

Brief Report

# Effect of Water Saturation on H<sub>2</sub> and CO Solubility in Hydrocarbons

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**Abstract:** The effect of water on the solubility of syngas in hydrocarbons has typically been ignored when developing models for Fischer-Tropsch slurry bubble column reactors (SBCR), despite water being a major by-product. Therefore, a generalized correlation was developed to predict water solubility in hydrocarbons at high temperatures, and was used to calculate the effect of water saturation on H<sub>2</sub> and CO solubility in hydrocarbons using the Span Wagner equation of state. The presence of water was shown to have a much more significant effect on H<sub>2</sub> solubility in hydrocarbons, compared to CO.

**Keywords:** solubility; water; hydrocarbons; syngas; Fischer-Tropsch; water-hydrocarbon mixtures

## 1. Introduction

The effect of the presence of water on syngas solubility in Fischer-Tropsch (F-T) Slurry Bubble Column Reactors (SBCR) has received little attention, despite water being a major by-product. Although there have been numerous investigations to measure solubilities and mass transfer parameters of CO and H<sub>2</sub> in F-T hydrocarbon fractions and slurries under a variety of operating conditions, the effect of water is typically neglected. Moreover, in most of the F-T SBCR models, liquid properties are typically determined for pure hydrocarbons or hydrocarbon mixtures, while disregarding the effect of water saturation on the physical properties of the hydrocarbons or on the gas solubilities. In fact, there only seems to be one publication concerned with the hydrodynamic effect of water on the F-T mass transfer [1,2]. Thus, the purpose of this work is to determine the solubility of water in various hydrocarbons using thermodynamic models, and to develop a generalized correlation for determining water solubility in hydrocarbons, which can then be used to estimate the effect of water saturation on the solubility of CO and H<sub>2</sub> in hydrocarbons.

## 2. Background

### 2.1. Empirical Solubility Correlations

Since the behavior of water's non-ideal behavior could not be explained using classical theoretical arguments, many researchers attempted to develop alternate empirical correlations to account for the temperature dependence of the solubility of hydrocarbons in aqueous systems. Numerous empirical correlations exist for water hydrocarbon mixtures at room temperature. Lindenberg [3] and McAuliff [4] observed an empirical relationship between the logarithms of aqueous solubility of water in hydrocarbons at room temperature and the hydrocarbon molar volume for homologous series. Klevens [5] suggested that the solubility of aromatic hydrocarbons is related to the molar volume, molecular length, and carbon number. Irmann [6] showed that the aqueous solubility can be determined from the sum of atomic and structural parameters for a variety of hydrocarbons. Other investigations have also correlated water solubility with a variety of readily measured or

calculated physical properties such as the octanol/water partition coefficient, normal boiling point, chromatographic retention indices, and molecular surface area and volume. Several studies [7,8] demonstrated a mechanistic relationship between the solubility and the molecular surface area of the hydrocarbon solute, similarly, Schatzberg [9] correlated the solubility of water in hydrocarbons ranging from paraffins to n-hexadecane at 298 and 313 K with solute surface tension.

Development of correlations for a wide range of temperatures has been one of the more difficult challenges. Theoretical studies suggest that the logarithm of solubility should be linear in inverse temperature for moderately non-ideal solutions i.e., if the solution operates under the assumption of being a random mixture of spherical particles [10]. Yet, this hypothesis seems to be more applicable to describe the hydrocarbon liquid phase with very low concentrations of the more non ideal liquid molecules (i.e., water), as shown by Hubbard [11]. Correlations for extended temperature ranges have been introduced by Tsonopoulos and Wilson [12] and Heidmann [13], which incorporated more complex dependencies on temperature into their Antoine-type correlations for the solubility of water in C<sub>6</sub> to C<sub>8</sub> hydrocarbons. Brady et al [14] developed graphical correlations for water solubility in heavy hydrocarbons as a function of temperature and the double bond index using a solution of groups theoretical approach.

Generally, the effect of pressure on binary water hydrocarbon mixtures could be readily estimated in the three phase region (VLE) as the sum of the pure component vapor pressures at various temperatures approaching the three phase critical point. However, the combined effect of temperature and pressure on the VLE and VLLE of water hydrocarbon mixtures are better correlated in terms of the hydrocarbon or the water volatility, or both. These relationships accounting for both temperature and pressure effects are restricted to temperatures which are far removed from the phase change boundary where the partial molal volume of the solute undergoes considerable change. The high solubility of water in hydrocarbons in general precludes representation of the hydrocarbon rich phase by the means of Henry constant.

## 2.2. Activity Coefficients for Water Hydrocarbon Mixtures

Saturated aqueous solutions of hydrocarbons at low to moderate temperatures are usually very dilute solutions, therefore hydrocarbon solubilities in water and vice versa could be directly related to the predictions of activity coefficients at infinite dilution. Deal et al. [15,16] presented an extensive correlation for activity coefficients at infinite dilution at 298 K with molecular structure and the interaction of various structural groups in the solution. The resulting correlations are simple and easily applicable to homologous series in water. Tsonopoulos and Prausnitz [17] extended the group contribution method approach to distinct classes of aromatic hydrocarbons and their derivatives. Other studies [18,19] correlated infinite dilution activity coefficients with specific physical properties which reflect the size, shape, and charge distribution of the hydrocarbon solute. Properties examined include carbon number, molecular volume, surface area, molecular connectivity, acentric factor, normal boiling point, melting point, total electronic energy, and dipole moment. These correlations, although specific to single hydrocarbon families and solvents, predicted activity coefficients at infinite dilution with very close agreement to the UNIQUAC and UNIFAC predictions.

Activity coefficient models for more miscible fluids are expected to reflect the thermodynamic effects of increased solubility; therefore, infinite dilution activity coefficients are not very applicable to mixtures of water with hydrocarbon oils or phenols, as they usually exhibit higher solubilities. Moreover, the effect of the solute composition must be incorporated directly into the activity coefficient expression. Black et al. [20] discussed the solubility of water in hydrocarbons using a regular solution model as well as the Flory-Huggins mixture equation of state to account for the discrepancies in the molal volume. Hildebrand [21] combined the two approaches into one model which was widely used in investigations for the modeling of the solubility of water in hydrocarbons at temperatures ranging from 273 to 348 K. More recent activity coefficient models such as the NRTL, UNIQUAC, and UNIFAC models are extremely popular for prediction of mutual solubility data for more miscible aqueous

hydrocarbon systems and have been applied in the design of many industrial processes in the oil and gas industry.

Extending activity coefficients to describe VLE and VLLE systems requires the use of an equation of state to describe the vapor phase; Li et al. [22] represented the fugacity coefficient of water in the vapor phase above the three phase crucial pressure using the virial equation of state in reduced form. The activity coefficient of light hydrocarbons in water was graphically correlated as a function of reduced temperature and the solubility parameter, whereas reference state fugacities were graphically correlated as functions of reduced temperatures and pressures. Alternatively, West et al. [23] conducted three phase calculations for light paraffin and water mixtures using the Suave Redlich Kwong equation of state for the vapor phase fugacities and proposed a modified Hilderbrand solubility parameter for the liquid phases.

This approach of mixing activity coefficient correlations with equations of state is mathematically inconvenient. The mathematical flexibility of activity coefficient models enables modeling of systems with very high liquid non-idealities, which is usually counterbalanced by the complex nature of most equations of state. This approach works well, however, for low temperature and moderate pressure systems, beyond which the accuracy and applicability has to be closely questioned. Moreover, combining different models for the vapor and liquid phases prevents the correct prediction of the mixtures critical and supercritical properties.

### 2.3. Equation of State Studies of Water-Hydrocarbon Mixtures

Hiedmann [24] was the first to demonstrate that the phase equilibria of water hydrocarbon mixture could be expressed using a single equation of state by using the Wilson modification of the Redlich-Kwong (RK) equation to predict the VLLE of n-paraffins and water. Using conventional mixing rules, the modified RK equation successfully predicted the water content of both the liquid hydrocarbon and the vapor phases; however, predictions for aqueous hydrocarbon solubilities were only qualitative. This sparked increasing interest into the development of Van der Waal type equations of state and mixing rules for the modeling of the phase equilibria of hydrocarbon + water systems. However, failure to successfully quantitatively replicate the water hydrocarbon behavior led to the superposition of specific solution models on simple equations of states to represent the solubility of hydrocarbons in water.

Moreover, a lot of effort has aimed at the development of conventional quadratic mixing rules for the simultaneous representation of both the hydrocarbon rich and aqueous phases. The introduction of temperature dependent, phase specific interaction constants to develop empirical extensions of quadratic mixing rules, has been deemed undesirable from a theoretical standpoint. The unique phase behavior of water indicates a more complex mechanism and dependency of water's mixing behavior in the presence of hydrocarbons, as such valuable information is lost in lumping all of these effects into binary interaction parameters. Although these empirical relations work and are easily applicable in phase equilibrium calculations, they fail to converge at two and three phase critical points. Attempts at overcoming the difficulties and limitations of quadratic mixing rules for the characteristic energy of van der Waal type equations of state aimed at the development of mixing rules which are cubic in mole fraction [25]. Other alternate approaches to the development of mixing rules for water hydrocarbon mixtures, include deriving them from complex solution chemistry principles. According to these principles, the formations of new associated species such as dimers, is postulated to account for the effects of hydrogen bonding and donor acceptor behavior. The concentrations of all coexisting species are then determined from pure component fugacities using empirically determined chemical equilibrium constants. These methods have been widely used to model low and moderate pressure phase equilibria of strongly non ideal vapors and liquid mixtures (eg. Acetic acids with alcohols or hydrocarbons), in conjunction with the use of activity coefficients [26]. This approach has also been superimposed on cubic equations of state to represent the phase equilibria at elevated pressure for polar substances and their mixtures and to model the self-association of water in the presence of

hydrocarbon solute, by treating water as a mixture of five polymeric species, the VLE and VLLE of polar and non-polar mixtures of the C<sub>1</sub>–C<sub>8</sub> alkanes with water were successfully modeled using the Schmidt-Wenzel equation.

However, there have been several drawbacks. Primarily, the proposed stoichiometry by which the association of pure water is represented is usually arbitrarily established. Moreover, the representation of the hydrogen bonding behavior of water by higher polymers cannot be readily justified, as the characteristic properties of these polymers cannot be readily determined for extended applications usually associated with equations of state. Other drawbacks include the computational complications associated with initially calculating the chemical equilibria, this complexity increases rapidly with the number of components and the severity of the conditions. At severe conditions, even the simplest of models would require complicated and time consuming computational solutions [27].

Another approach for modeling mixtures containing polar constituents involves the transposition of alternate activity coefficient models for the excess Gibbs free energy of the solution. Huron and Vidal [28] demonstrated that for the Soave equation of state, a simple relation exists between the ratio of energy and co-volume parameters (a,b) in addition to the limit of the Gibbs free energy at infinite pressure. They also suggested the modification of the NRTL model to account for the excess Gibbs free energy of the Soave equation. Although these models successfully represent the phase equilibria of simple systems containing polar components up to the critical point, they have not been tested on water hydrocarbon mixtures and are expected to deviate at the limit of low density due to their empirical nature.

A milestone was achieved by Mollerup [29,30] and Whiting and Prausnitz [31], when they derived density dependent mixing rules for van der Waals type equations of state using local composition averages of the residual internal energy of mixing. Using the analogy of the attractive energies of pure components, the authors expressed the local compositions in terms of bulk composition, temperature, and density. This model was then used to derive the mixing energy, the Helmholtz energy, and the solution pressure, which in turn were used to yield an equation of state for non-random mixtures. This mixing rule for the interaction energy parameter of the mixture represents an interpolation between the successful local composition activity coefficient models at high density and the theoretical quadratic mixing rule for the second virial coefficient in the limit of low density.

The density dependent mixing rules derived from the local composition methods improved on the correlation for the phase equilibria of polar and non-polar mixtures relative to the traditional random-mixing rules. However, this model overestimates the entropic contributions to mixing which making it inapplicable to asymmetric, non-polar mixtures. Dimitrelis and Prausnitz [32] tried to address this overestimation by reformulating the binary interaction parameters as deviations from the ideal values using quasi-chemical theory. Similarly, Mathias and Compeman [29] divided the residual internal energy of mixing into ideal and excess contributions to try and make the best use of the Peng-Robinson EOS's ability to model asymmetric non-polar mixtures, ultimately developing a truncated model with a low computational load. This simplified model reasonably predicts the VLE of a variety of mixtures as well as the mutual solubilities of water hydrocarbon mixtures.

Local composition mixing rules provide improved modeling and accuracy of mixtures involving polar components, there still remains some discrepancies regarding the formal definition and theoretical basis of the local composition concept based on the results of molecular dynamics and Monte Carlo simulations.

### 3. Calculating Water Solubility in Hydrocarbons

By taking the solubility of water in hydrocarbons to be linear in fugacity, Henry's law was used to determine the concentration of the water as shown in Equation (1).

$$C_1 = k_H^{-1}(T, P) \cdot f_1(T, P) \quad (1)$$

where  $C_1$  is the solubility of water,  $k_H^{-1}(T, P)$  is Henry's constant, and  $f_1(T, P)$  is the fugacity. Subscripts 1 and 2 refer to water and hydrocarbon respectively. The fugacity was determined from the departure of the molar Gibbs free energy from the ideal gas behavior as shown in Equation (2).

$$f_1(T, P) = P \cdot \exp\left(\frac{G(T, P) - G^{IG}(T, P)}{RT}\right) \quad (2)$$

The Gibbs free energy was determined using Equation (3), where the enthalpy and entropy were obtained from the steam tables [33], whereas the ideal gas Gibbs free energy were determined using the same equation, with the enthalpy, and entropy derived from the cubic heat equation as shown in Equations (4) to (6).

$$G = H - T \cdot S \quad (3)$$

$$C_p(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^3 \quad (4)$$

$$H^{IG} = \int_{T_r}^T C_p(T) dT \quad (5)$$

$$S^{IG} = \int_{T_r}^T \frac{C_p(T)}{T} dT - R \cdot \ln\left(\frac{P}{P_r}\right) \quad (6)$$

The inverse Henry's law constant was determined using the expression derived by Sanchez and Rodgers [34] for the solubility of gases in liquid polymers. It is based on equating the chemical potential of the absorbed gas to the ideal case, assuming infinite molecular weight of the polymer. A modified version that accounts for the molecular weight of the solvent was used as shown in Equation (7).

$$k_H^{-1} = \frac{M_1}{RT} \cdot \exp\left(-\check{\rho}_2 v_1^* \chi - \frac{v_1^*}{v_2^*} + r_1 \left[ \frac{\check{T}_2}{\check{T}_1} - 1 - \frac{(1 - \check{\rho}_2) \cdot \ln(1 - \check{\rho}_2)}{\check{\rho}_2} \right]\right) \quad (7)$$

where  $\chi$  is defined as the bare water-hydrocarbon interaction parameter defined in Equation (8).

$$RT\chi = P_1^* + P_1^* - 2 \cdot \zeta (P_1^* \cdot P_2^*)^{1/2} \quad (8)$$

$\zeta$  is a dimensionless parameter derived by Haschets [35] to account for deviations from the geometric mean for the solubility of water in n-alkanes between C<sub>6</sub> to C<sub>16</sub>, and is determined using Equation (9).

$$\zeta = 0.433799 + 2.6645 \cdot (10^{-3}) \cdot T \text{ (}^\circ\text{C)} \quad (9)$$

Additionally, the lattice volume equation of state [34] was also used to link the state parameters as shown in Equation (10).

$$\check{\rho}_2 + \check{P} + \check{T} \left[ \ln(1 - \check{\rho}) + \left(1 - \frac{1}{r}\right) \check{\rho} \right] = 0 \quad (10)$$

where  $\check{\rho}$ ,  $\check{P}$ , and  $\check{T}$  are reduced parameters defined in Equation (11), and  $\rho^*$ ,  $P^*$ , and  $T^*$  are reference parameters as shown in Table 1.

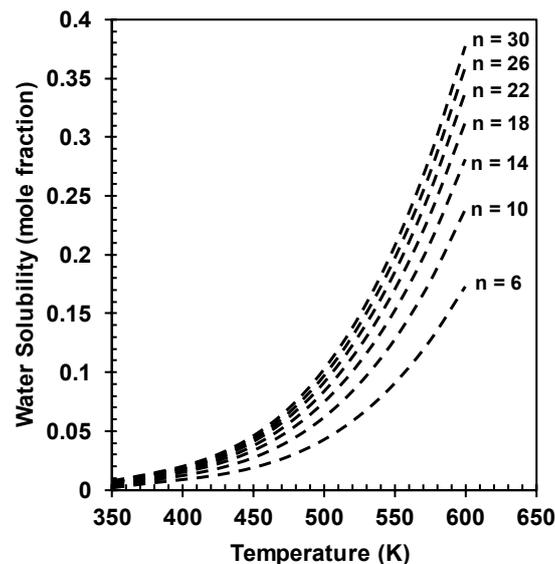
$$\check{\rho} = \frac{\rho}{\rho^*}, \quad \check{P} = \frac{P}{P^*}, \quad \check{T} = \frac{T}{T^*} \quad (11)$$

The solubility of water in Hexane, Octane, and Decane was subsequently calculated, the solubility of water in the hydrocarbons increased with increasing temperature and carbon number, with water having the highest solubility in Decane. The solubility of water in hydrocarbons was determined to range anywhere between 0.1 to 0.3 mole fraction, depending on the hydrocarbon. Subsequently, a correlation was fit to determine the equilibrium solubility of water in hydrocarbons over the temperature range of 350 to 650 K, as shown in Equation (12), and as highlighted in Figure 1. It is

important to note that there was no significant effect of pressure on the equilibrium solubility of water in hydrocarbons.

**Table 1.** Reference state parameters used in calculation [36].

Component	$\rho^*$ (kg/m <sup>3</sup> )	$P^*$ (MPa)	$T^*$ (K)	$r$
<i>n</i> -hexane	775	298	476	8.37
<i>n</i> -octane	815	307	502	10.34
<i>n</i> -decane	837	305	530	11.75
Water	1105	2690	623	8.46



**Figure 1.** Solubility of water in C<sub>6</sub> to C<sub>30</sub> hydrocarbons at 5 MPa.

When comparing the predicted solubilities with experimental data for water solubility in various hydrocarbons ranging from C<sub>6</sub> to C<sub>12</sub>, as summarized by Maaczyński et al. [37], the correlation predicted solubilities with errors ranging from 15% to 65%, with the highest deviations observed at higher temperatures. However, there were no qualitative deviations from the experimental data, and therefore the correlation was further used to analyze the effect of water saturation on the solubility of H<sub>2</sub> and CO in hydrocarbons.

$$X_w = [0.5704 \cdot \ln(n) + 0.3721] \cdot (10^{-8}) \cdot (T^3) - [0.5569 \cdot \ln(n) + 0.6112] \cdot (10^{-5}) \cdot (T^2) + [1.834 \cdot \ln(n) + 3.0314] \cdot (10^{-3}) \cdot (T) - [0.2006 \cdot \ln(n) + 0.4765] - 5.449 \cdot 10^{-3} \cdot (P - 5) \quad (12)$$

#### 4. H<sub>2</sub> and CO Solubilities in Pure and Water-Saturated Hydrocarbons

Once the solubility of water was determined, simple mixing rules were used to determine the effect of water saturation on H<sub>2</sub> and CO solubilities in hydrocarbons. Solubilities were determined Equation (13) [21], which accounts for the non-ideal interactions between the components:

$$-\log x_{solute} = \log P_{vapor-solute} + \frac{V_{m-solute}(\varphi_{solvent} - \varphi_{solute})^2}{4.58 \cdot T} - \log P_{system} \quad (13)$$

where  $\varphi$  is the Hildebrand solubility parameter, which is derived from the cohesive energy density of the solvent using Equation (14). This parameter provides an estimate of the degree of interaction between different components.

$$\varphi = \sqrt{\text{Cohesive Energy}} = \sqrt{\frac{\Delta H_v - RT}{V_{m-\text{solute}}}} \quad (14)$$

Values for the heat of vaporization were extracted from the NIST Chemistry Web book, whereas values for the molar volumes for each of the components were derived using the reduced Helmholtz energy. Subsequently, the Span and Wagner Equation of State [38], which has the form of a fundamental equation explicit in the Helmholtz Free Energy (HFE) where the function for the residual part of the HFE was fitted to selected data of the fugacity coefficient, as summarized in Equations (15) to (25), was used in an iterative manner to determine the molar volume of each of the components over a wide range of temperatures and pressures. Values of the Helmholtz energy constants for the determining the solubility of H<sub>2</sub> was obtained from Leachman [39], whereas those for CO were obtained from Kerley [40].

$$P_{\text{CO or H}_2}(\delta, \tau) = \rho RT(1 + \delta\phi'_\delta) \quad (15)$$

$$\phi^r = \sum_{i=1}^x n_i \delta^{d_i} \tau^{t_i} + \sum_{i=x+1}^y n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}} + \sum_{i=y+1}^z n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta-\epsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} + \sum_{i=z+1}^w n_i \Delta^{b_i} \delta \Psi \quad (16)$$

$$\delta = \rho / \rho_c \quad (17)$$

$$\tau = T_c / T \quad (18)$$

$$\Delta = \theta^2 + B_i [(\delta - 1)^2]^{\alpha_i} \quad (19)$$

$$\theta = (1 - \tau) + A_i [(\delta - 1)^2]^{1/(2\beta_i)} \quad (20)$$

$$\Psi = e^{-C_i(\delta-1)^2 - D_i(\tau-1)^2} \quad (21)$$

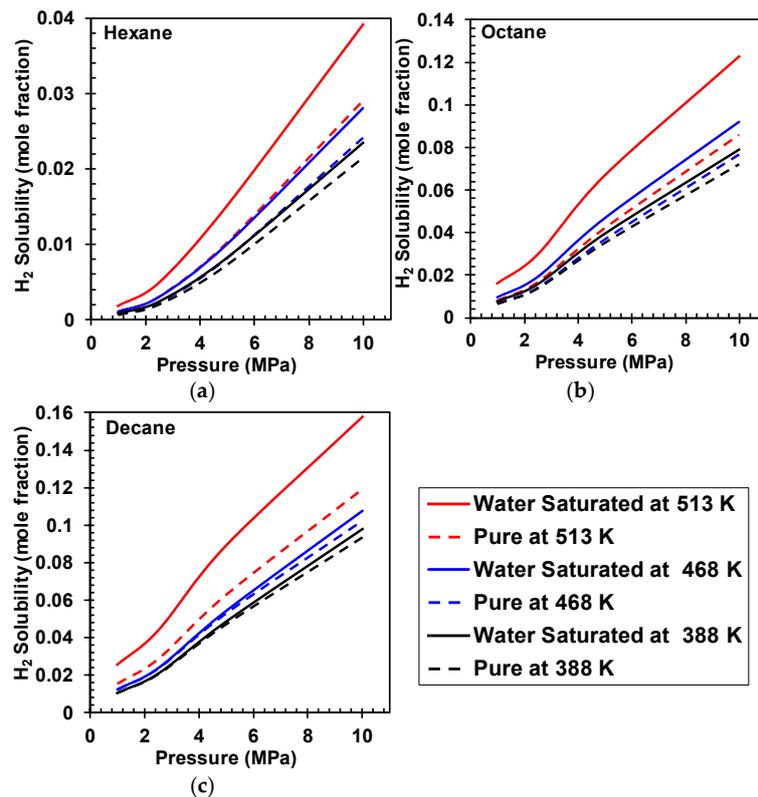
$$\begin{aligned} \phi'_\delta = & \sum_{i=1}^x n_i d_i \delta^{d_i-1} \tau^{t_i} + \sum_{i=x+1}^y n_i e^{-\delta^{c_i}} [\delta^{d_i-1} \tau^{t_i} (d_i - c_i \delta^{c_i})] \\ & + \sum_{i=y+1}^z n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta-\epsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \left[ \frac{d_i}{\delta} - 2\alpha_i(\delta - \epsilon_i) \right] \\ & + \sum_{i=z+1}^w n_i \left[ \Delta^{b_i} \left( \Psi + \delta \frac{\partial \Psi}{\partial \delta} + \frac{\partial \Delta^{b_i}}{\partial \delta} \delta \Psi \right) \right] \end{aligned} \quad (22)$$

$$\frac{\partial \Psi}{\partial \delta} = -2C_i(\delta - 1)\Psi \quad (23)$$

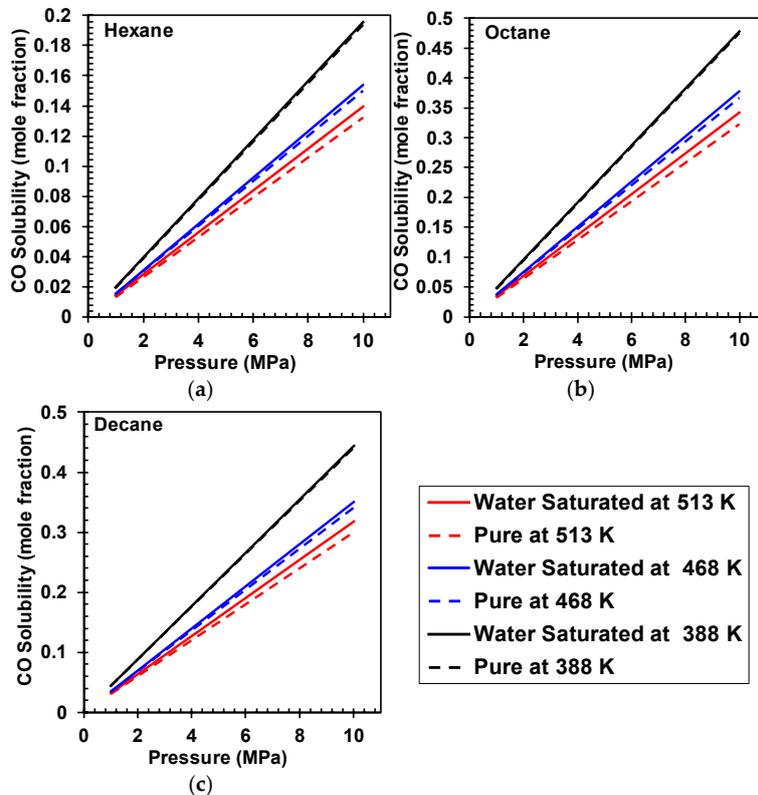
$$\frac{\partial \Delta^{b_i}}{\partial \delta} = b_i \Delta^{b_i} \left( \frac{\partial \Delta}{\partial \delta} \right) \quad (24)$$

$$\frac{\partial \Delta}{\partial \delta} = B_i(2\alpha_i)(\delta - 1)^{2(\alpha_i-1)} + 2\theta A_i(1/\beta_i)(\delta - 1)^{(1/\beta_i-1)} \quad (25)$$

Results for H<sub>2</sub> solubility in water saturated and unsaturated hydrocarbons is shown in Figure 2, and as can be seen in this figure, the solubility of H<sub>2</sub> is higher in water saturated hydrocarbons, and the effect of water saturation significantly increases with increasing temperatures. Moreover, results for CO solubility in water saturated and unsaturated hydrocarbons is shown in Figure 3, and as can be seen the presence of water does not have a significant effect on CO solubility. The effect of water solubility on H<sub>2</sub> solubility compared to CO could be attributed to hydrogen bonding effects.



**Figure 2.** Comparing H<sub>2</sub> solubility in pure and water saturated (a) Hexane, (b) Octane, and (c) Decane at various temperatures.



**Figure 3.** Comparing CO solubility in pure and water saturated (a) Hexane, (b) Octane, and (c) Decane at various temperatures.

## 5. Concluding Remarks

In this work, the solubility of water in hydrocarbons was calculated and a correlation was developed to predict the solubility of hydrocarbons over a wide range of temperatures and pressures. Subsequently, the effect of water saturation on H<sub>2</sub> and CO solubility in hydrocarbons was investigated. The solubility of water was found to increase with temperature and carbon number, whereas the presence of water in hydrocarbons was found to increase the solubility of H<sub>2</sub> and CO in hydrocarbons. However, this effect was significantly higher with H<sub>2</sub>, which could be attributed to synergistic effect induced by the presence of water.

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