationic or a nonionic surfactant.[33] They found that the reactivity and the yield, when compared to those obtained in a microhomogeneous medium, methanol-water, gave enhanced yields in the micellar system based on the cationic surfactant dodecyltrimethylammonium bromide.

Very early we realized that analysis of the properties of polyfunctional solutes in aqueous solution is not straightforward.[13] In the case of, for example, ioiic liquids as the basis for surfactants leading to microemulsions, account must be taken of the possible multitude of conformations for these structures. While the formation of microemulsions and phase behavior have been studied for many years, we wanted to utilize the discovery of Li and Kunieda that mixed surfactants are more effective than a single surfactant in forming microemulsions with low surfactant content.[34]

3.3 Transitions to ionic liquids (ILs)

Work by Bowers and coworkers[8] has given a boost to our conceptual model. Their work demonstrated that ILs based on 1-alkyl-3-methylimidazolium salts act as short-chain cationic surfactants in aqueous solution and form aggregates above a critical aggregation concentration (cac). We immediately realized that further studies must be done to define the role of chain length and counterion on the shape and size of the aggregates formed by these ILs. The issue regarding the bulk structure at concentrations below the cac values for the [C8mim][Cl] and [C8mim][I] systems also requires clarification. We have seen that knowledge of the aggregation behavior of these ILs is a vital part of understanding how they might participate as components in a mixed solvent system. Furthermore, the potential range of ordered structures formed in various solvents, such as the gel phases formed by [C10mim][Br][35] and [C8mim][Cl][8] in aqueous solution, may provide further information on potential designer ILs for use in decon/detox.

Prior to the work by Armstrong and co-workers,[36] limited work had been done on the dissolution of surfactants in ILs[6] or ionic liquids in aqueous surfactant solutions.[37] This new work showed us that [BMIM]Cl and [BMIM]PF_6 support the formation of micelles. Taken together, these support our premise that ILs can be utilized in the formation of microemulsions.

3.4 Biodegradable ILs

While room-temperature ionic liquids have been applied as solvents in both synthesis[38] and separation science,[39] there have always been concerns about their use as green solvents.[40] However, according to a recent review of the degradation or persistence of chemicals in the environment[41] in *Organic Process Research and Development*, it is clear that a further concern about degradation issues is essential before processes are scaled up in ionic liquids. In line with this, and given the fact that ILs possess a number of interesting properties such as high polarity and ionic conductivity, a wide window of electrochemical potential and excellent chemical and thermal stability, several authors have questioned the potential for ILs to accumulate in the environment.[1,40-42] Since we are purporting to use ILs as a constitutive element of a decon/detox formulation, it is important to address this issue immediately.

Jastorff and co-workers have reported a theoretical environment risk analysis on a test set of dialkylimidazolium ILs.[43] The strategy used a combination of structure-activity relationships (SAR), toxicological and ecotoxicological tests and modeling. This was in lieu of detailed experimental data on the biodegradability of ILs, which complicated predictions on bioaccumulation and spatiotemporal range and resulted in a high uncertainty level. More information will emerge, but until then, we have become motivated by the development of biodegradable surfactants.

At this point we were greatly assisted by work by Scammells and co-workers[1] in the design, preparation and evaluation of biodegradable ionic liquids containing ester or amide groups in the alkyl side chain. They described factors, which would improve the biodegradation of surfactants in newly designed ionic liquids. The key is the introduction of a group susceptible to enzymatic hydrolysis, which greatly improves the biodegradation compared with the commonly used dialkylimidazolium ionic liquids, [bmim]BF_4 and [bmim]PF_6.

4.0 Progress summary

4.1 Biodegradation of ILs

On examination of the literature regarding biodegradation of surfactant compounds a close resemblance between many quaternary ammonium compounds as well as surfactants based around an imidazolium core can be surmised.[1] (See Figure 8) These derivatives have a striking resemblance to the structure of many of the most important ILs prepared to date, so that much of the work developing biodegradable surfactants would be relevant to the design of a biodegradable ionic liquid. In particular the presence of the amide bonds can lead to improved biodegradation properties due to an extra hydrolysis degradation pathway.

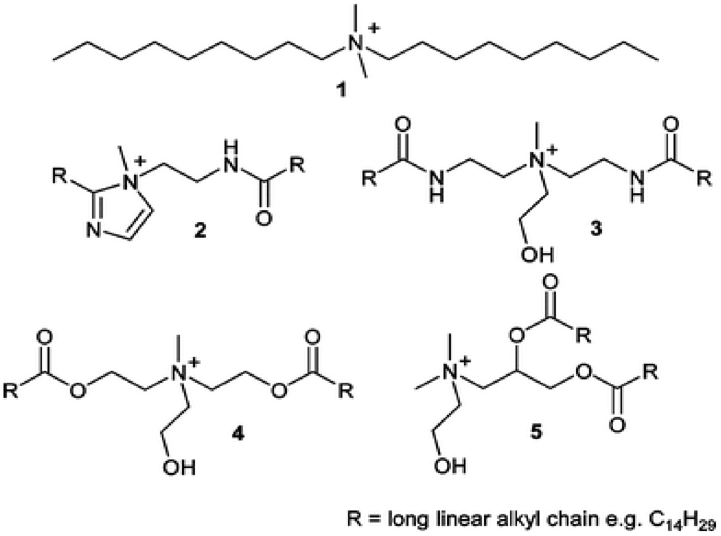
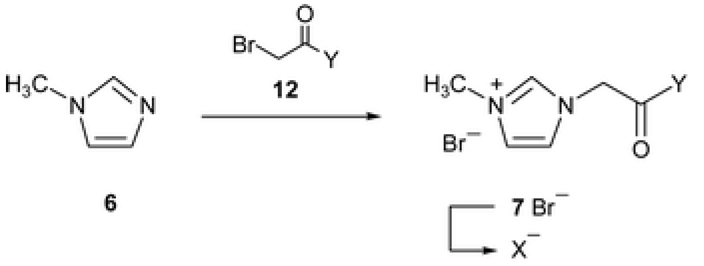


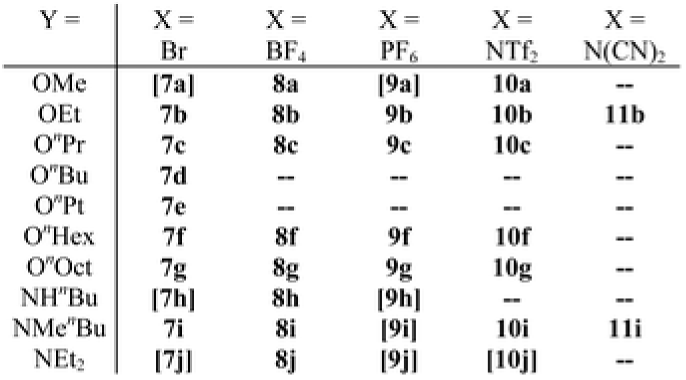
Figure 8: Common surfactants

Boethling[44] identified three factors which are important in the design of biodegradable compounds; (i) the presence of potential sites of enzymatic hydrolysis (for example, ester or amide groups), (ii) the introduction of oxygen in the form of hydroxyl, aldehyde or carboxylic acid groups, and (iii) the presence of unsubstituted linear alkyl chains (especially $\geq$ 4 carbons) and phenyl rings, which represent possible sites for attack by oxygenases. These principles have been followed during the development of biodegradable surfactants, and their inclusion in designer ionic liquids are invaluable.

A major concern at the design stage of this project was the physical properties of these modified imidazolium ionic liquids. Concerns which needed to be addressed were 1) melting points, 2) solubility, and 3) the effect of the ester/amide alkyl length on these properties. If the inclusion of an ester or amide bond into the side chain of an ionic liquid leads to increased order and crystallinity, it would result in these ionic liquids being liquid only at elevated temperatures. We are willing to take this risk, as the designer ILs would be incorporated into microemulsions.

Using the work by Scammells[1] as our starting point, we duplicated their work. This will become the basis for the task-specific ILs we hope to synthesize later in the project.





Y =	X = Br	X = BF_4	X = PF_6	X = NTf_2	X = $N(CN)_2$
OMe	[7a]	8a	[9a]	10a	--
OEt	7b	8b	9b	10b	11b
$O^{n}Pr$	7c	8c	9c	10c	--
$O^{n}Bu$	7d	--	--	--	--
$O^{n}Pt$	7e	--	--	--	--
$O^{n}Hex$	7f	8f	9f	10f	--
$O^{n}Oct$	7g	8g	9g	10g	--
$NH^{n}Bu$	[7h]	8h	[9h]	--	--
$NMe^{n}Bu$	7i	8i	[9i]	10i	11i
NEt_2	[7j]	8j	[9j]	[10j]	--

Figure 9: Synthesis of biodegradable ILs.[1]

It must be mentioned at this point that the biodegradation data of these compounds are not overly impressive.[1] It has been found that degradation rates of these compounds in natural environmental systems were better than some traditional ILs, but lower than biodegradable surfactants. Since imidazolium compounds are negatively charged ammonium ion-species, it yields similar results to the toxicity of antimicrobial compounds. This would mean that the ionic liquids may also have reduced biodegradation.

4.2 Microemulsions

Microemulsions are excellent solvents for hydrophobic organic compounds and are useful as reaction media to overcome the reagent incompatibility frequently encountered in chemical decontamination.[45] The solubilization capacity of microemulsions is generally much higher than that of micellar solutions. Aqueous solvent mixtures are not practically useful in decontamination of hydrophobic agents, especially if polymeric thickeners are present, but microemulsions (MEs) have good solubilizing power and are useful reaction media.

Microemulsions and other association colloids affect rates of bimolecular reactions in water by increasing (or decreasing) local concentrations in the micellar region and changing rate constants in that region. All three aspects of the use of microemulsions as medium for chemical reactivity, i.e. overcoming reagent incompatibility, providing specific rate enhancement (microemulsion catalysis) and inducing regiospecificity, are augmented. Reactions in these hybrid systems show the importance of both the large oil–water interface and the high dynamics of the system. Water was added to the formulation and it was found that the reaction rate changed abruptly when the system passed from water-in-oil to bicontinuous and again when the bicontinuous microemulsion was transformed into an oil-in-water microemulsion, opening new pathways to product recovery.

Recent work incorporating ionic liquids (ILs) in microemulsions leads to very high reactivity in these hybrid ionic liquids-microemulsions.[3,46-49] It has been demonstrated that an extra acceleration of a reaction may be obtained by proper choices of surfactant and ILs in the formulation. It is possible to find for almost any combination of water (or electrolyte solution) and organic liquid an amphiphile that stabilizes a ME.[34]

4.2.1 Preparation of MEs

An initial task was to make MEs and evaluate their solubilization capacities. This has included anionic, cationic, and neutral microemulsions. The work replicated previous work,[48] but also equipped us to formulate new designer ionic liquids (ILs) in MEs (designer IL/ME). The character of a ME, or whether one will be formed at all, is critically dependent upon structure of surfactants and their relative quantities. A microemulsion is an isotropic and optically clear dispersion of oil-in-water (o/w) or water-in-oil (w/o), where "oil" is a hydrocarbon. The name "microemulsion" derives from the fact that oil droplets in o/w systems or water droplets in w/o systems are stable, and they remain clear indefinitely. They form spontaneously when the following four components are mixed in specific proportions: water, oil, surfactant, and co-surfactant (generally a low molecular weight alcohol). The presence of a co-surfactant is critical in reducing the interfacial tension between the droplets and the continuous phase to near zero. In the absence of co-surfactant at the droplet interface, the emulsions become milky and unstable owing to the creation of much larger droplets.

Thus, microemulsions we made were prepared by weighing a mixture of alcohol, surfactant, and hydrocarbon into a 100 mL round bottom flask. This produced a white slurry, which was became a smooth paste. Water was then added with mild agitation to achieve clarity. Sometimes, we used a few minutes of sonication to hasten the process.

4.2.2 Microemulsions[3,50,51]

A series of test catalytic microemulsion were prepared at room temperature by adding drop-wise an aqueous solution of potassium hydrogen carbonate (1.15 g in 6 mL of water) to a magnetically stirred slurry of sodium dodecylsulfate (9.5 g), *n*-butanol (9.5 g), and methylene chloride (75 g). The transparent solution obtained after 5 min of mixing can be kept unchanged in a capped flask for several weeks. This work drew heavily upon previous results of Menger,[48] as we wanted to test the use of the sodium bicarbonate in the microemulsion system.

By using the following, and gradually introducing H_2O_2, we were beginning to develop our designer ionic liquid-microemulsion.

$KHCO_3$ (mmol/kg)	**water (%)**	**SDS (%)**	**butanol (%)**	**CH_2Cl_2 (%)**
48	6.0	9.5	9.5	75.0
5	5.0	7.7	15.3	72.0
	2.2	6.5	12.9	78.4
	8.3	7.3	14.6	69.8
	13.9	8.6	17.3	60.2
	21.0	9.6	19.3	50.1
	30.0	9.9	19.8	40.3
	39.9	9.9	20.0	30.2
	49.9	9.6	19.4	21.1

Figure 10: Initial microemulsion formulations

4.3 Proposed next class of MEs: decontamination of polymer-thickened agent (duplication of literature)

Mustard gas and Soman (3,3-dimethyl-2-butylmethylphosphonofluoridate) are often formulated with 5 to 10% (by weight) of an organic polymer. For example, Paraloid K125, a methylethylbutyl methacrylate copolymer of high molecular weight, developed by Rohm & Haas, is used to thicken such toxic agents. K125 will be used in order to prepare the model substrate (10% by weight with regard to the half-mustard).[52] Our intent is to formulate a microemulsion that can dissolve this polymer-thickened mustard agent.

The polymer has multiple roles: (*i*) it controls the rheology of toxin scattered by the weapon's explosion; (*ii*) its higher viscosity makes it adhere better to surfaces, so the toxin is more difficult to remove, extending its action; (*iii*) finally, because of its organic nature, the polymer prevents solubilization of the toxin in most aqueous decontaminant solutions. It has been observed that upon contact with water, a polymer film can form at the interface between the thickened agent and water: this prevents the thickened agent from dissolving into the decontaminant solution. The presence of a thickener in the poison adds constraints to the conception of an efficient decontamination medium.[53-57]

The choice of mustard gas analogue will be critical: indeed, the model must present a lipophilicity near that of yperite, and must also allow similar solubilization of the polymer (Paraloid K125). The rheology and the behavior of the couple polymer/model substrate must be as near as possible to those of the thickened mustard gas. With *p*-methoxyphenyl methyl sulfide and thioanisole, the polymer does not present the same solubilization characteristics, being insufficiently soluble. In contrast, the half-mustard 2-chloroethyl phenyl sulfide seems to mimic the thickened mustard gas satisfactorily: the polymer first expands, then dissolves.[52,58]

Following literature guidance, the relative proportion of polymer with regard to the half-mustard will be set at 10% by weight: in these proportions only part of the polymer was solubilized, the rest being present in an elastic and very viscous form. In order to be efficient, the microemulsion must contain two essential components: an organic solvent able to solubilize both toxin and polymer, and a decontaminating agent that reacts with the toxin and neutralizes it. It has been shown by Bunton et al.,[59] and we have duplicated it, that oxidations of sulfides and phosphorus(V) esters of thiols by H_2O_2 are catalyzed by H_2SO_4 and $HClO_4$. Rate constants are similar for given concentrations of H_2SO_4 and $HClO_4$, except that with greater than 50 wt.% H_2SO_4 peroxymonosulfuric acid is formed and the observed rate constants then increase. Strongly acidic ion-exchange resins also catalyze oxidations of the sulfides. Although these results are compelling, we wanted our system to be self-contained and functional without the use of H_2SO_4 and $HClO_4$.

4.4 Hydrogen peroxide oxidation/hydrolysis

Aqueous hydrogen peroxide is an ideal oxidant either alone or with a catalyst. It oxidizes alcohols, olefins, and sulfides in an environmentally, technically and economically satisfying manner.[60-62] Hydrogen peroxide, when uncatalyzed, is milder and yields the sulfoxide preferentially, but the reaction is too slow for the purpose of immediate decontamination. “Green chemistry” is a central issue in the chemical industry in the 21st century.[6,40] Current decontamination and detoxification (decon/detox) technologies produce unwanted wastes and are dangerous to both the environment and to those who handle them. Environmentally benign and clean technologies must be developed because oxidation and hydrolysis are core chemistries for decon/detox.

Aqueous hydrogen peroxide (H_2O_2) of <60% concentration is an ideal oxidant in view of an effective-oxygen content of as high as 47%, cleanness that produces only harmless water by reaction, safety in storage and operation, and the low cost of production and transportation. These obvious advantages have spurred the development of useful procedures for H_2O_2 oxidation of sulfides, however, there remains much room for improvement, because many of these procedures require either chlorohydrocarbon solvents that affect human health and the environment, or anhydrous H_2O_2 in ethanol.[54,63-65] Furthermore, parallel technologies to accomplish hydrolysis of the phosphorous esters (nerve agent analogues) must be developed. We found particularly instructive work by Chiarini and Bunton.[54] These authors found that rate constants of oxidation of thioanisole, PhSMe, by H_2O_2 mediated by tetraperoxomolybdate dianion, $Mo(O_2)^{4\ 2-}$ are almost unaffected by addition of hexan-1-ol or octan-1-ol to micellized cetylpyridinium chloride, CPyCl, although these hydrophobic alcohols should perturb the micellar interfacial region. These results differ from those for micellar-mediated reactions of hydrophilic anionic nucleophiles, which are inhibited by hydrophobic solutes.

4.4.1 Oxidation of sulfides

Aromatic and aliphatic sulfides are oxidized to sulfoxides or sulfones in high yield with 30% hydrogen peroxide without organic solvents or halogens. Dialkyl and alkyl aryl sulfides are cleanly oxidized to sulfoxides using aqueous hydrogen peroxide without catalysts. The oxidation of sulfides to sulfones proceeds through the sulfoxide intermediates, so the reaction must only proceed to the first step.[63]

4.4.2 Materials

All solvents and reagents were obtained from Aldrich, Acros or Fisher Chemical and were purified when necessary.

4.4.3 Representative procedure for oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide without catalyst

Figure 11: Hydrogen peroxide oxidation of sulfides

The H_2O_2 oxidation to sulfoxides has a long history since 1908, and it has frequently been used with or without catalysts in various organic solvents. However, the scope and limitations have not been clarified in the literature. Although solvent- and catalyst-free oxidation is highly desirable, no standard protocols utilizing mere aqueous H_2O_2 have been established.[64] For selective oxidation of dialkyl sulfides to the sulfoxides, we followed a simple procedure to treat a sulfide with an equimolar amount of 30% H_2O_2 at 35°C. Neither organic solvent nor metal catalyst is necessary. The second oxidation to dibutyl sulfone is very slow under such conditions. The oxidation below room temperature is slower, while raising the temperature to 50°C and with excess H_2O_2 forms an appreciable amount of the sulfone. Methyl phenyl sulfide is somewhat less reactive than dibutyl sulfide but behaves similarly. However, diaryl sulfides are different. Diphenyl sulfide is almost inert to 30% H_2O_2 below 50°C in the absence of catalysts. [59]

4.4.4 Hydrolysis of phosphorous esters

Basic peroxide has been known to rapidly decontaminate isopropyl methylphosphonofluoridate (GB or Sarin), **1**, for decades, via generation of the powerful nucleophile peroxy anion, OOH^-. This reaction is shown in Figure 12. The GB reaction consumes 2 mol of H_2O_2 and evolves 1 mol of O_2. GB in neutral peroxide exhibits an initial half-life of 67 h, apparently reacting with the background OOH^-. Yet, the reaction gradually slows prior to completion as the pH and concentration of OOH^- drop. However, with even small amounts of bicarbonate, the reaction rates for both GB and GD become too fast to measure by NMR spectroscopy ($t_{1/2}$ <<1 min) and go to completion.[59]

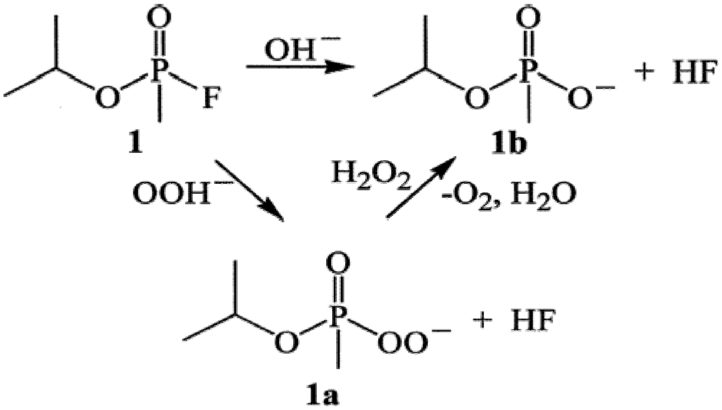


Figure 12: Hydrolysis of phosphorous esters

Thus, a simple solution of hydrogen peroxide, bicarbonate, and a suitable co-solvent for water-insoluble HD achieves the desired broad-spectrum decontamination of all three types of agents, even at low temperature. In some very preliminary experiments we were able to accomplish the hydrolysis of phosphorous esters. The environmental advantages of such formulations are self-evident. Further note that solid urea peroxide addition compound ($urea\cdot H_2O_2$) can be substituted for aqueous as this material yields solutions of the correct pH.[61,62,66,67]

Exploring microemulsions as media for both hydrolysis of phosphate esters (nerve agent analogs) and oxidation of sulfides (mustard analogs) provides evidence to support its use in decontamination of actual CAW.

4.5 Oxidation and hydrolysis in ionic liquids

The oxidation of sulphur compounds or the hydrolysis of phosphorous esters in ionic liquids (ILs) has not been thoroughly examined.[25,42,68,69] Room temperature ILs have gained recognition as environmentally benign alternative solvents for separations, chemical synthesis, electrochemistry and catalysis. Generally, they are non-volatile, non-explosive, recyclable, easy to handle, and thermally robust. Therefore, RTILs are regarded as "green solvents". The extractions of fuels using RTILs to remove sulfur compounds have been reported recently. To facilitate removal, the sulfides were oxidized. We, however, are attempting to combine the catalytic effect of ILs in oxidations and hydrolyses with the enhanced reactivity found in microemulsions (ME). The ILs [BMIM]PF_6^- and [BMIM]BF_4^-, which are immiscible with light oils, were selected as co-solvents for the MEs. To confirm the suitability of ILs we are performing both oxidation and hydrolysis in ILs.[2,6-8,31,38,70,71]

4.5.1 Oxidation

Oxidation of sulfides in ionic liquids was carried out as follows: each ionic liquid (5 mL) containing sulfides (0.022 g) was mixed carefully with H_2O_2 (30%, 1.36 mL) and $KHCO_3$ (0.36 mL). The resulting mixture was then stirred vigorously at room temperature. The solution was removed and analyzed by reversed-phase HPLC.

4.5.2 Hydrolysis

The use of imidazolium-based ionic liquids as promoters was found to be highly effective for the hydrolysis reaction of CF_3CH_2Cl with aqueous potassium acetate to produce 2,2,2-trifluoroethanol (TFE). Among ionic liquids tested, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) showed the highest yield of TFE, over 90%, which is almost two times higher than that obtained in the absence of an ionic liquid. This is the type of catalysis we hope to achieve by incorporating ILs into MEs. We are beginning these experiments, using [BMIM]Cl and moving toward designer ILs.

4.5.3 Designer ionic liquids

The incorporation of ILs into MEs presents some challenges. The preparation and testing of novel ionic liquids that will be useful in oxidation and hydrolysis chemical reactions have become our current task and we will highlight this effort now. We intend to use ionic liquids as the catalyst both for the chemical reaction and for recycling of the $KHCO_3$. The selective removal and catalytic transformation of removed contaminants will be the ultimate goal. The four-component system utilizes a unique detergent/surfactant system incorporating room temperature ILs that will, it is hypothesized, enable the decontamination and detoxification desired. The ME removes contaminants from surfaces. The isolated contaminants are then further reacted *in situ* oil phase in the o/w microemulsion.

5.0 Future work: Designer IL-Microemulsion(IL/ME)

Microemulsions are thermodynamically stable, fluid, and optically clear dispersions of two immiscible liquids. Microemulsion systems have utility in a broad range of applications including enhanced oil recovery, consumer and pharmaceutical formulations, nanoparticle synthesis, and chemical reaction media. One way to reduce surfactant requirements in microemulsion systems is through the use of efficient surfactants and interfacially active co-surfactants. We began exploring microemulsion systems based on efficient anionic surfactants and alcohol (or glycol ether) co-surfactants that are stable to temperature and compositional changes and yet employ low levels of non-volatile surfactants. To these we added H_2O_2 and designer ILs.

While new low-temperature oil-in-water (o/w) type microemulsions that resist freezing and phase separation at -18 C have been developed,[49] we have begun to extend their capabilities with ILs. These systems were shown to simultaneously destroy, via oxidative and hydrolytic mechanisms, simulants of three chemical warfare agents.[49] This extraordinarily complex chemical system resembles what happens in a living cell. Substantial practical issues remain: rates for a recalcitrant VX simulant should be increased and over-oxidation of the mustard simulant to a sulfone retarded. The challenge ahead of us is to insure that the same reactivity occurs within the designer ILs-microemulsion, and in an environmentally responsible manner.

As we showed in our previous report, we are using the following drawing as our conceptual model of the chemical processes occurring within the designer IL-microemulsion. In the pseudophase model for Bicarbonate Assisted Peroxide (BAP) oxidations in aqueous cationic micelles, the reactants are distributed rapidly between water and micelles. Kinetic treatments are based on the assumption that reactions occur in both the Stern layer and the bulk aqueous medium. [61]

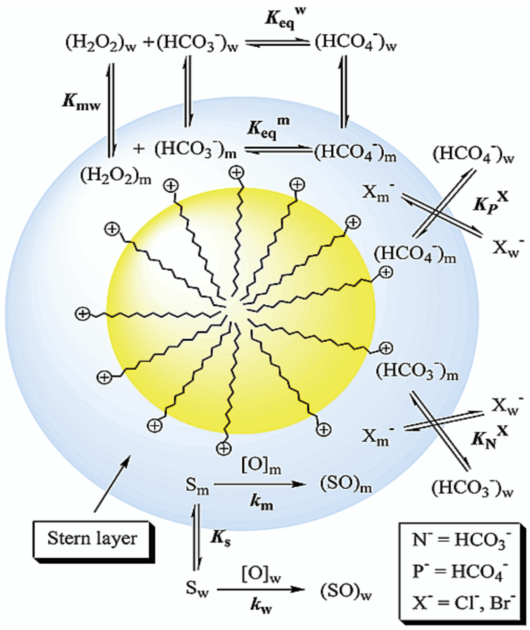


Figure 1 Pseudophase model for BAP oxidations in aqueous cationic micelles. [61]

The system we propose incorporates a combination of an ionic surfactant with a reactive counterion that is itself an oxidant or activates an oxidant from the bulk solution to form an oxidant counterion. The new catalytic cationic environment (designer ionic liquid/microemulsion) significantly will enhance the overall oxidation rates as compared to the addition of bicarbonate salts to the ME alone. Comparisons of designer IL/microemulsion will still need to be made to other highly reactive oxidants such as peroxymonosulfate (HSO_5^-) in aqueous surfactant media.

Reductions in the releases of ozone depleting substances, hazardous air pollutants, and the regeneration of the solvent are anticipated benefits of the newer technology. Disposal costs and regulatory enforcement issues will be minimized. Accomplishing this according to the principles of green chemistry is *a sine qua non* of all new methods in organic chemistry today.

5.1.1 Synthesis of [bmim][HCO_3]

84.55 g (0.484 mol) 1-butyl-3-methylimidazolium chloride ([bmim]Cl, commercial grade >98% purity) and 101.1 g ($\geq$0.379 mol) Na[HCO_3] (commercial grade; $\geq$87% purity) will be dissolved in 200 ml hot water (60 °C). The water was slowly removed under vacuum and solid product will be collected. The compound will be purified and its identity will be verified.

(1) Gathergood, N.; Garcia, M. T.; Scammells, P. J. *Green Chem.* **2004**, *6*, 166-175.

(2) Binks, B. P.; Dyab, A. K. F.; Fletcher, P. D. I. *Chem.Comm.* **2003**, 2540-2541.

(3) Menger, F. M.; Park, H. *Recl.Trav. Chim. Pays-Bas* **1994**, *113*, 176-180.

(4) Schwuger, M.-J.; Stickdornt, K.; Schomacker, R. *Chem. Rev.* **1995**, *95*, 849-864.

(5) Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourre, M.; Salager, J. L. *Langmuir* **1993**, *9*, 669-672.

(6) Hoffmann, M. M.; Heitz, M. P.; Carr, J. B.; Tubbs, J. D. *Journal of Dispersion Science & Technology* **2003**, *24*, 155-171.

(7) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081-3093.

(8) Bowers, J.; Butts, C. P.; Martin, P. J.; Vergara-Gutierrez, M. C.; Heenan, R. K. *Langmuir* **2004**, *20*, 2191-2198.

(9) Sheldon, R. A. *Pure & Applied Chemistry* **2000**, *72*, 1233-1246.

(10) Nijhuis, T. A.; Musch, S.; Makkee, M.; Moulijn, J. A. *Applied Catalysis A-General* **2000**, *196*, 217-224.

(11) Sun, J. M.; Fujita, S.; Bhanage, B. M.; Arai, M. *Catalysis Communications* **2004**, *5*, 83-87.

(12) Nardello, V.; Caron, L.; Aubry, J.-M.; Bouttemy, S.; Wirth, T.; Chantu, R. S.-M.; Adam, W. *J. Am. Chem. Soc.* **2004**, *126*, 10692 - 10700.
(13) Engberts, J. B. F. N.; Blandamer, M. J. *Chem. Commun.* **2001**, 1701 - 1708.
(14) Lake, L. W. *Enhanced Oil Recovery*; Prentice Hall: Englewood Cliffs, NJ, 1989.
(15) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B.; John Wiley & Sons: West Sussex, England, 1998, p 335.
(16) Meyers, D. *Surfactant Science and Technology*; 2nd ed.; VCH Publishers, Inc.: NY, NY, 1992.
(17) Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourrel, M.; Salager, J. L. *Langmuir* **1993**, *9*, 3371-3374.
(18) Sabatini, D. A.; Acostab, E.; Harwellc, J. H. *Current Opinion in Colloid & Interface Science* **2003**, *8*, 316-326.
(19) Seddon, K. R. *Nature Materials*, *2*, 363-365.
(20) Wilkes, J. S.; Zaworotko, T. *Chem.Comm.* **1992**, 965.
(21) Welton, T. *Chem. Rev.* **1999**, *99*, 2071-2083.
(22) Wasserscheid, P.; Sesing, M.; Korth, W. *Green Chem.* **2002**, *4*, 134 - 138.
(23) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391-1398.
(24) Sheldon, R. *Chemical Communications* **2001**, 2399-2407.
(25) Wasserscheid, P.; van Hal, R.; Bosmann, A. *Green Chem.* **2002**, *4*, 400-404.
(26) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
(27) Zhang, S. G.; Zhang, Z. C. *Green Chem.* **2002**, *4*, 376-379.
(28) Lo, W. H.; Yang, H. Y.; Wei, G. T. *Green Chem.* **2003**, *5*, 639-642.
(29) Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729-1743.
(30) Sethi, A. R.; Welton, T. In *Ionic Liquids*; Rogers, R. D., Seddon, K. R., Eds.; ACS: Washington, D.C., 2002, pp 241-258.
(31) Owens, G. S.; Abu-Omar, M. M. *J. Mol. Catal. A-Chemical.* **2002**, *187*, 215-225.
(32) Anastas, P. T. *Green Chem.* **2003**, *5*, G29-G34.
(33) Currie, F. *Journal of Colloid & Interface Science* **2004**, *277*, 230-234.
(34) Li, X.; Kunieda, H. *Current Opinion in Colloid & Interface Science* **2003**, *8*, 327-336.
(35) Firestone, M. A.; Dzielawa, J. A.; Zapol, P.; Curtiss, L. A.; Seifert, S.; Dietz, M. L. *Langmuir* **2002**, *18*, 7258 -7260.
(36) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. *Chem.Comm.* **2003**, 2444-2445.
(37) Friberg, S. E.; Yin, Q.; Pavel, F.; Mackay, R. A.; Holbrey, J. D.; Seddon, K. R.; Aikens, P. A. *J. Dispersion Sci. Technol.* **2000**, *21*, 185-197.

(38) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773-3789.

(39) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chemical Communications* **1998**, 1765-1766.

(40) Nelson, W. M. In *Ionic liquids: industrial applications for green chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS: Washington, DC, 2002; Vol. 818, pp 30-41.

(41) Laird, T.; Hermitage, S. A.; Tilstam, U. *Org. Proc. Res. Dev.* **2002**, *6*, 338-345.

(42) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2003**, *5*, 361-363.

(43) Jastorff, B.; Stormann, R.; Ranke, J.; Molter, K.; Stock, F.; Oberheitmann, B.; Hoffmann, W.; Hoffmann, J.; Nuchter, M.; Ondruschka, B.; Filser, J. *Green Chem.* **2003**, *5*, 136-142.

(44) Boethling, R. S. *Designing Safer Chemicals*; ACS: Washington, DC, 1996; Vol. 640.

(45) Holmberg, K. *Current Opinion in Colloid & Interface Science* **2003**, *8*, 187-196.

(46) Currie, F.; Holmberg, K.; Westman, G. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2001**, *182*, 321-327.

(47) Klier, J.; Tucker, C. J.; Kalantar, T. H.; Green, D. P. *Adv. Mater.* **2000**, *12*, 1751-1757.

(48) Menger, F. M.; Elrington, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 9621-9624.

(49) Menger, F. M.; Rourk, M. J. *Langmuir* **1999**, *15*, 309 -313.

(50) Kahlweit, M. *J. Phys. Chem.* **1995**, *99*, 1281-1284.

(51) Kahlweit, M.; Strey, R.; Schomacker, R. In *Reactions in Compartmentalized Liquids*; Knoche, W., Schomacker, R., Eds.; Springer-Verlag: New York, 1998, pp 1-10.

(52) Gonzaga, F.; Perez, E.; Rico-Lattes, I.; Lattes, A. *New Journal of Chemistry* **2001**, *25*, 151-155.

(53) Aubry, J.-M.; Bouttemy, S. *J. Am. Chem. Soc.* **1997**, *119*, 5286 - 5294.

(54) Chiarini, M.; Bunton, C. A. *Langmuir* **2002**, *18*, 8806-8812.

(55) Chiarini, M.; Gillitt, N. D.; Bunton, C. A. *Langmuir* **2002**, *18*, 3836 - 3842.

(56) Wagner, G. W.; Procell, L. R.; Yang, Y.-C.; Bunton, C. A. *Langmuir* **2001**, *17*, 4809 -4811.

(57) Wagner, G. W.; Yang, Y.-C. *Ind. Eng. Chem. Res.* **2002**, *41*, 1925 - 1928.

(58) Herrmann, H. W.; Selwyn, G. S.; Henins, I.; Park, J.; Jeffery, M.; Williams, J. M. *IEEE Transactions on Plasma Science* **2002**, *30*, 1460- 1470.

(59) Bunton, C. A.; Foroudian, H. J.; Gillitt, N. D.; Kumar, A. *Can J. Chem.* **1998**, *77*, 895-902.

(60) Adam, A.; Mehta, M. *Angew. Chem. Int. Ed.* **1998**, *37*, 1387 - 1388.

(61) Yao, H. R.; Richardson, D. E. *J . Am. Chem. Soc.* **2003**, *125*, 6211-6221.

(62) Yao, H.; Richardson, D. E. *J. Am. Chem. Soc.* **2000**, *122*, 3220 - 3221.

(63) Marques, A.; Marin, M.; Ruasse, M. F. *J. Org. Chem.* **2001**, *66*, 7588-7595.

(64) Neyens, E.; Baeyens, J. *J. Hazard. Mater.* **2003**, *98*, 33-50.

(65) Wahlen, J.; De Vos, D. E.; Jacobs, P. A. *Org. Lett.* **2003**, *5*, 1777 - 1780.

(66) Richardson, D. E.; Yao, H. R.; Frank, K. M.; Bennett, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 1729-1739.

(67) Richardson, D. E.; Regino, C. A. S.; Yao, H. R.; Johnson, J. V. *Free Radic. Biol. Med.* **2003**, *35*, 1538-1550.

(68) Lee, H.; Kim, K. H.; Kim, H.; Lee, S. D.; Kim, H. S. *Journal of Fluorine Chemistry* **2004**, *125*, 95-97.

(69) Pardey, A. J.; Rivas, A. B.; Longo, C.; Funaioli, T.; Fachinetti, G. *Journal of Coordination Chemistry* **2004**, *57*, 871-882.

(70) Sheldon, R. A.; Lau, R. M.; Sorgedrager, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002**, *4*, 147-151.

(71) Tong, K. H.; Wong, K. Y.; Chan, T. H. *Org. Lett.* **2003**, *5*, 3423-3425.