MODELING OF WATER SOLUBLE ORGANIC CONTENT IN PRODUCED WATER

J. McFarlane

Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37830-6181

INTRODUCTION

Off-shore 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 $mg \cdot L^{-1}$ and average of 29 $mg \cdot L^{-1}$ [1]. Although the solubility of most individual oil and grease compounds is lower than these levels, the analytical tests mandated by the United States Environmental Protection Agency (US EPA) for the measurement of total petroleum hydrocarbons also sample more soluble compounds such as carboxylic acids[2], which can augment the apparent total petroleum hydrocarbon (TPH) 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 $mg \cdot L^{-1}$ [3].

Effective remediation of produced water off-shore requires 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 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 would 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 US Department of Energy (DOE) to initiate work at Oak Ridge National Laboratory (ORNL) in produced water research.

The primary focus of 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. A brief summary of some of that work is given here.

DISCUSSION OF CURRENT ACTIVITIES

INTERNATIONAL DATA SETS ON PRODUCED WATER COMPOSITION

One task completed this year was a review of the literature on produced water with a particular focus on results from offshore wells.

Much of the information in the open literature on organics in produced water has been published for North Sea oil wells, because of increased environmental regulation. Results have been summarized in a review article by Utvik and Hasle (2002)[4]. Analyses from several studies of Norwegian produced water from 1995 onward show the predominant classes of water-soluble organic compounds to be dispersed oil, BTEX (benzene, toluene, ethylbenzene and xylene), NPD (napthalene, phenanthrene, dibenzothiophene, and C1-C3 substituted homologues), and PAH (polyaromatic hydrocarbons), organic acids, phenol and substituted phenols.

Older data come from Barth[5], who measured the concentrations of organic acids in formation and produced waters from wells on the Norwegian continental shelf using istachophoresis – a technique based on ionic mobility. The organic acids accounted for 70-100% of the water soluble organics in the water samples and acetic acid was the most predominant acid present. In addition, Barth noted that the composition of the produced water (after separation) was more complex than that of the formation water. This suggested to her that the formation water had been subject to bacterial action, or oxidation of organics, in the separation process.

The group of Brendehaug et al.[6] characterized water soluble organics in terms of broad chemical classifications: aliphatic, aromatic and polar, as well as performing a detailed analysis to identify compounds of toxicological importance. This group found that the dissolved hydrocarbons were dominated by the volatile components, such as benzene and its derivatives, rather than the oxidized hydrocarbons. Production chemicals, such as corrosion and scale inhibitors, flocculants, etc. were found to have an effect on organic concentrations.

Brown and co-workers[7] have provided information on water from Gulf of Mexico wells, in particular with and without treatment with silica gel. Their results show that the water soluble fraction is 79 to 98% polar in nature, predominantly organic acids, which are effectively extracted by silica get treatment. The group also analyzed for polyaromatic hydrocarbons, which they found at the extremely low levels of 10 to 30 ppb by weight.

Neff et al. published a detailed analysis of produced water from wells on the Louisiana shelf, in shallow water[8]. In comparison with deep water wells, the organic contamination was found to be very high, perhaps arising from a comparatively high level of biological activity.

A survey of produced water from international data was prepared by Tibbetts et al.[9], showing that organics in North Sea produced water are similar to world-wide averages.

However, the ranges of concentrations are very broad, some varying over 2 or 3 orders in magnitude. This paper also identified many of the chemicals that are added during the oil-water separation process, which can affect measurements of organic loading.

The produced water data sets mentioned above show a great degree of variation, but a few trends are apparent.

- Unless contamination of the reservoir occurs, the paraffinic oil and grease load in produced water is very low, within NPDES permits for offshore oil and grease. Entrained droplets can contribute up to 40 ppm to the measured TPH, and cannot be removed by gravity because of their small size, <20 μm^3.
- Oxidized organics are more soluble than aliphatic hydrocarbons, and their concentrations are difficult to predict from knowledge of the geochemistry of formation waters, because oxidation often occurs during separation and treatment. These organics, however, represent a large fraction of the total extractable material (TEM) sampled using EPA methods. Organic acids, which have a relatively high prevalence in all produced water fractions, can have concentrations as high as 1000 ppm.
- Other heteronuclear organics are not particularly prevalent in the water soluble fraction, unless introduced to enhance production, e.g., amines.
- Volatile aromatic compounds can represent a significant fraction of the water soluble organic material, depending on the source of the oil and the degree to which the oil and the water has been outgassed before sampling. The concentrations of volatile aromatic compounds will be difficult to predict with models based strictly on thermodynamic equilibrium calculations. Non-volatile polyaromatic hydrocarbons are much less soluble, and these are present in ppb amounts in the water.
- There are few data on some organic compounds that may be relatively soluble in produced water, such as: ketones, aldehydes, mixed heteronuclear organics, mercaptans, and thiols.

WATER CHARACTERIZATION AT ORNL

Because more information was needed on Gulf of Mexico wells, the characterization of simulated produced water at ORNL was carried out in previous years using standard US EPA analytical methods[10] with the objective to classify 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 were carried out to measure the effect of varying physical and chemical conditions on solubility and to derive data for model development.

Contact experiments were carried out with actual crude oil samples, with densities of about 0.85 $g \cdot cm^{-3}$. The aqueous phase; however, was prepared in the laboratory to approximate seawater composition. Most contacts were carried out under stirring for four days to ensure thermodynamic equilibrium. The oil, and after contact, the aqueous

phase, were analyzed by inductively coupled plasma analysis 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[11].

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, or water-to-oil ratio. Because the analyses for the second crude oil sample were done primarily as a comparison to the more detailed study of the first sample, few replicate tests were performed, and the resulting uncertainty was high, ±60%.

MODELS FOR ORGANIC UPTAKE

Results from the ORNL produced-water characterization studies were intended to support the development of a predictive model for produced water contamination with organic compounds. Last year, 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 non-miscible 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 data base 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 below. 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 contain moieties for which the activity coefficient database is weak (such as sulfur-containing chemicals).

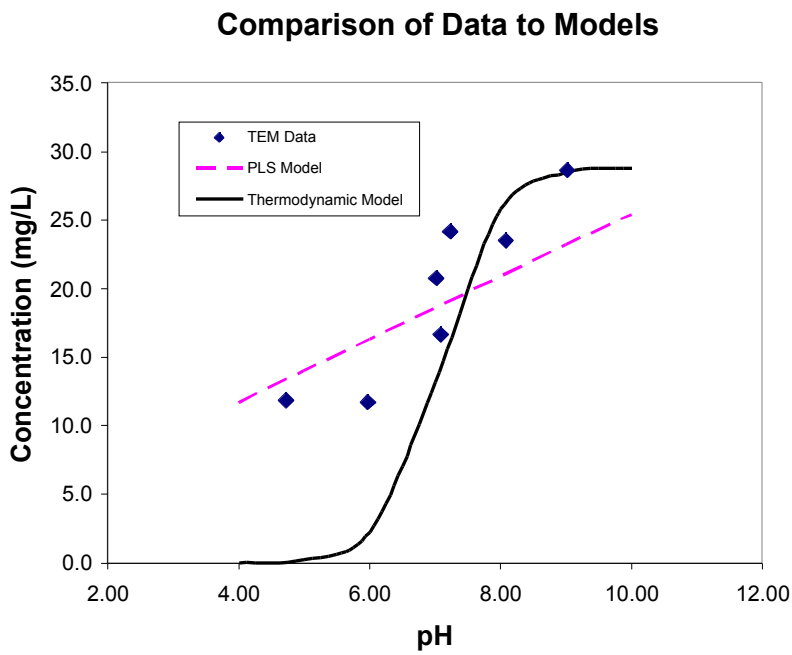

Figure 1: Graph showing comparison of models to total extractable material (TEM) data from contact experiments of simulated produced water brine with actual crude oil.

In addition to the thermodynamic modeling, prediction of solubility was based on a correlation 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, loadings, and weights 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 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, and 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 over as great a range as possible. If the input data set is modified to incorporate the degree of dissociation of the organic acid, Figure 2, the expected pseudo-titration curve can be generated that more accurately reproduces the data collected in the laboratory.

The statistical model will benefit from the results of work on produced water collected over the globe: offshore and near shore 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 well, addition of production chemicals) are similar across the world.

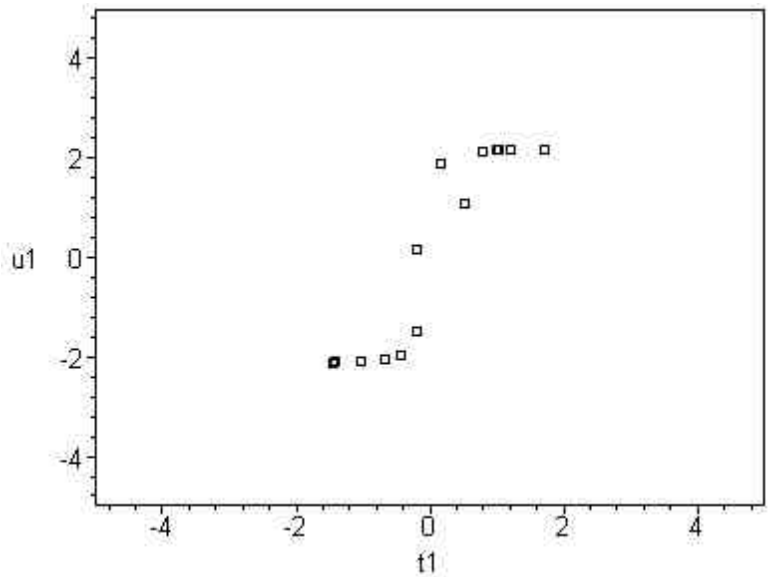

Figure 2: Results of partial least squares analysis showing the leading independent factor (best aligned with concentration) versus the leading dependent factor (best aligned with pH).

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