New Approaches to Produced Water Sampling, Analysis, and Remediation at ORNL

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Biographical Sketch

Joanna McFarlane (Ph.D., Chemistry, University of Toronto, 1990) has worked as a research chemist in the Separations and Materials Research Group of the Nuclear Science and Technology Division at Oak Ridge National Laboratory since 2001, where her primary focus has been on produced water analysis and remediation. She represents ORNL on the Natural Gas and Oil Technology Partnership, working with the U.S. Department of Energy to foster collaborations between the national laboratories and industry.

Abstract

Oil and natural gas production is often accompanied by large amounts of wastewater [1]. The volumetric ratio of water-to-oil will increase over the lifetime of an operation and can eventually exceed 90%. Water is also associated with some, but not all, gas production. For instance, dry sources of gas are found in Alberta, Canada. Produced water is often reinjected into the well to increase oil recovery. However, in the western states, the injected water is supplemented by “clean” groundwater—thus depleting a scarce resource. Water associated with fossil fuel production constitutes a high-volume waste stream, on the order of a trillion barrels of water a year [2]. Organic contamination from soluble and dispersed oil is monitored by the U.S. Environmental Protection Agency (EPA) for offshore production. Salinity, rather than organic contamination, is the primary concern for onshore discharge, although organics cause difficulties with some salt-removal methods, such as reverse osmosis. A thorough review of produced water issues and the research that has been undertaken to solve these problems was published in 2004 by Veil and coworkers [3].

Oak Ridge National Laboratory (ORNL) and other national laboratories, with the support of the U.S. Department of Energy (DOE), have been involved with produced water remediation technologies for several years. At ORNL, chemical engineering research has been applied to removal of organics from contaminated water (centrifugal separator, ozonation, and contacts with novel solvents such as ionic liquids). Water-soluble organics and inorganic ions have been analyzed and modeled using thermodynamic and statistical methods. Most of these projects have been supported by DOE/Fossil Energy (DOE/FE) through its oil program. Recent results from ORNL produced water studies, both experimental and theoretical, will be presented. The application of these investigations to technologies supporting both water conservation and energy initiatives will be explored.

Background

Offshore discharge of produced water associated with deep oil wells in the Gulf of Mexico is regulated by National Pollution Discharge Elimination System (NPDES) permits, to a daily maximum of 42 mg·L⁻¹ and an average of 29 mg·L⁻¹ oil and grease [4]. Although the solubility of most individual paraffinic hydrocarbons compounds is lower than these levels, the analytical tests mandated by the U.S. Environmental Protection Agency (EPA) for the measurement of total petroleum hydrocarbons also sample more-soluble compounds such as carboxylic acids [5], which can augment the apparent total petroleum hydrocarbon (TPH) concentration well above the permitting level. Crude oil from the Gulf of Mexico has a relatively high concentration of polar molecules, namely those containing oxygen, nitrogen, and sulfur. Many of these are water soluble, making the NPDES regulations particularly stringent and expensive to follow. In other
jurisdictions, the concerns are similar. For instance, discharge into the North Sea is limited to a monthly average of 40 mg·L⁻¹ [6].

Effective remediation of produced water offshore requires both understanding of the types and amounts of soluble hydrocarbons and the ability to predict the solubility as a function of variables that can be measured in the field. On-line monitoring of water-soluble organics can be applied to existing wells and would allow quick intervention should problems arise with organic removal. For new wells, prediction of water-soluble-organic content in produced water would allow an informed selection of cleanup technologies. Optimized removal methods could be included in the design phase, minimizing retrofit and construction costs. The petroleum industry has been addressing these issues through the Petroleum Energy Research Forum (PERF) and has collaborated with the U.S. Department of Energy (DOE) to support work in produced water research at Oak Ridge National Laboratory (ORNL).

Past Initiatives

ORNL has a long history of research focused on processing of radioactive waste streams. In some cases, the analyses and technologies that have been developed can be applied to problems of a more general nature, including contamination arising from industrial processing or energy production other than nuclear [7]. Hence, since 1997, ORNL has participated in investigations related to produced water in several areas: removal of the aqueous phase from the oil using centrifugal separation in a “downhole” separator [8], analysis of the organic and inorganic content in produced water [9], and remediation of produced water through oxidation of entrained hydrocarbons by ozonolysis [10].

Current Activities

The primary focus of recent produced water research at ORNL has been to characterize water-soluble organics in produced water and to develop models to explain and predict the concentrations of water-soluble organics under conditions similar to those encountered in the field. In addition, remediation of water contamination using ionic liquids, which are novel environmentally friendly solvents, has been explored. A brief summary of some of that work is given here.

Water Characterization

Because more information was needed on Gulf of Mexico wells, the characterization of simulated produced water at ORNL has been carried out using standard EPA analytical methods [11] with the objective of classifying the organics into size categories (roughly equivalent to carbon chain length,) and into chemical classes aliphatic, aromatic and polar. A sensitivity analysis was performed on solubility as a function of independent variables: temperature, pressure, pH, salinity and water-to-oil ratio. These experiments measured the effect of varying physical and chemical conditions on solubility and were used to derive data for model development.

Contact experiments were carried out with actual crude oil samples, with densities of about 0.85 g·cm⁻³. The aqueous phase was prepared in the laboratory to approximate seawater composition. Most contacts were carried out under stirring for 4 days to ensure thermodynamic equilibrium. The oil, and, after contact, the aqueous phase were analyzed by inductively coupled plasma for inorganic ions; by ion chromatography for organic acids; and by gas chromatography after fractionation on a packed column for aliphatic, aromatic, and polar components. Detailed experimental procedures are provided elsewhere [9].

The results of the characterization study [12] showed that of all of the physical variables tested, pH had the greatest effect on the solubility of organic compounds derived from oil. This suggested that a large fraction of these compounds are acidic, in agreement with work done elsewhere on North Sea crude oil [13].
Temperature, which was varied from 25 to 75°C, had a slight effect on solubility, which increased for heavier components. A decrease in solubility was observed for lighter components, attributed to losses through volatilization. No discernable trends were observed for the other physical variables: pressure, salinity (salting-out behavior), or water-to-oil ratio, within the uncertainty in the data. Pressure effects would have been most apparent in the solubilities of volatile organics, and these had previously been released from the oil samples before analysis.

**Models for Organic Uptake**

Results from the ORNL characterization studies of produced water were intended to support the development of a predictive model for produced water contamination with organic compounds. The modeling of produced water composition using a chemical thermodynamic equilibrium calculation was reported, the model being based on an iterative solution of the Rachford-Rice equation [14]. An activity coefficient model was used to describe component behavior in the two immiscible liquid phases: hydrocarbon and aqueous. As the compounds under consideration had little or no volatility under the conditions of the experiment, the vapor phase was not included in the model. The activity coefficients were determined from a liquid-liquid equilibrium database of UNIFAC coefficients based on a functional group analysis. The input to the calculation was randomly sampled to demonstrate how uncertainties in the input data were reflected in the results of the computation. The model successfully reproduced parametric studies carried out at ORNL, allowing explanation of changes in solubility observed with variations in pH (see the solid line in Figure 1). The main drawback to the chemical thermodynamic approach (or any phenomenological treatment), however, is that the system must be understood in sufficient detail to ensure that the assumptions of the model are valid. This may be problematic in a system comprising on the order of a thousand components, many of which are present in concentrations that are not well known, or that contain moieties for which the activity coefficient database is weak (such as sulfur-containing chemicals).

In addition to the thermodynamic modeling, a prediction of solubility based on a statistical correlation was developed using a partial least squares analysis (PLS) of the data. In this method, matrices of dependent and independent variables were prepared. Model development involved a stepwise breakdown of both matrices in terms of scores, loading, weight matrices, and regression parameters—to give an alternative description of the data in terms of a set of orthogonal eigenvectors. Predictions were based on the eigenvectors and regression parameters. Plots of scores allowed assessment of the goodness of fit (regression between predictor and response variables) and correlations between predictor variables or responses. The model was applied to the characterization data taken at ORNL [15]. Predictions for solubility as a function of pH are presented in the Figure 1 as the dashed straight line and show an increase in solubility with increasing pH. Although this model did not reproduce the “s”-shaped curve seen in the thermodynamic model, the analysis was performed without any assumptions concerning the chemistry of the water or the oil.

The advantage of the PLS model is that field data can be easily incorporated into the model. For this reason, it is the favored approach for implementation outside the laboratory. The validity of a statistical model depends on a wide breadth of data, which sample as many variables as possible over as great a range as can be obtained. When the input data set was modified to incorporate the degree of dissociation of the organic acid, the expected pseudo-titration curve was generated that more accurately reproduced the data collected in the laboratory (Figure 2).

The statistical model can include data on produced water collected over the globe: offshore and nearshore in the Gulf of Mexico, the North Sea, and elsewhere. The incorporation of a multitude of sources is possible because many of the production variables (temperature, pH, additives, age of the well, and addition of the production chemicals) are similar across the world.
Use of Ionic Liquids in Produced Water Remediation

There are a variety of methods for removal of trace amounts of hydrocarbon from an aqueous phase. However, physical methods (i.e., filtration) are subject to fouling while chemical methods (i.e., acidification) can be defeated by the chemistry of the oil [16]. The effectiveness of a new class of solvents, (i.e., ionic liquids) was tested in the uptake of typical water-soluble organics from aqueous brines. These 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 [17]. Their chemical and physical properties, such as solvent behavior and hydrophobicity, can be optimized by the choice of the anion and cation [18]. Although expensive to synthesize, ionic liquids may be recycled and used again in a cost effective process. In addition to waste remediation, applications of ionic liquids to oil production have been explored, such as in the extraction of hydrocarbons from oil shales [19].

In addition to remediation, it would be desirable to have on-line sampling of water-soluble organics in produced water so that any 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 organics. Thus, a sensitive method of analysis is required for on-line monitoring. One such technique may be provided by uptake on a quartz crystal microbalance [20]. 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. Ionic liquids have the advantage of high viscosities, which allow them to form a stable film on the quartz crystal microbalance [21].

ORNL 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.

Several ionic liquids were selected for investigation. The: 1-butyl-3-methylimidazolium bistrifluoromethanesulfonylimide (C₄mim NTf₂), 1-hexyl-3-methyl-imidazolium NTf₂ (C₆mim NTf₂), 1-octyl-3-methylimidazolium NTf₂ (C₈mim NTf₂), and C₄mim PF₆, were synthesized at ORNL [22]. Trihexyltetradecylphosphonium NTf₂ and 1-butyl-1-methyl-pyrrolidinium NTf₂ were purchased from Merck. Trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecylphosphonium methanesulfonate were synthesized by Rex Ren (Wesleyan University, Connecticut). The affinity to water was determined for most of these ionic liquids; 1 mL of ionic liquid and 10 mL of deionized 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 deionized 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.

Contact experiments were performed with 20 to 1000 µL of ionic liquid and 1 to 2 mL of aqueous solution shaken together in a small vial. Aqueous solutions of representative organics included 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 ± 2°C, 37°C, 75°C); in salinity (distilled-deionized water, 0.2 M NaCl, 1.8 M 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 g·L⁻¹). The sulfonate ionic liquids were extremely viscous and were diluted with 1-nonanol (1:1 by volume) to permit handling in the laboratory.
The two-phase systems were prepared, shaken for 2 minutes, centrifuged, and then allowed to come to equilibrium over several days. The aqueous phases were analyzed on a Waters high-performance liquid chromatograph (HPLC; refractive index detector 2410, autosampler 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 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 with these for controls, consisting of similarly treated aqueous solutions without addition of ionic liquid.

The measured distribution coefficients (i.e., the concentration ratio of organic in the ionic liquid to that in the aqueous phase) covered a wide range (see Table 1). The organics that were best extracted were toluene and 1-nonanol. The removal of other organics, such as cyclohexanone, showed a large variation in fraction removed from the aqueous phase. 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 (C₄mim N₂Tf) than the nonprotonated 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.

In these experiments, the salinity of the brine did not appear to change the solubility of the organic in C₄mim NTf₂ nor did the ionic liquid affect the salinity of the brine (as determined via chloride ion measurements of the aqueous phase). As a result, significant ion exchange was not observed. Similar results have been reported elsewhere in contacts with solutions of chlorophenols [23]. However, recent results 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 strength (I. Toh, private communication, July 2004).

Regeneration studies were performed on a series of three replicate samples of 100 µL C₄mim PF₆ in contact with 2 mL of an aqueous solution of hexanoic acid, toluene and 1-nonanol (all 1 g·L⁻¹) that were subjected to a number of washing steps: deionized water, pH 10, pH 10, pH 2, pH 10, pH 10. At each step, the rinse solutions were analyzed for the three organics of interest until the rinse concentrations were negligible. One of the samples of ionic liquid was then heated to 120°C to evaporate 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 with C₄mim NTf₂.

The results of the regeneration experiments on C₄mim PF₆ (Figure 3) show 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 effective at all for toluene. Heating of the C₄mim PF₆ above 100°C to remove the toluene was not successful, as it induced decomposition of the C₄mim PF₆, as seen by nuclear magnetic resonance (NMR). After heating at 120°C for several hours, the response to toluene and 1-nonanol returned for C₄mim NTf₂. However, the response to hexanoic acid did not return. This finding was confirmed by NMR studies on the regenerated ionic liquid, which showed small peaks from impurities in the spectra.

Octanol-water coefficients [24, 25], 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 [23, 26]. 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 nonreactive and weakly basic. Activity coefficients at infinite dilution have been measured for toluene and other hydrocarbons compounds in C₄mim NTf₂, C₆mim NTf₂, and C₄mim PF₆ [25, 27, 28]. These values are dependent not only on the ionic liquid but also on physical conditions such as temperature. Chemical interactions such as acid-
base phenomena [29], and the interactions between charged and noncharged molecules in both the aqueous and ionic liquid phases must be considered in understanding the behavior of multiphase systems involving ionic liquids [30].

Results of the project to date showed that ionic liquids will be very effective in the selective 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 pollutant [31] in produced water.

Summary and Future Focus
The goal of recent investigations at ORNL into produced water chemistry was to characterize and quantify organic content in produced water and to develop new methods for analysis and remediation. In many ways the efforts were successful, and progress has been gained towards understanding the behavior of these systems and how they might respond to new chemical treatments, such as extraction with ionic liquids. However, the step from laboratory experience to practical application is a large one and merits consideration of the following issues.

(i) Complexity. The systems investigated in the laboratory and the associated models necessarily include simplifications. In some circumstances these may be justified, as in the assumption that a large fraction of water-soluble organics are in the form of acetic acid. However, when developing new remediation technologies, it is necessary to test a new system with actual chemical systems. In the case of the work performed here, this means testing the model predictions against actual produced water data, or evaluating ionic liquid extraction with samples of actual produced water.

(ii) Chemical factors. Chemical interferences may change the effectiveness of the extraction method by changing the chemical environment of the solute/solvent relationship. Chemical stability is another aspect that should be examined when considering new solvents—as exemplified by the slow reaction between C₄mim PF₆ and H₂O-liberating HF [18].

(iii) Physical factors. The solubility of extractants, such as ionic liquids, may be one of the most difficult aspects to handle when these solvents are applied to industrial applications. Although many ionic liquids are termed hydrophobic and do indeed form a separate liquid phase with water, their solubility is not negligible. When dealing with industrial-scale implementation, this can give rise to significant losses and expense. This aspect requires additional attention before ionic liquids can be used in environmental or processing applications.

(iv) Toxicity. Toxicological research would benefit industry and regulators concerned about organic contamination. Much of the “oil and grease” measured by EPA methods is not paraffinic hydrocarbons. Instead, a large component is the nontoxic acetic acid. On the other hand, the environment may be harmed if remediation methods are implemented that add surfactants or solvents of unknown toxicity, to the system, even in small amounts. Hence, toxicological studies, as well as solubility studies, must be done along with measurements of chemical affinity.

Although much of the recent work described here focuses on organic contamination, the issue for onshore petroleum production is total dissolved solids or soluble sodium, calcium, and magnesium salts. Some of the methods discussed here should be directly applicable to onshore problems, as long as the assumptions underlying the methods and models do not change. But, other factors must be considered, such as incorporating expressions for pressure into the thermodynamic models, particularly if gas separations (CH₄, CO₂, and H₂S) are of interest. Data used in statistical models will likely be more limited, coming from a certain location or basin rather than worldwide. These are some of the issues concerning produced water analysis and remediation that will be addressed in future work at ORNL and elsewhere.
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<tr>
<th>Organic</th>
<th>$K_{ow}$</th>
<th>$K_{IL/W}$ Range</th>
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<tbody>
<tr>
<td>Toluene</td>
<td>2.73$^a$</td>
<td>13–200</td>
</tr>
<tr>
<td>1-Nonanol</td>
<td>3.77$^b$</td>
<td>5–410</td>
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<tr>
<td>Acetic acid</td>
<td>-0.17$^a$</td>
<td>Not extracted–6</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>1.92$^a$</td>
<td>Not extracted–25</td>
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<tr>
<td>Cyclohexanone</td>
<td>0.81$^a$</td>
<td>3–15</td>
</tr>
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$^a$Hansch et al. (Ref. 24).
$^b$Tewari et al. (Ref. 25).
Figure 1: Comparison of models with total extractable material (TEM) data from contact experiments of simulated produced water brine with actual crude oil.
Figure 2: Results of partial-least-squares analysis showing the leading independent factor (best aligned with concentration) versus the leading dependent factor (best aligned with pH).
Figure 3: Fraction of organic remaining in the C₄mim PF₆ after several sequential treatments, left to right. The initial amount of organic transferred into the ionic liquid from the aqueous phase was normalized to one.
References


5. U.S. Environmental Protection Agency 1999. Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-Polar Material) by Extraction and Gravimetry, EPA-821-R-98-002.


