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Thermodynamic Properties of Synthetic Natural Gases. 1. Dew-Point Curves of Synthetic Natural Gases and Their Mixtures with Water and Methanol. Measurement and Correlation

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Experimental measurements of dew points for five synthetic natural gas (SNG) mixtures between 1.9×10^5 and 106.0×10^5 Pa in the temperature range from 195.5 to 277.3 K and nine SNG + water + methanol mixtures between 1.4×10^5 and 73.1×10^5 Pa and at temperatures from 237.3 to 288.2 K were determined. The experimental results obtained on the multicomponent systems were analyzed in terms of an equation of state chemical reticular method, which reproduced experimental dew-point temperature data within an absolute average deviation between 0.8 and 3.7 K for the dry systems and from 0.5 to 1.9 K for the systems with water and methanol.

1. Introduction

Methanol is one of the main additives used in natural gas processing and pipeline transport. This chemical is used as a hydrate inhibitor and as a secant after the hydraulic tests of natural gas pipelines. In both applications, methanol is found with water in natural gases. To understand the influence of these two components on the vapor–liquid equilibrium (VLE) of natural gases which contain CO₂, five synthetic natural gases (SNGs) with CO₂ and their mixtures with water and methanol were studied. The compositions of the SNGs used are similar to the natural gas supplied through the Spanish pipeline network.

A water and methanol dew-point-generation experimental apparatus was built and commissioned, and the systems composed of water and methanol and the major components of natural gas were studied.^{1–3} The results on five SNG mixtures between 1.9×10^5 and 106.0×10^5 Pa and at temperatures from 195.5 to 277.3 K and nine SNG + water + methanol mixtures between 1.4×10^5 and 73.1×10^5 Pa and at temperatures from 237.3 to 288.2 K are presented here.

The demand for reliable calculation procedures to estimate these dew points in natural gases is becoming more and more important.⁴ Therefore, the experimental results obtained on the multicomponent systems were analyzed in terms of an equation of state chemical reticular (EOS-CR) method, which reproduced experimental dew-point temperature data within an absolute average deviation (AAD) between 0.8 and 3.7 K for SNGs and from 0.5 to 1.9 K for SNG + water + methanol mixtures.

2. Experimental Procedure

The experimental dew point ranged from 1.4×10^5 to 106.0×10^5 Pa at temperatures from 195.5 and 288.2

K. The five SNGs used in this work were prepared according to the gravimetric method (International Standard ISO 6142, 1981),⁵ by Air Liquide and Abelló-Linde. The compositions of these SNGs and their accuracies specified by the supplier are listed in Table 1.

The dew-point-generation apparatus used for our experimental data collection was built in a previous work.⁶ The experimental method used for this work is based on the generation of saturated gases with water and methanol by condensation of these compounds in a temperature-controlled condenser with continuous gas flow at specified pressures.

After controlled expansion, the gas is saturated with water and methanol vapor by flowing through a liquid mixture of these compounds in an isolated saturator held at laboratory temperature. The temperature of condensation of water and methanol is then achieved in one stainless steel condenser, which is located in a thermostat bath set at the desired equilibrium temperature. The concentration of water in the gas is measured at the outlet of the dew-point-generation system, using a Karl–Fischer titration, according to the standard method⁷ at atmospheric pressure. The concentration of methanol is determined by gas chromatography analysis. By doing so, the reference values for the contents of water and methanol in the gaseous phase are obtained.

The dew-point values of the SNGs and of SNG + water + methanol mixtures are measured by means of a chilled mirror instrument.⁸ The input pressure of the gas to the chilled mirror instrument is set using a regulator valve. When the apparatus reaches a stable value of dew-point temperature, both the pressure and temperature are recorded. In this way, the values of the temperature and pressure of the dew-point curve of the mixture generated are obtained.

The following instrumentation is used to analyze the contents of water and methanol and to carry out the dew-point measurements:

(i) Mitsubishi CA 06 Karl–Fischer titrator. Coupled with an Elster wet gasmeter type Gr. 00, E51, 0.2% accuracy.

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Table 1. Composition of SNGs (% mol) and Absolute or Relative Accuracy Specified by the Supplier

	gas 1	gas 2	gas 3	gas 4	gas 5
nitrogen	0.618 ± 2%	0.313 ± 2%	2.80 ± 0.06	6.90 ± 0.14	5.651 ± 1%
CO ₂	0.187 ± 2%	0.202 ± 2%	0.20 ± 0.01	0.51 ± 0.01	0.284 ± 2%
methane	the rest	the rest	the rest	the rest	the rest
ethane	0.082 ± 2%	8.038 ± 1%	0.18 ± 0.01	2.72 ± 0.06	7.526 ± 1%
propane	0.065 ± 2%	0.801 ± 2%	0.1029 ± 0.0020	0.85 ± 0.02	2.009 ± 2%
isobutane	0.050 ± 2%	0.081 ± 2%	0.0499 ± 0.0010	0.17 ± 0.01	0.305 ± 2%
<i>n</i> -butane		0.123 ± 2%	0.0095 ± 0.0002	0.32 ± 0.01	0.520 ± 2%
isopentane	0.017 ± 2%	0.010 ± 2%	0.0166 ± 0.0004	0.0850 ± 0.0020	0.120 ± 2%
<i>n</i> -pentane		0.0079 ± 2%		0.0940 ± 0.0020	0.144 ± 2%
<i>n</i> -hexane	0.032 ± 2%	0.0047 ± 2%	0.0160 ± 0.0004	0.119 ± 0.003	0.068 ± 2%
<i>n</i> -heptane	0.0027 ± 2%	0.0011 ± 2%	0.0054 ± 0.0003	0.0258 ± 0.0006	0.0138 ± 2%
<i>n</i> -octane	0.0033 ± 2%		0.0038 ± 0.0002	0.0180 ± 0.0004	0.011 ± 2%

(ii) HP 5890 gas chromatograph fit up with a Haysep Q column and thermal conductivity detector.

(iii) MBW dew-point instrument model DP3-D-HP-K2. The cooling of the mirror is achieved by cascaded Peltier elements, and the dew-point mirror temperature is optoelectronically controlled. The uncertainty in the dew-point temperature is better than ±0.1 K.

(iv) Pressure transmitter with a maximum error of 0.1% in the calibrated range.

Prior to this study of SNG and SNG + water + methanol dew points, the precision of both analytical methods and experimental procedures was determined.⁹

3. Results

The dew-point curves of the five SNGs, the water and methanol contents in the vapor phase, and the dew-point curves of the mixtures generated at the dew-point-generation system were determined, and the results of the experiments are collected in Table 2.

4. Theory

Introduction. Classical models such as UNIQUAC or NRTL allow the prediction of the VLE at low pressures for systems which contain one self-associating compound such as methanol, but these models are not suited for high-pressure calculations.¹⁰

In this work the EOS-CR model derived from the excess function equations of state model¹¹ and founded on the zeroth approximation on the quasi-reticular model is used. Other simpler models such as the Peng–Robinson EOS calculates properly the dew-point curves of the SNGs studied, but binary data are required to calculate the interaction parameters. In the EOS-CR model, these parameters can be calculated using a group contribution method. This makes it possible to predict dew-point curves of real natural gases. This is important because binary experimental data for all of the components of the so-called C₆+ fraction do not always exist. This work is part of research which aims to study SNGs, SNG + water, and SNG + water + methanol mixtures. The EOS-CR method used in this work has been chosen because it allows one to calculate properly the dew-point curves of these different systems.

To evaluate this method 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-point temperature of the vapor phase for the studied systems are calculated by means of the EOS-CR method using the experimental values of pressure and composition obtained in the present work. The values of the AAD

obtained after the comparison are between 0.8 and 3.7 K for SNGs and from 0.5 to 1.9 K for SNG + water + methanol mixtures.

Description of the VLE Model. To represent the VLE of 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 a constant packing fraction; the latter is described by v^0/v , with 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 one to evaluate the packing fraction by the ratio $\eta = b/v$. The packing fraction for the pure components and for the mixture are assumed to be the same.

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

The molar Helmholtz energy of a mixture, A , may be written as follows:

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

where A^{id} is the ideal mixture molar Helmholtz energy, a_i is the attractive parameter of component i of a translated Peng–Robinson cubic EOS,^{12,13} b_i is the covolume of component i , $A_{\text{res}}^{\text{E}}$ is the residual excess Helmholtz energy, and $Q(\eta)$ is expressed as follows:

$$Q(\eta) = \int_0^\eta \frac{Q'(\eta)}{\eta} d\eta \quad (3)$$

where

$$Q'(\eta) = \frac{\eta}{1 + \gamma\eta} \quad \text{and} \quad \gamma = 2(\sqrt{2} + 1) \quad (4)$$

The residual excess Helmholtz energy, $A_{\text{res}}^{\text{E}}$, can be separated into two terms, as shown in eq 5, where the

$$A_{\text{res}}^{\text{E}} = A_{\text{phys}}^{\text{E}} + A_{\text{chem}}^{\text{E}} \quad (5)$$

physical part, $A_{\text{phys}}^{\text{E}}$, is written by means of a formalism which enables one to separate the composition and packing fraction variables:

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

Table 2. Experimental Dew-Point Temperatures and Pressures for SNG and for SNG + $\bar{\rho}_{\text{water}}$ + $\bar{\rho}_{\text{methanol}}$ Mixtures

gas 1		gas 1 with $\bar{\rho}_{\text{water}} = 79.0 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 1098.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$		gas 1 with $\bar{\rho}_{\text{water}} = 40.5 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 3030.5 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$	
<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa
229.7	2.3	238.0	1.9	237.3	1.4
236.4	4.9	247.7	4.8	252.7	5.1
241.8	9.9	256.0	10.4	261.6	10.3
244.4	14.9	260.6	15.1	266.3	14.9
245.3	19.7	263.7	19.9	270.1	20.1
245.5	25.1	266.6	25.3	273.1	25.5
245.2	29.3	268.4	29.6	275.0	29.5
244.1	34.6	270.0	35.2	277.0	34.9
242.5	39.3	271.6	40.6	278.4	39.4
240.8	44.1	272.6	45.0	279.7	44.5
238.4	49.0	274.1	51.0	280.9	49.6
234.9	54.1	274.8	54.2	281.8	54.5
229.4	59.1	275.7	58.9	282.7	59.9
225.4	62.4	276.8	65.4	283.5	65.8
219.8	63.9	277.7	72.0	284.4	72.6
213.1	63.5				
210.0	62.3				
204.7	59.6				

gas 2		gas 2 with $\bar{\rho}_{\text{water}} = 82.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 991.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$		gas 2 with $\bar{\rho}_{\text{water}} = 69.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 2493.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$	
<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa
205.8	2.5	238.7	2.1	240.9	1.7
212.1	5.5	248.8	5.3	253.7	5.3
219.5	10.0	255.9	9.9	261.3	9.9
224.5	14.9	260.6	15.0	266.6	15.0
227.4	19.4	263.8	20.0	270.3	20.0
228.5	24.8	266.6	25.3	273.1	24.9
229.1	29.8	268.6	30.1	275.3	29.9
228.7	34.3	270.6	35.5	277.1	34.7
228.5	40.6	272.1	40.1	278.8	40.1
228.0	45.0	273.5	45.6	279.7	45.8
228.0	49.7	274.7	49.6	280.7	50.4
227.7	53.9	275.8	54.6	281.6	55.1
226.6	58.8	277.0	61.0	282.4	60.1
224.9	65.8	278.0	66.7	283.2	66.2
221.1	69.7	278.6	71.1	283.9	72.1
213.8	67.5				
211.6	62.7				

gas 3		gas 3 with $\bar{\rho}_{\text{water}} = 128.3 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 891.3 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$		gas 3 with $\bar{\rho}_{\text{water}} = 146.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 3459.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$	
<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa
236.8	4.7	245.9	3.1	245.6	1.9
241.8	8.9	252.5	5.6	249.9	2.6
245.0	15.1	260.0	10.6	253.8	3.6
246.5	20.0	264.0	14.9	257.8	5.1
246.4	25.0	268.0	20.3	261.1	6.5
245.5	30.0	270.5	25.1	264.1	8.2
244.7	35.6	272.6	29.7	266.9	10.1
243.3	40.0	274.6	35.1	269.9	12.6
241.5	45.0	276.2	39.9	272.9	15.2
238.9	50.3	277.6	44.5	275.2	17.4
235.8	54.7	279.0	49.5	277.2	20.3
230.0	59.0	280.1	54.4	278.6	22.3
221.2	64.1	281.3	60.2	280.4	25.4
213.4	63.8	282.3	64.6	281.5	27.5
203.0	59.7	283.3	69.0	282.9	30.6
197.0	54.7				
195.5	50.4				

Table 2. Cont'd.

gas 4		gas 4		gas 4 with $\bar{\rho}_{\text{water}} = 143.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 4611.0 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$	
<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa
247.7	1.9	267.1	84.4	248.0	1.7
252.8	3.0	265.6	87.7	253.1	2.6
260.7	5.2	263.7	91.4	260.6	4.6
266.5	9.2	262.0	95.5	263.7	5.9
271.3	14.4	258.7	100.0	266.6	7.2
274.1	19.9	249.7	105.3	271.1	10.0
275.8	25.0	247.6	106.0	274.2	12.7
276.6	29.4	245.3	105.9	276.6	15.0
277.1	35.0	241.5	105.8	278.4	17.0
277.3	39.3	237.7	102.2	280.5	19.8
277.0	44.5	231.8	99.2	282.0	22.0
276.5	49.5	229.2	95.1	283.7	24.9
275.5	54.8	226.1	90.2	284.7	27.0
274.8	60.0	222.7	85.4	286.4	30.2
273.4	64.9	221.3	82.8	287.3	32.2
272.4	70.3	218.5	78.2	288.2	34.6
270.9	75.9	216.4	73.7		
268.8	81.1	211.6	67.9		

gas 5		gas 5		gas 5 with $\bar{\rho}_{\text{water}} = 21.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 2365.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$		gas 5 with $\bar{\rho}_{\text{water}} = 25.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ and $\bar{\rho}_{\text{methanol}} = 3355.0 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$	
<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa	<i>T</i> /K	<i>P</i> /10 ⁵ Pa
243.4	2.0	271.8	60.1	274.4	41.0	245.2	2.6
249.8	3.4	269.4	66.2	275.1	44.8	257.2	6.8
254.1	5.0	267.6	71.4	276.1	50.4	260.9	9.1
258.3	7.0	264.6	75.3	276.9	55.6	266.0	13.4
262.4	9.9	262.1	80.2	277.3	59.9	268.8	16.5
266.7	14.7	257.9	84.8	277.8	65.7	272.3	21.9
269.7	20.1	252.1	88.5	278.1	72.4	274.3	25.6
271.4	24.6	246.1	91.4			276.6	30.9
272.7	30.6	241.9	92.3			278.2	35.5
273.2	35.1	231.4	90.5			279.6	40.2
273.3	40.0	228.1	88.7			280.7	44.5
273.5	45.0	223.3	82.8			281.8	49.9
273.2	50.0	215.7	74.2			282.7	55.1
272.5	55.0					283.4	59.8
						284.1	66.5
						284.6	73.1

The physical interactions between different compounds are represented by the physical term, A_{phys}^E , using eq 6.¹⁴ While the molecular associations, in the systems which contain methanol, are described by the chemical term, A_{chem}^E . For its calculation, the CREE model (Chimique Reticulaire Equation d'Etat) is used. It is a continuous association model defined by Rauzy and Berro.^{10,15}

For the first term on the right-hand side of eq 6, the following equations are used:¹⁴

$$E(T, x) = \frac{1}{2q_m} \left[\sum_{i=1}^p q_i x_i \left[\sum_{j=1}^p q_j x_j K_{ij} \right] + \sum_{i=1}^p q_i x_i \left[\sum_{j=1}^p q_j^{1/3} x_j L_{ji}^{1/3} \right] \right] \quad (7)$$

with

$$K_{ij} = \frac{E_{ij}^1 + E_{ij}^2}{2} \quad \text{and} \quad L_{ij} = E_{ij}^2 - E_{ij}^1 \quad L_{ij} = -L_{ji} \quad (8)$$

$$q_m = \sum_{k=1}^p q_k x_k \quad \text{and} \quad q_k = \delta_k b_k \quad (9)$$

where the subscripts i and j refer to the components i and j of the mixture with p components and q_i is the molecular surface of the component i . It is assumed that $q_i/q_j = (b_i/b_j)\delta$. δ is an adjustable parameter; the values of this parameter used in this paper are presented in Table 3. K_{ij} and L_{ij} are two binary interaction parameters between components i and j , which are calculated from eq 8. The interchange energies, E_{ij}^1 and E_{ij}^2 , are calculated using a group contribution method as follows:¹⁴

$$E_{ij}^1 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^1(T) \quad \text{with} \quad A_{kl}^1 = {}_1A_{kl}^0 \left(\frac{T^0}{T} \right)^{B_{kl}^0} \quad (10)$$

$$E_{ij}^2 = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}^2(T) \quad \text{with} \quad A_{kl}^2 = {}_2A_{kl}^0 \left(\frac{T^0}{T} \right)^{B_{kl}^0} \quad (11)$$

Table 3. Values of Parameter δ_i Used in This Work for Each Component of the Studied Mixtures

component	δ_i	component	δ_i
CH ₄	1.850	<i>n</i> -C ₆ H ₁₄	0.860
C ₂ H ₆	1.610	<i>n</i> -C ₇ H ₁₆	0.810
C ₃ H ₈	1.620	<i>n</i> -C ₈ H ₁₈	0.750
<i>i</i> -C ₄ H ₁₀	1.190	CO ₂	1.000
<i>n</i> -C ₄ H ₁₀	1.190	N ₂	1.000
<i>i</i> -C ₅ H ₁₂	0.980	H ₂ O	0.048
<i>n</i> -C ₅ H ₁₂	1.030	CH ₃ OH	1.000

Table 4. Number of Groups Which Constitute Each Component of the Studied Mixtures^{14,16,17}

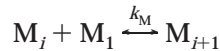
component	kind of group									
	1	2	3	4	8	9	10	11	17	18
CH ₄	0	0	0	0	1	0	0	0	0	0
C ₂ H ₆	0	0	0	0	0	1	0	0	0	0
C ₃ H ₈	0	0	0	1	0	0	0	0	0	0
<i>i</i> -C ₄ H ₁₀	2	1	0	0	0	0	0	0	0	0
<i>n</i> -C ₄ H ₁₀	0	0	1	0	0	0	0	0	0	0
<i>i</i> -C ₅ H ₁₂	2	2	0	0	0	0	0	0	0	0
<i>i</i> -C ₅ H ₁₂	1	0.5	3.5	0	0	0	0	0	0	0
<i>n</i> -C ₅ H ₁₂	2	3	0	0	0	0	0	0	0	0
<i>n</i> -C ₆ H ₁₄	2	4	0	0	0	0	0	0	0	0
<i>n</i> -C ₇ H ₁₆	2	5	0	0	0	0	0	0	0	0
<i>n</i> -C ₈ H ₁₈	2	6	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	1	0	0	0
N ₂	0	0	0	0	0	0	0	1	0	0
H ₂ O	0	0	0	0	0	0	0	0	1	0
CH ₃ OH	0	0	0	0	0	0	0	0	0	1

where ${}^1A_{kb}^0$, ${}^1B_{kb}^0$, ${}^2A_{kl}^0$ and ${}^2B_{kl}^0$ are group interaction parameters. The components of the studied mixture are divided into groups such as those shown in Table 4. The values for the group interaction parameters used for comparison calculations in this work are presented in Table 5.

The chemical contribution to the residual molar excess Helmholtz energy of a mixture, A_{chem}^E , is based on the self-association CREE model of Rauzy and Berro,^{10,15} where the alcohol (methanol in this work) is assumed to form continuous linear hydrogen-bounded polymers M₁, M₂, ..., M_{*i*}, etc., by successive chemical reactions:



⋮



described by a single equilibrium constant, k_M , of the form

$$k_M = \frac{\eta RT}{[b(1 - \eta)]} \exp\left(\frac{-\Delta A}{RT}\right) \exp\left(\frac{\beta Q(\eta)}{RT}\right) \quad (12)$$

The self-association Helmholtz energy, ΔA , is obtained as follows:

$$\Delta A = \Delta U^0 + C_T(T - T^0) - T \left[\Delta S^0 + C_T \ln\left(\frac{T}{T^0}\right) \right] \quad (13)$$

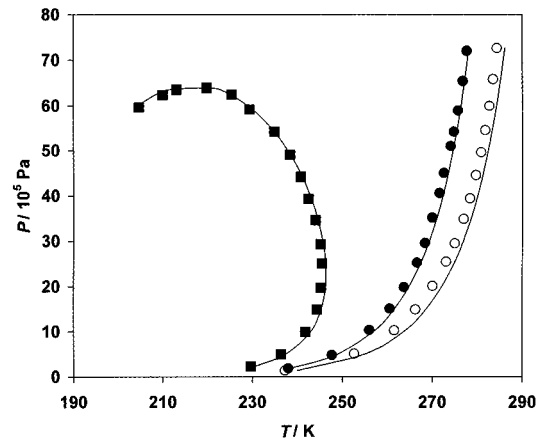


Figure 1. Comparison between experimental dew-point curves (symbol) and those calculated with the EOS-CR method (line) for the systems (■) gas 1, (●) gas 1 + 79.0×10^{-6} kg m⁻³(n) water + 1098.9×10^{-6} kg m⁻³(n) methanol, and (○) gas 1 + 40.5×10^{-6} kg m⁻³(n) water + 3030.5×10^{-6} kg m⁻³(n) methanol.

The values of ΔU^0 , C_T , ΔS^0 , and β used in this work are presented in Table 6.

The chemical contribution to the residual molar excess Helmholtz energy, A_{chem}^E , of a mixture with p components where the component M is self-associated is calculated as

$$A_{\text{chem}}^E = A_{\text{chem}} - A_{\text{chem}}^{\text{id}} \quad (14)$$

with

$$A_{\text{chem}} = (x_M - X)\Delta A \quad (15)$$

$$A_{\text{chem}}^{\text{id}} = x_M(1 - X_p)\Delta A \quad (16)$$

and

$$X = \frac{X_1}{1 - k_M X_1} \quad (17)$$

where X_1 is the monomer molar fraction that is expressed as

$$X_1 = \frac{(1 + 2k_M X_M) - (1 + 4k_M X_M)^{1/2}}{2k_M^2 X_M} \quad (18)$$

The self-association of water is not accounted for, and the same is true for cross-association between water and methanol.

5. Conclusions

In this work, the influence of water, methanol, and the usual components of natural gas on the VLE of natural gases supplied in Spain, through the European and Magreb gas pipeline network, has been studied.

The experimental dew-point data and the dew points calculated with the EOS-CR method are represented in Figures 1–5.

A comparison between experimental and calculated values of the dew-point temperature was carried out. The results of this comparison obtained for the dew-point curves of SNGs are presented in Table 7, and those obtained for SNG + water + methanol are given in Table 8. The values of the AAD obtained for

Table 5. Values of the Group Interaction Parameters, ${}_1A_{kp}^0$, ${}_1B_{kp}^0$, ${}_2A_{kp}^0$ and ${}_2B_{kp}^0$ Used in This Work

	1	2	3	4	8	9	10	11	17	18
${}_1A_{ki}^0/10^6 \text{ J m}^{-3}$										
1	0									
2	77.970 ¹⁶	0								
3	32.680 ¹⁶	7.700 ¹⁶	0							
4				0						
8	45.870 ¹⁶	97.440 ¹⁶	44.380 ¹⁶		0					
9	2.210 ¹⁶	67.080 ¹⁶	0.120 ¹⁶		7.860 ¹⁶	0				
10	438.210 ¹⁶	408.210 ¹⁶	409.240 ¹⁶		391.560 ¹⁶	397.980 ¹⁶	0			
11	314.350 ¹⁶	230.350 ¹⁶	231.100 ¹⁶		130.000 ¹⁶	284.770 ¹⁶	368.800 ¹⁶	0		
17	29.404 ¹⁴	3154.734 ¹⁴	2358.813 ¹⁴	3121.348 ¹⁷	1279.540 ¹⁴	1288.287 ¹⁴	1509.100 ¹⁴	2274.281 ¹⁴	0	
18	207.901 ¹⁴	502.358 ¹⁴	383.135 ¹⁴	347.285 ¹⁷	161.791 ¹⁷	285.621 ¹⁴	253.805 ¹⁴	675.206 ¹⁴	-1027.695 ¹⁴	0
${}_1B_{ki}^0/10^6 \text{ J m}^{-3}$										
1	1 ¹⁴									
2	0.920 ¹⁴	1 ¹⁴								
3	0.730 ¹⁴	1.840 ¹⁴	1 ¹⁴							
4				1 ¹⁴						
8	-3.650 ¹⁴	1.080 ¹⁴	-3.770 ¹⁴		1 ¹⁴					
9	18.680 ¹⁴	-0.330 ¹⁴	-22.970 ¹⁴		2.340 ¹⁴	1 ¹⁴				
10	0.370 ¹⁴	1.130 ¹⁴	0.730 ¹⁴		0.640 ¹⁴	0.940 ¹⁴	1 ¹⁴			
11	-0.910 ¹⁴	0.850 ¹⁴	0.740 ¹⁴		0.040 ¹⁴	-0.950 ¹⁴	0.620 ¹⁴	1 ¹⁴		
17	-4.795 ¹⁴	-1.257 ¹⁴	-1.248 ¹⁴	-1.793 ¹⁷	-0.726 ¹⁴	-1.560 ¹⁴	-0.831 ¹⁴	-1.115 ¹⁴	1 ¹⁴	
18	-0.027 ¹⁴	0.684 ¹⁴	0.475 ¹⁴	0.940 ¹⁷	2.390 ¹⁷	-0.304 ¹⁴	1.644 ¹⁴	-0.089 ¹⁴	0.131 ¹⁴	1 ¹⁴
${}_2A_{ki}^0/10^6 \text{ J m}^{-3}$										
1	0									
2	77.970 ¹⁶	0								
3	32.680 ¹⁶	7.700 ¹⁶	0							
4				0						
8	45.870 ¹⁶	97.440 ¹⁶	44.380 ¹⁶		0					
9	2.210 ¹⁶	67.080 ¹⁶	0.120 ¹⁶		7.860 ¹⁶	0				
10	438.210 ¹⁶	408.210 ¹⁶	409.240 ¹⁶		391.560 ¹⁶	397.980 ¹⁶	0			
11	314.350 ¹⁶	230.350 ¹⁶	231.100 ¹⁶		130.000 ¹⁶	284.770 ¹⁶	368.800 ¹⁶	0		
17	153213.172 ¹⁴	104763.141 ¹⁴	120420.43 ¹⁴	5553.582 ¹⁷	4279.212 ¹⁸	5946.637 ¹⁷	56629.527 ¹⁴	8712.375 ¹⁷	0	
18	198.106 ¹⁴	642.072 ¹⁴	468.877 ¹⁴	324.946 ¹⁷	1761.995 ¹⁷	239.985 ¹⁴	156.925 ¹⁴	486.890 ¹⁴	7538.737 ¹⁴	0
${}_2B_{ki}^0/10^6 \text{ J m}^{-3}$										
1	1 ¹⁴									
2	0.920 ¹⁴	1 ¹⁴								
3	0.730 ¹⁴	1.840 ¹⁴	1 ¹⁴							
4				1 ¹⁴						
8	-3.650 ¹⁴	1.080 ¹⁴	-3.770 ¹⁴		1 ¹⁴					
9	18.680 ¹⁴	-0.330 ¹⁴	-22.970 ¹⁴		2.340 ¹⁴	1 ¹⁴				
10	0.370 ¹⁴	1.130 ¹⁴	0.730 ¹⁴		0.640 ¹⁴	0.940 ¹⁴	1 ¹⁴			
11	-0.910 ¹⁴	0.850 ¹⁴	0.740 ¹⁴		0.040 ¹⁴	-0.950 ¹⁴	0.620 ¹⁴	1 ¹⁴		
17	0.065 ¹⁴	1.229 ¹⁴	0.589 ¹⁴	1.283 ¹⁷	5.537 ¹⁸	0.390 ¹⁷	-0.163 ¹⁴	7.140 ¹⁷	1 ¹⁴	
18	0.154 ¹⁴	1.476 ¹⁴	1.676 ¹⁴	1.186 ¹⁷	-11.605 ¹⁷	1.846 ¹⁴	6.172 ¹⁴	0.578 ¹⁴	-1.850 ¹⁴	1 ¹⁴

Table 6. Values of the Parameters of the Self-Association CREE (Chimique Réticulaire Equation d'Etat) Model of Rauzy and Berro^{10,15}

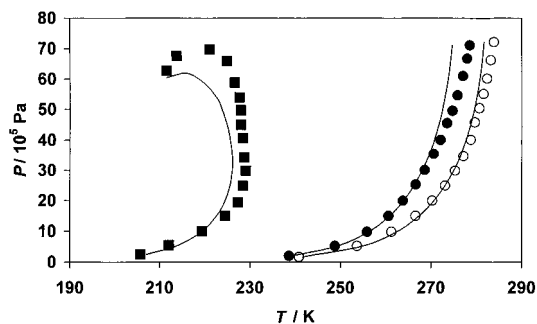
parameter	value	parameter	value
$\Delta U^0/(\text{J mol}^{-1})$	-21450.0 ¹⁴	$\Delta S^0/(\text{J K}^{-1} \text{ mol}^{-1})$	-127.767 ¹
$C_T/(\text{J K}^{-1} \text{ mol}^{-1})$	137.394 ¹⁴	β	720.629 ¹⁴

Table 7. Values of AAD and Experimental Ranges of Dew-Point Temperatures and Pressures for SNG Mixtures

SNG mixture	$T_{\text{range}}/\text{K}$	$P_{\text{range}}/10^5 \text{ Pa}$	AAD/K
gas 1	204.7–245.5	2.3–63.9	0.8
gas 2	205.8–229.1	2.5–69.7	3.0
gas 3	195.5–246.5	4.7–64.1	1.2
gas 4	211.6–277.3	1.9–106.0	3.7
gas 5	215.7–273.5	2.0–92.3	1.7

SNGs are between 0.8 and 3.7 K, and those for the SNG + water + methanol systems are from 0.5 to 1.9 K.

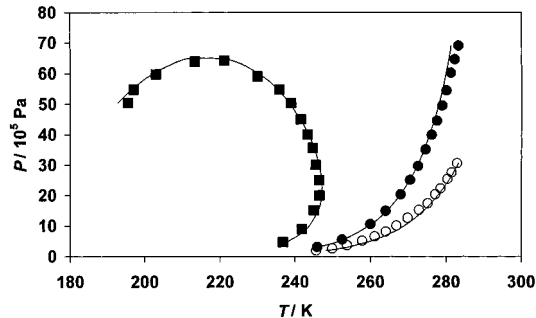
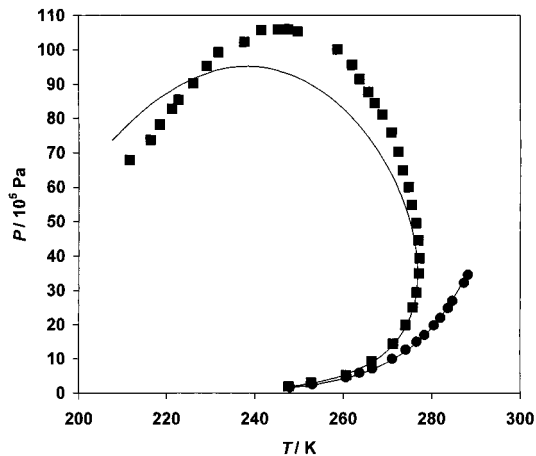
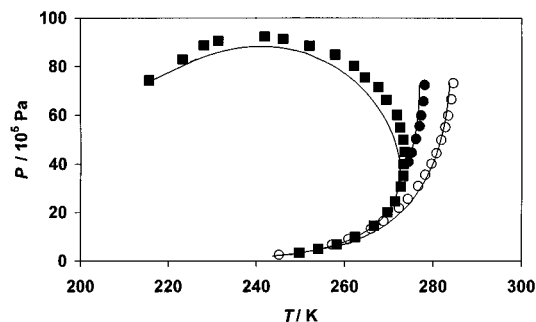
The EOS-CR method used allows one to predict properly both hydrocarbon and water + methanol dew points of the multicomponent systems in the studied temperature and pressure ranges. From the results obtained in this work with the SNGs, it can be concluded that the introduction of a group contribution method,

**Figure 2. Comparison between experimental dew-point curves (symbol) and those calculated with the EOS-CR method (line) for the systems (■) gas 2, (●) gas 2 + $82.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $991.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol, and (○) gas 2 + $69.8 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $2493.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol.**

as is used in the EOS-CR model, does not impair the predictions with respect to the EOS methods with interaction parameters obtained from binary experimental data. It makes the EOS-CR model very useful to predict both hydrocarbon and/or water + methanol dew points of real natural gases, provided that binary experimental data for all components of the so-called C_6+ fraction do not always exist.

Table 8. Values of AAD and Experimental Ranges of Dew-Point Temperatures and Pressures for Multicomponent Mixtures SNG + $\bar{\rho}_{\text{water}}$ + $\bar{\rho}_{\text{methanol}}$

SNG mixture	$\bar{\rho}_{\text{water}}/10^{-6} \text{ kg m}^{-3}(\text{n})$	$\bar{\rho}_{\text{methanol}}/10^{-6} \text{ kg m}^{-3}(\text{n})$	T range/K	P range/ 10^5 Pa	AAD/K
gas 1	79.0	1098.9	238.0–277.7	1.9–72.0	0.8
gas 1	40.5	3030.5	237.3–284.4	1.4–72.6	1.9
gas 2	82.8	991.7	238.7–278.6	2.1–71.1	1.5
gas 2	69.8	2493.6	240.9–283.9	1.7–72.1	1.0
gas 3	128.3	891.3	245.9–283.3	3.1–69.0	0.7
gas 3	146.7	3459.9	245.6–282.9	1.9–30.6	1.5
gas 4	143.4	4611.0	248.0–288.2	1.7–34.6	0.5
gas 5	21.1	2365.1	274.4–278.1	41.0–72.4	0.6
gas 5	25.6	3355.0	245.2–284.6	2.6–73.1	1.1

**Figure 3.** Comparison between experimental dew-point curves (symbol) and those calculated with the EOS-CR method (line) for the systems (■) gas 3, (●) gas 3 + $128.3 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $891.3 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol, and (○) gas 3 + $146.7 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $3459.9 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol.**Figure 4.** Comparison between experimental dew-point curves (symbol) and those calculated with the EOS-CR method (line) for the systems (■) gas 4 and (●) gas 4 + $143.4 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $4611.0 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol.**Figure 5.** Comparison between experimental dew-point curves (symbol) and those calculated with the EOS-CR method (line) for the systems (■) gas 5, (●) gas 5 + $21.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $2365.1 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol and (○) gas 5 + $25.6 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ water + $3355.0 \times 10^{-6} \text{ kg m}^{-3}(\text{n})$ methanol.

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Appendix 1

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

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

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

Nomenclature

- a = equation of state 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})
- b = covolume; equation of state size parameter ($\text{m}^3 \text{ mol}^{-1}$)
- \bar{b} = pseudo-covolume ($\text{m}^3 \text{ mol}^{-1}$)
- C_T = coefficient of the CREE (Chimique Réticulaire Equation d'Etat) model ($\text{J K}^{-1} \text{ mol}^{-1}$)
- E_{ij}^1, E_{ij}^2 = terms of the interchange energy (J m^{-3})
- k = constant of self-association equilibrium
- K_{ij}, L_{ij} = binary interaction parameters (J m^{-3})
- N = number of groups in a solution
- p = number of components in the mixture
- P = pressure (Pa)
- q = molecular surface (m^2)
- Q = integral of Q/η between 0 and η
- Q = packing fraction function
- 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 fraction ($\text{m}^3 \text{ mol}^{-1}$)
- x_M = nominal molar fraction of component M in the mixture
- X = sum of molar fractions of polymer in the mixture
- X_1 = molar fraction of monomer in the mixture
- X_p = value of X when x_M is unity

Greek Letters

- α_{ik} = surface area fraction of group k in molecule i
- γ = constant of the translated Peng–Robinson cubic equation of state
- δ = adjustable parameter, proportionality coefficient between the surface measure, q , and the covolume, v
- ΔA = molar Helmholtz energy of self-association (J mol^{-1})
- ΔS^0 = molar entropy of methanol self-association at T^0 ($\text{J K}^{-1} \text{ mol}^{-1}$)

ΔU^0 = molar energy of methanol self-association at T^0 (J mol⁻¹)

η = packing fraction

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

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

Subscripts

chem = chemical contribution

phys = physical contribution

i, j = components i and j

k, l = groups k and l

M = component M , which is considered self-associated

n = 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

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