



## Thermodynamic consistency of experimental VLE data for asymmetric binary mixtures at high pressures

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### ARTICLE INFO

#### Article history:

Received 8 October 2009

Received in revised form 14 February 2010

Accepted 16 February 2010

Available online 20 February 2010

#### Keywords:

Thermodynamic consistency

Vapor–liquid equilibrium

Peng–Robinson equation of state

Wong–Sandler mixing rules

### ABSTRACT

A thermodynamic consistency of isothermal vapor–liquid equilibrium data for 9 non-polar and 8 polar binary asymmetric mixtures at high pressures has been evaluated. A method based on the isothermal Gibbs–Duhem equation was used for the test of thermodynamic consistency using a  $\Phi$ – $\Phi$  approach. The Peng–Robinson equation of state coupled with the Wong–Sandler mixing rules were used for modeling the vapor–liquid equilibrium (VLE) within the thermodynamic consistency test. The VLE parameters calculations for asymmetric mixtures at high pressures were highly dependent on bubble pressure calculation, making more convenient to eliminate the data points yielding the highest deviations in pressure. However the results of the thermodynamic consistencies test of experimental data for many cases were found not fully consistent. As a result, the strategies for solving these problems were discussed in detailed.

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### 1. Introduction

Information about high-pressure phase equilibrium is essential for many chemical processes and separation operations involving higher pressures. Simulation of petroleum reservoirs, transportation, natural gas storage and carbon dioxide sequestration, and the study of geological processes are some examples in which high-pressure phase equilibrium data are necessary [1]. Many of the asymmetric mixtures at high pressures containing carbon dioxide and isoamyl acetate, ethyl laureate, ethyl caproate, among others compounds, have great industrial importance. For instance, in the field of the supercritical fluid extraction, designing and sizing equipments. These kind of binary mixtures are characterized by both high complexity and asymmetry, being the more common shortcoming for modeling vapor–liquid equilibrium (VLE). Therefore it is necessary to account models that provide good prediction for VLE [2].

There are many ways to obtain information about VLE for asymmetric mixtures. The direct experimental measurement of phase equilibrium data may be the preferred option, although these measurements can be difficult and expensive. There are some useful thermodynamic models that can be employed for predicting the VLE for binary mixtures at high pressures [3–11], especially when

a minimum number of experimental data is available, helping to reduce the number of experimental data points needed for a special design problem.

With the aim of generating adequate thermodynamic models, an accurate set of VLE data is required. This set is commonly tested by a thermodynamic consistency test in order to verify the reliability of the experimental data, which are increasingly in importance to have more accuracy. Among the most employed thermodynamic relations requiring to be satisfied for testing thermodynamic consistency are the Gibbs–Duhem and Gibbs–Helmholtz equations. Some common consistency thermodynamic tests (e.g. the overall area test method) are based on different mathematical rearrangement of the Gibbs–Duhem equation, which, in some cases, consider constant both temperature and pressure. Although the Gibbs–Duhem equation is also employed in the calculation of the fugacity coefficient among other thermodynamic relationships [12]. Furthermore, these thermodynamic equations, carried out in a rigorous manner, are really useful to prove the accuracy of the experimental data set [13].

The study of thermodynamic consistency of a binary system at low pressures is generally based on the equal-area criterion [13–17]. However, it is conveniently to use models different to the equal-area criterion when mixtures at high pressures are studied. Remarkable studies on thermodynamic consistency tests for these mixtures have been presented by Chueh et al. [18] by developing an equal-area test, based on extension of the Redlich and Kister's method for isothermal VLE data at low pressure. Won and Prausnitz [19] by proposing a method for isothermal data based on extension of the Baker's method. Christiansen and Frensdenslund [20]

Abbreviations: EoS, equation of state; NRTL, non-random two liquid; OF, objective function; PR, Peng–Robinson; VLE, vapor–liquid equilibrium.

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by considering an applicable model test to isothermal and isobaric data with a supercritical condition component. Bertuccio et al. [21] proposed a method to find the consistency VLE data for mixtures containing fluid in supercritical state. Also, Jackson and Wilsak [22] presented a review of several common thermodynamic consistency tests used mainly for mixtures at high pressures.

In many cases, thermodynamic consistency tests figure out the reliability of experimental data taken from literature. These tests provide a valuable tool when the experimental data satisfies and follows strictly a thermodynamic relationship (e.g. Gibbs–Duhem equation) assessing the data as thermodynamically consistent or inconsistent. In order to obtain VLE binary interaction parameters of asymmetric mixtures at high pressures, a suitable set of experimental data is required to generate reliable parameters coming from the minimization of a particular objective function.

In the present work, the thermodynamic consistency test for experimental VLE data of polar and non-polar asymmetric binary mixtures at high pressures proposed by Valderrama et al. [23] is analyzed. The Peng–Robinson (PR) equation of state [24] coupled with the Wong–Sandler mixing rules [25] has been used in thermodynamic consistency test and VLE estimation. NRTL model [26] was employed to predict the excess Helmholtz free energy into the Wong–Sandler mixing rules. The optimal parameters used in this work were calculated in previous works [27,28], and those were used for testing the thermodynamic consistency for twenty-two isothermal sets of non-polar mixtures and twenty-one isothermal sets of polar mixtures. Likewise the Levenberg–Marquardt minimization algorithm was used in all cases.

## 2. Thermodynamic consistency model

The Gibbs–Duhem equation requires a general coupling of molar partial properties of the components in a specific mixture that provides a basis for most of the methods for testing thermodynamic consistency of VLE experimental data. The general Gibbs–Duhem equation is expressed in terms of residual properties as [29]:

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT + \sum_i \frac{\bar{G}_i^R}{RT}dz_i \quad (1)$$

where  $z_i$  is the molar fraction of  $i$ -component in the reference phase (either  $x$  for liquid or  $y$  for the vapor phase) and the molar residual Gibbs property is defined by Eq. (2):

$$\bar{G}^R = \sum_i \bar{G}_i^R z_i \quad (2)$$

By replacing Eqs. (2) into (1):

$$\sum_i z_i \frac{d\bar{G}_i^R}{RT} = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \quad (3)$$

The residual Gibbs free energy properties can also be expressed in terms of fugacity coefficients ( $\bar{\phi}_i$ ) in the mixture:

$$\frac{\bar{G}_i^R}{RT} = \frac{\bar{G}_i - \bar{G}_i^{IGM}}{RT} = \ln(\bar{\phi}_i) \quad (4)$$

The fugacity coefficient can be replaced in Eq. (3), giving:

$$\sum_i z_i d \ln(\bar{\phi}_i) = \frac{V^R}{RT}dP - \frac{H^R}{RT^2}dT \quad (5)$$

where  $V^R$  and  $H^R$  are the molar residual volume and enthalpy of the mixture, respectively. Eq. (5) for a binary mixture, at constant temperature  $T$ , can be rewritten as:

$$z_1 \frac{d \ln(\bar{\phi}_1)}{dz_1} + z_2 \frac{d \ln(\bar{\phi}_2)}{dz_1} = \frac{1}{P}(Z-1) \frac{dP}{dz_1} \quad (6)$$

Eq. (6) is usually written in terms of solute concentration into a vapor phase mixture ( $z_i = y_i$ ). Thus, solute is termed as component 2 in the binary mixture. Taking into account these considerations the above equation can be expressed as:

$$\frac{1}{P} \frac{dP}{dy_2} = \frac{y_2}{(Z-1)} \frac{d \ln \bar{\phi}_2}{dy_2} + \frac{(1-y_2)}{(Z-1)} \frac{d \ln \bar{\phi}_1}{dy_2} \quad (7)$$

An analogous expression to (7), in terms of fugacity coefficients, has been reported by Bertuccio et al. [21]. Likewise Eq. (7) can be conveniently expressed in integral form, as follows:

$$\int \frac{1}{Py_2} dP = \int \frac{1}{(Z-1)\bar{\phi}_2} d\bar{\phi}_2 + \int \frac{(1-y_2)}{y_2(Z-1)\bar{\phi}_1} d\bar{\phi}_1 \quad (8)$$

where  $P$  is the absolute pressure,  $y_2$  is the molar fraction of solute in the vapor phase,  $Z$  is the compressibility factor of the vapor phase mixture, and  $\bar{\phi}_1$  and  $\bar{\phi}_2$  are the fugacity coefficients of species 1 and 2 in the vapor phase mixture. In Eq. (8) can also be written as:

$$A_p = \int \frac{1}{Py_2} dP = A_\phi = A_{\phi_1} + A_{\phi_2} \quad (9)$$

The right hand side of Eq. (8) is designated by  $A_\phi$  as follows:

$$A_\phi = A_{\phi_1} + A_{\phi_2} = \int \frac{1}{(Z-1)\bar{\phi}_2} d\bar{\phi}_2 + \int \frac{(1-y_2)}{y_2(Z-1)\bar{\phi}_1} d\bar{\phi}_1 \quad (10)$$

The parameters  $A_\phi$  and  $A_p$  are obtained using a convenient thermodynamic model and from  $P$ - $y$  experimental data set, respectively. The PR EoS coupled with the Wong–Sandler mixing rules was used to evaluate Eq. (10). Note the advantageous manner of Eq. (10) which overcomes the inconvenience in evaluating excess volume effects on the activity coefficient. As can be seen, Eq. (10) is a non-defined integral equation which can be solved using any integrator numerical method. Finally, in order to qualify an experimental data set,  $A_p$  must be equal to  $A_\phi$  within the defined deviations range [23].

## 3. Equation of state and mixing rules

The PR EoS has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (11)$$

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

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \quad (12)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (13)$$

where subscripts  $c$  and  $r$  denote critical and reduced conditions, respectively. The  $\alpha$  function is calculated from Eqs. (14) and (15):

$$\alpha(T_r) = \left[ 1 + \kappa \left( 1 - \sqrt{T_r} \right) \right]^2 \quad (14)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (15)$$

where  $\omega$  is the acentric factor. The PR EoS can be extended to mixtures by using the Wong–Sandler [25] mixing rules for both vapor and liquid phases. The parameters  $a_m$  and  $b_m$  are obtained from:

$$a_m = b_m \left[ \sum_i z_i \frac{a_i}{b_i} + \frac{A_\infty^E}{\sigma} \right] \quad (16)$$

with

$$b_m = \frac{\sum_i \sum_j z_i z_j (b - (a/RT))_{ij}}{1 - \sum_i z_i (a_i/b_i RT) - (A_\infty^E/\sigma RT)} \quad (17)$$

$$\sigma = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \quad (18)$$

and

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b - (a/RT))_i + (b - (a/RT))_j}{2} (1 - k_{ij}) \quad (19)$$

where  $k_{ij}$  is a binary interaction parameter of the second virial coefficient,  $z$  is the molar fraction and  $A_{\infty}^E$  is the excess Helmholtz free energy at infinite pressure which is calculated from NRTL model for binary mixtures according to equations:

$$\frac{A_{\infty}^E}{RT} = \sum_i z_i \left( \frac{\sum_j z_j \tau_{ji} g_{ji}}{\sum_k z_k g_{ki}} \right) \quad (20)$$

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (21)$$

where  $\alpha_{12}$  ( $=\alpha_{21}$ ),  $\tau_{12}$  and  $\tau_{21}$  are the three parameters of NRTL model. A constant value for  $\alpha_{12}$  of 0.3 was used. The PR EoS coupled with the Wong–Sandler mixing rules, the fitted NRTL parameters ( $\tau_{12}$  and  $\tau_{21}$ ), and the binary interaction parameters of the second virial coefficient ( $k_{12}$ ) were employed. These parameters have been previously determined using experimental phase equilibrium data at isothermal conditions for each of nine non-polar and eight polar asymmetric mixtures [27,28]. The corresponding fugacity coefficients and the values of  $P$ - $y$  variables for  $T$ - $x$  were calculated by using these fitted parameters in order to evaluate Eq. (10). The required variables to calculate Eq. (10), that are  $P$ ,  $y_2$ ,  $\phi_1$  and  $\phi_2$ , were found by using the thermodynamic condition expressing an equality-of-partial-fugacities for any component in all coexisting phases. This condition can be written in term of fugacity as:

$$\bar{f}_i^L(T, P, x_i; \tau_{12}, \tau_{21}, k_{12}) = \bar{f}_i^V(T, P, y_i; \tau_{12}, \tau_{21}, k_{12}) \quad (22)$$

where superscripts  $L$  and  $V$  denote the liquid and vapor phases, respectively. The expression (22) is the starting point for VLE calculations. Furthermore, these parameters were obtained from sets of experimental data using the following objective function [27]:

$$f_{ob} = \sum_{i=1}^{np} \sum_{j=1}^{nc} [y_i^{\exp} - x_i^{\exp} K^{cal}]^2 \quad (23)$$

where  $K$  is the distribution coefficient between vapor and liquid phases, the superscripts  $np$  and  $nc$  denote the numbers of experimental data points and components, and  $y$  and  $x$  are the molar fraction in the vapor and liquid phases, respectively. This objective function has shown very acceptable performances for VLE of asymmetric binary mixtures at high pressures [27,28].

#### 4. Asymmetric binary mixtures

In the present work, 9 non-polar (gas + non-polar solute) and 8 polar (gas + polar solute) asymmetric binary mixtures have been analyzed. The experimental conditions and their reference sources are shown in Tables 1 and 2. Data for 22 isotherms with 277 experimental points were studied for gas + non-polar mixtures and 21 isotherms with 191 experimental points were studied for gas + polar mixtures. Several asymmetric mixtures have widely been used in many applications and reported in literature [30–32].

#### 5. Thermodynamic consistency criteria

Asymmetric binary mixtures require a suitable thermodynamic model, such as PR coupled with Wong–Sandler mixing rules. Model correlation could be within an acceptable deviation range of molar fraction in vapor phase and pressure for values of (–20% to +20%) and (–10% to +10%) for molar fraction and pressure, respectively. The model is accepted only in the case of the deviations falling

**Table 1**  
Experimental conditions for non-polar asymmetric binary mixtures.

System	np	T (K)	Pressure range (bar)	Refs.
Carbon dioxide + propane	25	230.00	8.9–71.1	[33]
	17	270.00	32.0–79.5	
Carbon dioxide + <i>n</i> -pentane	12	310.15	5.6–73.1	[34]
	13	333.15	5.9–87.5	
	16	363.15	9.4–96.7	
Carbon dioxide + benzene	8	298.15	8.9–57.7	[35]
	9	313.15	14.8–77.5	
Carbon dioxide + styrene	9	333.15	60.3–112.0	[36]
	10	343.15	60.0–131.0	
	8	348.15	62.9–134.2	
Carbon dioxide + <i>n</i> -decane	22	344.30	63.8–127.4	[37]
	26	377.60	103.4–164.8	
<i>n</i> -Propylene + benzene	10	453.15	15.0–60.0	[38]
	10	473.15	20.0–60.0	
<i>n</i> -Pentane + toluene	11	293.15	0.02–0.56	[39]
	11	303.15	0.04–0.82	
	11	313.15	0.07–1.16	
<i>n</i> -Hexane + benzene	10	313.15	0.24–0.37	[39]
	10	323.15	0.36–0.54	
	10	333.15	0.52–0.76	
Carbon dioxide + limonene	8	313.18	8.30–84.5	[40]
	11	323.25	11.3–98.3	

within this range. These criteria were set up by Valderrama et al. [23], defining the individual percentage deviations in bubble point pressure and percentage of molar fraction deviation of vapor phase for each  $i$ -point as:

$$\% \Delta P_i = \frac{P_i^{\exp} - P_i^{cal}}{P_i^{\exp}} \times 100 \quad (24)$$

$$\% \Delta y_{2i} = \frac{y_{2i}^{\exp} - y_{2i}^{cal}}{y_{2i}^{\exp}} \times 100 \quad (25)$$

**Table 2**  
Experimental conditions for polar asymmetric binary mixtures.

System	np	T (K)	Pressure range (bar)	Refs.
Carbon dioxide + ethanol	6	314.50	5.7–81.1	[41]
	9	325.20	62.74–93.49	
	8	337.20	62.19–108.45	
Carbon dioxide + butanol	9	325.30	52.26–98.73	[41]
	11	337.20	61.78–117.76	
Carbon dioxide + isoamyl acetate	7	308.15	10.3–69.3	[42]
	8	318.15	10.0–80.3	
	9	328.15	10.3–90.7	
Carbon dioxide + ethyl caproate	8	308.20	17.0–64.6	[43]
	10	318.20	17.0–78.2	
	12	328.20	17.3–92.2	
Carbon dioxide + decanal	10	288.20	19.3–48.1	[44]
	11	303.20	21.7–67.6	
	12	313.20	82.2–16.8	
Carbon dioxide + ethyl laurate	8	308.15	14.8–70.0	[45]
	8	318.15	14.8–83.1	
	9	328.15	14.8–100.1	
Carbon dioxide + octanol	9	403.15	64.0–183.0	[46]
	7	453.15	64.0–188.0	
Ethylene + 1-decanol	9	308.15	10.3–103.6	[47]
	11	318.15	14.6–124.0	

Once the results from thermodynamic model are in agreement with the criteria, the individual percent area deviations must be calculated from Eq. (26):

$$\% \Delta A_i = \frac{A_{\phi i} - A_{p i}}{A_{p i}} \times 100 \quad (26)$$

In order to conclude that experimental data are thermodynamically consistent (TC), the individual area deviations (Eq. (26)) must fall within the range (−20% to +20%). Valderrama et al. [23] summarize these referred criteria including the required minimum number of experimental data and the decision rules for consistency test.

In summary, the calculation of pressure and solute concentration in the vapor phase ( $y_2$ ), as the evaluation of the expressions for  $A_\phi$  and  $A_p$ , requires both a suitable EoS and mixing rule. Furthermore, individual percentage deviations in the variables  $y_2$  and  $P$  must be low to accept the thermodynamic model. In some cases in which percentage  $\Delta y_2$  and percentage  $\Delta P_i$  are outside the defined margins of errors, it is concluded that another model must be applied, being this case commonly known as “try a different model” (TDM).

The consistency method studied in this article has some important aspects about multiple solutions, objective function and the best paired combinations of them. With the aim of determining the optimal parameters in each minimization of the objective function, the Levenberg–Marquardt minimization algorithm was used. Hence, the parameters  $\tau_{12}$ ,  $\tau_{21}$  and  $k_{12}$  for each isothermal temperature were calculated by optimizing the objective function until VLE predictions showed low deviations in bubble point pressure and vapor phase composition [27]. A substantial reduction in the computing time requirements was observed. Multiple solutions coming from the experimental data set for each mixture could appear in each minimization. These solutions were obtained into an acceptable predefined range taking into account, for example, available values for  $\tau_{12}$  and  $\tau_{21}$  calculated at low pressures. The  $k_{12}$  must be in concordance with the statistical thermodynamic postulates considering that such values were in acceptable range (0–1). Considering this objective function, it is expected to find all possible solutions for these parameters within the predefined range. The optimal parameters are chosen to be those that show the lowest

deviation both in bubble point pressure and vapor phase composition.

## 6. Results and discussion

The optimal parameters of the studied thermodynamic model, relative percentage deviations in bubble point pressure and absolute deviation in vapor phase molar fraction for polar and non-polar asymmetric mixtures have been previously reported in the supplementary material available online [27]. The parameters given in that material were used to predict the phase equilibrium and thermodynamic consistency test for the whole mixtures in the present study.

Results of thermodynamic consistency test for the propylene–benzene experimental data were considered consistent only if some points of data set are eliminated according to the decision rules proposed by the authors [23]. Table 3 shows the summary results for propylene–benzene mixture at 453.15 K. The data set for this system was found to be not fully consistent (NFC), denoting that some points in the obtained area deviations were out of the range (see bold face in Table 3). In the case when one point was eliminated from the initial data set, the area deviations for the remaining 9 points were within the previously defined limits. Therefore, the initial set of 10 data points was declared as NFC, but the remaining set of 9 data points was considered as TC.

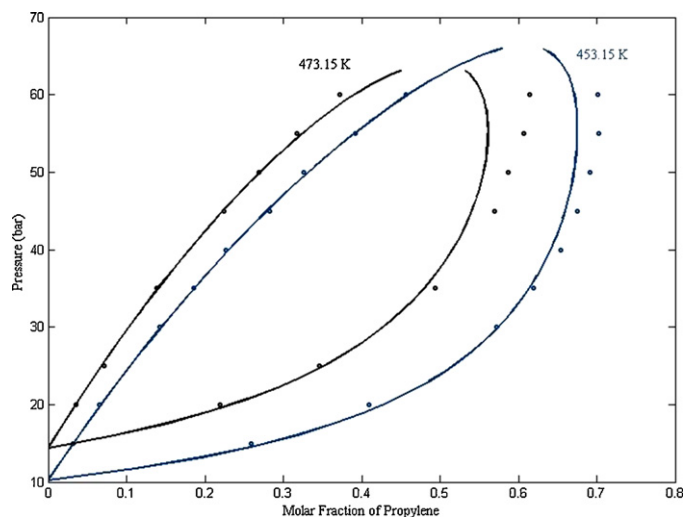
The predicted VLE data was in agreement with the experimental data as shown for propylene–benzene system in Fig. 1. Good predictions in the bubble point pressure ( $\Delta P = 1.14$  and  $\Delta P = 1.33$ ) at the two evaluated temperatures (473.15 and 453.15 K) were obtained. A good prediction was also obtained at the same temperatures for the absolute mean deviations in the vapor phase molar fraction for  $\Delta y_1 = 0.016$  and  $\Delta y_1 = 0.026$ . On the other hand, Fig. 2a–c shows the solution for each integral function in Eq. (8) corresponding to the propylene + benzene mixture at 453.15 K. Evaluation of the respective area under the curve for integral terms in this Eq. (8) was evaluated by inscribing  $N - 1$  trapezoids under the curve for a set of  $N$  experimental points. Finally, the sum of trapezoid areas was then obtained. Additionally, the results from the trapezoidal method calculations were validated by the alternative method by fitting parameters in the polynomial expressions coming from experi-

**Table 3**  
Detailed results for the system propylene + benzene at 453.15 K found to be thermodynamically consistent (TC) using PR+WS/NRTL model.

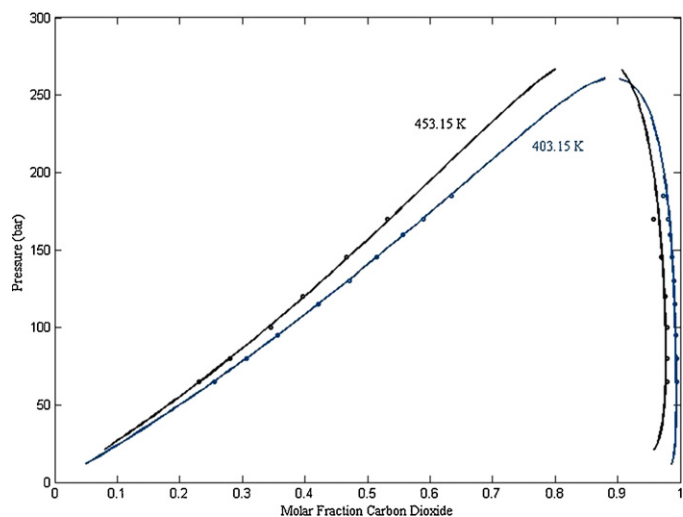
$A_p$	$A_\phi$	$\% \Delta A_i$	$p_i^{\text{exp}}$	$p_i^{\text{cal}}$	$\% \Delta P$	$y_2^{\text{exp}}$	$y_2^{\text{cal}}$	$\% \Delta y_{2i}$
0.436	0.425	−2.415	15	14.890	0.731	0.741	0.725	−2.070
<b>0.415</b>	<b>0.539</b>	<b>30.035</b>	<b>20</b>	<b>19.624</b>	<b>1.879</b>	<b>0.590</b>	<b>0.580</b>	<b>−1.795</b>
<b>0.398</b>	<b>0.296</b>	<b>−25.505</b>	<b>25</b>	<b>25.998</b>	<b>3.993</b>	<b>0.491</b>	<b>0.469</b>	<b>−4.429</b>
0.382	0.402	5.021	30	29.698	1.005	0.427	0.428	0.200
0.368	0.328	−10.777	35	34.970	0.083	0.380	0.386	1.680
0.351	0.393	12.114	40	39.537	1.157	0.346	0.361	4.335
<b>0.333</b>	<b>0.254</b>	<b>−23.629</b>	<b>45</b>	<b>45.377</b>	<b>0.839</b>	<b>0.325</b>	<b>0.339</b>	<b>4.488</b>
0.314	0.333	5.923	50	49.411	1.177	0.308	0.330	7.232
0.292	0.249	−14.640	55	55.105	0.191	0.297	0.325	9.130
–	–	–	60	59.774	0.375	0.298	0.328	10.027
Propylene + benzene, $T = 453.15$ K; $\tau_{12} = 1.087$ ; $\tau_{21} = 0.08$ ; $k_{12} = 0.180$ , 10 points result ( <sup>a</sup> NFC), $\% \Delta P = 1.1430$ , $\% \Delta y_2 = 2.879$ , $\% \Delta A_{av} = -2.6526$								
0.436	0.434	−0.526	15	15.058	0.387	0.741	0.719	−2.937
0.813	0.835	2.818	20	19.897	0.513	0.591	0.573	−2.870
0.382	0.398	4.010	30	30.009	0.033	0.427	0.424	−0.801
0.368	0.324	−11.820	35	35.226	0.646	0.380	0.382	0.689
0.351	0.390	11.148	40	39.720	0.699	0.346	0.357	3.269
0.333	0.254	−20.526	45	45.464	1.032	0.325	0.335	3.179
0.314	0.340	8.072	50	49.452	1.095	0.308	0.325	5.548
0.292	0.263	−9.904	55	55.158	0.288	0.297	0.317	6.737
–	–	–	60	59.969	0.0508	0.298	0.318	6.685
Propylene + benzene, $T = 453.15$ K; $\tau_{12} = 0.529$ ; $\tau_{21} = 0.436$ ; $k_{12} = 0.207$ , 9 points result ( <sup>b</sup> TC), $\% \Delta P = 0.139$ , $\% \Delta y_2 = 2.166$ , $\% \Delta A_{av} = 0.717$								

<sup>a</sup> NFC: not fully consistent.

<sup>b</sup> TC: thermodynamically consistent.



**Fig. 1.** Experimental and predicted VLE for propylene+benzene binary system. Experimental data taken from Guo et al. [38]. Prediction with PR EOS coupled with the WS mixing rules.



**Fig. 3.** Experimental and predicted VLE for carbon dioxide+1-octanol binary system. Experimental data taken from Lee et al. [46]. Prediction with Peng–Robinson EOS coupled with the WS mixing rules.

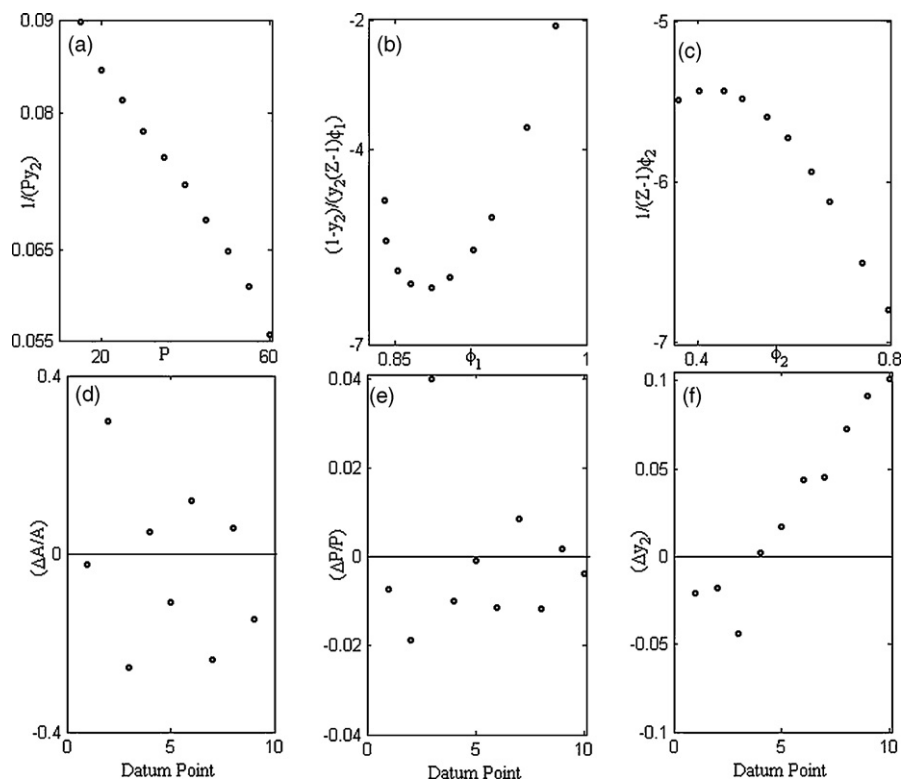
mental data. These referred methods were used to solve the integral expressions in Eq. (8), resulting in an area deviation below 1%. It was considered acceptable for our analysis.

Residual deviations in the individual areas for the propylene+benzene system at 453.15 K are shown in Fig. 2d–f. The margins of error were established by the calculation of individual area deviation percentage ( $\% \Delta A_i$ ) by the Eq. (26). Fig. 2d shows the deviations in the individual areas for the first set of experimental data. On the other hand, Fig. 2e and f shows the deviations for pressure and the vapor phase solute concentration. As can be seen in these figures, deviations in pressure and solute concentration were below 4% and 10%, respectively. It can be concluded that binary

interaction parameters were not enough good to predict the VLE for the studied system.

Carbon dioxide+1-octanol mixture data set at 403.15 K was found to be thermodynamically inconsistent (TI). The values of  $\% \Delta A_i$  were out of the adequate range (see bold face in Table 4). As a result, one point from the initial data set was not considered, and then  $\% \Delta A_i$  was calculated for the remaining 8 points. This last set was considered TC because their  $\% \Delta A_i$  were inside the range (Table 4).

According to the results obtained and shown in Fig. 3, the accuracy in VLE prediction for the experimental and predicted VLE for carbon dioxide+1-octanol system was verified. The parameters



**Fig. 2.** Integral functions in Eq. (8) and deviations in the individual areas for the propylene+benzene system at 453.15 K. Experimental data taken from Guo et al. [38].

**Table 4**  
Detailed results for the system carbon dioxide + 1-octanol at 403.15 K found to be thermodynamically consistent (TC) using PR+WS/NRTL model.

$A_p$	$A_\phi$	$\% \Delta A_i$	$p^{exp}$	$p^{cal}$	$\% \Delta P$	$y_2^{exp}$	$y_2^{cal}$	$\% \Delta y_{2i}$
38.024	32.089	-15.608	65	65.159	0.244	0.0055	0.00619	12.58
29.191	25.320	-13.260	80	79.852	0.184	0.0055	0.00659	19.90
26.671	24.269	-9.006	95	95.077	0.0813	0.0065	0.00732	12.69
13.249	13.451	1.525	115	115.210	0.182	0.0083	0.00879	5.928
9.310	9.103	-2.219	130	130.880	0.679	0.0107	0.0104	-2.868
6.675	7.081	6.070	145	144.960	0.0305	0.0132	0.0123	-7.160
<b>3.362</b>	<b>4.311</b>	<b>28.238</b>	<b>160</b>	<b>159.290</b>	<b>0.441</b>	<b>0.0170</b>	<b>0.0146</b>	<b>-13.83</b>
3.793	4.539	19.668	170	170.460	0.269	0.0193	0.0169	-12.21
-	-	-	185	185.520	0.282	0.0269	0.0208	-22.66
CO <sub>2</sub> + 1-octanol, T = 403.15 K, $\tau_{12} = 1.968$ , $\tau_{21} = -0.6095$ , $k_{12} = 0.7315$ , 9 points result ( <sup>a</sup> TI), $\% \Delta P_{av} = 0.266$ , $\% \Delta y_{2av} = -0.847\%$ , $\% \Delta A_{av} = 11.95$								
38.024	32.090	-15.606	65	65.159	0.244	0.0055	0.00619	12.543
29.191	25.321	-13.259	80	79.852	0.185	0.0055	0.00659	19.875
26.671	24.267	-9.013	95	95.077	0.081	0.0065	0.00733	12.703
13.249	13.450	1.514	115	115.210	0.182	0.0083	0.00879	5.9784
9.310	9.106	-2.196	130	130.880	0.679	0.0107	0.0104	-2.805
10.341	11.487	11.085	145	144.960	0.031	0.0132	0.0123	-7.123
3.793	4.539	19.674	170	170.460	0.269	0.0193	0.0169	-12.110
-	-	-	185	185.520	0.282	0.0269	0.0208	-22.550
CO <sub>2</sub> + 1-octanol, T = 403.15 K, $\tau_{12} = 1.968$ , $\tau_{21} = -0.6081$ , $k_{12} = 0.7303$ , 8 points result ( <sup>b</sup> TC), $\% \Delta P_{av} = 0.244$ , $\% \Delta y_{2av} = 0.813\%$ , $\% \Delta A_{av} = 10.33$								

<sup>a</sup> TI: thermodynamically inconsistent.

<sup>b</sup> TC: thermodynamically consistent.

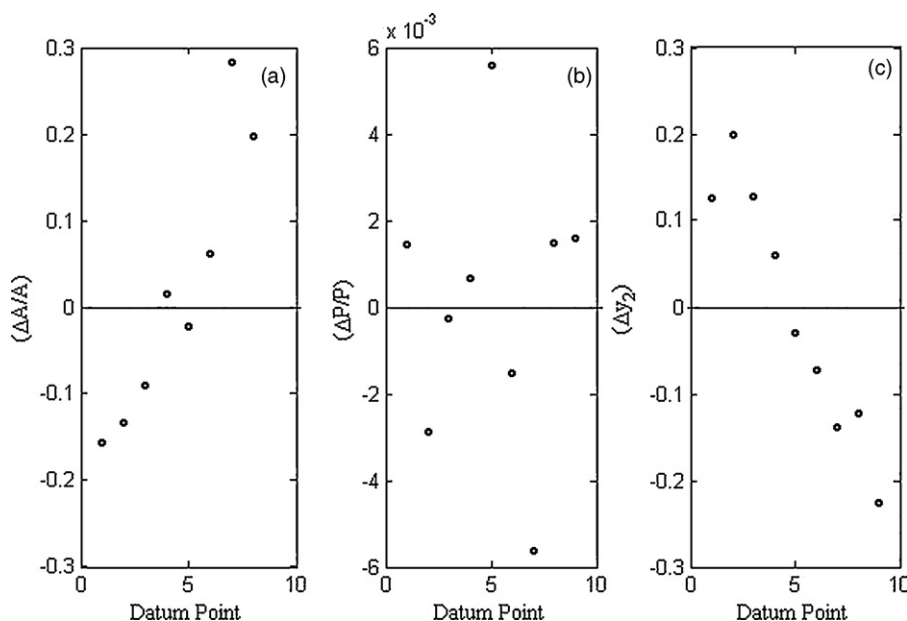
obtained by minimization at 453.15 and 403.15 K provided good predictions for pressure ( $\Delta P = 0.23$  and  $\Delta P = 0.266$ ). Furthermore, good predictions for vapor phase concentration were also obtained ( $\Delta y_1 = 0.0017$  and  $\Delta y_1 = 0.0045$ ).

Fig. 4 shows the deviations in the individual areas, pressure and the vapor phase solute concentration for the carbon dioxide + 1-octanol system at 403.15 K. As can be observed in Fig. 4a, there was only 1 point greater than 20% of area deviation from the initial data set. In the same way, deviations for pressure and the vapor phase solute concentration were less than 0.6% and 3%, respectively (see Fig. 4b and c).

After developing the consistency test for the ethylene + 1-decanol system at 318.15 K, it was found to be NFC. Their  $\% \Delta A_i$  were outside of the criterion range (see bold face in Table 5). Furthermore, total of  $\% \Delta A_i$  obtained were higher than one quarter of the data points initially considered. As a result, three points from

the initial data set were not considered, and then  $\% \Delta A_i$  were calculated for the remaining 8 points. Because of their  $\% \Delta A_i$  were outside of the range, this last set of data was newly considered NFC.

Fig. 5 shows the experimental and predicted VLE for the highly asymmetric ethylene + 1-decanol system. No good predictions for the data set parameters at 308.15 and 318.15 K were obtained ( $\Delta P = 2.5$  and  $\Delta P = 2.11$ ). However, good predictions for vapor phase concentration data ( $\Delta y_1 = 0.0004$  and  $\Delta y_1 = 1.84$ ) were obtained. Deviations in individual areas, pressure and the vapor phase solute concentration for this mixture at 318.15 K are given in Fig. 6. Here, it is observed that the deviation in the areas for the initial data set was exceeded in 60%. These results come from the fact that ethylene vapor phase concentration is close to 1. This fact made the term  $A_p$  from the integral in Eq. (9), and  $A_\phi$  from the integral in Eq. (10) bigger as 56,939 and 14,863, respectively (see Table 5). As a result,  $\Delta A_i$  defined by the Eq. (26) turns bigger as the single



**Fig. 4.** Deviations in the individual areas for the carbon dioxide + 1-octanol binary system at 403.15 K. Experimental data were taken from Lee et al. [46].

**Table 5**

Detailed results for the system ethylene + 1-decanol at 318.15 K found to be not fully consistent (NFC) using PR + WS/NRTL model.

$A_p$	$A_\phi$	$\% \Delta A_i$	$p^{exp}$	$p^{cal}$	$\% \Delta P$	$y_2^{exp}$	$y_2^{cal}$	$\% \Delta y_{2i}$
56939	14863	-73.89	14.65	14.849	1.361	$1 \times 10^{-5}$	$3.6 \times 10^{-5}$	260.57
31141	10177	-67.31	25.20	24.731	1.861	$1 \times 10^{-5}$	$3.5 \times 10^{-5}$	250.67
10458	6329.7	-39.47	36.90	36.308	1.604	$2 \times 10^{-5}$	$4.5 \times 10^{-5}$	123.57
638.58	2281.7	257.31	51.30	51.264	0.071	0.0002	$8.1 \times 10^{-5}$	-59.39
56.02	403.71	620.65	63.03	65.708	4.249	0.0013	0.000191	-86.28
75.522	446.95	491.82	69.53	72.173	3.802	0.0024	0.000304	-87.67
13.646	76.13	457.94	89.44	88.723	0.801	0.0063	0.00110	-82.57
7.8284	27.63	253.04	99.72	99.237	0.484	0.0112	0.00221	-80.32
4.5232	17.99	297.77	109.60	106.800	2.555	0.0131	0.00331	-74.81
3.6102	6.71	85.891	116.90	114.540	2.021	0.0156	0.00468	-70.12
56939	14863	-73.89	124.00	118.480	4.448	0.0171	0.00547	-68.02
Ethylene + 1-decanol, $T = 318.15$ K, $\tau_{12} = 1.847$ , $\tau_{21} = -1.033$ , $k_{12} = 0.702$ , 11 points result ( <sup>a</sup> NFC), $\% \Delta P_{av} = 2.11$ , $\% \Delta y_{2av} = 2.33\%$ , $\% \Delta A_{av} = 200.89$								
56939	13819	-75.73	14.65	14.794	0.983	$1 \times 10^{-5}$	$3.9 \times 10^{-5}$	285.87
31141	8942.7	-71.28	25.20	24.796	1.602	$1 \times 10^{-5}$	$3.9 \times 10^{-5}$	293.70
10458	5126.2	-50.98	36.90	36.529	1.005	$2 \times 10^{-5}$	$5.4 \times 10^{-5}$	168.06
638.58	1666.2	160.93	51.30	51.486	0.363	0.0002	0.000105	-47.01
56.02	276.13	392.92	63.03	65.446	3.833	0.00139	0.000260	-81.21
75.522	297.25	293.59	69.53	71.459	2.773	0.00247	0.000410	-83.15
38.613	105.21	172.48	89.44	86.008	3.837	0.00634	0.00141	-77.67
56939	13819	-75.73	124.00	109.920	11.355	0.0171	0.00692	-59.52
Ethylene + 1-decanol, $T = 318.15$ K, $\tau_{12} = 2.351$ , $\tau_{21} = -1.125$ , $k_{12} = 0.6762$ , 8 points result (NFC), $\% \Delta P_{av} = 3.21$ , $\% \Delta y_{2av} = 49.88\%$ , $\% \Delta A_{av} = 93.27$								

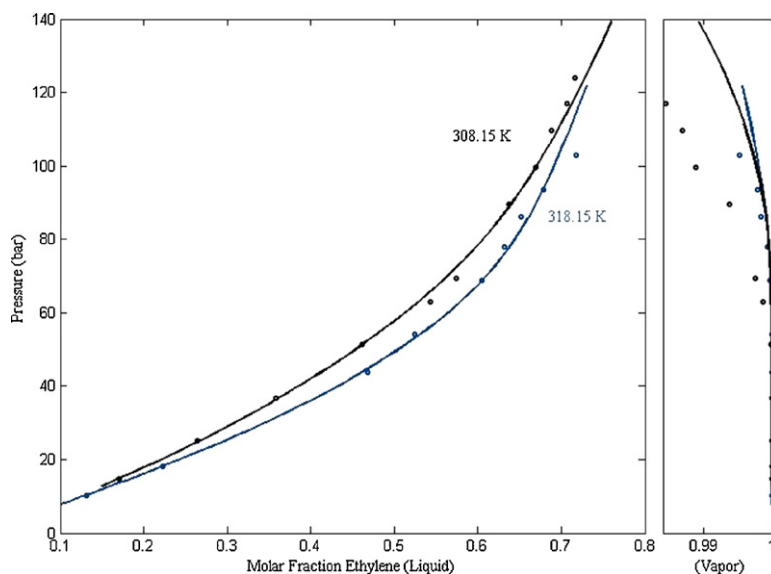
<sup>a</sup> NFC: not fully consistent.

terms turn equally bigger, obtaining results NFC. On the other hand, Fig. 6b and c shows the deviations in the individual pressure and the vapor phase solute concentration. Complete consistency results for all systems studied are shown in Table 6.

Experimental data for *n*-hexane + benzene system at 313.15, 323.15 and 333.15 K have been found thermodynamically inconsistent (TI). Some difficulties were found when a consistency test decision rules proposed by Valderrama and Alvarez [23] were applied. In this particular system, the initial data set was composed by 10 data points and the 25% of them with  $\% \Delta A_i$  outside of the criterion range is 2.5 points. This last value is an integer number and had to be rounded to 2 or 3 points to apply the test again for the remaining data set. Here the decision about TC, TI or NFC of the experimental data depends highly on this number.

Consequently, the reported decision rules [23] did not include a proper way to choose the suitable number of data that must be eliminated from the initial data set, suggesting that the points with

the highest deviation in the vapor phase concentration must be eliminated as the best choice. After this, the method should be implemented again. However, in the systems studied, the above referred procedure was unsuitable to be used because the VLE parameters calculations were highly dependent on bubble pressure calculation. It becomes more convenient to eliminate the data points, which yielded highest deviations in pressure. For example, the remaining 9 points of the initial data set of the propylene + benzene at 453.15 K system were found to be TC according to the defined error ranges proposed by the authors [23]. Furthermore, to obtain this result, the points with the highest deviation in bubble pressure from the initial data set were necessarily eliminated. Additionally, the points with highest deviation of  $\Delta y_2$  were eliminated from the initial data set and the consistency test was employed again using the remaining 9 points. The deviations in the obtained vapor phase solute concentration were not within the range (-20% to +20%). Therefore, TDM was the result of the



**Fig. 5.** Experimental and predicted VLE for ethylene + 1-decanol binary system. Experimental data taken from Gmehling et al. [47]. Prediction with PR EOS coupled with the WS mixing rules.

**Table 6**  
Summary of the final results for all non-polar and polar asymmetric binary mixtures.

Non-polar systems				Polar systems			
System	T (K)	np	Final result	System	T (K)	np	Final result
Carbon dioxide + propane	230.00	25	NFC	Carbon dioxide + isoamyl acetate	308.15	7	NFC
		22	NFC			6	NFC
		19	NFC		318.15	8	NFC
	270.00	27	NFC		6	NFC	
		20	NFC		328.15	9	NFC
Carbon dioxide + <i>n</i> -pentane	310.15	12	NFC	Carbon dioxide + ethyl caproate	308.20	8	NFC
		9	NFC			6	NFC
	333.15	13	TI		318.20	10	NFC
		10	TC			7	NFC
	363.15	16	NFC		328.20	12	NFC
12		NFC	9	NFC			
Carbon dioxide + benzene	298.15	8	NFC	Carbon dioxide + butanol	325.30	9	TI
		6	NFC			8	TC
	313.15	9	TC		337.20	11	TC
Carbon dioxide + styrene	333.15	9	NFC	Carbon dioxide + decanal	288.20	10	NFC
		6	NFC			7	NFC
	343.15	10	NFC		303.20	11	NFC
		7	NFC			8	NFC
348.15	8	NFC	313.20	12	NFC		
	6	NFC		8	NFC		
Carbon dioxide + <i>n</i> -decane	344.30	22	NFC	Carbon dioxide + ethanol	314.50	6	TC
		17	NFC			325.20	9
	377.60	26	NFC		337.20	8	TI
		19	NFC			6	TC
<i>n</i> -Propylene + benzene	453.15	10	NFC	Carbon dioxide + octanol	403.15	9	TI
		9	TC			8	TC
	473.15	9	TI		453.15	7	TI
7		TC	6	TC			
<i>n</i> -Pentane + toluene	293.15	11	TI	Carbon dioxide + ethyl laurate	308.15	8	NFC
		8	TI			6	NFC
	303.15	11	TC		318.15	8	NFC
		11	TI			6	NFC
313.15	11	TI	328.15	9	NFC		
	8	TC		6	NFC		
<i>n</i> -Hexane + benzene	313.15	10	TI	Ethylene + 1-decanol	308.15	9	NFC
		8	TC			6	NFC
	323.15	10	TI		318.15	11	NFC
		8	TC			8	NFC
	333.15	10	TI				
8		TC					
Carbon dioxide + limonene	313.18	8	TDM				
	323.25	11	TDM				

NFC: not fully consistent; TI: thermodynamically inconsistent; TC: thermodynamically consistent; TDM: try a different model.

test. Although the consistency test requires a high accuracy on the prediction of vapor phase solute concentration, for integral calculations in Eq. (8) is preferable to eliminate several points with the highest deviations in bubble point pressure from initial data set before applying the test again. Thus, the parameters obtained fitted better the remaining experimental data set when points with the highest deviations in bubble point pressure were eliminated. On the other hand, the  $y_2$  deviations for asymmetric mixtures are usually high and commonly not reported in literature [2,27,28,48].

According to the decision rules proposed by the authors [23], 6 points is the minimum experimental data from initial data set considered to apply the consistency test. For example, the initial data set of carbon dioxide + ethanol at 314.50 K was found to be TC. Thus, the initial data set was composed by 6 data points and if one point from the initial data set would not be considered, the thermodynamic test could not be applied and only one result could be obtained. Certainly, the thermodynamic consistency results and statistical analysis are improved when the availability of experimental data is big. In some cases, for example systems such as carbon dioxide + ethyl laurate at 308.15 K and 318.15 K, carbon dioxide + ethyl caproate at 308.20 K, the initial data set were considered NFC. As a result, two points from the initial data set were not considered, and the thermodynamic consistency test was applied again for the remaining 6 data points. Similar results were obtained. Therefore, the thermodynamic test cannot be applied again because the remaining data set was less of six points. Additionally, the parameters obtained by the minimization using the current data set were very similar to those calculated from the initial data set, and the thermodynamic consistency results were identical in both cases. On the other hand, experimental data for systems such as carbon dioxide + octanol at 453.15 K, and carbon dioxide + ethanol at 337.20 K, were found to be TI. As a result, two points with the lowest deviation in pressure from the initial data set were not considered, and this last set was again analyzed and found as TC.

The consistency test proposed by the authors [23], do not take into account the cases when data sets of vapor phase concentration is close to 1 (i.e. 0.9998–0.9999). This fact made big the terms  $A_p$  and  $A_\phi$ , and as a result,  $\Delta A_i$  turns bigger than



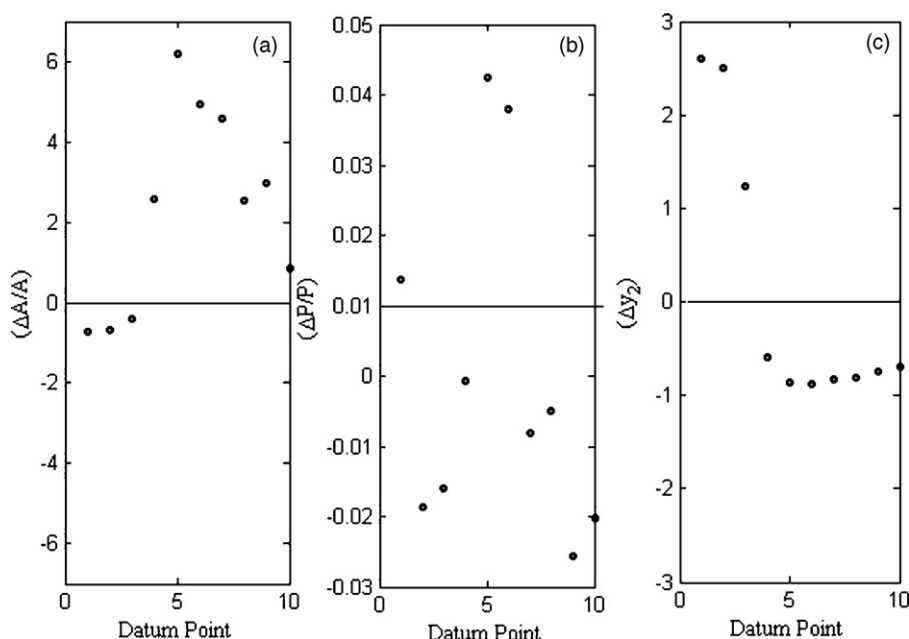


Fig. 6. Deviations in the individual areas for the ethylene + 1-decanol binary system at 318.15 K. Experimental data were taken from Gmehling et al. [47].

the single terms, obtaining results NFC. In this way, experimental data set for systems such as carbon dioxide + isoamyl acetate, carbon dioxide + ethylcaproate, carbon dioxide + decanal, carbon dioxide + ethyl laurate and ethylene + 1-decanol, were considered NFC. In the same way, for example, experimental data set for carbon dioxide + limonene at 313.18 and 323.25 K, were considered as TDM.

According to the consistency test proposed by Valderrama [23], it is important to remark the necessity for carrying out several minimizations procedures looking for new parameters that allow calculating the right hand side in the Eq. (8). In the same way, the set of parameters fitted in each minimization, depend strongly of the objective function used. According to that, the computing time requirements can be considerably increased [27].

## 7. Conclusions

In this work, thermodynamic consistency test of eight non-polar and eight polar asymmetric binary mixtures at high pressure were analyzed. Additionally, the ability of Peng–Robinson EoS coupled with the Wong–Sandler mixing rules and the NRTL model for representing fluid phase equilibrium within the thermodynamic test was demonstrated. Results of bubble point pressure, vapor phase concentration and the individual areas of relative percentage deviations, have demonstrated the capability and efficiency of the objective function used for minimizing VLE experimental data at high pressures. Finally the studied method gives an answer about consistency or inconsistency of a set of experimental  $P$ – $T$ – $x$ – $y$  data for the studied cases. A method to test the thermodynamic consistency of incomplete high-pressure VLE data in binary mixtures has been proved showing favorable results.

In some cases, the high asymmetry of these mixtures, is reflected in the way that the vapor phase concentration is close to 1, as a result of this, the left hand side of the Eq. (8) turns bigger than the other single terms, obtained as a result of the NFC test. Some difficulties with the experimental data set were analyzed and taken into account: (1) If the asymmetry of these mixtures makes grow the vapor phase concentration closer to 1, the left hand of the Eq. (8) turns into a big value. (2) Points must be removed from the remaining experimental data set, with the aim of reduce the devi-

ations for each  $i$ -point in bubble point pressure and vapor phase composition. Therefore, some examples and strategies for solving these problems were discussed. In the same way, the calculations of the VLE parameters for asymmetric mixtures at high pressures were highly dependent on bubble pressure calculation, making more convenient to eliminate the data points yielding the highest deviations in pressure. Finally the results obtained using the thermodynamic consistency test is a necessary, but no sufficient, condition for accepting the experimental data set.

### List of symbols

$A^E$	excess Helmholtz free energy
$a, b$	equation of state parameters
$(b-a/RT)_{ij}$	cross-second virial coefficient
$g_{ij}$	parameter defined by Eq. (11)
$K_{ij}$	distribution coefficient
$k_{ij}$	second virial coefficient interaction parameter
$nc$	number of components
$np$	number of experimental data points
$P$	pressure
$R$	gas constant
$T$	temperature
$V$	volume in molar units
$x$	liquid molar fraction
$y$	vapor molar fraction
$z$	molar fraction

### Greek letters

$\Delta$	deviation
$\alpha(T_r)$	temperature-dependent alpha function
$\alpha_{ij}$	NRTL model parameter
$\kappa$	Peng–Robinson alpha function parameter
$\tau_{12}, \tau_{21}$	NRTL model binary interaction parameter
$\omega$	acentric factor

### Subscripts

$c$	critical point
$m$	mixture
$r$	reduced conditions
$\infty$	infinite condition

## Superscripts

<i>E</i>	excess property
<i>exp</i>	experimental
<i>cal</i>	calculated

## Acknowledgments

Victor M. Trejos wants to acknowledge the financial support from the National University of Colombia at Manizales, through the program “Scholarship of Academic Excellence”, which made possible this work.

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