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# Thermodynamic consistency of high pressure ternary mixtures containing a compressed gas and solid solutes of different complexity

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**Abstract**

A thermodynamic consistency test applicable to high pressure binary gas–solid mixtures is extended to ternary mixtures containing a compressed gas and two solid solutes. A high pressure mixture containing carbon dioxide as solvent and two chemically similar solutes (2,3 dimethylnaphthalene and 2,6 dimethylnaphthalene) and a high pressure mixture containing carbon dioxide as solvent and two chemically different solutes (capsaicin and β-carotene), are considered in the study. Several sets of isothermal solubility data for binary and ternary mixtures are considered in the study. The Peng–Robinson equation of state with the mixing rules of Wong and Sandler have been employed for modeling the solubility of the solid in the case of binary mixtures, while the classical van der Waals mixing rules were used for modeling the ternary mixtures containing two solid solutes. Then the proposed thermodynamic consistency test has been applied. The results show that the thermodynamic test for ternary mixtures can be applied with confidence determining consistency or inconsistency of the experimental data used.


*Keywords:* Thermodynamic consistency; Supercritical fluids; Equations of state; Mixing rules; Solid–gas mixtures

## 1. Introduction

Different methods to test inherent inaccuracies of experimental phase equilibrium data have been published in the literature over the years. The important differences found in the data published by different researchers is one of the reasons that has motivated the proposals of these so-called “thermodynamic consistency tests”. 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 fundamental relationships, establishing that the data is or is not thermodynamically consistent. The thermodynamic relationship that is frequently used to analyze thermodynamic consistency of experimental phase equilibrium data is the Gibbs–Duhem equation. Depending on the way in which the Gibbs–Duhem equation is handled, different consistency tests have been derived. Among these are the Slope Test, the Integral Test, the Differential Test and the Tangent–Intercept Test. If the Gibbs–Duhem equation is not obeyed then the data is not consistent and can be considered as incorrect. If the equation is obeyed, the data is thermodynamically consistent but not necessarily correct. Good reviews of these methods are found in the books by Raal and Mühlbauer [1] and Prausnitz et al. [2].

Valderrama and Alvarez [3] presented an interesting method to test the thermodynamic consistency of phase equilibrium data in binary mixtures containing a liquid solute and a supercritical fluid. They analyzed the difficulties normally found when modeling these type of mixtures and proposed a methodology to analyzed the experimental data and to conclude about their thermodynamic consistency or inconsistency. In another communication, the same authors discussed the correct form of analyzing the accuracy of a model when dealing with high pressure phase equilibrium data [4], aspects that are taken into account in the proposed consistency method. More recently, Valderrama and Zavaleta [5] presented a thermodynamic test

*Abbreviations:* Aver, average value used for the area deviations; DMN, dimethylnaphthalene; eq., equation; EoS, equation of state; GAs, genetic algoritms; K, kelvin; Max, maximum value; NFC, not fully consistent; PR, Peng–Robinson EoS; Ref, reference to the literature; TC, thermodynamically consistent; TI, thermodynamically inconsistent; VL, van Laar; vdW, van der Waals; WS, Wong–Sandler

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Table 1
Properties of the substances considered in this work

| Compound | Formula | $M$ | $M/M_{CO_2}$ | $T_C$ (K) | $P_C$ (MPa) | $\omega$ | Ref. [1] | $V_i^{sol}$ (cm$^3$/gmol) | Ref. [2] |
|---|---|---|---|---|---|---|---|---|---|
| 2,3-DMN | $C_{12}H_{12}$ | 156.20 | 3.6 | 785.0 | 3.13 | 0.424 | Haselow et al. [40] | 138.3 | Haselow et al. [40] |
| 2,6-DMN | $C_{12}H_{12}$ | 156.20 | 3.6 | 777.0 | 3.14 | 0.420 | Haselow et al. [40] | 168.2 | Haselow et al. [40] |
| Capsaicin | $C_{18}H_{27}NO_3$ | 305.42 | 6.9 | 1062.1 | 1.71 | 1.180 | Skerget and Knez [19] | 289.8 | Vafai et al. [41] |
| β-Carotene | $C_{40}H_{56}$ | 536.85 | 12.2 | 1209.4 | 1.24 | 1.040 | Subra et al. [15] | 536.5 | Vafai et al. [41] |
| Carbon dioxide | $CO_2$ | 44.01 | 1.0 | 304.2 | 7.38 | 0.224 | Daubert et al. [42] | – | – |

Ref. [1] means literature sources for the critical properties and acentric factor and Ref. [2] means references for the solid molar volume.

to analyze high pressure binary gas–solid mixtures. So far, few attempts have been done to treat ternary mixtures as presented in this work.

The consistency method for ternary solid–solid–gas mixtures proposed in this work can be considered as a modeling procedure and can be easily extended to other multicomponent mixtures. In the method, a thermodynamic model that can accurately fit the experimental data must be first used to apply the consistency test. The fitting of the experimental data requires the calculation of some model parameters using a defined objective function that must be optimized.

Once a thermodynamic model (such an equation of state with appropriate mixing and combining rules) accurately fit the data fulfilling the equality of fugacities required by the fundamental phase equilibrium equation, that model is used to check that the Gibbs–Duhem equation is also fulfilled. Once should notice that these two steps, modeling of the data and the application of the Gibbs–Duhem equation are independent so that good modeling does not guarantee consistency and that consistent data cannot necessarily be well represented by a defined model.

The binary mixtures selected for this study present some interesting peculiarities that make them appropriate for the thermodynamic test for ternary mixtures that is presented here. The solutes themselves, 2,3 dimethylnaphthalene, 2,6 dimethylnaphthalene, capsaicin, and β-carotene, present some very different physicochemical characteristics and properties that determine different phase behavior (molecular size, molecular shape, polarity, chemical affinity). The dimethynaphthalene compounds (2,3DMN and 2,6DMN) are non-polar polycyclic aromatic hydrocarbons, chemical compounds that consist of fused aromatic rings. On the other hand, capsaicin is a cytotoxic alkaloid of the group known as capsaicinoid and β-carotene is a carotenoid made up of isoprene units as basic structures. Table 1 present some properties of these solutes included in the mixtures considered in this work. The literature sources from where the data were obtained are also given in the table.

The mixtures studied also have some special characteristics. For the binary mixtures, $CO_2$ + capsaicin and $CO_2$ + β-carotene, the concentration of the solid solutes (capsaicin and β-carotene) in the supercritical solvent ($CO_2$) is much lower than those for the binary mixtures $CO_2$ + 2,3DMN and $CO_2$ + 2,6DMN. The molecular weights ratio solute/solvent ($M/M_{CO_2}$) for $CO_2$ + capsaicin and $CO_2$ + β-carotene is much higher than those for $CO_2$ + 2,3DMN and $CO_2$ + 2,6DMN mixtures. Also, in all cases, the concentration of the solvent in the compressed phase is close to 1.0, but it cannot be considered as a pure gas, so mixture properties must be determined.

The solubility of 2,3DMN and 2,6DMN has been studied by Kurnik et al. [6] for the binaries $CO_2$ + 2,3DMN and $CO_2$ + 2,6DMN at 308, 318 and 328 K. The range of pressure was from 100 to 300 bars and the solubilities were all of the order of $10^{-3}$. To the best of our knowledge, the only published set of data for the ternary mixture $CO_2$ + 2,3DMN + 2,6DMN is that of Kurnik and Reid [7]. They presented experimental data for the ternary mixture at 308 and 318 K. The ranges of pressure and solubilities were about the same than those for the binary mixtures of Kurnik et al. [6]. Fig. 1 presents the data available on this ternary mixture $CO_2$ + 2,3DMN + 2,6DMN.

Solubility of capsaicin in high pressure $CO_2$ has been measured by Knez and Steiner [8], Hansen et al. [9], and more recently by de la Fuente et al. [10]. These authors used different experimental methodologies and comparable results, at several temperatures from 298 to 333 K and over a pressure range from 6 to 40 MPa were found. The solubility data for β-carotene in high pressure $CO_2$ can be found in the literature at temperatures ranging from 288 to 353 K and pressures ranging from 5 to 50 MPa [11–17]. The solubility data for this mixture reported

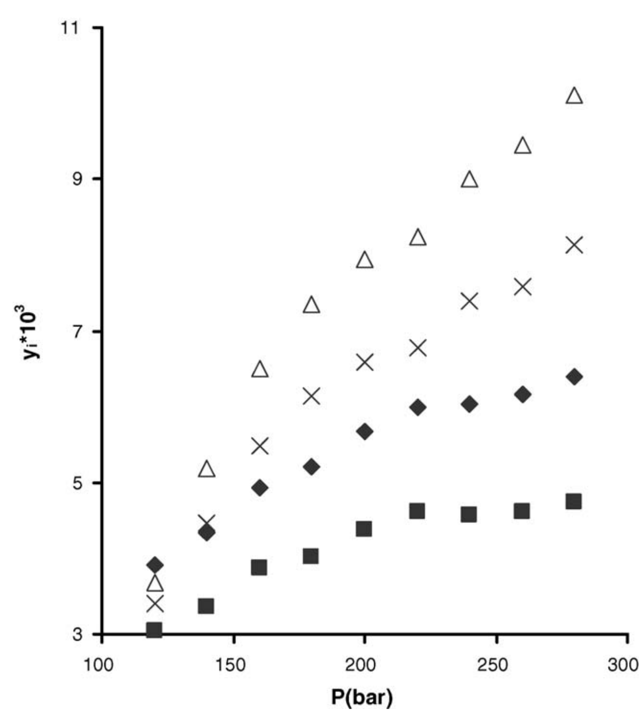


Fig. 1. Data for the ternary mixtures available in the literature: $CO_2$ + 2,3-DMN + 2,6-DMN at two temperatures. The data are from Kurnik and Reid [7]: (♦) 2,3-DMN at 308 K; (■) 2,6-DMN at 308 K; (△) 2,3-DMN at 318 K; and (×) 2,6-DMN at 318 K.