

Dew points of quaternary ethane + carbon dioxide + water + methanol mixtures — Measurement and modelling

C. Jarne, S.T. Blanco, S. Avila, C. Berro, S. Otín, and I. Velasco

Abstract: Dew points have been measured for eight ethane + carbon dioxide + water + methanol mixtures at pressures from 0.11 to 2.17 MPa and temperatures from 249.0 to 288.7 K. The results are 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 can be used to adequately predict the dew points of the mixtures in the temperature and pressure ranges used in the present study. In fact, the model reproduces the experimental dew point temperature data with ≤ 3.1 K average absolute deviation.

Key words: dew point, equation of state, excess function.

Résumé : On a mesuré les points de rosée de huit mélanges d'éthane + dioxyde de carbone + eau + méthanol, à des pressions allant de 0,11 à 2,17 MPa et à des températures allant de 249,0 à 288,7 K. On a analysé les résultats en termes d'une méthode basée sur une équation d'état de fonction d'excès permettant de faire des prédictions basées sur l'approximation zéro du modèle réticulaire de Guggenheim. On peut utiliser cette méthode pour prédire adéquatement les points de rosée de mélanges dans les plages de température et de pression utilisées dans la présente étude. En fait, le modèle permet de reproduire les données expérimentales de points de rosée avec une déviation absolue moyenne de moins de 3,1 K.

Mots clés : point de rosée, équation d'état, fonction d'excès.

[Traduit par la Rédaction]

Introduction

To investigate the influence of carbon dioxide, water, methanol and heavy hydrocarbons on the vapour-liquid equilibrium (VLE) of natural gas within the usual pressure and temperature conditions of natural gas transported by pipeline, we have previously studied the following systems: carbon dioxide + water and carbon dioxide + water + methanol (1), methane + carbon dioxide + water (2), ethane + carbon dioxide + water (2) and methane + carbon dioxide + water + methanol (3). Dew point data for the quaternary ethane + carbon dioxide + water + methanol system, which are not available in the literature, are reported in the present work. In addition, we have developed a theoretical model for dew point prediction.

A water + methanol dew point generation device was built and tested in previous studies (4, 5). The results for eight ethane + carbon dioxide + water + methanol mixtures at pressures from 0.11 to 2.17 MPa and temperatures from 249.0 to 288.7 K are presented here. The experimental results obtained for the quaternary mixtures are analysed in

terms of a predictive excess-function equation of state (EF-EOS) method based on the zero-order approximation of Guggenheim's reticular model, which reproduces the experimental dew point temperature data with an average absolute deviation (AAD) less than or equal to 3.1 K.

Experimental procedure

The experimental method used in this work is based on the generation of gases saturated with water and methanol by condensation of these components in a temperature-controlled condenser with continuous gas flow at specified pressures.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The gas supply bottles that contain ethane + carbon dioxide mixtures (Table 1) were prepared by weight by Abello-Linde (6). After controlled expansion (RV1), the gas from the ethane + carbon dioxide bottle was saturated with water and methanol vapour by flowing the gas through a saturator containing a liquid mixture of water and methanol at laboratory temperature (TI1). The temperature of con-

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Fig. 1. Schematic diagram of the experimental apparatus used in this work. Control valve (RV), ball valve (V), three-way valve (HV), temperature measurement (TI), pressure measurement (PI), water content analyser (QI), volume measurement (XI).

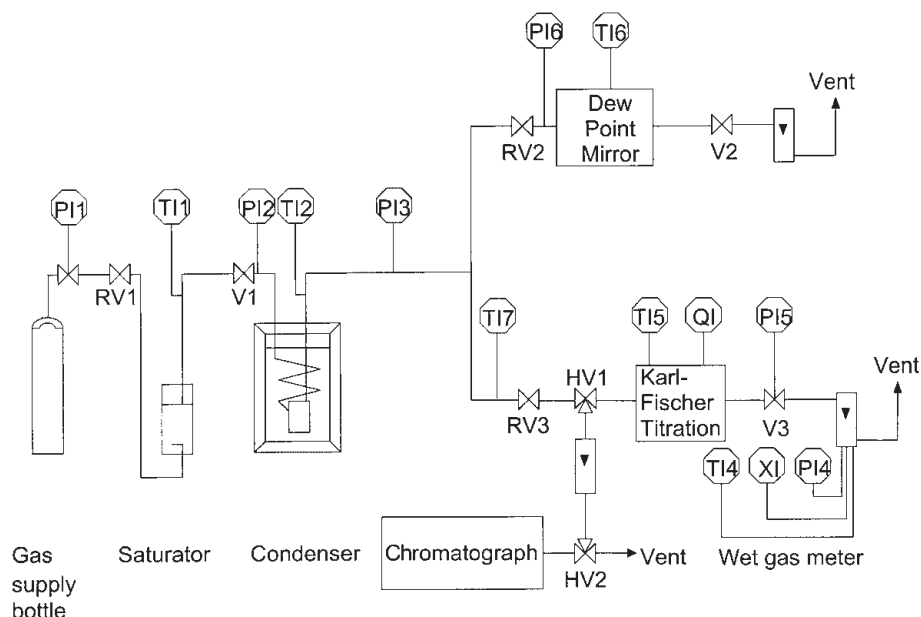


Table 1. Composition of ethane + carbon dioxide mixtures and relative accuracy specified by the supplier.

Component	Gas 1 (%)	Gas 2 (%)
Ethane	55±1	5±1
Carbon dioxide	45±1	95±1

densation of water and methanol was then achieved in a stainless-steel condenser, which was 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 and methanol contents in the gas phase of the generated VLE are obtained at the outlet of the condenser using the Karl Fischer titration (7) for water content and by gas chromatographic analysis for methanol content.

The dew point values for the ethane + carbon dioxide + water + methanol mixtures were measured by means of a chilled mirror instrument. The input pressure (PI6) of the gas in the chilled-mirror instrument was set using a regulator valve (RV2). When the apparatus reached a stable dew point temperature (TI6), both the pressure and temperature were 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 to measure the water content (0.2% accuracy); a HP 5890 gas chromatograph fitted with a Haysep Q column and a thermal conductivity detector to measure the methanol content; a MBW dew point instrument (model DP3-D-HP-K2) to measure the dew point temperatures. The cooling of the mirror as achieved by a cascaded-element Peltier cooling unit and the dew-point mirror temperature was opto-electronically controlled; a pressure transmitter to measure the dew point pressures (max error of 0.1%).

Prior to the study of ethane + carbon dioxide + water + methanol mixtures, the precision of the dew point measurements was determined as described previously (4, 5).

Results

We calculated the dew-point curves for gas 1 and gas 2 (Table 1) using the Peng–Robinson equation of state (8). The experimental dew points for the quaternary systems range from 0.11 to 2.17 MPa at temperatures from 249.0 to 288.7 K to avoid the presence of liquid ethane and carbon dioxide in the apparatus.

The water and methanol mol fractions and the dew point temperatures and pressures for the quaternary systems are collected in Table 2.

As shown in Table 2 for ethane + carbon dioxide + water + methanol mixtures with the same ethane and carbon dioxide contents and similar water mol fractions (such as gas 1 + 0.00048 water mol fraction + 0.0033 methanol mol fraction and gas 1 + 0.00040 water mol fraction + 0.0086 methanol mol fraction), increasing the methanol mol fraction in the mixture leads to an increase of the dew point temperature at a given pressure.

For the quaternary mixtures with the same ethane and carbon dioxide contents and similar methanol mol fractions (such as gas 1 + 0.00029 water mol fraction + 0.0049 methanol mol fraction and gas 1 + 0.00083 water mol fraction + 0.0053 methanol mol fraction), increasing the water content also increases the dew point temperature at a given pressure.

On the other hand, the dew point curve of gas 2 is on the right hand side of that of gas 1 in the pressure–temperature diagram. However, if we consider the mixtures gas 1 + 0.00040 water mol fraction + 0.0086 methanol mol fraction and gas 2 + 0.00044 water mol fraction + 0.0083 methanol mol fraction, we observe that, for a given pressure, the values of the dew temperatures are practically the same for the

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

T (K)	P (10^5 Pa)	T (K)	P (10^5 Pa)
<i>Gas 1: $\bar{x}_{\text{water}} = 0.00029$ and $\bar{x}_{\text{methanol}} = 0.0049$</i>			
249.0	1.1	278.6	9.7
251.3	1.3	281.8	12.3
255.6	1.9	284.1	14.6
261.0	2.8	284.7	15.2
266.1	4.0	286.4	17.2
270.3	5.5	287.3	18.3
273.9	7.1	287.9	19.1
276.4	8.4	288.6	20.0
<i>Gas 1: $\bar{x}_{\text{water}} = 0.00040$ and $\bar{x}_{\text{methanol}} = 0.0086$</i>			
255.3	1.1	277.1	4.8
256.2	1.2	281.3	6.3
262.6	1.8	284.1	7.6
265.9	2.3	287.3	9.3
271.1	3.2	288.6	10.1
275.0	4.2		
<i>Gas 1: $\bar{x}_{\text{water}} = 0.00048$ and $\bar{x}_{\text{methanol}} = 0.0033$</i>			
249.3	1.1	278.9	10.7
252.0	1.4	280.1	11.9
259.5	2.5	281.4	13.1
260.5	2.7	282.5	14.0
265.2	3.9	283.7	15.7
269.4	5.3	284.8	16.9
271.7	6.3	285.5	17.9
273.9	7.4	286.6	19.4
276.1	8.8	287.3	20.5
277.3	9.6	288.1	21.7
<i>Gas 1: $\bar{x}_{\text{water}} = 0.00083$ and $\bar{x}_{\text{methanol}} = 0.0053$</i>			
255.1	1.1	280.8	7.0
261.7	1.8	283.2	8.3
266.7	2.6	284.2	9.0
271.6	3.7	285.9	10.1
273.9	4.4	287.6	11.1
276.9	5.4	288.2	11.6
279.4	6.4		
<i>Gas 2: $\bar{x}_{\text{water}} = 0.00035$ and $\bar{x}_{\text{methanol}} = 0.0047$</i>			
249.6	1.1	278.9	9.9
257.3	2.0	282.1	12.5
263.3	3.2	282.9	13.3
267.1	4.2	284.7	15.3
269.7	5.1	286.1	17.0
272.0	6.0	287.2	18.7
274.4	7.1	288.5	21.0
<i>Gas 2: $\bar{x}_{\text{water}} = 0.00044$ and $\bar{x}_{\text{methanol}} = 0.0083$</i>			
255.9	1.1	280.9	6.1
259.3	1.4	282.9	7.0
263.9	1.9	285.5	8.2
268.0	2.6	287.2	9.2
272.2	3.4	288.7	10.1
277.2	4.8		
<i>Gas 2: $\bar{x}_{\text{water}} = 0.00057$ and $\bar{x}_{\text{methanol}} = 0.0034$</i>			
250.4	1.1	279.9	10.6

Table 2 (concluded).

T (K)	P (10^5 Pa)	T (K)	P (10^5 Pa)
250.9	1.1	281.5	12.0
256.8	1.8	284.1	14.7
260.8	2.4	285.1	16.1
266.8	3.9	286.0	17.1
270.6	5.2	286.9	18.2
274.2	6.9	287.8	20.0
276.3	8.0	288.3	20.9
<i>Gas 2: $\bar{x}_{\text{water}} = 0.00086$ and $\bar{x}_{\text{methanol}} = 0.0056$</i>			
255.4	1.2	281.5	7.3
262.7	1.8	283.0	8.1
267.1	2.6	284.8	9.3
268.9	3.0	286.0	10.1
273.2	4.1	287.3	11.0
276.0	5.0	288.2	11.7
279.0	6.1		

two quaternary mixtures. Therefore, it seems that the values of dew temperature and pressure for the quaternary mixtures are more sensitive to the water and methanol content than to the ethane and carbon dioxide content. Similar results were found for methane + carbon dioxide + water + methanol mixtures in an earlier work (3).

In a previous study (2), the dew points of ethane + carbon dioxide + water mixtures were studied. When comparing the results from the present work for ethane + carbon dioxide + water + methanol with the results of the previous study (2) for mixtures with the same ethane, carbon dioxide, and water content, we found that the presence of methanol in the mixtures leads to a displacement of the dew point curves to higher values of dew point temperature and pressure. This is observed for gas 1 + 0.00083 water mol fraction + 0.0053 methanol mol fraction (Table 2), gas 1 + 0.00082 water mol fraction (2), gas 2 + 0.00086 water mol fraction + 0.0056 methanol mol fraction (Table 2) and gas 2 + 0.00091 water mol fraction (2). At a given pressure, the difference between the dew temperature values of the mixture with methanol and without methanol are up to 7 K.

Discussion

As mentioned earlier, this work is part of a program of research investigating the influence of carbon dioxide, water, methanol, and heavy compounds of natural gases on the VLE of natural gas. Therefore, the ranges of dew temperature and pressure are studied within the typical ranges for natural gas transmission through pipelines, which means temperatures from 249 to 288 K and pressures up to 10 MPa. Although classical models such as UNIQUAC (9), DISQUAC (10), or modified UNIFAC (11) allow the prediction of vapour-liquid equilibria at low pressures for systems that contain polar compounds, they are not suitable for the present work. Instead, we use in this work the EF-EOS model, which is based on the zeroth-order approximation of Guggenheim's quasi-reticular model. In the EF-EOS model, which is an extension of the development originally presented by Vidal (12), the connection between excess functions and equations of state is established by equating excess

functions derived from Guggenheim’s quasi-lattice theory to expressions derived from equations of state (13).

A comparison between experimental and calculated dew point temperatures was carried out. The values of dew temperature for the system investigated were calculated by means of the EF-EOS method (13) using the experimental values of pressure and composition obtained in the present work.

The EF-EOS model has been chosen because it can be used to adequately predict the dew points of all the mixtures of present interest in the temperature and pressure ranges. The model satisfies two important conditions: (1) the Helmholtz energies of the pure components are calculated by an equation of state; (2) the excess functions are defined at a constant packing fraction described by v^0/v , where v^0 is 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 allows the evaluation of the packing fraction η by the ratio $\eta = b/v$. The packing fraction for the pure components and for the mixture is assumed to be the same, which means that the lattice on which the pure components are placed undergoes no distortion during the mixing process.

Regarding the EOS used in the EF-EOS model, given that the thermodynamic properties of carbon dioxide, such as saturation density, are often represented by cubic equations of state with poor accuracy, we have used for this component the more accurate IUPAC equation of state (14).

For ethane, water, and methanol, the translated Peng–Robinson cubic equation of state is used (13, 15). The name for this equation is due to the use of a translated molar volume \bar{v} called the pseudo-molar volume (16) instead of the molar volume as for the Peng–Robinson cubic equation of state.

$$[1] \quad P = \frac{RT}{\bar{v} - \bar{b}} - \frac{a(T)}{\bar{v}(\bar{v} + \gamma\bar{b})}$$

where P and T are the system pressure and temperature, R is the gas constant, \bar{b} is the pseudo-co-volume, and γ is a constant. For ethane, the equations proposed by Rauzy (15) are used to calculate a , and for \bar{b} , the equations proposed by P  neloux et al. (13) and Rauzy (15) are used.

For water and methanol, the attractive parameter a is calculated using the equations taken from Carrier et al. (16) and Carrier (17). For the pseudo co-volume \bar{b} , the equations used are those of P  neloux et al. (13) and Rauzy (15).

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

$$[2] \quad A = A^{\text{id}} - RT \ln(1 - \eta) - \sum_{i=1}^p \frac{x_i}{b_i} \psi_i(\eta) + A_{\text{res}}^E$$

where A^{id} is the ideal mixture molar Helmholtz energy, b_i is the molar co-volume for the component i , $\psi_i(\eta)$ is a function of the packing fraction, and x_i is the molar fraction for component i in the mixture. The residual excess Helmholtz energy (A_{res}^E) is a function in which composition x and packing fraction η are separated variables

Table 3. Values for E_{ij}^0 and r used in this work (eq. [6]).

Binary	E_{ij}^0 (J cm ⁻³)	r
CO ₂ + CH ₃ OH	673.15	-1.319
H ₂ O + CH ₃ OH	253.20	-3.068

$$[3] \quad A_{\text{res}}^E(T, x, \eta) = E(T, x) \int_0^\eta (Q'(\eta)/\eta) d\eta$$

where $Q'(\eta)$ is a function of the packing fraction.

For the first factor on the right-hand side of eq. [3], different equations are used depending on the binary interaction that is present in the mixture. For binary interactions between carbon dioxide and water, carbon dioxide and methanol, carbon dioxide and ethane, and water and methanol (18), we used

$$[4] \quad E(T, x) = \frac{1}{2} \sum_{i=1}^p \sum_{j=1}^p \frac{q_i q_j x_i x_j}{q_m} E_{ij}(T)$$

where the subscripts i and j refer to the components i and j of the mixture with p components, q_i is the molecular surface of the component i , q_m is the mean molecular surface, and E_{ij} is the interaction energy between components i and j . E_{ij} is calculated using the following equation for binary interactions between carbon dioxide and water (18)

$$[5] \quad E_{ij} = \alpha - \beta T \ln(T) + \lambda T$$

where $\alpha = 5018.172$ J cm⁻³, $\beta = 13.645$ J cm⁻³ K⁻¹, and $\lambda = 102.580$ J cm⁻³ K⁻¹ are adjusted parameters taken from Rauzy and P  neloux (1986) (18).

E_{ij} is calculated for binary interactions between carbon dioxide and methanol, and between water and methanol (18) using

$$[6] \quad E_{ij} = E_{ij}^0 \left[\frac{T^0}{T} \right]^r$$

E_{ij}^0 is the interaction energy at the reference temperature T^0 and r is an adjusted parameter taken from Rauzy and P  neloux (18) and listed in Table 3.

E_{ij} is calculated for binary interactions between carbon dioxide and ethane by means of a group contribution method as follows (19)

$$[7] \quad E_{ij} = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}(T)$$

where the subscripts k and l refer to the groups k and l of the components of the mixture with N groups, α_{ik} is the surface area fraction of group k in molecule i , and A_{kl} is the group interaction parameter between groups k and l taken from ref. 19.

The binary interactions between ethane and water and between ethane and methanol (20) were calculated using

Table 4. Values of the group interaction parameters ${}_1A_{kl}^0$, ${}_1B_{kl}^0$, ${}_2A_{kl}^0$, and ${}_2B_{kl}^0$ used in this work (eqs. [13] and [15]).

Binary	${}_1A_{kl}^0$	${}_1B_{kl}^0$	${}_2A_{kl}^0$	${}_2B_{kl}^0$
C ₂ H ₆ + H ₂ O	1288.287 (20)	-1.56 (20)	5946.637 (21)	0.39 (21)
C ₂ H ₆ + CH ₃ OH	264.046 ^a	0.783 ^a	1272.672 ^a	-0.931 ^a

^aThis work.

$$[8] \quad E(T, x) = \frac{1}{2q_m} \left[\sum_{i=1}^p q_i x_i \left(\sum_{j=1}^p q_j x_j K_{ij} \right) + \sum_{i=1}^p q_i x_i \left(\sum_{j=1}^p q_j^{1/3} x_j L_{ji}^{1/3} \right) \right]$$

where K_{ij} , L_{ij} are binary interaction parameters calculated using the following equations

$$[9] \quad K_{ij} = \frac{E_{ij}^1 + E_{ij}^2}{2}$$

$$[10] \quad L_{ij} = E_{ij}^2 - E_{ij}^1$$

$$[11] \quad L_{ij} = -L_{ji}$$

E_{ij}^1 the interchange energy between components i and j in a binary mixture where the mol fraction of j tends to zero, while E_{ij}^2 is the interchange energy in a binary mixture of i and j where the mol fraction of i tends to zero. E_{ij}^1 and E_{ij}^2 are calculated using a group contribution method as follows (20)

$$[12] \quad E_{ij}^1 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^1(T)$$

with

$$[13] \quad A_{kl}^1 = {}_1A_{kl}^0 \left(\frac{T^0}{T} \right)^{{}_1B_{kl}^0}$$

$$[14] \quad E_{ij}^2 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^2(T)$$

$$[15] \quad A_{kl}^2 = {}_2A_{kl}^0 \left(\frac{T^0}{T} \right)^{{}_2B_{kl}^0}$$

Superscripts 1 and 2 for A_{kl}^1 and A_{kl}^2 have the same meaning as previously explained for E_{ij}^1 and E_{ij}^2 and ${}_1A_{kl}^0$, ${}_1B_{kl}^0$ and ${}_2A_{kl}^0$, ${}_2B_{kl}^0$ are group interaction parameters at the reference temperature T^0 . The values for these parameters are presented in Table 4. The parameters for interchange energies between ethane + water were taken from previous studies (20, 21). In the present work, these parameters for the interchange energy between ethane and methanol are calculated using previously reported vapour-liquid equilibrium data for ethane + methanol mixtures (22–24).

Conclusions

The measured dew point curves and calculated values using the EF-EOS method are presented in Figs. 2–5. Values

Fig. 2. Comparison of measured dew points (symbols) and calculated values using the EF-EOS method (curves) for {Gas 1 + \bar{x}_{water} + $\bar{x}_{\text{methanol}}$ } systems: $\bar{x}_{\text{water}} = 0.00029$, $\bar{x}_{\text{methanol}} = 0.0049$ (●); $\bar{x}_{\text{water}} = 0.00040$, $\bar{x}_{\text{methanol}} = 0.0086$ (○).

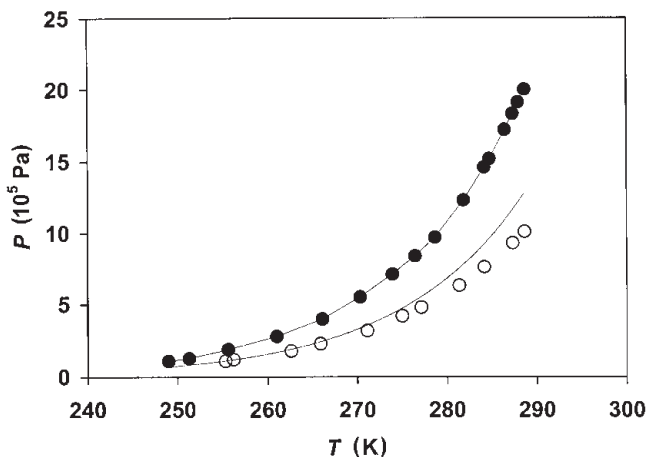
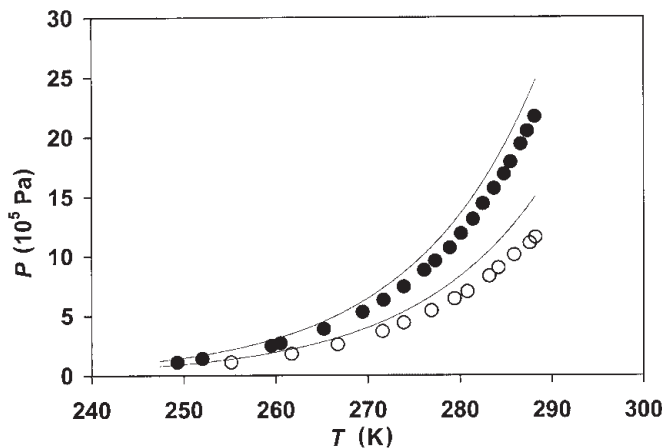


Fig. 3. Comparison of measured dew points (symbols) and calculated values using the EF-EOS method (curves) for {Gas 1 + \bar{x}_{water} + $\bar{x}_{\text{methanol}}$ } systems: $\bar{x}_{\text{water}} = 0.00048$, $\bar{x}_{\text{methanol}} = 0.0033$ (●); $\bar{x}_{\text{water}} = 0.00083$, $\bar{x}_{\text{methanol}} = 0.0053$ (○).



of AAD are calculated using eq. [16] and listed for each dew point curve in Table 5.

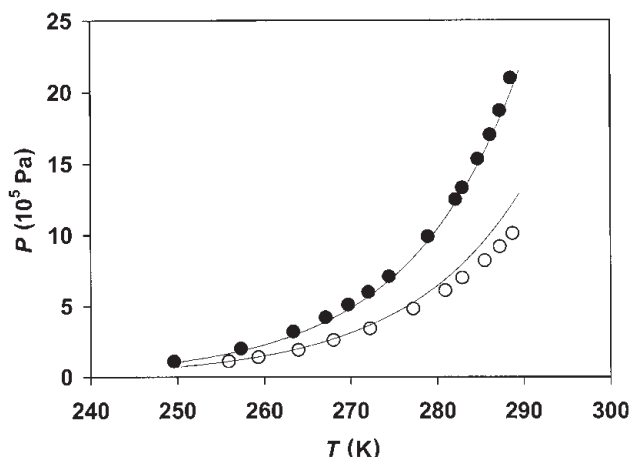
$$[16] \quad \text{AAD} = \frac{1}{N} \sum_{n=1}^N |T_n^{\text{exp}} - T_n^{\text{calc}}|$$

where N is the number of measured dew points that constitute an experimental dew point curve and T is the dew temperature.

Table 5. Water and methanol contents for ethane + carbon dioxide + water (\bar{x}_{water}) + methanol ($\bar{x}_{\text{methanol}}$) systems, experimental ranges of dew temperatures and pressures and values of AAD for the dew point curves.

Ethane + carbon dioxide mixture	\bar{x}_{water}	$\bar{x}_{\text{methanol}}$	T range (K)	P range (10^5 Pa)	AAD (K)
Gas 1	0.000 29	0.0049	249.0–288.6	1.1–20.0	0.0
Gas 1	0.000 40	0.0086	255.3–288.6	1.1–10.1	1.7
Gas 1	0.000 48	0.0033	249.3–288.1	1.1–21.7	2.0
Gas 1	0.000 83	0.0053	255.1–288.2	1.1–11.6	3.0
Gas 2	0.000 35	0.0047	249.6–288.5	1.1–21.0	0.7
Gas 2	0.000 44	0.0083	255.9–288.7	1.1–10.1	1.2
Gas 2	0.000 57	0.0034	250.4–288.3	1.1–20.9	1.9
Gas 2	0.000 86	0.0056	255.4–288.2	1.2–11.7	3.1

Fig. 4. Comparison of measured dew points (symbols) and calculated values using the EF-EOS method (curves) for {Gas 2 + \bar{x}_{water} + $\bar{x}_{\text{methanol}}$ } systems: $\bar{x}_{\text{water}} = 0.000\ 35$, $\bar{x}_{\text{methanol}} = 0.0047$ (●); $\bar{x}_{\text{water}} = 0.000\ 44$, $\bar{x}_{\text{methanol}} = 0.0083$ (○).



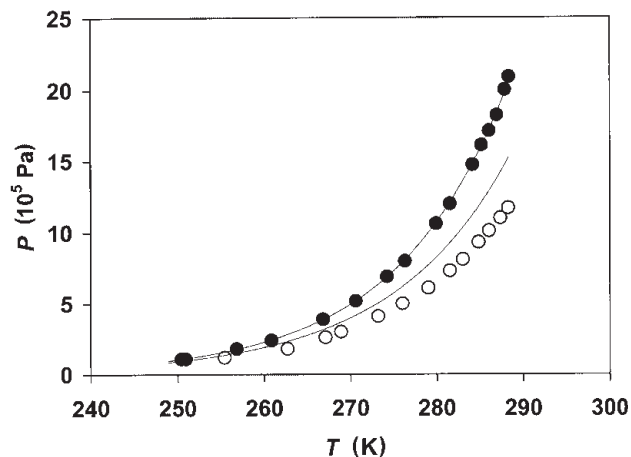
The AAD values for the studied quaternary systems are ≤ 3.1 K. No influence of temperature and pressure is found for the values of the deviations. The good agreement with the predictions obtained in this paper using the EF-EOS method validates this model for the prediction of dew points of the investigated ethane + carbon dioxide + water + methanol mixtures in our work.

Because the EF-EOS model uses a group contribution model, the availability of binary experimental data corresponding to every binary interaction in the mixture is not necessary. In view of this feature and the good results obtained with this model in this work and previous studies (1–3, 25), the EF-EOS model could be used to predict reliable dew points for hydrocarbons, water and water + methanol in real natural gases, even though binary experimental data for all components of the so-called C_6 + fraction are not available.

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Fig. 5. Comparison of measured dew points (symbols) and calculated values using the EF-EOS method (curves) for {Gas 2 + \bar{x}_{water} + $\bar{x}_{\text{methanol}}$ } systems: $\bar{x}_{\text{water}} = 0.000\ 57$, $\bar{x}_{\text{methanol}} = 0.0034$ (●); $\bar{x}_{\text{water}} = 0.000\ 86$, $\bar{x}_{\text{methanol}} = 0.0056$ (○).



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List of symbols

- a equation of state attractive energy parameter ($\text{Pa m}^6 \text{mol}^{-2}$)
- A molar Helmholtz energy (J mol^{-1})
- A_{kl} group interaction parameter between groups k and l (J m^{-3})
- AAD absolute average deviation (K)
- b co-volume; equation of state size parameter ($\text{m}^3 \text{mol}^{-1}$)
- \bar{b} pseudo co-volume ($\text{m}^3 \text{mol}^{-1}$)
- E_{ij} interchange energy (J m^{-3})
- E_{ij}^0 interaction energy at the reference temperature T^0 for binary interactions between carbon dioxide and methanol, and between water and methanol (J m^{-3})
- E_{ij}^1, E_{ij}^2 interchange energy between ethane and water or methanol (J m^{-3})
- K_{ij}, L_{ij} binary interaction parameters for ethane–water and ethane–methanol (J m^{-3})
- N number of groups in a solution

- 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 (m^2); $q_i = \delta_i b_i$ with d_i an adjustable parameter and b_i the co-volume for component i
- Q' a packing fraction function
- r adjusted parameter in the EF-EOS model
- R gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- T temperature (K)
- T^0 reference temperature (298.15 K)
- v molar volume ($\text{m}^3 \text{mol}^{-1}$)
- v^0 molar close packed volume ($\text{m}^3 \text{mol}^{-1}$)
- \bar{v} molar pseudo volume ($\text{m}^3 \text{mol}^{-1}$)
- x mol fraction
- \bar{x}_{water} experimental mean value of the water mol fraction
- $\bar{x}_{\text{methanol}}$ experimental mean value of the methanol mol fraction
- α adjusted parameter in the EF-EOS model (J cm^{-3})
- α_{ik} surface area fraction of group k in molecule i
- β adjusted parameter in the EF-EOS model ($\text{J cm}^{-3} \text{ K}^{-1}$)
- γ constant in the translated PR-EOS
- η packing fraction
- λ adjusted parameter in the EF-EOS model ($\text{J cm}^{-3} \text{ K}^{-1}$)
- Ψ function of the packing fraction

Superscripts and subscripts

- calc calculated
- exp experimental
- E excess property
- id ideal solution property
- i, j referring to components i, j
- k, l referring to groups k, l
- m referring to a mean molecular value
- n referring to a point of a dew point curve in the calculation of AAD
- res residual