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Sample of Proceedings

Solvent Effects of Ethyl Lactate as an Entrainer for the Separation of the Binary Azeotropic Mixture by Extractive Distillation

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Abstract

The object of this study is to consider a solvent effect of ethyl lactate as an entrainer candidate. We selected methyl acetate + methanol as a binary azeotropic system. Isobaric VLE for three binary systems methyl acetate + methanol, methyl acetate + ethyl lactate, and methanol + ethyl lactate were determined by an ebulliometric method. Experimental VLE data were represented by the Wilson and NRTL models. The solvent effects of ethyl lactate were evaluated by two approaches, i.e., the residue curve maps and the calculation of the separation factors α_{12} using the binary Wilson or NRTL parameters. Both of the calculated results for the residue curve maps and the separation factors show that ethyl lactate can be used as 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 this ternary system using the binary Wilson or NRTL parameters agreed well with the experimental VLE data.

Keywords

Vapor-liquid equilibria, Ethyl lactate, Entrainer

1. Introduction

Lactate esters have attracted a great deal of interest environmentally friendly solvents

from renewable feedstocks. Lactate esters, especially ethyl lactate, have excellent solvent properties and low toxicity and are candidates to replace toxic organic solvents and VOCs [1-3]. Ethyl lactate exists in beer, wine, and soy products, and it has been approved by the FDA for use in food industries for many years [1, 2]. If lactate esters can be used as a solvent for separation and purification process, a development of greener process would be possible.

In this work, we examine ethyl lactate as an environmentally friendly entrainer for the separation of the binary azeotropic system by extractive distillation. For the design of extractive distillation processes, a reliable knowledge of vapor-liquid equilibrium (VLE) data is required. In particular, the knowledge of the enhancement of the separation factor of the binary azeotropic system by addition of an entrainer is important.

The object of this study is to consider a solvent effect of ethyl lactate as an entrainer candidate. We selected methyl acetate + methanol as a binary azeotrope system. Ethyl lactate would satisfy criteria for the selection of entrainers for the separation of this system by extractive distillation shown by Gmehling and Möllmann [4]: (a) the entrainer is supposed to exhibit zeotropic behavior with all components of the system to be separated; (b) the entrainer should alter the activity coefficients of the components to be separated to different extents, in order to achieve separation factors far from unity; and (c) for convenient recovery of the entrainer, its boiling point must usually be sufficiently higher (e.g., $\Delta T = 40$ K) than that of any of the components of the system to be separated. Isobaric VLE for three binary systems methyl acetate + methanol, methyl acetate + ethyl lactate, and methanol + ethyl lactate were measured at pressures 40.00 to 101.3 kPa by an ebulliometric method. Experimental VLE data were represented by the Wilson and NRTL models. The solvent effects of ethyl lactate were evaluated by two approaches, i.e., the residue curve maps and the calculation of the separation factors α_{12} using the binary parameters obtained from the binary VLE data. VLE for the ternary system methyl acetate + methanol + ethyl lactate were also measured, and the prediction of this ternary system using the binary Wilson or NRTL parameters were compared with the experimental VLE data.

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 chromatograph (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. The purities were further confirmed by measuring normal boiling points (T_b) and densities (ρ) at 298.15 K. T_b were measured using a modified Swietoslawski-type ebulliometer (details are given in next section). ρ at 298.15 K were measured using a precision digital Anton

Paar oscillating u-tube densimeter (DMA 4500) with a reproducibility of 10^{-2} kg m⁻³. 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].

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 , liquid molar volumes at 298.15 K, v_i^L , of pure components used in this study.

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 ^a	927.10	927.9 ^a	79.90
Methanol	337.60	337.696 ^a	786.56	786.37 ^a	40.73
Ethyl lactate	426.10	427.7 ^a 424.98 ^b	1028.08	1027.2 ^a 1028.02 ^b	114.90

^a Ref. [5]

^b Ref. [6]

Tables 3 and 4, respectively, show the experimental vapor pressures and the Antoine constants of the compounds investigated in this study. Antoine constants in Table 4 were determined from the experimental vapor pressure data.

2.2. Apparatus and Procedure

A modified Swietoslowski-type ebulliometer was used to measure the boiling points. Details of the equipment and the measurement procedure have been described in previous papers [7, 8]. 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 supplied by Druck Co., Kirchentellinsfurt, Germany. The uncertainty in the pressure was estimated to be ± 0.03 kPa. For our measurements, a mixture (ca. 160 cm³) with known constituents was charged into the ebulliometer. 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 study, the ratio of the amount of vapor hold-up to that of the initially charged liquid was found to be less than 2.0×10^{-4} , and the effect of vapor hold-up was negligible, as in our previous work [7].

For the measurement of boiling point at 101.3 kPa, the ebulliometer was open to the atmosphere, and the atmospheric pressure in the ebulliometer was measured using a Fortin barometer with an accuracy of ± 0.013 kPa (± 0.1 mmHg). The experimental boiling points were corrected to 101.3 kPa by the following equation [9], because the atmospheric pressure fluctuated slightly during the measurements:

$$T = T_{\text{exptl}} + \frac{1}{2.303 \sum_{i=1}^{\text{NC}} B_i x_i / (T_{\text{exptl}} + C_i)^2} \frac{101.3 - P_{\text{exptl}}}{P_{\text{exptl}}} \quad (1)$$

where NC is the number of components; T_{exptl} is the experimental temperature at the actual atmospheric pressure; P_{exptl} , B_i and C_i are the Antoine constants of component i , as listed in Table 4; and x_i is the mole fraction in the liquid phase.

3. Experimental results of binary systems

In this study, VLE data for four binary systems, namely methyl acetate (1) + methanol (2), methyl acetate (1) + ethyl lactate (2), and methanol (1) + ethyl lactate (2), were measured at 40.00 to 101.3 kPa. These experimental VLE data are illustrated in Figs. 1 – 3 together with the literature values [6, 10-15]. From Fig. 1, the experimental VLE data of the system methyl acetate + methanol agreed well at reduced pressures and 101.3 kPa. In the systems methyl acetate + ethyl lactate and methanol + ethyl lactate, Resa et al. have reported the VLE data at 101.3 kPa [6]. Our experimental boiling point temperatures were higher than their ones at ethyl lactate rich region.

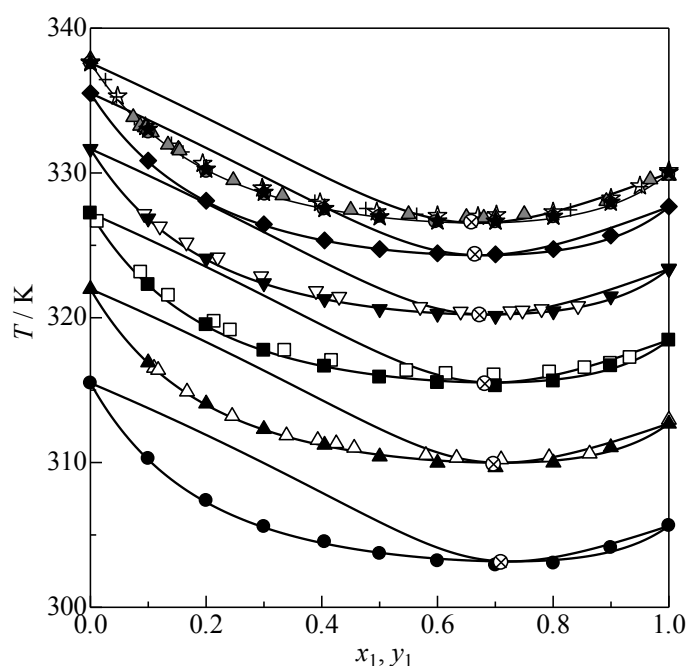


Fig. 1. Temperature–composition relationships for the system methyl acetate (1) + methanol (2). This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ◆, 93.32 kPa; ★, 101.3 kPa; Literature: Δ, Dobroserdov and Bagrov [10] at 53.33 kPa; □, Nagata and Ohta [11] at 66.66 kPa; ▽, Dobroserdov and Bagrov [10] at 79.99 kPa; ☆, Iliuta et al. [12] at 101.3 kPa; +, Nagata at 101.3 kPa [13]; ●; Tophhoff et al. [14] at 101.3 kPa; ▲, Tu et al. [15] at 101.3 kPa; —, Wilson; ⊗, azeotropic point.

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6. Conclusion

Isobaric VLE data of three binary mixtures, i.e., methyl acetate + methanol, methyl acetate + ethyl lactate, and methanol + ethyl lactate were measured at pressures 40.00 to 101.3 kPa. The experimental VLE data were represented by the Wilson and NRTL models with good accuracy. The solvent effects of ethyl lactate as an entrainer candidate were evaluated by two approaches, i.e., the residue curve maps and the calculation of the separation factors α_{12} using the binary Wilson parameters. Both of the calculated results for the residue curve maps and the separation factors show that ethyl lactate can be used 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 at a fixed $x_3 = 0.230$, which the apparent azeotropic point of the system methyl acetate + methanol disappears. The prediction of this ternary system using the binary Wilson or NRTL parameters agreed well with the experimental

VLE data.

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