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A new correlation for VLE data: Application to binary mixtures containing nitrogen

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Abstract−Recently we proposed simple analytical expressions for the calculation of the equilibrium pressure, as well as the mole fractions of both liquid and vapor phases at the vapor-liquid equilibrium of binary mixtures. They are based on a recently proposed molecular model for the vapor pressure of pure non-polar fluids, which, for a given temperature, only requires as input the values of the two Lennard-Jones molecular parameters and the acentric factor, which are parameters related to the molecular shape of each substance, and whose values are readily available. The mixing rules contain adjustable parameters that must be obtained for each mixture. In this work, we test the applicability of the models for some mixtures containing nitrogen. In particular, we find that the calculation of mole fractions must be performed with particular care in some cases. We show that the model for the pressure clearly improves the results obtained with classical equations of state for most of the mixtures studied.

Key words: Binary Mixtures, Molecular Parameters, Nitrogen, Vapor-liquid Equilibrium

INTRODUCTION

Prediction of fluid phase equilibria has always played an essential role in many industrial applications. Activity coefficient models and equations of state are generally considered the most appropriate procedures to obtain these properties. One of the clear advantages that equations of state (EOS) present is that the required procedures have been widely studied and are well-known. Nevertheless, as Ashour and Aly [1994] and Valderrama [2003] have indicated, no single EOS currently exists that is equally suitable for the prediction of vapor-liquid equilibrium (VLE) of all classes of binary systems, and over the whole range of temperature, pressure and molecular variety. The EOS method is accurate in a great number of cases, but it is not always simple or straightforward.

It is known that the computational methods used to solve the VLE equations obtained from EOS are not straightforward, and the choice of a particular method can affect the final result [Ashour and Aly, 1996; Englezos et al., 1990]. Moreover, the mixing rules involved range from the simple Lorentz-Berthelot proposal to more complex density-dependent or composition-dependent expressions [Wong and Sandler, 1992; Valderrama, 2003]. Thus, further laborious studies may be needed to know which mixing rule gives the best results for each mixture [Keshtkar et al., 1997; Valderrama, 2003]. The binary interaction parameters must be obtained by fitting the experimental phase equilibrium data at each temperature. This means that they must be calculated at each temperature from experimental data, and that for temperatures where there are no experimental data, estimates must be used. Also, these parameters are sensitive to many factors, including the ranges of temperature, pressure and composition, and the quality of the experimental data [Polishuk et al., 1999]. In order to improve results, several correlation expressions for the binary parameters have been presented in the literature. However, they are not always suitable for extrapolation [Coutinho et al., 1994] and in many cases are only applicable to particular mixtures [Gao et al., 1992].

Recently, a new kind of correlation which gives analytical expressions for the pressure-temperature-mole fraction relations in the vapor-liquid equilibrium of non-polar binary mixtures has been proposed [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004]. The model is based on a simple analytical expression for the vapor pressure of pure non-polar fluids, which, for a given temperature, requires as input only the Lennard-Jones molecular parameters and the acentric factor of the substance. The equilibrium mixture pressure is then expressed as a function of the vapor pressure of each component and of a mixture contribution. The molecular parameters required for this mixture contribution are related to those of the pure components through mixing rules where the interaction parameters are given as simple functions of the temperature and composition, with eight appropriate constants for each binary mixture. In addition, another simple expression, based on Raoult's Law, is used to obtain the vapor mole fraction, with another five constants for each mixture.

In previous works [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004], the above-mentioned new analytical expressions were used to study mixtures of non-polar fluids containing either carbon dioxide, or ethane, or propane, obtaining good results. In comparison with those methods using EOS, the proposed model permits one to calculate the VLE properties for simple binary mixtures directly from the values of the Lennard-Jones parameters and the acentric factor of each substance. As far as we now, this new kind of correlation is the only proposal based on molecular parameters. Another generalized model to correlate thermodynamic properties of mixtures was developed by Lemmon and Jacobsen [1999]. This model gives good results for different properties (not only VLE ones). However, the model here proposed is simpler for application.

In the present work, the aforementioned constants are calculated for some non-polar binary mixtures containing nitrogen. We show how the model permits one to calculate or predict the pressure and

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the liquid and vapor mole fractions by simple procedures once these constants are known. In particular, we find that special care must be taken in the calculation of mole fractions, where erroneous values can result in some cases if certain criteria are not considered. These criteria were not needed in the application of the model to other mixtures [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004].

The paper is organized as follows. We first describe the new kind of correlations by giving all the needed analytical expressions. Results are presented for six binary mixtures of non-polar fluids: nitrogen with simple alkanes, oxygen and benzene. Finally, we present our conclusions.

ANALYTICAL EXPRESSIONS

In a previous paper [Faúndez et al., 2000], a simple analytical expression to model a large number of non-polar fluids was proposed. As a first approximation, the molecules of non-polar fluids interact according to the Lennard-Jones (LJ) potential with suitable values for the molecular parameters ε and σ [Cuadros et al., 1996]. These represent, respectively, the depth of the potential well, and the distance at which the potential takes a null value. Any physical property is then expressed in dimensionless units by using these parameters. The pressure, P, and the temperature, T, in real units are related to the reduced quantities, P^* and T^*, by the following expressions:

$$P = P^*\frac{(\varepsilon/k)R}{N_a\sigma^3}(\mathrm{Pa}),$$
$$T = T^*(\varepsilon/k)(\mathrm{K}), \tag{1}$$

where k is Boltzmann's constant, N_a is Avogadro's number, and R is the molar gas constant. The parameters ε/k and σ are expressed in kelvin and meter, respectively.

Once the reduced properties are defined, the reduced vapor pressure at a given temperature for non-polar fluids, $P^*_V(\omega, T^*)$, can be obtained as

Table 1. Coefficients of Eq. (2) obtained by correlation of experimental vapor pressure data [DIPPR, 1996] for 42 non-polar fluids

i	a_i
0	0.020526
1	−0.061772
2	0.126176
3	−0.221552
4	0.159504
5	−1.585263
6	5.602518
7	−6.725159
8	3.043007
9	−0.417099
10	0.028668
11	−1.346791
12	2.699790
13	−1.302182

Table 2. Properties of pure components used in the present study [Cuadros et al., 1996; DIPPR, 1996]

Fluid	ε/k (K)	σ (nm)	ω
Nitrogen	91.85	0.3919	0.033
Oxygen	113.27	0.3654	0.021
Butane	287.20	0.6081	0.201
Pentane	309.75	0.6709	0.251
Hexane	327.47	0.7319	0.294
Heptane	340.97	0.7902	0.350
Benzene	377.46	0.6174	0.209

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

where ω is the acentric factor for each real substance [Poling et al., 2001] and represents the deviation of the real molecular shape with respect to the spherical form considered for the LJ fluids. The universal coefficients a_i's were obtained from a fit to vapor pressure data for 42 substances and 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 [DIPPR, 1996].

To model the properties relative to the VLE of binary mixtures we proposed the following correlation between the pressure, temperature and liquid mole fraction [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004]:

$$P_m(T, x_1) = x_1P_1(\omega_1, T) + x_2P_2(\omega_2, T) + x_1x_2P_{12}(\omega_{12}, T) \tag{3}$$

In this equation, $P_m(T, x_1)$ is the pressure of the mixture, and $P_1(\omega_1, T)$ and $P_2(\omega_2, T)$ are the vapor pressures of the pure components; $P_{12}(\omega_{12}, T)$ represent the contribution to the mixture vapor pressure due to the cross-interactions between unlike molecules; ω_1 and ω_2 are the acentric factors; and x_1 and x_2 are the mole fractions of the two components in the liquid phase. The analytical expression of Eq. (3), where all the quantities are expressed in real units (P in Pa and T in K), allows one to obtain the vapor pressure of either pure fluid 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 by using Eq. (2), i.e., using the same analytical expression proposed for the vapor pressure of pure fluids. Since Eq. (2) is given in terms of reduced units, one has to use the molecular parameters of the first component (ε_1, σ_1, ω_1) to obtain the real values of $P_1(\omega_1, T)$. Similarly, one has to use those of the second component (ε_2, σ_2, ω_2), to obtain real values of $P_2(\omega_2, T)$. Values for $P_{12}(\omega_{12}, T)$ will be obtained by using mixing rules for ε_{12}, σ_{12}, and ω_{12} in terms of the molecular parameters of the pure components.

Taking into account that, as was indicated in the introduction, the binary interaction parameters are quite sensitive to many factors, including the temperature, pressure and composition range, the following mixing rules are used:

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}\frac{T}{(\tau_1 + \tau_2T + \tau_3T^2 + \tau_4x_1)} \tag{4}$$

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}(\tau_5 + \tau_6T + \tau_7T^2 + \tau_8x_1) \tag{5}$$

and

$$\omega_{12}=\omega_1+\omega_2 \tag{6}$$

where τ_i are adjustable parameters with different values for each mixture, but are independent of temperature, pressure, and composition.

In summary, to obtain the vapor pressure of a given mixture for 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 this mixture. Moreover, the mole fraction x_1 may be obtained by solving Eq. (3) for a given temperature and pressure.

For the sake of simplicity in Eq. (3), the mole fractions of the vapor phases, y_i, were not included. We therefore propose a simple analytical expression for calculating the vapor mole fraction when the temperature and liquid mole fraction are known. The model for y_i is then [Cuadros et al., 2003]:

$$y_1=\frac{x_1P_1(\omega,T)}{x_1P_1(\omega_1,T)+(1-x_1)P_2(\omega_2,T)}g(T,x_1) \tag{7}$$

where $g(T, x_1)$ is an non-dimensional function given by

$$g(T,x_1)=c_0+c_1T+c_2Tx_1+c_3x_1^2+c_4x_1^3 \tag{8}$$

and x_1 is the liquid mole fraction. As can be seen, five constants must be calculated for each binary mixture.

More details about the application of the model can be found in previous papers [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2000, 2001, 2004]. In the following section, we shall discuss the results when these models are used to reproduce the VLE properties of some binary systems containing nitrogen. These mixtures were chosen to show that especial criteria must be considered in some cases when mole fractions are calculated. These criteria were not found in the application of the model to other mixtures [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004].

Table 3. Values for the τ_i coefficients for Eqs. (4), (5) for the binary systems studied in this paper

τ_i	Nitrogen+ Oxygen	Nitrogen+ Butane	Nitrogen+ Pentane
τ_1 (K)	1.2339E+05	6.2257E+07	4.1283E+05
τ_2	−2.5443E+03	−2.8772E+05	−1.0225E+03
τ_3 (K^{-1})	1.2433E+01	−1.8218E+02	−4.5877E+00
τ_4 (K)	7.0111E+02	3.0406E+07	2.5625E+05
τ_5	2.0157E+03	−5.3346E+01	−5.1636E+03
τ_6 (K^{-1})	−4.6639E+01	1.7814E+00	−2.3600E+00
τ_7 (K^{-2})	2.4369E-01	−7.8868E-04	5.6754E-02
τ_8	3.3575E+00	−4.2873E+02	5.3329E-05
τ_i	Nitrogen+ Hexane	Nitrogen+ Heptane	Nitrogen+ Benzene
τ_1 (K)	5.3740E+06	−2.5722E+06	−7.6928E+05
τ_2	−2.2872E+04	1.3089E+04	4.0003E+03
τ_3 (K^{-1})	−3.6946E+01	1.3680E+01	−5.2318E+00
τ_4 (K)	4.7976E+06	−2.3412E+06	3.8173E+03
τ_5	8.2583E+02	−5.3346E+01	8.2583E+02
τ_6 (K^{-1})	−4.2788E+00	1.7814E+00	−4.2788E+00
τ_7 (K^{-2})	5.5653E-03	−7.8868E-04	5.5653E-03
τ_8	−4.4963E+00	−4.2873E+02	−4.4963E+00

Table 4. Values for the c_i coefficients of Eq. (8) for the binary systems studied in this paper

Mixture	c_0	c_1 (K^{-1})	c_2 (K^{-1})	c_3	c_4
N_2+O_2	1.9658	−1.003E-02	9.590E-03	−2.9905	2.2232
$N_2+C_4H_{10}$	3.0835	−7.311E-03	6.360E-03	−7.5956	6.8709
$N_2+C_5H_{12}$	2.1650	−4.603E-03	1.545E-02	−23.6519	30.1731
$N_2+C_6H_{14}$	1.7483	−2.539E-03	2.768E-03	−2.7572	1.6277
$N_2+C_7H_{16}$	1.0963	−3.699E-04	4.234E-04	−0.3730	0.1468
$N_2+C_6H_6$	1.3238	−1.050E-03	2.188E-03	−6.2818	13.7685

RESULTS AND DISCUSSION

The selected binary systems are the mixtures of nitrogen with oxygen, butane, pentane, hexane, heptane, and benzene. Table 3 lists the values for the coefficients τ_i (i=1, 2, ...8) in Eqs. (4), (5) for each mixture. These values were obtained by non-linear fitting to experimental data to the vapor pressure values obtained from Eq. (3) for each system. Table 4 lists the values for the coefficients c_i (i=1, 2, ...5) for Eq. (8) for the six systems. These values were obtained by fitting experimental data to the vapor mole fraction obtained from Eq. (7).

Table 5 gives the VLE data used in this study and the results for P, x_1, and y_1 for each temperature by using Eqs. (3) and (7). The first column gives the system, and the second column the number of data points used in the fit for the vapor pressure. The third, fourth, and fifth columns list the temperature, pressure range, and experimental liquid mole fraction range, respectively. The sixth, seventh, and eighth columns give the absolute relative percentage deviation between experiment and calculation for the equilibrium pressure, ΔP, the liquid mole fraction, Δx_1, and the vapor mole fraction, Δy_1, for each isothermal set of data, and the mean deviations for each of the systems studied (numbers in bold face). The last column gives the source of data.

As one sees from Table 5, the proposed molecular model, Eq. (3), reproduces the vapor pressures of the selected binary mixtures with mean absolute deviations less than 5.5% for each temperature, with only two exceptions: for nitrogen+oxygen at 75 K and for nitrogen+butane at 310.93 K. In these cases, the high deviations are due to the use of data for low pressures, where the relative deviations are high although the absolute deviations are low.

In Table 6, we give a comparison of the mean deviations obtained when well-known equations of state (with one adjustable parameter for each temperature) are used to fit the same sets of data [Gmehling et al., 1982]. As can be seen, our molecular model gives a lower deviation except in the case of the nitrogen+oxygen mixture. In some cases (the mixtures of nitrogen with pentane, hexane, heptane, and benzene), the model clearly improves the equation of state results.

Figs. 1 to 4 show some of the results graphically. Thus, for nitrogen+butane Fig. 1 shows that the experimental data cross each other at low pressures, and there are data near the critical locus. Although both facts influence the validity of the model, the mean deviation in the calculated pressure is less than that obtained when equations

Table 5. Correlation of VLE data for the binary systems using Eqs. (3) and (7): number of data points; conditions and source of experimental data; and percentage absolute deviation between experimental and calculated values for the equilibrium pressure, the liquid mole fraction, Δx_1, and the vapor mole fraction, Δy_1, for each isothermal data set, together with the mean deviations for each of the systems studied (bold face numbers)

Mixture	Nº data	T (K)	Range of P (MPa)	Range of x_1	ΔP_m (%)	Δx_1 (%)	Δy_1 (%)	Ref.
Nitrogen+	110	75.00	0.0183-0.0709	0.0500-0.9000	16.05	36.77	8.74	Dodge
Oxygen		80.00	0.0367-0.1271	0.0500-0.9000	3.45	16.73	4.75	[1926]
		85.00	0.0673-0.2129	0.0500-0.9000	0.85	3.10	5.67	
		90.00	0.1147-0.3367	0.0500-0.9000	0.22	0.78	5.93	
		95.00	0.1831-0.5073	0.0500-0.9000	0.52	1.26	5.30	
		100.00	0.2818-0.7339	0.0500-0.9000	0.69	1.63	4.30	
		105.00	0.4160-1.0244	0.0500-0.9000	0.79	2.11	3.62	
		110.00	0.5938-1.3881	0.0500-0.9000	0.93	3.01	3.46	
		115.00	0.8207-1.8319	0.0500-0.9000	1.07	3.87	3.46	
		120.00	1.1085-2.3608	0.0500-0.9000	1.33	5.36	3.76	
		125.00	1.4571-2.8816	0.0500-0.9000	0.67	3.41	3.93	
					2.42	**7.09**	**4.81**	
Nitrogen+	27	310.93	1.6271-23.4558	0.0250-0.3880	8.53	8.78	4.15	Roberts and
Butane		344.26	3.5646-20.6703	0.0560-0.4650	5.39	7.01	4.30	McKetta
		377.59	5.8398-14.7271	0.1120-0.4490	3.83	9.27	5.54	[1961]
		410.93	4.1092-7.3704	0.0340-0.2440	4.16	12.40	10.85	
					5.30	**9.27**	**6.07**	
Nitrogen+	42	277.43	1.6616-20.7255	0.0250-0.2510	4.62	4.30	1.45	Kalra et al.
Pentane		310.71	0.2503-20.753	0.0037-0.2880	2.03	2.39	6.23	[1977]
		344.26	0.4137-20.7806	0.0022-0.3300	1.32	1.64	10.36	
		377.59	0.8136-20.7944	0.0032-0.4000	4.14	6.28	14.81	
					2.78	**3.44**	**8.56**	
Nitrogen+	52	310.93	1.7237-34.4735	0.0260-0.3590	5.43	4.41	1.53	Poston and
Hexane		344.26	1.7237-34.4735	0.0250-0.3910	2.66	2.34	1.59	McKetta
		377.59	1.7237-34.4735	0.0230-0.4790	3.30	3.58	3.44	[1966]
		410.93	1.7650-29.1025	0.0210-0.5760	1.69	2.34	5.29	
		444.26	3.4473-20.1946	0.0490-0.5050	5.40	7.50	8.34	
					3.60	**3.83**	**3.79**	
Nitrogen+	34	305.37	7.1015-69.1193	0.0800-0.5050	3.49	2.88	0.24	Akers et al.
Heptane		352.59	7.0326-69.1193	0.0960-0.7050	3.41	3.57	0.44	[1954]
		399.82	7.3084-55.1921	0.1160-0.7230	1.88	1.32	0.45	
		455.37	7.7979-24.3038	0.1280-0.4280	2.66	2.76	0.48	
					3.00	**2.64**	**0.36**	
Nitrogen+	18	348.15	6.2112-30.2603	0.0345-0.1458	0.48	0.43	0.27	Miller and
Benzene		373.15	6.2719-30.5592	0.0396-0.1750	1.00	0.93	0.40	Dodge
		398.15	6.4442-30.7111	0.0430-0.2044	0.55	0.55	0.21	[1940]
					0.65	**0.62**	**0.29**	

of state are used. For nitrogen+pentane, Fig. 2 illustrates the validity of the model even for the highest and the lowest temperatures, where the relative deviations are high. For nitrogen+hexane, Fig. 3, the model behaves very well for intermediate temperatures and pressures, with the mean deviations for each temperature being less than 5.5% (Table 5). For nitrogen+heptane, the experimental data are excellently reproduced, Fig. 4, with deviations less than or equal to 7% except for one datum. For nitrogen+benzene, only 18 experimental data were used. Nevertheless, the mean deviations obtained with the use of the model are significantly less than that obtained when equations of state are used. Individual deviations are less than or equal to 2%. In all cases, it must be taken into account that the model can be used at any intermediate temperature without introducing new constants, whereas for equations of state a new fitting procedure is needed.

As shown in Table 5, in the calculation of the liquid mole fraction, our molecular model, Eq. (3), gives mean absolute deviations greater than 10% for some temperatures in the nitrogen+oxygen and nitrogen+butane mixtures. Nevertheless, the mean deviations for these mixtures are less than 10%. Moreover, for the other four

Table 6. Mean deviations for the mixture pressure obtained with equations of state [Gmehling et al., 1982] and with our model (LKP: Lee-Kesler [1975] equation with mixing rules of Plöcker et al. [1978]; BWR: Benedict-Webb-Rubin [1940] equation; SRK: Soave-Redlich-Kwong [Soave, 1972] equation; PR: Peng-Robinson [1976] equation)

Mixture	Mean deviations (%)				
	LKP	BWR	SRK	PR	Eq. (3)
N_2+Oxygen	1.36	1.67	1.44	1.19	2.42
N_2+Butane	9.65	11.69	6.18	5.97	5.30
N_2+Pentane	6.09	14.94	4.79	4.82	2.78
N_2+Hexane	10.64	15.63	7.26	6.43	3.60
N_2+Heptane	11.66	24.5	5.28	5.14	3.00
N_2+Benzene	4.19	12.08	3.48	3.44	0.65

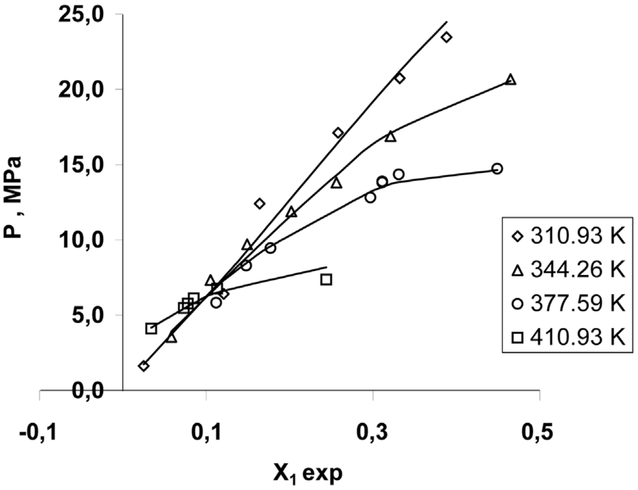

Fig. 1. Experimental data (symbols) [Roberts and McKetta, 1961] and fitted values (lines) obtained from our model Eq. (3) for the pressure of the nitrogen+butane system.

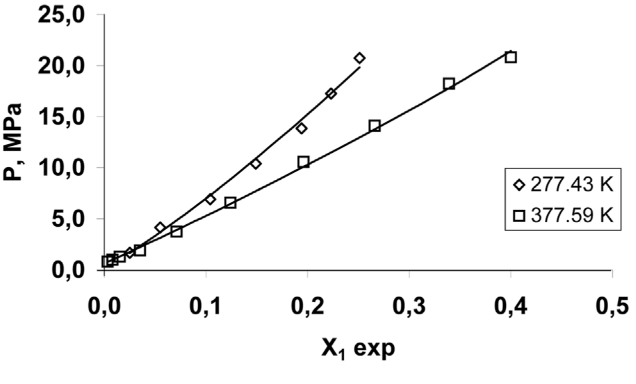

Fig. 2. Experimental data (symbols) [Kalra et al., 1977] and fitted values (lines) obtained from our model Eq. (3) for the pressure of the nitrogen+pentane system at the lowest and highest temperatures included in our study (Table 5).

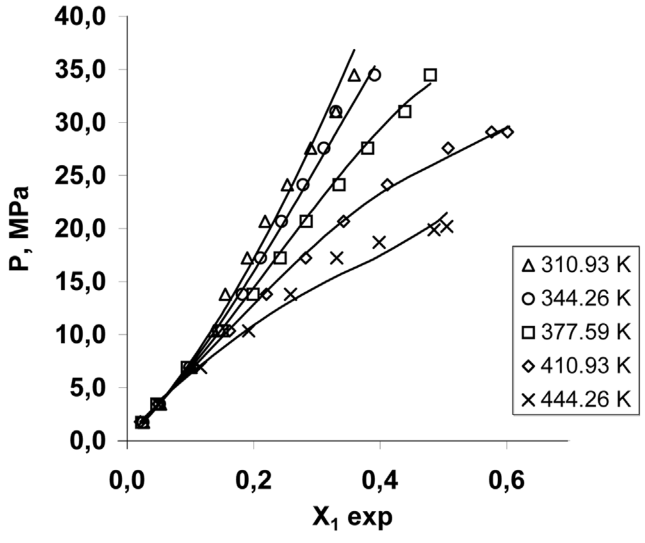

Fig. 3. Experimental data (symbols) [Poston and McKetta, 1966] and fitted values (lines) obtained from our model Eq. (3) for the pressure of the nitrogen+hexane system.

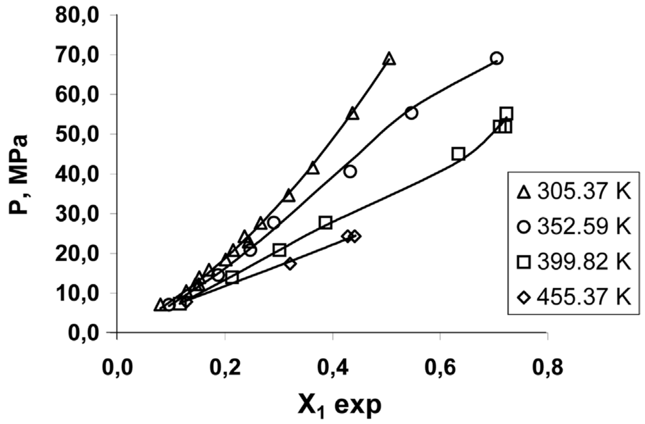

Fig. 4. Experimental data (symbols) [Akers et al., 1954] and fitted values (lines) obtained from our model Eq. (3) for the pressure of the nitrogen+heptane system.

mixtures, the model allows one to obtain the liquid mole fraction with mean absolute deviations less than or equal to 7.5% for each isothermal set of data studied, the mean deviation for each mixture being less than 4%. This is a reasonable result, because x_1 must be obtained by solving the equation resulting from substituting experimental values of temperature and pressure into Eq. (3). The deviations are of similar order to those obtained in the calculation of pressure.

We found that in some cases, when x_1 is extremely small, and hence close to zero, the model can give negative, but very near zero, solutions. We then took x_1=0 as the result. This occurs only for the two first data points at 75 K and the first datum at 80 K in the nitrogen+oxygen mixture, Fig. 5, and contributes greatly to the mean deviation at these temperatures (If we take x=0 the deviation with respect to any value different from zero is 100%.). As can be seen in Table 5, the mean deviation for the other temperatures is always less than 5.4%.

In other cases, the experimental pressure was slightly greater than the maximum pressure calculated with the model (although the absolute difference between them was small). In these cases, we took

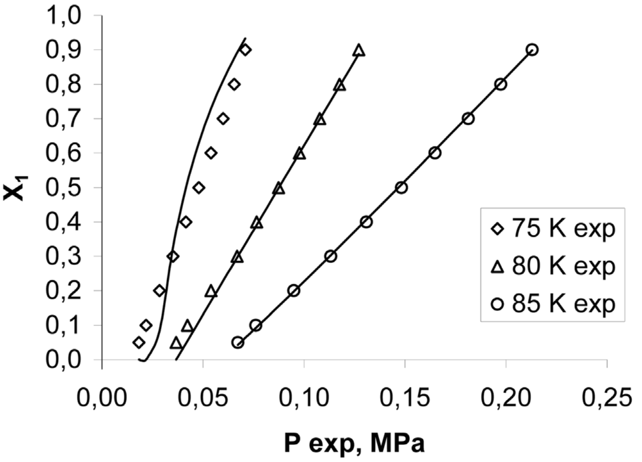

Fig. 5. Experimental data (symbols) [Dodge, 1926] and fitted values (lines) obtained from our model Eq. (3) for the liquid mole fraction of the nitrogen+oxygen system at low temperatures.

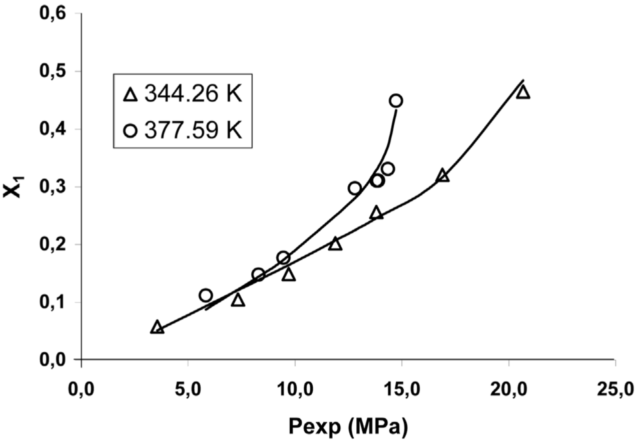

Fig. 6. Experimental data (symbols) [Roberts and McKetta, 1961] and fitted values (lines) obtained from our model Eq. (3) for the liquid mole fraction of the nitrogen+butane system at two temperatures.

as the calculated value of x_1 the value obtained at that maximum pressure. This occurs, for example, at the highest pressure for the nitrogen+butane mixture at 344.26 K and 377.59 K, Fig. 6, and for nitrogen+heptane at 352.59 K, and does not influence the mean deviation.

These two constraints for the application of our model were not found in our previous work. In any case, for future applications the indicated criteria (to take $x_1=0$ if negative values are found, and to take x_1 at the highest pressure given by the model if this pressure is less than the experimental value) must be taken into account.

With respect to the vapor mole fraction y_1, this quantity is calculated with mean deviations for each mixture ranging from 0.3% to 8.6% (the numbers in bold face in Table 5). There are three temperatures for which the means for the isothermal data (the non-bold-face numbers in Table 5) are greater than 10%, and nine for which they are less than 2%. Some of the greatest values of Δy_1 are due to the large deviations found for some particular experimental points.

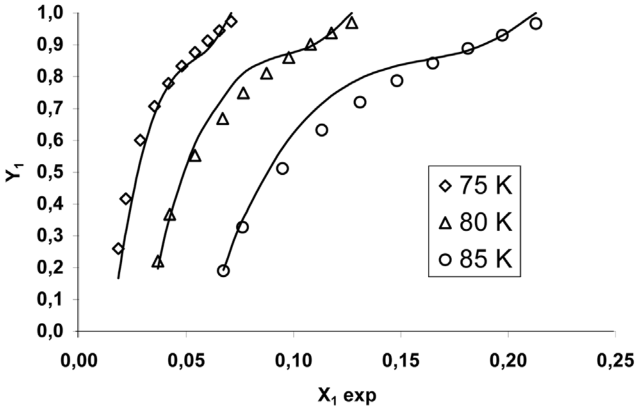

Fig. 7. Experimental data (symbols) [Dodge, 1926] and fitted values (lines) obtained from our model Eq. (7) for the vapor mole fraction of the nitrogen+oxygen system at low temperatures.

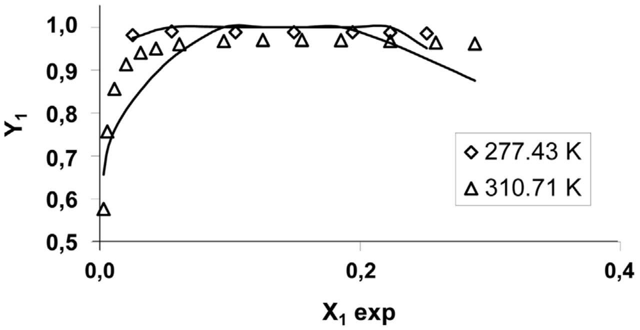

Fig. 8. Experimental data (symbols) [Kalra et al., 1977] and fitted values (lines) obtained from our model Eq. (7) for the vapor mole fraction of the nitrogen+pentane system at low temperatures.

Thus, for the nitrogen+oxygen mixture, the greatest Δy_1 is obtained at 75 K, where there is one datum with a deviation of 35% due to the vapor mole fraction value being close to zero. For the other temperatures the mean deviations are less than 6%. As can be seen in Fig. 7 (note the smallness of the range of x), the absolute deviation is large at intermediate mole fractions for the higher temperatures.

For nitrogen+butane, an individual deviation of 46% is found for the highest temperature and density. This experimental point is very close to the critical locus and hence is very difficult to correlate. As can be seen in Table 5, for the other temperatures the mean deviations are less than 6%.

For nitrogen+pentane, we find different degrees of accuracy at low and at high temperatures. Thus, although for the lower temperature the mean deviation is only 1.5%, it is important to take into account that Eq. (7) lead to values slightly greater than 1 for some cases, so that we set $y_1=1$. This also occurs for 310.71 K. These criteria do not influence the mean deviations, but, as is shown in Fig. 8, it leads to a disagreement between the model and the trend of the data. We would note also that these constraints were not found in previous uses of the model [Cuadros et al., 2000, 2002, 2003; Faúndez et al., 2001, 2004].

For nitrogen+pentane at higher temperatures the mean deviations

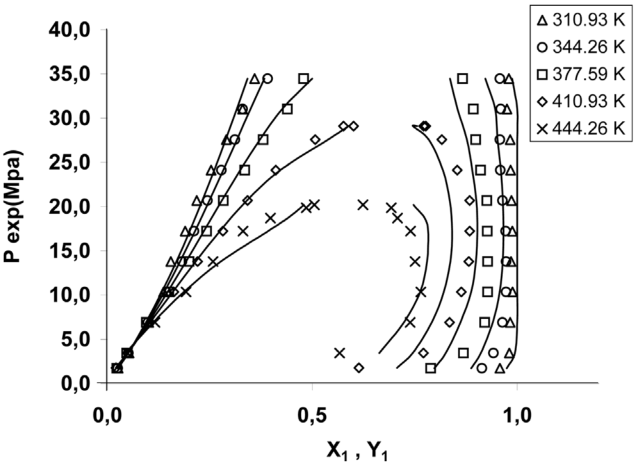

Fig. 9. Experimental data (symbols) [Poston and McKetta, 1966] and fitted values (lines) obtained from our model Eqs. (3) and (7) for the liquid and vapor mole fractions of the nitrogen+hexane system.

are greater than 10%, although most of the experimental points correspond to individual deviations less than 15%. However, there are three data at the lowest pressures and with the lowest values of y_1 for which deviations greater than 30% are reached.

As can be seen in Table 5 and Fig. 9, for the nitrogen+hexane mixture the mean deviation increases with temperature due to the increasing curvature in the experimental lines. At the lowest temperature, we found some values slightly greater than 1, which we replaced by the value 1 (Fig. 9). We note that for that temperature, the trend of the experimental points is practically vertical and very close to 1, and it is extremely difficult to match this trend with an analytical expressions at the same time as fitting the data at the higher temperatures (with a greater degree of curvature).

For the mixtures containing heptane or benzene, the accuracy of Eq. (7) is greater than that for the other mixtures. Thus, for the nitrogen+heptane mixture, despite the scatter of the data, all the individual deviations are less than 1% and the model clearly reproduces their trend (see Fig. 10, noting the scale of the figure). The same is the case for the nitrogen+benzene mixture.

In all cases, it must be taken into account that, once the constants are defined, the model can be easily applied for intermediate temperatures, pressures or mole fractions for which experimental data do not exist. Obviously, the simplicity of the model can lead to occasional large individual deviations that must be corrected by improving the model or the mixing rules.

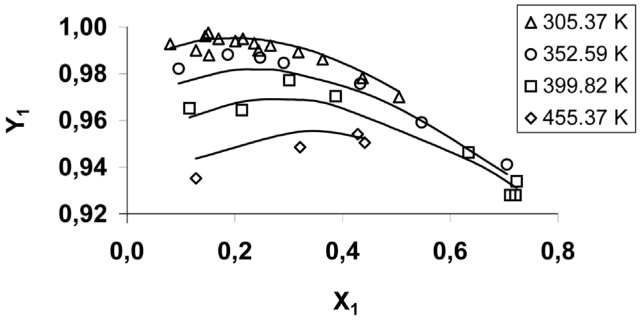

Fig. 10. Experimental data (symbols) [Akers et al., 1954] and fitted values (lines) obtained from our model Eq. (7) for the vapor mole fraction of the nitrogen+heptane system.

In summary, we have shown that the present model can reproduce, to a varying degree of agreement and taking into account different calculation criteria, different VLE diagrams. It could therefore serve as a basis for the development of at least an "almost" universal model for simple mixtures.

CONCLUSIONS

Analytical expressions relating properties of the vapor-liquid equilibrium of non-polar binary mixtures were used to correlate vapor-liquid equilibrium pressure and mole fractions for six mixtures containing nitrogen. The models were based on a simple analytical expression for the vapor pressure of the pure components. The equilibrium pressure for the mixture was then expressed in terms of the vapor pressure of each component and a mixture contribution was obtained from mixing rules, in which the interaction parameters are given as simple functions of the temperature and liquid composition, with eight adjustable parameters for each system. Since the mixing rules are defined by these constants, their final expressions have the same analytical form for any mixture.

A different model permits one to obtain the vapor mole fraction as a function of temperature and liquid mole fraction and five appropriate constants for each mixture. In all cases, the Lennard-Jones molecular parameters and the acentric factor of the components are the only input data, once the constants are known.

Good results were found for the calculation of the pressure, except for some particular experimental points. The model clearly improves the results of the classical equations of state for most of the mixtures that were studied.

The models were used in previous papers. Nevertheless in this work, we found that they can give values greater than 1 for the mole fractions in some particular cases. Also, the liquid mole fraction must be obtained by solving an equation, and in some cases no correct solution can be found. Thus, sometimes a negative, but near zero value, is obtained. In the use of the model, the solutions must be limited to the range from 0 to 1, so that some solutions must be appropriately rounded. Also, a far greater value of the liquid fraction may be obtained because for some states the maximum calculated pressure is slightly lower than the experimental pressure. In such a case, we recommend taking the value obtained at that maximum pressure as the calculated value.

To improve the model, a more complex mixing rule for the acentric factor could be defined, searching for the existence of an acentric factor for the mixture. We are now working on this and other ideas to define a more universal model for the correlation of vapor-liquid equilibrium data. We believe that the analytical expressions used here can serve as the basis for the development of new models. Moreover, the effect of different mixing rules on the predicted VLE properties obtained and the application to multicomponent mixtures should be considered.

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REFERENCES

Akers, W. W., Kehn, D. M. and Kilgore, C. H., "Volumetric and phase behavior of nitrogen-hydrogen system: nitrogen-n-heptane system," *Ind. Eng. Chem*., **46**, 2536 (1954).

Ashour, I. and Aly, G., "Representation of VLE using selected EOSs," *Fluid Phase Equilibria*, **98**, 55 (1994).

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. Engn.*, **20**, 79 (1996).

Benedict, M., Webb, G. B. and Rubin, L. C., "An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures," *J. Chem. Phys.*, **8**, 334 (1940).

Coutinho, J., Kontogeorgis, G. and Stenby, E., "Binary interaction parameters for nonpolar systems with cubic EOSs: a theoretical approach. 1. CO_2/hydrocarbons using SRK equation of state," *Fluid Phase Equilibria*, **102**, 31 (1994).

Cuadros, F., Cachadiña, I. and Ahumada, W., "Determination of Lennard-Jones interaction parameters using a new procedure," *Mol. Engng.*, **6**, 319 (1996).

Cuadros, F., Faúndez, C. A. and Mulero, A., "Molecular Thermodynamic Models for the VLE p-T-x relationships of binary mixtures," *Phase Transitions*, **72**, 309 (2000).

Cuadros, F., Faúndez, C. A., Renuncio, J. A. R. and Mulero, A., "An analytical pressure-temperature-composition correlation for the VLE of CO_2 binary mixtures," *Termochimica Acta*, **389**, 167 (2002).

Cuadros, F., Mulero, A., Okrasinski, W., Faúndez, C. A. and Parra, M. I., "VLE molecular thermodynamics of non polar fluids and their mixtures," *Int. Rev. Phys. Chem.*, **19**, 387 (2003).

DIPPR (Design Institute for Physical Property Data) files, American Institute of Chemical Engineers (1996).

Dodge, B. F. (1926) In: *Vapor-liquid data collection*, Gmehling, J., Onken, U., Arlt, M. (Eds.), DECHEMA, Frankfurt am Main (1982).

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 vapour-liquids equilibrium of non-polar fluids," *J. Phase Equilibria*, **21**, 364 (2000).

Faúndez, C. A., Mulero, A. and Cuadros, F., "Molecular models for the VLE of simple binary mixtures," *J. Phase Equilibria*, **22**, 531 (2001).

Faúndez, C. A., Tamblay, L. E. and Valderrama, J. O., "A molecular model for correlating vapor-liquid equilibrium of propane+hydrocarbon mixtures," *Korean J. Chem. Eng.*, **21**, 1199 (2004).

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 hydrocarbons systems," *Fluid Phase Equilibria*, **74**, 85 (1992).

Gmehling, J., Onken, U. and Arlt, M. (Eds.), *Vapor-liquid data collection*, DECHEMA, Frankfurt am Main (1982).

Kalra, N., Robinson, D. R. and Bessenger, G. J., "The equilibrium phase properties of nitrogen-n-pentane system," *J. Chem. Engng. Data*, **22**, 215 (1977).

Keshtkar, A., Jalali, F. and Moshfeghian, M., "Evaluation of VLE of CO_2 binary systems using UNIQUAC-based HV mixing rules," *Fluid Phase Equilibria*, **140**, 107 (1997).

Lee, B. I. and Kesler, M. G., "A generalized thermodynamic correlation based on three-parameter corresponding states," *AIChE J.*, **21**, 510 (1975).

Lemmon, E. W. and Jacobsen, R. T., "A Generalized model for the thermodynamic properties of mixtures," *Int. J. Thermophys.*, **20**, 825 (1999).

Miller, P. and Dodge, B. F., "The system benzene-nitrogen. Liquid-vapor equilibria at elevated pressures," *Ind. Eng. Chem.*, **32**, 434 (1940).

Peng, D. Y. and Robinson, D. B., "A new two-constant equation of state," *Ind. Engng. Chem. Fundamem.*, **15**, 59 (1976).

Plöcker, U., Knapp, H. and Prausnitz, J. M., "Calculation of high-pressure vapor-liquid equilibria from a corresponding states correlation with emphasis on asymmetric mixtures," *Ind. Eng. Chem. Pr. Des. Dev.*, **17**, 324 (1978).

Poling, B. E., Prausnitz, J. M. and O'Connell, J. P., *The properties of gases and liquids*, Fifth Edition, McGraw-Hill Book Co., New York (2001).

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).

Poston, R. S. and McKetta, J. J. (1966) In: *Vapor-liquid data collection*, Gmehling, J., Onken, U., Arlt, M. (Eds.), DECHEMA, Frankfurt am Main (1982).

Roberts, L. R. and McKetta, J. J., "Vapor-liquid equilibrium in the *n*-butane-nitrogen system," *AIChE J.*, **7**, 173 (1961).

Soave, G., "Equilibrium constants from a modified Redlich-Kwong equation of state," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Valderrama, J. O., "The state of the cubic equations of state," *Ind. Eng. Chem. Research*, **42**, 1603 (2003).

Wong, D. S. H. and Sandler, S. I., "A theoretical correct mixing rule for cubic equations of state," *AIChE J.*, **38**, 671 (1992).