

Objective functions analysis in the minimization of binary VLE data for asymmetric mixtures at high pressures

Jimmy A. López*, Victor M. Trejos, Carlos A. Cardona

Chemical Engineering Department, Universidad Nacional de Colombia sede Manizales, Apartado 127, Manizales, Colombia

Received 7 March 2006; received in revised form 28 July 2006; accepted 1 August 2006

Available online 5 August 2006

Abstract

Five different objective functions were studied with the purpose of analyzing their performance for parameters estimation of vapor–liquid equilibrium models for a series of 13 non-polar and 13 polar asymmetric binary mixtures at high pressures. Peng–Robinson equation of state coupled with the Wong–Sandler mixing rules were used for modeling the VLE in all cases. The first two objective functions are based on the calculation of the distribution coefficients for each component in the mixture and the remaining objective functions involve additional calculations of other quantities such as the bubble point pressure. In general, the optimal parameters obtained from all objective functions showed a good prediction capacity of the behavior of the vapor phase. It is also demonstrated that a good prediction of the pressure depends on the form of the objective function. It was found that one objective function has slight advantages over the other analyzed objective functions: first, it does not involve additional iterative calculations as the bubble point or isothermal flash for each data point; second, the optimal second virial coefficient interaction parameter shows to be in concordance with the statistical thermodynamic postulates; and finally, VLE predictions using the optimal parameters obtained with the help of this objective function show very good representations of both the vapor phase and pressure.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Parameters optimization; Objective function; Vapor–liquid equilibrium; Peng–Robinson equation of state; Wong–Sandler mixing rules

1. Introduction

In chemical processes design, an accurate prediction of the phase equilibria of the involved mixtures is essential. Therefore, an appropriate thermodynamic model for representing phase behavior is required. The selection of a model requires the knowledge of at least the main characteristics of components in the mixture (polar and, non-polar molecules, light gases and heavy components) and system temperature and pressure. Usually, a γ - Φ approach is considered at low and moderated pressures. As both system pressure and asymmetry (which can be identified by a noticeable difference among the infinite dilution activity coefficients of each component) increase, a Φ - Φ approach is most appropriate. In this case, an equation of state (EOS) coupled with an appropriate mixing rule for the attractive-term and the covolume is strongly

required for an accurate prediction of the vapor–liquid equilibrium (VLE).

The van der Waals (vdW) mixing rules can only represent mixtures of components with similar sizes. They are generally limited to non-polar and slightly polar mixtures. Moreover, its geometry is inadequate for composition variations and, although many works have been developed to improve the vdW mixing rules [1–9], they are, generally, unsuitable for describing complex systems. Since many mixtures involved in chemical processes are highly nonideal, mixing rules based on excess free energy takes great importance for representing the properties of nonideal mixtures. This kind of mixing rules has been originally developed by Huron and Vidal [10] who equated the excess Gibbs free energy at infinite pressure derived from a cubic EOS to that obtained from a liquid-activity coefficient model in order to calculate the attractive-term parameter, a_m . Additionally, they proposed a linear relationship for the covolume parameter, b_m . Due to inconsistencies in this mixing rule [11,12], some researchers have made several efforts to relax the infinite-pressure limit imposed on the Huron–Vidal mixing rule [13–18], obtaining satisfactory VLE predictions for many

* Corresponding author at: Planta Piloto de Ingeniería Química, PLAPIQUI-UNS-CONICET, Cmnno. La Carrindanga Km. 7, 8000 Bahía Blanca, Argentina. Tel.: +54 291 4861700x281; fax: +54 291 4861600.

E-mail address: jlopez@plapiqui.edu.ar (J.A. López).

complex mixtures. Other mixing rules based on zero reference pressure models have been developed by Twu and coworkers [19–21]. Such models reproduce the excess Gibbs free energy as well as the liquid activity coefficients of any activity model without requiring any additional binary interaction parameter.

Alternatively, the Wong–Sandler mixing rules [11], using the infinite pressure reference state and including the correct zero-pressure limit for the composition dependence of the second virial coefficient, are currently one of the most popular mixing rules for cubic EOS. Several authors have shown the applicability of these mixing rules in phase equilibrium prediction [22–33] and others have demonstrated their limitations [19–21,34].

Generally, VLE at high pressures can be calculated using activity coefficient model parameters from available values at low pressures. However, in the case of highly asymmetric mixtures, especially those containing light gases and heavy solutes, such parameters are not available. In such cases, it is possible to calculate the activity coefficient model parameters and the interaction parameter from VLE data by optimizing an appropriate objective function (OF). This approach has the advantage of achieving a moderate computing time and a good accuracy in the phase equilibrium prediction. These OF can be derived from the least squares principle or from the maximum likelihood principle [35]. In the least squares principle, the error is defined as the difference between the experimental point and the calculated value. Then, the OF to minimize is the quadratic error summation over the experimental data set:

$$f = \sum_{i=1}^{np} \sum_{j=1}^{nc} (u_{i,j}^{\text{exp}} - u_{i,j}^{\text{cal}})^2 \quad (1)$$

where np is the number of experimental data points, nc the number of components and u_{ij} are the dependent variables. The application of the maximum likelihood principle requires the knowledge of the measurement error for each experimental variable. In this case, the OF is similar to that of the least squares principle, but the statistical variance associated with the measured variables (σ_{ij}^2) should be taken into account:

$$f = \sum_{i=1}^{np} \sum_{j=1}^{nm} \frac{(w_{ij}^{\text{exp}} - w_{ij}^{\text{cal}})^2}{\sigma_{ij}^2} \quad (2)$$

where w_{ij} are the measured variables (liquid composition, x ; vapor composition, y ; temperature, T ; and pressure, P), and nm is the number of measured variables. The optimal parameters which minimize the Eq. (2) are those that maximize the likelihood function of the parameters [36]. The maximum likelihood principle requires that the measurements are only subject to random errors. In addition, the model must be capable of representing the measurements within an order less than the order of the experimental uncertainties [37]. At the present time, the least squares principle (Eq. (1)) is the most popular for obtaining interaction parameters from VLE data. Additionally, several of these computational methods applicable to parameters optimization from VLE data have been strongly analyzed [36–44].

In the present work five different OF were analyzed in order to evaluate their accuracy to represent both the vapor phase and the

pressure behavior in isothermal asymmetric binary mixtures at high pressures. The Peng–Robinson EOS [45] coupled with the Wong–Sandler mixing rules [11] have been used in the VLE estimation. The NRTL model [46] was utilized to predict the excess Helmholtz free energy. The second virial coefficient binary interaction parameter k_{12} and the NRTL model parameters τ_{12} and τ_{21} were calculated for 13 non-polar and 13 polar asymmetric mixtures at high pressures by optimizing each one of the five analyzed OF. A Levenberg–Marquardt minimization algorithm was used in all cases.

2. Equation of state and mixing rules

The Peng–Robinson (PR) equation of state [45] has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (3)$$

where P is the pressure, T the absolute temperature and R is the ideal gas constant. a and b are the energy and the size parameters, respectively, which are calculated from:

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \quad (4)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (5)$$

the subscripts c and r denote critical and reduced conditions, respectively. The correlation for the α function is:

$$\alpha(T_r) = [1 + \kappa(1 - \sqrt{T_r})]^2 \quad (6)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (7)$$

where ω is the acentric factor. In order to apply the PR EOS to mixtures, the Wong–Sandler [11] mixing rules were used. The a_m and b_m parameters have the following form:

$$a_m = b_m \left[\sum_i z_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right] \quad (8)$$

with

$$b_m = \frac{\sum_i \sum_j z_i z_j (b - \frac{a}{RT})_{ij}}{1 - \sum_i z_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \quad (9)$$

$$C = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \quad (10)$$

and

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{(b - (a/RT))_i + (b - (a/RT))_j}{2} (1 - k_{ij}) \quad (11)$$

where k_{ij} is a second virial coefficient binary interaction parameter, z is the molar fraction and A_∞^E is the excess Helmholtz free energy at infinite pressure which is calculated from an excess

Gibbs free energy model. The thermodynamic relation between these excess free energies is:

$$G^E(T, P, x) = A^E(T, P, x) + P V^E(T, P, x) \quad (12)$$

Since at low pressures, V^E is small, the difference between G^E and A^E is also small. Consequently, Wong and Sandler [11] established the following approximation:

$$G^E(T, P = \text{low}, x) = A^E(T, P = \text{low}, x) = A^E(T, P = \infty, x) \quad (13)$$

Therefore, the excess Helmholtz free energy is much less pressure-dependent than the excess Gibbs free energy. In this work, the excess Helmholtz free energy at infinite pressure was calculated with the NRTL model [46]:

$$\frac{A_\infty^E}{RT} = \sum_i z_i \left(\frac{\sum_j z_j \tau_{ji} g_{ji}}{\sum_k z_k g_{ki}} \right) \quad (14)$$

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (15)$$

In the case of binary mixtures, α_{12} ($=\alpha_{21}$), τ_{12} and τ_{21} are the three parameters of the NRTL model. As recommended by Renon and Prausnitz [46], a constant value of α_{12} (0.3) was used in this work. In this contribution, the adjustable parameters of the NRTL model: τ_{12} and τ_{21} and the second virial coefficient binary interaction parameter k_{12} have been determined using experimental phase equilibrium data at isothermal conditions for each of the 13 non-polar and the 13 polar asymmetric binary systems by the minimization of five different OF.

3. Asymmetric binary mixtures

In the present work, 13 non-polar (gas + non-polar solute) and 13 polar (gas + polar solute) asymmetric binary mixtures have been analyzed. The experimental conditions and the literature source of each data set are shown in Tables 1 and 2. Data for 37 isotherms with 364 experimental points were studied for gas + non-polar mixtures and 33 isotherms with 315 experimental points were studied for gas + polar mixtures. Several mixtures containing carbon dioxide and other compounds (limonene, isoamyl acetate, ethyl caproate, ethyl laurate, 1-heptanol, linalool, decanal) have a great importance in the field of supercritical fluid extraction. For example, the limonene and the linalool are the principal compounds of citrus oil. Since the linalool is one of the most important flavor fractions of this oil, it is common to remove the limonene to concentrate the oxygenated compounds as the linalool. On the other hand, esters as isoamyl acetate, ethyl caproate and ethyl laurate are widely used in the food, cosmetic and pharmaceutical industries. The production of these compounds is generally carried out by chemical synthesis, but the use of toxic organic solvents for food and health products is being progressively restricted. Therefore, the supercritical fluid extraction with carbon dioxide is one of the industrial alternatives to produce these and other esters [69].

The VLE study of carbon dioxide + styrene mixtures has a great importance in petrochemical industries. Styrene is com-

monly produced by dehydrogenation of ethylbenzene. As the reaction is not completed, separation of styrene + ethylbenzene mixtures using supercritical carbon dioxide as a solvent may be an attractive method [70]. Additionally, some works have shown that the synthesis of polystyrene from the polymerization of styrene in supercritical carbon dioxide has an increasing importance as production process [71–74].

4. Objective functions

In order to determine the optimal parameters for the VLE model, two OF that take into account the coefficient distribution calculation and three OF that require bubble point pressure calculation from an additional iterative process have been analyzed. The first two OF are implicit models which are based on the calculation of the distribution coefficients for each component:

$$f_1 = \sum_{i=1}^{np} \sum_{j=1}^{nc} \left[\ln K_{i,j}^{\text{cal}} - \ln K_{i,j}^{\text{exp}} \right]^2 \quad (16)$$

$$f_2 = \sum_{i=1}^{np} \sum_{j=1}^{nc} \left[y_{i,j}^{\text{exp}} - K_{i,j}^{\text{cal}} x_{i,j}^{\text{exp}} \right]^2 \quad (17)$$

where K is the distribution coefficient for both phases. The remaining OF involve additional iterative procedures for calculating their optimal values and are explicit models because the adjusted variables are calculated from a bubble point pressure calculation algorithm. Therefore, the implementation of these OF has larger computing time requirements in comparison with the implicit functions. The studied explicit OF are:

$$f_3 = \sum_{i=1}^{np} \left[\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right]^2 \quad (18)$$

$$f_4 = \sum_{i=1}^{np} \sum_{j=1}^{nc} \left[\frac{y_{i,j}^{\text{exp}} - y_{i,j}^{\text{cal}}}{y_{i,j}^{\text{exp}}} \right]^2 \quad (19)$$

$$f_5 = \sum_{i=1}^{np} \left[\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right]^2 + \sum_{i=1}^{np} \sum_{j=1}^{nc} \left[\frac{y_{i,j}^{\text{exp}} - y_{i,j}^{\text{cal}}}{y_{i,j}^{\text{exp}}} \right]^2 \quad (20)$$

where P is the bubble point pressure and y represents the molar fraction in vapor phase. As it has been shown, OF f_5 is a complement of functions f_3 and f_4 . However, this does not assure that the binary parameters obtained by these three functions will be identical. Although these OF have very similar computing times, the vapor–liquid equilibrium calculations using their optimal parameters will give a major precision represented in the pressure or the vapor phase composition (or both), but this depends of the objective function form.

In the literature, some authors have used OF f_1 for the parameters optimization of VLE data in asymmetric mixtures of light gases + hydrocarbons and alcohols [75] and carbon dioxide + n -alkanes [76], obtaining good predictions for pressure and not very good predictions for vapor composition. OF f_2 and f_4 are the less used to estimate binary interaction parameters in both

Table 1
Experimental conditions for non-polar asymmetric binary mixtures

System	np	T (K)	Pressure range (bar)	Reference
Hydrogen + <i>n</i> -hexadecane	7	461.65	20.3–252.7	[47]
	5	423.50	51.4–151.6	[48]
Helium + toluene	5	464.40	50.9–152.0	[48]
	5	505.20	51.4–153.2	[48]
	5	545.60	50.63–151.7	[48]
	5	464.50	51.9–152.2	[48]
Nitrogen + toluene	5	505.50	50.8–152.3	[48]
	5	545.20	51.1–151.6	[48]
	25	230.00	8.9–71.1	[49]
Carbon dioxide + propane	17	270.00	32.0–79.5	[49]
	12	310.15	5.6–73.1	[50]
Carbon dioxide + <i>n</i> -pentane	13	333.15	5.9–87.5	[50]
	16	363.15	9.4–96.7	[50]
	8	298.15	8.9–57.7	[51]
Carbon dioxide + benzene	9	313.15	14.8–77.5	[51]
	9	333.15	60.3–112.0	[52]
Carbon dioxide + styrene	9	338.15	62.4–119.0	[52]
	10	343.15	60.0–131.0	[52]
	8	348.15	62.9–134.2	[52]
	22	344.30	63.8–127.4	[53]
Carbon dioxide + <i>n</i> -decane	26	377.60	103.4–164.8	[53]
	5	313.20	39.4–78.7	[54]
	5	323.20	39.4–92.7	[54]
Carbon dioxide + limonene	5	333.20	49.9–102.6	[54]
	10	410.95	9.4–91.7	[55]
	12	444.25	7.0–115.0	[55]
Propylene + benzene	10	453.15	15.0–60.0	[56]
	9	473.15	20.0–60.0	[56]
	6	523.15	40.0–60.0	[56]
	3	543.15	45.0–55.0	[56]
	11	293.15	0.02–0.56	[57]
<i>n</i> -Pentane + toluene	11	303.15	0.04–0.82	[57]
	11	313.15	0.07–1.16	[57]
	10	303.15	0.15–0.25	[57]
<i>n</i> -Hexane + benzene	10	313.15	0.24–0.37	[57]
	10	323.15	0.36–0.54	[57]
	10	333.15	0.52–0.76	[57]

symmetric and asymmetric systems at high pressures. On the other hand, OF f_3 and f_5 are the most popular for estimating both the binary interaction parameter and the activity coefficient models parameters from VLE data at high pressures and temperatures. Therefore, it is necessary to develop a detailed study which involves explicit and implicit models and to find an adequate OF that guarantees small computing times and suitable exactitude for representing the VLE with respect to the correlated data.

5. Results and discussion

The parameters estimation was performed using the Levenberg-Marquardt minimization algorithm for each mixture

with OF f_1 – f_5 . Therefore, 185 minimizations in gas + non-polar binary mixtures and 165 minimizations in gas + polar binary mixtures were carried out. The optimal NRTL model parameters (τ_{12} and τ_{21}) and the second virial coefficient interaction parameter (k_{12}) are reported for the non-polar asymmetric binary mixtures and for the polar asymmetric binary mixtures in the [supplementary material](#).

The deviations between experimental data and calculated values with PR EOS and the Wong–Sandler mixing rules were established through the relative percentage deviations in the bubble point pressure:

$$\Delta P = \sum_{i=1}^{np} \frac{|P_{\text{exp}} - P_{\text{cal}}|}{P_{\text{exp}}} \left(\frac{100}{np} \right) \quad (21)$$

Table 2
Experimental conditions for polar asymmetric binary mixtures

System	np	T (K)	Pressure range (bar)	Reference
Nitrogen + methanol	8	298.15	6.7–101.9	[58]
	8	308.15	6.8–101.5	[58]
	8	318.15	7.4–98.5	[58]
Nitrogen + dimethylether	16	288.15	4.4–84.8	[59]
	15	308.15	7.8–84.3	[59]
	15	318.15	10.2–83.3	[59]
Carbon dioxide + isoamylacetate	7	308.15	10.3–69.3	[60]
	8	318.15	10.0–80.3	[60]
	9	328.15	10.3–90.7	[60]
Carbon dioxide + ethylcaproate	8	308.20	17.0–64.6	[61]
	10	318.20	17.0–78.2	[61]
	12	328.20	17.3–92.2	[61]
Carbon dioxide + ethyllaurate	8	308.15	14.8–70.0	[62]
	8	318.15	14.8–83.1	[62]
	9	328.15	14.8–100.1	[62]
Carbon dioxide + 1-heptanol	8	374.63	40.4–145.7	[63]
	6	431.54	68.3–168.1	[63]
Carbon dioxide + linalool	5	313.20	40.0–79.9	[64]
	5	323.20	40.0–97.8	[64]
Carbon dioxide + decanal	10	288.20	19.3–48.1	[65]
	11	303.20	21.7–67.6	[65]
	12	313.20	82.2–16.8	[65]
Ethane + 2-propanol	9	308.15	21.9–49.9	[66]
	8	313.15	31.7–53.6	[66]
Ethane + cyclohexanol	10	333.15	10.0–190.0	[67]
	10	393.15	10.0–190.0	[67]
	10	453.15	10.0–190.0	[67]
Ethylene + 1-decanol	9	308.15	10.3–103.6	[55]
	11	318.15	14.6–124.0	[55]
Propane + 1-decanol	7	408.15	12.2–63.5	[55]
	8	448.15	3.9–58.2	[55]
<i>n</i> -Hexane + 1-propanol	13	483.15	20.9–21.3	[68]
	14	493.15	25.1–24.5	[68]

The absolute mean deviation in the molar fraction in the vapor phase is as follows:

$$\Delta y = \sum_{i=1}^{np} |y_{\text{exp}} - y_{\text{cal}}| \frac{1}{np} \quad (22)$$

They are also reported in the supplementary material. The optimal parameters shown in Tables 1 and 2 in the supplementary material were used to predict the phase equilibrium of the considered mixtures. The agreement with the experimental data is generally satisfactory as shown in Figs. 1–10.

Experimental and predicted phase equilibrium for the carbon dioxide + limonene binary system is shown in Fig. 1. Predictions with the optimal parameters obtained from OF f_3 and f_5 are compared. It can be appreciated that predictions corresponding to f_5 are slightly better than those corresponding to f_3 . Figs. 2–4 show experimental and predicted VLE for ethane + *n*-decane, propylene + benzene and *n*-hexane + benzene binary mixtures, respectively. In these three figures, the OF that do not involve

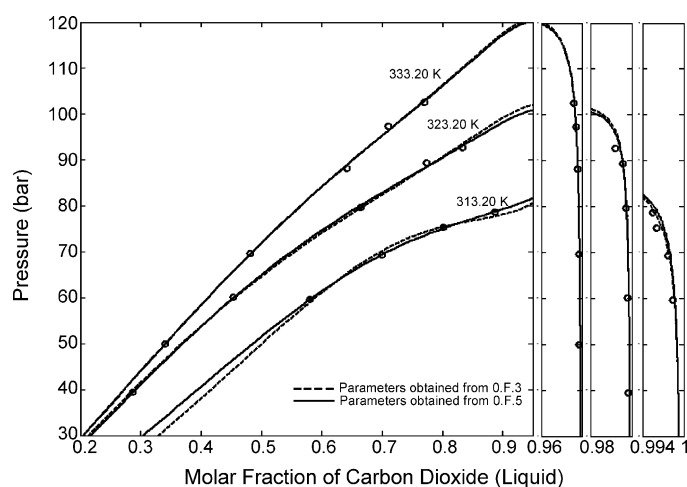


Fig. 1. Experimental and predicted VLE for carbon dioxide + limonene binary system. Comparison of accuracy of two objective functions. Experimental data taken from Iwai et al. [54]. Prediction with PR EOS coupled with the WS mixing rules.

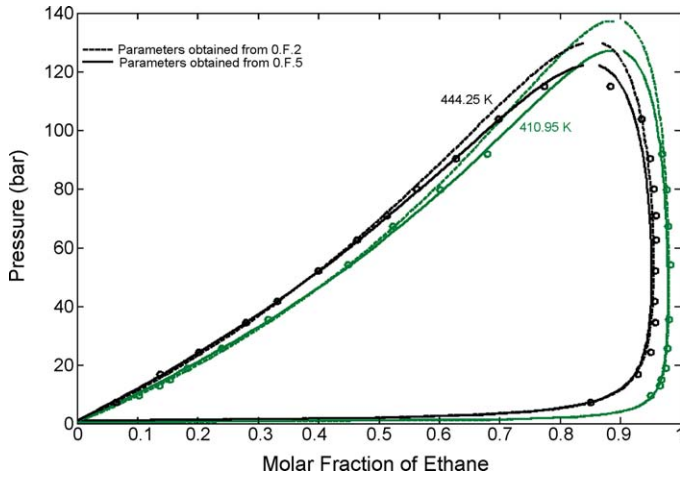


Fig. 2. Experimental and predicted VLE for ethane + *n*-decane binary system. Comparison of accuracy of two objective functions. Experimental data taken from Gardeler et al. [55]. Prediction with PR EOS coupled with the WS mixing rules.

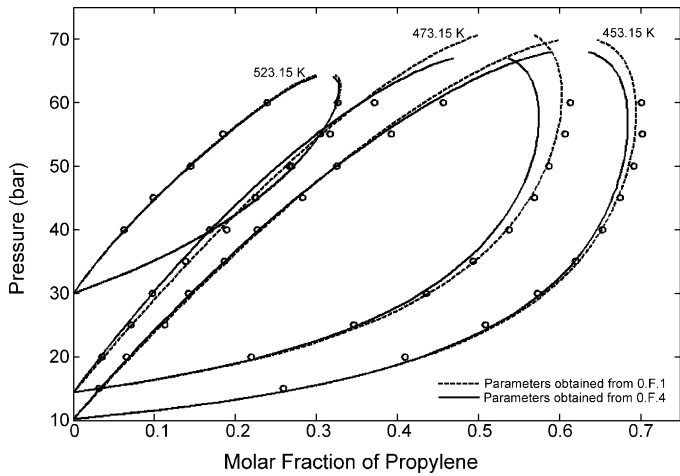


Fig. 3. Experimental and predicted VLE for propylene + benzene binary system. Comparison of accuracy of two objective functions. Experimental data taken from Guo et al. [56]. Prediction with PR EOS coupled with the WS mixing rules.

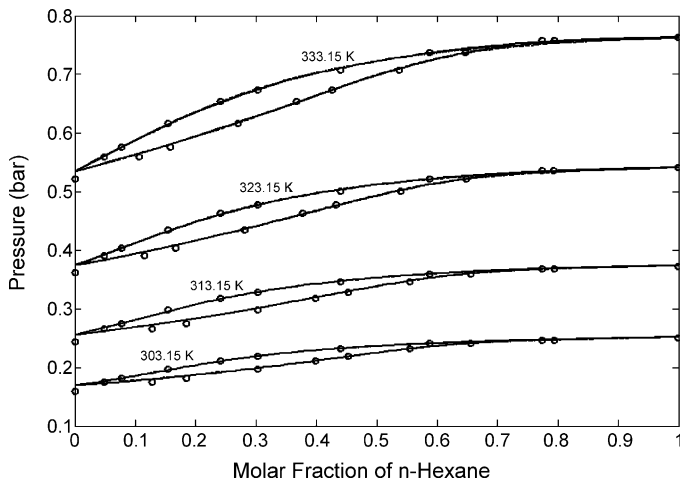


Fig. 4. Experimental and predicted VLE for *n*-hexane + benzene binary system. Comparison of accuracy of two objective functions (OF 2 and OF 3, identical predictions). Experimental data taken from Li et al. [57]. Prediction with PR EOS coupled with the WS mixing rules.

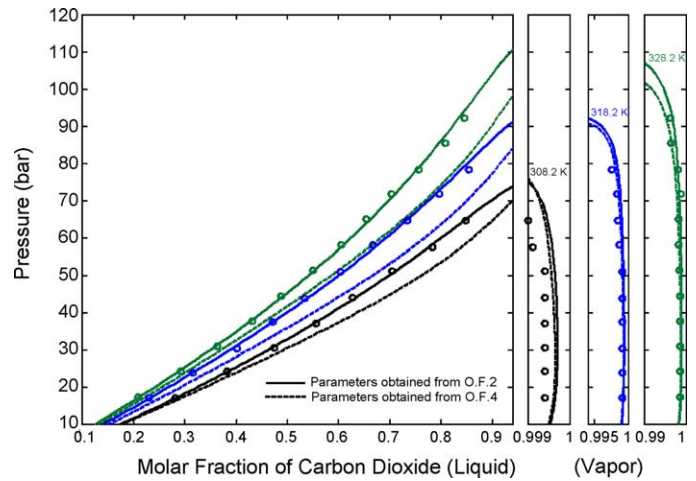


Fig. 5. Experimental and predicted VLE for carbon dioxide + ethyl caproate binary system. Comparison of accuracy of two objective functions. Experimental data taken from Hwu et al. [61]. Prediction with PR EOS coupled with the WS mixing rules.

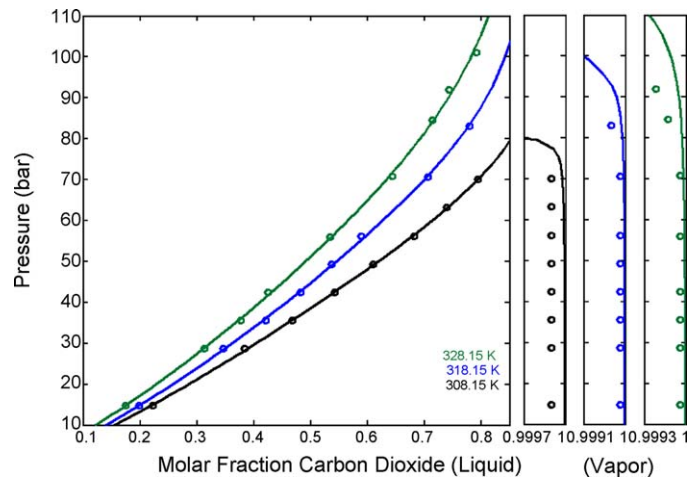


Fig. 6. Experimental and predicted VLE for carbon dioxide + ethyl laurate binary system. Experimental data taken from Cheng et al. [62]. Prediction with PR EOS coupled with the WS mixing rules with the obtained parameters from OF 2.

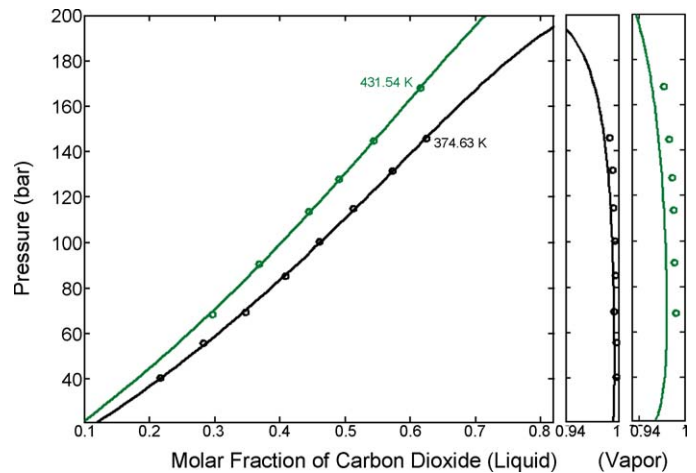


Fig. 7. Experimental and predicted VLE for carbon dioxide + 1-heptanol binary system. Experimental data taken from Elizalde-Solis et al. [63]. Prediction with PR EOS coupled with the WS mixing rules with the obtained parameters from OF 3.

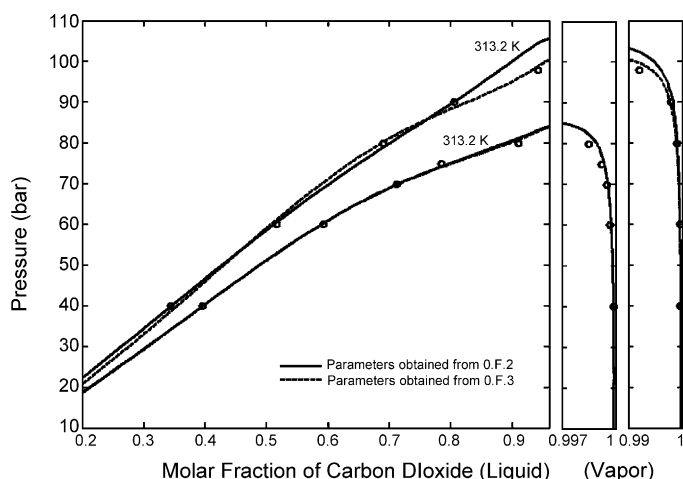


Fig. 8. Experimental and predicted VLE for carbon dioxide + linalool binary system. Comparison of accuracy of two objective functions. Experimental data taken from Iwai et al. [64]. Prediction with PR EOS coupled with the WS mixing rules.

additional iterative calculations as the bubble point pressure (f_1 and f_2) are compared with those that involve this kind of calculations (f_3 – f_5). It is important to note that the advantage of using implicit methods over explicit ones is the great reduction in the computing time. As it was mentioned in a previous work [76], explicit methods require on the average nine times more CPU time per iteration related to the implicit methods. A good agreement with the experimental data can be seen in these figures. Moreover, in ethane + *n*-decane and propylene + benzene asymmetric binary mixtures (see Figs. 2 and 3, respectively), the predictions obtained from implicit methods do not present very well the VLE near the critical point. In the case of *n*-hexane + benzene symmetric binary mixture (see supplementary material), the predictions with the optimal parameters obtained from OF f_2 and f_3 are almost identical. Moreover, differences between predictions from explicit and implicit methods can be found when the asymmetry of the mixtures was increased.

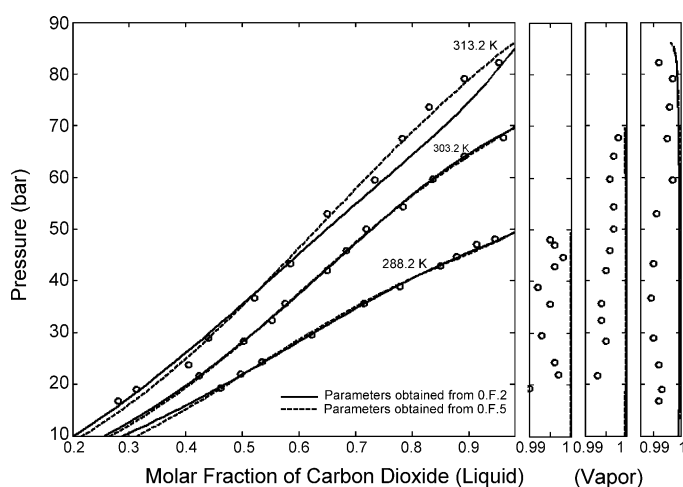


Fig. 9. Experimental and predicted VLE for carbon dioxide + decanal binary system. Comparison of accuracy of two objective functions. Experimental data taken from Vázquez da Silva et al. [65]. Prediction with PR EOS coupled with the WS mixing rules.

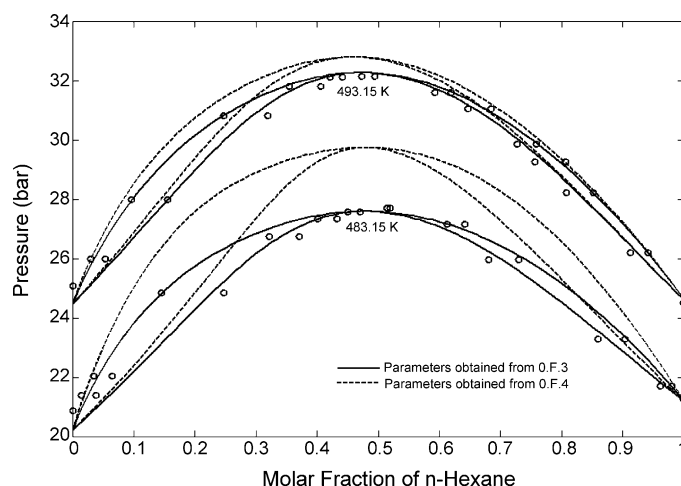


Fig. 10. Experimental and predicted VLE for *n*-hexane + 1-propanol binary system. Comparison of accuracy of two objective functions. Experimental data taken from Oh et al. [68]. Prediction with PR EOS coupled with the WS mixing rules.

Fig. 5 shows the experimental and predicted VLE for the highly asymmetric carbon dioxide + ethyl caproate binary system. Here, OF f_2 and f_4 are compared. In both cases, the vapor phase representations are very accurate taking into account the range of experimental data. It can be observed that OF f_4 gave poor predictions for pressure, while OF f_2 gave excellent predictions.

VLE for carbon dioxide + ethyl laurate asymmetric binary system is shown in Fig. 6. Experimental data are compared with the calculations with optimal parameters obtained from OF f_2 . At the three considered temperatures, all the predictions were accurate in both pressure and vapor phase composition.

The capability of OF f_3 is analyzed in Fig. 7. This figure shows the experimental and predicted phase equilibrium for carbon dioxide + 1-heptanol binary system. The predictions with the optimal parameters obtained using this OF are very accurate related to the experimental data. Moreover, for the two considered temperatures, the deviations corresponding to OF f_3 and f_5 are similar (see Table 2 in supplementary material).

Two important systems for the analysis of supercritical fluid extraction with carbon dioxide are shown in Fig. 8 (carbon dioxide + linalool) and Fig. 9 (carbon dioxide + decanal). Again, implicit and explicit models are compared. Although all predictions are very similar for both asymmetric mixtures, calculations developed with OF f_2 present light deviations near the critical point of both mixtures.

Experimental and predicted VLE (with the optimal parameters obtained from OF f_3 and f_4) for *n*-hexane + 1-propanol binary system are compared in Fig. 10. Both OF are explicit models. The predictions with OF f_4 are not accurate in the range of experimental data (see Fig. 10), while those ones with OF f_3 are very satisfactory.

In terms of numerical capacity, OF f_1 shows a bigger numerical instability than the other analyzed OF. First, for several binary mixtures (hydrogen + *n*-hexadecane at 461.65 K, helium + toluene at 505.20 and 545.60 K, nitrogen + toluene at 545.20 K, *n*-pentane + toluene at 303.15 and 313.15 K, carbon

dioxide + ethyl laurate at 318.15 K and carbon dioxide + decanal at 313.20 K), the optimal second virial coefficient interaction parameter violates the quadratic composition dependence of the second virial coefficient, since it takes unrealistic values (see the Tables in the supplementary material). In addition, in very few cases (hydrogen + *n*-hexadecane at 461.65 K, helium + toluene at 545.60 K, nitrogen + methanol at 308.15 and 318.15 K, and nitrogen + dimethyl ether at 288.15 K), the other OF also generated unrealistic values for this parameter. An explanation to this fact is that the second virial coefficient interaction parameter is used with the purpose of compensating the initial difference between the excess Helmholtz free energy at infinite pressure calculated using an EOS and the excess Gibbs free energy at low pressure calculated from activity coefficient model. Additionally, in highly asymmetric systems, its value is strongly dependent on the composition. This dependence becomes larger as the asymmetry increases. Therefore, a constant value of k_{ij} over the entire composition range will not be enough to reproduce the G^E activity model from an equation of state. These illogical values lead to the violation of the quadratic composition dependence of the second virial coefficient [34]. Therefore, for highly nonideal mixtures, it is necessary to find the virial coefficient binary interaction parameter as a function of the composition. On the other hand, in one case (carbon dioxide + decanal at 288.20 K), the OF f_1 did not show convergence in a real range of initial values. Additionally, in many systems (helium + toluene at 464.40 K, propylene + benzene at 543.15 K, *n*-pentane + toluene at 303.15 K, carbon dioxide + ethyl laurate at 308.15 and 318.15 K, carbon dioxide + linalool at 323.20 K,

Table 3

Average deviations in the VLE prediction of parameters obtained from each objective function for both non-polar and polar binary systems

Objective function	Non-polar systems		Polar systems	
	ΔP	Δy	ΔP	Δy
f_1	5.6838	0.0150	11.2268	0.0133
f_2	2.1224	0.0319	2.7097	0.0185
f_3	1.4706	0.0430	2.7518	0.0098
f_4	7.1928	0.0143	12.3279	0.0072
f_5	1.5833	0.0152	3.3485	0.0092

carbon dioxide + decanal at 288.20, 303.20 and 313.20 K and ethane + 2-propanol at 313.15 K), the minimization using this objective function presented satisfactory convergence, but when the deviations were calculated with the corresponding optimal parameters, illogical values were obtained, which were not reported here. This is because, OF f_1 does not involve procedures for bubble point pressure calculation, which are necessary to calculate those deviations. When OF f_1 fails, the other OFs satisfactory converge (see Tables 1 and 2 in the supplementary material). This error is directly due to the OF geometric form and not to the application of the Peng–Robinson equation of state coupled with the Wong–Sandler mixing rules.

With the purpose of comparing the accuracy of each OF for predicting the phase equilibrium of both gas + non-polar solute and gas + polar solute asymmetric binary mixtures at high pressures, Table 3 shows the average deviations of these predictions obtained from each OF. Also, for two of the studied asymmet-

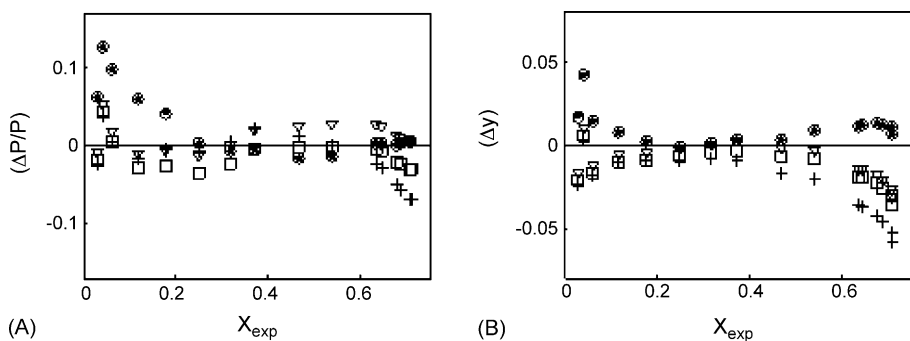


Fig. 11. Deviations between experimental points and calculated values of y and P for carbon dioxide + *n*-pentane at 363.15 K. Parameters obtained from: ▽, OF 1; +, OF 2; ●, OF 3; □, OF 4; ○, OF 5.

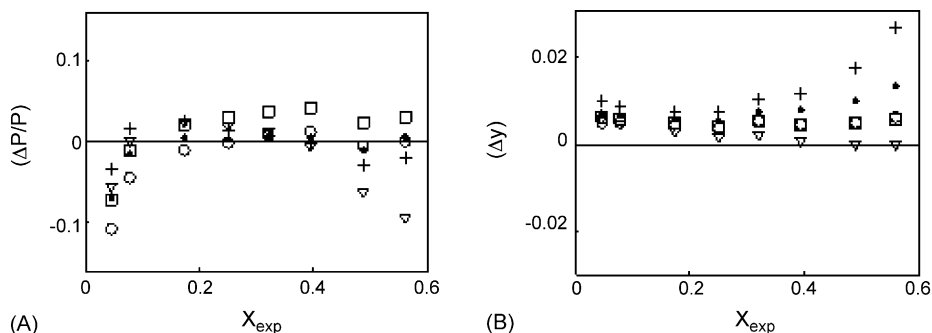


Fig. 12. Deviations between experimental points and calculated values of y and P for propane + *n*-decanol at 448.15 K. Parameters obtained from: ▽, OF 1; +, OF 2; ●, OF 3; □, OF 4; ○, OF 5.

ric systems, the residuals were calculated with the purpose of making more informative the quality of the obtained parameters. These residuals are the difference between the experimental point and the calculated value. Their statistical analysis can indicate how well the thermodynamic model represents the data and how precise the data are [38]. The residuals plots for carbon dioxide + *n*-pentane at 363.15 K and propane + *n*-decanol at 448.15 K are shown in Figs. 11 and 12, respectively. In general terms, the optimal parameters obtained from the different explicit models (OFs f_3 – f_5) are similar, but not identical. On the other hand, the optimal parameters obtained using implicit models (OFs f_1 and f_2) are very different. In terms of accuracy for representing the phase equilibria, all the OF gave good predictions for the vapor phase composition, but OF f_4 showed best results than the others in both gas + non-polar and gas + polar binary systems. The OF represented the bubble point pressure in a best way were f_2 , f_3 and f_5 .

6. Conclusions

In this work, five different OF were analyzed regarding its capability to represent the phase equilibrium in highly asymmetric binary mixtures at elevated temperatures and pressures. Additionally, the ability of Peng–Robinson EOS coupled with the Wong–Sandler mixing rules and the NRTL model for representing fluid phase equilibrium of these nonideal mixtures was demonstrated. All the OF gave good predictions for the vapor phase behavior. Only OF f_2 (based on coefficient distribution calculations), f_3 (based on bubble point pressure calculations) and f_5 (based on bubble point pressure and vapor phase composition calculations) represented the bubble point pressure satisfactory. Furthermore, it was found that OF f_2 has some advantages over the other analyzed OFs. Firstly, this OF does not involve additional iterative calculations as the bubble point or isothermal flash for each data point, resulting in a great reduction in the computing time requirements. Secondly, the optimal second virial coefficient interaction parameter showed to be concordant with the statistical thermodynamic postulates, since its value does not violate the quadratic composition dependence of the second virial coefficient. Finally, VLE predictions with the optimal parameters obtained using this OF showed very good predictions for both vapor phase and pressure. Therefore, objective function f_2 presents attractive features for parameter estimation of EOS and activity coefficient models from experimental data for appropriately representing the VLE.

List of symbols

a, b	equation of state parameters
A^E	excess Helmholtz free energy
$(b - a/RT)_{ij}$	cross second virial coefficient
C	constant defined by Eq. (10)
f	objective function (Eqs. (1) and (2))
f_1 – f_5	objective functions denoted by Eqs. (16)–(20), respectively
g_{ij}	parameter defined by Eq. (15)
G^E	excess Gibbs free energy
k_{ij}	second virial coefficient interaction parameter

K_{ij}	distribution coefficient
nc	number of components
nm	number of measured variables
np	number of experimental data points
P	pressure
R	gas constant
T	temperature
V	volume in molar units
V^E	excess volume
u_{ij}	dependent variables in Eq. (1)
w_{ij}	measured variables in Eq. (2)
x	liquid molar fraction
y	vapor molar fraction
z	molar fraction

Greek letters

$\alpha(T_r)$	temperature-dependent alpha function
α_{ij}	NRTL model parameter
γ	activity coefficient
Δ	deviation
κ	Peng–Robinson alpha function parameter
σ	statistical variance in Eq. (2)
τ_{12}, τ_{21}	NRTL model binary interaction parameter
Φ	fugacity coefficient
ω	acentric factor

Subscripts

c	critical point
m	mixture
r	reduced conditions
∞	infinite condition

Superscripts

E	excess property
exp	experimental
cal	calculated

Acronyms

EOS	equation of state
NRTL	non-random two liquid
OF	objective function
PR	Peng–Robinson
vdW	van der Waals
VLE	vapor–liquid equilibrium

Acknowledgment

Dr. Aníbal Blanco at Planta Piloto de Ingeniería Química (Argentina) for his critical review and valuable suggestions on early versions of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.fluid.2006.08.003](https://doi.org/10.1016/j.fluid.2006.08.003).

References

- [1] A.Z. Panagiotopoulos, R.C. Reid, New mixing rules for cubic equations of state for highly polar asymmetric mixtures, *ACS Symp. Ser.* 300 (1986) 571–582.
- [2] Y. Adachi, H. Sugie, A new mixing rule—modified conventional mixing rule, *Fluid Phase Equilib.* 28 (1986) 103–118.
- [3] R. Sandoval, G. Wilczek-Vera, J.H. Vera, Prediction of the ternary vapor–liquid equilibria with the PRSV equation of state, *Fluid Phase Equilib.* 52 (1989) 119–126.
- [4] J. Schwartzentruber, H. Renon, Development of a new cubic equation of state for phase equilibrium calculations, *Fluid Phase Equilib.* 52 (1989) 127–134.
- [5] J. Schwartzentruber, H. Renon, Extension of UNIFAC to high pressures and temperatures by use of a cubic equation of state, *Ind. Eng. Chem. Res.* 28 (1989) 1049–1055.
- [6] S.K. Shibata, S.I. Sandler, Critical evaluation of equation of state mixing rules for the prediction of high-pressure phase equilibria, *Ind. Eng. Chem. Res.* 28 (1989) 1893–1898.
- [7] G.A. Melhem, R. Saini, B.M. Goodwin, A modified Peng–Robinson equation of state, *Fluid Phase Equilib.* 47 (1989) 189–237.
- [8] R. Stryjek, J.H. Vera, PRSV—an improved Peng–Robinson equation of state with new mixing rules for strongly nonideal mixtures, *Can. J. Chem. Eng.* 64 (1986) 334–340.
- [9] P.M. Mathias, H.C. Klotz, J.M. Prausnitz, Equation-of-state mixing rules for multicomponent mixtures: the problem of invariance, *Fluid Phase Equilib.* 67 (1991) 31–44.
- [10] M.J. Huron, J. Vidal, New mixing rules in simple equations of state for representing vapour–liquid equilibria of strongly non-ideal mixtures, *Fluid Phase Equilib.* 3 (1979) 255–271.
- [11] D.S.H. Wong, S.I. Sandler, Theoretically correct mixing rule for cubic equations of state, *AIChE J.* 38 (1992) 671–680.
- [12] S.I. Sandler, *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York, 1994.
- [13] J. Mollerup, A note on the derivation of mixing rules from excess Gibbs energy models, *Fluid Phase Equilib.* 25 (1986) 323–327.
- [14] M.L. Michelsen, A method for incorporating excess Gibbs energy models in equations of state, *Fluid Phase Equilib.* 60 (1990) 47–58.
- [15] M.L. Michelsen, A modified Huron–Vidal mixing rule for cubic equation of state, *Fluid Phase Equilib.* 60 (1990) 213–219.
- [16] S. Dahl, M.L. Michelsen, A high-pressure vapor–liquid equilibrium with a UNIFAC based equation of state, *AIChE J.* 36 (1990) 1829–1836.
- [17] P.A. Gupte, P. Rasmussen, A. Fredenslund, A new group contribution equation of state for vapor–liquid equilibria, *Ind. Eng. Chem. Fund.* 25 (1986) 636–645.
- [18] G. Soave, A New Expression of $q(\alpha)$ for the modified Huron–Vidal methods, *Fluid Phase Equilib.* 72 (1992) 325–328.
- [19] C.H. Twu, J.E. Coon, CEOS/ A^E mixing rules constrained by vdW mixing rule and second virial coefficient, *AIChE J.* 42 (1996) 3212–3222.
- [20] C.H. Twu, J.E. Coon, D. Bluck, A zero-pressure cubic equation of state mixing rule for predicting high pressure phase equilibria using infinite dilution activity coefficients at low temperatures, *Fluid Phase Equilib.* 150–151 (1998) 181–189.
- [21] C.H. Twu, J.E. Coon, D. Bluck, Comparison of the Peng–Robinson and Soave–Redlich–Kwong equations of state using a new zero-pressure-based mixing rule for the prediction of high-pressure and high-temperature phase equilibria, *Ind. Eng. Chem. Res.* 37 (1998) 1580–1585.
- [22] D.S.H. Wong, H. Orbey, S.I. Sandler, Equation of state mixing rule for nonideal mixtures using available activity coefficient model parameters and that allows extrapolation over large ranges of temperature and pressure, *Ind. Eng. Chem. Res.* 31 (1992) 2033–2039.
- [23] K.A. Pividal, C. Sterner, S.I. Sandler, H. Orbey, Vapor–liquid equilibrium from infinite dilution activity coefficients: measurement and prediction of oxygenated fuel additives with alkanes, *Fluid Phase Equilib.* 72 (1992) 227–250.
- [24] H. Orbey, S.I. Sandler, D.S.H. Wong, Accurate equation of state predictions at high temperatures and pressures using the existing UNIFAC model, *Fluid Phase Equilib.* 85 (1993) 41–54.
- [25] H. Huang, S.I. Sandler, Prediction of vapor–liquid equilibria at high pressures using activity coefficient parameter obtained from low-pressure data: a comparison of two equations of state mixing rules, *Ind. Eng. Chem. Res.* 32 (1993) 1498–1503.
- [26] H. Huang, S.I. Sandler, H. Orbey, Vapor–liquid equilibria of some hydrogen + hydrocarbon systems with the Wong–Sandler mixing rule, *Fluid Phase Equilib.* 96 (1994) 143–153.
- [27] H. Orbey, S.I. Sandler, Reformulation of Wong–Sandler mixing rule for cubic equations of state, *AIChE J.* 41 (1995) 683–690.
- [28] P.T. Eubank, G.-S. Shyu, N.S.M. Hanif, New procedures for application of the Wong–Sandler mixing rules to the prediction of vapor–liquid equilibria, *Ind. Eng. Chem. Res.* 34 (1995) 314–325.
- [29] P. Ghosh, T. Taraphdar, Prediction of vapor–liquid equilibria of binary systems using PRSV equation of state and Wong–Sandler mixing rules, *Chem. Eng. J.* 70 (1998) 15–24.
- [30] G.N. Escobedo-Alvarado, S.I. Sandler, Study of EOS- G^{ex} mixing rules for liquid–liquid equilibria, *AIChE J.* 44 (1998) 1178–1187.
- [31] H. Orbey, C. Balci, G.A. Gürüz, Phase equilibrium of asymmetric systems by predictive equations of state models, *Ind. Eng. Chem. Res.* 41 (2002) 963–967.
- [32] M.B. Shiflett, S.I. Sandler, modeling fluorocarbon vapor–liquid equilibria using the Wong–Sandler model, *Fluid Phase Equilib.* 147 (1998) 145–162.
- [33] T. Yang, G.-J. Chen, W. Yan, T.-M. Guo, Extension of the Wong–Sandler mixing rule to the three parameter Patel–Teja equation of state: application up to the near-critical region, *Chem. Eng. J.* 67 (1997) 26–36.
- [34] P. Coutosik, N.S. Kalospiros, D.P. Tassios, Capabilities and limitations of the Wong–Sandler mixing rules, *Fluid Phase Equilib.* 108 (1995) 59–78.
- [35] Y. Bard, *Nonlinear Parameters Estimation*, Academic Press, 1974.
- [36] T.L. Sutton, J.F. MacGregor, The analysis and design of binary vapour–liquid equilibrium experiments. I. Parameter estimation and consistency test, *Can. J. Chem. Eng.* 55 (1977) 602–608.
- [37] V.G. Niesen, V.F. Yesavage, Application of a maximum likelihood method using implicit constraints to determine equation of state parameters from binary phase behaviour data, *Fluid Phase Equilib.* 50 (1989) 249–266.
- [38] T.F. Anderson, D.S. Abrams, E.A. Grens II, Evaluation of parameters for nonlinear thermodynamic models, *AIChE J.* 24 (1978) 20–29.
- [39] R. Paunovic, S. Jovanovic, A. Mihajlov, Rapid computation of binary interaction coefficients of an equation of state for vapor–liquid equilibrium calculations: application to the Redlich–Kwong–Soave equation of state, *Fluid Phase Equilib.* 6 (1981) 141–148.
- [40] D. Salazar-Sotelo, A. Boiveaut-Boudehen, H. Renon, Computer calculation of the optimal parameters of a model for the simultaneous representation of experimental binary and ternary vapor–liquid and liquid–liquid equilibrium data, *Fluid Phase Equilib.* 27 (1986) 383–403.
- [41] P. Englezos, N. Kalogerakis, P.R. Bishnoi, Estimation of binary interaction parameters for equations of state subject to liquid phase stability requirements, *Fluid Phase Equilib.* 53 (1989) 81–88.
- [42] P. Englezos, N. Kalogerakis, M.A. Trebble, P.R. Bishnoi, Estimation of multiple binary interaction parameters in equations of state using VLE data: application to the Trebble–Bishnoi equation of state, *Fluid Phase Equilib.* 58 (1990) 117–132.
- [43] P. Englezos, N. Kalogerakis, P.R. Bishnoi, A systematic approach for the efficient estimation of interaction parameters in equations of state using binary VLE data, *Can. J. Chem. Eng.* 71 (1993) 322–326.
- [44] J.R. Nunhez, C.B.B. Costa, R. Guirardello, A new spline approach for data fitting, *Fluid Phase Equilib.* 220 (2004) 171–180.
- [45] D.Y. Peng, D.B. Robinson, A new two constant equation of state, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64.
- [46] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE J.* 14 (1967) 135–144.
- [47] H.-M. Lin, H.M. Sebastian, K.-C. Chao, Gas–liquid equilibrium in hydrogen + *n*-hexadecane and methane + *n*-hexadecane at elevated temperatures and pressures, *J. Chem. Eng. Data* 25 (1980) 252–254.
- [48] H.-M. Lin, M.-J. Lee, R.-J. Lee, Phase equilibria of toluene in mixtures with helium or nitrogen at high temperatures, *J. Chem. Eng. Data* 40 (1995) 653–656.

- [49] L.A. Webster, A.J. Kidnay, Vapor–liquid equilibria for the methane–propane–carbon dioxide systems at 230 and 270 K, *J. Chem. Eng. Data* 46 (2001) 759–764.
- [50] K. Tochigi, K. Hasegawa, N. Asano, K. Kojima, Vapor–liquid equilibria for the carbon dioxide + pentane and carbon dioxide + toluene systems, *J. Chem. Eng. Data* 43 (1998) 954–956.
- [51] K. Ohgaki, T. Katayama, Isothermal vapor–liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol–carbon dioxide, *n*-hexane–carbon dioxide, and benzene–carbon dioxide systems, *J. Chem. Eng. Data* 21 (1976) 53–55.
- [52] M. Akgün, D. Emel, N. Baran, N.A. Akgün, S. Deniz, S. Dinçer, Styrene–carbon dioxide phase equilibria at high pressures, *J. Supercrit. Fluids* 31 (2004) 27–32.
- [53] N. Nagarajan, R.L. Robinson, Equilibrium phase compositions, phase densities, and interfacial tensions for CO₂ + hydrocarbon systems. 2. CO₂ + *n*-decane, *J. Chem. Eng. Data* 31 (1986) 168–171.
- [54] Y. Iwai, T. Morotomi, K. Sakamoto, Y. Koga, Y. Arai, High-pressure vapor–liquid equilibria for carbon dioxide + limonene, *J. Chem. Eng. Data* 41 (1996) 951–952.
- [55] H. Gardeler, K. Fischer, J. Gmehling, Experimental determination of vapor–liquid equilibrium data for asymmetric systems, *Ind. Eng. Chem. Res.* 41 (2002) 1051–1056.
- [56] J. Guo, T. Liu, Y.-C. Dai, W.-K. Yuan, Vapor–liquid equilibria of benzene and propylene under elevated temperature and pressure, *J. Chem. Eng. Data* 46 (2001) 668–670.
- [57] I.P.C. Li, Y.-W. Wong, S.-D. Chang, B.C.-Y. Lu, Vapor–liquid equilibria in systems *n*-hexane–benzene and *n*-pentane–toluene, *J. Chem. Eng. Data* 17 (1972) 492–498.
- [58] T. Laursen, S.I. Andersen, High-pressure vapor–liquid equilibrium for nitrogen + methanol, *J. Chem. Eng. Data* 47 (2002) 1173–1174.
- [59] M. Teodorescu, P. Rasmussen, High-pressure vapor–liquid equilibria in the systems nitrogen + dimethyl ether, methanol + dimethyl ether, carbon dioxide + dimethyl ether + methanol, and nitrogen + dimethyl ether + methanol, *J. Chem. Eng. Data* 46 (2001) 640–646.
- [60] Li.-C. Feng, K.-W. Cheng, M. Tang, Y.-P. Chen, Vapor–liquid equilibria of carbon dioxide with ethyl benzoate, diethyl succinate and isoamyl acetate binary mixtures at elevated pressures, *J. Supercrit. Fluids* 21 (2001) 111–121.
- [61] W.-H. Hwu, J.-S. Cheng, K.-W. Cheng, Y.-P. Chen, Vapor–liquid equilibrium of carbon dioxide with ethyl caproate, ethyl caprylate and ethyl caprate at elevated pressures, *J. Supercrit. Fluids* 28 (2004) 1–9.
- [62] K.-W. Cheng, M. Tang, Y.-P. Chen, Vapor–liquid equilibria of carbon dioxide with diethyl oxalate, ethyl laurate, and dibutyl phthalate binary mixtures at elevated pressures, *Fluid Phase Equilib.* 181 (2001) 1–16.
- [63] O. Elizalde-Solis, L.A. Galicia-Luna, S.I. Sandler, J.G. Sampayo-Hernández, Vapor–liquid equilibria and critical points of the CO₂ + 1-hexanol and CO₂ + 1-heptanol systems, *Fluid Phase Equilib.* 210 (2003) 215–227.
- [64] Y. Iwai, N. Hosotani, T. Morotomi, Y. Koga, Y. Arai, High-pressure vapor–liquid equilibria for carbon dioxide + linalool, *J. Chem. Eng. Data* 39 (1994) 900–902.
- [65] M. Vázquez da Silva, D. Barbosa, P.O. Ferreira, High pressure vapor–liquid equilibrium data for the system carbon dioxide + decanal at 288.2, 303.2, and 313.2 K, *J. Chem. Eng. Data* 47 (2002) 1171–1172.
- [66] D. Kodama, M. Ogawa, T. Kimura, H. Tanaka, M. Kato, High-pressure phase equilibrium for ethane + 2-propanol at 308.15 and 313.15 K, *J. Chem. Eng. Data* 47 (2002) 916–918.
- [67] J.T. Chen, M.J. Lee, Vapor–liquid equilibria of cyclohexanol with carbon dioxide, ethane, or nitrogen at elevated pressures, *J. Chem. Eng. Data* 41 (1996) 339–343.
- [68] B.C. Oh, Y. Kim, H.Y. Shin, H. Kim, Vapor–liquid equilibria for the system 1-propanol + *n*-hexane near the critical region, *Fluid Phase Equilib.* 220 (2004) 41–46.
- [69] Z. Knez, M. Habulin, Compressed gases as alternative enzymatic reaction solvent. A short review, *J. Supercrit. Fluids* 23 (2002) 29–42.
- [70] H.J. Dai, J.M. Simonson, H.D. Cochran, Density measurements of styrene solutions in supercritical CO₂, *J. Chem. Eng. Data* 46 (2001) 1571–1573.
- [71] V.P. Saraf, E. Kiran, Free radical polymerization of styrene in supercritical fluids, *Polymer* 31 (1990) 687–688.
- [72] H. Shiho, J.M. DeSimone, Preparation of micron-size polystyrene particles in supercritical carbon dioxide, *J. Polym. Sci.* 37 (1999) 2429–2437.
- [73] H. Shiho, J.M. DeSimone, Dispersion polymerizations of styrene in supercritical carbon dioxide utilizing random copolymers containing a fluorinated acrylate for preparing micron-size polystyrene particles, *J. Polym. Sci.* 38 (2000) 1146–1153.
- [74] D.A. Canelas, J.M. DeSimone, Dispersion polymerizations of styrene in carbon dioxide stabilized with poly(styrene-*b*-dimethylsiloxane), *Macromolecules* 30 (1997) 5673–5682.
- [75] I. Ashour, G. Aly, Effect of computation techniques for equation of state binary interaction parameters on the prediction of binary VLE data, *Comput. Chem. Eng.* 20 (1996) 79–91.
- [76] J.A. López, C.A. Cardona, Phase equilibrium calculations for carbon dioxide + *n*-alkanes binary mixtures with the Wong–Sandler mixing rules, *Fluid Phase Equilib.* 239 (2006) 206–212.