

## High-temperature vapour–liquid equilibrium for the water–alcohol systems and modeling with SAFT-VR: 1. Water–ethanol<sup>☆</sup>

A.F. Cristino<sup>a</sup>, S. Rosa<sup>a</sup>, P. Morgado<sup>b</sup>, A. Galindo<sup>c</sup>, E.J.M. Filipe<sup>b</sup>, A.M.F. Palavra<sup>b</sup>, C.A. Nieto de Castro<sup>a,\*</sup>

<sup>a</sup> Departamento de Química e Bioquímica and Centro de Ciências Moleculares e Materiais, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

<sup>b</sup> Departamento de Engenharia Química e Biológica and Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

<sup>c</sup> Department of Chemical Engineering and Centre for Process System Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

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### ABSTRACT

Linear alcohols represent an important alternative source of energy. The design of industrial processing equipment of these alcohols needs accurate vapour–liquid equilibrium (VLE) measurements of binary mixtures with water at high temperatures.

A flow apparatus was built to carry out vapour–liquid equilibrium at high temperatures for water–alcohol binary mixtures in the temperature range of 363–443 K and pressures up to 1.7 MPa. Experimental VLE data are presented for water–ethanol system for temperatures between 363.3 and 423.7 K, and pressures up to 1 MPa and compared with available literature data. Its performance was found to be commensurate with the design parameters and the required accuracy.

The statistical associating fluid theory for potentials of variable range (SAFT-VR) was used to correlate the data. The phase equilibria for this system are accurately described with this approach, especially considering that the parameters were obtained for a shorter region of the phase diagram.

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### 1. Introduction

The knowledge of the thermophysical properties of fluids is very important to the design of many processes in chemical engineering and for the development of new and alternative technologies [1–5]. In the area of vapour liquid equilibria (VLE) of binary mixtures there are a lot of experimental studies at low and room temperatures [6,7]. However, the situation is rather different at high temperatures. To fill this gap, a VLE experimental program, involving collaboration between the Experimental Thermodynamics Laboratory (CQE-IST) and Centre for Molecular Sciences and Materials (CCMM-FCUL), was developed in recent years.

Light aliphatic alcohols represent an important alternative source of energy with significant advantage in the environmental point of view. The project of industrial equipment for their processing needs accurate measurements on VLE of water + alcohol systems, such as C<sub>2</sub>H<sub>5</sub>OH, n-C<sub>3</sub>H<sub>7</sub>OH and n-C<sub>4</sub>H<sub>9</sub>OH, at high temperatures.

Some of these binary mixtures present azeotropes which disappear when the temperature increases. Therefore, these studies will be also theoretically important, since they will allow a better

knowledge on the intermolecular interactions existent in the liquid phase of these binary mixtures.

A flow method was chosen to carry out the measurements at high temperatures, because of possible thermal degradation of the alcohols. Minimizing the residence time of the compounds at high temperatures, this possibility decreases. On the other hand, this method can generate relatively large liquid and vapour samples required for characterization of vapour and liquid phases in VLE of more complex mixtures, such as pine resin, with several micro-components, which we intend to study in a near future.

An apparatus, based on this method was built at CCMM-FCUL, which allows carrying out VLE measurements in the temperature range from 363 to 443 K and pressures up to 1.7 MPa.

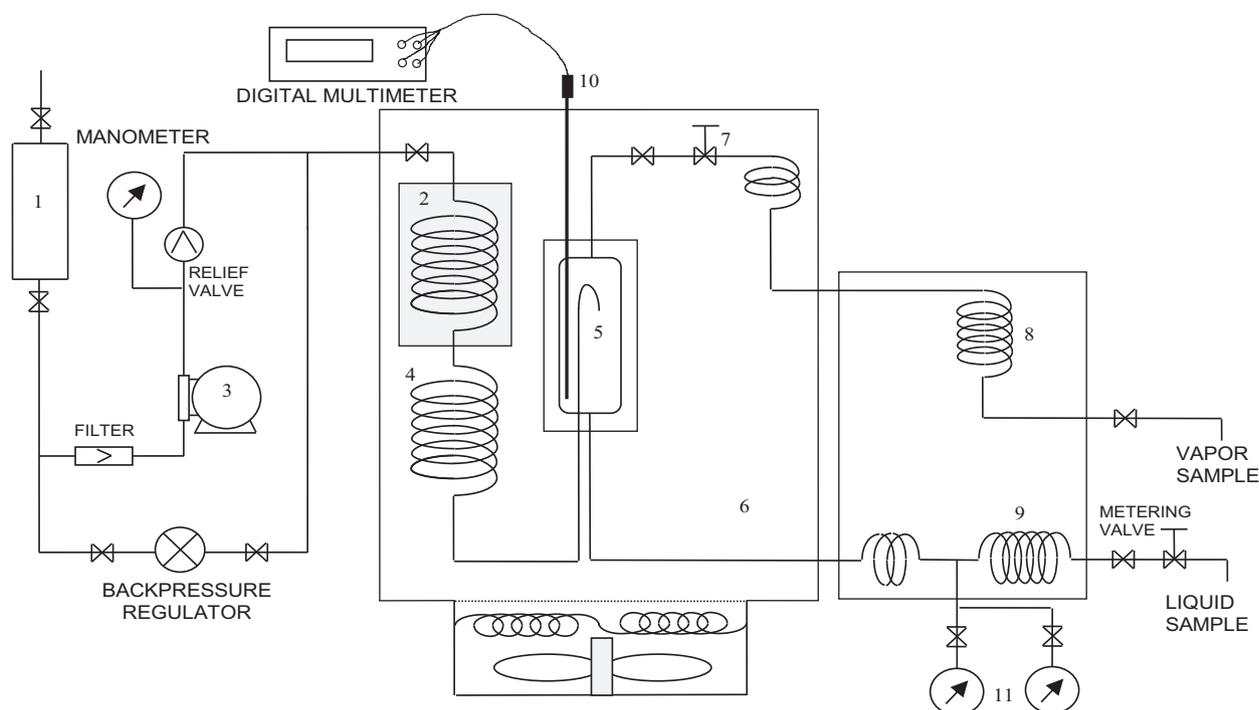
Several isothermal studies have been carried out in the temperature range from 283 to 363 K [8–19] and above 423 K [20–23] for ethanol + water system. Takigushi et al. [24] determined  $P,x$  at  $T=(340.00, 360.00, 380.00, 400.00$  and  $420.00)$  and Kleinert [25] reported  $P,x,y$  isothermal equilibrium data at  $T=(393.15$  and  $413.15)$  K. However, the only isothermal VLE study for the temperatures of 363.3, 381.4, 403.4 and 423.7 K was carried out by Kolbe and Gmehling [26], which involves the  $P,x$  diagram.

Correlation and predictive methods are necessary for scientific applications of phase equilibria if little information is available for the systems under study. Several theoretical semi-empirical and empirical methods have been proposed to correlate the VLE phase diagram with moderate success depending on the nature of the system.

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\* Corresponding author. Tel.: +351 217 500 918; fax: +351 217 500 088.

E-mail address: [cacastro@fc.ul.pt](mailto:cacastro@fc.ul.pt) (C.A. Nieto de Castro).



**Fig. 1.** Schematic diagram of the flow apparatus: (1) glass vessel, (2) preheater, (3) metering pump, (4) heat exchanger, (5) windowed equilibrium cell, (6) air bath, (7) micro-metering valve, (8) heat exchanger, (9) condenser, (10) platinum resistance thermometer and (11) pressure transducers.

From a theoretical point of view, a major step in our understanding of liquids and liquid mixtures has been the development of molecular-based equations of state (EOS), such as the SAFT equation [27–29]. Unlike typical engineering or cubic equations of state, SAFT explicitly takes into account the contribution of molecular details such as nonsphericity (molecular shape), polarity and association. In this work, we have used SAFT-VR, which describes molecules as homonuclear chains of hard-core monomers that interact through attractive potentials of variable range, typically a square well [30,31], and has been successfully used to describe the phase equilibria of a wide range of industrially important systems (see Ref. [32] and the references therein).

The aim of this work was to complement the existing data for this system, determining the  $P, x, y$  phase diagram of the water + ethanol mixtures at the temperatures of 363.2, 381.4, 403.4, 423.2 and 423.7 K. Moreover, a modelling of these experimental VLE results was carried out using SAFT-VR EOS.

## 2. Experimental

VLE data were obtained with flow apparatus formerly presented by Rosa et al. [33] and recently modified (Fig. 1). The mixture to be studied is introduced in a glass vessel (1) and a sample is pumped to the preheater (2) using a metering pump (3) (LDC Analytical, model 396-89). The preheater is made from an aluminium cylindrical block, filled with copper dust, through which a flowing tube passes. This preheater has a sufficient length to minimize the thermal degradation of the sample. A second heat exchanger (4) allows a fine tuning of the temperature of the liquid sample before entering the windowed equilibrium cell which is inside the oven.

The equilibrium cell (5) is a stainless steel 316 block rated for 13 MPa and 588 K, equipped with a borosilicate window (Jergusen 11R-20) to visualise the liquid vapour interface. The input line to the cell is made in an inverted U shape to increase the heat and mass transfer between the two phases after the liquid flash. The

thermostat is an air bath (6) controlled by a PID controller (Omron, model E5CN) from 293.2 to 523.2 K.

Inside the cell the vapour and liquid separate and the interface is easily seen, as the oven has a window. The vapour phase is removed from the top of the cell, using a micro-metering valve (7) to expand it to atmospheric pressure through a coil inside the thermostat. This metering valve also determines the vapour flow rate. The vapour after cooled and condensed in the heat exchanger (8) is collected in a small glass flask, prepared for the density determination.

The liquid sample is obtained from the bottom of the equilibrium cell and after passing through a condenser (9), where it cools down, is expanded to the atmospheric pressure using a micro-metering valve, and then collected in a small glass vessel for the density determination.

When the steady state is reached, the pressure and the temperature are measured and the liquid and vapour samples are collected. The equilibrium temperature is measured with a platinum resistance thermometer (10) (OMEGA Tech. Co.), calibrated at Electrónica Industrial de Alverca (EIA), and a 5½ digit multimeter (Keithley, model 197), with an uncertainty  $u_T = 0.1$  K, placed inside the high pressure cell (5).

The equilibrium pressure is read using two pressure transducers (11) (GE Druck, model UNIK5000) with ranges of 0–0.4 and 0–1.7 MPa with uncertainties of  $u_p = 0.0002$  MPa and 0.0009 MPa respectively, with two digital pressure readouts (4½ digits, GE Druck model DPI282).

The equilibrium compositions of the liquid and vapour phases are determined by densimetry. The method uses a relative vibrating tube densimeter (Paar, model 602), calibrated at 293.15 K with water, cyclohexane (Lab Scan) and toluene (Riedel De-Haën), with an estimated expanded uncertainty<sup>1</sup> of  $U_\rho = 0.04$  kg m<sup>-3</sup>. The cyclohexane and toluene were both purified and dried according to a

<sup>1</sup> The expanded uncertainty,  $U$  was assumed for an infinite number of degrees of freedom,  $k=2$ , i.e.  $U=2u$ .

**Table 1**  
Purity of densimeter calibrating liquids.

Compound	Purity (%) before drying process	Purity (%) after drying process	Impurities present
Toluene	99.7	100	–
Cyclohexane	99.0	99.76	2,2 Dimethylhexane or 2,2,3,3 tetramethylbutane

IUPAC recommendation [34]. Table 1 shows that their purity (confirmed by GC) after the purification process was highly successful. The water used in this work is obtained by a Millipore procedure with a resistivity of 180 kΩ m and the ethanol (Riedel De-Haën) with a confirmed purity of 99.80% by weight.

The values of the density of binary mixtures of ethanol–water were obtained from published data in a Portuguese Standard NP-753 (1969) [35]. The data from NP-753 (1969) was fitted to a third order polynomial in the molar fraction of ethanol within the range of the experimental measurements. The uncertainty of the molar fraction determination, taking into account the uncertainty in the density measurements was found to be  $u_x = 0.0001$ .

### 3. Theory

A quantitative interpretation of the results was performed using the molecular-based statistical associating fluid theory for potentials of variable attractive range, SAFT-VR, which has been successfully used to describe the phase behaviour of a wide range of systems, from simple molecules to complex multicomponent mixtures [36,37].

In the SAFT-VR approach, molecules are modelled as chains of  $m$  tangentially bonded hard spherical segments, with the attractive dispersive interactions described by a potential of variable attractive range such as the square-well potential used in this work. Each segment is characterized by three parameters, namely, the hard-sphere diameter  $\sigma$  and the depth  $\varepsilon$  and width  $\lambda$  of the potential well. In the case of associating molecules, such as water and ethanol which are hydrogen-bonding, embedded attractive square-well sites are included in the model, defined by their bonding volume  $K_{ab}^{HB}$  and the depth of the attractive potential  $\varepsilon_{ab,ij}^{HB}$ . The full expressions for the SAFT-VR equation of state can be found in references [30,31].

The molecular model parameters for the pure substances are determined by minimization of the differences between theoretical and experimental properties, normally the liquid density and vapour pressure. In the case of mixtures, the unlike interaction parameters also have to be specified. In this work, we have strictly followed the approach proposed by Mac Dowell et al. [38], both in the molecular models used and in the cross-interaction parameters for the mixture, as summarized below.

Water is represented as a single spherical segment ( $m = 1$ ) with four associating sites, two representing the hydrogen atoms and two the lone electron pairs. For ethanol one association site representing the hydroxyl hydrogen atom and two the oxygen lone electron pairs are included; in this case, the number of spherical segments is 1.533 accounting for the elongated molecular shape. It should be noted that, both in the pure compounds and in the mixture, the associative interactions are only allowed between sites of different type, namely “hydrogen-type” sites can only interact with “electron-type” sites and vice versa.

For the unlike interactions, pure arithmetic means have been used for the ranges and volumes, namely:

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

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

$$K_{ab,ij} = \left[ \frac{K_{ab,ii}^{1/3} + K_{ab,jj}^{1/3}}{2} \right]^3 \quad (3)$$

In order to quantitatively describe the mixture behaviour the unlike dispersive and associative energetic parameters have been adjusted to reproduce experimental results, by introducing adjustable correction factors ( $k_{ij}$  and  $k_{ab,ij}^{HB}$ ) to the usual geometric means:

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (4)$$

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

The unlike interaction parameters were obtained from Eqs. (1)–(5), using  $k_{ij} = -0.02297$  and  $k_{ij}^{HB} = 0.01989$ , optimized by fitting to experimental VLE data from the literature. Details of the procedure can be found in Ref. [38].

### 4. Results and discussion

Vapour pressure measurements of water in the temperature range of 383.2–423.2 K were performed for the initial certification of the apparatus. Water was chosen due to its characteristic of standard reference fluid for many physic-chemical properties. Table 2 compares our results of water vapour pressures with the results of reference [39]. It can be seen that the agreement is very good (up to a fraction of kPa), except for the lowest temperature, where the deviations are higher than the estimated uncertainty of our data (0.2 kPa).

Niesen et al. [22] tested their VLE apparatus studying the  $P,x,y$  of the ethanol–water system, at temperatures 423, 473 and 523 K. This system was chosen because it was believed that the VLE data obtained by Barr-David and Dodge [20] were accurate. However, significant differences occurred at 423 and 473 K, near the azeotrope. On the other hand, in 1985 Kolbe and Gmehling [26] published VLE data for ethanol + water system at 423.7 K. A fitting of these  $P,x$  data with an empirical equation of state allowed the calculation of data at 423.2 K. A comparison of these data with those of Niesen et al. [22] at the same temperature showed that there was an excellent agreement.

Thanking into account this agreement, a test of our apparatus was carried out through the vapour pressure measurements on the ethanol–water system at this temperature (Table 3). Fig. 2 compares our result with those obtained by Niesen et al. [22] for the  $P(x,y)$  diagram, while Fig. 3 shows both results for the vapour versus liquid compositions equilibrium curve. The results obtained by Niesen et al. [22] have an uncertainty in the pressure of 0.7 kPa in the range covered by this work, 0.1 K in temperature and 0.001 in molar fraction. The deviation between the two sets of data is

**Table 2**  
Vapour pressures (in MPa) for water at several temperatures.

T (K)	This work	Literature [36]	Deviations (kPa)
383.2	0.1425	0.143376	–0.9
393.2	0.1987	0.198665	0.0
403.2	0.2700	0.270260	–0.2
413.2	0.3617	0.361501	+0.2
423.2	0.4761	0.476101	0.0

**Table 3**

Experimental (vapour+liquid) equilibrium data for temperature  $T$ , pressure  $p$ , liquid-phase mole fraction  $x$ , and gas-phase mole fraction  $y$ , for the system ethanol (1) + water (2) system at 423.2 K.<sup>a</sup>

$T$ (K)	$p$ (MPa)	$x_1$	$y_1$
423.2	0.8082	0.1803	0.4490
423.2	0.8267	0.2290	0.4867
423.2	0.8233	0.2292	0.4704
423.2	0.8288	0.2296	0.4919
423.2	0.8363	0.2505	0.4799
423.2	0.8610	0.3141	0.5252
423.2	0.8624	0.3150	0.5250
423.2	0.8737	0.3399	0.5301
423.2	0.8867	0.3702	0.5453
423.2	0.8864	0.3712	0.5457
423.2	0.8901	0.3941	0.5572
423.2	0.9183	0.4564	0.5952
423.2	0.9190	0.4598	0.5947
423.2	0.9674	0.9983	0.9993

<sup>a</sup>  $u(T) = 0.1$  K,  $u(p < 0.4) = 0.0002$  MPa,  $u(p > 0.4) = 0.0009$  MPa, and  $u(x_1) = u(y_1) = 0.0001$ .

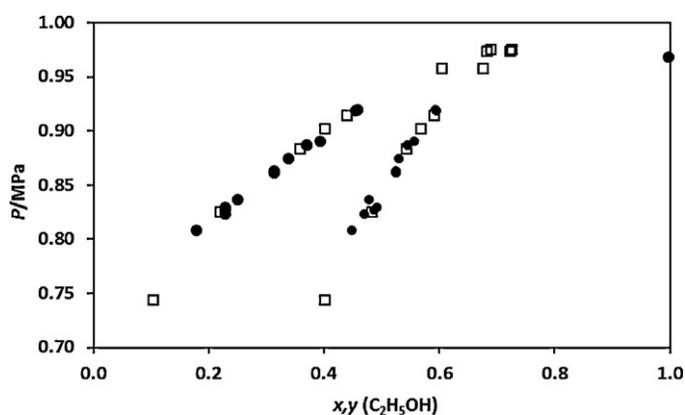


Fig. 2. Experimental vapour–liquid equilibrium compositions and pressures for ethanol+water mixtures at 423.2 K: (□) Niesen et al. [22], and (●) experimental data.

very small in the dew and bubble lines. On the other hand, the differences between the two sets of data in the  $y(x)$  diagram are also very small. The agreement between the two sets of data confirms the good performance of our flow apparatus.

The VLE study performed by Kolbe and Gmehling [26] occurred at the temperatures (363.2, 381.4, 403.4 and 423.7 K). To the best of our knowledge this is the only isothermal VLE study at these

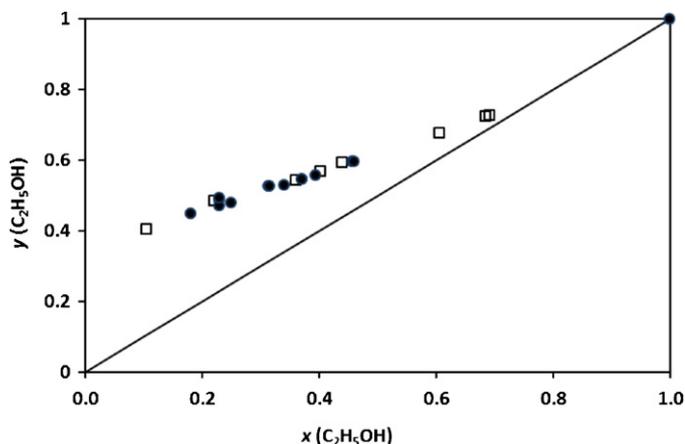


Fig. 3. Plot of vapour vs. liquid compositions of ethanol+water mixtures at 423.2 K: (□) Niesen et al. [22], and (●) present work.

**Table 4**

Experimental (vapour+liquid) equilibrium data for temperature  $T$ , pressure  $p$ , liquid-phase mole fraction  $x$ , and gas-phase mole fraction  $y$ , for the system ethanol (1) + water (2) system.<sup>a</sup>

$T$ (K)	$p$ (MPa)	$x_1$	$y_1$	$p$ (MPa)	$x_1$	$y_1$
363.3	0.1257	0.1601	0.4717	0.1460	0.4261	0.6157
363.3	0.1375	0.2791	0.5328	0.1478	0.4722	0.6061
363.3	0.1433	0.3696	0.5810	0.1554	0.6363	0.7076
363.3	0.1444	0.3963	0.5787	0.1561	0.7085	0.7468
363.3	0.1440	0.3993	0.5784	0.1589	0.7923	0.8101
363.3	0.1444	0.4223	0.5971	0.1576	0.9973	0.9971
381.4	0.1561	0.0172	0.1495	0.2735	0.4371	0.6017
381.4	0.1830	0.0430	0.2713	0.2740	0.4404	0.6092
381.4	0.1927	0.0563	0.3314	0.2750	0.4535	0.6144
381.4	0.2348	0.1592	0.4736	0.2752	0.4587	0.6198
381.4	0.2520	0.2643	0.5375	0.2761	0.4771	0.6119
381.4	0.2561	0.2894	0.5610	0.2799	0.4974	0.6294
381.4	0.2658	0.3585	0.5664	0.2806	0.5015	0.6312
381.4	0.2658	0.3618	0.5687	0.2827	0.5333	0.6526
381.4	0.2699	0.4173	0.5925	0.2830	0.5389	0.6491
381.4	0.2711	0.4215	0.5886	0.2878	0.6382	0.7024
381.4	0.2704	0.4256	0.5979	0.2906	0.7099	0.7371
381.4	0.2715	0.4271	0.5979	0.2954	0.7938	0.8089
381.4	0.2716	0.4367	0.5977	0.2884	0.9967	0.9977
403.5	0.3615	0.0431	0.2594	0.5631	0.6380	0.7010
403.5	0.4531	0.1450	0.4336	0.5665	0.7067	0.7404
403.5	0.5019	0.2971	0.5298	0.5761	0.7953	0.8059
403.5	0.5218	0.3778	0.5628	0.536	0.9991	0.9994
403.5	0.5322	0.4679	0.6041			
423.7	0.5328	0.0137	0.1100	0.8987	0.3926	0.5603
423.7	0.5825	0.0256	0.2017	0.9488	0.5669	0.6430
423.7	0.6229	0.0415	0.2390	0.9646	0.6417	0.6960
423.7	0.6297	0.0427	0.2587	0.9721	0.7094	0.7390
423.7	0.7608	0.1204	0.4009	0.9879	0.7947	0.8071
423.7	0.8459	0.2507	0.4881	0.9863	0.9980	0.9981
423.7	0.8550	0.2825	0.4975			

<sup>a</sup>  $u(T) = 0.1$  K,  $u(p < 0.4) = 0.0002$  MPa,  $u(p > 0.4) = 0.0009$  MPa, and  $u(x_1) = u(y_1) = 0.0001$ .

temperatures, which involves the  $P,x$  diagram. Table 4 presents the experimental results obtained for  $P,x,y$  diagram for the same temperatures. Our data and those from Kolbe and Gmehling [26] are also compared in Fig. 4 for the lowest temperature. The comparison shows that there is agreement between the two sets of data.

The results from the SAFT-VR equation of state, with the molecular model parameters used for water and ethanol displayed in Table 5, are presented in Fig. 5, along with the experimental data from this work. As can be seen, the agreement is remarkable, especially taking into account that the adjustable binary interaction parameters (Eqs. (4) and (5)) were optimized for a different set of experimental data, corresponding to a different region of the phase diagram. This confirms the ability of the theory to correctly predict the phase behaviour of real systems in extended ranges of

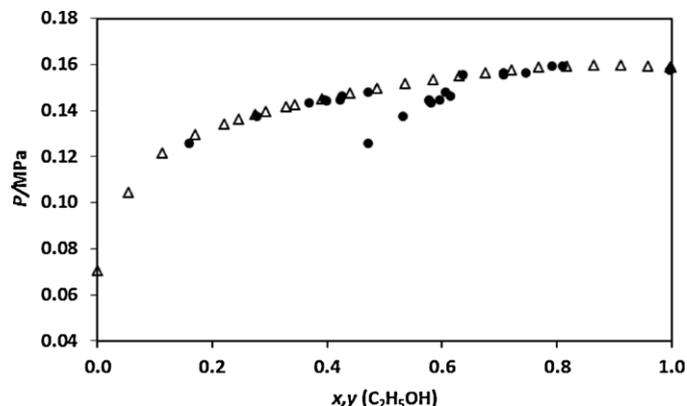
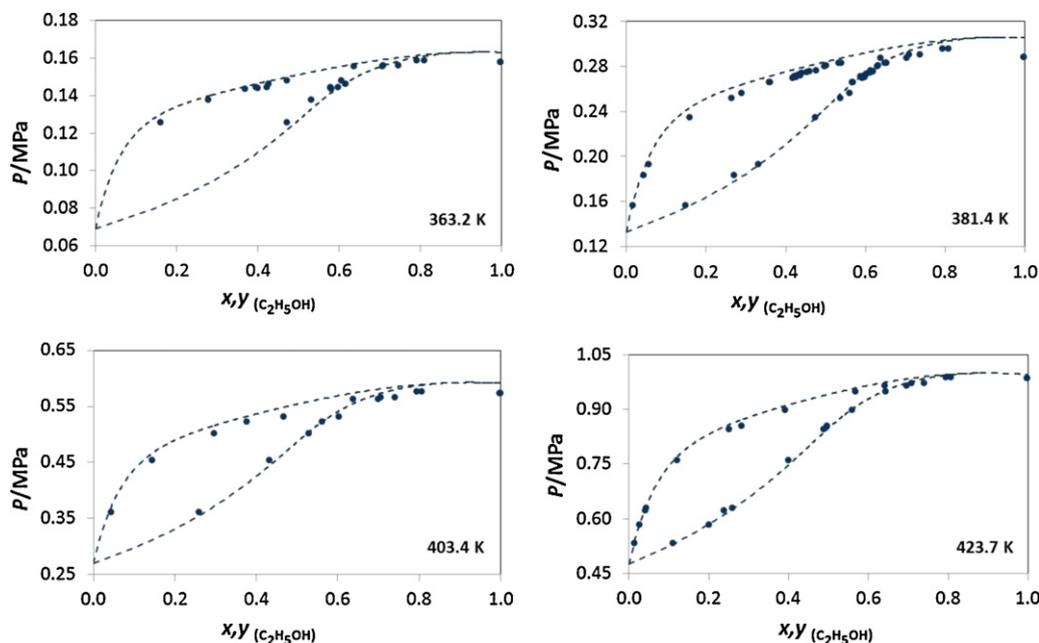


Fig. 4. Vapour–liquid equilibrium compositions vs. pressure for ethanol+water mixtures at 363.3 K: (△) Kolbe and Gmehling [26], and (●) present work.

**Table 5**  
SAFT-VR model parameters used in this work. The energy parameters  $\varepsilon$  and  $\varepsilon_{ab}^{\text{HB}}$  are divided by Boltzmann's constant  $k_B$ .

	$m$	$\sigma$ (Å)	$\frac{\varepsilon}{k_B}$ (K)	$\lambda$	H-sites	e-sites	$\frac{\varepsilon_{ab}^{\text{HB}}}{k_B}$ (K)	$K_{ab}^{\text{HB}}$ (Å <sup>3</sup> )
H <sub>2</sub> O	1	3.0342	250.000	1.7889	2	2	1400.00	1.066725
CH <sub>3</sub> CH <sub>2</sub> OH	1.533	3.7150	244.417	1.6730	1	2	2357.79	0.145637



**Fig. 5.** Comparison between vapour equilibrium data of the present work (●) and the application of the SAFT-VR theory (---) for water + ethanol system at the measured temperatures.

temperature and pressure. The transferability of these parameters to different water + alcohol systems will be tested in future work.

## 5. Conclusions

A flow apparatus was built to carry out vapour–liquid equilibrium at high temperatures for water–alcohol binary mixtures, in the temperature range of 363–443 K and pressures up to 1.7 MPa. Its performance was tested through measuring the vapour pressure of water between 383.2 and 423.2 K and of ethanol + water mixtures at 423.2 K. The data obtained agree with the mostly accurate experimental data available.

Experimental VLE data were obtained for the water–ethanol system for temperatures between 363.3 and 423.7 K, and pressures up to 1 MPa and compared with the only available literature  $P, x$  data for these temperatures given by Kolbe and Gmehling [26]. Once again our data agree with the literature.

The SAFT-VR theory was used to model the experimental results. The data are accurately described by this approach, using parameters obtained for a different set of literature results.

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