

Vapour-Liquid Equilibrium of Propyl Acetate - Ethanol and Propyl Acetate - 2 Propanol at 0.6 MPa

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VLE data for the binary systems of propyl acetate - ethanol and propyl acetate - 2-propanol at 0.6 MPa have been determined. The experimental data were verified with the point-to-point test of van Ness. These systems do not present an azeotropic point at 0.6 MPa. The different versions of UNIFAC and ASOG prediction models were applied.

Keywords: vapour-liquid equilibrium, VLE isobaric data, binary system, propyl acetate

Propyl acetate is obtained by esterification of acetic acid with propanol. It is a solvent that is used as raw material for adhesives as well as for ink formulations in the flexographic industry. This substance produces azeotropic mixtures with some alcohols.

Vapor-Liquid Equilibrium (VLE) of the binary system propyl acetate - ethanol has been investigated at 101.3 and 160.0 kPa [1], while the binary system propyl acetate - 2-propanol has been studied at 101.3 kPa [2]. An azeotropic point has been described for both systems [1-3]. Therefore, as in previous works [4, 5], the purpose of this study was to investigate the both systems for the azeotrope disappearance when pressure increases. To this effect, the isobaric data of VLE at 0.6 MPa for propyl acetate - ethanol and propyl acetate - 2-propanol has been obtained.

The VLE experimental data of phenyl acetate - ethanol and propyl acetate - 2-propanol were verified with the point-to-point test [6]. All data presented in this work agree with the global consistency criteria from literature [7]. After this, the contribution models UNIFAC [8-10] and ASOG [11] were verified with the consistent thermodynamic data of this paper.

Experimental parts

Materials

The physical properties, normal boiling temperature (T_{bp}), density (ρ) at 298.15 K, and refractive index (n_D) at 298.15 K, determined for propyl acetate with a purity of 99%, ethanol and 2-propanol both of 99.9% purity and their comparison with values found in literature are shown in table 1. These chemicals were used without further purification.

Equipment and procedure

The VLE experiments in this study were performed using

a dynamic recirculating still equipped with a Cottrell pump, which has been described in previous papers [4, 5]. Pt100 probes were threaded to the ebulliometer. The welding of the nut to the cover of the probes and the electric circuit were mounted by Dostmann Electronic GmbH. Temperature was measured with ± 0.02 K of uncertainty using a Pt-100 probe with a digital Dostmann Electronic P655 thermometer, both calibrated by Dostmann Electronic GmbH following laboratory standards calibration according to international agreement with NPL and NIST standards. The probe was mounted on the stainless steel ebulliometer, and verified by measuring the boiling point of distilled water.

Working pressure was measured using a pressure transmitter with a 0.0 to 4.0 MPa range (uncertainty of ± 0.005 MPa). A controller valve was included in order to regulate the flow of dry nitrogen into the equipment for obtaining VLE data in continuous operation. The system was kept at boiling conditions for 90 min to ensure the stationary state, and then samples of liquid and vapour were extracted into external sealed recipients.

The composition of the liquid (x_1) and vapor (y_1) samples for the binary systems were determined by measuring their densities at 298.15 K with a vibrating-tube density meter with a ± 0.1 kg·m⁻³ precision. The composition dependence on density was previously determined. The accuracy of the composition analysis was better than 0.002 mole fraction units.

Results and discussions

The VLE data T - x_1 - y_1 of propyl acetate (1) - ethanol (2) and propyl acetate (1) - 2-propanol (2) at 0.6 MPa are displayed in table 2. The thermodynamic consistency of these data has been verified using the literature properties [1, 7, 13]. The binary data of all the systems passed the

Table 1
PHYSICAL PROPERTIES OF THE PURE SUBSTANCES AT ATMOSPHERIC PRESSURE

compound	T_{bp}/K		ρ (298.15K)/(kg·m ⁻³)		n_D (298.15K)	
	Exp	Lit	Exp	Lit	Exp	Lit
ethanol	351.45	351.33 [1]	785.2	785.02 [1]	1.3598	1.3595 [1]
		351.443 [12]		784.93 [12]		1.35941 [12]
2-propanol	355.53	355.30 [2]	781.3	781.33 [2]	1.3751	1.3752 [2]
		355.55 [12]		781.26 [12]		1.3745 [12]
propyl acetate	374.61	374.55 [1]	882.4	882.4 [1]	1.3825	1.3816 [1]
		374.686 [12]		883.03 [12]		1.3828 [12]

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Table 2
EXPERIMENTAL DATA T - x_1 - y_1 AND CALCULATED VALUES FOR THE ACTIVITY COEFFICIENTS OF THE LIQUID PHASE

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
propyl acetate (1) + ethanol (2) at 0.6 MPa														
405.53	0.000	0.000		1.000	411.19	0.372	0.213	1.231	1.079	423.74	0.760	0.506	1.053	1.288
405.55	0.006	0.005	2.082	1.004	411.62	0.390	0.223	1.216	1.085	423.86	0.766	0.514	1.058	1.296
405.59	0.010	0.008	1.996	1.004	411.96	0.412	0.235	1.203	1.098	425.42	0.793	0.544	1.044	1.323
405.61	0.012	0.009	1.870	1.004	412.59	0.436	0.248	1.180	1.107	428.06	0.841	0.612	1.042	1.377
405.94	0.052	0.039	1.852	1.006	413.23	0.462	0.261	1.154	1.121	428.56	0.849	0.629	1.049	1.370
406.34	0.085	0.059	1.695	1.009	413.97	0.482	0.275	1.144	1.120	429.63	0.869	0.666	1.058	1.387
406.81	0.110	0.074	1.623	1.008	414.56	0.508	0.295	1.147	1.130	429.92	0.872	0.668	1.051	1.401
407.80	0.170	0.113	1.561	1.008	415.83	0.558	0.334	1.145	1.150	432.36	0.906	0.743	1.061	1.390
408.87	0.245	0.151	1.407	1.030	417.37	0.606	0.367	1.116	1.179	433.65	0.917	0.769	1.059	1.380
409.40	0.274	0.172	1.413	1.030	418.19	0.625	0.382	1.104	1.184	439.97	0.981	0.927	1.042	1.655
410.84	0.356	0.202	1.231	1.077	423.16	0.749	0.492	1.053	1.285	446.02	1.000	1.000	1.000	
propyl acetate (1) + 2-propanol (2) at 0.6 MPa														
410.08	0.000	0.000		1.000	415.11	0.284	0.183	1.249	0.996	427.35	0.736	0.544	1.071	1.116
410.50	0.025	0.018	1.565	0.991	415.89	0.321	0.206	1.220	1.000	430.01	0.789	0.615	1.069	1.114
410.80	0.037	0.025	1.457	0.988	416.62	0.371	0.226	1.138	1.033	435.02	0.880	0.746	1.041	1.155
411.21	0.059	0.039	1.411	0.986	416.64	0.375	0.229	1.140	1.035	438.16	0.929	0.825	1.018	1.253
411.83	0.097	0.068	1.473	0.980	416.65	0.378	0.234	1.156	1.033	439.63	0.953	0.868	1.012	1.384
412.29	0.124	0.086	1.441	0.979	417.88	0.454	0.292	1.165	1.055	441.08	0.966	0.903	1.007	1.363
412.55	0.157	0.102	1.341	0.993	418.74	0.483	0.306	1.125	1.069	442.44	0.978	0.934	1.001	1.393
413.07	0.184	0.120	1.329	0.992	419.96	0.525	0.346	1.136	1.064	443.60	0.988	0.962	0.996	1.436
413.89	0.219	0.143	1.304	0.988	420.64	0.566	0.375	1.124	1.094	446.02	1.000	1.000	1.000	
414.51	0.250	0.161	1.267	0.991	423.67	0.641	0.443	1.092	1.096					

consistency test [6], as the deviation between the calculated and experimental data resulted less than 0.01 mole fraction in the vapour phase [7].

Data treatment

The activity coefficients (γ_i) of the liquid phase for every system were determined by using the following equation:

$$\gamma_i = \frac{\phi_i y_i p}{x_i \phi_i^o p_i^o} \exp\left[\frac{(p_i^o - p) v_i^L}{RT}\right] \quad (1)$$

The fugacity coefficients (ϕ_i) were calculated using the virial state equation truncated at the second term, and from the following equation:

$$\phi_i = \phi_i^o \exp\left[\frac{p}{RT} \left(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}\right) - \frac{p_i^o B_{ii}}{RT}\right] \quad (2)$$

The second virial coefficients, B_{ii} and B_{ij} , were obtained by means of the Hayden and O'Connell method [14]. The liquid molar volumes of pure compounds (v_i^L) were estimated by the equation of Yen and Woods [15].

The activity coefficients of the liquid phase, calculated

from the VLE data (table 2) showed a positive deviation from ideal behavior, probably due to a molecular association. The negative deviation observed is possibly a consequence of experimental errors in temperature and pressure measurements.

After the thermodynamic consistency of the experimental data was verified, the calculated activity coefficients were correlated using excess Gibbs energies (G^E) with the relation G^E/RT vs. x_1 in the following thermodynamic models: Redlich-Kister, Van Laar, Margules, Wilson, NRTL and UNIQUAC. The simplex method [16] was applied, considering the minimization of the objective function (OF) as follows [17]:

$$OF = \sum_{i=1}^{i=n} \left(\gamma_i^{exp} - \gamma_i^{calc} \right)^2 + \sum_{j=1}^j \left(\gamma_j^{exp} - \gamma_j^{calc} \right)^2 \quad (3)$$

Good correlations were obtained from the thermodynamic models (table 3), and acceptable deviations were observed in the vapour phase prediction.

Correlation of data and prediction

All data processing was performed using the simplest method [16]. Results from the treatment of experimental

Table 3
CORRELATION PARAMETERS FOR G^E/RT WITH AVERAGE AND STANDARD DEVIATIONS

model	parameters	$\delta(y_1)$	$\delta(T)/K$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(G^E/RT)$
propyl acetate (1) + ethanol (2) at 0.6 MPa						
Redlich-Kister	$A_0 = 0.540$	$A_1 = -0.119$	0.012	0.62	0.06	0.02
Van Laar	$A_{12} = 0.681$	$A_{21} = 0.433$	0.012	0.57	0.06	0.02
Margules	$A_{12} = 0.684$	$A_{21} = 0.537$	0.015	0.85	0.04	0.02
Wilson	$\Delta\lambda_{12} = 4950.7$ (J·mol ⁻¹)	$\Delta\lambda_{21} = -2640.0$ (J·mol ⁻¹)	0.012	0.53	0.06	0.02
NRTL ($\alpha = 0.47$)	$g_{12} = -375.8$ (J·mol ⁻¹)	$g_{21} = 2739.3$ (J·mol ⁻¹)	0.012	0.61	0.05	0.02
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -1327.3$ (J·mol ⁻¹)	$\Delta u_{21} = -234.2$ (J·mol ⁻¹)	0.011	0.59	0.05	0.02
propyl acetate (1) + 2-propanol (2) at 0.6 MPa						
Redlich-Kister	$A_0 = 0.371$	$A_1 = -0.039$	0.011	0.62	0.05	0.01
Van Laar	$A_{12} = 0.416$	$A_{21} = 0.332$	0.011	0.62	0.05	0.01
Margules	$A_{12} = 0.429$	$A_{21} = 0.439$	0.012	0.92	0.03	0.02
Wilson	$\Delta\lambda_{12} = 1610.5$ (J·mol ⁻¹)	$\Delta\lambda_{21} = -201.2$ (J·mol ⁻¹)	0.011	0.61	0.05	0.01
NRTL ($\alpha = 0.47$)	$g_{12} = -14.8$ (J·mol ⁻¹)	$g_{21} = 1473.3$ (J·mol ⁻¹)	0.011	0.66	0.04	0.02
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 974.1$ (J·mol ⁻¹)	$\Delta u_{21} = -378.8$ (J·mol ⁻¹)	0.011	0.62	0.04	0.01

$$\delta(F) = \frac{1}{n} \sum_{i=1}^n |F_{exp} - F_{cal}|; \quad \sigma(F) = \sqrt{\frac{\sum_{i=1}^n (F_{exp} - F_{cal})^2}{n - m}} \quad (F \text{ being the properties})$$

Table 4
COEFFICIENTS AND STANDARD DEVIATIONS OBTAINED IN THE CORRELATION OF VLE DATA USING THE *FF* EQUATIONS

<i>FF</i>	R_T	A_3	A_1	A_2	A_3	
propyl acetate (1) + ethanol (2) at 0.6 MPa						
$(y_1 - x_1)[x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	1.269	-0.159	-2.226	2.858	-3.015	$\sigma(y_1-x_1) < 0.004$
$[T - x_1 T_{bp1} - (1 - x_1) T_{bp2}][x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	23.883	-33.556	-295.347	0.563		$\sigma(T)/K = 0.31$
$[T - y_1 T_{bp1} - (1 - y_1) T_{bp2}][y_1(1 - y_1)]^1 = \sum_{k=0} A_k Z_T^k$	1.980	-28.514	104.520	-141.199		$\sigma(T)/K = 0.16$
$(G^E / RT)[x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	25.000	0.495	1.128			$\sigma(G^E/RT) < 0.011$
propyl acetate (1) + 2-propanol (2) at 0.6 MPa						
$(y_1 - x_1)[x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	3.806	-0.269	-3.007	5.002	-4.258	$\sigma(y_1-x_1) < 0.003$
$[T - x_1 T_{bp1} - (1 - x_1) T_{bp2}][x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	8.038	-22.278	-101.895	0.049		$\sigma(T)/K = 0.42$
$[T - y_1 T_{bp1} - (1 - y_1) T_{bp2}][y_1(1 - y_1)]^1 = \sum_{k=0} A_k Z_T^k$	2.194	-9.645	-19.553	86.444	-90.953	$\sigma(T)/K = 0.20$
$(G^E / RT)[x_1(1 - x_1)]^1 = \sum_{k=0} A_k Z_T^k$	0.764	0.189	0.318			$\sigma(G^E/RT) < 0.005$

$$Z_T = \frac{x_1}{x_1 + R_T(1 - x_1)}$$

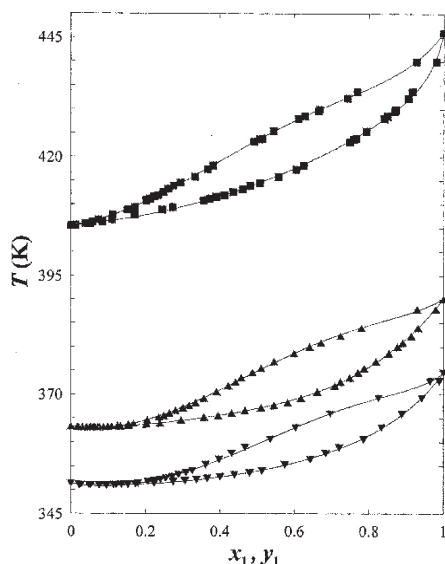


Fig. 1. Vapour-liquid equilibria and fitting curves of propyl acetate (1) + ethanol (2) at 0.6 MPa (■) and literature data [1] at 101.3 kPa (▲) or 160.0 kPa (▼)

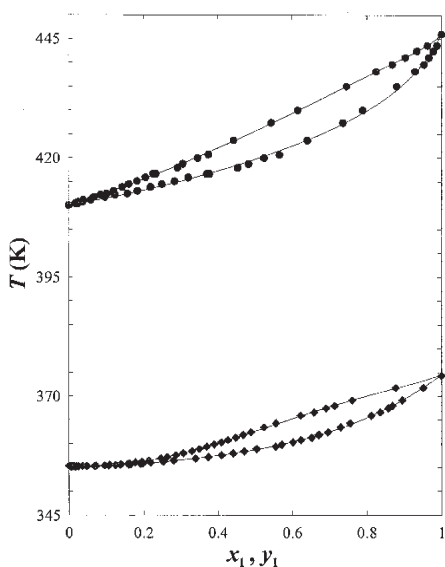


Fig. 2. Isobaric VLE and fitting curves of propyl acetate (1) + 2-propanol (2) at 0.6 MPa (●) and literature data [2] at 101.32 kPa (◆)

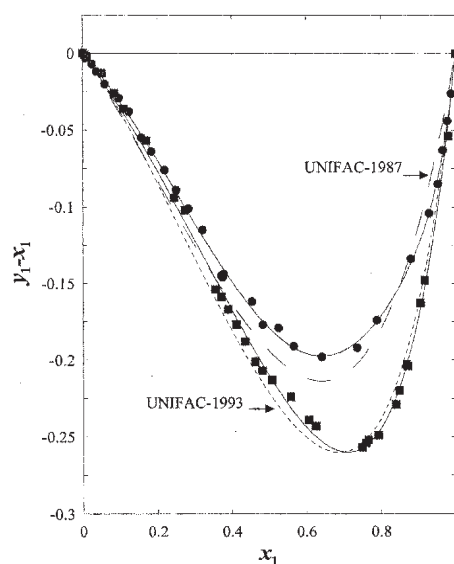


Fig. 3. Plot of experimental VLE data and fitting curves for propyl acetate (1) + ethanol (2) at 0.6 MPa (■) and propyl acetate (1) + 2-propanol (2) at 0.6 MPa (●). The curves represent predicted values for propyl acetate (1) + ethanol (2) from UNIFAC-1993 [9] (---) and for propyl acetate (1) + 2-propanol (2) from UNIFAC-1987 [7] (—)

consistency test [6], as the deviation between the calculated and experimental data resulted less than 0.01 papers [4, 5] are shown in table 4. The same process was applied to literature data [1, 2] [fig. 1, 2]. It can be observed that the experimental results at 0.6 MPa present for systems analyzed in this work a good correspondence with literature data at 0.1 and 0.16 MPa.

Figures 1 and 2 show a similar behaviour of T vs x_1 curves of both systems as well as the evolution of the systems with pressure. However, this trend disappears in T vs y_1 curves, when we observe a different effect of pressure on the mixture in the vapour phase.

On the other hand, these systems, for low ester mole fractions, show a decrease in the difference between $y_1 - x_1$ with pressure increasing. This produces a change between $y_1 - x_1$ going from positive to negative values from 0 to 1 ester mole fraction, thus generating the disappearance of the azeotrope mentioned in literature [1-3]. In figure 3 can be observed that there is no azeotropic data for the binary systems of this paper at 0.6 MPa.

model	group pairs	$\delta(\gamma_1)$	$\bar{\epsilon}(\gamma_1)\%$	$\delta(T)/K$
propyl acetate (1) + ethanol (2) at 0.6 MPa				
UNIFAC-1987 [8]	OH/COOC	0.015	7.44	1.91
UNIFAC-1991 [9]	OH/COOC	0.029	12.35	2.71
UNIFAC-1993 [10]	OH/COOC	0.008	5.16	1.20
ASOG [11]	OH/COO	0.011	3.47	0.80
propyl acetate (1) + 2-propanol (2) at 0.6 MPa				
UNIFAC-1987 [8]	OH/COOC	0.013	5.98	0.85
UNIFAC-1991 [9]	OH/COOC	0.025	13.69	2.75
UNIFAC-1993 [10]	OH/COOC	0.013	6.47	0.82
ASOG [11]	OH/COO	0.015	7.39	1.69

Table 5
MEAN ERRORS AND AVERAGE DEVIATIONS IN THE
PREDICTION OF VLE DATA USING ASOG AND
UNIFAC MODELS

$$\bar{\epsilon}(F) = \frac{100}{n} \sum_1^n \frac{|F_{\text{exp}} - F_{\text{cal}}|}{F_{\text{exp}}}$$

The UNIFAC [8-10] and ASOG [11] group contribution models are useful for the development of separation processes, reason why the experimental data in this paper were compared with the values obtained from these models. The overall results are presented in table 5. It should be noted that, globally, the ASOG and UNIFAC-1993 version provide the best results in the prediction of the activity coefficients. However, the best version of UNIFAC to predict the propyl acetate - ethanol system at 0.6 MPa was UNIFAC-1993 while for the propyl acetate - 2-propanol system at 0.6 MPa was UNIFAC-1987. Figure 3 shows the experimental data at 0.6 MPa with the fitting curves (see table 4) and the best results in the VLE prediction for the binary systems studied in this work.

Conclusions

The isobaric VLE data have been measured at 0.6 MPa for the binary systems propyl acetate-ethanol and propyl acetate-2-propanol by means of a stainless steel ebulliometer. The thermodynamic consistency of data has been verified with the point-to-point test and agree with the Fredenslund validation criterion.

Non azeotropic data for these propyl acetate-ethanol and propyl acetate-2-propanol binary systems at 0.6 MPa have been obtained; therefore, the disappearance of the azeotropes, which at low pressures are reported in the literature, has been verified. This allows the obtaining of these pure substances at 0.6 MPa.

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

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