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Isobaric (vapour + liquid + liquid) equilibrium data for (di-*n*-propyl ether + *n*-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) systems at 100 kPa

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Abstract

Isobaric (vapour + liquid + liquid) equilibria were measured for the (di-*n*-propyl ether + *n*-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) system at 100 kPa.

The apparatus used for the determination of (vapour + liquid + liquid) equilibrium data was an all-glass dynamic recirculating still with an ultrasonic homogenizer couple to the boiling flask.

The experimental data demonstrated the existence of a heterogeneous ternary azeotrope for both ternary systems. The (vapour + liquid + liquid) equilibria data were found to be thermodynamically consistent for both systems.

The experimental data were compared with the estimation using UNIQUAC and NRTL models and the prediction of UNIFAC model.

Keywords: (Vapour + liquid + liquid) equilibria; Di-*n*-propyl ether; *n*-Propyl alcohol; Diisopropyl ether; Isopropyl alcohol; Water

1. Introduction

Tertiary ethers with 5 or 6 carbons, like diisopropyl ether and di-*n*-propyl ether, have become important gasoline additives over the past decade. At first, oxygenates were used as octane-enhancing components, but then it was noticed that they also improve the combustion of gasoline and reduce emissions. For proper design of synthesis and separation processes of ethers we need a fundamental knowledge about multicomponent phase equilibria of the mixture.

The synthesis of ethers is difficult due to the phase behaviour. (Di-*n*-propyl ether + *n*-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) ternary systems form three binary azeotropes and one heterogeneous ternary azeotrope. Enhanced distillations could be attractive methods for the purification of the ethers and therefore the knowledge of the three-phase equilibria is essential for the simulation and design of the separation processes. However, measurements of (vapour + liquid + liquid) equilibria for ternary systems are not straightforward and usually time consuming. As a result, such data are not always available in the literature although they are frequently needed for design purposes. Therefore, the isobaric (vapour + liquid + liquid) equilibrium (VLLE) as well as (vapour + liquid) equilibrium (VLE) is indispensable to design and analyze the heterogeneous distillation process.

VLLE of partially miscible liquid mixtures involves simultaneously three-phase equilibrium conditions in the

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two-liquid phase region. On the one hand, the VLLE involves the (liquid + liquid) equilibria of both phases and on the other hand, the (vapour + liquid) equilibria of the liquid phases with the vapour phase. Assuming the vapour phase to be ideal, the condition of LLE is expressed as follows [1]:

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}}, \tag{1}$$

where I and II represent the liquid phases, γ_i the activity coefficient and x_i the molar liquid fraction. And the VLE as follows:

$$y_i = \frac{\gamma_i P_i^\circ}{P} x_i^{\mathrm{I}} = \frac{\gamma_i P_i^\circ}{P} x_i^{\mathrm{II}}, \tag{2}$$

where P_i° the saturated vapour pressure of the component i, P is the total pressure and y_i the molar vapour fraction.

VLLE calculation of partially miscible liquid mixtures is usually carried out using VLE and LLE data with the same set of parameters in activity models or using group contribution models like UNIFAC. Although the calculated ternary VLLE did not always agree with the experimental data. There are some studies [2,3] that concluded that the isobaric VLLE was better estimated by the parameters from the ternary LLE than those from the binary VLE data. On the other hand, other papers [4] reported that the isobaric VLLE was well estimated by the parameters determined from the binary VLE data. Those results suggest that the same set of parameters for VLE and LLE calculations may lead to different conclusions.

In order to correctly simulate and design azeotropic distillation columns, a set of fitted parameters that predict the equilibrium well is very important, since small deviations in the azeotropic compositions or in the non-isothermal binodal curve can lead to important deviations between the simulations and reality.

The objective of the present paper is to report VLLE data of (di-*n*-propyl ether + *n*-propyl alcohol + water) and (diisopropyl ether + isopropyl alcohol + water) systems at 100 kPa. These data will allow analyzing the reliability of models such as UNIFAC [5], NRTL [6] and UNIQUAC [7] to predict and correlate the equilibria data.

Different works have paid attention to the study of these ternary systems and several papers about the VLE [8–12] and LLE [13,14] equilibrium have been published.

However, it is not possible to find a complete experimental study of the isobaric VLLE of these ternary systems at 100 kPa in the literature.

2. Experimental section

2.1. Chemicals

Diisopropyl ether and *n*-propyl alcohol (mass fraction >0.99, *GC grade*) were purchased from Fluka, di-*n*-propyl ether (mass fraction 0.90, *for synthesis*) and isopropyl alcohol (mass fraction >0.998 *analysis grade*) were supplied by Merck and water was bidistillated. Di-*n*-propyl ether was purified to mass fraction 0.995 by batch distillation in a Fischer SPALTROHR-column HMS-500, controlled by a Fischer system D301-C. The other reagents were used without further purification after chromatography failed to show any significant impurities. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (mass fraction <0.0005). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracy in refractive index and density measurements are ±0.0002 and $\pm 0.01\ \mathrm{kg \cdot m^{-3}}$, respectively. The experimental values of these properties and the boiling points are given in table 1 together with those given in the literature. Appropriate precautions were taken when handling the reagents in order to avoid hydration.

2.2. Apparatus and procedure

The equilibrium vessel used in the measurements (Labodest VLE 602/D) was an all-glass dynamic recirculating still equipped with a Cottrell circulation pump, manufactured by Fischer Labor und Verfahrenstechnik (Germany) and referenced widely in the literature to obtain VLE data. For these VLE determinations, the still allows good mixing of the vapour and liquid phases and good separation of the

TABLE 1
Density d, refractive index n_{D}, and normal boiling point T_{b} of pure components

Component	$d/(\mathrm{kg \cdot m^{-3}})$ (298.15 K)		n_{D} (298.15 K)		$T_{\mathrm{b}}/\mathrm{K}$	
	Experimental	Literature[a]	Experimental	Literature[a]	Experimental	Literature[b]
Di-*n*-propyl ether	741.81	742.00	1.3784	1.3780	363.16	362.79
n-Propyl alcohol	799.62	799.51	1.3836	1.3837	369.75	370.35
Diisopropyl ether	718.32	718.20	1.3652	1.3655	341.40	341.45
Isopropyl alcohol	782.69	781.26	1.3754	1.3752	355.25	355.41
Water	997.00	997.04	1.3332	1.3325	373.15	373.15

[a] Taken from TRC tables [15].
[b] Taken from Daubert and Danner [16].