

Short communication

Experimental measurements of vapor–liquid equilibria at low pressure: Systems containing alcohols, esters and organic acids

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ABSTRACT

In this work the vapor–liquid equilibria for nine binary mixtures (methanol+acetic acid, methanol+methyl acetate, methanol+water, methyl acetate+acetic acid, water+acetic acid, ethyl acetate+acetic acid, ethanol+acetic acid, ethanol+ethyl acetate and ethanol+water) at subatmospherical pressure (580 mmHg) is presented. Peng–Robinson Stryjek–Vera equation of state coupled with the Wong–Sandler mixing rules were used for predicting phase equilibria of these mixtures. The measurements were developed using an apparatus with recirculation that can also be employed for liquid–vapor equilibrium with chemical reaction.

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1. Introduction

The interest in the reduction of both energetic and operation costs in chemical industries has allowed that technologies as reactive distillation acquire large importance at present time [1–5]. The applicability of this kind of processes where the reaction and separation stages are developed simultaneously is wide, due to the possibility to overcome thermodynamic limitations as chemical equilibrium and azeotropy. One of the main factors to take into account for the design of these processes is the thermodynamic behaviour of the system inside the column. Then, the simultaneous phase and chemical equilibria may be considered.

Experimentally, many types of apparatus for the study of the vapor–liquid equilibria (VLE) with or without chemical reaction have been used [6,7]. These equipments are classified according to their construction, operation and conversion reached inside the still. In this way, three configurations can be selected:

1. Static still: they are the simplest and economic equipments; their construction and operation is simple, but the time of stabilization is high, reason why they are obsolete and they are little used at the moment.

2. Recirculation still: the operation of these equipments is not so complex and the times of stabilization are smaller obtaining precise and reliable results. Implementation of the denominated Cottrell's bomb has allowed its extensive application at the present time.
3. Crossed flow stills: the main advantage of these equipments is that the kinetic of the system does not affect its performance, becoming a good selection alternative; however, it should be taken into account that their construction is expensive and the operation is complex.

The selection of the desirable configuration is done based on all of those considerations of cost, operation and conversion; under these conditions, several experimental works have been developed [7].

On the other hand, some authors have studied the VLE in the binary systems involving in this study [8–12]. But even though there are some similar investigations, there are not published VLE data of these mixtures at subatmospherical pressures.

In this work, nine binary systems (methanol+acetic acid, methanol+methyl acetate, methanol+water, methyl acetate+acetic acid, water+acetic acid, ethyl acetate+acetic acid, ethanol+acetic acid, ethanol+ethyl acetate and ethanol+water) have been studied experimentally. These systems are important in the design of reactive distillation processes, especially in the esterification of acetic acid with alcohols like methanol and ethanol to obtain methyl acetate and ethyl acetate, respectively. Experimental VLE data were obtained by using a recirculation still.

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Additionally, the binary interaction parameter of the second virial coefficient (k_{12}) and the non-random two liquid (NRTL) model parameters (τ_{12} and τ_{21}) were calculated for these nine binary systems at subatmospherical pressure (580 mmHg). Experimental data were correctly correlated using Peng–Robinson Stryjek–Vera equation of state (EOS) coupled with the Wong–Sandler mixing rules. Our principal goal is to examine experimentally only binary reactive systems at subatmospherical pressure, then to fit binary model parameters, and to extend from there on the calculation to multicomponent reactive systems.

2. Experimental

2.1. Apparatus and procedure

The studied binary systems were in their order: methanol–acetic acid, methanol–methyl acetate, methanol–water, methyl acetate–acetic acid, water–acetic acid, ethanol–acetic acid, ethanol–ethyl acetate, ethanol–water and ethyl acetate–acetic acid.

For the experimental determination of phase equilibrium, a recirculation still modified by Cardona [13] has been used. This equipment is also utilized to study phase equilibrium in systems with chemical reaction, and it is shown in Fig. 1. In this apparatus the fed sample is constantly recycled by means of a system type Cottrell (system that consists of a tube with an electrical resistance that vaporizes the mixture). This tube is connected to another one

of smaller diameter which allows an intense recirculation in whole system to assure that the phases are in contact. After the first operation hour, samples are extracted every 15 min until reaching the stabilization of the system in study (approximately 2 h).

Temperatures were measured by digital thermometers with $\pm 0.05^\circ\text{C}$. At the beginning of the every run, the pressure was measured with barometer CASIO. Alone if the pressure was of 580 mmHg (normal pressure in Manizales, 2167 m above sea level) the experiment were carried out. The samples of liquid and vapor obtained were analyzed together by means of refraction index and gas chromatography. The chromatograph used was a Perkin-Elmer Autosystem XL with identification column PE-WAX, which identifies the analyzed compounds correctly. The precision of the experimental measures was $\sigma(x_i) = \sigma(y_i) = 0.003$ for liquid and vapor concentrations, $\sigma(T) = 0.01\text{ K}$ for temperature and $\sigma(P) = 0.1\text{ mmHg}$ for pressure.

2.2. Chemicals

Acetic acid (GR grade, +99%), absolute ethanol (GR grade, +99%), methanol (GR grade, +99%), and ethyl acetate (GR grade, +99%) were purchased from Riedel-de Haen. Methyl acetate (GR grade, +99%) was purchased from Merck, and the deionized water (electric resistance, 18.2 M Ω /cm) was generated by a Millipore distilled water generator.

3. Equation of state and mixing rules used

The Peng–Robinson Stryjek–Vera (PRSV) equation of state [14] was used; this EOS has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (1)$$

where P denotes pressure, T is the temperature, R is the ideal gas constant and the parameters a and b are the energy and size parameters which are calculated as follows:

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

T_c and P_c are the critical temperature and pressure of each pure compound, respectively. And the correlation for the α function is

$$\alpha(T_r) = [1 + \kappa(1 - \sqrt{T_r})]^2 \quad (4)$$

Stryjek and Vera [14] modified the functional form of alpha function proposed by Soave [15] as follows:

$$\kappa = \kappa_0 + \kappa_1(1 + \sqrt{T_r})(0.7 - T_r) \quad (5)$$

and

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.171317848\omega^2 + 0.0196554\omega^3 \quad (6)$$

where κ_1 is a constant parameter for each pure component. To extend the PRSV EOS to mixtures the Wong–Sandler mixing rules [16] were used. Therefore, the a_m and b_m parameters have the following form:

$$b_m = \frac{\sum_i \sum_j z_i z_j (b - (a/RT))_{ij}}{1 - \sum_i z_i (a_i/b_i RT) - (A_\infty^E/\sigma RT)} \quad (7)$$

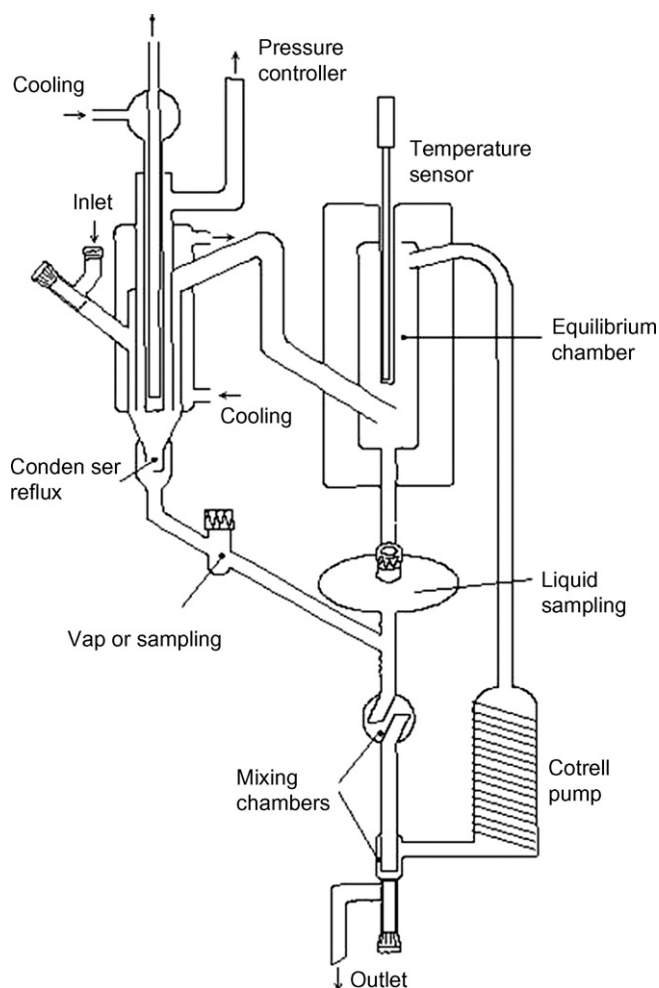


Fig. 1. Basic scheme of recirculation still.

and

$$a_m = b_m \left[\sum_i z_i \frac{a_i}{b_i} + \frac{A_\infty^E}{\sigma} \right] \quad (8)$$

where σ is a constant that depend of the EOS (-0.623225 for PRSV EOS) and A_∞^E is the excess Helmholtz free energy at infinite pressure

Table 1
Properties of substances included in the PRSV-WS model.

Substance	T_c , K	P_c , K	ω	κ_1	Ref.
Methanol	512.58	80.95	0.5653	-0.1681	[14]
Ethanol	513.92	61.48	0.6443	-0.0337	[14]
Acetic acid	592.00	57.86	0.4594	-0.1972	[14,18]
Methyl acetate	506.80	46.90	0.3253	0.0353	[19]
Ethyl acetate	523.25	38.30	0.3611	0.0693	[19]
Water	647.28	220.89	0.3438	-0.0663	[14]

Table 2
Experimental VLE results at 580 mmHg and deviations with PRSV-WS model.

Methanol (1) + acetic acid (2)					Methanol (1) + methyl acetate (2)						
Liquid		Vapor		Temperature		Liquid		Vapor		Temperature	
x_1	y_1	Δy^a	T , K	ΔT^b	x_1	y_1	Δy	T , K	ΔT		
0.181	0.383	0.151085	365.75	0.458976	0.187	0.241	0.016414	320.35	0.044665		
0.225	0.507	0.093278	361.95	0.463993	0.261	0.286	0.012157	320.15	0.032295		
0.552	0.841	0.029611	346.45	0.479023	0.418	0.382	0.023221	320.25	0.073362		
0.647	0.879	0.035870	343.35	0.094825	0.743	0.561	0.006078	322.85	0.312118		
0.767	0.943	0.014883	339.25	0.479029	0.852	0.687	0.004629	325.65	0.218378		
Average		0.064945		0.395169	Average		0.012499		0.136163		
Methanol (1) + water (2)					Methyl acetate (1) + acetic acid (2)						
Liquid		Vapor		Temperature		Liquid		Vapor		Temperature	
x_1	y_1	Δy	T , K	ΔT	x_1	y_1	Δy	T , K	ΔT		
0.062	0.265	0.031339	357.35	0.780166	0.183	0.538	0.080534	360.85	0.821730		
0.149	0.566	0.066824	352.15	0.464688	0.279	0.743	0.005881	353.85	1.734751		
0.155	0.595	0.086465	351.35	0.007884	0.565	0.939	0.020983	335.65	0.825639		
0.530	0.839	0.052733	340.95	0.049974	0.493	0.873	0.018478	336.95	2.695468		
0.781	0.895	0.026103	335.55	0.037847	0.743	0.987	0.024354	327.85	2.147988		
Average		0.052692		0.268111	Average		0.030046		1.645115		
Water (1) + acetic acid (2)					Ethanol (1) + acetic acid (2)						
Liquid		Vapor		Temperature		Liquid		Vapor		Temperature	
x_1	y_1	Δy	T , K	ΔT	x_1	y_1	Δy	T , K	ΔT		
0.346	0.470	0.039832	370.05	2.182894	0.190	0.382	0.064944	370.65	0.693430		
0.482	0.631	0.001043	369.45	0.499187	0.329	0.564	0.076599	364.95	0.132411		
0.621	0.719	0.018024	367.95	0.148741	0.615	0.845	0.010662	356.45	0.982352		
0.774	0.839	0.003902	366.95	0.296819	0.744	0.913	0.008338	352.05	0.240990		
0.871	0.895	0.001031	366.55	0.494338	0.796	0.981	0.036762	348.85	1.434415		
Average		0.012766		0.724395	Average		0.039461		0.696719		
Ethanol (1) + ethyl acetate (2)					Ethanol (1) + water (2)						
Liquid		Vapor		Temperature		Liquid		Vapor		Temperature	
x_1	y_1	Δy	T , K	ΔT	x_1	y_1	Δy	T , K	ΔT		
0.187	0.285	0.014643	338.85	0.190282	0.281	0.541	0.038729	348.85	0.048913		
0.258	0.334	0.001878	337.75	0.212584	0.356	0.579	0.034444	347.75	0.097925		
0.361	0.421	0.010705	337.25	0.148086	0.474	0.629	0.031455	346.55	0.199869		
0.605	0.524	0.014091	337.45	0.016927	0.620	0.705	0.019331	345.85	0.140563		
0.804	0.677	0.012235	338.95	0.017851	0.763	0.798	0.005860	344.95	0.020177		
Average		0.010710		0.117146	Average		0.025963		0.101489		
Ethyl acetate (1) + acetic acid (2)											
Liquid		Vapor		Temperature							
x_1	y_1	Δy	T , K	ΔT							
0.103	0.279	0.013876	375.25	0.085162							
0.222	0.452	0.066415	368.85	0.891232							
0.377	0.683	0.018920	360.75	0.276357							
0.546	0.829	0.004269	352.95	1.216496							
0.709	0.901	0.002704	347.75	1.570637							
Average		0.021236		0.807976							

^a $\Delta y = |y_{cal} - y_{exp}|$.

^b $\Delta T = |T_{cal} - T_{exp}|$.

Table 3
Optimal NRTL model parameters and binary interaction parameter at 580 mmHg.

Binary system	τ_{12}	τ_{21}	k_{12}
Methanol (1) + acetic acid (2)	0.483567	0.615656	-0.469085
Methanol (1) + methyl acetate (2)	0.485207	1.190302	-0.023033
Methanol (1) + water (2)	0.121012	-0.921983	0.505894
Methyl acetate (1) + acetic acid (2)	0.615550	-0.573038	0.025049
Water (1) + acetic acid (2)	-0.987897	1.968632	0.368501
Ethanol (1) + acetic acid (2)	0.319532	-1.799912	0.538691
Ethanol (1) + ethyl acetate (2)	0.322880	0.183000	0.323449
Ethanol (1) + water (2)	0.316016	0.787057	0.285228
Ethyl acetate (1) + acetic acid (2)	0.720461	-0.139218	-0.170304

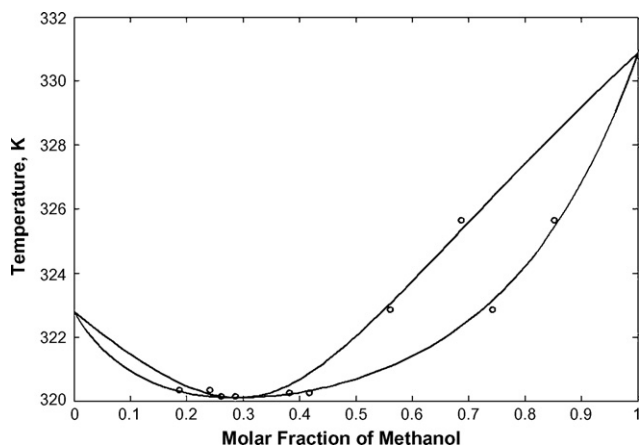


Fig. 2. Experimental and predicted T - x - y diagram for methanol (1) + methyl acetate (2) binary system at 580 mmHg. \circ , Experimental values; —, prediction with PRSV-W EOS.

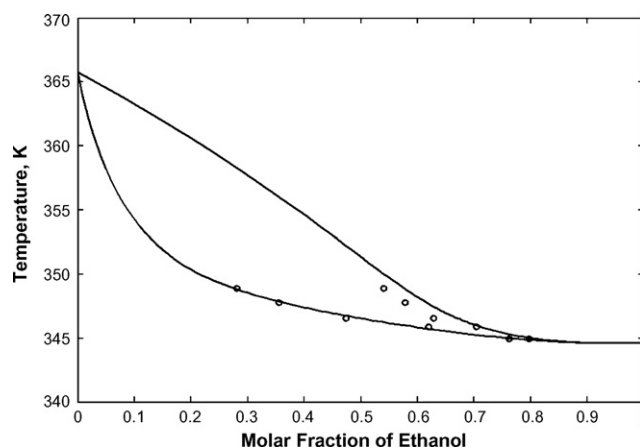


Fig. 4. Experimental and predicted T - x - y diagram for ethanol (1) + water (2) binary system at 580 mmHg. \circ , experimental values; —, prediction with PRSV-W EOS.

which was calculated from NRTL model [17]:

$$\frac{A_{\infty}^E}{RT} = \sum_i z_i \left(\frac{\sum_j z_j \tau_{ji} g_{ji}}{\sum_k z_k g_{ki}} \right) \quad (9)$$

with

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (10)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{(b - (a/RT))_i + (b - (a/RT))_j}{2} (1 - k_{ij}) \quad (11)$$

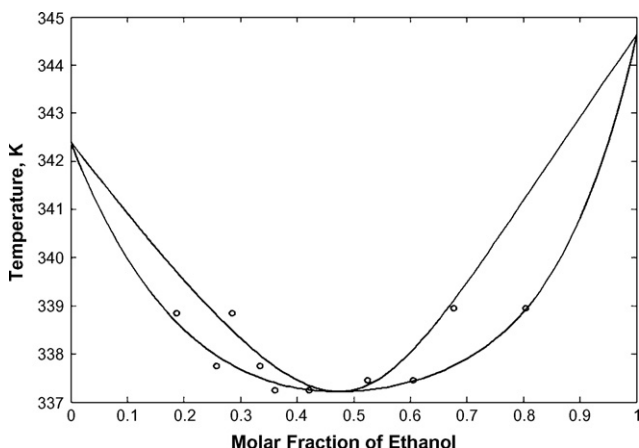


Fig. 3. Experimental and predicted T - x - y diagram for ethanol (1) + ethyl acetate (2) binary system at 580 mmHg. \circ , Experimental values; —, prediction with PRSV-W EOS.

k_{ij} is a second virial coefficient binary interaction parameter and z is the molar fraction. τ_{12} and τ_{21} are two adjustable parameters of the NRTL model [17].

4. Results and discussion

Table 1 shows the pure component properties for the PRSV-W EOS model. Experimental results of VLE for all binary mixtures involved in this study are presented in Table 2. In addition, the deviations for each experimental point for both the equilibrium temperature and vapor phase composition are calculated with respect to the used mathematical model.

The NRTL activity model parameters and binary interaction parameter of PRSV EOS were obtained using the Levenberg–Marquardt minimization algorithm in a similar way as it was made in previous works [20–22]. In this case, the following objective function was used:

$$f = \sum_{i=1}^{Np} ([T_{\text{exp},i} - T_{\text{calc},i}]^2 + [y_{\text{exp},i} - y_{\text{calc},i}]^2) \quad (12)$$

The optimal NRTL model parameters (τ_{12} and τ_{21}) and the second virial coefficient interaction parameter (k_{12}) are reported for the nine studied binary mixtures in Table 3. Based on these optimal parameters, experimental and predicted T - x - y diagrams for methanol + methyl acetate, ethanol + ethyl acetate, ethanol + water and ethyl acetate + acetic acid binary systems were constructed and are presented in Figs. 2–5. For all cases, the agreement between experimental data and calculated values was satisfactory. Then, these optimal interaction parameters can be correctly used in order to model the multicomponent reactive systems at 580 mmHg or similar subatmospherical pressures.

As it has been reported by other authors [8–11], binary systems methanol + methyl acetate, ethanol + water, and ethanol + ethyl

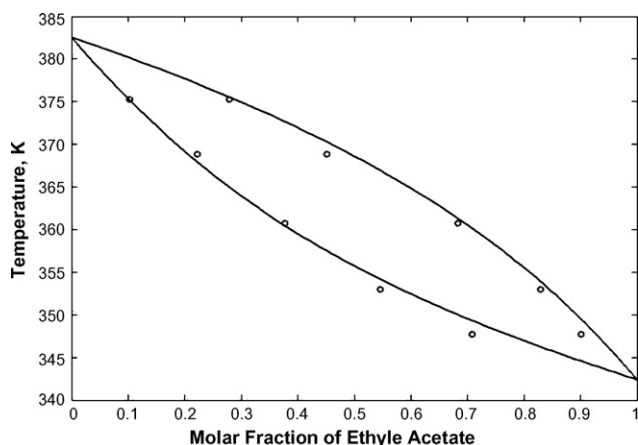


Fig. 5. Experimental and predicted T - x - y diagram for ethyl acetate (1) + acetic acid (2) binary system at 580 mmHg. ○, Experimental values; —, prediction with PRSV-EOS.

acetate have minimum temperature azeotropes. Here, these azeotropes were confirmed (see Figs. 2–4). However, due to pressure effects, in all cases the azeotropic temperatures were between 5 and 8 degrees below the azeotropic temperatures reported at 760 mmHg.

5. Conclusions

The VLE data of the binary systems methanol + acetic acid, methanol + methyl acetate, methanol + water, methyl acetate + acetic acid, water + acetic acid, ethyl acetate + acetic acid, ethanol + acetic acid, ethanol + ethyl acetate and ethanol + water were measured at subatmospherical pressure (580 mmHg) using a modified recirculation still. Experimental results were confronted with Peng–Robinson Stryjek–Vera equation of state coupled with the Wong–Sandler mixing rules, it was found good agreement with the experimental data. Also the NRTL activity model and second virial coefficient binary interaction parameters were optimized from these experimental results. These optimal parameters were also presented.

List of symbols

A^E	excess Helmholtz free energy
a, b	equation of state parameters
$(b - a/RT)_{ij}$	cross-second virial coefficient
g_{ij}	parameter defined by Eq. (10)
k_{ij}	second virial coefficient interaction parameter
N_p	number of experimental data points
P	pressure
R	gas constant
T	temperature
v	volume in molar units
x	liquid molar fraction
y	vapor molar fraction
z	molar fraction

Greek letters

Δ	deviation
$\alpha(T_r)$	temperature-dependent alpha function
α_{ij}	NRTL model parameter
κ	Soave alpha function parameter
σ	PRSV EOS constant
τ_{12}, τ_{21}	NRTL model binary interaction parameter
ω	acentric factor

Subscripts

c	critical point
m	mixture
r	reduced conditions
∞	infinite condition

Superscripts

E	excess property
exp	experimental
$calc$	calculated

Acronyms

EOS	equation of state
NRTL	non-random two liquid
PRSV	Peng–Robinson Stryjek–Vera
VLE	vapor–liquid equilibrium

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