

A Molecular Model for Correlating Vapor-Liquid Equilibrium of Propane+Hydrocarbon Mixtures

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Abstract—Simple analytical expressions are proposed for the calculation of the equilibrium pressure and the mole fractions of both liquid and vapor phases of propane+hydrocarbon binary mixtures. The new proposed expressions are based on a simple analytical expression for the vapor pressure of pure non-polar fluids, which, for a given temperature, only requires as input the values of the Lennard-Jones molecular parameters and the acentric factor. A properly modified Lorentz-Berthelot mixing rule is used, the interaction parameters being given as simple functions of the temperature and concentration with eight constants for each binary mixture. A different model is proposed to calculate the vapor mole fraction in which four appropriate constants are needed for each mixture. Here, it is shown how the models can reproduce accurately and straightforwardly the vapor liquid equilibrium properties (pressure, liquid mole fraction, and vapor mole fraction) of binary mixtures containing propane.

Key words: Vapor-liquid Equilibrium, Molecular Models, Propane-mixtures, Mixing Rules

INTRODUCTION

Reliable vapor-liquid equilibrium (VLE) correlation is constantly in demand for the design and simulation of separation processes. Propane is contained in oil reservoir fluids and in natural gases, so accurate means for correlating and predicting the phase-equilibrium variables are of special importance. Also, predicting the behavior of systems and processes at conditions for which experimental data are not available is common in industrial applications, and therefore accurate reliable correlations are needed. Equations of state (EoS) are generally considered the most appropriate models to correlate and predict phase equilibrium in mixtures, one of their clear advantages being that the required procedures have been widely studied and are well known.

When the properties of interest are those of VLE, the method of EoS, although accurate in a great number of cases, is neither simple nor straightforward. Thus, a first step in the study of a given mixture is the choice of an appropriate expression for the EoS. However, as it is well established, no single EoS currently exists that is equally suitable for the correlation of vapor-liquid equilibrium of all classes of binary systems, and over the whole range of temperature, pressure, concentration and molecular variety. Moreover, the application of an EoS to mixtures requires the use of mixing rules to represent the dependency of the EoS on concentration and combination rules to represent the interaction between the unlike components in the mixture. Mixing and combination rules range from the simple Lorentz-Berthelot or van der Waals rules to density-dependent or concentration dependent expressions [Huron and Vidal, 1979; Stryjeck and Vera, 1986; Wong and Sandler, 1992]. The accuracy in correlating VLE obtained by this method depends then on the EoS used and on the mixing rule employed [Englezos et al., 1990; Ashour and Aly, 1996]. Also, binary interaction parameters

must be introduced to obtain more accurate results. Such interaction parameters are obtained by fitting experimental phase equilibrium data at each temperature. These binary interaction parameters are sensitive to many factors, including the ranges of temperature, pressure and concentration and the quality of the experimental data [Polishuk et al., 1999]. In many cases, multiple binary interaction parameters are found, so a good and efficient searching and optimization algorithm must be used [Valderrama, 2003]. Some authors have proposed empirical and semi-empirical correlations for these interaction parameters [Chueh and Prausnitz, 1967; Graboski and Daubert, 1978; Arai and Nishiumi, 1987; Coutinho et al., 1994]. None of these proposals, however, have proven to be of general applicability, and at present there does not exist any accurate predictive or correlating way for evaluating the interaction parameters. The available correlations and estimation methods are not always suitable for extrapolation [Coutinho et al., 1994] and in many cases are only applicable to particular mixtures [Gao et al., 1992]. Some of the previous problems can be solved by using EoS based on molecular parameters [Cotterman et al., 1986; Cotterman and Prausnitz, 1986; Kiselev et al., 1998; Blas and Vega, 1998; Femeglia and Prici, 2001]. Although the results are in many cases more accurate when these expressions are used, the proposed analytical forms of the molecular EoS are generally difficult to handle.

The aim of the present work is to propose a simple expression based on a recently proposed molecular model for the vapor pressure of pure non-polar fluids [Faúndez et al., 2000]. A simple modified version of the Lorentz-Berthelot combination rules, in which the interaction parameters are given as functions of the temperature and the liquid-phase concentration, are also used. In addition, another simple expression is used to obtain the vapor mole fraction. Compared with methods that use EoS, the proposed model allows one to calculate directly and straightforwardly the VLE properties for simple binary mixtures by only knowing the Lennard-Jones (LJ) parameters and the acentric factor of each substance [Faúndez et al., 2001].

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First, the molecular model for the vapor pressure of non-polar pure fluids is described. Then, this model is extended to binary mixtures by using the modified new mixing rule, as explained by Faúndez et al. [2001]. Finally, results are presented for five binary mixtures containing propane, the results found are discussed, and their meaning analyzed.

PURE FLUIDS

As a first approximation, it is assumed that non-polar molecules interact according to the Lennard-Jones potential (Eq. (1)), with suitable values for the molecular parameters ε and σ [Cuadros et al., 1996], which represent, respectively, the depth of the potential well, and the distance at which the value of the potential vanishes.

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

Any physical property is then expressed in dimensionless form by using these parameters. The pressure P , the density ρ , and the temperature T , in real units are related to the reduced quantities P^* , ρ^* and T^* by the following expressions:

$$\begin{aligned} P &= P^* \frac{(\varepsilon/k)R}{N_a \sigma^3} \text{ (Pa)} \\ \rho &= \frac{\rho^*}{N_a \sigma^3} \text{ (mol} \cdot \text{m}^{-3}\text{)} \\ T &= T^* (\varepsilon/k) \text{ (K)} \end{aligned} \quad (2)$$

In these equations, k is Boltzmann's constant, N_a is Avogadro's number, and R the ideal gas constant. The parameters ε/k and σ are expressed in Kelvin and meters, respectively.

It has been shown that for a great number of non-polar fluids, the vapor pressure at a given temperature, $P_v^*(\omega, T^*)$, can be obtained from [Faúndez et al., 2000]:

$$P_v^*(\omega, T^*) = P_v^{*LJ}(T^*) + f(\omega, T^*) \quad (3)$$

Here, $P_v^{*LJ}(T)$ is the equilibrium pressure for the mixture formed by Lennard-Jones fluids and $f(\omega, T^*)$ is a universal function, in reduced units.

It has been also shown that the reduced equilibrium pressure in binary mixtures of Lennard-Jones fluids can be expressed, to a good approximation, as a polynomial expression, function of the reduced temperature T^* , as follows [Cuadros et al., 2000; Faúndez et al., 2000]:

$$\begin{aligned} P_v^{*LJ}(T^*) &= -0.530964 + 2.422916T^* - 4.074344T^{*2} \\ &+ 2.934668T^{*3} - 0.7242252T^{*4} \end{aligned} \quad (4)$$

The universal function $f(\omega, T^*)$ is:

Table 1. Coefficients of Eqn. (5) obtained by using vapor pressure data [DIPPR, 1996], for 42 pure non-polar fluids

a_0	0.5515
a_1	-2.4847
a_2	4.2006
a_3	-3.1562
a_4	0.8838
a_5	-1.5853
a_6	5.6025
a_7	-6.7252
a_8	3.0430
a_9	-0.4171
a_{10}	0.0287
a_{11}	-1.3468
a_{12}	2.6998
a_{13}	-1.3022

$$f(\omega, T^*) = \sum_{i=0}^4 a_i T^{*i} + \omega \sum_{i=5}^9 a_i T^{*i-5} + \omega^2 \sum_{i=10}^{13} a_i T^{*i-10} \quad (5)$$

In this equation, ω is the acentric factor [Reid et al., 1987] and the universal coefficients a_i 's have been obtained by fitting vapor pressure data for 42 substances [Faúndez et al., 2000]. These coefficients are listed in Table 1.

Table 2 lists the molecular parameter values used for the non-polar fluids chosen for the present study. The second and third columns give the LJ parameters [Cuadros et al., 1996] and the fourth column gives the corresponding values of the acentric factor. The fifth column gives the temperature interval covered for each substance, and the sixth column gives the mean absolute deviation ΔP_v between literature values for the vapor pressure [DIPPR, 1996] and those obtained from Eq. (3).

BINARY MIXTURES

The model for the vapor pressure of pure fluids presented in the previous section has been used to model the VLE properties of binary mixtures formed by non-polar components. To this end, it is assumed that the vapor pressure of a given mixture obeys the following model [Faúndez et al., 2001]:

$$P_m(T, x_1) = x_1 P_1(\omega_1, T) + x_2 P_2(\omega_2, T) + x_1 x_2 P_{12}(\omega_{12}, T) \quad (6)$$

In this equation, $P_1(\omega_1, T)$ and $P_2(\omega_2, T)$ are the vapor pressures of the pure components, ω_1 and ω_2 are the acentric factors of components 1 and 2, $P_{12}(\omega_{12}, T)$ is the contribution to the mixture vapor

Table 2. Pure component properties used in the present study, temperature range covered, and percentage mean absolute deviation ΔP_v between vapor pressure values [DIPPR, 1996] and those obtained from Eq. (3)

Substance	ε/k (K)	σ (Å)	ω	Temperature range (K)	ΔP_v (%)
Propane	255.18	5.471	0.1530	204.1-331.7	2.0
n-Butane	287.20	6.081	0.2010	236.9-373.4	2.1
Benzene	377.46	6.174	0.2090	311.4-490.7	2.8
n-Pentane	309.75	6.709	0.2510	263.3-402.7	2.3
n-Hexane	327.47	7.319	0.2940	286.5-425.7	4.3
n-Heptane	340.97	7.902	0.3500	298.4-443.3	3.1

Table 3. Values for the τ_i coefficients of Eqs. (7), (8) for the propane+hydrocarbon systems studied in this paper. Each set of τ_i values is obtained by comparison of experimental VLE data and values calculated by using Eq. (6)

τ_i	Propane+n-Butane	Propane+Benzene	Propane+n-Pentane	Propane+n-Hexane	Propane+n-Heptane
τ_1 (K)	2.471×10^{13}	3.169×10^{14}	5.583×10^{13}	1.164×10^{13}	-8.054×10^{11}
τ_2	-1.187×10^{11}	-2.110×10^{12}	-1.981×10^{11}	-6.070×10^{10}	2.959×10^9
τ_3 (K ⁻¹)	1.423×10^8	3.311×10^9	3.068×10^8	7.488×10^7	-3.614×10^6
τ_4 (K)	6.270×10^{11}	2.468×10^{12}	-8.911×10^{12}	-3.065×10^{11}	1.962×10^{11}
τ_5	-9.301×10^{10}	-3.215×10^{11}	-5.049×10^{11}	3.966×10^9	-1.778×10^9
τ_6 (K ⁻¹)	4.4993×10^8	1.756×10^9	2.080×10^9	-3.627×10^7	5.632×10^6
τ_7 (K ⁻²)	-5.437×10^5	-2.611×10^6	-2.327×10^6	5.643×10^4	-5.635×10^3
τ_8	-1.392×10^9	1.418×10^{10}	2.487×10^{10}	1.054×10^8	0.440×10^1

pressure due to the cross-interactions between unlike molecules, and x_1 and x_2 are the mole fractions of the two components in the liquid phase. The analytical expression (6), in which all the quantities are expressed in real units, allows one to obtain the vapor pressure for either of the pure fluids when $x_1=1$ or $x_2=1$. The three functions $P_1(\omega_1, T)$, $P_2(\omega_2, T)$, and $P_{12}(\omega_{12}, T)$, are calculated from Eqn. (3), i.e., using the same analytical expression proposed for the vapor pressure of pure fluids. Since Eq. (3) is given in terms of reduced units, molecular parameters for the first component ($\varepsilon_1, \sigma_1, \omega_1$) must be used to obtain the real values of $P_1(\omega_1, T)$. Similarly, molecular parameters for the second component ($\varepsilon_2, \sigma_2, \omega_2$) must be used to obtain real values of $P_2(\omega_2, T)$. Values for $P_{12}(\omega_{12}, T)$ are obtained by using combination rules for $\varepsilon_{12}, \sigma_{12}$ and ω_{12} in terms of the molecular parameters of the pure components.

The following combination rules have been previously used and good results were found for simple mixtures [Faúndez et al., 2001]:

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2} \frac{T}{(\tau_1 + \tau_2 T + \tau_3 T^2 + \tau_4 x_1)} \quad (7)$$

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} (\tau_5 + \tau_6 T + \tau_7 T^2 + \tau_8 x_1) \quad (8)$$

$$\omega_{12} = \omega_1 + \omega_2 \quad (9)$$

In these equations, the τ_i parameters adopt different values for each particular mixture, but are independent of temperature, pressure and concentration. Thus, to obtain the vapor pressure of a mixture at a given temperature and mole fraction, one only needs as input the parameters ε/k , σ , and ω for both pure fluids, and the τ_i coefficients for the mixture.

VAPOR PHASE CONCENTRATION

For a given pressure and temperature the liquid phase mole fraction is calculated by using Eq. (6).

For the vapor phase concentration a simple analytical expression, function of the temperature and the calculated mole fraction in the liquid phase, is used:

$$y_i(T, x_i) = c_0 x_i^{2/10} + c_1 (x_i T)^{1/3} + c_2 (x_i^{1/3} T^{2/10}) + c_3 T^3 \quad (10)$$

The basics of this equation is derived from different models for the equilibrium ratio $K_i = x_i/y_i$, presented in the literature [Walas, 1985]. From those models it can be easily seen that y is a complex function of T and x ; $y=f(T, x)$. After searching different functions we

found that series of the type $y = \sum c_i x^a T^{b_i}$ could model the data. Of the different series of this type explored in this work, the one shown in Eq. (10) gave the lowest deviations between experimental and calculated values of y_1 , as shown in the results.

The procedure then is straightforward: 1) for a given P and T , the liquid mole fraction x_1 is calculated by using Eq. (6); 2) the vapor mole fraction y_1 is calculated by using Eq. (10), completing the set of vapor-equilibrium properties of interest.

As can be seen, four appropriate constants must be calculated for each binary mixture. In the following section, the results obtained when the proposed model is used to predict the vapor pressure and the concentration in binary mixtures of propane+hydrocarbon mixtures, are presented.

RESULTS

Table 3 lists the values for the coefficients τ_i ($i=1, 2, \dots, 8$) in Eqs. (7) and (8) for the five systems studied in this work. These values were obtained by minimizing the deviations between predicted and experimental data for the pressure (Eq. (6)), for each system. Table 4 lists the values for the coefficients c_i ($i=0, 1, \dots, 3$) in Eq. (10) for the five systems. These values were obtained by minimizing the deviations between predicted and experimental data for the mole fraction of propane in the vapor phase, for each system.

Table 5 gives the VLE data used in this study and the results obtained for P_m, x_1 and y_1 using Eq. (6). The first column lists the system and the second column indicates the number of data points (N) used in the data fitting. The third, fourth, and fifth columns give the temperature, the pressure range, and the experimental mole fraction range, respectively. The sixth, seventh and eight columns give

Table 4. Values for the c_i coefficients of Eq. (10) for the propane+hydrocarbon systems studied in this paper. Each set of c_i values is obtained by comparison of experimental vapor mole fraction data and values calculated by using Eq. (10)

System	C_0	C_1	C_2	C_3
Propane+n-Butane	1.058	-0.073	0.912	-8.889×10^{-9}
Propane+Benzene	2.519	1.984	-4.609	-1.434×10^{-8}
Propane+n-Pentane	0.412	1.493	-2.861	-1.556×10^{-8}
Propane+n-Hexane	2.130	3.146	-6.933	-2.130×10^{-8}
Propane+n-Heptane	2.783	2.607	-6.042	-1.563×10^{-8}

Table 5. Correlation of VLE data for propane+hydrocarbon systems using Eq. (6) and (10): number of data points (N), conditions and source of experimental data (range of T, P and x), the percentage absolute deviation for the pressure $\Delta P_m(\%)$, for the liquid mole fraction, (Δx_1) and the vapor mole fraction, (Δy_1) for each set of data are presented

Binary mixture	N	T (K)	P range (MPa)	x_1 range	ΔP_m (%)	Δx_1 (%)	Δy_1 (%)	References
Propane+n-Butane	27	353.15	2.07-2.76	0.552-0.858	1.0	1.7	2.5	Kay [1970]
		363.15	2.07-3.45	0.382-0.905	0.3	0.4	3.0	
		373.15	2.07-4.07	0.226-0.898	0.3	0.5	3.4	
		383.15	2.07-4.07	0.331-0.731	0.4	0.8	2.1	
		393.15	2.76-4.07	0.179-0.564	0.4	0.9	0.7	
		403.15	2.76-4.07	0.238-0.410	0.4	1.2	3.2	
		413.15	3.44-4.07	0.182-0.211	0.3	1.3	1.2	
Propane+Benzene	56	310.93	0.28-1.03	0.106-0.792	3.6	5.6	4.7	Glanville et al. [1950]
		344.26	0.55-2.41	0.129-0.929	1.8	2.3	2.3	
		377.59	1.03-4.14	0.166-0.928	3.2	3.8	0.3	
		410.93	1.38-5.17	0.132-0.813	1.8	2.3	1.5	
		444.26	2.06-5.86	0.132-0.636	1.7	2.4	3.5	
		477.59	2.75-5.86	0.109-0.436	1.3	2.1	6.3	
					2.1	2.9	3.0	
Propane+n-Pentane	54	344.26	0.41-2.41	0.124-0.925	1.5	2.3	4.5	Sage and Lacey [1940]
		360.93	0.55-3.45	0.150-0.962	1.1	1.8	2.6	
		377.59	0.69-4.14	0.113-0.888	1.1	1.7	2.4	
		394.26	1.03-4.48	0.112-0.776	1.0	1.8	3.4	
		410.93	1.38-4.48	0.161-0.639	1.9	3.4	3.9	
		427.59	1.72-4.14	0.125-0.433	1.3	3.2	2.0	
		444.26	2.41-4.14	0.135-0.304	0.6	1.3	5.4	
Propane+n-hexane	32	333.15	1.72-2.06	0.852-0.985	0.7	0.6	0.8	Kay [1948]
		353.15	1.72-2.76	0.627-0.919	1.0	0.9	0.9	
		373.15	1.72-4.14	0.444-0.961	1.0	1.0	1.6	
		393.15	1.72-4.14	0.324-0.802	2.0	2.1	1.2	
		413.15	1.72-4.83	0.242-0.757	1.7	1.7	1.5	
		433.15	1.72-4.83	0.162-0.646	2.7	3.8	4.5	
		453.15	2.07-4.14	0.127-0.435	1.9	3.6	5.7	
Propane+n-heptane	35	473.15	2.76-3.45	0.131-0.241	1.5	4.2	4.1	Kay [1971]
					1.7	2.3	2.5	
		353.15	2.07-2.76	0.739-0.921	8.6	6.0	0.3	
		373.15	2.07-4.14	0.568-0.962	4.1	3.2	0.7	
		393.15	2.07-4.83	0.444-0.955	2.2	1.9	0.9	
		413.15	2.07-4.83	0.352-0.769	2.1	0.9	0.5	
		433.15	2.07-4.83	0.277-0.662	4.0	4.4	0.6	
453.15	2.07-4.83	0.211-0.570	5.6	5.3	1.1			
			473.15	2.07-4.83	0.146-0.505	7.3	9.8	2.0
			493.15	2.76-4.14	0.170-0.356	8.2	12.3	1.4
					4.7	5.0	1.0	

the absolute relative deviation between experimental and calculated vapor pressure, ΔP_m , liquid mole fraction Δx_1 , and the vapor mole fraction, Δy_1 , for each isothermal set of data. The mean deviations of all isotherms for each of the systems studied are given (in bold face). The last column gives the source of data.

The absolute deviation $\Delta P_m(\%)$, $\Delta x_1(\%)$ and $\Delta y_1(\%)$ for the N data points indicated in Table 5 are defined as follows:

$$\Delta P_m(\%) = (100/N) \sum |(P_{calc} - P_{exp})/P_{exp}|$$

$$\Delta x(\%) = (100/N) \sum |(x_{calc} - x_{exp})/x_{exp}|$$

$$\Delta y(\%) = (100/N) \sum |(y_{calc} - y_{exp})/y_{exp}| \quad (11)$$

As seen in Table 5, the proposed molecular model, Eq. (6), reproduces most of the saturation pressures of these binary mixtures with mean absolute deviations less than 4% for any temperature. Few data for the propane+n-heptane system give deviations of the order of 8%. The concentration in both phases also shows some higher deviation in a few cases. These few higher deviations do not diminish the goodness of the correlation, which can predict phase equilibrium properties from universal, generalized correlations.

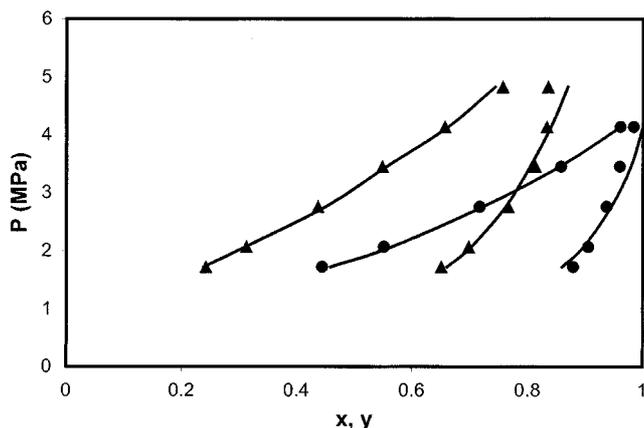


Fig. 1. Experimental data points [Kay, 1948] and theoretical values (lines) obtained from our models (Eqs. (6) and (10)) for the mole fractions of the propane+n-hexane system at two temperatures (● T=373.15 K and ▲ T=413.15 K).

As seen in Table 5, the molecular model allows one to obtain the liquid mole fraction in these binary mixtures with mean absolute deviation less than 12.5% for each isothermal data set studied. For each system, mean absolute deviations ranging from 0.9% to 5.0% are found. The vapor mole fraction “y” is predicted with mean absolute deviations less than 7% for each isothermal data set studied. Values of the mean deviations for each system range from 1.0% to 3.1%.

As an example, Fig. 1 shows the pressure versus concentration diagram for the propane+n-hexane system at two temperatures (● T=373.15 K and ▲ T=413.15 K). It can be seen that there is good agreement between model estimates and experimental data.

Fig. 2 shows a temperature versus concentration diagram for the propane+n-heptane system at pressure of 2.76 MPa. Good agreement between the model results and the experimental data is observed. The model for x, Eq. (5), gives a reasonable estimate of the experimental data. The only exception is the high deviation (17%) obtained at T=493.15 K, i.e., for the highest temperature considered. For y, the deviations found, for this pressure, are less than 2.1%.

Results obtained by using the proposed models, Eqs. (6) and (10),

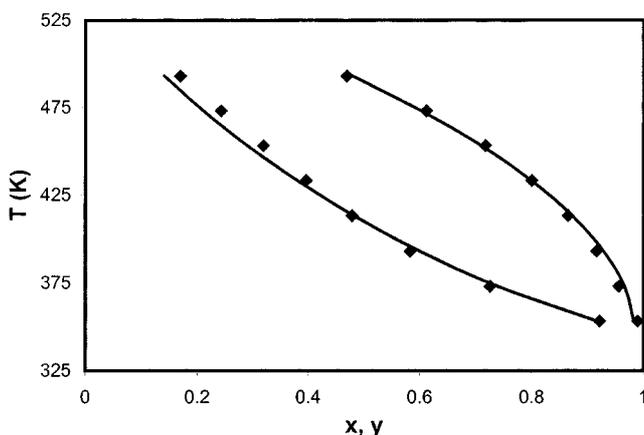


Fig. 2. Experimental data points [Kay, 1971] and theoretical values (lines) obtained from our models (Eqs. (6) and (10)) for the mole fractions of the propane+n-heptane system at P=2.76 MPa.

Table 6. Comparison between results obtained by using the proposed models (Eqs. (6) and (10)) and those obtained from the Peng-Robinson equation, as given Gao et al. [1992]

Binary mixture	Gao et al. [1992]		This work	
	% ΔP	% Δy_1	% ΔP	% Δy_1
Propane+n-Butane	0.4	1.8	0.4	2.2
Propane+Benzene	4.4	2.2	2.1	3.0
Propane+n-Pentane	3.0	2.7	1.2	3.1
Propane+n-hexane	1.1	1.3	1.7	2.5
Propane+n-heptane	1.6	3.6	4.7	1.0

are comparable with those obtained through traditional methods. For example, Gao et al. [1992] have used a correlation to evaluate binary interaction parameters in the Peng-Robinson EoS [Peng and Robinson, 1976] for light hydrocarbon mixtures. In Table 6, the deviations obtained with the proposed models are compared with those given by Gao et al. [1992] for five mixtures, at the same or similar temperature, pressure and mole fraction ranges. As seen, the saturation pressures and the vapor phase concentration are obtained with the proposed models with deviations less than or similar to those obtained by Gao et al. [1992] using an EoS.

CONCLUSIONS

An analytical expression relating the pressure, temperature, and concentration for the vapor-liquid equilibrium of non-polar binary mixtures was proposed. The model is based on a simple analytical expression for the vapor pressure of pure fluids. The equilibrium pressure for the mixture was then expressed in terms of the vapor pressure of each component and a mixture contribution. The molecular parameters for the mixture contribution were obtained from modified Lorentz-Berthelot mixing rules, in which the interaction parameters are given as simple functions of the temperature and concentration, with eight adjustable parameters for each system that were obtained from experimental data. Since the mixing rules are defined by these constants, their final expressions have the same analytical form for any mixture. An additional expression is proposed to obtain the vapor mole fraction as a function of the temperature and of the liquid mole fraction, with five appropriate constants for each mixture. The model is easy to use and the results are in good agreement with published experimental data.

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NOMENCLATURE

a_i : coefficients of Eq. (5)

c_i	: coefficients of Eq. (10)
k	: Boltzmann's constant
LJ	: Lennard-Jones
Na	: Avogadro's number
P	: vapor pressure in MPa
P^*	: vapor pressure in reduced Lennard-Jones units
P_m	: equilibrium pressure of the mixture
r	: intermolecular distance
R	: ideal gas constant
T	: temperature in Kelvin
T^*	: temperature in reduced Lennard-Jones units
x	: liquid mole fraction
y	: vapor mole fraction

Greek Letters

ε	: well-depth of the Lennard-Jones potential
ρ	: density in mol m^{-3}
ρ^*	: density in reduced Lennard-Jones units
σ	: intermolecular distance for zero LJ potential
τ_i	: coefficients of Eqs. (7) and (8)
ω	: acentric factor

REFERENCES

- Arai, T. and Nishiumi, H., "Correlation of the Binary Interaction Parameter of the Peng-Robinson Equation of State," *Bulletin of the College of Engineering, Hosei University*, **20**, 1 (1987).
- Ashour, I. and Aly, G., "Effect of Computation Techniques for Equation of State Binary Interaction Parameters on the Prediction of Binary VLE Data," *Computers in Chem. Eng.*, **20**, 79 (1996).
- Blas, F. and Vega, L., "Prediction of Binary and Ternary Diagrams Using the Statistical Associating Fluid Theory (SAFT) Equation of State," *Ind. Eng. Chem. Res.*, **37**, 660 (1998).
- Cotterman, R. L., Schwarz, B. J. and Prausnitz, J. M., "Molecular Thermodynamics for Fluids at Low and High Densities. Part I: Pure Fluids Containing Small or Large Molecules," *AIChE J.*, **32**(11), 1787 (1986).
- Cotterman, R. L. and Prausnitz, J. M., "Molecular Thermodynamics for Fluids at Low and High Densities. Part II: Phase Equilibria for Mixtures Containing Components with Large Differences in Molecular Size or Potential Energy," *AIChE J.*, **32**(11), 1799 (1986).
- Coutinho, J., Kontogeorgis, G. and Stenby, E., "Binary Interaction Parameters for Non-Polar Systems with Cubic EoS: a Theoretical Approach. 1. CO₂/hydrocarbons using SRK Equation of State," *Fluid Phase Equilibria*, **102**, 31 (1994).
- Chueh, P. L. and Prausnitz, J. M., "Vapor Liquid Equilibria at High Pressures: Calculations of Critical Temperatures, Volumes and Pressures of Non-Polar Mixtures," *AIChE J.*, **13**(6), 1107 (1967).
- Cuadros, F., Cachadaña, I. and Ahumada, W., "Determination of Lennard-Jones Interaction Parameters Using a New Procedure," *Molecular Engineering*, **6**, 319 (1996).
- Cuadros, F., Faúndez, C. A. and Mulero, A., "Vapour Pressure of Non-Polar Fluids and Their Repulsive and Attractive Contributions," *Phase Transitions*, **71**(1), 57 (2000).
- DIPPR (Design Institute for Physical Property Data) American Institute of Chemical Engineers (1996).
- Englezos, P., Kalogerakis, N., Trebble, M. A. and Bishnoi, P. R., "Estimation of Multiple Binary Interaction Parameters in Equations of State Using VLE Data: Application to the Trebble-Bishnoi Equation of State," *Fluid Phase Equilibria*, **58**, 117 (1990).
- Faúndez, C. A., Mulero, A. and Cuadros, F., "Molecular Thermodynamic Models for the Vapor-Liquid Equilibrium of Non-Polar Fluids," *Journal of Phase Equilibria*, **21**(4), 365 (2000).
- Faúndez, C. A., Mulero, A. and Cuadros, F., "A Simple Calculation of the Pressure and Liquid Mole Fraction at the VLE of Ethane/Light Hydrocarbon Binary Mixtures," *Chem. Eng. Comm.*, **187**, 215 (2001).
- Ferneglia, M. and Pricl, S., "Prediction of Phase Equilibria for Binary Mixtures by Molecular Modeling," *AIChE J.*, **47**(10), 2371 (2001).
- Gao, G., Dadiron, J. L., Saint-Guirons, H., Xans, P. and Montel, F., "A Simple Correlation to Evaluate Binary Interaction Parameters of the Peng-Robinson Equation of State: Binary Light Hydrocarbon Systems," *Fluid Phase Equilibria*, **74**, 85 (1992).
- Glanville, J. W., Sage, B. H. and Lacey, W. N., (1950). In: "Vapor-Liquid Equilibrium Data Collection," H. Knapp, R. Doring, L. Oellirch, U. Plocker and J. M. Prausnitz (eds.), DECHEMA, Frankfurt am Main (1982).
- Graboski, M. S. and Daubert, T. E., "A Modified Soave Equation of State for Phase Equilibrium Calculations. 2. Systems Containing CO₂, H₂S, N₂, and CO," *Ind. Eng. Chem. Process Des. Dev.*, **17**(4), 448 (1978).
- Huron, M. J. and Vidal, J., "New Mixing Rules in Simple Equations of State for Representing Vapor-Liquid Equilibria of Strongly Non-Ideal Solutions," *Fluid Phase Equilibria*, **3**, 255 (1979).
- Kay, W. B., (1948) In: "Vapor-Liquid Equilibrium Data Collection," H. Knapp, R. Doring, L. Oellirch, U. Plocker and J. M. Prausnitz (eds.), DECHEMA, Frankfurt am Main (1982).
- Kay, W. B., (1970) In: "Vapor-Liquid Equilibrium Data Collection," H. Knapp, R. Doring, L. Oellirch, U. Plocker and J. M. Prausnitz (eds.), DECHEMA, Frankfurt am Main (1982).
- Kay, W. B., (1971) In: "Vapor-Liquid Equilibrium Data Collection," H. Knapp, R. Doring, L. Oellirch, U. Plocker and J. M. Prausnitz (eds.), DECHEMA, Frankfurt am Main (1982).
- Kiselev, S. B., Rainwater, J. C. and Huber, M. L., "Binary Mixtures in and Beyond the Critical Region: Thermodynamic Properties," *Fluid Phase Equilibria*, **150**, 469 (1998).
- Polishuk, I., Wisniak, J. and Segura, H., "Prediction of the Critical Locus in Binary Mixtures Using Equation of State. I. Cubic Equation of State, Classical Mixing Rules, Mixtures of Methane-Alkanes," *Fluid Phase Equilibria*, **164**, 13 (1999).
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids," 4th ed., Chap. 2, pp. 23; Chap. 8, pp. 272, Mc Graw Hill Book Co., New York (1987).
- Sage, B. H. and Lacey, W. N., (1940). In: "Vapor-Liquid Equilibrium Data Collection," H. Knapp, R. Doring, L. Oellirch, U. Plocker and J. M. Prausnitz (eds.), DECHEMA, Frankfurt am Main (1982).
- Stryjek, R. and Vera, J. H., "PRSV: A Cubic Equation of State for Accurate Vapor-Liquid Equilibrium Calculations," *Can. J. Chem. Eng.*, **64**, 820 (1986).
- Valderrama, J. O., "The State of the Cubic Equations of State," *Ind. Eng. Chem. Research*, **42**(7), 1603 (2003).
- Walas, S. M., "Phase Equilibria in Chemical Engineering," 1st ed., Chap. 6, pp. 302-309, Butterworth Pub., Storeham, USA (1985).
- Wong, D. S. H. and Sandler, S., "A Theoretical Correct Mixing Rule for Cubic Equations of State," *AIChE J.*, **38**, 671 (1992).