MODELING OF WATER SOLUBLE ORGANIC CONTENT IN PRODUCED WATER

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INTRODUCTION

Produced water remediation to National Pollution Discharge Elimination System (NPDES) target levels can represent a significant cost for oil production in the Gulf of Mexico. Off-shore analysis and remediation of produced water is expensive, and the relatively high polar content of Gulf of Mexico crude oil also means a higher solubility of organic components in the aqueous phase. In addition, neither are the identities of the water-soluble components well known, nor are their concentrations in the produced water brines. These concentrations will be affected by physical variables such as pH and temperature, but also by the depth of the formation and the age of the well. The objective of this project was to address part of the gap in the knowledge base, building upon earlier work of the characterization of simulated produced water contacted with actual crude oil samples undertaken at ORNL, through the modeling of the produced water/crude oil system using chemical thermodynamics. Because of the focus on semi-volatile components, the chemical system was modeled as a liquid-liquid equilibrium with activity coefficients based on a UNIFAC functional group analysis. A random sampling method was introduced to allow uncertainties in the input data to be reflected in the results of the computation. The model has successfully reproduced parametric studies carried out at Oak Ridge National Laboratory, allowing explanation of changes in solubility observed with variations in pH and temperature.

DISCUSSION OF ACTIVITIES

BACKGROUND

Soluble organics in produced water and refinery effluents are treatment problems for the petroleum industry. Production facilities and refineries have to meet regulatory discharge requirements for dissolved organics. This is expected to become more difficult as environmental regulations become stricter and production from deep-water operations increases. Deep-water crude oil has a large polar constituent, which increases the amount of dissolved hydrocarbons in produced water and refinery effluents. Published work focused on North Sea crude oil suggests that the high polar content is mainly comprised of short-chain organic acids (Røe Utivk 1999). The oxidized organic material is formed from the redox-controlled decomposition of source rock or of organic precursors in the petroleum (Borgund and Barth 1994). Although the chemistry of formation water has been carefully studied (e.g., Barth and Riis 1991, Helgeson et al. 1993, Barth et al. 1996), further questions remain concerning the identity, chemistry, and toxicity of water-soluble organics in produced water after borehole separation, particularly for crude oil from the Gulf of Mexico. For instance, the concentration of carboxylic acids appears to be related to the

air exposure and age of the oil, as the acids can arise from biological breakdown of hydrocarbons in the separator (Barth 1987). There appears to be no direct correlation; however, between oxygen content and organic acid concentration (Borglund and Barth 1994) or pressure, temperature, or depth (Barth and Riis 1991). Hence, several petroleum companies, including Shell, ChevronTexaco, Phillips, and Statoil, developed a collaborative Petroleum and Environmental Research Forum (PERF) project to characterize and evaluate water solubles from Gulf of Mexico crude oil, to better understand the production of these contaminants.

Quantitative characterization data are needed as the first step in understanding the dissolution of water-soluble organic (WSO) compounds in produced water. Hence, between 1999 and 2002, Oak Ridge National Laboratory (ORNL) completed a study of the characterization of crude oils and water-soluble compounds in produced water under a variety of experimental conditions (Bostick et al. 2002, McFarlane et al. 2002). Industrial partners provided ORNL with two separate samples of crude oil from Gulf of Mexico deep-water wells. The oil samples had been stripped of their volatile components and little produced water was directly associated with the samples. Because of this, the study focused on the solubility behavior of semi-volatile organic compounds in simulated brine solutions, which were prepared to contain the principal inorganic components normally found in Gulf of Mexico seawater. Contact experiments between the crude oil and the brine were carried out under equilibrium conditions, to study the effects of brine pH, salinity, temperature, pressure and crude oil source on the transfer of organic compounds from the hydrocarbon to the aqueous phase. Of the six variables tested, the factor that most controlled the total WSO in produced water was that of aqueous phase pH. Trends in temperature were also observed. The overall concentrations of water-soluble organics derived from two different samples of crude oil were not substantially different; however, the water-soluble organics were almost exclusively polar from one of the crude oil samples, and were split between aromatic and polar from the other crude oil sample. The effects of water cut, pressure, and salinity on organic solubility were found to be very slight or not significant within the uncertainties of the experimental measurements. Hence, the modeling effort focused on deriving an explanation for the effect of pH and temperature on organic solubility rather than on the effect of these other physical variables.

CURRENT STATUS

The objective of the project is to develop a model of crude-oil derived organic solubility in produced water, ultimately to be used as a predictive tool. Aqueous-hydrocarbon systems can be modeled in a variety of ways. The option of using an empirical approach was considered, but ultimately it was decided that a model based on equilibrium thermodynamics was the most appropriate to the task. The advantage of a thermodynamic equilibrium model is that physical variables, such as temperature and salinity, can be

incorporated into the expressions for the activity coefficients (Huron and Vidal 1979). Volatile components and the dependence of solubility on pressure can be introduced with an additional gaseous phase, described by an equation of state. This approach has been successfully implemented to describe hydrocarbon-aqueous systems representative of those found in crude oil production, with solubility predicted by non-random two liquid (NRTL) activity coefficients in the aqueous and hydrocarbon phases (Pedersen et al. 1996).

The main difficulty of formulating the thermodynamic model is in the selection of which components will represent the system, comprising over 1000 different components. It was hoped that the compositional characterization of the crude oil would allow derivation of lumped parameter properties for different classes and sizes of soluble compounds; however, this approach was precluded by the large uncertainties in the data. In the current study, an activity coefficient model was used for both the hydrocarbon and aqueous phases, based on the UNIFAC group contribution formulation (e.g., Fredenslund and Sørensen 1993). In particular, UNIFAC parameters for liquid-liquid equilibrium were used in the model (Magnussen et al. 1981). Such an approach is often used to model aqueous and non-aqueous solubilities of environmentally important chemicals, for instance alkanes, alkyl benzenes, polyaromatic hydrocarbons and phenols (e.g., Kan and Tomson 1996). Limitations of the model have been documented in regards to systems involving solids (Gracin et al. 2002) and some interaction parameters are not available for selected functional groups, particularly for liquid-liquid equilibrium (Hansen et al. 1991). Hence, it is important to compare calculations to experimental measurements to validate the model.

Because the concentrations of the components were not individually determined, representative molecules were selected for the computational analysis, in particular hydrocarbons of various sizes, cyclohexane (a representative napthene or cyclic saturated hydrocarbon), aromatic compounds, organic acids, a ketone (acetophenone), and because these crudes contain 1–2% sulfur, a thiophene. These compounds were selected based on published descriptions of the composition of crude oil (Speight 1991, British Petroleum 2003). Large non-soluble compounds such as asphaltenes and resins were not included in the model, as they were assumed to have little impact on the solubility of other organic compounds. The quantities of each compound were also estimated, based on the results of the analyses of crude oil done at ORNL. The experimental uncertainties were used to derive distributions in feedstock concentrations, which were randomly sampled to provide input into the thermodynamic calculation. The thermodynamic model was run 100 times for each set of physical conditions, to give an output distribution in water-soluble organic concentration in produced water. The water-hydrocarbon ratios determined by the calculation were compared to the experimental results using a Welch 2 sample t-test, an analysis that gave the probability that the means of the two populations were the same. This statistical

test was required to assess the validity of the calculation. If agreement was good, then the compounds included in the calculation could include, or be similar in functionality to, the compounds that were actually present in the produced water.

The stochastic thermodynamic calculations were programmed in Maple 7 and were run on a personal computer. Besides the crude oil composition, inputs to the calculation included pressure, temperature, and brine. Salinity was incorporated as ionic strength in a Debye-Hückel correlation. Results of the calculation are presented in the table below, showing representative compounds and mean output water-hydrocarbon ratios and standard deviations. It was found that, with the exception of the phenols, the concentration of the compound in the crude oil had little effect on the distribution ratio between the oil and the brine. The distribution coefficients for selected hydrocarbons and aromatic compounds agreed very well with those measured in the experiment, with the probability for a particular component derived from the t-test shown in the table. A comparison was not done for the longer chain aliphatic compounds because the amounts measured in the produced water were so low. The calculated distribution coefficients for the polar components were very diverse, ranging from being fairly insoluble (dibenzothiophene) to miscible (formic acid), and so did not lend themselves to an overall comparison as done with the aliphatic and aromatic hydrocarbons. A cyclic aliphatic acid; however, was found to best match the measured distribution coefficient for the polar water-soluble fraction.

Results of Liquid-Liquid Equilibrium Calculations

Compound	Calculated water/hydrocarbon distribution coefficient pH7, 300 K, 1 bar, 65000 mg·L^{-1} Cl^-	Produced water analysis, Welch 2-sample t test probability	pKa values at 298K (Smith and March 2001, IUPAC 1979)
*n*hexane	5×10^{-5}		51
cyclohexane	8×10^{-5}		46
*n*octane	5×10^{-6}	Aliphatic C_6–C_{10} 4×10^{-6}, P = 0.59	51
*n*decane	4×10^{-7}		51
*n*eicosane	3×10^{-12}		51
$C_{28}H_{58}$	2×10^{-16}		51
benzene	3×10^{-4}		43
toluene	8×10^{-5}		43
napthalene	8×10^{-6}		43
methylnapthalene	2×10^{-6}	Aromatic 7×10^{-6}, P = 0.72	40
phenanthrene	2×10^{-7}		43
methanol	2		15.2
phenol	0.2		9.994
omethylphenol	0.03		10.02
formic acid	1×10^{4}		3.751

acetic acid	90		4.756
propanoic acid	20		4.874
nbutanoic acid	7		4.81
benzoic acid	5		4.205
naphthalene acetic acid	0.04		4.23
napthenic acid $(C_{13}H_{21})COOH$	2×10^{-4}	Polar 1×10^{-4}, P = 0.59	5
acetophenone	2×10^{-4}		19.2
dibenzothiophene	2×0^{-5}		43

The model was successfully used to fit the pH-dependence data that were generated in a crude-oil/simulated brine system, presented in Fig. 1. This model incorporated the acidity of the polar components (Khan et al. 1995). As can be seen in Fig. 1, the methylene-chloride extractable material (particularly in the C_{10}–C_{20} range) became more soluble as the brine became basic, pH > 7, as shown by the apparent inflection point in the data at ~pH7. This corresponded to the behavior calculated for naphthalene acetic acid. The pH behavior for the second crude oil sample, with monotonically increasing solubility as a function of pH, was more typical of the combination of naphthalene acetic acid and a cyclic carboxylic acid (or napthenic acid). Highly water-soluble acids, such as acetic acid, give a distribution coefficient between the organic and aqueous phases of one very close to their pKa values. Even though the degree of dissociation increases dramatically for less soluble acids at pH = pKa, the solubility doesn't trace the titration curve, because much of the acid remains in the organic phase even at higher pH values. Bases, such as quinoline, are present in their dissociated form at low pH, and hence exhibit the opposite trend in solubility behavior to that of an acid (Standal et al. 1999). It is probable that such weak bases were present in the crude oil samples, and would have transferred to the produced water simulant. They were not observed in the GC-MS analysis; however, a not unexpected result as nitrogen-containing species are expected to be present in much lower concentration that sulfur and oxygen containing species in the crude oil (Speight 1991), the latter dominating overall solubility behavior.

Testing of the model over a range of temperatures indicated that the solubility of many hydrocarbons did not change much over the temperature range of 300 to 350 K. For instance, no change in solubility was predicted for the short chain fatty acids, such as acetic acid, being already highly soluble in the aqueous phase at pH7. A slight increase in solubility was predicted for the bulky carboxylic acids, acetophenone and dibenzothiophene, Fig. 2, in agreement with characterization of the simulated produced water. Temperature effects have been measured (Cai et al. 2001) and predicted (Kojima and Ogawa 2001) for organic acids in aqueous systems, but these can be mainly attributed to dimerization equilibria which occur at higher concentrations than observed in produced water. At temperatures above

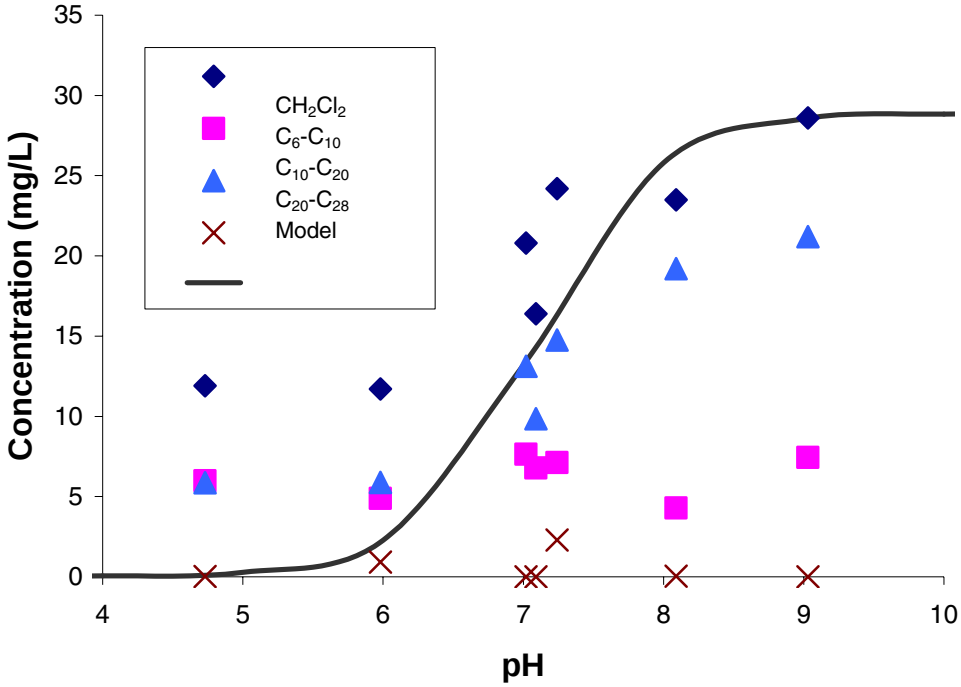

Fig. 1. Plot of water-soluble organic concentration for different carbon sizes as a function of pH. Superimposed on the plot are results of liquid-liquid equilibrium calculations for naphthalene acetic acid, salinity = 65,000 mg·L^{-1}.

320K, breakdown of organic acids via decarboxylation is a competing mechanism (Borglund and Barth 1994).

Equilibrium calculations on the hydrocarbon-brine system were run with salinity ranging from 40 to 115 g·L^{-1}, with results showing little apparent effect on solubility, in agreement with the experimental data. There was no evidence for the "salting" effect observed by Bennet and Larter (1997) for the substituted cresols that exhibited a greater partitioning into the hydrocarbon phase as the ionic strength of the aqueous phase increased. The phenomenon has been described as arising from the neutralization of charge about the molecule, increasing its absorption into the hydrocarbon layer. It is possible that many of the polar molecules in the produced water studied here behaved more like phenol than cresol, which demonstrated only a slight dependence on salinity in Bennet and Larter's studies. Khan and co-workers (1995) found that an increase in salinity caused an increase in the activity coefficient of the undissociated 2-oxopropanoic (pyruvic) acid in aqueous solution, yielding a decrease in solubility. However, the effect was not demonstrated with the shorter chain organic acids, which dissociate in aqueous solution.

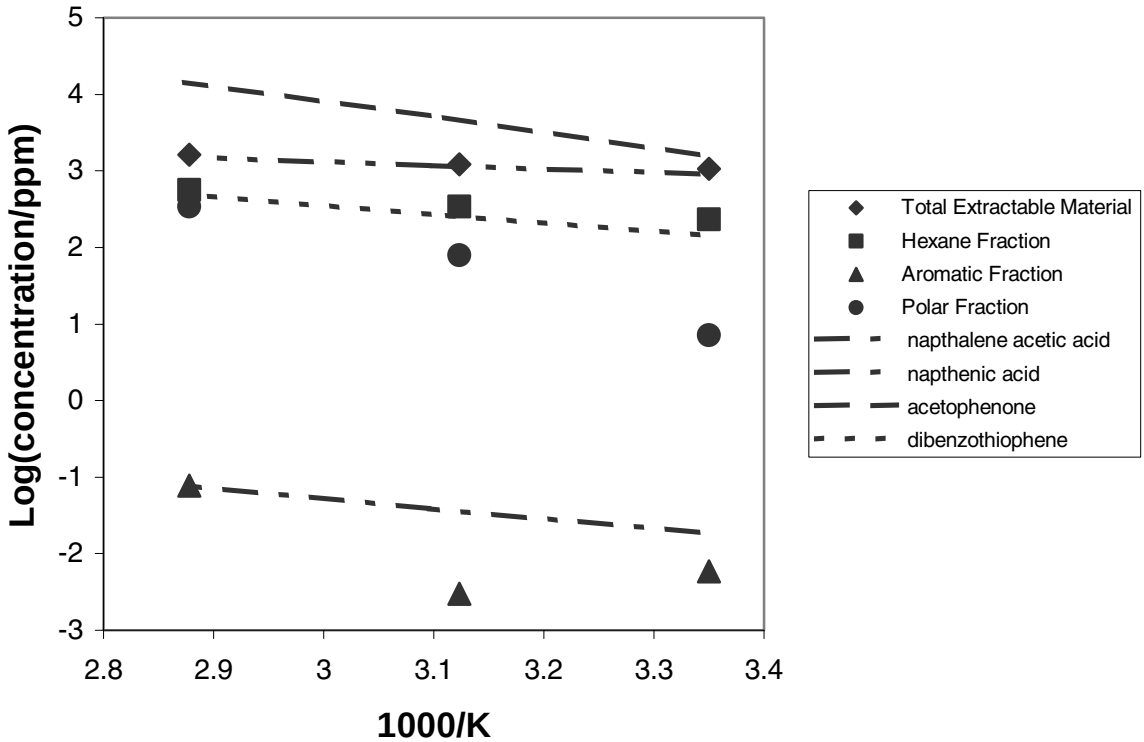

Fig. 2. Plot of water-soluble organic concentration as a function of inverse temperature for water contacted with crude #1. Superimposed on the plot are calculated concentrations of selected polar hydrocarbon compounds under reference conditions, and initial concentrations of 0.05 g·L^{-1} for each of the acids, 5.5 g·L^{-1} for acetophenone, and 29 g·L^{-1} for benzothiophene to make up the requisite polar fraction in the oil.

FUTURE PROGRESS

Future study will investigate cross-correlations between the variables that control solubility, such as water-soluble polar content, sulfur in the crude, and depth or location of formation, temperature and pH or carbonate concentration (Barth and Riis 1991) in the produced water. In addition, actual produced water may contain a colloidal precipitate after bulk separation from the crude oil. Under such conditions, the partitioning of molecules between the organic and aqueous phases will be affected by the droplet size and carbon chain length (Lang et al. 1992). Modeling such an effect will require consideration of mass transfer and the thermodynamic properties of the disperse phase (Gracin et al. 2002), and will be considered along with other variables related to the physical state of the oil during production and separation from the produced water.

Being able to fit laboratory data is the first step in demonstrating our ability to understand solubility of contaminants in produced water. It is expected that this knowledge will lead to the development of a predictive model for use in the design of new oil production facilities. The prediction of the effect of

changing production conditions on water soluble organic content will assist the petroleum industry to target produced water cleanup to best protect the environment.

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