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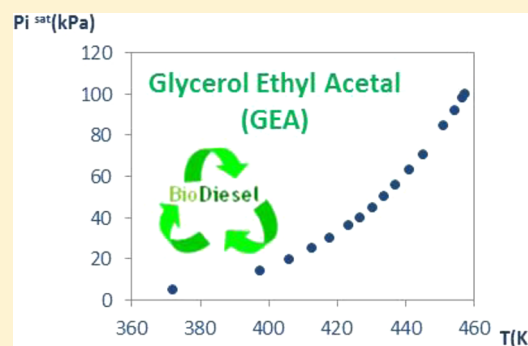
Isobaric Vapor–Liquid Equilibrium Data for Binary System of Glycerol Ethyl Acetal and Acetonitrile at 60.0 kPa and 97.8 kPa

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ABSTRACT: Isobaric vapor–liquid equilibrium (VLE) data for the binary mixture of glycerol ethyl acetal (GEA) and acetonitrile were measured at 60.0 kPa and 97.8 kPa, using a dynamic recirculating still. The VLE data were correlated using the nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models, and the interaction parameters of this mixture were estimated. The experimental procedure was checked by measuring VLE data at 97.8 kPa of the well-known system acetone/methanol showing high conformity, as given by applying a set of VLE consistency tests. The vapor pressure of GEA was measured, for the first time, in the temperature range from 371.85 K to 456.85 K, and it is described by the following expression: $\ln P_{\text{GEA}}^{\text{sat}}(\text{Pa}) = 24.17 - 5781/T(\text{K})$. The information collected is of utmost importance for the purification of GEA synthesized using simulated moving bed reactor technology.

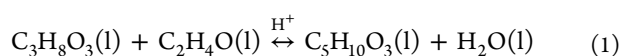


1. INTRODUCTION

In the last years, glycerol valorization has been the focus of much research, due its low cost and high availability. It is estimated that about 10 wt % of glycerol is obtained as a byproduct in the biodiesel production, and therefore, the transformation of glycerol into high added-value products has been studied in order to increase the economic viability of the biodiesel synthesis process.^{1–4} Among glycerol derivatives, glycerol acetals have been considered as promising chemicals, especially to be used as green oxygenates for diesel blending because of their ability to reduce particle emissions of exhaust gases without having a negative impact on the engine performance and to allow the control of the fuel properties.^{5–7}

For example, García et al.⁷ reported the benefits of glycerol acetal properties in biodiesel combustion process by improving the viscosity in order to achieve the flash point and oxidation stability required. Other applications, for these type of compounds, are as flavoring agents^{8,9} and surfactants antifreezing additives.¹⁰

Particularly, glycerol ethyl acetal (GEA) already proved its benefits when blended to fuel as octane number enhancer¹¹ and on the reduction of the particulate matter emissions.¹² GEA can be obtained from the acetalization of glycerol with acetaldehyde, catalyzed in acid medium, having water as a byproduct:



As written in eq 1, GEA has the general formula $\text{C}_5\text{H}_{10}\text{O}_3$, and it is composed by an isomeric mixture of 5- and 6-membered rings: *cis(trans)*-5-hydroxy-2-methyl-1,3-dioxane and *cis(trans)*-4-hydroxymethyl-2-methyl-1,3-dioxolane (see Figure 1).

The acetals synthesis involves thermodynamic equilibrium limited reactions, and the conventional process for their production makes use of a reactor followed by several separation steps (mostly distillation) to recover and recycle the unconverted reactants and to remove water in order to obtain acetals with the desired purity.¹³ However, this process represents high energy consumption and high capital costs (investment in several reaction/separation units). Therefore, the most feasible engineering solution for their production is the use of hybrid technologies, where reaction and separation occur, simultaneously, into the same piece of equipment, as the simulated moving bed reactor (SMBR). This technology combines the continuous countercurrent chromatographic separation with chemical reaction, since it is possible to achieve complete reactant conversion and product separation.

The SMBR was already successfully applied for the production of the following acetals: 1,1-diethoxyethane,^{14,15} 1,1-dimethoxyethane,¹⁶ and 1,1-dibutoxyethane,¹⁷ and is under development (within our research group) for the GEA synthesis.

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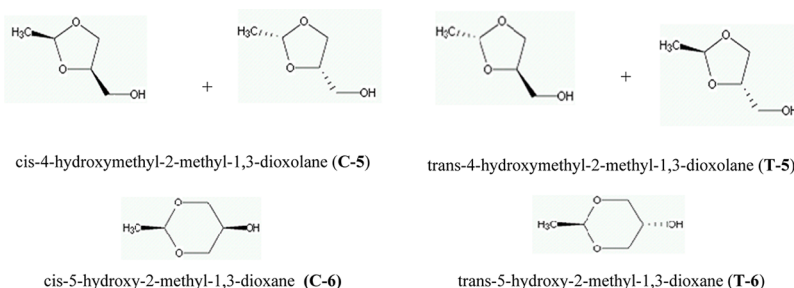


Figure 1. Glycerol ethyl acetal isomers from the reaction of acetaldehyde with glycerol.

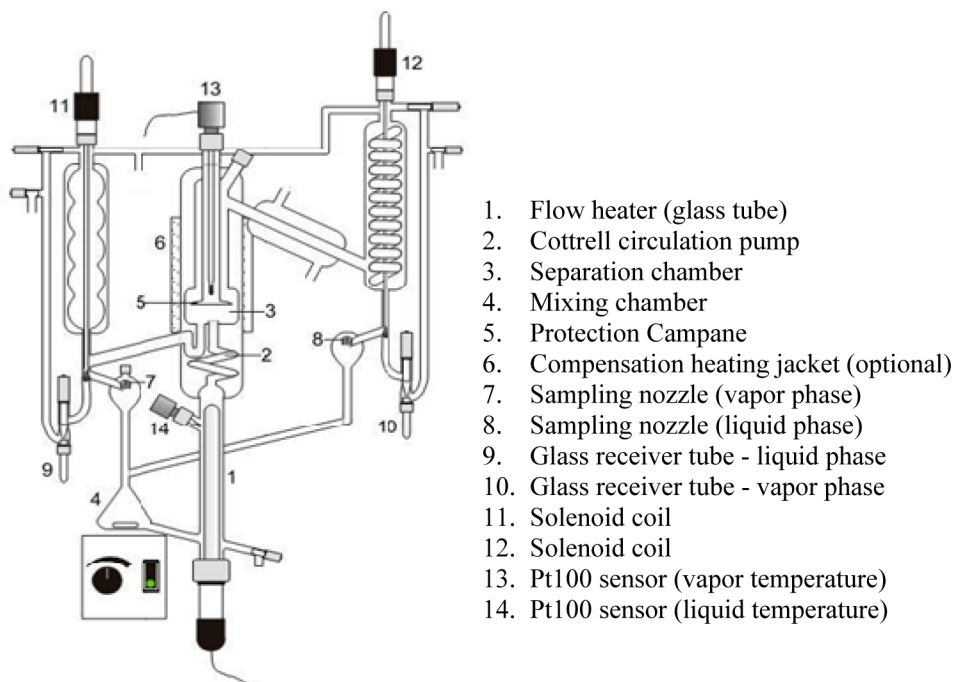


Figure 2. VLE 100 D apparatus.

In the SMBR, two outlet streams are obtained: the extract stream comprising the most adsorbed product and the raffinate stream comprising the less adsorbed one, both diluted in the desorbent (required in order to regenerate the adsorbent). Usually, in the acetalization SMBR processes, the alcohol is used as a desorbent; however, in the GEA synthesis this will not be possible due to the high glycerol viscosity (1.499 Pa·s at 25 °C¹⁸). Acetonitrile was pointed out as one of the most suitable solvents, based on miscibility, reactivity, and adsorption tests, to be applied on the GEA production by SMBR using a commercial resin, Amberlyst-15 wet, as a catalyst and selective adsorbent toward water.¹⁹ As a consequence, in this case, the outlet streams of the SMBR will be: (i) the extract stream comprising water/acetonitrile and (ii) the raffinate stream comprising the desired product (GEA) and acetonitrile.

To design, evaluate, and optimize an efficient separation unit to treat the raffinate stream to get pure GEA, it is important to know the thermodynamic properties of the pure compounds as well as of the binary system (GEA/acetonitrile). For this purpose, in this work, the isobaric vapor–liquid equilibrium (VLE) data were measured for the binary GEA/acetonitrile at two different pressures in a VLE apparatus (VLE 100D) manufactured by Fischer (Germany). The interaction parameters of this mixture were estimated by correlating the

VLE experimental data with the nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) thermodynamic models. The equipment was tested and the procedure validated measuring the VLE of acetone/methanol system at 97.8 kPa and the vapor pressures of the pure components.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Acetone by Absolve (> 0.997 mass fraction), acetonitrile by Fluka (> 0.999 mass fraction), methanol (> 0.998 mass fraction), acetaldehyde (> 0.99 mass fraction), and glycerol (> 0.99 mass fraction) from Sigma-Aldrich (U.K.) were used without any further purification.

2.2. GEA Production and Purification. To produce GEA, the reaction between acetaldehyde and glycerol, in a molar ratio of 2:1, was carried out in the presence of Amberlyst 15-wet resin (1 wt.%) from Rohm and Haas, on a glass-jacketed 1 L closed vessel, at atmospheric pressure and at 20 °C. After reaching the chemical equilibrium, the resin (heterogeneous catalyst) was separated by filtration, and the quaternary mixture comprising glycerol, acetaldehyde, GEA, and water was subjected to: (i) distillation at atmospheric pressure to remove acetaldehyde and (ii) vacuum distillation (20 mbar) to separate water and GEA from glycerol. The water/GEA mixture was

Table 1. Experimental Vapor Pressures of Acetone, Methanol, GEA, and Acetonitrile

acetone		methanol		GEA		acetonitrile	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
294.2	25.74	336.7	97.81	371.8	5.07	299.0	12.34
298.4	30.89	337.3	100.94	397.3	14.96	310.6	20.57
299.7	32.53	338.6	105.83	405.6	20.26	321.6	31.89
310.9	51.48	340.9	115.86	412.3	25.61	329.4	43.04
317.6	66.92	342.1	120.98	417.6	30.47	334.1	50.98
323.9	82.36	343.9	129.30	423.1	36.69	338.7	60.02
326.6	92.66	345.3	136.37	426.4	40.99	339.3	61.21
328.2	97.81	348.6	153.71	430.0	45.99	343.8	71.28
		351.9	172.86	433.5	51.17	348.3	82.73
		357.6	210.61	436.8	56.44	351.6	92.05
		361.2	237.64	437.2	60.02	354.4	100.75
		364.0	260.99	440.9	63.65	354.2	99.91
		367.7	294.29	444.8	71.34	357.1	109.31
		371.3	329.88	450.9	85.00	361.6	124.78
				453.9	92.12	365.8	141.08
				456.1	97.81	369.0	154.85
				456.9	100.08	372.3	169.67
						376.3	189.36
						382.3	221.97
						386.6	247.71
						390.1	270.69
						393.9	298.62

once again subjected to vacuum distillation, at 20 mbar, in order to obtain high-purity GEA (0.998 mass fraction according to the analytical method developed on gas chromatography with uncertainty of ± 0.0001) with the following molar basis composition: 68.0 % *trans*-5-hydroxy-2-methyl-1,3-dioxane, 25.3 % *trans*-4-hydroxymethyl-2-methyl-1,3-dioxolane, 6.2 % *cis*-4-hydroxymethyl-2-methyl-1,3-dioxolane, and 0.5 % *cis*-5-hydroxy-2-methyl-1,3-dioxane.

2.3. Apparatus and Experimental Procedure. In this study the VLE experiments were performed by using an all-glass dynamic recirculating still, apparatus model VLE 100D, which is manufactured by Fischer Company (Germany). A schematic representation is shown in Figure 2. This device is equipped with a Cottrell circulation pump, two temperature sensors Pt-100 class A with accuracy of ± 0.15 K, a vacuum pump, and an electrovalve activated by an on–off controller in order to minimize the pressure deviations from the setting. The pressure is measured by a vacuum (0 mbar to 1000 mbar abs. range) or a pressure (0 mbar to 4000 mbar rel. range) sensor, both presenting an accuracy of 0.35 % FSO and an uncertainty of ± 0.2 kPa.

Initially, the sensor accuracy was analyzed by measuring the vapor pressure at different temperatures of some well-known compounds. Deviations were found between the experimental vapor pressure and that calculated using the DIPPR chemical database,²⁰ more evidently at vacuum conditions. So, a calibration was performed to both pressure sensors using pure water (in the pressure range from 24.4 kPa to 209.6 kPa). This calibration was then validated through the measurement of the vapor pressure of acetone and methanol. After, isobaric VLE data were also measured for the well-known binary mixture containing both compounds. For each experiment, the pressure was fixed, and a suitable power of flow heater was defined to avoid a sudden and sharp boiling of the homogeneous mixture, at constant stirring. After reaching around 60 drops of both liquid and condensed vapor, the

system was kept at the boiling point for about 45 min before the first sampling. It was considered that the equilibrium was attained when the composition of two consecutive samples (taken every 5 min), from both vapor and liquid phases, present a deviation in their molar composition less than 0.1 %. The collection of vapor and liquid samples can be performed in two ways: one by using the glass receivers (9, 10) just raising the solenoid coils (11, 12) or using two gas syringes. The use of syringes is preferable, mainly for the vapor side, because it allows collecting directly the condensed drops formed, avoiding condensate losses through the walls. The new experimental data for the system GEA/acetonitrile were after being collected at two different pressures.

2.4. Analytical Method. All samples collected were analyzed in a Shimadzu-GC 2010 Plus gas chromatograph equipped with flame ionization and thermal conductivity detectors. The compounds were separated using a silica capillary column (CPWax52CB, 25 m \times 0.25 mm ID, film thickness of 1.2 μ m). Helium N50 was used as the carrier gas at a flow rate of 10.1 mL·min^{−1}. The temperature of the injector and of the both detectors was set to 573.15 K. The initial column temperature was 333.15 K for 3.0 min, and the temperature was then increased at 30 K·min^{−1} up to 513.15 K remaining constant for the following 7 min. In this way, the associated uncertainty of the measured molar fractions was ± 0.01 (except for binary acetone and methanol, which was ± 0.001).

3. RESULTS AND DISCUSSION

3.1. Pure Components. The equipment was initially tested to measure the vapor pressures of the pure compounds acetone, methanol, and acetonitrile. The experimental values are presented in Table 1, and a comparison with those calculated from the DIPPR database is given in Figure 3. In this plot the percentage relative deviation is shown for each experimental

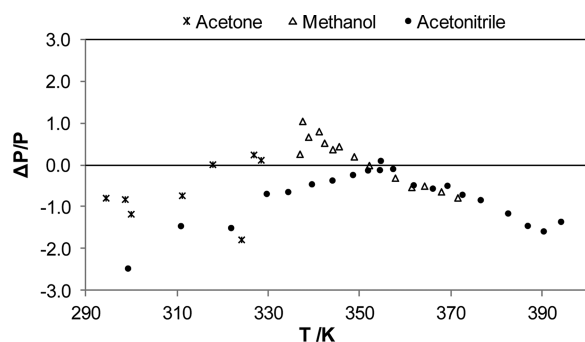


Figure 3. Percentage relative deviations of acetone, methanol, and acetonitrile.

point, varying from -2.4% up to 1.0% . The equation applied in the vapor pressure calculation is:

$$\ln P_i^{\text{sat}}(\text{Pa}) = A + \frac{B}{T} + C \ln T + DT^E \quad (2)$$

where T is the absolute temperature. Table 2 presents the coefficients found in the DIPPR database²⁰ and the average relative deviations as well. The average relative deviation is about 0.7% , which is within the values usually found,²¹ showing very good agreement between the experimental and calculated values. Regarding GEA, the experimental values are also presented in Table 1. For GEA a comparison to the values calculated by DIPPR is not possible. In fact, these are the first systematic measurements for the vapor pressures of GEA we are aware of. Equation 3 was fitted to the GEA vapor pressure experimental results leading to the following expression (valid in the temperature range 371.8 K to 456.9 K):

$$\ln P_{\text{GEA}}^{\text{sat}}(\text{Pa}) = 24.17 - \frac{5781}{T} \quad (3)$$

3.2. Binary Systems. VLE data for the acetone/methanol binary were first measured at 97.8 kPa to evaluate the performance of the equipment. The experimental data are reported in Table 3, where x_i is the mole fraction of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, and γ_i is the activity coefficient of component i calculated in accordance to eq 4:

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^{\text{sat}}} \quad (4)$$

where Φ_i is the fugacity coefficient ratio of component i and P is the total system pressure. The quality of the experimental data was analyzed in two ways. First, using the database available in the software AspenTech-AspenONE version 7.1, the VLE diagram was calculated at 97.8 kPa using either the NRTL or UNIQUAC model. As can be seen in Figure 4 a very good agreement was found, presenting average absolute deviations of $\delta y = 0.004$ and $\delta T = 0.08\text{ K}$ for the vapor phase composition and temperature, respectively. Second,

Table 3. Isobaric VLE Data for Acetone (1) and Methanol (2) System at 97.8 kPa

T/K	x_1	y_1	$\gamma_{1,\text{NRTL}}$	$\gamma_{1,\text{UNIQUAC}}$	γ_1^{exp}	γ_2^{exp}
327.6	0.9186	0.9049	0.9007	0.9072	1.0070	1.6996
327.4	0.7710	0.7676	0.7704	0.7763	1.0248	1.4887
327.8	0.6196	0.6693	0.6662	0.6669	1.0965	1.2542
328.2	0.5323	0.6177	0.6101	0.6073	1.1619	1.1594
328.8	0.4522	0.5526	0.5571	0.5512	1.1987	1.1295
330.4	0.2810	0.4182	0.4250	0.4129	1.3823	1.0470
331.3	0.2179	0.3564	0.3629	0.3491	1.4738	1.0260
332.1	0.1679	0.3024	0.3050	0.2906	1.5792	1.0117
332.9	0.1293	0.2566	0.2530	0.2388	1.6943	0.9972
333.8	0.0960	0.1973	0.2079	0.1882	1.7031	0.9999
335.2	0.0444	0.1009	0.0958	0.0963	1.8003	1.0015

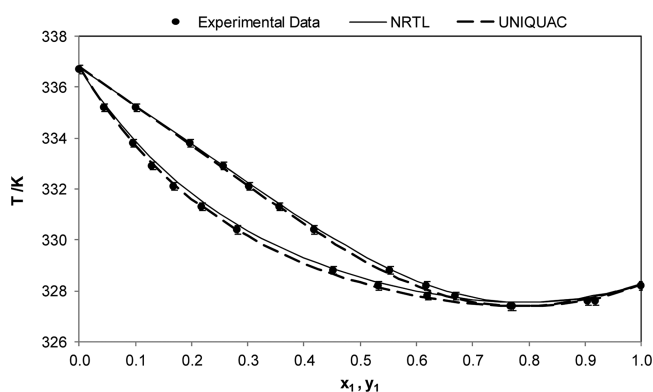


Figure 4. VLE for the acetone (1) and methanol (2) system at 97.8 kPa .

following the strategy suggested by Kang et al.,²² thermodynamic consistency tests were implemented: Herington test (test 1), Van Ness test (test 2), infinite dilution test (test 3), and pure component consistency test. The point test was not used because it is not applicable to isobaric data sets. Following their approach,²² the overall quality factor (Q) for a VLE data set of acetone/methanol system was about 0.99 , where $Q_{\text{VLE}} = [F_{\text{pure}}(F_{\text{test1}} + F_{\text{test2}} + F_{\text{test3}})]/0.75$, showing that the data are of very good quality. Finally, it is important to mention that, when using eq 4 to acetone/methanol system, the fugacity coefficients were obtained in accordance to the Tsonopoulos correlation,²³ calculating the second virial coefficient of pure substances using information available in the DIPPR database.²⁰

Afterward, VLE data of the system GEA and acetonitrile at two different pressures were measured. Tables 4 and 5 present the experimental data collected as well as the experimental activity coefficients for both components. The system presents positive deviations to the ideal solution behavior, suggesting that intermolecular forces between different species are less important than those in the pure liquids. For concentrated acetonitrile solutions self-association of GEA is favored since

Table 2. Coefficients Used To Calculate P_i^{sat} of Pure Components and Relation Deviations

component	T range/K	coefficients used on eq 2					$\Delta P/P$
		A	B	C	D	E	
acetone	178.45 to 508.20	$6.901 \cdot 10^1$	$-5.600 \cdot 10^3$	$-7.099 \cdot 10^0$	$6.224 \cdot 10^{-6}$	$2.000 \cdot 10^0$	0.007
methanol	175.47 to 512.50	$8.272 \cdot 10^1$	$-6.905 \cdot 10^3$	$-8.862 \cdot 10^0$	$7.466 \cdot 10^{-6}$	$2.000 \cdot 10^0$	0.005
acetonitrile	229.32 to 545.50	$5.830 \cdot 10^1$	$-5.386 \cdot 10^3$	$-5.495 \cdot 10^0$	$5.363 \cdot 10^{-6}$	$2.000 \cdot 10^0$	0.008

Table 4. Isobaric VLE Data of the GEA (1) and Acetonitrile (2) System at 60.0 kPa

T/K	x_1	y_1	γ_1	γ_2
338.9	0.034	0.000		0.981
339.4	0.055	0.000		0.987
340.2	0.079	0.000		0.994
341.6	0.118	0.001	0.363	1.009
343.6	0.181	0.001	0.214	1.04
345.3	0.245	0.002	0.292	1.072
347.3	0.309	0.003	0.315	1.104
348.1	0.358	0.004	0.349	1.126
349.6	0.395	0.003	0.221	1.144
352.3	0.443	0.004	0.231	1.163
357.4	0.549	0.009	0.332	1.196
359.8	0.592	0.013	0.399	1.206
361.9	0.611	0.018	0.488	1.207
363.8	0.638	0.022	0.526	1.212
364.9	0.666	0.024	0.524	1.221
368.6	0.691	0.029	0.520	1.226
371.6	0.722	0.034	0.514	1.236
374.3	0.751	0.04	0.520	1.248
385.6	0.833	0.082	0.611	1.288
386.8	0.837	0.095	0.673	1.277
397.4	0.876	0.16	0.727	1.280
398.6	0.885	0.182	0.783	1.278
404.9	0.907	0.242	0.811	1.283
412.6	0.936	0.361	0.898	1.288
420.4	0.954	0.525	0.988	1.158
423.6	0.957	0.579	0.980	1.071
430.4	0.981	0.76	1.011	1.116
436.3	0.996	0.917	1.002	1.578

Table 5. Isobaric VLE Data of the GEA (1) and Acetonitrile (2) System at 97.8 kPa

T/K	x_1	y_1	γ_1	γ_2
353.6	0.025	0.000		1.008
353.9	0.035	0.000		1.018
354.0	0.043	0.000		1.029
354.3	0.092	0.000		1.105
354.9	0.202	0.001	0.139	1.270
356.9	0.355	0.001	0.142	1.360
358.6	0.396	0.003	0.202	1.360
361.1	0.428	0.005	0.294	1.353
369.4	0.533	0.011	0.394	1.313
375.2	0.571	0.021	0.569	1.287
377.3	0.588	0.021	0.504	1.281
380.6	0.627	0.027	0.535	1.260
383.7	0.659	0.034	0.562	1.247
390.3	0.731	0.062	0.722	1.208
407.3	0.838	0.139	0.757	1.204
411.6	0.850	0.179	0.825	1.176
417.6	0.871	0.240	0.886	1.137
422.9	0.907	0.301	0.896	1.199
426.9	0.918	0.359	0.928	1.175
429.6	0.927	0.404	0.951	1.169
436.8	0.954	0.514	0.942	1.261
447.6	0.980	0.759	0.983	1.217
449.1	0.985	0.828	1.021	1.149

GEA activity coefficients are considerably lower than 1, which is also in accordance to the opposite trend for the acetonitrile activity coefficients.

Due to the lack of reliable values for the critical properties of GEA, in this system the fugacity coefficients had to be considered equal to 1, inhibiting the application of VLE consistency tests. Alternatively, data were correlated with NRTL and UNIQUAC models. The interaction parameters were estimated by minimizing the following objective function:

$$OF = \min \sum_{i=1}^N \left| \frac{T_{\text{exp}} - T_{\text{mod}}}{T_{\text{exp}}} \right| \quad (5)$$

where T_{exp} is the experimental equilibrium temperature, T_{mod} is the temperature calculated by the model, and N is the number of experimental data points. The area and volume parameters used in UNIQUAC model were found in Poling et al.²⁴ for acetonitrile, while for GEA were calculated by the group parameters published in the UNIFAC method ($r = 4.6315$, $q = 4.0640$).

The parameters for both models are given in Table 6, as well as the deviations in temperature and vapor phase composition. Similarly to the Van Ness test,²² which is regarded as a modeling capability test, the deviations presented in Table 6 allow the calculation of a quality factor (F), which indicates good consistency, as $F = 0.19$ for a maximum of 0.25. The temperature–composition diagrams (Txy) for the GEA (1) and acetonitrile (2) system are presented in Figures 5a (60.0 kPa) and 6a (98.7 kPa), while the $y-x$ diagrams are presented in Figures 5b and 6b, respectively.

Since the isomeric mixture was considered as a single compound and, consequently, the mixture taken as a pseudo binary, the interaction of isomers was not taken into account. This fact can contribute to the relative larger deviations when the GEA mole fraction is higher. Moreover, isomerization equilibria might change with temperature, which introduces a big challenge to model the behavior of this system, and new developments are needed to describe more correctly the physical and chemical equilibrium between isomers of GEA and other components. However, the modeling shows reasonable results considering also the large difference of the vapor pressures between the two compounds. This big difference leads to considerable difficulties in the experimental procedure, reducing the precision of the composition measurement (see section 2.4). The calculated activity coefficients for the GEA/acetonitrile system shown in Tables 4 and 5 present a curious trend with the composition, but such a variation is commonly found in this type of systems.^{25,26}

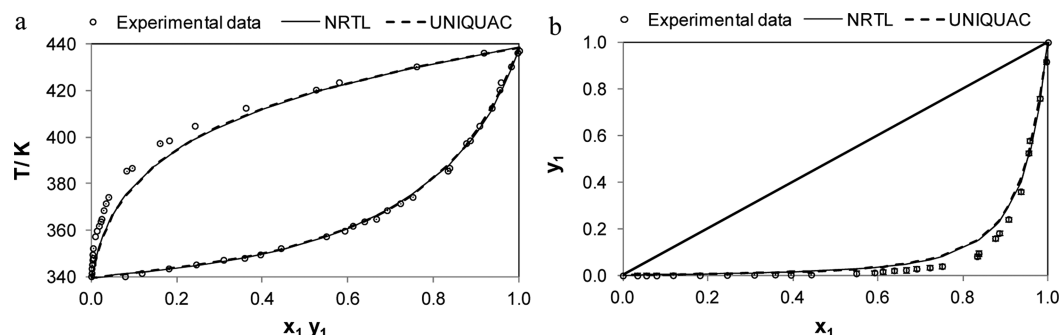
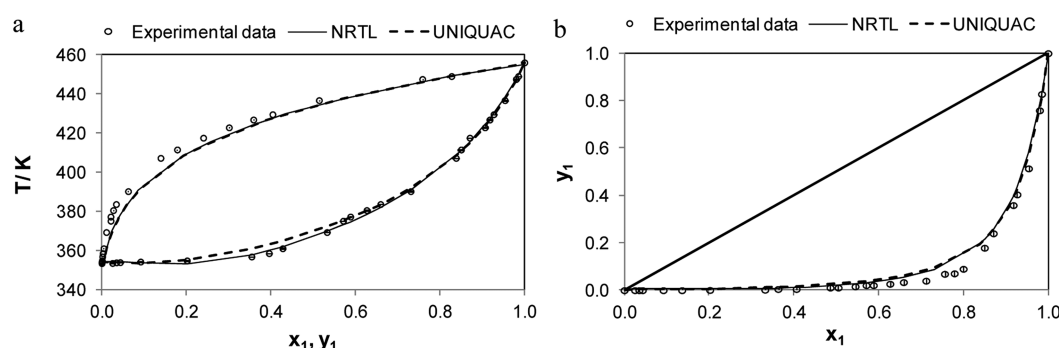
4. CONCLUSIONS

The main objectives of this work were the measurement of the isobaric VLE data for the binary system of GEA and acetonitrile at 60.0 kPa and 97.8 kPa, as well as the determination of GEA vapor pressure, leading to the following conclusions:

- The VLE data of the studied binary shows no azeotropic point.
- The vapor pressure of GEA, in the temperature range 371.85 K to 456.85 K, is given by: $\ln P_{\text{GEA}}^{\text{sat}}(\text{Pa}) = 24.17 - 5781/T$.
- The studied mixture behavior was reasonably described by both of NRTL and UNIQUAC thermodynamic models, taking into account that GEA is composed by four isomers and the high difference between the boiling temperatures of the both compounds involved. However, more realistic models must be developed considering the

Table 6. Binary Interaction Parameters ($\text{J}\cdot\text{mol}^{-1}$) and Deviations of Temperature and GEA Vapor-Phase Composition

model	P/kPa	parameters	$\delta T/\text{K}$	δy_1
NRTL ($\alpha = 0.3$)	60.0	$\Delta g_{12} = -3051.0$	$\Delta g_{21} = 6946.3$	0.89
	97.8	$\Delta g_{12} = -3912.8$	$\Delta g_{21} = 16682.3$	0.98
UNIQUAC	60.0	$\Delta u_{12} = 5.90$	$\Delta u_{21} = 1112.5$	0.75
	97.8	$\Delta u_{12} = -2084.9$	$\Delta u_{21} = 6459.1$	1.17

Figure 5. (a) Txy diagram of the binary GEA (1) and acetonitrile (2) system at 60.0 kPa. (b) $y-x$ diagram at 60.0 kPa.Figure 6. (a) Txy diagram of the binary GEA (1) and acetonitrile (2) system at 97.8 kPa. (b) $y-x$ diagram at 97.8 kPa.

physical and chemical equilibrium between isomers of GEA, besides the equilibrium of the mixture.

- (iv) Finally, the isobaric VLE data obtained in this work and the interaction parameters estimated are fundamental information for the design and optimization of separation processes such as distillation to get, efficiently, pure GEA.

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Notes

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