

# VAPOR-LIQUID EQUILIBRIUM MEASUREMENTS FOR THE BINARY SYSTEM METHYL ACETATE+ETHANOL AT 0.3 AND 0.7 MPa

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**Abstract** - This paper reports experimental data of the isobaric vapor-liquid equilibria (VLE) for the mixture methyl acetate + ethanol at 0.3 and 0.7 MPa, determined using a copper still ebulliometer. The activity coefficients obtained from the experimental data were correlated by using different thermodynamic mathematical models. All the binary systems show a positive consistency when subjected to the point-to-point test of Van Ness. The prediction of VLE data obtained with the UNIFAC and ASOG methods has been verified with experimental data.

**Keywords:** VLE isobaric data; Activity coefficient; Methyl ester; Ethanol.

## INTRODUCTION

Previous papers (Ortega and Susial, 1990; Ortega and Susial, 1993) have reported VLE data for methyl esters and alkanols at different pressures. The methyl acetate + ethanol binary system was reported at isothermal conditions of 323.15 K, 333.15 K, 343.15 K and 353.15 K by Perelygin and Volkov (1970) (see Gmehling and Onken, 1986). This system has also been reported at isobaric conditions by Perelygin and Volkov (1970) and Nishi (1972) (see Gmehling and Onken, 1986) and by Ortega et al. (1990) at 101.3 kPa, while Ortega and Susial (1990) have published data for the methyl acetate + ethanol system at 114.66 kPa and 127.99 kPa. In the present work, VLE measurements of methyl acetate + ethanol at 0.1, 0.3 and 0.7 MPa obtained with a copper still are presented.

The experimental data of this paper at 0.1, 0.3 and 0.7 MPa were verified thermodynamically using the point-to-point test of Van Ness (Van Ness et al., 1973) and by applying the procedure of Barker

(Barker, 1953) implemented in the computer program of Fredenslund et al. (1977).

All data included in this work have passed the consistency test according to the Fredenslund criteria (Fredenslund et al., 1977). These data were used to check the reliability of UNIFAC (Fredenslund et al., 1977; Fredenslund et al., 1975; Gmehling et al., 1993; Larsen et al., 1987) and ASOG (Kojima and Tochigi, 1979) group contribution models in order to expand the applicability of these predictive models.

## EXPERIMENTAL

### Materials and Apparatus

In this paper, ethanol and methyl acetate, both from Panreac Química S.A., were used as received. The purity and the experimental values of density, refractive index and normal boiling point of these products are shown in Table 1. The normal boiling

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point at 0.1 MPa was determined with the copper ebulliometer. 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 model 315RS Abbe refractometer with an uncertainty of  $\pm 0.0002$  units were used for density and refractive index determinations, respectively. The measures of the pure substance properties are compared with literature values.

### VLE Equipment and Procedure

A still ebulliometer developed and built in copper, with all its different pieces assembled with silver-weldings is presented in Figure 1. The still has a configuration similar to the apparatus made of glass by de Afonso et al. (1983). The equipment has a double-walled inverted vessel where a boiling mixture of liquid and vapor is generated by an electric heater. This boiling mixture rises in a tube that works like a Cottrell pump. The Cottrell tube is connected to a vessel that acts like an equilibrium

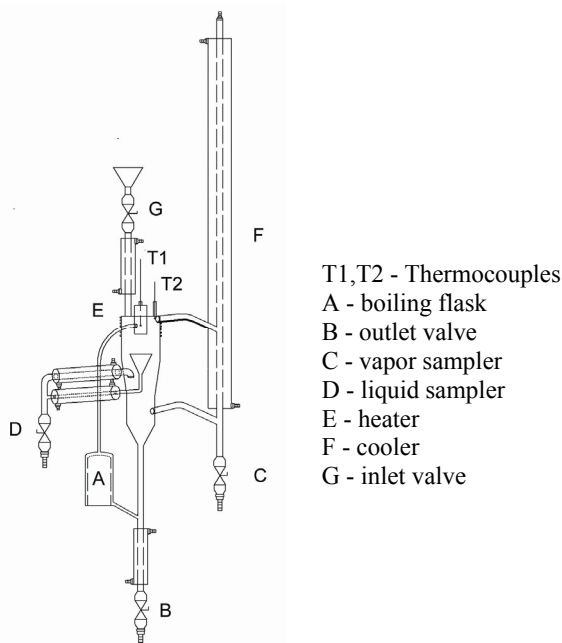
chamber. The liquid and vapor phases are carried out on separate paths from this equilibrium chamber. A tube connected to a funnel collects and circulates the liquid phase in the equipment. This tube has a lateral path that ends in a valve. The vapor phase is carried out to the cooler. The cooler has a coaxial tube that returns the condensate to the still and it has a lateral path with a finishing valve. Therefore, both phases are refluxed.

The equilibrium equipment has been designed to work at moderate pressures. Therefore, slight modifications were made to this copper still in order to ease sampling of both phases at the working pressures (see Figure 1). Some airtight outer vessels must be used. In addition, it was necessary to prepare J-type thermocouples with a ring silver-soldered to both its cover and the ebulliometer. Thermocouples of Thermocoax (range 1073 K) with 0.1% precision were used for the temperature measurements. The working pressure was measured with a NuovaFima manometer with a range from 0 to 1.0 MPa and 1% precision.

**Table 1: Physical properties of pure compounds at atmospheric pressure**

	purity/mass%	$T_{bp}/\text{K}$		$\rho (298.15 \text{ K})/(\text{kg}\cdot\text{m}^{-3})$		$n_D (298.15 \text{ K})$	
		exp	lit	exp	lit	exp	lit
<b>ethanol</b>	puriss. p.a. > 99.9	351.35	351.443 (A) 351.45 (B) 351.44 (C)	785.2	784.93 (A) 785.2 (B)	1.3600	1.35941 (A) 1.3594 (B,C)
<b>methyl acetate</b>	puriss. > 99	330.05	330.018 (A) 329.95 (B) 330.09 (C)	927.3	927.90 (A) 927.30 (B)	1.3590	1.3589 (A,C) 1.3587 (B)

(A) Riddick et al., 1986; (B) Nagata et al., 1976; (C) Yaws, 2003



**Figure 1: Equilibrium recirculation still used for the VLE measurements.**

The copper still described in this paper showed good agreement with the ebulliometer previously used, the operation procedure also being similar (de Afonso et al., 1983; Ortega et al., 1990; Susial et al., 1989). The procedure differs in the residence time of the mixture inside the ebulliometer and the sampling method. The ebulliometer has a 400 cm<sup>3</sup> mixture capacity, the reason why a 90 min recirculation time is necessary for the mixture. This was evaluated by a previous test of operation time vs. mole fraction of both phases (de Afonso et al., 1983). Samples of the liquid and vapor phases were removed from the airtight vessels with syringes and the compositions of the equilibrium phases were obtained by densimetry at 298.15 K, using a composition-density standard curve prepared for the mixture studied in this paper,

$$\rho = 785.2 + 181.1 \cdot x_1 - 51.5 \cdot x_1^2 + 12.5 \cdot x_1^3 \quad (1)$$

As in previous works (Ortega et al., 1990; Ortega and Susial, 1990; Susial et al., 1989), the values of the data pairs composition-density were correlated by using the Nelder and Mead (1967) procedure. Therefore, considering the different apparatus used, the estimated accuracy in the determination of both the liquid and vapor phase was better than  $\pm 0.002$  units of mole fraction.

## RESULTS AND TREATMENT

With the copper still ebulliometer, the experimental T-x<sub>1</sub>-y<sub>1</sub> data (Table 2) for methyl acetate+ethanol were obtained at 0.1, 0.3 and 0.7 MPa. Also included in Table 2 are the activity coefficients of the liquid phase for each system, calculated by using the following equation:

$$\gamma_i = \frac{\varphi_i y_i p}{x_i \varphi_i^o p_i^o} \exp \left[ \frac{(p_i^o - p) v_i^L}{RT} \right] \quad (2)$$

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

$$\varphi_i = \exp \left[ \frac{p}{RT} \left( 2 \sum_j y_i B_{ij} - \sum_i \sum_j y_i y_j B_{ij} \right) \right] \quad (3)$$

The second virial coefficients were calculated by the Hayden and O'Connell (1975) method. The liquid molar volumes of the pure compounds were estimated by the equation of Yen and Woods (1966).

VLE experimental data in this paper were verified by using the thermodynamic consistency test of Van Ness et al. (1973). The proposed computer program

of Fredenslund et al., (1977) was applied using physical properties from the literature (Fredenslund et al., 1977; Riddick et al., 1986; Yaws, 2003) and the correlations of the vapor pressures from a previous paper (Susial et al., 2010).

All the systems included in this work passed the point-to-point test because they have an average deviation of  $\delta(y_1) < 0.01$  (Fredenslund et al., 1977). The experimental data (Table 2) were correlated by using the calculated activity coefficients in the form of  $G^E/RT$  vs. x<sub>1</sub> with the Redlich-Kister, Van Laar, Margüles, Wilson, NRTL and UNIQUAC models. To calculate the constants of each model, a non-linear regression procedure was employed (Nelder and Mead, 1967), considering a minimization of the objective function (OF) (Holmes and Winkle, 1970; Postigo et al., 2009):

$$OF = \sum_1^n (\gamma_1^{\text{exp}} - \gamma_1^{\text{calc}})^2 + \sum_1^n (\gamma_2^{\text{exp}} - \gamma_2^{\text{calc}})^2 \quad (4)$$

The results of the correlations with thermodynamic mathematical models are presented in Table 3. The models give good fit to the experimental data and show acceptable mean deviations for the prediction of the vapor phase composition.

In addition, as in previous papers (Ortega et al., 1990; Ortega and Susial, 1990; Susial et al., 1989), the experimental data of each system were correlated to a fitting function (FF) with a polynomial form (see Table 4). Results of the experimental data treatment with the different FF, using the Nelder and Mead (1967) procedure to minimize the summation of the square of the deviations, are shown in Table 4.

A mathematical treatment similar to literature data (Ortega et al., 1990; Ortega and Susial, 1990) was made for the parameter of interest (y<sub>1</sub>-x<sub>1</sub>) or T. The fits of the experimental data of this paper (Table 4) are plotted in Figure 2 and 3, respectively).

The examination of the equilibrium data obtained in this work shows a good variation with pressure (see Figure 2) and an appreciable relation can be also observed between our systems at 0.1, 0.3 and 0.7 MPa and literature data at 127.99 kPa (Ortega and Susial, 1990). In Figure 2, some differences are seen between data from this study at 0.1 MPa and the data from literature at 101.32 kPa (Ortega et al., 1990), but these differences are also present between the data obtained by Ortega et al. (1990) at 101.32 kPa and literature data at 127.99 kPa (Ortega and Susial, 1990). The above mentioned relationship between the data from this work and literature data at 127.99 kPa (Ortega and Susial, 1990) is shown in the inset in Figure 3. On the other hand, the differences observed in Figure 3 between data from this paper at 0.1 MPa and literature data at 101.32 kPa (Ortega et al., 1990) may be due to the greater uncertainty in the determination of temperature in this work.

**Table 2: VLE experimental data and calculated values of activity coefficients of the liquid phase**

T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
<b>methyl acetate (1) + ethanol (2) at 0.1 MPa</b>				
351.35	0.000	0.000		1.000
349.05	0.038	0.127	1.789	0.979
345.95	0.079	0.254	1.892	0.991
341.35	0.168	0.418	1.691	1.037
339.75	0.211	0.496	1.681	1.014
337.25	0.291	0.577	1.538	1.056
336.75	0.335	0.602	1.417	1.083
336.05	0.372	0.635	1.377	1.084
334.45	0.441	0.686	1.323	1.125
333.75	0.488	0.703	1.254	1.199
332.95	0.569	0.738	1.160	1.302
331.95	0.643	0.773	1.112	1.425
331.55	0.686	0.791	1.081	1.519
331.15	0.720	0.809	1.068	1.586
330.45	0.855	0.874	0.995	2.085
330.25	0.874	0.892	1.000	2.075
330.15	0.902	0.911	0.993	2.208
330.15	0.911	0.921	0.994	2.158
329.95	0.959	0.959	0.990	2.453
330.05	1.000	1.000	1.000	
<b>methyl acetate (1) + ethanol (2) at 0.3 MPa</b>				
382.05	0.000	0.000		1.000
380.65	0.018	0.064	2.387	0.985
378.65	0.058	0.162	1.972	0.980
375.15	0.141	0.313	1.715	0.989
374.15	0.168	0.350	1.652	0.999
372.35	0.225	0.418	1.544	1.020
371.45	0.254	0.449	1.504	1.034
370.45	0.291	0.481	1.444	1.061
370.35	0.320	0.512	1.402	1.043
367.75	0.465	0.610	1.233	1.159
367.45	0.496	0.635	1.213	1.164
366.95	0.536	0.652	1.168	1.226
365.65	0.627	0.703	1.115	1.363
365.05	0.703	0.756	1.088	1.436
364.15	0.892	0.892	1.037	1.802
364.45	0.950	0.940	1.018	2.138
364.55	0.979	0.969	1.015	2.619
365.25	1.000	1.000	1.000	
<b>methyl acetate (1) + ethanol (2) at 0.7 MPa</b>				
410.75	0.000	0.000		1.000
410.05	0.031	0.052	1.328	0.992
409.05	0.045	0.092	1.653	0.990
407.65	0.092	0.168	1.521	0.991
407.15	0.113	0.204	1.520	0.983
406.35	0.141	0.247	1.500	0.981
404.55	0.197	0.312	1.410	1.007
404.05	0.232	0.350	1.358	1.009
402.95	0.298	0.410	1.269	1.032
401.65	0.388	0.481	1.177	1.080
399.95	0.504	0.577	1.129	1.138
399.35	0.561	0.618	1.101	1.181
398.25	0.686	0.703	1.050	1.324
398.25	0.809	0.791	1.002	1.531
398.65	0.911	0.892	0.994	1.677
399.15	0.989	0.979	0.994	2.600
399.35	1.000	1.000	1.000	

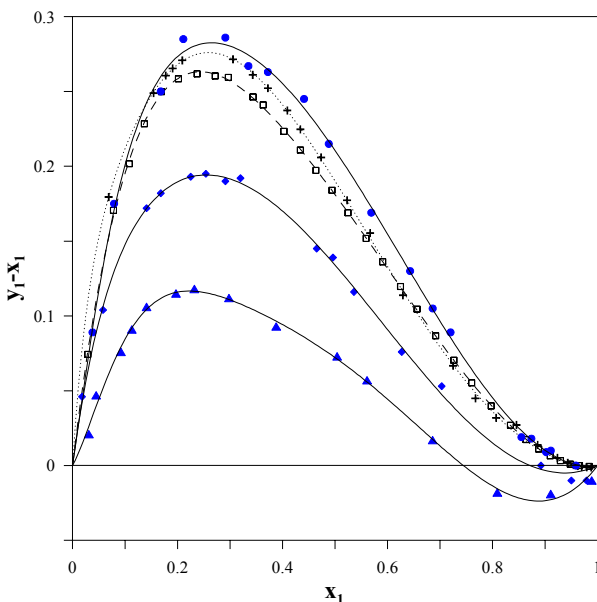
**Table 3: Correlation parameters of  $G^E/RT$  vs.  $x_1$ , mean deviations and standard deviations**

Model	parameters		$\delta(y_1)$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(G^E/RT)$
<b>methyl acetate (1) + ethanol (2) at 0.1 MPa</b>						
Redlich-Kister	$A_0 = 0.843$	$A_1 = 0.160$	0.007	0.05	0.05	0.01
Van Laar	$A_{12} = 0.712$	$A_{21} = 1.019$	0.007	0.06	0.05	0.01
Margules	$A_{12} = 0.671$	$A_{21} = 0.896$	0.008	0.04	0.12	0.01
Wilson	$\Delta\lambda_{12} = 1253.4 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta\lambda_{21} = 1605.0 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.006	0.05	0.05	0.01
NRTL( $\alpha = 0.47$ )	$\Delta g_{12} = 2489.7 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta g_{21} = 366.6 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.007	0.05	0.05	0.01
UNIQUAC ( $Z = 10$ )	$\Delta u_{12} = 2316.8 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta u_{21} = -744.0 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.007	0.05	0.05	0.01
<b>methyl acetate (1) + ethanol (2) at 0.3 MPa</b>						
Redlich-Kister	$A_0 = 0.806$	$A_1 = 0.048$	0.005	0.09	0.011	0.02
Van Laar	$A_{12} = 0.751$	$A_{21} = 0.865$	0.005	0.10	0.10	0.02
Margules	$A_{12} = 0.820$	$A_{21} = 0.667$	0.006	0.06	0.21	0.02
Wilson	$\Delta\lambda_{12} = 1927.9 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta\lambda_{21} = 880.9 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.005	0.09	0.10	0.02
NRTL( $\alpha = 0.47$ )	$\Delta g_{12} = 1800.2 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta g_{21} = 1084.1 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.006	0.09	0.10	0.03
UNIQUAC ( $Z = 10$ )	$\Delta u_{12} = 1836.6 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta u_{21} = -419.8 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.005	0.10	0.10	0.02
<b>methyl acetate (1) + ethanol (2) at 0.7 MPa</b>						
Redlich-Kister	$A_0 = 0.607$	$A_1 = 0.205$	0.012	0.09	0.12	0.02
Van Laar	$A_{12} = 0.426$	$A_{21} = 0.899$	0.012	0.09	0.09	0.02
Margules	$A_{12} = 0.441$	$A_{21} = 0.570$	0.009	0.08	0.24	0.01
Wilson	$\Delta\lambda_{12} = 63.9 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta\lambda_{21} = 3076.4 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.012	0.09	0.09	0.02
NRTL( $\alpha = 0.47$ )	$\Delta g_{12} = 4244.0 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta g_{21} = -970.3 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.014	0.10	0.08	0.02
UNIQUAC ( $Z = 10$ )	$\Delta u_{12} = 3604.5 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	$\Delta u_{21} = -1607.4 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	0.012	0.09	0.10	0.02

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

**Table 4: Fittings coefficients for FF and standard deviations**

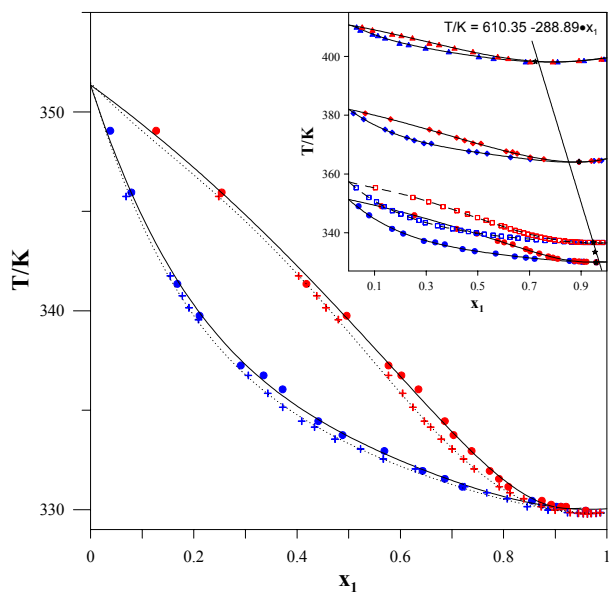
FF	$R_T$	$A_0$	$A_1$	$A_2$	$A_3$	
<b>methyl acetate (1) + ethanol (2) at 0.1 MPa</b>						
$(y_1 - x_1) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	0.758	2.865	-5.896	5.620	-2.677	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{\text{bp1}} - (1 - x_1) T_{\text{bp2}}] [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	0.267	-62.708	43.235			$\sigma(T)/K = 0.25$
$[T - y_1 T_{\text{bp1}} - (1 - y_1) T_{\text{bp2}}] [y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	2.807	4.393	-35.974			$\sigma(T)/K = 0.22$
$(G^E / RT) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	-0.018	1.764	-0.939			$\sigma(G^E/RT) < 0.01$
<b>methyl acetate (1) + ethanol (2) at 0.3 MPa</b>						
$(y_1 - x_1) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	0.344	2.621	-5.178	5.505	-3.107	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{\text{bp1}} - (1 - x_1) T_{\text{bp2}}] [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	1.226	-46.930	80.540	-71.950		$\sigma(T)/K = 0.17$
$[T - y_1 T_{\text{bp1}} - (1 - y_1) T_{\text{bp2}}] [y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	2.285	-2.199	-36.419			$\sigma(T)/K = 0.18$
$(G^E / RT) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	6.640	0.608	0.768			$\sigma(G^E/RT) = 0.01$
<b>methyl acetate (1) + ethanol (2) at 0.7 MPa</b>						
$(y_1 - x_1) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	1.181	1.180	-3.331	4.182	-2.557	$\sigma(y_1 - x_1) < 0.01$
$[T - x_1 T_{\text{bp1}} - (1 - x_1) T_{\text{bp2}}] [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	0.239	-9.833	-98.281	199.718	-116.830	$\sigma(T)/K = 0.18$
$[T - y_1 T_{\text{bp1}} - (1 - y_1) T_{\text{bp2}}] [y_1(1 - y_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	2.864	-4.576	-53.990	39.147		$\sigma(T)/K = 0.18$
$(G^E / RT) [x_1(1 - x_1)]^{-1} = \sum_{k=0} A_k \{x_1 [x_1 + R_T(1 - x_1)]^{-1}\}^k$	0.121	0.124	0.429			$\sigma(G^E/RT) = 0.01$



**Figure 2:** Experimental values and fitting curves for the mixture of methyl acetate (1) + ethanol (2) at 0.1 MPa (●), 0.3 MPa (◆) and 0.7 MPa (▲). Fitting curves and the literature values for methyl acetate (1) + ethanol (2) at different pressures: (+) 101.3 kPa (Ortega et al., 1990), and (□) 127.99 kPa (Ortega and Susial, 1990).

The experimental data from this paper at 0.1 MPa show that the methyl acetate + ethanol binary system has an azeotrope at  $x_{1az100} = y_{1az100} = 0.959$  and  $T_{az100} = 329.95$  K. This result does not differ significantly with the literature data (Gmehling et al., 2004) due to the fact that the small difference in temperature is within the range of error of the thermocouple used in this work. On the other hand, for 0.3 and 0.7 MPa a modification in the azeotropic data is verified. For these isobaric conditions, the location of the singular point is  $x_{1az300} = y_{1az300} = 0.892$ ,  $T_{az300} = 364.15$  K at 0.3 MPa; and  $x_{1az700} = y_{1az700} = 0.723$ ,  $T_{az700} = 398.25$  K at 0.7 MPa. A representation of the experimental azeotropic data of this paper and the bibliographic data (Gmehling et al., 2004) shows a relation between both (Figure 3). Azeotropic data at 0.1 and 0.7 MPa show a suitable position regarding the correlation equation; however, the azeotropic data at 0.3 MPa present an error of less than 5%, as shown in the inset in Figure 3.

The UNIFAC (Fredenslund et al., 1977; Fredenslund et al., 1975; Larsen et al., 1987) group contribution method and the ASOG (Kojima and



**Figure 3:** Experimental values and FF curves of  $T$  vs.  $x_1$  and  $T$  vs.  $y_1$  for methyl acetate (1) + ethanol (2) at 0.1 MPa (●), 0.3 MPa (◆) and 0.7 MPa (▲) compared with FF curves and the literature values for methyl acetate (1) + ethanol (2) at different pressures: (+) 101.3 kPa (Ortega et al., 1990), and (□) 127.99 kPa (Ortega and Susial, 1990).

Tochigi, 1979) model were used in previous papers (Ortega et al., 1990; Ortega and Susial, 1990; Susial et al., 1989) for the prediction of the VLE of isobaric data at pressures near atmospheric. This paper evaluates the behaviour in the prediction of VLE data by the different versions of UNIFAC and the ASOG group contribution models with respect to the experimental data obtained in this study at moderate pressures. Results are presented in Table 5.

Table 5 show that all group contribution models return reasonably good predictions, with mean deviations near 1% in the vapor phase mole fraction. However, all models generally return a higher average error in the prediction of the activity coefficient when applied to the systems studied at 0.3 and 0.7 MPa, the average error being greater at higher pressures. A new determination of the parameters of the different models will probably be required. On the other hand, the group contribution models (Table 5) yield acceptable predictions at 0.1 MPa for the azeotropic data. Nevertheless, at higher pressures, several models present significant discrepancy.

**Table 5: Mean deviations and average errors in the prediction of VLE data. Experimental and predicted azeotropic data**

	UNIFAC 1975 (A) COH/COO	UNIFAC 1977 (B) CCOH/COOC	UNIFAC 1987 (C) OH/COOC	UNIFAC 1993 (D) OH/COOC	ASOG 1979 (E) OH/COO
<b>methyl acetate (1) + ethanol (2) at 0.1 MPa</b>					
$\delta(y_i)$	0.01	0.01	0.01	0.01	0.01
$\bar{\epsilon}(\gamma_i)$	2.71	3.23	3.55	2.42	4.39
$\delta(T)/K$	0.36	0.76	0.33	0.38	0.45
<b>Azeotropic data</b>					
$x_{1\text{az exp}} = 0.959$	0.910	0.907	0.914	0.908	0.915
$T_{\text{az exp}} = 329.95 \text{ K}$	329.83	329.79	330.14	329.83	330.17
<b>methyl acetate (1) + ethanol (2) at 0.3 MPa</b>					
$\delta(y_i)$	0.01	0.01	0.02	0.01	0.01
$\bar{\epsilon}(\gamma_i)$	2.79	4.08	7.47	3.79	3.59
$\delta(T)/K$	0.38	1.29	1.52	0.44	0.83
<b>Azeotropic data</b>					
$x_{1\text{az exp}} = 0.892$	0.829	0.780	0.926	0.844	0.796
$T_{\text{az exp}} = 364.15 \text{ K}$	364.95	364.45	365.96	365.17	365.58
<b>methyl acetate (1) + ethanol (2) at 0.7 MPa</b>					
$\delta(y_i)$	0.01	0.02	0.02	0.01	0.01
$\bar{\epsilon}(\gamma_i)$	5.75	11.26	7.27	3.67	8.25
$\delta(T)/K$	1.74	3.18	1.16	1.03	2.12
<b>Azeotropic data</b>					
$x_{1\text{az exp}} = 0.723$	0.726	0.678	0.886	0.748	0.689
$T_{\text{az exp}} = 398.25 \text{ K}$	396.67	395.37	399.57	397.48	397.17

(A) Fredenslund et al., 1975; (B) Fredenslund et al., 1977; (C) Larsen et al., 1987; (D) Gmehling et al., 1993; (E) Kojima and Tochigi, 1979

## CONCLUSIONS

VLE data at moderate pressures have been obtained with a copper ebulliometer. Data for the methyl acetate + ethanol binary system at 0.1, 0.3 and 0.7 MPa are presented. The experimental data passed positively the consistency test of Van Ness and showed satisfactory agreement with literature data. This binary system forms an azeotrope at 0.1 MPa, which has been verified via good agreement with literature data. It has been also verified that the azeotropic data expressed as ester mole fraction decreases with a pressure increase.

The new isobaric data obtained at moderate pressures have been used to verify the predictive behavior of several group contribution models. The predictions achieved using the UNIFAC and ASOG models were verified by the determination of the mean deviations in the vapor phase mole fraction and the mean error in the estimation of the liquid phase activity coefficient. Results show that the predictions are good for the VLE at atmospheric pressure, while higher deviations were obtained with the pressure increase. When the UNIFAC and ASOG models were used for the azeotropic data prediction, the calculated values did not show a good agreement with the experimental data from this work at moderate pressures.

## NOMENCLATURE

$A_k$	Parameter	
$B_{ij}$	Cross second virial coefficient	$\text{m}^3 \cdot \text{mol}^{-1}$
$\bar{\epsilon}$	Average error	%
$F$	Property ( $F = y_i$ ; $F = (y_1 - x_1)$ ; $F = \gamma_1$ ; $F = \gamma_2$ ; $F = T/K$ ; $F = G^E/RT$ )	
$G^E$	Excess free energy	$\text{J} \cdot \text{mol}^{-1}$
$m$	Number of equation parameters	
$n$	Number of experimental data	
$n_D$	Refractive index	
$p_i^o$	Vapor pressure	kPa
$p$	Total pressure	kPa
$R$	Universal gas constant	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$R_T$	Parameter	
$T$	Temperature	K
$v_i^L$	Liquid molar volume	$\text{m}^3 \cdot \text{mol}^{-1}$
$x$	Liquid-phase mole fraction	
$y$	Vapor-phase mole fraction	

### Subscripts

az	Azeotrope
bp	Normal boiling point

cal	Calculated
exp	Experimental
i, j	Chemical substances
lit	Literature
1	Ester

### Greek Letters

$\delta$	Mean deviation	
$\phi$	Fugacity coefficient	
$\gamma$	Activity coefficient	
$\rho$	Density	$\text{kg}\cdot\text{m}^{-3}$
$\sigma$	Standard deviation	

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