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The overarching goals of this project were primarily three-fold: 1) to generate new classes of hydrophobic ionic liquids (IL) with great surfactant properties and grease dissolving abilities, 2) to achieve a greater scientific understanding of the key ionic liquid mechanisms and process variables for degreasing processes, and 3) to evaluate the potential for degreasing systems based on ILs in comparison with conventional solvents.

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ABSTRACT

The overarching goals of this project are primarily three-fold: 1) to generate new classes of hydrophobic ionic liquids with great surfactant properties and grease dissolving abilities, 2) to achieve a greater scientific understanding of the key ionic liquid mechanisms and process variables for degreasing processes, and 3) to evaluate the potential for degreasing systems based on ILs in comparison with conventional solvents.

The work consists of 3 tasks: 1) synthesis and characterization of new ionic liquids, 2) studies of degreasing technology based on ionic liquids, and 3) optimization of degreasing technology based on ionic liquids. The new types of ionic liquids are explored to tailor the chemistry for capability for removal of grease while mitigating corrosion. Bench-scale testing of contaminant removal is conducted in an interactive manner with synthesis. Optimization of degreasing is conducted in small scale testing, with systems characteristic of Department of Defense end-users.

Six aprotic ionic liquids with built-in surfactant nature have been synthesized and characterized. Effects of carbon chain length of ionic liquids' anions and the nature of cations on degreasing efficiencies have been investigated. The potential for the ionic liquid to act as a solvent for the contamination on the metal surface in question is promising.

OBJECTIVES

This project aims to develop an affordable, non-hazardous ionic liquids-based degreasing technology that will meet unique component requirements for Department of Defense (DoD) systems. The objective is to explore new chemistries and processes based on ionic liquids (ILs) for degreasing solvents that can be used to replace current high-volatile organic compounds (VOCs) solvents. Key elements include:

- Development of ionic liquid chemistries that provide suitable characteristics for degreasing in applications relevant to the military
- Characterization of performance, both in terms of contaminant removal and possibility for degradation of substrates
- Evaluation of the viability of degreasing processes based on ILs, taking into account contaminant buildup, cleaner recycling, losses, and waste production

We will perform synergistically linked research to address the following fundamental technical questions:

(1) Can IL cations and anions be exploited to generate new classes of hydrophobic ILs with enhanced surfactant nature as good degreasing solvents for applications relevant to the military?
(2) Can ILs provide the required level of degreasing comparable to conventional solvents?
(3) Can IL solvents be used in a cost-effective manner, with sustained degreasing efficiency, minimal losses, and acceptable waste generation?

TECHNICAL DISCUSSION OF WORK PERFORMED

CHAPTER 1. Introduction

Ionic liquids (ILs) are defined as room temperature molten salts. They are composed of cations and anions, and their melting points are generally below 100°C.[1] Walden et al.[2] synthesized IL, $[C_2H_5NH_3][NO_3]$, in 1914 by neutralizing ethylamine with concentrated HNO_3. Such an IL is protic because its synthesis occurs through a proton-transfer reaction. Hurley et al.[3] prepared a second class of ILs in 1951 by using alkylpyridinium chlorides with $AlCl_3$, which is aprotic. In 1992 Wilkes et al.[4] developed water-stable ILs composed of organic cations and inorganic or organic anions. This third class of ILs has been studied widely because of their stability in air and water. ILs are "designer solvents" – their physicochemical properties can be tuned through the appropriate combination of cations and anions.[5] It is possible to design an IL composition with specific chemical and physical properties that meet the user's needs[6]. Because ILs have unique properties unmatched by volatile organic compounds, ILs have enabled many achievements in the areas of catalysis,[7-9] separation,[10-11] lubricants,[12-13] electrochemistry,[14-16] and inorganic materials.[17]

Top performing degreasing solvents in use at military installations today include perchloroethylene (PCE), trichloroethylene (TCE), and normal propyl bromide (nPB). Both PCE and TCE have been identified as human carcinogens and hazardous air pollutants (HAPs), while a petition has been filed to list nPB as a HAP in response to emerging science regarding its toxicity. Both TCE and nPB are regulated as VOCs.

Vapor degreasing with chlorinated solvents has for many years been the industrial process of choice for removing wax materials. In the early 1990s, semi-aqueous processes began to see use, and in 1994, a process using an improved solvent was tested and approved by Pratt & Whitney Engines for removing wax and fixturing compounds from gas turbine engine parts [18]. Both General Electric and Rolls Royce subsequently approved this process and agent. A widely used semi-aqueous wax removal agent is isopropyl myristate and a polar organic compound (vapor pressure < 0.001 mm Hg at 20°C). A typical semi-aqueous process for wax removal is a three-step process composed of a hot water immersion tank, an agitated cleaning agent immersion tank, and agitated rinsing tanks (usually two rinse tanks); drying may be another necessary step in this process. When the cleaning agent is loaded with wax, it is typically disposed of by fuel blending. The cleaning agent is readily biodegradable and rinse water containing cleaning agent is usually disposed of by discharge to a sewer. Several new solvents have become available in recent years, such as n-propyl bromide, that could be alternatives to the use of chlorinated solvents.

Ionic liquids have a versatile chemistry that can be molecularly "tuned" in many ways,[19] as opposed to the limited chemistry of organic solvents. They can also be robust, thermally stable, minimally toxic, nonflammable, and nonvolatile. Most important, they are well known as excellent solvation media displaying high solubilities for both inorganic and organic species.[20]

In this work we synthesized and characterized six aprotic ionic liquids (AILs) with built-in surfactant nature. We investigated the effects of carbon chain length of ILs anions and the nature of cations on degreasing efficiencies. The potential for the IL to act as a solvent for the contamination on the metal surface in question is promising.

CHAPTER 2. Synthesis of Quaternary Ammonium Ionic Liquids

Quaternary ammonium cations entail no aromatic groups, which are different from alkylimidazolium-based and alkylpyridinium-based ILs. This key structural feature implies that their solvation environments are very different from those of alkylimidazolium-based and alkylpyridinium-based ILs, enabling the tailoring of their surfactant nature. In order to exploit the degreasing properties for tuning degreasing efficiency and associated with IL-based improved degreasing technologies, we synthesized two ionic liquids with quaternary ammoniums as cations.

2.1. $[N_{8888}]$ $[C_{17}H_{35}COO]$

Tetraoctylammonium bromide {$[N_{8888}]Br$, 14.12 g, 25.8 mmol} and stearic acid (white powder, 7.34 g, 25.8 mmol) were mixed in 30 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 40 mL of hexanes. The reaction mixture was stirred for two hours till all solids dissolved. To this stirred solution was added a solution of sodium hydroxide (NaOH, 1.032 g, 25.8 mmol) in 30 mL of D.I. H_2O drop wise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with D.I. H_2O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield $[N_{8888}]$ $[C_{17}H_{35}COO]$ as a viscous liquid (18.70 g, 24.9 mmol, yield: 96.6%).

^{1}H NMR ($CDCl_3$, ppm): 0.78-0.88 (m, 15H, $5CH_3$), 1.15-1.38 (m, 68H, $34CH_2$), 1.50-1.68 (m, 10H, 5 CH_2), 2.11 (m, 2H, $O{=}CCH_2$) ,3.24 (m, 8H, $4NCH_2$); ^{13}C NMR ($CDCl_3$, ppm): 13.91 (CH_3), 21.94 (CH_2), 22.45 (CH_2), 22.56 (CH_2), 26.20 (CH_2), 26.94 (CH_2), 28.90 (CH_2), 28.98 (CH_2), 29.23 (CH_2), 29.59 (CH_2), 29.66 (CH_2), 29.99 (CH_2), 31.53 (CH_2), 31.79 (CH_2), 38.68 ($O{=}CCH_2$), 58.67 (NCH_2), 179.37 (C=O).

2.2. $[N_{8888}]$ $[C_{13}H_{27}COO]$

Tetraoctylammonium bromide {$[N_{8888}]Br$, 8.91 g, 16.3 mmol} and myristic acid (white powder, 3.72 g, 16.3 mmol) were mixed in 20 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 25 mL of hexanes.To this stirred suspension was added a solution of sodium hydroxide (NaOH, 0.652 g, 16.3 mmol) in 18 mL of D.I. H_2O drop wise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with D.I. H_2O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield $[N_{8888}]$ $[C_{13}H_{27}COO]$ as a viscous liquid (11.22 g, 16.2 mmol, yield: 99.1%).

^{1}H NMR ($CDCl_3$, ppm): 0.80-0.88 (m, 15H, $5CH_3$), 1.17-1.36 (m, 60H, $30CH_2$), 1.50-1.68 (m, 10H, 5 CH_2), 2.12 (m, 2H, $O{=}CCH_2$) ,3.26 (m, 8H, $4NCH_2$); ^{13}C NMR ($CDCl_3$, ppm): 14.12 (CH_3), 22.19 (CH_2), 22.66 (CH_2), 26.44 (CH_2), 27.24 (CH_2), 29.11 (CH_2), 29.44 (CH_2), 29.82 (CH_2), 30.24 (CH_2), 31.73 (CH_2), 32.00 (CH_2), 39.07 ($O{=}CCH_2$), 58.92 (NCH_2), 179.47 (C=O).

CHAPTER 3. Synthesis of Quaternary Phosphonium Ionic Liquids

In order to exploit the degreasing properties for tuning degreasing efficiency and associated with IL-based improved degreasing technologies, several ionic liquids with quaternary phosphonium or ammonium as cations are synthesized. The details of some ILs are described as follows.

3.1. [P_{8888}] [$C_{17}H_{35}COO$]

Tetraoctylphosphonium bromide {Cyphons 482 [P_{8888}]Br, 15.69 g, 27.8 mmol} and stearic acid (white powder, 7.92 g, 27.8 mmol) were mixed in 35 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 40 mL of hexanes. To this stirred suspention was added a solution of sodium hydroxide (NaOH, 1.112 g, 27.8 mmol) in 35 mL of D.I. H_2O drop wise at room temperature. The mixture continued to be stirred at room temperature overnight. The reaction mixture was very cloudy and was added 30 mL more of hexanes. The mixture was stirred over weekend and the sticky white stuff floated in clear solution. The sticky white solid was filtered and added ~80 mL of $CHCl_3$, and washed with D.I. water four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield [P_{8888}] [$C_{17}H_{35}COO$] as a viscous liquid (16.20 g, 21.1 mmol, yield: 75.9%).

^{1}H NMR ($CDCl_3$, ppm): 0.82-0.88 (m, 15H, 5CH_3), 1.20-1.35 (m, 62H, 31CH_2), 1.42-1.65 (m, 18H, 9CH_2), 2.19 (m, 2H, O=CCH_2), 2.40 (m, 8H, 4PCH_2); ^{13}C NMR ($CDCl_3$, ppm): 14.15 (CH_3), 19.12 (CH_2), 21.79 (CH_2), 21.84 (CH_2), 22.50 (CH_2), 26.69 (CH_2), 28.88 (CH_2), 29.27 (CH_2), 29.57 (CH_2), 29.67 (CH_2), 29.90 (CH_2), 30.65 (CH_2), 30.80 (CH_2), 31.61 (CH_2), 31.83 (PCH_2), 38.10 (O=CCH_2), 179.03 (C=O).

3.2. [P_{8888}] [$C_{15}H_{31}COO$]

Tetraoctylphosphonium bromide {Cyphons 482 [P_{8888}]Br, 15.42 g, 27.3 mmol} and palmitic acid (white powder, 7.01 g, 27.3 mmol) were mixed in 35 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 40 mL of hexanes. To this stirred suspention was added a solution of sodium hydroxide (NaOH, 1.094 g, 27.3 mmol) in 35 mL of D.I. H_2O drop wise at room temperature. The reaction mixture was very cloudy and was added 25 mL more of hexanes and 25 mL more of D.I. H_2O. The mixture continued to be stirred at room temperature overnight. The mixture was still very cloudy, ~150 mL of $CHCl_3$ was added, and stand over weekend. The lower organic phase was separated and washed with D.I. water four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield [P_{8888}] [$C_{15}H_{31}COO$] as a viscous liquid (13.33 g, 18.0 mmol, yield: 65.9%).

^{1}H NMR ($CDCl_3$, ppm): 0.72-0.78 (m, 15H, 5CH_3), 1.10-1.25 (m, 58H, 29CH_2), 1.32-1.55 (m, 18H, 9CH_2), 2.07 (m, 2H, O=CCH_2), 2.23 (m, 8H, 4PCH_2); ^{13}C NMR ($CDCl_3$, ppm): 14.16 (CH_3), 19.01 (CH_2), 21.61 (CH_2), 22.39 (CH_2), 26.48 (CH_2), 28.78 (CH_2), 29.16 (CH_2), 29.46 (CH_2), 29.67 (CH_2), 29.55 (CH_2), 30.50 (CH_2), 30.64 (CH_2), 31.51 (CH_2), 31.72 (PCH_2), 37.78 (O=CCH_2), 178.88 (C=O).

3.3. [P_{8888}] [$C_{13}H_{27}COO$]

Tetraoctylphosphonium bromide {Cyphons 482 [P_{8888}]Br, 15.56 g, 27.6 mmol}and myristic acid (white powder, 6.30 g, 27.6 mmol) were mixed in 35 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 40 mL of hexanes. To this stirred suspension was added a solution of sodium hydroxide (NaOH, 1.10 g, 27.6 mmol) in 30 mL of D.I. H_2O drop wise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with D.I. H_2O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield [P_{8888}] [$C_{13}H_{27}COO$] as a viscous liquid (19.34 g, 27.2 mmol, yield: 98.5%).

^{1}H NMR ($CDCl_3$, ppm): 0.82-0.88 (m, 15H, 5CH_3), 1.18-1.25 (m, 54H, 27CH_2), 1.42-1.60 (m, 18H, 9CH_2), 2.16 (m, 2H, O=CCH_2), 2.32 (m, 8H, 4PCH_2); ^{13}C NMR ($CDCl_3$, ppm): 14.16 (CH_3), 18.82 (CH_2), 19.28 (CH_2), 21.99 (CH_2), 22.70 (CH_2), 27.03 (CH_2), 29.09 (CH_2), 29.48 (CH_2), 29.78 (CH_2), 30.15 (CH_2), 30.85 (CH_2), 31.81 (CH_2), 32.04 (NCH_2), 38.63 (O=CCH_2), 179.42 (C=O).

3.4. [P_{8888}] [n-$C_{11}H_{23}COO$]

Tetraoctylphosphonium bromide {Cyphons 482 [P_{8888}]Br, 15.48 g, 27.4 mmol}and dodecanoic acid (5.50 g, 27.4 mmol) were mixed in 35 mL of deionized water (D.I. H_2O, 18.2 MΩ-cm) and 40 mL of hexanes. To this stirred suspension was added a solution of sodium hydroxide (NaOH, 1.098 g, 27.4 mmol) in 30 mL of D.I. H_2O drop wise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with D.I. H_2O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^{O}C under vacuum for 4 hours to yield [P_{8888}][$C_{11}H_{23}COO$] as a viscous liquid (16.3 g, 23.9 mmol, yield: 87.1%).

^{1}H NMR ($CDCl_3$, ppm): 0.82-0.88 (m, 15H, 5CH_3), 1.20-1.35 (m, 50H, 25CH_2), 1.42-1.65 (m, 18H, 9CH_2), 2.17 (m, 2H, O=CCH_2), 2.35 (m, 8H, 4PCH_2); ^{13}C NMR ($CDCl_3$, ppm): 14.10 (CH_3), 18.70 (CH_2), 21.91 (CH_2), 22.65 (CH_2), 27.16 (CH_2), 29.02 (CH_2), 30.78 (CH_2), 30.92 (CH_2), 31.76 (CH_2), 32.00 (PCH_2), 38.97 (O=CCH_2), 179.64 (C=O).

CHAPTER 4. Characterization of Newly Synthesized Ionic Liquids

All six newly synthesized ionic liquids were characterized by nuclear magnetic resonance spectroscopy (NMR), FT-IR, and thermogravimetric gravity analysis (TGA).
NMR spectra of the ILs show essentially independent behavior of the cation and anion. For carboxyl anion, a single carbonyl resonance ~179 ppm exists, independent of the cation. For example, the [$C_{13}H_{27}COO$] anion resonance occurs as a singlet at approximately 179.5 ppm for either [P_{8888}] [$C_{13}H_{27}COO$] or [N_{8888}] [$C_{13}H_{27}COO$].

The physical properties of these ILs studied are compiled in Table 1. The thermal properties of ILs were examined by thermogravimetric analysis (TGA). The thermal decomposition temperatures (T_{onset}) range from 164 ^{o}C to 294 ^{o}C. This was typically greater than other most protic ionic liquids based on tertiary amines. The [P_{8888}] anion exhibited a distinctly higher thermal stability than [N_{8888}], see figure-1 below, a trend which was observed in earlier work.

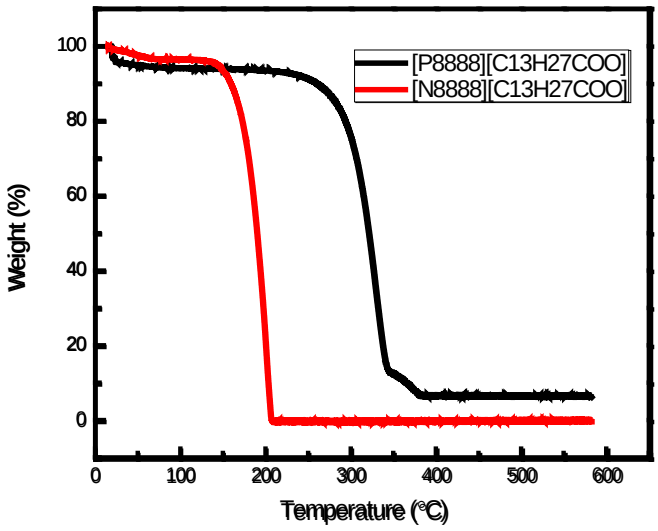

Figure 1. TGA plots of [P_{8888}] [$C_{13}H_{27}COO$] or [N_{8888}] [$C_{13}H_{27}COO$]

FTIR spectra of these ionic liquids are shown in Figure 2. They are consistent with structures of ILs

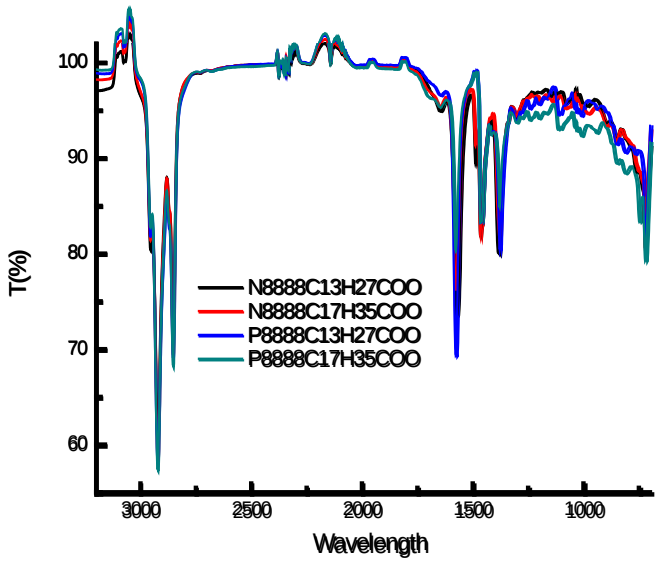

Figure 2. FTIR plots of newly synthesized ionic liquids

Table 1. Physical properties of newly synthesized ionic liquids.

Ionic liquids	Density (g/mL)	T_{onset} (°C)	$\nu_{C=O}$ (cm^{-1})	$\delta_{C=O}$ (ppm)
$[N_{8888}]$ $[C_{17}H_{35}COO]$	0.80	163.7	1571	179.37
$[N_{8888}]$ $[C_{13}H_{37}COO]$	0.85	168.2	1574	179.47
$[P_{8888}]$ $[C_{17}H_{35}COO]$	0.93	276.9	1577	179.03
$[P_{8888}]$ $[C_{15}H_{31}COO]$	0.92	271.2	nm	178.88
$[P_{8888}]$ $[C_{13}H_{27}COO]$	0.94	284.7	1577	179.42
$[P_{8888}]$ $[n\text{-}C_{11}H_{23}COO]$	0.87	293.5	nm	179.64

*nm: not measured

Chapter 5. Studies of Degreasing Technology Based on Ionic Liquids

A variety of experimental approaches are available to evaluate the degreasing capabilities of ionic liquids. Ideal testing approaches would need to facilitate limited sample vibration, minimize thermal variation, provide a clean controlled environment, and allow for instrumental access during each experimental trial. Two dominant methods were selected for the purposes of this effort: (1) droplet angle/shape analysis and (2) cleaning/deposition analysis using a quartz crystal microbalance. Droplet shape analysis employs an image capture system(Stanford Research Systems, QCM 200-USB) (examples from previous work are shown in Figure 3) combined with an instrument specific software driven shape fitting program with the ability of calculating/estimating droplet interfacial pension and/or surface contact angles. The QCM analysis utilizes a highly sensitive weight determination process based on the frequency a vibrating quartz crystal with the removal of mass (increase of frequency) or increase in mass (decrease of frequency). These techniques had the greatest potential to provide rapid screening of ionic liquid degreasing performance with the least ionic liquid material required for each test. Furthermore the sensitivity of these two approaches should allow for the demonstration of degreasing impacts based on ionic liquid structural differences.

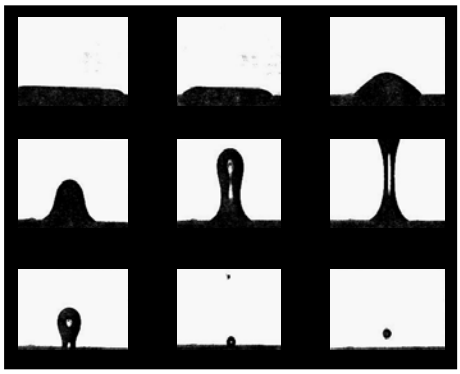

Figure 3. Droplet contact angle evolution and detachment

5.1. Droplet Shape Analysis.

All ionic liquids (ILs) were tested using the pendant droplet (PD) and contact angle (CA) measurement approaches to provide surface tension data and give an indication of cleaning capability. To benchmark processes and improve techniques before using ORNL produced ILs, procedures were first carried out using imidazolium based ILs, such as butyl-methylimidazolium chloride ([BMIM][Cl]) and butyl-methylimidazolium bromide ([BMIM][Br]).

Experimental Methods

Pendant Drop

Pendant droplets measure the surface tension of the liquid tested. Liquids were loaded into and were dispensed from a threaded gas-tight Hamilton syringe. Measurements can be taken with a stationary, receding, or advancing droplet. Stationary droplets provide the most consistent results. Best results are obtained when the droplet is advanced almost until it detaches but before it distorts. This point can be determined by advancing the droplet until detachment while recording frames for surface tension calculations. The point of distortion can then be recognized.

Contact Angle

Contact angle measurements were used for approximations of soil removal and confirmations of cleaning procedures. It is a good indication of surface to liquid interaction. Topological differences between even different coupons of the same material can result in variable results. Polishing can reduce this variability. Liquids tested were dropped from via a Hamilton gas tight threaded syringes from just over the droplets height onto the desired surface. The surface tension can be calculated from the frames taken during CA tests but for measuring cleaning the change in contact angle was emphasized.

Coupon Surface Preparation

All surfaces other than the already optically polished QCM crystals were polished with 400 grit wet sand paper to achieve a rough level of topological uniformity. Surfaces that appeared to have worn were again polished. Cleaning of surfaces consisted of a soak in petroleum ether and a water and non-residue soap bath agitated by a mechanical shaker. The minimum soak time for coated surfaces was 20 minutes at each stage. A progressive rinse of D.I. water, methanol, isopropanol, methanol, water followed each soak. Drying was performed with a nitrogen stream or 70 °C oven depending on the surface. Effectiveness of cleaning was confirmed via contact angle measurements.

Coating of crystals with the model soil, dotriacontane, {($C_{32}H_{66}$) [CAS#: 544-85-4]} was achieved via sublimation. Dotriacontane (abbrev as C-32) was selected as a model organic contaminant due to relevant published research focused on QCM soild studies and was a compromise with experimentally functional soils and DoD specific soils. C-32 was heated by a hot plate to 125 °C while a cold finger of 0.00 °C with the surface attached to it with double sided tape was suspended above. The pressure was adjusted to between 0.0-50.0 mbar depending on the desired thickness of the coating. Duration of sublimation was varied between 5-25 minutes but for most surfaces 10-15 minutes of sublimation produced a complete and visible coating. Twenty-five minutes of sublimation with a pressure below 25 mbar produced a visible white and complete coating on brass, stainless steel, and milled steel. Uniformity of coating was better achieved when all moisture was removed and the system was allowed to equilibrate before pressure was decreased. Anytime a surface coupon was tested for cleaning (HIS or TIS) it was thoroughly rinsed and dried before CAs were recorded.

Experimental Setup

Equipment

The camera used for recording CA and PD frames (Modified USB 2.0 Webcam with Thor labs focusing and extension lens) is mounted to be focused on a calibration bead set just below the tip

of a Hamilton threaded syringe. The entire apparatus is placed inside an incubator which can be flushed with nitrogen. Incubator controls temperature and removes unwanted air currents.

Software and Calibration

KSV Instruments software is using the Young/Laplace fit equations for calculations of surface tension. The software is originally for Windows 2000 but has been laboriously made to run on a Virtual Windows XP. Calibration is achieved with a calibration bead: 3.125 and 4.000047 mm beads have been used.

5.1.1. Pendant Droplet Testing

The pendant droplet measurements were performed to develop an understanding of the air/ionic liquid surface tension for a particular ionic liquid. These measurements were performed to determine if significant viscosity differences existed between tested ionic liquids which could have a detrimental effect on the consistency of the experimental results and consequently on any estimation of cleaning.

It was observed that the capillary behavior of the liquids on the end of the syringe made it difficult to produce a stationary droplet for many of the ionic liquids. Therefore, only select frames could be used to calculate surface tension. Each frame was determined and a baseline set individually (Figure 4). The baseline was established by a visual inspection to be where the droplet curvature appeared to cease. The center of the droplet had to be clearly visible and for three consecutive frames on a forward moving droplet before the frame could be used. If gas bubbles were observed in the droplet the frame was not selected.

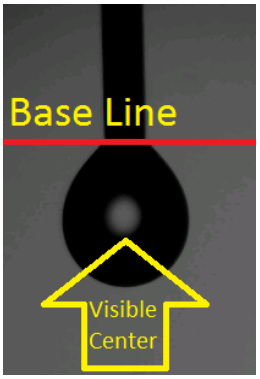

Figure 4. Example Droplet Baselining

The following table (Table 2) shows surface tension measurements as determined for the imidazolium family group of ionic liquids. As stated earlier these ionic liquids were used to establish procedure quality and verification that the experimental systems were testable by this method. All accepted data sets are included (hence the extra measurements for some ionic liquids).

Table 2. Surface Tension Determination of Imidazoilum Based Ionic Liquids

Ionic Liquid	Ionic Liquid Abbreviation	Surface Tension [mN/m]	# of Frames Used
1-butyl-3-methyl-imidazolium bromide	[BMIM] Br	49.68 ± 0.24	30
		49.45 ± 0.22	12
		52.00 ± 1.39	12
		51.99 ± 0.29	28
		51.98 ± 0.06	5
		47.78 ± 0.05	12
		47.38 ± 0.58	10
1-butyl-3-methyl-imidazolium chloride	[BMIM] Cl	41.43 ± 0.36	19
1-hexyl-3-methyl-imidazolium chloride	[HMIM]Cl	34.40 ± 0.63	30
		32.82 ± 0.35	12
		32.34 ± 0.05	30
1-octyl-3-methyl-imidazolium chloride	[OMIM] Cl	33.35 ± 1.14	24
		31.46 ± 0.21	3
		33.15 ± 0.49	5
		32.50 ± 0.17	6
		32.17 ± 0.12	8
		31.94 ± 0.21	121
1-decyl-3-methyl-imidazolium chloride	[DMIM] Cl	36.80 ± 0.41	12
1-hexyl-3-methyl-imidazolium hexaflourophosphate	[BMIM] PF_6	41.17 ± 1.15	7
		40.32 ± 0.42	13
		41.23 ± 0.19	30
		39.16 ± 0.67	7
		37.88 ± 0.11	30
1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide	[OMIM] TF_2N	29.10 ± 0.19	9
		29.14 ± 0.21	56

The following table (Table 3) shows surface tension measurements as determined for the ORNL synthesized group of ionic liquids.

Table 3. Surface Tension Determination of ORNL Synthesized Ionic Liquids

Ionic Liquid		Surface Tension [mN/m]	# of Frames Used
$[P_{8888}][C_{17}H_{35}COO]$	ORNL-168	30.28 ± 0.25	65
		30.35 ± 0.14	260
$[N_{8888}][C_{17}H_{35}COO]$	ORNL-160	27.04 ± 2.99	89
		27.02 ± 0.18	56
$[P_{8888}]$ $[C_{13}H_{27}COO]$	ORNL 164	30.70 ± 0.15	101
		30.65 ± 0.18	259
		31.17 ± 0.06	180
		31.13 ± 0.13	13
$[N_{8888}]$ $[C_{13}H_{27}COO]$	ORNL 167	28.83 ± 0.21	158

As can be seen from the data the experimental surface tensions for ORNL ILs were within a reasonably consistent band of values between 27 – 31 mN/m for all ionic liquids measured. Furthermore the ORNL tested ionic liquids were observed to have highly consistent surface tensions (within ± 4 mN/m). This effectively demonstrates that any substantive differences in contact angle and subsequent cleaning efficiency will be attributable to detergency effects and not limited uniquely by viscosity effects. For clarity, the number of frames used in a specific data set are based on measurement/droplet stability. Larger frame numbers were acquired for droplets where external vibrational phenomena (door being shut, drawer being shut, etc) were potential disrupting equilibrium. While no significant differences were identified during the course of the research the larger number of frames were incorporated in an abundance of caution.

5.1.2. Contact Angle Testing

Contact angle measurements were performed to develop an estimation of the extent of surface cleaning related to the ionic liquid/ionic liquid solutions exposure to the surface. Previous work by the co-PI and his collaborators employed water droplet contact angles on surfaces as indicators of surface cleaning.[22-31] The general approach being that a change from a pre-cleaned contact angle measurement was indicative of cleaning. More specifically, if the contact angle decreased, the resulting assumption of cleaning could be made based on the reduction of the organic (or hydrophobic) surface contamination, thus allowing the droplet to spread.

A number of challenges existed for this approach with the most significant being the quantity of ionic liquid available for testing. Two additional concerns for these experiments were the type of surface material to be tested and the strategy for introducing the surface into the ionic liquid/ionic liquid solution.

5.1.2.1. Testing Surface Selection

Initially a variety of surfaces were to be tested using the contact angle approach. This project focused on materials that meet DoDs particular needs, materials tested so far and shown in

Figure 5 include gold (surface of the QCM crystal), brass, aluminum, Teflon, Nylon, and Acrylic.

Figure 5. Surface materials to be tested

Following initial testing it was determined that effectively only metal surfaces could be prepared consistently (polished, contaminated, cleaned, etc) enough to reduce the impacts of unintentional surface topography changes indicative of use. As a result only milled steel and brass metal coupons were initially tested using the contact angle approach. During the initial course of these tests it was determined that the imidazolium ionic liquids induced some degree of surface corrosion. Figure 6 shows a milled steel coupon that had been treated with the imidazolium ionic liquid and left overnight in a shallow tray of water.

Figure 6. Milled steel coupon demonstrating IL induced corrosion

Testing showed that even newly polished coupons rusted quickly when in contact with imidazolium based ionic liquid in atmospheric conditions. Figure 7 shows the visual evidence of surface corrosion (rust) on both a milled steel and brass coupon 24 hours after contact with [BMIM][Cl] and only in contact with ambient laboratory humidity.

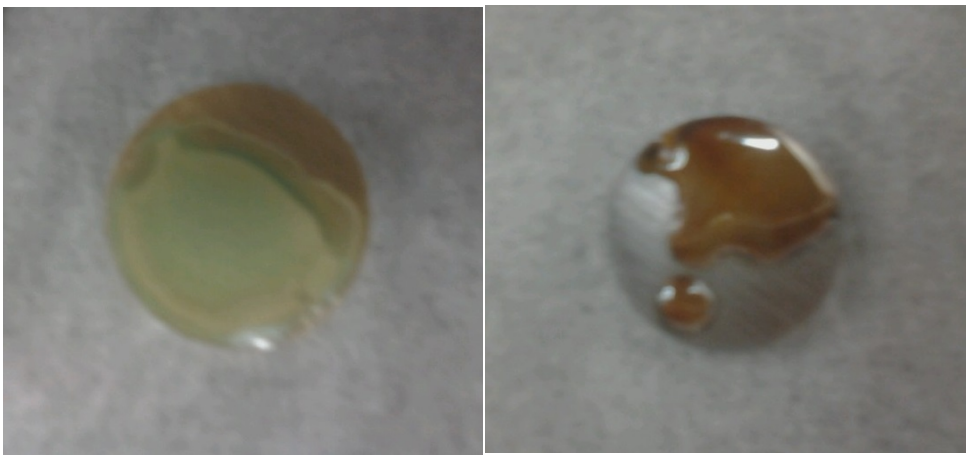

Figure 7. Steel and brass 24 hours after contact with [BMIM]Cl

The ionic liquids supplied by ORNL did not appear to oxidize either brass or steel. Figure 8 shows the observed surface corrosion from an imidazolium ionic liquid and the lack of apparent corrosion due to the ORNL supplied ionic liquids. In this figure only milled steel was tested and a single ORNL liquid was observed but is expected to be consistent with effects from the ionic liquid family grouping. It is important to note here that both the cation and anion present in the

Figure 8. Steel surface in contact with [BMIM] Cl on right ORNL IL on left after 24 hours

two groups of ionic liquids could potentially be different. It is not directly possible to use the above evidence to eliminate corrosion from the ORNL ionic liquids. It is also not possible to assign the corrosion to the cation since non-halide imidazolium ionic liquids were not used in the contact angle measurements. It was possible to speculate that the rate of rusting could be rapid enough to alter the surfaces of coated coupon surfaces without directly removing any dotriacontane. Stainless steel coupons were therefore selected so that any corrosion could be reduced. It is still recommend that the stainless steel be polished regularly to remove any beginnings of rust that could occur and maintain as pristine a surface as possible.

5.1.2.2. Immersion Test Selection

Two potential techniques were proposed for use in the demonstration of cleaning using ionic liquid/ionic liquids solutions. Initially a series of tests that employed a full immersion of the test coupon in the cleaning liquid were performed. A major challenge for this approach was that a limited amount of ionic liquids were available which necessitated the use of an ionic liquid solution approach. Subsequent testing was performed using a second immersion approach, hanging immersion, which allowed for the testing of only half of a coupon at a given time. This approach allowed for the use of pure ionic liquids when the quantity needed was available.

The total immersion soak (TIS) approach was used on coupons with 1 inch in diameter, primarily milled steel. TIS consists of a beaker (beaker size depends on number of coupons being tested) of some concentration of solution or solvent therein. The coupon tested was placed at the bottom of the beaker and allowed to sit for 30 minutes. The coupon was then removed and rinsed with a solution solvent (selected based on IL solubility) and dried. The surface was then placed on the contact angle apparatus and DI water droplets placed on the surface and allowed to stabilize. These post cleaning contaminated surface measurements were compared to pre-cleaning contaminated surface measurement and the degree of cleaning estimated. Testing was performed to identify and eliminate the potential that the ionic liquid specific solvent rinse was impacting the cleaning efficiency. Results indicated that no substantive cleaning was occurring from the post-immersion rinse and drying steps.

TIS tests with imidazolium based ILs in water were undertaken with some evidence for cleaning activity being observed. Table 4 shows typical data for these tests using a [BMIM][Cl] solution.

Table 4. CAs for (concentration) [BMIM][Cl] solution soak.

Solution #	CA after 10-Min Sublimation	CA after Post Soak Post Rinse	Change in CA
1	64	52	- 12
2	62	47	-15
3	57	45	-12
4	55	37	-18

TIS tests with ORNL synthesized ILs in methanol were undertaken with similar evidence for cleaning activity being observed. Table 5 shows typical data for these tests.

Table 5. CAs for low concentration ORNL soak tests.

Solution #	CA after 10-Min Sublimation	CA after Post Soak Post Rinse	Change in CA
1. IL 168	72	60	-12
2. IL 164	78	58	-20
3. IL 160	72	52	-20
4. IL 167	67	57	-10

The data above is a limited set of the available data. Significant time was spent attempting to refine the TIS approach with little improvement in consistency. Figure 9 shows the results for [BMIM][Cl] over a range of concentrations (this is inclusive of all experiments using this ionic liquid for all polishing levels). It was observed that the TISs approach was highly variable unless the surface is perfectly polished (as with a QCM crystal). The considerable variability in the contact angles was largely attributed to topological imperfections and the corrosion effect of [BMIM][Cl]. This is seen in the variability of cleaned surfaces that have the same polishing and/or milling. Without a high confidence in the specific changes in CA no further testing with the limited supplies of ionic liquids was attempted. The consequential qualitative evidence for cleaning was accepted and testing moved on to the QCM experimental work.

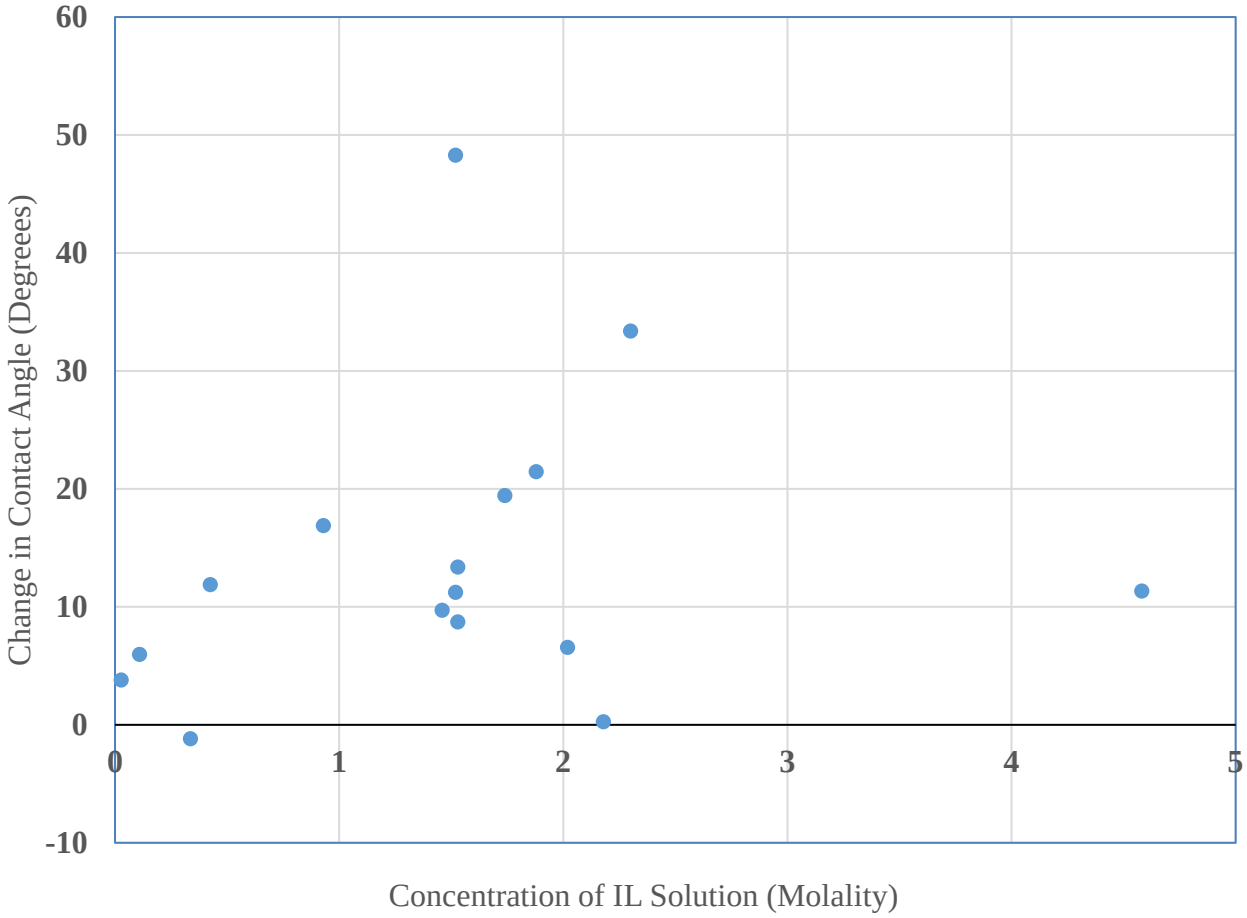

Figure 9. Wide variability in data for [BMIM][Cl] cleaning solutions.

During the course of the QCM experimental work significant challenges to data accuracy and interpretation were discovered (shown more extensively in section 5.2) and a revisiting and improvement of the immersion soak tests was performed.

With the previously outlined issues with the TIS approach, a new approach using a hanging coupon technique, hanging immersion soak (HIS), was developed. It was determined based on lessons learned during the previous work that new surfaces would be acquired and employed in all subsequent tests. Ten new surfaces were acquired (5 brass and 5 stainless steel). A hole was drilled near the edge of each coupon and a line scored across the width creating two halves with the drilled hole at the top of one half. The undrilled side was used as the testing side (side 1). The drilled side was used as the permanent benchmark (side 2). From the hole the coupon was suspended from a boom with side one immersed in the solution or solvent. Except for the solution soak testing, side 2 underwent all the procedures that side 1 underwent thereby significantly reducing coincidental experimental noise. HIS soaks were performed with the prepared brass and stainless steel coupons for 60 to 90 minutes at a time. The model grease used was dotriacontane (C-32) used as received from Sigma Aldrich. The general experimental arrangement can be seen in Figure 10.

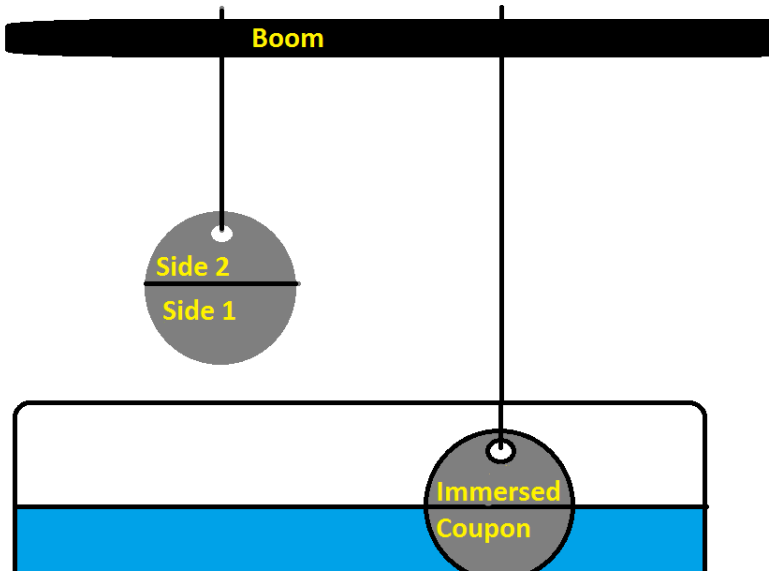

Figure 10. Schematic of HIS apparatus setup

As a proof of concept a series of tests were performed using the HIS apparatus. These tests were designed to determine if the comparisons between the two sides held true throughout the process of contamination, cleaning, and returning the coupon to a highly cleaned state. Additionally, as time and resources (ILs) were becoming limited it was determined that the HIS testing process would have to suffice as our main analysis of cleaning potential/efficiency.

The first of these tests was focused on demonstrating the consistency between the two coated coupon sides. It was a fundamental assumption of the work we undertook that the general roughness of each coupon, while likely unique between coupons, would be consistent for each test on a specific coupon. The process employed the 10 new one inch diameters metal coupons. Five brass and five stainless steel coupons were sublimated with C-32: brass for 12 min at 50-45mbar and stainless steel for 15 min at 45-50 mbar. These coupons had been scored through their centers creating two sides to be used in HISs. Side one will be further tested. Side 2 is a permanent reference which will be only put through the rinse and dry procedure of the testing process. The CAs of the all measured coupons shortly after sublimation are recorded in Table 6.

Table 6. CAs post sublimation on modified brass and stainless steel coupons.

Coupon #	**Brass CAs**			**Stainless Steel CAs**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	65	65	1.00	74	76	0.97
II	66	65	1.02	77	70	1.10
III	68	61	1.11	77	80	0.96
IV	71	72	0.99	78	71	1.10
V	71	70	1.01	70	70	1.00

Values are in degrees and unless otherwise specified are the average of 60 frames. This set frame number was determined to represent the establishment of an equilibrium state (60 frames represents one hour of immersion). As can be seen the resulting CAs are largely consistent. A quick analysis technique is to determine the ratio of side1 to side 2, in which values closer to unity indicate greater uniformity, values less than unity indicate a slightly lower coating on side 1 than side 2, and values larger than unity indicate a larger coating on side 1 than side 2. This specific technique can be used to provide greater inside into cleaning/deposition performance in the later cleaning studies. As can be seen in the data, the results from brass are generally more consistent than the results for stainless steel. This could be explained by brass coating more evenly and/or stainless steel have more topological imperfections. This could be the case as brass is softer and polishes more easily and evenly. Additionally, the C-32 may bind more readily to the brass versus stainless steel as a result of surface properties. In general, it is expected that a thicker coat of C-32 would give more consistent CAs. This was tested initially during the development of the TIS procedures and was based on observational data. Actual coating thickness was not measured nor was such measurement possible at the time of this work.

The second set of tests were performed using the coated coupons from the above test. These coupons were immersed in DI H_2O for 30 minutes to show that CAs do not have significant change from being soaked in water. The results from this test can be seen in Table 7.

Table 7. CAs of Coupons from Table 5 after H_2O immersion.

Coupon #	**Brass CAs**			**Stainless Steel CAs**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	59	65	0.91	64	73	0.88
II	67	65	1.03	71	66	1.08
III	72	61	1.18	78	71	1.10
IV	67	68	0.99	68	63	1.08
V	--	--	--	80	78	1.03

As with the previous analysis the closer to unity the S1/S2 ratio, the closer to negligible cleaning was observed. In general, both brass and stainless steel do not have significantly different contact angle ratios and thus there is no indication of cleaning for either surface. This further confirms that simple water immersion is insufficient to remove any appreciable quantities of the surface contaminant.

A third set of tests were performed to provide some clarification as to the validity of the approach for ionic liquid solutions. In this test only the stainless steel coupons were used (an experimental error resulted in the invalidation of the brass coupons for this test). For this test, three stainless steel coupons were selected and immersed for one hour in a solution of 15 grams [DMIM][Cl] and 100 grams DI H_2O. The coupons were then removed and rinsed thoroughly than dried with a nitrogen gas stream. As with the previous tests involving pure DI H_2O, the [DMIM][Cl] solution does not appear to affect any significant cleaning as indicated by CA and S1/S2 ration for the C-32 coated stainless steel. There are a number of experimental variations that could be performed for this type of test; however, owing to resource limitations no further

tests in this vein were perform at the time of this report. The results from this set of tests can be seen in Table 8 and indicate negligible cleaning performance.

Table 8. CAs of Stainless Steel Coupons following immersion in [DMIM][Cl] solution

Coupon #	**Stainless Steel CAs**		
	S1	*S2*	*S1/S2*
I	71	71	1.00
II	67	72	0.93
III	84	87	0.97
IV	71	--	--
V	71	65	1.09

Following the experimental trials using water and a standard ionic liquid, the ORNL ionic liquid with the greatest available quantity was tested. Only the first three stainless steel coupons were tested as a direct result of the limited quantity of ORNL prepared ionic liquid solutions These stainless-steel coupons were immersed for 1 hour in a previously made solution of ORNL IL 167 and methanol. Following immersion, the coupons were rinsed w/ methanol (selected for ionic liquid solubility) and then dried with N_2. The results from this set of tests can be seen in Table 9.

Table 9. CAs of Stainless Steel Coupons following immersion in ORNL IL 167 solution.

Coupon #	**Stainless Steel CAs**		
	S1	*S2*	*S1/S2*
I	62	63	0.98
II	61	79	0.77
III	76	62	1.23

There may be some cleaning, but these tests do not convincingly confirm or provide any understanding of said cleaning from a quantitative view. The coupons have been rinsed and handled enough that the mechanical abrasion appeared to be a potential factor, specifically coupon III. It is difficult to draw any significant conclusions from this data set; however, a potential interpretation is that the strength of the ionic liquid solution is critical to cleaning efficiency and that the tested concentration was too low.

In order to verify that we could return the coupons to a functionally pristine clean state, a test focused on verifying our approach using the HIS method was performed. All ten coupons, five brass and five stainless steel were cleaned with an initial petroleum ether soak and rinse followed up with a non-residue soap solution agitated by mechanical shaker. Each cleaning stage is followed by a progressive rinse through water, methanol and isopropanol. The data for this test is shown in Table 10. The lower the contact angle becomes, the lower the residual soil is assumed to remain. It is clear from this data that the cleaning procedure was effective in significantly

removing any contamination and further confirmed that the inherent surface imperfection (such as roughness) will have significant impacts on contact angles.

Table 10. CAs of post testing post cleaning procedure coupons.

Coupon #	**Brass CAs**			**Stainless Steel CAs**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	46	51	0.90	CA on steel were either between 25-35 degrees or too irregular to measure. It spread fast along and adhered to the surface, making it difficult to achieve a uniform droplet.		
II	48	42	1.14			
III	40	40	1.00			
IV	49	44	1.11			
V	54	48	0.90			

The final test was focused specifically on the cleaning performance of ORNL IL/methanol solutions. Three ORNL IL solutions were prepared with what remained of the ORNL produced ionic liquids (160, 167, and 168). ORNL IL 164 was not tested using this new HIS approach as it was expended during QCM testing. The concentrations were selected based on the available ionic liquid and the total required solution volume for the immersion soak test and are as follows: 160: 0.04 M; 167: 0.15 M; 168: 0.07 M. The data for these tests is shown in Table 11.

Table 11. CAs of Stainless Steel Coupons following immersion in ORNL IL solutions

Stainless Steel Coupon #	**CAs after 20 min sublimation**			**CAs after soak, rinse, and dry**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	65	71	0.92	57	57	1.00
II	65	65	1.00	62	60	1.03
III	68	70	0.97	62	67	0.93

It is difficult to determine if cleaning occurred for these solutions as there is little indication from either the relative contact angle changes or the S1/S2 ratio. The consistency of the approach is significant in that this data set represented the optimal sublimation conditions and the experience of the experimental technician. Despite the lack of significant evidence of cleaning (which could be explained due to the low concentrations of the liquid solutions based on measured weight) it was determined that this testing approach provided the most significant chance of demonstrating cleaning for any ionic liquid, either pure or in solution. Unfortunately, the limited ILs available where expended in these tests and recovery and purification did not return enough IL for further testing. Additional ILs were requested, prepared, and sent from ORNL and the subject of the experimental activities outlined in Chapter 6.

5.2. Quartz Crystal Microgravimetry Analysis

A selection of the ORNL ionic liquids (ILs) were tested using the quartz-crystal microgravimetry approaches to provide a direct measurement of the detergency process. To benchmark this

processes and improve techniques before using ORNL produced ILs, procedures were first carried out using imidazolium based ILs, butyl-methylimidazolium chloride ([BMIM][Cl]) specifically in this case.

Experimental Equipment and Methods

QCM

A QCM200 Quartz Crystal Microbalance Digital Controller with a QCM25 5 MHz Crystal Oscillator from Stanford Research Systems (SRS) was used for all QCM measurements. The electrode surface was gold overlaid on chrome. All tests were undertaken in a temperature controlled incubator with the capability of being nitrogen flushed. The QCM gate interval was set to 1 second for these tests, allowing for 0.1 Hz change or less than a microgram of mass change detection.[33] Though not on the order of a reaction time, a gate interval of 1 second also allows for real time kinetic detection of the detergency process.
The flow cell tests were undertaken with the SRS Flow Cell Adapter (SRS Part# O100FC) connected via 1/16 inch tubing to a KD scientific syringe pump. A reservoir was connected to the outlet to allow for the withdraw/infuse function of the pump.

Crystal Surface Preparation
Coating of crystals with dotriacontane (C-32) was achieved via sublimation. C-32 was heated by a hot plate to 125 °C while a cold finger of 0.00 °C with the surface attached to it with double sided tape was suspended above. The pressure was adjusted to around 50 mbar. Duration of sublimation was somewhat varied but generally was set at 20 minutes. Anytime a crystal was tested for cleaning (IST or FCT) it was thoroughly rinsed and dried before CAs or base frequencies were recorded.

5.2.1. QCM Baseline/Qualification Tests

Two types of tests where utilized using the QCM instrumentation: (1) an immersion soak test (IST) and, (2) a flow cell test (FCT). These tests employ standard experimental strategies for use of the specific QCM instrument employed in this work. Expansions on the challenges and advantages for these methods are outlined in the QCM operations manual.[33] Major challenges are the introduction of noise from external vibration sources, sudden atmospheric changes (pressure, temperature, etc) and from inconsistencies in solution flow. All of these limitations can obscure any detergency effects if the introduced noise is sufficiently large. To mitigate impacts from external factors, extensive measures were taken to isolate the QCM apparatus from ambient phenomena impacts. Flow inconsistencies were addressed using a variety of syringe pump flow schemes. As will be shown in the follow sections, significant issues were discovered and dramatically reduced the utility of this approach.

5.2.1.1 Immersion Soak Test (IST)

As shown in Figure 11, the IST approach requires that the supporting apparatus suspends the QCM oscillator and crystal holder at 90 degrees relative to the ground above a 100 mL beaker containing solution. The entire apparatus is inside a constant temperature incubator with

vibration minimizing pads to dampen the impacts of external ambient vibrations. The IST method requires a minimum of 40 mL of solution to completely immerse the QCM crystal holder head. During these test, the dry baseline of the coated or clean crystal is determined. Next the crystal is immersed into the solution. Following initial wetting of the crystal, the crystal holder/wand is removed and reemerged into solution to remove any bubbles that might have been present on the crystal surface. The experimental process can involve multiple removals each of which will be followed by rinsing with solvent and drying with nitrogen. The crystal was allowed to stabilize after each removal, rinse, and dry. In general stabilization was determined by observation and normally required less than 5 minutes upon disruption of equilibrium.

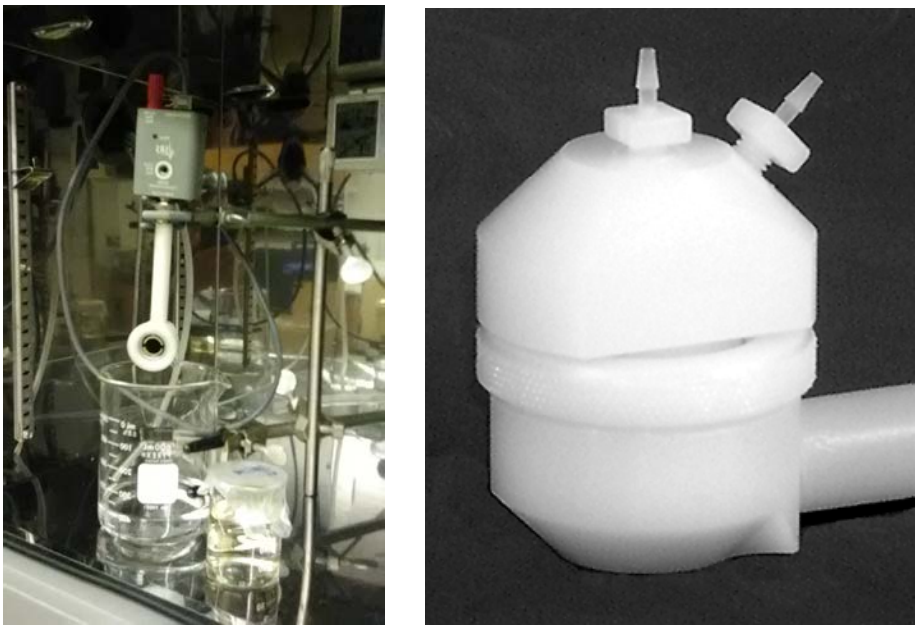

Figure 11. (Left) Picture of QCM apparatus setup for IST. Smaller beaker (100mL) next to large beaker is placed below QCM wand and wand is lowered to immerse crystal. (Right) Flow cell on QCM wand.

5.2.1.2 Flow Cell Test (FCT)

The FCT apparatus holds the oscillator and wand in the same orientation as the IST. A PTFE flow cell attaches to the face of the crystal holder with an inlet in the center (Figure 11). Solution flows through the inlet, spreads over the gold surface of the crystal, and exits through an outlet near the edge of the crystal. Both inlet and outlet connections attach to 1/16-inch PTFE tubing. The tubing is connected to a syringe push/pull syringe pump with a programmable flow rate. A minimum of 2 mL is necessary fill the cell and tubing but over 6 mL is desirable to flush all bubbles from the system. Larger volumes in a reservoir are easier to use. The tubing can be transferred from solution and attached to a nitrogen flow to rinse and dry the cell, tubing and crystal. Drying times were nominally greater than five minutes.

5.2.1.3 Water Baseline Performance Tests

The IST and FCT were benchmarked with deionized water using both clean and coated crystals. Figures 12 and 13 show a dry baseline at a higher frequency interspersed with lower frequency

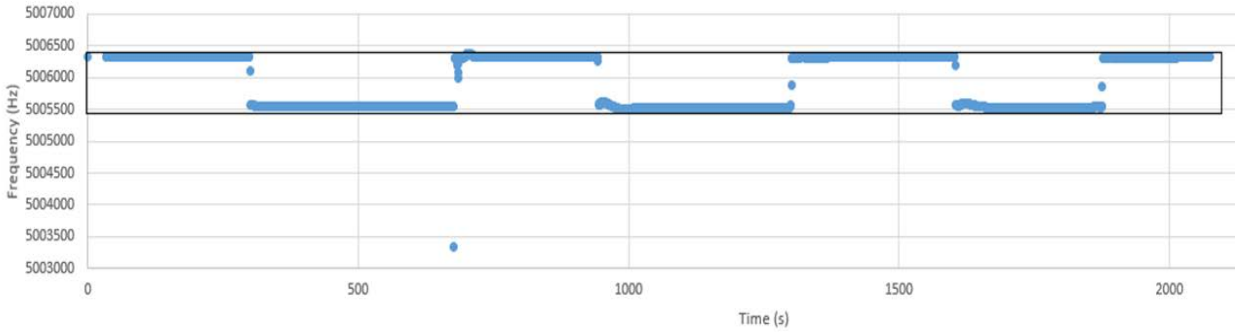

Figure 12. 100% water IST with a clean crystal

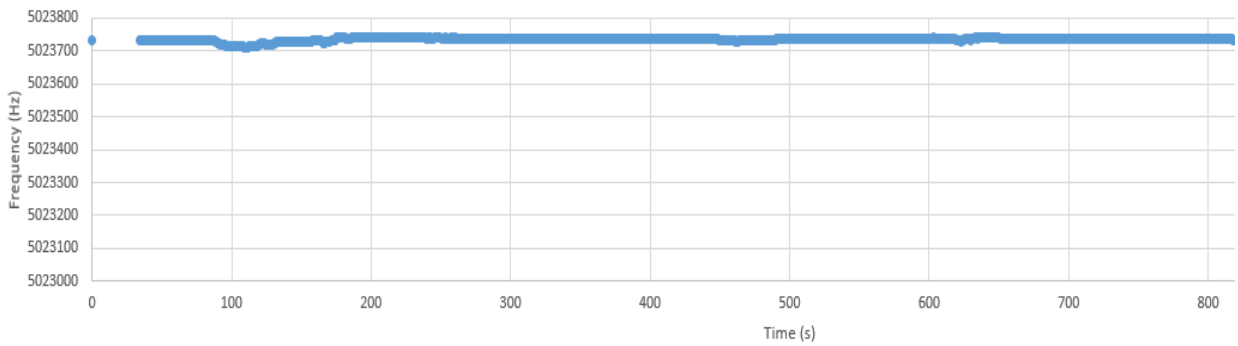

Figure 13. 100% water IST with a coated crystal

immersion periods for clean and coated crystals respectively. The coated crystal exhibited a lower dry baseline frequency which is consistent with the crystal having adhered mass on the surface. FCT benchmarking showed that the method was less precise and easily disrupted by bubbles or vibrations from the building as it did not have a large solution surrounding it to act as a dampener. Additionally, flushing the line and flow cell removes bubbles that many have been introduced during the previous pull step, the time for this process was normally between three to five minutes. This process produces a cyclic response as shown in the QCM graph, therefore, FCTs are recorded after the line has been flushed. This could potentially remove C-32 before the recording is started. Figure 14 shows the results of a programmed push/pull pumping scheme, the data looks very erratic, but the y-axis range is small enough that the benchmark serves its purpose in showing that water does not remove any C-32. The repeating pattern is a result of pressure changes at the crystal surface relating to the push/pull programming.

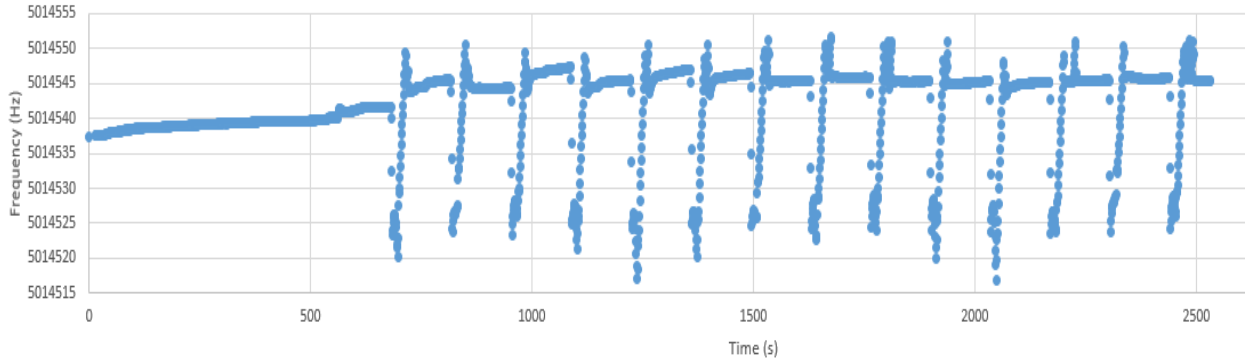

Figure 14. 100% water FCT with push pull programing on a coated crystal and no dry baseline

5.2.1.4 Methanol Baseline Performance Tests

The IST approach was benchmarked with methanol using both clean and coated crystals. Figures 15 and 16 show a dry baseline at a higher frequency interspersed with lower frequency

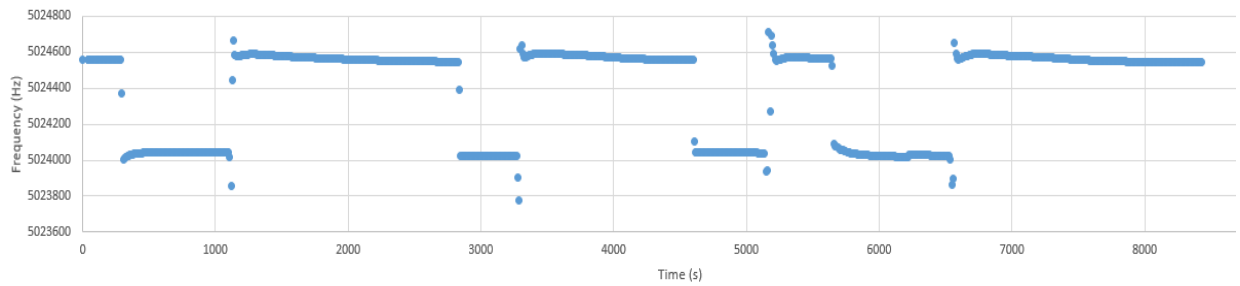

Figure 15. 100% methanol IST with a clean crystal.

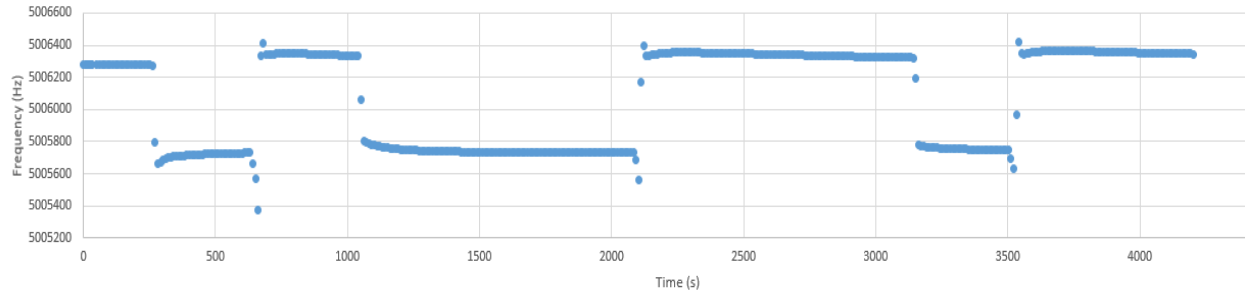

Figure 16. 100% methanol IST with a coated crystal.

immersion periods for clean and coated crystals respectively. The coated crystal exhibited a lower dry baseline frequency which is consistent with the crystal having adhered mass on the surface. With no removal from the coated crystal (determined by the negligible change in mass) for the methanol solvent during repeated ISTs it was assumed that it would not remove during FCT and no baseline was performed. The variation in equilibrium length was included to demonstrate that stability was truly achieved at the minimum step length.

5.2.1.5 Imidazolium Ionic Liquid Baseline Performance Tests

As the focus of this study is the use of ionic liquids as cleaning agents, a series of benchmark tests were performed using imidazolium ionic liquid solutions (Table 11). The results from

Table 11. QCM immersions using IST in [BMIM]Cl solutions.

Approximate Concentration of [BMIM][Cl] in H_2O	Δ Resistance (ohm)	Δ Frequency (Hertz)
0.71 M	373.8	-803
1.42 M	441.6	-910
2.82 M	610.9	-1181
Pure IL	1938	-380274

imidazolium based ILs are not readily understood and the lack of a clear trend for the increasing [BMIM][Cl] concentrations is a concern. A significant change in viscosity and charge of the liquid media has the potential to produce erratic behavior form the QCM instrumentation and ionic liquids are obvious contributors to such phenomena.

The response of the QCM to IL solutions is also shown in Table 11. From earlier tests, we expect the QCM to increase in resistance and decrease in frequency when transitioning from air to ionic liquid solution (as in water and methanol solutions). If cleaning is observed the frequency should gradually increase and the resistance stay approximately the same. For low concentrations (below 0.5 M) the expected resistance and frequency changes are observed but no cleaning is observed. As a proof of performance, a series of tests were undertaken with low (typical of surfactant concentrations) ionic liquid quantities, 0.35 M, 0.19 M, 0.035 M, 0.019 M, 0.0035 M [BMIM][Cl] in DI H_2O. The results from these tests are shown in Figures 17 – 21 respectively.

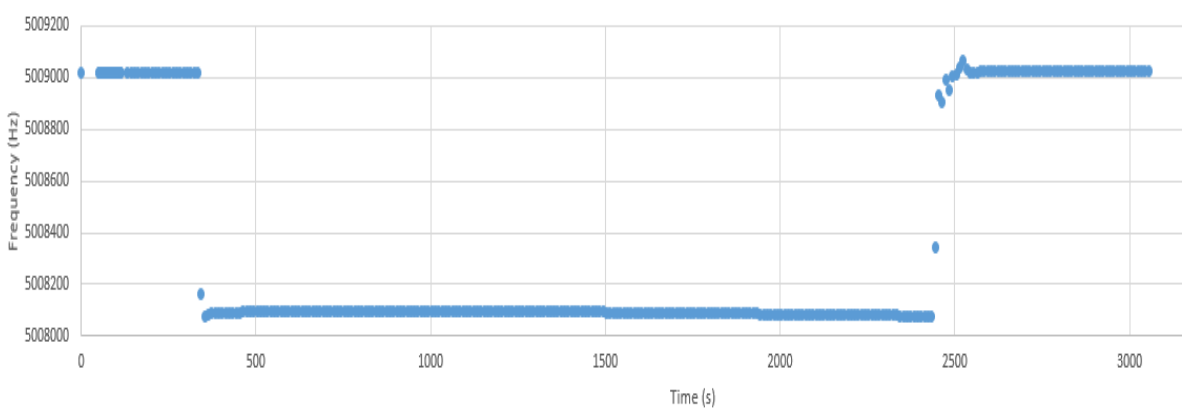

Figure 17. 0.35 M [BMIM][Cl] for a coated crystal using IST

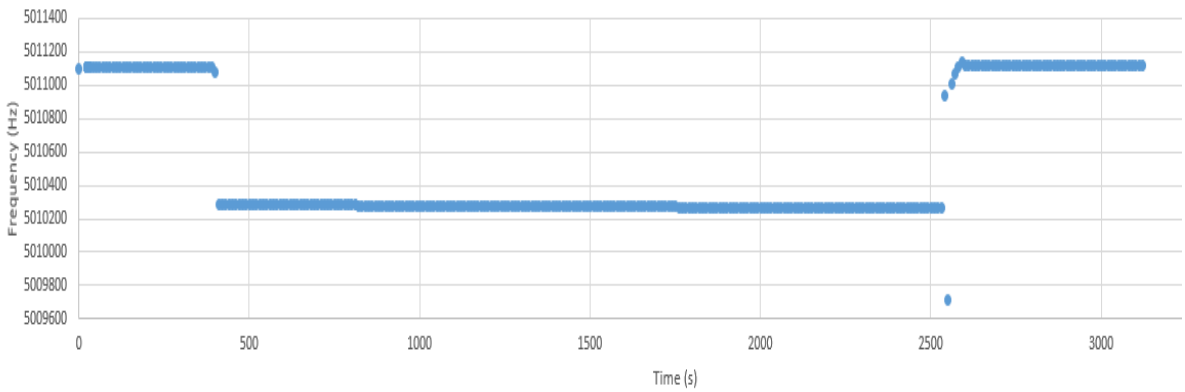

Figure 18. 0.19 M [BMIM][Cl] for a coated crystal using IST

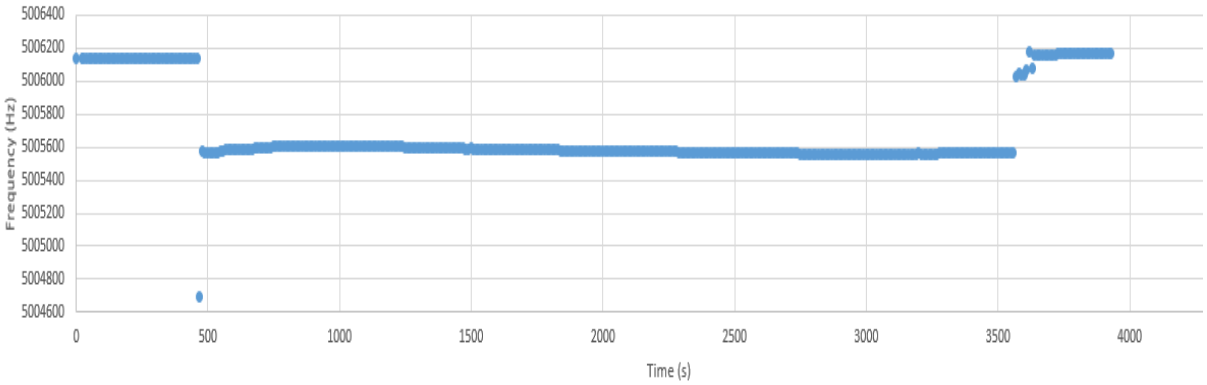

Figure 19. 0.035 M [BMIM][Cl] for a coated crystal using IST

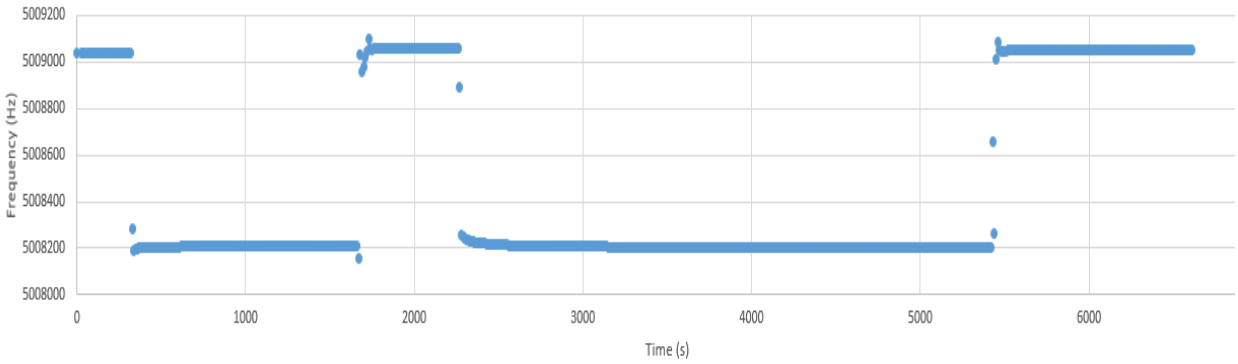

Figure 20. 0.019 M [BMIM][Cl] for a coated crystal using IST

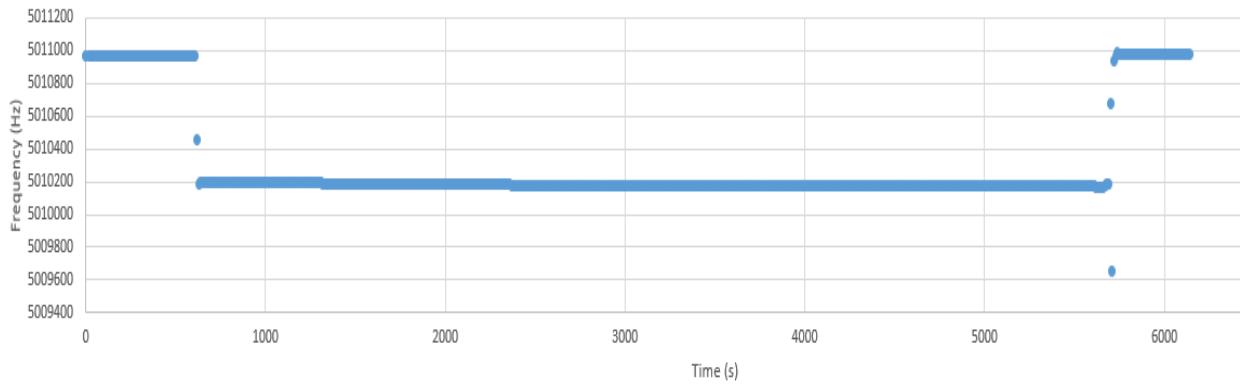

Figure 21. 0.0035 M [BMIM][Cl] for a coated crystal using IST

The unchanging nature of the data over time in Figure 17-21 leads to the interpretation that ionic liquid solutions in this concentration range are not effective cleaning solutions. Further complicating this analysis, the higher concentration experiments (specifically the pure IL test shown in Table 11) are not as useful in developing correlations. Regardless, based on the low concentration data set the IST approach appears to work for measuring solution related frequency changes.

5.2.1.6 ORNL Ionic Liquid Baseline Performance Tests

While the IST approach was functional with respect to experimental time constraints, the quantity of ionic liquid/ionic liquid solution required (40 – 100 mL) was prohibitive when considering the small quantity of ORNL produced ionic liquids remaining after CA testing. With this in mind the FCT approach was employed with two specific process variations. The first was replacement of water with methanol, selected due to ORNL ionic liquid solubility, and the second was the exploration of a push/pull programmed loop scheme. This would allow for a small amount of pure ionic liquid or ionic liquid solution (no more than 6 mL for operational constraints). The specific nature of the push/pull program was not clear initially so a test low flow/stagnant rate (Figure 22), and one of alternative medium/high push/pull flow rates (Figure 23) was performed. The concentration used for the ORNL IL/methanol solutions, 0.035 M ORNL Il/methanol was selected to be near to the value as published in the work of Weerawardena *et al.* (the study on which our QCM work was based).[33] These tests used ORNL IL-167 as it was the only remaining IL of any sufficient pure amount at this time of these studies.

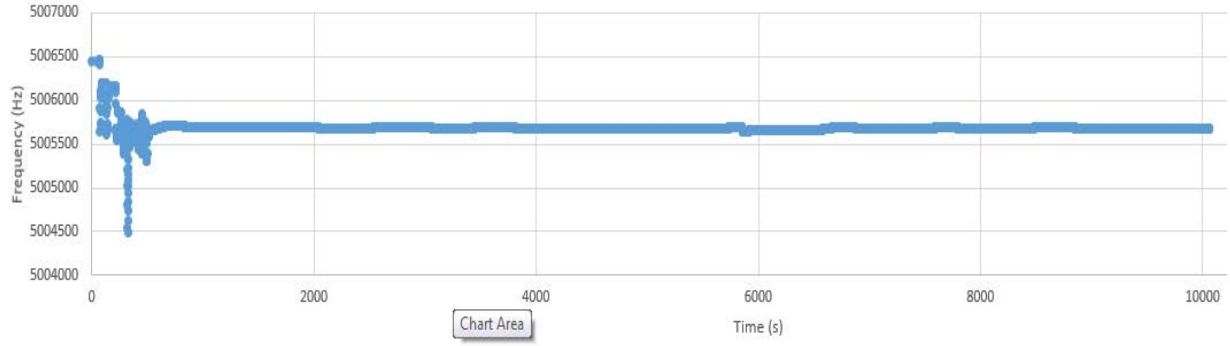

Figure 22. 0.035 M ORNL IL-164/methanol solution with low rate and stagnant flow

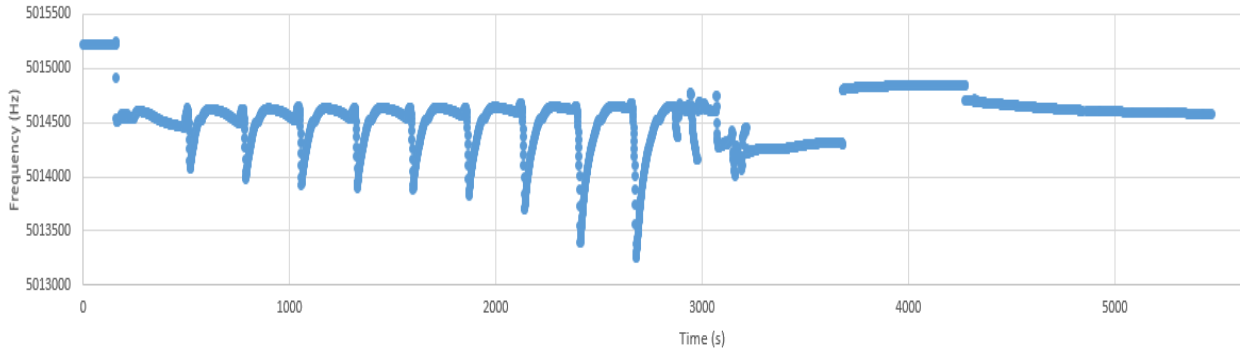

Figure 23. 0.035 M ORNL IL-167/methanol solution with alternating high and medium flow

As can be seen from the data above, the instability in the base value made analysis problematic at best for alternative flow rates, with less uncertainty from low flow followed by a stagnant contact period. From this we inferred that a test following this approach would result in the best representation of detergency. Figure 24 show the result from such a test with both the air contacting frequency followed by the cleaning frequency.

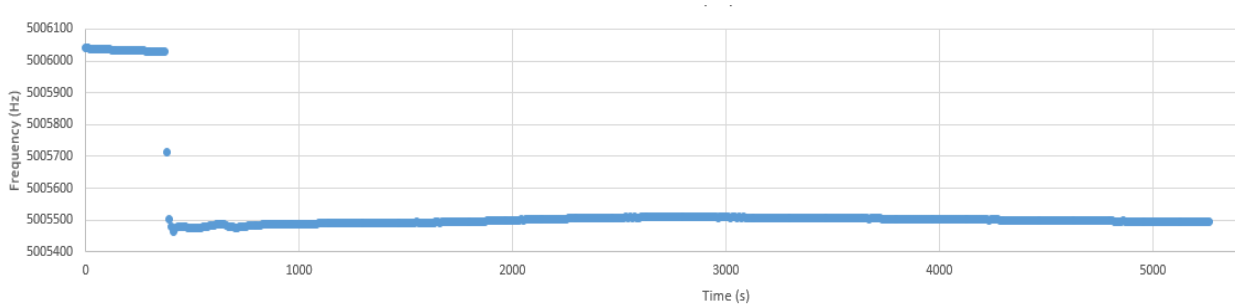

Figure 24. 0.035 M ORNL IL-167/methanol solution FCT based soak test with air baseline

This lack of detergency was unexpected (since the CA tests had indicated some potential cleaning) and forced us to rethink the QCM measurement approach. In an attempt to develop an instrumentation baseline (basic analytical performance outside ionic liquid work) we repeated one of the better performing condition test from the work of Weeawardena *et al*.[34] The results from these tests were inconclusive as we were fundamentally not able to demonstrate the same detergency results in line with the published data. Figure 25 shows the absorbance of water as the surfactant helps it bind to the C-32 but upon removal from solution, rinsing and drying there is no frequency change and therefore no permanent mass change. There are several potential explanations; however, the most logical is that a fundamental problem exists with our QCM apparatus and as such with limited time and ionic liquid quantities a decision to rely on the HIS CA determination approach for cleaning was made for optimization studies.

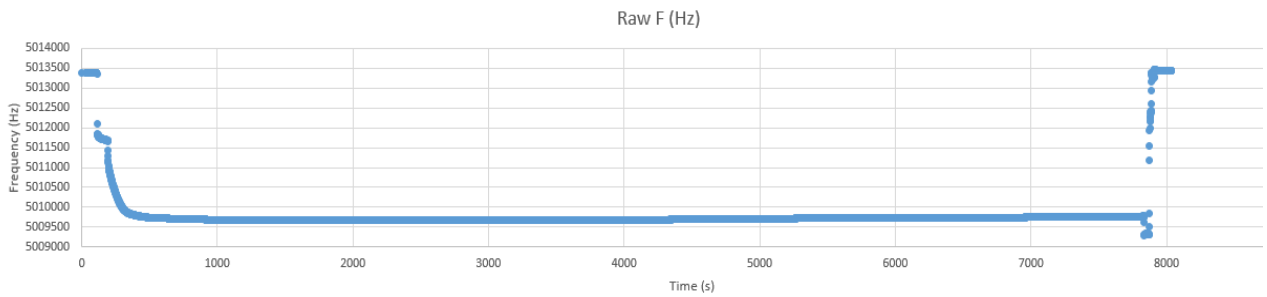

Figure 25. 0.00075 M C12E8 H_2O solution ICT QCM test on a coated crystal.

Chapter 6. Optimization of Degreasing Technology Based on Ionic Liquids

6.1. Optimization of Coating Method

As indicated earlier, significant variations existed in the sublimation process and without the optimal conditions determined it was suggested that we seek an external vendor for pre-contaminated coupons. Unfortunately, we were not able to find any such vendor for pre-greased coupons in any way conducive to our work at the small scale. Therefore we have refined the method for coating our metal coupons via the vacuum sublimation process. We have further clarified that a sublimation time of 10 minutes at 125 °C allowed for a more uniform surface coating of dotriacontane (C-32) on our target stainless steel coupons as determined by multiple water droplet contact angles placed at various sites on the coupon. As uniformity was desired, this method change was accepted without surface thickness measurements (which as indicated previously were not available at the time of this work).

6.2. Determination of Cleaning Activity for Pure ORNL Ionic Liquids

As a result of the previous efforts, the initial ionic liquids synthesized at ORNL were exhausted or unreliably purified such that a new batch of ionic liquids was required for the final determination of detergency. These new ionic liquids were $[P_{8888}][C_{15}H_{31}COO]$ (ORNL IL-175-1), $[P_{8888}]$[C13H27COO] (ORNL IL-164-2), $[P_{8888}][n\text{-}C_{11}H_{23}COO]$ (ORNL IL-175-2), and $[P_{8888}][i\text{-}C_{11}H_{23}COO]$ (ORNL IL-184-1) and were in marginally larger (> 5mL) quantities. Due to the limited quantities of these liquids at the time of this work, surface tension measurements were not performed.

This final series of tests reverted to the HIS CA approach outlined in Chapter 5 and was focused on providing a robust data set for use in selecting an ideal ionic liquid with which to initiate any future work. Each of the final four ionic liquids were subjected to the same experimental conditions. One challenge to acquiring consistent data is the presence of significant variations in surface roughness. When combined with the limited number of tests that could be performed the data is limited to four to five coupons. In the tables that follow, two notations are important to recognize: (1) “NM“are used to denote the absence of a measurement for said coupon/condition due to some experimental error (specifically Table 12 Coupon #2 the technician marred the coated surface with a gloved hand), and (2) italics are used to indicate an apparent outlining data value that was excluded from the final averages for the S1/S2 ratios. Traditionally a statistical test would be applied to the data to determine if said value was a true outlier; however, insufficient data was available at the completion of experimental trials. It was administratively determined that any values 10% greater than unity for S1/S2 were would be reported but excluded from the final average. The exclusion was premised on the unlikely situation that wetting would be decreased (indicating increased hydrophobicity) and the likelihood that operator error resulted in the deviation. The results for each of these ionic liquids can be seen in Tables 12-15.

Table 12. CAs on stainless steel after treatment with $[P_{8888}][i\text{-}C_{11}H_{23}COO]$ using HIS

Coupon #	**CAs on Stainless Steel (Post Sublimation)**			**CAs on Stainless Steel (Post HIS Test)**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	86	96	0.896	45	77	0.584
II	NM	NM	NM	NM	NM	NM
III	90	95	0.947	47	70	0.671
IV	*95*	*86*	*1.116*	*48*	*42*	*1.143*
V	109	111	0.982	57	106	0.538

**Italicized data indicates data excluded from final average*
**NM stands for not measured.*

Table 13. CAs on stainless steel after treatment with $[P_{8888}][C_{15}H_{31}COO]$ using HIS

Coupon #	**CAs on Stainless Steel (Post Sublimation)**			**CAs on Stainless Steel (Post HIS Test)**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	143	143	1.00	111	140	0.79
II	130	130	1.00	102	132	0.77
III	152	150	1.01	109	138	0.79
IV	140	140	1.00	132	138	0.96
V	146	150	0.97	146	130	1.12

Table 14. CAs on stainless steel after treatment with $[P_{8888}][n\text{-}C_{11}H_{23}COO]$ using HIS

Coupon #	**CAs on Stainless Steel (Post Sublimation)**			**CAs on Stainless Steel (Post HIS Test)**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	*157*	*111*	*1.41*	*109*	*96*	*1.14*
II	160	156	1.03	159	156	1.02
III	145	136	1.07	105	111	0.95
IV	160	157	1.02	110	116	0.95
V	154	152	1.01	--	--	--

**Italicized data indicates data excluded from final average*

Table 15. CAs on stainless steel after treatment with $[P_{8888}][C_{13}H_{27}COO]$ using HIS

Coupon #	**CAs on Stainless Steel (Post Sublimation)**			**CAs on Stainless Steel (Post HIS Test)**		
	S1	*S2*	*S1/S2*	*S1*	*S2*	*S1/S2*
I	105	112	0.94	67	109	0.61
II	111	116	0.96	105	117	0.90
III	107	106	1.01	81	105	0.77
IV	116	118	0.98	96	107	0.90
V	155	166	0.93	109	150	0.73

Table 16 shows the accepted average S1/S2 ratios for each ORNL ionic liquid tested. Additionally, the difference between the two calculated values can be used as a rough representation of surface coverage changes (cleaning is indicated if the differences between cleaned and contaminated coupon ratios are positive).

Table 16. Average S1/S2 ratios for each new batch ORNL ionic liquid tested.

ORNL IL #	**Post Sublimation S1/S2 Ratio**	**Post Soak/Rise/Dry S1/S2 Ratio**	**% Change in S1/S2 Ratios**
184-1	0.942	0.598	36.5
175-1	1.003	0.828	17.5
175-2	1.037	0.971	6.35
164-2	0.964	0.781	18.9

With the noted limits in the above data in mind, Figure 24 shows a visual comparison of the averages of the coated S1/S2 and cleaned S1/S2 ratios for the data above. The dashed line represents no change in the values before and after cleaning. As the data approaches the x-axis the cleaning ratio is approaching absolute cleaning. If a data point were to be above the dashed line the results would be indicative of surface deposition (increase in mass). Conversely, if the data point resides below the line the result would be indicative of surface cleaning. Furthermore, data values residing closer to unity are indicative of no change in surface contamination as a result of simple cleaning (not related to ionic liquid treatment).

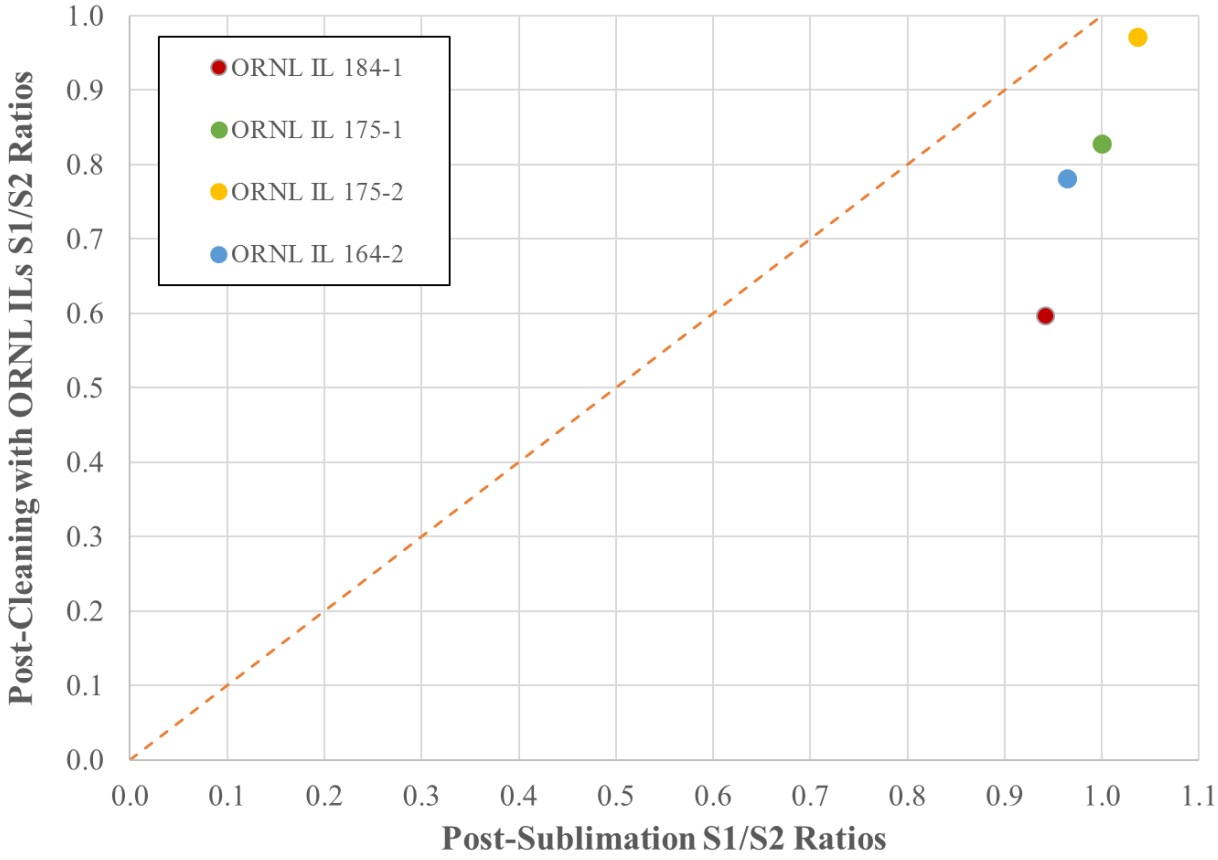

Figure 24. Comparison of S1/S2 Ratios as an Indicator of Cleaning Potential

6.3. Conclusions

From the work outlined in this report, a few conclusions can be reached. These conclusions naturally divide into: (1) experimental activities and (2) the question of ionic liquid facilitated degreasing.

With respect to experimental activities, it is observable that the contact angle approach was effective in providing a screening of ionic liquid/ionic liquid solution potentials for degreasing. It is less apparent that the results can provide complete understanding of cleaning. The lack of reliability with regards to the QCM measurements precluded the use of that technique for directly measuring cleaning performance and no explanation other than a failure of the analytical deceive can be reached at this time.

With respect to ionic liquid facilitated degreasing, the data from our study (such as Table 16) would indicate that $[P_{8888}][C_{11}H_{23}COO]$ had the greatest cleaning potential. The recommendation from our project would be that this is ionic liquid can be the subject of future targeted cleaning and to be produced in greater quantities. From the data related to molecular mass and cleaning ratios a general trend begins to emerge where the more effective degreasing solvent had the lower carbon chain length on anion. This could indicate that the length of the

long chain on anion is crucial in interacting with and removing the surface contamination by limiting local interference between the soil and the organic moiety of the ionic liquid.

Overarching conclusions are that several new ILs have been synthesized and evaluated for grease removal and $[P_{8888}][C_{11}H_{23}COO]$ is found to have the greatest cleaning potential. Many unknown factors are remained and future research is definitely necessary.

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