

OFFSHORE VERSUS ONSHORE PRODUCED WATER CHARACTERIZATION AND MODELS

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ABSTRACT

Organic contamination of produced water is of direct environmental concern. Offshore discharge is regulated by the Environmental Protection Agency through National Pollution Discharge Elimination System permits. Onshore, remediation issues are centered about total dissolved solids (or salinity); however, organics must be removed in pretreatment before desalinization of produced water for beneficial end use. Oak Ridge National Laboratory, with support of the US Department of Energy and the Petroleum Energy Research Forum, has embarked on a program to characterize produced water contaminants and to model the solubilities of these contaminants as a function of such variables as pH, temperature, and salinity. Although these efforts have primarily been directed toward offshore remediation, it is recognized that there may be parallels in the concerns of onshore producers. These issues are explored in this paper, with a particular focus on organic contaminants in produced water.

BACKGROUND

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 $42 \text{ mg}\cdot\text{L}^{-1}$ and average of $29 \text{ mg}\cdot\text{L}^{-1}$. 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 acids², 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 $40 \text{ mg}\cdot\text{L}^{-1}$ 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. In addition, this paper addresses the similarities and differences between soluble organics in produced water offshore and onshore, and how research in either area can complement the other.

ORGANICS IN PRODUCED WATER

Offshore

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 were summarized in a review article by Utvik and Hasle (2002)⁴. Tables 1 through 7 present data pertinent to the discussion here. The first table represents a compilation of analyses from several studies of Norwegian produced water from 1995 onward. The predominant classes of water-soluble organic compounds are shown in the graph: dispersed oil, BTEX (benzene, toluene, ethylbenzene and xylene), NPD

(naphthalene, phenanthrene, dibenzothiophene, and C1-C3 substituted homologues), and PAH (polyaromatic hydrocarbons), organic acids, phenol and substituted phenols.

Table 2 presents older data from Barth⁵, who measured the concentrations of organic acids in formation (slight grey shading) and produced waters from wells on the Norwegian continental shelf, using isotachopheresis – 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.

Another set of data from the North Sea is presented in Table 3. 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-workers⁷ have provided information on water from Gulf of Mexico wells, in particular with and without treatment with silica gel. Their results, Table 4, show that the water soluble fraction is 79 to 98% polar in nature, predominantly organic acids, which are well extracted by the silica gel 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. has published a detailed analysis of produced water from wells on the Louisiana shelf, in shallow water⁸, Table 5. In comparison with deep water wells, the organic contamination is 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, Table 6. This shows that organics in North Sea produced water are similar to world-wide averages. However, the ranges indicated in some of the concentration data are very broad, 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.

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 using standard US EPA analytical methods¹⁰ 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 $0.85 \text{ g}\cdot\text{cm}^{-3}$. 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 elsewhere¹¹.

The results of the characterization study¹², Table 7, 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 oil¹³. 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, $\pm 60\%$.

Onshore

In contrast to offshore produced water, analysis of water associated with onshore sources of petroleum tends to focus on the determination of inorganic species and total dissolved solids. However, there are examples of the measurement of organic contamination, such as from Fillo et al.¹⁴, who detected the following compounds in water from onshore production.

- Volatile organic carbon - benzene (<10 ppm on average), toluene (<10 ppm on average), ethylbenzene (<2 ppm on average),
- Semi volatile organics - C₁₀ to C₃₀ straight chain hydrocarbons (2-20 ppm), and
- Phenols, carboxylic acids and naphthalene (poly aromatic hydrocarbons were very low).

Recent data from the analysis of onshore produced water indicated that a major component of soluble organics was fatty acids, namely acetic up to hexanoic acid¹⁵. The amounts were low, however, with acetic acid having the highest concentration at about 11 ppm. The analyses for acids and other organic components pointed to direct contamination from oil seepage from a nearby well, rather than local uptake. This work highlights a general problem with environmental analysis, in that the source of the target chemicals may not be that which is being investigated.

General Comment

The examples from the literature presented here do not show some of the detailed analyses that have been published for produced water contamination, based on gas-chromatography mass spectrometry, which target priority pollutants. These have been done both for Gulf of Mexico water^{11,12} and for North Sea water¹³. Individual compounds can be identified, however, because of the large number of compounds and isomers, this type of analysis is very complicated. The concentrations of important compounds may be obscured by the signal of isomers, and often the analyses give a distorted picture of what is actually driving the chemistry of the brine/oil system.

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. Three approaches to the model were considered: an empirical model based on trends in the characterization data, a model based on thermodynamic equilibrium calculations, and a statistical model.

The simplest approach to a model is an empirical formulation, i.e., generation of parameters describing the chemical system based on the regression analysis of an input data set. The assumptions underlying such an approach are: 1) the physical variables in the data set span the range of conditions that are to be used in the model, 2) the chemical system in the training data set approximates that of the systems it is meant to represent, 3) the scatter in the data is small compared to the effect of the trends, and 4) physical effects on solubility act essentially independently of one another. In consideration of the current data set, the first and second conditions were met, but the scatter in the data precluded quantification of the trends in all areas except that of pH dependence.

Hence, the next approach selected was to model produced water composition using a chemical thermodynamic equilibrium calculation, based on the iterative solution of the Rachford-Rice equation¹⁶. 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. Non-random two liquid (NRTL) coefficients were also tested in the model, but were found to be limited in their application to multiphase systems and did not include all of the compounds present in crude oil. 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 third approach to modeling was to base predictions 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 ORNL¹⁷. Predictions for solubility as a function of pH are presented in the figure as the dashed straight line. 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.

DISCUSSION AND CONCLUSIONS

The produced water data sets given in the paper show a great degree of variation, but a few trends are apparent. These general statements appear to apply to water produced from onshore, offshore, and “near” shore sources.

- 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, $<20 \mu\text{m}^3$.
- 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 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.

A phenomenological approach to produced water modeling was performed, employing the assumption of chemical equilibrium. An advantage of the thermodynamic equilibrium approach is that it gave a physical basis for calculated solubility; and hence, would allow for extrapolation to conditions outside the original data set, unlike other

modeling approaches. The model selected for the activity coefficients was empirical; however, derived from experimental measurements. This is true even of newly formulated databases of coefficients that have been published recently^{18,19}, which are only available for liquid-vapor not liquid-liquid systems. In addition, the database is missing some information for functional group moieties present in crude oil (particularly sulfur containing groups). Yet, the main drawback to the chemical thermodynamic approach (or any phenomenological treatment) is that the system must be understood in sufficient detail to ensure that the assumptions of the model are valid.

Should the chemical system be well characterized, which at a minimum means that individual compounds and their concentrations in the oil are available; the chemical thermodynamic approach is a method for prediction supported by many fundamental studies²⁰. Although our focus to date has been on produced water associated with Gulf of Mexico deep water crude oil, the principles behind thermodynamic analysis and modeling could apply to onshore as well as offshore organic/aqueous systems. The model could also be extended to include volatile organics, which were not included in the ORNL contact experiments, but will be of particular importance to natural gas/aqueous systems.

The PLS statistical approach also provided reasonable agreement with the data, showing an increase in solubility with pH and with temperature. 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. This 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.

The modeler will have to be much more cautious about using off site data for statistical modeling of onshore produced water. Local conditions can vary widely. For instance, gas wells can range from being dry to having copious amounts of produced water. Terrestrial wells or samples are more easily subject to contamination from local sources. Smaller capacity wells are also more influenced by local changes in geology or temporal effects, such as the age of the well. Statistical analysis can be used for onshore produced water, but with a more selective sample set and with the understanding that extrapolation to other situations will not be appropriate.

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Table 1: North Sea Produced Water Contamination from Utvik and Hasle⁴

Compound	Low Concentration (mg·L ⁻¹)	High Concentration (mg·L ⁻¹)
Dispersed oil	10	40
BTEX	1	40
NPD	0.9	10
PAH	0.01	0.13
Organic Acids	55	760
Phenol	0.1	6
C ₁ -C ₄ alkylated phenols	0.17	11.3
C ₄ -C ₇ alkylated phenols	0.1	0.8

Table 3: Speciation of Organics in Produced Water from Brendehaug et al⁶.

Wells	Gulfaks A Flotation Cell	Gulfaks B Flotation Cell	Statfjord B Flotation Cell	Statfjord B Degas Tank	Statfjord B Flotationa Cell	Statfjord B Degas Tank
Main fractions	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Aliphatic	2.45	5.81	0.0254	1.65	0.316	0.888
Aromatic	1.04	3.99	1.5	1.63	1.05	2.12
Polar	6.77	15.7	72.4	31.8	27.5	65.3
Fatty acids	36.7	53.5	690	790	543	lost
Total Organic	47	79	763	825	575	lost
Aromatic	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
BTEX	582	533	168	130	145	159
Napthalenes	49.3	2160	622	942	708	845
Phenanthrenes	12.5	90	23	41.7	36.8	21-3
Dibenzothiophenes	3.17	22.7	8.16	10.8	10.2	5.07
Acenaphthene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Acenaphthylene	0.047	1.53	1.11	1.04	0.666	0.787
Fluorene	0.254	11.3	12	12	8.89	9.5
Anthracene	<0.001	<0.001	0.032	0.046	0.0341	0.0396
Fluoranthene	0.0269	0.195	0.0415	0.0892	0.0854	0.0458
Pyrene	0.0291	0.194	0.0559	0.121	0.118	0.0669
Benzo(a)anthracene	<0.001	0.0311	0.0045	0.0193	0.0151	0.012
Chrysene/triphenylene	0.329	0.3398	0.0403	0.203	0.226	0.112
Benzo(bjk)fluoranthene	<0.001		<0.001		<0.001	<0.001
Benzo(a)pyrene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Benzo(ghi)perylene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Phenols	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Phenol	0.262	0.152	4.86	2.59	2.84	2.3
C1	0.209	0.375	2.84	3.09	2.92	2.51
C2	0.0603	0.107	1.26	0.72	0.771	0.884
C3	0.054	0.725	0.634	0.253	0.322	0.603
C4	0.0117	0.237	0.0658	0.0217	0.0279	0.0805
C5	0.0124	0.0946	0.0235	0.0048	0.0081	0.0352
C6	0.006	0.0243	0.0073	<.001	0.0016	0.0127
C7	0.0026	0.0062	<.001	<.001	<.001	<.001
Total	0.618	1.72	9.69	6.69	6.89	6.43

Table 4: Data from Brown and Co-workers⁷ Showing Effectiveness of Silica Gel Treatment

	platform 1	platform 2	platform 3
	mg/L	mg/L	mg/L
Pre treatment	7.28	54.7	80.2
Post silica gel treatment	0.26	11.4	1.44
% After treatment	3.6	20.8	1.8
Hexane	0.08	5.1	0.72
Aromatic	0.04	2.94	0.32
Polar	<.01	1.04	<.01
More polar	0.08	0.32	0.28
% Fractions recovered	77	82	92

Table 5: Organic contamination in near-shore Louisiana, from Neff et al.⁸

	Eugene Island	Lake Pelto
	µg/L*	µg/L*
Total Organic Carbon	220000	298000
Saturates	28400	17100
Aromatics	2500	3300
Total hydrocarbons	30900	20400
C ₁₀ -C ₃₄	3677	606
PAH	80	142
Volatile hydrocarbons	11308	5515
Steranes	63	92
Triterpanes	76	80
Ketones	2230	1320
Phenols (C ₀ -C ₄)	2720	675
Salinity (ppt)	183	150
Metals		
Barium	37400	11500
Cadmium	0.32	0.12
Chromium	1.11	0.71
Copper	6.36	0.4
Lead	17.9	1.5
Mercury	0.06	0.07
Nickel	0.4	1.27
Silver	<.2	<.2
Zinc	1200	125

* Unless noted otherwise.

Table 6: Comparison of North Sea Produced Water Contamination to World-Wide Averages, from Tibbetts et al.⁹

	world	north sea	sea water	Murchison	Hutton	Hutton
density(kg/m3)	1014-1140	1014-1085		1020-1021	1019-1025	1019-1022
surface tension (dynes/cm)	43-78			50-58	59-73	59-73
TOC (mg/L)	0-1500	100-1000		441-869	15-552	139-522
COD (mg/L)	1220		392	441-869	127-2070	420-2070
TSS (mg/L)	1.2-1000		2.4-2.8	15-85	3-29	3-29
pH	4.3-10	6.7-7.3	7.6-8.3	7.1-8.1	6.9-8.3	6.9-8.3
Temperature (deg.C)				50-94	66-81	66-81
Total Oil (mg/L)	2-565	2.0-64		7.-75	9-220	9-220
BTX (mg/L)	.39-35	4.5-35		2.2-43	1.3-92.6	1.3-92.6
Base/ neutrals (mg/L)	<140	<140	<0.1	3.2-22	4.-96	7.1-96
Oil and Grease (ug/L)	275			24-4360	62-7530	69-7530
Chloride (mg/L)	80-200,000	12,400-81,000	20020-20820	16900-18690	163210-21035	16310-19040
Bicarbonate (mg/L)	77-3990	420-1430	134-155	500-715	260-995	565-995
Sulphate	<2-1650	18-1650	2810-2960	1295-1800	705-2895	705-1920
ammoniacal nitrogen (mg/L)	10-300	10-250		0-17	0-8.9	0-8.9
Sulphide	10			0-0.2	0-1.2	0-1.2
Total polars (mg/L)	9.7-600	25-520	0-9.6	0-21	1.-36	1.-36
Higher acids (mg/L)	<1-63	.1-53	1.2-11.9	3.7-9.5	1.7-9.3	3.1-9.3
Phenol (mg/L)	.009-23	2.-23		2.2-6.8	1.4-6.2	3.6-6.2
Volatile fatty acids (mg/L)	2.-4900	200-930		178-237	20-626	238-626

Table 7: Characterization of Simulated Produced Water from Contacts with Gulf of Mexico Crude Oil

Reference conditions	Total Extractable Material	Hexane Fraction	Aliphatic C ₆ -C ₂₈	Aromatic	Polar
25°C, 1 bar, 65 g·L ⁻¹ Cl ⁻ , pH7, 80% water	±4 mg/L	±5 mg/L	±0.02 mg/L	±0.09 mg/L	±1mg/L
Temp. (°C)					
25±1	21	11	0.0170.22	0.11	2.3
47	22	13	0	0.08	6.7
74	25	16		0.33	13
% Water					
20.00±0.01	30	14	0.051	0.24	NA
50.00	31	16	0.050	0.30	5.8
66.67	12	10	0.062	0.030	NA
Salinity (g·L⁻¹ Cl⁻)					
40 ± 4	12	5.4	0.066	0.030	4.6
114 ± 11	14	6.6	0.25	0.050	6.1
Press. (bar) @ 50°C					
1	3.9	3.5	0.016	0.17	4.1
14±2	48	24	0.10	0.31	3.4
35±2	6.1	2.7	0.015	0.024	6.2
60±2	4.1	6.0	0.071	0.090	2.1
pH crude oil#1					
4.73±0.01	12	5.8	0.040	0.07	3.1
5.98	12	5.2	0.005	0.04	5.3
8.09	24	10	0.010	0.11	28
9.03	29	10	NA	0.28	NA
pH crude oil#2	(±60%)	(±60%)	(±60%)	(±60%)	(±60%)
7.12	5.8	5.0	0.22	3.0	1.0
8.52	11	4.5	0.14	2.4	1.7
9.48	4.1	8.6	0.14	0.71	1.2

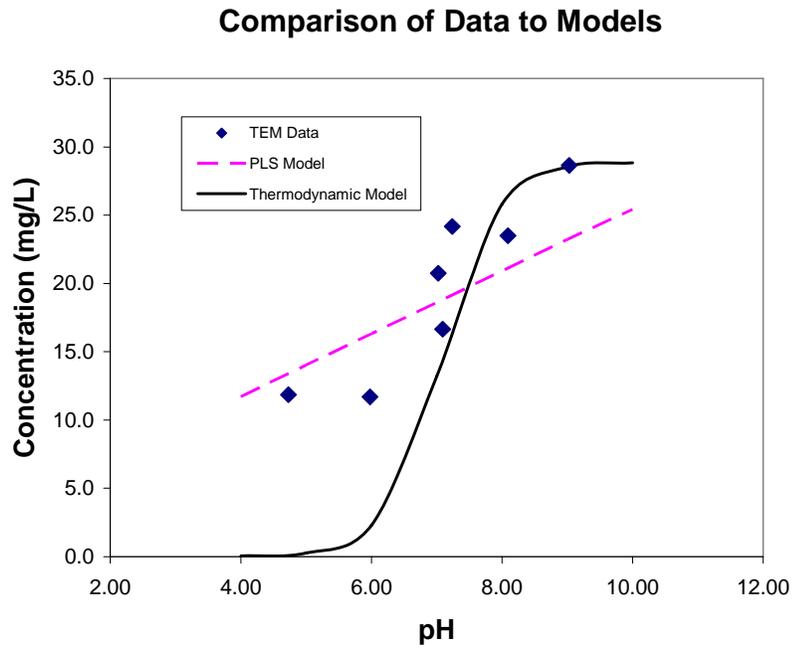


Figure 1: Graph showing comparison of models to total extractable material (TEM) data from contact experiments of simulated produced water brine with actual crude oil.

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