See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/231373577

# Gas Solubility: A Key to Estimating the Water Content of Natural Gases

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · MAY 2006

Impact Factor: 2.59 · DOI: 10.1021/ie051337i

**CITATIONS** 

20

**READS** 

59

# 4 AUTHORS:



Amir H. Mohammadi

**557** PUBLICATIONS **4,821** CITATIONS

SEE PROFILE



**Antonin Chapoy** 

**Heriot-Watt University** 

105 PUBLICATIONS 1,667 CITATIONS

SEE PROFILE



Bahman Tohidi

**Heriot-Watt University** 

216 PUBLICATIONS 3,095 CITATIONS

SEE PROFILE



**Dominique Richon** 

**Aalto University** 

**533** PUBLICATIONS **6,599** CITATIONS

SEE PROFILE

# Gas Solubility: A Key to Estimating the Water Content of Natural Gases

Amir H. Mohammadi,† Antonin Chapoy,† Bahman Tohidi,† and Dominique Richon\*.‡

Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, United Kingdom, and Centre Energétique et Procédés, Ecole Nationale Supérieure des Mines de Paris, CEP/TEP, 35 Rue Saint Honoré, 77305 Fontainebleau, France

Experimental water content data, at low temperatures, for hydrocarbons and non-hydrocarbon gases are scarce and often rather dispersed. This is partly due to the fact that water content of gases is indeed very low at low temperatures and high pressures and hence generally very difficult to measure. However, measuring gas solubility in water is easier than measuring water content of gases. In this work, we examine the need for water content data in the gas phase for tuning binary interaction parameters between water and gaseous components in an equation of state. We consider three cases for tuning: (1) gas solubility in the liquid-phase only, (2) water content of the gas phase, and (3) mutual solubilities. The Valderrama modification of the Patel—Teja equation of state with the nondensity dependent mixing rules is used for modeling the fluid phases. These results show that using only gas solubility data in tuning the thermodynamic model leads to accurate predictions of water content data, and, therefore, experimental gas-phase water contents are not indispensable. Furthermore, we report new experimental data on the water content of the gas phase for a gas mixture consisting of 94% methane, 4% ethane, and 2% n-butane at low temperatures. The data were measured in the 277.82-292.88 K temperature range and at pressures up to 3.028 MPa, using a static-analytic technique taking advantage of a Rolsi sampling device. To examine the consistency of the new experimental data they are compared with the results of a previously reported semi-empirical approach and the developed thermodynamic model. The agreements between the experimental and predicted data are good, demonstrating the reliability of the data and the techniques used in this work.

#### Introduction

Natural gases normally contain significant quantities of water. During production, transportation and processing, undesired amounts of dissolved water may condense, altering the physical state from vapor to condensed water and to gas hydrates/ice. The condensed phase may lead to corrosion and/or two-phase flow problems. The formation of gas hydrates and/or ice could result in pipeline blockage and shutdown. To avoid such troubles, accurate knowledge of water-hydrocarbon phase behavior over a wide range of temperatures and pressures is of great interest to the petroleum industry. On the other hand, estimating the water content is crucial in the design and operation of natural gas facilities. Accurate data, especially at low temperatures, are necessary to develop and validate predictive methods. Unfortunately, data for most natural gas components at low temperatures were found to be scarce and often rather dispersed.<sup>1,2</sup>

The main objective in this work is to examine the need for generating water content data for tuning binary interaction parameters (BIPs) in an equation of state (EoS) and whether it is possible to achieve an acceptable accuracy using the gas in water solubility data.

A thermodynamic model based on uniformity of fugacity of each component throughout all the phases is employed to model the phase equilibrium.<sup>1</sup> The Valderrama modification of the Patel and Teja equation of state (VPT-EoS)<sup>3</sup> with the nondensity dependent (NDD) mixing rules<sup>4</sup> is used for predicting fugacities of components in fluid phases. The BIPs are tuned using a Simplex algorithm. It is shown that using only gas solubility

data in tuning the thermodynamic model<sup>1</sup> can lead to accurate predictions of water content data and, therefore, less need to measure water solubility in the gas phase.

Furthermore, we report new water content data for a gas mixture consisting of 94% methane, 4% ethane, and 2% *n*-butane at low temperatures (277.82-292.88 K) and pressures up to 3.028 MPa. The gas-phase compositions are measured by the gas chromatography method. The isotherms presented in this work were determined using an apparatus based on a static-analytic method taking advantage of a new Rolsi electromagnetic capillary sampler.<sup>2</sup> To examine the consistency of the experimental data they are compared with the predictions of a previously reported semi-empirical approach and the thermodynamic model<sup>1</sup> developed in this work. Good agreement between experimental data and predictions demonstrates the reliability of the data generated in the present work. The results provide better understanding and evaluation of mutual solubility of the natural gas-water system associated with production and transportation.

# **Experimental Section**

**Materials.** Helium (carrier gas), from Air Liquide, is pure grade with traces of water (3 ppm) and of hydrocarbons (0.5 ppm). The gas mixture, 94% methane, 4% ethane ( $\pm 2\%$ ), and 2% n-butane ( $\pm 2\%$ ), was purchased from Messer Griesheim. Deionized water was used after degassing.

**Apparatus and Procedures.** The apparatus used in this work (Figure 1) is based on a static-analytic method with vapor phase sampling, which is similar to that previously described by Chapoy et al.<sup>2</sup>

The phase equilibrium is achieved in a cylindrical cell made of sapphire, and the cell is immersed in a constant-temperature liquid bath that controls and maintains the desired temperature within  $\pm 0.02~\mathrm{K}$ . To perform accurate temperature measurements

<sup>\*</sup> To whom correspondence should be addressed. E-mail: richon@ paris.ensmp.fr. Tel.: +(33) 1 64 69 49 65. Fax: +(33) 1 64 69 49 68.

<sup>†</sup> Heriot-Watt University.

<sup>&</sup>lt;sup>‡</sup> Ecole Nationale Supérieure des Mines de Paris.

**Figure 1.** Flow diagram of the equipment: <sup>1,2,5-7,10,12</sup> C, carrier gas; d.a.s, data acquisition system; DH<sub>2</sub>O, degassed water; EC, equilibrium cell; FV, feeding valve; GCy, gas cylinder; LB, liquid bath; MS, magnetic stirrer; PP, platinum resistance thermometer probe; PT, pressure transducer; SM, sampler monitoring; ST, sapphire tube; Th, thermocouple; TR, temperature regulator; Vi, valve i; VS, vapor sampler; VSS, variable speed stirrer; and VP, vacuum pump.

Table 1. Critical Properties and Acentric Factors<sup>8</sup>

compound	$P_{\rm c}$ , MPa	$T_{\rm c}$ , K	$v_{\rm c}$ , m <sup>3</sup> ·kmol <sup>-1</sup>	ω
water	22.048	647.30	0.0560	0.3442
methane	4.604	190.58	0.0992	0.0108

Table 2. Measured (This Work) and Predicted Water Contents (Mol Fraction) of a Gas Mixture Containing 94 mol % Methane, 4 mol % Ethane, and 2 mol % *n*-Butane

			semi-empirical approach1	
<i>T</i> , K	P, MPa	measured water content (this work)	predicted water content <sup>a</sup>	AD%
277.82	1.721	$5.25 \times 10^{-4}$	$5.38 \times 10^{-4}$	2.5
278.08	0.501	$1.82 \times 10^{-3}$	$1.77 \times 10^{-3}$	2.7
282.76	1.076	$1.17 \times 10^{-3}$	$1.17 \times 10^{-3}$	0.0
282.76	3.028	$4.44 \times 10^{-4}$	$4.55 \times 10^{-4}$	2.5
282.77	1.235	$1.04 \times 10^{-3}$	$1.03 \times 10^{-3}$	1.0
282.79	1.868	$7.00 \times 10^{-4}$	$7.00 \times 10^{-4}$	0.0
282.91	0.521	$2.43 \times 10^{-3}$	$2.38 \times 10^{-3}$	2.1
292.76	0.503	$4.66 \times 10^{-3}$	$4.64 \times 10^{-3}$	0.4
292.77	0.986	$2.44 \times 10^{-3}$	$2.42 \times 10^{-3}$	0.8
292.88	1.785	$1.38 \times 10^{-3}$	$1.39 \times 10^{-3}$	0.7

<sup>&</sup>lt;sup>a</sup> Ignoring the effect of gas gravity.

in the equilibrium cell and to check for thermal gradients, the temperature is measured at two locations corresponding to the vapor and liquid phases through two  $100~\Omega$  platinum resistance thermometers (Pt100,  $\pm 0.02~\rm K$  in the 273–393 K range) connected to an HP data acquisition unit (HP34970A). Pressure is measured by means of a Druck pressure transducer connected to the same data acquisition unit; the pressure transducer is calibrated against a dead weight pressure balance (Desgranges & Huot 5202S, CP 0.3–40 MPa, Aubervilliers, France).

Table 3. BIPs for the VPT-EoS<sup>3</sup> and NDD Mixing Rules<sup>4</sup> (w, Water; g, Gas)

system	objective function	$k_{\mathrm{w-g}}{}^{a}$	$l_{\mathrm{w-g}}^{}0b}$	$l_{\mathrm{w-g}}^{-1} \times 10^{4 b}$
methane-water	eq 1	0.5044 0.5075	1.8302 1.8406	51.72 50.02
	eq 2 eq 3	0.5073	1.8224	52.06

 $^a\,k_{\rm w-g}$ : BIP for the classical mixing rules.  $^{1,4}$   $^b\,l_{\rm w-g}{}^0$  and  $l_{\rm w-g}{}^1$ : constants for the BIP for the asymmetric term.  $^{1,4}$ 

Pressure measurement uncertainties are estimated to be within  $\pm 1$  kPa in the 0.2-5 MPa range.

The analytical work was carried out using a gas chromatograph (GC; VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected to a data acquisition system fitted with BORWIN software (version 1.5, from JMBS, Le Fontanil, France). The analytical column is Hayesep T 100/120 Mesh column (silcosteel tube, length: 1.5 m, diameter: 1/8 in.). The FID and TCD were utilized to detect the hydrocarbons and water, respectively. The FID was repeatedly calibrated by introducing known amounts of the gas mixture through a gas syringe in the injector of the GC. The uncertainties on the moles are estimated to be  $\pm 2.0\%$  in the 3.8  $\times$  10<sup>-6</sup> to 2.0  $\times$  10<sup>-5</sup> mol range,  $\pm 2.2\%$  in the  $1.6 \times 10^{-7}$  to  $8.2 \times 10^{-7}$  mol range, and within  $\pm 3.5\%$  in the  $8.2 \times 10^{-8}$  to  $4.1 \times 10^{-7}$  mol range for methane, ethane, and n-butane, respectively. As the water concentration is expected to be very low, calibrating the TCD is very difficult and requires a special instrument described by Chapoy et al.6,7 and Mohammadi et al.1,5 along with the calibration procedure. The experimental accuracy of the TCD calibration with water, in the  $7.5 \times 10^{-9}$  to  $3.4 \times 10^{-7}$  mol range, is estimated to be  $\pm 4\%$  in the worst case.

Table 4. Experimental and Calculated/Pro	edicted Gas Solubilities (Mol Fraction) in	n the Liquid Phase of the Methane-	Water System

<i>T</i> , K	$P_{ m exp},$ MPa	experimental gas solubility <sup>12</sup>	model <sup>1</sup> results using BIPs based on eq 1 (dependent data)	AD% using BIPs based on eq 1	model <sup>1</sup> results using BIPs based on eq 2 (independent data)	AD% using BIPs based on eq 2	model <sup>1</sup> results using BIPs based on eq 3 (partially dependent data)	AD% using BIPs based on eq 3
275.11	0.973	$3.99 \times 10^{-4}$	$3.61 \times 10^{-4}$	9.5	$3.71 \times 10^{-4}$	7.0	$3.49 \times 10^{-4}$	12.5
275.11	1.565	$6.31 \times 10^{-4}$	$5.67 \times 10^{-4}$	10.1	$5.82 \times 10^{-4}$	7.8	$5.48 \times 10^{-4}$	13.2
275.11	2.323	$9.01 \times 10^{-4}$	$8.15 \times 10^{-4}$	9.5	$8.37 \times 10^{-4}$	7.1	$7.88 \times 10^{-4}$	12.5
275.11	2.82	$1.06 \times 10^{-3}$	$9.69 \times 10^{-4}$	8.7	$9.95 \times 10^{-4}$	6.1	$9.36 \times 10^{-4}$	11.7
283.13	1.039	$3.29 \times 10^{-4}$	$3.27 \times 10^{-4}$	0.6	$3.38 \times 10^{-4}$	2.7	$3.16 \times 10^{-4}$	4.0
283.12	1.81	$5.58 \times 10^{-4}$	$5.53 \times 10^{-4}$	0.9	$5.71 \times 10^{-4}$	2.3	$5.34 \times 10^{-4}$	4.3
283.13	2.756	$7.72 \times 10^{-4}$	$8.12 \times 10^{-4}$	5.2	$8.39 \times 10^{-4}$	8.7	$7.84 \times 10^{-4}$	1.6
283.13	5.977	$1.50 \times 10^{-3}$	$1.56 \times 10^{-3}$	4.3	$1.61 \times 10^{-3}$	7.3	$1.51 \times 10^{-3}$	0.7
298.16	0.977	$2.38 \times 10^{-4}$	$2.38 \times 10^{-4}$	0	$2.49 \times 10^{-4}$	4.6	$2.30 \times 10^{-4}$	3.4
298.16	2.542	$6.13 \times 10^{-4}$	$5.89 \times 10^{-4}$	3.9	$6.16 \times 10^{-4}$	0.5	$5.70 \times 10^{-4}$	7.0
298.15	5.922	$1.24 \times 10^{-3}$	$1.23 \times 10^{-3}$	0.4	$1.29 \times 10^{-3}$	4.0	$1.19 \times 10^{-3}$	4.0
298.13	15.907	$2.46 \times 10^{-3}$	$2.50 \times 10^{-3}$	1.6	$2.61 \times 10^{-3}$	6.1	$2.41 \times 10^{-3}$	2.0
313.11	1.025	$2.04 \times 10^{-4}$	$2.05 \times 10^{-4}$	0.5	$2.16 \times 10^{-4}$	5.9	$1.98 \times 10^{-4}$	2.9
313.11	2.534	$4.43 \times 10^{-4}$	$4.86 \times 10^{-4}$	9.7	$5.12 \times 10^{-4}$	15.6	$4.70 \times 10^{-4}$	6.1
313.11	7.798	$1.31 \times 10^{-3}$	$1.30 \times 10^{-3}$	0.8	$1.37 \times 10^{-3}$	4.6	$1.25 \times 10^{-3}$	4.6
313.11	17.998	$2.33 \times 10^{-3}$	$2.35 \times 10^{-3}$	0.9	$2.47 \times 10^{-3}$	6.0	$2.27 \times 10^{-3}$	2.6
	AAI	0%	4.2		6.0		5.8	

The equilibrium cell and its loading lines are evacuated down to 0.1 Pa prior to introduction of about 5 cm<sup>3</sup> of degassed water at room temperature. Then, the gaseous hydrocarbon mixture is introduced into the cell directly from the commercial cylinder (through preliminary evacuated transfer lines) to the pressure level corresponding to the pressure of the first measurement. More gas is introduced after each sampling and analysis step up to the new desired pressure. After each introduction of gas into the cell, efficient stirring is started, and pressure is stabilized within a few minutes; measurements are performed only when the pressure is constant within the experimental uncertainty for at least 10 min (pressure remains constant during sampling as withdrawn amounts are negligible compared to total phase volumes).

The sampling is carried out using a Rolsi capillary sampler injector.<sup>2</sup> The sampler injector is connected to the cell through 0.1 mm internal diameter capillary tubing. The withdrawn samples are then swept to the GC for analysis. For each equilibrium condition, at least 10 samples are withdrawn from the vapor phase in equilibrium with the liquid phase, using the sampler, and analyzed to check for measurement repeatability.

# Thermodynamic Model

**Pure Compound Properties.** The critical temperatures  $(T_c)$ , critical pressures ( $P_c$ ), critical volumes ( $v_c$ ), and acentric factors  $(\omega)$  for water and methane are provided in Table 1.8

Description of the Model. A detailed description of the model for predicting the water content of gases is given elsewhere.1 Briefly, a thermodynamic model based on uniformity of the fugacity of each component throughout all the phases<sup>8,9</sup> is used to model the phase equilibrium. In this model, the VPT-EoS<sup>3</sup> with the NDD mixing rules<sup>4</sup> is employed in calculating fugacities in all fluid phases. This combination has proved to be a strong tool in modeling systems with polar and nonpolar compounds.4

#### **Results and Discussion**

The new experimental water content data are reported in Table 2 and are compared with the predictions of a previously reported semi-empirical approach.<sup>10</sup> The agreements between the experimental and predicted data are good, with absolute deviation (AD) values in the (0.0 to 2.7) % range. The average absolute deviation (AAD) among all the experimental and predicted data is 1.3%, demonstrating good consistency.

As the water content of sweet gases with low concentrations of heavy hydrocarbons is approximately equal to the water content of methane, especially at low temperatures, 10,11 the model1 is developed for the methane-water system, and it is then used for predicting the water content of the gas mixture. For tuning the BIPs between methane and water, three cases are considered. They are as follows: (a) only gas solubility data previously measured<sup>12</sup> are used for tuning the BIPs using the objective function displayed in eq 1; (b) only water content data of the gas phase are used for tuning the BIPs using the objective function shown in eq 2; and (c) only mutual solubility data are used for tuning the BIPs using the objective function indicated in eq 3.

objective function 1

$$FOB = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}} \right|$$
 (1)

objective function 2

$$FOB = \frac{1}{M} \sum_{1}^{M} \left| \frac{y_{i,exp} - y_{i,cal}}{y_{i,exp}} \right|$$
 (2)

objective function 3

$$FOB = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}} \right| + \frac{1}{M} \sum_{i=1}^{M} \left| \frac{y_{i,exp} - y_{i,cal}}{y_{i,exp}} \right|$$
(3)

where N and M are the number of gas solubility data points and water content data points, respectively,  $x_{i,exp}$  and  $y_{i,exp}$  stand for the measured gas solubility and water content, respectively, and  $x_{i,cal}$  and  $y_{i,cal}$  represent the calculated gas solubility and water content, respectively.

Although the values of the BIPs depend on different factors, such as the number, accuracy, and measurement conditions of experimental data as well as appropriate initial guesses for the BIPs in the Simplex algorithm,1 preliminary study shows that using the above objective functions leads to approximately the same values of the BIPs. Table 3 reports the optimized BIP values between methane and water based on the objective

	-		model <sup>1</sup> results using BIPs	AD%	model <sup>1</sup> results using BIPs	AD%	model <sup>1</sup> results using BIPs	AD%
<i>T</i> , K	<i>P,</i> MPa	experimental water content	based on eq 1 (independent data)	using BIPs based on eq 1	based on eq 2 (dependent data)	using BIPs based on eq 2	based on eq 3 (partially dependent data)	using BIPs based on eq 3
	IVII a	water content	* *				(partially dependent data)	based on eq 3
282.98	1.147	$1.14 \times 10^{-3}$	$1.11 \times 10^{-3}$	experimental war 2.6	ter content data from $1.11 \times 10^{-3}$	1 ref 1 2.6	$1.11 \times 10^{-3}$	2.6
283.08	1.005	$1.14 \times 10^{-3}$ $1.24 \times 10^{-3}$	$1.11 \times 10^{-3}$ $1.27 \times 10^{-3}$	2.4	$1.11 \times 10^{-3}$ $1.27 \times 10^{-3}$	2.4	$1.11 \times 10^{-3}$ $1.26 \times 10^{-3}$	1.6
283.15	1.003	$1.24 \times 10^{-3}$ $1.26 \times 10^{-3}$	$1.27 \times 10^{-3}$ $1.28 \times 10^{-3}$	1.6	$1.27 \times 10^{-3}$ $1.28 \times 10^{-3}$	1.6	$1.28 \times 10^{-3}$	1.6
288.11	1.003	$1.78 \times 10^{-3}$	$1.78 \times 10^{-3}$	0.0	$1.28 \times 10^{-3}$ $1.77 \times 10^{-3}$	0.6	$1.28 \times 10^{-3}$ $1.78 \times 10^{-3}$	0.0
288.15	1.005	$1.73 \times 10^{-3}$ $1.77 \times 10^{-3}$	$1.78 \times 10^{-3}$ $1.77 \times 10^{-3}$	0.0	$1.77 \times 10^{-3}$	0.0	$1.73 \times 10^{-3}$ $1.77 \times 10^{-3}$	0.0
293.01	2.051	$1.17 \times 10^{-3}$	$1.77 \times 10^{-3}$ $1.23 \times 10^{-3}$	5.1	$1.77 \times 10^{-3}$ $1.23 \times 10^{-3}$	5.1	$1.77 \times 10^{-3}$ $1.23 \times 10^{-3}$	5.1
293.01	0.992	$2.41 \times 10^{-3}$	$2.43 \times 10^{-3}$	0.8	$2.43 \times 10^{-3}$	0.8	$2.44 \times 10^{-3}$	1.2
293.01	0.572	$4.64 \times 10^{-3}$	$4.64 \times 10^{-3}$	0.0	$4.64 \times 10^{-3}$	0.0	$4.64 \times 10^{-3}$	0.0
293.11	0.99	$2.40 \times 10^{-3}$	$2.45 \times 10^{-3}$	2.1	$2.45 \times 10^{-3}$	2.1	$2.45 \times 10^{-3}$	2.1
297.97	0.563	$5.69 \times 10^{-3}$	$5.69 \times 10^{-3}$	0.0	$5.69 \times 10^{-3}$	0.0	$5.70 \times 10^{-3}$	0.2
298	1.697	$1.96 \times 10^{-3}$	$1.98 \times 10^{-3}$	1.0	$1.98 \times 10^{-3}$	1.0	$1.98 \times 10^{-3}$	1.0
298.01	0.608	$5.19 \times 10^{-3}$	$5.30 \times 10^{-3}$	2.1	$5.29 \times 10^{-3}$	1.9	$5.30 \times 10^{-3}$	2.1
298.01	2.846	$1.22 \times 10^{-3}$	$1.24 \times 10^{-3}$	1.6	$1.23 \times 10^{-3}$	0.8	$1.24 \times 10^{-3}$	1.6
298.11	1.01	$3.27 \times 10^{-3}$	$3.26 \times 10^{-3}$	0.3	$3.26 \times 10^{-3}$	0.3	$3.26 \times 10^{-3}$	0.3
303.11	1.03	$4.40 \times 10^{-3}$	$4.28 \times 10^{-3}$	2.7	$4.28 \times 10^{-3}$	2.7	$4.28 \times 10^{-3}$	2.7
308.11	0.99	$5.82 \times 10^{-3}$	$5.88 \times 10^{-3}$	1.0	$5.88 \times 10^{-3}$	1.0	$5.88 \times 10^{-3}$	1.0
313.12	1.09	$7.34 \times 10^{-3}$	$7.03 \times 10^{-3}$	4.2	$7.03 \times 10^{-3}$	4.2	$7.03 \times 10^{-3}$	4.2
	AAI	30%	1.6		1.6	5	1.6	
	AAL	770					1.0	
277.0	0.401	1 72 10-3			ter content data from		1.77 10-3	2.2
277.8	0.491	$1.73 \times 10^{-3}$	$1.77 \times 10^{-3}$	2.3 0.2	$1.77 \times 10^{-3}$	2.3	$1.77 \times 10^{-3}$	2.3
277.8 277.8	1.081 2.196	$8.30 \times 10^{-4}$ $4.36 \times 10^{-4}$	$8.28 \times 10^{-4}$ $4.29 \times 10^{-4}$	1.6	$8.28 \times 10^{-4}$ $4.29 \times 10^{-4}$	0.2 1.6	$8.28 \times 10^{-4}$ $4.30 \times 10^{-4}$	0.2 1.4
277.8	3.136	$3.21 \times 10^{-4}$	$3.14 \times 10^{-4}$	2.2	$3.14 \times 10^{-4}$	2.2	$3.15 \times 10^{-4}$	1.4
		$8.61 \times 10^{-4}$	$8.47 \times 10^{-4}$		$8.46 \times 10^{-4}$	1.7		
279.3 282.9	1.178 0.493	$2.64 \times 10^{-3}$	$2.50 \times 10^{-3}$	1.6 5.3	$2.50 \times 10^{-3}$	5.3	$8.47 \times 10^{-4} $ $2.50 \times 10^{-3}$	1.6 5.3
282.9	0.493	$1.83 \times 10^{-3}$	$1.81 \times 10^{-3}$	3.3 1.1	$1.81 \times 10^{-3}$	3.3 1.1	$1.81 \times 10^{-3}$	3.3 1.1
283	1.081	$1.83 \times 10^{-3}$ $1.22 \times 10^{-3}$	$1.81 \times 10^{-3}$ $1.18 \times 10^{-3}$	3.3	$1.81 \times 10^{-3}$ $1.18 \times 10^{-3}$	3.3	$1.81 \times 10^{-3}$ $1.18 \times 10^{-3}$	3.3
282.9	1.458	$9.26 \times 10^{-4}$	$8.84 \times 10^{-4}$	3.3 4.5	$8.83 \times 10^{-4}$	3.3 4.6	$8.84 \times 10^{-4}$	4.5
283	2.822	$5.30 \times 10^{-4}$	$4.89 \times 10^{-4}$	7.7	$4.88 \times 10^{-4}$	7.9	$4.89 \times 10^{-4}$	7.7
283	4.374	$3.13 \times 10^{-4}$	$3.38 \times 10^{-4}$	8	$3.37 \times 10^{-4}$	7.7	$3.38 \times 10^{-4}$	8.0
287.7	0.993	$1.85 \times 10^{-3}$	$1.74 \times 10^{-3}$	5.9	$1.74 \times 10^{-3}$	5.9	$1.74 \times 10^{-3}$	5.9
287.7	1.985	$9.33 \times 10^{-4}$	$9.09 \times 10^{-4}$	2.6	$9.08 \times 10^{-4}$	2.7	$9.09 \times 10^{-4}$	2.6
287.7	2.393	$7.75 \times 10^{-4}$	$7.67 \times 10^{-4}$	1	$7.66 \times 10^{-4}$	1.2	$7.67 \times 10^{-4}$	1.0
292.7	0.976	$2.52 \times 10^{-3}$	$2.43 \times 10^{-3}$	3.6	$2.43 \times 10^{-3}$	3.6	$2.43 \times 10^{-3}$	3.6
292.7	2.69	$9.26 \times 10^{-4}$	$9.44 \times 10^{-4}$	1.9	$9.43 \times 10^{-4}$	1.8	$9.45 \times 10^{-4}$	2.1
292.7	2.735	$9.08 \times 10^{-4}$	$9.31 \times 10^{-4}$	2.5	$9.29 \times 10^{-4}$	2.3	$9.31 \times 10^{-4}$	2.5
292.7	3.667	$7.03 \times 10^{-4}$ $7.03 \times 10^{-4}$	$7.21 \times 10^{-4}$	2.6	$7.20 \times 10^{-4}$	2.4	$7.22 \times 10^{-4}$	2.7
297.6	1.008	$3.10 \times 10^{-3}$	$3.17 \times 10^{-3}$	2.3	$3.17 \times 10^{-3}$	2.3	$3.17 \times 10^{-3}$	2.3
297.5	2.342	$1.44 \times 10^{-3}$	$1.43 \times 10^{-3}$	0.7	$1.43 \times 10^{-3}$	0.7	$1.43 \times 10^{-3}$	0.7
297.9	3.675	$1.00 \times 10^{-3}$	$9.82 \times 10^{-4}$	1.8	$9.81 \times 10^{-4}$	1.9	$9.83 \times 10^{-4}$	1.7
297.6	3.865	$8.76 \times 10^{-4}$	$9.25 \times 10^{-4}$	5.6	$9.23 \times 10^{-4}$	5.4	$9.25 \times 10^{-4}$	5.6
	AAI	0%	3.1		3.1	l	3.1	

Table 6. Experimental and Predicted Water Contents (Mol Fraction) in the Gas Phase of Gas Mixture-Water System

<i>T</i> , K	P, MPa	measured water content (this work)	model <sup>1</sup> predictions using BIPs based on eq 1 <sup>a</sup>	AD% using BIPs based on eq 1	model <sup>1</sup> predictions using BIPs based on eq 2 <sup>a</sup>	AD% using BIPs based on eq 2	model <sup>1</sup> predictions using BIPs based on eq 3 <sup>a</sup>	AD% using BIPs based on eq 3
277.82	1.721	$5.25 \times 10^{-4}$	$5.37 \times 10^{-4}$	2.3	$5.36 \times 10^{-4}$	2.1	$5.37 \times 10^{-4}$	2.3
278.08	0.501	$1.82 \times 10^{-3}$	$1.77 \times 10^{-3}$	2.7	$1.77 \times 10^{-3}$	2.7	$1.77 \times 10^{-3}$	2.7
282.76	1.076	$1.17 \times 10^{-3}$	$1.17 \times 10^{-3}$	0.0	$1.17 \times 10^{-3}$	0.0	$1.17 \times 10^{-3}$	0.0
282.76	3.028	$4.44 \times 10^{-4}$	$4.52 \times 10^{-4}$	1.8	$4.52 \times 10^{-4}$	1.8	$4.53 \times 10^{-4}$	2.0
282.77	1.235	$1.04 \times 10^{-3}$	$1.02 \times 10^{-3}$	1.9	$1.02 \times 10^{-3}$	1.9	$1.02 \times 10^{-3}$	1.9
282.79	1.868	$7.00 \times 10^{-4}$	$6.97 \times 10^{-4}$	0.4	$6.97 \times 10^{-4}$	0.4	$6.98 \times 10^{-4}$	0.3
282.91	0.521	$2.43 \times 10^{-3}$	$2.37 \times 10^{-3}$	2.5	$2.37 \times 10^{-3}$	2.5	$2.37 \times 10^{-3}$	2.5
292.76	0.503	$4.66 \times 10^{-3}$	$4.63 \times 10^{-3}$	0.6	$4.63 \times 10^{-3}$	0.6	$4.63 \times 10^{-3}$	0.6
292.77	0.986	$2.44 \times 10^{-3}$	$2.41 \times 10^{-3}$	1.2	$2.41 \times 10^{-3}$	1.2	$2.41 \times 10^{-3}$	1.2
292.88	1.785	$1.38\times10^{-3}$	$1.39 \times 10^{-3}$	0.7	$1.39 \times 10^{-3}$	0.7	$1.39 \times 10^{-3}$	0.7
	AAL	0%	1.4		1.4		1.4	

<sup>&</sup>lt;sup>a</sup> Ignoring the effect of gas gravity.<sup>10</sup>

functions displayed in eqs 1–3. Comparisons of the results of the model<sup>1</sup> with experimental data from the literature and new experimental data measured in the present work are reported in Tables 4–6 along with ADs. As can be seen, the experimental data and the predictions of the model<sup>1</sup> based on the BIPs obtained using the objective function displayed in eq 1 show satisfactory agreement, demonstrating the reliability of the tuning technique using only gas solubility data.

## Conclusions

New experimental data on the water content of a gas mixture containing 94% methane, 4% ethane, and 2% *n*-butane were generated in the 277.82–292.88 K temperature range and for pressures up to 3.028 MPa using a static-analytic method with equipment that takes advantage of a high-pressure new capillary sampler. The new experimental data were compared with

predictions of a previously reported semi-empirical approach. Good agreement between all data was observed, demonstrating the reliability and consistency of the experimental data and the technique and predictive method used in this work.

A previously reported thermodynamic model was then used with various databases to model the phase behavior of waterhydrocarbon systems. It was shown that using only gas solubility data in tuning the thermodynamic model leads to accurate predictions of the water content data. This is a very useful remark to the reduce experimental information required to evaluate mutual solubility of the natural gas-water system, especially at low-temperature conditions, where measuring gas solubilities in water is much easier than measuring natural gas water contents.

### Acknowledgment

The financial support by the European Infrastructure for Energy Reserve Optimization (EIERO), the Gas Processors Association (GPA), and a joint industrial project supported by Shell, TOTAL, Statoil, and Petrobras provided the opportunity for this joint work, which is gratefully acknowledged.

#### **Nomenclature**

AAD = average absolute deviation

AD = absolute deviation

BIP = binary interaction parameter

EoS = equation of state

FID = flame ionization detector

FOB = objective function

GC = gas chromatograph

NDD = nondensity dependent mixing rules

TCD = thermal conductivity detector

VPT-EoS = Valderrama modification of Patel—Teja equation of state

M = number of water content data points

N = number of gas solubility data points

P = pressure

T = temperature

k = BIP for the classical mixing rules

l = constant for the BIP for the asymmetric term

v = molar volume

x = mole fraction in liquid phase

y = mole fraction in vapor phase

Greek letters

 $\omega$  = acentric factor

Superscripts

1 = non-temperature-dependent term in NDD mixing rules

2 = temperature-dependent term in NDD mixing rules

**Subscripts** 

cal = calculated property

exp = experimental property

c = critical property

i, j = index for data

w = water

#### **Literature Cited**

- (1) Mohammadi, A. H.; Chapoy, A.; Richon, D.; Tohidi, B. Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems. Ind. Eng. Chem. Res. 2004, 43, 7148-7162.
- (2) Chapoy, A.; Mohammadi, A. H.; Tohidi, B.; Richon, D. Estimation of Water Content for Methane + Water and Methane + Ethane + n-Butane + Water Systems Using a New Sampling Device. J. Chem. Eng. Data 2005, 50, 1157-1161.
- (3) Valderrama, J. O. A generalized Patel-Teja equation of state for polar and non-polar fluids and their mixtures. J. Chem. Eng. Jpn. 1990, 23, 87-
- (4) Avlonitis, D.; Danesh, A.; Todd, A. C. Prediction of VL and VLL equilibria of mixtures containing petroleum reservoir fluids and methanol with a cubic EoS. Fluid Phase Equilib. 1994, 94, 181-216.
- (5) Mohammadi, A. H.; Chapoy, A.; Tohidi, B.; Richon, D. Measurements and Thermodynamic Modeling of Vapor-Liquid Equilibria in Ethane-Water Systems from 274.26 to 343.08 K. Ind. Eng. Chem. Res. **2004**, 43, 5418-5424.
- (6) Chapoy, A.; Coquelet, C.; Richon, D. Solubility measurement and modeling of water in the gas phase of the methane/water binary system at temperatures from 283.08 to 318.12 K and pressures up to 34.5 MPa. Fluid Phase Equilib. 2003, 214, 101-117.
- (7) Chapoy, A.; Coquelet, C.; Richon, D. Measurement of the Water Solubility in the Gas Phase of the Ethane + Water Binary System near Hydrate Forming Conditions. J. Chem. Eng. Data 2003, 48, 957-966.
- (8) Avlonitis, D. A. Thermodynamics of Gas Hydrate Equilibria. Ph.D. Thesis, Heriot-Watt University, Edinburgh, U.K., 1992. Also: Avlonitis, D. A. Multiphase Equilibria in Oil-Water Hydrate Forming Systems. M.Sc. Thesis, Heriot-Watt University, Edinburgh, U.K., 1988.
- (9) Tohidi-Kalorazi, B. Gas Hydrate Equilibria in the Presence of Electrolyte Solutions. Ph.D. Thesis, Heriot-Watt University, Edinburgh, U.K., 1995.
- (10) Mohammadi, A. H.; Chapoy, A.; Tohidi, B.; Richon, D. A Semi-Empirical Approach for Estimating the Water Content of Natural Gases. Ind. Eng. Chem. Res. 2004, 43, 7137-7147.
- (11) Mohammadi, A. H.; Chapoy, A.; Tohidi, B.; Richon, D. Advances in Estimating Water Content of Natural Gases. Presented at the 85th Annual GPA Convention, Grapevine, TX, March 5-8, 2006.
- (12) Chapoy, A.; Mohammadi, A. H.; Richon, D.; Tohidi, B. Gas solubility measurement and modeling for methane-water and methaneethane-n-butane-water systems at low temperature conditions. Fluid Phase Equilib. 2004, 220, 113-121.

Received for review November 30, 2005 Revised manuscript received April 13, 2006 Accepted April 17, 2006

IE051337I