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Thermodynamic consistency of low pressure equilibrium data of water + congener mixtures using a versatile equation of state

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ABSTRACT

A general thermodynamic consistency test is applied to analyze phase equilibrium data (TPxy data) for binary water + congener mixtures found in alcoholic distillation processes. The congeners, substances that are present at very low concentration in a must, considered in this study are: acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 1-propanol, methyl acetate and 2-butanol. The thermodynamic test combines the Peng–Robinson equation of state modified by Kwak and Mansoori for correlating phase-equilibrium data and the Gibbs–Duhem equation to check for consistency. The test is applied to analyze twenty five isothermal P-x-y data of water+congener mixtures obtained from the literature. Of the 25 sets of data, 18 are found to be thermodynamically inconsistent. In several cases, the results are in agreement with information from the literature in which these same systems are considered to be thermodynamically inconsistent using a test that uses activity coefficients for the liquid phase.

1. Introduction

Musts and wines employed in alcoholic distillation contain two major components, water and ethanol, and several substances that are present at very low concentrations. Despite these low concentrations, the presence of these substances, known as "congeners", is of paramount importance since they are essential part of the aroma of a distilled product. Because of the great number of congeners and their low concentration, modeling distillation processes is a difficult task [1,2].

Most processes in which alcoholic beverages are obtained from musts and wines operate at atmospheric pressure so methods for the correct modeling of equilibrium data must be carefully chosen. The treatment of low pressure vapor–liquid equilibrium data commonly use the so-called activity coefficient method, through the so-called Gamma-Phi (γ-ϕ) method in which the activity coefficient γ is employed to represent non-idealities in the liquid phase and the fugacity coefficient ϕ is employed to represent non-idealities in the vapor phase. The Dechema collection (Gmehling et al. [3]) presents binary vapor–liquid equilibrium data for many systems (including most of those analyzed in this paper). The book also includes the results of a consistency test for low pressure systems using the γ-ϕ method. An alternative approach is the equation of state method, also known as Phi–Phi (ϕ–ϕ) method, in which non-idealities in both phases are represented by the fugacity coefficient (ϕ) determined using an equation of state [4,5]. This is the method used in this work.

Thermodynamic consistency (TC) of phase equilibrium data is of especial importance for the checking of experimental data used in process design and simulation of alcoholic distillation [6,7]. That a set of phase equilibrium data is declared as thermodynamically consistent means that the data fulfills some rigorous thermodynamic equations within defined and acceptable limits of accuracy. Therefore, the data can be accepted as reliable for being used in other calculations such as in design and process simulation. However if the data do not pass the consistency test, it does not mean that the data is erroneous but gives the user a warning about this situation. It should be also mentioned that since some assumptions and arbitrariness are frequently introduced in defining a consistency test, different tests may give different answers, "*a situation that may question their usefulness*" according to Wisniak et al. [8]. These authors defined a set of guidelines to critically analyze a consistency test and conclude that "*as with any approximation, application of consistency tests requires rigor, reasonable assumptions and models, and an examination of the data and results of the test*".

To the best of the authorś knowledge, consistency analysis of water+congener mixtures using the equation of state method has

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Symbols

a_c, b	Parameter in the PR EoS
a_m, b_m, c_m, d_m	Interaction parameters in the mixing rules
k_{ij}	Binary interaction parameter
M	Molecular weight
P	Pressure
P_c	Critical pressure
P_i^0	Pressure of component “i” in the reference state
R	Ideal gas constant
T	Temperature
T_c	Critical temperature
T_R	Reduced temperature
V	Volume
V_c	Critical volume
x_1	Liquid mole fraction
y_1	Vapor mole fraction

Abbreviations

EoS	Equation of state
NFC	Not fully consistent
PR	Peng-Robinson
PR/KM	Peng-Robinson+ Kwak-Mansoori model
TC	Thermodynamic consistent
TI	Thermodynamic inconsistent
%Δ	Percent deviation
%ΔA	Area deviation

Greek letters

α(T)	Temperature function in the PR EoS
β_{ij}	Binary interaction parameter
δ_{ij}	Binary interaction parameter
γ	Activity coefficient
ω	Acentric factor

Super/subscripts

cal	Calculated
exp	Experimental
i, *j*	Components *i* and *j*

not been presented in the literature. During the last years we have analyzed a number of binary and ternary mixtures containing water+congener, ethanol+congener, water+ ethanol+ congener but consistency analysis as the one presented in this paper has not been done [9-14]. However some related studies are found in the literature.

Góral et al. [15] analyzed VLE data for 36 binary alcohol+hydrocarbon systems. The method combined thermodynamic consistency tests, data correlation, comparison with enthalpy of mixing data, and comparison of VLE data for various mixtures. Kurihara et al. [7] evaluated data for 46 alcohol+hydrocarbon systems at low pressures using the PAI test (Point, Area, Infinite dilution test). The PAI test is combined with the NRTL equation for the activity coefficient. Kato [16] proposed a thermodynamic consistency test for binary constant-temperature VLE data for the systems methanol+water and ethanol+water. The binary parameters involved in the activity coefficients equations are numerically optimized to satisfy the Gibbs–Duhem equation. Kato [17] investigated an empirical consistency test for binary constant-temperature and for constant-pressure VLE data of the systems methanol+water, ethanol+water, ethanol+(methanol, 1-propanol, 2-propanol). Alvarez et al. [18] reported isobaric VLE data at 101.3 kPa for the binary mixtures: methanol+ (methylacetate, ethanol, water) and ethanol+water. The experimental data were tested for thermodynamic consistency by means of the Wisniak method and were demonstrated to be consistent. Susial et al. [19] reported experimental data of the isobaric VLE for the mixture methyl acetate+ethanol at 0.3 and 0.7 MPa. The experimental data passed the consistency test of Van Ness. No application has been found on the use of the Kwak–Mansoori approach with the Peng-Robinson EoS (PR/KM) to determine thermodynamic consistency of phase equilibrium data.

In other advances, Marcilla et al. [20] proposed as a method for evaluating the quality of experimental VLE data the inspection of the Gibbs energy function for the liquid mixtures, which is derived from the experimental values for the liquid and vapor concentrations. This method would be convenient to consider in addition to the consistency test. In their study they analyze the experimental data of some binary systems, such as water + butanol at 760 mmHg and water + propanol at 323 K, among others. They also discuss situations associated with the distribution of experimental data, such as water + propanol system, where the experimental data are very limited to concentrations very close to both pure components. More recently, Carrero-Mantilla et al. [21] propose to simultaneously use a test that combines a statistical consistency analysis and a thermodynamic condition established by the Gibbs–Duhem equation. The VLE data was described using the NRTL equation, with two different sets of parameters.

The PR/KM model has been previously discussed in the literature and has demonstrated to have acceptable accuracy and adequate flexibility for correlating VLE data of different types of mixtures, requirements of the consistency test [22,23]. The test employed to check the thermodynamic consistency of isothermal P-x-y equilibrium data has been previously described by the authors for other type of mixtures [24,25].

2. Thermodynamic consistency

As explained in previous papers, the consistency method proposed by the authors is model-dependent; meaning that the method requires a thermodynamic model that can accurately fit the experimental to then applying the consistency test. In this work the chosen model is the Peng–Robinson equations modified by Kwak and Mansoori [26]. These authors presented an attractive approach that, according to the authors, is consistent with statistical-mechanical theory of the van der Waals mixing rules and is based on the fact that mixing rules in van der Waals type equations of state are for constants and not for thermodynamic state function, such as the α(T) function commonly used in the attractive pressure term of van der Waals-type EoS. The approach of Kwak and Mansoori considers rewriting the Peng–Robinson EoS so that the transformed equation of state contains three temperature-independent parameters (c_m, b_m and d_m). The three EoS parameters are expressed using the classical van der Waals mixing rules, each one including one adjustable parameter.

The Peng–Robinson model belongs to the so-called van der Waals type equations of state, and can be written as follows [27]:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{1}$$

In this equation “*a*” is a function of the reduced temperature ($T_R = T/T_c$) and “*b*” is a parameter determined using the critical properties of the substance of interest:

$$a = a_c \alpha(T_R) \tag{2}$$

$$a_c = 0.4572\frac{R^2T_c^2}{P_c} \tag{3}$$

$$\alpha(T_R) = \left[1 + F(1 - T_R^{0.5})\right]^2 \tag{4}$$

$$b = 0.0778\,\frac{RT_c}{P_c} \tag{5}$$

$$F = 0.3746 + 1.5423\omega - 0.2699\omega^2 \tag{6}$$

For mixtures, the PR equation is written as follows:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b_m(V - b_m)} \tag{7}$$

In this equation a_m and b_m are the equation of state parameters for the mixture, to be calculated using defined mixing rules.

The PR/KM model

The modified EoS proposed by Kwak and Mansoori that has been designated as PR/KM is:

$$P = \frac{RT}{V - b} - \frac{c + RTd - 2\sqrt{RTcd}}{V(V + b) + b(V - b)} \tag{8}$$

With

$$c = a_c(1 + F^2) \tag{9}$$

$$a_c = 0.4572\,\frac{R^2T_c^2}{P_c} \tag{10}$$

$$F = 0.3746 + 1.5423\omega - 0.2699\omega^2 \tag{11}$$

$$b = 0.0778\,\frac{RT_c}{P_c} \tag{12}$$

$$d = \frac{a_cF^2}{RT_c} \tag{13}$$

For mixtures, the modified PR/KM equation is:

$$P = \frac{RT}{V - b_m} - \frac{c_m + RTd_m - 2\sqrt{RTc_md_m}}{V(V + b_m) + b(V - b_m)} \tag{14}$$

and the mixing and combining rules proposed by Kwak and Mansoori are:

$$c_m = \sum_i\sum_j x_ix_jc_{ij} \quad c_{ij} = \sqrt{c_ic_j}(1 - k_{ij}) \quad c_i = c_{ci}(1 + F_i^2) \tag{15}$$

$$b_m = \sum_i\sum_j x_ix_jb_{ij} \quad b_{ij} = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2}\right)^3(1 - \beta_{ij})$$

$$b_i = 0.0778\frac{RT_{ci}}{P_{ci}} \tag{16}$$

$$d_m = \sum_i\sum_j x_ix_jd_{ij} \quad d_{ij} = \left(\frac{d_i^{1/3} + d_j^{1/3}}{2}\right)^3(1 - \delta_{ij})$$

$$d_i = \frac{\alpha(T_{ci})F_i^2}{RT_{ci}} \tag{17}$$

In these equations, x_i is the mole fraction of component "i" in the liquid or gas phase. As seen in Eqs. (15-17), the PR/KM model contains up to three adjustable parameters (k_{ij}, β_{ij}, δ_{ij}), one for each of the constants, and they are assumed to be the same for both phases, liquid and gas. Usually the parameter that most affect the accuracy of the model is k_{ij}, the interaction parameter for "c" in the PR/KM model, and several mixtures can be modeled with $\beta_{ij} = \delta_{ij} = 0$ [4]. Additionally, the model requires the critical properties (T_c and P_c) and the acentric factor (ω) for each of the components in the mixture.

The relative deviations $\%\Delta P$ *and* $\%\Delta y_1$ for a set of N data, given in the tables, are defined as:

$$\%\Delta P = \frac{100}{N}\sum\left(\frac{P^{cal} - P^{exp}}{P^{exp}}\right)_i \tag{18}$$

$$\%\Delta y_1 = \frac{100}{N}\sum\left(\frac{y_1^{cal} - y_1^{exp}}{y_1^{exp}}\right)_i \tag{19}$$

The absolute deviations in the calculated pressure in the binary system for each point "i" are used to determine the accuracy of the thermodynamic model:

$$|\%\Delta P| = \frac{100}{N}\sum\frac{\left|P^{cal} - P^{exp}\right|_i}{P_i^{exp}} \tag{20}$$

The thermodynamic consistency test can be applied if these deviations, expressed as $|\%\Delta P|$ are within pre-established ranges. Once the model is accepted, the Gibbs–Duhem equation is applied as explained elsewhere [28]. The equations that describe the consistency test are as follows.

The Gibbs–Duhem equation in terms of residual properties is written as [29].

$$\sum x_id\left[\frac{G^R}{RT}\right] = -\frac{H^R}{RT^2}dT + \frac{V^R}{RT}dP \tag{21}$$

In terms of fugacity coefficients Eq. (21) is reduced to:

$$\sum x_id\,Ln\varphi_i = -\frac{H^R}{RT^2}dT + \frac{V^R}{RT}dP$$

and

$$\left[\frac{(Z - 1)}{P}\right]dP = x_1d(Ln\varphi_1) + x_2d(Ln\varphi_2) \tag{22}$$

And at constant temperature one gets:

$$\left[\frac{(Z - 1)}{P}\right]dP = x_1d(Ln\varphi_1) + x_2d(Ln\varphi_2) \tag{23}$$

Arranging terms:

$$\frac{1}{P}dP{=}\frac{x_1}{(Z - 1)\varphi_1}d\varphi_1 + \frac{(1 - x_1)}{(Z - 1)\varphi_2}d\varphi_2$$

and

$$\int\frac{1}{\mathrm{P}x_1}\mathrm{dP} = \int\frac{1}{(Z - 1)\varphi_1}\mathrm{d}\varphi_1 + \int\frac{(1{-}x_1)}{x_1(Z - 1)\varphi_2}\mathrm{d}\varphi_2 \tag{24}$$

The fugacity coefficient for the PR/KM model is [22]:

$$\begin{aligned}\ln\varphi_i &= \frac{\left(2\bar{B}_i - b_m\right)(Z - 1)}{b_m} - \ln(Z - B)\\ &\quad - \frac{A}{2\sqrt{2}B}\left[\frac{2\bar{A}_i + 2RT\overline{D}_i - \frac{2\sqrt{RT}\left(a_m\overline{D}_i + d_m\bar{A}_i\right)}{\sqrt{a_md_m}}}{c} - \frac{\left(2\bar{B}_i - b_m\right)}{b_m}\right]\\ &\quad \times\ln\left[\frac{Z + B\left(1 + \sqrt{2}\right)}{Z + B\left(1 - \sqrt{2}\right)}\right]\end{aligned}$$

$$A = \frac{cP}{R^2T^2} \qquad B = \frac{b_mP}{RT} \qquad c = a_m + d_mRT - 2\sqrt{a_md_mRT}$$

$$\bar{A}_i = \sum_j^N x_ja_{ij} \quad \bar{B}_i = \sum_j^N x_jb_{ij} \quad \overline{D}_i = \sum_j^N x_jd_{ij} \tag{25}$$

The final test is reduced to the calculation of two integral terms designated as A_P and A_φ [30].

$$\begin{aligned}A_P &= \int\frac{1}{Px_1}dP\\ A_\varphi &= \int\frac{1}{(Z - 1)\varphi_1}d\varphi_1{+}\int\frac{(1{-}x_1)}{x_1(Z - 1)\varphi_1}d\varphi_1\end{aligned} \tag{26}$$

In the equations above, x_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, $\underline{H}^R$ is the residual enthalpy, V^R

Table 1
Properties for all substances involved in this study. The values for these properties, were obtained from Daubert et al. [35].

Components	M (kg/kg mol)	T_c (K)	P_c (bar)	V_c (m^3/kmol)	ω
Water	18.0	647.1	220.6	0.056	0.3449
Acetic acid	60.1	592.0	57.9	0.180	0.4665
Acetaldehyde	44.0	466.0	55.5	0.154	0.2907
Ethyl acetate	88.1	523.4	38.8	0.286	0.3664
Furfural	96.1	670.2	56.6	0.252	0.3678
Methanol	32.0	512.7	80.8	0.117	0.5659
1-Propanol	60.1	536.7	51.7	0.218	0.6204
Methyl acetate	74.1	506.6	47.5	0.228	0.3313
2-Butanol	74.1	536.2	42.0	0.269	0.5768

is the residual volume, T is the temperature, and P is the pressure of the system.

Thus, if a set of data is considered to be consistent, A_P should be equal to A_φ within acceptable defined deviations. 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:

$$\%\Delta A_i = 100\left(\frac{A_\phi - A_p}{A_p}\right)_i \tag{27}$$

$$|\%\Delta A_i| = 100\left|\frac{A_\varphi - A_P}{A_P}\right|_i \tag{28}$$

In Eq. (26) A_P is determined using the experimental P-x data at fixed temperature, while a thermodynamic model (an equation of state), is employed to evaluate A_φ in Eq. (26). If the data are adequately correlated, meaning that the deviations in the calculated pressure are within acceptable margins (as defined later here) and the individual area deviation $\%\Delta A_i$ are within defined margins of errors, then the data set is considered to be consistent.

To evaluate the integrals given by Eqs. (26), the following must be defined: (i) an equation of state; (ii) a set of mixing rules; and (iii) a set of combining rules. In principle, any appropriate equation of state and any mixing and combining rules can be used to evaluate the pressure. This model must be used to determine the fugacity coefficients φ_i and the compressibility factor Z. Once the model is defined and the optimum parameters are determined from the experimental P-T-x data, the area A_φ is calculated. For a set of N experimental data points at a fixed temperature there are $(N-1)$ values of the area A_P and $(N-1)$ values of the area A_φ to be calculated [28].

To define the criteria for consistency and inconsistency it is first required to check if the model is able to correlate the data within acceptable deviations. The model is accepted if the deviation defined by Eq. (20) is lower than 10% for $|\%\Delta P|$. After the model is found appropriate, it is required that the deviations in the individual areas $|\%\Delta A_i|$ defined by Eq. (28) are all lower than 20% to declare the data as being thermodynamically consistent. All these criteria that have been used by the authors for several years are available in the literature [24,25,28,30-34]. However, not only the criteria of deviations are considered for determining consistency or inconsistency, but also the distribution of such deviations. If some few points (up to 25% of the original points) do not pass the area test but the rest of the data does pass the test, there is no reason to eliminate the whole set of data. So the rest of the data is declared consistent, and the original set of data is not fully consistent (NFC). If more than 25% of the data do not pass the test, then the whole original set is declared to be thermodynamically inconsistent (TI).

3. Experimental data and classical consistency models

The study considers data of eight binary congener + water mixtures at pressures ranging from 0.077 to 4.86 bar and temperatures ranging from 308 to 373 K. These include 25 isotherms with a total of 322 data points. The congeners included in these mixtures are: acetic acid, acetaldehyde, ethyl acetate, 2-butanol, furfural, methanol, methyl acetate and 1-propanol. Table 1 shows pure component properties for all the substances considered in this study. In this Table, M is the molecular weight, T_c is the critical temperature, P_c is the critical pressure, V_c is the critical volume and ω is the acentric factor. The values for these properties were obtained from Daubert et al. [35].

Table 2 gives some details on the experimental data used in the study including the literature source for each of the twenty five data set [3,36]. In this Table, T is the temperature (expressed in kelvin), N is the number of experimental data, P is the pressure (expressed in bar), Δx_1 is the liquid mole fraction range for component 1 and Δy_1 is the vapor mole fraction range for component 1. The component 1 is the congener substance.

As observed in Table 2, most of the data were obtained from the Dechema collection [3]. This collection not only the data is presented but also includes two tests to check the thermodynamic consistency of the data listed. The tests are based on the so-called γ-ϕ method for correlating the PTxy data. This low pressure technique is a method in which the low pressure gas phase is considered to be an ideal mixture ($\phi = 1$) and the non-idealities of the liquid phase are considered using a model for the activity coefficient (γ) [5].

The Dechema method considers a simplified form of the fundamental equation of phase equilibrium for low pressure cases and determines the activity coefficients of each component in the binary mixture as:

$$\gamma_i = \frac{y_i P}{x_i P_i^o} \tag{29}$$

where P_i^0 is the pressure of component "i" in the reference state.

The Gibbs–Duhem equation is integrated to obtain:

$$\int_0^1 \left[Ln\frac{\gamma_1}{\gamma_2} \right] dx = 0 \tag{30}$$

For the calculation of the activity coefficients using Eq. (30) the experimental equilibrium mole fractions are used and also experimental vapor pressure of the pure components. Eq. (30) means that if one plots $Ln(\gamma_1/\gamma_2)$ from $x = 0$ to $x = 1$, a positive area (A_P above the x-axis and a negative area (A_N below the x-axis) will be obtained and they should have the same value. Since experimental data have intrinsic experimental errors and because of the assumptions done in obtaining Eq. (30), the integral will not be

Table 2
Details on the phase equilibrium data for the systems considered in this study. In the table the temperature values have been rounded to the closest integer.

Systems water (2)+	Ref.	T(K)	N	Range of date		
				P(bar)	Δx_1	Δy_1
Acetic acid	[3]	333	10	0.1414–0.1939	0.0300–0.8507	0.0220–0.7824
		343	11	0.1957–0.3045	0.0500–0.9500	0.0420–0.9083
		353	11	0.2974–0.4664	0.0500–0.9500	0.0415–0.9060
		363	11	0.4297–0.6908	0.0500–0.9500	0.0410–0.9010
Acetaldehyde	[3]	348	5	1.2156–4.0520	0.0250–0.2600	0.6850–0.9300
		373	5	1.7728–4.8624	0.0100–0.1500	0.4800–0.7950
Ethyl acetate	[36]	313	19	0.1710–0.2770	0.0500–0.9500	0.5860–0.8960
		328	19	0.2610–0.5250	0.0500–0.9500	0.4250–0.8730
		343	19	0.4750–0.9270	0.0500–0.9500	0.3740–0.8600
Furfural	[3]	323	7	0.1112–0.1399	0.0038–0.0180	0.0190–0.0530
		338	7	0.2410–0.2559	0.0038–0.0180	0.0200–0.0560
		353	7	0.4290–0.5065	0.0038–0.0180	0.0209–0.0570
Methanol	[36]	308	19	0.0770–0.2700	0.0500–0.9500	0.2920–0.9850
		313	19	0.0960–0.3400	0.0500–0.9500	0.2750–0.9810
		323	19	0.1670–0.5380	0.0500–0.9500	0.2960–0.9810
		333	19	0.2695–0.8130	0.0500–0.9500	0.2920–0.9800
		338	19	0.3482–1.000	0.0500–0.9500	0.2340–0.9800
		373	19	1.3216–3.3630	0.0500–0.9500	0.2360–0.9770
1-propanol	[36]	333	19	0.2260–0.3098	0.0500–0.9500	0.3210–0.8500
		363	19	0.8090–1.0303	0.0500–0.9500	0.3850–0.8740
Methyl acetate	[3]	333	8	0.3945–1.1009	0.0095–0.9636	0.5121–0.9497
		343	8	0.5692–1.7248	0.0095–0.9636	0.4913–0.9420
		353	8	0.8304–2.1833	0.0095–0.9636	0.4740–0.9320
2-butanol	[3]	333	6	0.2439–0.3146	0.0130–0.8500	0.2550–0.6550
		353	9	0.5705–0.7478	0.0130–0.8500	0.2730–0.7020

zero. A deviation is defined as

$$\%D = 100 \cdot \left[\frac{A_P - A_N}{A_P + A_N} \right] \tag{31}$$

Although D is arbitrary and the Dechema collection [3] establishes that “as a rule it should not be larger than a few percent”, and fixes %D as 10. When a set of data passes the test ($\%D < 10\%$) a plus sign is reported (+) and when the data do not pass the test ($\geq 10\%$) a minus sign is shown (−).

4. Results and discussion

Table 3 presents the results of the consistency test for the mixtures considered in this study. As observed in the table, 2 of the 25 data sets were found to be thermodynamically consistent (TC), 5 sets were found to be not fully consistent (NFC), and 18 sets were found to be thermodynamically inconsistent (TI). Of the 18 sets found to be thermodynamically inconsistent 17 did not fulfill the area test and one set was declared TI because the model could not fit the data in an accurate way ($\%P_{max}$ greater than 10%).

As indicated in Table 3, the PR/KM model reproduces bubble pressures of these binary mixtures with mean absolute deviations below 7.6% for any temperature. In 20 of 25 isotherms studied, pressure deviations are below 5.0%. With respect to the congener concentration in the vapor phase y_1, this quantity is predicted in all cases studied, with mean absolute deviations from 3.1% to 13.0%. It should be mentioned that the highest deviations are generally found for those cases in which the congener concentration in the vapor phase is very low. For the 2 isotherms considered to be thermodynamically consistent, for instance the system methanol (1) + water (2) at two temperatures, the modeling is acceptable as seen in Table 3 and deviations in the areas are within the established limits.

Five cases are declared to be Not Fully Consistent (NFC), for instance the system acetic acid (1)+ water (2) at two temperatures (353 K and 363 K). This is so in these cases because there are some few points in the original data set that give high area deviations but the remaining areas give deviations within the established limits. If those points showing high deviation are not considered in the analysis (one or two points for each one of the systems) the remaining data give area deviations below the established limits (20%). Thus, the remaining set is TC but the original set is declared to be NFC.

For the 18 cases considered to be thermodynamically inconsistent (TI), 17 did not fulfill the area test. For instance for the system ethyl acetate+water, at all temperatures, area deviations are very high for more than 25% of the points of the original data set, despite that the modeling is acceptable and within the limits established by the method. The system furfural + water at $T = 323$ K was declared to be TI because the modeling is not accurate enough; this means that some deviations in the individual pressures are higher than 10%. This is indicated with the symbol∗ in Table 3 (TI∗ in the last column).

Despite these results showing that most of the analyzed data sets resulted to be thermodynamically inconsistent, it is important to mention that the same data have been previously tested by others using a different consistency test. The mixtures acetaldehyde (1)+water (2); ethyl acetate (1) + water (2); furfural (1)+water (2) at 338 K are declared to be thermodynamically inconsistent, in agreement with the consistency test reported by Gmehling et al. [3] in the Dechema Collection. For the mixture methyl acetate (1)+water (2) and 2-butanol (1)+water (2) the results found in this work are in disagreement with the analysis of the literature. These data are found TI, while in the Dechema collection the data are declared to be TC. The data for the systems ethyl acetate (1)+water (2), methanol (1)+water (2) and 1-propanol (1)+water (2) were taken from the compilation by Ohe [36] which does not report consistency analysis. However some of the sets are also included in the Dechema collection and the consistency results are in agreement with our findings for the mixture ethyl acetate (1) + water (2) at all temperatures and for the mixture methanol (1) + water (2) at 333 K.

For the system fulfural (1)+water (2) the data used were those points at low concentration of furfural in the liquid phase. All these

Table 3
Results obtained for the modeling and consistency test. In the column designated as Dechema [3], NI means No-Information available in that collection, and the sings plus (+) and minus (−) mean that the data pass or did not pass the two, respectively.

Systems water (2) +	T(K)	k_{12}	β_{12}	δ_{12}	$\lvert\Delta P\%\rvert$	$P_{max}\%$	$\lvert\Delta y_1\%\rvert$	$\lvert\Delta A\%\rvert$	Dechema [3]	This work
Acid acetic	333	0.1643	−0.0921	0.6755	7.5	−9.5	10.4	47.9	NI	TI
	343	0.1310	−0.1336	0.6254	4.4	−9.2	10.7	21.4	NI	TI
	353	0.0329	−0.1984	0.4879	5.8	−9.9	8.1	12.3	NI	NFC
	363	0.0081	−0.2730	0.5091	4.0	−6.4	7.6	19.9	NI	NFC
Acetaldehyde	348	0.3157	0.1197	0.7738	2.9	−6.3	3.1	29.9	−	TI
	373	-0.2108	0.2364	−0.7711	2.4	4.3	5.2	25.1	−	TI
Ethyl acetate	313	0.0784	0.4419	−0.3509	3.5	7.1	3.2	110.3	−	TI
	328	0.1198	0.5063	−0.3253	4.5	−6.4	4.1	88.7	−	TI
	343	0.1202	0.5311	−0.3560	4.5	7.3	4.9	140.2	−	TI
Furfural	323	0.0261	−0.0188	0.0977	6.9	−18.1	13.0	—	+	TI*
	338	0.0320	−0.0074	0.0905	7.1	−8.5	7.8	51.8	−	TI
	353	0.0284	−0.0181	0.0799	4.3	−9.9	4.9	67.5	+	TI
Methanol	308	−0.1154	−0.2702	0.2160	4.0	−6.3	5.9	12.2	+	NFC
	313	−0.0639	−0.3349	0.4161	1.6	4.1	4.9	15.4	NI	TI
	323	−0.1154	−0.3237	0.2759	2.6	−3.9	3.6	6.8	−	TC
	333	−0.0661	−0.1930	0.2126	0.4	−0.7	3.8	6.4	+	TC
	338	−0.0683	−0.1921	0.2021	0.6	−2.8	5.8	10.4	−	NFC
	373	−0.1520	−0.1512	−0.0582	3.2	9.7	5.4	13.5	−	NFC
1-propanol	333	0.0940	0.1271	0.1931	2.4	8.1	5.2	236.6	+	TI
	363	0.0430	−0.1318	0.3601	1.0	6.3	4.8	98.8	NI	TI
Methyl acetate	333	0.2845	0.1525	0.6119	0.9	2.1	3.3	49.8	+	TI
	343	0.5400	0.2942	0.9733	3.6	−8.0	3.4	151.7	+	TI
	353	0.1508	0.1247	0.3094	5.3	9.9	4.1	267.4	+	TI
2-butanol	333	0.1367	0.2187	0.2011	1.4	−5.4	10.6	56.7	+	TI
	353	0.0526	−0.0371	0.3239	1.4	−4.5	8.2	90.2	+	TI

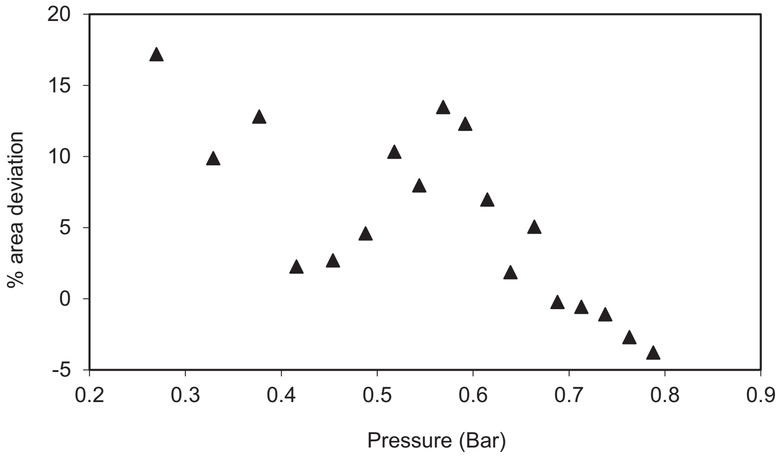

Fig. 1. Area deviations for the liquid phase $\%\Delta A_i$ for the system methanol (1) + water (2) at T = 333 K, declared to be thermodynamically consistent (TC).

results and comments are summarized in Table 3. In the Table, results of this work and those reported by the Dechema collection [3] are listed. In the column designated as Dechema [3], NI means that there is no information available in that collection for the Dechema consistency test, and the sings plus (+) and minus (-) mean that the data passed (+) or did not pass (-) the consistency test.

Some examples of the results obtained are presented in Figs. 1, 2 and 3. Fig. 1 shows the relative area deviations for the liquid phase $\%\Delta A_i$ for the system methanol (1) + water (2) at T = 333 K, declared to be thermodynamically consistent (TC). As observed in the figure, all area deviations are below 20%. Fig. 2 shows the relative area deviations for the liquid phase $\%\Delta A_i$ for the system acetic acid (1) + water (2) at T = 353 K, declared to be not fully consistent (NFC). In this case, one point present area deviations higher than 20%. Fig. 3 shows the relative area deviations for the system ethyl acetate (1) + water (2) at T = 328 K, declared to be thermodynamically inconsistent (TI). As shown in the figure, in this case 83% of the original data give deviations higher than 20%.

Some final remarks are necessary to clarify what would be the consequences of having inconsistent data and how this can affect future research. More than thirty years ago Harg [37] summarized these aspects in a conference in the USA, speech that was later published in the journal Fluid Phase Equilibria. Inconsistent data are not only unreliable but their potential errors may affect good design of new processes or introducing errors in improving over existing processes, since calculations are done based on wrong data. And certainly accuracy of those calculations cannot be better than the accuracy of the data used in the calculations (unless such errors cancel each other). According to Harg, at that time (the beginnings of the 1980‘s) the ultimate wish was “*to have all the validated, experimental data that we need for the system in question at the specified conditions*”. Harg also added that priority on accuracy in industrial processes should be given to vapor-liquid equilibrium data, the type of data analyzed in this paper.

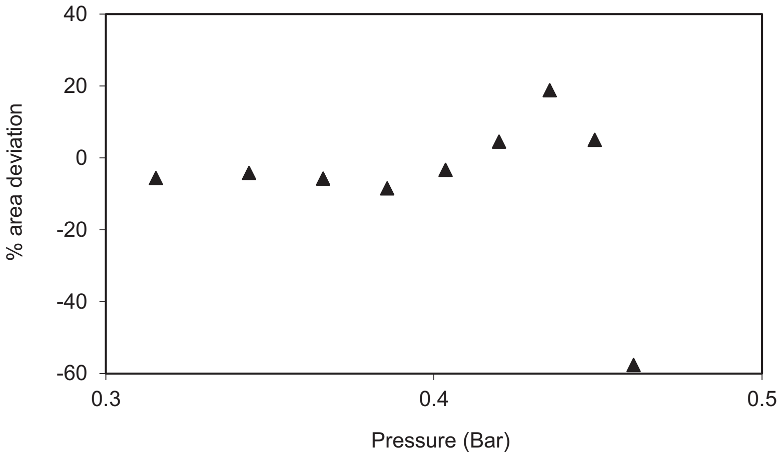

Fig. 2. Area deviations for the liquid phase $\%\Delta A_i$ for the system acetic acid (1) + water (2) at $T = 353$ K, declared to be not fully consistent (NFC).

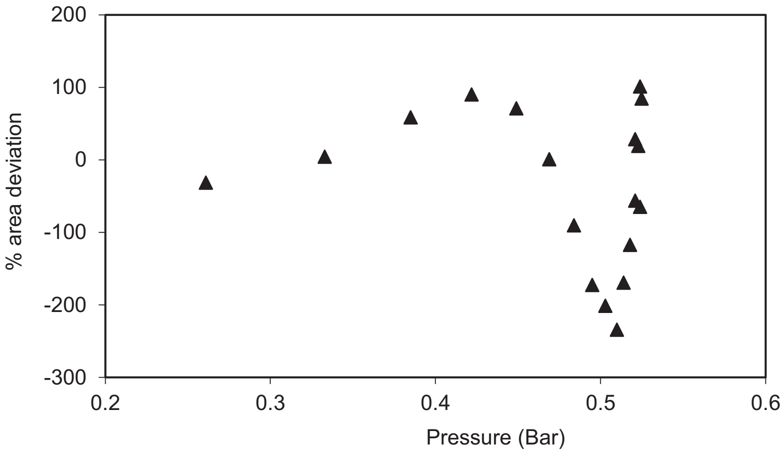

Fig. 3. Area deviations for the system ethyl acetate (1) + water (2) at $T = 328$ K, declared to be thermodynamically inconsistent (TI).

5. Conclusions

Based on the results, the following main conclusions can be drawn: (i) the equation of state method using appropriate mixing rules such as the one of Kwak–Mansoori can be used to model low pressure VLE data in water + congener mixtures; (ii) bubble pressures can be correlated with good accuracy with the PR/KM model, giving absolute average deviations below 7.6% for each isothermal data set and the overall absolute average deviations is 3.4%; (iii) the congener concentration in the vapor phase, y_1, can be obtained with good accuracy, giving absolute average deviations below 13.1% for each isothermal data set and the overall absolute average deviations is 6.1%; (iii) the proposed consistency test method allows to globally analyze P-T-y data; (iv) the method gives an adequate answer about consistency or inconsistency of a set of experimental P-T-y data.

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