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**High pressure CO₂ solubility in food model solutions and fruit juices.**

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Graphical abstract

$$\ln S \left(\frac{gCO_2}{100\ g\ liquid}\right) = k \cdot \ln(\rho_{sc-co_2}) + \frac{a}{T(K)} + \frac{b}{^\circ Brix} + c$$
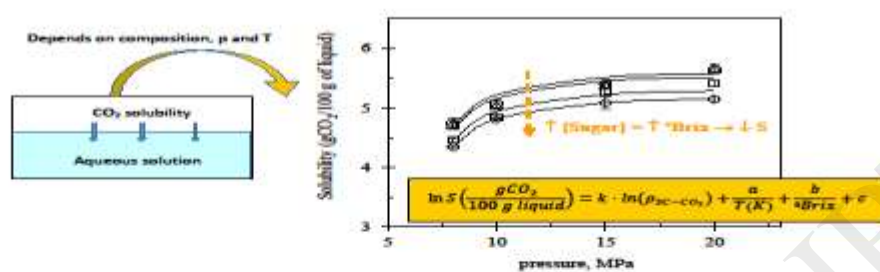
Highlights

- CO_2 solubility depend on pressure, temperature and composition of the liquid phase.
- The presence of sugars led to lower solubility values of CO_2.
- A Chrastill-type equation according to Fornari's approach described CO_2 solubility.
- A new term was introduced to account the presence of sugars.

Abstract

Measurements of CO_2 solubility were performed in different media, pure water, model citrate buffer solutions at different pH values and in the presence of different sugar content and in real apple and carrot juices. Solubility was determined in the pressure range from 8 to 20 MPa and in the temperature range from 308 to 318 K. CO_2 solubility in citrate buffer solutions at pH=3.8 and pH= 6.2 was slightly lower than CO_2 solubility in pure water. A Chrastil-type equation according to Fornari's approach was used to fit CO_2 solubility data in pure water and model solutions. A new term was introduced in this equation to account for the decrease in solubility of CO_2 in the presence of sugar in the liquid media.

1. Introduction

Thermal treatments are usually employed in the food industry as preservation technique, however they cause undesirable changes in several physical parameters and can also destroy heat-sensitive nutritional components. Non-thermal technologies have gained interest and acceptance as food processing methods due to the consumer demand for fresh-like products. Among them, high pressure carbon dioxide (HPCD) has been proposed as an alternative non-thermal pasteurization technique for foods. In HPCD treatments, operating temperatures do not exceed 60ºC and pressures are usually below 50 MPa. The use of HPCD in the food industry is very attractive since CO_2 is non-toxic, chemically inert, and ready available. HPCD has been used to inactivate some microorganism and enzymes that cause deleterious effects in fruit and vegetable juices [1–3]

The mechanism of pressurized CO_2 on microorganism and enzyme inactivation is not yet fully understood. Knowledge of CO_2 solubility in liquid foods is of interest for a better understanding of the action of CO_2 as pasteurizing agent. Additionally, the amount of CO_2 employed in HPCD

processes could be optimized by knowing the solubility of CO_2 at different operating pressures and temperatures and the process would be more economical [4].

In the literature, there are a few studies dealing with the determination of CO_2 solubility in liquid foods or in model media containing different food components. Dohrn et al. [5] determined the phase equilibria for ternary and quaternary systems of glucose, water, CO_2 and ethanol. They observed that the solubility of glucose in the vapor phase was very small, and it increased with pressure and ethanol in the medium, while the CO_2 solubility in the aqueous solution decreased when glucose was in the medium at a concentration of 15 wt.%. Calix et al. [6] determined the CO_2 solubility at 40ºC in different model aqueous solutions with ascorbic or citric acid (0.01 wt.%) and different sugars, from 11.5 to 13 wt. % and in commercial orange and apple juices in the pressure range from 7.58 to 15.86 MPa. These authors also found that CO_2 solubility decreased in the presence of solutes compared with pure water. Following the previous work of Calix et al. [6], Ferrentino et al [4] determined CO_2 solubility in ternary and quaternary mixtures with malic acid (from 0.01 to 2.68 wt.%) and glucose (from 4 to 12 wt.%) in the pressure and temperature range from 7.5 to 15.0 MPa and 308 to 333 K, respectively. These authors observed that organic acids hardly affected CO_2 solubility while the CO_2 solubility significantly decreased with glucose concentration. These authors also found that CO_2 solubility decreased with the presence of sodium phosphate monobasic concentrations [7].

In this work, CO_2 solubility was determined in two different citrate buffer solutions at pH of 3.8 and 6.2, similar to the pH of apple and carrot juices, respectively. The effect of different sugars (glucose, sucrose and fructose) found in apple and carrot juices, on CO_2 solubility was also determined in citrate buffer solutions. CO_2 solubility in model buffer solutions has been compared with pure water and with CO_2 solubility in real apple and carrot juices. CO_2 solubility data have been fitted to an empirical equation based on the Chrastil's equation [8] according to Fornari's

approach [9] that correlates CO_2 solubility in different media with the density of the CO_2 at the operating pressure and temperature. The effect of sugar concentration, by determining ºBrix of the liquid mixture, was also considered in the Chrastil-type equation proposed in this work.

2. Materials and methods

2.1 Equipment for measurement of CO_2 solubility

The high pressure equipment used for measurement of CO_2 solubility has been previously described for fluid phase equilibrium measurements [10]. The equipment was built by Eurotechnica GmbH (Germany) and consists of an equilibrium cell made of stainless steel (SS-316) and equipped with a sapphire window for observing the content of the cell during measurements. The maximum specifications of the apparatus are p = 32 MPa and T = 393 K. Internal volume of the cell ranges from 40 to 70 mL, adjustable through a manual screw piston. The cell includes a pressure transducer and an immersed thermocouple. Both of them calibrated and connected to a Data Acquisition System (DAS). Overall standard uncertainties in the equilibrium measurements were u(p) = ± 0.15 MPa, u(T) = ± 0.1 K.

The equipment was placed inside an oven that allowed temperature control of the system. Once the operating temperature was achieved the system was purged with low pressure CO_2 and 25 mL of the liquid media were introduced into the cell. Using the manual screw piston, the volume of the cell was adjusted to 50 mL. A certain amount of CO_2 was then charged into the cell by using a high-pressure syringe pump (ISCO 260D) and measured by a Coriolis mass flow meter (Rheonik RHE015). The desired pressure was adjusted by actuating the manual screw piston. Mixing of the components of the system was achieved by continuously recirculating the vapour phase through the liquid phase by means of a gear pump (Micropump IDEX). First, the speed of the pump was set to the maximum during 30 min in order to achieve a convenient mixture. Then, speed was set to a lower value for at least 1 h to assure equilibrium. The system was then let to stand for 30 min

at constant temperature and pressure. Samples from the liquid phase were taken by a micro-metering valve connected to the bottom of the equilibrium cell through a 1/16" capillary. Pressure drop during sampling was compensated with the manual screw piston.

Samples were decompressed to atmospheric pressure and released CO_2 was measured using an upturned burette and a thermal mass flow meter (Bronkhorst F-110C). The liquid separated from CO_2, was collected in an ice-cooled glass trap and the vials weighed in a precision analytical balance (accurate to $\pm$ 0.0001 g). The ratio between the grams of CO_2 and the grams of liquid gave the solubility value, expressed in grams of CO_2 per 100 g of noncarbonated solution [4].

2.2 Effect of different components on CO_2 solubility

CO_2 solubility was determined in different liquid media at different temperatures, from 308 to 328 K, in the pressure range from 8 to 20 MPa. This pressure and temperature range was chosen based on previous studies of enzyme inactivation by HPCD in cloudy juice from *Golden Delicious* apples [2].

First, CO_2 solubility was determined in pure water at 318 K to verify the reliability of the solubility data obtained with the equipment.

In liquid foods, many components such as amino acids and organic acids can exert buffer action [11]. Therefore, the solubility of CO_2 was determined in different citrate buffer solutions to study the effect of a buffer action on CO_2 solubility. Solubility was determined at two different values of pH in the citrate buffer, according to the natural pH values of apple and carrot juices, pH = 3.8 and pH =6.2, respectively.

The effect of the main sugars present in fruits on solubility of CO_2 was also determined in a citrate buffer solution at pH =3.8. CO_2 solubility was determined in pseudo-ternary mixtures, considering the citrate buffer as one component, of glucose-citrate buffer-CO_2, sucrose-citrate buffer-CO_2 and fructose-citrate buffer-CO_2. The concentration of glucose, fructose and sucrose in the buffer

solution was 2.91 wt.%, 2.51 wt.% and 5.85 wt.%, respectively. The sugar content was taken from Wu et al. [12] as determined for apple fruit of *Golden Delicious* cultivar. Further solubility measurements were carried out in a multicomponent mixture formed by glucose-sucrose-fructose-citrate buffer-CO_2, at the same sugar content as the reported above. Finally, CO_2 solubility was also determined in a more complex mixture formed by all the sugars and pectin.

The effect of sugars on solubility of CO_2 was also carried out at a pH value of the citrate buffer of 6.2, similar to the pH of carrot juice. Although sugar content of carrot juice is lower than the previously reported values for apple juice [13], the same sugar content was kept to compare with the data determined pH 3.8.

Finally, solubility of CO_2 was determined in real apple and carrot juices. Cloudy apple juice was prepared from *Golden delicious* apples. Apples were peeled and cut in cubes and then added to a 0.3 wt.% of L-ascorbic acid solution to avoid enzymatic browning. Apple cubes were wiped and immediately squeezed with a screw juice extractor. Carrot juice was prepared from fresh carrots (Daucus carota *cv. Natesa*). Carrots were washed, peeled and the juice was extracted by an electronic juicer (Moulinex® Junior 864). Both liquors, apple and carrot juices, were filtered with 2 layers of cheesecloth. The pH of apple and carrot juice was 3.72 and 6.34, respectively.

°Brix of all the liquid media employed in this work were measured with a Milton Roy refractometer at 25°C (Model 334610) and are reported in Table 1.

2.3 CO_2 solubility data correlation

In this work, CO_2 solubility data were correlated to an empirical equation based on the Chrastil's equation traditionally employed to correlate the solubility of a compound in a supercritical fluid with the density of the supercritical gas [8]. Fornari et al. [9] demonstrated that the liquid phase

composition could be also related with the density of the supercritical fluid and they successfully

correlated solubility (S) of different supercritical gases in different liquids:

$$\ln S \ (g \ CO_2/100 \ g \ liquid) = k \cdot \ln(\rho_{SC-CO_2}) + c \qquad \text{at constant temperature} \qquad [1]$$

According to Fornari et al. [9] this equation establishes a Chrastil-type relationship between the

composition of the liquid phase and the density of the SC-CO$_2$.

When CO$_2$ solubility data were obtained at different temperatures, the following equation, based

on the one proposed by Chrastil [8], was used:

$$\ln S \ (g \ CO_2/100 \ g \ liquid) = k \cdot \ln(\rho_{SC-CO_2}) + a/T(K) + c \qquad [2]$$

In the present work, Fornari's model has been extended to multicomponent mixtures, due to the

nature of the components present in the liquid phase. Components such as sugar, salts an citric

acid can be considered almost insoluble in SC-CO$_2$ [14,15].

2.4 Statistical analysis

Statistical analyses were conducted using the software Statgraphics X64. The results are presented

as a mean ± standard deviation of CO$_2$ solubility in the liquid phase by sampling three times. The

significance of the differences was determined based on an analysis of the variance with the

Fisher's least significant method at p-value ≤ 0.05.

The mean relative deviation (MRD) between experimental and calculated solubility of CO$_2$ was

evaluated:

$$MRD = \frac{1}{n}\left(\sum_{all \ samples}\left|\frac{S_{calc} - S_{exp}}{S_{exp}}\right|\right) \cdot 100 \qquad [3]$$

where the subscripts exp and calc are calculated and experimental values and n is the number of

experimental solubility data.

3 Results and discussion

3.1 Validation of the equipment. CO_2 solubility in water

In order to check the reliability of the apparatus and the experimental procedure, CO_2 solubility in water was determined at 318 K in the pressure range from 8 to 20 MPa (Table 2). Figure 1 shows that solubility data obtained in this work at 318 K lie between data obtained from literature at 308 K and 328 K [16,17] proving that the apparatus can provide reliable values of solubility being of the order of previous published results. For instance, at 10 MPa Bamberger et al. [16] reported a solubility value of 5.11 g CO_2/100 g water at 323 K, while 5.46 g CO_2/100 g water was reported by Wiebe et al. at 313 K [17]. In this work at the same pressure and 313 K, the solubility was 5.33 g CO_2/100 g, laying between both temperatures. In the literature graphical representations of CO_2 solubility as a function of temperature at different pressures can be found and solubility data at 45ºC can be easily obtained, having values similar to this work [17,18].

CO_2 solubility data in pure water were fitted to equation 1. Parameters are reported in Table 2 and represented in Figure 1, yielding a good fitting quality ($R^2 > 0.94$).

3.2 CO_2 solubility in citrate buffer solutions

The effect of the pH on CO_2 solubility was assessed by means of a citrate buffer solution at two different values of pH, 3.8 and 6.2, in the pressure and temperature range from 8 to 20 MPa and from 318 to 328 K, respectively (Figure 2 and Table 3). For each liquid medium, it can be observed that CO_2 solubility depends on pressure and temperature. At a constant temperature, an increase in pressure led to an increase in solubility of CO_2 while solubility at a constant pressure, increased by decreasing temperature.

Results obtained with pure water at 318 K are also listed for a better comparison of the effect of the buffer capacity of the media on CO_2 solubility. Slightly differences can be observed in CO_2 solubility for pure water and the two buffer systems with the highest values obtained in pure water and the lowest in the citrate buffer solution at pH =6.2. Although, according to the Fisher's least significant method, no differences were observed in CO_2 solubility in the different liquid media for each pressure. The small differences observed in CO_2 solubility in the different liquid media, especially at the highest pressures, can be related with the composition of the liquid media. The concentration of citric acid and sodium citrate salt at pH = 3.8 and 6.2 were 0.74 wt.% and 0.15 wt.% of citric acid and 0.39 wt.% and 1.10 wt.% of sodium citrate, respectively. In this regard, Ferrentino et al. [4] reported CO_2 solubility data in a water-malic acid system, at 313 K in the pressure range from 7.5 to 15 MPa, finding no significant dependence of the CO_2 solubility value on the malic acid concentration in the solutions, in the range from 0 g to 2.68 g of malic acid in a 100 g solution. Based on these results, in this work, it was assumed that the citric acid concentration would not play an important role on the values of CO_2 solubility. In a different study, Ferrentino et al. [7] also determined CO_2 solubility in the system water-sodium phosphate monobasic solutions at different salt concentration in the range from 0.24 to 4.8 g of sodium phosphate monobasic in 100 g of water. These authors found that an increase in the amount of the solute decreased solubility of the CO_2. For instance, at 313 K and 10.34 MPa, CO_2 solubility decreased from values of 5.32 ± 0.19 g CO_2/100 g in pure water to values of 5.16 ± 0.03 and 4.61 ± 0.06 g CO_2/100 g for a sodium phosphate monobasic concentration of 0.240 g /100 g water and 4.8 g/100 g water, respectively. These results agree with the trend in the CO_2 solubility data obtained in this work, since the lowest solubility values were obtained at pH value of 6.2, corresponding with the highest sodium citrate concentration.

Similar trend was observed for the other two isotherms, at 308 and 328 K, for each operating pressure.

Based on the results presented in Table 3, CO_2 solubility data in the citrate buffer solutions at both pH values were fitted all together to equation [2], in the temperature and pressure range from 308 to 328 K and from 8 to 20 MPa, respectively. Parameters are listed in Table 2. Based on the quality of the fitting, it can be concluded that a Chrastil-type relationship can be successfully applied to fit CO_2 solubility data in buffer aqueous solution, according to Fornari's approach [9].

3.3 CO_2 solubility in different sugars solutions

Solubility of CO_2 in the liquid system citrate buffer-glucose was measured at 318 K, in the pressure range from 8 to 20 MPa at the two values of pH, 3.8 and 6.2. The weight fraction of glucose in the liquid feed was 2.91 wt.% [12]. The experimental results for the citrate buffer at pH = 3.8 are listed in Table 4. CO_2 solubility increased with increasing pressure at constant temperature. For the citrate buffer at pH = 6.2 and same glucose concentration, no significant differences were obtained with the values reported in Table 4 at pH = 3.8 for each operating pressure (4.78 ± 0.04, 5.10 ± 0.05, 5.36 ± 0.01 and 5.57 ± 0.09 g/100 g of liquid mixture at 8, 10, 15 and 20 MPa, respectively). The presence of glucose led to a decrease in CO_2 solubility compared to the corresponding buffer solution, also listed in Table 4 for a better comparison. This fact has been also observed in the literature for water + glucose + CO_2 systems [4,5] . Dohrn et al. [5] observed a decrease in CO_2 solubility of 6.2 % and 8.9 % per gram of glucose at 323 K and 10 and 20 MPa, respectively, compared with pure water. In this work, a decrease of the same order was obtained for CO_2 solubility, 5.2 wt.% and 7.4 wt.% per gram of glucose at 313 K at 10 and 20 MPa, respectively, compared with the citrate buffer solution (at pH value of 3.8).

The effect of other sugars, such as sucrose and fructose on CO_2 solubility was only determined in the citrate buffer solution at pH = 3.8, at 318 K in the pressure range from 8 to 20 MPa. Sucrose and fructose concentration was fixed at 2.51 wt.% and 5.85 wt.%, respectively [12]. CO_2 solubility was also determined in the citrate buffer solutions at pH = 3.8 in presence of all sugars: 2.91 wt.% of glucose, 2.51 wt.% of sucrose and 5.85 wt.% of fructose. Results are collected in Table 4 and plotted in Figure 3. For each pressure, an increase in sugar concentration led to a decrease in CO_2 solubility with significant differences among the sugar concentration for each pressure when applying the LSD test (p ≤ 0.05).

Figure 3 clearly shows that the higher the sugar content the lower the solubility of CO_2. CO_2 solubility at 318 K and the ºBrix of the corresponding sugar feed solutions has been plotted in Figure 4 for each operating pressure. A linear relationship can be observed for each pressure, the corresponding linear regressions have been listed in Table 5, together with the quality of the fitting. An ANOVA was performed to test the statistical significance of the terms in the regression model and it was found no significant differences among the slope for the various values of pressure at 90 % or higher confidence level. Based on this finding, CO_2 solubility data obtained in the presence of sugars were fitted to an equation similar to Eq. [2], but taking also into account the effect of sugar content, expressed as ºBrix of the solution, in a similar way as the effect of temperature on CO_2 solubility:

$$\ln S \ (g \ CO_2/100 \ g \ liquid) = k \cdot \ln(\rho_{SC-CO_2}) + a/T(K) + b/ºBrix + c \qquad [4]$$

At the highest pressure studied in this work, 20 MPa, CO_2 solubility has been also determined at 308 and 328 K in the citrate buffer solution for the two pH values of 3.8 and 6.2 in presence of all sugars (2.91 wt.% of glucose, 2.51 wt.% of sucrose and 5.85 wt.% of fructose). Results are plotted in Figures 5a and 5b. As previously described, CO_2 solubility decreased with temperature and, for

each temperature, no significant differences ($p \leq 0.05$) were found between both values of pH, although, in general, slightly lower values were obtained at pH = 6.2 (Table 6). Solubility data obtained at these two temperatures were also fitted to Eq. 4 together with the previous data at different sugar concentration. Fitted parameters are listed in Table 2 and good fitting can be observed.

Finally, the effect of the presence of pectin on CO_2 solubility was also determined in a complex mixture of citrate buffer at pH = 3.8 in presence of all the sugars (2.91 wt.% of glucose, 2.51 wt.% of sucrose and 5.85 wt.% of fructose) and for a pectin concentration similar to the pectin content of apple juice, 22 mg/L expressed as D-galacturonic acid [2]. CO_2 solubility was determined for that mixture at 20 MPa and 318 K obtaining a value of 5.27 ± 0.04 g/100 g of liquid mixture, finding no significant difference with the value of solubility for the same mixture in the absence of pectin ($p \leq 0.05$).

3.4. CO_2 solubility in real apple and carrot juice

CO_2 solubility was finally determined in real apple and carrot juices at 20 MPa in the temperature range from 308 to 328 K. Results are plotted in Figure 5a and 5b together with the results obtained for the corresponding citrate buffer in presence of all sugars for a better comparison. Surprisingly CO_2 solubility is higher in the real juices than in the model solutions in presence of all sugars. This result could be attributed to the ºBrix of the real juices compared to the ºBrix of the corresponding model solutions at both pH values.

Apple juice presented a value of 10.83 ºBrix while the citrate buffer solution with all the sugars at pH= 3.8 presented a slightly higher value, 11.17 ºBrix. The same behaviour was determined for carrot juice with a ºBrix of 9.06 while the ºBrix of the model solution at pH = 6.2 was higher, 11.63. As it was explained in the experimental section 2.2, higher sugar content than the usual found in carrot juice was chosen at pH close to the carrot juice, to compare the CO_2 solubility at

different pH values. In any case, differences could be also attributed to the presence of minor components present in the real juices that could exert an effect on CO_2 solubility.

5. Conclusions

CO_2 solubility in aqueous solutions depends on the composition of the solutions. Slightly lower values, but not significant different according to LSD test, of CO_2 solubility in citrate buffer solutions were obtained compared to water, probably due to presence of sodium citrate salt. Sugars present in fruit or vegetable juices, such as sucrose, glucose or fructose led to significant lower values of CO_2 solubility. The presence of other minor components such as pectin did not affect the solubility values.

CO_2 solubility data were successfully fitted to a Chrastill type equation, according to Fornari's approach to relate the liquid phase composition with the density of the supercritical fluid. In this work an additional term was added, to account for the decrease in solubility of CO_2 in the presence of sugars taking into account the ºBrix of the aqueous solutions, obtaining a good fitting.

Solubility of real apple and carrot juices did not fit to the proposed model, since minor components present in natural juices could affect the CO_2 solubility.

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Table 1. ºBrix of the different citrate buffer solutions and apple and carrot juices employed in this work.

Solution	ºBrix
pH = 3.8, 2.91% glucose	3.60 ± 0.08
pH = 3.8, 2.51% sucrose	3.23 ± 0.1
pH = 3.8, 5.85% fructose	6.17 ± 0.06

pH = 3.8, 2.91% glucose, 2.51% sucrose and 5.85% fructose	11.17 ± 0.06
pH = 6.2, 2.91 % glucose	3.73 ± 0.06
pH = 6.2, 2.91% glucose, 2.51% sucrose and 5.85 % fructose	11.63 ± 0.06
Apple juice	10.83 ± 0.06
Carrot juice	9.06 ± 0.06

Table 2. Parameters of Eq (1), (2) and (4) for different CO2 + liquid media systems, n number of experimental data fitted, MRD, mean relative deviation (Eq. 3)

Liquid media	Equation	k	a	b	c	R^2	n	MRD
Water	1	0.139 ± 0.023			0.82 ± 0.14	0.9484	4	1.47 %
Citrate buffer solutions (pH =3.8 and 6.2)	2	0.170 ± 0.009	422 ± 55		-0.71 ± 0.16	0.9669	24	1.54 %
Citrate buffer solutions + sugars	4	0.140 ± 0.008	446 ± 96	0.366 ± 0.042	-0.74 ± 0.30	0.9391	25	1.42 %

Table 3. Solubility of CO_2 in pure water at 318 K and two different citrate buffer solutions at pH values of 3.8 and 6.2 in the temperature range from 308 to 328 K and pressure range from 8 to 20 MPa

p, MPa	T, K	water	pH = 3.8	pH = 6.2
8	308		5.40 ± 0.05^a	5.43 ± 0.05^a
10	308		$5.94 \pm 0.11^{b,c}$	5.85 ± 0.11^b
15	308		$6.05 \pm 0.08^{c,d}$	$5.92 \pm 0.08^{b,c}$
20	308		$6.18 \pm 0.05^{d,e}$	6.29 ± 0.11^e
8	318	4.95 ± 0.10^a	4.86 ± 0.07^a	4.87 ± 0.13^a
10	318	5.33 ± 0.08^b	5.22 ± 0.04^b	5.18 ± 0.07^b
15	318	5.69 ± 0.11^c	$5.70 \pm 0.11^{c,d}$	5.62 ± 0.11^c
20	318	5.94 ± 0.08^e	$5.87 \pm 0.02^{d,e}$	$5.77 \pm 0.03^{c,d}$
8	328		4.27 ± 0.23^a	4.30 ± 0.07^a
10	328		4.86 ± 0.12^b	4.83 ± 0.04^b
15	328		5.38 ± 0.07^c	5.29 ± 0.06^c
20	328		5.62 ± 0.03^d	$5.55 \pm 0.15^{c,d}$

For each isotherm (308, 318 and 328 K), same letters in the same raw and column mean no significant difference according to LSD test at p-value ≤0.05.

Table 4. CO_2 solubility in citrate buffer solutions at pH = 3.8 in the presence of different sugars: glucose (2.91 wt.%), sucrose (2.51 wt.%), fructose (5.85 wt.%) and a mixture of all of them.

p, MPa	Citrate buffer	Glucose	Sucrose	Fructose	All sugars
8	4.86 ± 0.07^b	4.75 ± 0.09^b	4.73 ± 0.09^b	4.46 ± 0.03^a	4.33 ± 0.02^a
10	5.22 ± 0.04^d	5.07 ± 0.06^c	5.05 ± 0.04^c	4.84 ± 0.01^b	4.66 ± 0.01^a
15	5.70 ± 0.11^c	5.41 ± 0.01^b	5.39 ± 0.06^b	5.27 ± 0.08^b	4.97 ± 0.10^a
20	5.87 ± 0.02^d	5.65 ± 0.08^c	5.66 ± 0.04^c	5.47 ± 0.05^b	5.26 ± 0.05^a

For each pressure, same letters in the same raw mean no significant difference according to LSD test at p-value ≤ 0.05.

Table 5. Terms of the linear regression model of CO_2 solubility as a function of ºBrix at 318 K at different operating pressures

Pressure, MPa	Intercept	Slope*	R^2
8	4.886 ± 0.091	-0.0532 ± 0.0134	0.9423
10	5.213 ± 0.057	-0.0514 ± 0.0083	0.9749
15	5.592 ± 0.025	-0.0552 ± 0.0036	0.9957
20	5.808 ± 0.064	-0.0519 ± 0.0095	0.9681

(*) The ANOVA performed for variables in the order fitted determined no significant differences among the slope at the 90 % (or higher) confidence level.

Table 6. CO_2 solubility in citrate buffer solutions at pH = 3.8 and pH =6.2 in the presence of glucose (2.91 wt.%), sucrose (2.51 wt.%) and fructose (5.85 wt.%) at 20 MPa and at different temperatures.

pH	Temperature, K	Solubility g/100 g of liquid
3.8	308	5.43 ±0.01[c]
6.2	308	5.46 ±0.08[c]
3.8	318	5.26 ±0.05[b]
6.2	318	5.15 ±0.06[b]
3.8	328	4.93 ±0.02[a]
6.2	328	4.85 ±0.03[a]

Same letters in the solubility column mean no significant difference according to LSD test at p-value ≤ 0.05.
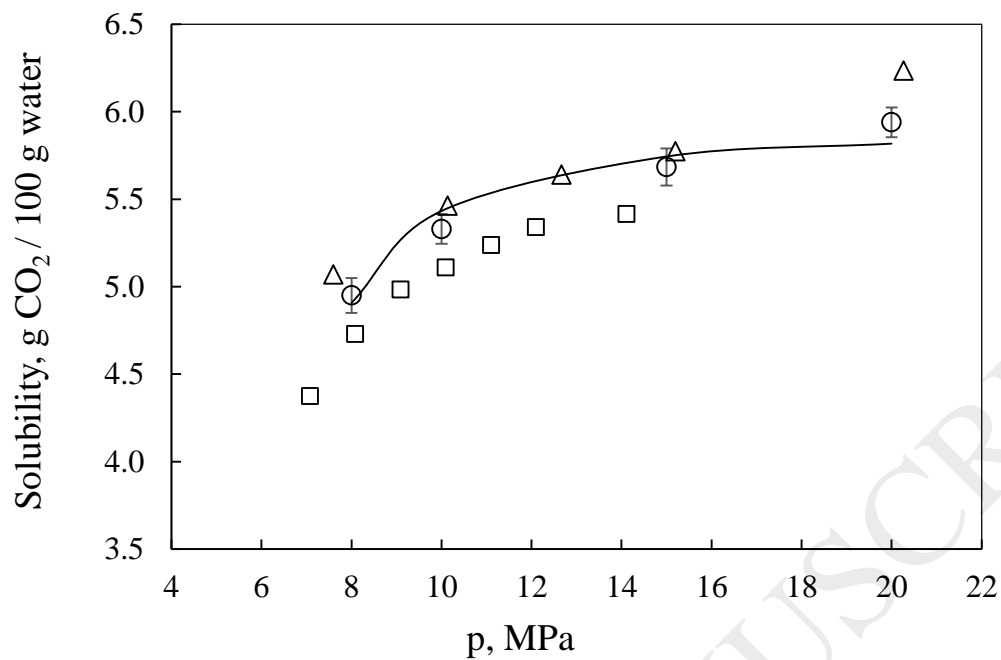
Figure 1. Solubility of CO_2 in pure water at different temperatures: 318 K (o, this work), 323 K (□, [16]) and 313 K (Δ, [17].). Continuous line corresponds to Eq [1], parameters are listed in Table 2.
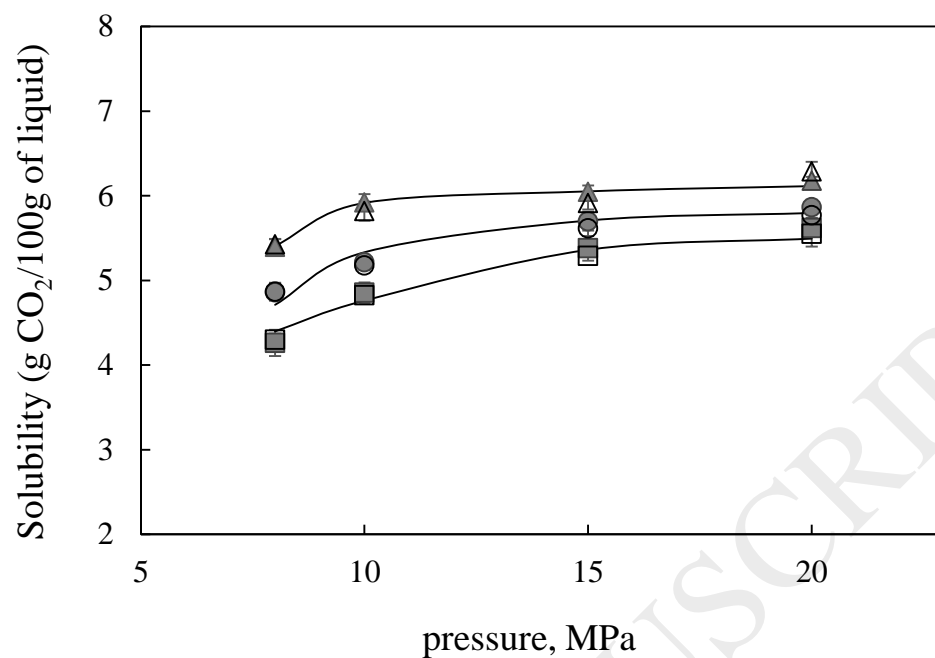
Figure 2. Solubility of CO_2 in citrate buffer solutions at two values of pH, 3.8 (grey symbols) and 6.2 (white symbols) at different temperatures: 308 K (Δ ▲), 318 K (o, ●), 323 K (□, ■). Continuous lines correspond to Eq [2], parameters are listed in Table 2.
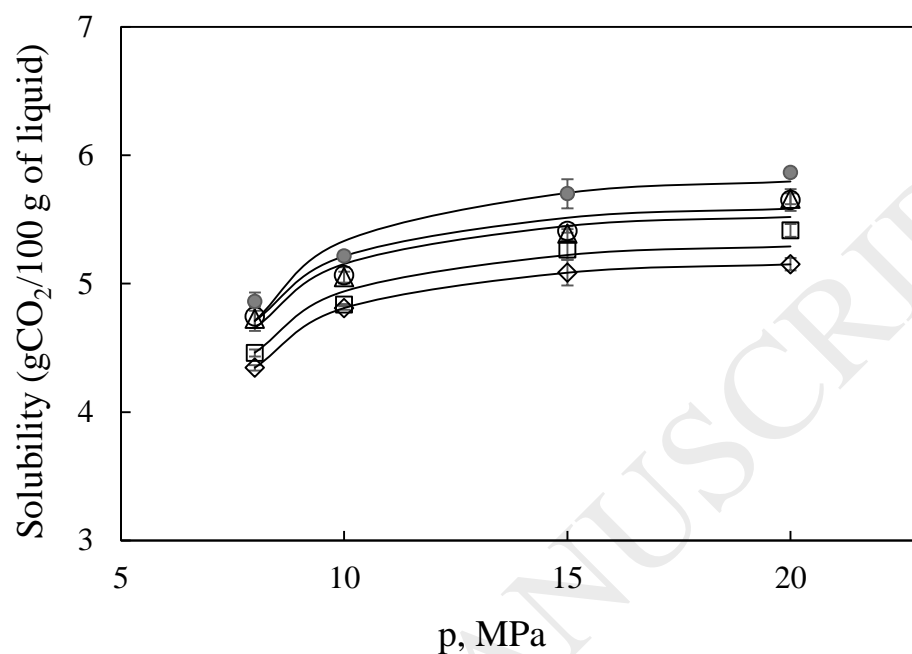
Figure 3. CO_2 solubility at 318 K in a buffer citrate solution (pH = 3.8) with different sugars in the medium (o glucose 2.91 %, Δ sucrose 2.51 %, $\square$, fructose 5.9 % $\Diamond$ mixture of sugars: glucose 2.91 %, sucrose 2.51 % and fructose 5.85 %). CO_2 solubility in the citrate buffer solution (pH= 3.8) has been also plotted for comparison ($\bullet$). Continuous lines correspond to Eq. 2 (buffer solution) and Eq. 4 (in the presence of sugars), parameters are listed in Table 2.
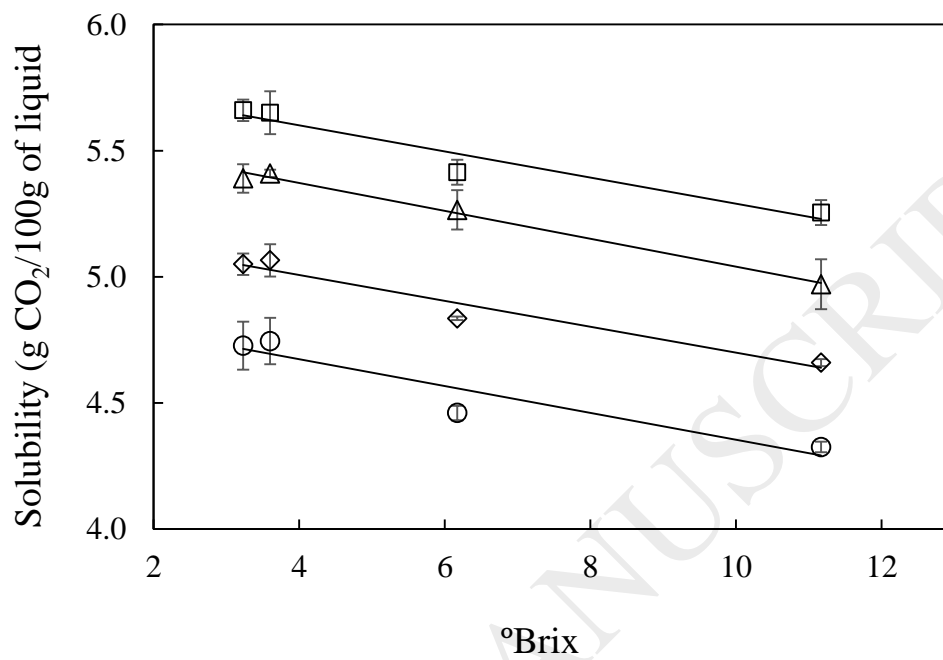
Figure 4. CO_2 solubility at 318 K as a function of ° Brix of different sugar solutions (see Table 1) in a citrate buffer solution at pH= 3.8. at different operating pressure (□ 20 MPa, Δ 15 MPa, ◊ 10 MPa and ○ 8MPa). Continuous lines correspond to the linear regression of solubility with ºBrix (Table 6).
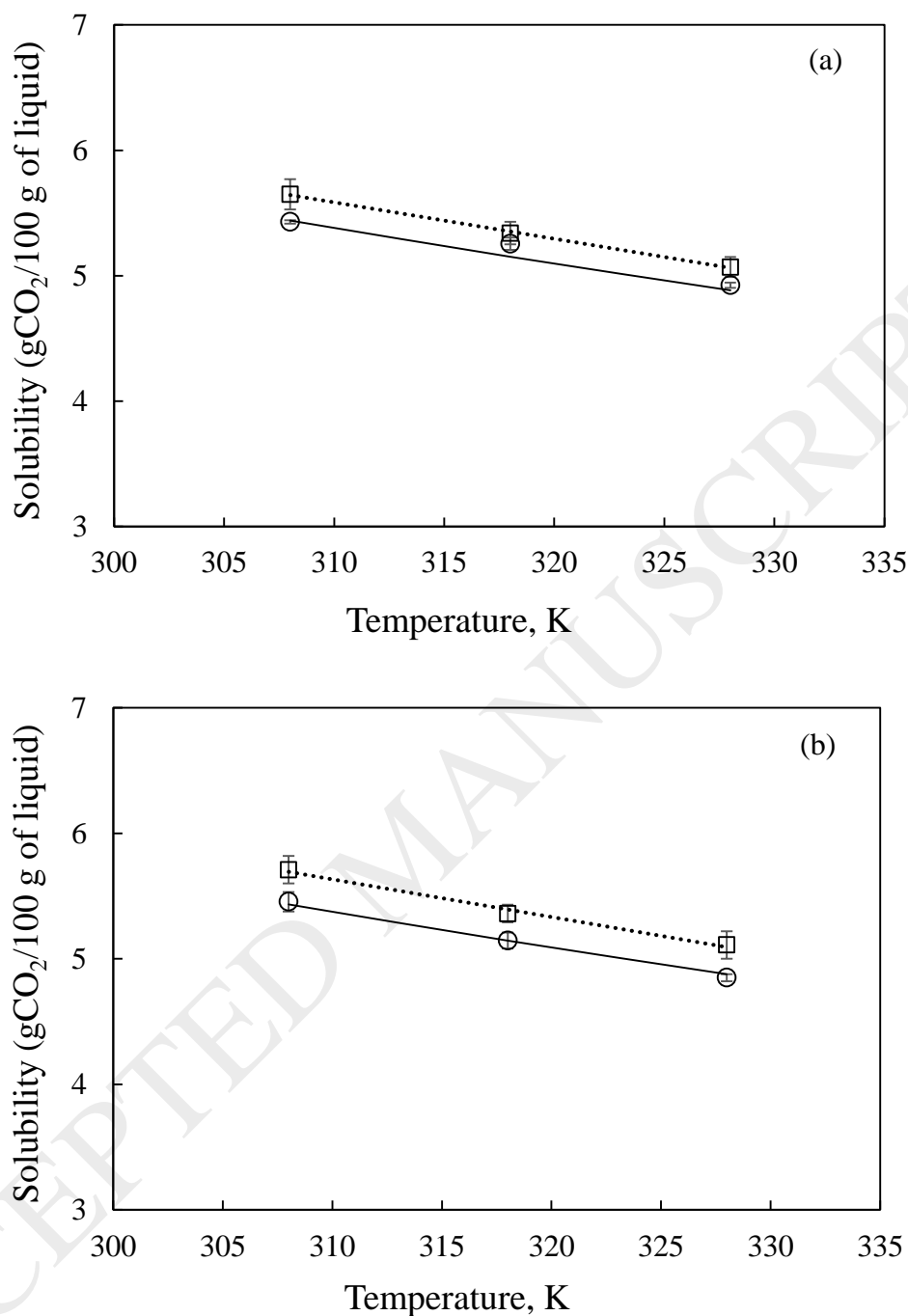
Figure 5. CO_2 solubility at 20 MPa (a) In a citrate buffer solution with 2.5 % glucose, 2.9 % sucrose and 5.2 % fructose at pH =3.8 (o) and real apple juice (□) (b) In a citrate buffer solution with 2.5 % glucose, 2.9 % sucrose and 5.2 % fructose at pH = 6.2 (o) and real carrot juice, (□). Continuous lines represent the fitting to Eq. 4 and parameters are listed in Table 2. Discontinuous lines are to guide the eye.