

Comparison of Models for Determination of Supercritical Fluids Solubility in Heavy Oils

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Abstract

In this work a comparison between a simple model, cubic equations of state and SAFT model to calculate supercritical fluids solubility in heavy oils is presented. The first thermodynamic model is based on activity coefficient which is calculated by a group-contribution method (UNIFAC). The results were compared with experimental and convex – body SAFT model represented better the solubility data.

Keywords: supercritical fluids solubility, thermodynamic models, UNIFAC model, SAFT model, cubic equation of state

1. Introduction

Systems containing gases and oils are frequently found in great areas of chemical engineering studies. In the petroleum industry plenty of steps can be pointed out in which the direct contact of the components shows a considerable relevance. From the petroleum generation until its commercialization, several steps, as its migration to the underground reservoirs, exploration, transport and storage, have an intensive contact not only of the gases originally present with the oil fractions, but also of those injected gases for a better use of the reservoir.

A correct characterization of the gas solubilities in the oil fractions has its own importance for an accurate determination of the behavior between the presented phases in some operations conditions. However, those conditions can vary according to each reservoir type or process and its detailed study becomes essential.

Some models are presented in the literature to determine the phase equilibrium of the studied systems operating at low experimental pressure. However, supercritical behavior of some gases is observed, where the carbon dioxide is commonly presented in those kinds of systems. For the characterization of this kind of equilibrium, a very little quantity of models is available in the literature.

The aim of the present work is to compare some models to calculate the supercritical fluids solubilities in heavy oil fractions. A simple model (M2) is presented and its results compared with the Prausnitz and Shair correlation (M1), the Peng-Robinson equation of state with one (M3) and two (M4) parameters estimated in

the quadratic mixing rule, the conventional SAFT model (M5) and the SAFT convex body model (M6).

In the literature there are lots of experimental works showing the gas (carbon dioxide, nitrogen, methane) solubility in oil fractions represented by a heavy hydrocarbon (n-octane, n-decane, n-hexadecane) at elevated conditions. Three systems presented in the literature ($\text{CO}_2 + \text{C}_{10}\text{H}_{22}$, $\text{CO}_2 + \text{C}_{16}\text{H}_{34}$, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$) were chosen to verify the applicability of each described model.

2. Thermodynamic Modeling

In the development of thermodynamic models to determine the phase equilibria of gas - oil systems, numerous works are presented in the literature and some works can be pointed out: Horstman et al. (2000), Kontogeorgis et al. (1996), Voutsas et al. (2000), Islam et al. (2000), Passarello et al. (2000), Gross and Sadowski (2001), Li et al. (2001), Haruki et al. (2001), Yang and Zhong (2001), Ahlers and Gmehling (2002a,b), Nasrifar and Moshfeghian (2002a,b), Duan and Sun (2003), Solms et al. (2003), Polishuk et al. (2003a,b), Ghosh et al. (2003), Diamond and Akinfiev (2003), Garcia et al. (2004), Polishuk et al. (2004), Sánchez et al. (2004), Gao et al. (2004), Fu et al. (2006), Ferrando et al. (2006), Voutsas et al. (2006), Falabella et al. (2006), Shimoyama et al. (2006), Collinet and Gmehling (2006), Hashemi et al. (2006), Mao and Duan (2006) and Folas et al. (2006).

To determine the vapor liquid equilibrium, one starts from the isofugacity criteria considering the non ideality only in the liquid phase.

The fugacity for a substance i presented in the liquid phase can be described by Eq. (1) and for a substance in the vapor phase, by Eq. (2).

$$f_i^L = x_i \gamma_i f_i^{ref} \quad (1)$$

$$f_i^V = y_i \phi_i P \quad (2)$$

As the vapor phase behavior had been considered ideal, Eq. (2) reduces to Eq. (3).

$$f_i^V = y_i P \quad (3)$$

Applying the expressions for the fugacities of the substances in each phase and knowing that the product $y_i P$ corresponds to the partial pressure of each substance, one can do the sum of these partial pressures and obtains Eq. (4) to represent the total pressure of the system in the vapor liquid equilibria.

$$P = x_{\text{CO}_2} \gamma_{\text{CO}_2} f_{\text{CO}_2}^{ref} + x_{\text{oil}} \gamma_{\text{oil}} f_{\text{oil}}^{ref} \quad (4)$$

The UNIFAC group contribution model modified by Hansen et al (1992) was chosen to represent the non ideality of the petroleum phase due to that the interaction functional group parameters are available in the literature.

In general, a number of works use the reference state as being the fugacity of a pure liquid in the pressure and temperature of the system. For the oil, this approach was adopted and its fugacity calculated through the oil vapor pressure. However, in the usual conditions of reservoirs and in the operating conditions involving petroleum, carbon dioxide has a supercritical behavior and the correlation proposed by Prausnitz and Shair (1961,1999) can be used to describe its hypothetical reference fugacity as shown in Eq. (5) below. So, this model incorporating this correlation in the fugacity reference expression was called as model (M1).

$$\ln(f_{CO_2}^{ref} / P_c) = 7.81 - 8.06 / T_r - 2.94 \ln T_r \quad (5)$$

3. Results and discussions

Experimental data for supercritical carbon dioxide solubility in heavy oil (n-decane) from Gallegos et al. (2006) were used to evaluate M1. Table 1 shows the pure component properties and the Antoine constants for Eq. (6).

Table 1. Pure component properties.

Properties	Substance				Reference
	CO ₂	CH ₄	C ₁₀ H ₂₂	C ₁₆ H ₃₄	
Molecular Weight	44.01	16.03	142.286	226.45	Reid et al. (1977)
Critical Pressure (bar)	73.7646	45.5	21.0756	14.01	
Critical Temperature (K)	304.2	190.6	617.6	720.6	
Acentric factor	0.225	0.008	0.490	0.7471	
A	-	-	16.0114	16.1841	
B	-	-	3456.80	4214.91	
C	-	-	-78.67	-118.7	

$$\ln P_i^{vap} (mmHg) = A - B / (T(K) + C) \quad (6)$$

From the first results, it was possible to observe the existence of a constant deviation factor in the results obtained by the Prausnitz and Shair (1961,1999) correlation, model M1. Multiplying the reference state fugacity by a unique factor (F), the calculated values from experimental data showed a satisfactory proximity to the experimental data. Thus, a new equation to calculate the vapor liquid equilibrium is presented in Eq. (7) as shown.

$$P = x_{CO_2} \gamma_{CO_2} f_{CO_2}^{ref} F + x_{oil} \gamma_{oil} f_{oil}^{ref} \quad (7)$$

For each temperature, a factor F was obtained which adjusts the calculated values to the experimental data. With these values F, new parameters (PA= 26.5571, PB= -26.5434, PC= -19.8052) were obtained for reference fugacity through Eq. (8). Incorporating this new expression in Eq. (4), the second model (M2) is developed.

$$\ln(f_{CO_2}^{ref} / P_c) = PA + PB / T_r + PC \ln T_r \quad (8)$$

Table 2 presents the pressure (DP) and the vapor phase compositions (DY) deviations obtained using models M1 and M2 for characterization of the vapor liquid equilibrium for the binary system CO₂ + decane, where T1 represents the temperature of 319.11 K, T2, 344.74 K and T3, 372.94 K.

Table 2. First results.

Temperatures	M2				M1			
	DP (bar)	DP (%)	DY (-)	DY (%)	DP (bar)	DP (%)	DY (-)	DY (%)
T1 = 319.11 K	4.36	5.99	0.0050	0.51	18.61	28.05	0.0050	0.51
T2 = 344.74 K	2.29	3.00	0.0160	1.11	24.54	27.25	0.0160	1.11
T3 = 372.94 K	5.99	6.79	0.0277	1.86	22.53	20.68	0.0275	1.84

Analyzing the results presented in Table2, the vapor phase deviations obtained with model M2 didn't present any significant difference from those obtained with model M1. However, the pressure deviations calculated by model M2 were sufficiently reduced in comparison with the calculate values with model M1.

Then, the performance of these two described models, M1 and M2, were compared with other four thermodynamic models: Peng-Robinson with one (M3) and two parameters (M4); conventional SAFT model (M5) and convex – body SAFT model (M6) proposed by Pfohl and Brunner (1998). For these calculations the software Phase Equilibria (PE) developed in Professor Brunner's research group at the Technical University of Hamburg-Harburg (2000) was used, but some differences in the calculations were observed and presented in Table 3. In the first column, it is shown the models used, in the second the kind of calculations realized for each model and in the last one the respective objective functions (FOBJ).

Table 3. Differences observed in each calculation.

Model	Kind of calculations	FOBJ
M1 M2	$P = x_{gas} \gamma_{gas} f_{gas}^{ref} + x_{oil} \gamma_{oil} P_{oil}^{vap}$	$\sum_{i=1}^{NP} \left(\frac{P^{exp} - P^{calc}}{P^{exp}} \right)^2 + \sum_{i=1}^{NP} \left(\frac{y^{exp} - y^{calc}}{y^{exp}} \right)^2$
M3 M4 M5 M6	$y_{gas} = \frac{x_{gas} \phi_{gas}^L}{\phi_{gas}^V}; x_{oil} = \frac{y_{oil} \phi_{oil}^V}{\phi_{oil}^L}$	$\sqrt{\frac{1}{NP} \sum_{i=1}^{NP} \left(\frac{\xi^{exp} - \xi^{calc}}{\xi^{exp}} \right)^2}$, where ξ = molar fractions

Table 4 presents absolute [DY(ABS)] and relative deviations [DY(REL)] in the vapor molar fraction calculated with the six presented models for the experimental data obtained from Reamer et al. (1963) for the CO₂ + C₁₀H₂₂ system, Sebastian et al.

(1980) for the CO₂ + C₁₆H₃₄ system and Lin et al. (1980) for the CH₄ + C₁₆H₃₄ system. The absolute deviations [DY(ABS)] were calculated according to Eq. (9) and the relative deviations [DY(REL)%] from Eq. (10). In Table 5 is presented the values of the parameters obtained for each model.

$$DY(ABS) = \frac{1}{NP} \sum_{i=1}^{NP} |y_i^{\text{exp}} - y_i^{\text{calc}}| \quad (9)$$

$$DY(REL)\% = \frac{1}{NP} \sum_{i=1}^{NP} \frac{|y_i^{\text{exp}} - y_i^{\text{calc}}|}{y_i^{\text{exp}}} * 100 \quad (10)$$

In order to illustrate these results, Figure 1 shows a P-x plot and Figure 2 a P-y plot for CO₂ + C₁₀H₂₂ system at 410.93 K, where the points represent the experimental data and the solid lines the calculated values for each model.

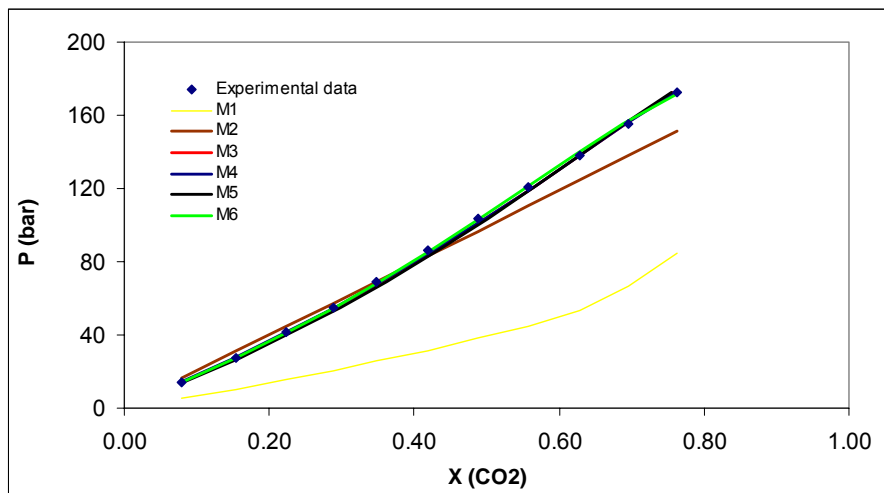
The results show that convex – body SAFT model represent vapor molar fraction better than other models, however, the parameters obtained using PE software were in different way of the parameters obtained to M2 model, as can be seen in Table 3.

Table 4. Absolute and relative deviations.

Systems	T(K)	NP	M1		M2		M3		M4		M5		M6	
			DY	DY	DY	DY	DY	DY	DY	DY	DY	DY	DY	DY
			(ABS)	(REL) %	(ABS)	(REL) %	(ABS)	(REL) %	(ABS)	(REL) %	(ABS)	(REL) %	(ABS)	(REL) %
CO ₂ + C ₁₀ H ₂₂ Reamer et al. (1963)	277.6	11	9.52E-05	0.0095	8.58E-05	0.0086	2.97E-05	0.0030	1.04E-04	0.0104	NC	NC	6.76E-05	0.0068
	310.9	11	8.33E-04	0.0738	7.07E-04	0.0707	5.41E-04	0.0541	5.25E-04	0.0525	NC	NC	4.25E-04	0.0425
	344.3	8	5.82E-03	0.4725	4.62E-03	0.4668	5.27E-03	0.5717	2.60E-03	0.2628	8.50E-04	0.0861	2.30E-03	0.2331
	377.6	10	1.54E-02	1.0946	1.07E-02	1.0882	4.17E-03	0.4400	3.90E-03	0.3978	1.51E-03	0.1529	3.34E-03	0.3425
	410.9	11	3.35E-02	2.0206	1.97E-02	2.0345	5.49E-03	0.5640	5.94E-03	0.6109	4.72E-03	0.4882	3.16E-03	0.3297
	444.3	11	6.69E-02	3.5215	3.44E-02	3.6282	7.03E-03	0.7374	7.34E-03	0.7696	8.30E-03	0.8817	2.97E-03	0.3164
	477.6	11	1.25E-01	6.4482	4.83E-02	5.3714	1.12E-02	1.2235	1.15E-02	1.2623	1.72E-02	1.9440	5.91E-03	0.6735
	510.9	9	2.37E-01	9.9891	9.29E-02	11.1466	1.21E-02	1.4626	1.09E-02	1.3355	2.56E-02	3.2632	4.23E-02	4.8435
CO ₂ + C ₁₆ H ₃₄ Sebastian et al. (1980)	463.1	4	3.37E-03	0.3383	2.83E-03	0.2839	4.62E-04	0.0464	5.24E-04	0.0526	NC	NC	7.89E-04	0.0793
	542.9	4	2.42E-02	2.1576	1.31E-02	1.3547	5.92E-03	0.6109	4.01E-03	0.4139	9.81E-03	1.0112	7.89E-04	0.2039
	623.6	4	1.35E-01	13.2435	6.36E-02	7.5488	1.79E-02	2.1410	1.26E-02	1.5124	5.92E-03	0.7210	2.32E-02	2.6455
	663.8	4	3.61E-01	32.9632	1.27E-01	18.2052	2.62E-02	3.8774	1.48E-02	2.2781	NC	NC	3.46E-02	4.9622
CH ₄ + C ₁₆ H ₃₄ Lin et al. (1980)	462.5	7	3.44E-03	0.3459	3.45E-03	0.3473	1.90E-03	0.1914	8.92E-04	0.0896	1.29E-03	0.1297	2.85E-04	0.0286
	542.7	7	2.18E-02	1.8844	1.79E-02	1.8393	4.98E-03	0.5116	1.37E-03	0.1408	2.08E-03	0.2133	4.70E-04	0.0483
	623.7	7	1.09E-01	10.0000	7.72E-02	8.8398	1.29E-02	1.4916	1.93E-02	2.2150	7.85E-03	0.9192	8.23E-03	0.9555
	703.6	3	6.14E-01	87.5570	1.22E-01	26.6611	4.49E-02	10.6565	6.21E-02	14.9714	1.15E-01	20.9079	2.15E-01	46.3352

Table 5. Parameters obtained for each model.

Systems	T(K)	M2			M3	M4		M5		M6	
		PA	PB	PC	kij	kij	lij	kij	lij	kij	lij
CO ₂ + C ₁₀ H ₂₂ Reamer et al. (1963)	277.59	35.7728	-35.0858	-26.0941	0.1219	0.1210	-0.0035	-	-	0.1904	-0.0059
	310.93	27.7386	-27.6387	-20.6115	0.0988	0.1114	0.0107	-	-	0.1881	0.0100
	344.26	26.1136	-26.1324	-19.5026	0.0973	0.0930	-0.0168	0.1683	-0.0435	0.1947	0.0231
	377.59	26.0563	-26.0793	-19.4635	0.1001	0.0968	-0.0091	0.1741	-0.0035	0.1990	0.0352
	410.93	26.8781	-26.8411	-20.0243	0.1023	0.1006	-0.0038	0.1763	0.0083	0.1989	0.0595
	444.26	28.3599	-28.2146	-21.0355	0.1069	0.1058	-0.0020	0.1784	0.0300	0.1904	0.1068
	477.59	26.0681	-26.0902	-19.4715	0.1149	0.1126	-0.0057	0.1712	0.0775	0.1678	0.1897
	510.93	33.4410	-32.9244	-24.5029	0.1471	0.1409	-0.0069	0.1565	0.1603	0.1692	0.1580
CO ₂ + C ₁₆ H ₃₄ Sebastian et al. (1980)	463.05	-4.8529	6.3758	3.7874	0.0474	0.1040	0.0206	-	-	0.1614	0.1115
	542.85	-5.0020	6.6613	3.9726	0.0596	0.1424	0.0305	-0.1038	0.5230	0.1638	0.1733
	623.55	-4.8541	6.3782	3.7889	0.0850	0.2169	0.0318	0.0293	0.5215	0.0572	0.4690
	663.75	-4.6254	5.9403	3.5047	0.2529	0.3659	0.0504	-	-	0.0445	0.5313
CH ₄ + C ₁₆ H ₃₄ Lin et al. (1980)	462.45	10.5397	-10.6179	-4.8129	0.0257	0.0786	0.0250	0.1144	0.1319	0.1008	0.1264
	542.65	10.7562	-10.7983	-4.8845	0.0654	0.1243	0.0372	0.1279	0.1665	0.1066	0.1642
	623.65	10.6208	-10.6854	-4.8397	0.1377	0.0765	-0.0301	0.0154	0.3647	-0.0382	0.3968
	703.55	8.1795	-8.6508	-4.0331	0.6405	0.1485	-0.2203	-0.1764	-0.0556	-0.1615	-0.2726

**Figure 1.** P-x plot for CO₂ + C₁₀H₂₂ system at 410.93 K.

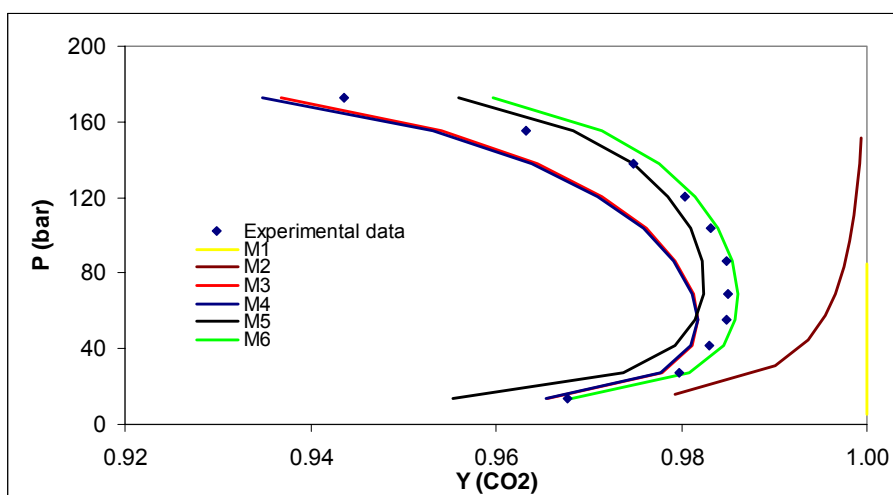


Figure 2. P-y plot for $\text{CO}_2 + \text{C}_{10}\text{H}_{22}$ system at 410.93 K.

4. Conclusions

The conclusion of this work is that convex – body SAFT model showed better results in most of temperatures for each system studied. The next step of this research is to develop a software to compare all of the models with the same objective function. We believe that the parameters obtained via PE software will not give so good results when used to calculate bubble point, as model based on Prausnitz and Shair approach, model M2.

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Nomenclature

ABS – absolute
PA – parameter A
PB – parameter B
PC – parameter C
f – fugacity
F – constant factor
NC – not converged
P – pressure
REL – relative
T – temperature
x – molar fraction in the liquid phase
y – molar fraction in the vapor phase

Greek letters

γ – activity coefficient
 ϕ – fugacity coefficient

Subscripts

i – component i
c – critical state
r – reduced

Superscripts

L – liquid phase
ref – reference
V – vapor phase
vap – vapor

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