J. Chem. Thermodynamics 128 (2019) 215–224

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Measurement and correlation of vapor–liquid equilibrium data for binary and ternary systems composed of (−)-β-caryophyllene, p-cymene and 3-carene at 101.33 kPa

Guangyan Yao, Linlin Wang *, Xiaopeng Chen *, Dankui Liao, Xiaojie Wei, Jiezhen Liang, Zhangfa Tong

Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

ARTICLE INFO

Article history:
Received 14 November 2017
Received in revised form 11 July 2018
Accepted 10 August 2018
Available online 11 August 2018

Keywords:
(−)-β-caryophyllene
p-cymene
3-carene
Vapor–liquid equilibrium

ABSTRACT

New experimental vapor–liquid equilibrium (VLE) data for three binary systems composed of p-cymene + (−)-β-caryophyllene, 3-carene + (−)-β-caryophyllene, and 3-carene + p-cymene and for the ternary system of (−)-β-caryophyllene + p-cymene + 3-carene were obtained using a modified Ellis equilibrium still over the temperature range from 444.44 to 528.78 K at 101.33 kPa. The compositions of these mixtures were assessed using gas chromatography. The VLE data for the binary systems passed thermodynamic consistency tests based on the Herington method and Van Ness test. The thermodynamic consistency of the ternary system was checked by a Van Ness test. The VLE data for binary systems were correlated using the Wilson, NRTL, and UNIQUAC activity coefficient models with minor deviations. The ternary VLE data were also satisfactorily correlated using the Wilson, NRTL and UNIQUAC models. By comparing the experimental values for the ternary system with the values calculated using the three models, the average absolute deviation of the equilibrium temperature and vapor–phase composition were determined to be less than 0.57 K and 0.0060, respectively. These results indicated excellent agreement of the models with experimental values.

1. Introduction

Heavy turpentine is derived from wood turpentine obtained from pine trees, and its primary components are sesquiterpenes such as (−)-β-caryophyllene and longifolene. Heavy turpentine also contains some monoterpenes, including p-cymene and 3-carene, which are widely used in the synthesis of drugs and fragrances. (−)-β-Caryophyllene is a type of natural bicyclic sesquiterpene [1] linked to rotenone and is reported to be effective against Parkinson's disease [2]. Basha et al. [3] also determined that (−)-β-caryophyllene can effectively decrease the hyperglycemia caused by streptozotocin. In addition, (−)-β-caryophyllene has been commonly used as a fragrance chemical since the 1930s [4]. In Sköld's study [5], 45% of deodorants on the European market in 1998 contained (−)-β-caryophyllene. The chemical p-cymene is an important organic synthesis intermediate [6] and has a wide range of applications, including as an additive in musk fragrances and perfumes [7], anti-inflammatory and antimicrobial agents [8] and solvent for varnishes and dyes [9]. It is known that p-cymene is having an increasing effect on the environment [10]. Meanwhile, 3-carene is one of the few natural chiral compounds with a special ternary ring structure along with biological activity [11]. This compound has applications in a variety of edible flavors [12,13], as well as in pesticides and pharmaceuticals [14], and is also important in many precious chemicals such as plasticizers and non-toxic solvents [15].

The vapor–liquid equilibrium (VLE) data for binary and ternary mixtures containing heavy turpentine represent fundamental thermodynamic properties, and play a major role in the design and operation of industrial separation processes. These data are also important for the testing and extension of fluid mixture theories. However, it is difficult to obtain VLE data for such mixtures because of their high boiling points and viscosities. Thus, VLE data for the heavy turpentine systems have not yet been reported; only some values for binary or ternary mixtures of light turpentine are found in the literature. For example, Bernardo-Gil et al. provided data for the binary systems consisting of α-pinene + p-cymene [16] and α-pinene + β-pinene [17]. Existing ternary VLE information is insufficient. The same group published some VLE results for the α-pinene + β-pinene + (S)-(−)-limonene system [18], and Sun et al. [19] reported VLE results for β-pinene + p-cymene + (S)-(−)-limonene.

* Corresponding author.
E-mail addresses: wanglinlin1971@163.com (L. Wang), lilm@gxu.edu.cn (X. Chen).

https://doi.org/10.1016/j.jct.2018.08.015
0021-9614/

In this work, a modified Ellis apparatus was used to allow the investigate of the vapor–liquid phase behavior of mixtures containing heavy turpentine system components with high boiling-points and viscosities. Experimental VLE data for the binary systems *p*-cymene + (−)-*β*-caryophyllene, 3-carene + (−)-*β*-caryophyllene and 3-carene + *p*-cymene as well as the ternary system (−)-*β*-caryophyllene + *p*-cymene + 3-carene are acquired at 101.33 kPa. The thermodynamic consistency of the VLE measurements is checked using the Herington method [20] and Van Ness test [21]. In addition, the activity coefficients are calculated and correlated with the Wilson [22], NRTL [23], and UNIQUAC [24] models using Aspen Plus V8.4. The binary interaction parameters are obtained for use in the optimization and design of separation processes of these systems.

2. Experimental

2.1. Chemicals

The (−)-*β*-caryophyllene (minimum mass fraction of 0.98), *p*-cymene (minimum mass fraction of 0.97), and 3-carene (minimum mass fraction of 0.97) used in this work were all of analytical-reagent grade and purchased from Tokyo Chemical Industry Co., Ltd., Shanghai (TCI). These compounds were purified by redistillation under the protection of high-purity nitrogen (each to a mass fraction of greater than 0.995) before use. The purity of these materials was determined by gas chromatography (GC, Agilent7890B) in conjunction with a flame ionization detector and HP-5 column (30 m × 0.32 mm × 0.25 μm). The sources, purity, and analysis method of reagents are summarized in Table 1. The experimental densities of the three pure compounds were determined using an Anton Paar DMA 4500 M densimeter, calibrated with dry air and pure water at atmospheric pressure. The uncertainty in the resulting density values was 0.001 g·cm^{-3} . The physical properties of these reagents are summarized in Table 2.

2.2. Apparatus and procedure

The Ellis equilibrium still is commonly used for the determination of VLE data [43] at normal pressure and temperature below 423.15 K [43,44]. To our knowledge, few report has been published about the VLE data above 473.15 K.

A modified Ellis equilibrium still was used to assess the vapor–liquid phase behavior of mixtures containing heavy turpentine with high boiling points and viscosities. A diagram of the equipment is presented in Fig. 1. An ordinary Ellis equilibrium still placed in the open environment and would be expected to exhibit considerable heat dissipation via convection when operated at high temperature (above 473.15 K), thus making it difficult to balance the liquid and vapor temperature ($T_{vapor} = T_{liquid}$) and produce in inaccurate data, especially when the mixtures contain heavy turpentine. Therefore, a variety of techniques were used to avoid convection. First, we designed a thermally insulating wooden case (430 × 260 × 700 mm) coated on the inside with a temperature-resistant silver anti-radiation paint. A glass door with a black flannel curtain was installed in the front of the wooden case to allow visual observation of the interior. In addition, the exterior of the equilibrium still was wrapped with fiberglass acting as a thermal insulation material, with heating wires coiled inside. The heating wires were controlled by an external artificial intelligence industrial regulator to adjust the heat preservation temperature. The temperature was measured by a precision mercury-in-glass thermometer. The dew neck calibration of the thermometer was determined using Eq. (1):

$$T = t_{obs} + 0.00016 \times h \times (t_{obs} - t_{amb}) + 273.15 \quad (1)$$

where T is the boiling point temperature (K), t_{obs} and t_{amb} are the observed and room temperatures (°C), respectively, and h is the thermometer height of the external part of the still (°C).

The modified Ellis equilibrium still had a total capacity of about 250 mL and was heated with stirring at a set speed. Cooling water was circulated through the reflux condenser. After boiling

Table 1
Materials description.

Chemical name	CAS	Source	Initial mole fraction purity	Final mole fraction purity	Purification method	Analysis Method
3-carene	13466-78-9	TCI	0.97	>0.995	Distillation	GC[a]
p-cymene	99-87-6	TCI	0.97	>0.995	Distillation	GC[a]
(−)-*β*-caryophyllene	87-44-5	TCI	0.98	>0.995	Distillation	GC[a]

[a] Gas chromatograph.

Table 2
Normal boiling point (T_b) and density (ρ) of pure components.

Substance	T_b (101.33 kPa)/K[a]		ρ(298.15 K)/(g·cm^{-3})[b]		
	This work	Literature	This work		Literature
3-carene	444.44	445.15 ~ 446.15 [25] 444.75 [26] 443.14 [27] 444.84 [28]	P_{exp}/kPa 100.51	0.8638	0.8618 [25] 0.8623 [29] 0.8611[26] 0.8609 [30]
p-cymene	450.28	429 ~ 450.30 [31] 450.40 [32] 450.38 [33] 451.99 [34]	100.35	0.8532	0.8535 [28,34] 0.8521 [35] 0.8523 [36] 0.8533 [37] 0.8529 [38]
(−)-*β*-caryophyllene	528.78	527.15 ~ 530.15 [39] 528.15 [40]	100.68	0.8968	0.8995 [41] 0.8971 [42]

[a] Standard uncertainties u are $u(T) = 0.6$ K, $u(P) = 0.2$ kPa.
[b] Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(\rho) = 0.001$ g·cm^{-3}.