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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:

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

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

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

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