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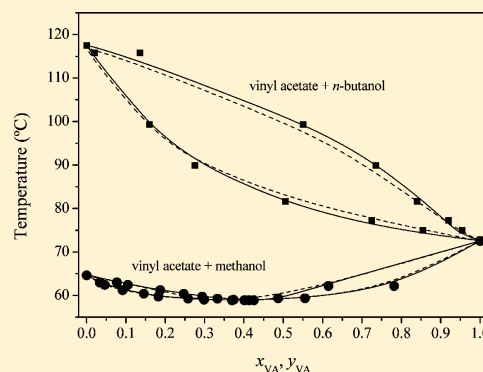
Vapor–Liquid Equilibrium at $p/\text{kPa} = 101.3$ of the Binary Mixtures of Ethenyl Acetate with Methanol and Butan-1-ol

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ABSTRACT: The vapor–liquid equilibrium (VLE) at the constant pressure of $p/\text{kPa} = 101.3$ has been determined for the binary mixtures of ethenyl acetate with both methanol and butan-1-ol. The consistency of the data was checked with the Wisniak L–W test, and the data were found to be consistent. The experimental data were also satisfactorily adjusted to nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) activity coefficient models, as well as to Peng–Robinson and perturbed-chain statistical associating fluid theory (PC-SAFT) equations of state, with the aim of obtaining the binary interaction parameters of both mixtures. With these parameters, the VLE of both mixtures can be accurately predicted, which includes the azeotropic point of the ethenyl acetate + methanol pair. The PC-SAFT and Peng–Robinson equations of state were also employed as purely predictive.



1. INTRODUCTION

Recently, distillation-based processes are gaining importance as a reliable alternative to separate a wide variety of binary and also multicomponent systems. As a consequence, the importance of accurately knowing the vapor–liquid equilibrium (VLE) data of these systems is extremely high, if wanting to calculate the dimensions of the equipment which is necessary to carry out the separation.

In many polymer production processes, after the polymerization step, there are VLE-based stages, such as distillation or devolatilization, with the aim of purifying the desired product as well as the unreacted monomers; such is the case of the ethylene–ethenyl acetate copolymer (EVA). This copolymer is becoming one of the most important polymeric materials due to its wide range of applications (coatings of photovoltaic cells, tires, cables, etc.), depending on the ethenyl acetate content.^{1,2}

When the ethenyl acetate content of the final product is between 40 % and 70 %, the copolymer is usually obtained by a solution process, the most common solvents being methanol and butan-1-ol.³ In these processes, although the polymerization reaction is clearly the core of the overall process, both purification and separation steps are equally important, to obtain a final product with the required specifications, but also to recover as much unreacted monomers as possible and to purify the solvent, so that the process is economically feasible.⁴ The importance of recovering the ethenyl acetate is due to this compound is one of the two monomers which constitute the EVA copolymer.

In the EVA solution process, the separation between ethenyl acetate and solvents is usually carried out by employing a series of flashes and distillation columns.⁵ This implies that, to model

these stages, is indubitably essential to accurately know the VLE; for this reason, we have decided to obtain these data as a previous stage before modeling the separation columns.

The paper shows the results of the VLE measurements that were performed for the binary systems of ethenyl acetate with methanol and butan-1-ol at $p/\text{kPa} = 1.013$. All of the obtained data were initially fitted to nonrandom two-liquid (NRTL)⁶ and universal quasichemical (UNIQUAC)⁷ activity coefficient models, but also to Peng–Robinson⁸ and perturbed-chain statistical associating fluid theory (PC-SAFT)^{9,10} equations of state (EoS). The great potential of recently developed EoS such as PC-SAFT is that they allow extrapolating from low pressure VLE to high pressures; for this reason, they are suitable to be employed for simulation purposes. All of the adjustments were carried out by employing ASPEN PLUS commercial software.¹¹

2. EXPERIMENTAL SECTION

2.1. Materials. All of the analytical grade materials employed in this work were purchased directly from Aldrich. Their purities, expressed in mass fraction, are shown in Table 1.

Table 1. Mass Fraction Purities of the Employed Reagents

chemical name	source	mass fraction purity
methanol	Aldrich	0.999
butan-1-ol	Aldrich	0.998
ethenyl acetate	Aldrich	0.990

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2.2. Apparatus and Procedure. The experiments were carried out with an apparatus entirely glass-made that had been successfully employed with other systems.^{12,13} In this equipment, the vapor and liquid phases are constantly being recirculated with the purpose of obtaining an accurate mixing of the phases and also to guarantee that the equilibrium has been reached. To keep pressure constant and under control, the vapor condenser is attached to a constant-pressure system controlled by a Cartesian manostat, with an accuracy in the measurement of pressure of $\Delta p/\text{Pa} = \pm 133$. The measurement of the equilibrium temperatures was performed with two certified type J thermocouples, with an accuracy of $T/\text{K} \pm 0.1$.

The analysis of both liquid and condensed vapor analyses was made by means of gas chromatography technique. For ethenyl acetate + methanol mixture, a Perkin-Elmer A/S chromatograph with a flame ionization detector and a J&W DB-23 capillary column were employed. For ethenyl acetate + butan-1-ol mixture, an Agilent A/S gas chromatograph with a mass spectrometer detector and also a J&W DB-23 capillary column was employed. In this last case, pentan-1-ol was used as a solvent to prepare the samples, and hexan-1-ol was employed as an internal standard.

3. RESULTS AND DISCUSSION

The VLE data (x_1, y_1, T) and the calculated activity coefficients of components in the liquid phase are shown in Tables 2 and 3. As it

Table 2. Ethenyl Acetate (1) + Methanol (2) VLE Data (Mole Fraction) at $p/\text{kPa} = 101.3$

x_1	y_1	T_b/K	γ_1	γ_2
0.000	0.000	64.6		1.000
0.033	0.077	63.0	3.160	1.084
0.046	0.105	62.5	3.169	1.088
0.092	0.187	61.2	2.964	1.089
0.145	0.247	60.4	2.550	1.109
0.183	0.294	59.8	2.470	1.114
0.258	0.333	59.3	2.018	1.183
0.299	0.374	59.0	1.972	1.187
0.367	0.401	58.9	1.717	1.268
0.413	0.425	58.9	1.630	1.306
0.555	0.487	59.4	1.367	1.510
0.782	0.615	62.2	1.107	2.069
1.000	1.000	72.6	1.000	

$$^a u(T) = 0.1 \text{ K}, u(x_1) = 0.005, u(y_1) = 0.001.$$

Table 3. Ethenyl Acetate (1) + Butan-1-ol (2) VLE Data (Mole Fraction) at $p/\text{kPa} = 101.3$

x_1	y_1	T_b/K	γ_1	γ_2
0.000	0.000	117.5		1.000
0.020	0.135	115.8	1.924	0.946
0.160	0.550	99.4	1.537	1.044
0.275	0.735	89.9	1.507	1.045
0.505	0.840	81.7	1.227	1.314
0.725	0.920	77.2	1.077	1.447
0.855	0.955	75.0	1.018	1.709
1.000	1.000	72.6	1.000	

$$^a u(T) = 0.1 \text{ K}, u(x_1) = 0.007, u(y_1) = 0.007.$$

can be noticed, the ethenyl acetate + methanol mixture presents an azeotrope; for this reason, the majority of the experimental data points are distributed around this value, due to this area of

the T - xy curve is going to be the critical one to obtain a reliable set of interaction parameters.

To calculate the activity coefficients, an excel algorithm with eqs 1 and 2 was employed. According to these equations the nonideality of the vapor phase is considered by determining the vapor-phase fugacity with the virial equation, truncated after second term.

$$\gamma_i = \frac{y_i \cdot P}{x_i \cdot P_i^0} \cdot \exp \left[\frac{(B_{ij} - v_i) \cdot (P - P_i^0) + (1 - y_i) \cdot P \cdot \delta_{ij}}{R \cdot T} \right] \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

In these eqs 1 and 2, γ_i represents the liquid phase activity coefficient of component i , and x_1 and y_1 are the mole fractions of component i in liquid and vapor phases, respectively, P is the total pressure, P_i^0 is the vapor pressure of the pure components, v_i is the liquid molar volume of component i , and R and T are the universal gas constant and the absolute temperature, respectively. The terms B_{ii} and B_{ij} are the second virial coefficient of the pure gas and the cross second virial coefficient, respectively; both coefficients were obtained following Tsonopoulos correlation.¹⁴ Finally, the calculation of the pure component vapor pressure was performed by means of Antoine equation (the Antoine constants taken from NIST database¹⁵ are shown in Table 4). According to the activity coefficient values, it can be seen in Tables 1 and 2 that both the two binary systems have a positive deviation of ideality.

Table 4. Pure Component Antoine Equation Parameters^a

compound	A	B	C	temperature range/K
ethenyl acetate	5.22841	1807.332	0.7	280–380
metanol	5.15853	1569.613	−34.846	245–370
butan-1-ol	4.54607	1351.555	−93.34	310–411

^a

$$\log P_i^0 (\text{Pa}) = A - \frac{B}{[T(\text{K}) + C]}$$

The thermodynamic consistency of the experimental data was assessed with the L–W method of Wisniak.¹⁶ Following this method, the obtained $D = 100(L - W)/(L + W)$ values were less than 5 in both cases (2.8 for ethenyl acetate + methanol and 4.1 for ethenyl acetate + butan-1-ol), which indicates that the data are thermodynamically consistent (this value has to be lower than 5 whenever the values of the enthalpy of vaporization are estimated).

Later on, the equilibrium data were adjusted to the NRTL⁶ and UNIQUAC⁷ activity coefficient models, as well as with Peng–Robinson⁸ and PC-SAFT^{9,10} equations of state, by means of ASPEN PLUS commercial software.¹¹ In all cases the fitting was carried out using an objective function called “maximum likelihood”;¹⁷ this function is characterized by simultaneously minimizing the difference between the experimental and the adjusted values of all of the variables that can be manipulated (in this study, liquid and vapor composition of both components pressure and temperature).

As recommended in literature,¹¹ the NRTL and UNIQUAC binary interaction parameters were assumed to be temperature dependent, according to eqs 3 and 4, respectively.

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (3)$$

In this last expression, τ_{ij} , τ_{ji} and α_{ij} are the binary interaction parameters of the NRTL equation.

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij}T\right) \quad (4)$$

In this last expression, τ_{ij} and τ_{ji} are the binary interaction parameters of the UNIQUAC equation.

With both NRTL and UNIQUAC models, we only adjusted the b_{ij} and b_{ji} terms of the binary interaction parameters. On the other hand, the NRTL equation nonrandomness α factor was kept constant at 0.3, for the two studied binary systems.

Concerning the Peng–Robinson EoS, the pure component parameters (critical pressure, critical temperature, critical volume, and acentric factor) which are required for this model, were taken from NIST database,¹⁵ and the employed mixing rules were the classical ones⁸ defined in the original Peng–Robinson article. The binary interaction parameter (k_{ij}^{PR}) was determined by adjusting the experimental data of each mixture; besides, this model was also employed in a purely predictive way, by evaluating the VLE assuming a value of the binary interaction parameter equal to zero.

In relation to PC-SAFT EoS, the pure component parameters (segment diameter, σ ; segment number, m ; segment energy parameter, ε/k ; association energy, ε^{ABi}/k , and effective association volume, κ^{ABi}) were taken from ASPEN PLUS database¹⁸ and are summarized in Table 5; the binary interaction

Table 5. PC-SAFT Pure Component Parameters

parameter	ethenyl acetate	methanol	butan-1-ol
σ	3.2570	3.2300	3.6139
m	3.4442	1.5255	2.7515
$\varepsilon/k/K$	232.25	188.90	259.59
$\varepsilon^{ABi}/k/K$	0.0	2899.5	2544.6
κ^{ABi}	0.035176/6.692·10 ⁻³	0.035176	6.692·10 ⁻³

parameter ($k_{ij}^{PC-SAFT}$) was obtained by fitting the experimental data. It has to be considered that, according to literature,¹⁹ when dealing with a binary mixture of a polar compound (ethenyl acetate) and an associating compound (methanol or butan-1-ol), the association-energy parameter, ε^{ABi}/k , of the nonself-associating (polar) component ought to be set to zero, while the association volume parameter, κ^{ABi} , of the nonself-associating component must be assumed to be equal to the value of the associating component in the mixture. The PC-SAFT model was also employed as a purely predictive one, like it had been previously done with the Peng–Robinson equation (assuming a zero-value for the binary interaction parameter).

Figure 1 shows the experimental T – x y data of both mixtures, as well, as the regressed values with NRTL and UNIQUAC models. Figure 2 shows the same experimental data along with the regressed values with Peng–Robinson and PC-SAFT equations of state. Finally, Figure 3 shows the experimental data compared with the predictions made by Peng–Robinson and PC-SAFT equations of state (by fixing the binary interaction parameter at zero).

As it can be observed, both NRTL and UNIQUAC models (Figure 1) are perfectly capable of fitting the VLE data by adjusting only the b_{ij} terms of the binary interaction parameters; as a consequence no more than these two terms were considered.

Regarding the EoS models (Figure 2), it can be noticed that PC-SAFT is perfectly capable of adjusting the experimental data; nevertheless, the fitting to Peng–Robinson EoS is not so accurate, maybe because the studied mixtures are a combination of a relatively high polar compound (ethenyl acetate) with an associating compound (methanol or butan-1-ol), and this EoS was first developed for nonpolar systems.

For the two mixtures involved in this work, PC-SAFT EoS presents a clear advantage over the other models, such as NRTL or UNIQUAC because, to accurately describe the equilibrium, it is only necessary a temperature-independent binary interaction parameter.

When the two EoS models act in a purely predictive way (Figure 3), it can be noticed that, despite the incapability of the Peng–Robinson EoS to accurately predict the equilibrium of

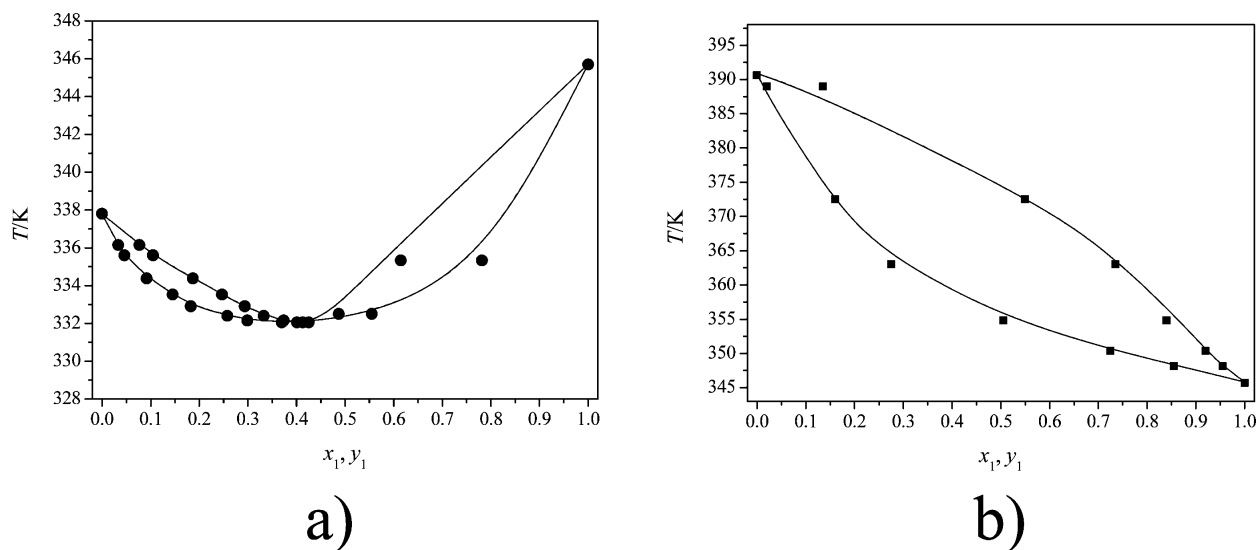


Figure 1. VLE of ethenyl acetate (1) + methanol (2) and ethenyl acetate (1) + butan-1-ol (2) mixtures. (a) ●, experimental T – x y data of the ethenyl acetate + methanol mixture. (b) ■, experimental T – x y data of the ethenyl acetate + butan-1-ol mixture. Solid lines (—), NRTL regressed values; dashed lines (---), UNIQUAC regressed values.

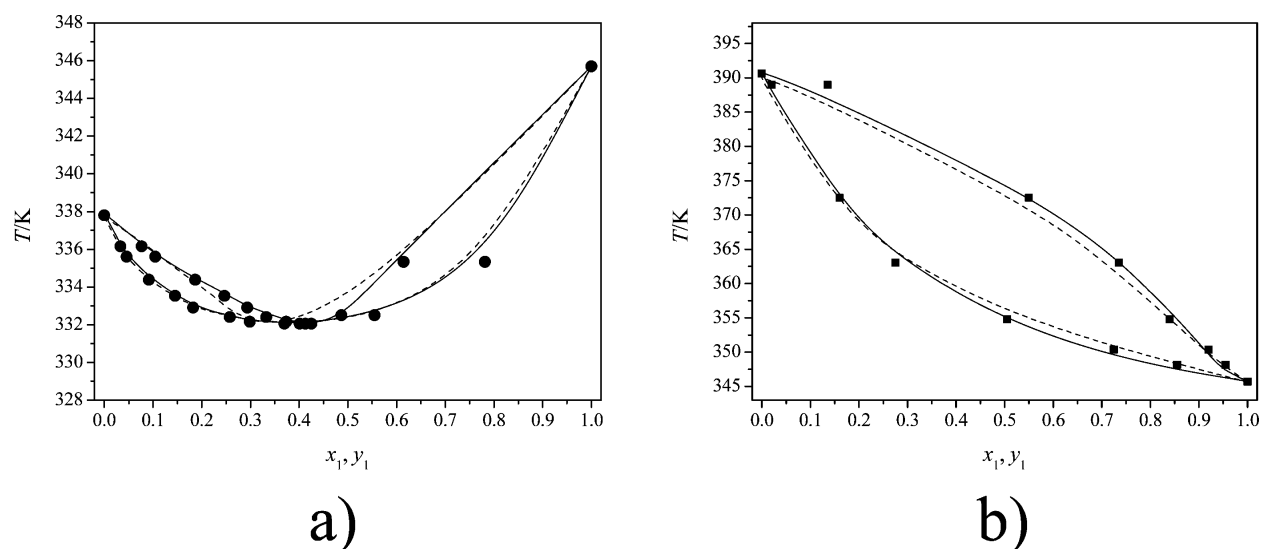


Figure 2. VLE of ethenyl acetate (1) + methanol (2) and ethenyl acetate (1) + butan-1-ol (2) mixtures. (a) ●, experimental T - xy data of the ethenyl acetate + methanol mixture. (b) ■, experimental T - xy data of the ethenyl acetate + butan-1-ol mixture. Solid lines (—), PC-SAFT regressed values; dashed lines (---), Peng–Robinson regressed values.

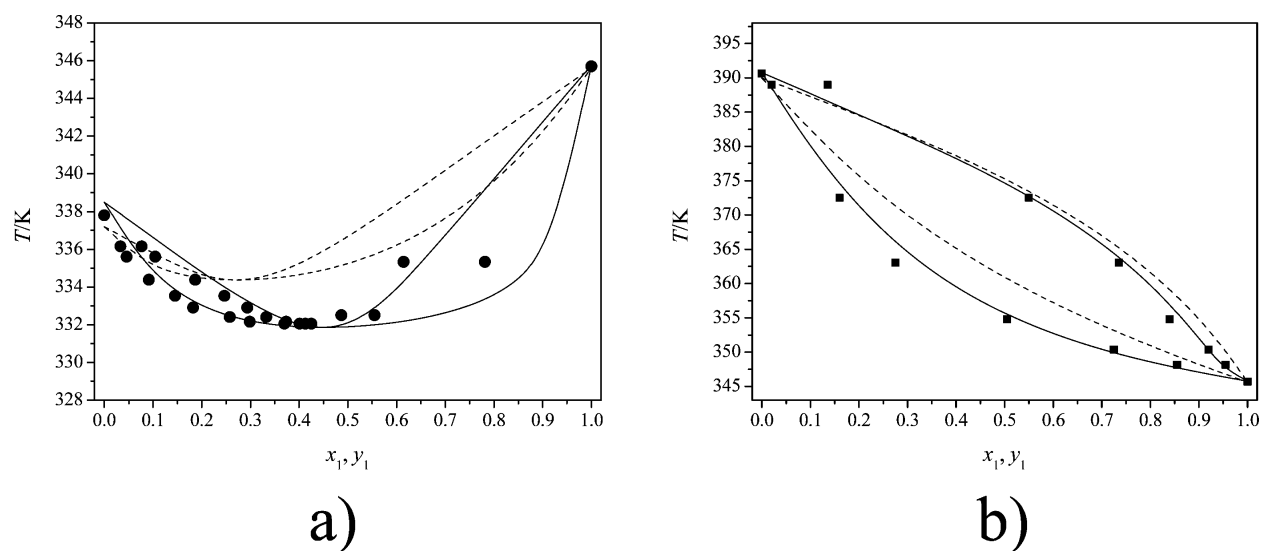


Figure 3. VLE of ethenyl acetate (1) + methanol (2) and ethenyl acetate (1) + butan-1-ol (2) mixtures. (a) ●, experimental T - xy data of the ethenyl acetate + methanol mixture. (b) ■, experimental T - xy data of the ethenyl acetate + butan-1-ol mixture. Solid lines (—), PC-SAFT predicted values; dashed lines (---), Peng–Robinson predicted values.

both mixtures, the PC-SAFT equation is clearly able to give a good approximation to the equilibrium data.

Analyzing more in detail the ethenyl acetate + methanol mixture, as it was previously indicated, this mixture presents an azeotrope at a value of ethenyl acetate mole fraction of 0.41. According to Figure 1, both NRTL and UNIQUAC models are perfectly capable of adjusting the equilibrium data of this mixture around the azeotropic point; this allows drawing the conclusion that the binary interaction parameters of both models can be employed to accurately predict the azeotropic point; the same comment can be applied to the PC-SAFT equation (Figure 2, continuous line). However, the Peng–Robinson equation (Figure 2, dotted line), despite performing a reasonable good overall adjustment, is not able to provide an accurate value of the azeotropic value. When these last two equations are employed as purely predictive (Figure 3), it can be observed that, by

employing the PC-SAFT equation, a reasonable value of the azeotropic point can be obtained.

Tables 6, 7, 8, and 9 show the binary interaction parameters determined from fitting the experimental data of both mixtures

Table 6. NRTL Binary Interaction Parameters

	ethenyl acetate (1) + methanol (2)	ethenyl acetate (1) + butan-1-ol (2)
b_{ij}	336.8	351.6
b_{ji}	171.4	−17.7

Table 7. UNIQUAC Binary Interaction Parameters

	ethenyl acetate (1) + methanol (2)	ethenyl acetate (1) + butan-1-ol (2)
b_{ij}	−464.0	−149.6
b_{ji}	65.8	37.7

Table 8. PC-SAFT k_{ij} Binary Interaction Parameter

	ethenyl acetate (1) + methanol (2)	ethenyl acetate (1) + butan-1-ol (2)
k_{ij}	-0.0059	0.0060

Table 9. Peng–Robinson k_{ij} Binary Interaction Parameter

	ethenyl acetate (1) + methanol (2)	ethenyl acetate (1) + butan-1-ol (2)
k_{ij}	0.017	0.044

to the four studied models. The main point to be emphasized is that the k_{ij} values of PC-SAFT EoS are close to zero. This confirms the ability of this model of acting as purely predictive.

With the aim of assessing the quality of the adjustments, in Table 10, the average absolute deviations, in percentage, of

Table 10. Temperature, $\sigma(T) = 1/k \sum (T_{\text{calc}} - T_{\text{exp}})/T_{\text{exp}}$, and Ethenyl Acetate Vapor Mole Fraction, $\sigma(y_1) = 1/k \sum (y_{1,\text{calc}} - y_{1,\text{exp}})/y_{1,\text{exp}}$, Root-Mean-Square Deviations for the Methods Tested

ethenyl acetate (1) + methanol (2)			ethenyl acetate (1) + butan-1-ol (2)		
method	$\sigma(T)$	$\sigma(y_1)$	method	$\sigma(T)$	$\sigma(y_1)$
NRTL	0.072	2.12	NRTL	0.54	2.60
UNIQUAC	0.074	2.10	UNIQUAC	0.54	2.60
Peng–Robinson	0.142	10.26	Peng–Robinson	0.79	4.16
PC-SAFT	0.148	1.83	PC-SAFT	0.62	4.00

temperature (eq 5) and ethenyl acetate vapor mole fraction (eq 6) are presented.

$$\sigma(T) = \frac{1}{k} \left| \sum_k \frac{T_{\text{calc}} - T_{\text{exp}}}{T_{\text{exp}}} \right| \quad (5)$$

$$\sigma(y) = \frac{1}{k} \left| \sum_k \frac{y_{1,\text{calc}} - y_{1,\text{exp}}}{y_{1,\text{exp}}} \right| \quad (6)$$

In both eqs 5 and 6, T indicates the temperature, y_1 the ethenyl acetate vapor mole fraction, and k the number of data points; the subscript exp represents experimental data and the subscript calc represents regressed data. As it can be observed, except for Peng–Robinson EoS, all the values are lower than 5 % and also similar among them. This reaffirms the previously made comments indicating that NRTL, UNIQUAC and PC-SAFT equations are suitable to adjust the experimental data of the two studied binary systems.

4. CONCLUSION

In this work, experimental and consistent VLE data of the binary systems methanol + ethenyl acetate and butan-1-ol + ethenyl acetate have been determined at $p/kPa = 101.3$; their consistency was evaluated with the Wisniak L–W method.

The NRTL and UNIQUAC activity coefficient models and PC-SAFT EoS are capable of accurately fitting the experimental data, while a much higher deviation is obtained when the Peng–Robinson EoS is employed.

PC-SAFT and Peng–Robinson EoS were also employed in a predictive way (by assuming a zero value for the binary interaction parameter), and it was found that the PC-SAFT equation is able to give a good approximation to the equilibrium data.

The regressed interaction parameters of NRTL, UNIQUAC, and PC-SAFT models can be employed to obtain an accurate value of the azeotropic point of the ethenyl acetate + methanol mixture.

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Notes

The authors declare no competing financial interest.

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