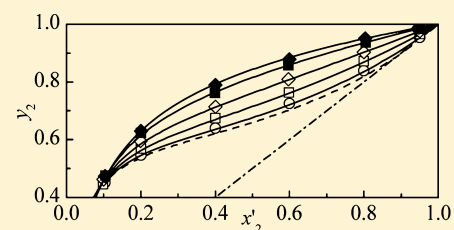


Vapor–Liquid Equilibrium of Water + Ethanol + Glycerol: Experimental Measurement and Modeling for Ethanol Dehydration by Extractive Distillation

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ABSTRACT: The present work aims at establishing reliable activity coefficient model for vapor–liquid equilibrium (VLE) of the system water + ethanol + glycerol, with an emphasis on the application in ethanol dehydration by extractive distillation. New experimental data were reported for ternary VLE at 100 kPa, boiling temperature of water + glycerol at 101.33 kPa, and infinite dilution activity coefficient of water and ethanol, respectively, in glycerol at five temperatures of 313.15 K to 393.15 K. The NRTL equation was used for the modeling. For extending the composition and temperature range of data source, literature data of binary VLE of water + ethanol, infinite dilution activity coefficients of water + ethanol, and excess enthalpies of water + glycerol were also used for optimization of the NRTL parameters. The correlation showed that the azeotrope of water + ethanol can be removed at a glycerol mass fraction of 0.0902. The experimental results were compared graphically with those of calculations, showing good agreement. Comparisons were also presented for experimental results and correlations available in the literature.



■ INTRODUCTION

Using glycerol as entrainer for ethanol dehydration is an interesting topic because it aims at reducing the energy demand for bioethanol production by use of a coproduct of biodiesel. Herein, bioethanol and biodiesel are both biofuels that have received worldwide interest in recent years. Glycerol has many attractive features. It is nontoxic and environment compatible. Due to the large-scale production of biodiesel, glycerol is highly available and inexpensive. Under temperatures below 100 °C, the vapor pressure of glycerol is very low. It is regarded as a typical example of biobased solvent and has received increasing attention for its use in the chemical industry.¹

The mixture of water + ethanol forms a minimum boiling point azeotrope at about 0.96 mass fraction of ethanol. Simple distillation cannot be used to distill ethanol above the azeotropic composition. The feasibility of using glycerol for extractive distillation has been verified by vapor–liquid equilibrium (VLE) measurements by Lee et al.,² Souza et al.,³ and Pla-Franco et al.⁴ Results showed that the azeotrope of water + ethanol will be effectively removed by the addition of glycerol. Energy evaluation and process optimization have also been reported by García-Herreros et al.,⁵ Navarrete-Contreras et al.,⁶ and Gil et al.^{7,8} NRTL parameters in the database of Aspen Plus process simulator were frequently used for the calculation of activity coefficients in the liquid phase.

We have calculated VLE for the ternary system water (1) + ethanol (2) + glycerol (3) using NRTL parameters suggested by Souza et al.,³ Pla-Franco et al.,⁴ and Aspen Plus (APV80 VLE-IG), respectively. Results showed significant deviations for different sources. Moreover, the infinite dilution activity coefficient of water in glycerol, γ_{13}^{∞} , deviated greatly and showed

different trends of temperature dependence. Using the parameters of APV80 VLE-IG, the calculated value of γ_{13}^{∞} was less than unity and decreased rapidly with the rise of temperature. This trend appears to be quite unusual. The differences in ternary VLE and infinite dilution activity coefficients would have important influence on the design of extractive distillation.

The present work aims at establishing reliable activity coefficient model for water + ethanol + glycerol, with emphasis on the application in extractive distillation of ethanol using glycerol as entrainer. New experimental data were measured for ternary VLE of water + ethanol + glycerol, boiling temperature of water + glycerol, and infinite dilution activity coefficient of water and ethanol, respectively, in glycerol. These data, together with literature results for binary VLE and infinite dilution activity coefficients of water + ethanol, were used in the modeling. For the verification of temperature dependence of γ_{13}^{∞} , literature values for excess enthalpies of water + glycerol were also used. To the best of our knowledge, this is the first work using such a wide range of data for the modeling of VLE for water + ethanol + glycerol.

■ EXPERIMENTAL SECTION

Materials. Water was double distilled. Ethanol (mass fraction purity 0.998) and glycerol (mass fraction purity 0.995) were supplied by Sinopharm Chemical Reagent Co. Ltd. and used without further treatment. By Karl Fischer

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Table 1. Experimental Vapor–Liquid Equilibrium Data for Temperature T , Liquid-Phase Mole Fraction on Glycerol-Free Basis x' , Liquid-Phase Mass Fraction w , and Vapor-Phase Mole Fraction y , and Calculated Results for Activity Coefficient γ , and Relative Volatility α , for the Ternary System Water (1) + Ethanol (2) + Glycerol (3) at $p = 100$ kPa^a

x'_2	w_3	T K	y_1	y_2	γ_1	γ_2	α_{21}	x'_2	w_3	T K	y_1	y_2	γ_1	γ_2	α_{21}
$x'_2 = 0.1$								$x'_2 = 0.6$							
0.104	0.807	379.33	0.525	0.474	0.91	3.20	7.78	0.598	0.603	359.00	0.166	0.834	1.09	1.62	3.37
0.104	0.695	370.62	0.525	0.475	0.96	3.34	7.78	0.597	0.505	357.09	0.191	0.809	1.18	1.48	2.86
0.104	0.601	366.64	0.529	0.471	0.99	3.38	7.68	0.599	0.404	355.64	0.213	0.787	1.28	1.38	2.47
0.0999	0.508	364.36	0.538	0.462	1.00	3.44	7.73	0.598	0.301	354.50	0.237	0.763	1.37	1.30	2.17
0.0985	0.402	362.45	0.541	0.459	1.01	3.47	7.77	0.601	0.200	353.52	0.253	0.747	1.44	1.23	1.96
0.0980	0.302	361.17	0.554	0.446	1.04	3.39	7.42	0.600	0.102	352.69	0.274	0.726	1.53	1.18	1.77
0.0996	0.199	359.99	0.550	0.450	1.04	3.38	7.40	$x'_2 = 0.8$							
0.103	0.100	359.25	0.549	0.451	1.04	3.27	7.16	0.803	0.804	366.03	0.0499	0.9499	0.91	1.89	4.66
$x'_2 = 0.2$								0.804	0.704	361.79	0.0647	0.9353	1.02	1.58	3.52
0.201	0.800	373.04	0.370	0.630	0.93	2.83	6.77	0.801	0.601	358.85	0.0805	0.9194	1.13	1.41	2.84
0.201	0.701	366.25	0.377	0.623	0.96	2.81	6.58	0.800	0.503	357.04	0.0966	0.9034	1.26	1.29	2.33
0.200	0.604	362.55	0.390	0.610	0.99	2.74	6.25	0.800	0.403	355.61	0.112	0.888	1.39	1.20	1.98
0.199	0.504	360.16	0.405	0.595	1.02	2.65	5.92	0.800	0.303	354.38	0.128	0.872	1.53	1.14	1.70
0.199	0.402	358.61	0.417	0.583	1.04	2.56	5.61	0.800	0.206	353.29	0.144	0.856	1.68	1.09	1.49
0.200	0.285	357.38	0.430	0.570	1.06	2.45	5.29	0.800	0.101	352.15	0.161	0.839	1.86	1.05	1.30
0.201	0.207	356.79	0.437	0.563	1.06	2.39	5.13	$x'_2 = 0.95$							
0.201	0.101	356.18	0.453	0.547	1.09	2.29	4.80	0.948	0.814	366.20	0.0118	0.9881	0.89	1.83	4.63
$x'_2 = 0.4$								0.950	0.698	361.58	0.0158	0.9841	1.01	1.47	3.29
0.401	0.801	368.61	0.211	0.789	0.93	2.32	5.59	0.950	0.604	359.10	0.0196	0.9803	1.13	1.32	2.65
0.399	0.700	362.91	0.238	0.762	0.99	2.11	4.81	0.950	0.503	357.20	0.0243	0.9757	1.29	1.21	2.13
0.400	0.602	359.75	0.263	0.737	1.05	1.95	4.21	0.949	0.405	355.89	0.0293	0.9706	1.45	1.13	1.77
0.400	0.503	357.72	0.285	0.715	1.11	1.82	3.75	0.950	0.301	354.60	0.0339	0.9661	1.64	1.07	1.49
0.400	0.403	356.32	0.306	0.694	1.15	1.72	3.40	0.949	0.201	353.42	0.0398	0.9602	1.84	1.03	1.29
0.400	0.304	355.33	0.326	0.674	1.20	1.62	3.10	0.950	0.102	352.22	0.0455	0.9545	2.11	1.01	1.10
0.400	0.205	354.54	0.345	0.655	1.24	1.54	2.85	$x'_2 = 0.6$							
0.400	0.103	353.90	0.359	0.641	1.27	1.48	2.67	0.600	0.801	366.53	0.121	0.879	0.95	2.06	4.86
0.598	0.702	361.90	0.143	0.857	1.00	1.79	4.04	0.598	0.702	361.90	0.143	0.857	1.00	1.79	4.04

^a $u(T) = 0.08$ K, $u(p) = 0.05$ kPa, $u(w_3) = 0.003$, $u_r(x'_2) = 0.01$, $u_r(y_1) = 0.01$, and $u_r(y_2) = 0.01$.

titration, water mass fraction was typically 4.1×10^{-4} for ethanol and 6.8×10^{-4} for glycerol.

Determination of Vapor–Liquid Equilibrium. Apparatus and procedure for ternary VLE measurement have been described in detail previously.^{9–12} At the beginning of measurement, water content of ethanol and glycerol was analyzed. Certain amount of glycerol was first added into an ebulliometer. Then, ethanol and additional water were introduced quantitatively so that liquid-phase glycerol mass fraction, w_3 , had a value of 0.8. The overall synthetic masses were thus obtained for the first data point. When equilibrium was established, vapor condensate was sampled and analyzed. Glycerol mass fraction of the vapor sample was analyzed by gas chromatograph (Fuli 9790J).¹² A capillary column of OV-1301 (20 m \times 0.32 mm \times 0.25 μ m) was used. Carrier gas was nitrogen, and detection was by FID. 1,6-Hexanediol was used as internal standard. Each sample was analyzed three times. Deviations were less than 15 %. Water mass fraction was measured by Karl Fischer titration (SF-3 Titrator, Zibo Zifen Instrument, Ltd.). Consequently, vapor-phase mole fractions of water and ethanol were obtained. Liquid-phase compositions were calculated on the basis of mass balance.^{9,11} By replacing certain amount of the mixture in the boiler with water and ethanol, w_3 was changed from high to low, whereas x'_2 , defined as $x'_2 = x_2/(x_1 + x_2)$, remained approximately unchanged. This process repeated until w_3 was reduced to 0.1. Standard

uncertainties were estimated to be 0.08 K for temperature, 0.05 kPa for pressure, and 0.003 for liquid-phase glycerol mass fraction. Relative standard uncertainty for liquid-phase ethanol mole fraction was estimated to be 0.01. Relative standard uncertainty for vapor-phase mole fraction of water or ethanol was estimated to be 0.01.

For the measurement of boiling temperature of water + glycerol, the liquid phase mole fractions were determined by Karl Fischer titration.

Determination of Infinite Dilution Activity Coefficients. Activity coefficients at infinite dilution were measured using inverse gas chromatography. The experiments were performed by use of a Fuli 9790J gas chromatograph equipped with a thermal conductivity detector (TCD). The carrier gas was helium. Using a rotary evaporation preparatory technique, a 0.5 m length stainless steel column was packed with a stationary phase consisting of 0.396 mass fraction of glycerol on Chromosorb W AW (60/80 mesh). The amount of packing was calculated from the masses of the packed and empty column and was checked throughout experiments. The mass of glycerol as the stationary phase was 0.322 g. Loss of glycerol during the measurements was estimated to be less than 0.002 g. Solute injections were typically 0.2 μ L, and each experiment was repeated at least twice to confirm reproducibility.

Using the retention data of inverse chromatography experiments the net retention volume, V_{N_i} , was calculated by

$$V_N = (t_R - t_G) \frac{p_o - p_w}{p_o} \frac{T}{T_0} U_0 \quad (1a)$$

$$J = \frac{3 \left(\frac{p_i}{p_o} \right)^2 - 1}{2 \left(\frac{p_i}{p_o} \right)^3 - 1} \quad (1b)$$

where t_R is the retention time of a particular solute, t_G is the retention time of air, U_0 is the flow rate of the carrier gas measured at room temperature (T_0), T is the column temperature, p_w is the vapor pressure of water at T_0 , J is the James–Martin correction factor for pressure gradient and gas compressibility inside the column, and p_i and p_o are the inlet and outlet pressures, respectively. Consequently, activity coefficients at infinite dilution for solute (i , $i = 1$ for water, and $i = 2$ for ethanol) in glycerol (3), γ_{i3}^∞ , were calculated by the equation developed by Everett¹³ and Cruickshank et al.¹⁴

$$\ln \gamma_{i3}^\infty = \ln \left(\frac{n_3 R T}{V_N p_i^{\text{sat}}} \right) - \frac{p_i^{\text{sat}} (B_{ii} - V_i^{\text{sat}})}{R T} + \frac{J^{-1} p_o (2B_{i4} - V_i^\infty)}{R T} \quad (2)$$

where n_3 is the number of moles of glycerol in the column, R is the gas constant, B_{ii} is the second virial coefficient of the solute (i) at temperature T , B_{i4} is the cross second virial coefficient between solute (i) and carrier gas (4), p_i^{sat} is the vapor pressure of solute at temperature T , V_i^{sat} is the saturated liquid molar volume at temperature T , and V_i^∞ is the partial molar volume of the solute in glycerol at infinite dilution. In the calculations V_i^∞ is assumed to be equal to V_i^{sat} . The Hayden–O’Connell correlation¹⁵ was used for the calculation of the Virial coefficients. Relative standard uncertainty for γ_{i3}^∞ was estimated to be 0.05.

RESULTS AND DISCUSSION

The experimental results for ternary VLE data of water (1) + ethanol (2) + glycerol (3) are listed in Table 1, including liquid phase mole fraction of ethanol on an glycerol free basis (x'_2), liquid phase mass fraction of glycerol (w_3), vapor phase mole fraction of ethanol (y_2), equilibrium temperature (T), activity coefficients of water (γ_1) and ethanol (γ_2), and relative volatility of ethanol to water (α_{21}). The measurements were performed at $p = 100$ kPa. In the calculation of the activity coefficients the vapor phase was regarded as an ideal gas and the saturated vapor pressures of ethanol and water were calculated by parameters in the literature.¹⁶ Boiling temperatures of water (1) + glycerol (3) are listed in Table 2. The boiling temperature measurements were performed at $p = 101.33$ kPa. The

Table 2. Experimental Results for Boiling Temperature, T , in Relation with Glycerol Mass Fractions, w_3 , for System Water (1) + Glycerol (3) at $p = 101.33$ kPa^a

w_3	T
	K
0.7996	392.18
0.8957	407.44
0.9247	416.55
0.9502	428.63

^a $u(T) = 0.08$ K, $u(w_3) = 0.003$.

experimental results for infinite dilution activity coefficients of water in glycerol and ethanol in glycerol are listed in Table 3. The measurements were performed at five temperatures in a range of 313.15 K to 393.15 K.

Table 3. Experimental Results for Infinite Dilution Activity Coefficients of Water, γ_{13}^∞ , and Ethanol, γ_{23}^∞ , in Glycerol^{a,b}

solute	313.15 K	333.15 K	353.15 K	373.15 K	393.15 K
	γ_{i3}^∞ or γ_{23}^∞				
water	0.73	0.75	0.78	0.79	0.80
ethanol	4.76	3.98	3.73	3.52	3.25

^a $u_r(\gamma_{13}^\infty) = 0.05$, $u_r(\gamma_{23}^\infty) = 0.05$. ^bAccording to eq 2, the infinite dilution activity coefficients have been corrected to zero pressure.

The NRTL equation¹⁷ was used for the modeling of VLE for water (1) + ethanol (2) + glycerol (3). The binary parameters were optimized by use of the experimental results in Tables 1 to 3, as well as literature results of various data type. These include binary VLE data for water + ethanol (Zhang et al.,¹⁸ at 100 kPa; Arce et al.,¹⁹ at 101.32 kPa; Kurihara et al.,²⁰ at 101.3 kPa), infinite dilution activity coefficients for water + ethanol (Kojima and Tochigi, cited in ref 21), and excess enthalpies of water + glycerol (Huemer et al.²² at 323.15 and 353.15 K). The objective function used for the optimization was

$$F = F_{\text{ternary}} + \sum F_{\text{binary}} + 0.2 \times F_{\text{inf}} + 0.2 \times F_{\text{HE}} \quad (3)$$

$$F_{\text{ternary}} = \sqrt{\frac{1}{N} \sum_N (\gamma_{1,\text{cal}}/\gamma_{1,\text{exp}} - 1)^2 + \frac{1}{N} \sum_N (\gamma_{2,\text{cal}}/\gamma_{2,\text{exp}} - 1)^2} \quad (3a)$$

$$F_{\text{binary}} = \sqrt{\frac{1}{N} \sum_N (\gamma_{1,\text{cal}}/\gamma_{1,\text{lit}} - 1)^2 + \frac{1}{N} \sum_N (\gamma_{2,\text{cal}}/\gamma_{2,\text{lit}} - 1)^2} \quad (3b)$$

$$F_{\text{inf}} = \sqrt{\frac{1}{N} \sum_N (\gamma_{13,\text{cal}}^\infty/\gamma_{13,\text{exp}}^\infty - 1)^2 + \frac{1}{N} \sum_N (\gamma_{23,\text{cal}}^\infty/\gamma_{23,\text{exp}}^\infty - 1)^2 + \sqrt{(\gamma_{12,\text{cal}}^\infty/\gamma_{12,\text{lit}}^\infty - 1)^2 + (\gamma_{21,\text{cal}}^\infty/\gamma_{21,\text{lit}}^\infty - 1)^2}} \quad (3c)$$

$$F_{\text{HE}} = \sqrt{\frac{1}{N} \sum_N (H_{\text{cal}}^E/H_{\text{lit}}^E - 1)^2} \quad (3d)$$

where N is the number of data points for a particular data set. In the construction of the objective function, weighing factors were used for the terms of infinite dilution activity coefficient (F_{inf}) and excess enthalpy (F_{HE}). The value 0.2 was chosen somewhat arbitrarily. It was found that, by use of the weighing factors having a common value of 0.2, the resulting correlation was satisfactory for all the data sets. In the correlation, temperature-dependent energy parameters were used for the three binary pairs. It was found that the correlation was sensitive to the choice of the nonrandomness factor c_{23} . For best correlation, c_{23} should have a relatively small value of 0.1. Meanwhile, the values of c_{12} and c_{13} did not show significant

Table 4. Estimated Values of Binary Parameters in the NRTL Equation^a

component <i>i</i>	component <i>j</i>	a_{ij}	b_{ij}	a_{ji}	b_{ji}	c_{ij}
			K		K	
water	ethanol	13.4033	-4099.93	-6.1599	2136.89	0.3
water	glycerol	-1.0486	669.79	0.5754	-527.01	0.3
ethanol	glycerol	-0.9555	702.17	0.3310	19.40	0.1

$${}^a\tau_{ij} = \Delta g_{ij}/RT = a_{ij} + b_{ij}/T; G_{ij} = \exp(-c_{ij}\tau_{ij}).$$

influence on the quality of correlation and were set as 0.3. Results are summarized in Table 4.

Using the obtained parameters, ternary VLE data were calculated in comparison with experimental values. Results are shown in Table 5, in which δT and δy are, respectively, mean

Table 5. Mean Average Deviations, δT and δy , in the Calculation of Ternary VLE of Water (1) + Ethanol (2) + Glycerol (3), and Binary VLE of Water (1) + Ethanol (2), Based on Correlation by NRTL Equation

data type	source of data	data points	δT	δy
			K	
ternary VLE at 100 kPa	this work	48	0.18	0.0032
ternary VLE at 100 kPa	Lee et al. ²	8	2.74	0.0035
ternary VLE at 101.33 kPa	Souza et al. ³	27	4.77	0.0555
ternary VLE at 101.3 kPa	Pla-Franco et al. ⁴	36	0.90	0.0147
binary VLE at 100 kPa	Zhang et al. ¹⁸	9	0.09	0.0007
binary VLE at 101.32 kPa	Arce et al. ¹⁹	23	0.26	0.0032
binary VLE at 101.3 kPa	Kurihara et al. ²⁰	18	0.12	0.0032

absolute deviations of equilibrium temperature and vapor phase mole fraction. The calculated results are in good agreement with experimental values, with $\delta T = 0.17$ K and $\delta y = 0.0032$. The same ternary system has been measured by Lee et al.,² Souza et al.,³ and Pla-Franco et al.⁴ By using parameters proposed in Table 4, the literature data were calculated. As compared with the results of Pla-Franco et al., the calculation has relatively small deviations, with $\delta T = 0.90$ K and $\delta y = 0.0147$. For the results of Lee et al., the deviation in vapor phase mole fraction is small ($\delta y = 0.0035$), whereas the deviation in temperature is relatively large ($\delta T = 2.74$ K). The calculated results show significant deviations for those of Souza et al., having $\delta T = 4.77$ K and $\delta y = 0.0555$.

Experimental and calculated results for the ternary VLE are also shown in Figures 1 to 4. Owing to the regular distribution of the experimental compositions, at eight w_3 and six x'_2 , quality of the present correlation can be in some sense visualized in terms of relative volatility and activity coefficients. Generally, good agreement can be observed. Effects of glycerol on the phase behavior of water and ethanol are also demonstrated in these figures. As shown by the experimental results in Figure 1, the relative volatility of ethanol to water, α_{21} , increases with the addition of glycerol. This is related with a salting-out effect that may enhance the separation of water + ethanol. At $x'_2 = 0.1$, the correlation indicates that α_{21} tends to have a maximum with increasing w_3 . This trend can be verified by the correlation shown in Figure 2, in which a salting-in effect can be observed in the water-rich region. Because the relative volatility is very high in this region, such a salting-in effect will not cause problem to the process of extractive distillation.

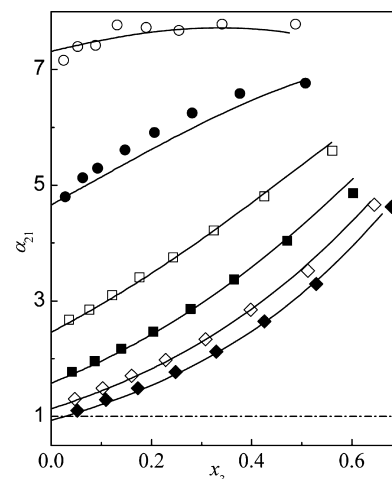


Figure 1. Experimental and calculated relative volatility of ethanol to water, α_{21} , in relation with glycerol mole fraction, x_3 , for the saturated mixture water (1) + ethanol (2) + glycerol (3) at $p = 100$ kPa: \circ , $x'_2 = 0.1$; \bullet , $x'_2 = 0.2$; \square , $x'_2 = 0.4$; \blacksquare , $x'_2 = 0.6$; \diamond , $x'_2 = 0.8$; \blacklozenge , $x'_2 = 0.95$; lines were calculated by NRTL parameters in Table 4.

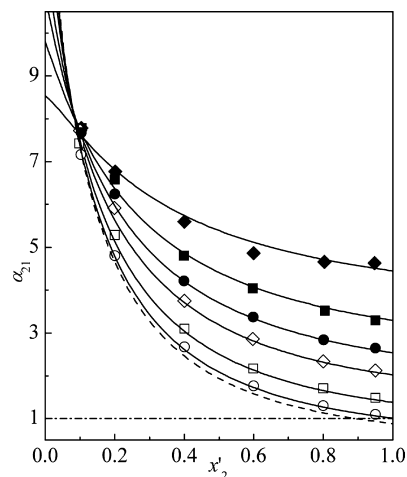


Figure 2. Experimental and calculated relative volatility of ethanol to water, α_{21} , in relation with ethanol mole fraction on solvent-free basis, x'_2 , for water (1) + ethanol (2) + glycerol (3) at $p = 100$ kPa: \circ , $w_3 = 0.1$; \square , $w_3 = 0.3$; \diamond , $w_3 = 0.5$; \bullet , $w_3 = 0.6$; \blacksquare , $w_3 = 0.7$; \blacklozenge , $w_3 = 0.8$. Lines were calculated by NRTL with parameters in Table 4: solid lines, $w_3 = 0.1, 0.3, 0.5, 0.6, 0.7, \text{ and } 0.8$, respectively; dashed line, $w_3 = 0$.

Mechanism for the effect of glycerol on relative volatility can be described by the effect on activity coefficients, using the relation $\alpha_{21} = (\gamma_2/\gamma_1) \cdot (p_2^{\text{sat}}/p_1^{\text{sat}})$. Because the ratio of vapor pressures is independent of composition and insensitive to temperature, the effect of glycerol on α_{21} is mainly decided by its effect on γ_1 and γ_2 . As shown in Figure 3, the salting-out effect is caused by both the decrease of γ_1 and the increase of γ_2 . In the water-rich region, as indicated by the correlation shown

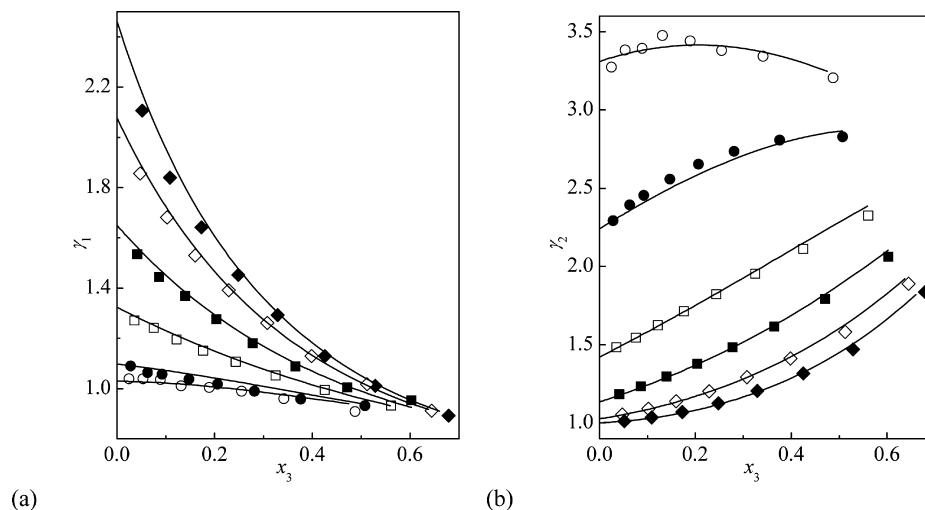


Figure 3. Experimental and calculated activity coefficients of (a) water, γ_1 , and (b) ethanol, γ_2 , in relation with glycerol mole fraction, x_3 , for water (1) + ethanol (2) + glycerol (3) at $p = 100$ kPa: \circ , $x'_2 = 0.1$; \bullet , $x'_2 = 0.2$; \square , $x'_2 = 0.4$; \blacksquare , $x'_2 = 0.6$; \diamond , $x'_2 = 0.8$; \blacklozenge , $x'_2 = 0.95$; lines were calculated by NRTL parameters in Table 4.

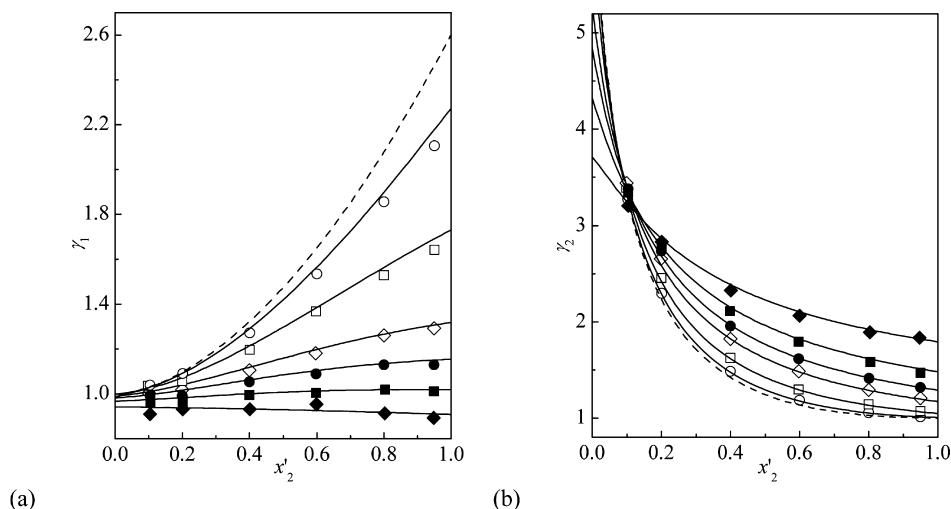


Figure 4. Experimental and calculated activity coefficients of (a) water, γ_1 , and (b) ethanol, γ_2 , in relation with ethanol mole fraction on solvent-free basis, x'_2 , for the saturated mixture water (1) + ethanol (2) + glycerol (3) at $p = 100$ kPa: \circ , $w_3 = 0.1$; \square , $w_3 = 0.3$; \diamond , $w_3 = 0.5$; \bullet , $w_3 = 0.6$; \blacksquare , $w_3 = 0.7$; \blacklozenge , $w_3 = 0.8$. Lines were calculated by NRTL with parameters in Table 4: solid lines, $w_3 = 0.1, 0.3, 0.5, 0.6, 0.7$, and 0.8 , respectively; dashed line, $w_3 = 0$.

in Figure 4, γ_2 decreases rapidly with the addition of glycerol. This accounts for the salting-in effect observed in Figure 2.

Using the binary parameters, isobaric VLE data for water (1) + ethanol (2) were calculated and compared with literature values, as shown in Table 5. Results are satisfactory. For the VLE data of Zhang et al.,¹⁸ the present correlation has very small deviations of $\delta T = 0.09$ K and $\delta y = 0.0007$. Good agreement can also be observed for the results of Arce et al.¹⁹ ($\delta T = 0.26$ K and $\delta y = 0.0032$) and Kurihara et al.²⁰ ($\delta T = 0.12$ K and $\delta y = 0.0032$). Moreover, activity coefficients at infinite dilution were calculated for the binary system. Results are given in comparison with those of Kojima and Tochigi (cited in Kojima et al.²¹) in Table 6. The calculated value of γ_{12}^∞ is 2.59, having very small deviation with the literature value of 2.58. For γ_{21}^∞ , the calculated and literature value is, respectively, 6.84 and 6.85, indicating very good agreement.

NRTL parameters for VLE of water (1) + ethanol (2) + glycerol (3) have been proposed by Souza et al.³ and Pla-Franco et al.,⁴ and are available in the database of Aspen Plus

Table 6. Deviations in the Calculation of Infinite Dilution Activity Coefficients, γ^∞ , of Water (1) + Ethanol (2), Based on Correlation by NRTL Equation

data	T K	literature value ^a	calculated value	relative deviation
γ_{12}^∞	351.45	2.58	2.59	0.4 %
γ_{21}^∞	373.15	6.85	6.84	0.2 %

^aKojima and Tochigi (1970, cited in ref 21).

process simulator, for example, APV80 VLE-IG. As shown in Figure 5, the present correlation was compared with those in literature in terms of α_{21} in relation with w_3 at $p = 100$ kPa and $x'_2 = 1$. When the glycerol mass fraction is low, the present correlation provide similar results as compared with those of Souza et al.³ The calculated relative volatilities of Pla-Franco et al.⁴ and APV80 VLE-IG are somewhat larger. On the basis of calculations using APV80 VLE-IG, the minimum mass fraction

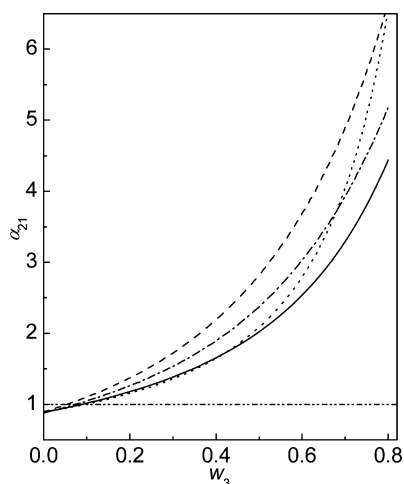


Figure 5. Calculated results for relative volatility of ethanol to water, α_{21} , for water (1) + ethanol (2) + glycerol (3) at $x'_2 = 1$ and $p = 100$ kPa: solid line, this work in Table 4; dotted line, Souza et al. (ref 3); dashed line, APV80 VLE-IG; dash-dot line, Franco et al. (ref 4).

of glycerol needed for breaking the water + ethanol azeotrope is 0.0545. This value is apparently smaller compared with the result of the present correlation, which requires a minimum mass fraction of 0.0902. At higher glycerol mass fractions, for example, $w_3 > 0.5$, the deviations become larger for the three literature sources.

For further comparison of the correlations, boiling temperatures were calculated for binary systems of water (1) + glycerol (3) and ethanol (2) + glycerol (3). When glycerol mass fraction is low, for example, $w_3 < 0.5$, all the correlations provide similar results for the boiling temperature. With the increase of glycerol mass fraction, however, deviations may be significantly high. Comparisons for the boiling temperature of water (1) + glycerol (3) at $p = 101.33$ kPa are shown in Figure 6. Using parameters in this work, the calculated boiling temperatures are in good agreement with the experimental values. The results are slightly lower than those of Mokbel et

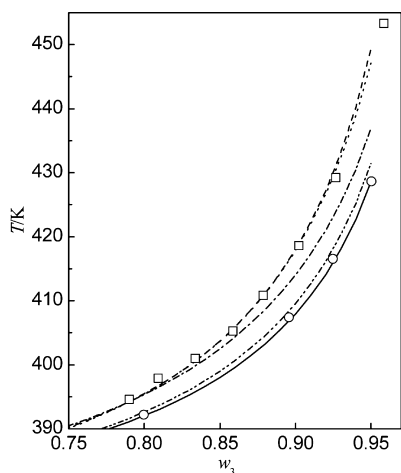


Figure 6. Boiling temperature for the binary system water (1) + glycerol (3) at $p = 101.33$ kPa: \square , Oliveira et al. (ref 24). Lines were calculated by model parameters: solid line, this work in Table 4; dotted line, Souza et al. (ref 3); dashed line, APV80 VLE-IG; dash-dot line, Franco et al. (ref 4); dash-dot-dot line, Mokbel et al. (ref 23).

al.²³ and are apparently much lower than those of Pla-Franco et al.⁴ Although the results of Souza et al.³ and APV80 VLE-IG are in good agreement with the literature values of Oliveira et al.,²⁴ they show significant positive deviation from the results of this work and those of Mokbel et al.²³ At $w_3 = 0.95$, the deviation in boiling temperature may be as large as 20 K. This might cause significant overestimation of the boiler temperature in extractive distillation. For the boiling temperature of ethanol (2) + glycerol (3) at $p = 101.33$ kPa, as shown in Figure 7, the

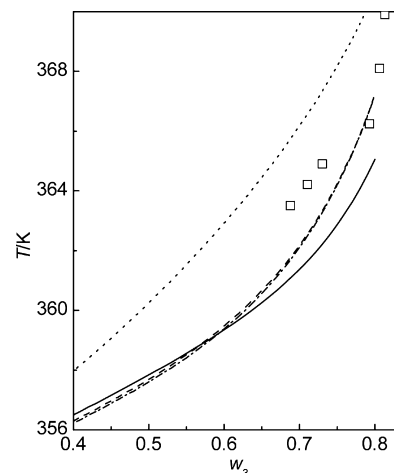


Figure 7. Boiling temperature for the binary system ethanol (2) + glycerol (3) at $p = 101.33$ kPa: \square , Oliveira. Lines were calculated by model parameters: solid line, this work in Table 4; dotted line, Souza et al. (ref 3); dashed line, APV80 VLE-IG; dash-dot line, Franco et al. (ref 4).

correlation in this work provide similar results as compared with those of Pla-Franco et al.⁴ and APV80 VLE-IG, especially at $w_3 < 0.6$. At $w_3 = 0.8$, the deviation has a value of 2.15 K. Meanwhile, the boiling temperatures reported by Oliveira et al.²⁴ are relatively high. The correlation of Souza et al.³ show largest deviations, which has a positive value of 5.61 K at $w_3 = 0.8$. In extractive distillation, this might cause overestimation of the temperature for the feeding plate of glycerol.

To compare the correlations in a wider composition range, infinite dilution activity coefficients were calculated for water in glycerol, γ_{13}^∞ , and ethanol in glycerol, γ_{23}^∞ . The calculated results are compared with the experimental and literature values and shown in Figure 8. As γ_{13}^∞ is concerned, the results of the present correlation are in good agreement with the experimental values and are slightly larger than the literature values of Ikari and Ayabe (cited in Kojima et al.²¹) and the calculated values of Mokbel et al.²³ Further, the literature values of Bestani and Shing²⁵ appears to be unusually great, whereas the correlations of Souza et al.,³ Pla-Franco et al.,⁴ and APV80 VLE-IG provide values that are unusually small. Because the infinite dilution state is closely related to the process of glycerol recovery, such large deviations in γ_{13}^∞ would have significant impact on the design of the recovery unit. For γ_{23}^∞ , results of the present correlation are similar to those of Souza et al.,³ and are in good agreement with the experimental values. Meanwhile, the correlations of Pla-Franco et al.⁴ and APV80 VLE-IG provide values that are relatively small.

As indicated in Figure 8, the calculated values of γ_{13}^∞ decrease rapidly with the rise of temperature, so far as the parameters of APV80 VLE-IG are used. Because γ_{13}^∞ is less than unity, this

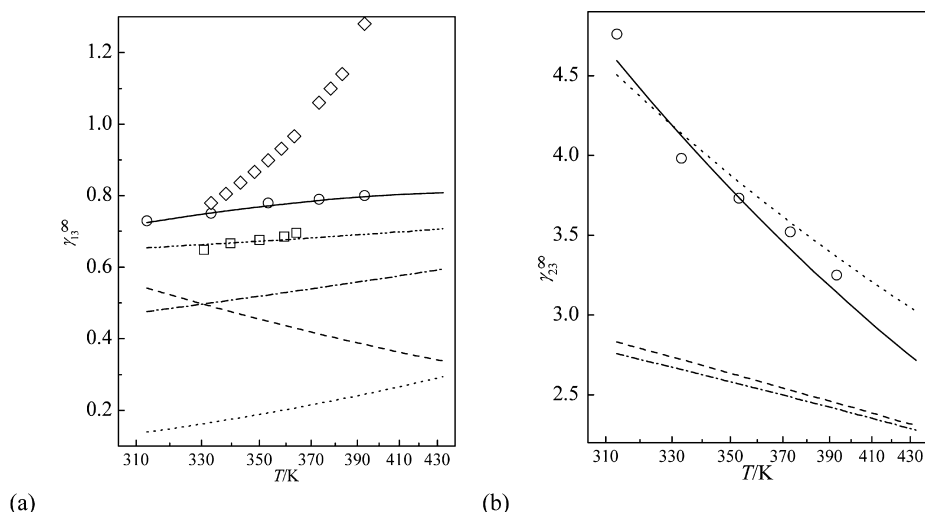


Figure 8. Infinite dilution activity coefficients of (a) water, γ_{13}^{∞} , and (b) ethanol, γ_{23}^{∞} , in glycerol: \circ , this work; \square , Ikari and Ayabe (1967, cited in ref 21); \diamond , Bestani and Shing (ref 25). Lines were calculated by model parameters: solid line, this work in Table 4; dotted line, Souza et al. (ref 3); dashed line, APV80 VLE-IG; dash-dot line, Franco et al. (ref 4); dash-dot-dot line, Mokbel et al. (ref 23).

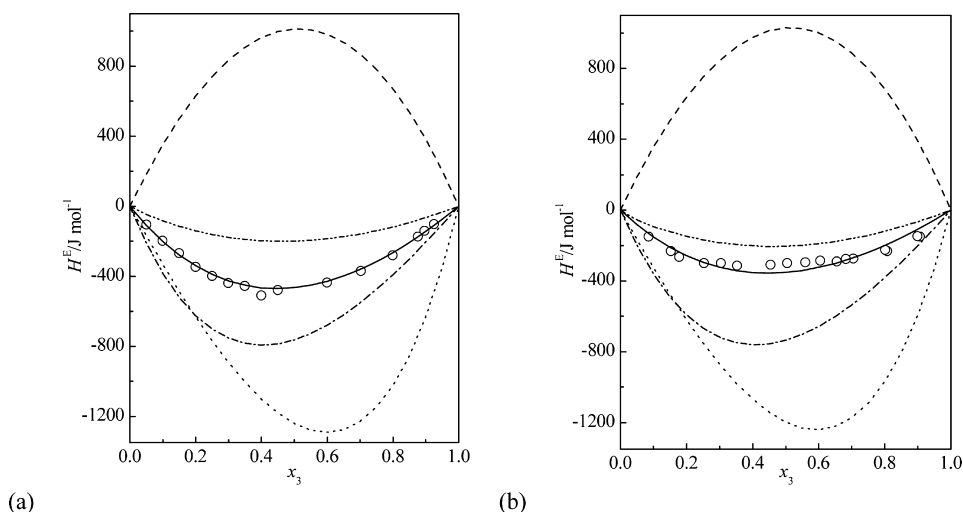


Figure 9. Excess enthalpies, H^E , for the binary system water (1) + glycerol (3) at (a) 323.15 K and (b) 353.15 K: \circ , Huemer et al. (ref 22). Lines were calculated by model parameters: solid line, this work in Table 4; dotted line, Souza et al. (ref 3); dashed line, APV80 VLE-IG; dash-dot line, Franco et al. (ref 4); dash-dot-dot line, Mokbel et al. (ref 23).

trend seems to be very unusual. For verification of the temperature dependence of the activity coefficients, excess enthalpies, H^E , were calculated by the relation

$$H^E = -RT^2 \left(x_1 \frac{d(\ln \gamma_1)}{dT} + x_2 \frac{d(\ln \gamma_2)}{dT} \right) \quad (4)$$

Results at 323.15 and 353.15 K are shown in Figure 9, in comparison with the literature values of Huemer et al.²² As expected, the correlation of APV80 VLE-IG provide positive values of H^E , which should be erroneous. Although the correlations by Souza et al.,³ Pla-Franco et al.,⁴ and Mokbel et al.²³ provide results with correct sign, there are significant deviations as compared with the literature values. Using the parameters in this work, the calculated results are in good agreement with the literature values.

CONCLUSIONS

Vapor–liquid equilibrium of the system water + ethanol + glycerol were modeled using experimental and literature data

over wide ranges of composition and temperature, with emphasis on the application in ethanol dehydration by extractive distillation. New experimental data were reported for isobaric ternary VLE, boiling temperature of water + glycerol, and infinite dilution activity coefficient of water and ethanol in glycerol. The NRTL equation was used for the modeling. Literature data of binary VLE of water + ethanol, infinite dilution activity coefficients of water + ethanol, and excess enthalpies of water + glycerol were also used for optimization. The correlation showed that the azeotrope of water + ethanol can be removed at a glycerol mass fraction of 0.0902. The experimental results were compared graphically with those of calculations, showing good agreement. Comparisons were also presented for experimental results and correlations available in the literature.

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