Thermochimica Acta 499 (2010) 85–90

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermodynamic consistency test of high pressure gas–liquid equilibrium data including both phases

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ARTICLE INFO

Article history:
Received 7 August 2009
Received in revised form 7 November 2009
Accepted 12 November 2009

Keywords:
Thermodynamic consistency
Phase equilibrium
Gibbs–Duhem equation
High pressure mixtures

ABSTRACT

A method to test the thermodynamic consistency of high pressure gas–liquid equilibrium data in binary mixtures which considers data for a single phase has been extended to propose an overall test using the whole set of *PTxy* data. The method previously proposed by the authors was applied before to situations in which the concentration in the gas phase only was known (a solid dissolved in a high pressure gas) and to situations in which the concentration in the liquid phase only was known (ionic liquid and a high pressure gas). The extension is done here by proposing a combined analysis in which the test is applied to both phases while the modeling is done using bubble pressure calculations as recommended in the literature. Data for water + carbon dioxide mixtures at nine temperatures and for pressures ranging from 100 to 1500 bar and temperatures 383 to 598 K were used. Results indicate that the proposed method is reliable and can be used to check the thermodynamic consistency using all experimental phase equilibrium data available.

1. Introduction

The inaccuracies that arise in measuring experimental phase equilibrium properties has made it necessary to come up with methods to test inherent inaccuracies of such data. Although it is difficult to be absolutely certain about the correctness of a given set of experimental data, it is possible to check whether such data satisfy certain thermodynamic relationships, thereby establishing that the data are thermodynamically consistent or inconsistent. The thermodynamic relationship that is frequently used to analyze thermodynamic consistency of experimental phase equilibrium data is the fundamental Gibbs–Duhem equation. The Gibbs–Duhem equation relates the activity coefficients, the partial Gibbs free energy, or the fugacity coefficients of all components in a given mixture. Depending on the way in which the Gibbs–Duhem equation is handled, different consistency tests have been derived [1–3]. If the Gibbs–Duhem equation is not obeyed then the data are inconsistent and can be considered as incorrect. If the equation is obeyed, the data are thermodynamically consistent but not necessarily correct. More details and discussion on all these methods are given by Raal and Mühlbauer [4] and Poling et al. [5].

In previous communications the authors presented a thermodynamic consistency test and applied it to several situations: (i) Valderrama and Alvarez [6] applied the test to high-pressure phase equilibrium using the gas phase experimental data to determine the consistency; (ii) Valderrama and Zavaleta [7] applied the test to high pressure solid–gas equilibrium using the concentration of the solid in the gas phase to test consistency; (iii) Valderrama and Robles [8] applied the test to ternary solid + solid + gas phase equilibrium and used the concentration of the solids in the gas phase to determine consistency; Valderrama et al. [9] extended the method to binary mixtures containing an ionic liquid and high pressure CO_2 and used the concentration of CO_2 in the liquid phase to apply the test. These and other methods presented in the literature are described in Table 1.

As seen in Table 1 the different approaches presented in the literature not only use different equilibrium data but also different thermodynamic functions that are calculated either directly using experimental data or including thermodynamic models. For instance Mühlbauer [13], Jackson and Wilsak [14], Bertucco et al. [15] and Valderrama and Alvarez [6] use (P, y) data and fugacity coefficients. The more complex methods of Chueh et al. [10] and of Won and Prausnitz [11] both use (P, x, y) data and other derived thermodynamic properties (equilibrium ratios, saturation

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Abbreviations: EoS, equation of state; eqn., equation; GLE, gas–liquid equilibrium; NFC, not fully consistent; PR, Peng–Robinson EoS; PR/WS/VL, Peng–Robinson/Wong–Sandler/van Laar; Ref, reference; TC, thermodynamically consistent; TI, thermodynamically inconsistent; VL, van Laar; WS, Wong–Sandler.

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doi:10.1016/j.tca.2009.11.006

Nomenclature

Symbols

a	force constant in the PR equation of state
a_m	force constant for a mixture
$A_\infty^E(x)$	Helmholtz free energy at infinite pressure
$A_o^E(x)$	Helmholtz free energy at low pressure
A_P	integral for point x_{2i} to x_{2i+1} using P–y experimental data
A_φ	integral for point x_{2i} to x_{2i+1} using a thermodynamic model
$\%\Delta A_i$	individual relative percent area deviation
$\lvert\%\Delta A_i\rvert$	individual absolute percent area deviation
$\%\Delta A_i^G$	individual percent area deviation for the gas phase
$\%\Delta A_i^L$	individual percent area deviation for the liquid phase
b	volume constant in the PR equation of state
b_m	volume constant for a mixture
d	derivative operator
F_{PR}	acentric factor function for the PR equation of state
$g_o^E(y)$	Gibbs free energy at low pressure
H^R	residual enthalpy
k_{ij}	binary interaction parameters for the force constant in an EoS
k_{12}	interaction parameters for the force constant in an EoS for a binary mixture
L_{12}, L_{21}	parameters in the van Laar model
Ln	natural logarithm
N_D	number of data points in a data set
P	pressure
$\%\Delta P_i$	percent deviation in the system pressure for a point "i"
P_c	critical pressure
R	ideal gas constant
T	temperature
T_c	critical temperature
T_r	reduce temperature ($T_r = T/T_c$)
V	volume
V^E	excess volume
x	mole fraction in the liquid phase
y	mole fraction in the gas phase
Z	compressibility factor (Z = PV/RT)

Greek letters

α	temperature function for the PR equation of state
Δ	deviation
$\Delta A\%$	deviation between A_P and A_φ (eqns. (8) and (9))
φ	fugacity coefficient
ω	acentric factor
Ω	constant in the WS mixing rule. $\Omega = 0.34657$ for the PR EoS

Super/subscripts

cal	calculated
exp	experimental
i, j	component i or j

pressure, liquid volumes). In another approach, consistency tests that use the liquid phase concentration and that have been applied to high-pressure phase equilibrium were presented by Christiansen and Fredenslund [12] and more recently by Valderrama et al. [9]. The first method includes calculated variables such as excess enthalpy, liquid-phase volume and activity coefficients, while the latter uses the fugacity coefficient and compressibility factor of the liquid phase which are simultaneously calculated using an equation of state.

As explained in previous papers, the consistency method proposed by the authors can be considered as a modeling procedure. This is because a thermodynamic model that can accurately fit the experimental data must be used to apply the consistency test, based on the Gibbs–Duhem equation. The Gibbs–Duhem equation in terms of residual properties applied to any of the phases of a given mixture is [3]:

$$\sum \xi_i d\left[\frac{G^R}{RT}\right] = -\frac{H^R}{RT^2}dT + \frac{V^R}{RT}dP \qquad (1)$$

$$\sum \xi_i d\mathrm{Ln}\ \varphi_i = -\frac{H^R}{RT^2}dT + \frac{V^R}{RT}dP \qquad (2)$$

In these equations, ξ_i is the concentration of component "i" in the liquid or gas phase, φ_i is the fugacity coefficient of component "i" in the corresponding phase, H^R is the residual enthalpy, V^R is the residual volume, T and P are the temperature and pressure of the system, respectively.

For high-pressure phase equilibrium, either gas–solid or gas–liquid, there are some general problems for testing experimental data: (i) the gas-phase non-idealities are important and a good model to evaluate the fugacity coefficients φ_i in eqn. (2) is needed; (ii) for isothermal data the term involving the residual enthalpy (H^R) vanishes, but the term involving the residual volume (V^R) cannot be ignored as done at low pressure; (iii) the data available do not cover the whole concentration range for both, the liquid and the gas phase in gas–liquid mixtures or the solid and the gas phases in gas–solid mixtures; and (iv) the concentration of one of the components in one of the phases is usually low and commonly unknown.

In some cases simplifications can be introduced to derive a consistency test that makes use of the incomplete data available. For instance in supercritical fluid applications such as extraction of substances from a liquid solution, the solute concentration in the gas phase is low while the gas concentration in the liquid phase could reach high values (*PTx* data available). In supercritical fluid applications such as extraction of substances from a solid matrix, the solute concentration in the gas phase is low while the gas concentration in the solid phase is negligible (*PTy* data available). In some situations, however, the concentration of all components in the different phases cover wider ranges of concentration and the whole set of data (*PTxy*) should be used to define a reasonable consistency test.

The authors have established certain requirements to define a good consistency test method to analyze high-pressure phase equilibrium data [7]. The test should fulfill the following ten basic requirements: (i) use the Gibbs–Duhem equation; (ii) use the fundamental equation of phase equilibrium, that is the equality of fugacities of a component in all phases; (iii) use for testing, all the experimental *PTxy* data available; (iv) does not necessarily require experimental data for the whole concentration range and be applicable for data in any range of concentration; (v) be able to correlate the data within acceptable limits of deviations, deviations that must be evenly distributed; (vi) requires few calculated properties; (vii) be able to detect erroneous experimental points; (viii) makes appropriate use of necessary statistical parameters; (ix) be simple to be applied, considering the complexity of the problem to be solved; and (x) be able to conclude about consistency if the defined criteria are not fulfilled.

The method proposed by the authors fulfills these basic requirements and can conclusively determine the consistency or inconsistency of data in most cases, as demonstrated in previous works. However, the method has not been used to test data using the whole set of *PTxy* data, as done in this paper.

Table 1
Selected studies on methods for thermodynamic consistency for high pressure mixtures.

The method	Some characteristics	Properties involved	Data used	Comments	Ref
Chueh–Muirbrook–Prausnitz (1965)	Equal-area test, based on the Gibbs–Duhem equation.	φ^V, V^L, k_i	P, x_i, y_i	The method requires a model for calculating the fugacity coefficients but some problems arise for evaluating the areas in the zero concentration limit.	[10]
Won–Prausnitz (1973)	For analyzing isothermal data that requires the definition of arbitrary functions.	P^s, φ^V, V^L	P, x_i, y_i	Functions are required to represent the variation of the activity coefficient with concentration and the molar volume of the mixture with pressure.	[11]
Christiansen–Fredenslund (1975)	Test for isobaric or isothermal high-pressure data.	H^E, γ_i, V^L	P, x_i	This method includes the calculation of several thermodynamic properties, all which make the method complex to be applied.	[12]
Mühlbauer (1991)	Test based only on the concentration of the vapor phase.	φ^V, V^V	P, y_i	The method is essentially similar to that of Chueh–Muirbrook–Prausnitz, but liquid volume is not required.	[13]
Jackson–Wilsak (1995)	Tests applicable to low and high pressures.	φ^V	P, y_i	The choice of an inappropriate model for the vapor-phase properties will introduce incorrect thermodynamic inconsistencies.	[14]
Bertucco–Barolo–Elvassore (1997)	Method to analyze isothermal data that need a model to estimate incomplete VLE data	Z^V, φ^V	P, y_i	Expressed the Gibbs–Duhem equation for a binary mixture at constant temperature in terms of the fugacity coefficients.	[15]
Valderrama and Alvarez (2004)	Method for cases in which the gas phase contains practically one component.	Z^V, φ^V	P, y_i	Adjustable parameters were found by minimizing the errors between predicted and experimental bubble pressure.	[6]
Valderrama–Reategui–Sanga (2008)	Applicable to mixtures containing a liquid solute and a supercritical fluid.	Z^L, φ^L	P, x_i	Based on the Gibbs–Duhem equation, on the fundamental equation of phase equilibrium and on an equation of state.	[9]
This work	Applicable to any mixture and complete or incomplete VLE data	Z^L, φ^L, Z^V, φ^V	P, x_i, y_i	The data are modeled using an EoS and then data are analyzed for both phases, liquid and vapor.	–

2. Development of equations

Bertucco et al. [15] expressed the Gibbs–Duhem equation for a binary mixture at constant temperature T in terms of the fugacity coefficients φ_1 and φ_2 of the components in the mixture. Using $\bar{G}_i^R = RT\,\mathrm{Ln}\,\varphi_i$ and $V^R = RT(Z-1)/P$ for a binary mixture at constant T, eqn. (2) becomes [3]:

$$\left[\frac{Z-1}{P}\right] dP = \xi_1 d(\mathrm{Ln}\,\varphi_1) + \xi_2 d(\mathrm{Ln}\,\varphi_2) \tag{3}$$

In this equation ξ is the mole fraction of component 1 and 2 in the liquid or gas phase (x for the liquid and y for the gas), P is the system pressure, φ_1 and φ_2 are the fugacity coefficients of components 1 and 2 in the corresponding phase, and Z is the compressibility factor of the corresponding phase.

For the method proposed in this work, this equation must be applied independently for the liquid and the gas phase. Also, for binary mixtures $\xi_1 = 1 - \xi_2$ so eqn. (3) can be written in function of ξ_2 only, as follows:

$$\frac{1}{P} dP = \frac{\xi_2}{(Z-1)\varphi_2} d\varphi_2 + \frac{1-\xi_2}{(Z-1)\varphi_1} d\varphi_1 \tag{4}$$

This equation can be conveniently expressed in integral form, as follows:

$$\int \frac{1}{P\xi_2} dP = \int \frac{1}{(Z-1)\varphi_2} d\phi_2 + \int \frac{1-\xi_2}{\xi_2 (Z-1)\varphi_1} d\varphi_1 \tag{5}$$

In eqn. (5) the left hand side is designated by A_P and the right hand side by A_φ, as follows:

$$A_P = \int \frac{1}{P\xi_2} dP \tag{6}$$

$$A_\phi = \int \frac{1}{(Z-1)\phi_2} d\phi_2 + \int \frac{1-\xi_2}{\xi_2 (Z-1)\phi_1} d\phi_1 \tag{7}$$

Thus, if a set of data is considered to be consistent A_P should be equal to A_φ within acceptable defined deviations. This must be true for both phases, liquid and gas, in independent form. To set the margins of errors the individual relative percent area deviation $\%\Delta A_i$ and individual absolute percent area deviation $|\%\Delta A_i|$ between experimental and calculated values are defined as:

$$\%\Delta A_i = 100 \left[\frac{A_\varphi - A_P}{A_P}\right]_i \tag{8}$$

$$|\%\Delta A_i| = 100 \left| \left[\frac{A_\varphi - A_P}{A_P}\right]_i \right| \tag{9}$$

To evaluate A_φ for a given phase (liquid or gas) a thermodynamic model, such as an equation of state, must be used to determine the fugacity coefficients φ_i and the compressibility factor Z. Once the model is defined and the optimum parameters determined from the experimental $PTxy$ data, the area A_φ is calculated. It is also relevant to mention that for a set of N experimental data points there are $(N-1)A_P$ areas and $(N-1)A_\varphi$ areas to be calculated for a given mixture at a fixed temperature [9].

For the gas phase, A_P^G is determined using the P–y data of the experimental data set $PTxy$, while the chosen thermodynamic model is employed for A_φ^G. If the individual area deviations $\%\Delta A_i^G$ are within defined margins of errors, the gas phase data are considered to be consistent. For the liquid phase, A_P^L is determined using the P–x data of the experimental data set $PTxy$, while the same thermodynamic model is employed for A_φ^L. If the individual area deviations $\%\Delta A_i^L$ are within defined margins of errors, the liquid phase data are considered to be consistent. A detailed description about the acceptable errors in predicting these GLE properties and the areas A_P and A_φ have been discussed by the authors elsewhere [7].

The absolute deviations in the calculated pressure and solute concentration in the gas phase for each point "i" are defined as:

$$|\%\Delta P| = \frac{100}{N} \sum \frac{\left|P^{\mathrm{cal}} - P^{\mathrm{exp}}\right|_i}{P_i^{\mathrm{exp}}} \tag{10}$$

$$|\%\Delta y| = \frac{100}{N}\sum \frac{\left|y^{\mathrm{cal}} - y^{\mathrm{exp}}\right|_i}{y_i^{\mathrm{exp}}} \tag{11}$$

The Peng–Robinson EoS with the Wong–Sandler–van Laar mixing rules with one interaction parameter k_{12} is used as the default thermodynamic model, to evaluate the fugacity coefficients and the variables P–y, for given values of T–x in the integrals that appear in eqn. (7). Despite some limitations of the Wong–Sandler mixing rule pointed out in the literature [16], several works and our own findings have clearly demonstrated that the Wong–Sandler mixing rule has the accuracy and necessary flexibility to correlate phase equilibrium variables in high-pressure systems [17–21]. This proved to be equally applicable to the cases of mixtures containing high pressure CO_2 and water, as the results show.

The Peng–Robinson equation and the Wong–Sandler mixing rule used as a default model can be expressed as follows [22]:

$$P = \frac{RT}{V-b} + \frac{a}{V(V+b)+b(V-b)} \tag{12}$$

$$\begin{aligned} a &= 0.457235(R^2T_c^2/P_c)\alpha(T_r)\\ b &= 0.077796(RT_c/P_c)\\ \alpha(T_r)^{0.5} &= [1+F_{\mathrm{PR}}(1-T_r^{0.5})]\\ F_{\mathrm{PR}} &= 0.37646 + 1.54226\omega - 0.26992\omega^2 \end{aligned} \tag{13}$$

For mixtures:

$$P = \frac{RT}{V-b_m} + \frac{a_m}{V(V+b_m)+b_m(V-b_m)} \tag{14}$$

In this equation a_m and b_m are the equation of state constants to be calculated using defined mixing rules. For the PR equation the WS mixing rule can be summarized as follows [23]:

$$\begin{aligned} b_m &= \left(\Sigma\Sigma\xi_i\xi_j\left(b-(a/RT)\right)_{ij}\right) / \left(1-(\Sigma\xi_i a_i/b_i RT) - (A^E_\infty(\xi)/\Omega RT)\right)\\ \left(b-(a/RT)\right)_{ij} &= (1/2)[b_i+b_j] - (\sqrt{a_i a_j}/RT)(1-k_{ij})\\ a_m &= b_m\left(\sum \xi_i[a_i/b_i] + (A^E_\infty(\xi)/\Omega)\right) \end{aligned} \tag{15}$$

In these equations, k_{ij} is a binary interaction parameter, a_m and b_m are the equation of state constants, $\Omega = 0.34657$ for the PR equation, and $A^E_\infty(\xi)$ is calculated using the van Laar model and assuming that $A^E_\infty(\xi) \approx A^E_o(\xi) \approx g^E_o(\xi)$, being $g^E_o(\xi)$ the excess Gibbs free energy at low pressure [24].

The van Laar model (VL) for a binary mixture is described by the following equation [7]:

$$\frac{g_0^E(\xi)}{RT} = \frac{(L_{12}/RT)\xi_1\xi_2}{\xi_1(L_{12}/L_{21})+\xi_2} \tag{16}$$

For a binary mixture, the van Laar equation includes two empirical parameters L_{12} and L_{21}, and therefore for a binary mixture the Peng–Robinson + Wong–Sandler + van Laar model (PR/WS/VL) includes three adjustable parameters (k_{12}, L_{12} and L_{21}). The equations for Z, φ_1 and φ_2 using the Peng–Robinson equation and the WS mixing rules are given by Orbey and Sandler [18].

3. Consistency criterion

Although the concept of consistency seems to be different from consistency tests applied to low pressure gas–liquid equilibrium data, the situation is conceptually the same. At low pressures the equilibrium equation is applied and the activity coefficients are determined. Then the Gibbs–Duhem equation is applied to determine consistency of the data. At high pressures the equilibrium equation is applied and the fugacity coefficients are determined to then apply the Gibbs–Duhem equation. Therefore, for the case being analyzed, an appropriate model to evaluate the fugacity coefficients of each component in both phases and the compressibility factor of the mixture in both phases is needed. As explained above, the PR/WS/VL model is used to evaluate these properties.

The model is accepted and the consistency test is then applied if the average absolute pressure deviations $\%\Delta P$ and the average absolute deviations for the gas phase mole fraction $\%\Delta y_{CO_2}$ defined by eqns. (10) and (11) are below 10%. After the model is found appropriate, it is required that the average absolute deviations in the individual areas for both phases $|\%\Delta A_i^G|$ and $|\%\Delta A_i^L|$, defined by eqn. (9), are below 20% to declare the data as being thermodynamically consistent. The data are considered to be thermodynamically inconsistent (TI) if the deviations in correlating the equilibrium bubble pressure and gas phase concentration are within the established limits but the individual deviations in the areas are outside the established limits, for more than 25% of the data points in the data set. The test cannot be applied if the equilibrium pressure and gas phase concentration are not well correlated, that means if deviations in the calculated pressure (eqn. (10)) are greater than 10%. If the deviations in correlating the equilibrium pressure and gas phase concentration are within the established limits (10%) but the individual deviations in the areas are outside the established limits for less than 25% of the points, the data are considered to be not fully consistent (NFC).

4. Data selection and modeling

Nine isotherms for the mixture CO_2 + water from moderate to high pressures were used for applying the method. These systems were chosen because they cover wide ranges of temperature, pressure and concentration in both phases, so the method could be fully evaluated. Table 2 gives details on the selected experimental gas–liquid equilibrium data for the nine sets considered in the analysis. The temperatures for which data are available are between 383 and 598 K while the pressure ranges from 100 to 1500 bar. Bubble pressure calculations for binary mixtures were performed using the PR/WS/VL model. The adjustable parameters of the model (L_{12}, L_{21}, and k_{12}), were determined by non-linear optimization using the Lebenverg–Marquardt method. The margins of acceptable errors (10% for the calculated pressure, 10% for the gas phase concentration, and 20% for the areas) have been previously explained by the authors [6,7]. Table 3 shows the parameters for each isotherm and the deviations in modeling the pressure and the gas phase concentration.

As observed in Table 3, the model parameters (k_{12}, L_{12} and L_{12}), do not follow a well defined pattern as the temperature increases. Although this fact could be desirable when modeling systems with

Table 2

Properties of the substances involved and details on the phase equilibrium data to be tested for consistency. In the table, the temperature and pressure values have been rounded to the closest integer.

Properties of each component [25]

Compound	M (kg/kmol)	T_c (K)	P_c (bar)	ω
CO_2	44.0	304.2	73.8	0.2240
H_2O	18.0	647.1	220.6	0.3449

Range of data for CO_2 + H_2O mixtures [26]

No.	T (K)	P (bar)	x_{CO_2}	y_{CO_2}
1	383	100–1500	0.014–0.040	0.800–0.958
2	423	100–1500	0.013–0.048	0.752–0.910
3	473	100–1500	0.013–0.072	0.690–0.825
4	523	100–1500	0.012–0.144	0.410–0.680
5	533	100–1500	0.027–0.175	0.500–0.642
6	543	100–1300	0.027–0.288	0.288–0.590
7	548	100–885	0.010–0.270	0.256–0.558
8	573	100–550	0.004–0.170	0.080–0.456
9	598	150–435	0.010–0.180	0.106–0.180

Table 3
Calculated parameters in the Wong–Sandler mixing rules, pressure deviations and deviation of gas mole fraction for all isotherms studied.

No.	T (K)	N_D	k_{12}	L_{12}	L_{21}	$\lvert\%\Delta P\rvert$	$\lvert\%\Delta y_{CO_2}\rvert$
1	383	15	0.0520	3.5757	2.1628	4.1	1.4
2	423	15	0.0740	3.4886	2.2433	5.3	2.4
3	473	15	0.0731	3.2861	2.0071	3.7	1.9
4	523	15	0.3401	2.7911	1.3461	6.7	9.9
5	533	15	0.3659	2.6408	1.4079	2.4	8.8
6	543	13	0.3134	2.7056	1.2563	2.0	6.1
7	548	11	0.1446	3.0796	1.1937	1.9	6.9
8	573	10	0.1471	2.9698	1.2435	2.6	6.1
9	598	7	0.1659	2.7903	1.2106	1.6	6.2

the objective of generalizing models and methods, it is not that important in the case of performing thermodynamic consistency of GLE data. What is more important is the accuracy of the model used to represent the variables being modeled. In this case we wanted low deviations in correlating the bubble pressure and the vapor phase concentration.

5. Results and discussion

Table 4 presents the results of the consistency test for all the mixtures considered in this study. As seen in the table, four of the nine data sets were found to be thermodynamically consistent (TC), three sets were found to be not fully consistent (NFC) and two sets were found to be thermodynamically inconsistent (TI). For the four isotherms considered to be thermodynamically consistent (523, 548, 573 and 598 K), the modeling was acceptable as seen in Table 3 and deviations in the areas for both phases are within the established limits. For the two cases considered to be thermodynamically inconsistent (TI at 383 and 473 K), area deviations are very high for more than four point of the original data set, despite that the modeling is low and clearly between the limits established by the method. For the three cases declared to be not fully consistent (NFC at 423, 533 and 543 K), there are a few points with high area deviations but the remaining areas give deviations within the established limits. If high deviation points are not considered in the analysis (three points at 423 K, one at 533 K and two at 543 K) the remaining data give area deviations below the established limits (20%). Thus, at 423 K the original 15 data are NFC while the remaining 12 points are considered to be TC. Also, at 533 K, the original 15 data are NFC while the remaining 14 points are considered to be TC and finally at 543 K, the original 13 data are NFC while the remaining 11 points are considered to be TC. It should be mentioned, however, that care must be taken with this, since the defined percentages have a frontier character only and the explanatory character of the eliminated data depends on the system, on the pressure and on the temperature of the data.

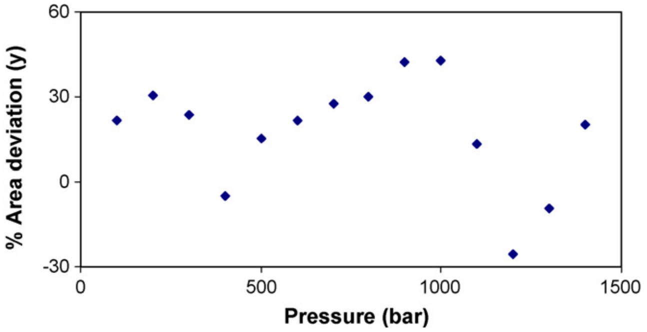

Fig. 1. Error in the area for the gas phase $\%\Delta A_i^G$ (eqn. (8)) for the isotherm 523 K, declared as thermodynamically consistent (TC).

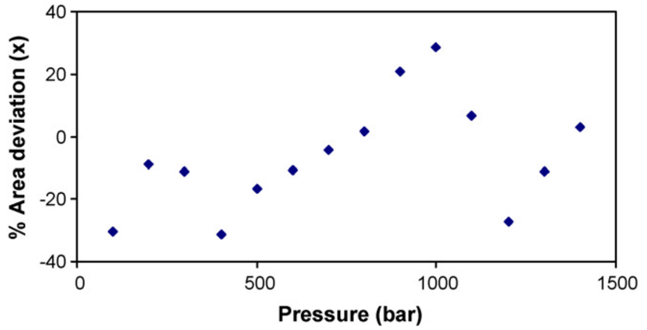

Fig. 2. Error in the area for the liquid phase $\%\Delta A_i^L$ (eqn. (8)) for the isotherm 523 K, declared as thermodynamically consistent (TC).

A graphical description of the results is shown in Figs. 1–4. Figs. 1 and 2 show the deviation in the areas for the gas phase $\%\Delta A_i^G$ and for the liquid phase $\%\Delta A_i^L$ for the isotherm 523 K, declared as thermodynamically consistent (TC). Figs. 3 and 4 show the deviation in the areas for the gas phase $\%\Delta A_i^G$ and for the liquid phase $\%\Delta A_i^L$ for the isotherm 423 K, declared as not fully consistent (NFC). It should be noted that for all cases shown in the figures and in Table 3, pressure deviations and deviation in the gas mole fraction are below the established limit of 10%, indicating the acceptable accuracy of the PR/WS/VL model used in correlating the data. This fact, however, does not guarantee consistency of the data in the way defined in this work, as shown in Table 4. It should be noticed that at 383 K, modeling is accurate enough (4.1% for the pressure and 1.4% for the gas phase mole fraction) but high area deviations are found for several points, so finally the set is declared to be thermodynamically inconsistent.

Table 4
Area deviations and results of the consistency test for all isotherms studied.

No.	T (K)	N_D	$\%\Delta A_i^G$	$\lvert\%\Delta A_i^G\rvert$	$\%\Delta A_i^L$	$\lvert\%\Delta A_i^L\rvert\rvert$	Result
1	383	15	−12.1	41.0	−11.3	25.7	TI
2	423	15	13.2	60.1	−2.7	15.9	NFC
		12	8.9	16.7	−2.7	15.9	TC
3	473	15	0.8	38.0	1.8	21.8	TI
4	523	15	14.9	21.6	−3.8	17.9	TC
5	533	15	17.3	26.8	−2.5	14.0	NFC
		14	10.6	20.7	−7.3	16.1	TC
6	543	13	7.0	26.4	−2.3	18.8	NFC
		11	18.2	18.2	6.8	11.2	TC
7	548	11	−8.3	10.9	−6.4	7.1	TC
8	573	10	10.2	15.4	4.6	18.1	TC
9	598	7	−16.1	18.2	−6.3	9.4	TC

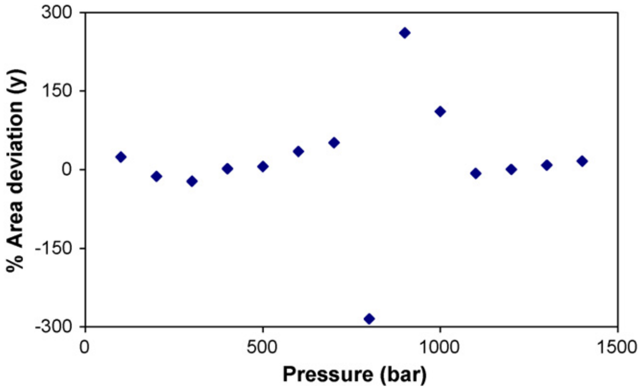

Fig. 3. Error in the area for the gas phase $\%\Delta A_i^G$ (eqn. (8)) for the isotherm 423 K, declared as not fully consistent (NFC).

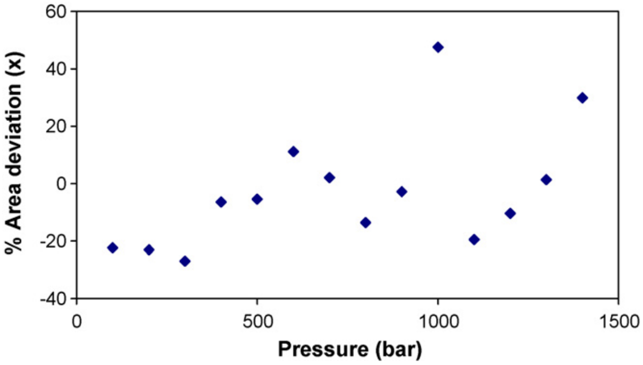

Fig. 4. Error in the area for the liquid phase $\%\Delta A_i^L$ (eqn. (8)) for the isotherm 423 K, declared as not fully consistent (NFC).

6. Conclusions

A reasonable and flexible method to test the thermodynamic consistency of complete *PTxy* data of binary mixtures at high pressure has been presented. Based on the results the following three main conclusions can be drawn: (i) the proposed consistency test method allows to globally analyze gas–liquid equilibrium data in both phases using complete *PTxy* data; (ii) the numerical technique used to find the optimum model parameters for the PR/WS/VL model is shown to be efficient and accurate for modeling the required variables; and (iii) the method gives an answer about consistency or inconsistency of a set of experimental *PTxy* data for all cases that are well correlated by a thermodynamic model.

Acknowledgements

The authors thank the National Council for Scientific and Technological Research (CONICYT), for its research grant FONDECYT 1070025. JOV thanks the Direction of Research of the University of La Serena for permanent support and the Center for Technological Information of La Serena-Chile for using its library and computer facilities. CAF thanks the Dept. of Physics of the University of Concepción for special support during the preparation of this work.

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