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Vapor–liquid equilibrium for propylene glycols binary systems: Experimental data and regression

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ABSTRACT

Vapor–liquid equilibrium (VLE) data are reported for five binary systems involving propylene glycols. VLE data have been measured in the temperature range of 350.15–510.15 K and pressure up to 34.374 kPa for the binary systems: 1,2-propanediol (monopropylene glycol, MPG) + 2-[2-(2-hydroxypropoxy) propoxy] propan-1-ol (tripropylene glycol, TPG), MPG + 2-(2-[2-(2 hydroxypropoxy) propoxy]propoxy) propan-1-ol (tetrapropylene glycol, TePG), 1-(2-hydroxypropoxy) propan-2-ol (dipropylene glycol, DPG) + TPG, DPG + TePG and TPG + TePG. These experimental data are obtained using an equilibrium apparatus build in our laboratory. For the binary system MPG + DPG there are VLE data available in literature. The experimental data obtained were correlated using the NRTL model. These VLE data are essential for the process design in order to separate propylene glycols mixtures by distillation.

1. Introduction

Propylene glycol mixture is obtained by hydrolysis of 1,2-epoxy propane and contains: water, 1,2-propanediol (monopropylene glycol, MPG), 1-(2-hydroxypropoxy) propan-2-ol preponderant in mixtures isomers (dipropylene glycol, DPG), 2-[2-(2-hydroxypropoxy) propoxy]propan-1-ol preponderant in mixtures isomers (tripropylene glycol, TPG), 2-(2-[2-(2-hydroxypropoxy) propoxy]propoxy) propan-1-ol preponderant in mixtures isomers (tetrapropylene glycol, TePG) and poly(propylene glycol). The importance of the separation for propylene glycols mixture in order to obtain pure components is reflected in the numerous applications in which they are used, such as: plasticizers, as functional fluids, obtaining unsaturated polyester resins and more [1]. We are developing a new industrial process to separate the propylene glycols mixture [2]. For synthesis and simulation of this process is necessary to have accurate vapor–liquid equilibrium (VLE) data for the components of the mixture [3]. The essential VLE data for the design of distillation columns to separate propylene glycols mixtures are divided into two categories: water–propylene glycols systems and propylene glycols systems. The VLE data for the water–propylene glycols binary systems were published in our previous article [3]. In this paper we report *p-T-x* experimental VLE data for MPG + TPG, MPG + TePG, DPG + TPG, DPG + TePG and TPG + TePG in the temperature range of 350.15–510.15 K and pressure up to 34.374 kPa. For these five propylene glycols binary systems there are no data in the literature. We used our equilibrium apparatus for measurements of the VLE data, described in a previous work [4]. The experimental data were correlated with NRTL (non-random two-liquid) using the PRO II simulation software [5]. In this software we defined TePG as a new component by using the physical and transport properties of these component that were presented in our previous work [4]. The VLE data for the binary system MPG + DPG system that belong to the propylene glycols systems category, are available in the literature. We used these known data to validate the experimental procedure.

2. Experimental

The specifications of all propylene glycols used are presented in Table 1. The pressure was measured using a DPI 705 sensor with the measuring range between 0 and 0.35×10^5 Pa and the temperature was measured with VWR International, LLC, NIST traceable digital thermometer (±0.05% accuracy and 0.001 K resolution).

The vapor–liquid equilibrium experimental data were performed using an equilibrium apparatus build in our laboratory. The construction and operation of this apparatus have been described in our previous work [4].

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Nomenclature

a,b,c	binary interaction parameters of the NRTL model
G	adjustable parameter which depends on the interaction energy between molecules of component i and component j
P	pressure
p	vapor pressure
R	universal gas constant (J mol-1id=6#K-1)
T	temperature (K)
u	uncertainty
x	concentration of the component in liquid phase of the mixture expressed as molar fraction
Δ	difference
γ_i	activity coefficient
τ	adjustable parameter
α, α', β'	nonrandomness parameters of the NRTL model
i, j	components i and j
ij	pair interaction
ji	pair interaction
k	component k
calc	calculated value
expt	experimental value

The experimental procedure used to determine the VLE data was the following:

- the preparation of the mixtures at laboratory conditions by mass [6,7] using a Mettler Toledo AB204-S electronic balance accurate to 0.0001 g;
- the mixture sample (about 30 ml) was introduced in the equilibrium cell (made from transparent glass with an inner volume of about 50 ml), was cooled and then was degassed;
- the equilibrium cell was connected to an U-shaped tube and were placed in thermostatic oil bath where the desired temperature was maintained within ±0.05 K [4];
- the temperature was maintained, until the level of the manometric liquid in the two branches of the U shaped tube remained constant;
- finally, when the pressure of the system did not change for 30 min (the level of manometric liquid was the same in the two branches) the vapor pressure was measured [4].

The ELV experimental data for MPG + TPG, MPG + TePG, DPG + TPG, DPG + TePG and TPG + TePG were obtained for five mixture compositions. We also measured the vapor pressure at different temperatures for the pure components. The standard uncertainties [8] for temperature and concentration of the more volatile component in the mixture were ±0.01 K and ±0.0002 mole fraction. We measured the vapor pressure three times, for each fixed temperature and concentration and we reported the average value together with it uncertainty [8]. As we did not measure the compositions of vapor phases, thermodynamic consistency was not determined.

3. Results and discussions

In Tables 2 and 3 are presented the VLE measurements for the binary mixtures that have monopropylene glycol like volatile component, MPG + TPG and MPG + TePG, in the temperature ranges of 350.15–485.15 K and of 355.15–510.15 K.

In Tables 4 and 5 are presented the VLE measurements for the binary mixtures that have dipropylene glycol like volatile component, DPG + TPG and DPG + TePG, in the temperature ranges of 395.15–470.15 K and of 380.15–470.15 K.

The p-T-x experimental data of the TPG + TePG system are shown in Table 6, these measurements have been performed in the temperature interval of 400.15–470.15 K.

For the binary system MPG + DPG there are VLE data available in literature [5,9]. The experimental data for this system, in the temperature range of 350.15–460.15 K, determined using the same apparatus like in this paper, presented Nicolae and Oprea [9], are compared with those calculated with the simulation software [5]. This comparison validates the experimental procedure.

The experimental data for these five binary systems are regressed with the NRTL model using the PRO II simulation software. We used this model due to its large usage and simple implementation [10]. NRTL model is based on local composition of the liquid mixtures and was proposed by Renon and Prausnitz [11,12]. Eqs. (1)–(5) are the general relations which define the NRTL model, as they are available in the PRO II reference manual. These equations describe the NRTL binary interaction parameters specific for each binary [5].

$$\ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_{ji}}{\sum_j G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj}}{\sum_k G_{kj} x_k}\right) \quad (1)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + \frac{c_{ij}}{T^2}(\text{unit is K}) \quad (2)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{RT} + \frac{c_{ij}}{R^2T^2}(\text{unit is kcal or kJ}) \quad (3)$$

$$G_{ij} = \exp(-\alpha_{ji}\tau_{ij}) \quad (4)$$

$$\alpha_{ji=}\alpha_{ji}' + \beta_{ji}'T \quad (5)$$

In the PRO II database there are binary interaction parameters for the MPG + DPG system for the NRTL model with three parameters. Because of this, the VLE experimental data of these system, presented by Nicolae and Oprea [9], are regressed using the NRTL model only with three parameters. Table 7 contains the values of the binary

Table 1
Specifications of the used chemicals

Chemical name	Source	Mass fraction Purity	Water content, % weight	Purification method	Analysis method
Monopropylene glycol	S.C. Oltchim S.A.	0.9993	0.070	none	–
Dipropylene glycol	Dow Chemical	0.9989	0.003	none	–
Tripropylene glycol	Dow Chemical	0.9993	0.005	none	–
Tetrapropylene glycol	Dow Chemical, purified in our laboratory	0.9940	0.008	distillation	GC[a]

[a] Gas-liquid chromatography