Fluid Phase Equilibria 287 (2010) 141–145

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Short communication

Experimental measurements of vapor–liquid equilibria at low pressure: Systems containing alcohols, esters and organic acids

Iván R. Navarro-Espinosa[a,1], Carlos A. Cardona[a], Jimmy A. López[b,*]

[a] Departamento de Ingeniería Química, Universidad Nacional de Colombia sede Manizales, Apartado 127, Manizales, Colombia
[b] Planta Piloto de Ingeniería Química, PLAPIQUI–UNS–CONICET, Camino "La Carrindanga" Km. 7, 8000 Bahía Blanca, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 17 July 2009
Received in revised form
30 September 2009
Accepted 2 October 2009
Available online 9 October 2009

Keywords:
Vapor–liquid equilibrium
Low pressure
Parameters optimization
Reactive mixtures

ABSTRACT

In this work the vapor–liquid equilibria for nine binary mixtures (methanol + acetic acid, methanol + methyl acetate, methanol + water, methyl acetate + acetic acid, water + acetic acid, ethyl acetate + acetic acid, ethanol + acetic acid, ethanol + ethyl acetate and ethanol + water) at subatmospherical pressure (580 mmHg) is presented. Peng–Robinson Stryjek–Vera equation of state coupled with the Wong–Sandler mixing rules were used for predicting phase equilibria of these mixtures. The measurements were developed using an apparatus with recirculation that can also be employed for liquid–vapor equilibrium with chemical reaction.

Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.

1. Introduction

The interest in the reduction of both energetic and operation costs in chemical industries has allowed that technologies as reactive distillation acquire large importance at present time [1–5]. The applicability of this kind of processes where the reaction and separation stages are developed simultaneously is wide, due to the possibility to overcome thermodynamic limitations as chemical equilibrium and azeotropy. One of the main factors to take into account for the design of these processes is the thermodynamic behaviour of the system inside the column. Then, the simultaneous phase and chemical equilibria may be considered.

Experimentally, many types of apparatus for the study of the vapor–liquid equilibria (VLE) with or without chemical reaction have been used [6,7]. These equipments are classified according to their construction, operation and conversion reached inside the still. In this way, three configurations can be selected:

1. Static still: they are the simplest and economic equipments; their construction and operation is simple, but the time of stabilization is high, reason why they are obsolete and they are little used at the moment.
2. Recirculation still: the operation of these equipments is not so complex and the times of stabilization are smaller obtaining precise and reliable results. Implementation of the denominated Cottrell's bomb has allowed its extensive application at the present time.
3. Crossed flow stills: the main advantage of these equipments is that the kinetic of the system does not affect its performance, becoming a good selection alternative; however, it should be taken into account that their construction is expensive and the operation is complex.

The selection of the desirable configuration is done based on all of those considerations of cost, operation and conversion; under these conditions, several experimental works have been developed [7].

On the other hand, some authors have studied the VLE in the binary systems involving in this study [8–12]. But even though there are some similar investigations, there are not published VLE data of these mixtures at subatmospherical pressures.

In this work, nine binary systems (methanol + acetic acid, methanol + methyl acetate, methanol + water, methyl acetate + acetic acid, water + acetic acid, ethyl acetate + acetic acid, ethanol + acetic acid, ethanol + ethyl acetate and ethanol + water) have been studied experimentally. These systems are important in the design of reactive distillation processes, especially in the esterification of acetic acid with alcohols like methanol and ethanol to obtain methyl acetate and ethyl acetate, respectively. Experimental VLE data were obtained by using a recirculation still.

---

* Corresponding author. Tel.: +54 291 4861700x281; fax: +54 291 4861600.
E-mail address: jlopez@plapiqui.edu.ar (J.A. López).

[1] Current address: School of Chemical Engineering, Universidad del Valle, P.O. Box 25360, Cali, Colombia.

0378-3812/$ – see front matter. Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2009.10.002

Additionally, the binary interaction parameter of the second virial coefficient (k_{12}) and the non-random two liquid (NRTL) model parameters (τ_{12} and τ_{21}) were calculated for these nine binary systems at subatmospherical pressure (580 mmHg). Experimental data were correctly correlated using Peng–Robinson Stryjek–Vera equation of state (EOS) coupled with the Wong–Sandler mixing rules. Our principal goal is to examine experimentally only binary reactive systems at subatmospherical pressure, then to fit binary model parameters, and to extend from there on the calculation to multicomponent reactive systems.

2. Experimental

2.1. Apparatus and procedure

The studied binary systems were in their order: methanol–acetic acid, methanol–methyl acetate, methanol–water, methyl acetate–acetic acid, water–acetic acid, ethanol–acetic acid, ethanol–ethyl acetate, ethanol–water and ethyl acetate–acetic acid.

For the experimental determination of phase equilibrium, a recirculation still modified by Cardona [13] has been used. This equipment is also utilized to study phase equilibrium in systems with chemical reaction, and it is shown in Fig. 1. In this apparatus the fed sample is constantly recycled by means of a system type *Cottrell* (system that consists of a tube with an electrical resistance that vaporizes the mixture). This tube is connected to another one of smaller diameter which allows an intense recirculation in whole system to assure that the phases are in contact. After the first operation hour, samples are extracted every 15 min until reaching the stabilization of the system in study (approximately 2 h).

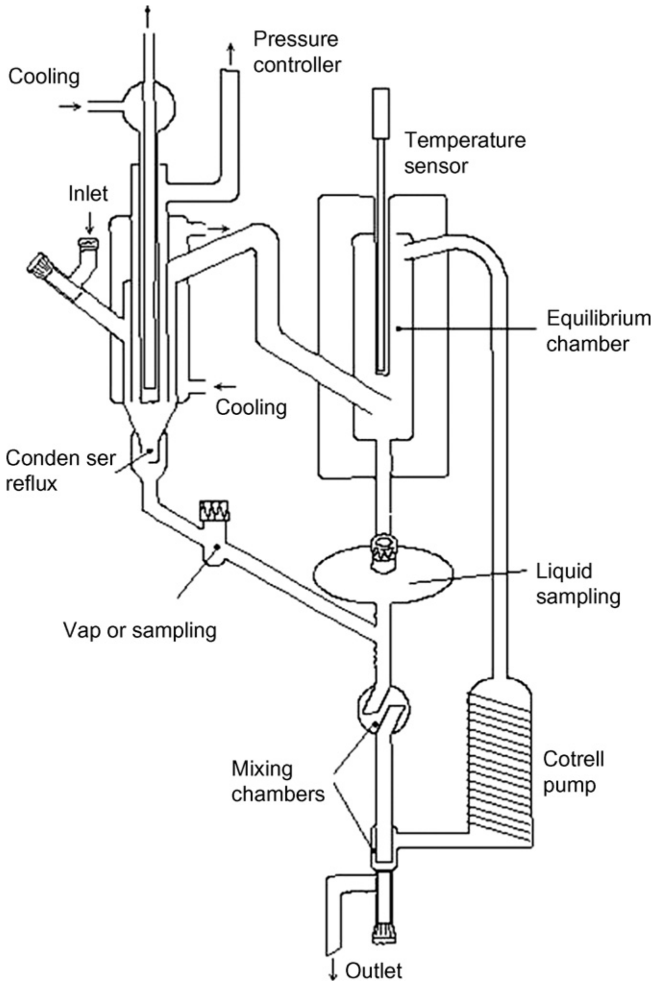

Fig. 1. Basic scheme of recirculation still.

Temperatures were measured by digital thermometers with ±0.05 °C. At the beginning of the every run, the pressure was measured with barometer CASIO. Alone if the pressure was of 580 mmHg (normal pressure in Manizales, 2167 m above sea level) the experiment were carried out. The samples of liquid and vapor obtained were analyzed together by means of refraction index and gas chromatography. The chromatograph used was a Perkin-Elmer Autosystem XL with identification column PE-WAX, which identifies the analyzed compounds correctly. The precision of the experimental measures was $\sigma(x_i) = \sigma(y_i) = 0.003$ for liquid and vapor concentrations, $\sigma(T) = 0.01$ K for temperature and $\sigma(P) = 0.1$ mmHg for pressure.

2.2. Chemicals

Acetic acid (GR grade, +99%), absolute ethanol (GR grade, +99%), methanol (GR grade, +99%), and ethyl acetate (GR grade, +99%) were purchased from Riedel-de Haen. Methyl acetate (GR grade, +99%) was purchased from Merck, and the deionized water (electric resistance, 18.2 MΩ/cm) was generated by a Millipore distilled water generator.

3. Equation of state and mixing rules used

The Peng–Robinson Stryjek–Vera (PRSV) equation of state [14] was used; this EOS has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

where P denotes pressure, T is the temperature, R is the ideal gas constant and the parameters a and b are the energy and size parameters which are calculated as follows:

$$a = 0.457235\frac{R^2T_c^2}{P_c}\alpha(T_r) \tag{2}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{3}$$

T_c and P_c are the critical temperature and pressure of each pure compound, respectively. And the correlation for the α function is

$$\alpha(T_r) = [1+\kappa(1-\sqrt{T_r})]^2 \tag{4}$$

Stryjek and Vera [14] modified the functional form of alpha function proposed by Soave [15] as follows:

$$\kappa = \kappa_0 + \kappa_1(1+\sqrt{T_r})(0.7-T_r) \tag{5}$$

and

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.171317848\omega^2 + 0.0196554\omega^3 \tag{6}$$

where κ_1 is a constant parameter for each pure component. To extend the PRSV EOS to mixtures the Wong–Sandler mixing rules [16] were used. Therefore, the a_m and b_m parameters have the following form:

$$b_m = \frac{\sum_i\sum_j z_i z_j (b-(a/RT))_{ij}}{1-\sum_i z_i(a_i/b_iRT)-(\underline{A}_{\infty}^{E}/\sigma RT)} \tag{7}$$

Download English Version:

https://daneshyari.com/en/article/203333

Download Persian Version:

https://daneshyari.com/article/203333

Daneshyari.com