MUTUAL SOLUBILITIES OF HYDROCARBON-WATER SYSTEMS WITH F-SAC

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ABSTRACT – In this paper, the F-SAC model was extended in order to better represent the very low mutual solubility of hydrocarbons (alkanes, cycloalkanes, alkenes, cycloalkenes and aromatics) and water. Infinite dilution activity coefficient and liquid-liquid equilibrium data were considered. A new parameter for the computation of the water self-association energy was proposed, enabling a better agreement with experimental data in wide temperature ranges. The results were compared with some UNIFAC variants, found in the literature. For the systems studied, the proposed method performed better, including the quantitative representation of the experimentally observed minimum solubility point. None of UNIFAC models tested was capable of predicting such behavior. Finally, the model was used to predict the water solubility in petroleum fractions by using a pseudo-components approach. With this approach, the F-SAC model was capable of satisfactory represent the experimental data.

1. INTRODUCTION

The prediction of simultaneous solubilities of hydrocarbon-water systems is of great importance in refineries and petrochemical plants in the design, control and optimization of products and processes. In addition, it is necessary for modeling and evaluating the environmental impacts of hydrocarbon contaminants and oil spills (Polak and Lu, 1973).

In general, the miscibility of hydrocarbons-water systems is very low, in order of parts per million. Moreover, an interesting behavior of hydrocarbon-water systems is the minimum of hydrocarbon solubility in the water-rich phase, around room temperature (Polak and Lu, 1973; Tsonopoulos, 1999, 2001; Klamt, 2001) while the solubility of water in hydrocarbons increases monotonically with temperature.

In IUPAC-NIST Solubility Data Series, volume 81, the authors compiled in a series of 12 papers the hydrocarbons with water and seawater solubility data for binary systems which appeared in the literature to end of 2002. According to the authors, all experimental data available was critically reviewed and (when possible) evaluated, using a reference data (Maczynzski, 2005).

Several empirical expressions for predicting the mutual solubilities in hydrocarbon-water systems have been proposed in literature – *e.g.* (Polak and Lu, 1973; Huibers and Katritzky, 1998;

Tsonopoulos, 1999, 2001). Although the proposed expressions are useful for determining the solubilities of such systems, a model with a sound theoretical basis is always desirable. For Instance, Oliveira *et. al.* (2007) used the equation of state CPA-EoS to correlate hydrocarbon-water systems in a wide range of temperature and pressure. Very accurate results were observed, however it was noticed that the CPA-EoS was not capable of predicting the LLE minimum of solubility. Klamt (2003) used published data (Tsonopoulos, 1999, 2001) for the analysis of COSMO-RS - no particular solubility data for the systems studied was considered in the COSMO-RS parametrization. Surprisingly, the temperature dependence of the water solubility in various hydrocarbons was reproduced quite well. In the water-rich phase, COSMO-RS was capable of predicting the minimum of solubility, although the calculated and experimental curves disagree by around 40 K.

In the UNIFAC(Do) parametrization of Jakob *et. al.* (2006), the authors tried to correlate different types of data, including VLE and LLE. However, this model usually predicts low activity coefficients, therefore high solubility, for mixtures with quite low miscibility, such as hydrocarbon-water systems. Furthermore, the UNIFAC-type models usually have poor performance when applied in predicting IDAC in mixtures involving very polar components (such as water), since the largest non-idealities occur in the diluted region (Voutsas and Tassios, 2006). This distortion was allowed in the several versions of the model in order to correctly represent the VLE and the occurrence of a miscibility gap of alcohol-water systems (Jakob *et. al.*, 2006). Similar poor performance for aqueous systems was also shown in the studies of Gerber and Soares (2010). Thus, the representation of the mutual solubilities of hydrocarbon-water systems with theoretically sound models is still an interesting challenge in thermodynamics

A more recent alternative for the prediction of hydrocarbon-water mutual solubilities is the F-SAC (Functional-Segment Activity) model. This model was first formulated for non-hydrogen bonding mixtures (Soares and Gerber, 2013) and then extended for mixtures were hydrogen bonds (HB) can form (Soares *et al.*, 2013). In Possani *et. al.* (2014), the model was extended and modified in order to represent simultaneously IDAC, LLE and VLE data for an industrially relevant set of non hydrogen bonding mixtures.

In the present work we have continued the investigation of the F-SAC model, in this case, to simultaneously represent IDAC and LLE data for alkanes, cycloalkanes, alkenes, cycloalkenes and aromatics + water systems. The parameters obtained were then used to predict the water solubility in petroleum fractions by using a pseudo-components approach.

2. THE PROPOSED EXTENSION

In the F-SAC model, the activity coefficients for the liquid phase γ_i are calculated by:

$$\ln\gamma_i = \ln\gamma_i^{comb} + \ln\gamma_i^{res} \tag{1}$$

where $\ln\gamma_i^{comb}$ and $\ln\gamma_i^{res}$ are, respectively, the combinatorial and the residual contributions. The interaction energy for each contact between segments *m* and *n* is given as follows:

$$\Delta W\left(\sigma_m,\sigma_n\right)=\theta\left(T,m,n\right)\frac{\alpha\left(\sigma_m,\sigma_n\right)}{2}+\frac{E^{HB}\left(\sigma_m,\sigma_n,T\right)}{2} \tag{2}$$

where $\theta(T,m,n)$ is an empirical temperature (T) dependence; α is the constant for the misfit energy; and $E^{HB}(\sigma_m,\sigma_n)$ takes into account for hydrogen bond formation.

As it has already been suggested in the original papers (Soares and Gerber, 2013), new effects or parameters need to be incorporated into the model in order to better represent mutual miscibility. Therefore, in this work, a new HB temperature dependence is introduced as follows:

$$E^{HB}=\Delta W^{HB}\left(\sigma_m,\sigma_n\right)\times\exp\left[-\psi_{HB}\left(\sigma_m,\sigma_n\right)\left(T/T^o-1\right)\right] \tag{3}$$

where $\Delta W^{HB}(\sigma_m,\sigma_n)$ is the HB interaction energy at the reference temperature T^o, taken as 323.15 K; $\psi_{HB}(\sigma_m,\sigma_n)$ is the HB temperature correction parameter, here introduced for each HB acceptor-donor segment.

3. RESULTS AND DISCUSSION

In the present work, the F-SAC parameters tables are revised and extended in order to correlate the simultaneous solubility of mixtures containing hydrocarbons and water. The parameter optimization methodology is the same described in the previous F-SAC papers. The parameter estimation was accomplished considering infinite-dilution activity coefficient (IDAC) experimental databases (Gerber and Soares, 2010; Soares, 2011; Gerber and Soares, 2013), containing IDAC data for mixtures of hydrocarbons and hydrocarbons with water. In addition, the liquid-liquid equilibrium data collected from the IUPAC-NIST Solubility Data Series, volume 81, was considered. Only data labeled as “Reliable” or “Tentative” was used; no “Doubtful” data was taken into account.

3.1. Parameter Calibration

The model was calibrated using a local search optimization algorithm which minimizes the absolute average deviation (AAD) for IDAC and LLE experimental data according to the following objective function (OF):

$$OF=AAD_{IDAC}+w\times AAD_{LLE} \tag{4}$$

where w is a weight factor, chosen as 10, as indicated elsewhere (Possani *et. al.*, 2014), with:

$$AAD_{IDAC}=\frac{1}{NP}\sum_i \ln\left|\gamma_{i,\exp}^{\infty}-\gamma_{i,calc}^{\infty}\right| \tag{5}$$

$$AAD_{LLE}=\frac{1}{NP}\sum_i \ln\left|x_{i,\exp}^{\infty}-x_{i,calc}^{\infty}\right| \tag{6}$$

The resulting parameters are shown in Tables 1 and 2. Calculation results using the present modifications are referred hereinafter as F-SAC*.

Table 1 – F-SAC* parameters determined in this work.

Group	$Q_k^+/\text{Å}^2$	$Q_k^-/\text{Å}^2$	$\sigma_k^+/e\,\text{nm}^{-2}$	$\beta_k\times10^6 K$	Subgroup	$R_k/\text{Å}^2$	$Q_k/\text{Å}^2$
C=C	10.83	5.55	0.39	686.13	CH_2=CH	48.16	82.61
					CH=CH	36.86	45.55
					c-CH_2=C	38.52	50.95
					c-CH=CH	36.86	59.61
					CH=C	28.54	13.61
ACH	15.69	4.60	0.25	480.73	ACH	19.26	34.05
					AC	10.89	-0.52
H_2O	30.23	15.11	0.57		H_2O	29.45	45.46

Table 2 – F-SAC* hydrogen bond formation energies for acceptor-donor pairs, optimized in this work.

Donor	Acceptor	$\Delta W^{HB}(\sigma_m,\sigma_n)/kJ\cdot mol^{-1}$	Ψ_{HB}
H_2O	H_2O	5.79	0.42
	ACH	1.95	-0.12

3.2. IDAC Results

In this section, IDAC calculations using the F-SAC* were compared with the UNIFAC-LLE (Magnussen *et. al.*, 1981) model. Figure 1 shows the parity plots for the studied systems.

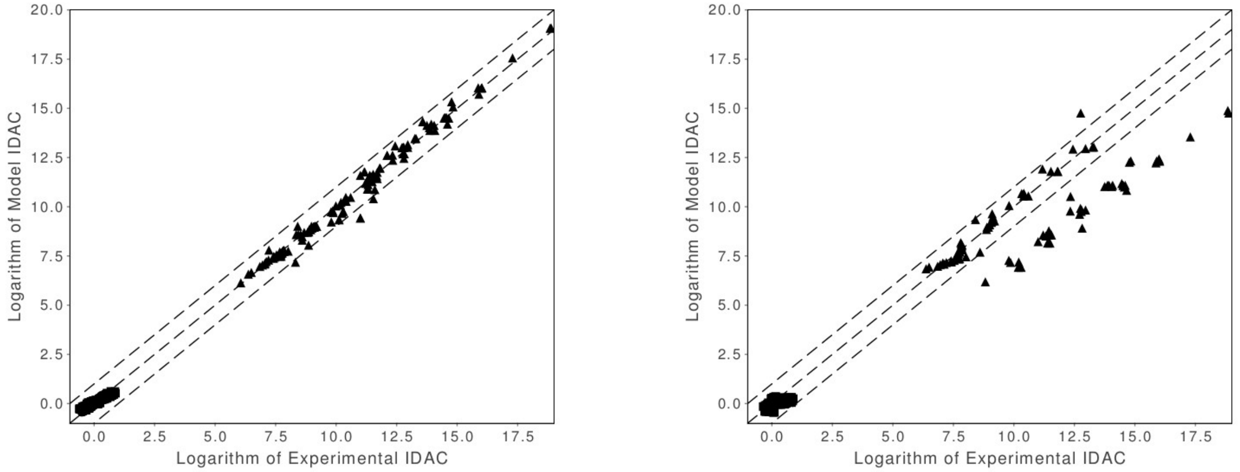
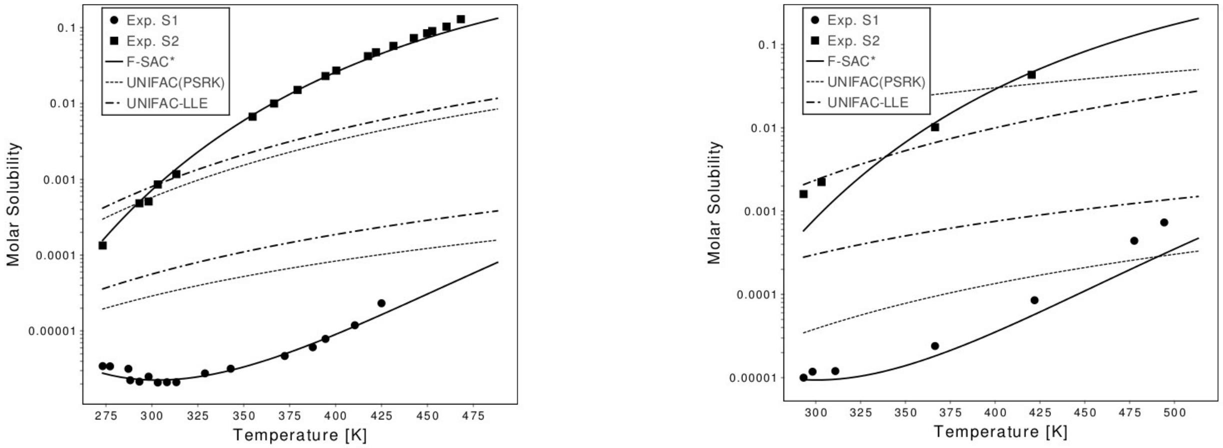


Figure 1 – Experimental versus calculated IDAC for F-SAC* and UNIFAC-LLE, respectively.

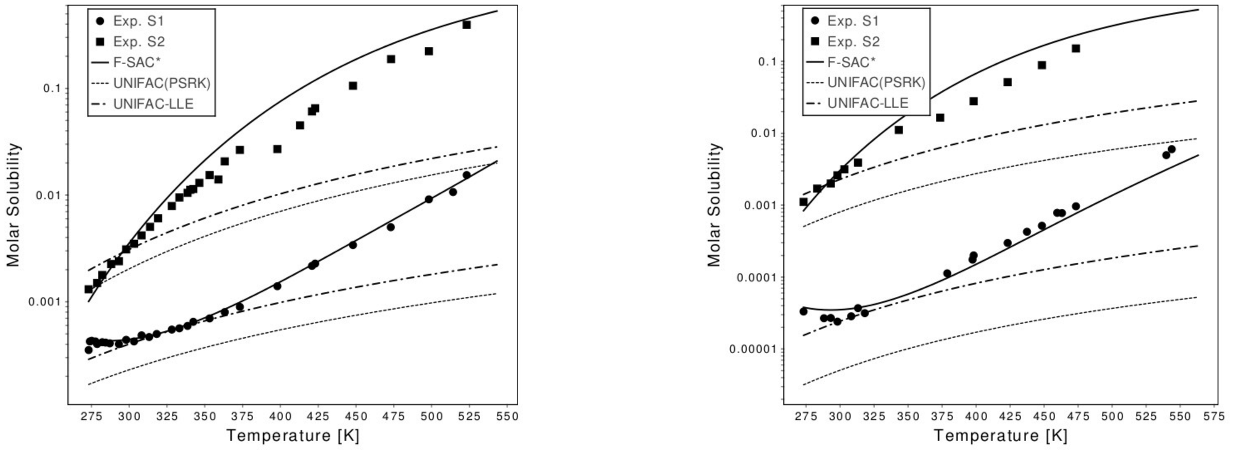
As can be seen in Figure 1, F-SAC performed better, with an AAD_{IDAC} of 0.1179 for F-SAC against 0.6211 for UNIFAC-LLE. The nearly ideal results (ln IDAC approximately zero) are for hydrocarbon-hydrocarbon systems. The higher values of ln IDAC represent hydrocarbon-water systems. Systematic negative deviations (points under the diagonal lines) are observed in UNIFAC-LLE calculations for hydrocarbons in aqueous phase.

3.3. LLE Results

Figure 2 shows some selected LLE results, calculated using F-SAC*, UNIFAC(PSRK) and UNIFAC-LLE. As it can be observed, the F-SAC model has shown a very good agreement with experimental data, with the smaller deviations. Furthermore, it was capable to correctly reproduce the minimum solubility point of hydrocarbons in the water phase. The overall deviations (AAD_{LLE}) are 0.314 for F-SAC against 1.585 and 1.393 for UNIFAC(PSRK) and UNIFAC-LLE.



(a) n-hexane – water (b) 1-hexene – water



(c) benzene – water (d) m-xylene – water

Figure 2 – LLE results for hydrocarbon-water systems.

3.3. Extension for Oil Fractions

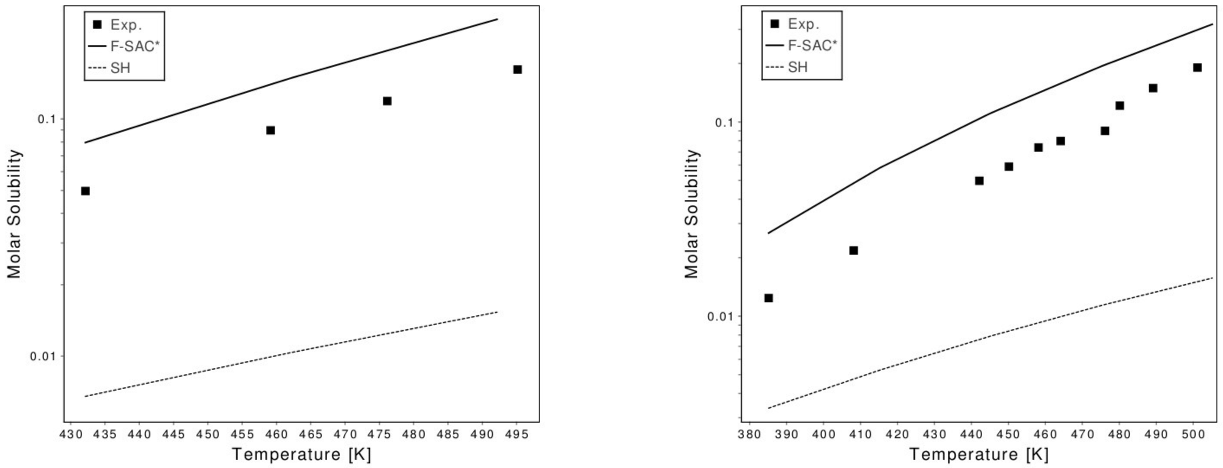
In this section, a pseudo-components approach was used to predict the water solubility in oil fractions using F-SAC*. As an initial attempt, each pseudo-component (average molar mass: M_{pseudo}) was considered to be a linear alkane: $CH_3-CH_2-\cdots-CH_2-CH_3$. The number of CH_3 subgroups is $\nu_{CH3}=2$, because these subgroups appear only in the molecule's terminals. Thus, by a mass balance the number of CH_2 subgroups is given simply by:

$$\nu_{CH2}=\frac{\left(M_{pseudo}-n_{CH3}\times M_{CH3}\right)}{M_{CH2}} \tag{7}$$

where $M_{CH3}\simeq 15\,g/mol$ and $M_{CH2}\simeq 14\,g/mol$. The average molar mass for each pseudo-component was obtained by (Riazi, 2005):

$$M_{pseudo}=\left[\frac{6.98291-\ln\left(1070-T_b\right)}{0.02013}\right]^{3/2} \tag{8}$$

where T_b is the pseudo-component average boiling point. The pseudo-component average boiling point was obtained using the oil characterization package available in the iiSE process simulator (VRTech, 2014). The oil fractions chosen to test the proposed methodology were the Naphtha and Kerosene of Griswold and Kasch (1942). Figure 3 shows the results calculated using F-SAC* and Scatchard – Hilderbrand (SH) Gibbs free energy models. Both models were combined with the SRK equation of state by the SCMR - Self Consistent Mixing Rule (Staudt and Soares, 2012). The combination of the activity models with an equation of state was mandatory for proper representation of these systems, since the high-temperature LLE results were obtained in pressures up to 60 bar.



(a) naphtha – water (b) kerosene – water

Figure 3 – LLE results for oil-water systems.

Actually, all results in Figure 3 were obtained by simulating a three-phase flash within the iiSE simulator. Experimental temperature and pressure (not shown) were specified in the simulation. If the simulation results at the experimental pressure also produced a vapor phase then the pressure was slightly increased in the simulation in order to get a genuine LLE result. As can be seen in Fig. 3, a satisfactory agreement of F-SAC* predictions with experimental data was obtained for the systems tested. This is particularly interesting because no oil data were used in the parametrization of the suggested model and a very crude approximation (only linear akanes) was assumed.

4. CONCLUSIONS

In this work, the F-SAC model was extended in order to better represent the very low mutual solubility of hydrocarbons and water in wide temperature ranges. This was accomplished by the addition of a new parameter, leading to temperature dependent hydrogen bond association energies. The IUPAC-NIST Solubility Data Series, volume 81, was used to collect liquid-liquid equilibrium (LLE) experimental data. The model's calibration was performed using, simultaneously, infinite dilution activity coefficient (collected in previous works) and the IUPAC-NIST binary LLE data. The extended model results were compared with some UNIFAC parametrizations freely available in the literature. A good agreement with all experimental data was obtained using the suggested model. Further, it was possible to correctly represent the temperature behavior of hydrocarbons in the water-rich phase, including the correct prediction of the solubility minimum. Finally, the model was used to compute the solubilities of water in petroleum fractions using a pseudo-components approach. As an initial attempt a very simple methodology for describing the pseudo-components was used and good results were already obtained. Currently, a more sophisticated representation is being elaborated by taking into account the differences between n-paraffins, isoparaffins, naphtenes, and aromatics.

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