SOLUBILITY AND THERMODYNAMIC PROPERTIES OF CARBON DIOXIDE IN MEG/WATER MIXTURES

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Abstract. Solubility of gases in mixtures of monoethylene glycol (MEG)/water is an important issue for petroleum industry when is considered the MEG regeneration process after its use as a hydrate inhibitor. This work aims to measure the solubility and excess properties of CO_2 (carbon dioxide) in MEG/water mixtures at different concentrations and temperatures. A static methodology was used for measure the value of Henry constant and solubilities up to 5 bar in the temperature range from 298 to 348 K at molar compositions of the solvent mixture MEG:water of 0, 10, 50, 90 and 100 %. All mixtures were degassed before the gas solubility measurement by freezing the sample under liquid nitrogen and melting the mixture by heating under vacuum. Results indicated that temperature has a remarkable negative influence on solubility of carbon dioxide in the liquid mixture. Pressure, on the other hand present a positive linear effect on the gas solubility. Phase diagrams of pressure in function of mole composition were constructed for the binary and ternary mixtures. Also, the results indicated that MEG concentration has an important role on solubility of CO_2 in the liquid mixture. Excess solution enthalpy and entropy were also determined from binary and ternary henry constant evaluated for the mixtures.

Keywords: solubility, monoethylene glycol, carbon dioxide, water

1. Introduction

Oil companies are continually working to increase the exploration and production of oil and gas. In this context, the development of projects offshore are increasing, especially at great depths. In some petroleum fields, fluids from reservoir (gas, oil and water) are routed directly to the platform through pipes where the processing is performed. These pipelines remain under high pressures and low temperatures, providing favorable conditions for the formation of gas hydrates (Psarrou et al. [1]).

Hydrates can block pipelines, subsea transfer lines, and, in the event of a gas kick. During drilling, can form in the well, in risers, blow-out preventers (BOPs) and chokelines (Masoudi et al. [2]). Gas hydrates are non-stoichiometric compounds, which are formed by water (host) and small gas molecules (guests) (eg, methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2) and hydrogen sulfide (H_2S)) under conditions of low temperature and high pressure (Sloan and Koh [3], Lee et al. [4]).

In order to avoid the formation of hydrates during the disposing of petroleum to platform, the industry usually does the injection of inhibitors in the head of the wells. These inhibitors can be classified in thermodynamic or kinetic types, and are injected depending on the temperature and pressure conditions of well (Masoudi et al. [2]).

The monoethylene glycol (MEG) is one of the most important thermodynamic inhibitors to avoid hydrate formation (Galvão and Francesconi [5], Afzal et al. [6]). On the other hand, due to the large amounts of MEG used for hydrate control, its recycle is a lot of common (Psarrou et al. [1])

The separation of water comes with an unwelcome effect: the glycol also dissolves an amount of the gaseous components. In order to design, to operate and to optimize an effective dehydration system, it is fundamental to know the amount of gas dissolved and the influence of temperature and pressure on the dissolution phenomena (Galvão and Francesconi [5]).

In particular, the knowledge of the amount of carbon dioxide dissolved in MEG/water mixtures is very helpful for the MEG regeneration process, once CO_2 is responsable for carbonate formation (salt precipitation) and pH decreasing (corrosion) (MASOUDI et al. [2], Psarrou et al. [1]).

In this context, the objective of this work is to report experimental data on gas solubility and calorimetric properties involving binary and ternary systems of carbon dioxide with water and MEG in the temperature range of 288–348,15 K and pressures up to 5 bar. The experimental methodology is based on the work of Ohgaki et al. [7] and Nitta et al. [8], in which the gas liquid phase composition is determined through an iterative procedure assuming the validity of Henry's law for the liquid phase fugacity of the lighter component.

2. Experimental

2.1. Materials

For the experimental procedures were used as the solute carbon dioxide provided by White Martins, with minimum purity of 99,99%, doubly distilled water (Milli-Q) and monoethylene glycol (99,5%, Merck) as solvent. This latter used as received, without any additional treatment.

2.2. Apparatus and Experimental Procedure

The apparatuses used to determine the experimental data for this work have been reported in detail by Dalmolin et al. [9]. Experimental unit, shown schematically in Figure 1, consists of a cylinder of carbon dioxide, a pressure regulating valve connected to it directly, a vacuum pump and the unit for the collection of data (called the mobile part).

Gas cylinder and vacuum pump are connected to the unit through pipes and Swagelok (QC4-S/D-400) fast connections. Mobile part (parts 4, 5, 6 and valves V1, V2, V3 in Figure 1) is constituted by equilibrium cell, a gas reservoir and a pressure transducer. There are ball valves (Swagelok 42XS4-SS) in the inputs the mobile part, equilibrium cell and gas reservoir. Equilibrium cell is connected to the mobile part via a Cajon VCO connection and the ball valve by a Cajon (Ultra Torr, SS-4-UT-6) metal connection glass. All lines of the mobile part are 1/4 in OD tubing of stainless steel. Mobile part of the unit is inserted into ultra-thermostatic bath (Julabo, model MC) which allows the temperature control accuracy of 0,1 K. System pressure is obtained with the aid of a transducer (accuracy of 0,015 bar) and, through its calibration, the value is obtained in atmospheres (absolute pressure).
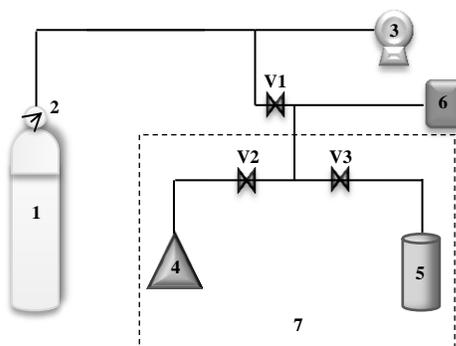
Figure 1. Schematic diagram of the experimental apparatus: (1) gas cylinder; (2) control valve; (3) vaccum pump; (4) equilibrium cell; (5) gas reservoir; (6) pressure transducer; (7) water bath; V1, bellow valve; and V2 and V3, ball valves.

Methodology to be employed in the solubility tests has a first and important step the degassing of the solvent. Cell was emptied, weighed and filled with solvent, typically covering 2/3 of its total capacity. Degassing was accomplished by freezing (using liquid nitrogen) and melting (at room temperature) the solvent under moderate vacuum, repeatedly, until no gas bubbles were observed in the melting process. Afterwards the cell was dried, weighed and connected to the mobile part of the equipment. It is worth mentioning that the degassing step has led in all circumstances to very negligible solvent mass losses. With the aid of the vacuum pump, the entire line is evacuated - from the mobile part (gas reservoir open) to the cylinder pressure regulating valve. The vacuum pump is then isolated from the system and the gas is admitted to the mobile part (gas reservoir open) at a pressure slightly greater than that which is desired to obtain the first data of balance. The ball valve located at the entrance of the mobile part is closed and await the stability of the pressure reading. Then, equilibrium cell ball valve is opened and closed in rapid movements, thereby enabling the solubilization of the gas to reach equilibrium, noting the value of the ultimate pressure. Solubility is then calculated by an iterative scheme using the thermodynamic equilibrium laws. New equilibrium points can be obtained by closing the equilibrium cell, evacuating to the mobile part and adding gas at increased pressures.

2.3. Theoretical Considerations

Phase equilibria can be described by isofugacity criteria

$$\hat{f}_1^V = \hat{f}_1^L \tag{1}$$

where $\hat{f}_1^V$ and $\hat{f}_1^L$ represent fugacities of component 1 in the vapor phase (gas) and liquid phase, respectively. Once the CO_2 has limited solubility in the solvents and solvent mixtures of interest of this work, it is assumed Henry's law valid for the component of low solubility. As the gases are at infinite dilution, the asymmetric activity coefficient Henry's law (γ_1^*) can, safety, be approximated to unity. Equilibrium "Equation 1" can be described by:

$$y_1 \hat{\emptyset}_1^V P = x_1 H_1 \tag{2}$$

where $\hat{\emptyset}_1^V$ is the fugacity coefficient of component 1 in the vapor phase; P is the system pressure, H_1 is Henry's constant; and x_1 and y_1 are the mole fractions of the vapor and liquid phases, respectively.

The gas liquid phase composition was calculated by an iterative procedure according to "Equation 2" and schemes presented in the literature (Ohgaki et al. [7] and Nitta et al. [8]). The partial molar volume of carbon dioxide at infinite dilution in both solvents was estimated using a corresponding state correlation (Lyckman et al. [10], Handa and Benson [11]). The vapor phase fugacity coefficient of the gas was calculated through the P–R EoS (Peng and Robinson [12]).

The enthalpy and entropy of solution is obtained by straight-forward thermodynamics (Prausnitz et al. [13]):

$$\left(\frac{\partial \ln H_1}{\partial(1/T)}\right) = \frac{\bar{h}_1^{1,\infty} - h_1^{ig}}{R} = \frac{\Delta \bar{h}_1}{R} \tag{3}$$

$$\left(\frac{\partial T \ln H_1}{\partial T}\right) = \frac{\bar{s}_1^{1,\infty} - s_1^{ig}}{R} = -\frac{\Delta \bar{s}_1}{R} \tag{4}$$

where, $\bar{h}_1^{1,\infty}$ and h_1^{ig} denote, respectively, the partial molar enthalpy of the solute in liquid solution at infinite dilution and molar enthalpy of solute in the ideal gaseous phase, $\bar{s}_1^{1,\infty}$ and s_1^{ig} stand for, respectively, the partial molar entropy of the solute in liquid solution at infinite dilution and molar entropy of the solute in the ideal gaseous phase.

In the case of gas liquid solubility, the mixture consists of molecules of the chemical nature, different shape and size. Furthermore, in systems containing glycols, the molecules of liquid are strongly polar. These characteristics make the mixture, in general, not ideal and to quantify these non-idealities, excess properties can be employed. The excess Henry's constant, directly related to solubility, is usually defined as:

$$\ln H_{l,m}^{ex} = \ln H_{l,m}^{rs} - \ln H_{l,m}^{is} \tag{5}$$

where $H_{l,m}^{ex}$ is the excess Henry's constant for a solute in the binary solvent mixture, $H_{l,m}^{rs}$ and $H_{l,m}^{is}$ denote the Henry's constants for a real and ideal solution, respectively.

The last term in "Equation 5" is the well-known Henry's constant of a component in an ideal solution, given by:

$$\ln H_{l,m}^{is} = \sum_{j:2}^{ns} x_j' \cdot \ln H_{i,j} \tag{6}$$

where x_j' is the solute-free solvent mole fraction, $H_{i,j}$ represents the binary Henry's constant of a solute in solvent j and ns means the number of heavier compounds (solvents).

All the values for CO_2 solubility shown in the graphs and tables are on molar basis (molar fraction) calculated according to the expression:

$$x_1 = \frac{n_1}{n_2 + n_1} \tag{7}$$

where n_1 is the number of moles of solute and n_2 is the number of moles of solvent in the liquid phase.

An algorithm has been implemented in Fortran for calculating the solubilities and Henry's constant. Details of the calculation procedure can be found in Ohgaki et al. [7] and Nitta et al. [8].

3. Results and Discussion

3.1. Unit and Procedure Validation

Using the methodology described previously, the unit and experimental procedure were validated using solubility data of CO_2 in water under pressure up to 5 bar and different temperatures (298 and 323,15 K).

The Henry's constants values are reported in Figures 2(a) and 2(b). As expected, a linearity between the measured values was noticed in the experimental range investigated (low solubility), where Henry's constant values increases with temperature.

It can be noted a good agreement between the results obtained in this study with the data available in the literature at different temperatures, suggesting thereby that the unit and procedures adopted are appropriate to measure the solubility of gases in liquids.

(a)   (b)
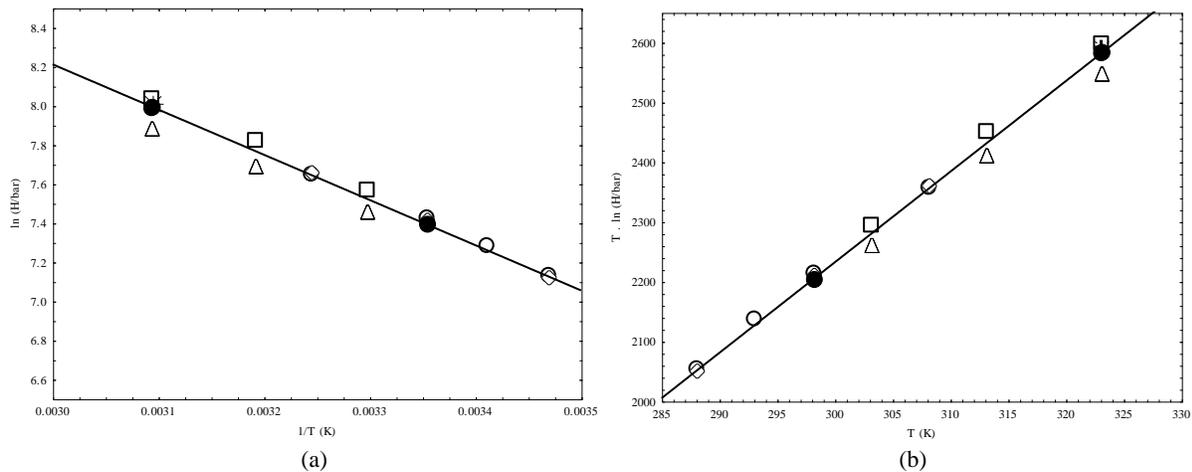
Figure 2. Dependence of Henry's law constant with temperature: (a) (ln H) versus 1/T; (b) T·ln H) versus T. (△) Ohgaki et al. [7]; (○) Dalmolin et al. [9]; (□) Campos *et al*. [14]; (◇) Postigo e Katz [15]; (✽) Zawlsza e Malesliska [16]; (●) This work.

3.2. Solubility measurements of CO_2 in solvents mixtures

To realize solubility measurements of CO_2 in MEG/water mixtures, the same procedure used for experimental measurements of solubility of CO_2 in water was adopted.

Table 1. Solubility (x) and Henry's (H) constants for $CO_2(1)$ in mixtures of MEG(2)/water(3). Values of the composition of the solvent mixture in free base solute

$x_2 = 0,00$

T (K) = 298,50 H = 1624 bar				T (K) = 323,35 H = 2960 bar			
P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$
1,535	0,087	1,210	0,089	1,250	0,035	1,053	0,026
2,529	0,151	2,010	0,136	2,154	0,065	1,673	0,048
3,259	0,194	2,653	0,176	2,887	0,092	2,062	0,060
3,783	0,227	3,209	0,208	3,486	0,114	2,438	0,073
		3,811	0,241	4,083	0,136	3,020	0,093
			0,265			3,359	0,106
			0,293			3,839	0,123

$x_2 = 0,10$

T (K) = 288,15 H= 1303 bar		T (K) = 303,15 H=1745 bar		T (K) = 318,15 H= 2199 bar		T (K) = 333,15 H= 2883 bar		T (K) = 348,15 H= 3563 bar	
P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$
1,110	0,086	1,089	0,067	1,148	0,051	1,160	0,032	1,230	0,029
2,116	0,165	2,114	0,121	2,139	0,094	2,182	0,073	2,188	0,047
3,134	0,230	3,503	0,178	3,104	0,131	3,159	0,106	3,162	0,090

$x_2 = 0,50$

T (K) = 288,15 H= 731 bar		T (K) = 303,15 H= 1018 bar		T (K) = 318,15 H= 1227 bar		T (K) = 333,15 H= 1575 bar		T (K) = 348,15 H= 2171 bar	
P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$
1,163	0,151	1,098	0,105	1,265	0,093	1,215	0,062	1,410	0,052
2,014	0,292	2,118	0,206	2,172	0,174	2,144	0,132	2,187	0,092
3,003	0,404	3,098	0,306	2,890	0,248	3,150	0,204	3,142	0,147
						4,056	0,271		

$x_2 = 0,90$

T (K) = 288,15 H= 496 bar		T (K) = 303,15 H= 655 bar		T (K) = 318,15 H= 782 bar		T (K) = 333,15 H= 971 bar		T (K) = 348,15 H= 1241 bar	
P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$
1,165	0,215	1,172	0,185	1,198	0,144	1,199	0,110	1,238	0,094
2,048	0,415	2,082	0,324	2,081	0,271	2,153	0,221	2,154	0,175
2,975	0,655	3,010	0,479	3,069	0,402	3,072	0,326	3,050	0,262
		4,044	0,655	4,038	0,536	4,033	0,439		

$x_2 = 1,00$

T (K) = 288,15		T (K) = 303,15		T (K) = 318,15		T (K) = 333,15		T (K) = 348,15	
H= 456 bar		H=551 bar		H=725 bar		H= 934 bar		H= 1040 bar	
P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$	P (bar)	$x_1 \times 10^2$
1,060	0,214	1,051	0,186	1,125	0,151	1,151	0,115	1,245	0,110
2,050	0,457	2,006	0,355	2,087	0,282	2,124	0,221	2,152	0,206
3,020	0,711	2,994	0,533	3,064	0,422	3,110	0,332	3,111	0,321
		3,961	0,703	4,060	0,561	4,111	0,449		
		4,910	0,889			5,050	0,546		

Table 1 shows the experimental results regarding the solubility of CO_2 in the MEG/water mixture in different molar concentrations of solvents (0, 10, 50, 90 and 100%), ranging between 288 and 348 K and pressures up to 5 bar. The composition of the mixture is always displayed on a CO_2 free molar basis. For each condition, it was assessed the solubility as a function of pressure.

Analyzing the solubility data for the gas-liquid system it is possible to verify the temperature influence upon solubility. The increasing of temperature leads to a decrease in gas solubility since the kinetic energy of the molecules and the strength of their collisions are larger at higher temperatures, contributing to the release of gas molecules from the liquid. The fact of carbon dioxide solubility decreases with temperature indicates that the interaction among molecules of solute and solvent releases energy (an exothermic effect) (Galvão and Francesconi [5]).

For CO_2/water and CO_2/MEG pure systems, it can be noted that carbon dioxide is much more soluble in MEG than in water. It also can be observed that the increase of MEG concentration induces an increase in the amount of gas solubility in the solvent mixture. This tendency can be best viewed in Figure 3, at 303,15 K, which a linear relationship exists between the pressure and the amount of CO_2 in the liquid phase solubilized. An inspection of Table 1 indicated that similar observations were obtained for other temperatures investigated and, as usually observed for most liquid-gas systems, temperature has an opposite effect on gas solubility when compared to pressure.
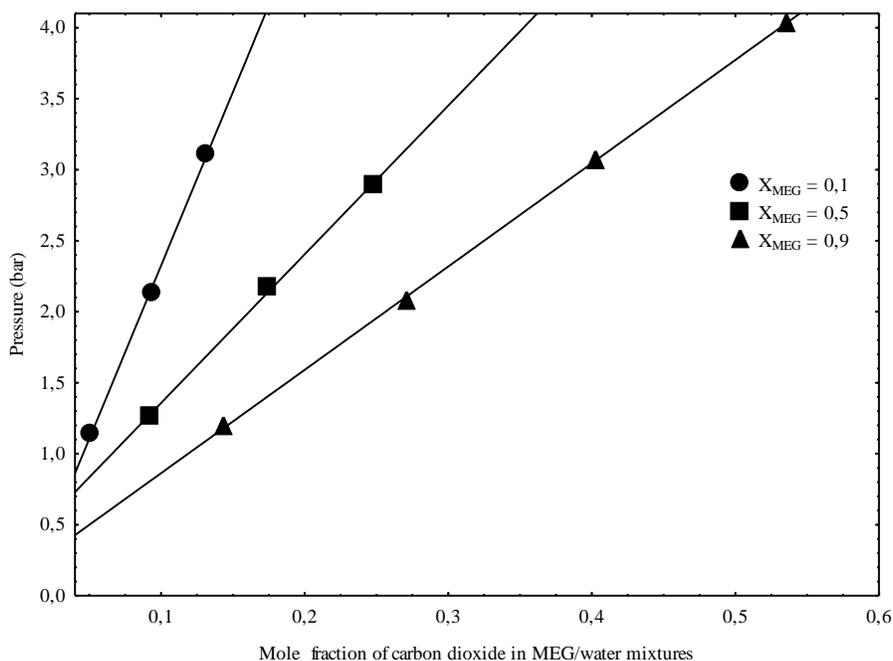
Figure 3. P–x diagram for carbon dioxide in MEG(2)/water(3) mixtures at 303,15 K expressed as mole fraction (x).

Figure 4(a) and 4(b) present the natural logarithm of Henry's law constant versus inverse temperature for different MEG compositions. As expected, the H values for carbon dioxide increase with temperature. The calorimetric properties values for the CO_2/MEG/water system were obtained from these figures. Table 2 depicts enthalpy and entropy values for carbon dioxide in MEG/water mixtures.

(a)

(b)
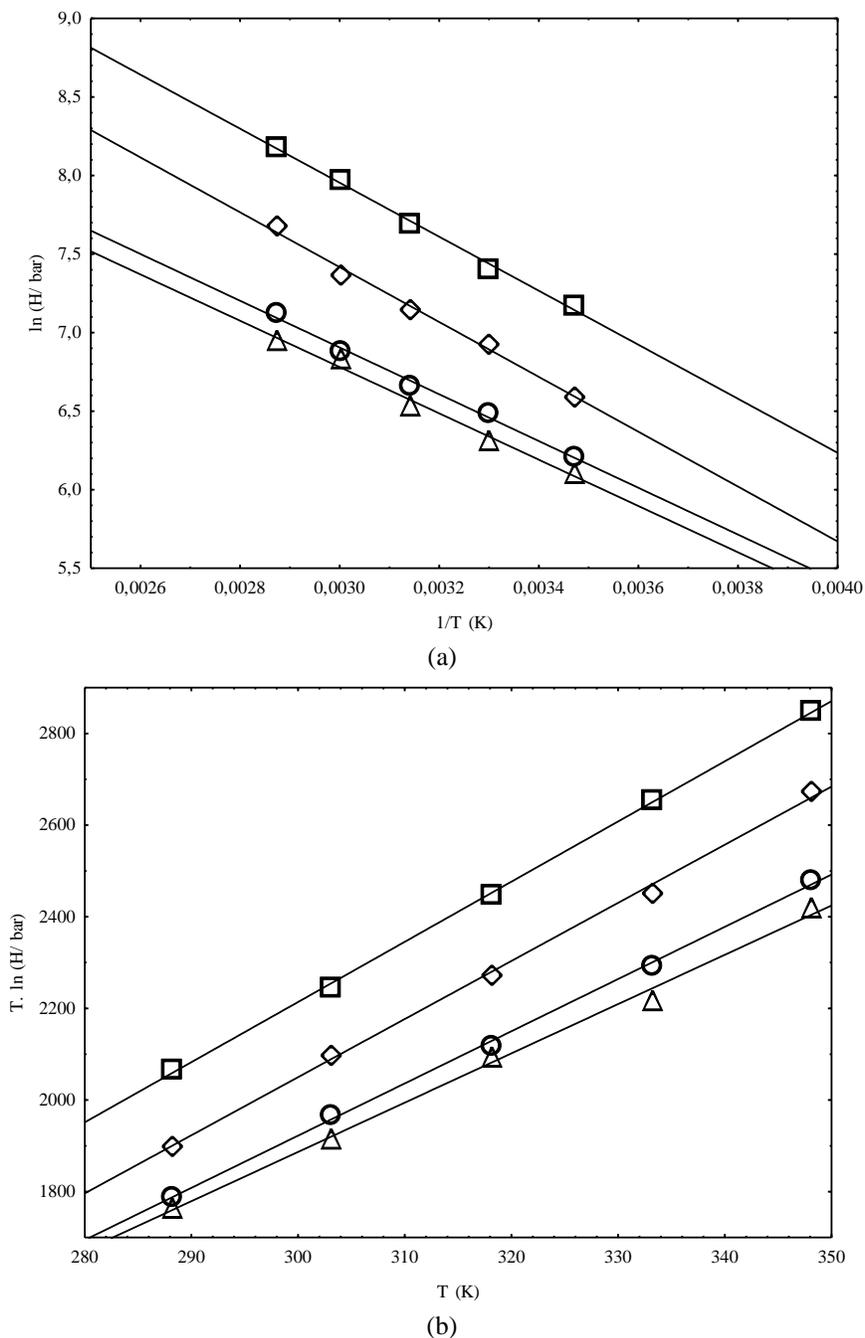
Figure 4. Dependence of Henry's law constant with temperature at different MEG compositions: (□) $x_{MEG} = 0,10$; (◇) $x_{MEG} = 0,50$; (○) $x_{MEG} = 0,90$; (△) $x_{MEG} = 1,0$. (a) ln(H) versus 1/T and (b) T·ln(H) versus T.

Table 2. Values of the enthalpy ($\triangle \bar{h}$) and entropy ($\triangle \bar{s}$) of solution for carbon dioxide in MEG/water mixtures in the temperature range investigated 288–348,15 K

x_{MEG}	$-\triangle \bar{h}(J/mol)$	$-\triangle \bar{s}(J/mol \cdot K)$
0	19237; 18712 [9]; 19430 [17]	126,0; 124,1 [9]
0,1	14292	109,2
0,5	14515	105,4
0,9	12375	94,7
1,0	11777	91,6

Figure 5 presented experimental excess Henry's constant and carbon dioxide solubility data in MEG/water systems as calculated by the "Equation 5". It can be seen that the mixture induces negative deviations from ideality (pure solvents) regarding the Henry constant. In other words, the mixture presents the H constant value smaller than those expected for pure solvents. Once the H constant is related to solubility inverse, it can be concluded that the molecular interactions between water and MEG provide an increase in solubility of CO_2 in mixture, when it compared to each pure solvent contribution.
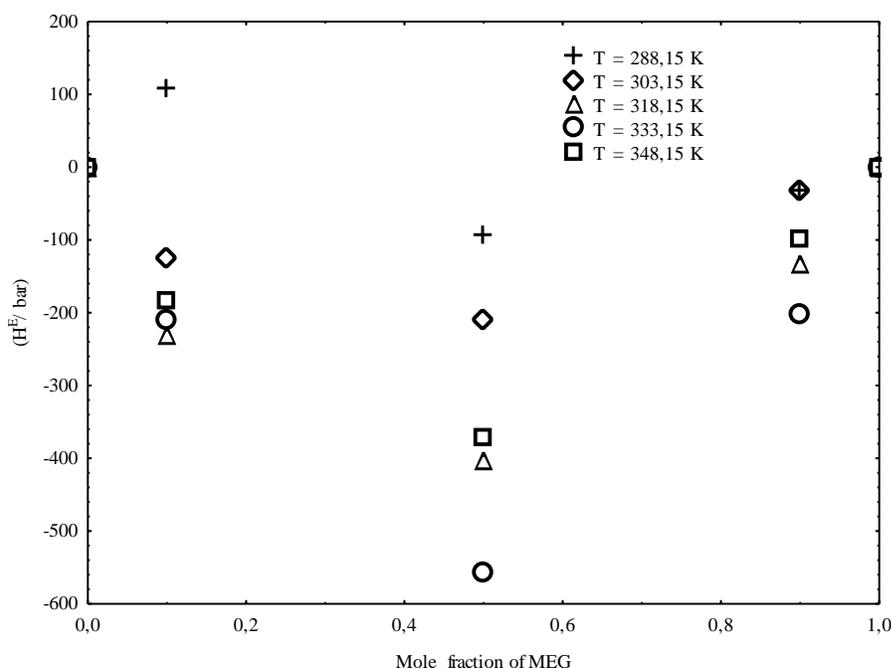
Figure 5. Excess Henry's constant (H^E) for carbon dioxide in MEG/water mixtures at various temperatures and some solvent mixture compositions (x_{MEG}).

4. Conclusion

Solubilities of gases in pure liquids and in solvents mixtures are of considerable industrial and theoretical importance. In this work, gases solubility data, Henry's constants values and calorimetric properties values for carbon dioxide in binary and ternary mixtures involving water and MEG were measured from 288 to 348,15 K, pressures up to 5 bar and for different compositions. It was experimentally verified that temperature has a remarkable negative influence on solubility of carbon dioxide, as demonstrated by the decrease of solubility with temperature. However, negative excess Henry's constant shows that the interactions between water and MEG promote the solubility of carbon dioxide in the mixture in the range of temperature and pressure studied.

Acknowledgements

References

[1]   M.N. Psarrou, L.O. Josang, K. Sandengen, T. Ostvold, Carbon dioxide solubility and monoethylene glycol (MEG) degradation at MEG reclaiming/regeneration conditions, Journal of Chemical and Engineering Data 56 (2011) 4720–4724.

[2]   R. Masoudi, B. Tohidi, R. Anderson, R.W. Burgass, J. Yang, Experimental measurement and thermodynamic modeling of clathrate hydrate equilibria and salt solubility in aqueous ethylene glycol and electrolyte solutions, Fluid Phase Equilibria 219 (2004) 157–163.

[3]   E.D. Sloan, C.A. Koh, Clathrate hydrates of natural gases. Colorado, 2008, 720p.

[4]   H.H. Lee, S.H. Ahn, B.U. Nam, B.S. Kim, G.W. Lee, D. Moon, H.J. Shin, K.W. Han, J.H. Yoon, Thermodynamic stability, spectroscopic identification and gas storage capacity of $CO_2-CH_4-N_2$ mixture gas hydrates: Implications for landfill gas hydrates, Environmental Science and Technology 46(7) (2012), 4184−4190.

[5]   A.C. Galvão, A.Z. Francesconi, Solubility of methane and carbon dioxide in ethylene glycol at pressures up to 14 MPa and temperatures ranging from (303 to 423) K, Journal of Chemical Thermodynamics 42 (2010) 684–688.

[6]   W. Afzal, A.H. Mohammadi, D. Richon, Experimental study and phase equilibrium modeling of systems containing acid gas and glycol, Fluid Phase Equilibria 318 (2012) 40–50.

[7]   K. Ohgaki, H. Nishii, T. Katayama, A method for gas-solubility measurement, Journal of Chemical Engineering of Japan 16 (1983) 72–73.

[8]   T. Nitta, T. Akimoto, A. Matsui, T. Katayama, An apparatus for precise measurement of gas solubility and vapor pressure of mixed solvents, Journal of Chemical Engineering of Japan A 16 (1983) 352–356.

[9]   I. Dalmolin, E. Skovroinski, A. Biasi, M.L. Corazza, C. Dariva, J.V. Oliveira, Solubility of carbon dioxide in binary and ternary mixtures with ethanol and water, Fluid Phase Equilibria 245 (2006) 193–200.

[10] E.W. Lyckman, C.A. Eckert, J.M. Prausnitz, Generalized reference fugacities for phase equilibrium thermodynamics, Chemical Engineering Science 20 (1965) 685–691.

[11] Y.P. Handa, G.C. Benson, Partial molar volumes of gases dissolved in liquids. Part I. Selected literature data and some estimation techniques, Fluid Phase Equilibria 8 (1982) 161–180.

[12] D.Y. Peng, D. B. Robinson, Industrial and Engineering Chemistry Fundamentals 15 (1976) 59–64.

[13] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, Molecular thermodynamics of Fluid Phase Equillibria. New Jersey, 1999.

[14] C.E.P.S. Campos, H.G.D. Villardi, F.L.P. Pessoa, A.M.C. ULLER, Solubility of carbon dioxide in water and hexadecane: experimental measurement and thermodynamic modeling, Journal of Chemical and Engineering Data 54 (2009) 2881–2886.

[15] M.A. Postigo, M. KATZ, Solubility and thermodynamics of carbon dioxide in aqueous ethanol solutions, Journal of Solution Chemistry 16 (1987) 1015–1024.

[16] A. Zawlsza, B.Y. Malesliska, Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2-5 MPa and at temperatures up to 473 K, Journal of Chemical and Engineering Data 26 (1981) 300–391.

[17] J.J. Carrol, J.D. Slupsky, A.E. Mather, The solubility of carbon dioxide in water at low pressure, Journal of Physical Chemistry 20(6) (1991).