

# **CARBON DIOXIDE INFLUENCE ON WATER DEW POINT CURVES OF MIXTURES CONTAINING METHANE OR ETHANE OR A SYNTHETIC NATURAL GAS**

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## **ABSTRACT**

Dew points have been measured for two binary carbon dioxide + water between  $1.2 \times 10^5$  Pa and  $30.6 \times 10^5$  Pa in the temperature range from 251.9 K to 288.2 K, four ternary methane + carbon dioxide + water between  $1.1 \times 10^5$  Pa and  $31.6 \times 10^5$  Pa in the temperature range from 248.5 K to 288.1 K, four ternary ethane + carbon dioxide + water between  $1.1 \times 10^5$  Pa and  $20.3 \times 10^5$  Pa in the temperature range from 252.2 K to 288.4 K and three multicomponent mixtures; one synthetic natural gas (SNG) from  $1.2 \times 10^5$  Pa to  $60.2 \times 10^5$  Pa in the temperature range between 213.6 K and 252.2 K and two SNG + water from  $1.1 \times 10^5$  Pa to  $40.9 \times 10^5$  Pa in the temperature range between 246.1 K and 288.1 K.

The results were analysed in terms of a predictive excess function - equation of state (EF-EOS) method based on the zeroth-approximation of Guggenheim's reticular model. This method has been chosen because can be used to adequately predict the dew points of the all mixtures of our interest in the dew temperature and pressure ranges. In fact, the model reproduces the experimental dew-point temperature data within average absolute deviation (AAD) between 0.1 and 2.1 K.

The results obtained for the studied mixtures with water mole fraction lower than 0.00174, at pressures higher than  $5 \times 10^5$  Pa were also compared to a predictive equation of state (EOS) model. It reproduced experimental dew-point temperature data within AAD between 0.2 and 5.3 K.

## INTRODUCTION

This work is part of a research study which objective is to investigate the influence of carbon dioxide, water, methanol and heavy hydrocarbons of natural gases on the vapour-liquid equilibrium (VLE) of natural gas within the usual pressure and temperature conditions of natural gas transported by pipeline in Europe.

The present work studies the influence of carbon dioxide on dew points of ternary methane or ethane + carbon dioxide + water mixtures and of multicomponent SNG and SNG + water mixtures. To achieve this objective, experimental dew points and composition data for these mixtures and for binary carbon dioxide + water were determined, and a theoretical model was developed for dew-point prediction.

The study of gases with a higher carbon dioxide content than the usual ones in natural gases is justified because there are natural gases such as those from Lacq (France), St. Faust Meillon (France) or Kapuni (New Zealand), with high carbon dioxide contents; also because carbon dioxide is found as a remains after having been used to extract hydrocarbons from exhausted natural gas fields.

The presences in the apparatus of both, solid hydrates and liquid carbon dioxide or hydrocarbon + carbon dioxide were avoided. As a consequence, the measured dew points of the studied systems are on the right-hand side, in the pressure-temperature diagram, of both the vapour-hydrate equilibrium curve for carbon dioxide + water or hydrocarbon + carbon dioxide + water and the dew-point curve of pure carbon dioxide or hydrocarbon + carbon dioxide.

The experimental apparatus used in this work for water dew point generation, and hydrocarbon and water dew-point determination, was built and tested for previous studies [1,2]. The results presented here are for:

- Two binary carbon dioxide + water mixtures at pressures of  $1.2 \times 10^5$ - $30.6 \times 10^5$  Pa and temperatures of 251.9-288.2K.
- Four ternary methane + carbon dioxide + water mixtures at pressures  $1.1 \times 10^5$ - $31.6 \times 10^5$  Pa and temperatures of 248.5-288.1 K.
- Four ternary ethane + carbon dioxide + water mixtures at pressures  $1.1 \times 10^5$ - $20.3 \times 10^5$  Pa and temperature 252.2- 288.4 K.
- Three multicomponent mixtures; one SNG from  $1.2 \times 10^5$  Pa to  $60.2 \times 10^5$  Pa in the temperature range between 213.6 K and 252.2 K and two SNG + water from  $1.1 \times 10^5$  Pa to  $40.9 \times 10^5$  Pa in the temperature range between 246.1 K and 288.1 K.

The results obtained for the studied mixtures were analysed in terms of a predictive EF-EOS method, which reproduced experimental dew-point temperature data within AAD between 0.1 and 2.1 K. The results obtained for the studied mixtures with water mole fraction lower than 0.00174, at pressure values higher than  $5 \times 10^5$  Pa were also compared to a classical EOS model, which reproduced experimental dew-point temperature data within AAD between 0.2 and 5.3 K.

## EXPERIMENTAL PROCEDURE

The experimental dew points range from  $1.1 \times 10^5$  Pa to  $60.2 \times 10^5$  Pa at temperatures from 246.1 K and 288.4 K. The methane or ethane + carbon dioxide mixtures and SNG used in this work were prepared by Abelló-Linde according to the gravimetric method [3]. The compositions of these mixtures and their accuracies, as specified by the supplier, are listed in Table 1.

Table 1. Composition of mixtures (% mol.) and relative accuracy specified by the supplier.

component	gas 1	gas 2	gas 3	gas 4	gas 5	gas 6
nitrogen						$1.559 \pm 1\%$
CO <sub>2</sub>	$100 \pm 1$	$20 \pm 1$	$70 \pm 1$	$45 \pm 1$	$95 \pm 1$	$25.908 \pm 1\%$
methane		$80 \pm 1$	$30 \pm 1$			$69.114 \pm 0.2\%$
ethane				$55 \pm 1$	$5 \pm 1$	$2.620 \pm 1\%$
propane						$0.423 \pm 2\%$
<i>i</i> -butane						$0.105 \pm 2\%$
<i>n</i> -butane						$0.104 \pm 2\%$
<i>i</i> -pentane						$0.034 \pm 2\%$
<i>n</i> -pentane						$0.023 \pm 2\%$
<i>n</i> -hexane						$0.110 \pm 2\%$

The apparatus used for our experimental data collection was described in previous works [1,2]. In this apparatus, the dew point of pure gaseous compounds and their mixtures can be determined; in addition, the mixtures composed of water and pure gaseous compounds or their mixtures can be generated and their dew points determined. For the mixtures with water, the experimental method used is based on the generation of saturated gases with water by condensation of this compound in a temperature-controlled condenser with continuous gas flow at specified pressures.

A scheme of the experimental apparatus is shown in Figure 1

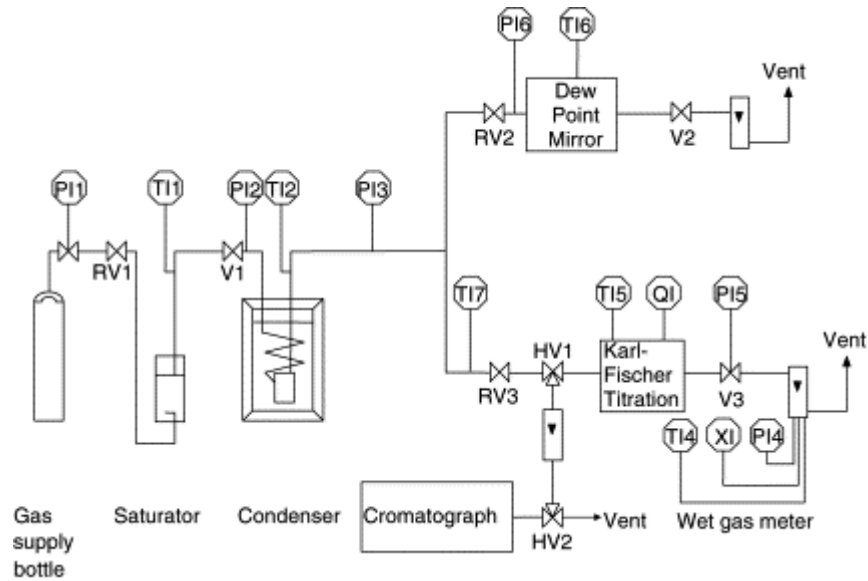


Figure 1. Schematic diagram of the experimental apparatus used in this work. Legend is as follows: RV, control valve; V, ball valve; HV, three-way valve; TI, temperature measurement; PI, pressure measurement; QI, coulometric measurement; and XI, volume measurement.

After controlled expansion (RV1), the gas from the bottle is saturated with water by flowing the gas through a saturator containing water at laboratory temperature (TI1). The condensation temperature of water is then achieved in a stainless-steel condenser, which is located in a thermostatic bath set at the desired temperature of condensation (TI2). This temperature (TI2) is lower than the temperature in the saturator (TI1). The values for the water content in the gas phase of the generated VLE are obtained at the outlet of the condenser using Karl Fischer titration, following the standard method [4] at atmospheric pressure.

The dew point values of the carbon dioxide + water mixtures, methane or ethane + carbon dioxide + water mixtures, SNG and of SNG + water mixtures are measured by means of a chilled mirror instrument. The input pressure (PI6) of the gas to the chilled mirror instrument is set using a regulator valve (RV2). When the apparatus reaches a stable dew-point temperature value of the dew temperature (TI6), both pressure and temperature are recorded.

The following instrumentation is used in the experimental apparatus:

- A Mitsubishi CA 06 Karl Fischer Titrator, coupled with an Elster wet gasmeter (Type Gr. 00, E51, 0.2% accuracy) to analyse the content of water.
- A MBW dew-point instrument Model DP3-D-HP-K2 to measure the dew-point temperature. The cooling of the mirror is achieved using cascaded Peltier elements and the dew-point mirror temperature is opto-electronically controlled. The uncertainty on the dew-point temperature is better than  $\pm 0.1$  K.
- A pressure transmitter with a maximum error of 0.1 % in the calibrated range to measure the dew-point pressure.

Prior to the study of the carbon dioxide + water mixtures, methane or ethane + carbon dioxide + water mixtures, SNG and SNG + water mixtures, the precision of experimental procedure was determined [5,6].

## RESULTS

The water contents and dew-point temperatures and pressures for the studied systems are collected in Table 2 to 5.

Table 2. Experimental water contents and dew-point temperatures and pressures for carbon dioxide + water ( $\bar{\rho}_{\text{water}}$ ) systems

<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)
<b>gas 1 ; <math>\bar{\rho}_{\text{water}} = 644.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>				<b>gas 1 ; <math>\bar{\rho}_{\text{water}} = 1515.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>			
251.9	1.2	281.2	16.1	259.4	1.3	285.5	8.0
256.6	1.9	281.9	17.0	263.2	1.7	286.5	8.5
265.1	4.0	282.7	18.4	264.5	1.9	287.7	9.3
267.2	5.0	283.2	19.5	266.9	2.2	288.2	9.7
271.1	6.4	283.9	20.8	269.2	2.6		
272.1	7.3	284.3	21.3	271.3	3.0		
273.3	8.1	284.6	22.1	274.9	3.9		
273.4	8.4	285.0	22.9	276.4	4.3		
274.9	9.6	285.8	24.6	278.1	4.8		
276.1	10.7	286.1	25.6	279.1	5.2		
277.0	11.4	286.6	26.6	280.3	5.6		
278.0	12.3	287.0	27.5	281.8	6.2		
278.8	13.2	287.4	28.2	282.4	6.6		
279.6	14.2	287.8	29.2	283.4	7.0		
280.6	15.3	288.2	30.6	283.9	7.2		

Table 3. Experimental water contents and dew-point temperatures and pressures for methane + carbon dioxide + water ( $\bar{\rho}_{\text{water}}$ ) systems.

<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)
<b>gas 2; <math>\bar{\rho}_{\text{water}} = 478.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>				<b>gas 2; <math>\bar{\rho}_{\text{water}} = 1329.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>			
248.5	1.2	277.5	13.6	257.3	1.1	279.6	5.4
252.8	1.7	279.0	15.3	264.1	2.0	281.0	6.0
260.1	3.3	280.7	17.3	266.9	2.5	283.6	7.1
264.8	4.9	281.8	18.9	268.9	3.1	285.1	7.8
267.2	6.1	282.5	19.8	271.0	3.5	286.7	8.5
270.8	7.8	283.6	21.6	272.8	4.0	288.1	9.0
272.0	8.8	285.4	24.4	275.7	4.6		
273.3	9.8	286.2	25.6				
274.5	10.9	286.8	26.6				
276.0	12.3	287.4	28.2				
<b>gas 3; <math>\bar{\rho}_{\text{water}} = 439.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>				<b>gas 3; <math>\bar{\rho}_{\text{water}} = 1123.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>			
249.1	1.1	279.4	15.6	255.4	1.2	279.9	6.5
256.8	2.2	280.7	17.3	258.9	1.5	281.0	7.1
263.3	3.9	282.2	19.3	263.6	2.1	282.7	8.0
267.0	5.1	283.4	21.5	266.6	2.5	284.7	9.3
269.6	6.8	284.1	22.7	272.1	3.8	286.4	10.4
272.1	8.5	285.2	25.0	274.2	4.4	287.2	11.2
273.8	9.9	286.1	27.1	278.1	5.8	287.9	11.9
275.9	11.7	287.2	29.8				
277.8	13.8	287.8	31.6				

Table 4. Experimental water contents and dew-point temperatures and pressures for ethane + carbon dioxide + water ( $\bar{\rho}_{\text{water}}$ ) systems.

<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)
<b>gas 4 ; <math>\bar{\rho}_{\text{water}} = 661.5 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>				<b>gas 4 ; <math>\bar{\rho}_{\text{water}} = 1274.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>			
252.2	1.1	281.0	12.0	257.0	1.1	280.2	5.9
256.1	1.5	282.5	13.3	259.8	1.4	282.8	7.1
259.4	2.0	284.0	14.8	264.2	1.9	285.2	8.3
264.4	3.0	284.9	15.7	272.1	3.4	287.4	9.5
271.2	5.6	286.3	17.5	274.9	4.0	288.4	10.2
274.4	7.3	287.3	19.1				
276.8	8.8	287.9	20.1				
279.1	10.5						
<b>gas 5 ; <math>\bar{\rho}_{\text{water}} = 728.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>				<b>gas 5 ; <math>\bar{\rho}_{\text{water}} = 1285.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>			
253.0	1.1	276.6	8.5	256.7	1.1	280.0	6.0
254.7	1.3	279.8	10.7	265.6	2.0	282.1	7.2
257.3	1.7	281.7	12.4	269.8	3.0	284.2	8.3
262.2	2.4	283.4	14.3	272.1	3.5	284.9	8.6
264.7	3.2	285.9	17.0	273.9	4.0	285.8	9.2
269.4	4.9	286.6	18.1	276.0	4.6	287.0	9.9
272.7	6.2	287.2	19.2	277.3	5.0	288.2	10.7
273.2	6.5	288.0	20.3	278.7	5.5		

Table 5. Experimental dew-point temperatures and pressures for SNG and experimental water contents and dew-point temperatures and pressures for SNG + water ( $\bar{\rho}_{\text{water}}$ ) systems.

<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)	<i>T</i> (K)	<i>P</i> (10 <sup>5</sup> Pa)
<b>gas 6</b>				<b>gas 6 ; <math>\bar{\rho}_{\text{water}} = 277.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>		<b>gas 6 ; <math>\bar{\rho}_{\text{water}} = 1392.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})</math></b>	
213.6	1.2	248.9	18.0	246.1	1.1	261.3	1.5
216.2	1.2	249.5	19.4	252.6	2.1	265.2	2.0
216.4	1.2	249.8	20.2	256.8	3.0	268.4	2.6
217.0	1.2	250.1	20.9	260.1	4.1	270.8	3.1
217.5	1.3	250.5	22.2	264.8	6.0	272.8	3.5
218.6	1.3	250.7	23.0	266.9	7.9	274.6	4.0
219.5	1.4	251.1	24.2	268.7	9.0	272.6	4.5
221.1	1.6	251.3	25.3	270.6	10.5	277.9	5.0
222.0	1.7	251.5	26.4	272.9	12.4		
222.7	1.8	251.7	27.6	274.4	14.1		
224.5	2.1	251.9	28.8	276.0	15.9		
226.6	2.5	252.0	30.4	277.0	17.2		
228.5	2.9	252.1	31.4	278.9	19.8		
229.3	3.1	252.2	32.5	279.9	21.4		
231.5	3.8	252.2	33.7	281.6	24.6		
232.6	4.1	252.2	34.0	282.6	26.6		
233.4	4.4	252.2	35.3	283.3	28.1		
235.1	5.0	252.2	36.8	284.0	29.5		
235.6	5.2	252.2	38.3	285.0	32.4		
236.7	5.8	252.0	39.6	286.2	35.1		
237.8	6.3	251.9	40.8	286.9	37.1		
238.4	6.7	251.6	43.0	287.8	40.0		
239.4	7.2	251.3	45.0	288.1	40.9		
240.4	7.9	251.0	46.3				
241.3	8.5	250.7	47.9				
242.1	9.2	250.2	50.0				
243.2	10.1	249.5	52.0				
244.1	11.0	248.8	54.2				
245.1	12.0	248.1	56.1				
245.8	12.9	247.6	58.3				
246.7	14.2	246.4	60.2				
247.4	15.2						



From the investigated mixtures containing water (Tables 2 to 5), it can be concluded that for a given system and for a given pressure, increasing the water content increases the dew-point temperature. The increase is higher for high values of pressure than for low values. For instance, for SNG +  $277.9 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 5), the dew temperature at  $4.1 \times 10^5$  Pa is 260.1 K and for SNG +  $1392.1 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 5), the dew temperature at  $4.0 \times 10^5$  Pa is 274.6 K. On the other hand, the dew temperature for SNG is 232.6 K at  $4.1 \times 10^5$  Pa (Table 5). Comparing this dew temperature with that for SNG +  $277.9 \times 10^{-6}$  kg m<sup>-3</sup>(n) water at the same pressure, it can be seen that the addition to the dry mixture of  $277.9 \times 10^{-6}$  kg m<sup>-3</sup>(n) water leads to an increasing of 27.5 K in the dew temperature.

As shown in Table 3, the dew points are similar for methane + carbon dioxide + water mixtures with similar water contents independently on the methane and carbon dioxide contents in the mixtures. Such is the case of gas 2 +  $478.7 \times 10^{-6}$  kg m<sup>-3</sup>(n) water and gas 3 +  $439.4 \times 10^{-6}$  kg m<sup>-3</sup>(n) water.

From Tables 3, 4 and 5, comparing experimental dew points for gas 2 +  $1329.1 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 3), gas 4 +  $1274.6 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 4), gas 5 +  $1285.2 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 4) and gas 6 +  $1392.1 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 5), it can be concluded that similar dew points are obtained for mixtures with similar water contents, independently on the hydrocarbon, nitrogen and carbon dioxide contents. It seems to point out that, in the studied mixtures, the dew points exclusively depend on the water content of the mixture, but not on the composition of hydrocarbon + carbon dioxide or hydrocarbon + nitrogen + carbon dioxide of the mixture.

Comparing the results for carbon dioxide + water mixtures with those for methane or ethane + carbon dioxide + water, we found that the experimental dew temperature and pressure for gas 2 +  $478.7 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 3), gas 3 +  $439.4 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 3) are similar to those obtained for gas 1 +  $644.2 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 2). We have found similar results for dew points for gas 2 +  $1329.1 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 3), gas 4 +  $1274.6 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 4), gas 5 +  $1285.2 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 4), gas 6 +  $1392.1 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 5) and for gas 1 +  $1512.2 \times 10^{-6}$  kg m<sup>-3</sup>(n) water (Table 2). From these results it could be concluded that, if the vapour phase of the VLE is composed by carbon dioxide and water, the water content in this phase is higher than in the vapour phase of VLE with hydrocarbon, carbon dioxide and water or with hydrocarbon, nitrogen, carbon dioxide and water. This behaviour is observed even if the content of hydrocarbon in the vapour phase is quite smaller than the carbon dioxide content, such is the case, as an example, of gas 5 (95% carbon dioxide + 5% ethane).

## **THEORY**

### **Introduction**

Equations of state such as the Santis-Breedveld- Prausnitz EOS [7], the Nakamura-Breedveld-Prausnitz EOS [8], the Peng-Robinson EOS [9], and the Robinson-Peng-Ng EOS [10], yield good results in calculation of water dew point of natural gases at higher temperatures than the temperature of the natural gas pipeline network. Instead of them, we

use two models, one is the EF-EOS method, which is derived from the excess function-equation of state model [11], and based on the zeroth order approximation of the quasi-reticular model. This model has been chosen because it allows the adequate prediction of dew points for the whole studied mixtures in the dew temperature and pressure ranges of our interest. The second model is an EOS based on a modified Peng-Robinson EOS [6, 12]. This equation allows predicting adequately the water dew point curve in the usual temperature and pressure range of importance for natural gas pipelines.

To evaluate the theoretical models used in this paper for the prediction of the dew points of the multicomponent systems in the studied temperature and pressure ranges, a comparison between experimental and calculated values of dew point temperature was carried out. The values of dew temperature of the vapour phase for the investigated systems are calculated by means of the EF-EOS method [11], and the EOS model [6, 12] using the experimental values of pressure and composition obtained in the present work.

### Description of the EF–EOS model

To represent the vapour-liquid equilibrium in the mixtures, a model founded on the zeroth approximation of Guggenheim’s reticular model was selected. The model satisfies two important conditions:

- (1) The Helmholtz energies of pure components are calculated by an equation of state.
- (2) The excess functions are defined at constant packing fraction, the latter described by  $v^0/v$ ,  $v^0$  being the molar close-packed volume and  $v$  the molar volume. It is assumed that it is possible to define a “covolume”  $b$  proportional to  $v^0$ , which enables to evaluate the packing fraction by the ratio  $\eta = b/v$ . The packing fraction for the pure components and for the mixture it is assumed to be the same, then:

$$\eta = \frac{b}{v} = \frac{b_i}{v_i} \quad (i = 1, \dots, p) \quad (1)$$

The EOS used in the EF-EOS model is the translated Peng-Robinson cubic equation of state [13], for components different from carbon dioxide and the IUPAC equation [14] for carbon dioxide. The reason for this choice is that thermodynamic properties of carbon dioxide such as saturated density are often poorly represented by cubic equations of state especially near of the critical point. The IUPAC equation [14] is easy to use given its polynomial form, even if the parameters used are numerous.

$$z = 1 + \frac{\rho}{\rho_c} \sum_{i=0}^{i=9} \sum_{j=0}^{j=6} c_{ij} \left( \frac{T_c}{T} - 1 \right)^j \left( \frac{\rho}{\rho_c} - 1 \right)^i \quad (2)$$

where  $\rho_c$  is the mass of carbon dioxide per unit of volume at critical temperature and pressure.

The translated Peng-Robinson cubic equation of state [13] is of the form:

$$P = \frac{RT}{\bar{v} - \bar{b}} - \frac{a(T)}{\bar{v}(\bar{v} + \gamma\bar{b})} \quad (3)$$

The values of the parameters  $a$  and  $\bar{b}$  depend on the component as follows.

For nitrogen and hydrocarbons with less than six carbon atoms the following equation is used for the covolume,  $\bar{b}$  [13]

$$\bar{b} = 0.045572 \frac{RT_c}{T_c} \quad (4)$$

The attractive parameter  $a$  as a function of the temperature,  $T$ , is calculated using various equations taken from Pénélox et al. [13].

For hydrocarbons with more than five carbon atoms the covolume,  $\bar{b}$ , is calculated by means of a group contribution method [15]. The attractive parameter,  $a$ , is obtained using the equations proposed by Coniglio et al. [15] and Carrier et al [16].

For water the eqn (3) is used for the calculation of the covolume,  $\bar{b}$  [13] and the equations proposed by Carrier et al. [16] for the attractive parameter,  $a$ .

The excess function of the EF–EOS model is the residual excess Helmholtz energy,  $A_{\text{res}}^E$ , which contribute to the molar Helmholtz energy of a mixture,  $A$ , as follows:

$$A = A^{\text{id}} - RT \ln(1 - \eta) - \sum_{i=1}^p \frac{x_i}{b_i} \Psi_i(\eta) + A_{\text{res}}^E \quad (5)$$

The residual excess Helmholtz energy,  $A_{\text{res}}^E$ , can be written by means of a formalism which enables to separate the composition and packing fraction variables:

$$A_{\text{res}}^E = E(T, x) Q(\eta) \quad (6)$$

where  $Q(\eta)$  is expressed as [13]:

$$Q(\eta) = \int_0^\eta \left( \frac{1}{1 + \gamma\eta} \right) d\eta \quad (7)$$

where the value of the parameter  $\gamma$  is [17] 20 when the IUPAC equation is used. If the translated Peng-Robinson cubic equation of state is used the value for parameter  $\gamma$  is  $2(\sqrt{2} + 1)$ .

The first term on the right hand side of eq. 5 is expressed as follows.

For carbon dioxide + water binary using the equations taken from Rauzy et al. [18].

For carbon dioxide + alkane or nitrogen binaries, the equations proposed by Berro et al. [19] are used.

$$E(T,x) = \frac{1}{2} \sum_{i=1}^p \sum_{j=1}^p \frac{q_i q_j x_i x_j}{q_m} E_{ij}(T) \quad (7)$$

$$E_{ij} = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl}(T) \quad (8)$$

$$A_{kl} = A_{kl}^0 [1 + \exp(\alpha_1 l_{\text{hyd}} + \alpha_2)] \left[ \frac{T_0}{T} \right]^r \quad (9)$$

with

$$r = \beta_1 (l_{\text{hyd}})^{1.5} + \beta_2 l_{\text{hyd}} \quad (10)$$

The values of these parameters used in later calculations in this work are presented in Table 6. The value for the interchange energy,  $A_{kl}^0$ , between carbon dioxide and nitrogen is obtained in this work using the experimental results of vapour-liquid equilibrium for carbon dioxide + nitrogen from literature [20-23] and the value for the interchange energy,  $A_{kl}^0$ , between carbon dioxide and methane is obtained in this work using the experimental results of vapour-liquid equilibrium carbon dioxide + methane from literature [24-27]

Table 6. Values of the group interaction parameters,  $A_{kl}^0$ , used in eq. (9) for the EF-EOS model.

Binary	$A_{kl}^0 / 10^6 \text{ J m}^{-3}$
CO <sub>2</sub> + N <sub>2</sub>	28.278*
CO <sub>2</sub> + CH <sub>4</sub>	253.278*
CO <sub>2</sub> + -CH <sub>3</sub>	442.314 <sup>19</sup>
CO <sub>2</sub> + -CH <sub>2</sub> -	442.314 <sup>19</sup>
CO <sub>2</sub> + -CH- 	328.303 <sup>19</sup>

\*this work

For alkane + alkane or water and nitrogen + alkane or water binaries, the equations proposed by Hocq [28] are used:

$$E(T, x) = \frac{1}{2q_m} \left[ \sum_{i=1}^p q_i x_i \left[ \sum_{j=1}^p q_j x_j K_{ij} \right] + \sum_{i=1}^p q_i x_i \left[ \sum_{j=1}^p q_j^{1/3} x_j L_{ji}^{1/3} \right] \right] \quad (11)$$

with

$$q_m = \sum_{k=1}^p q_k x_k \quad (12)$$

and

$$q_k = \delta_k b_k \quad (13)$$

$$K_{ij} = \frac{E_{ij}^1 + E_{ij}^2}{2} \quad (14)$$

$$L_{ij} = E_{ij}^2 - E_{ij}^1 \quad (15)$$

$$L_{ij} = -L_{ji} \quad (16)$$

The interchange energies,  $E_{ij}^1$  and  $E_{ij}^2$ , are calculated using a group contribution method as follows [28]:

$$E_{ij}^1 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^1(T) \quad (17)$$

with

$$A_{kl}^1 = {}_1A_{kl}^0 \left( \frac{T^0}{T} \right)^{{}_1B_{kl}^0} \quad (18)$$

$$E_{ij}^2 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^2(T) \quad (19)$$

with

$$A_{kl}^2 = {}_2A_{kl}^0 \left( \frac{T^0}{T} \right)^{{}_2B_{kl}^0} \quad (20)$$

where  ${}_1A_{kl}^0$ ,  ${}_1B_{kl}^0$ ,  ${}_2A_{kl}^0$  and  ${}_2B_{kl}^0$  are group interaction parameters.

The values for the group interaction parameters for interchange energies are the same as in previous works [5, 6, 12, 29].

## Description of the EOS model

The EOS model used in this work is based on a modified Peng-Robinson EOS in order to obtain a good description of vapour pressure of ice and liquid water [6, 12].

The equation of state used is the Peng–Robinson cubic equation of state of the form:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \quad (21)$$

The binary interaction coefficients,  $k_{ij}$ , used for the calculation of attractive parameter,  $a$ , in eqn. (21) are temperature dependent for CO<sub>2</sub> + H<sub>2</sub>O, CH<sub>4</sub> + H<sub>2</sub>O and C<sub>2</sub>H<sub>6</sub> + H<sub>2</sub>O binaries. The following temperature dependent equation has to be used [6, 12]:

$$k_{ij}(T) = k_{ij,0} + k_{ij,1} \left( \frac{T}{273.15} - 1 \right) \quad (22)$$

Values for the binary interaction parameters  $k_{ij,0}$  and  $k_{ij,1}$  used in this work for carbon dioxide + nitrogen or water or alkane are collected in Table 7. These coefficients for the other binary interactions are the same as in previous works [6, 12].

Table 7. Values of binary interaction parameters,  $k_{ij,0}$ , used in eq. 22 for the EOS model

component	$k_{ij,0}$	$k_{ij,1}$
<b>N<sub>2</sub></b>	-0.0170	
<b>H<sub>2</sub>O</b>	0.1840	0.2360
<b>CH<sub>4</sub></b>	0.0919	
<b>C<sub>2</sub>H<sub>6</sub></b>	0.1322	
<b>C<sub>3</sub>H<sub>8</sub></b>	0.1241	
<b><i>i</i>-C<sub>4</sub>H<sub>10</sub></b>	0.1200	
<b><i>n</i>-C<sub>4</sub>H<sub>10</sub></b>	0.1333	
<b><i>i</i>-C<sub>5</sub>H<sub>12</sub></b>	0.1219	
<b><i>n</i>-C<sub>5</sub>H<sub>12</sub></b>	0.1222	
<b><i>n</i>-C<sub>6</sub>H<sub>14</sub></b>	0.1100	

## DISCUSSION AND CONCLUSIONS

In this work; the dew points of carbon dioxide + water, methane or ethane + carbon dioxide + water, SNG and SNG + water systems have been studied.

The measured dew-point curves and calculated values using the EF-EOS method and the EOS model are represented in Figures 2-7.

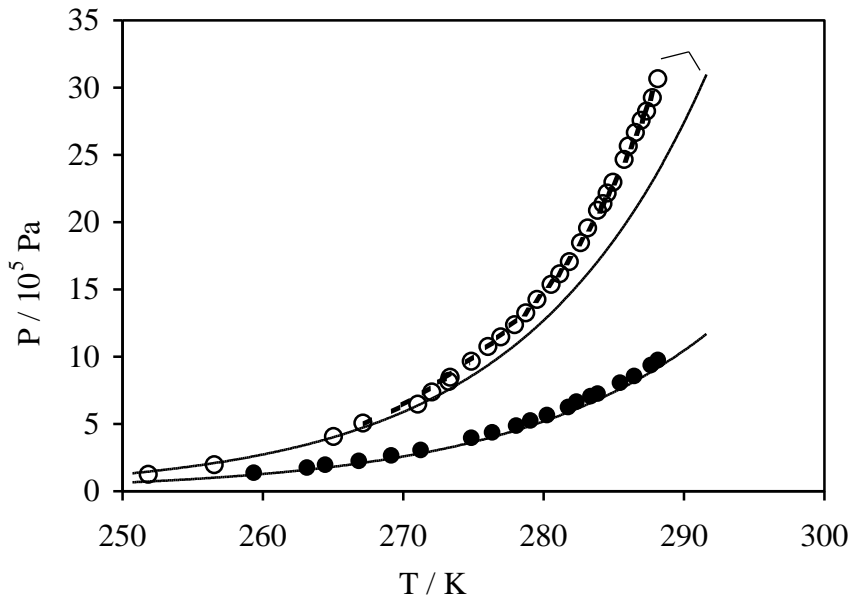


Figure. 2. Comparison between measured dew-point curves (symbols) and calculated values using the EF-EOS method (curves) and using the EOS model (dotted curve) for gas1 + water ( $\bar{\rho}_{\text{water}}$ ) systems:  $\circ$ ,  $\bar{\rho}_{\text{water}} = 644.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ ;  $\bullet$ ,  $\bar{\rho}_{\text{water}} = 1512.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$

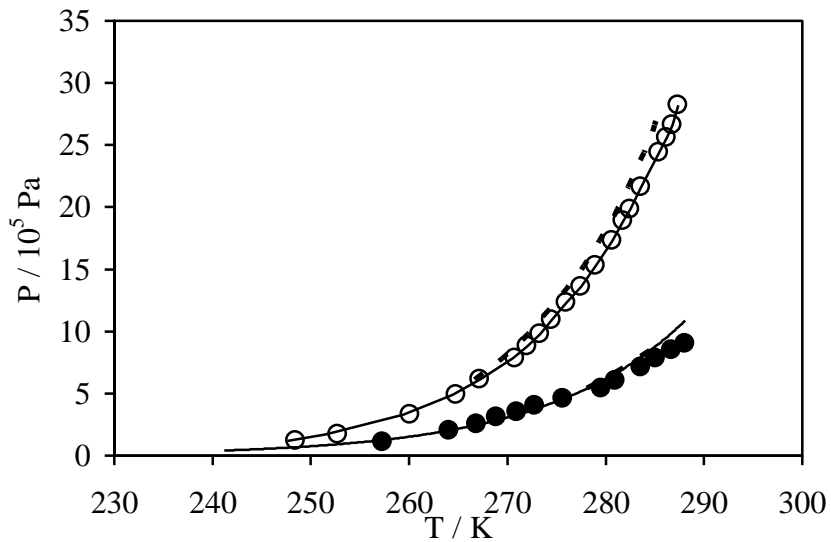


Figure. 3. Comparison between measured dew-point curves (symbols) and calculated values using the EF-EOS method (curves) and the EOS model (dotted curves) for gas 2 + water ( $\bar{\rho}_{\text{water}}$ ) systems:  $\circ$ ,  $\bar{\rho}_{\text{water}} = 478.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ ;  $\bullet$ ,  $\bar{\rho}_{\text{water}} = 1329.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$

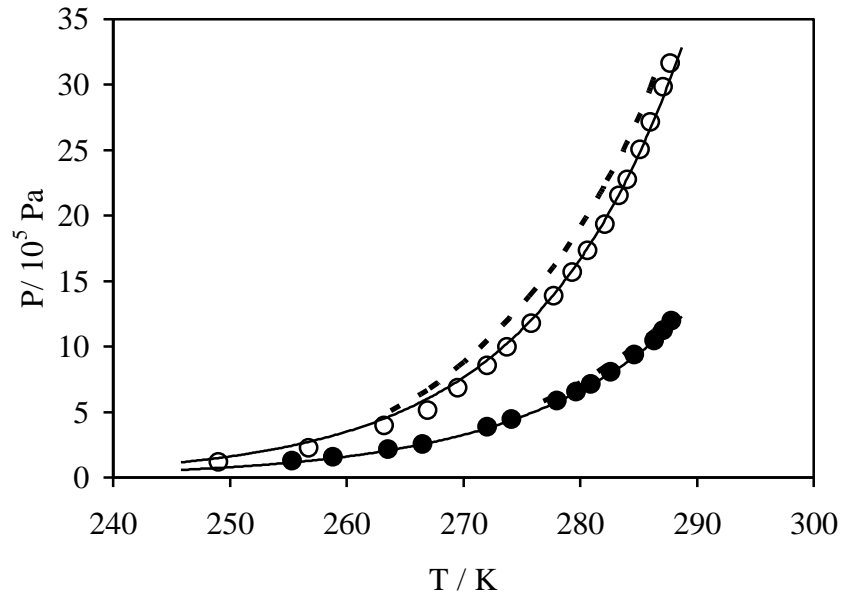


Figure. 4. Comparison between measured dew-point curves (symbols) and calculated values using the EF-EOS method (curves) and the EOS model (dotted curves) for gas 3 + water ( $\bar{\rho}_{\text{water}}$ ) systems: ●,  $\bar{\rho}_{\text{water}} = 439.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ ; ○,  $\bar{\rho}_{\text{water}} = 1123.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$

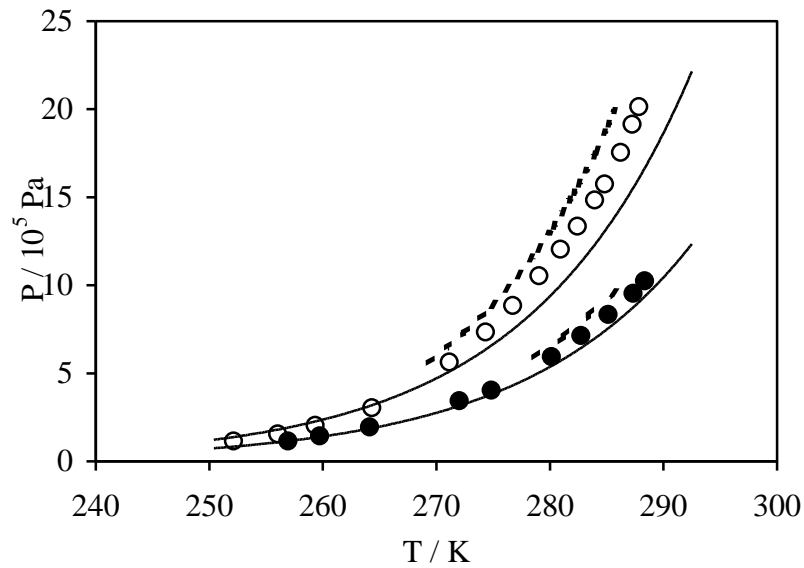


Figure 5. Comparison between measured dew-point curves (symbols) and calculated values using the EF-EOS method (curves) and the EOS model (dotted curves) for gas 4 + water ( $\bar{\rho}_{\text{water}}$ ) systems: ○,  $\bar{\rho}_{\text{water}} = 661.5 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ ; ●,  $\bar{\rho}_{\text{water}} = 1274.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ .



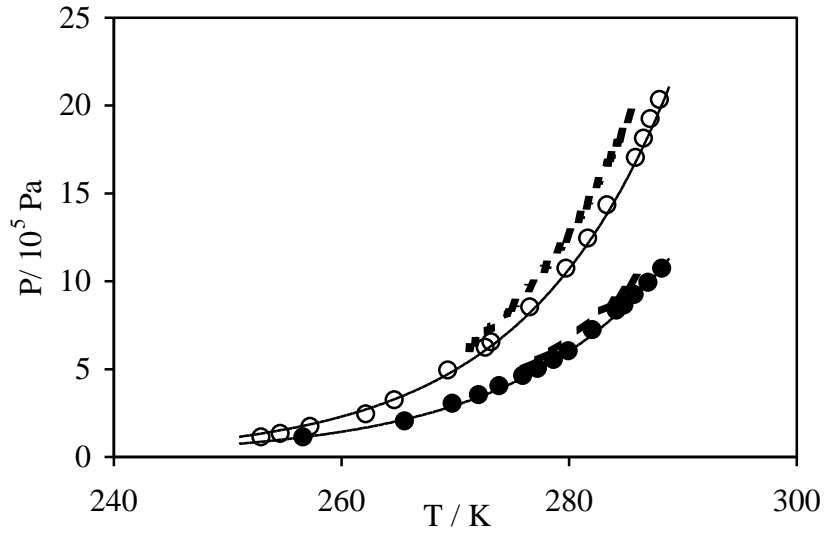
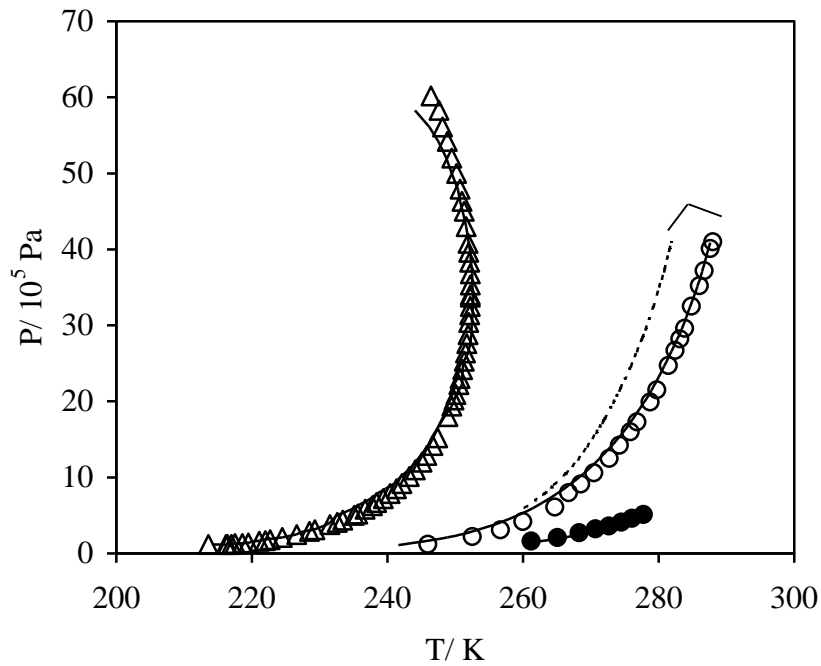


Figure. 6. Comparison between measured dew-point curves (symbols) and calculated values using the EF-EOS method (curves) and the EOS model (dotted curves) for gas 5 + ( $\bar{\rho}_{\text{water}}$ ) systems:  $\circ$ ,  $\bar{\rho}_{\text{water}} = 728.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ ;  $\bullet$ ,  $\bar{\rho}_{\text{water}} = 1285.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ .

Figure 7. Comparison between measured dew-point curves (symbols) and calculated



values using the EF-EOS method (curves) and the EOS model (dotted curves) for the systems:  $\Delta$ , gas 6;  $\circ$ , gas 6 +  $277.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$  water;  $\bullet$ , gas 6 +  $1392.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$  water

Values of average absolute deviation (AAD) are calculated using eqn. (23) and listed

for each dew-point curve in Table 7.

$$AAD = \frac{1}{N} \sum_{n=1}^N |T_n^{\text{exp}} - T_n^{\text{calc}}| \quad (23)$$

Comparing the experimental and calculated values for dew-point temperature, it can be concluded that both theoretical methods used in this work adequately reproduce the experimental dew-point data. As explained previously, the calculated values for dew temperatures with both theoretical models are obtained using the experimental values of pressure and composition obtained in this work.

Table 7. Water contents for carbon dioxide + water ( $\bar{\rho}_{\text{water}}$ ) mixtures, methane or ethane + carbon dioxide + water ( $\bar{\rho}_{\text{water}}$ ) mixtures and SNG + water ( $\bar{\rho}_{\text{water}}$ ) mixtures. Experimental ranges of dew temperatures and pressures and values of AAD<sup>1</sup> (EF-EOS model) and of AAD<sup>2</sup> (EOS model) for the dew-point curves.

System	$\bar{\rho}_{\text{water}}$ ( $10^{-6} \text{ kg m}^{-3}(\text{n})$ )	<i>T</i> range (K)	<i>P</i> range ( $10^5 \text{ Pa}$ )	AAD <sup>1</sup> (K)	AAD <sup>2</sup> (K)
gas 1 + water	644.2	251.9 – 282.2	1.2 – 30.6	1.8	0.2
	1512.2	259.4 – 288.2	1.3 – 9.7	0.8	
gas 2 + water	478.7	248.5 – 287.4	1.2 – 28.2	0.2	1.3
	1329.1	257.3 – 288.1	1.1 – 9.0	0.8	1.9
gas 3 + water	439.4	249.1 – 287.8	1.1 – 31.6	0.8	2.0
	1123.9	255.4 – 287.9	1.2 – 11.9	0.1	1.1
gas 4 + water	661.5	252.2 – 287.9	1.1 – 20.1	2.1	2.1
	1274.6	257.0 – 288.4	1.1 – 10.2	0.8	1.7
gas 5 + water	728.8	253.0 – 288.0	1.1 – 20.3	0.6	1.9
	1285.2	256.7 – 288.2	1.1 – 10.7	0.1	1.4
gas 6		213.6 – 252.2	1.2 – 60.2	0.9	
gas 6 + water	277.9	246.1 – 288.1	1.1 – 40.9	1.6	5.3
	1392.1	261.3 – 277.9	1.5 – 5.0	0.4	0.3

The EF-EOS model predicts the dew temperature within AAD between 0.1 and 2.1 K for the studied mixtures. No influence of temperature and pressure is found for the obtained values of deviations. The good agreement with predictions obtained in this paper using the EF-EOS method validates this model for the prediction of dew points for the investigated systems in our work.

The EOS model reproduced experimental dew point temperature data within AAD between 0.2 and 5.3 K. No influence of temperature and pressure is found for the obtained

values of deviations between experimental and calculated data of dew temperature. This model calculates systematically lower values for dew temperature than the experimentally obtained for the studied mixtures. The EOS model is not applicable to mixtures with water mole fraction higher than 0.00174.

Because of the EF–EOS model uses a group contribution model, the availability of every binary experimental data corresponding to every binary interaction in the mixture is not necessary. Considering this property and the good results obtained with this model in this work and previous studies [5, 6, 12, 29], EF–EOS model could be used for properly prediction of hydrocarbon, water and water + methanol dew-point of real natural gases, although binary experimental data for all components of the so-called C<sub>6+</sub> fraction are not available.

## NOMENCLATURE

$A$	equation of state attractive energy parameter (Pa m <sup>6</sup> mol <sup>-2</sup> )
$A$	molar Helmholtz energy (J mol <sup>-1</sup> )
$A$	coefficients in EOS model
$A_{kl}$	group interaction parameter between groups $k$ and $l$ (J m <sup>-3</sup> )
AAD	absolute average deviation (K)
$b$	covolume; equation of state size parameter (m <sup>3</sup> mol <sup>-1</sup> )
$\bar{b}$	pseudo covolume (m <sup>3</sup> mol <sup>-1</sup> )
$c_{ij}$	parameters of the accurate equation of state, the IUPAC equation
$E_{ij}^1, E_{ij}^2$	terms of the interchange energy between alkane and alkane or water or methanol and between nitrogen and alkane or water or methanol (J m <sup>-3</sup> )
$k_{ij}$	binary interaction coefficients in EOS model
$K_{ij}, L_{ij}$	binary interaction parameters (J m <sup>-3</sup> )
$l_{\text{hyd}}$	parameter related to the chain-length of the hydrocarbons
$N$	number of groups in a solution
$N$	for calculating AAD, number of dew points which constitute a dew point curve
$p$	number of components in the mixture
$P$	pressure (Pa)
$q$	molecular surface (m <sup>2</sup> )
$Q$	integral of $Q'/\eta$ between 0 and $\eta$
$R$	gas constant (8.314 J mol <sup>-1</sup> K <sup>-1</sup> )
$r$	adjusted parameter
$T$	temperature (K)
$T^0$	reference temperature (298.15 K)
$v$	molar volume (m <sup>3</sup> mol <sup>-1</sup> )
$\bar{v}$	molar pseudo-volume (m <sup>3</sup> mol <sup>-1</sup> )
$z$	compressibility factor

## Greek symbols

$\alpha_1, \alpha_2$	adjusted parameters in EF-EOS model
$\alpha_{ik}$	surface area fraction of group $k$ in molecule $I$
$\beta_1, \beta_2$	adjusted parameters in EF-EOS model
$\gamma$	constant of the translated Peng-Robinson cubic equation of state
$\delta$	adjustable parameter, proportionality coefficient between the surface measure, $q$ , and the covolume, $v$
$\eta$	packing fraction
$\rho$	mass of carbon dioxide per unit of volume ( $\text{g cm}^{-3}$ )
$\bar{\rho}_{\text{water}}$	experimental mean value of water content ( $10^{-6}\text{kg m}^{-3}(\text{n})$ )
$\bar{\rho}_{\text{methanol}}$	experimental mean value of methanol content ( $10^{-6}\text{kg m}^{-3}(\text{n})$ )
$\Psi$	function of the packing fraction
$\omega$	acentric factor

## Subscripts

$c$	critical value
$eb$	value at normal vaporization temperature
$i, j$	referring to components $i, j$
$k, l$	referring to groups $k, l$
$n$	referring to a point of a dew point curve in the calculation of AAD
$N$	number of dew points which constitute a dew point curve
$res$	residual

## Superscripts

$cal$	calculated
$exp$	experimental
$E$	excess property
$id$	ideal solution property

## Acknowledgment

This work is part of a research project 2FD97-2078 financially supported by Science and Technology Ministry of Spain, and FEDER funds. The authors also acknowledge the technical support of ENAGAS, S. A. during the experimental part of this work.

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