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Solubility and Diffusivity of CO_2 in Natural Methyl Cellulose and Sodium Carboxymethyl Cellulose

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Supporting Information

ABSTRACT: The diffusion coefficients and solubility of CO_2 in methyl cellulose (M_w = 40 000 g·mol^{-1}) and sodium carboxymethyl cellulose (CMC) of different molecular weights, M_w = (90 000, 250 000, and 700 000) g·mol^{-1}, were determined by a gravimetric method. The MBS (magnetic suspension balance) was used for measurements at three different temperatures, (313, 333, and 353) K, and pressures up to 30 MPa. High values of solubility (up to 36.11 mol %) and diffusion coefficients [$(2.55 \cdot 10^{-9}$ to $8.61 \cdot 10^{-8})$ cm^2·s^{-1}] were obtained. The solubility of CO_2 in the polymers depends on the temperature and pressure, while diffusion coefficients are concentration-dependent. The solubility and diffusivity in the various CMCs are influenced by molecular weight and the degree of substitution.

INTRODUCTION

The application of supercritical carbon dioxide ($SCCO_2$) in polymerization reactions and polymer processing is rapidly expanding.[1] $SCCO_2$ has also shown to be an attractive solvent and processing aid for the chemical and physical modification of polysaccharides such as cellulose and starch.[2,3]

Using supercritical fluids is one possibility to carry out chemistry and chemical technologies in a sustainable manner ("green chemistry").[4] $SCCO_2$ and other dense fluid technologies are an environmentally benign alternative to conventional industrial processes.[4] The use of $SCCO_2$ has increased significantly because of its importance in a variety of fields, including synthetic chemistry, analytical chemistry, material science, food industry, and powder technology.[5] Particularly, its characteristics (such as low cost, nontoxicity, nonflammability, and chemical inertness[6]), have been exploited in extraction, separation, and crystallization processes.[5,6] Its supercritical conditions are easily attained (T_c/K = 304, p_c/MPa = 7.38), and it can be removed from a system by simple depressurization.[5−7]

Methyl cellulose (MC) is a chemical compound derived from cellulose.[8] It may be used as a thickener in food industry, as a matrix for the controlled release of drugs in the pharmaceutical industry, mixed with concrete in civil engineering, and as an agent for modifying water viscosity in the petrochemical industry for heavy oil recovery.[9] It is nontoxic, nondigestible, nonallergenic, and nonirritant. MC is used in oral and topical pharmaceutical formulations[9] and in cosmetics and food products as an emulsifier and stabilizer.[8−10]

Sodium carboxymethyl cellulose (CMC) is a white granular powder in its pure state. Its properties are similar to those of MC. It is used in food industry as viscosity modifier or as thickener or to stabilize emulsions but can also be found in many nonfood products such as water-based paints, detergents, and paper products.[8−12]

Solubility and diffusivity data are important when designing technologies for processing natural or synthetic polymers. CO_2 has been proposed for sustainable processing of polysaccharides; however, the phase equilibrium data are highly scarce.[13] Therefore, this study represents an original contribution to the understanding of the interactions between cellulose derivatives and CO_2 as a potential "green" solvent.

In the present work, the solubility and diffusivity of CO_2 in MC (M_w = 40 000 g·mol^{-1}) and sodium CMC of different molecular weights [M_w = (90 000, 250 000, and 700 000) g·mol^{-1}] (Table 1) have been measured using a magnetic suspension balance. The solubility data were studied for each polymer at three different temperatures, (313, 333, and 353) K, in the pressure range (0 to 30) MPa.

EXPERIMENTAL SECTION

Materials. CO_2 (purity 2.5) was obtained from Messer (Ruše, Slovenia). Methyl cellulose (catalog no. 274429; MC, M_w = 40 000 g·mol^{-1}) and sodium carboxymethyl cellulose of different molecular weights (catalog no. 419273; CMC, M_w = 90 000 g·mol^{-1}, catalog no. 419303; M_w 250 000 g·mol^{-1}, catalog no. 419338; M_w 700 000 g·mol^{-1}) were provided by Sigma-Aldrich (Maribor, Slovenia). MC and CMC were delivered as a white powder, and they were compressed to tablets before the measurements. The reagents were used without further purification.

Apparatus. The solubility and diffusion coefficients of CO_2 in MC and CMC were measured using a magnetic suspension balance (MSB; RUBOTHERM, Germany). The MSB allows the gravimetric measurements of the quantity of gas dissolved in the polymer, with a resolution and accuracy of the microbalance of 10 μg and ± 0.002 %, respectively. The measurements can be performed over a wide range of temperature and pressure, due to the location of the balance outside the measuring cell, in normal conditions of pressure and temperature. A detailed description

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Table 1. Properties of Cellulose Derivatives: Molecular Weight (M_w), Density (ρ), and Viscosity (η)

component	M_w g·mol^{-1}	ρ g·mL^{-1}	degree of substitution	η^a cPs
MC	40 000		1.60−1.90[b]	300−560
sodium CMC	90 000	1.59	0.70	50−200
sodium CMC	250 000	1.59	0.90	400−800
sodium CMC	700 000	1.59	0.90	2500−6000

[a] 2 %, water, 25 °C. [b] Moles of methoxy/moles of cellulose.

of the device and of the working procedure can be found in literature.[14,15] The measuring cell of MSB is also equipped with a window, which allows an observation of the sample and the estimation of volume changes during the sorption measurements. The polymers were shaped into discs with a diameter of 14.7 mm and placed in a glass sample container inside the measuring cell of MSB, so that only one surface was in contact with the gas.

The solubility and diffusivity of CO_2 in MC and CMC were measured at three different temperatures, (313, 333, and 353) K, in the pressure range (0 to 30) MPa (with an uncertainty u_c = 0.005 MPa). The measurements were performed using a step-by-step method: increasing the pressure with approximately 2 MPa, allowing the system to reach equilibrium, while recording the sorption curve, before applying the next pressure step.

Solubility Calculations. To determine the solubility of CO_2 in polymers, it is necessary to know the mass of the polymer and the quantity of absorbed gas. The solubility is thus expressed as the mass of gas, in grams, absorbed by the unit mass of substrate. The mass of the substrate was obtained by weighing the sample in vacuum.

For solubility measurements the pressure of the gas inside the MSB cell was increased stepwise at constant temperature. The recorded balance reading during solubility measurements need to be corrected for the buoyancy effect acting on the sample and the sample container. For these corrections it is necessary to know the density of the gas inside the MSB cell and the volume of the sample and of the sample container. The density of CO_2 inside the measuring cell was obtained from the NIST Chemistry WebBook for the applied temperature and pressure. The volume of the sample container was previously determined by measurements in the absence of the polymer sample. The volume of the polymer samples [(0.25 to 0.30) cm^3] was recorded by a photo camera. Since the volume of the samples changes during absorption of CO_2, the volume variation was estimated by image processing, using the diameter of the sample container as an internal reference. The uncertainty of volume measurements was u_c = 0.01 cm^3, which stands for an error in solubility calculations of ± 2 %. These values were then used for determining the corrected mass and the mass of the absorbed gas.

Diffusion Coefficient. To determine the diffusion coefficient, a one-dimensional diffusion process was considered as described by Fick's second law:[16−23]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the concentration of diffusing substance, x is the direction normal to the section, and D (assumed constant) is the diffusion coefficient.

It was assumed that Fick's second law is valid in the very first moment following the application of the pressure step. That is, the diffusion is one-dimensional, with all gas entering through a single sample surface, and the variation in concentration is small enough so that the thickness of the sample and the diffusion coefficient can be assumed not to vary during the short time considered.[21]

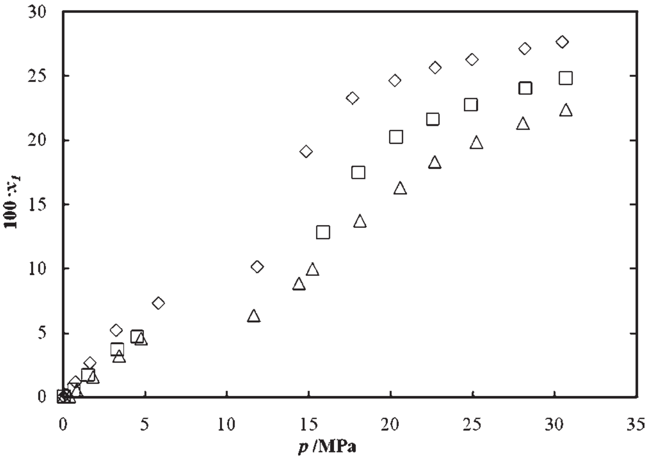

Figure 1. Solubility of CO_2 (1) in sodium MC (M_w = 40 000 g·mol^{-1}) (2): ◊, 313 K; □, 333 K; △, 353 K.

When considering the diffusion along a cylindrical rod of length l, with one end and its surface sealed and the other end maintained at a constant concentration of gas, the following boundary conditions can be used:[18]

$$\begin{aligned} C &= C_0 \quad \text{for} \quad 0 < x < l, \quad t = 0 \\ \frac{\partial C}{\partial x} &= 0 \quad \text{for} \quad x = l, \quad t \geq 0 \\ C &= C_1 \quad \text{for} \quad x = 0, \quad t \geq 0 \end{aligned} \tag{2}$$

According to Crank,[16] by applying the above boundary conditions the solution of eq 1 is:

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n + 1}\exp\left[-\frac{(2n + 1)^2\pi^2}{4l^2}Dt\right]\cos\left[\frac{(2n + 1)\pi x}{2l}\right] \tag{3}$$

By integrating over the length l, and by considering M_t as the total amount of diffusing substance which has entered the polymer at time t and M_∞ as the corresponding quantity after infinite time, the corresponding solution for small times is:[16−18]

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{l^2}\right)^{1/2}\left[\pi^{-1/2} + 2\sum_{n=1}^{\infty}(-1)^n \text{ierfc}\frac{nl}{\sqrt{Dt}}\right] \tag{4}$$

For small values of M_t/M_∞ (< 0.5), eq 4 can be approximated to:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{5}$$

The value of D can be deduced from the initial gradient, Γ, of the plot M_t/M_∞ as a function of $t^{1/2}$ (reduced sorption curve).[16−23]

$$D = \frac{\pi}{4}\Gamma^2 l^2 \tag{6}$$

The experimental error for diffusivity calculations was ± 7 %.

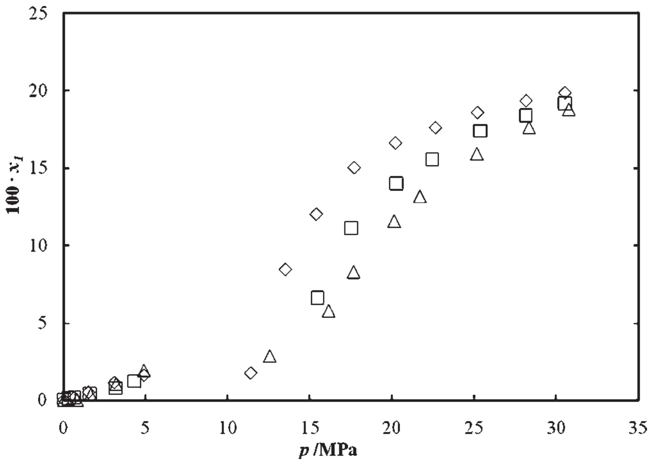

Figure 2. Solubility of CO_2 (1) in sodium CMC (M_w = 90 000 $g\cdot mol^{-1}$) (2): ◊, 313 K; □, 333 K; △, 353 K.

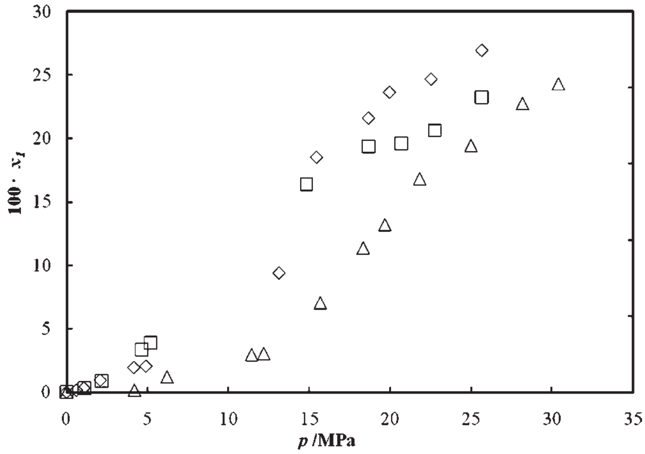

Figure 3. Solubility of CO_2 (1) in sodium CMC (M_w = 250 000 $g\cdot mol^{-1}$) (2): ◊, 313 K; □, 333 K; △, 353 K.

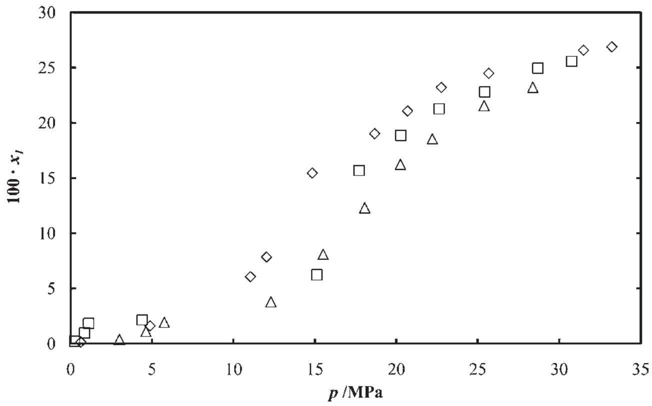

Figure 4. Solubility of CO_2 (1) in sodium CMC (M_w = 700 000 $g\cdot mol^{-1}$) (2): ◊, 313 K; □, 333 K; △, 353 K.

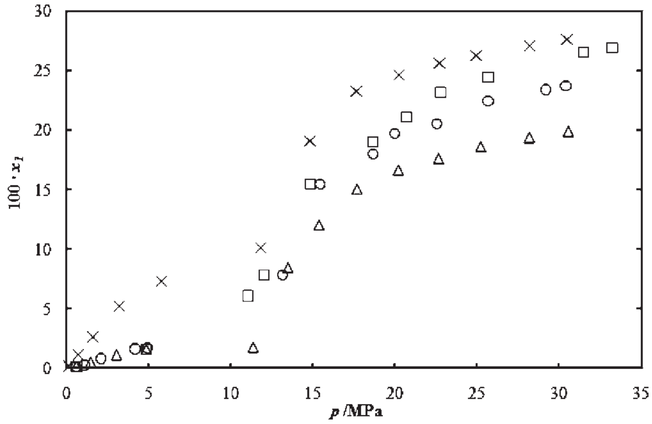

Figure 5. Solubility of CO_2 (1) in different cellulose derivatives (2) at 313 K: ×, MC (M_w = 40 000 $g\cdot mol^{-1}$); △, CMC (M_w = 90 000 $g\cdot mol^{-1}$); ○, CMC (M_w = 250 000 $g\cdot mol^{-1}$); □, CMC (M_w = 700 000 $g\cdot mol^{-1}$).

■ RESULTS AND DISCUSSION

Solubility of CO_2 in MC and CMC. The solubility data of CO_2 in the studied cellulose derivatives are presented in Figures 1 to 4 (mole fraction). The solubility isotherms for MC are presented in Figure 1. The solubility of CO_2 in MC increases with increasing pressure and decreasing temperature. This phenomenon is generally observed during measurements concerning the absorption of CO_2 in polymers. It can be explained by the plasticization effect of CO_2 and by the effect of pressure and temperature on gas density.[14]

Figure 2 shows the solubility of CO_2 in CMC (M_w = 90 000 $g\cdot mol^{-1}$). The solubility of CO_2 in CMC (M_w = 250 000 $g\cdot mol^{-1}$) and CMC (M_w = 700 000 $g\cdot mol^{-1}$) are presented in Figures 3 and 4. The maximum solubility of CO_2 in CMC (M_w = 250 000 $g\cdot mol^{-1}$) is 22.47 mol %, at 353 K and 30.38 MPa. Figure 4 shows that the maximum solubility of CO_2 in CMC (M_w = 700 000 $g\cdot mol^{-1}$) is 23.74 mol % at 30.76 MPa and 333 K. As mentioned previously, the solubility increases with pressure and decreases with temperature. The sorption isotherms in Figures 1 to 4 show that solubility increases fast at lower pressures, and it tends to reach a constant value at higher pressures. This may be due to the hydrostatic pressure and to a saturation of the substrate with gas.

Figure 5 shows a comparison between the solubility of CO_2 in the studied biopolymers at 313 K. It can be noticed that all CMC derivatives absorb less gas than MC. This is due to different molecular weights and side groups. A higher molecular weight and a larger size of the side groups, as is the case of CMCs, may cause steric hindrance which accounts for a smaller free volume available to gas molecules and thus a smaller solubility of CO_2.

The different solubility of CO_2 in CMC of different molecular weight may be explained by the structure of the polymers. As indicated by the producer, CMC (M_w = 90 000 $g\cdot mol^{-1}$) has a smaller degree of substitution than CMC (M_w = 250 000 $g\cdot mol^{-1}$) and CMC (M_w = 700 000 $g\cdot mol^{-1}$). Therefore, there is a smaller number of carboxyl groups present in CMC (M_w = 90 000 $g\cdot mol^{-1}$) than in the other two CMCs. Carboxyl groups are responsible for the polymer's affinity for CO_2 due to Lewis acid–base interactions with gas molecules, as previously demonstrated by other groups.[24–26] As a conclusion, CMC (M_w = 250 000 $g\cdot mol^{-1}$) and CMC (M_w = 700 000 $g\cdot mol^{-1}$) show a higher affinity for CO_2, which would explain the higher values of solubility recorder for these polymers in comparison to CMC (M_w = 90 000 $g\cdot mol^{-1}$).

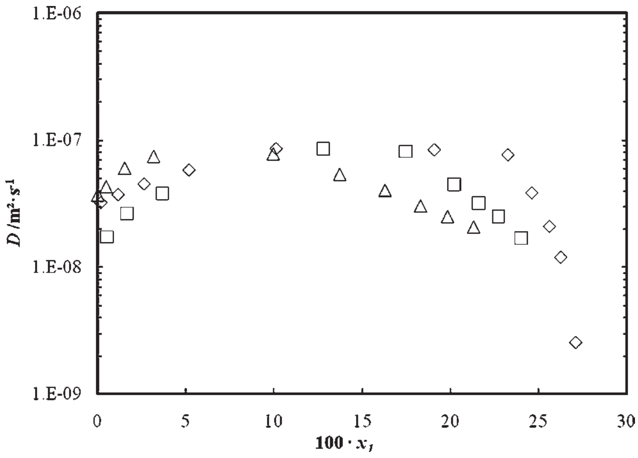

Figure 6. Diffusion coefficients for the system CO_2 (1)/MC (2): ◇, 313 K; □, 333 K; △, 353 K.

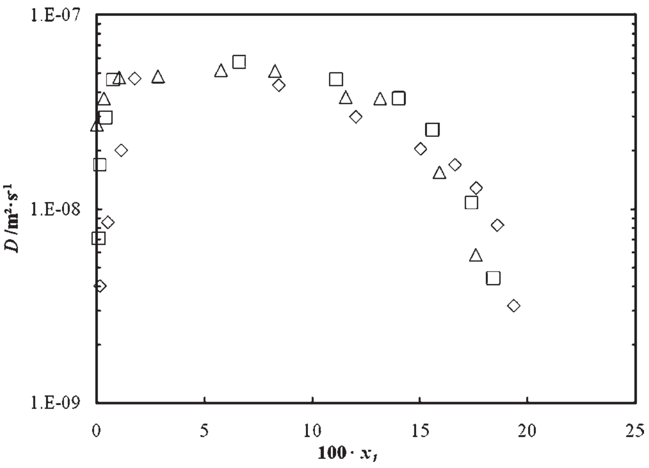

Figure 7. Diffusion coefficients for the system CO_2 (1)/sodium CMC ($M_w = 90\,000\ \mathrm{g \cdot mol^{-1}}$) (2): ◇, 313 K; □, 333 K; △, 353 K.

Similar results were observed when comparing the CO_2 solubility in the studied cellulose derivatives at (333 and 353) K.

Diffusion Coefficients. For the design of processes involving polymer−gas systems, it is necessary to know the mechanism of diffusion and how the rate of diffusion is affected by variables such as temperature or gas concentration.[18,19]

The diffusion coefficients of the system CO_2/polysaccharide derivative were measured at three different temperatures, (313, 333, and 353) K, for a pressure range from (0.5 to 30) MPa. The volume variation was measured during absorption measurements, and the values were used to account for the buoyancy effect on the sample. The maximum volume variation for MC, CMC ($M_w = 250\,000\ \mathrm{g \cdot mol^{-1}}$), and CMC ($M_w = 700\,000\ \mathrm{g \cdot mol^{-1}}$) was approximately 25 %, while CMC ($M_w = 90\,000\ \mathrm{g \cdot mol^{-1}}$) exhibited a much lower swelling (a maximum of 10 %). An explanation to this phenomenon may be correlated to the effect of the polymer structure on CO_2 solubility. The diffusion coefficients as a function of the CO_2 solubility are presented in Figures 6 to 9 for the different studied systems.

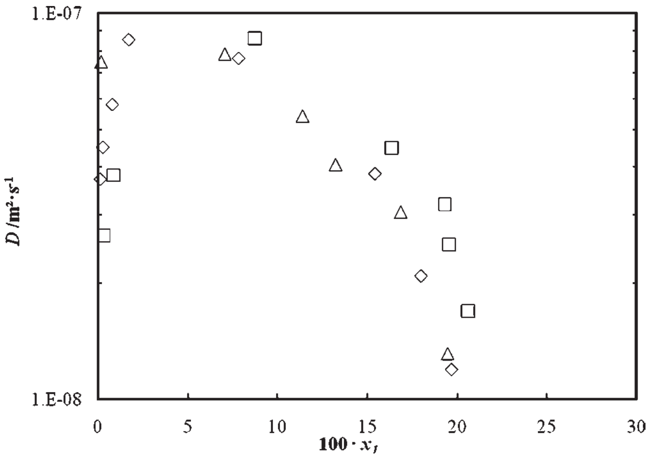

Figure 8. Diffusion coefficients for the system CO_2 (1)/sodium CMC ($M_w = 250\,000\ \mathrm{g \cdot mol^{-1}}$) (2): ◇, 313 K; □, 333 K; △, 353 K.

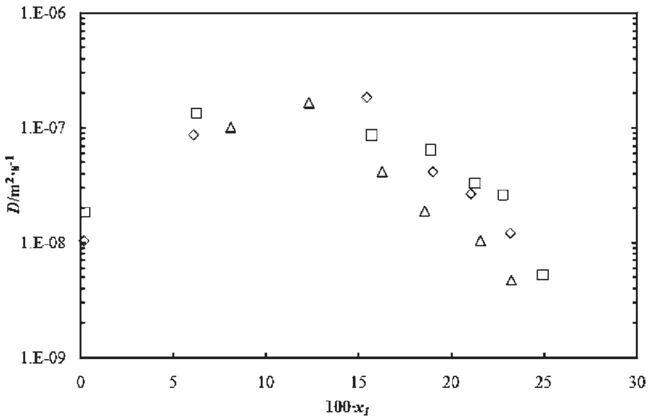

Figure 9. Diffusion coefficients for the system CO_2 (1)/sodium CMC ($M_w = 700\,000\ \mathrm{g \cdot mol^{-1}}$) (2): ◇, 313 K; □, 333 K; △, 353 K.

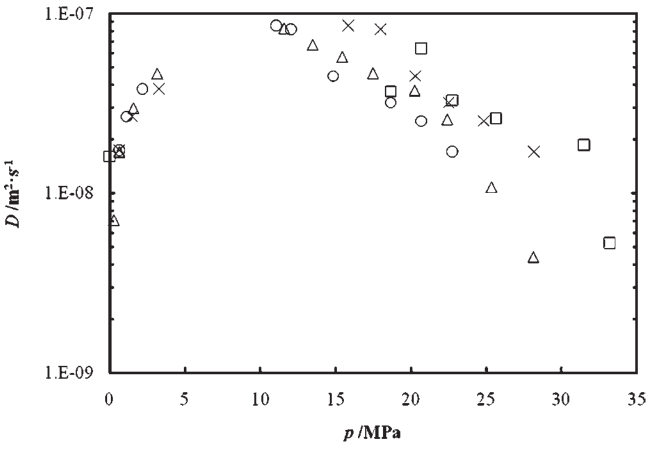

Figure 10. Diffusivity of CO_2 (1) in different cellulose derivatives (2) at 333 K: ×, MC; △, CMC ($M_w = 90\,000\ \mathrm{g \cdot mol^{-1}}$); ○, CMC ($M_w = 250\,000\ \mathrm{g \cdot mol^{-1}}$); □, CMC ($M_w = 700\,000\ \mathrm{g \cdot mol^{-1}}$).

At lower pressure (from 0.1 MPa to approximately 15 MPa), the diffusion coefficients increase with increasing pressure for all studied systems (Figures 6 to 9), and afterward they stay constant over a small range, (15 to 16) MPa; finally they decrease with a further increase in the pressure. The rate of diffusion depends on the number and size distribution of existing holes and the ease of hole formation which are influenced by chain mobility.[17] For small gas concentrations, equivalent to low pressures, chain mobility is high due to the plasticizing effect of CO_2. At higher concentrations however chain mobility decreases; therefore, diffusivity decreases. The hydrostatic pressure may play a role in this decreased diffusivity through reducing the available free volume in the system.[13,17]

The effect of polymer structure on diffusivity can be observed in Figure 10. As expected, a higher diffusivity was obtained for the CO_2/MC system, due to a smaller size of the side groups compared to CMC, which provide a less hindered path for gas diffusion. In the case of CO_2/CMC a higher molecular weight suggests a more packed configuration of the macromolecules, which accounts for the smaller values of the diffusion coefficient.

The high values obtained in this study for the solubility and diffusivity of CO_2 in cellulose derivatives suggest that supercritical fluids represent a viable "green" alternative to the traditional methods of processing biopolymers. The data presented above represent an insight in the phenomena that may occur during $SCCO_2$ processing technologies of polysaccharides, with potential applications in a large number of fields and industries.

CONCLUSIONS

This study presents the experimental results for the solubility and diffusivity of CO_2 in cellulose derivatives: MC and sodium CMC of different molecular weights, M_w = (90 000, 250 000, and 700 000) $g \cdot mol^{-1}$. The measurements were performed with the help of a magnetic suspension balance for various temperatures, (313, 333, and 353) K, and pressures (up to 30 MPa). The results show a high solubility of CO_2 in all substrates (up to 36.11 mol %), the values being influenced by nature and size of the side groups. A larger side group accounts for the smaller solubility of gas in CMCs. The molecular weight and side groups of the polymeric chains also influence the diffusion coefficient, which is strongly concentration-dependent. These data may find applications in developing new, sustainable technologies of processing biopolymers.

ASSOCIATED CONTENT

Supporting Information. Experimental results of solubility data (Tables 1−8). This material is available free of charge via the Internet at http://pubs.acs.org.

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