

USE OF IONIC LIQUIDS IN PRODUCED WATER CLEAN UP

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INTRODUCTION

Oil and gas production usually involves pumping of large amounts of contaminated water along with the hydrocarbon phase, termed “produced water” by the industry¹. This high-volume waste stream, on the order of a trillion gallons of water a year, is subject to National Pollution Discharge Elimination System permits. For Gulf of Mexico wells, the Environmental Protection Agency (EPA) limit on oil and grease content in produced water discharged in the ocean is a daily maximum of 42 mg·L⁻¹ and a monthly average of no more than 29 mg·L⁻¹ (ref. 2). Waste water is analyzed for total petroleum hydrocarbon content, an analysis that not only measures the less soluble paraffinic hydrocarbons, but also soluble polar molecules: phenols and organic acids³. There are a variety of methods for removal of trace amounts of hydrocarbon, but physical methods (i.e., filtration) are subject to fouling and chemical methods (i.e., acidification) can be defeated by the chemistry of the oil⁴. It would be desirable to have on-line sampling of water soluble organics in produced water so that a problem with separation of the organics could be detected quickly should it arise, thus lessening any impact to the environment.

After separation of the aqueous phase from the hydrocarbon phase, the water is expected to contain a low concentration of organics⁵, and hence a sensitive method of analysis is required for on-line monitoring. One such technique may be provided by uptake on a quartz crystal microbalance⁶. A quartz oscillator is covered with a film into which the analyte can dissolve, and a change in frequency corresponds to the mass of the substance that is taken up onto the microbalance. Classes of solvents that promise to have good properties for film formation include ionic liquids, because of their unique physical and chemical properties⁷. Ionic liquids are organic salts that are liquid at room temperature with low vapor pressures, suggesting that they are more environmentally friendly than other organic solvents. Their chemical and physical properties, such as solvent behavior and hydrophobicity, are determined by the choice of the anion and cation, allowing them to be tailor-made for a particular application⁸. Ionic liquids have high viscosities, which is an advantage in this research, as they will form a stable film on the quartz crystal microbalance⁹. Although expensive to synthesize, ionic liquids may be recycled and used again in a cost effective process. In addition to waste remediation, other applications of ionic liquids in oil production have been explored elsewhere¹⁰, such as in the extraction of hydrocarbons from oil shales.

The experiments done this year tested the effectiveness of nine different ionic liquids in removing organics from the aqueous phase as a function of temperature, salinity, and pH. The organic compounds selected were representative of various classes of water soluble organics that have been shown to contaminate produced water. Saturation behavior and regeneration were also investigated. The effect on organic removal by addition of a diluent to the ionic liquid phase was also examined, as this has been shown to enhance organic acid uptake in studies with amine/aqueous systems¹¹. A diluent can have the effect of reducing viscosity, which assists interfacial dispersion and speeds mass transfer between two immiscible phases.

Demonstration of organic solubility in selected ionic liquids is the first step into the development of an on-line sensor for produced water contamination.

DISCUSSION OF CURRENT ACTIVITIES

The uptake of organics into the ionic liquid from the aqueous phase was measured using liquid-liquid contact experiments. Nine different ionic liquids were selected for investigation: 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide - bmim Tf₂N, 1-octyl-3-methylimidazolium Tf₂N – omim Tf₂N, and bmim PF₆, were synthesized at ORNL¹². Trihexyltetradecylphosphonium bistrifluoromethylsulfonylimide, 1-hexyl-3-methyl-imidazolium Tf₂N, and 1-butyl-1-methyl-pyrrolidinium Tf₂N were purchased from Merck. Trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecylphosphonium methanesulfonate were synthesized by Rex Ren (Wesleyan University, Connecticut). The affinity to water was checked for most of these ionic liquids; 1mL of ionic liquid and 10 mL de-ionized H₂O were shaken in a vibrating mixer for 60 min. Karl-Fischer titration (Brinkman 652 KF-Coulometer) was used to determine the water solubility in the ionic liquid, and UV spectroscopy (on a Varian Cary 50000 UV-Vis-NIR spectrophotometer) was used to determine the ionic liquid solubility in de-ionized water. Although all of these ionic liquids were considered to be hydrophobic, they had measurable solubility in H₂O and in some cases allowed water uptake of over 1% by weight.

Thermal analyses were performed on some of the ionic liquids, using a Harrop model ST-736 DTA/TGA apparatus (30°C·h⁻¹, 100 cm³·min⁻¹ N₂ or O₂). The ionic liquids were all stable to at least 280°C, even in 100% O₂, except for bmimPF₆ that decomposed at 180°C in 99.97% N₂. Viscosities were recorded using a Brookfield Model DV-III Rheometer and were generally much higher than that of water or most organic solvents.

Contact experiments typically used 50 or 100 µL of ionic liquid and 1 to 2 mL of aqueous solution shaken together in a small vial. For some experiments as little as 20 µL or as much as 1 mL of ionic liquid was used. Aqueous solutions of representative organics were used (0.1 to 10 g·L⁻¹): hexanoic acid (Sigma 99-100%), glacial acetic acid (J.T.

Baker), 1-nonanol (Aldrich 98%), toluene (Aldrich 99%), cyclohexanone (Spectrum Quality Products 97%), and octane (MCB Manufacturing 98%) without further purification.

Contacts took place over a range of conditions: in temperature ($22\pm 2^\circ\text{C}$, 37°C , 75°C), in salinity (distilled-deionized water, 0.2M NaCl, 1.8M NaCl), in pH (<2 to 12), in ionic liquid-to-water ratio (0.02 to 1.0), and in organic concentration (0.1 to $10\text{ g}\cdot\text{L}^{-1}$). A diluent, 1-nonanol, was added to some of the ionic liquids, bmim PF₆, trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecyl methanesulfonate. In the case of the bmim PF₆, the tests were carried out to compare results on organic acid extraction with and without a diluent. Ratios of ionic liquid to diluent ranged from 0.2 to 2, and the diluent was found to enhance organic recovery from aqueous solution. The sulfonate ionic liquids were extremely viscous, and a 1:1 volumetric dilution ratio was required to be able to test extraction in the laboratory. 1-nonanol was chosen as the diluent because of its high solubility in the ionic liquids.

The two-phase systems were prepared, shaken for two minutes, centrifuged, and then allowed to settle for a few days. The aqueous phases were analyzed on a Waters high performance liquid chromatograph (refractive index detector 2410, auto sampler 717 Plus) or acidified and extracted with methylene chloride and measured on a Hewlett Packard 5890 gas chromatograph (GC) using a flame ionization detector (FID). To simplify the analysis, separate extraction experiments were carried out for mixtures of the organic acids and butane diol, followed by HPLC analysis. Aqueous solutions of toluene, 1-nonanol, and cyclohexanone, were treated separately and analyzed by GC. Hexanoic acid could be analyzed using both methods. Results were compared to controls, consisting of similarly treated aqueous solutions without addition of ionic liquid.

The measured distribution coefficients covered a broad range, Table 1, from no extraction to complete extraction from the aqueous phase into the ionic liquid. The organics that were best extracted were toluene and 1-nonanol. Other organics, such as cyclohexanone and hexanoic acid, transferred into the ionic liquid phase only under certain conditions. Still others, such as acetic acid, were not taken up into the ionic liquid in significant amounts in most of the ionic liquids tested. For instance, the extraction of hexanoic acid was sensitive to pH, as the protonated form was better removed from the aqueous phase by the ionic liquid (bmim Tf₂N) than the non-protonated form. Removal of acetic acid with the sulfonate ionic liquids; however, did not demonstrate such a pH dependence. In the case of hexanoic acid, the pH sensitivity suggested a mechanism for recycling the ionic liquid by rinses with controlled pH.

Table 1: Distribution Coefficients and Activity Coefficients for Organics in Ionic Liquids

Organic	K_{ow}	$K_{IL/W}$ Range
Toluene	2.73 [27]	13 – 200
1-nonanol	3.77 [28]	5 – 410
Acetic acid	-0.17 [27]	Not extracted – 6
Hexanoic acid	1.92 [27]	Not extracted – 25
Cyclohexanone	0.81 [27]	3 – 15

The salinity of the brine did not appear to change the solubility of the organic in the ionic liquid. Nor did the bmim Tf_2N affect the salinity of the brine, from chloride ion measurements of the aqueous phase, so significant ion exchange was not observed. Similar results have been reported elsewhere in contacts with solutions of chlorophenols¹³. Recent results that will be reported elsewhere; however, indicate that the solubility of the ionic liquid has a complex dependence on salinity, and at higher concentrations (up to 3 M) is inversely proportional to solution ionic strength¹⁴.

Temperature effects were complicated by the enhanced solubility of the ionic liquid in the aqueous phase and losses through volatilization. Hence, the effect of temperature on organic solubility could not be quantified.

Regeneration studies were carried on a series of three replicate samples, of 100 μ L bmim PF_6 in contact with 2 mL of a 1 $g \cdot L^{-1}$ solution of hexanoic acid, toluene and 1-nonanol in deionized water, that were subjected to a number of washing steps: deionized water, pH10, pH10, pH2, pH10, pH10. At each step, the rinse solutions were analyzed for the three organics of interest, until rinse concentrations were negligible. One of the samples of ionic liquid was then heated to 120°C to drive off the toluene, and the other two were reused in contact experiments to measure the change, if any, in distribution coefficient after the cycle of rinses. A similar procedure was carried out for contacts with 3-methyl-1-butylimidazolium bistrifluoromethylsulfonylimide.

The results of the regeneration experiments on bmim PF_6 , Figure 1, showed that the remediation of the ionic liquid through rinsing was successful in the case of 1-nonanol, but less so for hexanoic acid, and not at all for toluene. Heating of the bmim PF_6 above 100°C ionic liquid to remove the toluene was not successful, as it induced decomposition of the bmim PF_6 , as seen by NMR. After heating at 120°C for several hours, the response to toluene and 1-nonanol returned for bmim Tf_2N , Figure 2, but not for hexanoic acid. This finding was borne out by nuclear magnetic resonance (NMR) studies on the regenerated ionic liquid, which showed small peaks from impurities in the spectra.

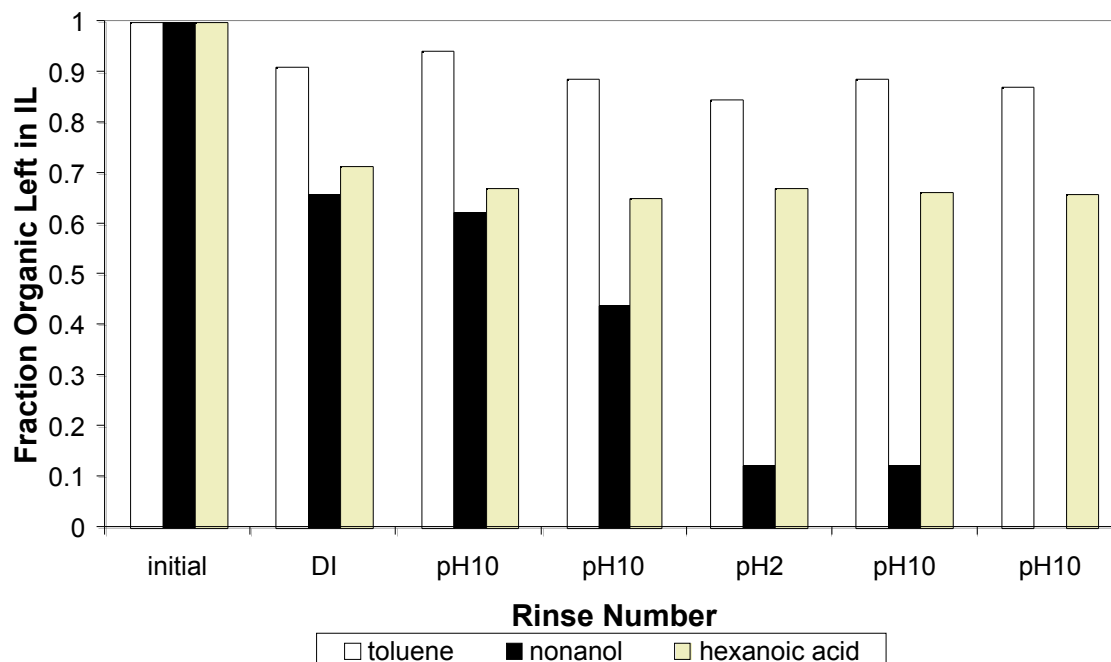


Figure 1: Fraction of organic remaining in the ionic liquid after treatment. The initial amount of organic transferred into the ionic liquid from the aqueous phase was normalized to one.

Octanol-water coefficients^{15,16}, K_{ow} values, for various organic species studied are listed in Table 1, along with the range of distribution coefficients observed in the ionic liquids in this work. Arguments have been presented in the literature that the K_{ow} values correlate with the uptake into ionic liquids^{13,17}. It is apparent that one distribution coefficient does not predict the behavior in the ionic liquids studied, even though the ionic liquids that were selected for this study could all be classified as non-reacting, weakly basic ionic liquids. Activity coefficients at infinite dilution have been measured for toluene and other hydrocarbons compounds in bmimTf₂N, emimTF₂N, and bmimPF₆^{17,18,19}. These are not only dependent on the ionic liquid, but also on physical conditions such as temperature. Chemical interactions such as acid-base phenomena²⁰, and the interactions between charged and non-charged molecules in both the aqueous and ionic liquid phases²¹ must be considered in understanding the behavior of multiphase systems involving ionic liquids.

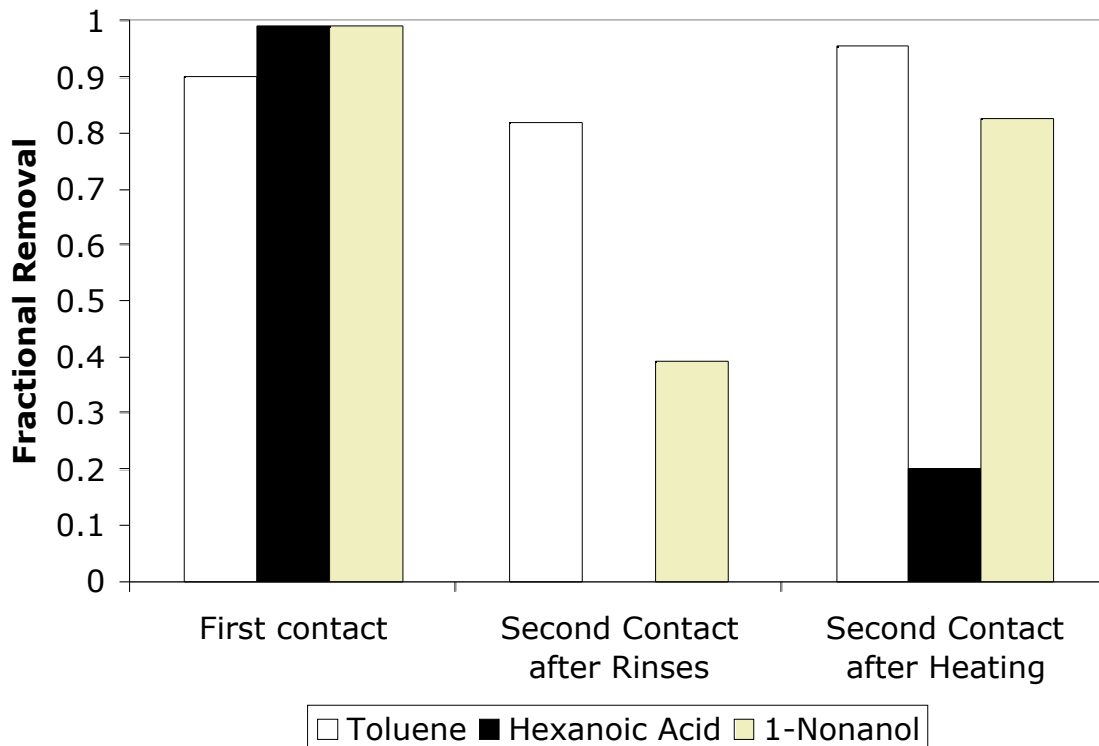


Figure 4: Fractional removal of various organics for aqueous contacts with fresh ionic liquid (bmim Tf₂N) (cycle 1), rinsed ionic liquid (cycle 2), and ionic liquid both rinsed and heated (cycle 3).

Results of the project to date showed that ionic liquids will be very effective in the selecting removal of particular contaminants in produced water, and yet will be fairly blind to other constituents. Although this would present difficulties in across-the-board remediation, it may prove advantageous in sampling for a particular priority pollutant²² in produced water.

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