Equation of state dependency of thermodynamic consistency methods. Application to solubility data of gases in ionic liquids

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A B S T R A C T

A thermodynamic method to check the consistency of phase equilibrium data developed by the authors and applied to several situations by different researchers is analyzed to determine the effect of the equation of state employed to correlate the data on the final response of the consistency test. The consistency test method, in fact, uses an equation of state to correlate the equilibrium data and to calculate some properties such as volume, fugacity and compressibility factor. After these properties are determined the Gibbs-Duhem equation is applied to determine data consistency. If the data fulfill the Gibbs-Duhem equation the data are considered to be consistent and if the data do not fulfill de Gibbs-Duhem equation the data are of doubtful thermodynamic consistency. The equation of state dependency of the method has been recognized by the authors and other researchers but discussion of the real effects of the equation of state used on the results of the consistency method has not been presented. This work demonstrates that after a good and accurate thermodynamic model is used to correlate the data, the consistency test can be considered equation-of-state independent.

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1. Introduction

During the last several years the authors have developed and applied a thermodynamic test to check the consistency of phase equilibrium data presented in the literature for many different types of systems. Cases studied by the authors include PTxy, PTy and PTx data, being P the pressure, T the temperature, y the gas phase mole fraction, and x the liquid mole fraction. The first work of the authors [1] analyzed gas-liquid mixtures at supercritical conditions. After that, several applications to solid-gas mixtures, gas-water systems and more recently to gas + ionic liquid mixtures have been reported in the literature [2–6].

Initially and for simple mixtures, common cubic equations of state were successfully employed, such as the Peng-Robinson equation with classical mixing and combining rules. However, in several cases the equation of state cannot accurately correlate the phase equilibrium data and, therefore, the consistency test cannot be applied. This because the application of the consistency test needs values of the compressibility factor (Z) and of the fugacity coefficients (φ) of the components in the mixture. As known, when equations of state are applied to mixtures, it is necessary to introduce mixing and combining rules to account for the concentration effect on the equation of state parameters. Several models for mixing and combining rules have been discussed in the literature [7] being the proposal of Kwak and Mansoori an interesting approach that has been several times explored [8]. Kwak and Mansoori state that van der Waals mixing rules were proposed for temperature-independent parameters and not for temperature-dependent parameters, as commonly done when cubic equations of state are applied to mixtures. Thus, they rewrote the Peng-Robinson expression obtaining an equation of state that includes three temperature-independent parameters: c_m, b_m and d_m [9]. The three EoS parameters are expressed using the classical van der Waals mixing rules, each one including an adjustable parameter.

The inclusion of the Kwak-Mansoori proposal has not been done for three parameter equations of state, a method that is also presented in this work. In particular, in this paper, the Valderrama-Patel-Teja (VPT) equation of state, a generalization of the Patel-Teja equation proposed by Valderrama in 1990 is employed for modeling the phase equilibrium data [10]. The VPT equation of state contains three parameters: two volume-type parameters (b and c)

that are temperature independent and a force-type parameter (a) which is temperature dependent. When the VPT equation is transformed following the concepts of Kwak and Mansoori, a new parameter appears (d) but the force parameter becomes temperature independent. In this way, the VPT + Kwak-Mansoori expression fulfills with a basic requirement of the van der Waals model. This means that the parameters of the EoS are constant and not functions of the temperature.

One aspect that has been mentioned in the past by the authors is that their consistency test, as it happens with all consistency test methods, is model dependent. In the method analyzed in this paper, the model is the equation of state chosen for correlating the data and for calculating the properties needed in the consistency method (Z and φ). In a series of paper by the authors and by other researchers it is implicitly assumed that once the set of data is well represented by an equation of state, the results of the test are independent of the equation of state employed. However, this aspect has not been clearly proved and constitutes the novelty of this paper: to demonstrate that once an equation of state accurately correlates the phase equilibrium data, the consistency test is meaningful and the results about consistency or inconsistency of a set of experimental data can be accepted with confidence.

2. Thermodynamic analysis

The consistency test is based on the Gibbs-Duhem equation and has been presented with details in the literature [11]. In the test, the equation of state method is used for phase equilibrium correlation and prediction in complex systems. In this method, the same equation is used for the liquid and gas phases to apply the fundamental equation of phase equilibrium. That is the equality of fugacities of a given component in both phases, $f_i^L = f_i^G$. In terms of the fugacity coefficients φ_i, the equality of fugacities becomes $x_i \varphi_i^L = y_i \varphi_i^G$. To evaluate the fugacity coefficients φ_i^L and φ_i^G an equation of state is used. To describe the concentration dependency of the equation of state parameters, appropriate mixing and combining rules are included. Therefore, as stated in the Introduction, if the consistency test give similar results when different equations of state are used to model the phase equilibrium data, the consistency test can be considered equation-of-state independent. This is the main and novel objective of this work.

As detailed in the several papers published by the authors, the consistency test for isothermal data is summarized in an expression derived from the Gibbs-Duhem equation [1]:

$$\int \frac{1}{Px_1} dP = \int \frac{1}{(Z-1)\varphi_1} d\varphi_1 + \int \frac{(1-x_1)}{x_1(Z-1)\varphi_2} d\varphi_2 \tag{1}$$

For simplicity of the explanation that follows the left-hand side is denoted by A_P and the right-hand side is denoted by A_φ.

$$A_P = \int \frac{1}{Px_1} dP \tag{2}$$

$$A_\varphi = \int \frac{1}{(Z-1)\varphi_1} d\varphi_1 + \int \frac{(1-x_1)}{x_1(Z-1)\varphi_2} d\varphi_2 \tag{3}$$

Therefore, Eq. (1) becomes:

$$A_P = A_\varphi \tag{4}$$

The term A_P is calculated from experimental data only (pressure P and solubility x_1), while A_φ is determined by calculating the compressibility factor Z and the fugacity coefficients (φ_1 and φ_2) from an equation of state. If a set of data is considered to be consistent, A_P should be equal to A_φ, within acceptable defined

deviations [1]. To analyze this aspect of the equation of state influence on the consistency test results, this paper considers two models: the Peng-Robinson (PR) and the Valderrama-Patel-Teja (VPT) equations, both with the approach of Kwak and Mansoori for the equation of state parameters, and for the mixing and combining rules. Table 1 summarizes these models.

In Table 1, ξ_i is the mole fraction of component "i" in either phase: $\xi_i = x_i$ when the equations are applied to the liquid phase and $\xi_i = y_i$ when the equations are applied to the gas phase. Also, the PR/KM model contains three adjustable parameters (k_{ij}, β_{ij}, δ_{ij}), one for each of the constants: k_{ij} for α_m, β_{ij} for b_m, and δ_{ij} for d_m. The VPT/KM model contains four adjustable parameters (k_{ij}, l_{ij}, m_{ij}, n_{ij}), one for each of the constants: k_{ij} for α_m, l_{ij} for b_m, m_{ij} for c_m and n_{ij} for d_m. It is also assumed that these adjustable parameters are the same for both the liquid and the gas phases. Additionally, the model requires the critical temperature T_c the critical pressure P_c, the acentric factor ω and the critical compressibility factor for each component in the mixture.

The average absolute deviations in the calculated bubble pressure in the binary system for each point "i" are used to determine the accuracy of the PR/KM and VPT/KM models. This deviation is defined as:

$$|\%\Delta P| = \frac{100}{N} \sum \frac{|P^{cal}-P^{exp}|_i}{P_i^{exp}} \tag{5}$$

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 consistency test model can be applied [11,12]. The equations that define the consistency test have been published in previous papers, so they are not repeated here. These are summarized in Eq. (1) in which (N-1) values for the area A_P (Eq. (2)) and (N-1) values for the area A_φ (Eq. (3)) are calculated if a set of N experimental data points at constant temperature is available [11].

One should notice that is in the calculations of A_φ (Eq. (3)) where the equation of state plays its role. As observed in Eq. (3) the integral term A_φ includes the compressibility factor (Z) and the fugacity coefficient (φ) both determined using an equation of state. Accurate equations of state will give similar values of Z and φ and the areas A_φ should be the same. Simple equations of state with simple mixing rules cannot accurately calculate these values of Z and φ, the areas A_φ will have different erroneous values, and the conclusion of the test may not be the correct one.

As mentioned above, if a set of data is considered to be consistent, A_P (from Eq. (2)) should be equal to A_φ (from Eq. (3)) within acceptable defined deviations. To set the margins of errors, the individual relative percent area deviation $\%\Delta A_i$ and the individual absolute percent area deviation $|\%\Delta A_i|$ between experimental and calculated values are defined as:

$$\%\Delta A_i = 100 \left[\frac{A_\varphi - A_P}{A_P}\right]_i \tag{6}$$

$$|\%\Delta A_i| = 100 \left|\frac{A_\varphi - A_P}{A_P}\right|_i \tag{7}$$

In Eqs. (6) and (7), A_P is determined using experimental phase equilibrium data at constant temperature, while different equations of state models can be employed to evaluate A_φ. If the data are correlated with deviations within established limits (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 thermodynamically consistent.

The criteria established to define if a set of data is consistent or