A Peng-Robinson based model for an equation of state using a non symmetric mixing rule for prediction of density of highly polar, asymmetric mixture of CO_2 and n-decane.

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Abstract

The purpose of this work was obtain a Φ–Φ thermodynamical model based on Peng-Robinson EOS to calculate in a accurate way the volumetric properties of carbon dioxide-n-decane mixtures. The procedure used is described as follow: a) Obtention of reliable equations for a and b parameter of Peng Robinson EOS for both subcritical and supercritical compound using liquid compressibility and acentric factor correlations. B) Fitting Panagiotopoulos-Reid mixing rules's kij to the mixture VLE equilibria using a combination of a logical search plan and a generalization of secant method. The correlation for B and A based on liquid compressibility of n-decane describes exactly way the pure saturated region for the subcritical component. It was obtained a pair of binary interaction parameters, whose values are 0.0922 and 0.114. It was observed an accurate prediction of bubble pressure in the low range pressure and an underestimation of carbon dioxide composition at high pressure.

Introduction

There is a kind of articulation between the transport phenomena and thermodynamical model to find a way to predict the flux of oil from wells, when CO_2 is supplied. The aim of this work is to provide a technique of modeling Vapor Liquid Equilibria (VLE) of binary mixtures containing CO_2 in the simplest way possible, in spite of the inherent

difficulties associated to this kind of systems, due principally to the supercritical condition of CO_2.

Φ–Φ based models are often chosen for VLE calculation, even more if the experimental data available to which this models are going to be fitted, is into high pressure range. In this sense, the Peng-Robinson EOS [1], is one of the most commonly used equations of state in industry on generating thermodynamical properties in process simulation.

Panagiotopoulos and Kumar [2] proposed a generalized technique for the calculation of the pure component parameter for use in a general two-parameter EOS. This technique is essentially equal to the Martin-Hou Criteria [3] and is an extension of the technique of Joffe and Zudkevitch [4], from which Peng-Robinson's α functional form was obtained. This technique allows one to compute values of a and b for any two parameter EOS, given the vapor pressure and the liquid volume of the component at the temperature of interest. They proposed a pair of correlations for B and A, where

$$A = \frac{bP}{RT} \quad (1.)$$

$$B = \frac{aP}{(RT)^2} \quad (2.)$$

The expressions were based on a power series in $\ln Z_L$, which proved be superior to other schemes attempted. Ventura and Santos [5] found a similar correlations for refrigerants, thought this equations were based on temperature instead of Z^L.

To use the Panagiotopoulos *et. al.*'s correlation, it's necessary to know the vapor pressure and the saturated liquid volume of the component at the given temperature in order to compute Z^L.

Vapor pressure can be computed using any particular correlation available and saturated liquid volume can be calculated using the Spencer Danner modified Rackett equation. Spencer *et. al*. [6] said that the modified equation of Rackett is as accurate as, or more accurate than presently available generalized correlations for predicting the effect of temperature on saturated liquids.

Oellrich [7] developed an wide list containing van der Waals mixing rule binary interaction for Peng-Robinson equation of state, in which the value of k_{ij} for CO_2-n-decane binary mixture is 0.114. Panagiotopoulos and Reid [8] proposed a cubic mixing rule to model phase equilibria in both polar an non polar systems, whose expressions are given by the equations (3), (4) and (5)

$$b_m = \sum_i x_i b_i \quad (3.)$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (4.)$$

where

$$a_{ij} = \sqrt{a_i a_j}\left[1 - k_{ij} + \left(k_{ij} - k_{ji}\right)x_i\right] \quad (5.)$$

The equation (5) is reduced to van der Waals mixing rule when k_{ij} is equal to k_{ji}. Lee *et al.*[9] have mentioned that the Panagiotopoulos-Reid mixing rule violates the quadrature composition dependence of the second virial coefficient. Lee *et al.*[10] reported that Panagiotopoulos and Reid mixing rule and Soave-Redlich-Kwong EOS model understimate the composition of CO_2 in the liquid phase. The cause of this behavior would be due to the Michelsen-Kistenmacher syndrome [11] known as dilution effect. Thought, Vera *et al* [12] has developed a technique to test mixing rules for dilution effect.

Panagiotopoulos and Reid fitted k_{12} and k_{21} to the experimental supercritical fluid phase composition (y_1) and the liquid phase composition (x_2) of a carbon dioxide-water mixture at 323K, respectively. They reported an excellent agreement between model prediction and experiment, even quite close to mixture critical region.

Methodology Description

The binary interaction parameters k_{12} and k_{21} were fitted using the objective function π, developed by Paunovic *et al.* [13]

$$\pi = \sum_i \left[\left(\frac{\left| f_1^L - f_1^V \right|}{f_1^V} \right)_i + \left(\frac{\left| f_2^L - f_2^V \right|}{f_2^V} \right)_i \right] \quad (6.)$$

Each term of the equation (6) can be evaluated if an experimental data base of P, T, x and y are available and a set of values of k_{12} and k_{21} are specified. The equation for the liquid and vapor fugacities is

$$\ln \phi_k = \ln \frac{\hat{f}_k}{x_k P} = \frac{b_k}{b_m}\left(\frac{Pv}{RT} - 1\right) - \ln \frac{P(v - b_m)}{RT} + \left[\frac{\sum_i x_i (a_{ik} + a_{ki}) - \sum_i \sum_j x_i^2 x_j (k_{ij} - k_{ji}) \sqrt{a_i a_j} + x_k \sum_i x_i (k_{ki} - k_{ik}) \sqrt{a_k a_i}}{a_m} - \frac{b_k}{b_m} \right] * \frac{a_m}{\sqrt{u^2 - 4w}} \ln \left(\frac{2v + b_m \left(u - \sqrt{u^2 - 4w} \right)}{2v + b_m \left(u + \sqrt{u^2 - 4w} \right)} \right) \quad (7.)$$

where both a_m and b_m can be computed using the equations (3), (4) and (5).

Following a slightly different technique to Panagiotopoulos and Kumar one, a correlation in terms of Z^L was proposed for B and A parameter of Peng Robinson EOS for the subcritical component. The main difference between the technique used in this work and those proposed by Panagiotopoulos *et al.* lays on the nature of the equation solved.

Panagiotopoulos and Reid solved the equation (8) for both liquid and gas compressibility and the equality of pure fugacities for B, A and Z^V, fixing Z^L varying B, A and Z^V until a tolerance is satisfied. The method applied in this work considers an additional variable Z^I, which has no physical importance. An additional equation is required. However, there is an advantage on avoiding the procedure of solving the cubic equation for Z^L and Z^V. The set of equations solved to computed B and A were derived applying the Martin and Hou criteria [3] to the saturated data of n-decane available from Bach equation [14]. The equations derived from an analysis similar to the one applied in the critical point.

$$Z3 - C_1 * Z2 + C_2 * Z - C_3 = (Z - Z^L)(Z - Z^I)(Z - Z^V) \qquad (8.)$$

$$Z^L + Z^I + Z^V - C_1 = 0 \qquad (9.)$$

$$Z^L\left(Z^I + Z^V\right) + Z^I Z^V - C_2 = 0 \qquad (10.)$$

$$Z^L Z^I Z^V - C_3 = 0 \qquad (11.)$$

where C_1, C_2 and C_3 are 1-B , A-B(2+3B) and AB-B^2-B3, respectively, for the Peng-Robinson EOS.

The equations (9), (10), (11) and the equality of both vapor and liquid fugacities of the subcritical component were solved simultaneously for Z^L, Z^V, B and A fixing the Z^L, P and T values from the saturated data using a modified algorithm based on generalization of secant method [15] to solve nonlinear equations. Furthermore, a set of expressions for B and B was proposed to be suitable of being fitted to the calculated values of B and A, which are shown in equations

$$B = Z^L\left(\eta_1 + \eta_2 Z^L\sqrt{Z^L} + \eta_3 \Big/ \sqrt{Z^L} + \eta_4 \ln Z^L \Big/ \left(Z^L\right)^2\right) \qquad (12.)$$

$$A = B\sum_{i}\left[\varepsilon_i\left(\ln Z^L\right)^i\right] \quad ($$

13.)

For the supercritical compound, it was considered the correlation based on acentric factor, following Panagiotopoulos and Reid [8].

A logic research plan based on Hooke and Jeeves [16], and the generalization of secant method based algorithm [15] were used together, with a tolerance of 10^{-4} and 10^{-6} each one, to compute k_{12} and k_{21} defining a pair of equations, conformed by equaling to zero the differential of the equation (6) with respect to each k_{12} and k_{21}, in turn.

Results and Discussion

On solving the equality of fugacities and the equations (9), (10) and (11) a set of coupled B and A were obtained to each temperature (Z^L). A further fitting of equations (12) and (13) to the calculated points was carried out, splitting the data range into two regions: one belongs to the low temperature range and the other is close to the critical region. The values of parameters are summarized in the Table 1.

It was necessary to split the total data range into two regions due to the high deviation from the calculated points observed at low temperature (-50%). The agreement between equation (12) and the values of B calculated was excellent, providing a maximum deviation of 10% over the complete range. A similar result was obtained on fitting the equation (13) to A, with a maximum deviation from the calculated values of 6% over the entire range.

It was obtained a set of values of k_{12} and k_{21} for the temperature and pressure , which are shown in table 2. It was defined in equations (14) and (15), in the sense of Chen and Lee [17], a pair of deviation equations as for P as for y_1

$$\Delta P/P = \frac{1}{n}\sum_{k=1}^{n}\frac{\left|P_k^{calc} - P_k^{exp}\right|}{P_k^{exp}} \quad ($$

14.)

$$\Delta y_1 = \sum_{k=1}^{n}\left|y_{1_k}^{calc} - y_{1_k}^{exp}\right| / n \quad ($$

15.)

It's remarkable that the k_{21} value reported in table 3 is exactly to the value obtained by Oellrich [7] using either Peng-Robinson EOS. It observed that the Panagiotopoulos-Reid mixing rule predicts bubble pressure more accurately than Peng-Robinson with van der Waals mixing rule at low pressures. This situation changes when pressure and temperature increases. In this case, the Peng-Robinson EOS with Panagiotopoulos-Reid mixing rule overestimate the bubble pressure, as can be observed in figure 1. This is in agreement with the tendency mentioned by Chen and Lee [17].

Conclusion

The equilibrium data for n-decane, from Bach's equation, were correlated for B and A using a functional expression based on a linear, squared root and natural logarithm of Z^L combinations for B and the Panagiotopoulos-Kumar correlation for A, respectively, achieving an excellent agreement with the experimental values of Z^L. The expressions for A and B, and the Rackett equation for V^L were used together to find the k_{ij} values for a binary mixture of CO_2 and n-decane, that fits the experimental VLE data in a wide temperature and pressure range, with a reasonable error on predicting bubble pressure and vapor mole concentration of CO_2 . The Peng-Robinson equation of state with Panagiotopoulos-Reid mixing rule predicts bubble pressure more accurately than Peng-Robinson with van der Waals mixing rule. However, underestimate CO_2 composition at high pressure.

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List of Symbols

a,b parameters in an equation of state (dimensions are dependent on the form of the EOS)

C Constans of equation (10) (dimensioless)

f fugacity of a pure component (N m^{-2})

k binary interaction parameter

P pressure (N m^{-2})

R universal gas constant ($JxK^{-1x}(mole^{-1})$)

T temperature (K)

u,w arithmetic constants in a cubic EOS

v specific volume ($m^3x(mole^{-1})$)

x,y molar concentration in liquid and vapour, respectivelly (mole of component/ total moles of mixture)

Z compressibility (=Pv/RT)

Subscripts-Superscripts

I root of equation (10) between liquid and vapor compressibility.

i,j,k components: 1 for carbon dioxide, 2 for n-decane.

L,V refered to vapor and Liquid phase, respectively

m referred to mixture parameter

SAT saturated state of pure component

Greek Letters

π Objective function defined in equation (8)

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Table 1. Approximate expressions for the functions $B(Z^L)$ and $A(Z^L)$ shown in equations (12) and (13)

	$0.000118 \leq Z_L \leq 0.0117$		$0.0117 \leq Z_L \leq 0.249$	
i	η_i	ε_i	η_i	εi
0	0.750787	46.941680	0.329891	22.877721
1	-32.255837	28.988877	-1.315577	30.432990
2	0.00295	7.765157	0.071754	19.061713
3	$3.32202*10^{-10}$	0.854234	$1.00877*10^{-05}$	4.920940
4	-	0.034479	-	0.459667

Table.2. Results of Bubble-Pressure Calculations from the Peng-Robinson

T [K]	P [kPa]	k_{12}	k_{21}	$100\Delta P/P$[b]	$100\Delta y_1$[c]
344-510	1378-14600[a]	0.0922	0.114	7.13	0.78

(a): For T=510 K is only up to 6900 kPa. (b): See equation (14). (c): See equation (15)

Figure 1. Bubble Pressure at 344,26K for carbon dioxide n-decane mixture

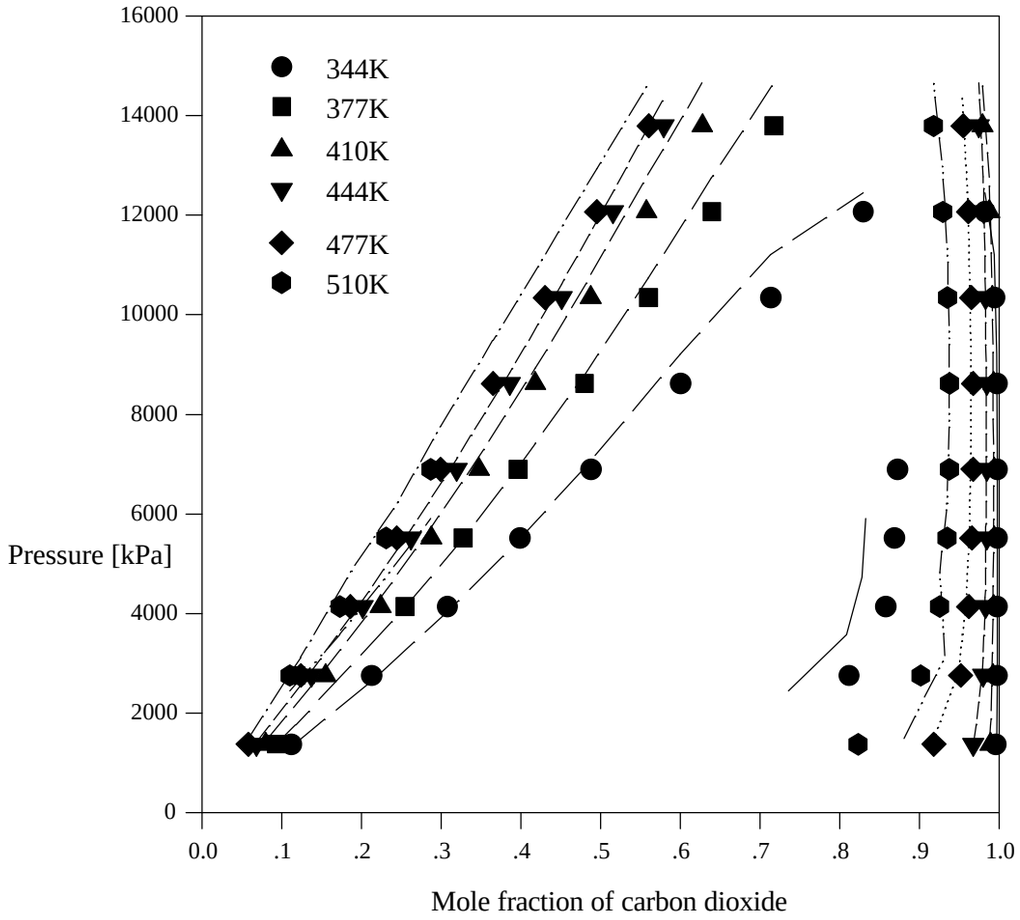
16000
14000
12000
10000
8000
6000
4000
2000
0
Pressure [kPa]
344K
377K
410K
444K
477K
510K
0.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Mole fraction of carbon dioxide

Figure 1