On correlating water solubility in ill-defined hydrocarbons

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HIGHLIGHTS

- Heavy oils + water exhibit Type IIIb pseudo binary phase behavior.
- The database used to create water solubility models do not account for this.
- Consequently, prior correlations diverge from data at high temperature.
- Two new options are presented to resolve this issue.
- Correlation of supercritical water solubility in hydrocarbons requires further study.

GRAPHICAL ABSTRACT
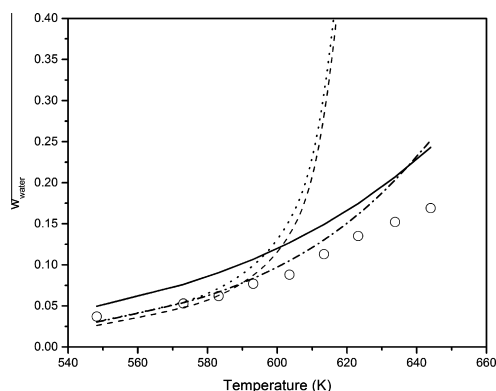
ABSTRACT

Saturated water solubility values in hydrocarbon liquids span more than four orders of magnitude and are characterized by high relative error. Development of reliable correlations is particularly challenging for ill-defined and asymmetric hydrocarbon mixtures where fluid characterization and pseudo binary phase behavior type are uncertain. In this work, predictive correlations targeting this application, below the critical temperature of water, are explored and two promising models are compared with computation methods available in the literature. The model inputs include easily measurable properties (hydrogen mass fraction, fluid density at ambient conditions) as well as K_{Watson}, mean molar mass and the average boiling point of the hydrocarbon mixture. These latter three inputs are complex and frequently difficult to define parameters encountered in refinery characterization of ill-defined organic mixtures. Models comprising one or two input variables were fit using a training data set comprising pure hydrocarbons and Athabasca bitumen. The average deviation of the models from these reference experimental data was found to be comparable to the uncertainty of the reference data in most cases. However most of the models exhibited high deviation and bias relative to the test data set comprising ill-defined hydrocarbon mixtures. Two models are shown to be robust numerically, insensitive to the uncertainty of input variables, and applicable irrespective of the pseudo binary phase behavior type with water (Type II, Type IIIa, or Type IIIb) up to their upper critical end point (UCEP). At temperatures above the UCEP, a hydrocarbon rich liquid phase only arises for Type IIIb pseudo binary mixtures. In this region, above 647 K, correlation extrapolation options beyond the range of experimental data are discussed, and only fluid-specific Henry-like constant models are proposed.

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1. Introduction

Thermodynamic data and accurate models for the properties of hydrocarbons mixtures containing water, including solubility, are

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often required to design unit operations, to develop processes for production and refining, and to perform environmental assessments. For ill-defined hydrocarbons such as Athabasca bitumen, examples include, hot water extraction processes (mined bitumen), in situ production processes such as steam assisted gravity drainage (SAGD), crude distillation towers, and refining more broadly. One important application of mixtures of water and heavy ill-defined hydrocarbons is in refining where the use of near-critical and supercritical water as a reaction medium has been proposed [1–9]. Water solubility models are essential for the design, development and optimization of such processes.

As water solubility in hydrocarbons and hydrocarbon solubility in water vary over many orders of magnitude with temperature variations from room temperature to the critical temperature of water (Tc = 647.1 K), and the values are typically small at low temperatures, solubility measurement and correlation efforts encounter numerous challenges. Typically, water solubility in hydrocarbons can be estimated to within one order of magnitude, and hydrocarbon solubility in water to within two orders of magnitude over this temperature range using general-purpose correlations. Solubility models for water + hydrocarbon mixtures fall into two categories. Some models attempt to estimate mutual solubilities, based on equations of State, activity models or correlations, while others focus on correlations for hydrocarbon solubility in water (outside the scope of this review) or on water solubility in hydrocarbons. These methods generally rely on fitting parameters to limited numbers of fluids or to specific homologous series, and calculation outcomes are sensitive to the choice of properties used in fluid characterization and to the uncertainties of these input properties. Due to the many experimental difficulties encountered, solubility data quality is also an issue. Care must be exercised in data selection for model training and testing. Maczynski et al. [10–21] provide detailed reviews of mutual solubility data for hydrocarbons and water published before 2003. This body of work is a key resource for work in this field.

There are a number of thermodynamics models that predict the mutual solubility of water and low molar mass hydrocarbons. De Hemptinne et al. [22] reviewed the available methods to describe mutual solubility of water and hydrocarbons. They noted that both aqueous and organic liquid phases cannot be described adequately with a single model and that different models for each phase are preferred. Kabadi and Danner [23] proposed asymmetric mixing rules for water + hydrocarbon mixtures using the Soave–Redlich–Kwong equation of state. Michel and co-workers [24] investigated the application of cubic equations of state in calculations of mutual solubilities of water and hydrocarbons. They found that conventional mixing rules for cubic equation did not led to reliable results for practical applications. Soreide and Whitson [25] and Dhima et al. [26] also used different sets of binary interaction parameters for water-rich and hydrocarbon-rich phases. They also proposed a composition-based energy parameter for the Peng–Robinson equation to consider impacts of the aqueous phase salinity. Haruki and co-workers [27–30] proposed an exponent-type mixing rule for the energy parameter in SRK equation. They adjusted the binary parameters to give improve fits to the experimental data. Economou and Tsonopoulos [31] showed that the application of the Huron–Vidal mixing rule with the PR equation of state improved phase equilibria predictions for the 1-hexene + water binary mixture vis-à-vis the van der Waals mixing rules. Li et al. [32] coupled a modified Huron–Vidal mixing rule with the UNIFAC method to predict solubility and phase equilibria for light hydrocarbon–water binary mixtures. Yan et al. [33] applied a cubic + association (CPA) model to estimate the solubility of water in hydrocarbon mixtures containing C_7^+ components. These models illustrate the capability of equations of state to predict phase equilibria for a limited range of hydrocarbon + water binary and pseudo binary mixtures. These

models predict mutual solubilities of liquid phases qualitatively, but no general recommendation have been proposed to extend these models to ill-defined hydrocarbon + water mixtures. Estimation of properties based on these methods for reservoir fluids, and for ill-defined hydrocarbons, such as heavy oils and vacuum residues, in particular where the oils are characterized using distillation curves that are extrapolated beyond the limits of experimental data, can be very poor. In a recent effort to extend mutual solubility calculations to reservoir fluids, and distillation cuts, Satyro et al. [34] proposed a predictive NRTL-based approach to estimate mutual solubilities of hydrocarbons and water using hydrocarbon specific gravity and K_{Watson}:

$$K_{Watson} = \frac{\sqrt[3]{T_b}}{S.G.} \tag{1}$$

where S.G. is the specific gravity of hydrocarbons and T_b (molar average normal boiling point) in degrees Rankin as correlating parameters. Their general model was fit and evaluated using reliable mutual solubility data for pure hydrocarbons + water. For heavy hydrocarbons, their model diverged from the solubility data, and they proposed a modified approach for predicting the solubility of water in heavy hydrocarbons and reservoir fluids.

Empirical correlations are generally simpler than equation of state calculation approaches. They require fewer input parameters because they focus only on water solubility in the hydrocarbon phase. Tsonopoulos and co-workers [35–37] investigated the solubility of water in hydrocarbons at high temperatures, and analyzed available experimental solubility data from the perspective of prediction based on simple empirical correlations. The API handbook [38] suggests correlations to predict water solubility as a function of temperature and hydrogen to carbon ratio for pure and mixed hydrocarbons. Yaws et al. [39–41] also developed simple empirical models to estimate mutual solubility of hydrocarbons and water for three categories of hydrocarbons. As these models were developed based on the solubility of water in low molar mass hydrocarbons, they diverge from water solubility values for reservoir fluid + water mixtures at high temperatures.

The goal of this work is to develop simple and reliable predictive methods to estimate the solubility of water in ill-defined hydrocarbons at temperatures below the UCEP (Type II, Type IIIa and Type IIIb) and above the UCEP (Type IIIb) for heavy oil + water mixtures. This work also attempts to provide a path toward developing readily applicable numerical tools that support the design calculation needs related to high-temperature heavy oil and bitumen production and refining applications in particular. Reviewed experimental solubility data for water + pure hydrocarbons [10–21,42,43] and Athabasca bitumen [44], shown in Table 1, comprise a training data set. The test data set, shown in Table 2, comprises solubility data for water in 13 ill-defined mixtures. For mixtures comprising the test data set, limited fluid characterization is available and some potential input parameters for the models must be estimated. Further, composite input parameters such as K_{Watson}, while frequently encountered as inputs for thermodynamic models, and applicable to pure compounds and narrow boiling fractions (refinery characterization approach), are of limited value for heavy hydrocarbons such as Athabasca bitumen where mean molar mass and molar mass distribution and mean boiling point and boiling distribution are not readily measured, and where mean values are not representative of the wide range of components present. For the solubility models described in detail, the impact of input variable uncertainty on computed solubility outcomes is addressed explicitly. Correlations providing reliable water solubilities in ill-defined heavy hydrocarbons mixtures from room temperatures up to the UCEP of the mixtures are presented. Above the UCEP options to estimate water in heavy hydrocarbon solubility as a function of temperature and pressure are also explored, in