



Bubble point pressures of binary system of methanol and methyl propionate

Alireza Shariati ^{a,*}, Louw J. Florusse ^b, Maaike C. Kroon ^c, Cor J. Peters ^{c,d}

^a Natural Gas Engineering Department, School of Chemical and Petroleum Engineering, Shiraz University, Molla Sadra Avenue, Shiraz, 71345, Iran

^b DelftChemTech, Delft University of Technology, Julianalaan 136, 2628, BL, Delft, The Netherlands

^c Separation Technology Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612, AZ, Eindhoven, The Netherlands

^d Chemical Engineering Department, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:

Received 30 October 2015

Received in revised form

18 February 2016

Accepted 21 February 2016

Available online 24 February 2016

Keywords:

Vapor–liquid equilibria

Raoult's law

Margules equation

Saturation pressure

ABSTRACT

In this work, bubble point pressures of the system of methanol + methyl propionate were measured for several isopleths within temperature and pressure ranges of 382–444 K and 0.437–2.285 MPa, respectively. The vapor pressures of pure methanol and methyl propionate were also measured. The two-suffix Margules equation was used to represent the nonidealities of the liquid phase and the virial equation of state was used to take into account the nonidealities of the vapor phase. The temperature-dependent parameter of the two-suffix Margules equation was determined using Barker's method. The results show that the model can successfully estimate the bubble points of this system with average errors less than 0.69%.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Methyl propionate is an ester which has a number of industrial applications; for example, it is used as a flavor or fragrance in the food or cosmetic industries, or as an intermediate in the chemical industry for producing other chemicals such as methyl methacrylate [1]. Methanol is one of the reactants which is used for producing methyl propionate along with ethylene and carbon monoxide, and therefore, for the design of a methyl propionate production plant, it is necessary to have accurate knowledge on the phase behavior of the constituents of the system.

Polak and Lu [2] reported the isothermal vapor–liquid equilibria of the system of methanol + methyl propionate for one isotherm (298 K) within a low pressure range ranging from 11.5 to 19.78 kPa. Blanco and Ortega [3] have also reported the vapor–liquid equilibria of the system of methanol + methyl propionate for one isobar (0.141 MPa) within a temperature range of 345–361 K. However, the investigated pressures and temperatures, which were studied by these groups, did not cover the complete range of industrial production pressures and temperatures. In this work, we have

measured the vapor pressures of pure methanol and methyl propionate in the temperature ranges of 391.86–444.52 K and 402.94–444.51 K, respectively, and the bubble point pressures of the binary mixtures of methanol + methyl propionate for several isopleths in the temperature range of 381.67–444.88 K. In this way, new data within the industrial range of operational temperatures and pressures for producing methyl propionate is presented [4]. In addition, using the isothermal pressure-composition data obtained from our experimental data, we have determined, and presented, the activity coefficient parameter of the two-suffix Margules model for the binary system of methanol and methyl propionate.

2. Experimental

Methanol was purchased from J.T. Baker with a purity of over 99.8%, and methyl propionate was obtained from Fluka with a purity of 99.8%. Table 1 shows the purity and supplier information of these chemicals. The bubble point pressures of several samples with different compositions were measured at a number of temperatures using an equipment called the Cailletet apparatus. The equilibrium cell of the Cailletet apparatus is a glass tube with an inside diameter of 3–4 mm. This tube is about 50 cm long and one end of the tube is closed. The sample with known composition is

* Corresponding author.

E-mail address: shariati@shirazu.ac.ir (A. Shariati).

Table 1
The suppliers and purities of the chemicals.

Chemical	Supplier	Purity, %
Methanol	J.T. Baker	99.8
Methyl Propionate	Fluka	99.8

injected into the Cailletet tube from the open end and mercury is used to seal the tube and also to transmit pressure to the sample. A glass jacket is fixed around the equilibrium tube in order to circulate thermostat fluid around the sample to keep the temperature fixed at a certain desired value. Shariati and Peters [5] have extensively explained the Cailletet apparatus.

For measuring the vapor pressures of pure methanol and pure methyl propionate, and also the bubble point pressures of binary mixtures of methanol + methyl propionate at several concentrations, visual measurements were performed for a sample with a fixed and known overall composition, the pressure was varied at a certain temperature until the last bubble of vapor disappeared. This pressure was recorded as the bubble point pressure of the mixture at that specific temperature [6].

In this work, silicone oil was used as the thermostat fluid. The bath temperature fluctuated no more than 0.04 K. For temperature measurements, a platinum-resistance thermometer was used very close to the equilibrated sample. The accuracy of the temperature readings were ± 0.01 K. The pressure was kept constant and measured using a dead weight gauge with an accuracy of ± 0.003 MPa. Shariati and Peters have previously explained the gas solubility measurements extensively [7].

3. Modeling

In this work, the gamma–phi formulation [8] was used to calculate the bubble point pressures. Such an approach should be used instead of the Raoult's law for systems whose vapor and liquid phases are considered to be nonideal. Including the fugacity coefficient in the formulation corrects for the vapor phase nonidealities, while the nonidealities in the liquid phase are taken into account by including the activity coefficient term. For the binary system of methanol + methyl propionate, the gamma–phi formulation becomes:

$$P = \frac{x_1 \gamma_1 P_1^{sat} \varphi_1^{sat}}{\hat{\varphi}_1} + \frac{x_2 \gamma_2 P_2^{sat} \varphi_2^{sat}}{\hat{\varphi}_2} \quad (1)$$

In Eq. (1), P is the bubble point pressure, x_1 and x_2 are the mole fractions, γ_1 and γ_2 are the activity coefficients, P_1^{sat} and P_2^{sat} are the vapor pressures of methanol (1) and methyl propionate (2), respectively. In addition, φ_1^{sat} and φ_2^{sat} are the corresponding fugacity coefficients at the system temperature and the vapor pressures of the pure components, and $\hat{\varphi}_1$ and $\hat{\varphi}_2$ are the fugacity coefficients of components 1 and 2 in the mixture at the system temperature and pressure, respectively.

It is also possible to calculate the vapor phase compositions using the gamma–phi formulation, by the following equation:

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat} \varphi_1^{sat}}{P \hat{\varphi}_1} \quad (2)$$

and

$$y_2 = 1 - y_1 \quad (3)$$

The two-suffix Margules [9] model was selected for considering the nonidealities in the liquid phase:

$$\frac{G^E}{RT} = Ax_1 x_2 \quad (4)$$

where, G^E is the excess Gibbs energy and A is the model parameter which is only a function of temperature. Using the excess Gibbs energy model of Eq. (4) and the definition of the partial properties, the activity coefficients of methanol and methyl propionate have the following relations, respectively, with composition and temperature:

$$\ln \gamma_1 = Ax_2^2 \quad (5)$$

and

$$\ln \gamma_2 = Ax_1^2 \quad (6)$$

The virial equation of state was used to determine φ_1^{sat} and φ_2^{sat} for the pure components, and $\hat{\varphi}_1$ and $\hat{\varphi}_2$ for components 1 and 2 in the mixture using the following equations:

$$\ln \varphi_1^{sat} = \frac{B_{11} P_1^{sat}}{RT} \quad (7)$$

$$\ln \varphi_2^{sat} = \frac{B_{22} P_2^{sat}}{RT} \quad (8)$$

$$\ln \hat{\varphi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12}) \quad (9)$$

and

$$\ln \hat{\varphi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12}) \quad (10)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (11)$$

In the above equations, B 's indicate the second virial coefficients which are determined by the approximation methods described in Ref. [8].

4. Results and discussion

Table 2 presents the experimentally measured pressure–temperature (P – T) data for the binary system of methanol + methyl propionate for eight different isopleths in the temperature and pressure ranges of 381.67–444.88 K and 0.437–2.285 MPa, respectively. The data at 0 and 1 in mole fraction are the vapor pressure data of pure methyl propionate and methanol, respectively, and the remaining data represent the bubble point curves of the binary mixture of methanol and methyl propionate at six different isopleths. Table 3 shows the parameters of the Antoine equation for methanol and methyl propionate, which were optimized based on the vapor pressure data of Table 2. It is clear from the pure-component data that methanol is more volatile than methyl propionate, with higher vapor pressures at each temperature. Fig. 1 shows the P – T data of this binary system graphically. The isopleths of Fig. 1 indicate that with increasing methanol mole fraction at constant temperature, the bubble point pressure of the system reaches a maximum and then marginally decreases. Fig. 2 shows this phenomenon on a P – x diagram for the four isotherms of 410, 420, 430, and 440 K. These isothermal P – x diagrams were determined by fitting polynomial functions to the experimental P – T data at each composition. Each isotherm has a

Download English Version:

<https://daneshyari.com/en/article/200819>

Download Persian Version:

<https://daneshyari.com/article/200819>

[Daneshyari.com](https://daneshyari.com)