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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

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Abstract: The vapour pressures of *n*-propyl acetate, *iso*-butyl acetate and 2-propanol from 0.004 to 1.6 MPa absolute pressure and vapour–liquid equilibria (VLE) data for the binary systems *n*-propyl acetate+ethanol, *n*-propyl acetate+2-propanol, *iso*-butyl acetate+ethanol and *iso*-butyl acetate+2-propanol at 0.15 MPa were determined. The experimental VLE data were verified with the van Ness Test and the Fredenslund Criterion. The *n*-propyl acetate+ethanol and +2-propanol binary systems have an azeotropic point at 0.15 MPa. Different versions of the universal quasichemical functional group activity coefficients and analytical solutions of groups contribution models were applied.

Keywords: vapour–liquid equilibria isobaric data; phase equilibrium; binary system; esters; alcohols.

INTRODUCTION

Esters, including *n*-propyl acetate and *iso*-butyl acetate, are used in fermentation processes for the synthesis of antibiotics, as solvents for paints, lacquers and varnishes, and in various applications in the graphic arts industry. These substances generate azeotropic mixtures with some alcohols. However, the components of the azeotropic mixtures can be separated by modifying the pressure in the process, in order to obtain pure substances. For this reason, it may be of interest to know the operating conditions under which the azeotropic point disappears. Thus, laboratory data becomes necessary, meaning that ebulliometers and components of experimental facilities must be analyzed.

The construction of a metallic ebulliometer for the determination of the vapour–liquid equilibrium (VLE) data at moderate pressures was previously re-

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ported.^{1,2} Considering this, together with the necessity for reliable data, different modifications were accomplished in the experimental installation,² which are verified in this study.

The VLE of the binary system *n*-propyl acetate+ethanol (PAE) was studied at 101.3 and 160.0 kPa,³ and the system *n*-propyl acetate+2-propanol (PA2P) at 101.32 kPa.⁴ The azeotropic point was described for these two systems.^{3–5} Therefore, both systems could be used as references in the analysis of the modifications introduced in the experimental equipment. For this purpose, VLE data of the binary system PAE and PA2P at 0.15 MPa were determined. The experimental data for the isobutyl acetate+ethanol (IBAE) and isobutyl acetate+2-propanol (IBA2P) systems, which have not been described in literature, are also presented in this paper at 0.15 MPa.

On the other hand, the thermodynamic validation of VLE data depends on the vapour pressures of the pure substances. Accordingly, the vapour pressures of *n*-propyl acetate, isobutyl acetate and 2-propanol, which are required for the application of the point-to-point test, were determined in this study over a wide temperature range.⁶ The data used for ethanol was published in previously.² The VLE data obtained at 0.15 MPa for the binary systems PAE, PA2P, IBAE and IBA2P met the consistency criteria established in literature.⁷ After the thermodynamic consistency was proven, the experimental data were predicted with the universal quasichemical functional group activity coefficients (UNIFAC)^{8–10} and analytical solutions of groups and analytical solutions of groups (ASOG)¹¹ group contribution models for the activity coefficients.

EXPERIMENTAL

Chemicals and apparatus

The physical properties, normal boiling point, density at 298.15 K, and refractive index at 298.15 K, determined for *n*-propyl acetate (Alfa Aesar GmbH & Co. with a purity of 99 %), *iso*-butyl acetate (Panreac Química S.A. with a purity of 99 %) and 2-propanol (99.8 % purity from Panreac Química S.A.), and a comparison with values from literature are given in Table I. The physical properties of ethanol (Panreac Química S.A. of 99.8 % purity) are not different from those previously published.² These chemicals were used without further purification. The normal boiling point at 0.1 MPa was determined with a stainless steel ebulliometer.^{1,2} A Kyoto Electronics DA-300 vibrating tube density meter with an uncertainty of $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$ and a Zusi 315RS Abbe refractometer with an uncertainty of ± 0.0002 units were used for density and refractive index determinations, respectively.

Equipment and procedure

The experimental work in this paper was performed with a dynamic ebulliometer equipped with a Cottrell pump and where the recirculation of both phases is verified, as was previously described.¹ Dostmann Electronic GmbH Pt100 probes, to which a nut and welded ring were included, were placed in the experimental equipment.¹ The electrical system was later assembled inside a sheath, allowing the probe to be screwed to the stainless-steel ebulliometer. The digital Dostmann Electronic GmbH p655 probes used allowed temperature measu-

rements with a ± 0.02 K uncertainty. The welding of the ring to the sheath and the calibration of the system was realised by Dostmann Electronic GmbH. National Physical Laboratory (NPL) and National Institute of Standards and Technology (NIST) standards were applied during calibration of the device. After the probes had been installed, their correct operation was verified by measurement of the boiling point of distilled water.

TABLE I. Physical properties of pure substances and the Antoine constants; tw – this work

T_{bp} / K	$\rho / \text{kg}\cdot\text{m}^{-3}$	n_{D}	A	B	C	$\Delta T / \text{K}$	$\sigma(p_i^0) / \text{MPa}$
2-Propanol							
355.53 ^(tw)	781.3 ^{tw}	1.3751 ^{tw}	6.4727 ^{tw}	1162.30 ^{tw}	95.25 ^{tw}	303–452	0.001
355.30 ⁴	781.33 ⁴	1.3752 ⁴	6.8729 ⁴	1365.38 ⁴	70.04 ⁴	330–370	–
355.41 ¹²	781.26 ¹²	1.3752 ¹²	6.86618 ¹²	1360.13 ¹²	75.56 ¹²	–	–
<i>n</i> -Propyl acetate							
374.61 ^{tw}	882.4 ^{tw}	1.3825 ^{tw}	6.2797 ^{tw}	1371.09 ^{tw}	55.27 ^{tw}	302–503	0.002
374.686 ¹²	883.03 ¹²	1.3828 ¹²	6.14362 ⁴	1284.08 ⁴	64.364 ⁴	–	–
374.55 ³	882.40 ³	1.3816 ³	6.50975 ¹²	1523.13 ¹²	36.38 ¹²	320–430	–
Isobutyl acetate							
389.44 ^{tw}	866.2 ^{tw}	1.3882 ^{tw}	6.4101 ^{tw}	1487.45 ^{tw}	51.07 ^{tw}	300–516	0.001
389.80 ¹²	867.7 ¹²	1.3880 ¹²	6.3546 ⁴	1462.4 ⁴	53.45 ⁴	–	–
389.85 ¹³	866.06 ¹⁴	1.3876 ¹³	6.4088 ¹²	1500.59 ¹²	49.088 ¹²	307–392	–

In order to determine work pressure, a digital display pressure transmitter type 8311 from Burket Fluid control systems (0.0–4.0 MPa range, ± 0.002 MPa uncertainty) was included in the experimental installation.² A controller valve (Binks MFG Co.) was included in the experimental setup in order to control dry nitrogen flow into the equipment during continuous operation and for the determination of the experimental VLE data. However, for the determination of vapour pressure, a controller valve with a 0.6–2.4 MPa range from Trufflo International and a discharge pressure regulator with a 0.035–2.8 MPa range from Fairchild Ind. Prod. Co., were employed. The experimental installation² was also equipped with a Bourdon manometer with a -0.1 – 0.15 MPa range and ± 0.001 MPa uncertainty.

The mixtures studied in this work were kept under boiling conditions for 90 min to ensure a stationary state. After recirculation of both phases, the liquid and vapour condensate samples were extracted from the ebulliometer into external sealed recipients. Once the sample was extracted, the equipment was recharged with a small amount of one of the compounds, in order to modify the composition of the mixture inside the ebulliometer in a continuous operation. The composition of the liquid and vapour phases in the collected samples was determined by density measurement at 298.15 K. A calibration curve composition vs. density had previously been obtained. The greatest uncertainty found for these systems by this composition analysis method was better than 0.002 units in the mole fraction of vapour phase.

RESULTS AND DISCUSSION

The vapour pressures of *n*-propyl acetate, *iso*-butyl acetate and 2-propanol in this work were obtained previously with the stainless-steel ebulliometer,¹ and the new equipment included in the installation previously detailed.² The vapour pressures and temperature data (Table S-I, Supplementary material) were correlated to the Antoine Equation:

$$\log_{10}(p_i^0 / \text{kPa}) = A - \frac{B}{T / \text{K} - C} \quad (1)$$

and the Nelder and Mead¹⁵ procedure was used. The constants obtained are given in Table I together with literature data.

The vapour pressures were verified by calculating the enthalpy of vaporization using the Clapeyron Equation:¹⁶

$$\frac{dp^0}{dT} = \frac{\Delta H_{\text{vap}}}{T(v_i^{\text{G}} - v_i^{\text{L}})} \quad (2)$$

and introducing the Antoine Equation into Eq. (2) as follows:

$$\Delta H_{\text{vap}} = \frac{(v_i^{\text{G}} - v_i^{\text{L}})p^0 BT}{(T - C)^2} \quad (3)$$

The constants of Eq. (1) given in Table I and the vapour pressures from Table S-I were applied in Eq. (3). Data of the critical properties⁷ were employed in the determination of the vapour and liquid molar volumes of the pure compounds using the Hayden and O'Connell¹⁸ method and the Yen and Woods Equation,¹⁹ respectively. When considering as a reference all the data in Table II for each of the substances and the Antoine constants from the literature,¹² the results show that the average errors in the enthalpy of vaporization were less than 2.6, 1.4 and 0.4 %, for 2-propanol, *n*-propyl acetate and isobutyl acetate, respectively. On the other hand, the application of Eq. (3) together with the normal boiling points and the Antoine constants of this work returns deviations of less than 1.3, 1.6 and 1.4 % for 2-propanol, *n*-propyl acetate and isobutyl acetate, respectively, when considering as a reference the enthalpy of vaporization from literature.¹⁷ The acentric factor was obtained using the properties in the literature⁷ and from the correlation of the experimental data from Table S-I, as reduced properties in the Antoine Equation. The acentric factors showed values of 0.665; 0.411 and 0.441 with deviations of less than 5.6, 4.1 and 2.9 % for 2-propanol, *n*-propyl acetate and isobutyl acetate, respectively; literature data¹⁷ were taken for comparison.

The VLE data T - x_1 - y_1 of PAE, PA2P, IBAE and IBA2P at 0.15 MPa are shown in Tables S-II and S-III (Supplementary material). The experimental data were verified to evaluate the thermodynamic consistency using the method described by Fredenslund *et al.*⁷ To develop the test, a three-term Legendre polynomial was used to correlate the excess Gibbs free energy. According to this criterion, the experimental data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapour phase is less than 0.01. In the present study, the values obtained were $\delta y = 0.0089$

for the PAE system, $\delta y = 0.0092$ for the PA2P system, $\delta y = 0.0032$ for the IBAE system and $\delta y = 0.0079$ for the IBA2P system.

Data treatment

The activity coefficients of the liquid phase for each system were determined using the following equation:

$$\gamma_i = \frac{y_i p}{x_i p_i^0} \exp \left[\frac{p}{RT} \left(2 \sum_j y_i B_{ij} - \sum_i \sum_j y_i y_j B_{ij} \right) - \frac{p_i^0 B_{ii}}{RT} + \frac{(p_i^0 - p) v_i^L}{RT} \right] \quad (4)$$

The virial state equation truncated at the second term was employed and the second virial coefficients were obtained by means of the Hayden and O'Connell¹⁸ method. The liquid molar volumes of the pure compounds were estimated using the Yen and Woods equation.¹⁹

The activity coefficients of the liquid phase (Tables S-II and S-III), calculated from the VLE data applying the previous procedure showed a positive deviation from ideal behaviour, probably due to molecular association. The negative deviation observed is possibly a consequence of the experimental uncertainty in the temperature and pressure measurements.

After the thermodynamic consistency of the experimental data had been verified, the calculated activity coefficients were correlated using the excess Gibbs free energy with the relation G^E/RT vs. x_1 in the following thermodynamic models: Wilson, non-random two-liquid (NRTL) and universal quasichemical (UNIQUAC). To obtain the interaction parameters for the activity-coefficient models, the simplex method¹⁵ was applied, using the minimization of the objective function (OF) as follows:²⁰

$$OF = \sum_1^n \left(\gamma_1^{\text{exp}} - \gamma_1^{\text{calc}} \right)_i^2 + \sum_1^n \left(\gamma_2^{\text{exp}} - \gamma_2^{\text{calc}} \right)_i^2 \quad (5)$$

Good correlations were obtained with the thermodynamic models (Table II), and acceptable deviations were observed in the prediction of temperature and vapour phase mole fractions.

Correlation of data and prediction

As in previous studies,^{1,2} the experimental data from every system were correlated to a fitting function (FF) with a polynomial structure:

$$(y_1 - x_1) [x_1(1 - x_1)]^{-1} = \sum_{k=0}^m A_k \left\{ x_1 [x_1 + R_T(1 - x_1)]^{-1} \right\}^k \quad (6)$$

$$\left[T - x_1 T_{\text{bp1}} - (1 - x_1) T_{\text{bp2}} \right] [x_1(1 - x_1)]^{-1} = \sum_{k=0}^m A_k \left\{ x_1 [x_1 + R_T(1 - x_1)]^{-1} \right\}^k \quad (7)$$

$$\left[T - y_1 T_{bp1} - (1 - y_1) T_{bp2} \right] [y_1(1 - y_1)]^{-1} = \sum_{k=0}^m A_k \left\{ x_1 [x_1 + R_T(1 - x_1)]^{-1} \right\}^k \quad (8)$$

The data correlations were performed using the simplex method.¹⁵ The results from the treatment of experimental data are given in Table III. The same process was applied to literature data^{3,4} (Figs. 1–3). It can be observed that the experimental results at 0.15 MPa present good agreements with literature data at 0.1013 and 0.160 MPa for the PAE and PA2P systems studied in this work. For these reason, it seems obvious that the new apparatus for temperature and pressure control are appropriate.

TABLE II. Correlation parameters for G^E/RT with average and standard deviations and predictions of the azeotropic points:

$$\delta(F) = \frac{1}{n} \sum_1^n |F_{\text{exp}} - F_{\text{cal}}|; \quad \sigma(F) = \sqrt{\frac{\sum_1^n (F_{\text{exp}} - F_{\text{cal}})^2}{n - m}}; \quad \bar{e}(F) = \frac{100}{n} \sum_1^n \frac{|F_{\text{exp}} - F_{\text{cal}}|}{F_{\text{exp}}}$$

Model	Parameters, J mol ⁻¹		$\delta(y_1)$	$\bar{\alpha}(T)$ / K	$\sigma(G^E/RT)$
<i>n</i> -Propyl acetate (1) + ethanol (2) at 0.15 MPa					
Wilson	$\Delta\lambda_{12} = 4339.4$	$\Delta\lambda_{21} = -1193.7$	0.005	0.77	0.02
NRTL ($\alpha = 0.47$)	$g_{12} = 954.0$	$g_{21} = 2250.5$	0.005	0.90	0.03
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 1959.4$	$\Delta u_{21} = -411.2$	0.005	0.81	0.03
<i>n</i> -Propyl acetate (1) + 2-propanol (2) at 0.15 MPa					
Wilson	$\Delta\lambda_{12} = 3754.0$	$\Delta\lambda_{21} = -1368.0$	0.009	0.24	0.02
NRTL ($\alpha = 0.47$)	$g_{12} = -553.6$	$g_{21} = 3129.3$	0.011	0.30	0.02
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 397.2$	$\Delta u_{21} = 344.5$	0.009	0.23	0.02
Isobutyl acetate (1) + ethanol (2) at 0.15 MPa					
Wilson	$\Delta\lambda_{12} = 5113.0$	$\Delta\lambda_{21} = -1508.3$	0.003	0.18	0.01
NRTL ($\alpha = 0.47$)	$g_{12} = 1060.2$	$g_{21} = 2536.9$	0.003	0.22	0.01
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 2365.7$	$\Delta u_{21} = -548.5$	0.003	0.25	0.01
Isobutyl acetate (1) + 2-propanol (2) at 0.15 MPa					
Wilson	$\Delta\lambda_{12} = 4183.1$	$\Delta\lambda_{21} = -1866.8$	0.005	0.54	0.02
NRTL ($\alpha = 0.47$)	$g_{12} = -269.5$	$g_{21} = 2598.1$	0.004	0.51	0.02
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 778.2$	$\Delta u_{21} = -12.9$	0.004	0.49	0.02
Azeotropic data					
<i>n</i> -Propyl acetate (1) + ethanol (2) at 0.15 MPa					
Model	This work	Wilson	NRTL	UNIQUAC	
$x_{1\text{az exp}}$	0.051	0.046	0.049	0.046	
$T_{\text{az exp}} / \text{K}$	361.93	361.61	361.60	361.64	
<i>n</i> -Propyl acetate (1) + 2-propanol (2) at 0.15 MPa					
Model	This work	Wilson	NRTL	UNIQUAC	
$x_{1\text{az exp}}$	0.011	0.024	0.028	0.023	
$T_{\text{az exp}} / \text{K}$	365.77	365.70	365.69	365.71	

The symmetrical behaviour of the T vs. x_1 curves in for systems, as well as the influence of pressure, are shown in Figs. 1 and 2. However, the effect of pressure on the vapour phase of the substances seems to create a certain asymmetry in the T vs. y_1 curves, which is highlighted at higher system pressures and ester composition. The different development between the IBAE and IBA2P systems as a consequence of the differences in the boiling points of these alcohols is shown in Fig. 3.

TABLE III. Coefficients and standard deviations obtained in the correlation of the VLE data using the FF equations

FF Equation	R_T	A_0	A_1	A_2	A_3	Condition
<i>n</i> -Propyl acetate (1) + ethanol (2) at 0.15 MPa						
(6)	2.22	0.12	-4.26	5.89	-6.26	$\sigma(y_1-x_1) < 0.003$
(7)	2.11	-29.85	2.42	-88.99		$\sigma(T) = 0.17$ K
(8)	0.60	-38.33	45.79	-0.40		$\sigma(T) = 0.11$ K
<i>n</i> -Propyl acetate (1) + 2-propanol (2) at 0.15 MPa						
(6)	1.99	-0.13	-1.57	0.69	-1.62	$\sigma(y_1-x_1) < 0.003$
(7)	3.52	-23.12	-50.04	18.06	-49.11	$\sigma(T) = 0.13$ K
(8)	1.24	-24.00	-14.98	112.41	-90.11	$\sigma(T) = 0.12$ K
Isobutyl acetate (1) + ethanol (2) at 0.15 MPa						
(6)	2.94	-0.21	-4.58	5.24	-7.47	$\sigma(y_1-x_1) < 0.003$
(7)	9.60	-38.66	-249.20	0.65		$\sigma(T) = 0.11$ K
(8)	0.85	-56.50	178.59	-136.64		$\sigma(T) = 0.22$ K
Isobutyl acetate (1) + 2-propanol (2) at 0.15 MPa						
(6)	9.29	-0.42	-7.15	5.58	-0.01	$\sigma(y_1-x_1) < 0.003$
(7)	11.06	-31.53	-237.47	262.30		$\sigma(T) = 0.18$ K
(8)	0.07	6.05	-144.42	148.93		$\sigma(T) = 0.17$ K

The VLE data for the binary systems PAE, PA2P, IBAE and IBA2P at 0.15 MPa were predicted using the following group contribution methods to calculate the liquid-phase activity coefficients: the ASOG¹¹ method; the original UNIFAC⁷ method, with the structural and group-interaction parameters recommended by Hansen *et al.*,⁹ the UNIFAC-Lyngby⁸ method; and the UNIFAC-Dortmund¹⁰ method. The mean errors and average deviations between the experimental VLE data and those predicted by the different group contribution models are listed in Table IV.

It should be noted that, globally, the ASOG¹¹ method and UNIFAC-1987⁸ version provide the best results in the prediction of the activity coefficients, temperature and vapour phase mole fraction. However, the best method for the prediction of the vapour phase mole fraction at 0.15 MPa was UNIFAC-1991⁹ in the IBAE system. The experimental data for PAE and for PA2P both at 0.15 MPa, together with the data fitting curves predicted with the different group contribution models are shown in Fig. 4. For the PAE and the PA2P systems at 0.15 MPa,

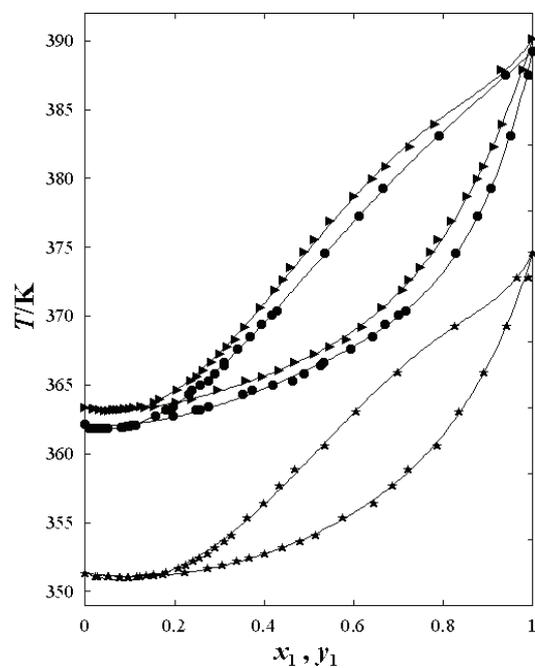


Fig. 1. Plot of experimental VLE data and curves for *n*-propyl acetate (1) + ethanol (2) at 0.15 MPa (●). Fitting curves and literature data³ for 0.1013 (★) and 0.1600 MPa (▲).

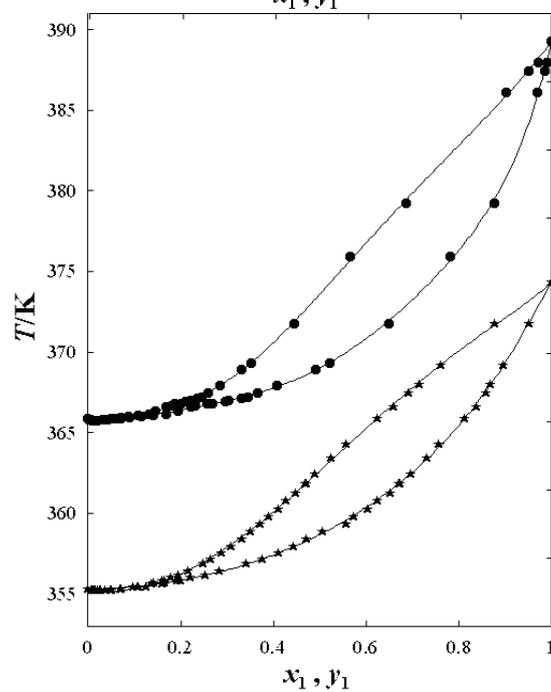


Fig. 2. Isobaric VLE representation of *n*-propyl acetate (1) + 2-propanol (2) at 0.15 MPa (●) with literature data⁴ at 0.10132 MPa (★) and fitting curves.

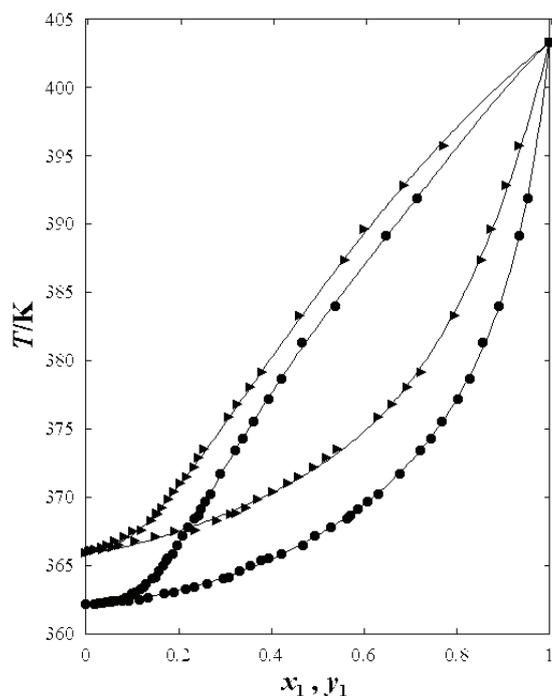


Fig. 3. Plot of experimental VLE data for isobutyl acetate (1) + ethanol (2) (●) and isobutyl acetate (1) + 2-propanol (2) (▲), at 0.15 MPa.

the UNIFAC-1991⁹ and UNIFAC-1987⁸ methods gave lower mean deviations for the ester vapour phase mole fraction, as shown in Fig. 4; however, the ASOG¹¹ model globally represents the behaviour of these systems acceptably (see the inset in Fig. 4). The UNIFAC-1991⁹ version was the best model to predict the IBAE system and the IBA2P system was well represented by the UNIFAC-1987⁸ model, as shown in Fig. 5. However, the ASOG¹¹ model gave a good prediction for the IBA2P system at 0.15 MPa, as can be seen in the inset of Fig. 5.

TABLE IV. Mean errors and average deviations in the prediction of the VLE data using the ASOG and UNIFAC models

Parameter	UNIFAC-1987 ⁸	UNIFAC 1991 ⁹	UNIFAC 1993 ¹⁰	ASOG ¹¹
	OH/COOC	OH/COOC	OH/COOC	OH/COO
<i>n</i> -Propyl acetate (1) + ethanol (2) at 0.15 MPa				
$\delta(y_1)$	0.012	0.006	0.018	0.013
$\bar{e}(\gamma_1)$	4.89	4.80	7.42	4.89
$\delta(T) / \text{K}$	0.47	1.26	0.73	0.50
Azeotropic data				
$x_{1\text{az exp}} = 0.051$	0.030	0.059	0.018	0.034
$T_{\text{az exp}} / \text{K} = 361.93$	361.68	361.51	361.70	361.68

TABLE IV. Continued

Azeotropic data				
<i>n</i> -Propyl acetate (1) + 2-propanol (2) at 0.15 MPa				
$\delta(\gamma_1)$	0.007	0.013	0.013	0.009
$\bar{e}(\gamma_1)$	4.61	8.51	10.18	5.78
$\delta(T) / \text{K}$	0.44	0.47	1.23	0.19
Azeotropic data				
$x_{1\text{az exp}} = 0.011$	0.012	0.049	0.002	0.031
$T_{\text{az exp}} / \text{K} = 365.77$	365.77	365.61	365.87	365.67
Isobutyl acetate (1) + ethanol (2) at 0.15 MPa				
$\delta(\gamma_1)$	0.014	0.004	0.022	0.017
$\bar{e}(\gamma_1)$	5.85	1.89	10.48	7.87
$\delta(T) / \text{K}$	1.24	0.41	2.21	1.59
Isobutyl acetate (1) + 2-propanol (2) at 0.15 MPa				
$\delta(\gamma_1)$	0.003	0.017	0.014	0.005
$\bar{e}(\gamma_1)$	2.20	8.58	8.66	2.61
$\delta(T) / \text{K}$	0.45	1.26	1.78	0.30

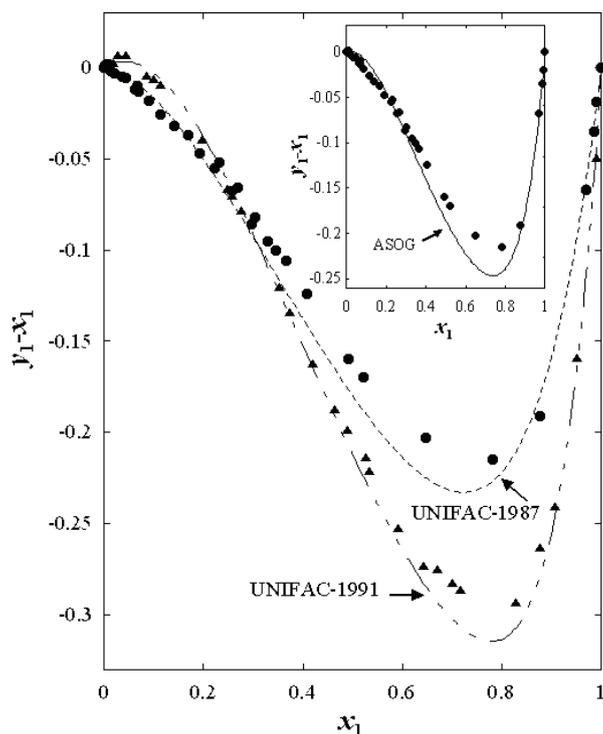


Fig. 4. Experimental points of $(y_1 - x_1)$ vs. x_1 for *n*-propyl acetate (1) + ethanol (2) at 0.15 MPa (\blacktriangle) and *n*-propyl acetate (1) + 2-propanol (2) at 0.15 MPa (\bullet). Fitting curves of data prediction for *n*-propyl acetate (1) + ethanol (2) with UNIFAC-1991⁹ and for *n*-propyl acetate (1) + 2-propanol (2) with UNIFAC-1987⁸ or ASOG¹¹ for the inset.

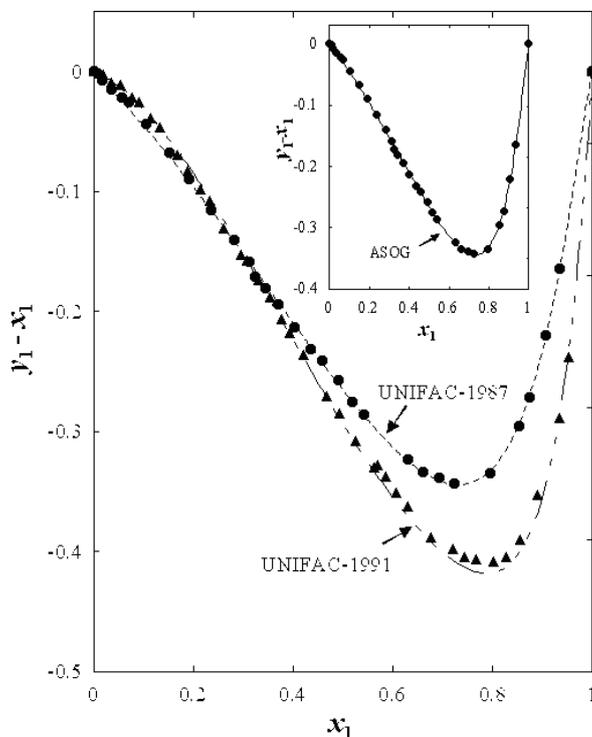


Fig. 5. Experimental points of $(y_1 - x_1)$ vs. x_1 for *iso*-butyl acetate (1) + ethanol (2) at 0.15 MPa (\blacktriangle) and isobutyl acetate (1) + 2-propanol (2) at 0.15 MPa (\bullet). Fitting curves of data prediction for isobutyl acetate (1) + ethanol (2) with UNIFAC-1991⁹ and for isobutyl acetate (1) + 2-propanol (2) with UNIFAC-1987⁸ or ASOG¹¹ for the inset.

Azeotropic data

The azeotropic points have been described in various works⁵ for the PAE system. Ortega *et al.*³ established that the composition and temperature of the azeotrope at 0.1600 MPa were $x_{1az} = 0.041$ and $T_{az} = 363.14$ K. On the other hand, for the system PA2P at 0.10132 MPa, the only azeotropic point was reported by González *et al.*⁴ as $x_{1az} = 0.037$ and $T_{az} = 355.2$ K. Accordingly, the singular points in both systems, studied in this paper at 0.15 MPa ($x_{1az} = 0.051$ and $T_{az} = 361.93$ K for PAE system and $x_{1az} = 0.011$ and $T_{az} = 365.77$ K for PA2P system), are plotted in Fig. 6, together with literature data,³⁻⁵ in order to verify, by means of the evolution of the azeotrope, the modifications introduced in the experimental installation. The azeotropic data from the literature³⁻⁵ together with the azeotropic data from this work are presented in Fig. 6. For the PAE system these are indicated by the composition of the ester in $x_1 - T_r$ coordinates; and for the PA2P system in $\log_{10}(p_r) - T_r$ coordinates. The azeotropic points of this paper are also indicated by pressure in $x_1 - \log_{10} p_r$ coordinates.

The azeotropic data from this work present a good agreement with those in the literature.³⁻⁵ The systems PAE and PA2P show a modification in the T - x_1 - y_1 values with increasing pressure (Figs. 1 and 2); *i.e.*, the azeotrope moves towards lower ester mole fractions with increasing pressure. This produces a change in the y_1 - x_1 values, which decrease, thus leading to the disappearance of the azeotrope with increasing pressure. This behaviour can be observed from the data presented in Fig. 6.

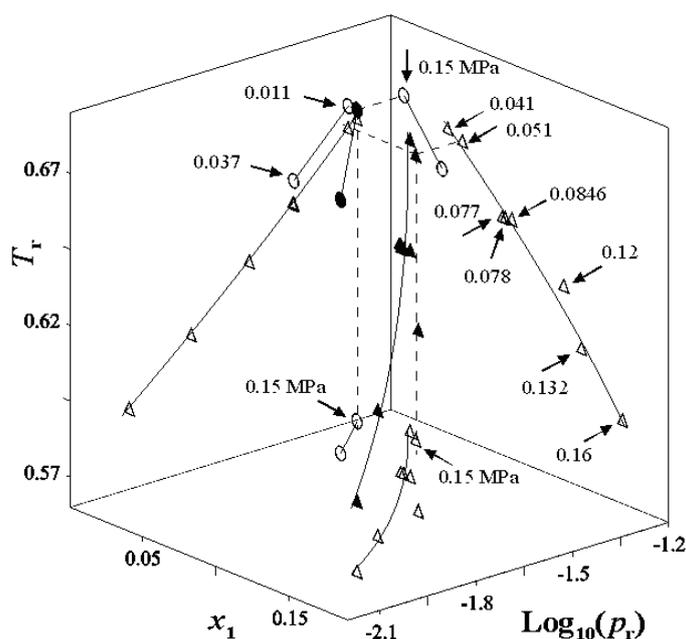


Fig. 6. Azeotropic data in reduced coordinates for the systems *n*-propyl acetate (1) + ethanol (2) (▲, △) and *n*-propyl acetate (1) + 2-propanol (2) (●, ○) from literature³⁻⁵ and this work at 0.15 MPa.

On the other hand, Table II shows the predictions made by the thermodynamic models for the azeotropic point for the systems studied in this work. It can be seen that, generally, they all give good predictions. However, when considering the group contribution models (Table IV) the ASOG¹¹ model is the one that globally best represents the azeotropic data of this work, while the UNIFAC-1991⁹ model predicts well the singular point of the PAE system at 0.15 MPa; although the UNIFAC-1987⁸ model predicts well the azeotropic data in the PA2P system at 0.15 MPa. In addition, the model UNIFAC-1993¹⁰ does not give a good prediction of the azeotropic point, as shown in Table IV.

CONCLUSIONS

The isobaric VLE data for the binary systems *n*-propyl acetate + ethanol, *n*-propyl acetate + 2-propanol, isobutyl acetate + ethanol and isobutyl acetate + 2-propanol at 0.15 MPa have been measured using a stainless steel ebulliometer. The thermodynamic consistencies of the experimental data were checked by the van Ness Test⁶ and agree with the Fredenslund validation criterion.⁷

Thermodynamically consistent VLE data and vapour pressures of 2-propanol, *n*-propyl acetate and isobutyl acetate were obtained and compared to those in the literature. The results showed that the new equipment introduced in the experimental installation enabled reliable data to be obtained.

The singular points of the systems *n*-propyl acetate + ethanol and *n*-propyl acetate + 2-propanol at 0.15 MPa were determined. The azeotropic data were correlated and discussed considering literature data and the effect of the system pressure on the elimination of azeotropes.

Several thermodynamic mathematical models, as well as group contribution models, the ASOG, the original UNIFAC, the UNIFAC-Lyngby and the UNIFAC-Dortmund, were applied, and the predictions were verified and discussed with respect to the experimental data obtained in this study.

SUPPLEMENTARY MATERIAL

Tables S-I-S-III (experimental data) are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

NOMENCLATURE

A, B, C	Antoine Equation parameters (Eqs. (1) and (3))
A_k	Parameter of Eqs. (6)–(8)
B_{ii}	Second virial coefficient of the pure component, $\text{m}^3 \cdot \text{mol}^{-1}$
B_{ij}	Cross second virial coefficient, $\text{m}^3 \cdot \text{mol}^{-1}$
ΔH_{vap}	Enthalpy of vaporization, $\text{J} \cdot \text{mol}^{-1}$
\bar{e}	Average error, %
F	Property ($F = y_1$; $F = (y_1 - x_1)$; $F = \gamma_1$; $F = \gamma_2$; $F = T$; $F = G^E/RT$)
G^E	Excess free energy, $\text{J} \cdot \text{mol}^{-1}$
m	Number of equation parameters
n	Number of experimental data
n_D	Refractive index
p_i^0	Vapour pressure for pure substance, kPa
p	Total pressure, kPa
R	Universal gas constant, $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
R_T	Parameter of Eqs. (6)–(8)
T	Temperature, K
v_1^L, v_1^G	Pure substances liquid and gas molar volumes, $\text{m}^3 \cdot \text{mol}^{-1}$
x	Liquid-phase mole fraction
y	Vapour-phase mole fraction
Z_T	Active fraction of vapour phase or liquid phase.

Greek symbols

γ	Activity coefficient
δ	Mean deviation
ρ	Density, $\text{kg}\cdot\text{m}^{-3}$
σ	Standard deviation.

Subscripts

az	Azeotrope
bp	Normal boiling point
cal	Calculated
exp	Experimental
i, j	Chemical substances
Lit	Literature
1	Ester.

ИЗВОД

НАПОНИ ПАРА И РАВНОТЕЖА ПАРА–ТЕЧНОСТ ПРОПИЛАЦЕТАТА И
ИЗОБУТИЛАЦЕТАТА СА ЕТАНОЛОМ ИЛИ 2-ПРОПАНОЛОМ НА
ПРИТИСКУ 0,15 МПа. БИНАРНИ СИСТЕМИ

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Одређени су напони пара пропилацетата, изобутилацетата и 2-пропанола, на апсолутном притиску од 0,004 МПа до 1,6 МПа, као и подаци за равнотежу пара-течност бинарних система пропилацетат + етанол, пропилацетат + 2-пропанол, изобутилацетат + етанол и изобутилацетат + 2-пропанол на притиску од 0,15 МПа. Експериментални подаци за равнотежу пара-течност су проверени преко теста van Ness-а и Fredenslund-овог критеријума. Бинарни системи пропилацетат+етанол и пропилацетат+2-пропанол имају тачку азеотропа на притиску 0,15 МПа. Примењене су различите верзије модела коефицијената активности универзалних квази-хемијских функционалних група и аналитичких решења за групе да би се описали доприноси група.

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