

A Thermodynamic Model to Calculate the Solubilities of Heavy Oils in Supercritical Carbon Dioxide

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Over the past few years, significant interest has been expressed in a separation concept wherein a condensed phase is contacted with a supercritical fluid phase in a solvent extraction process, which is the basis for several industrial processes, such as the petroleum refining. The thermodynamic formulations for correlating and predicting phase equilibrium behavior in the supercritical fluid region are in a crescent development as can be found in several works in the literature. So, there is a frequently necessity for a correct characterization of the phase behavior of this kind of systems, calculating the solubilities of heavy oils in the supercritical fluids. The aim of this work is to present a thermodynamic model to correlate and predict the experimental data available in the literature for two selected systems formed by supercritical carbon dioxide with decane and hexadecane. This model was based on the Peng – Robinson equation of state and two different mixing rules, Heideman and Kokal (HK) and LCVM, were tested. The results show a satisfactory characterization of the phase behavior of the selected systems.

Introduction

The extraction process with supercritical fluids is considered an alternative technology in the conventional processes of physical separations. Substances, like supercritical carbon dioxide, are frequently used in this kind of processes, since they have characteristics as ideal conditions of inert solvents, gaseous in the normal conditions, non-toxic, non-inflammable, non aggressive to the environment, low critical temperatures, and low costs. This technique is considered attractive, mainly in the atmosphere protection and product quality, free of residues and doesn't degrade the extract. In this kind of process can be pointed out the facility of solute recovery, the solvent recovery by a simple modification on the pressure or temperature and the possibility to select the direction of the separation through the correct choice for the thermodynamics conditions.

In the petroleum refine, there is a heavy fraction of its processing which contains an elevated aggregate value. So, it is very interesting to apply these extraction processes with supercritical fluids to obtain a better production of some interesting products. Moreover, others examples in this industry can be mentioned as some studies on asphaltene that achieved considerable attention in the last few decades due to the increase of the raw heavy oil reserves and consequent reduction of the light oil reserves. It can be observed from lots of available works in literature the ROSE (Residuum Oil Supercritical Extraction) process as the main technology of petroleum desasphalting.

The supercritical fluid extraction presents a thermodynamic equilibrium at elevated pressures. The thermodynamic modeling using equations of state is very important to do a correct characterization of the phase equilibrium of these systems. Therefore, the solubility determination of oils in supercritical fluids has an extreme importance and applicability for the areas which contain these heavy oils systems.

Thus, the objective of the present work is to develop a thermodynamic model based on Peng-Robinson equation of state with two different mixing rules, Heideman and Kokal (HK) and LCVM, to determine the solubility of two heavy hydrocarbons, decane and hexadecane, in supercritical carbon dioxide, characterizing these phase behaviors.

Thermodynamic Modeling

In the development of thermodynamic models to determine the phase equilibria (PE) of gas – oil systems, numerous works are presented in the literature and those ones more recent are shown next: Horstman et al. [1], Kontogeorgis et al. [2], Voutsas et al. [3], Islam et al. [4], Passarello et al. [5], Gross and Sadowski [6], Li et al. [7], Haruki et al. [8], Yang and Zhong [9], Ahlers and Gmehling [10,11], Nasrifar and Moshfeghian [12,13], Duan and Sun [14], Solms et al. [15], Polishuk et al. [16,17], Ghosh et al. [18], Diamond and Akinfiyev [19], Garcia et al. [20], Polishuk et al. [21], Sánchez et al. [22], Gao et. [23], Fu et al. [24], Ferrando et al. [25], Voutsas et al. [26], Falabella et al. [27], Shimoyama et al. [28], Collinet and Gmehling [29], Hashemi et al. [30], Mao and Duan [31] and Folas et al. [32].

In the present work, the non ideality situation was considered in both phases (liquid and vapor), incorporating this deviation in the fugacity coefficients calculus for the substances presented.

To determine the vapor liquid Equilibria (VLE), one starts from the chemical potential equality and from the classical thermodynamics, one obtains the equality for the fugacities of a component i presented in both phases. The fugacity of a substance i presented in the liquid phase can be expressed by equation (1) and for a substance in the vapor phase, by equation (2) as shown bellow, where ϕ_i represent the fugacity coefficients.

$$f_i^L = x_i \phi_i^L \quad (1)$$

$$f_i^V = x_i \phi_i^V \quad (2)$$

Applying the expressions for the fugacities of the substances in each phase in the fugacity equality mentioned earlier, one obtains the expression for the bubble point calculation as show in equation (3).

$$x_i \phi_i^L = y_i \phi_i^V \quad (3)$$

The equation of state proposed by Peng and Robinson (PR) [33] was applied to calculate the fugacity coefficients of the substances in each phase as can be shown in equation (4) for a mixture containing k components and its original mixing rule, van der Waals, is represented by equations (5) and (6).

$$\ln \frac{\phi_i}{x_i P} = \frac{b_k}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_i x_i a_{ik}}{a} - \frac{b_k}{b} \right) * \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (4)$$

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

A different mixing rule was incorporating to the PR equation and compared to the original one. This mixing rule, called LCVM, was proposed by Boukouvalas et al. [34] and was created by a linear combination of the Huron – Vidal [35] and MHV1 [36] mixing rules. The LCVM mixing rule can be represent by equation (7), where λ is a parameter to be optimize, which ranges from zero to one, and G^E represents a free excess energy model to be incorporated. In this study the UNIQUAC model was applied to represent these calculations for G^E and its parameters (a_{12} and a_{21}) were estimated.

$$\alpha = \left(\frac{\lambda}{0.623} - \frac{1-\lambda}{0.52} \right) \frac{G^E}{RT} - \frac{1-\lambda}{0.52} \sum_i x_i \ln \frac{b}{b_i} + \sum_i x_i \alpha_i \quad (7)$$

The second model proposed to calculate the VLE of this kind of system was developed by Heideman and Kokal [37] which incorporates a free excess energy model in the mixing rule applied in the PR equation of state. The final expression to calculate the fugacity coefficients is represented in equation (8). The UNIQUAC model was applied to represent the G^E and the expression for α is expressed by equation (9).

$$\ln \phi_i = \ln \left(\frac{V}{V-b} \right) + \frac{b_i}{V-b} - \frac{ab_iV}{(V+2.41b)(V-0.41b)} - \ln \left(\frac{PV}{RT} \right) - \left(\frac{b}{V} \right) g \left(\frac{b}{V} \right) \left[\frac{\partial(n\alpha)}{\partial n_i} \right]_{T,n_j} \quad (8)$$

$$\alpha_i = \frac{a_i}{b_i RT} \quad (9)$$

Results and Discussion

In order to compare the three presented models (PR-vdW, PR-LCVM and PR-HK), experimental data available in the literature for the systems carbon dioxide + decane and carbon dioxide + hexadecane were used to calculate the VLE. Table 1 represents a resume from the experimental data with its references and ranges of experimental conditions applied in the present work.

Table 1: Experimental data used in this work.

System	Reference	Number of points	T (K)	P (bar)
CO ₂ + decane	Gallegos et al. [38]	29	319.11 – 372.94	34.85 – 160.6
	Nagarajan et al. [39]	44	344.3 – 377.6	63.85 – 164.6
	Sebastian et al. [40]	16	462.55 – 583.65	19.62 – 51.07
CO ₂ + hexadecane	Spee et al. [41]	16	393.2	101 – 256
	Breman et al. [42]	43	305.7 – 512.3	12.42 – 32.92
	Sebastian et al. [40]	16	462.55 – 663.75	20.06 – 50.66

Table 2 shows the pure component properties of each substance presented.

Table 2: Pure component properties.

Properties	Substance			Reference
	CO ₂	C ₁₀ H ₂₂	C ₁₆ H ₃₄	
Molecular Weight	44.01	142.285	226.446	[43]
Critical Pressure (bar)	73.74	21.10	14.00	
Critical Temperature (K)	304.12	617.70	723.00	
Acentric factor	0.225	0.490	0.718	

Table 3 represents all the results obtained in the modeling of the studied experimental data, where DP and DY represent the deviation in pressure and in the molar fraction of the vapor phase calculations, respectively.

Table 3: Results.

Systems	Equations	PR-OR			PR-LCVM			PR-HK		
CO ₂ + C ₁₀ H ₂₂	References	[38]	[39]	[40]	[38]	[39]	[40]	[38]	[39]	[40]
	DP (%)	2.54	1.83	2.67	9.71	10.64	4.98	13.28	4.12	1.90
	DY	0.0025	0.0043	0.1125	0.0082	0.0235	0.4615	0.0713	0.1722	0.7959
CO ₂ + C ₁₆ H ₃₄	References	[42]	[41]	[40]	[42]	[41]	[40]	[42]	[41]	[40]
	DP (%)	1.98	1.88	11.50	12.02	1.72	7.81	107.35	11.35	1.77
	DY	0.0029	0.4098	0.2850	0.0040	0.2657	0.6992	0.0015	0.1405	0.8034

Table 4 shows the final value for the parameters of each equation. It is important to be noticed that in the first equation (PR-OR) only the binary interaction parameter of the mixing rule (k_{ij}) was estimated; in the second one (PR-LCVM) the λ parameter from the mixing rule and the binary interaction parameters from the UNIQUAC model (a_{12} and a_{21}) were estimated; and in the third equation (PR-HK) only the binary interaction parameters from the UNIQUAC model were estimated.

Table 4: Final parameters for each equation.

Systems	Equation	PR-OR		
CO ₂ + C ₁₀ H ₂₂	References	[38]	[39]	[40]
	k_{ij}	0.105580	0.096586	0.120625
CO ₂ + C ₁₆ H ₃₄	References	[42]	[41]	[40]
	k_{ij}	0.113062	0.086250	0.290806
Systems	Equation	PR-LCVM		
CO ₂ + C ₁₀ H ₂₂	References	[38]	[39]	[40]
	Λ	0.466365	0.501793	0.485086
	a_{12}	888.62	910.11	1401.71
	a_{21}	-888.69	-910.14	-1398.11
CO ₂ + C ₁₆ H ₃₄	References	[42]	[41]	[40]
	λ	0.616444	0.614432	0.596472
	a_{12}	1351.60	1076.37	1064.38
	a_{21}	-1350.89	-1076.21	-1064.25
Systems	Equation	PR-HK		
CO ₂ + C ₁₀ H ₂₂	References	[38]	[39]	[40]
	a_{12}	978.73	1743.76	14392.50
	a_{21}	-978.77	-1702.88	-12120.00
CO ₂ + C ₁₆ H ₃₄	References	[42]	[41]	[40]
	a_{12}	1234.56	1051.27	1363.51
	a_{21}	-989.75	-210.19	-1351.23

From the Table 3, the original Peng – Robinson equation of state shows satisfactory results to determine the phase behavior of the carbon dioxide + decane system. For the other system, carbon dioxide + hexadecane, the PR-OR equation represents with good precision the experimental data for the first reference; PR-LCVM equation for the second data; and PR-HK for the third data. So, for systems with hydrocarbons with a great number of carbons, it is necessary to develop some modifications in these equations to improve the results. One possible solution is to apply the UNIFAC model to represent the free excess energy, which is already in study in our group of research.

Figure 1 represents the qualitative behavior for the pressure versus the molar fraction of both phases (x and y) for the CO₂ + decane system and Figure 2, for the CO₂ + hexadecane system. The

solid lines represent the calculated values from PR-OR equation of state for the first system and for the PR-LCVM equation for the second one.

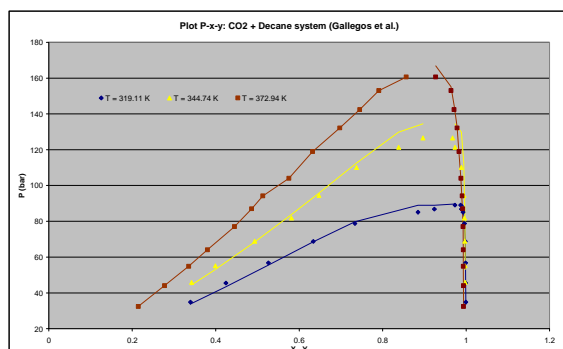


Figure 1: PR-OR calculated values vs. experimental data.

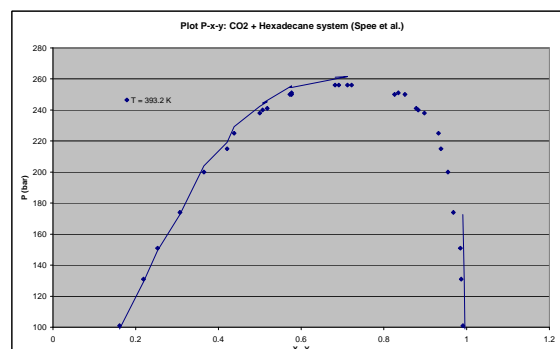


Figure 2: PR-LCVM calculated values vs. experimental data.

Conclusions

A correct characterization of the VLE of systems with gases and heavy oils has an important aspect for the petroleum industry. Some equations of state are being used to represent the solubilities of the gases in oils fractions. In this study, the PR-OR equation of state shows a satisfactory determination of the VLE for the $\text{CO}_2 + \text{C}_{10}\text{H}_{22}$ system. However, for the $\text{CO}_2 + \text{C}_{16}\text{H}_{34}$ system, all proposed equations presented good results only for one reference studied. So, some modifications need to be done in these equations, as apply the UNIFAC model to calculate the free excess energy term (G^E), which alternative is already in development in our group of research.

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