

Mutual solubilities of hydrocarbons and water with the CPA EoS

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Abstract

The knowledge of hydrocarbon/water phase equilibria is important in the design and operation of equipment for petroleum transport and refining and petrochemical plants. The presence of water in a hydrocarbon mixture can affect the product quality and damage the operation equipment due to corrosion and formation of gas hydrates. Tracing the concentration of hydrocarbons in aqueous media is also important for technical purposes like preventing oil spills and for ecological concerns such as predicting the fate of these organic pollutants in the environment.

In spite of its huge interest there was no model able for a qualitative description of the mutual solubility of water and hydrocarbons for a broad range of systems in a wide range of thermodynamic conditions.

In this work it is shown that an equation of state incorporating association known as the CPA EoS is able to produce an excellent description of the mutual solubilities of water and several aliphatic and aromatic hydrocarbons in a broad range of pressures and temperatures.

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1. Introduction

Describing the mutual solubilities of hydrocarbons and water is very important in the energy industry. Natural gas is generally saturated with water and during production, transportation, and processing, some of the dissolved water in the vapor phase may condense. Predicting the water solubility in a hydrocarbon mixture to prevent the formation of this aqueous phase is necessary to conform to product specifications and to protect the operation equipment from corrosion, the most common adverse effect. Imposing a maximum value for the water solubility is also necessary even when a water rich phase is deliberately created for the transport of heavy oils or to remove salts that deposit on the pipelines [1].

Beside corrosion, the presence of water in hydrocarbon mixtures, can also lead to the formation of gas hydrates which can cause problems in the petroleum industry, since they can form in pipelines and block the flow during transportation, drilling and production of oil or natural gas. They can also cause the hampering of the operation of heat exchangers and expanders. Thus, modeling the water content is required to determine the extent of drying or the amount of gas hydrate inhibitor necessary to avoid gas hydrate formation [2,3]. On the other hand gas hydrates can be used as an unconventional natural gas energy storage since the gas hydrates can contain more than 150 times as much natural gas than gaseous natural gas at standard temperature and pressure. Most light hydrocarbons are known to form stable gas hydrates only under high pressure and low temperature conditions [4].

Being able to model the water solubility in hydrocarbon fluids is also useful in predicting the water content of fuels.

The knowledge of the phase equilibria of aqueous mixtures with hydrocarbons is important for environmental purposes since hydrocarbons, like other pollutants, must be removed from refinery and petrochemical plant wastewater streams and from sea or fresh waters when oil spills occur. For this purpose, knowing the solubility and volatility of hydrocarbons is required

Abbreviations: AAD, average absolute deviation; APACT, associated perturbed anisotropic chain theory; CPA, cubic plus association; EoS, equation of state; LLE, liquid–liquid equilibria; MHV2, second-order modified Huron–Vidal mixing rules; NP, number of data points; SAFT, statistical associating fluid theory; SRK, Soave–Redlich–Kwong; UNIFAC, universal functional activity coefficient model

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to describe their phase distribution through the removal process and also to assist in the design of separation equipment [1].

Despite the importance of these systems it is quite difficult to describe their phase equilibria since aqueous solutions of hydrocarbons have an extreme nonideal behavior resulting in a very limited miscibility over a broad temperature range. Moreover the solubility of a hydrocarbon in water is several orders of magnitude lower than the counterpart solubility of water in the hydrocarbon. In addition, the solubility of hydrocarbons in water has a minimum value at lower temperatures (where the enthalpy of solution is zero), while the water solubility in hydrocarbons is a monotonic function of temperature [5].

Over the last three decades a number of approaches to the description of the mutual solubilities of hydrocarbons and water have been attempted. Several quantitative structure–property relationships (QSPR) have been used to estimate the solubility of organic compounds in water. The hydrocarbon content can be correlated with the molecular surface area [6], the different group contributions or fragment structure information [7]. These QSPRs can also involve self-organizing maps (SOMs) and fuzzy ARTMAP neural systems, as in the work of Giralt et al., developed to estimate infinite dilution activity coefficients of organics compounds in water [8].

Also, different thermodynamic models have been evaluated for hydrocarbon/water mutual solubilities. The property of practical interest for the description of low pressure mutual solubilities is the Henry's law constant which is a direct measure of the partition of a given solute between two phases. This property expressed as a function of temperature and pressure is useful for correlating or predicting hydrocarbon solubility in water, provided that the fugacity of the coexisting organic phase can be calculated. A group contribution scheme based on a hydration model was already used to predict the Henry's law constant of aqueous systems of alkanes, alkenes, alkylcycloalkanes, and alkylbenzenes [9].

However, until recently the state of art model for water solubility modeling was the UNIFAC model, in spite of its poor accuracy for the systems under study. In fact, the existing UNIFAC-type models perform poorly when applied to the prediction of infinite-dilution activity coefficients in polar mixtures, especially in aqueous mixtures [10]. Even the model of Hooper et al. [11] which was developed only to correlate liquid–liquid equilibria for water/hydrocarbon mixtures, degrades its performance as the carbon number in the *n*-alkane increases. Empirical approaches are possible to overcome these limitations but involve reducing the general predictive character of the group contribution [12]. Moreover this model is limited to low pressure applications. There are better alternative approaches for UNIFAC that are specifically designed for aqueous solutions such as the linear solvation energy relationship (LSER) but work is still in progress to increase its range of applicability [13]. Other activity coefficient models, such as the non-random two liquid model (NRTL), was also used in combination with the Debye–Hückel theory to calculate the solubility of a number of molecular solutes in water in the presence of a hydrotrope [14].

The extension to high pressures was first achieved through excess Gibbs energy models in cubic equation of state mixing rules (EoS-GE) such as the modified Huron-Vidal, mixing rules (MHV2), but still with limited success towards the mutual solubilities of water and hydrocarbons [15].

A novel, a priori prediction method for thermodynamic equilibria of fluids is COSMO-RS. This method was used to predict the mutual solubilities of hydrocarbons and water with a good qualitative and an even satisfactory quantitative agreement with the experimental data. Further improvements of the hydrogen bond temperature dependence in COSMO-RS parameterizations or the inclusion of the shape effects existing in pure chain liquids, for instance, are still necessary to improve the description of mutual solubilities of hydrocarbons and water [16].

Recently, Bidart et al. employed the Carnahan Starling van der Waals equation of state with quadratic mixing rules for obtaining the global phase diagrams of water + *n*-alkane mixtures [*n* = 1–36] with qualitative agreement with experimental results [17].

The breakthrough in the modeling of aqueous systems came with the development of association models such as the statistical associating fluid theory (SAFT) [18], the associated-perturbed-anisotropic-chain-theory (APACT) [5] and the cubic plus association (CPA) EoS [18–20]. All these models have previously been applied to the description of the hydrocarbon/water mutual solubilities and the SAFT EoS was already applied for the prediction of the thermodynamic inhibiting effect of methanol on gas hydrate formation [21]. However, the original SAFT approach has problems in describing aqueous solutions of hydrocarbons. As shown by Economou and co-workers [5,22], increasing the complexity of SAFT and explicitly accounting for hydrogen bonding, by several mixing rules and association schemes for water, does not improve the fitting of the water solubility neither provide a quantitative description of the hydrocarbon solubility. Possible explanations for the SAFT limitations in these systems are its inadequacy to account for the high polarity of the water molecule, or the use of inappropriate water parameters. The same study showed that the APACT model when applied for aqueous hexane and decane systems provided hydrocarbon solubilities too low by one to four orders of magnitude, and that the 3-site model predicts a minimum in the aromatic hydrocarbon solubility but at much higher temperatures and solubilities than the experimental values.

After the original development of the SAFT model several new versions were proposed for modeling hydrocarbon/water binary systems. The Lennard-Jones SAFT (LJ-SAFT), exhibited better agreement with experimental data than the original version, however it can only be applied to a limited range of density [23]. Grenner et al., employed the simplified perturbed chain SAFT model (PC-SAFT) using a different set of water pure component parameters based on some physically justified arguments to predict very satisfactorily the solubilities in the hydrocarbon rich phase but the obtained solubility of the hydrocarbon in water was higher than the experimental values [24]. Improved results were also recently obtained by Karakatsani et al. using a polar term in PC-SAFT (tPC-SAFT). With a polar contribution, mutual solubilities of water + *n*-hexane and

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