

# THERMODYNAMIC CONSISTENCY TESTS FOR PHASE EQUILIBRIUM IN LIQUID SOLUTE+SUPERCRITICAL SOLVENT MIXTURES

José O. Valderrama<sup>1,2</sup> and Víctor H. Alvarez<sup>2</sup>

<sup>1</sup>Fac. de Ingeniería, Depto. Ing. Mecánica, Univ. de la Serena, Casilla 554, La Serena, Chile

<sup>2</sup>Centro de Información Tecnológica (CIT), Casilla 724, La Serena, Chile

## Abstract

A new method to test the thermodynamic consistency of phase equilibrium data in binary mixtures containing a liquid solute and a supercritical fluid is presented. The method is specially designed for treating incomplete PTxy data. That is, data that do not cover the whole range of concentration of the components in the mixture, as those usually found in supercritical fluid mixtures. The method is based on the Gibbs-Duhem equation and on an appropriate combination between equations of state, mixing rules and combining rules. For the systems of interest, not only the PTxy data is not available for the whole concentration range (as usually available for low-pressure data), but also the solute concentration in the gas phase is very low. For these cases, the classical differential or integral methods described in standard books, are not applicable. In this paper, the new method is applied to three high-pressure binary mixtures and consistency criteria are defined.

## 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 relationship, establishing that such data is or is not thermodynamic consistent. The thermodynamic relationship that is frequently used to analyze thermodynamic consistency of experimental phase equilibrium data is the fundamental Gibbs-Duhem equation (Prausnitz et al., 1999). This equation interrelates the activity coefficients or the fugacity coefficients of all components in a given mixture. If the equation is not obeyed then the data is inconsistent and can be considered as incorrect. If the equation is obeyed, the data is thermodynamically consistent but not necessarily correct. The Gibbs-Duhem equation in terms of residual properties applied to the gas phase mixture is (Smith et al., 2001):

$$\sum y_i d [ \bar{G}_i^R ] = - \frac{H^R}{RT^2} dT + \frac{V^R}{RT} dP \quad (1)$$

Using  $\bar{G}_i^R = RT \ln \phi_i$  and  $V^R = RT(Z-1)/P$  for a binary mixture at constant T, eqn. (1) becomes:

$$[ (Z-1)/P ] dP = y_1 d ( \ln \phi_1 ) + y_2 d ( \ln \phi_2 ) \quad (2)$$

The way in which the Gibbs-Duhem equation is arranged and applied to the experimental data has given origin to several Consistency Test Methods, most of them designed for low-pressure data. Among these, are the Slope Test, the Integral Test, the Differential Test and the Tangent-Intercept Test. A good review of these methods is found in the books by Raal and Mühlbauer (1998), by Prausnitz et al. (1999) and by Poling et al. (2001). Also, Jackson and Wilsak (1995) analyzed several consistency tests, mainly for complete high pressure vapor-liquid equilibrium data. For the cases of interest in this work, high pressure mixtures containing a supercritical component for which incomplete experimental data are available, the classical differential or integral methods described in standard books, are not applicable. Thus, a new method is proposed in this work.

## Development of Equations

Bertucco et al. (1997), expressed the Gibbs-Duhem equation for a binary mixture at constant temperature T in terms of the fugacity coefficients  $\phi_1$  and  $\phi_2$  of the components in the mixture. For a solute (component 2) in a gas phase mixture, the equation developed by Bertucco et al. becomes:

$$\frac{1}{P} \frac{dP}{dy_2} = \frac{y_2}{(Z-1)} \frac{d \ln f_2}{dy_2} + \frac{(1-y_2)}{(Z-1)} \frac{d \ln \phi_1}{dy_2} \quad (3)$$

The above equation can be conveniently written in integral form, as follows:

$$\int \frac{1}{P(1-y_2)} dP = \int \frac{y_2}{(1-y_2)(Z-1)\phi_2} df_2 + \int \frac{1}{(Z-1)\phi_1} d\phi_1 \quad (4)$$

In this equation P is the system pressure,  $y_2$  is the gas phase solute mole fraction,  $\phi_1$  and  $\phi_2$  are the fugacity coefficients of components 1 and 2 in the gas phase mixture, and Z is the compressibility factor of the gas mixture. In eqn. (4) the left hand side of the above equation is designated by  $A_P$  and the right hand side by  $A_\phi$ .

In eqn. (5),  $A_P$  is determined using the P-y data of the experimental data set PTxy while a thermodynamic model, such as the equation of state, is employed for  $A_\phi$ . If the data is adequately correlated and eqn. (5) is fulfilled between defined margins of errors, the data set is considered to be consistent. To define the margins of errors a percent area deviation  $\% \Delta A_i$  between experimental and calculated values is defined as:

$$\% \Delta A_i = 100 * \left( \left[ \int \frac{1}{P(1-y_2)} dP \right]_{\text{exp}} - \left[ \int \frac{y_2}{(1-y_2)(Z-1)\phi_2} df_2 + \int \frac{1}{(Z-1)\phi_1} d\phi_1 \right]_{\text{cal}} \right) / \left[ \int \frac{1}{P(1-y_2)} dP \right] \quad (5)$$

To evaluate the integrals in eqns. (5) for a set of N experimental points, two consecutive data points are used, obtaining N-1 values of the integrals. To evaluate  $A_P$  only the experimental data is used, while to evaluate  $A_\phi$  a model is used to evaluate the fugacity coefficients. The Peng-Robinson equation of state (Peng and Robinson, 1976), with classical mixing rules and one interaction parameter  $k_{ij}$  is employed in the proposed method. The optimum parameter is that which gives the minimum value of the average individual percent area deviation  $\% \Delta A_{av}$ . Therefore, the first condition imposed in our test is that the model be able to fulfill the Gibbs-Duhem equation within acceptable pre-defined deviations. Once this is fulfilled, the total percent area deviation ( $\% \Delta A_T$ ), the deviation in the gas phase solute concentration ( $\% \Delta y_2$ ), and the deviation in the pressure ( $\% \Delta P$ ), are observed and analyzed. A set of data is considered to be consistent if the criteria shown in Table 1 are fulfilled.

**Table 1:** Defined parameters for the proposed Consistency Test

Parameter	Formula	Criterion
Average individual percent area deviation	$\% \Delta A_{av} = 100 * [(A_\phi - A_P) / A_P] / (N-1)$	<5%
Total percent area deviation	$\% \Delta A_T = 100 * [(\Sigma A_\phi - \Sigma A_P) / \Sigma A_P]$	<10%
Overall deviation in the gas phase solute concentration	$\% \Delta y_2 = 100 \Sigma [(y_2^{\text{cal}} - y_2^{\text{exp}}) / y_2^{\text{exp}}] / N$	<10%
Overall deviation in the system pressure	$\% \Delta P = 100 \Sigma [(P^{\text{cal}} - P^{\text{exp}}) / P^{\text{exp}}] / N$	<5%

## Applications

Three binary systems were chosen to demonstrate the application of the thermodynamic test. The mixtures were carefully selected so that various features of the thermodynamic consistency test could be emphasized. Details on the systems are shown in Table 2. The necessary properties of the pure substances (critical temperature  $T_c$ , critical pressure  $P_c$ , and acentric factor  $w$ ) involved in the mixtures selected for study, are presented in Table 3. The mixtures Carbon Dioxide/n-Butane and Ethylene/1-Butene were already examined by Bertucco et al. (1997). The third mixture Carbon Dioxide/1-Octanol has not previously checked for consistency.

**Table 2:** Details for the systems

<i>System</i>	<i>Solvent(1) / Solute(2)</i>	<i>Range P(atm)</i>	<i>T(K)</i>	<i>Range <math>x_2</math></i>	<i>Range <math>y_2</math></i>	<i>Ref.</i>
1	CO <sub>2</sub> / n-Butane	8 / 81	344	0.382 / 0.998	0.970 / 0.713	Olds et al. (1949)
2	Ethylene / 1-Butene	5 / 47	293	0.155 / 0.951	0.042 / 0.520	Bae et al (1981)
3	CO <sub>2</sub> / 1-Octanol	64 / 187	403	0.366 / 0.745	0.006 / 0.027	Weng et al. (1994)

**Table 3:** Properties of Components of the systems

<i>Components</i>	<i>MW</i>	<i>T<sub>c</sub> (K)</i>	<i>P<sub>c</sub> (atm)</i>	<i>w</i>	<i>Ref.</i>
Carbon Dioxide	44.01	304.2	72.83	0.225	Prausnitz et al. (1986)
n-Butane	58.12	425.2	37.50	0.201	Daubert et al. (1996)
Ethylene	28.05	282.4	49.66	0.087	Daubert et al. (1996)
1-Butene	56.11	419.6	39.67	0.191	Daubert et al. (1996)
1-Octanol	130.23	652.5	28.23	0.594	Daubert et al. (1996)

A summary of the results is given in Table 4 and Fig. 1. For the systems studied, besides detailed calculations for every data point in the data set, the average individual percent area deviation  $\% \Delta A_{av}$ , the overall percent area deviation  $\% \Delta A_T$ , the overall deviation in the gas phase solute concentration  $\% \Delta y_2$ , and the overall deviation in the pressure  $\% \Delta P$ , are presented.

The values  $-2.8 \% \Delta A_{av}$ , 0.8 for  $\% \Delta y_2$  and 2.7 for  $\% \Delta P$  with the maximum  $\% \Delta A_i$  of 18.6, lead to the conclusion that the system Carbon Dioxide /n-Butane can be considered as thermodynamically consistent. The values  $-23.1 \% \Delta A_{av}$ , 10.2 for  $\% \Delta y_2$  and -1.8 for  $\% \Delta P$  with the maximum  $\% \Delta A_i$  of  $-40.3$ , lead to the conclusion that the system Ethylene/1-Butene can be considered as thermodynamically inconsistent. For the third mixture studied, 1-Octanol/Carbon Dioxide the value  $-24.1 \% \Delta A_{av}$ , 7.6 for  $\% \Delta y_2$ , and  $-5.9$  for  $\% \Delta P$  with the maximum  $\% \Delta A_i$  of  $-31.7$ , lead to the conclusion that this system is thermodynamically inconsistent.

Figure 1 presents a graphical picture of the different parameters considered to define consistency of a given set of experimental data. As observed in the figure, for the mixture Carbon Dioxide/n-Butane, deviations in average individual areas and in gas phase solute concentration are reasonable distributed with pressure deviations below 5%. For the systems Ethylene/1-Butene and Carbon Dioxide/1-Octanol, area and gas phase solute concentration deviations are high. For this case, the average pressure deviation is not very high, but still higher than the established 5% shown in Table 1.

**Table 4:** Results for the three mixtures studiedCarbon Dioxide (1)/n-Butane(2) ( $k_{ij} = 0.15147$ )

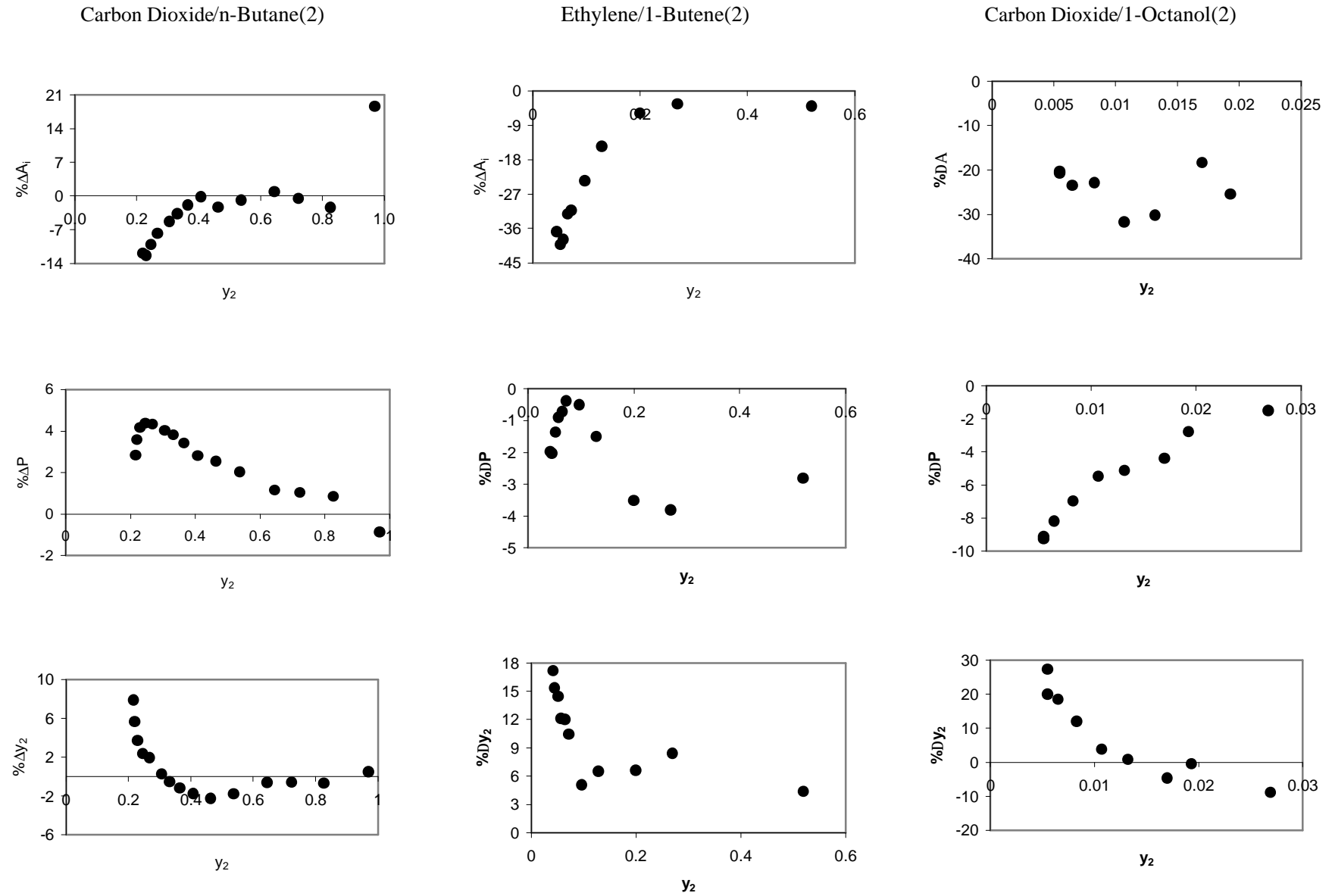
$P_i/P_{i+1} (exp)$	$P_i/P_{i+1} (cal)$	$y_{2i}/y_{2i+1} (exp)$	$y_{2i}/y_{2i+1} (cal)$	$\%DA_i$	$\%DP_i/\%DP_{i+1}$	$\%Dy_{2i}/\%Dy_{2i+1}$	
8.5 / 10.2	8.4 / 10.3	0.97 / 0.82	0.97 / 0.82	18.6	-0.9 / 0.8	0.5 / -0.7	
10.2 / 11.9	10.3 / 12.0	0.83 / 0.72	0.82 / 0.72	-2.4	0.8 / 1.0	-0.7 / -0.6	
11.9 / 13.6	12.0 / 13.8	0.72 / 0.64	0.72 / 0.64	-0.5	1.0 / 1.1	-0.6 / -0.6	
13.6 / 17.0	13.8 / 17.4	0.64 / 0.54	0.64 / 0.53	0.8	1.1 / 2.0	-0.6 / -1.8	
17.0 / 20.4	17.4 / 20.9	0.54 / 0.46	0.53 / 0.45	-0.9	2.0 / 2.5	-1.8 / -2.3	
20.4 / 23.8	20.9 / 24.5	0.46 / 0.41	0.45 / 0.40	-2.3	2.5 / 2.8	-2.3 / -1.8	
23.8 / 27.2	24.5 / 28.2	0.41 / 0.36	0.40 / 0.36	-0.2	2.8 / 3.4	-1.8 / -1.2	
27.2 / 30.6	28.1 / 31.8	0.36 / 0.33	0.36 / 0.33	-1.9	3.4 / 3.8	-1.2 / -0.5	
30.6 / 34.0	31.8 / 35.4	0.33 / 0.31	0.33 / 0.31	-3.7	3.8 / 4.0	-0.5 / 0.2	
34.0 / 40.8	35.4 / 42.6	0.31 / 0.27	0.31 / 0.27	-5.3	4.0 / 4.3	0.2 / 1.9	
40.8 / 47.6	42.6 / 49.7	0.27 / 0.25	0.27 / 0.25	-7.8	4.3 / 4.4	1.9 / 2.4	
47.6 / 54.4	49.7 / 56.7	0.25 / 0.23	0.25 / 0.24	-10.1	4.4 / 4.2	2.4 / 3.7	
54.4 / 61.2	56.7 / 63.4	0.23 / 0.22	0.24 / 0.23	-12.4	4.2 / 3.6	3.7 / 5.6	
61.2 / 68.0	63.4 / 70.0	0.22 / 0.22	0.23 / 0.23	-12.0	3.6 / 2.8	5.6 / 7.9	
				$\% \Delta A_T = 7.7$	$\% \Delta A_{av} = -2.8$	$\% \Delta P = 2.7$	$\% \Delta y_2 = 0.8$

Ethylene(1)/1-Butene(2) ( $k_{ij} = 0.01462$ )

$P_i/P_{i+1} (exp)$	$P_i/P_{i+1} (cal)$	$y_{2i}/y_{2i+1} (exp)$	$y_{2i}/y_{2i+1} (cal)$	$\%DA_i$	$\%DP_i/\%DP_{i+1}$	$\%Dy_{2i}/\%Dy_{2i+1}$	
4.8 / 9.3	4.7 / 8.9	0.52 / 0.27	0.54 / 0.29	-4.0	-2.8 / -3.8	4.3 / 8.4	
9.3 / 12.5	8.9 / 12.1	0.27 / 0.20	0.29 / 0.21	-3.4	-3.8 / -3.5	8.4 / 6.6	
12.5 / 19.1	12.1 / 18.8	0.20 / 0.13	0.21 / 0.14	-5.9	-3.5 / -1.5	6.6 / 6.5	
19.1 / 25.4	18.8 / 25.3	0.13 / 0.10	0.14 / 0.10	-14.6	-1.5 / -0.5	6.5 / 5.1	
25.4 / 32.0	25.3 / 31.9	0.10 / 0.07	0.10 / 0.08	-23.6	-0.5 / -0.4	5.1 / 10.4	
32.0 / 34.7	31.9 / 34.5	0.07 / 0.06	0.08 / 0.07	-31.3	-0.4 / -0.7	10.4 / 12.0	
34.7 / 38.6	34.5 / 38.3	0.06 / 0.06	0.07 / 0.06	-32.3	-0.7 / -0.9	12.0 / 12.1	
38.6 / 41.0	38.3 / 40.4	0.06 / 0.05	0.06 / 0.06	-38.9	-0.9 / -1.4	12.1 / 14.4	
41.0 / 45.4	40.4 / 44.4	0.05 / 0.04	0.06 / 0.05	-40.3	-1.4 / -2.0	14.4 / 15.3	
45.4 / 46.9	44.4 / 46.0	0.04 / 0.04	0.05 / 0.05	-36.9	-2.0 / -2.0	15.3 / 17.1	
				$\% \Delta A_T = -10.8$	$\% \Delta A_{av} = -23.1$	$\% \Delta P = -1.8$	$\% \Delta y_2 = 10.2$

Carbon Dioxide(1)/1-Octanol(2) ( $k_{ij} = 0.08261$ )

$P_i/P_{i+1} (exp)$	$P_i/P_{i+1} (cal)$	$y_{2i}/y_{2i+1} (exp)$	$y_{2i}/y_{2i+1} (cal)$	$\%DA_i$	$\%DP_i/\%DP_{i+1}$	$\%Dy_{2i}/\%Dy_{2i+1}$	
64.2 / 79.0	58.2 / 71.7	0.006 / 0.006	0.007 / 0.007	-20.7	-9.3 / -9.1	20.0 / 27.3	
79.0 / 93.8	71.7 / 86.1	0.006 / 0.006	0.007 / 0.007	-20.3	-9.1 / -8.2	27.3 / 18.5	
93.8 / 113.5	86.1 / 105.6	0.006 / 0.008	0.008 / 0.009	-23.5	-8.2 / -7.0	18.5 / 12.0	
113.5 / 128.3	105.6 / 121.3	0.008 / 0.011	0.009 / 0.011	-22.9	-7.0 / -5.5	12.0 / 3.7	
128.3 / 143.1	121.3 / 135.8	0.011 / 0.013	0.011 / 0.013	-31.7	-5.5 / -5.1	3.7 / 0.8	
143.1 / 158.0	135.8 / 151.0	0.013 / 0.017	0.013 / 0.016	-30.2	-5.1 / -4.4	0.8 / -4.7	
158.0 / 167.8	151.0 / 163.1	0.017 / 0.019	0.016 / 0.019	-18.4	-4.4 / -2.8	-4.7 / -0.5	
167.8 / 182.6	163.1 / 179.9	0.019 / 0.027	0.019 / 0.024	-25.4	-2.8 / -1.5	-0.5 / -8.9	
				$\% \Delta A_T = -23.7$	$\% \Delta A_{av} = -24.1$	$\% \Delta P = -5.9$	$\% \Delta y_2 = 7.6$



**Fig. 1:** Deviations in the individual areas, the system pressure and the gas phase solute concentration for the three mixtures studied.

## Conclusions

A new method to test the thermodynamic consistency of incomplete high pressure phase equilibrium data in binary mixtures, that is data that do not cover the whole range of concentration of the components in the mixture, has been presented.

The defined criteria for thermodynamic consistency must be refined by studying more systems, establishing the weight of each parameter on the final decision of consistency or inconsistency of a set of experimental data.

For the cases studied, one set of data (Carbon Dioxide/n-Butane) showed to be thermodynamically consistent while the other two sets (Ethylene/1-Butene and Carbon Dioxide/1-Octanol) did not fulfill the consistency criteria and are considered to be thermodynamically inconsistent.

The preliminary results presented in this work indicate that the proposed method is appropriate to demonstrate the thermodynamic consistency or inconsistency of incomplete experimental PTxy data in binary mixtures containing a supercritical gas.

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