Thermodynamic Consistency of Vapor-Liquid Equilibrium Data at High Pressure

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A method for testing the thermodynamic consistency of binary and isothermal vapor-liquid equilibrium data at moderate and high pressures is proposed, using a φ-φ approach. The Redlich-Kwong-Soave equation of state with Huron-Vidal mixing rules at infinite pressure is used in the data-reduction procedure, and a Margules equation is used to calculate the activity coefficients at infinite pressure. This model is shown to be thermodynamically consistent. The proposed method allows us to check consistency of vapor-liquid equilibrium data in the presence of components at the gaseous and supercritical states.

Introduction and Background

The check of thermodynamic consistency in vapor–liquid equilibrium (VLE) experimental data sets is a very important issue, one that arises when the data measured are more than needed for the complete simulation of the behavior of the system. For consistency to be ensured, basic thermodynamic equations must be satisfied by the experimental data. Among these equations, the Gibbs–Duhem equation is the most widely referenced and used. This equation can be handled in a number of ways, leading to different consistency tests; an exhaustive discussion on these possibilities is provided by Jackson and Wilsak (1995). A classic method for checking thermodynamic consistency is contained in Van Ness et al. (1973), which was further developed and finally summarized in Van Ness and Abbott's textbook (1982). This method is, in fact, a data-reduction procedure, according to which a thermodynamically consistent model is fitted to the experimental data by regression of the adjustable parameters of the model. The data turn out to be thermodynamically consistent if the model enables an accurate reproduction of the experimental pressures (or vapor compositions, or both), with pressure- (P-) and vapor composition- (y-) residuals that scatter randomly around zero and within the experimental uncertainty of the measured data.

The γ-φ approach is usually adopted to model VLE in these checks. As long as the system pressure is not too high and the temperatures are well below the critical temperatures of all components in the mixture, the vapor phase is not far from the ideal state; accordingly, vapor-phase fugacities can be calculated by simplified models, for example, the ideal-gas one (i.e., $\varphi_i = 1$) or the two-term virial equation in pressure. However, it has been noted that such a procedure may be unreliable even at moderate pressure (Jackson and Wilsak, 1995), and the use of more accurate equations of state (EOSs), such as cubic EOSs, has been suggested. Liquid-phase nonidealities are always encapsulated in the activity coefficient γ. The nonideal behavior of the liquid phase can also be clearly discerned at low pressure, so an accurate representation of γ is required in the whole pressure (i.e., composition) range. Therefore, there has been a considerable effort to develop excess Gibbs energy (G^E) models with enough flexibility to yield random scattering about zero of the P- and y-residuals, as well as with a sufficiently small number of adjusting parameters with respect to the experimental points available. The Redlich–Kister and the Margules equations are widely used G^E expressions; more flexible correlating equations have been proposed, such as the 5-parameter modified Margules equation (Abbott and Van Ness, 1975) and the sum of symmetric functions equation (Rogalsky and Malanowski, 1977). All of these models provide pressure-independent activity coefficients and are inherently thermodynamically consistent (in the Gibbs–Duhem's sense) only at constant temperature and constant pressure. However, if the system pressures are not very high, these models can claim inherent thermodynamic consistency even if only the isothermal condition is satisfied, since the term of the Gibbs–Duhem equation for the total pressure differential is negligible; thus, a simple data-reduction procedure can be used to assess thermodynamic consis-

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tency, where predicted pressures and vapor-phase compositions are evaluated through simple bubble-point calculations.

In this work we address the problem of checking the thermodynamic consistency of binary and isothermal VLE data at moderate and high pressures. As was pointed out in a review by Mühlbauer and Raal (1995), such tests have been reported in the literature in only a limited number of cases. Unfortunately, the extension of the γ-φ approach, developed for low-pressure data, to the regression of high-pressure data is a difficult task, mainly for two reasons:

1. At the system temperature, one or both of the components may be supercritical. In this case, the liquid-phase standard state of their activity must be chosen at the component infinite dilution (and not at the pure component) reference state, which requires calculating the pertinent Henry's constants;
2. The term of the Gibbs–Duhem equation containing the differential of total pressure cannot be neglected. This requires the Gibbs–Duhem equation to be explicitly introduced in the VLE calculations, either in an integral form (Won and Prausnitz, 1973) or in a differential one (Christiansen and Fredenslund, 1975). This second problem can be overcome by properly accounting for the effect of pressure on the activity coefficients, as suggested, for example, by Jackson and Wilsak (1995).

On the other hand, checking thermodynamic consistency of high-pressure data in the framework of a φ-φ approach would be advisable, because the previously mentioned problem (1) would clearly hold no longer; as far as problem (2) is concerned, we will show in the article that it can be bypassed as well. In spite of these facts, thermodynamic consistency tests based on the φ-φ approach are reported less frequently in the literature, possibly because, although EOSs have been extensively used with good results to model the VLE of nonpolar or slightly polar mixtures, their reliability for predicting the VLE of strongly nonideal mixtures is not satisfactory when classic mixing rules are employed. In other words, such mixing rules are not flexible enough to deal with this kind of mixture. However, the use of highly flexible nonclassic mixing rules can help overcome this problem; among the wealth of G^E-based mixing rules so far proposed (see, e.g., the papers by Voutsas et al. (1995), and by Orbey and Sandler (1995)), we have used the Huron–Vidal (HV) mixing rule at infinite pressure (Huron and Vidal, 1979). In the referenced article, these authors applied a φ-φ approach to high-pressure VLE calculations, in order to prove that their mixing rule provided enough flexibility for evaluating experimental data scattering.

As a matter of fact, the problem of checking thermodynamic consistency with the φ-φ data-reduction procedure was not examined in detail in any of the references indicated; for instance, it was mentioned by Malanowski and Anderko (1992) in their textbook, but no examples are reported there. The purpose of our article is to show how a consistency test can be performed in the case of high-pressure isothermal VLE data of binary systems. The Redlich–Kwong–Soave (RKS) EOS (Soave, 1972) will be used with HV mixing rules (Huron and Vidal, 1979): the fact that such rules are not consistent with the mixture second virial coefficient dependency on composition does not influence VLE calculations at high pressure, at least for the systems considered.

It will be shown that the proposed approach is inherently consistent for isothermal data and can be used as a powerful tool for checking the thermodynamic consistency of VLE data that cannot be handled by the existing methods.

The Reduction Model

In a binary homogeneous system, the classic Gibbs–Duhem equation at constant temperature T is a constraint between the values of the activity coefficients γ_i of the two components and the molar excess volume V^E of the mixture:

$$\frac{V^E}{RT}dP = z\,d\ln\gamma_1 + (1-z)d\ln\gamma_2 \qquad T = \text{const.}, \tag{1}$$

where z is the mole fraction of component 1 in the reference phase (either x for the liquid or y for the vapor phase).

However, the Gibbs–Duhem equation can also be expressed in terms of fugacity coefficients φ_i in the mixture

$$-\frac{V^R}{RT}dP = z\,d\ln\varphi_1 + (1-z)d\ln\varphi_2 \qquad T = \text{const.}, \tag{2}$$

where V^R is the molar residual volume of the mixture.

A binary system at isothermal VLE conditions has only one degree of freedom, so that the mole fraction z in the reference phase can be taken as the independent variable. Therefore, Eqs. 1 and 2 can be rewritten as

$$\frac{V^E}{RT}\frac{dP}{dz} = z\frac{d\ln\gamma_1}{dz} + (1-z)\frac{d\ln\gamma_2}{dz} \qquad T = \text{const.}, \tag{3}$$

$$-\frac{V^R}{RT}\frac{dP}{dz} = z\frac{d\ln\varphi_1}{dz} + (1-z)\frac{d\ln\varphi_2}{dz} \qquad T = \text{const.} \tag{4}$$

Equation 3 is commonly used at constant temperature and pressure, with the liquid phase taken as the reference one; here, it becomes the well-known isothermal and isobaric Gibbs–Duhem equation:

$$x\frac{d\ln\gamma_1}{dx} + (1-x)\frac{d\ln\gamma_2}{dx} = 0 \qquad T = \text{const.},\quad P = \text{const.} \tag{5}$$

Since in any VLE binary data set, T and P cannot be simultaneously constant, Eq. 5 is applied instead of Eq. 3 only in an approximate way, which is reasonable at low pressure; however, at moderate and high pressures the lefthand-side term of Eq. 3 may not be negligible, so that such an approximation is no longer justified and either excess volumes must be considered in the calculation or the activity coefficient values must be corrected for pressure dependency. Using a different procedure, we intend to check thermodynamic consistency on the basis of Eq. 4. According to the currently proposed method, calculation of the fugacity coefficients is performed by means of an RKS EOS with HV mixing rules; in a dimensionless form it is expressed by

$$Z^3 - Z^2 + BZ\left(\frac{A}{B} - 1 - B\right) - \frac{A}{B}B^2 = 0, \tag{6}$$

where Z is the mixture compressibility factor ($Z = PV/RT$) and R is the universal gas constant. The mixture parameters are defined by

$$\frac{A}{B} = \sum_{i=1}^{2} z_i \left[\left(\frac{A}{B} \right)_i - \frac{\ln \gamma_i^\infty}{\ln(2)} \right] \tag{7}$$

$$B = \sum_{i=1}^{2} z_i B_i. \tag{8}$$

In Eq. 7, γ_i^∞ is the activity coefficient of component i at infinite pressure. The pure component parameters can be evaluated by

$$\left(\frac{A}{B} \right)_i = \frac{\Omega_a}{\Omega_b} \left(\frac{\alpha(T)}{T_r} \right)_i \tag{9}$$

$$B_i = \Omega_b \frac{P_r}{T_r}, \tag{10}$$

where P_r and T_r are the reduced pressure and temperature; Ω_a and Ω_b are constant values, typical of the RKS EOS ($\Omega_a = 0.42748$, $\Omega_b = 0.08664$);

$$\frac{\alpha}{T_r} = f\left(\frac{P_r^{\text{sat}}}{T_r} \right), \tag{11}$$

according to the work of Soave (1986), and P_r^{sat} is the reduced vapor pressure. The expression f in Eq. 11 is a generalized polynomial that turns out to be very accurate for representing pure component vapor pressures.

The expression of the fugacity coefficient of component i in the mixture can be derived from Eqs. 6 to 8:

$$\ln \varphi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) - \left(\frac{A}{B} - \frac{\ln \gamma_i^\infty}{\ln(2)} \right) \ln\left(1 + \frac{B}{Z}\right). \tag{12}$$

In the examples presented below, the activity coefficients at infinite pressure are calculated by a modified Margules equation, according to Barker's method (Barker, 1953). Typically, 2-, 4-, and 6-parameter Margules equations were used.

It can be shown that condition 4 is identically verified if the fugacity coefficients are expressed by Eq. 12 and the activity coefficients by a model (such as the Margules equations) that satisfies Eq. 5. The proof is reported in the Appendix.

As a consequence, the proposed equation of state can be correctly used with any suitable G^E-based mixing rule to assess the thermodynamic consistency of isothermal VLE experimental data of binary systems. This means that the experimental data can be consistently reduced by performing VLE calculations through the proposed model. The calculated values of y and P can then be compared with the experimental ones, in order to check thermodynamic consistency.

Note that the proposed procedure overcomes the problem of evaluating excess volume or pressure effects on the activity coefficients, as should be done when using Eq. 3 in a pressure range where the pressure differential term of this Gibbs–Duhem equation cannot be neglected. In order to apply our method, the following pure-component parameters need to be known:

- The critical-temperature-to-critical-pressure ratio
- The vapor pressure at the experimental temperature, for components below their critical temperature
- The $\alpha(T)$ value at the experimental temperature, for supercritical components.

Data-Reduction Procedure

According to Barker's method (Barker, 1953), we have assumed that the liquid composition is not affected by experimental errors, thus ascribing to P and y all the measurement uncertainties. However, it should be noted that statistical methods that account for errors in the other measured variables can also be used (Kemeny et al., 1982). Given N_p experimental data points of the *PTxy* type, one of the following different objective functions was minimized in order to evaluate the model parameters:

$$obf_1 = \sum_{i=1}^{N_p} (\delta P)^2 \tag{13}$$

$$obf_2 = \sum_{i=1}^{N_p} [\delta(\Delta P/P)]^2 \tag{14}$$

$$obf_3 = \sum_{i=1}^{N_p} (\delta y)^2 \tag{15}$$

$$obf_4 = \sum_{i=1}^{N_p} \frac{1}{\sigma_{\Delta P/P}^2} [\delta(\Delta P/P)]^2 + \sum_{i=1}^{N_p} \frac{1}{\sigma_y^2} (\delta y)^2, \tag{16}$$

where the residuals on pressure, δP and $\delta(\Delta P/P)$, and on vapor composition, δy, are defined as

$$\delta P = P_{\text{calculated}} - P_{\text{experimental}}$$

$$\delta(\Delta P/P) = \frac{P_{\text{calculated}}}{P_{\text{experimental}}} - 1$$

$$\delta y = y_{\text{calculated}} - y_{\text{experimental}}. \tag{17}$$

In Eq. 16 the symbols $\sigma_{\Delta P/P}$ and σ_y indicate the root-mean-square (RMS) values of $\delta(\Delta P/P)$ and δy, respectively. They are obtained, as suggested by Van Ness and Abbott (1982), by minimizing separately Eq. 15 (for $\sigma_{\Delta P/P}$) and Eq. 14 (for σ_y).

The fitting ability of the model and the thermodynamic consistency of the data set were checked by examining pres-

Table 1. Results of the Consistency Tests Performed

	System ①**		System ②†	System ③††			System ④‡	
	Van Ness and Abbott (1982)	This Work	This Work	Jackson and Wilsak (1995)	This Work (7 Points)	This Work (All Points)	This Work obf: Eq. 14	This Work obf: Eq. 16
Average $\lvert\delta(\Delta P/P)\rvert(\%)$	n.a.*	0.0005	0.1106	0.47	0.4976	0.1298	0.1386	0.1949
Average $\delta(\Delta P/P)(\%)$	n.a.	0.0000	0.0006	n.a.	0.0039	0.0005	0.0004	0.0155
Maximum $\lvert\delta(\Delta P/P)\rvert(\%)$	n.a.	n.c.*	0.4853	n.a.	n.c.	0.3670	0.4530	0.4490
RMS $\delta(\Delta P/P)(\%)$	0.0007	0.0006	0.1598	n.a.	0.6106	0.1649	0.2030	0.2327
Average $\lvert\delta y\rvert$	n.a.	0.0025	0.0033	n.a.	0.0076	0.0085	0.0291	0.0020
Average δy	0.0012	0.0012	0.0016	n.a.	0.0076	0.0085	0.0290	0.0008
Maximum $\lvert\delta y\rvert$	n.a.	n.c.	0.0090	n.a.	n.c.	0.0132	0.0638	0.0047
RMS δy	0.0030	0.0030	0.0039	0.006	0.0084	0.0090	0.0360	0.0023

*n.a. = not available; n.c. = not calculated

**System ①: *Chloroform/Ethanol at 318.15 K*. Comparison between the classic procedure by Van Ness and Abbott (1982) and the proposed method for the same 4-parameter Margules equation. The objective function is Eq. 13. Note that pressure deviations are not expressed in % for this system; absolute deviations are in bar.

†System ②: *n-Butane/Carbon Dioxide at 344.26 K*. Summary of the consistency test with objective function (Eq. 14) and a 4-parameter Margules equation.

††System ③: *Ethene/1-Butene at 293.15 K. Columns 5 and 6:* comparison between the results reported by Jackson and Wilsak (1995) with 7 experimental data points and the proposed method with a 2-parameter Margules equation and the same data points. *Column 7:* summary of the consistency tests performed on the whole data set with a 6-parameter Margules equation. The objective function is Eq. 14.

‡System ④: *Hydrogen-Ethene at 235.15 K*. Summary of the consistency test by minimizing the two different objective functions (Eqs. 14 and 16) (6-parameter Margules equation).

sure vs. liquid composition, pressure residual vs. liquid composition, and vapor composition-residual vs. liquid composition diagrams.

Following Abbott and Van Ness (1977), a two-step fitting procedure was used in order to minimize the possibility that the vapor pressures may act as primary fitting parameters. First, it was necessary to decide the number of adjustable parameters of the Margules equation; thus, values of the vapor pressures coming from correlating expressions taken from the literature were used when the experimental data at $x_i = 0$ were not available, while for supercritical components, an extrapolated value of the $\alpha(T)$ function calibrated on vapor pressures was employed at the experimental temperature T_{exp}. Then, once the suitability of the Margules equation was demonstrated, the vapor pressure(s) (and possibly the value of $\alpha(T_{\mathrm{exp}})$) were treated as further parameters to be fitted by data reduction.

Results and Discussion

Validation of the proposed method for high-pressure binary systems was performed with reference to examples already referenced and discussed in the literature (Jackson and Wilsak, 1995, and Won and Prausnitz, 1973). A summary of the results is given in Table 1.

However, first we show that the procedure is also reliable in the case of low-pressure VLE data reduction. Figure 1a, 1b, 1c refer to the system *Chloroform/Ethanol at 318.15 K (System* ①*)*, which is also reported in Van Ness and Abbott's textbook (Van Ness and Abbott, 1982). The data set comes from Scatchard and Raymond (1938). The data reduction, carried out in Eq. 13, leads to the conclusion that the residuals δy are not scattering randomly around zero: the average value of the scatter is 0.0012. Note that the results provided by the proposed method (Table 1, column 3) are equivalent to those obtained when the classic procedure is adopted (Table 1, column 2); of course, the latter is definitely simpler. Three systems were examined at high pressure:

n-Butane/Carbon Dioxide at 344.26 K (System ②*)*. In dealing with this system, Won and Prausnitz (1973) had to devise a special modification of their method in order to correctly reproduce the experimental measurements. On the other hand, the currently proposed procedure, with Eq. 14 as the objective function, readily yields a good fitting of the experimental data, as can be seen in Figure 2a. Note that the datum at $x = 0$, provided in the data set by Olds et al. (1949), was not included in the regression because it is not clear if it represents an experimental determination or the result of the vapor pressure equation. With reference to Table 1 (column 4) and Figure 2b, a random scatter of the $\delta(\Delta P/P)$ residuals is obtained with a value of the RMS $\delta(\Delta P/P)$ not far from the experimental error of 0.1%; however, the δy residual distribution is clearly biased (Figure 2c) and the RMS δy is almost twice the experimental uncertainty of 0.002. Thus, the data appear not to be fully consistent.

Ethene/1-Butene at 293.35 K (System ③, data set from Bae et al., 1981). Jackson and Wilsak (1995) examined this system, but, since their model could not be used for VLE calculations near the critical region, they included only seven data points in the regression; moreover, they calculated an erroneous behavior on the supercritical-component side of the *P-x,y* diagram. The same seven points were first regressed by using the proposed method, in order to allow a comparison with Jackson and Wilsak's procedure: the results, which are summarized in Table 1 (columns 5 and 6), are similar. On the other hand, our method is able to overcome the supercritical-component detection problem, so that all the available data points can be used in the regression, and column 7 in Table 1 can be derived along with Figure 3. Figure 3b shows that random scattering of the $\delta(\Delta P/P)$ residuals is obtained; however, the RMS value of $\delta(\Delta P/P)$ is almost three times larger than the experimental uncertainty of 0.06%, which indicates that the data set is believed to be inconsistent. Jackson and Wilsak (1995) had the same result, although type also observed nonrandom scattering of the $\delta(\Delta P/P)$ residuals. Confirming our conclusion, Figure 3c

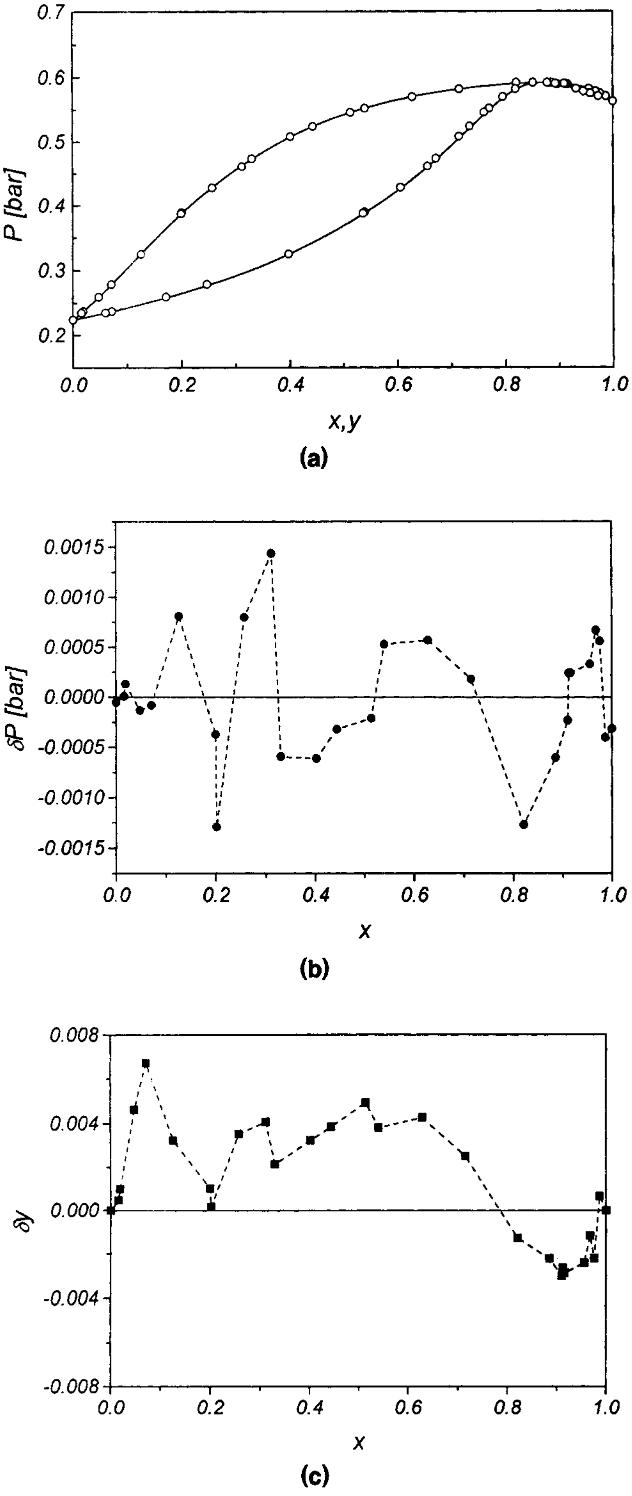

Figure 1. System chloroform/ethanol at 318.15 K: P-x,y diagram (a), δP residuals (b), and δy residuals (c): the objective function is Eq. 13.

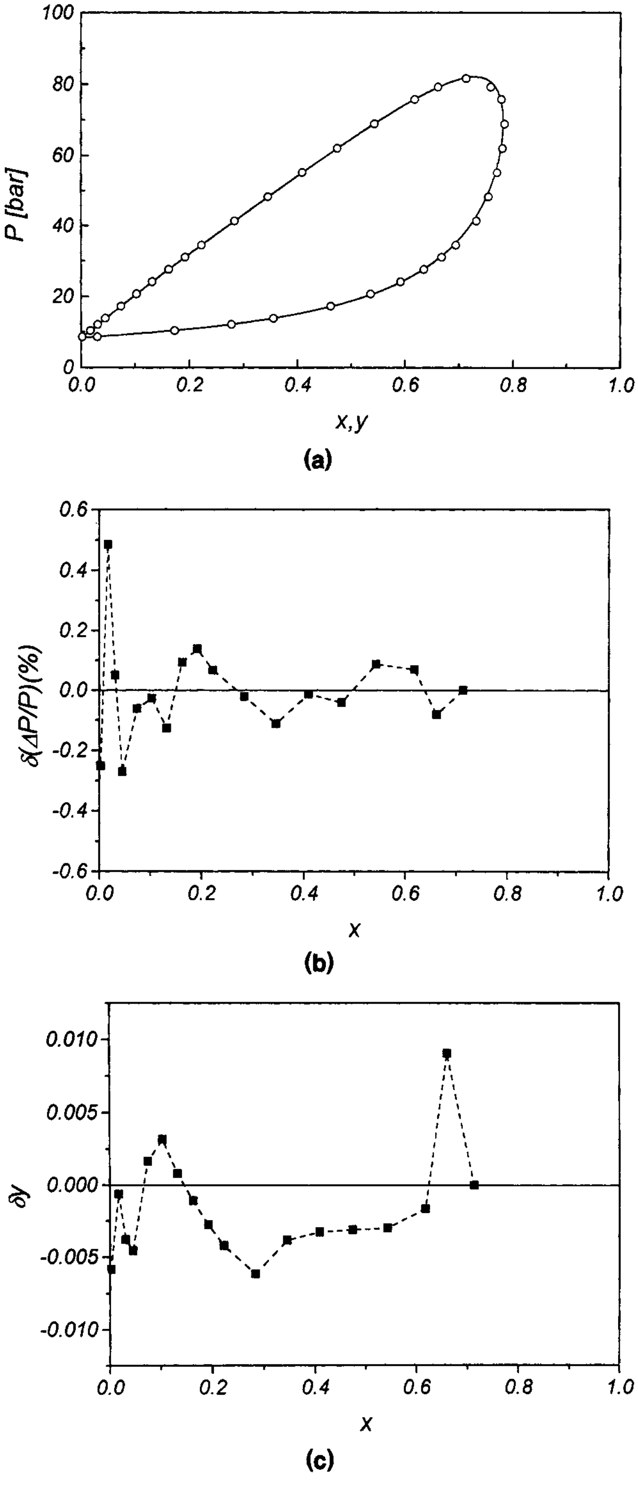

Figure 2. System n-butane/carbon dioxide at 344.26 K: P-x,y diagram (a), $\delta(\Delta P/P)$ residuals (b), and δy residuals (c): the objective function is Eq. 14.

shows that the δy residuals are undoubtedly biased, with an RMS value 4.5 times higher than the reported experimental error of 0.002. Once again, it should be remembered that the proposed method was able to capture the presence of the supercritical component and predict a reasonable critical point for the mixture.

Hydrogen/Ethene at 235.15 K (System ④*).* A considerable amount of equilibrium data were measured by Heintz and

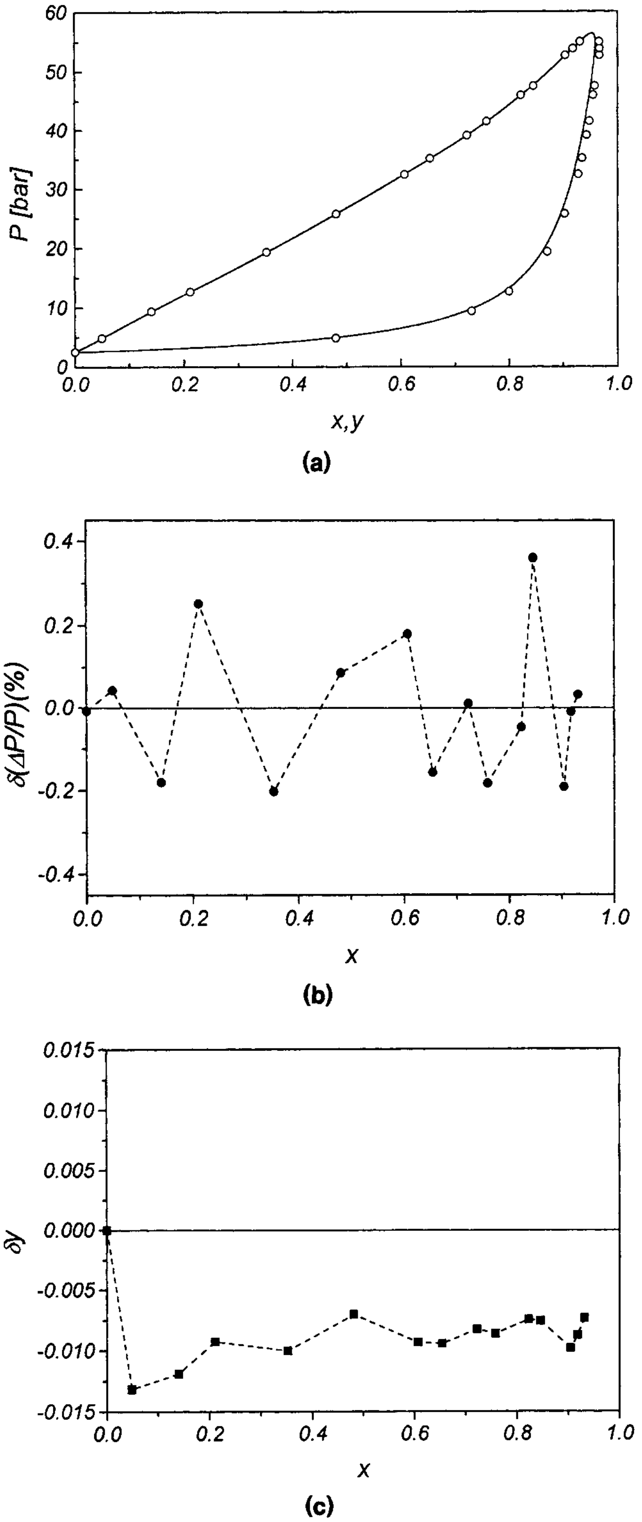

Figure 3. System ethene/1-butene at 293.35 K: P-x,y diagram (a), $\delta(\Delta P/P)$ residuals (b), and δy residuals (c): the objective function is Eq. 14.

Streett (1983) for this system. However, erratic results are presented in the literature when treating them in view of thermodynamic consistency (Jackson and Wilsak, 1995). A preliminary analysis with our model suggested exclusion of one equilibrium point from the regression. In this way, the model enables a correct reduction of the data points (Figure 4a). For this system, better results were obtained, on the whole, by considering Eq. 16 as the objective function to min-

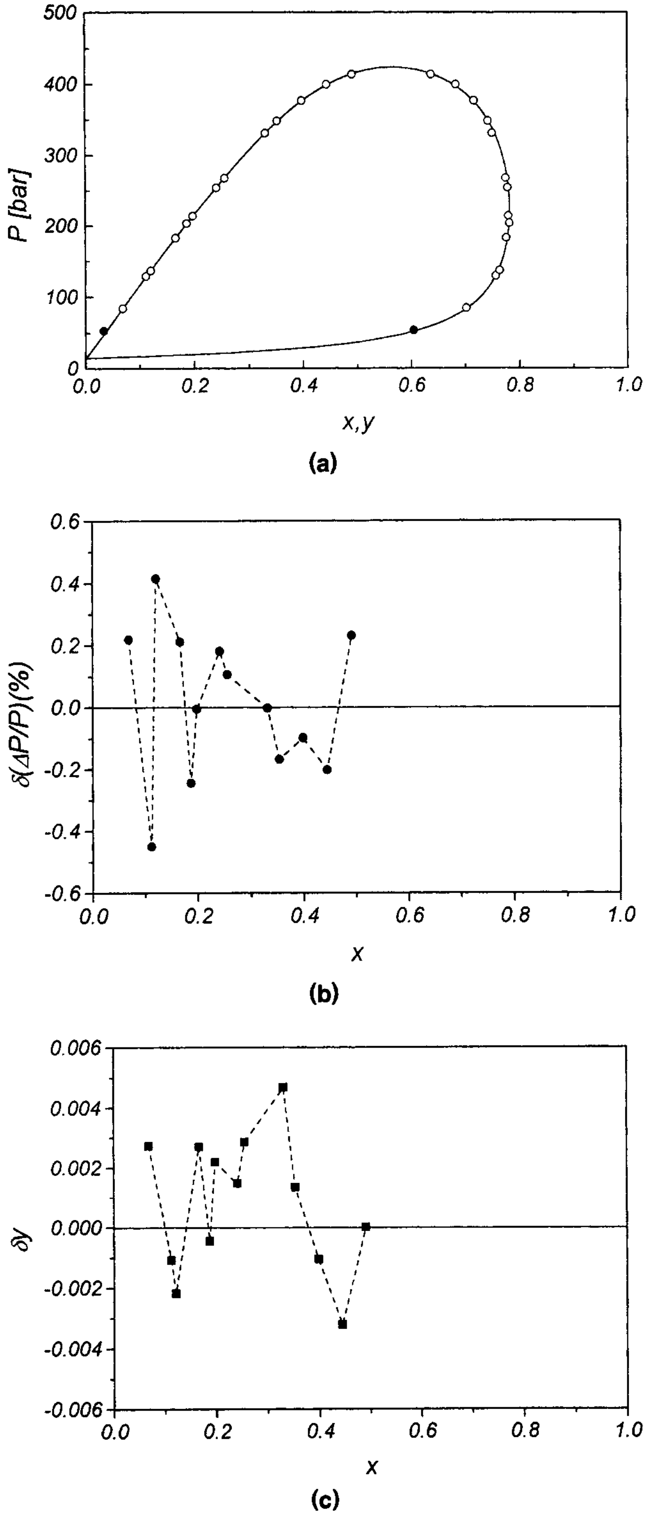

Figure 4. System hydrogen-ethene at 235.15 K: P-x, diagram (a), $\delta(\Delta P/P)$ residuals (b), and δy residuals (c): the objective function is Eq. 16.

The data points indicated by (●) were not included in the regression.

imize (Table 1, column 9); in fact, when only pressure values were regressed (Eq. 14), the model was not able to capture accurately the vapor compositions at the higher pressures (Table 1, column 8). Figure 4b indicates that the scatter of the $\delta(\Delta P/P)$ residuals is acceptably random, with an RMS value of $\delta(\Delta P/P)$ less than the experimental error (0.5%). A similar consideration can be drawn for the vapor compositions from the analysis of the δy residuals plot (Figure 4c); also, the measurement error (0.003) is larger than the RMS δy. On the whole, this data set can be regarded as thermodynamically consistent. Note that in this case the value of $\alpha(T_{\mathrm{exp}})$ has not been fitted to the data set, but that a simple extrapolation of the Melhem equation (Melhem, 1989) has been used.

Conclusions

A novel approach was proposed for checking the thermodynamic consistency of vapor–liquid equilibrium data at moderate and high pressures. The Soave–Redlich–Kwong equation of state, with Huron–Vidal mixing rules at infinite pressure and a suitable G^E model, was shown to be thermodynamically consistent for the treatment of isothermal data sets. Application of the method allowed us to carry out, with satisfactory results, consistency tests of vapor–liquid equilibrium data, which is otherwise impossible or hard to do with classic procedures. These results are obtained at the expense of slight complications in the development and computer implementation of the fitting model.

Acknowledgment

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Appendix: Thermodynamic Consistency of the Model (Eqs. 6 through 15) for Binary Systems at Constant *T*

To prove that Eq. 4,

$$-\frac{V^R}{RT}\frac{dP}{dz} = z\frac{d\ln\varphi_1}{dz} + (1-z)\frac{d\ln\varphi_2}{dz}, \tag{4}$$

is identically satisfied by the proposed model at constant T, let us take the first derivative of Eq. 12 with respect to the mole fraction z of component 1 in either phase:

$$\begin{aligned}\frac{d\ln\varphi_i}{dz} = {}& \frac{(Z-1)}{B}\frac{dB_i}{dz} - \frac{B_i(Z-1)}{B^2}\frac{dB}{dz} + \frac{B_i}{B}\frac{dZ}{dz} \\ & - \frac{1}{(Z-B)}\left(\frac{dZ}{dz} - \frac{dB}{dz}\right) \\ & - \left(\frac{d(A_i/B_i)}{dz} - \frac{1}{\ln(2)}\frac{d\ln\gamma_i^\infty}{dz}\right)\ln\left(1+\frac{B}{Z}\right) \\ & - \left(\frac{A_i}{B_i} - \frac{\ln\gamma_i^\infty}{\ln(2)}\right)\frac{Z}{Z+B}\left(\frac{1}{Z}\frac{dB}{dz} - \frac{B}{Z^2}\frac{dZ}{dz}\right).\end{aligned} \tag{A1}$$

Then, we obtain:

$$z\frac{d\ln\varphi_1}{dz} + (1-z)\frac{d\ln\varphi_2}{dz} = ❶+❷+❸+❹+❺+❻, \tag{A2}$$

where

$$\text{❶} = z\frac{(Z-1)}{B}\frac{dB_1}{dz} + (1-z)\frac{(Z-1)}{B}\frac{dB_2}{dz} \qquad \text{(A3)}$$

$$\text{❷} = -z\frac{B_1(Z-1)}{B^2}\frac{dB}{dz} - (1-z)\frac{B_2(Z-1)}{B^2}\frac{dB}{dz} \qquad \text{(A4)}$$

$$\text{❸} = z\frac{B_1}{B}\frac{dZ}{dz} + (1-z)\frac{B_2}{B}\frac{dZ}{dz} \qquad \text{(A5)}$$

$$\text{❹} = -\frac{1}{(Z-B)}\left(\frac{dZ}{dz} - \frac{dB}{dz}\right) \qquad \text{(A6)}$$

$$\text{❺} = -z\left(\frac{d(A_1/B_1)}{dz} - \frac{1}{\ln(2)}\frac{d\ln\gamma_1^\infty}{dz}\right)\ln\left(1+\frac{B}{Z}\right)$$
$$-(1-z)\left(\frac{d(A_2/B_2)}{dz} - \frac{1}{\ln(2)}\frac{d\ln\gamma_2^\infty}{dz}\right)\ln\left(1+\frac{B}{Z}\right) \qquad \text{(A7)}$$

$$\text{❻} = -z\left(\frac{A_1}{B_1} - \frac{\ln\gamma_1^\infty}{\ln(2)}\right)\frac{Z}{Z+B}\left(\frac{1}{Z}\frac{dB}{dz} - \frac{B}{Z^2}\frac{dZ}{dz}\right)$$
$$-(1-z)\left(\frac{A_1}{B_1} - \frac{\ln\gamma_1\infty}{\ln(2)}\right)\frac{Z}{Z+B}\left(\frac{1}{Z}\frac{dB}{dz} - \frac{B}{Z^2}\frac{dZ}{dz}\right). \qquad \text{(A8)}$$

By recalling that for the pure component,

$$B_i = \frac{b_i P}{RT}, \qquad \text{(A9)}$$

a differentiation along the VLE curve yields

$$\frac{dB_i}{dz} = \frac{b_i}{RT}\frac{dP}{dz}, \qquad \text{(A10)}$$

so that

$$z\frac{dB_1}{dz} + (1-z)\frac{dB_2}{dz} = \frac{b}{RT}\frac{dP}{dz} = \frac{B}{P}\frac{dP}{dz}. \qquad \text{(A11)}$$

Therefore it can be easily derived:

$$\text{❶} = \frac{(Z-1)}{P}\frac{dP}{dz}. \qquad \text{(A12)}$$

On the other hand, from the mixing rule of parameter B, Eq. 8, we can simplify:

$$\text{❷} = -\frac{(Z-1)}{B}\frac{dB}{dz} \qquad \text{(A13)}$$

$$\text{❸} = \frac{dZ}{dz}. \qquad \text{(A14)}$$

Since parameter A/B, according to Eq. 9, does not depend upon pressure, it follows that:

$$\text{❺} = \frac{1}{\ln(2)}\left(z\frac{d\ln\gamma_1^\infty}{dz} + (1-z)\frac{d\ln\gamma_2^\infty}{dz}\right)\ln\left(1+\frac{B}{Z}\right). \qquad \text{(A15)}$$

Finally, from the mixing rule of parameter A/B, Eq. 7, we obtain

$$\text{❻} = -\frac{A}{B}\frac{Z}{Z+B}\left(\frac{Z\dfrac{dB}{dz} - B\dfrac{dZ}{dz}}{Z^2}\right). \qquad \text{(A16)}$$

According to the Huron–Vidal hypothesis:

$$z\frac{d\ln\gamma_1^\infty}{dz} + (1-z)\frac{d\ln\gamma_2^\infty}{dz} = \frac{V^{E\infty}}{RT}\frac{dP}{dz} = 0. \qquad \text{(A17)}$$

With a suitable model for the activity coefficient, such as the Margules equation, Eq. A15 is identically equal to zero.

If Eq. A2 is rewritten by taking Eqs. A3 to A17 into account, and all terms containing dZ/dz (and dB/dz) are grouped together, the following relationship can be derived:

$$z\frac{d\ln\varphi_1}{dz} + (1-z)\frac{d\ln\varphi_2}{dz}$$
$$= \frac{AZ - AB - Z^2 - BZ + Z^3 - B^2Z}{Z(Z+B)(Z-B)}\frac{dZ}{dz}$$
$$+ \frac{-AZ + AB + Z^2 + BZ - Z^3 + B^2Z}{B(Z+B)(Z-B)}\frac{dB}{dz}$$
$$+ \frac{(Z-1)}{P}\frac{dP}{dz}, \qquad \text{(A18)}$$

and considering the RKS EOS expressed by Eq. 6,

$$Z^3 - Z^2 + ZB\left(\frac{A}{B} - 1 - B\right) - \frac{A}{B}B^2 = 0, \qquad (6)$$

we finally have

$$z\frac{d\ln\varphi_1}{dz} + (1-z)\frac{d\ln\varphi_2}{dz} = \frac{(Z-1)}{P}\frac{dP}{dz}$$
$$= \left(\frac{V}{RT} - \frac{1}{P}\right)\frac{dP}{dz} = -\frac{V^R}{RT}\frac{dP}{dz}, \qquad \text{(A19)}$$

which is exactly Eq. 4.

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