Fluid Phase Equilibria 389 (2015) 28–40

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Densities, surface tensions, and isobaric vapor–liquid equilibria for the mixtures of 2-propanol, water, and 1,2-propanediol

Chih-Wei Chang, Ta-Lung Hsiung, Chih-Ping Lui, Chein-Hsiun Tu *

Department of Applied Chemistry, Providence University, Shalu 43301, Taiwan, ROC

ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 5 December 2014
Accepted 28 December 2014
Available online 31 December 2014

Keywords:
Density
Surface tension
Isobaric VLE
Aqueous 2-propanol
1,2-Propanediol

ABSTRACT

Densities and surface tensions of the ternary system (2-propanol + 1,2-propanediol + water) at $T = 298.15$ K and its constituent binary systems (2-propanol + 1,2-propanediol and 1,2-propanediol + water) at $T = 298.15$, 308.15, 318.15, and 328.15 K were measured under atmospheric pressure. Densities were determined using a vibrating-tube densimeter. Surface tensions were determined by the Wilhelmy-plate method. From the experimental binary and ternary data, the excess molar volumes and deviations in surface tension were calculated. These excess quantities were fitted to the Redlich–Kister equation, a simple equation based on Connors and Wright, and a modified equation of Cibulka, respectively. The results were used to study the nature of mixing behaviors between mixture components.

Isobaric vapor–liquid equilibrium (VLE) at $P = 101.3$ kPa have been measured for the ternary system of 2-propanol + water + 1,2-propanediol using an equilibrium still with circulation of both vapor and liquid phases. The effect of 1,2-propanediol on the VLE of 2-propanol + water was studied with three mass fractions (0.10, 0.30, and 0.50) of 1,2-propanediol in the overall liquid mixtures. The equilibrium compositions of mixtures were analyzed by gas–liquid chromatography. The results showed that the azeotropic point between 2-propanol and water can be eliminated when the mass fraction of 1,2-propanediol in the feed is up to 0.50. The relative volatilities of 2-propanol with respect to water were also determined. The new ternary VLE data were successfully correlated with the Wilson, NRTL, and UNIQUAC models, for which the binary interaction parameters are reported. The comparison of the volatility effect of 1,2-propanediol with that of 1,3-propanediol on 2-propanol + water was illustrated.

1. Introduction

Alcohol type such as 2-propanol is widely used as solvent in industries. Especially, it can be treated as a dehydration agent to clean the parts and electric circuit in the electronic processes. Accordingly, the purification of the aqueous 2-propanol solution to recover 2-propanol becomes a necessary step to reduce the pollution problem and the capital cost. However, at atmospheric pressure this alcohol forms a minimum boiling azeotrope with water, which is hard to be separated with ordinary distillation and requires special methods to facilitate the separation. Among all of separation techniques toward the above mixture, extractive distillation, which acts to introduce a higher-boiling homologue to increase the relative volatility of one component, has been proved to be promising [1,2].

In order to design the separating process efficiently, a wide range of information is desired. Data such as densities, surface tensions, and vapor–liquid phase equilibria of the homogeneous mixtures are fundamental in the design of process units that involve fluid flow, interface heat, and mass transfer. Thus their experimental values are essential for modeling the extractive distillation process with these transport phenomena. Besides this practical application, their data are important for elucidating the nature of interactions between the molecular components. Propylene glycol such as 1,2-propanediol finds its broad usage as an excipient in the development of injectable formulations for poorly water soluble drugs [3]. It is a compound of low toxicity, low vapor pressure, and high water solubility, which enables its use as a potential solvent for the extractive separation of the aqueous 2-propanol solution.

In our previous studies the isobaric vapor–liquid equilibria, densities, viscosities, and surface tensions of the ternary and binary mixtures containing 2-propanol, water, and 1,3-propanediol have been investigated [4,5], and the obvious volatility improvement for 2-propanol using 1,3-propanediol was observed. Accordingly, 1,2-propanediol, which has a boiling point of 460.8 K [6] and a 26.8 K lower than 1,3-propanediol, could be a good entrainer as 1,3-propanediol but is expected to have a significant difference on vapor–liquid equilibria from 1,3-propanediol upon

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* Corresponding author. Tel.: +886 4 26328001; fax: +886 4 26327554.
E-mail address: chtu@pu.edu.tw (C.-H. Tu).

http://dx.doi.org/10.1016/j.fluid.2014.12.040

Nomenclature

a_k	Correlation parameters in Eqs. (3) and (4) for binary V^E and $\Delta\sigma$
A_{ij}, A_{ji}	Binary parameters of liquid activity-coefficient model
A, B, C, D, E	Parameters of the vapor pressure equation, Eq. (8)
a, b, c, d, e	Coefficients in the liquid molar volume equation, Eq. (9)
C_k	Correlation parameters in Eq. (6) for ternary V^E and $\Delta\sigma$
g_{ij}, g_{jj}	NRTL binary interaction parameters
N	Number of components
n	Number of experimental data
P	System pressure, 101.3 kPa
P°	Vapor pressure of pure component, Pa
q	Surface area parameter of the UNIQUAC model
r	Volume parameter of the UNIQUAC model
R	Universal gas constant
T	Equilibrium temperature, K
V^E	Excess molar volume, cm^3/mol
v^L	Liquid molar volume of pure liquid for the Wilson equation, m^3/kmol
U_{ij}, U_{jj}	UNIQUAC binary interaction parameters
w_s	Weight fraction of 1,2-propanediol in the feed
x_i	Equilibrium mole fraction of component i in the liquid phase
x'_1	Liquid-phase mole fraction of 2-propanol on a 1,2-propanediol free basis
y_i	equilibrium mole fraction of component i in the vapor phase
y'_1	Vapor-phase mole fraction of 2-propanol on a 1,2-propanediol free basis

Greek letters

α_{ij}	NRTL binary interaction parameter
β'_{12}	Relative volatility of 2-propanol to water on a 1,2-propanediol free basis
γ_i	Liquid-phase activity coefficient of component i
δ	Standard deviation defined in Eq. (5)
ε	Pre-determined constants for $\Delta\sigma$ in Eq. (4)
λ_{ij}, λ_{ii}	Wilson binary interaction parameters
ρ	Density
σ	Surface tension

Superscripts

calc	Calculated value
expt	Experimental value
E	Excess quantity
L	Liquid state
o	Pure component

Subscripts

1, 2	Component
i, j	Component
ij	i–j pair interaction

mixing with 2-propanol + water. Hence, this work is to extend the measurement for the mixtures of 2-propanol + water involving 1,2-propanediol, and to compare its volatility effect with that of 1,3-propanediol on the basis of the results of vapor–liquid equilibria, which will be important toward a more suitable solvent for the separation of 2-propanol and water. Meanwhile, the densities and surface tensions were included for the efficient design of the extractive distillation process.

In the past, experimental excess molar volumes have been determined at $T = 298.15$ K for 2-propanol + 1,2-propanediol by Pal et al. [7] on a continuous dilution dilatometer, in addition, experimental densities of 1,2-propandiol + water in the temperature range of 278.15–338.15 K have been reported by George et al. [8], Geyer et al. [9], and Kapadi et al. [10]. Using the method of capillary rise for the surface tensions of 1,2-propanediol + water, Romero and Paéz [11] obtained the experimental data at $T = 298.15$ K, and Horibe et al. [12] carried out the determination for the low-temperature range of −5 to 22 °C. On vapor–liquid equilibrium, isobaric data at $P = 101.3$ kPa [13,14] and isothermal results at temperatures 80, 98, and 110 °C [15,16] have been presented for 1,2-propanediol + water, moreover, one set of isobaric data at $P = 101.3$ kPa could be located for 2-propnanol + 1,2-propanediol [17]. As for the binary system of 2-propanol + water, the studies on its densities and surface tensions at $T = 298.15$ to 328.15 K and isobaric vapor–liquid equilibria at $P = 101.3$ kPa have been done in our previous work [4,5].

Having this in mind, the densities and surface tensions of the ternary system of 2-propanol + water + 1,2-propanediol at $T = 298.15$ K were measured under atmospheric pressure 0.1 MPa. The isobaric vapor–liquid equilibrium (VLE) behavior for the same ternary system has been investigated at $P = 101.3$ kPa by means of a dynamic method using a re-circulating still. As far as we know, no such information has been provided in the open literature. In addition, the experimental densities and surface tensions for two constituent binary systems (2-propanol + 1,2-propanediol and 1,2-propanediol + water) at $T = 298.15$, 308.15, 318.15, and 328.15 K have been included. The experimental data of density and surface tension are used to calculate the excess molar volumes and deviations in surface tension which are discussed on the basis of molecular interaction. The results of the VLE investigation were used to analyze the effect of 1,2-propanediol on the azeotropic behavior of aqueous 2-propanol solution. Smooth representations of these experimental data are described, and their best fitted parameters were collected.

2. Experimental section

2.1. Materials

The chemicals such as 2-propanol, 1,2-propanediol, and water were of analytical grade. They were used without further purification. 2-Propanol and 1,2-propanediol were stored over molecular sieves (Merck 0.4 nm beads) before use. The purity of all chemicals was checked using a PerkinElmer Autosystem gas chromatograph (GC), and no impurity peak was detected. The electrical conductivity of $\kappa = 1.25$ μS/cm at 298.15 K were obtained for pure water with a Kyoto model CM-117 conductivity meter. The specifications of these chemicals are shown in Table 1.

2.2. Apparatus and procedure

A set with compositions varying from 0.05 to 0.95 mole fractions for each of the binary systems (2-propanol + 1,2-propanediol and 1,2-propanediol + water) at $T = 298.15$, 308.15, 318.15, and 328.15 K along with a total of 55 compositions, which cover a wide range of mole fractions, for the ternary system of 2-propanol + 1,2-propanediol + water at $T = 298.15$ K were used in the measurement over the densities and the surface tensions. All samples were prepared by mass using a Mettler AB204 balance with a precision of ±0.1 mg. The possible error of composition in mole fraction was estimated to be ±0.0001. At least four measurements which were