Molecular Models for the Vapor-Liquid Equilibrium of Simple Binary Mixtures

C.A. Faúndez, A. Mulero, and F. Cuadros

(Submitted 28 February 2001)

Simple analytical expressions are proposed for the calculation of the equilibrium pressure, as well as (for a given temperature and pressure) 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 nonpolar fluids, which, for a given temperature, only requires as input the values of the two Lennard-Jones (LJ) molecular parameters and the acentric factor, which are parameters related to the molecular shape of each substance and whose values are readily available. The model for the equilibrium pressure of a binary mixture (which also permits one to obtain the liquid phase mole fraction) is similar to that derived from Raoult's law, where a properly modified Lorentz-Berthelot mixing rule is used, the interaction parameters being given as simple functions of the temperature and composition with eight appropriate constants for each binary mixture. A different model is needed to calculate the vapor mole fraction in which five appropriate constants are needed for each mixture. Here, we show how the models reproduce accurately and straightforwardly the vapor liquid equilibrium properties (pressure, liquid mole fraction, and vapor mole fraction) of eight binary systems over a broad temperature range, including some data at or near the critical locus.

1. Introduction

Prediction of fluid phase equilibria has always played an essential role in many industrial applications. For this reason, it is essential to use reliable models that generate accurate phase equilibrium properties using, if possible, a simple procedure. Different thermodynamic models have been developed and reported in the literature: these include activity coefficient models, which describe liquid-phase nonideality; and equations of state (EOS), generally considered the most appropriate models to calculate the phase equilibrium of mixtures [1986Pra].

One of the clear advantages that EOS present is that the required procedures have been widely studied and are well-known. Nevertheless, when the properties of interest are those of a phase equilibrium and, in particular, of vapor-liquid equilibrium (VLE), the method, although accurate in a great number of cases, is not simple or straightforward. Thus, as Ashour and Aly [1994Ash] have indicated, no EOS currently exist that are equally suitable for the prediction of VLE of all classes of binary systems, and over the entire range of temperature, pressure, and molecular variety. Moreover, the application of EOS to mixtures requires the use of mixing rules giving the interaction parameters between the different components of the mixture. These mixing rules range from the simple Lorentz-Berthelot proposal to more complex density-dependent or composition-dependent expressions [1979Hur, 1986Str, 1992Won]. Thus, further laborious studies may be needed to know what mixing rule gives the best results for each mixture [1997Kes].

An added difficulty is that the computational methods used to solve the VLE equations are not straightforward, and the choice of which particular method can even affect the final result [1996Ash, 1990Eng]. Moreover, 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, estimated values of these parameters must be used. It must be taken into account that the binary interaction parameters are sensitive to many factors, including the ranges of temperature, pressure, and composition and the quality of the experimental data [1999Pol]. 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 [1994Cou] and, in many cases, are only applicable to particular mixtures [1992Gao].

Some of the previous questions can be solved by using EOS based on molecular parameters [1986Cot1, 1986Cot2, 1998Kis, 1998Bla, 2000Lee]. Although the results are 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 an expression that is simple to use and that is based on a recently proposed molecular model for the vapor pressure of pure nonpolar fluids [2000Fau]. A simple modified version of the Lorentz-Berthelot rules, where the interaction parameters are given as functions of temperature and liquid-phase composition [2000Cua2], must also be used. In addition, another simple expression, based on Raoult's law, is used to obtain the

C.A. Faúndez, Dpto. de Física, Universidad de La Serena, La Serena, Chile; and **A. Mulero** and **F. Cuadros,** Dpto. de Física, Universidad de Extremadura, 06071 Badajoz, Spain. Contact e-mail: cuadros1@unex.es.

vapor mole fraction. In comparison with the methods that use EOS, the proposed model permits one to calculate directly and straightforwardly the VLE properties for simple binary mixtures from only a knowledge of the Lennard-Jones (LJ) parameters and the acentric factor of each substance [2000Cua2].

The paper is organized as follows. We first describe the molecular model for the vapor pressure of nonpolar pure fluids. Then, we propose their extension to binary mixtures and the new mixing rules. Finally, results are presented for eight binary mixtures containing ethane and dioxide carbon.

2. Molecular Model for Pure Fluids

In a previous paper [2000Fau], we proposed a simple analytical expression to model a large number of nonpolar fluids. As a first approximation, we consider that the molecules of nonpolar fluids interact according to the LJ potential with suitable values for the molecular parameters ε and σ [1996Cua]. 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 adimensional units 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:

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

$$\rho = \frac{\rho^*}{\mathrm{N_a}\sigma^3} \ (\mathrm{mol \cdot m^{-3}}) \tag{Eq 1}$$

$$T = T^* \ (\varepsilon/\mathrm{k}) \ (\mathrm{K})$$

where k is the Boltzmann's constant, $\mathrm{N_a}$ the Avogadro's number, and R the ideal gas constant. The parameters ε/k and σ are expressed in kelvin and meters, respectively.

Once the reduced properties are defined, we showed [2000Fau] that, for nonpolar fluids, the vapor pressure at a given temperature, $P_v^*\ (\omega, T^*)$ can be obtained as

$$P_v^*(\omega,T^*) = P_v^{*\mathrm{LJ}}(T^*) + f(\omega,T^*) \tag{Eq 2}$$

where $P_v^*\mathrm{LJ}(T)$ is the vapor pressure for an LJ fluid, which can be expressed, to a good approximation, as a polynomial in the temperature [2000Cua1, 2000Fau]:

$$P_v^{*\mathrm{LJ}}(T^*) = -0.530964 + 2.422916T^* - 4.074344T^{*2}$$
$$+ 2.934668T^{*3} - 0.724252T^{*4} \tag{Eq 3}$$

In Eq 2, $f(\omega, T^*)$ is a universal (in reduced units) polynomial expression given by

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

$$\tag{Eq 4}$$

Table 1 Coefficients of Eq 4 obtained by correlation of experimental vapor pressure data [1996DIP] for 42 nonpolar fluids

a_0	0.551490
a_1	−2.484688
a_2	4.200572
a_3	−3.156220
a_4	0.883756
a_5	−1.585263
a_6	5.602518
a_7	−6.725159
a_8	3.043007
a_9	−0.417099
a_{10}	0.028668
a_{11}	−1.346791
a_{12}	2.699790
a_{13}	−1.302182

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

Substance	ε/k (K)	σ (Å)	ω	Temperature range (K)	ΔP_v (%)
Ethane	216.12	4.782	0.0990	172.9–281.0	1.2
Cyclopentane	346.11	6.100	0.1960	285.5–449.9	2.3
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
Carbon dioxide	201.71	4.444	0.2310	216.8–262.2	0.2
n-Pentane	309.75	6.709	0.2510	263.3–402.7	2.3
n-Heptane	340.97	7.902	0.3500	298.4–443.3	3.1
n-Octane	351.42	8.498	0.3980	316.3–456.9	5.0

where ω is the acentric factor for each real substance [1987Rei] 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 were obtained [2000Fau] from a fit to vapor pressure data for 42 substances [1996DIP] and are listed in Table 1.

Table 2 lists the molecular parameter values used for the nonpolar fluids chosen for this present study. The second and third columns give the LJ parameters [1996Cua] and the fourth column gives the corresponding values of the acentric factor. The fifth column gives the temperature interval covered for each substance in the fit to the vapor pressure, and the sixth column gives the mean absolute deviation ΔP_v between the experimental values of the vapor pressure [1996DIP] and those obtained from Eq 2. These deviations range from 0.2% for carbon dioxide to 5% for n-octane (for the temperature range that was considered). A complete list for 42 substances can be found in our earlier article [2000Fau].

The procedure described above was also used to model the density of the liquid phase and the latent heat of vaporization of these nonpolar fluids [2000Fau]. In all cases, the models start out from the corresponding property of the LJ reference system, which is perturbed appropriately.

3. Molecular Model for Binary Mixtures

The model for the vapor pressure of pure fluids presented in the previous section will now be used to model the properties relative to the VLE of binary mixtures of nonpolar fluids. To this end, we shall assume that the vapor pressure of a given mixture obeys the law [2000Cua2]

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

(Eq 5)

In this equation, $P_1(\omega_1, T)$ and $P_2(\omega_2, T)$ are the vapor pressures of the pure components; $P_{12}(\omega_{12}, T)$ represents 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 5, where all the quantities are expressed in real units, 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 using Eq 2, *i.e.*, using the same analytical expression proposed for the vapor pressure of pure fluids. Because 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 using the 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 Section 1, the binary interaction parameters are quite sensitive to many factors, including the temperature, pressure, and composition range, we propose the following mixing rules [2000Cua2]:

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

(Eq 6)

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

(Eq 7)

and

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

(Eq 8)

where τ_i terms are parameters that adopt different values for each particular mixture, but are independent of temperature, pressure, or composition.

In sum, 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 5 for a given temperature and pressure.

Because of the simplicity of Eq 5, the mole fractions of the vapor phases, y_i, are 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

$$y_1 = \frac{x_1 P_1(\omega_1, T)}{x_1 P_1(\omega_1, T) + (1 - x_1) P_2(\omega_2, T)} g(T, x_1)$$

(Eq 9)

where $g(T, x_1)$ is given by

$$g(T, x_1) = c_0 + c_1 T + c_2 T x_1 + c_3 x_1^2 + c_4 x_1^3$$

(Eq 10)

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

In the following section, we shall discuss the results obtained when these models are used to reproduce the VLE properties of some binary systems.

4. Results

The selected binary systems are four mixtures containing ethane and another four mixtures containing CO_2. Ethane is a simple hydrocarbon with a low acentric factor, whereas CO_2 is interesting because of its practical applications.

Table 3 lists the values for the coefficients τ_i ($i = 1, 2, \ldots 8$) in Eq 6 and 7 for the eight systems studied. These values were obtained by comparing the vapor pressure values obtained from Eq 5 for a broad temperature and liquid mole fraction range and the experimental data for each system. Average absolute deviations between theoretical and experimental pressures are given in Table 5.

Table 4 lists the values for the coefficients c_i ($i = 0, 1, \ldots 4$) for Eq 10 for the eight systems. These values were obtained by comparing the vapor mole fraction obtained from Eq 9 and the experimental data.

Table 5 gives the VLE data used in this study and the results obtained for P, x_1, and y_1 using Eq 5 and 9, respectively, for each temperature. The first column lists the system and the second column indicates the number of data points used in the fit for the vapor pressure. The third, fourth, and fifth columns list the temperature, the pressure range, and the experimental liquid mole fraction range, respectively. The sixth, seventh, and eighth columns give the absolute relative percentage deviation between experimental and calculated equilibrium pressure, ΔP_m, 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 one of the systems studied (numbers in bold). The last column gives the source of data.

As one sees from Table 5, the proposed molecular model, Eq 5, reproduces the vapor pressures of the selected binary mixtures with mean absolute deviations less than 5.5% for each temperature, except at temperatures near 300 K for the ethane + benzene mixture. For mixtures containing ethane, the mean absolute deviations vary from 0.4 to 3.4%, whereas these deviations vary from 1.9 to 4.3% for the CO_2 mixtures.

As may be seen in Table 5, our molecular model, Eq 5, permits one to obtain the liquid mole fraction of these binary

Table 3   Values for the τ_i coefficients of Eq 6 and 7 for the binary 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 5

τ_i	Ethane + n-butane	Ethane + benzene	Ethane + n-heptane	Ethane + n-octane
τ_1 (K)	-4.54172×10^{12}	-5.38247×10^{11}	-4.22455×10^{12}	-1.09756×10^{11}
τ_2	3.86687×10^{9}	2.52515×10^{9}	2.14675×10^{10}	1.34088×10^{9}
τ_3 (K^{-1})	1.27093×10^{8}	-2.83935×10^{6}	-3.58822×10^{7}	-3.67498×10^{6}
τ_4 (K)	-1.18757×10^{13}	5.96863×10^{10}	1.06361×10^{12}	1.97741×10^{10}
τ_5	9.85799×10^{10}	1.46178×10^{8}	-2.62035×10^{9}	4.26181×10^{8}
τ_6 (K^{-1})	-6.37492×10^{8}	-1.05616×10^{6}	7.07234×10^{6}	-2.55043×10^{6}
τ_7 (K^{-2})	$769,149$	1462.75	-12444.2	2205.03
τ_8	3.19982×10^{10}	-5.30781×10^{7}	1.68813×10^{9}	1.01964×10^{8}

τ_i	CO$_2$ + cyclopentane	CO$_2$ + n-butane	CO$_2$ + benzene	CO$_2$ + n-pentane
τ_1 (K)	6.56528×10^{10}	1.19365×10^{12}	2.7281×10^{12}	6.46683×10^{10}
τ_2	-3.4592×10^{8}	-6.01087×10^{9}	-1.09439×10^{10}	2.93758×10^{8}
τ_3 (K^{-1})	483115.0	6.93922×10^{6}	9.06454×10^{6}	-1.62499×10^{6}
τ_4 (K)	-7.62388×10^{9}	-3.40784×10^{10}	-8.8206×10^{10}	2.08347×10^{10}
τ_5	3.91625×10^{8}	1.49909×10^{9}	-9.99734×10^{9}	2.97592×10^{8}
τ_6 (K^{-1})	-2.53626×10^{6}	-9.0129×10^{6}	5.4266×10^{7}	-1.73241×10^{6}
τ_7 (K^{-2})	4019.0	12203.4	-75353.7	1629.52
τ_8	6.18075×10^{6}	5.20862×10^{7}	4.36649×10^{7}	4.27593×10^{7}

Table 4   Values for the c_i coefficients of Eq 10 for the binary 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 9

Binary mixture	c_0	c_1	c_2	c_3	c_4
Ethane + n-butane	3.01657	-0.00670170	0.00245003	-1.70592	1.09123
Ethane + benzene	2.2528	-0.00383873	0.00371281	-3.86875	2.81588
Ethane + n-heptane	1.7582	-0.00210177	-0.000072101	0.1218	-0.233955
Ethane + n-octane	1.04964	-0.000281481	0.000336251	-0.10402	0.0361889
CO$_2$ + cyclopentane	1.40003	-0.000981366	-0.00201775	1.19894	-0.710175
CO$_2$ + n-butane	2.62885	-0.00555544	0.00123233	-0.807582	0.480164
CO$_2$ + benzene	1.19138	-0.000910427	0.000320116	-3.34391	3.15653
CO$_2$ + n-pentane	1.66108	-0.00230665	0.00111646	-0.917626	0.611665

mixtures with mean absolute deviations less than 7.8% for each isothermal set of data studied, the only exceptions being for the ethane + benzene system at temperatures near 300 K. This is a reasonable result, because high deviations have also been found in the calculation of the pressure of this mixture at these temperatures. For each system, mean absolute deviations ranging from 0.6 to 6.0% are found. Note that x_1 must be obtained by solving the equation obtained by introducing experimental values of temperature and pressure into Eq 5.

With respect to the vapor mole fraction y_1, this quantity is predicted with mean absolute deviations less than 6% for each isothermal set of data studied, the only exception being for the ethane + benzene system at the two highest temperatures (Table 5). Values of the mean deviations for each system range from 0.5 to 4.6%.

We note that the given percentages are mean deviations, so that their values can be affected by a lack of accuracy for only a few points instead of the complete range. Thus, for example, we can consider the ethane + benzene mixture, which gives the highest deviations of the ethane mixtures that were considered. Figure 1 shows a temperature versus composition diagram for the ethane + benzene system at $P = 5.5158$ MPa. A good agreement between our results and the experimental data may be observed. The model for y_1, Eq 9, gives a reasonable estimate of the experimental data. The only exception is the very high deviation obtained at $T = 533.15$ K, $i.e.$, for the highest temperature considered. This high individual deviation leads to a mean deviation of 14.3% for that temperature, which is the highest mean deviation found in our calculations. For other temperatures (at the same pressure), the deviations are considerably lower. For example, Fig. 2 shows the experimental data (points) [1952Kay] and our theoretical values (lines) for the composition of the ethane + benzene system at two temperatures ($\bullet$, $T = 373.15$ K; and $\blacktriangle$, $T = 473.15$ K). At $T = 373.15$ K, the agreement between our results and the experimental data is good for both compositions. For $T = 473.15$ K, the agreement is good also, except for the points at the highest experimental equilibrium pressure value. As can be seen in Fig. 2, the data of the vapor mole fraction present a strong curvature, which is adequately reproduced by Eq 9.

We note that, while in these and the following figures we plot pressure (or temperature) versus composition, it

Table 5 Correlation of VLE data for the binary systems using Eq 5 and 9: number of data points for each system; conditions and source of experimental data; and percentage absolute deviation between experimental and calculated values for the equilibrium pressure, ΔP_m, the liquid mole fraction, Δx_1, and the vapor mole fraction, Δy_1, for each isothermal set of data, and also the mean deviations for each of the systems studied (numbers in bold)

| Binary mixture	Data number	Temperature (K)	P range (MPa)	x_1 range	ΔP_m (%)	Δx_1 (%)	Δy_1 (%)	Reference
Ethane + n-butane	19	338.71	3.54–5.55	0.482–0.753	0.1	0.1	0.7	[1965Meh]
		366.48	3.51–5.48	0.299–0.529	0.5	0.7	0.7	
		394.26	3.24–5.03	0.118–0.312	0.4	1.1	1.9	
					0.4	**0.6**	**1.0**	
Ethane + benzene	80	273.15	2.07	0.8723	0.3	0.3	1.8	[1952Kay]
		293.15	2.07–3.45	0.4398–0.9554	6.9	10.4	4.2	
		313.15	2.07–4.83	0.2916–0.9164	8.6	10.2	4.8	
		333.15	2.07–4.83	0.2210–0.6400	5.6	6.6	5.9	
		353.15	2.07–4.83	0.1780–0.4711	1.6	2.0	3.9	
		373.15	2.07–4.83	0.1467–0.3763	2.5	3.0	1.1	
		393.15	2.07–6.89	0.1228–0.4793	3.2	3.8	2.4	
		413.15	2.07–6.89	0.1017–0.4099	3.7	4.6	4.1	
		433.15	2.07–8.27	0.0795–0.4506	3.9	5.0	4.4	
		453.15	2.07–8.27	0.0556–0.4004	3.6	4.8	4.1	
		473.15	2.07–8.27	0.0305–0.3611	3.3	4.2	2.8	
		493.15	2.07–6.89	0.0048–0.2322	1.0	2.2	4.2	
		513.15	2.76–6.89	0.0066–0.2060	1.7	3.8	2.4	
		533.15	3.45–5.52	0.0015–0.1012	1.4	6.7	14.3	
		553.15	4.83	0.0177	0.3	2.6	8.1	
					3.4	**4.7**	**4.6**	
Ethane + n-heptane	62	338.71	2.76–6.62	0.460–0.940	5.3	3.7	2.0	[1964Dat]
		366.48	2.76–8.14	0.353–0.888	1.9	1.6	1.4	
		394.26	2.76–8.79	0.299–0.830	2.1	2.0	1.7	
		422.02	2.76–8.82	0.235–0.759	3.0	3.0	2.2	
		449.82	2.76–8.27	0.188–0.678	3.1	4.0	2.1	
					2.9	**2.8**	**1.9**	
Ethane + n-octane	64	273.15	0.41–2.23	0.178–0.952	2.2	2.1	1.2	[1968Rod]
		298.15	0.41–4.05	0.112–0.984	0.8	0.7	0.5	
		313.15	0.41–5.27	0.093–0.973	2.8	2.5	0.3	
		323.15	0.41–5.27	0.084–0.863	4.0	3.6	0.2	
		348.15	0.41–5.27	0.057–0.663	2.1	1.9	0.4	
		373.15	0.41–3.65	0.047–0.405	1.7	1.7	0.8	
					2.4	**2.2**	**0.5**	
CO_2 + Cyclopentane	39	310.86	0.18–6.55	0.0067–0.857	5.4	7.8	2.6	[1986Eck]
		318.17	0.65–7.36	0.048–0.844	4.3	6.2	1.0	
		333.17	1.07–8.26	0.058–0.726	3.1	3.9	2.1	
					4.3	**6.0**	**1.8**	
CO_1 + n-Butane	106	311.09	0.59–7.52	0.0245–0.9388	2.6	3.8	1.8	[1989Nie]
		344.43	0.99–8.06	0.0108–0.7000	1.6	2.6	4.6	
		394.60	2.48–6.51	0.0110–0.3535	1.1	3.6	4.8	
					1.9	**3.3**	**3.4**	
CO_2 + Benzene	29	313.4	2.12–5.92	0.190–0.661	1.3	1.5	1.2	[1986Kim]
		353.0	0.49–6.27	0.020–0.332	3.4	4.2	1.9	
		373.5	0.67–5.91	0.023–0.280	1.5	1.7	2.4	
		393.2	0.73–5.95	0.017–0.249	1.5	2.0	1.6	
					1.9	**2.4**	**1.8**	
CO_2 + n-Pentane	48	277.65	0.23–3.90	0.0290–0.9791	1.4	1.7	2.6	[1973Bes]
		311.04	0.46–7.38	0.0344–0.9416	4.0	5.4	1.2	
		344.15	0.41–9.22	0.0072–0.7796	3.8	5.7	2.6	
		377.59	0.91–9.63	0.0119–0.6447	3.7	6.3	3.4	
					3.4	**4.9**	**2.4**	
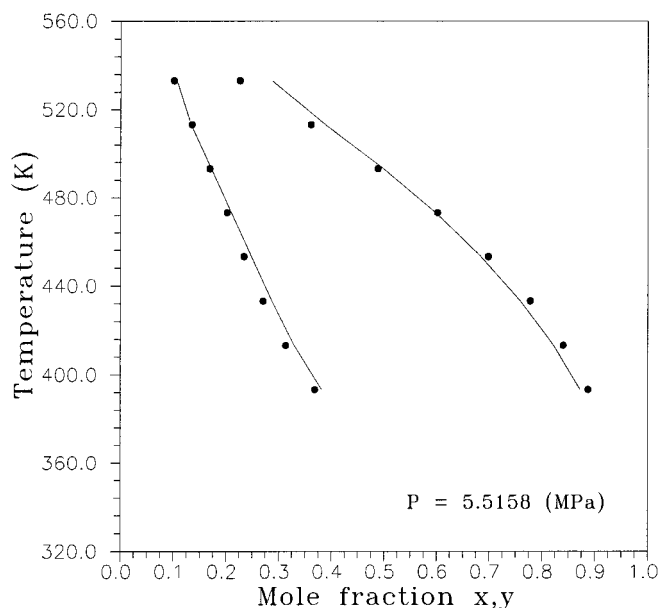
Fig. 1 Experimental data points [1952Kay] and theoretical values (lines) obtained from our models (Eq 5 and 9) for the mole fractions of the ethane + benzene system, vs temperature at $P = 5.5158$ (MPa)
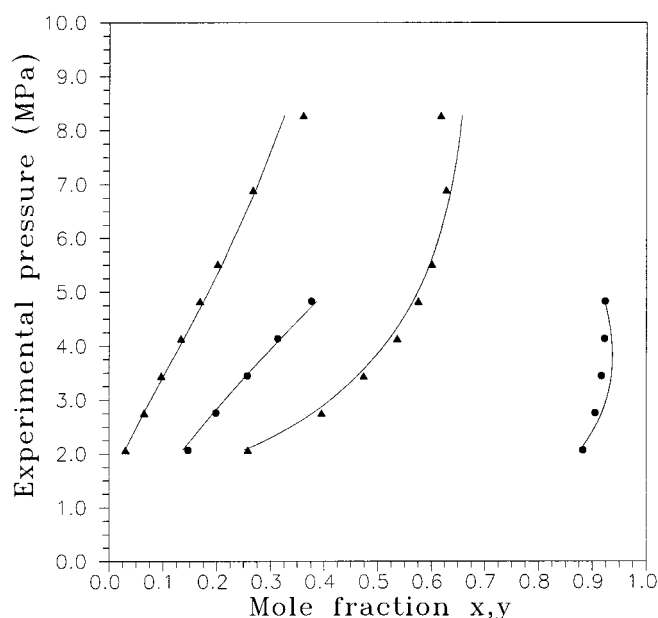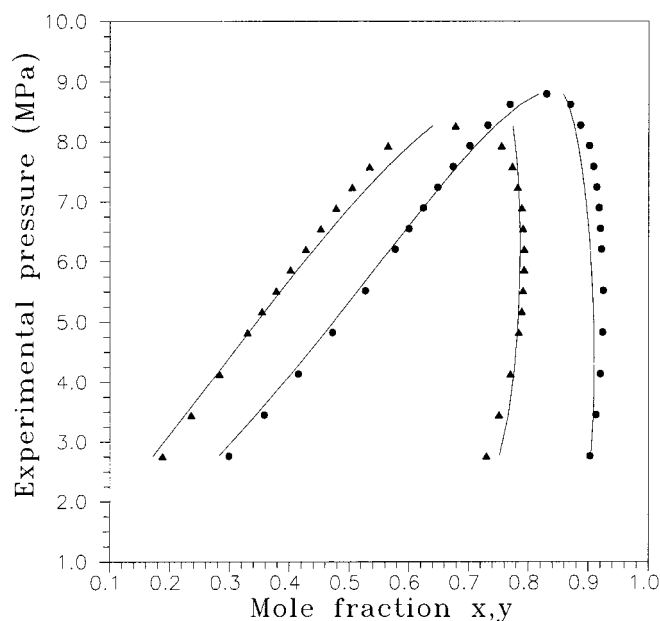

Fig. 2 Experimental data points [1952Kay] and theoretical values (lines) obtained from our models (Eq 5 and 9) for the mole fractions of the ethane + benzene system, vs pressure at two temperatures ($\bullet$, $T = 373.15$ K; and $\blacktriangle$, $T = 473.15$ K)

Fig. 3 Experimental data points [1964Dat] and theoretical values (lines) obtained from our models (Eq 5 and 9) for the mole fractions of the ethane + heptane system, vs pressure at two temperatures ($\bullet$, $T = 394.26$ K; and $\blacktriangle$, $T = 449.82$ K)

must be clear that the input properties are pressure and temperature, and the calculated values are the liquid and vapor mole fractions.

In the preceding systems, no data are available near the critical locus, which is the case of the ethane + heptane system. Figure 3 shows plots of experimental pressure versus composition for that system at two temperatures ($\bullet$, $T = 394.26$ K; and $\blacktriangle$, $T = 449.82$ K). As can be seen, the validity of the proposed models clearly depends on the

agreement found for points near the critical locus. Thus, for $T = 394.26$ K, the deviation in the calculation of the mole fraction of the liquid is less than in the case of $T = 449.8$ K, due mainly to the presence of an experimental point at P greater than 8 MPa, which is not reached in our model. Thus, for intermediate or low pressures, the accuracy of the models is practically the same at any temperature.

Other examples of the results, but now for mixtures containing carbon dioxide, are shown in Fig. 4 to 6. A common feature of the CO_2 composition diagram is that, for a given temperature, the liquid mole fraction is practically linear with pressure, whereas the vapor mole fraction versus P presents a strong curvature at low pressures. For example, Fig. 4 shows the results obtained using our models for the CO_2 + benzene system at two temperatures ($\bullet$, $T = 353$ K; and $\blacktriangle$, $T = 393.2$ K). As can be seen, the proposed models for y_1 behave well even at low pressures, where the curvature is greatest.

Data near the critical locus are available for CO_2 + butane and CO_2 + pentane systems. Figure 5 shows the experimental data (points) and our theoretical values (lines) for the composition data of the CO_2 + butane system [1989Nie] versus the experimental pressure of the system at $T = 311.09$ K. One sees that there is good agreement between our theoretical estimates and the experimental results: the individual deviations found for x_1 are less than 10.5%, except for two points at the lowest experimental equilibrium pressure value. For y_1, the individual deviations found are less than 3.6%. The critical point is reproduced almost exactly.

Figure 6 plots the pressure versus composition diagram for the CO_2 + pentane system at two temperatures ($\bullet$, $T = 311.04$ K; and $\blacktriangle$, $T = 377.59$ K). For $T = 311.04$ K, the individual deviations found for x_1 are less than 7%, except

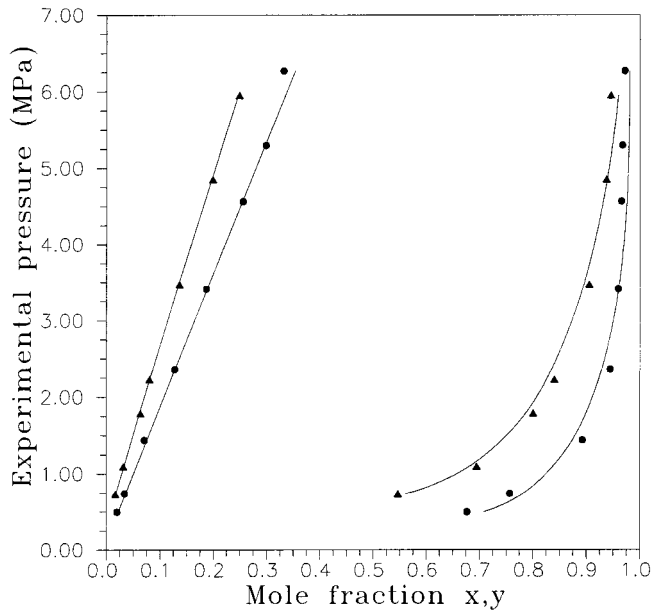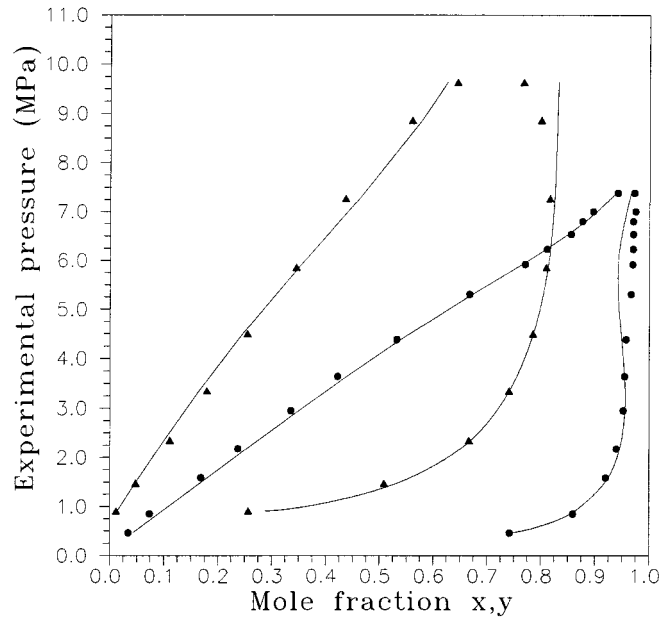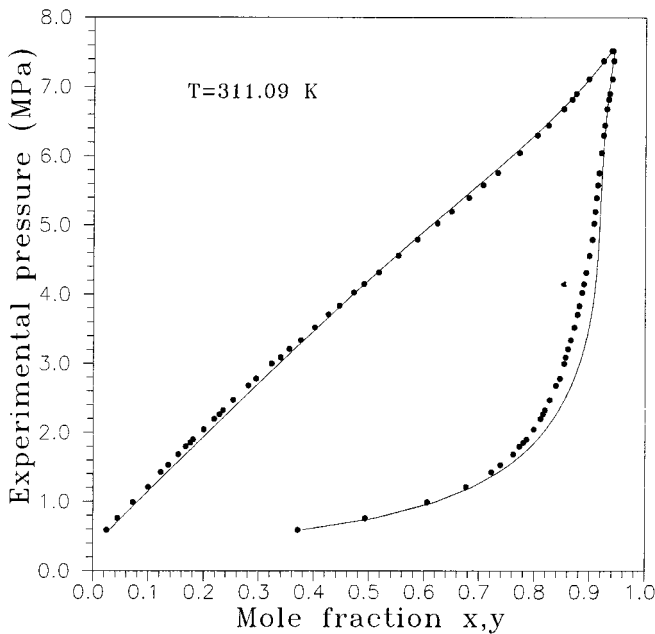**Fig. 4** Experimental data points [1986Kim] and theoretical values (lines) obtained from our models (Eq 5 and 9) for the mole fractions of the CO_2 + benzene system, vs pressure at two temperatures ($\bullet$, $T = 353$ K; and $\blacktriangle$, T $= 393.2$ K)

Fig. 6 Experimental data points [1973Bes] and theoretical values (lines) obtained from our models (Eqs 5 and 9) for the mole fractions of the CO_2 + pentane system, vs pressure at two temperatures ($\bullet$, $T = 311.04$ K; and $\blacktriangle$, $T = 377.59$ K)

Fig. 5 Experimental data points [1989Nie] and theoretical values (lines) obtained from our models (Eq 5 and 9) for the mole fractions of the CO_2 + butane system, vs pressure at $T = 311.09$ K

for two points at the lowest experimental equilibrium pressure values. For the same temperature, the agreement between our theoretical estimates and the experimental results for y_1 is very good, the individual deviations found being less than 3%. As can be seen, for $T = 377.59$ K, the results obtained for x_1 are excellent. For y_1, the individual deviations found are less than 12.5%. As can be clearly seen, the model works less well when the experimental

curve near the critical locus is narrow than when the curve is sharp. In any case, the agreement is very good for any low pressure.

To sum up, we have shown that the present model can reproduce, with a greater or lesser degree of agreement, different diagrams, even those including points near the critical locus. Therefore, it could be an almost universal model for simple mixtures.

5. Conclusions

Analytical expressions relating properties for the VLE of nonpolar binary mixtures were proposed. The models were 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 was obtained from modified Lorentz-Berthelot mixing rules, where 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, pressure, and liquid mole fraction and five appropriate constants for each mixture. In all cases, the LJ molecular parameters and the acentric factor of the components are the only input data, once the constants are known.

In any case, the models are very easy to use and the agreement with the experimental data is good, even near the

critical locus in those cases where the experimental pressure-composition curve is sharply defined. Applications to other mixtures of nonpolar fluids are being made.

Acknowledgments

References

1952Kay: W.B. Kay and T.D. Nevens (1952): in *Vapor-Liquid Equilibrium Data Collection,* J. Gmehling, U. Onken, and M. Arlt, eds., DECHEMA, Frankfurt am Main, 1982.

1964Dat: S.P. Datsur (1964): in *Vapor-Liquid Equilibrium Data Collection,* J. Gmehling, U. Onken, and M. Arlt, eds., DECHEMA, Frankfurt am Main, 1982.

1965Meh: V.S. Mehta and G. Thodos (1965): in *Vapor-Liquid Equilibrium Data Collection,* J. Gmehling, U. Onken, and M. Arlt, eds., DECHEMA, Frankfurt am Main, 1982.

1968Rod: A.B.J. Rodrigues, D.S. Mc Caffrey, and J.P. Kohn (1968): in *Vapor-Liquid Equilibrium Data Collection,* J. Gmehling, U. Onken, and M. Arlt, eds., DECHEMA, Frankfurt am Main, 1982.

1973Bes: G.J. Besserer and D.B. Robinson (1973): in *Vapor-Liquid Equilibrium Data Collection,* J. Gmehling, U. Onken, and M. Arlt, eds., DECHEMA, Frankfurt am Main, 1982.

1979Hur: M.J. Huron and J. Vidal: *Fluid Phase Equilibria,* 1979, vol. 3, pp. 255-71.

1986Cot1: R.L. Cotterman, B.J. Schwarz, and J.M. Prausnitz: *AIChE J.,* 1986, vol. 32 (11), pp. 1787-98.

1986Cot2: R.L. Cotterman and J.M. Prausnitz: *AIChE J.,* 1986, vol. 32 (11), pp. 1799-1812.

1986Eck: C. Eckert and S.I. Sandler: *J. Chem. Eng. Data,* 1986, vol. 31, pp. 26-28.

1986Kim: C.H. Kim, P. Vimalchand, and M.D. Donohue: *Fluid Phase Equilibria,* 1986, vol. 31, pp. 299-311.

1986Pra: J.M. Prausnitz, R.N. Lichtenthaler, and E. Gomes de Azevedo: *Molecular Thermodynamics of Fluid-Phase Equilibria,* Prentice-Hall Inc., Englewood Cliffs, NJ, 1986.

1986Str: R. Stryjek and J.H. Vera: *Can. J. Chem. Eng.,* 1986, vol. 64, pp. 820-26.

1987Rei: R.C. Reid, J.M. Prausnitz, and B.E. Poling: *The Properties of Gases and Liquids,* McGraw-Hill Book Co., New York, NY, 1987.

1989Nie: V.G. Niesen: *J. Chem. Thermodyn.,* 1989, vol. 21, pp. 915-23.

1990Eng: P. Englezos, N. Kalogerakis, M.A. Trebble, and P.R. Bishnoi: *Fluid Phase Equilibria,* 1990, vol. 58, pp. 117-23.

1992Gao: G. Gao, J.L. Dadiron, H. Saint-Guirons, P. Xans, and F. Montel: *Fluid Phase Equilibria,* 1992, vol. 74, pp. 85-93.

1992Won: D.S.H. Wong and S.I. Sandler: *AIChE J.,* 1992, vol. 38, pp. 671-80.

1994Ash: I. Ashour and G. Aly: *Fluid Phase Equilibria,* 1994, vol. 98, pp. 55-69.

1994Cou: J.Coutinho, G. Kontogeorgis, and E. Stenby: *Fluid Phase Equilibria,* 1994, vol. 102, pp. 31-60.

1996Ash: I. Ashour and G. Aly: *Computers Chem. Eng.,* 1996, vol. 20, pp. 79-91.

1996Cua: F. Cuadros, I. Cachadiña, and W. Ahumada: *Mol. Eng.,* 1996, vol. 6, pp. 319-25.

1996DIP: DIPPR (Design Institute for Physical Property Data), American Institute of Chemical Engineers, STN International, Germany, via on-line, 1996.

1997Kes: A. Keshtkar, F. Jalali and M. Moshfeghian: *Fluid Phase Equilibria,* 1997, vol. 140, pp. 107-28.

1998Bla: F. Blas and L. Vega: *Ind. Eng. Chem. Res.,* 1998, vol. 37, pp. 660-74.

1998Kis: S.B. Kiselev, J.C. Rainwater, and M.L. Huber: *Fluid Phase Equilibria,* 1998, vol. 150, pp. 469-78.

1999Pol: I. Polishuk, J. Wisniak, and H. Segura: *Fluid Phase Equilibria,* 1999, vol. 164, pp. 13-47.

2000Cua1: F. Cuadros, C.A. Faúndez, and A. Mulero: *Phase Transitions,* 2000, vol. 71 (1), pp. 57-72.

2000Cua2: F. Cuadros, C.A. Faúndez, and A. Mulero: *Phase Transitions,* 2000, vol. 72, pp. 309-29.

2000Fau: C.A. Faúndez, A. Mulero, and F. Cuadros: *J. Phase Equilibria,* 2000, vol. 21 (4), pp. 364-70.

2000Lee: Y.P. Lee, Y.C. Chiew, and G.P. Rangaiah: *Ind. Eng. Chem. Res.,* 2000, vol. 39, pp. 1497-1502.