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Vapor−Liquid Equilibria for Ethyl Acetate + Methanol at (0.1, 0.5, and 0.7) MPa. Measurements with a New Ebulliometer

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A new dynamic still for the determination of vapor−liquid equilibrium (VLE) data has been constructed in stainless steel. Both the liquid and vapor phases are recirculated. The operating procedure is based on the Cottrell pump principle. The liquid mixture is placed in an inverted double-walled vessel and heated. The equipment performance has been verified by measurements on mixtures that have been previously studied by various authors. VLE data have been determined for the ethyl acetate + methanol binary system at (0.1, 0.5, and 0.7) MPa. The experimental data have been tested with the point-to-point test of Van Ness, employing the program of Fredenslund, and are shown to be consistent.

Introduction

Distillation is one of the procedures used in chemical engineering to separate substances from a mixture. However, when an azeotrope is present at atmospheric pressure, the separation is not possible. In these situations, pure substances can be obtained if the process pressure is modified.

Ethyl acetate is a widely used solvent in industrial processes. This compound forms an azeotrope with methanol.[1] The ethyl acetate + methanol mixture has been studied under isothermal and isobaric conditions in various investigations.[2] Despite this fact, vapor−liquid equilibrium (VLE) isobaric data for this system at pressures above 141.3 kPa[3] have not been found.

Consequently, the ethyl acetate + methanol mixture can be used to evaluate a new ebulliometer at low pressures. The ebulliometer, made of stainless steel, takes as a reference the copper-made still formerly introduced by the authors.[4] Experimental VLE determinations have been made with the binary system ethyl acetate + methanol at (0.1, 0.5, and 0.7) MPa, studying the behavior of the azeotrope at different pressures.

The experimental data obtained in this work have been verified with the consistency point-to-point test of Van Ness.[5] The isobaric data show a positive consistency when the Fredenslund criterion[6] is applied. Therefore, these data can be used to corroborate the predictions of the group contribution models under moderate pressures.

Experimental Section

Products. 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 the ethyl acetate (Panreac) and methanol (Panreac) and their comparison with values found in the literature[7–9] are shown in Table 1. These products were used without further purification.

Apparatus and Procedure. An equilibrium still made of stainless steel 316 L has been developed and constructed (Figure 1) using a configuration similar to that of the ebulliometer of de-Afonso et al.[10] with some modifications in the design to that previously presented by our research group.[11] The main difference between this new still and the copper-made ebulliometer consists in the diameter used for the vapor outlet, modified to satisfy the observed necessity for the vapor to circulate into the cooler, due to the countercurrent resistance created by the gas pressure. In addition, the recirculation circuit of the liquid phase has been simplified and built in such a way that the retained volumes of both recirculated phases are similar.

Table 1. Physical Properties of the Pure Compounds at Atmospheric Pressure

		T_{bp}		ρ (298.15 K)			
		K		kg·m^{-3}		n_{D} (298.15 K)	
compound	purity	exptl	lit.	exptl	lit.	exptl	lit.
methanol	puriss. p.a. $w > 0.999$	337.85	337.696^{a} 337.85^{b,c}	786.8	786.64^{a} 786.8^{b}	1.3270	1.32652^{a} 1.3265^{b,c}
ethyl acetate	puriss. $w > 0.995$	350.15	350.26^{a} 350.21^{c}	894.6	894.55^{a} 894.0^{c}	1.3700	1.36978^{a} 1.3704^{c}

[a] From ref 7. [b] From ref 8. [c] From ref 9.

As shown in Figure 1, an apparatus with a 400 cm^{3} capacity has been built to work at moderate or high pressures. The liquid volumes employed inside the equipment are a consequence of the commercial tubes that have been used in the construction of the ebulliometer. The general description of the equilibrium ebulliometer and the disposal of the different elements in the installation can therefore be consulted in previous papers.[4,10–12]

It was also necessary to prepare J-type thermocouples with a soldered nut. The nut was threaded onto a bolt which had a hole in its center that perforated entirely, and was welded to the ebulliometer. Thermocoax thermocouples calibrated by a commercial firm following the IEC 5842 standards were verified by us with the ice and steam points of distilled water. The temperature was measured with an uncertainty of ± 0.05 K.

The pressure was controlled with a pressure-regulating valve (Binks MFG Co.) included in the nitrogen supply line. The pressure was measured with a NouvaFima manometer with a (0 to 1.0) MPa range (uncertainty of ± 0.005 MPa) and a Bourdon manometer with a (−0.1 to +0.15) MPa range (uncertainty of ± 0.001 MPa). Both provide a 1 % accuracy of full scale.

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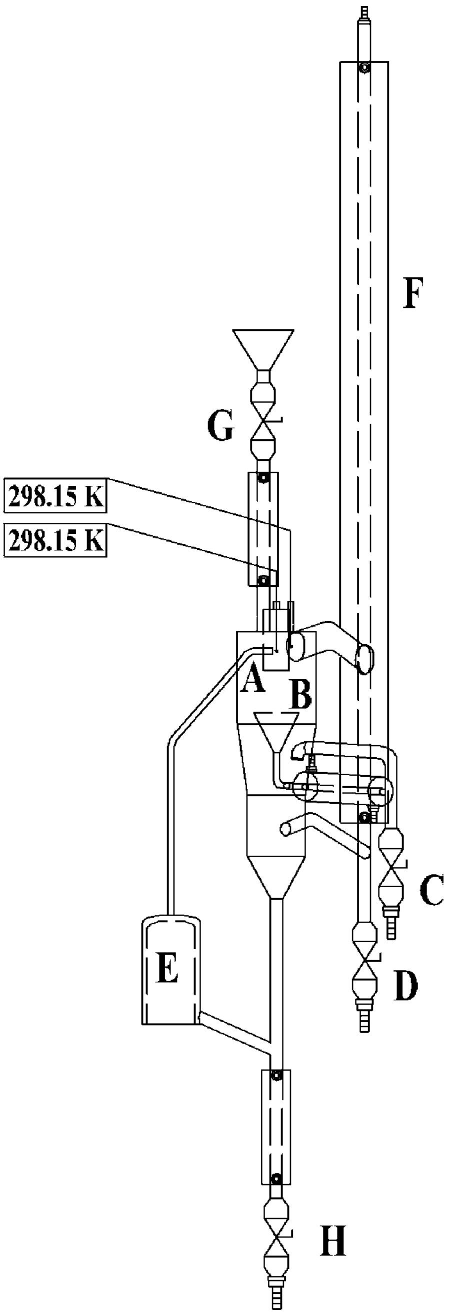

Figure 1. Schematic diagram of the equilibrium recirculation still used for VLE measurements: A, equilibrium chamber; B, liquid funnel; C, liquid sampler; D, vapor sampler; E, boiling flask; F, cooler; G, inlet valve; H, outlet valve.

A Kyoto Electronics DA-300 vibrating tube density meter, with an uncertainty of ± 0.1 $\text{kg}\cdot\text{m}^{-3}$ was used to measure the composition of both phases in equilibrium. Ester + alcohol mixtures were determined with this apparatus, proceeding as in previous works.[12,13] Such composition as ester mole fraction x_1 vs density pairs (Table 2) were correlated to a polynomial function by means of the Nelder−Mead procedure.[14] To check the error in the density measurements, the data shown in Table 2 were verified with the literature data.[15–17] The results of the relative deviations on the densities measured in this work are shown in Table 2. The uncertainty in the composition of both phases is estimated to be better than 0.002 mole fraction unit.

Results and Treatment

The experimental data T, x_1, and y_1 of ethyl acetate + methanol at (0.1, 0.5, and 0.7) MPa obtained with the new still are shown in Table 3. The liquid-phase activity coefficients, γ_i, are also included in Table 3 for each of the systems studied and have been calculated by using the following equation:

Table 2. Densities and Excess Volumes, v^{E}, for the Binary System Ethyl Acetate + Methanol at 298.15 K

x_1	ρ / $\text{kg}\cdot\text{m}^{-3}$	$10^9\cdot v^{E}$ / $\text{m}^3\cdot\text{mol}^{-1}$	$e = 100\cdot\lvert(\rho_{\text{exptl}} - \rho_{\text{lit.}})/\rho_{\text{exptl}}\rvert$ ref 15	ref 16	ref 17
0.0000	786.8	0.0	0.03	0.01	0.06
0.0513	799.6	−18.6	0.00	0.02	0.03
0.1009	810.4	−33.4	0.03	0.02	0.02
0.1537	820.5	−48.7	0.05	0.02	0.02
0.2028	828.9	−65.5	0.06	0.02	0.01
0.2535	836.5	−72.5	0.07	0.01	0.02
0.3517	849.2	−88.1	0.05	0.01	0.00
0.4527	859.9	−95.3	0.02	0.02	0.02
0.4983	864.1	−95.7	0.00	0.03	0.03
0.6042	872.7	−93.5	0.01	0.03	0.04
0.7012	879.3	−78.2	0.01	0.01	0.04
0.7500	882.3	−72.4	0.02	0.00	0.03
0.8036	885.3	−58.5	0.04	0.02	0.02
0.8500	887.7	−43.8	0.05	0.03	0.01
0.8964	890.0	−32.7	0.05	0.03	0.01
0.9391	892.0	−22.8	0.04	0.02	0.01
1.0000	894.6	0.0	0.00	0.00	0.03

$$\gamma_i = \frac{\varphi_i y_i p}{x_i \varphi_i^{\circ} p_i^{\circ}} \exp\left[\frac{(p_i^{\circ} - p)v_i^{\mathrm{L}}}{RT}\right] \qquad (1)$$

The fugacity coefficients, φ_i, were determined from the virial equation of state truncated at the second term, as follows:

$$\varphi_i = \exp\left[\frac{p}{RT}\left(2\sum_j y_i B_{ij} - \sum_i \sum_j y_i y_j B_{ij}\right)\right] \qquad (2)$$

The second virial coefficients, B_{ij}, for the pure components and mixtures were calculated by the Hayden and O’Connell method.[18] The liquid molar volumes of pure compounds, v_i^{L} were estimated from the equation of Yen and Woods.[19] The results for the activity coefficients obtained in this work present a moderate deviation from ideal values, perhaps as a result of molecular association by hydrogen bonds.

The thermodynamic consistency test of Van Ness et al.[5] was used to verify the VLE experimental data introduced in this paper. The computer program proposed by Fredenslund[6] was applied. The Antoine constants previously determined[11] were applied.

As in previous studies,[4,12] the experimental data from every system were correlated to a fitting function (FF) with a polynomial structure:

$$\mathrm{FF} = \sum_{k=0} A_k Z_{\mathrm{T}}^{\,k} \qquad (3)$$

In eq 3 the Ocón active fraction,[20,21] Z_{T}, is given by the following equation:

$$Z_{\mathrm{T}} = \frac{x_1}{x_1 + R_{\mathrm{T}}(1 - x_1)} \qquad (4)$$

The Ocón parameter R_{T} in eq 4 has been established[20,21] to be pressure and temperature dependent, as it is related to the

Table 3. Experimental Data of VLE

T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
Ethyl Acetate (1) + Methanol (2) at 0.1 MPa											
337.85	0.000	0.000		1.000	0.000	336.25	0.478	0.379	1.254	1.274	0.235
337.65	0.013	0.026	3.024	0.999	0.014	336.45	0.513	0.397	1.215	1.316	0.234
337.35	0.026	0.049	2.879	1.000	0.028	336.75	0.550	0.416	1.175	1.363	0.228
336.85	0.067	0.101	2.343	1.007	0.063	337.05	0.591	0.436	1.134	1.432	0.221
336.65	0.081	0.117	2.260	1.012	0.077	337.95	0.667	0.478	1.066	1.572	0.193
336.35	0.111	0.149	2.122	1.020	0.101	338.45	0.701	0.501	1.045	1.641	0.179
335.95	0.166	0.201	1.940	1.038	0.141	339.65	0.773	0.564	1.022	1.804	0.151
335.85	0.189	0.220	1.872	1.046	0.155	342.75	0.872	0.684	0.987	2.062	0.081
335.65	0.246	0.260	1.711	1.076	0.187	343.95	0.912	0.755	1.000	2.224	0.070
335.65	0.260	0.267	1.662	1.086	0.193	344.85	0.932	0.793	0.997	2.352	0.055
335.65	0.288	0.281	1.579	1.107	0.204	345.95	0.952	0.832	0.987	2.597	0.033
335.75	0.327	0.304	1.499	1.129	0.214	347.05	0.972	0.892	0.999	2.749	0.027
335.95	0.397	0.336	1.354	1.193	0.227	350.15	1.000	1.000	1.000		0.000
336.15	0.446	0.361	1.285	1.240	0.231						
Ethyl Acetate (1) + Methanol (2) at 0.5 MPa											
385.35	0.000	0.000		1.000	0.000	384.15	0.240	0.208	1.596	1.088	0.176
384.85	0.022	0.034	2.821	1.009	0.032	384.35	0.289	0.234	1.482	1.119	0.194
384.75	0.029	0.044	2.775	1.009	0.038	384.65	0.344	0.261	1.377	1.160	0.207
384.65	0.039	0.055	2.583	1.011	0.047	384.85	0.370	0.275	1.341	1.178	0.212
384.55	0.045	0.063	2.570	1.011	0.053	385.05	0.388	0.289	1.336	1.183	0.215
384.45	0.058	0.077	2.442	1.013	0.064	385.85	0.467	0.328	1.232	1.255	0.219
384.35	0.072	0.092	2.354	1.015	0.075	386.35	0.501	0.344	1.189	1.290	0.214
384.25	0.092	0.112	2.247	1.017	0.090	387.75	0.591	0.388	1.095	1.412	0.195
384.15	0.113	0.130	2.127	1.023	0.106	388.35	0.620	0.406	1.075	1.451	0.186
384.05	0.144	0.155	1.993	1.033	0.127	392.35	0.773	0.538	1.030	1.693	0.142
384.05	0.161	0.166	1.908	1.041	0.137	396.65	0.872	0.667	1.017	1.930	0.099
384.05	0.190	0.178	1.733	1.062	0.153	400.65	0.932	0.773	1.002	2.232	0.056
384.05	0.207	0.188	1.679	1.072	0.162	407.45	0.991	0.952	0.991	3.009	0.001
384.05	0.221	0.197	1.647	1.079	0.170	408.75	1.000	1.000	1.000		0.000
Ethyl Acetate (1) + Methanol (2) at 0.7 MPa											
397.55	0.000	0.000		1.000	0.000	397.05	0.312	0.234	1.398	1.130	0.189
396.75	0.035	0.047	2.552	1.008	0.041	397.65	0.370	0.261	1.295	1.172	0.195
396.65	0.046	0.060	2.482	1.009	0.050	398.25	0.416	0.282	1.225	1.209	0.195
396.55	0.058	0.072	2.366	1.011	0.061	398.55	0.446	0.297	1.194	1.238	0.197
396.35	0.077	0.092	2.285	1.016	0.078	399.65	0.513	0.336	1.142	1.293	0.193
396.25	0.099	0.112	2.166	1.020	0.095	401.25	0.591	0.378	1.072	1.383	0.174
396.25	0.112	0.122	2.086	1.024	0.103	403.35	0.667	0.436	1.041	1.460	0.153
396.25	0.128	0.133	1.987	1.030	0.113	405.15	0.718	0.478	1.016	1.525	0.130
396.25	0.144	0.144	1.911	1.036	0.123	406.35	0.754	0.513	1.009	1.583	0.120
396.25	0.161	0.155	1.839	1.043	0.134	408.85	0.812	0.577	0.994	1.692	0.094
396.25	0.178	0.166	1.780	1.051	0.144	418.45	0.952	0.832	0.988	2.101	0.024
396.45	0.227	0.190	1.587	1.080	0.164	420.85	0.972	0.892	0.986	2.193	0.009
396.65	0.254	0.208	1.544	1.089	0.174	423.95	1.000	1.000	1.000		0.000
396.85	0.289	0.227	1.472	1.109	0.185						

Table 4. Fitting Coefficients for Eq 3 and Standard Deviations[a]

FF	R_T	A_0	A_1	A_2	A_3	
Ethyl Acetate (1) + Methanol (2) at 0.1 MPa						
$(y_1 - x_1)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.779	0.690	−4.904	6.849	−5.688	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{bp1} - (1 - x_1) T_{bp2}][x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	4.351	−27.231	−5.747	−68.043		$\sigma(T)/K = 0.17$
$[T - y_1 T_{bp1} - (1 - y_1) T_{bp2}][y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.095	−18.321	−90.275	249.042	−166.225	$\sigma(T)/K = 0.09$
$(G^E/RT)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.251	1.060	−0.294			$\sigma(G^E/RT) < 0.01$
Ethyl Acetate (1) + Methanol (2) at 0.5 MPa						
$(y_1 - x_1)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.507	0.495	−4.919	7.825	−6.599	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{bp1} - (1 - x_1) T_{bp2}][x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	2.484	−38.458	15.243	−103.096		$\sigma(T)/K = 0.13$
$[T - y_1 T_{bp1} - (1 - y_1) T_{bp2}][y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	0.248	−31.044	−45.416	66.927		$\sigma(T)/K = 0.15$
$(G^E/RT)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	0.156	1.333	−0.550			$\sigma(G^E/RT) < 0.01$
Ethyl Acetate (1) + Methanol (2) at 0.7 MPa						
$(y_1 - x_1)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.646	0.404	−4.901	7.666	−6.400	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{bp1} - (1 - x_1) T_{bp2}][x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	1.339	−45.129	38.29	−86.663		$\sigma(T)/K = 0.15$
$[T - y_1 T_{bp1} - (1 - y_1) T_{bp2}][y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	0.205	−33.446	−62.219	94.75		$\sigma(T)/K = 0.11$
$(G^E/RT)[x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k Z_T^k$	0.569	1.148	−0.602			$\sigma(G^E/RT) < 0.01$

[a] The standard deviation $\sigma(F) = [\sum_1^n (F_{exptl} - F_{calcd})^2/(n - m)]^{1/2}$, with F being $y_1 - x_1$, T/K, or G^E/RT, n the number of data, and m the number of parameters.

properties of the pure compounds. The results of the experimental data treatment including the different FF values obtained from the Nelder and Mead[14] procedure, considering the summation of square deviations by minimization, are shown in Table 4. A similar mathematical treatment on the literature data[2,3] was made with FF being $y_1 - x_1$. These FF values, together with the experimental data of this paper and its correlations (Table 4), were plotted (Figure 2).

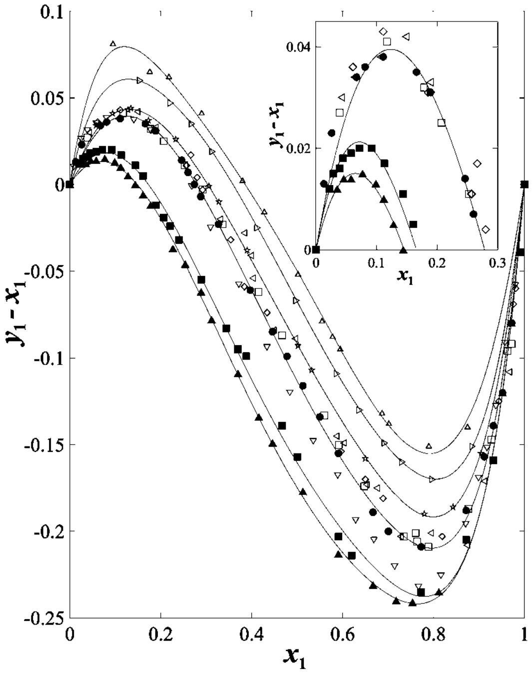

Figure 2. Experimental points and fitting curves for the mixture ethyl acetate (1) + methanol (2): ●, at 0.1 MPa; ■, at 0.5 MPa; ▲, at 0.7 MPa. Literature[2,3] values for ethyl acetate (1) + methanol (2) with fitting curves: △, right-pointing triangle, and ☆, at (13.33, 26.66, and 66.66) kPa by Park et al., 1973; left-pointing triangle, at 97.33 kPa by Nakanishi et al., 1967; ◇, at 101.33 kPa by Akita and Yoshida, 1963; □, at 101.33 kPa by Nagata, 1962; ▽, at 141.3 kPa by Blanco and Ortega, 1998.

The experimental data obtained from this work show an evolution with pressure that agrees with data[2] obtained by Park et al. at (13.33, 26.66, and 66.66) kPa and by Nagata at 101.33 kPa. Particularly, the data presented in this paper at 0.1 MPa show good agreement with those presented by Nagata[2] at 101.33 kPa and are quite similar to those provided by Akida and Yoshida[2] at 101.3 kPa. The data presented by Nagata[2] show an average error $\bar{e}(y_1 - x_1)$ equal to 10 % (see Table 5) with respect to the data obtained in this work when considering $y_1 - x_1$ in the FF shown in Table 4. On the contrary, those obtained by Blanco and Ortega[3] at 141.3 kPa present some differences in their evolutionary development when compared with the data presented in this paper. These differences appear mainly between 0.6 and 0.8 in the ester mole fraction, so they can be attributed to a possible systematic error in the indicated range of the mole fraction of ester.

The inset included in Figure 2 represents data corresponding to the liquid mole fraction within the range of 0.0 to 0.3. It is observed from this diagram that the differences mentioned are small in this composition range. Moreover, it should be considered that the experimental error of all data has been magnified in the diagram for the indicated composition interval.

By considering $y_1 - x_1$ as FF, as shown in Table 4, the mean deviations $\delta(y_1 - x_1)$ (see Table 5) of the data presented in the inset included in Figure 2 are 0.38 % from the Akida and Yoshida[2] data 0.32 % from the Nakanishi et al.[2] data, 0.22 % from the Nagata[2] data, and 0.21 % from the data from this work, when all these data are compared to the FF taken as the reference. Therefore, the data presented in this paper fit well with those obtained by Nagata[2] at 101.33 kPa. For these reasons, it can be pointed out that the ebulliometer introduced in this work seems to be reliable for VLE determinations under moderate pressures.

The ethyl acetate + methanol system presents an azeotrope that has been widely studied and mentioned in the literature.[1] Therefore, it was decided to analyze the evolution of this azeotrope with pressure modifications.

The azeotropic data of the ethyl acetate + methanol system obtained in this study are shown in Table 5 and have been illustrated together with the literature data[1–3] in Figure 3. From the representation it is observed that the distribution of the experimental azeotropic data can be interrelated in the previously indicated way.[11] This connection can be better observed in the inset included in Figures 3 and 4. Figure 4 shows good agreement between the evolution of the T, p, and x_1 azeotropic data found in the literature and those obtained in this study at (0.1, 0.5, and 0.7) MPa. In the inset of Figure 4, the relation T vs x_1 has been magnified to verify the azeotropic data obtained in this work at 0.1 MPa, and it is observed that the azeotrope

Table 5. Mean Deviations and Average Errors in the Prediction of VLE Data. Experimental and Predicted Azeotropic Data[a]

	UNIFAC-1987,[22] $CH_3OH/COOC$	UNIFAC-1991,[23] $CH_3OH/CCOO$	UNIFAC-1993,[24] $CH_3OH/CCOO$	ASOG-1979,[25] OH/COO
		Ethyl Acetate (1) + Methanol (2) at 0.1 MPa		
$\delta(y_1)$	0.01	0.01	0.01	0.01
$\bar{e}(\gamma_1)$/%	2.59	3.12	2.57	4.00
$\delta(T)$/K	0.26	0.57	0.21	0.82
		Azeotropic Data		
$x_{1\mathrm{az,exptl}} = 0.282$	0.304	0.327	0.309	0.288
$T_{\mathrm{az,exptl}}/\mathrm{K} = 335.65$	335.64	335.36	335.92	334.83
		Ethyl Acetate (1) + Methanol (2) at 0.5 MPa		
$\delta(y_1)$	0.01	0.01	0.01	0.01
$\bar{e}(\gamma_1)$/%	7.05	3.86	6.73	3.52
$\delta(T)$/K	2.27	0.60	2.10	1.18
		Azeotropic Data		
$x_{1\mathrm{az,exptl}} = 0.172$	0.102	0.187	0.094	0.147
$T_{\mathrm{az,exptl}}/\mathrm{K} = 384.05$	385.78	384.67	385.87	384.58
		Ethyl Acetate (1) + Methanol (2) at 0.7 MPa		
$\delta(y_1)$	0.02	0.01	0.02	0.01
$\bar{e}(\gamma_1)$/%	7.04	3.48	6.69	3.54
$\delta(T)$/K	2.44	1.01	2.08	1.12
		Azeotropic Data		
$x_{1\mathrm{az,exptl}} = 0.144$	0.061	0.153	0.060	0.115
$T_{\mathrm{az,exptl}}/\mathrm{K} = 396.25$	397.91	396.80	397.96	396.86

[a] The mean deviation $\delta(F) = (1/n)\sum_1^n |F_{\mathrm{exptl}} - F_{\mathrm{calcd}}|$, and the average error $\bar{e}(F) = (100/n)\sum_1^n(|F_{\mathrm{exptl}} - F_{\mathrm{calcd}}|)/(F_{\mathrm{exptl}})$ with F being y_1, γ_1, or T/K.

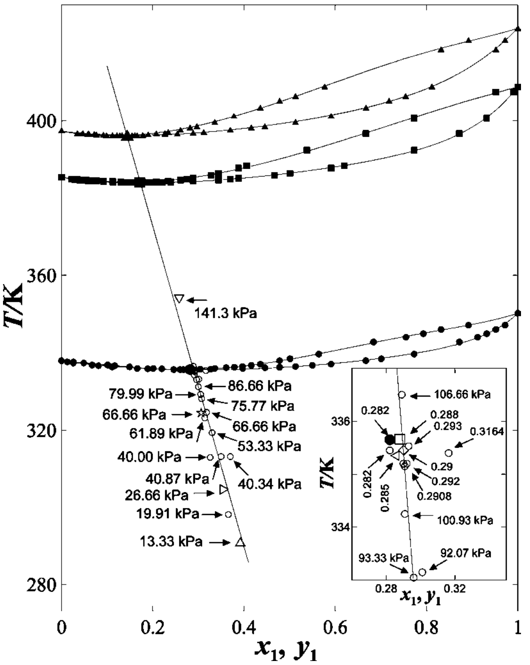

Figure 3. Experimental data T, x_1, and y_1 and fitting curves for the mixture ethyl acetate (1) + methanol (2): ●, at 0.1 MPa; ■, at 0.5 MPa; ▲, at 0.7 MPa. Azeotropic data[3] for ethyl acetate (1) + methanol (2) at 141.3 kPa and other different pressures with fitting lines (T/K = 455.59 − 414.35·x_1):[1,2] △, right-pointing triangle, and ☆, by Park et al., 1973; left-pointing triangle, by Nakanishi et al., 1967; ◇, by Akita and Yoshida, 1963; □, by Nagata, 1962.

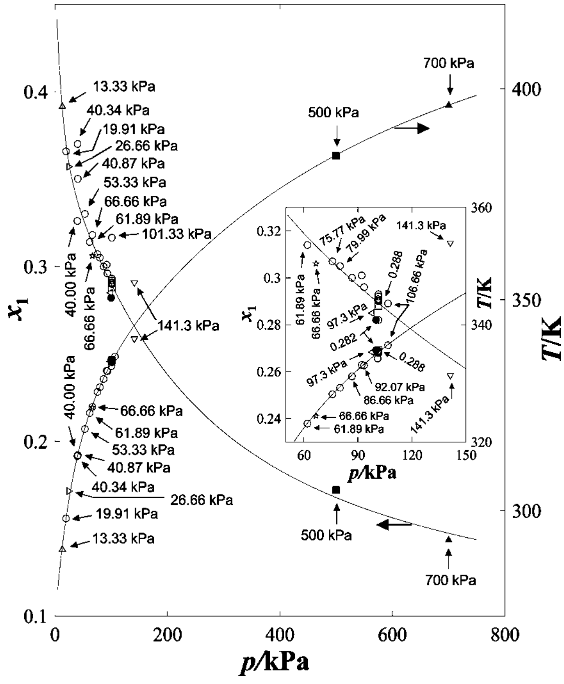

Figure 4. Representation of the azeotropic data. Experimental points T, p, and x_1 and fitting curves for the mixture ethyl acetate (1) + methanol (2): ●, at 0.1 MPa; ■, at 0.5 MPa; ▲, at 0.7 MPa. Bibliographic data[3] at 141.3 kPa and other different pressures:[1,2] △, right-pointing triangle, and ☆, by Park et al., 1973; left-pointing triangle, by Nakanishi et al., 1967; ◇, by Akita and Yoshida, 1963; □, by Nagata, 1962.

composition obtained at 0.1 MPa in this paper is well correlated with the bibliographic data. The azeotropic data of this paper at (0.1, 0.5, and 0.7) MPa also return a good correlation with the literature data, when p vs x_1 and p vs T are considered, as shown in Figure 4.

Finally, the thermodynamically consistent data shown in Table 3 were used to verify the predictive behavior of the UNIFAC[22–24] and ASOG[25] models. Table 5 shows the results obtained from the comparison between the experimental data provided in this paper and the results obtained with the UNIFAC and ASOG models for the same isobaric systems. The results in Table 5 show that the conventional version of the UNIFAC[23] model returns a better prediction of the experimental data than the ASOG[25] model, probably because the ASOG model does not contain a specific group pair parameter for methanol.

The three different versions of the UNIFAC model return similar deviations in the prediction of the vapor phase, and although the mean error in the prediction of the liquid-phase activity coefficient is less in the conventional version of the UNIFAC[23] model, all versions give a higher mean error with a pressure increase. However, predictions obtained with the ASOG model do not seem to be influenced by a pressure increase.

Referring to the prediction of the azeotrope, the ASOG model fails in the estimation of this point with a pressure increase, maybe for the reason previously described. On the other hand, the three versions of the UNIFAC model return a worse prediction than the ASOG model for the azeotropic point at 0.1 MPa, the ASOG model providing results similar to those found in the literature[1] at this pressure. Nevertheless, an increase in the system pressure results in a less reliable prediction, the conventional version of the UNIFAC[23] model once again being the one that most approximates the experimental value.

Conclusions

The VLE data for the ethyl acetate + methanol system at (0.1, 0.5, and 0.7) MPa have been determined. The system presents an azeotrope that moves toward compositions richer in alcohol when the pressure is increased.

The experimental data obtained in this work have been contrasted with the literature data to evaluate the behavior of the new equilibrium still. The evolution of the azeotrope with pressure and the comparison between the experimental data of this work and those found in the literature have also been analyzed. The results show that the main modification made in the ebulliometer may be reliable, as it facilitates the vapor-phase circulation as a consequence of an increase in the diameter of the tube that connects the body of the still with the cooler.

The UNIFAC and ASOG models have been used to estimate the vapor-phase compositions in the binary system. The predictions made by the ASOG model are acceptable. The conventional version of the UNIFAC model returns a good prediction of the data in this work. However, globally all models lose prediction quality with a pressure increase.

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