

INSIGHTS INTO THE SOLUBILITY OF HYDROCARBONS IN WATER BY THE SOFT-SAFT EQUATION OF STATE

*Lourdes F. Vega**, Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC) and MATGAS Research Center, Bellaterra, Barcelona, Spain.

Fèlix Llovell, Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC) and Departament d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Spain.

Felipe J. Blas, Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, Huelva, Spain

Introduction

Water is a fascinating molecule, essential to our lives, and present in most of the chemical and industrial processes. As for any other compound, an accurate model of water is essential to design and optimize any industrial process in which water is present. Several models, based on *ab-initio* calculations and/or semi-empirical models have been proposed in recent years and some improvements have been obtained with respect to the previous ones. However, even today there is not a single model available, accurate enough to describe its thermodynamic and structural behavior over a wide range of thermodynamic conditions, including its subtle behavior in mixtures.

One of these cases is the description of the mutual solubilities between water and hydrocarbons, essential for the petrochemical industry. The thermodynamic behavior of aqueous solutions of hydrocarbons is extremely non-ideal due to the microscopic nature of the associating interactions among water molecules. It results in some anomalous properties that are challenging to model. For example, the solubility of the hydrocarbon in water is several orders of magnitude lower than the solubility of water in the hydrocarbon-rich liquid phase. Moreover, the solubility of the hydrocarbon exhibits a minimum at room temperature, while the solubility of water is a monotonic function that increases with the temperature [1]. The presence of the minimum means that, at a certain (low) temperature, the solubility of the hydrocarbon in water increases when the temperature is decreased. This phenomenon is related to the strong anisotropy of the hydrogen bonding formed among water molecules. As a consequence, the entropic effect becomes more important than the thermal molecular agitation.

The purpose of this work is twofold: (1) to provide an accurate molecular model for water using the soft-SAFT equation of state [2,3], and (2) to check the capability of this molecular-based equation of state for capturing the solubility minima of n-alkanes in water found experimentally at room temperature.

The soft-SAFT Equation of State

Within the framework of SAFT, the equation of state (EoS) of a fluid is a perturbation expansion given in terms of the residual molar Helmholtz energy, defined as the difference between the total Helmholtz energy and that of an ideal gas at the same temperature T and

molar density ρ . SAFT implicitly assumes that there are three major contributions to the total intermolecular potential of a given molecule: a) the repulsion-dispersion contribution typical of individual segments b) the contribution due the fact that these segments can form long lived chains and c) the contribution due to the possibility that some segments form association complexes with other molecules. Furthermore, we added a new term a^{polar} which takes into account the quadrupolar interactions between molecules, in case they exist. According to this scheme, the residual Helmholtz energy can be written as:

$$a^{res} \equiv a - a^{ideal} = a^{ref} + a^{chain} + a^{assoc} + a^{polar} \quad (1)$$

where, a^{res} is the residual Helmholtz free energy density of the system. The superscripts *ref*, *chain*, *assoc* and *polar* refer to the contributions from the reference term, the formation of the chain, the association, and the polar interactions, respectively, depending on the system under study.

In the soft-SAFT EoS, [2]-[4] the reference term is a Lennard-Jones (LJ) spherical fluid, which accounts for both the repulsive and attractive interactions of the monomers forming the chain. As in previous works the accurate EoS of Johnson et al. [5] is used here. For the case of mixtures the same equation is used by applying the van der Waals one-fluid theory, with generalized Lorentz-Berthelot mixing rules: $\sigma_{ij} = \eta_{ij} \left(\frac{\sigma_i + \sigma_j}{2} \right)$ and $\epsilon_{ij} = \xi_{ij} (\epsilon_i \epsilon_j)^{1/2}$, where

η and ξ are the size and energy binary adjustable parameters, respectively. The equation is used in a fully predictive manner from the pure component parameters when η and ξ are equal to unity, while values different from unity mean the use of one or two binary parameters, taking into account the differences in size and/or energy of the segments forming the two compounds in the mixture.

The chain and association terms come from Wertheim's theory [6], and they are formally identical in the different versions of SAFT:

$$a^{chain} = \rho k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (2)$$

$$a^{assoc} = \rho k_B T \sum_i x_i \sum_\alpha \left(\ln X_i^\alpha - \frac{X_i^\alpha}{2} \right) + \frac{M_i}{2} \quad (3)$$

being ρ is the molecular density, T is the temperature, m is the chain length, x_i is the molar fraction of component i , k_B the Boltzmann constant and g_{LJ} is the radial distribution function of a fluid of LJ spheres at density $\rho_m = m\rho$, evaluated at the bond length σ . M_i the number of associating sites of component i , and X_i^α the mole fraction of molecules of component i non bonded at site α , which accounts for the contributions of all the associating sites in each specie.

In soft-SAFT it is possible to explicitly account for multipolar interactions by the addition of a perturbative multipolar term. In particular, an expansion of the Helmholtz free energy density in terms of the perturbed quadrupole-quadrupole potential with the Padé approximation was proposed by Stell et al. [7]:

$$a^{qq} = a_2^{qq} \left(1 - \frac{a_3^{qq}}{a_2^{qq}} \right)^{-1} \quad (4)$$

Expressions for a_2 and a_3 , the second and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential and involve the state variables, molecular parameters, and the integral for the reference fluid. A detailed derivation of these expressions is given elsewhere [8]. This new term involves an additional molecular parameter, Q , the quadrupolar moment, which is usually taken from experimental data.

The classical formulation of SAFT makes the theory unable to correctly describe the scaling of thermodynamic properties as the critical point is approached. A possible solution is to splice together an equation which incorporates the fluctuation-induced scaled thermodynamic behavior of fluids asymptotically close to the critical point, but that also accounts for a crossover to classical behavior of the thermodynamic properties far away from the critical point, where the effect of fluctuations becomes negligible. This contribution is obtained when the renormalization group (RG) theory [9]-[10] is applied. The treatment followed, based on White's work, [11]-[12] is done by incorporating the scaling laws governing the asymptotic behavior close to the critical point, while reducing to the original equation of state far from the critical point. It is expressed mathematically as a set of recursive equations that incorporate the fluctuations in a progressive way.

$$a = \rho k_B T \sum_{i=1}^{\infty} (a_{n-1} + a_n^{cross}) \quad (5)$$

It is important to remark that the value of a_{n-1} for the first iteration correspond to the original soft-SAFT value. Details on the implementation of the crossover term can be found in the original references [13]-[14].

The molecular model for water and hydrocarbons

Several semi-empirical models for water have been developed along the years (see, for instance references [15]-[17] for excellent reviews). The goal is to capture its structure, on the basis that if the computed model can successfully predict the physical properties of liquid water, then the (unknown) structure of liquid water can be determined. Most of these models involve orientation electrostatic effects and LJ sites that may or may not coincide with one or more of the charged sites. The LJ interaction accounts for the size of the molecules. It is repulsive at short distances, ensuring that the structure does not completely collapse due to the electrostatic interactions. At intermediate distances it is significantly attractive but non-directional and competes with the directional attractive electrostatic interactions. This competition ensures a tension between an expanded tetrahedral network and a collapsed non-directional one. Generally each model is developed to fit well with one particular physical structure or parameter (for example, the density anomaly, the radial distribution function or the critical parameters) and it comes as no surprise when a model developed to fit certain parameters gives good compliance with these same parameters; the challenge is then to use

this model to accurately predict the behavior of the system at conditions far away from which the parameters were fitted, or for other properties. Figure 1a shows a bidimensional sketch of water, showing the orientation of the 2 hydrogen atoms and the 2 other pairs of electrons around the central oxygen atom of the molecule (image taken from Ref.[18]). According to the image, it seems that water presents 4 different associating sites. However, some simulations have shown that in the clusters of liquid water, only three sites are bonded per molecule in most of the cases [19]. Although there is still a controversy in literature about the number of sites to be used when modeling water we have decided to use a simple four sites model, as several modeling works done with SAFT [20]-[21] and CPA [22], with the same level of description as the model used here, have confirmed a superior performance of the four-site associating model.

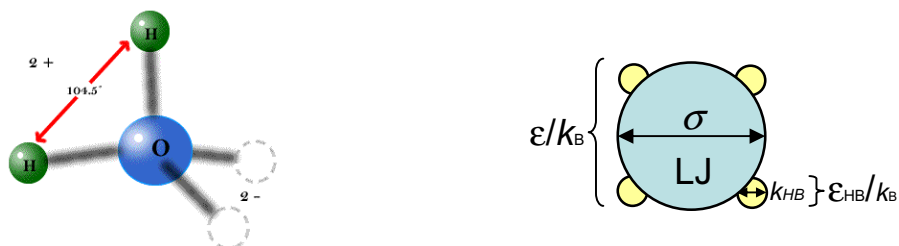


Figure 1. Bidimensional sketch of the model used for water. a) Ball and stick classical sketch (image from reference [18]) b) soft-SAFT model. The big circle represents the LJ center, while the small circles stand for the square-well sites mimicking the associating sites..

The most important features of the water + hydrocarbon mixtures can be defined at a microscopic level: repulsive and dispersive intermolecular forces between atoms or units in the real molecules, covalent-like bonds to form the hydrocarbon chain, and the association bonds due to the formation of hydrogen bonds among the water molecules. Following several other authors we have decided not to explicitly include electrostatic interactions among water molecules; this effect is taken into account in an effective manner through the association molecular potential parameters of water. The water molecules are modeled as a single spherical LJ core, accounting for the repulsive and dispersive forces between different molecules of the fluid, with four embedded off-center square well bonding sites (see Figure 1b). These four sites account for the two electron lone pairs and the two hydrogen sites of the water molecule.

Hydrocarbon molecules are represented as united atoms or sites: each site is assigned parameter values to represent a group of atoms in the molecule of interest, such as CH₃, CH₂ or CH groups. In the soft-SAFT approach these molecules are modeled as *m* LJ segments of equal diameter, σ , and the same dispersive energy, ϵ , bonded tangentially to form the chain.

Results I: Pure compounds

The application of soft-SAFT to any mixture first requires values for the molecular parameters of the pure compounds. These parameters are obtained by fitting to experimental data, usually vapor-liquid equilibrium data. We have followed different approaches for water in this work. First, as with any other molecule, an overall optimization of the parameters for a

wide range of temperature was done. For this purpose, two versions of the equation were used, the original soft-SAFT equation [2] and the crossover version of the equation [3], designed to accurately predict the phase envelope close to and far from the critical region. Results from the calculations are depicted in Figure 2a; temperature data from the critical region down to $T = 400\text{K}$ was used in the optimization. As shown in the graph, both versions of the equation perform equally well in a wide range of temperatures, while, as expected, only crossover soft-SAFT also captures the critical point. Quantitative agreement with experimental data [23] up to 350K is obtained with the crossover soft-SAFT version of the equation. Figure 2b shows these two calculations, but it also includes two more sets: a set obtained by fitting experimental vapor-liquid equilibrium data over a limited range of temperatures ($300\text{--}450\text{K}$) and calculations performed with parameters from Müller and Gubbins [21] with a LJ-SAFT equation of state. Parameters for the different sets are provided in table 1.

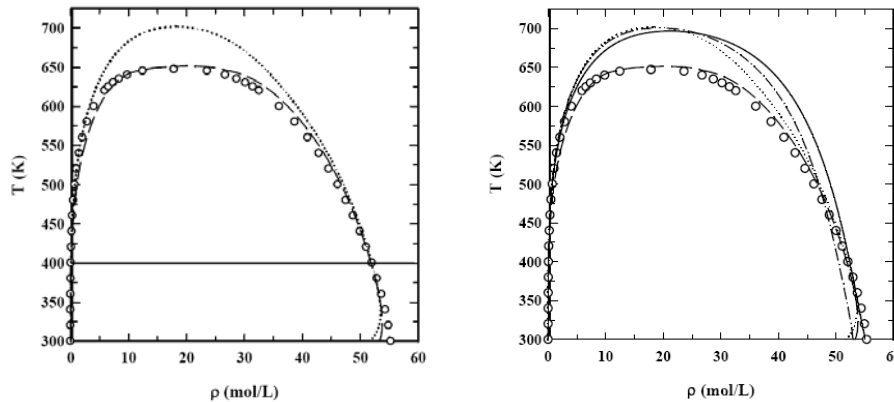


Figure 2: Vapor-liquid equilibrium of water. Symbols represented experimental data from [23], while lines represent different model calculations. Dotted line: calculations with the original soft-SAFT EoS; dashed line calculations with crossover soft-SAFT (using data from the critical point up to 400K); solid line: soft-SAFT calculations optimized in the range $300\text{--}450\text{K}$; dashed and dotted line correspond to the soft-SAFT performance using Müller and Gubbins water parameters [21]. The graph is split in two for clarity purposes

Several comments are in order here: first, the parameters obtained with the global optimization (figure 2a) give unphysical results for liquid densities at near ambient temperatures (below 350K). This is due to the fact that for these values of the energy parameter the reference equation is well outside the range for which it was fitted (the reduced temperature). Since this reference equation is just a fitting to available simulation data, no good extrapolations should be expected outside this range. Second, the parameters provided by Müller and Gubbins give a good description of the vapor phase, while the description of the liquid phase is worse than that obtained with the parameters used with soft-SAFT for global optimization. A final comment: the parameters obtained by carefully fitting the narrow range of temperatures of interest (solid line in figure 2b) give an excellent description of both densities for this range of temperatures, while deviating from experimental results at higher temperatures. Since the mixtures under investigation are found experimentally at these temperatures, these are the parameters used for the mixture study. Note that the crossover version was not used in this case, as the conditions are far away from the critical region (and the crossover equation reduces to the original equation at these conditions).

Table 1. Molecular parameters for a four associating model for water using soft-SAFT with and without a crossover term and different options of optimization. Parameters obtained by Müller and Gubbins are also provided for comparison. See text for details.

Procedure	m	$\sigma(\text{\AA})$	$\varepsilon/k_B(\text{K})$	$\varepsilon_{\text{HB}}/k_B(\text{K})$	$k_{\text{HB}}(\text{\AA}^3)$
Optimized in range (300-450K)	1.000	3.154	365	2932	2388
Global without crossover	1.000	3.137	480	2612	923.2
Global with crossover*	1.000	3.137	458	2501	1037
Müller and Gubbins parameters	1.000	3.190	408.54	2707	2367.7

* $L=1.00$, $\phi=5.0$

Results II: Solubility of selected hydrocarbons in water

We now turn on the prediction of the phase behavior of several water + n-alkane binary mixtures. In particular, the main interest of this work is to check the ability of the soft-SAFT approach for predicting the existence of a minimum in the solubility of hydrocarbons in water at low temperatures. This minimum is observed at approximately 320K in the LLG three-phase line of the water + n-alkane homologous mixtures.

We first studied the water + n-hexane, which can be considered a regular member of the homologous series. A binary energy parameter, $\xi=0.68$, was used to fit the solubility of water in n-hexane, and the same value is used to predict the solubility of n-hexane in water. Figure 3 shows the mutual solubilities of water and n-hexane, as functions of temperature, in a wide range of temperatures, from near the triple point of water to near the upper-critical end-point of the mixture. As can be seen, agreement between theoretical predictions and experimental data taken from the literature is excellent at all temperatures considered. Apart from the obvious agreement between both results in the solubility of water in n-hexane (this property has been fitted during the optimization), it is remarkable the agreement between both data along the solubility curve of n-hexane in water. The soft-SAFT approach is not only able to capture the correct order of magnitude of these solubilities, but also *the minimum of the solubility of n-hexane in water at low temperature*, in excellent agreement with experimental data. To our knowledge, this is the first SAFT approach able to predict quantitatively the existence of this minimum.

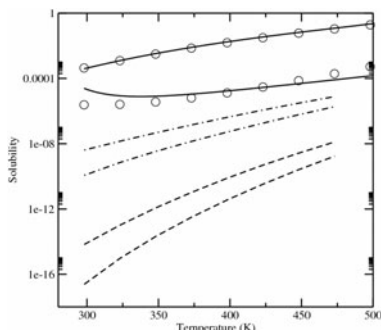


Figure 3: Mutual solubilities of the system n-hexane + water. Circles represent experimental data [24]. The solid lines are soft-SAFT predictions while the dashed and dotted-dashed lines represent, from bottom to top, SAFT 3-site (vdW rule), SAFT 4-site (vdW rule), SAFT 3-site (PHCT) and SAFT 4-site (PHCT) calculations.

The performance of the soft-SAFT equation is also compared (figure 3) with calculations performed with the original SAFT EoS with different water models (three- and four-site models) and two mixing rules: the vdW one-fluid approximation and the PHCT

mixing rules [25]. All of them are able to describe the solubility of water in n-hexane (as expected since this property has been fitted directly to obtain the value of ξ) but they are unable to predict, even qualitatively, the solubility of n-hexane in water.

The binary parameter fitted for the mixture water + n-hexane ($\xi = 0.68$) was used to predict the behavior of the water + methane binary mixture, with no further fitting. This is the only mixture of the series that does not exhibit LLG equilibria, which may be due to the small size of the methane molecule that permits to be dissolved in water. Although the solubility issue of this work is not observed in this mixture, its vapor-liquid equilibrium (at room temperatures) is of crucial interest because of the hydrate formation at low temperatures, which often results in the blockage and shutdown of the gas and oil subsea pipelines. Figure 4 depicts the solubility of water in methane (gas phase) at different temperatures, from 308.11K (close to hydrate formation) up to 477K. As can be seen, the equation is able to predict the behavior of the solubility, as a function of composition, at all temperatures, in excellent agreement with the experimental data taken from the literature.

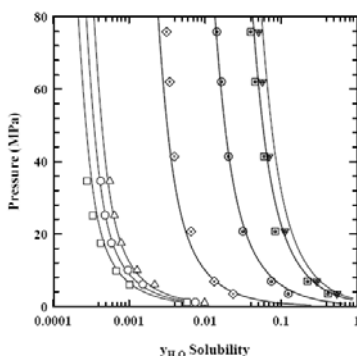


Figure 4: Solubility of water in methane (gas phase) at different isotherms from 308.11K till 477K. Empty squares (308.11K), circles (313.12K) and triangles (318.12K) represent experimental data from reference [26]. Dotted diamonds (366.5K), circles (422.04K), squares (466.5K) and triangles (477.5K) are experimental data from reference [27]. The solid lines are soft-SAFT predictions.

The model has also been checked for the rest of the water + n-alkanes mixtures, from water + methane up to + n-decane. Soft-SAFT is able to predict, without need of any adjustable parameter, the existence of the solubility minimum of n-alkanes in water. However, if a quantitative description of the thermodynamic properties of these mixtures is desired, one binary parameter with a constant value is required to achieve a quantitative agreement with experimental data. We have observed, not shown here, that the value $\xi = 0.68$ (obtained by fitting water in n-hexane) can be used in a transferable way to predict the behavior of the rest of the family mixtures, without any further adjustment.

Conclusions

The soft-SAFT equation of state has been successfully applied to accurately model water + hydrocarbon binary mixtures, including the mutual solubility of water and hydrocarbons. A four-site LJ sphere model was used to describe the phase behavior of pure water. The theoretical predictions were able to provide a quantitative agreement with the experimental data over a wide range of temperatures, although some unphysical results were observed at room temperature. These problems were attributed to the high value of the dispersive energy of water found during the optimization procedure of the molecular parameters. An additional set of soft-SAFT parameters was fitted in a (more reduced) range of temperature, from 300 to 450K. This choice allowed to describing the thermodynamic properties of water in excellent agreement with experimental data in this range. The model

was able to predict the solubility minima of hydrocarbons in water at low temperatures, in excellent agreement with experimental data. The theoretical approach uses only a (temperature-independent) single binary energy parameter to describe the non-idealities of the mixtures. The same value is employed for the whole water + n-alkane homologous series, although only results for methane and n-hexane were shown here. To our knowledge, this is the first time that a theoretical treatment based on the SAFT approach is able to capture the solubility minima of hydrocarbons in water. This successful result is a consequence of the accurate and realistic reference term used in the soft-SAFT equation of state, including the radial distribution function of the reference fluid, used in both the chain and the association terms.

Acknowledgements

We are indebted to Ioannis Economou for several discussions, for encouraging us to perform this work several years ago, and for providing data for comparison. This research has been possible thanks to the financial support received from the Spanish Government (projects PPQ2001-0671, CTQ2004-05985-C02-01, CTQ2005-00296/PPQ and CTQ2008-05370/PPQ) and the Catalan Government (2005SGR-00288). F. Llovell acknowledges a predoctoral FPU grant from the Ministerio de Educación y Ciencia of Spain (MEC). F. J. Blas also acknowledges the financial support from the Spanish Government project FIS2007-66079-C02-02.

References

1. Economou, I. G.; Tsonopoulos, C. *Chem. Eng. Sci.* **1997**, 52, 511.
2. Blas, F.J. and Vega, L.F. *Mol. Phys.* **1997**, 92, 135
3. Llovell, F. ; Pàmies, J.C. and Vega, L.F. *J. Chem. Phys.* **2004**, 121, 10715
4. Pàmies, J.C.; Vega, L. F. *Ind. Eng. Chem. Res.* **2001**, 40, 2532.
5. Johnson, J.K.; Zollweg, J.; Gubbins, K.E., *Mol. Phys.*, **1993**, 78, 591.
6. Wertheim, M.S., *J. Stat. Phys.*, **1984**, 35, 19, *Ibid.*, **1986**, 42, 459, 477.
7. Stell, G. ; Rasaiah, J.C.; Narang, H., *Mol. Phys.*, **1974**, 27, 1393.
8. Gubbins, K.E.; Two, C.H. *Chem. Eng. Sci.*, **1978**, 33, 863.
9. Wilson, K. G. *Phy. Rev. B* **1971**, 4, 3174.
10. Wilson, K. G.; Fisher, M. E. *Phys. Rev. Lett.* **1972**, 28, 240.
11. White, J. A. *Fluid Phase Equilibria* **1992**, 75, 53.
12. Salvino, L. W.; White, J. A. *J. Chem. Phys.* **1992**, 96, 4559.
13. Llovell, F.; Pàmies, J. C.; Vega, L. F. *J. Chem. Phys.* **2004**, 121, 10715.
14. Llovell, F.; Vega, L.F. *J. Phys. Chem. B* **2006**, 110, 1350.
15. Wallqvist A.; Mountain, R. D. *Reviews in Comp. Chem.* **1999**, 13, 183.
16. Jorgensen, W. L.; Tirado-Rives, J. *Proc. Natl. Acad. Sci. USA* **2005**, 102, 6665.
17. Guillot, B. *J. Mol. Liq.* **2002**, 101, 219.
<http://ghs.gresham.k12.or.us/science/ps/sci/ibbio/chem/notes/chpt2>
18. Wei, S.; Shi, Z.; Castelman, A.W Jr. *J. Chem. Phys.* **1991**, 94, 3268.
19. Kraska, T.; Gubbins, K. E. *Ind. Eng. Chem. Res.* **1996**, 35, 4738.
20. Muller, E. A.; Gubbins, K. E. *Ind. Eng. Chem. Res.* **1995**, 34, 3662.
21. Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; von Solms, N.; Stenby, E. H.; *Ind. Eng. Chem. Res.* **2006**, 45, 4855.
22. NIST Chemistry Webbook, <http://webbook.nist.gov/chemistry> (2007)
23. Tsonopoulos, C.; Wilson, G.M. *AIChE J.* **1983**, 29, 990.
24. Economou, I. G.; Donohue, M. D. *Ind. Eng. Chem. Res.* **1992**, 31, 2388.
25. Chapoy, A.; Coquelet, C.; Richon, D. *Fluid Phase Equilib.* **2003**, 214, 101.
26. Yarrison, M.; Cox, K.R.; Chapman, G. *Ind. Eng. Chem. Res.* **2006**, 45, 6770.
- 27.