Fluid Phase Equilibria 420 (2016) 50–57

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Vapor-liquid equilibria of binary and ternary mixtures containing ethyl lactate and effect of ethyl lactate as entrainer

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ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form
4 December 2015
Accepted 17 December 2015
Available online 21 December 2015

Keywords:
Vapor–liquid equilibria
Ethyl lactate
Entrainer

ABSTRACT

This work investigated the effect of ethyl lactate as an entrainer for separation of a binary azeotropic system. Isobaric vapor–liquid equilibria (VLE) were determined for three binary systems, including methyl acetate + methanol, methyl acetate + ethyl lactate, and methanol + ethyl lactate using ebulliometry. Experimental VLE data were represented by the Wilson and NRTL models. The effect of ethyl lactate was evaluated by two approaches, including residue curve maps and calculation of S_{12} separation factors using binary Wilson parameters. Both the residue curve maps and the separation factors showed that ethyl lactate acted as an entrainer for extractive distillation of the binary azeotropic system methyl acetate + methanol. VLE for the ternary system methyl acetate + methanol + ethyl lactate were also measured, and the prediction of the behavior of this ternary system using the binary Wilson or NRTL parameters showed excellent agreement with the experimental VLE data.

1. Introduction

Ethyl lactate is a biomass-derived solvent. It can be easily produced from ethanol and lactic acid, which are obtained by fermentation of biomass. It is found in beer, wine, and soy products. Ethyl lactate has excellent properties as a solvent, such as low toxicity, relatively low volatility, low viscosity, and good biodegradability, and recyclability. Consequently, it has attracted much attention in recent years as a promising candidate to replace toxic organic solvents and volatile organic compounds [1–3]. Because of its low toxicity, ethyl lactate is approved by the US Food and Drug Administration as a pharmaceutical and food additive [1,2]. It has been widely used as a green solvent in several applications, such as organic synthesis, and in fragrances, inks, and coatings. Because of its features, ethyl lactate could be used as a solvent for green separation and purification.

Ethyl lactate could be applied as an entrainer for the separation of a binary azeotropic system by extractive distillation. To design an extractive distillation process, vapor–liquid equilibrium (VLE) data are required. In particular, knowledge of the enhancement of the separation factor in a binary azeotropic system with addition of an entrainer is important. Gmehling and Möllmann [4] have defined the following criteria for selection of an entrainer for extractive distillation: (a) the entrainer should exhibit zeotropic behavior with all components of the system to be separated; (b) to achieve separation factors far from unity, the entrainer should alter the activity coefficients of the components to be separated to different extents; and (c) for convenient recovery of the entrainer, its boiling point must be sufficiently higher (e.g., $\Delta T = 40$ K) than that of any of the components of the system to be separated.

The aim of this work was to investigate the use of ethyl lactate as an entrainer. Ethyl lactate would satisfy the criteria of Gmehling and Möllmann [4]. We selected methyl acetate + methanol as the binary azeotrope system. Isobaric VLE data for three binary systems, methyl acetate + methanol, methyl acetate + ethyl lactate, and methanol + ethyl lactate, were measured at pressures between 40.00 and 101.3 kPa by ebulliometry. The experimental VLE data were evaluated using the Wilson and non-random two-liquid (NRTL) models. The solvent effects of ethyl lactate were evaluated by two approaches, including residue curve maps and calculation of separation factors (S_{12}) using the binary parameters obtained from the binary VLE data. VLE data for the ternary system methyl acetate + methanol + ethyl lactate were also measured, and the predicted behavior of this ternary system using binary Wilson or NRTL parameters was compared with the experimental VLE data.

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http://dx.doi.org/10.1016/j.fluid.2015.12.029
0378-3812/

Table 1
Chemicals used in this work.

Component	Source	Grade	Molecular sieve	Purity (mass fraction)
Methyl acetate	Wako Pure Chemical Industries	Special grade	4A	>0.999
Methanol			3A	>0.999
Ethyl lactate			13X	>0.995

Table 2
Normal boiling points (T_b), densities at 298.15 K (ρ), and liquid molar volumes at 298.15 K (v_i^L) of the pure components used in this study.[a]

Component	T_b (K)		ρ (298.15 K) (kg m^{-3})		$v_i^L \times 10^6$ (m^3 mol^{-1})
	Experimental	Literature	Experimental	Literature	
Methyl acetate	330.04	330.018[b]	927.10	927.9[b]	79.90
Methanol	337.60	337.696[b]	786.56	786.37[b]	40.73
Ethyl lactate	426.10	427.7[b] 424.98[c]	1028.08	1027.2[b] 1028.0[c]	114.90

[a] Standard uncertainties u are $u(\rho) = \pm 0.01$ kg/m^3, $u(T) = \pm 0.01$ K, $u(P) = \pm 1$ kPa.
[b] Ref. [5].
[c] Ref. [6].

Table 3
Experimental vapor pressures of the pure components used in this work.[a]

P (kPa)	T (K)		
	Methyl acetate	Methanol	Ethyl lactate
40.00	305.65	315.49	396.91
53.33	312.68	321.98	405.49
66.66	318.45	327.23	412.44
79.99	323.36	331.66	418.34
93.32	327.68	335.51	423.47
101.3	330.04	337.60	426.10

[a] Standard uncertainties u are $u(T) = \pm 0.03$ K, $u(P) = \pm 0.03$ kPa.

2. Experimental

2.1. Materials

The chemicals used in this work are summarized in Table 1. The purities of the materials were checked by gas chromatography (GC-4000, GL Sciences Co., Ltd., Tokyo, Japan) with a thermal conductivity detector. The water contents of all chemicals were checked using a Karl Fischer moisture meter (CA-200, Mitsubishi Chemical Co., Ltd., Tokyo, Japan), and were less than 100 ppm. Normal boiling points (T_b) were measured using a modified Swietoslawski-type ebulliometer (details are given in Section 2.2). The densities (ρ) at $T = 298.15$ K and $P = 0.1$ MPa were also measured using a precision digital oscillating U-tube density meter (DMA 4500, Anton Paar, Graz, Austria) with a reproducibility of 10^{-2} kg/m^3. The experimental T_b and ρ at 298.15 K of the chemicals used in this work are shown in Table 2 together with the literature values [5,6].

Tables 3 and 4 show the experimental vapor pressures and the Antoine constants, respectively, of the compounds investigated in this work. The Antoine constants in Table 4 were determined from the experimental vapor pressure data. The average deviations between the experimental values and those calculated using the Antoine constants in the literature [7,8] were within 0.47 kPa. Except for ethyl lactate, the vapor pressures calculated using the Antoine constants determined in this work deviated from those in the literature [9,10] by 0.51 kPa on average.

2.2. Apparatus and procedure

A modified Swietoslawski-type ebulliometer was used to measure the boiling points. The equipment and the measurement procedure have been described elsewhere [11,12]. The apparatus consisted of an ebulliometer, a pressure-controlling circuit, and a computer to analyze the data. Boiling points were measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K. The pressure in the apparatus was established by a pressure controller (DPI515, Druck Co., Kirchentellinsfurt, Germany). The uncertainty in the pressure was estimated to be ±0.03 kPa. For our measurements, the ebulliometer was charged with approximately 160 cm^3 of a mixture with known constituents. The liquid mole fraction was determined gravimetrically (Mettler digital balance model AX504, Mettler-Toledo Inc., Columbus, OH, USA) with a sensitivity of 0.1 mg. The uncertainty in the mole fraction was estimated to be ±0.0001. Steady state was assumed when the temperature oscillated by no more than 0.02 K/min. The uncertainty in the experimental temperature boiling point was estimated to be ±0.03 K. Boiling point measurements for a given mixture were performed at progressively higher system pressures. For this work,

Table 4
Antoine equation constants[a] determined for pure components used in this work.

Component	Determined Antoine constants			Literature Antoine constants				$\lvert \Delta P_i^s \rvert_{av.}$ (kPa)[b]	Reference (vapor pressure)	$\lvert \Delta P_i^s \rvert_{av.}$ (kPa)[c]
	A	B	C	A	B	C	Reference			
Methyl acetate	6.20814	1168.97	−51.831	6.18621	1156.43	−53.46	[7]	0.22	[9]	0.13
Methanol	7.13230	1553.46	−34.588	7.20277	1580.08	−33.65	[7]	0.44	[10]	0.51
Ethyl lactate	6.74990	1776.94	−51.719	6.60607	1673.80	−62.21	[8]	0.47		

[a] $\log(P_i^s/\text{kPa}) = A - B/[(T/\text{K}) + C]$.
[b] $\lvert \Delta P_i^s \rvert_{av.} = \sum_{k=1}^{NDP} \left| P_{i,\text{exptl}}^s - P_{i,\text{calcd}}^s \right|_k / \text{NDP}$, where $P_{i,\text{exptl}}^s$ is the experimental vapor pressure, and $P_{i,\text{calcd}}^s$ is the vapor pressure calculated using Antoine constants from the literature values.
[c] $\lvert \Delta P_i^s \rvert_{av.} = \sum_{k=1}^{NDP} \left| P_{i,\text{lit}}^s - P_{i,\text{calcd}}^s \right|_k / \text{NDP}$, where $P_{i,\text{lit}}^s$ is the literature vapor pressure, and $P_{i,\text{calcd}}^s$ is the vapor pressure calculated using the Antoine constants determined in this work.