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Phase Behavior Studies of 2-Hydroxyethyl Methacrylate and Methyl Methacrylate in High-Pressure Carbon Dioxide

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Herein, we report the cloud point measurements of the CO_2 + 2-hydroxyethyl methacrylate (HEMA) and CO_2 + methyl methacrylate (MMA) systems. Experimental data were obtained at (313.15, 323.15, and 338.15) K and pressures up to (10.5 and 21.1) MPa, respectively. The Soave−Redlich−Kwong equation of state with the Mathias−Klotz−Prausnitz mixing rule was used to model experimental results, and a good correlation was achieved. Both systems were shown to be temperature dependent, with a solubility decrease with increasing temperature. Comparing the two studied systems, it was possible to notice that CO_2 + HEMA experimental data were shifted to higher pressures than those observed for the CO_2 + MMA system. This behavior suggests that CO_2−HEMA interactions are weaker than those established between CO_2 and MMA.

Introduction

Over the last years, acrylated polymers have been widely used in biomedical devices, specially due to their high biocompatibility. They have found applications in diverse biomedical fields such as tissue engineering, ophthalmology, bone repair, and many others.[1−3]

Poly(methyl methacrylate) (PMMA) is nowadays one of the acrylates with more applications in the biomedical field mostly due to its inertness and mechanical properties,[3] and poly(hydroxyethyl methacrylate) (PHEMA) was the first hydrogel being developed for biomedical applications. It was used as a soft contact lens material due to its high water content at equilibrium, rubbery behavior, and good biocompatibility, resembling natural tissues more closely than other synthetic materials.[4]

Many conventional polymerizations involve excessive use of hazardous organic solvents. Due to environmental and human safety concerns, chemists and chemical engineers are currently seeking new and cleaner methods for polymer processing.[5] Supercritical fluids are considered an interesting alternative to most traditional solvents because of their physical and chemical properties. Supercritical carbon dioxide ($scCO_2$), in particular, possesses innumerous properties that made it emerge as the most extensively studied supercritical fluid for polymerization reactions.[6] It is inexpensive, has a low critical point, and is a gas under ambient conditions. Therefore, by simply reducing the pressure of the system, it is possible to easily separate the solvent from the polymer, leading to highly pure materials and avoiding the need of an energy-consuming step.[7−10]

An important condition for polymer synthesis in $scCO_2$ is the knowledge of the phase behavior[11] to optimize and decide the best operation conditions to perform the reaction.[12]

Lora and McHugh[13] have already reported the phase behavior study of the CO_2 + methyl methacrylate (MMA) system at (313.15, 353.15, and 378.65) K. To the best of our knowledge, the CO_2 + hydroxyethyl methacrylate (HEMA) system has never been studied before.

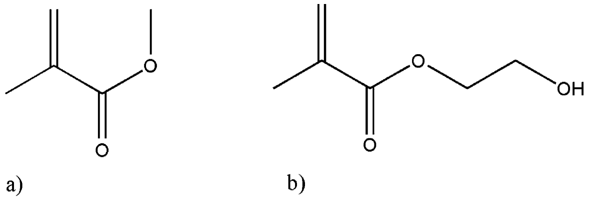

Figure 1. Chemical structure of the monomers: (a) MMA; (b) HEMA.

The focus of this work is to study the CO_2 + HEMA system phase envelope, to know and predict the thermodynamic behavior of mixtures involved in polymerization reactions. As one of the most usual polymerization temperatures is 338.15 K,[8] cloud points were measured for several mixtures of CO_2 + HEMA at (313.15, 323.15, and 338.15) K and pressures up to 21.1 MPa. To evaluate the accuracy of our experimental data, the CO_2 + MMA system was also studied. Our data were compared with the work from Lora and McHugh.[13]

Experimental Section

Materials. Methyl methacrylate (MMA, > 99 % purity, Sigma-Aldrich) and 2-hydroxyethyl methacrylate (HEMA, > 99 % purity, Sigma-Aldrich) were used as received. Their structures are shown in Figure 1. Carbon dioxide was obtained from Air Liquide with 99.998 % purity.

Apparatus and Procedure. The cloud point apparatus used in this work is similar to the one described in our earlier publications[14,15] and is schematically represented in Figure 2. The cloud point measurements were undertaken in a high-pressure variable volume steel cell with a front sapphire window and a bottom screw-tap connected to a Teflon piston that can be moved with water under pressure. Pressure was generated via a hand pump (High-Pressure Equipment Co., model 37-6-30) and monitored with a pressure transducer (Setra Systems Inc., model 204) with a precision of ± 0.0001 MPa. The high-pressure cell was immersed in a 40 L thermostated water bath and heated by means of a PID controller (Hart Scientific, model

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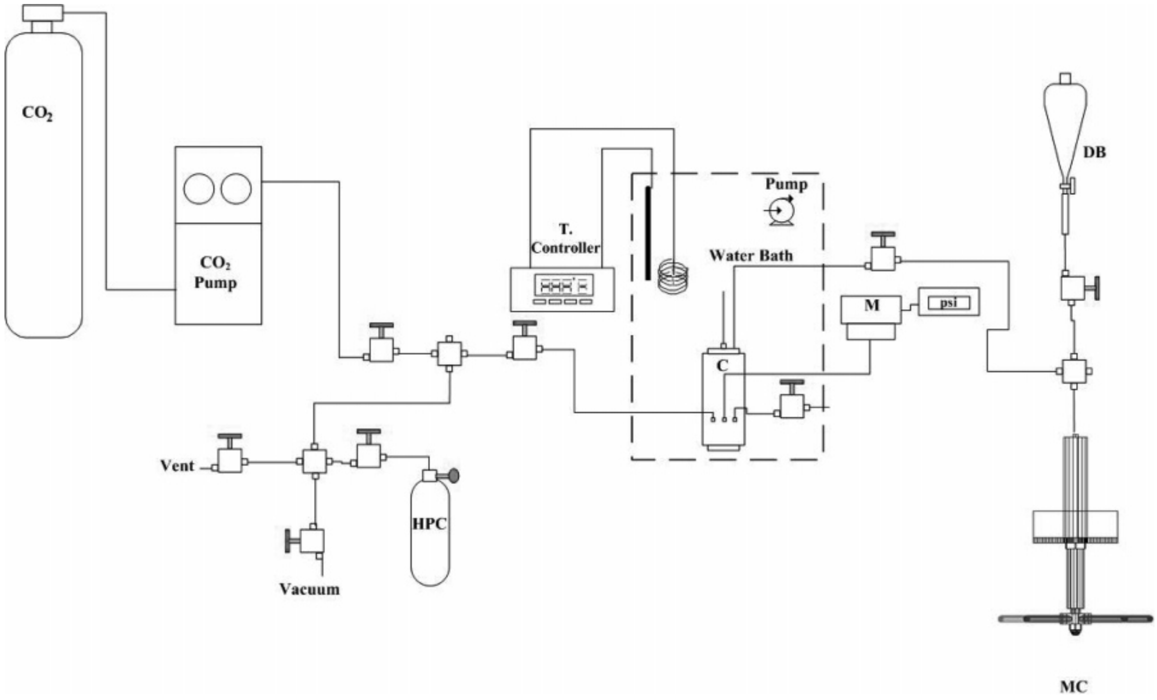

Figure 2. Cloud point measurements apparatus scheme. HPC, high-pressure cylinder; MC, manual controller; C, cell; M, manometer; DB, decantation blister.

Table 1. Experimental Data for the CO$_2$ + Methyl Methacrylate System

T/K	xCO$_2$	p/MPa	transition[a]
313.15	0.8173	6.38	BP
	0.8494	6.55	BP
	0.9103	7.22	BP
	0.9309	7.39	BP
	0.9567	7.78	BP
	0.9660	7.93	BP
	0.9738	7.95	BP
323.15	0.8173	7.46	BP
	0.8494	7.81	BP
	0.9103	8.50	BP
	0.9309	8.69	BP
	0.9567	9.05	BP
	0.9660	9.10	BP
	0.9738	9.12	CP
338.15	0.8173	8.97	BP
	0.8494	9.41	BP
	0.9103	10.34	BP
	0.9309	10.47	BP

[a] BP, bubble point; CP, critical point.

2000) that maintained the temperature within ± 0.01 K. The monomer was introduced into the cell to within ± 0.00001 g, which was then closed. Carbon dioxide was introduced into a cylinder, using a high-pressure compressor (NWA PM-101), which was then weighted in a balance (Precisa, 1212 M) to within ± 0.001 g. The weighted cylinder was connected to the system, and CO$_2$ was transferred to the cell. The system is then closed, and the CO$_2$ remaining in the lines was collected again inside the cylinder with the help of liquid nitrogen. The cylinder is weighted again, and the CO$_2$ composition is determined gravimetrically.

The pressure was increased with the hand pump, and the system was allowed to equilibrate for 15 min at the desired temperature to guarantee that a homogeneous phase was present. A good mixing was provided by means of a magnetic bar. The measurements were undertaken at constant temperature, and the pressure was slowly decreased until two phases were observed.

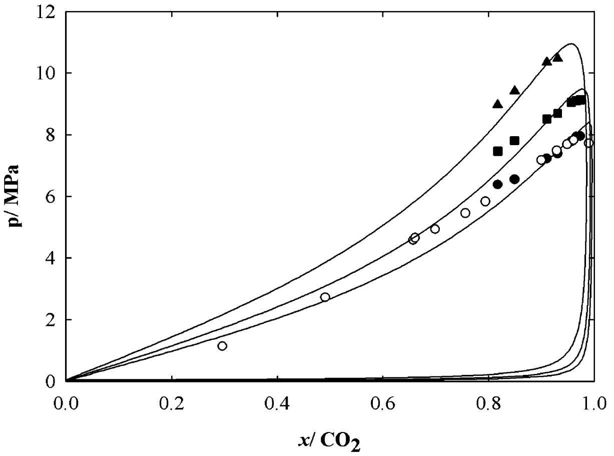

Figure 3. Comparison of experimental data (symbols) for the CO$_2$ + MMA system with calculated data (solid lines) obtained with the Soave–Redlich–Kwong equation of state with $k_{ij} = -0.055$, $\lambda_{ij} = 0.041$, and $l_{ij} = -0.0004$. This work: ●, 313.15 K; ■, 323.15 K; ▲, 338.15 K. Lora and McHugh data: ○, 313.15 K.[13]

The cloud point pressure recorded was the pressure at which the cell became completely cloudy (white opaque). Cloud points were measured and reproduced at least three times to within ± 0.03 MPa.

Results and Discussion

(*1*) *CO$_2$ + MMA System.* To further evaluate the feasibility of our method and the accuracy of the measurements, cloud point data of CO$_2$ + MMA were obtained and compared with Lora and McHugh[13] values. Pressure–composition isotherms were obtained at (313.15, 323.15, and 338.15) K over the pressure range of (6.38 to 10.47) MPa and are shown in Table 1 and Figure 3. Experimental data obtained in this study were modeled using the Soave–Redlich–Kwong (SRK) equation of state[16] (EOS) with the Mathias–Klotz–Prausnitz (MKP) mixing rule.[17,18] The Soave–Redlich–Kwong EOS was the first

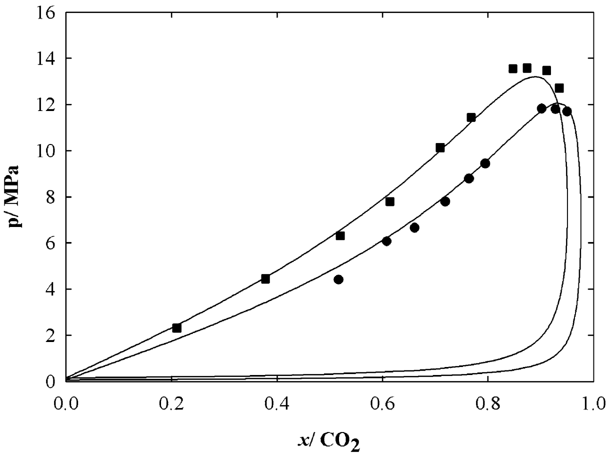

Figure 4. Calculation results (solid lines) for the CO_2 + MMA system using the Soave−Redlich−Kwong equation of state with $k_{ij} = -0.055$, $\lambda_{ij} = 0.041$, and $l_{ij} = -0.0004$ and comparison with values from the work of Lora and McHugh: ●, 353.15 K; ■, 378.65 K.[13]

Table 2. Critical Constants and Acentric Factor for CO_2,[20] Methyl Methacrylate (MMA),[21] and 2-Hydroxyethyl Methacrylate (HEMA)

component	T_c/K	p_c/MPa	ω
CO_2	304.15	7.38	0.225
MMA	563.95	3.68	0.317
HEMA	641.88[a]	3.67[a]	0.986[b]

[a] Estimated critical constants.[24] [b] Estimated acentric factor.[19]

Table 3. Experimental Data for the CO_2 + 2-Hydroxyethyl Methacrylate System

T/K	xCO2	p/MPa	transition[a]
313.15	0.4210	5.30	BP
	0.5338	6.80	BP
	0.6134	7.59	BP
	0.6772	8.48	BP
	0.7150	9.95	BP
	0.8196	11.29	BP
	0.8464	12.55	BP
	0.8778	13.87	BP
	0.9074	14.26	CP
	0.9450	14.00	DP
	0.9584	12.98	DP
	0.9650	12.09	DP
	0.9702	11.48	DP
	0.9745	10.99	DP
323.15	0.1491	2.88	BP
	0.4210	5.83	BP
	0.5338	7.45	BP
	0.6134	8.81	BP
	0.6772	10.61	BP
	0.7150	11.92	BP
	0.8196	13.64	BP
	0.8464	15.06	BP
	0.8778	16.30	BP
	0.9074	16.65	CP
	0.9450	16.32	DP
	0.9584	15.33	DP
	0.9650	14.63	DP
	0.9702	13.87	DP
	0.9745	13.43	DP
338.15	0.1491	2.75	BP
	0.4210	7.00	BP
	0.5338	8.89	BP
	0.6134	10.71	BP
	0.6772	14.12	BP
	0.7150	16.90	BP
	0.8196	17.25	BP
	0.8464	18.27	BP
	0.8778	19.42	BP
	0.9074	21.04	CP
	0.9450	19.39	DP
	0.9584	18.35	DP
	0.9650	17.76	DP
	0.9702	16.89	DP
	0.9745	16.41	DP

[a] BP, bubble point; CP, critical point; DP, dew point.

modification of the simple Redlich−Kwong EOS where the parameter a was made temperature dependent. This equation is given by

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \qquad (1)$$

$$a(T) = a(T_c)\alpha(T,\omega) \qquad (2)$$

$$a(T_c) = 0.42747 \cdot \frac{R^2 T_c^{\ 2}}{P_c} \qquad (3)$$

$$\alpha(T,\omega) = \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \qquad (4)$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \qquad (5)$$

$$b = 0.08664\,\frac{RT_c}{P_c} \qquad (6)$$

The Mathias−Klotz−Prausnitz (MKP) mixing rule includes three adjustable interaction parameters, k_{ij}, λ_{ij}, and l_{ij}

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}\,(1 - k_{ij}) + \sum_{i=1}^{N} x_i[\sum_{j=1}^{N} x_j\,(\sqrt{a_i a_j}\,\lambda_{ij})^{1/3}]^3 \qquad (7)$$

with $k_{ij} = k_{ji}$ and $\lambda_{ij} = -\lambda_{ji}$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \qquad (8)$$

with $l_{ij} = l_{ji}$.

The SRK equation of state requires three input parameters per pure compound: critical temperature (T_c), critical pressure (p_c), and acentric factor (ω).[19] Critical constants (T_c, p_c) of carbon dioxide and methyl methacrylate are known from experimental measurements[13,20,21] and are listed in Table 2 along with the acentric factors. The pressure−composition isotherm at 313.15 K was correlated using PE,[19] a noncommercial program for high-pressure phase equilibria calculations, and the SRK equation of state and MKP mixing rule. The best agreement between measured and calculated values was obtained with $k_{ij} = -0.055$, $\lambda_{ij} = 0.041$, and $l_{ij} = -0.0004$, and the fitting led to an average absolute relative deviation (AARD) of less than 5 %. Figure 3 represents a comparison of experimental data obtained in this work (dark symbols) with the data reported by Lora and McHugh (open symbols) and with calculated pressure−composition isotherms (solid line). The good agreement of our data with the literature at 313.15 K validates the accuracy of the experimental data obtained in this work.

To check the applicability of the correlation model to other temperatures, pressure−composition isotherms were calculated at (353.15 and 378.65) K. The predicted results compared well with the Lora and McHugh experimental data for the CO_2 + MMA system with an AARD less than 6 %, as can be confirmed in Figure 4.

(2) CO_2 + HEMA System. Experimental data for the CO_2 + HEMA system at (313.15, 323.15, and 338.15) K are shown in

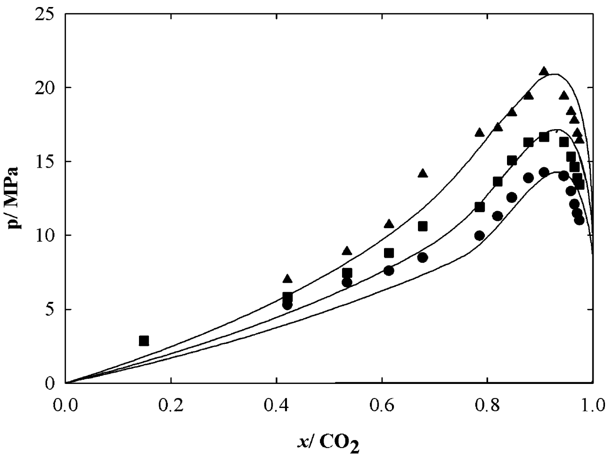

Figure 5. Comparison of experimental data (symbols) for the CO_2 + HEMA system with calculated data (solid lines) obtained with the Soave−Redlich−Kwong equation of state with $k_{ij} = -0.0085$, $\lambda_{ij} = 0.004$, and $l_{ij} = -0.003$: ●, 313.15 K; ■, 323.15 K; ▲, 338.15 K.

Table 3 and are graphically presented in Figure 5. As expected, cloud point dependence with temperature was similar to that observed for the CO_2 + MMA system. In fact, as the temperature increased, a higher pressure was needed to obtain a single-phase solution from a two-phase solution. This means that the solubility decreases with increasing temperature. In general, this solubility dependence with temperature is a well-known phenomenon for systems where a component is at supercritical conditions.[13,22] Bubble point portions of the $p-x$ isotherms for the CO_2 + HEMA system are convex toward lower pressures, as was observed for the CO_2 + MMA system, meaning that CO_2 is also highly soluble in the HEMA-rich liquid phase; however, comparing these two systems, it is possible to notice that CO_2 + HEMA $p-x$ isotherms are shifted to higher pressures than those observed for the CO_2 + MMA system. This behavior suggests that CO_2−HEMA interactions are weaker than those established between CO_2 and MMA, which results in smaller solubility of CO_2 in HEMA. An analogous difference was found between the CO_2 + MMA system and the CO_2 + butyl acrylate system.[13] The authors explained that the lower solubility of carbon dioxide in butyl acrylate, when compared with MMA, was likely due to the steric hindrance of the butyl chain that complicates the complex formation between CO_2 and the acrylate carbonyl oxygen. A recent work from Temtem et al.[23] showed that steric hindrances can have an important contribution to solubility due to different entropic variations between diverse CO_2−solute complexes.

Cloud point data of the CO_2 + HEMA system were also correlated using the Soave−Redlich−Kwong equation of state with the Mathias−Klotz−Prausnitz mixing rule. The input parameters, critical constants, and acentric factor for 2-hydroxyethyl methacrylate were estimated, as no available values were found in the literature. The critical constants were obtained using the ChemDraw Ultra 8.0 program,[24] and the acentric factor was calculated from PE.[19] The resulting parameters are listed in Table 2. The most optimal fit to $p-x$ isotherms of CO_2 + HEMA systems was obtained with $k_{ij} = -0.0085$, $\lambda_{ij} = 0.004$, and $l_{ij} = -0.003$. From Figure 5, it can be seen that SRK equation of state calculations predict lower pressures than those found experimentally for the portion of the bubble curve with $x_{CO_2} \leq 0.7$. The course of the bubble and dew point curves can be predicted satisfactorily with an AARD less than 9 %, and an inflection point seems to be present in the range $0.7 \leq x_{CO_2} \leq 0.8$ for the isotherm at lower temperature. In the region close to the critical point, the deviation in pressure is smaller.

Conclusions

Pressure−composition isotherms for CO_2 + MMA and CO_2 + HEMA systems at (313.15, 323.15, and 338.15) K were obtained for pressures up to (10.5 and 21.1) MPa, respectively. Equilibrium data were correlated using the Soave−Redlich−Kwong equation of state with the Mathias−Klotz−Prausnitz mixing rule. Good correlation results were obtained. Phase equilibria of the studied systems were shown to be temperature dependent. Solubility decreased with increasing temperature, and a higher pressure was needed to obtain a single homogeneous phase. By comparing $p-x$ isotherms for both systems, CO_2 + MMA and CO_2 + HEMA, it was possible to notice that CO_2 + HEMA cloud points are shifted to higher pressures than those observed for the CO_2 + MMA system, suggesting that CO_2−HEMA interactions are weaker than those established between CO_2 and MMA.

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