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Solubility of CO₂ in methanol, ethanol, 1,2-propanediol and glycerol from 283.15 K to 373.15 K and up to 6.0 MPa

*Marie Décultot**, Alain Ledoux, Marie-Christine Fournier-Salaiin, Lionel Estel

*marie.decultot@insa-rouen.fr

Normandie Univ, INSA Rouen, UNIROUEN, LSPC, 76000 Rouen, France

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ABSTRACT:

Capture, storage and valorisation of CO₂ are efficient solutions to reduce the emissions of greenhouse gas. To improve these technologies, there is a need to have a good knowledge of the interactions between CO₂ and some current solvents. In this article, the solubility of CO₂ in methanol, ethanol and 1,2-propanediol is measured by a constant-volume method for temperatures between 283.15 K and 373.15 K and for pressures below 6.0 MPa. The same method is used for glycerol for pressures up to 2.0 MPa. For all of the studied solvents, the solubility increases when temperature decreases and when pressure increases. No literature data was available for this wide range of temperature for ethanol, methanol, 1,2-propanediol and

glycerol. Henry's law constants are calculated for each temperature and are compared between to one another. The solubility of CO₂ in these solvents increases in the following order: glycerol < 1,2-propanediol < methanol ≈ ethanol.

1. Introduction

With 34 Gt emitted each year in the atmosphere, carbon dioxide is the most human emitted greenhouse gases in the world. These emissions are increasing due to an economic and demographic growth, which implies an elevation of the consumption of fossil energy[1]. The elevation of the global temperature can reach up to + 5 °C in 2100 if these emissions are not limited. Capture and storage of CO₂ have received a lot of attention as a solution to reduce these emissions[2]. In addition, to face up to the rarefaction of fossil fuels and in a perspective of circular economy, the valorisation of CO₂ is developing. In this new chemistry, CO₂ is no more seen as a waste but as a source of carbon used to produce value-added chemicals[3]. However, only few examples are developed on the industrial scale.

In this context, our work is focused on the synthesis of organic carbonate by associating CO₂ with alcohol or diol or glycerol. The main carbonates that could be obtained are dimethylcarbonate, diethylcarbonate, propylene carbonate or glycerol carbonate. Due to their very low toxicity, they have many potential applications like fuel additive, solvent or monomer [4]. Currently, they are produced by using some toxic and harmful components like phosgene. The synthesis via the route (CO₂ + alcohol) has been proven to be the more interesting concerning the environmental aspect and the sequestration of CO₂[5].

Many homogeneous and heterogeneous catalysts have been tested for this synthesis[6,7]. Some of them give high selectivity but the yield is still low because of the unfavourable thermodynamics of the reaction. Chemical reactions take place at about 373.15 K and pressure

until 6.0 MPa. To study the kinetics of this reaction, it is important to take into account the data of phase equilibria in these conditions.

The aim of this article is to provide a wide range of solubility of carbon dioxide in four different solvents: methanol, ethanol, 1,2-propanediol and glycerol. The experiments are performed by a constant-volume method at temperatures between 283.15 K and 373.15 K and pressures up to 6.0 MPa for methanol, ethanol and 1,2-propanediol. This range of temperature is higher than the one shown in literature data. The solubility of CO₂ in glycerol is measured with the same method and for pressures below 2.0 MPa. Only one data set is available in the literature for this range of pressure [8]. The originality of this paper is to present new relevant data about CO₂ solubility into alcohols.

2. Experimental

2.1. Materials.

The source and the purity of all compounds used are described in Table 1. All the chemicals are used as received. Water contents of ethanol, methanol, 1,2-propanediol and glycerol were determined using Metrohm Karl Fischer coulometer 899t itrator.

Chemical name	CAS	Source	Volume fraction purity ^a	Mass fraction of water	Analysis Method	Purification method
Carbon Dioxide	124-38-9	Air Liquide	0.999			-
Absolute ethanol	64-17-5	Fisher Scientific	> 0.995	0.0003	Karl - Fischer	-
Absolute methanol	67-56-1	Fisher Scientific	> 0.995	0.0002	Karl - Fischer	-

1,2- propanediol	57-55-6	Alfa Aesar	0.995	0.0028	Karl- Fischer	-
Glycerol	56-81-5	Appl ichem Par reac	0.99	0.0028	Karl- Fischer	-

^a The purity was provided by the supplier

Table 1. Chemical compounds used in this study.

2.2 Apparatus

Figure 1 represents a schematic diagram of the apparatus used to measure the solubility. The experiments were carried out in a stainless steel cell from Mettler-Toledo with a capacity of 1.61 L (± 0.01 L). The cell was equipped with two temperature sensors, one for the liquid in the vessel (T_r) and one for the jacket (T_j). A heat carried fluid circulated through the jacket to regulate the temperature in the vessel with an accuracy of ± 0.01 K. The pressure inside the cell was also measured by a pressure gauge with an accuracy of ± 0.01 bar. An anchor type agitator was used to stir the solution at about 300 rpm. This kind of reactor is described in more detail by

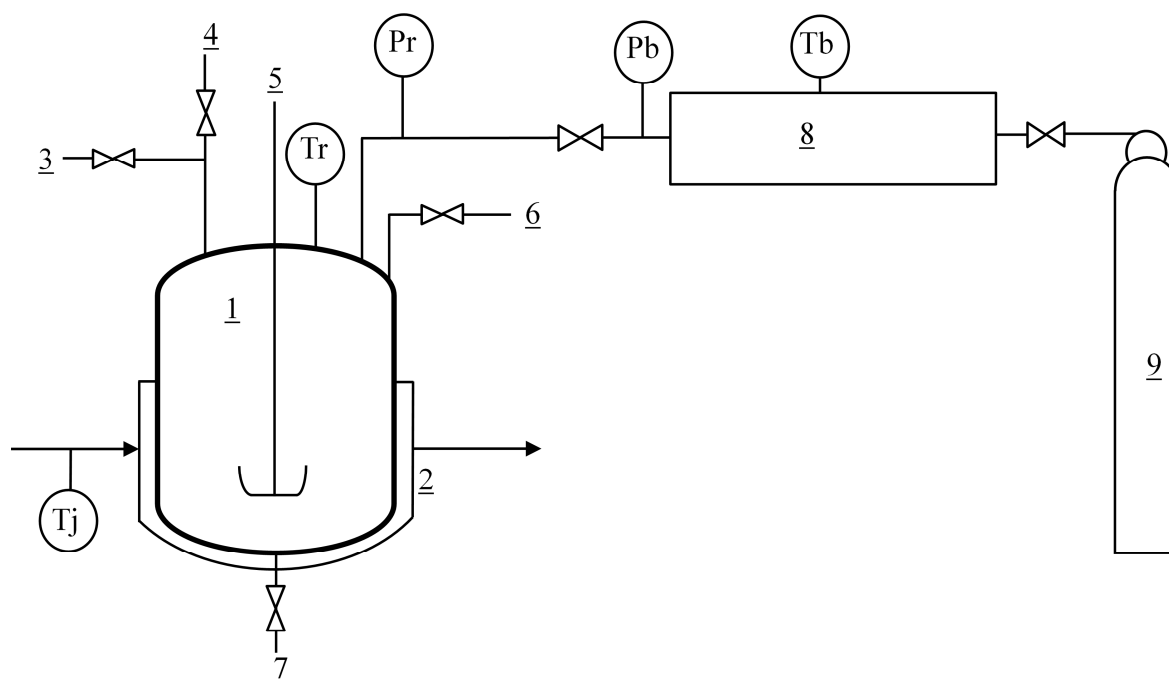


Figure 1. Schematic diagram of the apparatus: 1. cell, 2. jacket, 3. vacuum connector, 4. event valve, 5. stirrer, 6. liquid inlet, 7. liquid outlet, 8. buffer tank, 9. CO₂ gas cylinder

Balland *et al.* [9].

The CO₂ cylinder was connected to a stainless steel buffer tank with a capacity of 2.12 L (± 0.01 L). The temperature (T_b) and pressure (P_b) of this buffer tank were recorded with two sensors with accuracies of ± 0.01 K and ± 0.01 bar respectively. A valve controlled the injection of CO₂ from the buffer tank to the cell. All the temperatures and pressures measured during the experiments were recorded continuously using an acquisition system.

2.3 Experimental procedure.

Before each experiment, an amount of nitrogen was injected in the cell and the pressure was recorded during 2 hours to test the gas leakage of the apparatus. Then, the cell was emptied with a vacuum pump to 100 Pa. The temperature in the cell was maintained at 283.15 K and around 800 mL of solvent were injected into the cell through the liquid inlet. The exact weight of the solvent injected, m_s , was measured, with an accuracy of ± 0.2 g, by a double weighing of the bottle containing the solvent: before and after the injection. The mixture was stirred during all the experiment at around 300 rpm. The cell was emptied again with the vacuum pump to be sure that there is no inert gas in the cell. The buffer tank was purged with CO₂ three times and then it was filled with CO₂. After few minutes the pressure and the temperature in the buffer tank were constant. An amount of CO₂ was injected in the cell to obtain approximately 0.1 MPa, the temperature in the cell was maintained at 283.15 K. When the pressure and temperature were stabilised, the temperature was raised from 283.15 K up to 373.15 K by step of 10 K. At each step, we considered that the equilibrium was reached when the pressure was constant. The stabilisation period to reach this equilibrium depended on the solvent used: for the ethanol, methanol and 1,2-propanediol the stabilisation time was about 50 minutes. A total of 150

minutes was used for the glycerol because the absorption of CO_2 in glycerol is a very slow process. At the end of the experiments, three other steps at 343.15 K, 313.15 K and 283.15 K were made to control the repeatability. Thanks to this method, we insured that there is no leakage, that CO_2 did not react with the solvent and that the stabilisation time was sufficiently

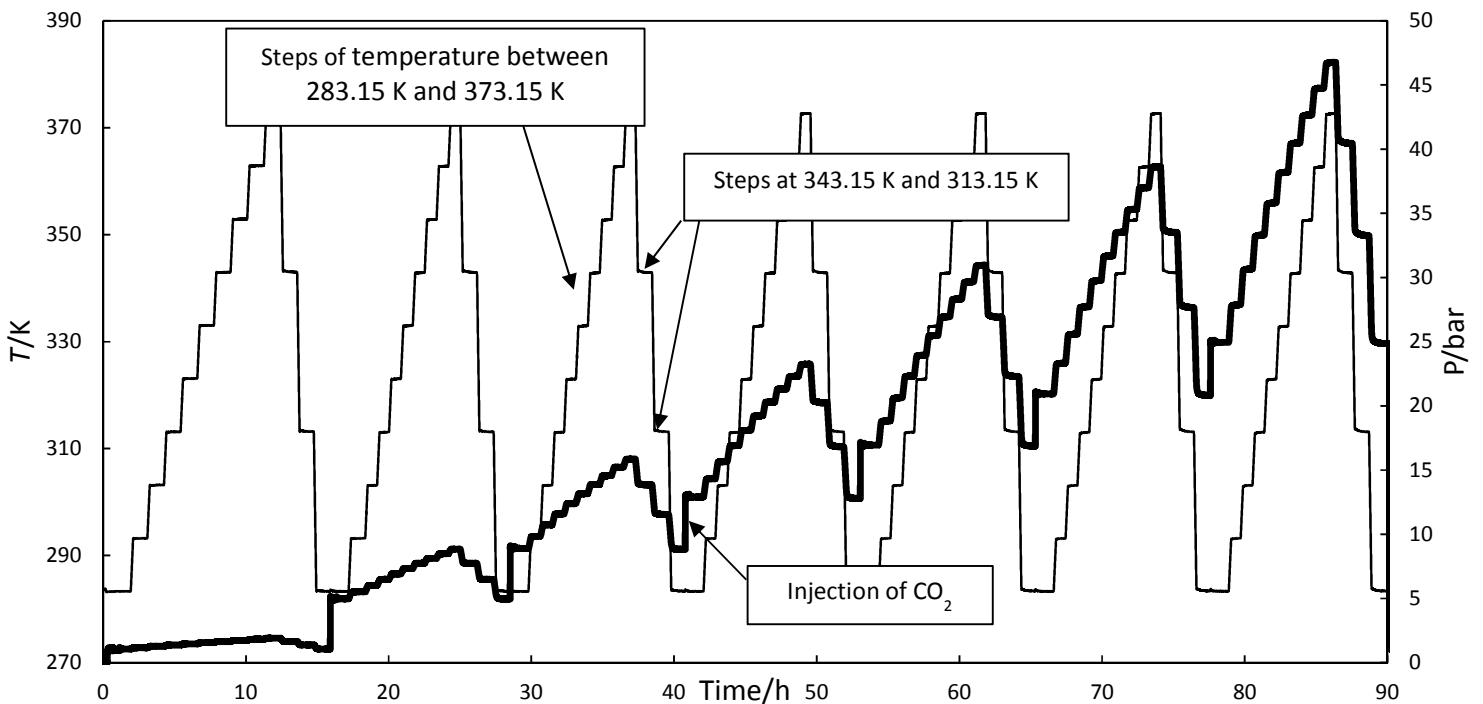


Figure 2: Evolutions of temperature (—) and pressure (—) in the cell during the experiment in 1,2-propanediol long. When the temperature in the cell came back to 283.15 K, the pressure was increased by introducing CO_2 again. Several injections of CO_2 were made for each solvent. The temperature and pressure in the cell recorded during all the experiments are plotted in Figure 2 for the 1,2-propanediol.

3. Results and discussion

3.1 Calculation of the solubility

The CO_2 solubility in the solvent is expressed using the mole fraction :

$$x = \frac{n_{CO_2}^{sol}}{n_{CO_2}^{sol} + n_s} \quad \text{Eq 1}$$

introduced in the cell which is calculated as :

$$n_s = \frac{m_s}{M_s} \quad \text{Eq 2}$$

Here m_s corresponds to the mass of solvent injected in the cell and M_s is the molar mass of the solvent .

The moles of CO₂ absorbed in the solvent are calculated by a mass balance:

$$n_{CO_2}^{sol} = n_{CO_2}^{inj} - n_{CO_2}^{Eq} \quad \text{Eq 3}$$

$n_{CO_2}^{Eq}$ is the amount of CO₂ at the equilibrium in the gas phase in the cell .

$n_{CO_2}^{inj}$ is calculated by the difference of the amount of CO₂ in the buffer tank before the injection ($n_{CO_2}^1$) and after the injection ($n_{CO_2}^2$):

$$n_{CO_2}^{inj} = n_{CO_2}^1 - n_{CO_2}^2 \quad \text{Eq 4}$$

All the amounts of CO₂ in the cell and in the buffer tank were calculated by using the Peng-Robinson equation of state[10]:

$$P_{CO_2} = \frac{RT_r}{v-b} - \frac{\alpha(T_r)a}{v^2 + 2vb - b^2} \quad \text{Eq 5}$$

The T_r represents the temperature of the cell and v is the molar volume of CO₂. a and b are two constants calculated with the following equations:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad \text{Eq 6}$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad \text{Eq 7}$$

$\Omega_a=0.457, \Omega_b=0.07780$;

$T_c = 304.25$ K and $P_c = 7.382$ MPa are the critical temperature and pressure of CO₂.

$\alpha(T_r)$ is a function of the temperature inside the cell and of the CO₂ acentric factor which is equal to 0.228:

$$\alpha(T_r) = [1 + m(1 - (T_r/T_c)^2)]^2 \quad \text{Eq 8}$$

$$m = 0.374640 + 1.542260\omega - 0.26992\omega^2 \quad \text{Eq 9}$$

We assumed that liquids are ideal and follow the Raoult's law to calculate the partial pressure of CO₂ at each equilibrium in the cell:

$$P_{CO_2} = P_{cell} - P_{liq}^s(1 - x) \quad \text{Eq 10}$$

where P_{cell} represents the pressure measured in the cell by the transducer and P_{liq}^s corresponds to the saturated vapour pressure of the solvent calculated for each temperature in Table 2 using the Antoine's equation. The Antoine's coefficients are reported in Table 3. These calculated saturated vapour pressures are in good agreement with literature data [11–13]. The vapour pressures of ethanol in this range of temperature were measured in the cell to ensure that the residual pressure correspond to these calculated vapour pressures.

Temperature/K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
$0.01P_{\text{methanol}}^s$ /Pa	0.074	0.130	0.219	0.354	0.555	0.845	1.251	1.807	2.553	3.534
$0.01P_{\text{ethanol}}^s$ /Pa	0.031	0.059	0.105	0.179	0.294	0.468	0.722	1.083	1.582	2.258
$0.01P_{\text{1,2-propanediol}}^s$ /Pa					0.002	0.003	0.006	0.011	0.019	0.032

Table 2. Saturated vapour pressure of methanol, ethanol and 1,2-propanediol for temperatures from 283.15 K to 373.15 K

	Temperature/K	A	B	C	References
Methanol	283.15 – 373.15	5.20409	1581.341	-33.5	[14]
Ethanol	283.15 – 343.15	5.37229	1670.409	-40.191	[15]
	343.15 - 373.15	5.24677	1598.673	-46.424	[14]
1,2-propanediol	323.15 – 373.15	6.07936	2692.187	-17.94	[16]

Table 3. Antoine's coefficients [17] used to calculate the saturated vapour pressure of methanol, ethanol and 1,2-propanediol with the following equation, with P_{liq}^S in bar and T in K :

$$\text{Log}(P_{liq}^S) = A - \frac{B}{T + C}$$

3.2. Reliability of the apparatus

The standard uncertainty of the solubility for each equilibrium was calculated from:

$$\begin{aligned} \frac{\delta x}{x} &= \sqrt{\left(\frac{\delta(n_{CO_2}^{sol})}{n_{CO_2}^{sol}}\right)^2 + \left(\frac{\delta(n_{CO_2}^{sol} + n_{liq})}{n_{CO_2}^{sol} + n_{liq}}\right)^2} \\ &= \sqrt{\left(\frac{\delta(n_{CO_2}^{inj})^2 + \delta(n_{CO_2}^{Eq})^2}{n_{CO_2}^{sol\ 2}}\right) + \left(\frac{\delta(n_{CO_2}^{inj})^2 + \delta(n_{CO_2}^{Eq})^2 + \delta(n_{liq})^2}{(n_{CO_2}^{sol} + n_{liq})^2}\right)} \end{aligned} \quad \text{Eq 11}$$

$$\frac{\delta(n_{CO_2}^i)}{n_{CO_2}^i} = \sqrt{\left(\frac{\delta(P_i)}{P_i}\right)^2 + \left(\frac{\delta(V_i)}{V_i}\right)^2 + \left(\frac{\delta(T_i)}{T_i}\right)^2} \quad \text{Eq 12}$$

where P_i , T_i and V_i correspond respectively to the pressure, temperature and volume of CO_2 at the equilibrium in the cell for $\delta(n_{CO_2}^{Eq})$ and in the buffer tank before injection for $\delta(n_{CO_2}^{inj})$.

And n_s is estimated by:

$$\delta(n_s) = \frac{\delta(m_s)}{M_s} \quad \text{Eq 13}$$

3.3. Results and discussion

Table 4 to Table 7 report the partial pressure of CO₂ at the equilibrium P_{CO_2} , the solubility x and the estimated standard uncertainties $\pm x$ for the absorption of CO₂ in ethanol, methanol, 1,2-propanediol and glycerol. The calculated standard uncertainties are below 2.0×10^{-3} , which represents mainly (1-2) % of the values of solubility for each solvent.

Figure 3 to Figure 6 represent the partial pressure of CO₂ plotted against the solubility for the four solvents for each temperature. As expected, the solubility for each solvent increases when the pressure increases but decreases when the temperature increases. In the temperature and pressure ranges studied, linear plots are obtained between partial pressure of CO₂ and solubility. For ethanol, methanol, 1,2-propanediol and glycerol, the correlation coefficients obtained for each temperature were higher than 0.997. In our range of temperature and pressure, the solubility of CO₂ is proportional to the pressure of the gas over the solvent, according to the Henry's law:

$$P_{CO_2} = k_H x \quad \text{Eq 14}$$

The k_H represents the Henry's law constant. It refers to the slope of the line P_{CO_2} to x . All the Henry's law coefficients are reported in Table 8. Comparisons of the Henry's law constants obtained in this work and in the literature are represented in Figure 7 and Figure 8 where k_H is plotted against the temperature for methanol and ethanol. The solubility of CO₂ in methanol is the most studied alcohol, the data of eleven articles are plotted in Figure 7. [18–28]. For ethanol, the comparison with seven articles is made in Figure 8 [21,25,26,29–32]. These data are in good agreement with our results, this comparison validates our method to measure solubility. It can be seen in Figure 7 and Figure 8 that Henry's law constant is generally determined for temperatures lower than 353.15 K, so our work presents new values of solubility for higher temperatures up to 373.15 K.

Only two articles have been found about the solubility of CO₂ in 1,2-propanediol [25,33]. The

Henry's law constants in these two works are different as we can see in Figure 9. Our work is closer to the results obtained by Galvao *et al.*[33] than to the results from Gui *et al.*[25]. This difference can be explained by the degassing of the solvent. Indeed, Galvao *et al.* used a method to degas the solvent before it is used, so they did not consider any inert gas. On the contrary, Gui *et al.* did not use any degassing method but considered an amount of inert gas. This gas could have an impact on the solubility of CO₂, which could explain this difference. In our work, we also degassed our solvent by evacuating the cell when the solvent was inside. Thanks to this method, we ensured that no inert gas interacted with the solubilisation of CO₂ in the solvent. This difference in the methodology could explain why our results are close to the results of Galvao *et al.* In some other works, researchers studied the solubility of 1,2-propanediol in supercritical carbon dioxide [34] or the phase equilibria for temperature higher than 373.15 K [35]. These results are not comparable to ours.

For glycerol, only one literature reference has been found which is represented in Figure 10 [8]. The Henry's law constants obtained by Ostonen *et al.* are very similar to our results. Some other papers studied the solubility of CO₂ in glycerol but for higher pressures[36–38], where the Henry's law is not applicable.

All the Henry's law constants for the four solvents are reported in Table 8 and plotted in Figure 10. Methanol and ethanol have a similar behaviour toward the solubility of CO₂. CO₂ is less soluble in 1,2-propanediol and very slightly soluble in glycerol. These results are in agreement with the explanation given in previous studies[25,39] where the solubility of a gas in a solvent is divided in two main steps: first, the interactions solvent-solvent must be broken to create cavities, and then the solute molecules must fill these cavities with the interaction solute-solvent. In our case, we have two alcohols, 1,2-propanediol with two hydroxyl groups and

glycerol with three hydroxyl groups. This difference in the structure of molecules can explain the difference observed in the solubility of CO_2 . Indeed, the hydroxyl groups can form internal hydrogen bonds, so glycerol which has 3 hydroxyl groups has a better internal interaction than 1,2-propanediol. That could explain why it absorbs less CO_2 than 1,2-propanediol. Similarly, the internal interactions of 1,2-propanediol are stronger than the interactions between alcohols.

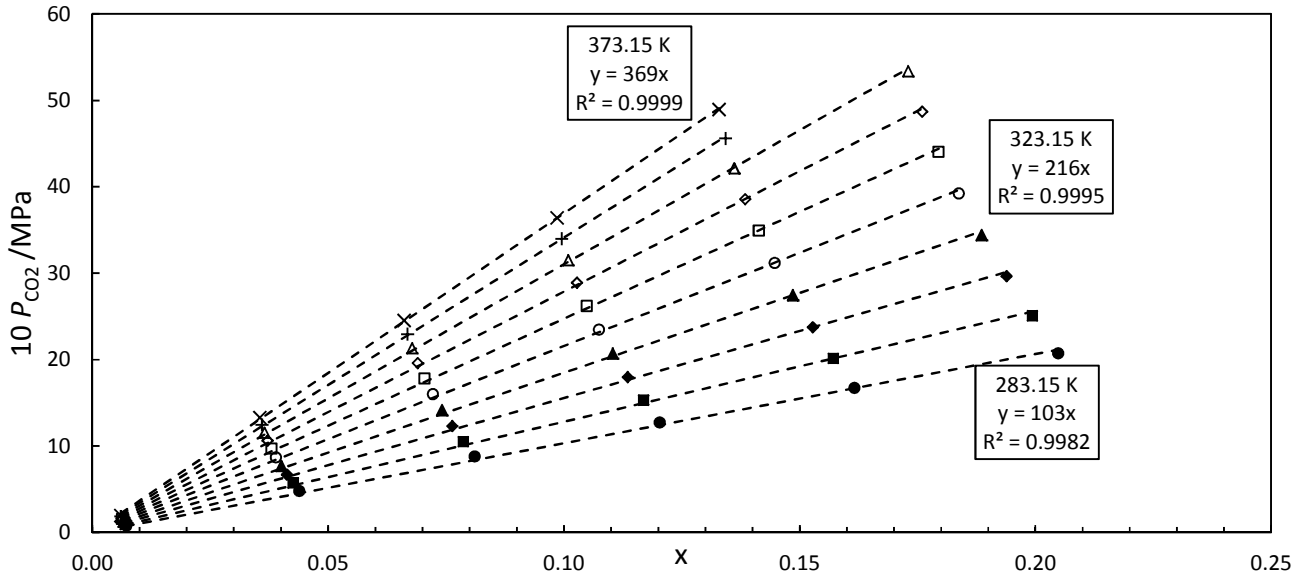


Figure 3. Pressure-solubility diagram for CO₂ and liquid methanol at different temperatures, ●, T = 283.15 K; ■, T = 293.15 K; ◆, T = 303.15 K; ▲ T = 313.15 K; ○, T = 323.15 K; □, T = 333.15 K; ◇, T = 343.15 K; △, T = 353.15 K; +, T = 363.15 K; ×, T = 373.15 K. P_{CO₂} is the partial pressure of CO₂ in the cell at the equilibrium, and x is the mole fraction of CO₂ in the liquid phase.

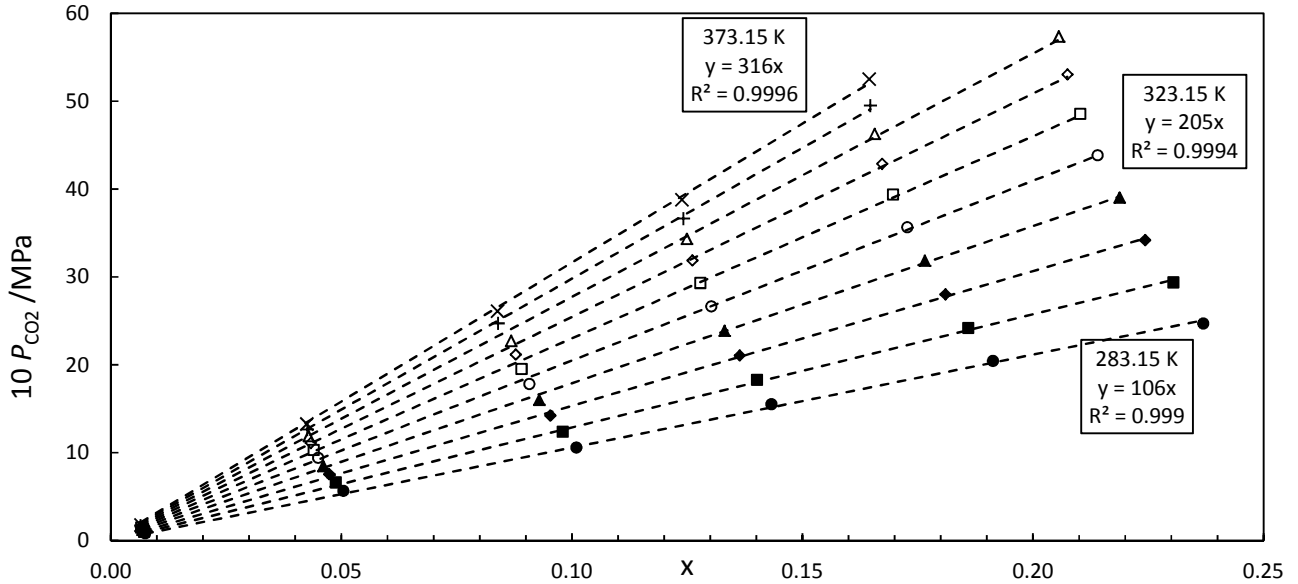


Figure 4. Pressure-solubility diagram for CO₂ and liquid ethanol at different temperatures, ●, T = 283.15 K; ■, T = 293.15 K; ◆, T = 303.15 K; ▲ T = 313.15 K; ○, T = 323.15 K; □, T = 333.15 K; ◇, T = 343.15 K; △, T = 353.15 K; +, T = 363.15 K; ×, T = 373.15 K. P_{CO₂} is the partial pressure of CO₂ in the cell at the equilibrium, and x is the mole fraction of CO₂ in the liquid

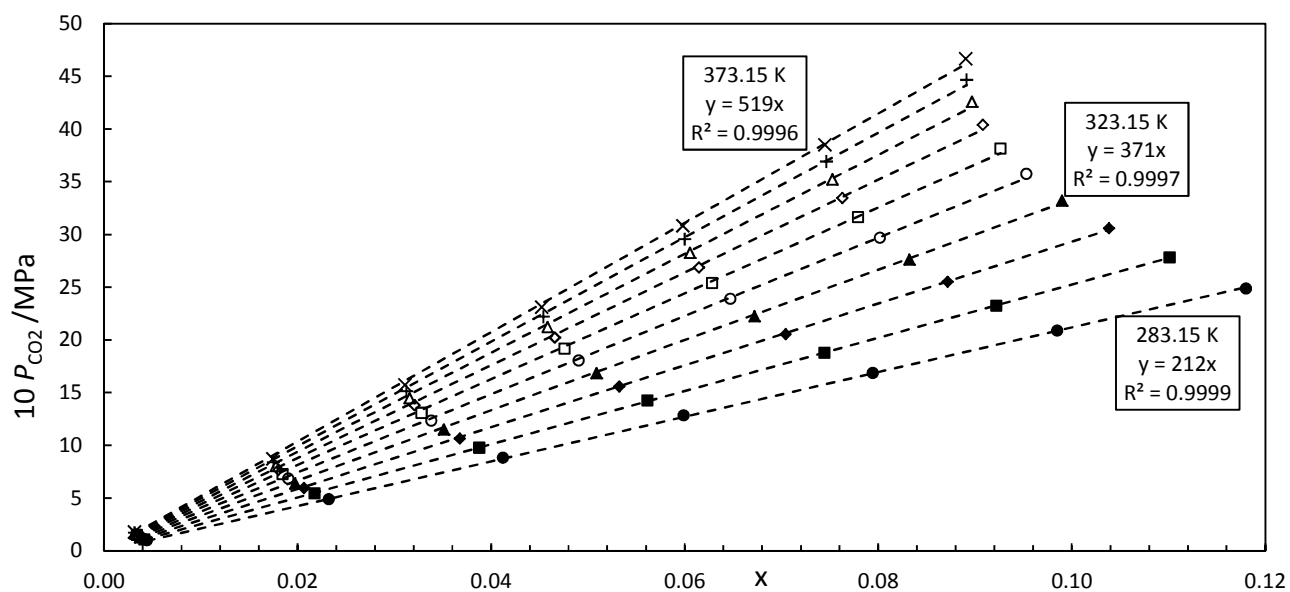


Figure 5. Pressure-solubility diagram for CO₂ and liquid 1,2-propanediol at different temperatures, ●, T = 283.15 K; ■, T = 293.15 K; ◆, T = 303.15 K; ▲, T = 313.15 K; ○, T = 323.15 K; □, T = 333.15 K; ◇, T = 343.15 K; △, T = 353.15 K; +, T = 363.15 K; ×, T = 373.15 K. P_{CO₂} is the partial pressure of CO₂ in the cell at the equilibrium, and x is the mole fraction of CO₂ in the liquid

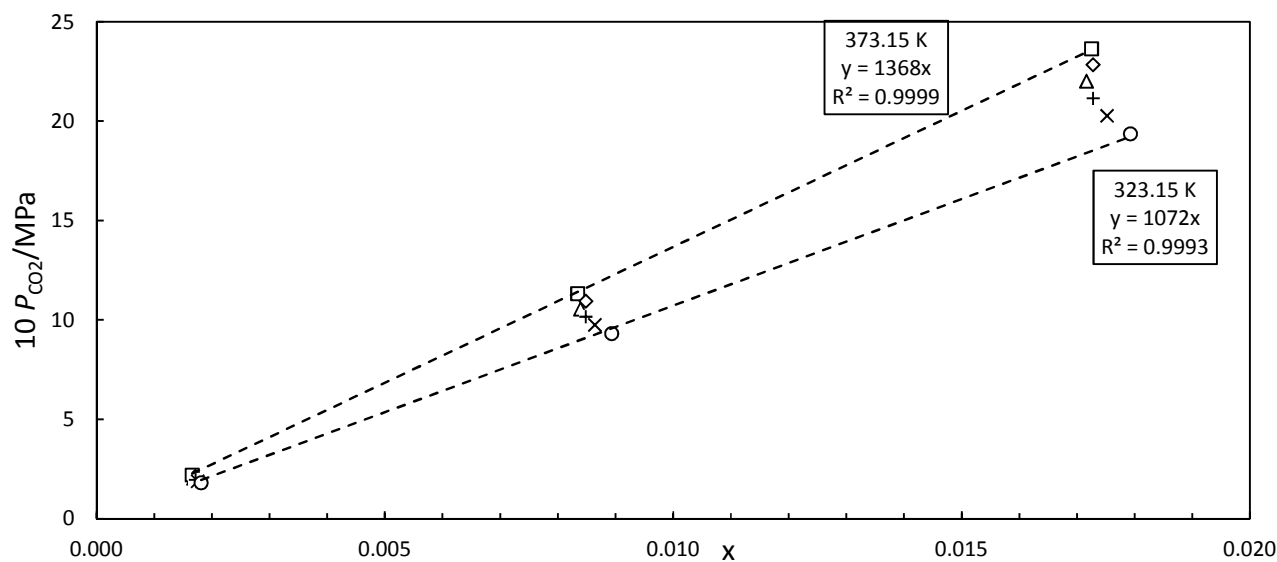


Figure 6. Pressure-solubility diagram for CO₂ and liquid glycerol at different temperatures, ○, T = 323.15 K; ×, T = 333.15 K; +, T = 343.15 K; △, T = 353.15 K; ◇, T = 363.15 K; □, T = 373.15 K. P_{CO₂} is the partial pressure of CO₂ in the cell at the equilibrium, and x is the mole fraction of CO₂ in the liquid phase.

$10^{-2} P_{\text{CO}_2}/\text{Pa}$	x	δx	$10^{-2} P_{\text{CO}_2}/\text{Pa}$	x	δx
T=283.15 K			T=293.15 K		
0.79	0.0072	0.0001	0.94	0.0070	0.0001
4.79	0.0439	0.0002	5.73	0.0425	0.0002
8.78	0.0811	0.0003	10.52	0.0786	0.0003
12.74	0.1203	0.0004	15.30	0.1169	0.0005
16.73	0.1616	0.0006	20.15	0.1572	0.0007
20.73	0.2048	0.0008	25.08	0.1993	0.0009
T=303.15 K			T=313.15 K		
1.12	0.0067	0.0001	1.27	0.0065	0.0001
6.71	0.0412	0.0002	7.70	0.0400	0.0002
12.33	0.0763	0.0004	14.17	0.0741	0.0004
17.98	0.1135	0.0005	20.72	0.1103	0.0006
23.76	0.1527	0.0007	27.46	0.1485	0.0008
29.68	0.1938	0.0010	34.43	0.1886	0.0011
T=323.15 K			T=333.15 K		
1.42	0.0064	0.0001	1.56	0.0063	0.0001
8.70	0.0389	0.0002	9.69	0.0380	0.0003
16.00	0.0722	0.0004	17.83	0.0705	0.0004
23.48	0.1075	0.0006	26.22	0.1049	0.0006
31.20	0.1447	0.0008	34.93	0.1413	0.0009
39.23	0.1838	0.0011	44.05	0.1795	0.0012
T=343.15 K			T=353.15 K		
1.67	0.0062	0.0001	1.79	0.0061	0.0001
10.64	0.0372	0.0003	11.58	0.0365	0.0003
19.61	0.0690	0.0005	21.33	0.0678	0.0005
28.90	0.1027	0.0007	31.52	0.1009	0.0007
38.60	0.1384	0.0009	42.16	0.1361	0.0010
48.71	0.1760	0.0013	53.41	0.1730	0.0014
T=363.15 K			T=373.15 K		
1.89	0.0061	0.0001	1.96	0.00610	0.0001
12.47	0.0360	0.0003	13.31	0.03558	0.0003
22.98	0.0668	0.0005	24.56	0.06617	0.0005
34.00	0.0996	0.0007	36.43	0.09855	0.0008
45.61	0.1343	0.0010	48.95	0.13295	0.0011

^a Standard uncertainties are $u(P_{\text{CO}_2}) = 1 \text{ Pa}$ and $u(T) = 0.01 \text{ K}$

Table 4. Partial pressure of CO_2 (P_{CO_2}), solubility (x) and standard uncertainties (δx) of CO_2 in liquid methanol from 283.15 K to 373.15 K at the equilibrium^a.

$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	δx	$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	Δx
T=283.15 K			T=293.15 K		
0.82	0.0075	0.0002	0.96	0.0072	0.0002
5.67	0.0505	0.0004	6.61	0.0489	0.0004
10.59	0.1010	0.0006	12.39	0.0980	0.0007
15.51	0.1433	0.0008	18.27	0.1402	0.0009
20.44	0.1914	0.0012	24.18	0.1860	0.0012
24.68	0.2369	0.0015	29.36	0.2305	0.0016
T=303.15 K			T=313.15 K		
1.10	0.0070	0.0002	1.24	0.0068	0.0002
7.56	0.0474	0.0004	8.51	0.0461	0.0004
14.22	0.0953	0.0007	16.03	0.0929	0.0007
21.09	0.1364	0.0009	23.89	0.1331	0.0010
28.03	0.1810	0.0013	31.87	0.1765	0.0014
34.19	0.2243	0.0017	39.05	0.2188	0.0018
T=323.15 K			T=333.15 K		
1.35	0.0067	0.0002	1.47	0.0066	0.0002
9.43	0.0450	0.0004	10.29	0.0441	0.0004
17.81	0.0908	0.0007	19.52	0.0891	0.0008
26.64	0.1302	0.0010	29.32	0.1279	0.0011
35.65	0.1727	0.0014	39.37	0.1696	0.0015
43.85	0.2141	0.0019	48.54	0.2103	0.0019
T=343.15 K			T=353.15 K		
1.57	0.0065	0.0002	1.66	0.0065	0.0002
11.13	0.0434	0.0005	11.91	0.0429	0.0005
21.17	0.0878	0.0008	22.74	0.0868	0.0008
31.87	0.1262	0.0011	34.32	0.1249	0.0011
42.90	0.1673	0.0015	46.29	0.1657	0.0016
53.07	0.2075	0.0020	57.38	0.2056	0.0021
T=363.15 K			T=373.15 K		
1.73	0.0065	0.0002	1.78	0.0066	0.0002
12.62	0.0426	0.0005	13.28	0.0425	0.0005
24.72	0.0840	0.0008	26.12	0.0838	0.0008
36.64	0.1242	0.0011	38.81	0.1239	0.0012
49.51	0.1647	0.0016	52.53	0.1645	0.0016

^a Standard uncertainties u are $u(P_{\text{CO}_2}) = 1 \text{ Pa}$ and $u(T) = 0.01 \text{ K}$

Table 5. Partial pressure of CO_2 (P_{CO_2}), solubility (x) and standard uncertainties (Δx) of CO_2 in liquid ethanol from 283.15 K to 373.15 K at the equilibrium^a.

$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	δx	$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	δx
T=283.15 K			T=293.15 K		
0.98	0.0044	0.0003	1.08	0.0042	0.0003
4.90	0.0232	0.0005	5.44	0.0217	0.0005
8.81	0.0412	0.0007	9.76	0.0388	0.0007
12.84	0.0599	0.0009	14.26	0.0562	0.0009
16.86	0.0794	0.0011	18.76	0.0744	0.0012
20.86	0.0985	0.0013	23.25	0.0922	0.0014
24.87	0.1180	0.0016	27.81	0.1101	0.0017
T=303.15 K			T=313.15 K		
1.19	0.0039	0.0003	1.29	0.0037	0.0003
5.94	0.0206	0.0005	6.40	0.0197	0.0005
10.66	0.0368	0.0007	11.52	0.0351	0.0007
15.58	0.0532	0.0009	16.84	0.0509	0.0010
20.56	0.0704	0.0012	22.26	0.0672	0.0012
25.51	0.0872	0.0015	27.65	0.0832	0.0015
30.60	0.1038	0.0017	33.24	0.0990	0.0018
T=323.15 K			T=333.15 K		
1.38	0.0035	0.0003	1.48	0.0034	0.0003
6.84	0.0190	0.0005	7.26	0.0185	0.0005
12.32	0.0338	0.0008	13.08	0.0328	0.0008
18.02	0.0490	0.0010	19.15	0.0476	0.0010
23.87	0.0647	0.0013	25.40	0.0628	0.0013
29.69	0.0802	0.0015	31.61	0.0779	0.0016
35.74	0.0953	0.0019	38.13	0.0926	0.0019
T=343.15 K			T=353.15 K		
1.56	0.0033	0.0003	1.64	0.0032	0.0003
7.66	0.0180	0.0005	8.03	0.0177	0.0005
13.80	0.0321	0.0008	14.48	0.0316	0.0008
20.22	0.0466	0.0010	21.24	0.0458	0.0010
26.86	0.0615	0.0013	28.25	0.0605	0.0013
33.47	0.0763	0.0016	35.22	0.0752	0.0016
40.41	0.0908	0.0019	42.58	0.0897	0.0019
T=363.15 K			T=373.15 K		
1.72	0.0031	0.0003	1.79	0.0031	0.0003
8.39	0.0175	0.0005	8.73	0.0174	0.0005
15.13	0.0312	0.0008	15.75	0.0311	0.0008
22.21	0.0454	0.0010	23.13	0.0452	0.0010
29.57	0.0600	0.0013	30.84	0.0598	0.0013
36.92	0.0746	0.0016	38.53	0.0744	0.0016
44.66	0.0891	0.0020	46.67	0.0890	0.0020

^a Standard uncertainties u are $u(P_{\text{CO}_2}) = 1 \text{ Pa}$ and $u(T) = 0.01 \text{ K}$

Table 6. Partial pressure of CO₂ (P_{CO_2}), solubility (x) and standard uncertainties (δx) of CO₂ in liquid 1,2-propanediol from 283.15 K to 373.15 K at the equilibrium^a.

$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	δx	$10^{-2}P_{\text{CO}_2}/\text{Pa}$	x	δx
$T=323.15\text{ K}$			$T=333.15\text{ K}$		
1.80	0.0018	0.0002	1.89	0.0018	0.0002
9.31	0.0089	0.0005	9.76	0.0086	0.0005
19.36	0.0179	0.0009	20.27	0.0175	0.0009
$T=343.15\text{ K}$			$T=353.15\text{ K}$		
1.97	0.0017	0.0002	2.05	0.0017	0.0002
10.16	0.0085	0.0005	10.56	0.0084	0.0005
21.15	0.0173	0.0009	22.01	0.0172	0.0009
$T=363.15\text{ K}$			$T=373.15\text{ K}$		
2.12	0.0017	0.0002	2.19	0.0017	0.0002
10.95	0.0085	0.0005	11.32	0.0083	0.0005
22.84	0.0173	0.0009	23.65	0.0173	0.0009

^a Standard uncertainties are $u(P_{\text{CO}_2}) = 1\text{ Pa}$ and $u(T) = 0.01\text{ K}$

Table 7. Partial pressure of CO₂ (P_{CO_2}), solubility (x) and standard uncertainties (δx) of CO₂ in liquid glycerol from 323.15 K to 373.15 K at the equilibrium^a.

T	methanol	ethanol	1,2-propanediol	glycerol
283.15 K	103 ($\pm 0.8\%$)	106 ($\pm 0.6\%$)	212 ($\pm 1.6\%$)	
293.15 K	128 ($\pm 0.1\%$)	129 ($\pm 0.9\%$)	252 ($\pm 1.7\%$)	
303.15 K	155 ($\pm 0.6\%$)	153 ($\pm 0.7\%$)	293 ($\pm 1.4\%$)	
313.15 K	185 ($\pm 0.4\%$)	179 ($\pm 0.8\%$)	333 ($\pm 1.8\%$)	
323.15 K	216 ($\pm 0.5\%$)	205 ($\pm 0.8\%$)	371 ($\pm 2.0\%$)	1072 ($\pm 5.1\%$)
333.15 K	247 ($\pm 0.6\%$)	230 ($\pm 0.9\%$)	407 ($\pm 2.1\%$)	1151 ($\pm 5.2\%$)
343.15 K	279 ($\pm 0.9\%$)	254 ($\pm 0.9\%$)	440 ($\pm 2.1\%$)	1218 ($\pm 5.3\%$)
353.15 K	310 ($\pm 0.8\%$)	277 ($\pm 1.0\%$)	469 ($\pm 2.2\%$)	1277 ($\pm 5.4\%$)
363.15 K	341 ($\pm 0.6\%$)	298 ($\pm 1.0\%$)	496 ($\pm 2.2\%$)	1315 ($\pm 5.3\%$)
373.15 K	369 ($\pm 0.6\%$)	316 ($\pm 1.0\%$)	519 ($\pm 2.2\%$)	1368 ($\pm 5.4\%$)

liquid glycerol from 323.15 K to 373.15 K at the equilibrium^a.

Henry's law constants $10 k_{\text{H}}/\text{MPa}$

^a Standard uncertainty u is $u(T) = 0.01\text{ K}$

Table 8. Henry's law constants k_H for methanol, ethanol, 1,2-propanediol and glycerol from 283.15 K to 373.15 K

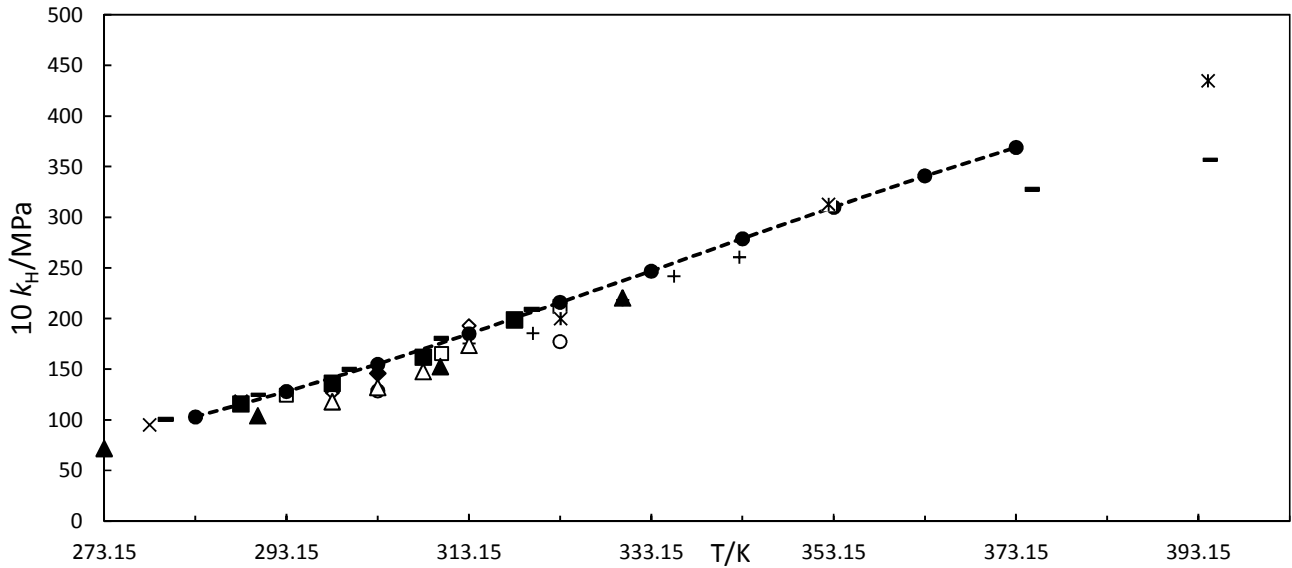
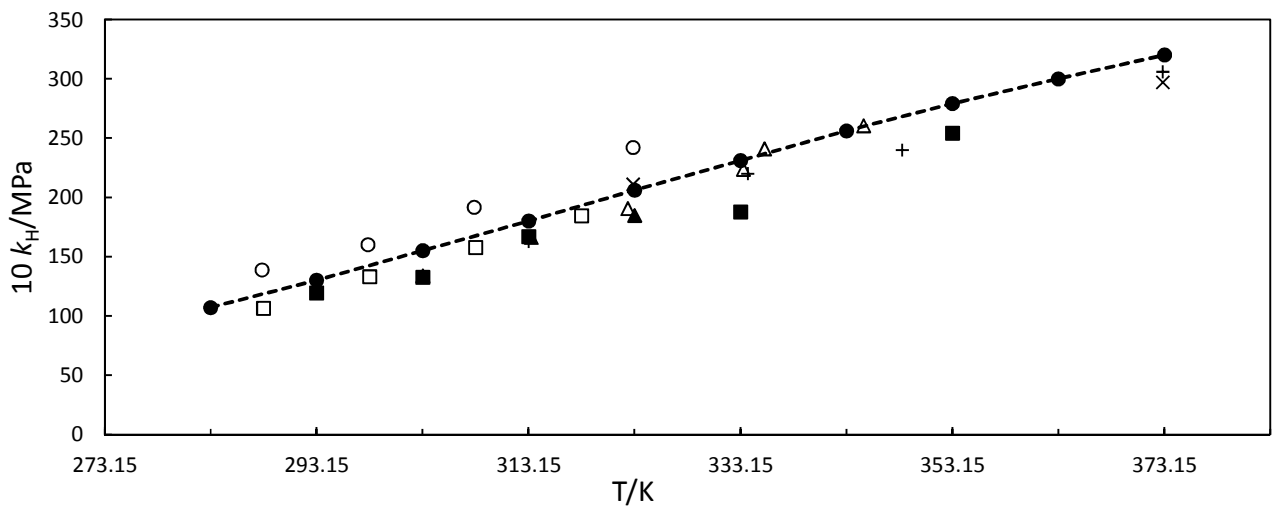
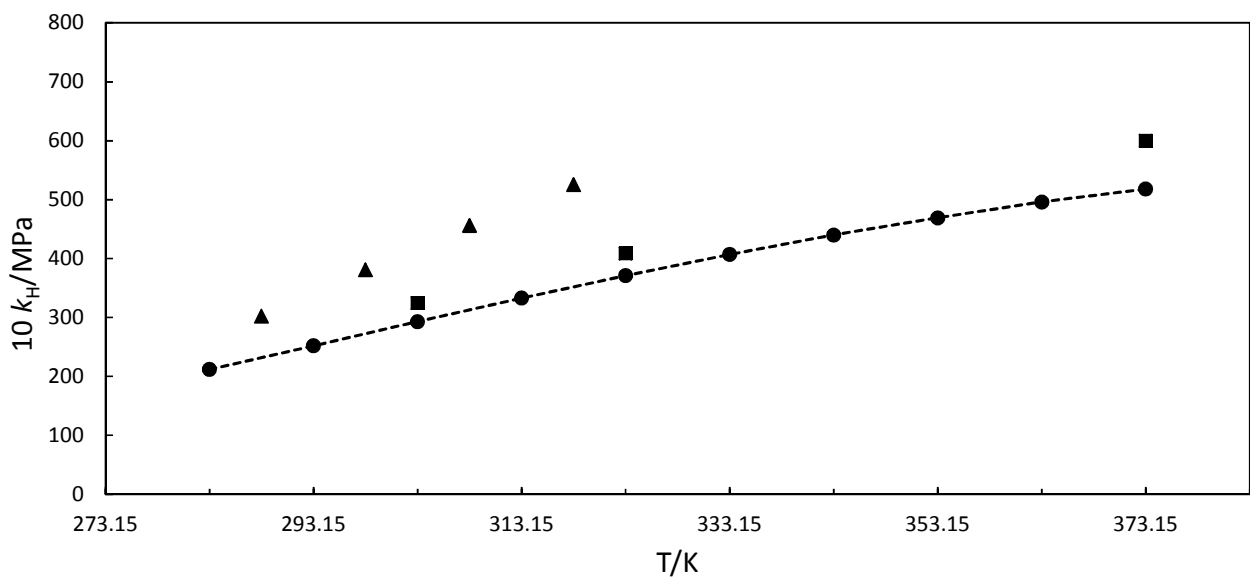


Figure 7. Henry's law constant k_H of CO_2 in liquid methanol versus temperature: \square Ohgaki *et al.* (1976)[18]; \square Hong *et al.* (1988)[19]; \square Chang *et al.* (1997)[20]; + Joung *et al.* (2001)[21]; \times Bezahtak *et al.* (2002)[22]; \blacklozenge Schwinghammer *et al.* (2006)[23]; \square Secuianu *et al.* (2009)[24] \blacksquare Gui *et al.* (2011)[25]; \circ Kariznovi *et al.* (2013)[26]; \ast Leu *et al.* (1991)[27]; -



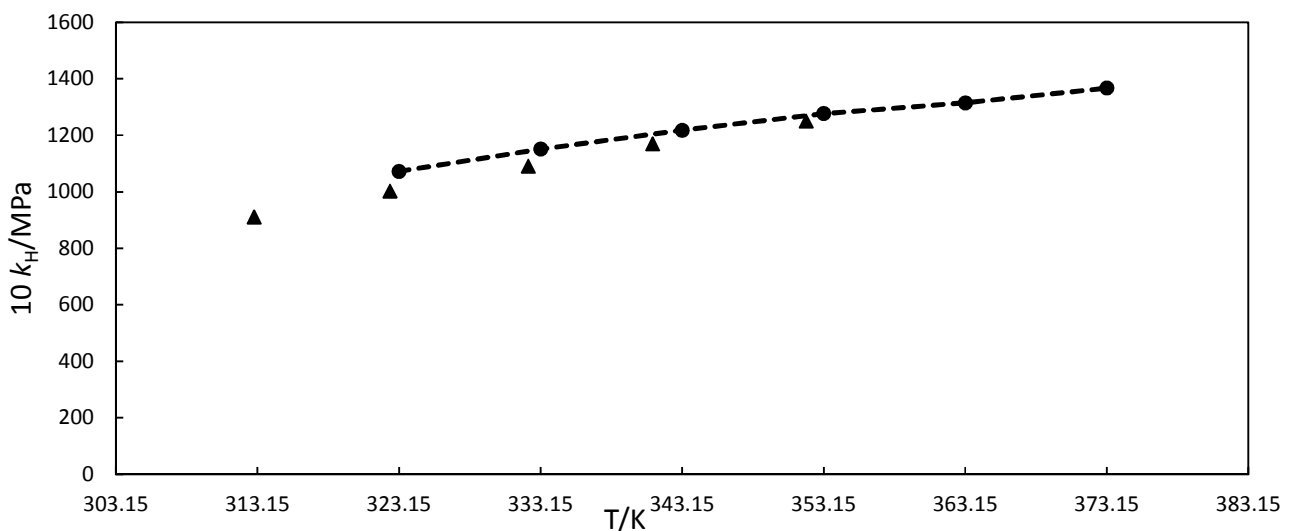
Miyano *et al.* (2004)[28]; ● this study (2019)

Figure 8. Henry's law constant k_H of CO₂ in liquid ethanol versus temperature: □ Joung *et al.* (2001)[21] ; ○ Dalmolin *et al.* (2006)[30] ; ■ Secuianu *et al.* (2008)[29] ; □ Gui *et al.* (2011)[25] ; □ Kariznovi *et al.* (2013) [26]; +Galicia-Luna *et al.* (2000)[31]; × Friend *et al.*



(2005)[32]; ● this study (2019)

Figure 9. Henry's law constant k_H of CO₂ in liquid 1,2-propanediol versus temperature: ■



calculated from Galvao *et al.* (2010)[33] □ Gui *et al.* (2011)[25] ● this study (2019)

Figure 10. Henry's law constant k_H of CO₂ in liquid glycerol versus temperature: □ Ostonen *et al.* (2014)[8] ● this study (2019)

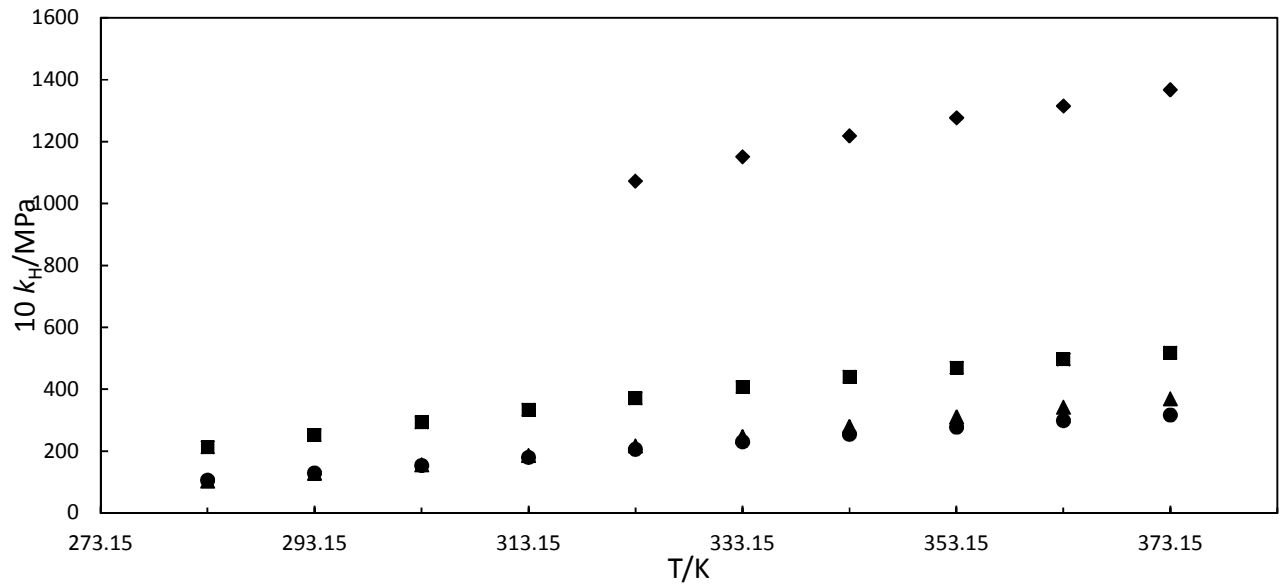


Figure 11. Henry's law constant k_H of CO₂ in liquid methanol (▲), liquid ethanol (●), liquid 1,2-propanediol (■) and liquid glycerol (◆) versus temperature.

4. Conclusions

The solubility of CO₂ in methanol, ethanol and 1,2-propanediol was measured from 283.15 K to 373.15 K and up to 6.0 MPa. In glycerol, a temperature range of 323.15 K to 373.15 K was studied up to 2.0 MPa. The constant-volume method used in this work is validated by comparison with literature. For each solvent, the solubility of CO₂ increases with a decrease of temperature and with an increase of pressure. Henry's law constant was calculated for each temperature and for each solvent, the solubility increases in this order: glycerol < 1,2-propanediol < methanol, ethanol. These differences can be explained by the different structures of the solvents.

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REFERENCES

- [1] IEA, Energy and Climate Change, (2015).
- [2] Carbon Dioxide Capture and Storage, Intergov. Panel Clim. Change. (2005).
- [3] A.A. Olajire, Valorization of greenhouse carbon dioxide emissions into value-added products by catalytic processes, *J. CO₂ Util.* 3 (2013) 74–92. doi:10.1016/j.jcou.2013.10.004.
- [4] S. Huang, B. Yan, S. Wang, X. Ma, Recent advances in dialkyl carbonates synthesis and applications, *Chem. Soc. Rev.* 44 (2015) 3079–3116. doi:10.1039/C4CS00374H.
- [5] J.G.M.-S. Monteiro, O. de Q.F. Araújo, J.L. de Medeiros, Sustainability metrics for eco-technologies assessment, part I: preliminary screening, *Clean Technol. Environ. Policy.* 11 (2009) 209–214. doi:10.1007/s10098-008-0189-9.
- [6] Y. Cao, H. Cheng, L. Ma, F. Liu, Z. Liu, Research Progress in the Direct Synthesis of Dimethyl Carbonate from CO₂ and Methanol, *Catal. Surv. Asia.* 16 (2012) 138–147. doi:10.1007/s10563-012-9140-5.
- [7] M. Tamura, M. Honda, Y. Nakagawa, K. Tomishige, Direct conversion of CO₂ with diols, aminoalcohols and diamines to cyclic carbonates, cyclic carbamates and cyclic ureas using heterogeneous catalysts, *J. Chem. Technol. Biotechnol.* 89 (2014) 19–33. doi:10.1002/jctb.4209.
- [8] A. Ostonen, E. Sapei, P. Uusi-Kyyny, A. Klemelä, V. Alopæus, Measurements and modeling of CO₂ solubility in 1,8-diazabicyclo-[5.4.0]-undec-7-ene—Glycerol solutions, *Fluid Phase Equilibria.* 374 (2014) 25–36. doi:10.1016/j.fluid.2014.04.021.
- [9] L. Balland, N. Mouhab, S. Alexandrova, J.-M. Cosmao, L. Estel, Determination of Kinetic and Energetic Parameters of Chemical Reactions in a Heterogeneous Liquid/Liquid System,

- Chem. Eng. Technol. 22 (1999) 321–329. doi:10.1002/(SICI)1521-4125(199904)22:4<321::AID-CEAT321>3.0.CO;2-8.
- [10] C. Coquelet, D. Richon, Propriétés thermodynamiques-Détermination pour les fluides purs, Tech. Ing. (2007).
- [11] J. Safarov, I. Kul, M. Talibov, A. Shahverdiyev, E. Hassel, Vapor Pressures and Activity Coefficients of Methanol in Binary Mixtures with 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide, J. Chem. Eng. Data. 60 (2015) 1648–1663. doi:10.1021/je501033z.
- [12] P. Sauer mann, K. Holzapfel, J. Oprzynski, F. Kohler, W. Poot, T.W. de Loos, The p-T properties of ethanol + hexane, Fluid Phase Equilibria. 112 (1995) 249–272. doi:10.1016/0378-3812(95)02798-J.
- [13] E.M. Fendu, F. Oprea, Vapor-liquid equilibrium for propylene glycols binary systems: Experimental data and regression, Fluid Phase Equilibria. 382 (2014) 244–253. doi:10.1016/j.fluid.2014.09.015.
- [14] D. Ambrose, C.H.S. Sprake, Thermodynamic properties of organic oxygen compounds XXV. Vapor pressures and normal boiling temperatures of aliphatic alcohols, J. Chem. Thermodyn. 2 (1970) 631–645. doi:10.1016/0021-9614(70)90038-8.
- [15] C.B. Kretschmer, R. Wiebe, Liquid-Vapor Equilibrium of Ethanol-Toluene Solutions, J. Am. Chem. Soc. 71 (1949) 1793–1797. doi:10.1021/ja01173a076.
- [16] D.R. Stull, Vapor Pressure of Pure Substances. Organic and Inorganic Compounds, Ind. Eng. Chem. 39 (1947) 517–540. doi:10.1021/ie50448a022.
- [17] NIST Chemistry WebBook, SRD 69, n.d.

- [18] K. Ohgaki, T. Katayama, Isothermal vapor-liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol-carbon dioxide, n-hexane-carbon dioxide, and benzene-carbon dioxide systems, *J. Chem. Eng. Data.* 21 (1976) 53–55. doi:10.1021/je60068a015.
- [19] J.H. Hong, R. Kobayashi, Vapor-liquid equilibrium studies for the carbon dioxide-methanol system, *Fluid Phase Equilibria.* 41 (1988) 269–276. doi:10.1016/0378-3812(88)80011-6.
- [20] C.J. Chang, C.-Y. Day, C.-M. Ko, K.-L. Chiu, Densities and P-x-y diagrams for carbon dioxide dissolution in methanol, ethanol, and acetone mixtures, *Fluid Phase Equilibria.* 131 (1997) 243–258. doi:10.1016/S0378-3812(96)03208-6.
- [21] S.N. Joung, C.W. Yoo, H.Y. Shin, S.Y. Kim, K.-P. Yoo, C.S. Lee, W.S. Huh, Measurements and correlation of high-pressure VLE of binary CO₂-alcohol systems (methanol, ethanol, 2-methoxyethanol and 2-ethoxyethanol), *Fluid Phase Equilibria.* 185 (2001) 219–230. doi:10.1016/S0378-3812(01)00472-1.
- [22] K. Bezanehtak, G.B. Combes, F. Dehghani, N.R. Foster, D.L. Tomasko, Vapor-Liquid Equilibrium for Binary Systems of Carbon Dioxide + Methanol, Hydrogen + Methanol, and Hydrogen + Carbon Dioxide at High Pressures, *J. Chem. Eng. Data.* 47 (2002) 161–168. doi:10.1021/je010122m.
- [23] S. Schwinghammer, M. Siebenhofer, R. Marr, Determination and modelling of the high-pressure vapour-liquid equilibrium carbon dioxide-methyl acetate, *J. Supercrit. Fluids.* 38 (2006) 1–6. doi:10.1016/j.supflu.2005.11.014.

- [24] C. Secuianu, V. Feroiu, D. Geana, Phase equilibria experiments and calculations for carbon dioxide + methanol binary system, *Cent. Eur. J. Chem.* 7 (2009) 1–7. doi:10.2478/s11532-008-0085-5.
- [25] X. Gui, Z. Tang, W. Fei, Solubility of CO₂ in Alcohols, Glycols, Ethers, and Ketones at High Pressures from (288.15 to 318.15) K, *J. Chem. Eng. Data.* 56 (2011) 2420–2429. doi:10.1021/je101344v.
- [26] M. Kariznovi, H. Nourozieh, J. Abedi, Experimental measurements and predictions of density, viscosity, and carbon dioxide solubility in methanol, ethanol, and 1-propanol, *J. Chem. Thermodyn.* 57 (2013) 408–415. doi:10.1016/j.jct.2012.10.002.
- [27] A.-D. Leu, S.Y.-K. Chung, D.B. Robinson, The equilibrium phase properties of (carbon dioxide + methanol), *J. Chem. Thermodyn.* 23 (1991) 979–985. doi:10.1016/S0021-9614(05)80178-8.
- [28] Y. Miyano, I. Fujihara, Henry's constants of carbon dioxide in methanol at 250–500 K, *Fluid Phase Equilibria.* 221 (2004) 57–62. doi:10.1016/j.fluid.2004.04.017.
- [29] C. Secuianu, V. Feroiu, D. Geană, Phase behavior for carbon dioxide+ethanol system: Experimental measurements and modeling with a cubic equation of state, *J. Supercrit. Fluids.* 47 (2008) 109–116. doi:10.1016/j.supflu.2008.08.004.
- [30] I. Dal Molin, 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. doi:10.1016/j.fluid.2006.04.017.
- [31] L.A. Galicia-Luna, A. Ortega-Rodriguez, D. Richon, New Apparatus for the Fast Determination of High-Pressure Vapor–Liquid Equilibria of Mixtures and of Accurate Critical Pressures, *J. Chem. Eng. Data.* 45 (2000) 265–271. doi:10.1021/je990187d.

- [32] D.G. Friend, D.J. Frurip, E.W. Lemmon, R.E. Morrison, J.D. Olson, L.C. Wilson, Establishing benchmarks for the Second Industrial Fluids Simulation Challenge, *Fluid Phase Equilibria*. 236 (2005) 15–24. doi:10.1016/j.fluid.2005.04.020.
- [33] A.C. Galvão, A.Z. Francesconi, Methane and carbon dioxide solubility in 1,2-propylene glycol at temperatures ranging from 303 to 423 K and pressures up to 12 MPa, *Fluid Phase Equilibria*. 289 (2010) 185–190. doi:10.1016/j.fluid.2009.12.006.
- [34] K. Chyliński, J. Gregorowicz, Solubilities of 1-propanol and 1,2-propanediol in supercritical carbon dioxide. New analytical procedure and measurements, *Fluid Phase Equilibria*. 143 (1998) 163–172. doi:10.1016/S0378-3812(97)00290-2.
- [35] M. Škerget, D. Plšek, Ž. Knez, Phase equilibria of the propylene glycol/CO₂ and propylene glycol/ethanol/CO₂ systems, *J. Supercrit. Fluids*. 95 (2014) 129–136. doi:10.1016/j.supflu.2014.08.019.
- [36] Y. Medina-Gonzalez, T. Tassaing, S. Camy, J.-S. Condoret, Phase equilibrium of the CO₂/glycerol system: Experimental data by in situ FT-IR spectroscopy and thermodynamic modeling, *J. Supercrit. Fluids*. 73 (2013) 97–107. doi:10.1016/j.supflu.2012.11.012.
- [37] A.V.M. Nunes, G.V.S.M. Carrera, V. Najdanovic-Visak, M. Nunes da Ponte, Solubility of CO₂ in glycerol at high pressures, *Fluid Phase Equilibria*. 358 (2013) 105–107. doi:10.1016/j.fluid.2013.07.051.
- [38] H. Sovová, J. Jez, M. Khachatryan, Solubility of squalane, dinonyl phthalate and glycerol in supercritical CO₂, *Fluid Phase Equilibria*. 137 (1997) 185–191. doi:10.1016/S0378-3812(97)00102-7.

- [39] B. Gwinner, D. Roizard, F. Lapique, E. Favre, R. Cadours, P. Boucot, P.-L. Carrette, CO₂ Capture in Flue Gas – Semiempirical Approach to Select a Potential Physical Solvent, *Ind. Eng. Chem. Res.* 45 (2006) 5044–5049. doi:10.1021/ie0580396.