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Isothermal Vapor−Liquid Equilibrium of Ethanol + Glycerol and 2-Propanol + Glycerol at Different Temperatures

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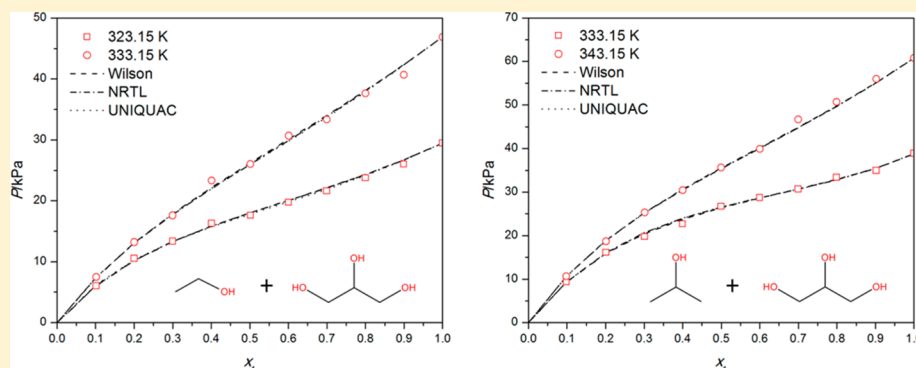
ABSTRACT: Isothermal vapor−liquid equilibrium (VLE) data for two binary mixtures of ethanol + glycerol and 2-propanol + glycerol were determined at the temperature range from (323.15 to 343.15) K using a simple quasistatic ebulliometer. The experimental data were correlated with the Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models. Both systems show that the vapor pressures increase with increasing alcohols concentrations, and no azeotropic behaviors are exhibited. In addition, both systems show positive deviations from the Raoult's Law.

1. INTRODUCTION

The production of biodiesel is gaining great attention in recent years because of environmental concerns and its possibility as a substitute for fossil fuels. Biodiesel is also considered to be a renewable and environmentally friendly fuel due to it being biodegradable, nontoxic, and lower emission.[1−3] Biodiesel can be derived from vegetable oils or animal fats[4−6] by a transesterification reaction with an excess of alcohols in the presence of a catalyst.[7,8] By this method, glycerol may be generated as a commercial value byproduct. Glycerol is a useful compound in pharmaceutical, cosmetic, and food industries and as a possible entrainer in the extractive distillation for separating azeotropic mixtures.[9,10] One of the major stage processes in biodiesel production is glycerol recovery section to separate glycerol with unreacted alcohols which is recycled into a transesterification reactor.[11] In order to design and optimize the glycerol recovery process, the vapor−liquid equilibrium (VLE) data for a binary system of alcohols + glycerol are required.

Many works related to the VLE measurements of alcohols + glycerol are available in the open literature. To the best of our knowledge, VLE data of these binary systems still remain scarce especially involving higher chain alcohols (i.e., 2-propanol). (Methanol or ethanol) + glycerol systems were studied at low pressures in the previous works.[12−14] Ethanol + glycerol systems were also measured at different temperatures by Dulitskaya[15] and Zaoui-Djelloul-Daouadji et al.[16] The isothermal VLE data for methanol + glycerol and ethanol + glycerol systems near the critical temperatures of the alcohols were reported by Shimoyama et al.[17] In another works, Oliveira et al.[11] also reported VLE data of alcohols + glycerol mixtures containing higher chain alcohols at atmospheric pressure.

The compilation of VLE data sources for alcohols + glycerol with each measurement conditions are presented in Table 1. Most of the VLE measurements for a binary system of ethanol + glycerol in the previous work were reported in the isobaric conditions. Experimental data for the 2-propanol + glycerol system were reported by Oliveira et al.[11] However, the measured data are only for a limited condition namely, at atmospheric pressure and in the 2-propanol mole fractions ranges of (0.0064 to 0.3850). None of the previous work reported the VLE measurements for the binary system of 2-propanol + glycerol in the wide range of pressures and compositions. Therefore, in the present study, the VLE data (P-T-x_i) were measured with a simple quasistatic ebulliometer for two binary systems of ethanol + glycerol and 2-propanol + glycerol at the temperatures of (323.15 and 333.15) K and (333.15 and 343.15) K, respectively. The experimental data were correlated with the Wilson,[18] nonrandom two-liquid (NRTL),[19] and universal quasichemical (UNIQUAC)[20] models.

Table 1. Vapor−Liquid Equilibrium Data Sources for Alcohols + Glycerol

alcohols	type	measurement conditions	source
methanol	isobaric	101.325 kPa	ref 11
	isobaric	(32.02 to 45.3) kPa	ref 12
	isobaric	(6.7 to 66.7) kPa	ref 14
	isothermal	(493 to 573) K	ref 17
ethanol	isobaric	101.325 kPa	ref 11
	isobaric	(15.1 to 93.2) kPa	ref 13
	Isobaric	(6.7 to 66.7) kPa	ref 14
	isothermal	(298.14 to 348.12) K	ref 15
	isothermal	(493 to 573) K	ref 17
	isothermal	(273.15 to 353.15) K	ref 16
	isothermal	(323.15 to 333.15) K	this work
1-propanol	isobaric	101.325 kPa	ref 11
2-propanol	isobaric	101.325 kPa	ref 11
	isothermal	(333.15 to 343.15) K	this work
1-butanol	isobaric	101.325 kPa	ref 11

2. EXPERIMENTAL SECTION

2.1. Materials. The materials used in this study were ethanol (purity better than 0.999), 2-propanol (purity better than 0.998), and glycerol (purity better than 0.995). All materials were purchased from Merck, Germany and used without additional purification. The material descriptions are presented in Table 2 including the pure properties of each material.

2.2. Apparatus and Procedures. In this study, the vapor pressures were measured using a simple quasistatic ebulliometer with the schematic diagram; details and reliability test of the experimental apparatus were described in our previous work.[21]

The experiment was started by measuring the vapor pressures of pure ethanol at (323.15 and 333.15) K and 2-propanol at (333.15 and 343.15) K. For measurements of alcohols and glycerol binary mixtures, the compositions of initial liquid were prepared gravimetrically by weighing the required amounts of the pure components on an Ohaus balance with an accuracy of ± 0.0002 g. The uncertainty of liquid phase composition was estimated to be less than 0.05 % in mole fractions. The temperature was maintained to within ± 0.1 K of the desired value. The vapor pressures at various temperatures and compositions were measured using a pressure gauge (model Wika, USA) with a precision of ± 0.05 kPa.

The VLE measurement was started by charging the liquid mixtures of a certain composition into the ebulliometer cell. Then, the vacuum pump was turned on to remove air and impurities from the equilibrium cell. The prepared solution was slowly heated by an electric heater and stirred homogeneously with a magnetic stirrer. This procedure was also applied while meassuring the vapor pressure of pure substances. The temperature was adjusted with a controller (model TZN4S, Autonics, USA) connected with a platinum RTD probe and temperature display. The equilibrium condition was attained

when the pressure in the equilibrium cell reached a constant value. The equilibrium composition of the liquid phase was assumed to be the same as the initial composition of the mixture as proved in our previous work.[21] The experimental procedure was repeated at different temperatures and compositions.

3. RESULTS AND DISCUSSION

The experimental VLE data $(P−T−x_i)$ have been determined for two binary systems of ethanol + glycerol and 2-propanol + glycerol within the temperatures ranges of (323.15 to 333.15) K and (333.15 to 343.15) K, respectively. The experimental data obtained in this work are presented in Tables 3 and 4.

Table 3. Vapor−Liquid Equilibrium Data for the Binary System of Ethanol (1) + Glycerol (2) from T = (323.15 to 333.15) K[a]

	P/kPa	
x_1	T = 323.15 K	T = 333.15 K
0.1018	6.00	7.47
0.2005	10.53	13.20
0.3002	13.33	17.60
0.4013	16.27	23.33
0.5018	17.60	26.00
0.6008	19.73	30.66
0.6995	21.60	33.33
0.7999	23.73	37.60
0.8994	26.00	40.66
1.0000	29.44	46.86

[a]$u(T)$ = 0.1 K, $u(P)$ = 1 %, and $u(x_1)$ = 0.005.

Table 4. Vapor−Liquid Equilibrium Data for the Binary System of 2-Propanol (1) + Glycerol (2) from T = (333.15 to 343.15) K[a]

	P/kPa	
x_1	T = 333.15 K	T = 343.15 K
0.0986	9.33	10.67
0.2015	16.13	18.67
0.3017	19.73	25.33
0.3999	22.66	30.40
0.4998	26.66	35.66
0.5998	28.66	39.93
0.6995	30.66	46.66
0.7993	33.33	50.66
0.9024	34.93	56.00
1.0000	38.84	60.75

[a]$u(T)$ = 0.1 K, $u(P)$ = 1 %, and $u(x_1)$ = 0.005.

Both systems indicate that the vapor pressures increase with increasing alcohols mole fractions. The measured vapor pressures of pure alcohols agreed well with those calculated from the Antoine equation with a magnitude within ± 0.15 %.

Table 2. Material Description and Properties of Pure Components

component	source	mass fraction purity	MW/g·mol^{-1}	boiling point/K	density^a/g·cm^{-3}
ethanol	Merck, Germany	0.999	46.069	351.80[b]	0.78515[c]
2-propanol	Merck, Germany	0.998	60.096	355.39[b]	0.78099[d]
glycerol	Merck, Germany	0.995	92.095	563.00[e]	1.25780[f]

[a]T = 298.15 K. [b]Reference 23. [c]Reference 24. [d]Reference 25. [e]Reference 26. [f]Reference 27.

The vapor pressure measurement of pure glycerol could not be performed in this study due to the extremely low vapor pressure of pure glycerol at these temperatures range. The used Antoine constants are obtained from the Thermodynamics Research Center (TRC) data bank, College Station, TX, USA as listed in Table 5.

Table 5. Parameters of the Antoine Equation for Pure Compounds

component	A	B	C
ethanol[a]	5.33675	1648.220	230.918
2-propanol[a]	5.24268	1580.920	219.610
glycerol[b]	10.6190	4487.040	−140.200

[a]Reference 23, $\log(P^s) = A - B/(T + C - 273.15)$, where P^s is in bar and T is in K. [b]Reference 26, $\ln(P^s) = A - B/(T + C)$, where P^s is in bar and T is in K.

The experimental data of the binary system were correlated with the Wilson, NRTL, and UNIQUAC equations, and the physical properties of each component are given in Table 6.

Table 6. Physical Properties and Parameters of Pure Components Used in the Activity Coefficients Correlation

component	molar volume/cm^3·mol^{-1}	r^a	q^a
ethanol	58.68[b]	2.5755	2.588
2-propanol	76.92[b]	3.2491	3.124
glycerol	73.03[c]	4.7957	4.908

[a]References 28 and 29. [b]Reference 23. [c]Reference 26.

Barker's method[22] was used to obtain the optimal values of the binary interaction parameters for the mixtures studied in this work by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^{n} (P_{i,cal} - P_{i,exp})^2 \tag{1}$$

where n is the number of data points and the subscripts cal and exp refer to calculated and experimental values, respectively. Since the experimental pressures were below the atmospheric pressure, the vapor phase behavior was assumed to be close to ideal so that equilibrium pressures might be calculated using the following equation:

$$P_{cal} = \sum_{i=1}^{m} x_i \gamma_i P_i^s \tag{2}$$

where x_i are the mole fractions of the liquid phase, γ_i are the activity coefficients of the components, and m are the number of the component in the mixtures. P_i^s are the vapor pressures of the pure components.

The best fitted binary interaction parameters (A_{12}, A_{21}, B_{12}, and B_{21}) obtained in this work and the average absolute deviations (AAD) between the experimental and the calculated vapor pressures are listed in Table 7. This table showed that the experimental data were well correlated with the Wilson, NRTL, and UNIQUAC equations. The comparison between experimental data and calculated vapor pressures with the Wilson, NRTL, and UNIQUAC activity coefficient models are presented in Figures 1 and 2. In these figures, solid points represent experimental data, dash lines represent calculated values by the Wilson model, dash dot lines represent the calculated values by the NRTL model, and dotted lines

Table 7. Fitted Binary Interaction Parameters of Activity Coefficient Models and Average Absolute Deviations (AAD)

model	parameters				AAD^a/%
	A_{12}	A_{21}	B_{12}/K	B_{21}/K	
Ethanol (1) + Glycerol (2) at T = (323.15 to 333.15) K					
Wilson[b]	0.3624	11.5082	−389.23	−3763.54	1.9
NRTL[c]	−7.4194	−5.0624	2308.02	2067.40	1.8
UNIQUAC[d]	1.8165	1.5407	−455.92	−797.25	1.6
2-Propanol (1) + Glycerol (2) at T = (333.15 to 343.15) K					
Wilson	−2.1683	22.7095	576.54	−7886.11	1.2
NRTL	−39.3952	22.1856	13487.42	−7328.31	1.3
UNIQUAC	9.0100	−8.0588	−2968.20	2532.16	1.3

[a]AAD $= (1/n)\Sigma_{i=1}^{n}|(P_{cal} - P_{exp})/P_{exp}|_i100$ %, where n is the number of data points. [b]$\Lambda_{ij} = (V_j/V_i)\exp((A_{ij} + B_{ij}/T))$, where V is the molar volume of the component. [c]$\tau_{ij} = A_{ij} + B_{ij}/T$, the value of α was fixed to be 0.2 for each binary system. [d]$\tau_{ij} = \exp(A_{ij} + B_{ij}/T)$.
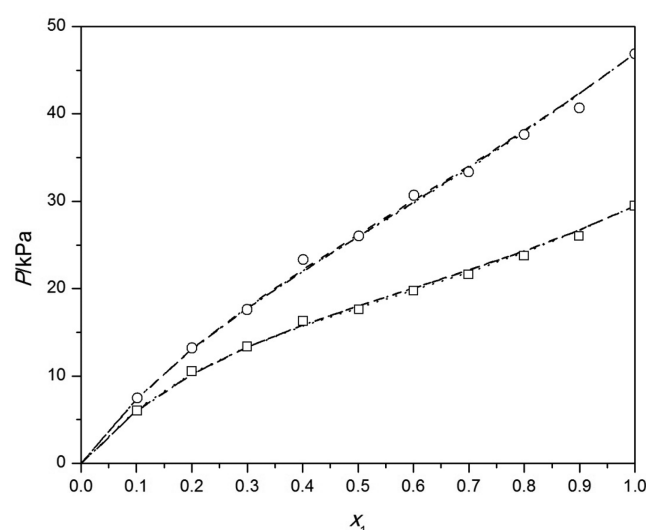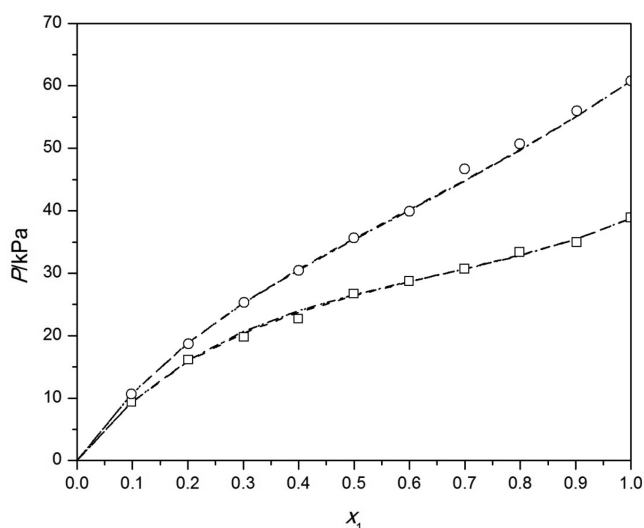

Figure 1. VLE phase ($P-x_1$) diagram for binary system of ethanol (1) + glycerol (2): (□) experimental data at 323.15 K; (○) experimental data at 333.15 K; (----) calculated values from the Wilson model; (−●−) calculated values from the NRTL model; and (●●●) calculated values from the UNIQUAC model.

represent the calculated values by the UNIQUAC model. The binary systems of ethanol (1) + glycerol (2) and 2-propanol (1) + glycerol (2) showed positive deviations from ideal solution (Raoult's law).

The vapor phase compositions (y_i) were determined, and the results showed that the vapor phase was made up of pure alcohols ($y_1 = 1$) because the vapor pressure of glycerol is close to zero in the range of studied temperatures. On the other hand, no azeotrope point was exhibited by the binary systems studied in this work.

4. CONCLUSIONS

In the present study, isothermal VLE data for two binary systems of (ethanol or 2-propanol) + glycerol have been measured using a simple quasistatic ebulliometer at different temperatures. The experimental data were well correlated using the Wilson, NRTL, and UNIQUAC models. Both systems exhibit positive deviations from the Raoult's law without any azeotrope formation.

Figure 2. VLE phase ($P-x_1$) diagram for binary system of 2-propanol (1) + glycerol (2): (□) experimental data at 333.15 K; (○) experimental data at 343.15 K; (----) calculated values from the Wilson model; (−●−) calculated values from the NRTL model; and (●●●●) calculated values from the UNIQUAC model.

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Notes
The authors declare no competing financial interest.

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