Experimental Measurement and Thermodynamic Modeling for the Solubility of Methane in Water and Hexadecane

C. Eduardo Pereira Siqueira Campos,*,† J. Ribas Penello,‡ F. Luiz Pellegrini Pessoa,‡ and A. Maria Cohen Uller†

PEQ/COPPE/UFRJ, Cidade Universitária, CT, Bl. G, Sala 115, CEP 21949-900, RJ, Brasil, and DEQ/EQ/UFRJ,
Cidade Universitária, CT, Bl. E, Sala 207, Gabinete K, CEP 21945-970, RJ, Brasil

In the petroleum industry, there is direct contact among oil, gases, and water in many steps of petroleum exploitation and refining operations. The main constituent of the natural gas is methane, presenting on its composition 95 % of this substance. To design and optimize these operations a correct characterization of the phase equilibrium is essential, which depends on accurate experimental data and thermodynamic models. So, the main goal of this work was the experimental measurement of methane solubility in water and hexadecane, since this organic compound has properties similar to the average properties of Brazilian heavy oil. The experimental conditions used were a temperature range from (303.2 to 323.2) K and a low pressure range from (60.8 to 638.5) kPa. Moreover, the results were correlated using the best thermodynamic model, the Peng−Robinson equation of state for both phases with original mixing rules, to describe the behavior of the systems, demonstrating satisfactory bubble-point calculation.

Introduction

One of the most important exploited products from a petroleum reservoir is natural gas, whose composition shows methane contents higher than 95 %. Among other existing substances, there is oil, corresponding to hydrocarbons with elevated molecular weights, and the so-called production water, which presents a great number of ionic compounds (salts).

Along several steps of oil processing in offshore and onshore units, it is possible to identify a direct contact among oil, water, and gas, where the gas solubility determination in the liquids is extremely important for a correct description of the behavior of these systems.

For a satisfactory representation of these complex systems, a good knowledge of the behavior for the binaries systems formed by the mentioned substances is recommended. In a previous work, Siqueira Campos et al.[1] measured carbon dioxide solubility in water and hexadecane in a temperature range from (303.2 to 323.2) K and pressures from (51.7 to 535.4) kPa. In the present work, solubilities of methane were measured in water and hexadecane in a temperature range from (303.2 to 323.2) K and pressure range from (60.8 to 638.5) kPa. Hexadecane was chosen to represent the oil, since Brazilian petroleum can be characterized as a heavy oil with average properties similar to those of this alkane.

In the literature, there are some experimental data for methane solubility in water, but most of them are at elevated pressure, reporting the hydrate compound formation; for the methane + hexadecane system, these data are very scarce where only two works report this solubility. It is important to note that to measure experimental data at elevated pressures the costs are higher and there are many safety issues to be considered. So, it is possible to obtain the experimental measurements at low pressures, correlate these data, and predict the points at elevated pressures with satisfactory results, reducing the mentioned problems. Table 1 shows methane solubility in water and hexadecane data available in the literature.

Thus, because of the necessity of data for methane solubility in liquids for the correct characterization of phase behavior in the petroleum industry systems and the limited quantity of experimental data at low pressures of particular systems, the objective of this work was to determine methane solubilities in two different liquids: water and hexadecane. Furthermore, a thermodynamic modeling of the reported data is presented to calculate the phase equilibrium of the systems.

Experimental Section

Materials. Methane was supplied by Linde Gas Ltd. and hexadecane from Vetec Química Fina Ltd., both with 0.999 purity in mass fraction, and water was once-distilled.

Methods. In a previous work, an apparatus for gas solubility measurement was built and described in detail. It was validated with literature data and used to determine carbon dioxide solubility in water and hexadecane. In the present work, this equipment was used for the current measurements, where Figure 1 represents its schematic flowchart reported by Siqueira Campos et al.[1] for this synthetic method.

Experimental Procedure. The same experimental procedure adopted by Siqueira Campos et al.[1] was used in this work, and it is briefly discussed. The initial step was the weighing of a liquid sample inside the cell using an analytical digital balance. After the liquid degassing process, the system was completely evacuated, methane filled into the reservoir cell, and the bath temperature stabilized. The first pressure value was set by feeding the gas into the lines, and the valve close to the cell was periodically opened to prevent any solvent diffusion until the pressure was stabilized (final pressure). Thus, at the end of each experimental point, a pressure drop

---

* Corresponding author. Phone: +55 21 2562-7603; fax: +55 21 2562-8300. E-mail address: carlos@peq.coppe.ufrj.br.
† PEQ/COPPE/UFRJ, Cidade Universitária. E-mail: jojo_penello@hotmail.com; pessoa@eq.ufrj.br.
‡ DEQ/EQ/UFRJ, Cidade Universitária. E-mail: angela@pr2.ufrj.br.

10.1021/je9007958

Table 1. Literature Data for Methane Solubility in Water and Hexadecane

gas	liquid	ref	T/K	P/MPa
methane	water	O'Sullivan and Smith[2] (1970)	324.65 to 398.15	10.1 to 60.8
methane	hexadecane	Lin et al.[3] (1980)	462.45 to 703.55	2.03 to 25.33
methane	hexadecane	Rijkers et al.[4] (1993)	293.15 to 313.15	0.11 to 69
methane	water	Lekvam and Bishnoi[5] (1997)	274.19 to 285.67	0.57 to 9.08
methane	water	Kim et al.[6] (2003)	298.15	2.3 to 16.6
methane	water	Kiepe et al.[7] (2003)	313 to 373	up to 10
methane	water	Chapoy et al.[8] (2003)	283.08 to 318.12	up to 35
methane	water	Wang et al.[9] (2003)	283.2 to 303.2	2 to 40
methane	water	Mohammadi et al.[10] (2004)	282.98 to 313.32	up to 2.99
methane	water	Chapoy et al.[11] (2004)	275.11 to 313.11	up to 18
methane	water	Chapoy et al.[12] (2005)	277.8 to 361.4	up to 4.9
methane	water	Mohammadi et al.[13] (2006)	275.11 to 313.11	0.97 to 18
methane	water	Yarrison et al.[14] (2006)	310 to 477	3.45 to 110.32
methane	water	Qin et al.[15] (2008)	323.6 to 375.8	30.1 to 49.9

Table 2. Methane (1) + Water (2) System Solubility Data

T/K = 303.2		T/K = 313.2		T/K = 323.2	
P/kPa	$10^5 \cdot x_1$	P/kPa	$10^5 \cdot x_1$	P/kPa	$10^5 \cdot x_1$
111.5	1.83 ± 0.01	111.5	1.66 ± 0.01	111.5	0.9 ± 0.1
182.4	5.11 ± 0.01	182.4	4.45 ± 0.01	182.4	3.6 ± 0.1
243.2	8.4 ± 0.2	253.3	7.4 ± 0.1	243.2	6.20 ± 0.01
374.9	13.99 ± 0.01	374.9	12.4 ± 0.1	374.9	10.90 ± 0.01
506.6	19.7 ± 0.5	486.4	16.8 ± 0.9	506.6	15.7 ± 0.5
638.3	25.96 ± 0.01	628.2	22.5 ± 0.8	638.3	21.0 ± 1.0

Table 3. Methane (1) + Hexadecane (2) System Solubility Data

T/K = 303.2		T/K = 313.2		T/K = 323.2	
P/kPa	$10^3 \cdot x_1$	P/kPa	$10^3 \cdot x_1$	P/kPa	$10^3 \cdot x_1$
60.8	2.7 ± 0.4	60.8	1.78 ± 0.01	60.8	1.5 ± 0.5
121.6	7.5 ± 0.5	121.6	6.2 ± 0.2	121.6	5.9 ± 0.7
182.4	12.8 ± 0.5	182.4	11.1 ± 0.4	182.4	10.8 ± 0.7
283.7	20.5 ± 0.5	283.7	18.9 ± 0.5	273.6	18.5 ± 0.7
395.2	31.0 ± 0.8	395.2	28.8 ± 0.7	385.0	28.4 ± 0.6
506.6	43.9 ± 0.6	506.6	40.8 ± 0.7	506.6	39.7 ± 0.5

was observed, and discounting the dead volume (≈ 50 cm^3), one can obtain the real pressure drop referring to gas solubility in the liquid, evaluating its mole fraction through the algorithm presented by Siqueira Campos et al.[1] To measure consecutively equilibrium pressures using only one liquid sample, other higher initial pressures were adjusted. Each experiment was conducted three times to obtain repeatability of the proposed data.

The influence of some experimental variables on the gas solubility in liquids was verified before measurements. The quantity of solvent inside the equilibrium cell, partial molar volume of the gas in the algorithm calculations, compressibility factor in the vapor phase, and maximum time for total gas solubility were checked. The final values confirmed that 90 % of the cell volume needed to be filled with solvent, the Peng−Robinson (PR) equation of state was used to correct the vapor-phase deviations, and a time between (40 and 60) min was sufficient to complete the process.

The estimated accuracy for each measurement was 0.1 K for the temperature, 0.04 % for the pressure, and 0.1 mg for the weighed mass. The uncertainty for the mass determination was 0.05 mg and for the mole fraction of each substance was $5 \cdot 10^{-6}$.

Results and Discussion

Methane solubilities in water and hexadecane were obtained, and they can be seen in Tables 2 and 3 for the methane + water and methane + hexadecane systems, respectively. Moreover, Figure 2 shows a satisfactory behavior for the methane + water system data when compared with literature reports. All necessary data input and the calculation sequence for each experimental data reduction are the same as those presented by Siqueira Campos et al.[1]

From the results, it is possible to observe that the gas solubilities decrease in both liquids with increasing the temperature. On the other hand, it is also detected that methane solubilities in both liquids presented small values, demonstrating that any kind of loss or experimental uncertainty leads to deviations in the measured pressure drop. Thus, periodic tests to verify the equipment conditions are recommended during the experiments.

Moreover, apparent Henry constants, as shown by Ohgaki et al.,[16] were evaluated through eq 1, where k'_H represents this constant; y_{gas}, the vapor-phase mole fraction of the gas; x_{gas},

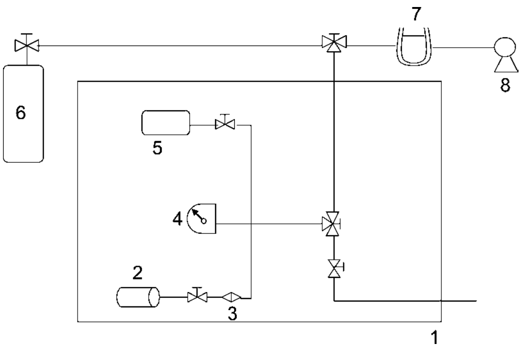

Figure 1. Schematic: 1, thermostatic bath; 2, equilibrium cell; 3, quick connection; 4, pressure transducer; 5, gas reservoir; 6, gas cylinder; 7, vacuum pump protection; 8, vacuum pump.

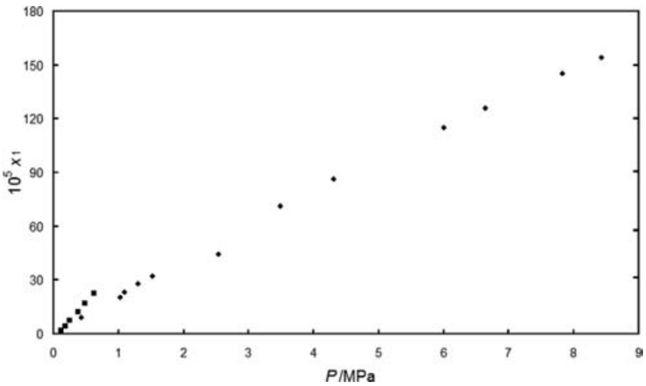

Figure 2. CH_4 (1) solubility in H_2O (2) as function of pressure at 313.2 K: ●, Kiepe et al.;[7] ■, this work.

Table 4. Apparent Henry's Constant[16] for the Methane + Water System

T/K = 303.2		T/K = 313.2		T/K = 323.2	
P/kPa	k'_H/MPa	P/kPa	k'_H/MPa	P/kPa	k'_H/MPa
111.5	5925.9	111.5	6465.4	111.5	11292.9
182.4	3485.5	182.4	3967.3	182.4	4767.8
253.3	2919.8	253.3	3306.3	253.3	3833.8
374.9	2604.8	374.9	2935.9	374.9	3291.6
506.6	2504.4	486.4	2807.3	506.6	3101.7
638.3	2398.8	628.2	2749.4	638.3	2940.7

Table 5. Apparent Henry's Constant[16] for the Methane + Hexadecane System

T/K = 303.2		T/K = 313.2		T/K = 323.2	
P/kPa	k'_H/MPa	P/kPa	k'_H/MPa	P/kPa	k'_H/MPa
60.8	23.7	60.8	38.1	60.8	43.7
121.6	16.3	121.6	20.2	121.6	21.0
182.4	14.5	182.4	16.8	182.4	17.2
283.7	13.6	283.7	14.7	273.6	15.0
395.2	12.5	395.2	13.5	385.0	13.6
506.6	11.6	516.8	12.4	506.6	12.8

Table 6. Henry's Law Constants

systems	$CH_4 + H_2O$	$CH_4 + C_{16}H_{34}$
T/K	k_H/MPa	k_H/MPa
303.2	15198.8	35.4
313.2	16212.0	77.7
323.2	39516.8	95.3

Table 7. UNIFAC Group Interaction Parameters[18]

n	m	A_{nm}/K	A_{mn}/K	B_{nm}	B_{mn}
CH_4	H_2O	41.10	950.50	4.7289	2.5081
CH_4	CH_2	−25.00	88.00	−0.3000	0.3000

Table 8. Area and Volume Parameters[19]

substance	R	Q
CH_4	1.2900	1.1240
$C_{16}H_{34}$	11.2438	9.2560
H_2O	0.9200	1.4000

Table 9. Antoine Parameters[26]

substance	A	B	C
water	5.1156	1687.537	230.170
hexadecane	4.1536	1830.510	154.450

the liquid-phase mole fraction of the gas; ϕ_{gas}, the fugacity coefficient of the gas, and P, the system equilibrium pressure. Table 4 shows the calculated values of this thermodynamic property for the methane + water system and Table 5 for methane + hexadecane. However, when the pressure tends to zero, one can determine Henry's law constants, and these values are presented in Table 6. To compare the values reported in Table 6, there are two literature reports for the infinite dilution Henry's constant at 298 K for the system methane + hexadecane: 17.35 MPa (Richon and Renon[17]) and 21.18 MPa (Lenoir et al.[18]). From these values, it is possible to verify that the Henry's constants presented in this work show satisfactory measurements.

$$k'_H = \frac{y_{gas}\phi_{gas}P}{x_{gas}} \tag{1}$$

Thermodynamic Modeling

To calculate the vapor−liquid equilibrium (VLE), one starts from the isofugacity criteria. Considering the nonideality in the liquid phase, the fugacity for a substance i presented in this phase can be described by eqs 2 or 3 and in the vapor phase by eq 4.

$$f_i^L = x_i\gamma_i f_i^{ref} \tag{2}$$

$$f_i^L = x_i\phi_i^L f_i^0 \tag{3}$$

$$f_i^V = y_i\phi_i^V f_i^0 \tag{4}$$

Applying these equations in the isofugacity criteria, one obtains eqs 5 and 6 which represent traditional $\gamma - \phi$ and $\phi - \phi$ approaches, respectively.

$$x_i\gamma_i f_i^{ref} = y_i\phi_i^V P \tag{5}$$

$$x_i\phi_i^L = y_i\phi_i^V \tag{6}$$

For the first approach three thermodynamic models (M1, M2, and M3) were analyzed. These models were implemented using the universal functional activity coefficient (UNIFAC) group contribution method proposed by Hansen et al.[19] to represent the nonideality of the liquid phase and the group interactions parameters presented by Voutsas et al.[20] Table 7 illustrates these parameters, and Table 8 shows the surface and area parameters obtained from Reid et al.[21]

Moreover, several works in the literature use as the reference state for the substances in the liquid phase a pure liquid at the same pressure and temperature of the system, and its fugacity is calculated through the vapor pressure, as shown in eq 7. Table 9 presents the Antoine parameter[21] values for each substance. For the gas, the strategy proposed by Prado[22] was used, and the gas fugacity reference was obtained by estimating the parameters F1, F2, and F3 presented in a correlation similar to the one proposed by Prausnitz and Shair,[23] as shown in eq 8.

$$\log_{10}[P^{vap}/\text{bar}] = A - \frac{B}{T/\text{K} + C - 273.15} \tag{7}$$

$$\ln\left(\frac{f_{CH_4}^{ref}}{P_c}\right) = \text{F1} - \frac{\text{F2}}{T_r} - \text{F3}\ln T_r \tag{8}$$

Finally, an ideal behavior for the substances presented in the vapor phase was adopted in model M1, while on the models M2 and M3 the nonideality deviations on this phase were accounted for using the virial and PR equations of state, respectively.

For the second approach, two thermodynamic models were tested, where the fugacity coefficients for the both phases were calculated from an equation of state. Model M4 uses the PR equation of state with the original mixing rule[24] (van der Waals: vdW), and model M5 uses the same equation with Heideman and Kokal[25] (HK) mixing rule.

Table 10 summarizes the five analyzed models with their particular characteristics and the expressions for equilibrium constants (K_i).

Initially, the model parameters were obtained using experimental data presented in Table 1 to determine the best proposed model and afterward using them to correlate the experimental measurements presented in this work. Pressure deviations were evaluated using eq 9, where P represents the experimental pressure and P^{CALC} the calculated pressure. Table 11 presents the results obtained for both systems using all proposed models with literature data. The parameters presented in each model were estimated using all experimental points in each system, achieving a simple group of parameters that simultaneously represents all isotherms. The Simplex fitting method was applied

Table 10. Thermodynamic Models

model	approach	liquid phase	vapor phase	$(f_i^0)_{\text{liq}}$	$(f_i^0)_{\text{vap}}$	K_i
M1	$\gamma - \phi$	UNIFAC	ideal gas	eq8	P	$K_i = (\gamma_i f_i^0)/P$
M2	$\gamma - \phi$	UNIFAC	virial equation	eq8	P	$K_i = (\gamma_i f_i^0)/(\phi_i^V P)$
M3	$\gamma - \phi$	UNIFAC	PR-vdW	eq8	P	$K_i = (\gamma_i f_i^0)/(\phi_i^V P)$
M4	$\phi - \phi$	PR-vdW	PR-vdW	f_i^0	f_i^0	$K_i = \phi_i^L/\phi_i^V$
M5	$\phi - \phi$	PR-HK	PR-HK	f_i^0	f_i^0	$K_i = \phi_i^L/\phi_i^V$

Table 11. Thermodynamic Modeling Results with Literature Experimental Data

	DP (%)				
system	M1	M2	M3	M4	M5
$CH_4 + H_2O$	26	55	> 30	7	17
$CH_4 + C_{16}H_{34}$	8	8	> 10	3	> 10

Table 12. Pressure Deviations and Parameters Obtained for the Experimental Data of this Work

system	DP (%)	k_{ij}	l_{ij}
$CH_4 + H_2O$	21	0.0001	0.1316
$CH_4 + C_{16}H_{34}$	10	0.0181	0.0089

in this optimization step, and the objective function is presented in eq 10, where NP represents the number of experimental points.

$$\text{MD} = \left(\frac{|P - P^{\text{CALC}}|}{P}\right) \tag{9}$$

$$F_{\text{obj}} = \sum_{i=1}^{\text{NP}} \left(\frac{P_i - P_i^{\text{CALC}}}{P_i}\right)^2 \tag{10}$$

Analyzing Table 11, it can be verified that the model M4 presented satisfactory results for the calculations of gas solubilities in liquids, where the achieved deviations are in the same magnitude of other experimental and theoretical works developed in the literature. Table 12 presents the results achieved for the modeling of experimental values of the present work and the final estimated parameters for model M4.

Conclusions

Methane solubilities in water in a range from $(9 \cdot 10^{-6}$ to $26 \cdot 10^{-5})$ and in hexadecane in a range from $(1 \cdot 10^{-3}$ to $44 \cdot 10^{-3})$ were experimentally determined in a temperature range from (303.2 to 323.2) K and pressure range from (60.8 to 638.5) kPa using the equipment developed by Siqueira Campos et al.[1] Apparent Henry's constants were also calculated for each experimental measurement. Furthermore, five thermodynamic models were analyzed to represent the phase equilibrium of the studied systems. The best results were achieved using the model M4, which consists of a $\phi - \phi$ thermodynamic approach where the Peng−Robinson equation of state was implemented for each phase calculation. The best values of k_{ij} and l_{ij} for the system methane−water were 0.0001 and 0.1316, respectively, and for methane−hexadecane system were 0.0181 and 0.0089, respectively. Using these parameters, the final deviations in pressure were equal to 21 % for the first system and 10 % for the second one. Experimental and theoretical results were satisfactory when compared with other works available in the literature.

Supporting Information Available:

Equations of state used to correct the deviations for the studied substances and Table A1 with the properties of these substances. Figure 3 presents the flow chart for the data reduction of gas solubility. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Siqueira Campos, C. E. P.; Villardi, H. G.; Pessoa, F. L. P.; Uller, A. M. C. Solubility of Carbon Dioxide in Water and Hexadecane: Experimental Measurement and Thermodynamic Modeling. *J. Chem. Eng. Data* **2009**, *54*, 2881–2886.

(2) O'Sullivan, T. D.; Smith, N. O. The Solubility and Partial Molar Volume of Nitrogen and Methane in Water and in Aqueous Sodium Chloride from 50 to 125 and 100 to 600 atm. *J. Phys. Chem.* **1970**, *74*, 1460–1466.

(3) Lin, H.; Sebastian, H. M.; Chao, K. Gas-Liquid Equilibrium in Hydrogen + *n*-Hexadecane and Methane + *n*-Hexadecane at Elevated Temperatures and Pressures. *J. Chem. Eng. Data* **1980**, *25*, 252–254.

(4) Rijkers, M. P. W. M.; Peters, C. J.; Arons, J. S. Measurements on the phase behavior of binary mixtures for modeling the condensation behavior of natural gas: Part III. The system methane + hexadecane. *Fluid Phase Equilib.* **1993**, *85*, 335–345.

(5) Lekvam, K.; Bishnoi, P. R. Dissolution of methane in water at low temperatures and intermediate pressures. *Fluid Phase Equilib.* **1997**, *131*, 297–309.

(6) Kim, Y. S.; Ryu, S. K.; Yang, S. O. Liquid Water - Hydrate Equilibrium Measurements and Unified Predictions of Hydrate-Containing Phase Equilibria for Methane, Ethane, Propane, and Their Mixtures. *Ind. Eng. Chem. Res.* **2003**, *42*, 2409–2414.

(7) Kiepe, J.; Horstmann, S.; Fischer, K. Experimental Determination and Prediction of Gas Solubility Data for Methane + Water Solutions Containing Different Monovalent Electrolytes. *Ind. Eng. Chem. Res.* **2003**, *42*, 5392–5398.

(8) Chapoy, A.; Coquelet, C.; Richon, D. Solubility Measurement and Modeling of Water in the Gas Phase of the Methane/Water Binary Systems at Temperatures from 283.08 to 318.12 K and Pressures up to 34.5 MPa. *Fluid Phase Equilib.* **2003**, *214*, 101–117.

(9) Wang, L. K.; Chen, G. J.; Han, G. H. Experimental study on the solubility of natural gas components in water with or without hydrate inhibitor. *Fluid Phase Equilib.* **2003**, *207*, 143–154.

(10) Mohammadi, A. H.; Chapoy, A.; Richon, D. Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems. *Ind. Eng. Chem. Res.* **2004**, *43*, 7148–7162.

(11) Chapoy, A.; Mohammadi, A. H.; Richon, D.; Todihi, B. Gas solubility measurement and modeling for methane-water and methane-ethane-*n*-butane-water systems at low temperature conditions. *Fluid Phase Equilib.* **2004**, *220*, 113–121.

(12) Chapoy, A.; Mohammadi, A.; Tohidi, H. B. 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.

(13) Mohammadi, A. H.; Chapoy, A.; Richon, D. Gas Solubility: A Key to Estimating the Water Content of Natural Gases. *Ind. Eng. Chem. Res.* **2006**, *45*, 4825–4829.

(14) Yarrison, M.; Cox, K. R.; Chapman, W. G. Measurement and Modeling of the Solubility of Water in Supercritical Methane and Ethane from 310 to 477 K and Pressures from 3.4 to 110 MPa. *Ind. Eng. Chem. Res.* **2006**, *45*, 6770–6777.

(15) Qin, J.; Rosenbauer, R. J.; Duan, Z. Experimental Measurements of Vapor-Liquid Equilibria of the $H_2O + CO_2 + CH_4$ Ternary System. *J. Chem. Eng. Data* **2008**, *53*, 1246–1249.

(16) Ohgaki, K.; Nishii, H.; Katayama, T. A Method for Gas-Solubility Measurement. *J. Chem. Eng. Jpn.* **1983**, *16*, 72–73.

(17) Richon, D.; Renon, H. Infinite Dilution Henry's Constants of Light Hydrocarbons in *n*-Hexadecane, *n*-Octadecane, and 2,2,4,4,6,8,8-Heptamethylnonane by Inert Gas Stripping. *J. Chem. Eng. Data* **1960**, *25*, 59–60.

(18) Lenoir, J. Y.; Renauk, P.; Renon, H. J. Gas chromatographic determination of Henry's constants of 12 gases in 19 solvents. *J. Chem. Eng. Data* **1971**, *16*, 340–342.

(19) Hansen, H. K.; Coto, B.; Kuhlmann, B. *Phase Equilibria and Separation Process*, SEP-9212; Technical University of Denmark: Copenhagen, Denmark, 1992.

(20) Voutsas, E. C.; Boukouvalas, C. J.; Kalospiros, N. S.; Tassios, D. P. The Performance of EoS/G^E Models in the Prediction of Vapor−Liquid Equilibria in Asymmetric Systems. *Fluid Phase Equilib.* **1996**, *116*, 480–487.
(21) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw Hill: New York, 1977.
(22) Prado, M. P. Predictive model for carbon dioxide solubilities calculations in polymers. MSc. Thesis, COPPE/UFRJ, Brazil, 2004.
(23) Prausnitz, J. M.; Shair, F. H. Thermodynamic Correlation of Gas Solubilities. *AIChE J.* **1961**, *7*, 682–687.
(24) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
(25) Heideman, R. A.; Kokal, S. L. Combined Excess Free Energy Models and Equations of State. *Fluid Phase Equilib.* **1990**, *56*, 17–37.
(26) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The properties of gases and liquids*, 5th ed.; McGraw Hill: New York, 2001.

Received for review October 1, 2009. Accepted April 28, 2010. The authors would like to thank CNPq and FAPERJ for the financial support.

JE9007958