

# Evolution and Testing of a Metallic Ebulliometer for VLE Determination

*Susial Badajoz, Pedro; García Montesdeoca, Isabel; García Vera, Diego; Marrero Pérez, Aníbal.; Dunia E. Santiago*<sup>\*+</sup>

*Escuela de Ingenierías Industriales y Civiles. Universidad de Las Palmas de Gran Canaria  
35017 Las Palmas de Gran Canaria, Canary Islands, SPAIN*

**ABSTRACT:** *An ebulliometer designed with automated feeding was tested and verified in this work. The ebulliometer is made of stainless steel. The feeding of the substances is automatically controlled with a computer. In the equipment, both the liquid and vapor phases are recirculated. The binary mixtures isobutyl acetate + 1-propanol and isobutyl acetate + 2-propanol was studied and the vapor-liquid equilibrium of these mixtures was determined at 101 kPa. The isobaric T-x-y data are reported, including the azeotropic point of the isobutyl acetate + 1-propanol binary system. The calculations have been carried out considering the non-ideal vapor phase and the activity coefficients of the liquid phase have been obtained. The thermodynamic consistency of the system was verified with the Van Ness point-to-point test. The  $\phi$ - $\phi$  approach was used to evaluate the data reproducibility by considering the Perturbed Chain-Statistical Associating Fluid Theory (PC-SAFT).*

**KEYWORDS:** *Vapor-liquid Equilibri; Isobutyl acetate; 1-propanol; 2-propanol; PC-SAFT*

## INTRODUCTION

Esters and alcohols are compounds frequently used as solvents in different types of industrial processes and circumstances. These are also used as extraction agents and as raw materials in organic synthesis. The use of these substances increases with the decrease in the use of chlorinated and aromatic solvents.

The recovery of these compounds and their purification for subsequent applications is necessary to attain a rational use of solvents. For this reason, it seems appropriate to study these substances and their mixtures to determine observable and easily measurable parameters that provide information on their behavior.

On the other hand, distillation is one of the most important mass transfer operations in chemical industries. Consequently, the use of automatic substance feeding systems for the experimental determination of the Vapor-Liquid Equilibrium (VLE) in isobaric conditions provides knowledge of the mixtures and allows to obtaining of reliable data that can be used in the dimensioning of separation equipment. To our knowledge, no other authors have reported the design of the automatic feeding of substances into an ebulliometer.

In this work, the VLE of the binary systems isobutyl acetate + 1-propanol (AIB1P) and isobutyl acetate +

---

*\*To whom correspondence should be addressed.*

*+ E-mail: dunia.santiago@ulpgc.es*

*1021-9986/2023/6/1925-1937 13/\$/6.03*

2-propanol (AIB2P) at 101 kPa were determined. Both systems are described in literature [1–3]. AIB2P does not present an azeotrope at 101 kPa, but AIB1P has azeotropes at 150 and 600 kPa [1,2]. Moreover, in this work an azeotrope for this last system at 101 kPa has been determined.

VLE data must be validated before being used; for this reason, the binary mixtures studied in this work have been verified with the point-to-point test [4] employing the routine proposed in FORTRAN by Fredenslund et al. [5]. Results indicate that the systems are consistent considering the global criteria found in the literature [5]. This allowed to apply the data to the model that employs the Perturbed Chain–Statistical Associating Fluid Theory (PC–SAFT) [6,7], to determine the prediction capacity of the cited model. PC–SAFT is a commonly used model that has been employed in the study of a wide variety of industrial processes, such as those related to: amino acids solutions [6], pharmaceuticals [7], polymer foams [8] or petroleum [9], among others.

## EXPERIMENTAL SECTION

### *Substances and measuring equipment*

The substances were used as received from the manufacturer, Panreac Química S.A., with no further purification. All substances were received with purity grade higher than 99% w/w. The boiling temperature ( $T_{bp}$ ), density ( $\rho_{ii}$ ), and refractive index ( $n_D$ ) of the pure substances, determined at 298.15 K and 101 kPa, agree with those published previously [1]. The equipment used to determine density and the refractive index were those described in the literature [1,12]. Namely, a Mettler Toledo DM-40 digital density meter with an accuracy of 0.0001 g/mL was used to register density, and an Atago RX-7000 $\alpha$  digital refractometer with an accuracy of 0.0001 units was used to measure the refractive index.

Mass fraction mixtures of AIB1P and AIB2P were prepared using an Entris–224i–1S balance from Sartorius Lab Instruments GmbH & Co. with an accuracy of  $10^{-4}$  g. Samples with a molar fraction ( $x_i$ ) between 0 and 1 were prepared in this study to verify the calibration curve that can be found in previous work [1]. The mixtures were prepared using glass bottles with an airtight stopper. For each of the prepared mixtures, density ( $\rho_{ij}$ ) was measured at 298.15 K and the excess volume was calculated [1], to verify the quality of the obtained data. Next, calibration curves of mole fraction versus density were determined.

### *Experimental Equipment*

In previous works [13], a continuous operation copper-made ebulliometer was presented and described. For the construction of the mentioned ebulliometer, a glass-made ebulliometer was taken as model [10]. The measurement and control devices associated to the copper-made ebulliometer and the successive modifications that were made on the ebulliometer to facilitate the experimental work are reported in previous works [1,8,11,12].

To be able to work at high pressure and to avoid the inconveniences found previously with the glass-made and copper-made ebulliometers [13,14] a stainless steel ebulliometer was constructed and it was provided with internal recirculation of fluids to study Vapor–Liquid Equilibria (VLE). In this equipment all the joints of the different parts were soldered with silver. The equipment has a similar configuration than the one made of glass by Casiano de Afonso [14]. Therefore, a continuous and dynamic equipment in which both phases can be recirculated was designed. In the present study, both the system and the experimental procedure are developed and described, as well as the new automatic system to feed the substances into the equipment.

The equipment (Fig. 1) has a double-walled inverted chamber (1) with a Cottrell tube on the upper side (2), and another tube on the lower side, that connects with the lower part of the equipment. The mixture is introduced between the two walls and an electric heater is placed inside the boiling flask to generate a vapor lift pump effect.

The Cottrell tube (2) is introduced into the equipment from the top and is connected inside the equipment to the equilibrium chamber (3) that is composed of an inverted vessel with a Pt100 probe (4); a second Pt100 probe is located on the right side (5). This Pt100 probe (5) is located at the entrance of a curved pipe (21) that connects the ebulliometer with the cooler (6). The outer part of the equipment is heated by a surrounding electrical resistance (7) to prevent the condensation of the vapor phase.

Beside the Pt100 probes but at a certain distance from the equilibrium chamber a cooler is placed (8) to thermally protect the valve (9) that is situated above. Following this valve, a damping vessel is found (10), which is composed of two equal-diameter tubes on the sides and one tube with a larger diameter in the middle. Immediately above there is a second valve (11) and the loading funnel (12).

The heat exchanger (6) is composed of two concentric tubes. The interior tube is connected to the equipment on one of its sides (21) and can be connected to nitrogen gas at its upper end. On its lower side, the exchanger includes two branches; one of them connects the exchanger to the main equipment (20) and the other is connected to the valve (13).

Below the equilibrium chamber a funnel (14) is placed with a slightly larger diameter than the equilibrium chamber (3). The funnel is connected to a pipeline on its bottom that leads to the outside of the equipment, where two refrigerants (15,16) are located, and next, a valve (17).

The diameter of the main equipment is progressively reduced on its bottom part, until it is transformed into a pipeline that goes through a cooling system (18). Before reaching the cooling system, the pipeline is connected to the double-walled inverted chamber (1) with an ascending tube. Below this, on the lowest part of the equipment, there is a valve (19).

### **Operating procedure**

To study the VLE in previous works [15, 16], the metallic ebulliometer constructed in stainless steel (2 mm thickness) and provided with internal recirculation, as shown in Fig. 1, was loaded with 600 mL of pure substance (A). Next, the heating of the equipment was started.

The liquid-vapor mixture that is produced in the inverted vessel (1) rises through the Cottrell tube (2) and reaches the equilibrium chamber (3). The Pt100 probe (4) records the temperature of the mixture, and the heat electrical resistance (7) prevents the condensation of vapor in the equilibrium chamber. This is controlled with another Pt100 probe (5). The vapor exits through the curved pipe (21) and rises through the cooler (6) where it is condensed. The resulting liquid is collected in the outlet valve (13). The excess vapor is recirculated back to the ebulliometer through the pipe (20) above the valve (13) to guarantee an adequate homogenization of the mixture.

The hot liquid falls from the equilibrium chamber to the funnel (14) where it is collected and channeled through the cooler (16) to the outlet valve (17). This liquid is cooled using the cooling system (15,16) to thermally protect the outlet valve (17). The excess liquid is recirculated to the main body of the ebulliometer through the cooler (15).

In the lower part of the equipment, the entrance to the inverted vessel is preceded by a concentric heat exchanger (18) that operates like those previously described, although this last exchanger collects the mixture from the body of the equipment and allows its homogenization before it enters the inverted vessel. The heat exchanger (18) acts as a thermal protector of valve (19), through which the equipment is emptied.

The equipment, as was informed in previous works [15,16], was loaded with substance (A) through the loading funnel (12) and valves (9, 11) and next the electrical resistances were switched on once the equipment was charged and closed. Once the boiling temperature of the pure substance (A) was reached at atmospheric pressure, the equipment could be connected on the upper side of the cooler (6) to nitrogen. The introduction of nitrogen allows to control pressure, if necessary, and thus allows to work at 101 kPa and other pressures.

The ebulliometer was kept working in this situation 4 hours to allow the homogenization of temperature inside the equipment. Next, 15 mL of substance (B) were introduced into the equipment through the loading funnel (12) and with the help of the valves (9, 11).

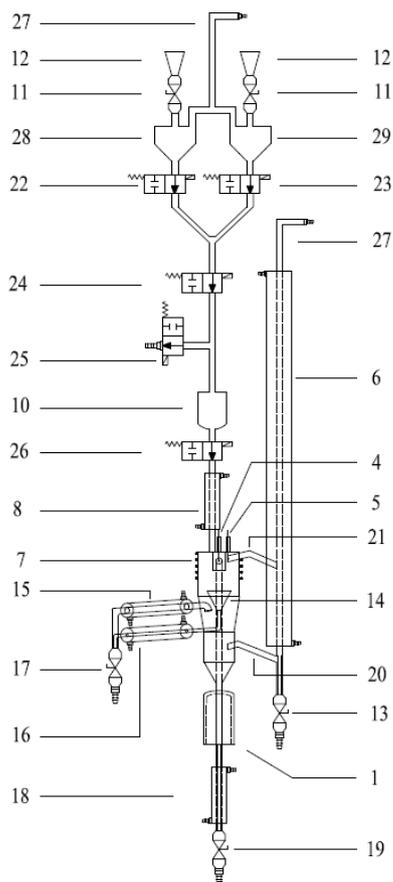
The resulting mixture was kept boiling for 90 minutes to ensure the stationary state to acquire VLE data. After the recirculation of phases for 90 minutes, samples of the liquid and vapor phases were taken through valves (16) and (13), respectively. The samples were stored in sealed recipients until they tempered and next, density was measured at 298.15 K.

After the extraction of samples, the ebulliometer was loaded again with another 15 mL of substance (B) to modify the composition of the mixture inside the ebulliometer. This process was done in continuous using valves (9) and (11) sequentially, and, thus, the process was not stopped to load substance (B).

Moreover, the configuration of valves (13) and (17) allows the continuous recirculation of the phases that are separated in the equilibrium chamber (3) and that circulate due to the Cottrell effect along tube (2), which is connected to the inverted vessel (1) and the equilibrium chamber (3), and along which the redistribution of substances between non-miscible phases is attained in co-current flow.

To determine the composition of the liquid and vapor phases of the samples collected through valves (17) and (13) density data were introduced in a calibration curve of

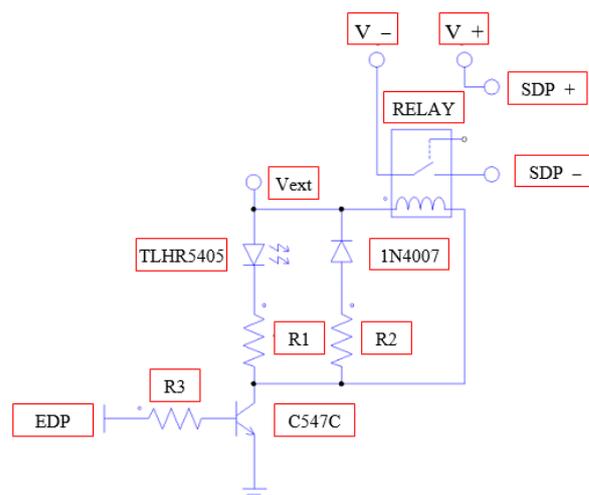




**Fig. 2:** Diagram of the ebulliometer used for VLE measurements with the electronic device for the introduction of the substances: 1. Boiling flask; 4. Pt100 probe of equilibrium; 5. Pt100 probe of vapor heating; 6. Cooler with nitrogen line connection; 7. Electric heater resistance; 8. Cooler; 10. Damping vessel; 11. Inlet valves; 12. Funnels for the inlet of substances; 13. Vapor sampler valve; 14. Liquid funnel; 15, 16. Coolers; 17. Liquid sampler valve; 19. Outlet valve; 20. Tube of vapor phase circulation; 21. Outlet vapor phase curved tube; 22, 23, 24, 25, 26. Solenoid valves; 27. Nitrogen supply line; 28, 29. Vessels to load the substances.

For this purpose, from the 5 digital outputs of the USB-202 module, 5 electronic circuits were connected (see one of the circuits in Fig. 3) to adapt the signals and avoid internal problems due to derived currents that could appear as a result of discharges from the coils of the relays to which the solenoid valves were connected.

Therefore, each of the 5 outputs used in the USB-202 controller was connected to an EDP circuit on the electronic board (see Fig. 3). In addition, the EDP input in Fig. 3 refers to the digital input of the external electronic board of the USB-202 module, that is, the point at which one of the 5 outputs used in the USB-202 module was connected.



**Fig. 3:** Electronic switching circuit between the USB-202 and the normally closed solenoid valves, designed to supply the substances to the ebulliometer.

Upon receiving the signal in mA generated in the USB-202 module, based on the C547C transistor, current began to circulate through the line, and, consequently, through the relay coil (see Fig. 3). When the relay worked, it allowed the external power supply that was connected between (V -) and (V +), to provide energy to the circuit of the solenoid valve. This circuit was arranged between the terminals (SDP +) and (SDP -).

The operating sequence, corresponding to the opening and closing of the solenoid valves (see Fig. 2), for the introduction of the substances in the equipment, begun after feeding the substances (A) and (B) to be studied in the VLE determination, through the funnels (12) that are connected to hermetic tanks (28 and 29).

The solenoid valves (22-26) are normally closed, but the solenoid valves (22, 24 and 26) are opened to introduce the substance (A) in the equipment. This was done after the circuit (11-23) was verified as closed, and before introducing the pressure gas into the equipment (27). This way, an initial volume was guaranteed, and this volume was kept constant throughout the experiment. Next, the solenoid valves (22, 24 and 26) were closed.

Consequently, the hydraulic circuit between the solenoid valves (22) and (26) was left empty and at atmospheric pressure after this process. After loading the equipment with substance (A), the installation was operated as previously indicated [12,15,16]. However, in this study, the solenoid valves (24 and 25) were opened, and the vacuum pump was connected to the solenoid valve

(25). A negative pressure was established in the (22–26) hydraulic circuit. After this, the solenoid valves (24, 25) were closed.

The system was left 4 h for thermal and pressure stabilization. During this time, the equipment was subjected to the working pressure. Next, 15 mL of substance (B) was introduced according to the following sequence, which was programmed in a computer.

The solenoid valve for the feeding of the second substance (23) was opened for a given time (the process is immediate, although 2 min were established for the pre-loading operation). This way, the 15 mL circuit situated between the solenoid valves (22), (23) and (24) was filled with substance (B). Note that the solenoid valves (22) and (24) were closed at this time.

Next, the solenoid valve (23) was closed, and a timeout of 15 s was set before opening the general feeding solenoid valve (24). Once the valve opened, the liquid subjected to atmospheric pressure fell to the damping vessel (10). This process was fast, as the liquid was subjected to pressure, but the damping vessel was at negative pressure. Following this, the solenoid valve (24) was closed and, 15 s later, solenoid valve (26) opened. Note that valves (24) and (25) were closed at this moment.

The liquid in the damping vessel and the ebulliometer were connected under this situation and after the stabilization of pressure between both fluids, the liquid fell into the ebulliometer. At this time, the necessary loading of substance (B) to generate a perturbation in the ebulliometer was accomplished.

After 5 minutes, which was the time programmed to load the substance with total security (although the process was fast and was carried out in about 1 min), valve (26) was closed. The ebulliometer was kept working normally with the mixture inside. The equipment was heated and insulated thanks to the resistances located in (1) and (7).

After about 15 s, the solenoid valves (24) and (25) opened to extract the pressure gas retained in the circuit between the solenoid valves (22), (23) and (26). After 2 min, these areas were considered empty and both valves (24) and (25) were closed. After 15 s, the feed solenoid valve (23) of the second substance (B) was opened as indicated above, and in this way, the volume between said valves was once again occupied by 15 mL of the second substance (B) and ready to be introduced into the ebulliometer. After 90 min which were necessary to

reach stable conditions [12–14], the mixture of each phase was extracted for analysis.

### VLE modelling with PC-SAFT

The equation of state that considers the Perturbed–Chain Statistical Associating Fluid Theory (PC-SAFT) has been described applying the perturbation theory of Barker–Henderson [17,18] and considering the different contributions of the Helmholtz free energy ( $A^{res}/Nk_B T$ ). For this reason, the compressibility factor ( $Z$ ) can be calculated considering the sum of the contributions that correspond to the ideal gas ( $Z^{id}=1$ ), the hard chain contribution ( $Z^{hc}$ ), the dispersion contribution ( $Z^{disp}$ ), and the contribution of the associating interactions ( $Z^{assoc}$ ), as follows:

$$Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc} \quad (3)$$

Each of the terms in Eq. (3) represents different contributions to the total free energy of the fluid. The equation of state is presented in detail by Gross–Sadowski [10,11], who used a new term of dispersion and the same hard chain term, applied to mixtures within the statistical associating fluid theory developed by Chapman [19,20], together with the associating term of the Wertheim's first order thermodynamic perturbation theory [21–24].

To calculate the different thermodynamic properties using PC-SAFT [10,11], five parameters for each substance, and one correlation parameter for the mixture ( $k_{1ij}$ ) may be needed. Among these, three simulation parameters are needed for each non-associative pure substance: the segment number ( $m_i$ ), the segment diameter ( $\sigma_i$ ) and the segment–segment interaction energy ( $\varepsilon_i/k_B$ ). Two additional parameters may be necessary for the pure substance if the association interactions were to be described. Those are the association volume ( $\kappa^{AiBi}$ ) and the association energy ( $\varepsilon^{AiBi}/k_B$ ).

The dispersion contribution term, as described by Gross–Sadowski [10,11], is needed to describe the segment–segment interactions of some combination rules. To calculate the segment diameter ( $\sigma_{ij}$ ) and the segment–segment interaction energy ( $\varepsilon_{ij}/k_B$ ) of the mixture, the following mixing rules are applied:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (4)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1 - k_{1ij}) \quad (5)$$

being  $kI_{ij}$ , the specific binary interaction parameter for each mixture.

The Helmholtz free energy association contribution is used to describe cross-combining interactions between associating substances needs of corresponding mixing rules. The mixing rules of *Wolbach* and *Sandler* [25] were applied:

$$\varepsilon^{AiBj} = \frac{1}{2}(\varepsilon^{AiBi} + \varepsilon^{AjBj}) \quad (6)$$

$$\kappa^{AiBj} = \sqrt{\kappa^{AiBi}\kappa^{AjBj}} \left[ \frac{\sqrt{\sigma_{ii}\sigma_{jj}}}{0.5(\sigma_{ii} + \sigma_{jj})} \right]^3 \quad (7)$$

We checked several software and found that the associating term of the PC-SAFT [10,11] is not programmed or is incorrectly included. For this reason, we applied the PC-SAFT model [10,11] in a FORTRAN routine that was developed and verified.

We compared the results obtained with our programme with those presented in the work reported by *Gross-Sadowski* [11], using the same constants than those used by *Gross-Sadowski* [11], and did not observe significant differences in the results. Additionally, the data from *Zach Baird* [26], who used PC-SAFT [10,11] with the terms dipole and ionic was also employed to verify our programme and once again no significant differences were observed.

Next, to obtain the parameters of the pure fluid from the PC-SAFT [10,11] model, the vapor pressures [1,3] and the critical properties [27] reported in literature were used. To obtain the association parameters ( $\varepsilon^{AiBi}/k_B$  association energy and  $\kappa^{AiBi}$  association volume) of 1-propanol and 2-propanol, a 2B scheme with 2 association positions in the alcohol was applied. The only position considered for the association of isobutyl acetate was estimated as a solvation parameter; thus, the same association volume ( $\kappa^{AiBi}$ ) as that of the alcohol was applied.

A multiobjective function was used, as in previous work [13], to minimize errors in the data corresponding to molar densities and vapor pressures. Data from literature [13,28,29] include the parameters for the PC-SAFT model [10,11] for the substances used in this work. The Standard Deviation (SD), the Mean Absolute Deviation (MAD), and the Mean Percentage Deviation (MPD) were calculated from the experimental data for comparison purposes.

With the parameters of the pure substances [13,28,29], and applying an isobaric bubble point algorithm (scheme

$p-x_1$ ) in FORTRAN, as described before [13,29], the PC-SAFT [10,11] model was obtained for the binary systems studied in this work.

To minimize error in the correlations and to optimize the prediction of data, the simplex method of Nelder and Mead [30] was employed, both in the determination of the parameters of the pure substances and when applying the bubble point method during the modeling of VLE data.

## RESULTS AND DISCUSSION

The isobaric  $T-x_1-y_1$  data for the VLE of the systems AIB1P and AIB2P at 101 kPa are shown in Table 1. The data were verified using the  $\gamma$ - $\phi$  approximation. The fugacity coefficients ( $\phi$ ) were calculated considering that the vapor phase was non-ideal. The procedure of *Fredenslund et al.* [5] was used for calculations employing the Hayden and O'Connell method [31] and the correlation of Yen and Woods [32].

The critical properties and Antoine constants to calculate the vapor pressure ( $p^0$ ) of each substance  $i$  were taken from literature [1-3,27]. The activity coefficients ( $\gamma$ ) used to describe the liquid phase of substance  $i$  were calculated following Eq. (1):

$$\gamma_i = \frac{y_i p}{x_i p_i^0} \exp \left[ \frac{p}{RT} \left( 2 \sum_{j=1}^2 y_j B_{ij} - \sum_{i=1}^2 \sum_{j=1}^2 y_i y_j B_{ij} \right) - \frac{p_i^0 B_{ii}}{RT} + \frac{(p_i^0 - p) v_i^L}{RT} \right] \quad (1)$$

The factors involved in Eq. (1) are pressure ( $p$ ), temperature ( $T$ ), the mole fractions of the liquid ( $x$ ) and vapor phases ( $y$ ) of substance  $i$  or  $j$ , the second virial coefficients of the pure substances ( $B_{ii}$ ), the cross-second virial coefficients ( $B_{ij}$ ), the molar volume of the liquid phase ( $v_i^L$ ) of substance  $i$  and the universal gas constant ( $R$ ). The activity coefficients of the liquid phase (see Table 1), calculated from VLE data as indicated previously, showed a positive deviation compared to the ideal state. The hydrogen bonding in the alcohol and the dipole force with the  $\pi$  electrons in the ester could be the reason for this deviation. In a previous work we found that the positive deviation decreases when pressure is increased because there is greater difficulty for the delocalization of electrons at higher pressure [33]. The point-to-point test [4] was used to evaluate the thermodynamic consistency. For this purpose, Legendre

Table 1: Experimental data of VLE and calculated values<sup>a</sup>

T/K	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	γ <sub>2</sub>	g <sup>E</sup> /RT	T/K	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	γ <sub>2</sub>	g <sup>E</sup> /RT
Isobutyl acetate (1) + 1-Propanol (2)											
370.44	0.000	0.000		1.000		371.80	0.466	0.339	1.245	1.162	0.183
370.18	0.011	0.015	2.471	0.991	0.001	371.90	0.473	0.346	1.248	1.161	0.184
370.10	0.025	0.031	2.253	0.992	0.013	372.09	0.494	0.359	1.232	1.177	0.186
369.89	0.043	0.050	2.127	0.999	0.031	372.51	0.532	0.378	1.188	1.217	0.183
369.80	0.058	0.065	2.056	1.002	0.043	372.82	0.563	0.390	1.146	1.264	0.179
369.64	0.084	0.089	1.954	1.010	0.065	372.94	0.576	0.399	1.141	1.278	0.180
369.56	0.102	0.103	1.867	1.017	0.079	373.16	0.590	0.407	1.128	1.294	0.177
369.56	0.123	0.119	1.788	1.023	0.091	373.35	0.610	0.419	1.117	1.324	0.177
369.58	0.142	0.134	1.743	1.027	0.102	373.46	0.617	0.425	1.116	1.329	0.176
369.63	0.158	0.147	1.715	1.029	0.109	373.79	0.639	0.438	1.098	1.362	0.171
369.71	0.183	0.165	1.658	1.035	0.121	374.50	0.681	0.467	1.073	1.425	0.161
369.77	0.217	0.188	1.589	1.048	0.137	375.14	0.715	0.492	1.055	1.486	0.151
369.96	0.256	0.214	1.523	1.060	0.151	376.07	0.745	0.518	1.034	1.526	0.132
370.15	0.283	0.233	1.490	1.066	0.159	376.50	0.763	0.535	1.028	1.560	0.126
370.32	0.306	0.248	1.459	1.073	0.165	377.02	0.780	0.551	1.018	1.594	0.117
370.65	0.342	0.270	1.405	1.086	0.171	379.27	0.853	0.638	1.003	1.779	0.087
370.80	0.355	0.279	1.392	1.088	0.172	380.06	0.868	0.661	0.996	1.806	0.075
370.94	0.379	0.292	1.358	1.104	0.178	381.63	0.900	0.719	0.995	1.874	0.058
371.33	0.412	0.310	1.309	1.121	0.178	383.60	0.932	0.793	0.996	1.900	0.040
371.38	0.417	0.312	1.299	1.125	0.178	385.60	0.968	0.886	1.001	2.066	0.024
371.61	0.445	0.331	1.281	1.140	0.183	386.83	0.979	0.921	1.001	2.119	0.017
371.67	0.448	0.332	1.274	1.142	0.182	389.76	1.000	1.000	1.000		
371.72	0.455	0.334	1.260	1.151	0.182						
Isobutyl acetate (1) + 2-Propanol (2)											
355.53	0.000	0.000		1.000		361.50	0.455	0.233	1.249	1.115	0.160
355.79	0.027	0.020	2.223	0.994	0.015	361.70	0.477	0.239	1.213	1.144	0.163
355.87	0.044	0.033	2.244	0.995	0.031	362.23	0.510	0.249	1.160	1.182	0.157
356.31	0.073	0.047	1.895	0.994	0.041	363.11	0.543	0.265	1.124	1.200	0.147
356.60	0.101	0.062	1.788	0.997	0.056	363.60	0.580	0.287	1.120	1.244	0.157
357.03	0.131	0.078	1.707	0.997	0.068	363.96	0.607	0.293	1.079	1.301	0.150
357.46	0.155	0.096	1.748	0.989	0.077	364.79	0.639	0.313	1.064	1.335	0.144
357.92	0.204	0.115	1.564	1.010	0.099	365.24	0.656	0.324	1.056	1.356	0.140
358.58	0.237	0.138	1.577	1.000	0.108	366.18	0.691	0.346	1.036	1.411	0.131
359.07	0.283	0.153	1.439	1.026	0.122	367.08	0.723	0.371	1.029	1.465	0.127
359.82	0.327	0.179	1.418	1.030	0.134	368.57	0.762	0.412	1.031	1.512	0.121
359.98	0.343	0.182	1.366	1.045	0.136	370.52	0.803	0.461	1.025	1.563	0.108
360.52	0.393	0.203	1.304	1.079	0.151	373.84	0.854	0.540	1.011	1.604	0.078
361.02	0.434	0.224	1.280	1.106	0.164	380.87	0.943	0.754	1.019	1.740	0.050
361.60	0.448	0.230	1.247	1.101	0.152	389.44	1.000	1.000	1.000		

<sup>a</sup> The expanded uncertainties  $U(k=2)$  are:  $U(T)=0.2$  K,  $U(p)=1$  kPa,  $U(x_1)=U(y_1)=0.004$ .  $T$ ,  $x_1$ ,  $y_1$ ,  $\gamma_1$ ,  $\gamma_2$  stand for: temperature, mole fraction of the ester in the liquid phase, mole fraction of the ester in the vapor phase, activity coefficient of the ester, activity coefficient of the alcohol.

polynomials of degree four were used to correlate the excess Gibbs free energy ( $g^E/RT$ ). The experimental data were considered consistent when the mean absolute deviation between the calculated and measured mole fractions of substance 1 in the vapor phase ( $\delta y_1$ ) was lower than 0.01 [5]. In the present study, the obtained values were  $\delta y_1=0.0056$  for AIB1P and  $\delta y_1=0.0060$  for AIB2P, both at 101 kPa.

The  $T-x_1-y_1$  experimental results for the binary systems AIB1P and AIB2P at 101 kPa are included in Table 1. These were compared with bibliographic data [1–3] (see Fig. 4). An adequate evolution with pressure was observed for the data obtained in this work. The effect of pressure in these systems varies depending on the position of the hydroxyl group in the alcohol. We verified the

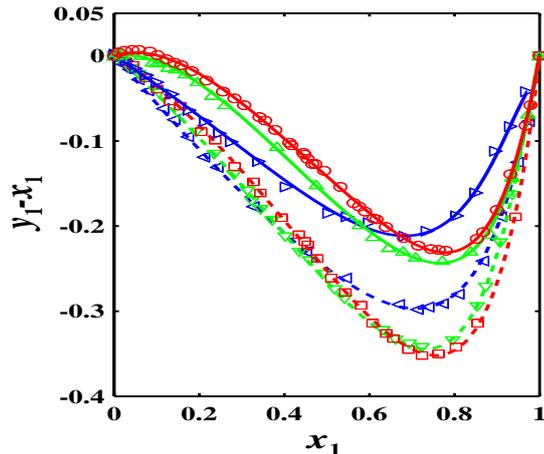


Fig. 4: Plot of  $(y_1 - x_1)$  vs.  $x_1$  for VLE of AIB1P (○) and AIB2P (□), isobaric systems at 101 kPa, and correlation curves. Data for AIB1P (△) [2] and AIB2P (▽) [3] at 150 kPa, and AIB1P (▷) [1] and AIB2P (◁) [1] at 600 kPa from literature are also included, with their correlation curves.

compressive–expansive effect related to compositions with high alcohol content; this effect is greater for alcohols with higher molecular weight.

It is known that azeotropic data must be specially considered in the process of separation of liquid mixtures. For this reason, many systems that present an azeotrope are found in literature [34]. However, for the systems studied here, AIB1P and AIB2P, to our knowledge, azeotropic data has only been reported before for AIB1P [1,2].

Considering the data obtained in this work, the coordinates of the azeotrope for AIB1P, calculated with a system of lineal equations with a tridiagonal matrix algorithm, also known as the natural cubic spline method [35], resulted in:  $x_1=0.1059$ ;  $T=369.55$  K at 101 kPa, from the interpolation of the data shown in Table 1. The following data are reported for the same system in the bibliography:  $x_1=0.0576$ ;  $T=380.67$  K at 150 kPa and  $x_1=0.0109$ ;  $T=426.86$  K at 600 kPa [1,2].

The azeotropic data from this work for AIB1P are presented in Fig. 5, together with the correlation curve between the azeotrope ( $x_{1,az,exp}=y_{1,az,exp}$ ), reduced temperature ( $T_R$ ) and reduced pressure ( $p_R$ ), as follows:

$$\frac{1}{T_R} = 1.0105 - 0.2648 \cdot (\text{Log}_{10} p_R) \quad (2a)$$

$$x \left( \frac{1}{T_R} \right) (\text{Log}_{10} p_R)^2_{1az, exp} \quad (2b)$$

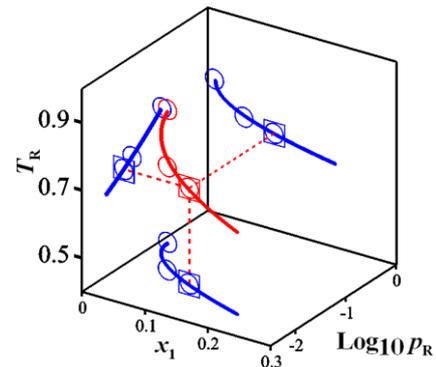


Fig. 5: Azeotropic data for AIB1P at 101 kPa, this work (◻). Bibliographic data (○) for AIB1P at 150 kPa [2] and 600 kPa [1]. Data for AIB1P at 101 kPa, this work (◻). Bibliographic data (◻) for AIB1P at 150 kPa [2] and 600 kPa [1]. The correlation curves were obtained using Eqs. (2a, 2b).

From Fig. 5 an adequate evolution of the azeotropic data with temperature is observed, and a good correlation between the properties, the reason why we can deduce that the azeotrope of system AIB1P could be removed at pressures above 600 kPa. Despite this, it should be noted that, due to the reduced number of available data, Eqs. (2a, 2b) can be only employed to correlate data and thus these are not suitable for the prediction of the azeotropic point under new conditions.

The results for  $k_{1ij}=0.0038$ , obtained for AIB1P and  $k_{1ij}=0.0119$ , obtained for AIB2P, were determined (see Table 2) as previously described, with the simultaneous correlation of all data for each of the mixtures; that is: 95 values of AIB1P (43 from this work at 101 kPa, 26 at 150 kPa from Ref. [2] and 26 at 600 kPa from Ref. [1]; and 79 values of AIB2P (28 from this work at 101 kPa, 29 at 150 kPa from Ref. [3] and 22 at 600 kPa from Ref. [1]). We can indicate that the binary parameters of each mixture have been determined because these were obtained independent of the operating conditions.

In Table 2 the statistical results for the predictions obtained with the PC–SAFT [10,11] model are included for the systems AIB1P and AIB2P at 101 kPa. Data are also shown for the systems reported in bibliography [1–3] for comparison purposes.

The composition–composition and temperature–composition data obtained from the PC–SAFT [10,11] modelling were plotted (see Figs. 6 and 7) together with the experimental results obtained in this work (see Table 1), for AIB1P and AIB2P at 101 kPa. Additionally, for

**Table 2: Standard deviation (SD), mean absolute deviation (MAD) and mean percentage deviation (MPD) obtained from the modelling of experimental VLE data using PC–SAFT<sup>a</sup>**

	p/kPa	MAD		MPD		SD		k <sub>1ij</sub>	Azeotrope	
		T/K	y <sub>1</sub>	T/K	y <sub>1</sub>	T/K	y <sub>1</sub>		x <sub>1,az</sub>	T <sub>az</sub> /K
Isobutyl acetate (1) + 1–propanol (2)										
TW	101								0.1059	369.55
PC–SAFT <sup>[10-11],[13],[28-29]</sup>		0.49	0.017	0.13	5.83	0.59	0.02	0.0038	0.0436	370.26
PC–SAFT <sup>[10-11],[36]</sup>		0.35	0.012	0.09	5.66	0.45	0.01	-0.0053	0.0111	369.15
TW	150								0.0576	380.67
PC–SAFT <sup>[10-11],[13],[28-29]</sup>		0.95	0.018	0.25	9.48	0.48	0.00	0.0038	0.0061	381.27
PC–SAFT <sup>[10-11],[36]</sup>		0.81	0.017	0.21	11.62	0.41	0.00	-0.0053	NA	NA
TW	600								0.0109	426.86
PC–SAFT <sup>[10-11],[13],[28-29]</sup>		1.60	0.018	0.36	13.71	2.16	0.02	0.0038	NA	NA
PC–SAFT <sup>[10-11],[36]</sup>		1.44	0.009	0.33	10.94	1.44	0.01	-0.0053	NA	NA
Isobutyl acetate (1) + 2–propanol (2)										
PC–SAFT <sup>[10-11],[13],[28-29]</sup>	101	0.59	0.01	0.16	3.71	0.67	0.01	0.0119	NA	NA
PC–SAFT <sup>[10-11],[36]</sup>		0.69	0.018	0.19	10.34	0.80	0.02	-0.0110	NA	NA
PC–SAFT <sup>[10-11],[13],[28-29]</sup>	150	0.61	0.013	0.16	7.01	0.33	0.00	0.0119	NA	NA
PC–SAFT <sup>[10-11],[36]</sup>		1.12	0.018	0.30	10.34	0.96	0.00	-0.0110	NA	NA
PC–SAFT <sup>[10-11],[13],[28-29]</sup>	600	0.48	0.012	0.11	8.51	0.56	0.01	0.0119	NA	NA
PC–SAFT <sup>[10-11],[36]</sup>		1.56	0.005	0.36	4.64	1.70	0.01	-0.0110	NA	NA
<sup>a</sup> TW = this work	NA = non azeotrope									

$$\text{MAD}(F) = \frac{1}{n-2} \sum_1^n |F_{\text{exp}} - F_{\text{cal}}|; \text{MPD}(F) = \frac{100}{n-2} \sum_1^n \frac{|F_{\text{exp}} - F_{\text{cal}}|}{F_{\text{exp}}}; \text{SD}(F) = \sqrt{\frac{\sum_1^n (F_{\text{exp}} - F_{\text{cal}})^2}{n-2}}$$

*F* being *y*<sub>1</sub> or *T*/K; *n* is the number of data

comparison purposes the PC–SAFT model [10,11] was applied to literature data [1–3], and results are included in Table 2.

The parameters of the pure substances obtained using different objective functions and different vapor pressures and molar volumes are found in the literature [11,36]. We used these reported parameters and proceeded identically to determine the interaction parameters of the mixtures.

The results of the model, the parameter  $k_{1ij} = -0.0053$  obtained for AIB1P and the parameter  $k_{1ij} = -0.0110$  obtained for AIB2P, are included in Table 2. Likewise, correlations using the data obtained from the prediction of the systems AIB1P and AIB2P at 101 kPa are also included in Figs. 6 and 7.

It is observed that, in general, the PC–SAFT model reproduced adequately the systems AIB1P and AIB2P. It must be noted that, globally, better predictions were obtained when the parameters of the pure substances obtained by us [13,28,29] were used, rather than those taken from bibliography [11,36]. This can be verified if the statistical results, MAD, MPD and SD, included

in Table 2 are considered, together with the reproduction of the azeotrope.

However, better prediction results were obtained for the AIB2P system at 600 kPa when we used the parameters reported by other authors [11,36]. The slightly better reproduction of temperatures is a consequence of the different objective functions used; the one described by us [15], uses weights in the properties, so the predictions are rationalized, and random parameters are not generated mathematically.

Moreover, the nature of the substances studied in this work indicate that, to adequately represent the molecular interactions, the polar contribution could be significant, although an interaction parameter of the mixture as function of temperature could be estimated previously.

In any case, for ester + alcohol mixtures, such as AIB1P and AIB2P, which are composed of a component that self–associates with a non–associative substance with a proton receptor position, cross–associations can occur. For these reasons, these mixtures are difficult to describe, probably due to the associative contribution of

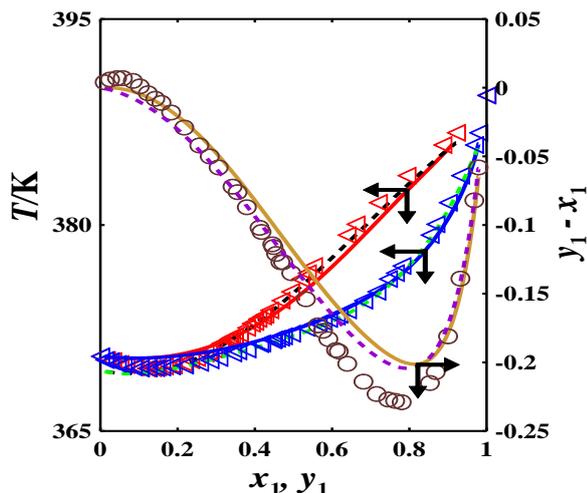


Fig. 6: Experimental data for AIB1P at 101 kPa:  $(y_1 - x_1)$  vs.  $x_1$  (O), and  $T$  vs.  $x_1, y_1$  ( $\Delta$ ,  $\triangle$ ). Correlation curves of  $(y_1 - x_1)$  vs.  $x_1$  (—) and  $T$  vs.  $x_1, y_1$  (—, —): modelling with PC-SAFT [10,11] using the parameters [13,28,29] determined by us. Correlation curves of  $(y_1 - x_1)$  vs.  $x_1$  (- - -) and  $T$  vs.  $x_1, y_1$  (- - -, - - -): modelling with PC-SAFT [10,11] using parameters from bibliography [11,36].

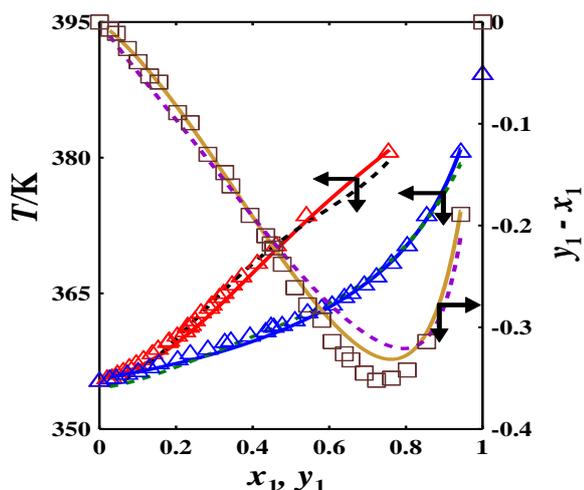


Fig. 7: Experimental data for AIB2P at 101 kPa:  $(y_1 - x_1)$  vs.  $x_1$  (□) and  $T$  vs.  $x_1, y_1$  ( $\Delta$ ,  $\triangle$ ). The correlation curves for  $(y_1 - x_1)$  vs.  $x_1$  (—) and for  $T$  vs.  $x_1, y_1$  (—, —) represent the model obtained with PC-SAFT [10,11] using the parameters determined by us [13,28,29]. The correlation curves for  $(y_1 - x_1)$  vs.  $x_1$  (- - -) and  $T$  vs.  $x_1, y_1$  (- - -, - - -) represent the model obtained with PC-SAFT [10,11] with the parameters from the bibliography [11,36].

the model since the substance that acts as a proton acceptor does not have association parameters. The problem is approached using as solvation parameter the one corresponding to the volume of association of the alcohol

( $\kappa^{\text{AiBi}}$ ), before using the polar contribution in the model, although the solution does not seem to be definitive.

On the other hand, AIB1P presents an azeotrope that was calculated in this work at different pressures (Table 2). The model obtained with PC-SAFT when the parameters from literature were applied [11,13,28,29,36] must verify the prediction of the singular point.

Results are shown in Table 2. The prediction of the azeotrope for the system AIB1P at 101 and 150 kPa is adequate when we used the parameters obtained by us for the pure substances [13,28,29]. When the parameters reported by other authors [11,36] are employed in the prediction, however, the azeotropic point was only reproduced at 101 kPa for AIB1P, although with an error in the composition of the azeotrope of 89%.

## CONCLUSIONS

This work addresses the evolution of an ebulliometer designed and made by the authors. Namely, an automatic system for the introduction of substances into the stainless steel ebulliometer is described. The equipment can work at high pressures. To verify the correct operation of the equipment, VLE data have been obtained for the AIB1P and AIB2P binary systems at 101 kPa.

The obtained data satisfied the van Ness thermodynamic consistency test using the Fredenslund et al. routine. Based on this, the azeotrope for the AIB1P system at 101 kPa was calculated, and additionally, using the same natural spline cubic method, azeotropes were calculated at 150 and 600 kPa using data from the literature.

For the AIB1P and AIB2P systems, the data from this work together with data from literature, were applied to the PC-SAFT model, to obtain the interaction parameter of the mixture. The prediction with the PC-SAFT model was obtained using the parameters determined by us as well as with those reported by other authors.

The predictions that were obtained when we used the parameters determined by us improved the reproduction of the experimental data compared to the predictions that were obtained when we used the parameters reported in literature instead. For this reason, it is appropriate to use an objective function that weighs the contributions of the vapor pressures and molar volumes in the process used to obtain the parameters of the model.

However, it is evident that the ester + alcohol mixtures are difficult to reproduce as a consequence of

imperfections in the determination of the associative interactions between the substances, even after employing equal association volumes for the ester and the alcohol, that is, considering the molecular solvation phenomena.

In the future, the authors recommend assessing other mixtures in the ebulliometer and different working pressures, and to analyse different contributions in the model, such as polar contributions.

### Acknowledgments

The authors declare that they have no conflicts of interest. This research did not receive any specific grant from funding agencies in the public sector.

Received : Jun.18,2022 ; Accepted : Oct.24, 2022

### REFERENCES

- [1] Susial P., Apolinario J.C., Rodríguez–Henríquez J.J., Castillo V.D., Estupiñan E.J., [Isobaric VLE at 0.6 MPa for Binary Systems Isobutyl Acetate + Ethanol, +1–Propanol or +2–Propanol](#), *Fluid Phase Equilib*, **331**: 12–17 (2012).
- [2] Susial P., Apolinario J.C., Castillo V.D., Estupiñan E.J., Rodríguez–Henríquez J.J., [Isobaric VLE for the binary systems Isobutyl Acetate+Methanol or +1–Propanol at 0.15 MPa](#), *Afinidad*, **69**: 95–100 (2012).
- [3] Susial P., Rodríguez–Henríquez J.J., Apolinario J.C., Castillo V.D., Estupiñan E.J., [Vapour Pressures and Vapour–Liquid Equilibria of Binary Systems of \*n\*–Propyl Acetate and Isobutyl Acetate with Ethanol or 2–Propanol at 0.15 MPa](#), *J. Serb. Chem. Soc*, **77**: 1243–1257 (2012).
- [4] Van Ness H.C., Byer S.M., Gibbs R.E., [Vapor–Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods](#), *AIChE J*, **19**: 238–244 (1973).
- [5] Fredenslund A., Gmehling J., Rasmussen P., “[Vapor–Liquid Equilibria Using UNIFAC, A Group Contribution Model](#)”, *Elsevier, Amsterdam*, (1977).
- [6] Shadloo A., Peyvandi K., [A Simple Method to Reduce the Optimized Parameters of Aqueous Amino Acid Solutions Using Association EOSs](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **40** (3): 920–933 (2021).
- [7] Mahmoudabadi S.Z., Pazuki G., [Application of PC-SAFT EOS for Pharmaceuticals: Solubility, Co-Crystal and Thermodynamic Modelling](#), *J. Pharm. Sci.* **110** (6): 2442–2451 (2021).
- [8] Feng Z., Panuganti S.R., Chapman W.G., [Predicting Solubility and Swelling Ratio of Blowing Agents in Rubbery Polymers Using PC-SAFT Equation of State](#), *Chem. Eng. Sci.* **183**: 306–328 (2018).
- [9] Seitmaganbetov N., Rezaei N., Shafiei A., [Characterization of Crude Oils and Asphaltenes Using the PC-SAFT EoS: A Systematic Review](#), *Fuel*, **291**: 120180 (2021).
- [10] Gross J., Sadowski G., [Perturbed–Chain, SAFT An Equation of State Based on a Perturbation Theory for Chain Molecules](#), *Ind. Eng. Chem. Res.*, **40**: 1244–1260 (2001).
- [11] Gross J., Sadowski G., [Application of the Perturbed–Chain SAFT Equation of State to Associating Systems](#), *Ind. Eng. Chem. Res.*, **41**: 5510–5515 (2002).
- [12] Susial P., Sosa–Rosario A., Rios–Santana R., [Vapor–Liquid Equilibria for Ethyl Acetate + Methanol at \(0.1, 0.5, and 0.7\) MPa. Measurements with a New Ebulliometer](#), *J. Chem. Eng. Data*, **55**: 5701–5706 (2010).
- [13] Susial P., Rios–Santana R., Sosa–Rosario A., [VLE Data of Methyl Acetate+Methanol at 1.0, 3.0 and 7.0 bar with a New Ebulliometer](#), *J. Chem. Eng. Jpn.*, **43**: 650–656 (2010).
- [14] De–Afonso C., Ezama R., Losada P., Calama M.A., Llanas B., Pintado M., Saenz de la Torre A.F., [Isobaric Vapor–Liquid Equilibrium. III. Development and Testing of a Small Capacity Equilibrium Still](#), *An. Quim*, **79**: 243–253 (1983) (in Spanish).
- [15] Susial P., García–Vera D., Montesdeoca I., Santiago D.E., López–Beltrán J., [Measurements and Modeling of VLE Data for Butyl Acetate with 2–Propanol or 2–Butanol. Binary Systems at 0.15 and 0.6 MPa](#), *J. Chem. Eng. Data*, **62**: 2296–2306 (2017).
- [16] Susial P., García–Vera D., Marrero–Pérez A.J., Herrera–Vega P., Rodríguez–Domínguez C., Tauste–Sánchez Y., [Experimental Setup with Automatic Control. High Pressure VLE Data of Binary Systems 2–Butanol with \*n\*–Heptane and 2, 2, 4–Trimethylpentane at Both 1.5 MPa and 2.0 MPa](#), *J. Chem. Thermodyn.*, **142**: 105997 (2020).
- [17] Baker J.A., Henderson D., [Perturbation Theory and Equation of State for Fluids: The Square–Well Potential](#), *J. Chem. Phys.*, **47**: 2856–2861 (1967).
- [18] Baker J.A., Henderson D., [Perturbation Theory and Equation of State for Fluids: The Square–Well Potential. II. A Successful Theory of Liquids](#), *J. Chem. Phys.*, **47**: 4714–4720 (1967).

- [19] Chapman W.G.; Jackson G.; Gubbins K.E. **Phase Equilibria of Associating Fluids. Chain Molecules with Multiple Bonding Sites.** *Mol. Phys.*, **65**: 1057–1079 (1988).
- [20] Chapman W.G., Gubbins K.E., Jackson G., Radosz M., **SAFT: Equation-of-State Solution Model for Associating Fluids.** *Fluid Phase Equilib.*, **52**: 31–38 (1989).
- [21] Wertheim M.S., **Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics.** *J. Stat. Phys.*, **35**: 19–34 (1984).
- [22] Wertheim M.S., **Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations.** *J. Stat. Phys.*, **35**: 35–47 (1984).
- [23] Wertheim M.S., **Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites.** *J. Stat. Phys.*, **42**: 459–476 (1986).
- [24] Wertheim M.S., **Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization.** *J. Stat. Phys.*, **42**: 477–492 (1986).
- [25] Wolbach J.P., Sandler S.I., **Using molecular Orbital Calculations to Describe the Phase Behavior of cross-Associating Mixtures.** *Ind. Eng. Chem. Res.*, **37**: 2917–2928 (1988).
- [26] Baird Z., “PC-SAFT” GitHub, <https://github.com/CoolProp/PC-SAFT> (last accessed 10/05/2022).
- [27] Daubert T.E., Danner R.P., “Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation”, Hemisphere Publishing Co., New York (1989).
- [28] Susial P., García D., Susial R., Clavijo Y.C., Martín A., **Measurement and Modelization of VLE of Binary Mixtures of Propyl Acetate, Butyl Acetate or Isobutyl Acetate with Methanol at Pressure of 0.6 MPa.** *Chin. J. Chem. Eng.*, **24**: 630–637 (2016).
- [29] Susial P., García-Vera D., González-Domínguez J. D., Herrera-Vega P., **Measurement and Modelization of VLE for Butyl Acetate with Methanol, Ethanol, 1-Propanol, and 1-Butanol. Experimental Data at 0.15 MPa.** *J. Chem. Eng. Data*, **63**: 2228–2242 (2018).
- [30] Nelder J., Mead R., **A Simplex Method for Function Minimization.** *Comput., J.* **7**: 308–313 (1965).
- [31] Hayden J.G., O’Connell J.P., **A Generalised Method for Predicting Second Virial Coefficients.** *Ind. Eng. Chem. Process Des. Dev.*, **14**: 209–216 (1975).
- [32] Yen L.C., Woods S.S., **A Generalized Equation for Computer Calculation of Liquid Densities.** *AIChE J.*, **12**: 95–99 (1966).
- [33] Susial P., Sosa-Rosario A., Rodríguez-Henríquez J.J., Ríos-Santana R., **Vapor Pressure and VLE Data Measurements on Ethyl Acetate/Ethanol Binary System at 0.1, 0.5 and 0.7 MPa.** *J. Chem. Eng. Jpn.*, **44**: 155–163 (2011).
- [34] Gmehling J., Menke J., Krafczyk J., Fischer K., “Azeotropic Data. 2<sup>nd</sup> ed., part 1”, Ed. Wiley-VCH Verlag, Weinheim, Germany (2004).
- [35] Raviart P.A., Thomas, J.M. **Primal Hybrid Finite Element Methods for 2<sup>nd</sup> order Elliptic Equations.** *Math. Comp.*, **31**: 391–413 (1977).
- [36] Tihic A., Kontogeorgis G.M., Von Solms N., Michelsen M.L., **A Predictive Group Contribution Simplified PC-SAFT Equation of State: Application to Polymer Systems.** *Ind. Eng. Chem. Res.*, **47**: 5092–5101 (2008).