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Dew Points of Ternary Methane (or Ethane) + Carbon Dioxide + Water Mixtures: Measurement and Correlation

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Experimental measurements of dew points for seven methane + carbon dioxide + water mixtures in the pressure range of 1.1×10^5 – 60.5×10^5 Pa in the temperature range of 243.1–288.1 K, and four ethane + carbon dioxide + water mixtures at pressures of 1.1×10^5 – 20.3×10^5 Pa and temperatures of 252.2–288.4 K, were determined. The experimental results obtained on the ternary systems were analyzed in terms of a predictive excess function–equation of state (EF–EOS) method, which reproduced experimental dew-point temperature data within an absolute average deviation (AAD) of 0.1–2.1 K. The experimental results obtained for the studied mixtures at pressures of $>5 \times 10^5$ Pa were also compared to a predictive equation of state (EOS) model. It reproduced experimental dew-point temperature data within AAD values of 0.9–2.1 K.

1. Introduction

This work is part of research whose intent is to investigate the influence of carbon dioxide, water, methanol, and heavy hydrocarbons of natural gases on the vapor–liquid equilibrium (VLE) of natural gas, within the usual pressure and temperature conditions of natural gas transport by pipeline. We initially intended to study the systems with the lowest number of components: the carbon dioxide + water and carbon dioxide + water + methanol systems, and their mixtures with the major components of natural gas, which are methane and ethane. Given that experimental dew-point data for these systems were not found in the literature (at least not within the temperature and pressure ranges of interest), they were determined and the obtained results for methane (or ethane) + carbon dioxide + water are presented here. The results obtained for carbon dioxide + water and carbon dioxide + water + methanol systems are presented in other work;¹ similar data have been published elsewhere for methane + carbon dioxide + water + methanol.² Therefore, the purposes of the present work were (i) to obtain experimental data of methane (or ethane) + carbon dioxide + water dew points within the usual

pressure and temperature conditions of a natural gas pipeline, and (ii) to achieve a theoretical model that allows adequate prediction of the experimental results obtained. The compositions of methane (or ethane) + carbon dioxide gaseous mixtures were chosen to cover a broad hydrocarbon/carbon dioxide composition range.

The presence of solid hydrates of water and methane (or ethane) + carbon dioxide, and liquid methane (or ethane) + carbon dioxide, was 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 vapor–hydrate equilibrium curve of methane (or ethane) + carbon dioxide + water and the dew-point curve of methane (or ethane) + carbon dioxide.

The experimental apparatus used in this work to generate the water dew point was built and commissioned as described in previous works.^{3,4} The results on seven methane + carbon dioxide + water mixtures at pressures of 1.1×10^5 – 60.5×10^5 Pa and temperatures of 243.1–288.1 K, and four ethane + carbon dioxide + water mixtures at pressures of 1.1×10^5 – 20.3×10^5 Pa and temperatures of 252.2–288.4 K, are presented here.

The experimental results obtained on the ternary systems were analyzed in terms of an excess function–equation of state (EF–EOS) method, which reproduced experimental dew-point temperature data within an absolute average deviation (AAD) of 0.1–2.1 K. The

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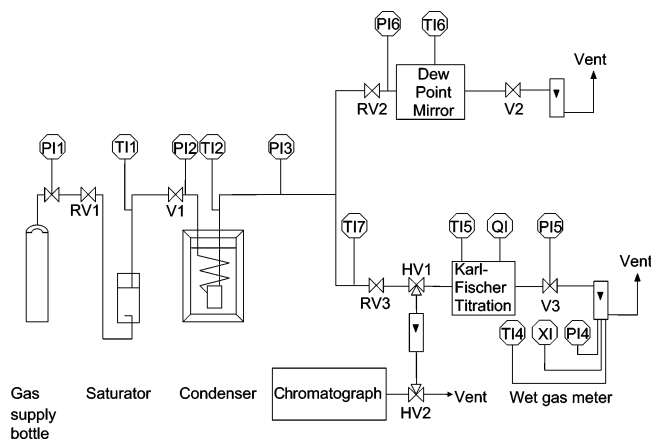


Figure 1. Schematic diagram of the experimental apparatus used in this work. Legend is as follows: RV, control valve; V, ball valve; HV, three-way valve; TI, temperature measurement; PI, pressure measurement; QI, coulometric measurement; and XI, volume measurement.

Table 1. Composition of Methane (or Ethane) + Carbon Dioxide Mixtures and Relative Accuracy, as Specified by the Supplier

component	Amount (mol %)			
	mixture 1	mixture 2	mixture 3	mixture 4
carbon dioxide	20 ± 1	70 ± 1	45 ± 1	95 ± 1
methane	80 ± 1	30 ± 1		
ethane			55 ± 1	5 ± 1

experimental results obtained on the studied mixtures at pressures of $>5 \times 10^5$ Pa were also analyzed by means of an equation of state (EOS) model, which reproduced experimental dew-point temperature data within an AAD of 0.9–2.1 K.

The good agreement obtained between experimental and calculated values serves as validation of both predictive models.

2. Experimental Section

The experimental dew points are in the range of 1.1×10^5 – 60.5×10^5 Pa at temperatures of 243.1–288.4 K.

The apparatus used for our experimental data collection was described in previous works.^{3,4} In this apparatus, the dew point of pure gaseous compounds and their mixtures can be determined; in addition, the mixtures constituted by water or water + methanol and pure gaseous compounds or their mixtures can be generated and their dew points can be determined. For the mixtures with water or water + methanol, the experimental method used is based on the generation of saturated gases with water or with water and methanol by condensation of these compounds in a temperature-controlled condenser with continuous gas flow at specified pressures. In this work, the methane (or ethane) + carbon dioxide mixtures were saturated with water. The four methane (or ethane) + carbon dioxide mixtures used were prepared according to the gravimetric method (International Standard ISO 6142, 1981)⁵ by Abelló Linde. The compositions of these mixtures, and their accuracy (as specified by the supplier), are listed in Table 1.

A schematic diagram of the experimental apparatus is shown in Figure 1. After controlled expansion (RV1), the gas is saturated with water vapor by making it flow through an

isolated saturator that contains water at laboratory temperature (TI1). Later, the gas is allowed into a stainless-steel condenser, where the condensation temperature of water is attained. The condenser is located in a thermostatic bath set at the desired condensation temperature (TI2). This temperature (TI2) is lower than the temperature in the saturator (TI1). The water concentration in the gas is measured at the outlet of the condenser, using Karl Fischer titration, following the standard method⁶ at atmospheric pressure. By doing so, the reference value for the water content in the gaseous phase is obtained.

The dew points of the methane (or ethane) + carbon dioxide + 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 (TI6), both the pressure and temperature are recorded. In this way, the values of the temperature and pressure of the dew-point curve of the generated mixture are obtained.

The following instrumentation is used to analyze the contents of water and to perform the dew-point measurements: a Mitsubishi CA 06 Karl Fischer Titrator, coupled with an Elster wet gasmeter (Type Gr. 00, E51, 0.2% accuracy); MBW Dew Point Instrument, Model DP3-D-HP-K2 (the cooling of the mirror is achieved using cascaded Peltier elements, and the dew-point mirror temperature is optoelectronically controlled; the uncertainty on the dew-point temperature is better than ± 0.1 K); and a pressure transmitter with a maximum error of 0.1% in the calibrated range.

Prior to the study of the dew points of the methane (or ethane) + carbon dioxide + water systems, the precision of both analytical methods and experimental procedures was determined.^{7,8}

3. Results

The water contents for the generated methane + carbon dioxide + water and ethane + carbon dioxide + water mixtures at the dew-point generation system, and their dew-point curves, were determined and the results of the experiments are collected in Tables 2 and 3.

From the investigated mixtures (Tables 2 and 3), it can be concluded that, for a given pressure value, the dew-point temperature increases when the water amount also increases. The increase is greater for high pressures than for low pressures.

As shown in Table 2, the measured dew points are similar for methane + carbon dioxide + water mixtures with a similar water concentration; such is the case of mixture 1 + 478.7×10^{-6} kg m^{-3} (n) water and mixture 2 + 439.4×10^{-6} kg m^{-3} (n) water. From Tables 2 and 3 and by comparing experimental dew points obtained for mixture 1 + 1329.1×10^{-6} kg m^{-3} (n) water (from Table 2), mixture 3 + 1274.6×10^{-6} kg m^{-3} (n) water (from Table 3), and mixture 4 + 1285.2×10^{-6} kg m^{-3} (n) water (from Table 3), it can be concluded that similar

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Table 2. Experimental Water Content and Dew-Point Temperatures and Pressures for {Methane + Carbon Dioxide + $\bar{\rho}_{\text{water}}$ } Systems

temp, T (K)	pressure, P (10^5 Pa)	temp, T (K)	pressure, P (10^5 Pa)
Mixture 1; $\bar{\rho}_{\text{water}} = 272.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
243.1	1.1	277.8	24.8
248.7	1.9	279.4	28.6
253.7	3.1	281.3	33.4
257.7	4.5	281.5	34.2
262.7	7.0	282.4	36.9
265.3	8.8	284.2	42.7
267.2	10.6	285.0	46.6
271.4	13.3	285.7	49.4
272.6	15.1	286.6	55.1
273.8	17.3	287.1	58.3
274.8	19.2	287.4	60.5
276.1	21.3		
Mixture 1; $\bar{\rho}_{\text{water}} = 343.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
245.3	1.1	281.2	26.6
246.1	1.2	282.0	28.3
251.3	2.0	282.8	30.1
257.7	3.5	283.5	32.0
267.8	8.9	284.4	34.0
271.2	11.1	285.1	35.7
272.1	12.3	285.5	36.7
273.7	14.1	286.0	38.9
274.9	15.7	286.5	40.6
276.6	18.1	286.9	42.3
277.8	19.9	287.3	44.2
279.0	22.0	287.9	45.8
280.1	24.2		
Mixture 1; $\bar{\rho}_{\text{water}} = 478.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
248.5	1.2	277.5	13.6
252.8	1.7	279.0	15.3
260.1	3.3	280.7	17.3
264.8	4.9	281.8	18.9
267.2	6.1	282.5	19.8
270.8	7.8	283.6	21.6
272.0	8.8	285.4	24.4
273.3	9.8	286.2	25.6
274.5	10.9	286.8	26.6
276.0	12.3	287.4	28.2
Mixture 1; $\bar{\rho}_{\text{water}} = 1329.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
257.3	1.1	279.6	5.4
264.1	2.0	281.0	6.0
266.9	2.5	283.6	7.1
268.9	3.1	285.1	7.8
271.0	3.5	286.7	8.5
272.8	4.0	288.1	9.0
275.7	4.6		
Mixture 2; $\bar{\rho}_{\text{water}} = 439.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
249.1	1.1	279.4	15.6
256.8	2.2	280.7	17.3
263.3	3.9	282.2	19.3
267.0	5.1	283.4	21.5
269.6	6.8	284.1	22.7
272.1	8.5	285.2	25.0
273.8	9.9	286.1	27.1
275.9	11.7	287.2	29.8
277.8	13.8	287.8	31.6
Mixture 2; $\bar{\rho}_{\text{water}} = 677.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
252.5	1.2	281.8	13.0
257.8	1.8	283.0	14.4
263.7	3.0	283.6	15.2
268.4	4.5	284.3	16.1
273.1	6.2	285.3	17.2
275.0	7.5	286.4	18.5
276.9	8.8	287.0	19.4
278.1	9.7	287.8	20.4
279.7	10.9	288.0	20.7
281.2	12.1		
Mixture 2; $\bar{\rho}_{\text{water}} = 1123.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$			
255.4	1.2	279.9	6.5
258.9	1.5	281.0	7.1
263.6	2.1	282.7	8.0
266.6	2.5	284.7	9.3
272.1	3.8	286.4	10.4
274.2	4.4	287.2	11.2
278.1	5.8	287.9	11.9

Table 3. Experimental Content of Water and Dew-Point Temperatures and Pressures for {Ethane + Carbon Dioxide + $\bar{\rho}_{\text{water}}$ } Mixtures

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

measured dew points are obtained for mixtures with similar water content, independent of the composition of methane (or ethane) + carbon dioxide mixtures. The data from the table seem to show that, in the studied mixtures, the dew-point temperature and pressure are exclusively dependent on the water concentration of the mixture, but not on the composition of the methane (or ethane) + carbon dioxide mixtures. The same conclusion was obtained in a previous work³³ about the study of dew points of synthetic natural gas (SNG) + water.

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In a previous work,¹ the carbon dioxide + water mixtures were studied; when comparing the results from the present work with the latter, we found that the experimental dew-point temperatures and pressures for mixture 1 + $478.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water and mixture 2 + $439.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water are similar to those obtained for the mixture of carbon dioxide + $644.2 \text{ kg m}^{-3}(\text{n})$ water.¹

We have found similar results for the experimental dew points for mixture 1 + $1329.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water, mixture 3 + $1274.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water, and mixture 4 + $1285.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water, as well as for the mixture of carbon dioxide + $1512.2 \text{ kg m}^{-3}(\text{n})$ water.¹

From these experimental results, it could be concluded that, if the vapor phase of the VLE is composed of carbon dioxide and water,¹ the water content in this phase is higher than in the vapor phase of VLE with methane (or ethane), carbon dioxide, and water (from this work). This behavior is observed even if the content of methane (or ethane) in the vapor phase is quite smaller than the carbon dioxide content, as is the case of mixture 4 (95% carbon dioxide + 5% ethane) in this work.

4. Theory

4.1. Introduction. Equations of state such as the Peng–Robinson EOS⁹ and the Robinson–Peng–Ng EOS¹⁰ yield good results in the calculation of water dew points of natural gas at temperatures higher than the usual temperature of the natural gas pipeline network.

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Classical models such as UNIQUAC,¹¹ DISQUAC,¹² or modified UNIFAC¹³ allow the prediction of the VLE at low pressures for systems that contain a polar compound; however, these models are not suitable for high-pressure calculations,¹⁴ as is the case in this work.

As mentioned previously, this work is part of research that studies the influence of carbon dioxide, water, methanol, and heavy compounds of natural gases on the VLE of natural gas. Therefore, the studied ranges of dew-point temperature and pressure are within the usual temperature and pressure of natural gas transmission through a pipeline, which means low temperatures at high pressures. For this reason, the above-mentioned theoretical models are not suitable for the present work. Instead of them, we use two models. One model is the EF–EOS method, which is derived from the EF–EOS model¹⁵ and founded on the zeroth approximation on the quasi-reticular model. This model has been chosen because it allows adequate prediction of the dew points of all the mixtures of our interest in the dew-point temperature and pressure ranges. The second model is an EOS that is based on a modified Peng–Robinson EOS.¹⁶ This equation, which has been developed by the European Gas Research Group (GERG), allows adequate prediction the water dew-point curve in the usual temperature and pressure ranges of importance for natural gas pipelines.

A comparison between experimental and calculated values of the dew-point temperature was performed. The values of dew-point temperature of the vapor phase for the studied systems were calculated by means of the EF–EOS method¹⁵ and the EOS model¹⁶ using the experimental values of pressure and composition that were obtained in the present work.

4.2. Description of the Excess Function–Equation of State (EF–EOS) Model. To represent the VLE 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 EOS.

(2) The excess functions are defined at a 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 “co-volume” b proportional to v^0 , which enables evaluation of the packing fraction η , using the ratio $\eta = b/v$. The packing fractions for the pure components and for the mixture are assumed to be the same; therefore,

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

In regard to the EOS used in the EF–EOS model, for methane, ethane, and water, the translated Peng–Robinson cubic equation of state^{17,18} is used, and for carbon dioxide, an accurate EOS (the IUPAC equation¹⁹) is used, given that the thermodynamic properties of carbon dioxide (such as saturated density) are often represented by cubic equations of state with poor accuracy, especially near the critical point. Instead of improving these equations, we have chosen an accurate EOS—the IUPAC equation¹⁹—that is easy to use, given

its polynomial form, even if the parameters used are numerous.

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

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

As previously mentioned, for methane, ethane, and water, the translated Peng–Robinson cubic equation of state^{17,18} of the form

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

was used. The values of the parameters a and \bar{b} are dependent on the component as follows.

4.2.1. Methane and Ethane. For methane and ethane, the following equation is used for the co-volume, \bar{b} :^{17,18}

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

The attractive parameter a , as a function of the temperature T , is calculated using the equations proposed by Rauzy in 1982:¹⁸

$$a(T) = a_c \left\{ 1 - m_s \left[1 - \left(\frac{T}{T_c} \right)^{0.4450} \right] \right\}^2 \quad (5)$$

where

$$a_c = 0.45724 \left(\frac{R^2 T_c^2}{P_c} \right) \quad (6)$$

and

$$m_s = \frac{\sqrt{a_{eb}/a_c} - 1}{1 - (T_{eb}/T_c)^{0.4450}} \quad (7)$$

4.2.2. Water. For water, eq 4 is used for the calculation of the co-volume \bar{b} , and the equations proposed by Carrier and co-workers^{20,21} are used to calculate the attractive parameter a :

$$a(T) = a_{eb} \left[1 + m_1 \left(1 - \frac{T}{T_{eb}} \right) - m_2 \left(1 - \frac{T}{T_{eb}} \right) \right] \quad (8)$$

The excess function of the EF–EOS model is the residual excess Helmholtz energy (A_{res}^E), which contributes to the molar Helmholtz energy of a mixture (A), as follows:¹⁵

$$A = A^{id} - RT \ln(1 - \eta) - \sum_{i=1}^p \frac{x_i}{b_i} \Psi_i(\eta) + A_{res}^E \quad (9)$$

A_{res}^E can be written by means of a formalism that allows the composition and packing fraction variables to be separated:

$$A_{res}^E = E(T, x) Q(\eta) \quad (10)$$

where $Q(\eta)$ is expressed as¹⁸

$$Q(\eta) = \int_0^\eta \frac{Q'(\eta)}{\eta} d\eta \quad (11)$$

with

$$Q'(\eta) = \frac{\eta}{1 + \gamma\eta} \quad (12)$$

where the value of the γ parameter²² is 20 when the accurate EOS (the IUPAC equation¹⁹) is used as the equation of state of the EF–EOS model. If the translated Peng–Robinson cubic equation of state^{17,18} were to be used, the value of parameter γ would be $2(\sqrt{2} + 1)$.

For the first term on the right-hand side of eq 11, the following equations are used:

(1) For carbon dioxide + water,²³

$$E(T, x) = \frac{1}{2} \sum_{i=1}^p \sum_{j=1}^p \frac{q_i q_j x_i x_j}{q_m} E_{ij}(T) \quad (13)$$

with

$$q_m = \sum_{i=1}^p q_i x_i \quad (14)$$

and

$$q_i = \delta_i b_i \quad (15)$$

where q_m is the mean molecular surface. The value of δ_i in eq 15 for carbon dioxide is the unity, whereas for water, the following equation is used for δ_i :

$$\delta_i = A + BT \quad (16)$$

E_{ij} is calculated using the following equation for carbon dioxide + water binary interactions:²³

$$E_{ij} = \alpha - \beta T \ln T + \lambda T \quad (17)$$

where α , β , and λ are adjusted parameters whose values are taken from Rauzy et al.²³

(2) For carbon dioxide + methane (or ethane), eqs 13–15 are used.²⁴ In eq 13, E_{ij} is calculated by means of a group contribution method as follows:²⁴

$$E_{ij} = - \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl}(T) \quad (18)$$

where α_{ik} is the surface area fraction of group k in molecule i , and N is the number of groups in the solution. In eq 18,

$$A_{kl} = A_{kl}^0 \left[1 + \exp(\alpha_1 I_{hyd} + \alpha_2) \right] \left[\frac{T_0}{T} \right]^r \quad (19)$$

with

$$r = \beta_1 (I_{hyd})^{1.5} + \beta_2 I_{hyd} \quad (20)$$

where I_{hyd} is a parameter that is related to the chain length of the hydrocarbons, and the variables α_1 , α_2 , β_1 , and β_2 are adjusted parameters from Berro et al.²⁴ A_{kl}^0 is a group interaction parameter. The values for A_{kl}^0

Table 4. Value of the Group Interaction Parameter A_{kl}^0 Used in eq 19 for the EF–EOS Model

binary system	A_{kl}^0 (10 ⁶ J m ⁻³)	reference
CO ₂ + CH ₄	253.278	this work
CO ₂ + –CH ₃	442.314	Berro et al. ²⁴

used in this work are presented in Table 4. The value of this parameter for carbon dioxide + –CH₃ is taken from the literature,²⁴ and the value of this parameter for the interchange energy between carbon dioxide and methane was obtained in this work using the experimental VLE results for the carbon dioxide + methane mixture from the literature.^{25–29}

(3) For alkane + water,³⁰

$$E(T, \mathbf{x}) = \frac{1}{2q_m} \left[\sum_{i=1}^p q_i x_i \left(\sum_{j=1}^p q_j x_j K_{ij} \right) + \sum_{i=1}^p q_i x_i \left(\sum_{j=1}^p q_j^{1/3} x_j L_{ji}^{1/3} \right) \right] \quad (21)$$

with

$$q_m = \sum_{k=1}^p q_k x_k \quad (22)$$

and

$$q_k = \delta_k b_k \quad (23)$$

$$K_{ij} = \frac{E_{ij}^1 + E_{ij}^2}{2} \quad (24)$$

$$L_{ij} = E_{ij}^2 + E_{ij}^1 \quad (25)$$

$$L_{ij} = -L_{ji} \quad (26)$$

where the subscripts i and j refer to components i and j of the mixture with p components, and δ_i is an adjusted parameter for each component of the mixture. The values for δ_i used in this work are those of Hocq.³⁰ K_{ij} and L_{ij} are parameters for binary interaction between components i and j , which are calculated from eqs 24–26. The interchange energies, E_{ij}^1 and E_{ij}^2 , are calculated using a group contribution method as follows:³⁰

$$E_{ij}^1 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^1(T) \quad (27)$$

with

$$A_{kl}^1 = {}_1A_{kl}^0 \left(\frac{T^0}{T} \right)^{{}_1B_{kl}^0} \quad (28)$$

and

$$E_{ij}^2 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^2(T) \quad (29)$$

with

$$A_{kl}^2 = {}_2A_{kl}^0 \left(\frac{T^0}{T} \right)^{{}_2B_{kl}^0} \quad (30)$$

where ${}_1A_{kl}^0$, ${}_1B_{kl}^0$, ${}_2A_{kl}^0$, and ${}_2B_{kl}^0$ are group interaction parameters. The values for the group interaction pa-

Table 5. Values of the Group Interaction Parameters ${}_1A_{kl}^0$, ${}_1B_{kl}^0$, ${}_2A_{kl}^0$, and ${}_2B_{kl}^0$ Used in eqs 28 and 30 for the EF–EOS Model

component	Value (10 ⁶ J m ⁻³)		
	CH ₄	C ₂ H ₆	H ₂ O
	${}_1A_{kl}^0$		
CH ₄	0 ^a		
C ₂ H ₆	7.860 ^b	0 ^a	
H ₂ O	1279.540 ^a	1288.287 ^a	0 ^a
	${}_1B_{kl}^0$		
CH ₄	1 ^a		
C ₂ H ₆	2.340 ^a	1 ^a	
H ₂ O	–0.726 ^a	–1.560 ^a	1 ^a
	${}_2A_{kl}^0$		
CH ₄	0 ^b		
C ₂ H ₆	7.860 ^b	0 ^b	
H ₂ O	6234.785 ^c	5946.637 ^c	0 ^b
	${}_2B_{kl}^0$		
CH ₄	1 ^a		
C ₂ H ₆	2.340 ^a	1 ^a	
H ₂ O	1.476 ^d	0.390 ^d	1 ^d

^a From ref 30. ^b From ref 31. ^c From ref 4. ^d From ref 32.

rameters used for comparison calculations in this work are taken from the literature^{4,30–32} and are presented in Table 5.

4.3. Description of the Equation of State (EOS) Model. The EOS model used in this work is based on a modified Peng–Robinson EOS, which is used to obtain a good description of the vapor pressure of ice and liquid water.¹⁶

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

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \quad (31)$$

with

$$b(T) = b(T_c) \quad (32)$$

and

$$a(T) = a(T_c) \alpha(T_r, \omega) \quad (33)$$

where

$$a^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \quad (34)$$

and

$$\kappa = 0.374640 + 1.54226\omega - 0.26992\omega^2 \quad (35)$$

The modification of the Peng–Robinson equation, for water, is made using the following equation:¹⁶

$$\alpha^{1/2} = A_0 + A_1(1 - T_r^{1/2}) + A_2(1 - T_r^{1/2})^2 + A_3(1 - T_r^{1/2})^4 \quad (36)$$

where different values for coefficients A_0 , A_1 , A_2 , and A_3 are used for $T > 273.15$ K and for $T < 273.15$ K (see Table 6). For the attractive parameter a and the co-volume b , in the case of mixtures, classical mixing rules are used.

For the calculation of the binary interaction parameter (k_{ij}) between the components of the mixtures, the

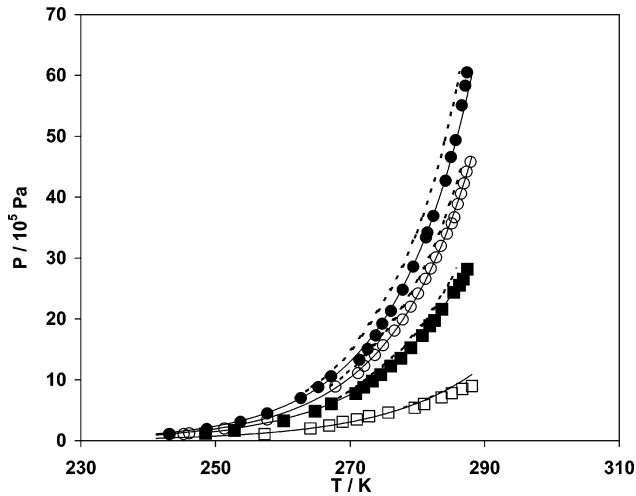


Figure 2. Comparison between experimental dew points (symbols) and dew points calculated with the EF-EOS method (solid line) and with the EOS model (dotted line) for {mixture 1 + $\bar{\rho}_{\text{water}}$ } systems: (●) $\bar{\rho}_{\text{water}} = 272.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$; (○) $\bar{\rho}_{\text{water}} = 343.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$; (■) $\bar{\rho}_{\text{water}} = 478.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$; and (□) $\bar{\rho}_{\text{water}} = 1329.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$.

Table 6. Values of the Coefficients A_0 , A_1 , A_2 , and A_3 Used in the EOS Model, for Various Temperature Ranges^a

coefficient	Value	
	223.15 K \leq T < 273.15 K	273.15 K \leq T \leq 313.15 K
A_0	0.77404	1
A_1	1.58484	0.90544
A_2	0	-0.21378
A_3	-2.28241	0.26

^a From ref 16.

Table 7. Values of the Binary Interaction Parameters $k_{ij,0}$ and $k_{ij,1}$ Used in eq 37 for the EOS Model^a

component	Value			
	H ₂ O	CO ₂	CH ₄	C ₂ H ₆
	$k_{ij,0}$			
H ₂ O	0			
CO ₂	0.1840	0		
CH ₄	0.6510	0.0919	0	
C ₂ H ₆	0.6350	0.1322	-0.0026	0
	$k_{ij,1}$			
H ₂ O	0			
CO ₂	0.2360	0		
CH ₄	-1.3850	0	0	
C ₂ H ₆	-0.9300	0	0	0

^a From ref 16.

following temperature-dependent equation must be used:¹⁶

$$k_{ij}(T) = k_{ij,0} + k_{ij,1} \left(\frac{T}{273.15 \text{ K}} - 1 \right) \quad (37)$$

Values for the binary interaction parameters $k_{ij,0}$ and $k_{ij,1}$ used in this work are taken from the literature¹⁶ and are given in Table 7.

5. Discussion

In this work, the dew points of ternary methane (or ethane) + carbon dioxide + water systems have been studied.

The experimental dew-point data and the dew points calculated with the EF-EOS method and with the EOS model are represented in Figures 2–5.

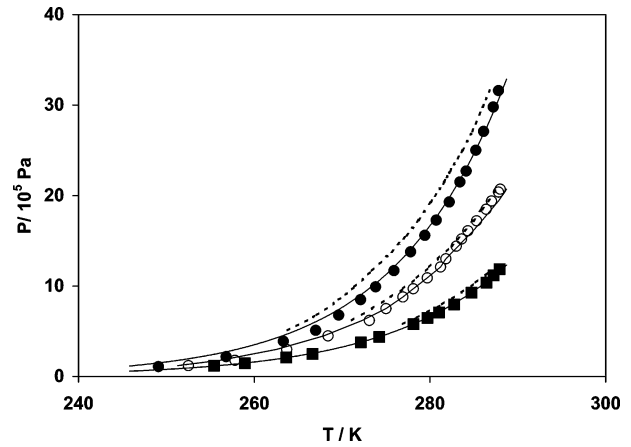


Figure 3. Comparison between experimental dew points (symbols) and dew points calculated with the EF-EOS method (solid line) and with the EOS model (dotted line) for {mixture 2 + $\bar{\rho}_{\text{water}}$ } systems: (●) $\bar{\rho}_{\text{water}} = 439.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$; (○) $\bar{\rho}_{\text{water}} = 677.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$; and (■) $\bar{\rho}_{\text{water}} = 1123.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$.

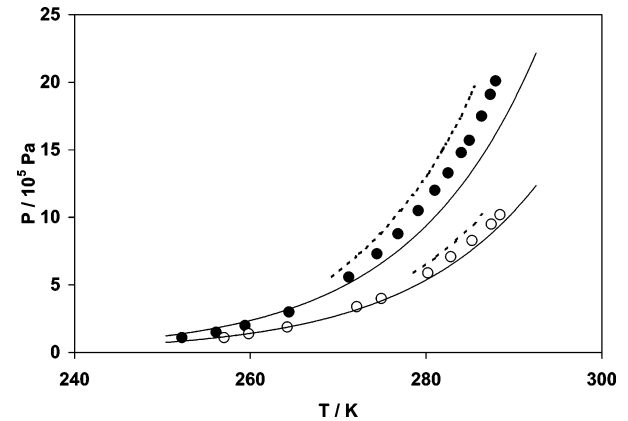


Figure 4. Comparison between experimental dew points (symbols) and dew points calculated with the EF-EOS method (solid line) and with the EOS model (dotted line) for {mixture 3 + $\bar{\rho}_{\text{water}}$ } systems: (●) $\bar{\rho}_{\text{water}} = 661.5 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and (○) $\bar{\rho}_{\text{water}} = 1274.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$.

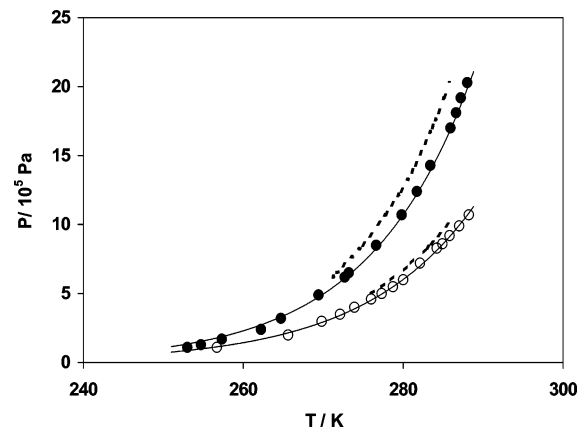


Figure 5. Comparison between experimental dew points (symbols) and dew points calculated with the EF-EOS method (solid line) and with the EOS model (dotted line) for {mixture 4 + $\bar{\rho}_{\text{water}}$ } systems: (●) $\bar{\rho}_{\text{water}} = 728.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and (○) $\bar{\rho}_{\text{water}} = 1285.2 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$.

The AAD values obtained for each dew-point curve are presented in Table 8. Comparing the experimental and calculated values of the dew-point temperature, it can be concluded that both theoretical methods used in

Table 8. Experimental Water Content for the {Methane (or Ethane) + Carbon Dioxide + $\bar{\rho}_{\text{water}}$ } Systems, Experimental Ranges of Dew-Point Temperatures and Pressures for the {Methane (or Ethane) + Carbon Dioxide + $\bar{\rho}_{\text{water}}$ } Mixtures, and AAD Values for the EF–EOS Model and the EOS Model for the Measured Dew-Point Curves

$\bar{\rho}_{\text{water}}$ (10 ⁻⁶ kg m ⁻³ (n))	temp range (K)	pressure range (10 ⁵ Pa)	AAD (K)	
			EF–EOS	EOS
Mixture 1				
272.7	243.1–287.4	1.1–60.5	0.3	1.6
343.9	245.3–287.9	1.1–45.8	0.2	1.2
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
Mixture 2				
439.4	249.1–287.8	1.1–31.6	0.8	2.0
677.7	252.5–288.0	1.2–20.7	0.5	0.9
1123.9	255.4–287.9	1.2–11.9	0.1	1.1
Mixture 3				
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
Mixture 4				
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

this work adequately reproduce the experimental dew-point data. As it has been explained previously, the calculated values for dew-point temperatures with both theoretical models are obtained using the experimental values of pressure and composition obtained in this work.

The EF–EOS model predicts the dew-point temperature within an AAD range of 0.1–2.1 K for methane (or ethane) + carbon dioxide + water mixtures. No influence of water content or of temperature and pressure is observed for the obtained values of deviations.

The EOS model reproduced experimental dew-point temperature data within an AAD range of 0.9–2.1 K. No influence of water content or of temperature and pressure is observed for the obtained values of deviations between the experimental and calculated dew-temperature data. This model systematically calculates lower values for the dew-point temperature than those experimentally obtained for the studied mixtures.

The EF–EOS method used allows proper prediction of the water dew points of the ternary systems in the studied temperature and pressure ranges. In previous works, good results were obtained with this model for the prediction of the dew points of SNG, SNG + water mixtures, and SNG + water + methanol mixtures with low and high carbon dioxide concentrations.³³ The EF–EOS model uses a group contribution model; therefore, the calculation of binary interaction parameters from binary experimental data is not necessary. The latter and the fair results obtained with the EF–EOS model in this work and in previous works^{7,8,33–35} make the EF–EOS model very useful to predict the dew point of hydrocarbon, water, and water + methanol mixtures of

(34) Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otin, S. Thermodynamic Properties of Synthetic Natural Gases. 1. Dew-Point Curves of Synthetic Natural Gases and Their Mixtures with Water and Methanol. Measurement and Correlation. *Ind. Eng. Chem. Res.* **2002**, *15*, 3714–3721.

(35) Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otin, S. Thermodynamic Properties of Synthetic Natural Gases. Part 3. Dew Point Curves of Synthetic Natural Gases and Their Mixtures with Water. Measurement and Correlation. *Energy Fuels* **2003**, *17*(2), 338–343.

real natural gases with high or low contents of carbon dioxide, provided that binary experimental data for all components of the so-called C₆+ fraction are not always available.

List of Symbols

a = equation of state (EOS) attractive energy parameter (Pa m⁶ mol⁻²)

A = molar Helmholtz energy (J mol⁻¹)

A = coefficient in the EOS model

A_{kl}, B_{kl} = group interaction parameters in the EF–EOS model.

AAD = absolute average deviation (K)

b = co-volume; equation of state (EOS) size parameter (m³ mol⁻¹)

\bar{b} = pseudo co-volume (m³ mol⁻¹)

c_{ij} = parameters of the accurate equation of state (EOS), the IUPAC equation

E_{ij} = terms of the interchange energy between carbon dioxide and water (J m⁻³)

k_{ij} = binary interaction coefficients in the EOS model

K_{ij}, L_{ij} = binary interaction parameter in EF–EOS model

m_1, m_2 = parameters used for the calculation of a for polar molecules

m_s = parameter used for the calculation of a for methane and ethane

N = for calculating AAD, number of dew points that constitute a dew-point curve

p = number of components in the mixture

P = pressure (Pa)

q = molecular surface area (m²)

Q = integral of $Q(\eta)/\eta$ between 0 and η

Q = a packing fraction function

R = gas constant (8.314 J mol⁻¹ K⁻¹)

T = temperature (K)

T^0 = reference temperature (298.15 K)

v = molar volume (m³ mol⁻¹)

v^0 = molar close-packed volume (m³ mol⁻¹)

\bar{v} = molar pseudo volume (m³ mol⁻¹)

x = molar fraction

z = compressibility factor

Greek Symbols

α = function of the acentric factor and the reduced temperature in EOS model

α, β, λ = adjusted parameters in the EF–EOS model

γ = constant of the function $Q(\eta)$

δ = adjustable parameter; proportionality coefficient between the surface measure (q) and the co-volume (v)

η = packing fraction

κ = function of the acentric factor in the EOS model

ρ = mass of carbon dioxide per unit of volume (g cm⁻³)

$\bar{\rho}_{\text{water}}$ = experimental mean value of water content (10⁻⁶ kg m⁻³(n))

$\bar{\rho}_{\text{methanol}}$ = experimental mean value of methanol content (10⁻⁶ kg m⁻³(n))

Ψ = function of the packing fraction

ω = acentric factor

Subscripts

c = critical value

eb = value at normal vaporization temperature

i, j = refers to components i, j

k, l = refers to groups k, l
 n = refers to a point of a dew-point curve in the calculation of AAD
 r = reduced value
 res = residual

Superscripts

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

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Appendix

For comparison between calculated and experimental dew-point temperatures for each studied dew-point curve, we use the deviation

$$AAD = \frac{1}{N} \sum_{n=1}^N |T_n^{\text{exp}} - T_n^{\text{cal}}|$$

where N is the number of dew points that constitute a dew-point curve.

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