



Isobaric vapor-liquid equilibrium for binary system of methyl caprate + methyl laurate at 2, 4 and 6 kPa



Hui Ding^a, Wenjing Ke^b, Dan Zhao^a, Lulu Wang^a, Yujie Gao^c, Shejiang Liu^{a,*}

^a School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China

^b School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^c Tianjin Academy of Environmental Sciences, Tianjin 300191, China

ARTICLE INFO

Article history:

Received 22 December 2016

Received in revised form 27 August 2017

Accepted 17 September 2017

Available online 20 September 2017

Keywords:

Methyl caprate

Methyl laurate

Vapor-liquid equilibrium

NRTL

UNIFAC

COSMO-SAC

ABSTRACT

In this work, we measured the isobaric vapor-liquid equilibrium (VLE) data for the binary system of methyl caprate (1) + methyl laurate (2) at 2, 4 and 6 kPa with a modified Othmer still. The point consistency test of Van Ness test method was applied to check the thermodynamic consistency of all the experimental values, which guaranteed the reliability of our measurements. Afterwards, the experimental data were regressed by two activity coefficient models (Wilson, NRTL). Furthermore, we made the data prediction with the group contribution method (UNIFAC) and the COSMO-SAC model. The results of all the regressions and predictions are satisfying and reasonable, while the results provided by the NRTL model are relatively better than the other three models, with the root mean square deviations of temperature and vapor-phase mole fraction less than 0.33 K and 0.0069, respectively.

© 2017 Elsevier Ltd.

1. Introduction

Methyl caprate and methyl laurate are two significant vegetable-based fatty acid esters which typically exist in the biodiesel production [1–3]. However, the fine separation of them from the biodiesel could generate higher added values. In recent years, they are enjoying widely application in the chemical industry, such as in the preparation of food, pharmaceuticals, cosmetics [4], solvents, plasticizers [5], detergents, surfactants, lubricants [6], and antibacterial agents [7]. Furthermore, new applications of them have been exploited now. Leah C. Liston et al. [8] and Yaghoob Farnam et al. [9] have revealed the novel use of methyl laurate as the phase change materials in concrete pavements. For another, they have also been used as raw materials to produce higher alcohols [10,11].

To the best of our knowledge, the physicochemical properties and the VLE data are essential information for the fine separation and better application of them. However, the related study is far from adequate. Currently, quite a few researches relevant to their physicochemical properties have been reported. Monika Zarska et al. [12] measured the speed of sound and the densities of methyl caprate and methyl laurate. Based on the experimental results, a

function has been established for the calculation of their densities, isobaric thermal expansivities and isentropic compressibilities. By determining the densities and viscosities of seven ethyl esters and eight methyl esters, reliable models for the computation of the densities and the viscosities of biodiesel fuel were proposed by Maria Jorge Pratas et al. [13]. Using the pulse-heating method, Nikitin et al. [14] obtained the critical temperatures and pressures of methyl esters $C_nH_{2n}O_2CH_3$ ($n = 6, 7, 8, 9, 10, 11, 12$), and the equations for the calculation of the critical temperatures and pressures were hereby developed. In addition, Xiangyang Liu et al. [3] determined the isobaric molar heat capacities of methyl caprate and methyl laurate within the temperatures from 300 K to 380 K and at pressures from 0.1 MPa to 4.25 MPa.

All the above researches have provided important basic information about their physicochemical properties, which is of great help for their industrial application. Nevertheless, the works concerning the phase equilibrium behavior are scarce. It is known to all that the phase equilibrium behavior is a significant property for their fine separation in the field of distillation. Only few works have been revealed. The work by N. Bureau et al. [15] reported the vapor pressure of some heavy fatty acid esters including methyl laurate and the work by Troy A. Scott et al. [16] presented the vapor pressure of both methyl caprate and methyl laurate. As for the vapor-liquid equilibrium for binary system of methyl caprate and methyl laurate, we have only located the work by Rose et al. [17], in which 3 to 6 VLE data points at 30, 40, 50 and 100 mmHg

* Corresponding author.

E-mail address: liushejiang@163.com (S. Liu).

were covered and are now provided in the Supplementary Material (Table S1). None of the data were checked or regressed by any thermodynamic models. Regrettably, obvious mistakes also existed in the data. Hence, the industrial cannot use these data as a guide for the vacuum distillation directly. For more complete research and considering the significance of the VLE data in the vacuum distillation, here in this work, the isobaric VLE data for binary system of methyl caprate and methyl laurate at 2, 4 and 6 kPa were measured with a modified Othmer still. First, the Van Ness test [18] was employed to check the thermodynamic consistency of the obtained data. Then, the experimental values were regressed with the Wilson and the Nonrandom two-liquid (NRTL) activity coefficient models. Furthermore, the UNIFAC model was applied to make a data prediction. Finally, the newly established COSMO-SAC model was also adopted for the prediction of the VLE data of the binary system. The activity coefficients of each material were acquired from the COSMO-SAC model. And based on the calculated activity coefficients, the composition of vapor-phase at each point was achieved.

2. Experiment

2.1. Materials

The purities, sources, water contents and CAS registry numbers of the reagents used are recorded in Table 1. Only trace impurities in the two reagents were detected by gas chromatography (GC 2060, China) with flame ionization detector (FID). The water contents of the two reagents were determined by the method of Karl Fischer titration. Thus, the materials were used without further dehydrating or purification.

2.2. Apparatus and procedure

All the VLE data were measured with a modified Othmer still, which has a total internal volume of about 50 ml. The reliability of the still was validated in our previous works [19,20]. The flow-chart of the experimental apparatus and the details of the still were shown in Fig. 1. In this modified Othmer still, continuous and intimate contacts between the liquid phase and the condensed vapor phase were achieved and thus the system could be equilibrated rapidly. First, a liquid solution with a volume of 40 ml was added into the still from the liquid-phase sampling port. After all the connectors were sealed, the vacuum pump (Deying, Shanghai, China) was started to evacuate the system. The operational pressures were measured with a U-shaped differential manometer filled with mercury, whose standard uncertainty was $0.05 \cdot P$ (P represented the operational pressure). The desired pressures were reached by adjusting the needle valve. And after the pressures were kept fixed for about 30 min, the heating bar started to heat the liquid solution. A mercury thermometer with a standard uncertainty of 0.3 K was used to determine the temperatures. When the pressure and temperature were kept constant for about 45 min, the equilibrium was assumed to be achieved. Then the samples of the liquid

phase and condensed vapor phase were taken from both sampling ports and analyzed by GC.

2.3. Analysis

A gas chromatography (GC 2060, China) equipped with a flame ionization detector (FID) and a PC-88 column (30 m, 0.45 mm, 2.55 μm) was applied to analyze the liquid-phase and vapor-phase compositions. And high purity nitrogen (99.999%) was used as the carrier gas with a fixed flow rate of 1 ml/min. The temperatures of the injector and the detector were both kept at 523.15 K. While the column temperature was first fixed at 413.15 K for 2 min, and then increased to 463.15 K at 5 K/min, and held for 1 min.

The calibration of the GC was made with 15 standard solutions gravimetrically prepared by an electronic balance (FA2004N, uncertainty of ± 0.0001 g). For each sample, three paralleled analyses were made. When the deviations between the measurements were less than 0.5%, we recorded the mean values and converted the data to mole fractions according to the standard curve.

3. Results and discussion

3.1. Experimental results

The isobaric VLE data of the binary system of methyl caprate and methyl laurate were determined and recorded in Tables 2–4. The boiling points of the two pure components at 2, 4, and 6 kPa were measured in this work and the corresponding comparisons to earlier measurements from other publications [15–17,21–30] were made. The corresponding percent deviations of pressure of all the experimental data from the Antoine equation for the two pure components were calculated and illustrated in Figs. 2 and 3. In Fig. 2, all the percent deviations of pressure for pure methyl caprate are within $\pm 15\%$, except for individual data points. While what is shown in Fig. 3 is that most of the percent deviations of pressure for pure methyl laurate are between -30% and 20% , except for some individual points. However, the percent deviations of pressure for the two pure components measured in this work are located in the range of -5% to 10% , which demonstrates that our measurements are reasonable and reliable. In addition, a comparison of our measured VLE data at 4 kPa for the binary system with the data provided by Rose, A. et al. was made and graphically shown in Fig. 4. Noticeable yet acceptable deviations between our measurements and the literature data were seen, which were mainly due to the equipments that used for the analysis of the liquid phase and condensed vapor phase samples. In this work, a gas chromatography (GC 2060, China) was used to determine all the samples and the data provided by Rose, A. et al. were obtained from a refractometer. Obviously, a GC and a refractometer have different systemic errors. Also different researchers may practice differently in the data reading. Thus, noticeable yet accredited deviations exist. And for more complete analysis, a deviation plot of the data of Ref. [17] relative to the NRTL model developed in this work were shown in Fig. 5.

Table 1
Specification of chemical reagents.

Chemical name	Sources	CAS RN	Mass fraction purity	Water content ^b (mass %)	Analysis
Methyl caprate	Shanghai Macklin Biochemical Co., Ltd	110–42–9	0.995	0.090%	GC ^a
Methyl laurate	Shanghai Aladdin Bio-Chem Technology Co., Ltd	111–82–0	0.998	0.077%	GC

^a Gas chromatography: Fig. S1, Supplementary Material.

^b Karl Fischer titration.

Download English Version:

<https://daneshyari.com/en/article/4907215>

Download Persian Version:

<https://daneshyari.com/article/4907215>

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