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Fluid Phase Equilibria

Vapor-liquid and liquid-liquid equilibrium modeling of systems involving ethanol, water, and ethyl valerate (valeric acid) using the PC-SAFT equation of state

Luís R.S. Kanda, Kallynca C. dos Santos, Julia T.F. Santos, Francisco C. Paes, Fernando A.P. Voll, Marcos L. Corazza*

Department of Chemical Engineering, Federal University of Parana, CEP 81531-990, Curitiba, PR, Brazil

ABSTRACT

Valeric biofuels are renewable and environmental friendly fuels whose production avoids the competition with the food industry for edible oils since its route of production uses lignocellulose of residue from crops as raw material. After the reaction steps several purification operations are necessary for the valeric biofuels to meet purity standards. Therefore, it is of utter importance the knowledge of both liquid-liquid (LLE) and vapor-liquid (VLE) equilibrium behavior of species present in the process, such as ethyl valerate, valeric acid, ethanol and water. In this sense, the objective of this work is to provide a general overview for the phase equilibria of the system aforementioned using experimental data collected as background for the thermodynamic modeling. Experimental data concerning to LLE were evaluated at local atmospheric pressure (around 90.9 kPa) and 293.15 K and 318.15 K, while VLE data were collected at several different controlled pressures, ranging from approximately 7 kPa to local atmospheric pressure (around 91 kPa). UNIFAC and PC-SAFT (Perturbed Chain form of the Statistical Associating Fluid Theory) were used to perform the thermodynamic modeling. The results obtained in this work are helpful to prove the importance of carefully evaluate the interactions between the molecules present in the system. Otherwise, the design of unit operations could underestimate the number of stages required for the purification, causing the products to not reach purity specifications.

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1. Introduction

Environmental and sustainability concerns provided the major inspiration for researchers in the quest for renewable fuels to replace the conventional petroleum-based fuels. The most recent technologies, also known as new generation biofuels, points towards the use of alternative raw materials that also have less impact on food industry [1]. Low-cost bio-wastes such as wood residues (left over from forestry operations), municipal solid wastes, dedicated energy crops and agricultural or food wastes can be used as raw materials to obtain a promising class of advanced generation fuels [2]. Among the renewable fuels, the named valeric biofuels comprehend compounds derived from levulinic acid (LA), such as γ-valerolactone and valeric esters, which can be employed as additives either in gasoline or in diesel fuels to improve engine

performance [3,4].

Valeric esters are produced after multiple sequential reactions, including hydrolysis, hydrogenation and, finally, esterification. The latter reaction occurs between valeric acid and a short chain alcohol, resulting in a mixture containing a carboxylic acid alkyl ester, which depends upon the alcohol used, non-converted valeric acid, alcohol and water [5—10]. Several phase-separation steps can be performed after the reaction in order to obtain a high purity valeric ester.

The design of separation units in chemical plants requires the determination of phase equilibrium conditions. Both the recovery of the short chain alcohol, such as the ethanol, and the purification of the biofuel are usually carried out by distillation, which demands an understanding of the vapor-liquid equilibrium (VLE) phenomenon [11]. In addition, liquid-liquid equilibrium (LLE) data are useful to comprehend the behavior of liquid phases providing information to perform washing and liquid-phase separation steps [12].

Therefore, it is of summit importance to improve thermodynamic models to accurately predict both liquid-liquid and vapor-liquid equilibriums. The nature of the molecules present in this process requires both a robust model, due to its large deviation from ideality, and a significant amount of data to perform the regression of model parameters [13]. The Perturbed Chain form of the Statistical Associating Fluid Theory, PC-SAFT [14,15], is able to predict very well such systems, as demonstrated previously by several authors [13,16–20]. Furthermore, SAFT-based equations of state have presented very interesting engineering applications and can provide reliable and accurate predictions of both physical properties and phase equilibria of complex systems, mainly related to biodiesel production systems [13,21–27].

Considering the importance of the predictive thermodynamic models in the design, modeling, simulation and optimization of industrial processes involving valeric biofuels, the objective of this work is to provide a general overview for both LLE and VLE using the PC-SAFT equation of state. Experimental data for the LLE were obtained from the previous work from our research group [28] at local atmospheric pressure (around 91 kPa) and 293.15 K and 318.15 K for the ternary systems ethanol + ethyl valerate + water, ethanol + valeric acid + water and ethyl valerate + valeric acid + water, while new VLE data were measured at several different controlled pressures, ranging from approximately 7 kPa to the local atmospheric pressure (around 91 kPa) for the binary system ethanol + ethyl valerate.

This study is fundamental for a better understanding of the phase behavior of species present during the valeric acid esterification with ethanol and it can also provide information for the design, simulation and optimization of the unit operations related to the purification of the desired products.

2. Materials and methods

2.1. Chemicals

Ethanol and ethyl valerate were used in this work as received from the suppliers, without any purification. Table 1 presents IUPAC nomenclatures, suppliers and minimum purities.

2.2. Vapor-liquid equilibrium data measurements

Vapor-liquid equilibrium (VLE) data were measured for the pure components and for the binary system ethanol + water with the intent to check the reliability of both the experimental apparatus and the procedure used, and thereafter VLE data were measured for the ethanol + ethyl valerate system. The VLE data were performed using a rather simple bench unit that was composed by a 250 mL three-neck round-bottom flask, with a Graham condenser connected to an ultrathermostatic bath kept at 10 °C attached to one neck and a thermocouple fixed in the central neck, whilst the remaining neck remained sealed with a silicone stopper, as described in previous studies [29,30]. The top of the condenser was connected to a vacuum system, composed by a trap, a vacuum pump and a valve to regulate the pressure inside the distillation flask, which was fitted on a heating mantle that provided the necessary heating for the boiling of the mixture.

Each binary mixture with the desired global composition was prepared by weighing the proper amounts of each compound. The total volume inside the flask was set as the maximum as possible (around 2/3 of the total volume), ensuring that the extension of the vapor-phase was much smaller when compared to the liquid-phase extension. Hence, the composition of the liquid-phase can be considered nearly identical to the fixed global composition. This hypothesis was required for the determination of data at low pressures, in which it was not possible to sample the mixture and determine the composition, and it was confirmed at local atmospheric pressure. In this case, after the visual observation of well-defined bubbles (the system reached the boiling point), both the temperature and the pressure were checked from time to time, until the temperature reached a nearly constant value, indicating that the vapor-liquid equilibrium was reached.

After the VLE was reached, a sample of the mixture was collected and its density was measured and the composition of the liquid phase was determined using a calibration curve previously set (Equation (1)), in which a, b and c are adjustable parameters fitted for each binary mixture, w_i is the mass fraction of component i, and ρ is the density measured at 20.0 °C. The samples used in the calibration curves were prepared by weighing specific amounts of each component, so as their true compositions are known. Prior to the preparation of the samples, each pure component was left for 10 min in an ultrasound bath and after the weighing the same procedure was applied to the samples. The mass fraction of a sample with unknown composition is determined by solving the quadratic Equation (1), which results in two roots. In the case of this work, every sample with unknown composition have presented only one root in the interval expected for a mass fraction ($0 < w_i < 1$). The composition of the second component (w_j) was found by using the material balance, represented by Equation (2).

$$a \cdot w_i^2 + b \cdot w_i + (\rho - c) = 0 \tag{1}$$

$$w_j = 1 - w_i \tag{2}$$

Several different controlled pressures were set for the measurements of the boiling point of each mixture, ranging from approximately 7 kPa to the local atmospheric pressure (around 91 kPa). Data sets obtained using this procedure are presented for each pressure in temperature-composition diagrams.

2.3. Liquid-liquid equilibrium data

The liquid-liquid equilibrium (LLE) data (binodal curves and tie-lines) for the ternary mixtures ethanol + ethyl valerate + water, ethanol + valeric acid + water and ethyl valerate + valeric acid + water were presented by Paes et al. (2017) [28], at 293.15 K and 318.15 K and atmospheric pressure (around 91 kPa). Basically, binodal curves were obtained by the cloud-point method, using a closed jacketed glass cell whose temperature was kept constant using an ultrathermostatic bath and the content was stirred by a magnetic stirrer. This procedure comprises the titration of a single-phase binary mixture with known composition by the third component, until the appearance of the second phase, identified by the cloud point of the mixture. As for the tie-lines determination,

Table 1
Chemicals information.

Compound	IUPAC nomenclature	Supplier (city/state)	Minimum purity (mass fraction)
Ethanol	Ethanol	Neon (São Paulo/SP)	0.998
Ethyl valerate	Ethyl pentanoate	Sigma-Aldrich (São Paulo/SP)	0.980