Solubility of Carbon Dioxide in Butyl Methacrylate at Temperatures of (323 and 333) K

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Experimental data on the solubility of carbon dioxide in butyl methacrylate are reported at temperatures of 323 and 333 K and pressures in the range of (2 to 10) MPa. Volumetric expansion data for the liquid phase are also reported over the same range of temperature and pressure. The solubility data are correlated with the Peng−Robinson equation of state using two interaction parameters.

Introduction

Supercritical carbon dioxide ($scCO_2$) has been widely investigated as a reaction solvent in chemical synthesis. Concern over the emission of volatile organic solvents has led to numerous applications in polymer synthesis and processing.[1,2] Despite the proven benefits of $scCO_2$ as a polymerization solvent, the need for elevated pressure continues to be a major disadvantage associated with its use. Homogeneous reaction conditions typically require operating pressures in the range of (10 to 40) MPa. This problem is compounded by the limited solubility of common polymers in $scCO_2$, as solubility is facilitated by an increase in pressure.

Recent investigations have shown that many of the advantages gained under supercritical conditions (one-phase system) can also be attained in a liquid medium expanded with dense CO_2 at greatly reduced operating pressures (two-phase system). CO_2-expanded liquids (CXLs) combine the tunability and transport properties of $scCO_2$ with the solvating power of organic solvents to generate a continuum of reaction media. CXLs offer much improved solubilities of polymers and homogeneous catalysts at significantly lower pressures due to the presence of the organic solvent in the liquid phase. Compared to neat organic solvents, CXLs also offer advantages such as increased solubilities of reactant gases and enhanced reaction rates and selectivities.[3−7]

Very few studies have been reported on the polymerization in CXLs. The polymerization of methyl methacrylate and styrene in a variety of CO_2-expanded solvents has been investigated.[8,9] These studies demonstrate that the properties of the polymers can be tuned by controlling the extent of volumetric expansion of the solvent. More recently, Kemmere et al.[10] have successfully carried out the ultrasound-induced radical polymerization of CO_2-expanded methyl methacrylate. This process eliminates the use of initiators and enhances the rate of polymerization via the reduced viscosity of the monomer. In these preceding examples, the advantages associated with CO_2-expanded liquids were realized at pressures well below 10 MPa.

Polymerization of CO_2-expanded monomers offers the additional benefit of eliminating organic solvents in the polymerization process. The solubility of CO_2 in the monomer and the associated volumetric expansion of the liquid phase are important parameters in such a process and provide a point of reference in the investigation of the phase behavior of the CO_2/monomer/polymer system. In kinetic studies, phase equilibria are also required in conjunction with kinetic measurements for the estimation of concentration terms that appear in reaction rate expressions.

Methacrylates are an important class of monomer that are widely used in the manufacture of plastic products. The solubility of CO_2 in methyl methacrylate has been examined extensively.[11−13] However, no experimental data on the solubility of CO_2 in butyl methacrylate have been reported in the literature. The polymerization of methacrylates is typically conducted at temperatures above 323 K. In this work, we present experimental data on the solubility of CO_2 in butyl methacrylate at temperatures of 323 and 333 K and pressures in the range of (2 to 10) MPa. Volumetric expansion data for the liquid phase are also reported over the same range of temperature and pressure. The solubility data are correlated with the Peng−Robinson equation of state (PREOS).

Experimental Section

Materials. Butyl methacrylate (99 %) was obtained from Sigma-Aldrich and used without further purification. The particular grade of butyl methacrylate used contains 10 ppm of 4-methoxyphenol to prevent polymerization of the monomer. Liquid carbon dioxide (99.5 %) was purchased from Linde Gas. 2-Propanol (99.5 %) was obtained from Ajax Finechem.

Apparatus and Procedure. The apparatus used for solubility and volumetric expansion measurements is similar to that reported in earlier studies.[12,14,15] A schematic diagram of the apparatus is shown in Figure 1. The equilibrium cell consisted of a high-pressure sight gauge immersed in a water bath (± 0.2 K). The system pressure was monitored with a pressure transducer with an uncertainty of ± 0.035 MPa. The liquid phase in the sight gauge was withdrawn from the bottom of the sight gauge and recirculated through the vapor phase with a metering pump. Samples of liquid phase were removed from the sight gauge via a 6-port switching valve, located at the outlet of the metering pump, and directed to a solvent trap containing 2-propanol. The outlet of the solvent trap was connected to an inverted buret, which was used to measure the volume of CO_2 released from a sample.

Volumetric expansion data were determined prior to the measurement of solubility data. The initial observation of the

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10.1021/je0504820 CCC: $33.50

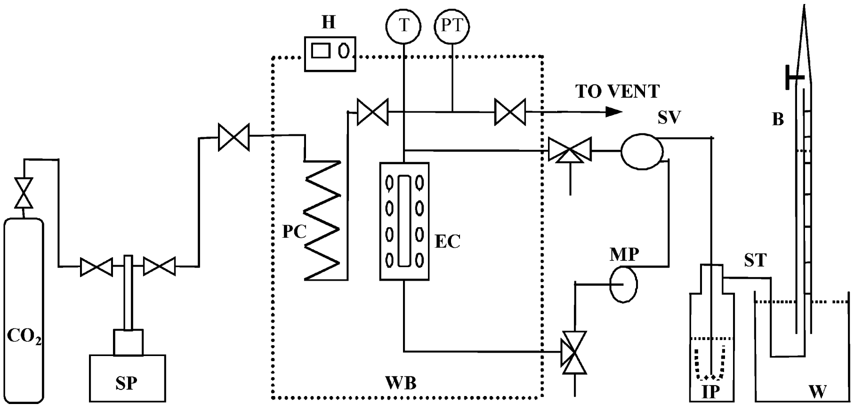

Figure 1. Schematic diagram of the experimental apparatus: B, buret; CO$_2$, carbon dioxide cylinder; EC, equilibrium cell; H, heater; IP, 2-propanol; MP, metering pump; PC, preheating coil; PT, pressure transducer; SP, syringe pump; ST, solvent trap; SV, switching valve; T, thermocouple; W, water; WB, water bath.

expansion of butyl methacrylate provided a means of determining the allowable range of pressure for which two phases (liquid and vapor) were always present at a given temperature. The glass face of the sight gauge was fitted with a ruler (1 mm graduations) to determine the level of the liquid phase. The volume of liquid corresponding to a given level was determined by calibration with ethanol at atmospheric pressure. The ruler was placed on that part of the gauge where the internal cross-sectional area is constant. A linear relationship was therefore observed between the volume of ethanol and the indicated level.

In the determination of the volumetric expansion of butyl methacrylate, around 20 mL of butyl methacrylate was initially loaded into the sight gauge such that the liquid level exceeded the zero mark on the ruler. The metering pump was primed, and the recirculation of the liquid phase was commenced. The sight gauge and the connecting lines were then thoroughly purged by pressurizing the vapor space with CO$_2$ at low pressure (~ 0.5 MPa) and releasing the pressure slowly while maintaining the recirculation of the liquid phase. The purging step was repeated several times. After the last depressurization, the recirculation of the liquid phase was continued until the liquid level stabilized. This last step was particularly important for ensuring that the recirculation line was free from any gas bubbles.

The equilibrium cell was then pressurized with CO$_2$ in several stages to obtain incremental amounts of expansion of the liquid phase, within the limits imposed by the ruler on the sight gauge. For each stage of addition of CO$_2$, the temperature, pressure, and liquid level were recorded at regular time intervals to verify that equilibrium conditions had been reached. Equilibrium was typically established within a period of 30 min with recirculation. The volumetric expansion of the liquid phase (E) at a given temperature (T) and pressure (P) was calculated according to the following equation:

$$E(T,P) = \frac{V_L(T,P) - V_L^*(T)}{V_L^*(T)} \times 100\ \% \qquad (1)$$

where V_L is the volume of the expanded liquid phase and V_L^* is the initial volume of the liquid-phase saturated with CO$_2$ at atmospheric pressure. The estimated uncertainty in the liquid volumes is ± 0.2 mL. The volumetric expansion of butyl methacrylate at a given temperature was repeated twice, and the deviations between runs were generally less than 5 %.

In the determination of solubility data, the procedure used for loading and purging the equilibrium cell was identical to that described above. The attainment of equilibrium was confirmed by monitoring the composition of the liquid phase over time. The time taken to obtain equilibrium was marginally longer than that required for the expansion measurements. Prior to the sampling of the liquid phase, the 2-propanol in the solvent trap was saturated with CO$_2$. The solution in the solvent trap was analyzed by gas chromatography to determine the total mass of butyl methacrylate in the sample.

The gas that evolved from the solvent trap was allowed to pass into the buret where the volume displacement of water was recorded. Since the solvent trap was operated at near atmospheric pressure, the amount of CO$_2$ collected was calculated using the ideal gas equation as follows:

$$n_c = \frac{P_f V_f - P_i V_i}{RT} \qquad (2)$$

where n_c is the number of moles of CO$_2$, P is the pressure, and V is the combined volume of gas in the solvent trap and buret. The subscripts i and f refer to the initial and final conditions in the solvent trap, respectively. The pressure in the solvent trap was deduced from the height of water in the buret. Each pressure term in eq 2 was corrected for the vapor pressure of 2-propanol. The composition of the liquid phase was calculated from the mean of at least three measurements, with a relative standard deviation (RSD) of less than 4 %. The RSD was calculated with respect to the molar ratio of butyl methacrylate to CO$_2$ in the sample.

Data Correlation

The two-parameter version of the PREOS was used in the correlation of the solubility data. The relevant equations for the standard model[16] are well-known and are not reproduced here. In the two-parameter model, the expressions for the attractive (a_{mix}) and repulsive (b_{mix}) terms of the fluid mixture are as follows:

$$a_{mix} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \qquad (3)$$

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \qquad (4)$$

$$b_{mix} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \qquad (5)$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2}(1 - l_{ij}) \qquad (6)$$

Table 1. Pure Component Critical Properties and Acentric Factors

component	T_c/K	P_c/MPa	ω
carbon dioxide[17]	304.12	7.374	0.225
butyl methacrylate[18]	616	2.63	0.4655

Table 2. Mole Fraction Solubility of CO_2 (x) in Butyl Methacrylate

P/MPa	x	E/%[a]
	T = 323.2 K	
1.99	0.2469	10.0
3.49	0.4109	21.1
6.00	0.6312	58.0
6.98	0.7237	88.7
7.98	0.8151	152
8.48	0.8604	219
	T = 333.2 K	
2.00	0.2201	8.1
3.50	0.3727	18.1
6.01	0.5749	45.2
7.99	0.7186	88.0
9.00	0.7975	136
9.49	0.8330	176
10.0	0.8726	250

[a] Values of the volumetric expansion obtained from interpolation of the experimental data shown in Figure 3.

where k_{ij} and l_{ij} are the binary interaction parameters, x represents either the vapor or liquid-phase composition, a_{ii} and b_{ii} are the pure-component attractive and repulsive terms, and N is the number of components in the system. The introduction of the second interaction parameter l_{ij} leads to a different expression for the fugacity coefficient of the fluid mixture. The reader is referred elsewhere for the relevant equations.[12] The critical properties and acentric factors used for calculating a_{ii} and b_{ii} are listed in Table 1.

Values of the binary interaction parameters were regressed from the solubility data using bubble-pressure calculations. The procedure involves the calculation of the vapor-phase composition and the system pressure from the liquid-phase composition and the system temperature. The binary interaction parameters were allowed to vary with temperature. At a given temperature, the optimum values of k_{ij} and l_{ij} were obtained by minimizing the sum of squared relative deviations (SSRD) with respect to pressure:

$$\mathrm{SSRD} = \sum_{i=1}^{M} \left(\frac{P_{\mathrm{calc}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}} \right)_i^2 \tag{7}$$

where M is the number of data points, and P_{calc} and P_{exp} are the calculated and experimental values of pressure, respectively.

Results and Discussion

Solubility Data. Experimental data for the solubility of CO_2 in butyl methacrylate are presented in Table 2. Some general features of the liquid-phase composition can be observed in Figure 2. Mole fractions of 0.2 to 0.9 CO_2 are attained in the range of pressure from (2 to 10) MPa. At constant pressure, the solubility of CO_2 increases with decreasing temperature in accordance with the increase in the density of pure CO_2. Data on the solubility of CO_2 in methyl methacrylate are also included in Figure 2. For monomers in the same homologous series, the solubility of CO_2 would be expected to decrease with an increase in the molecular weight of the monomer. This result is clearly evident in Figure 2.

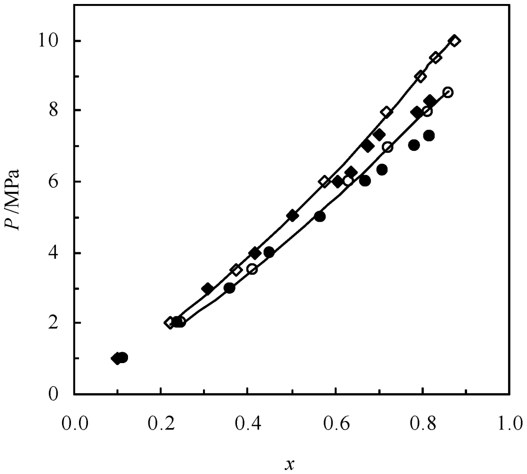

Figure 2. Comparison of $P-x$ data for the CO_2 + butyl methacrylate (BMA) and CO_2 + methyl methacrylate (MMA) systems: ○, BMA − 323 K; ◇, BMA − 333 K; ●, MMA − 323 K;[12] ◆, MMA − 333 K.[12] The solid lines represent the correlation of the butyl methacrylate data with the PREOS.

Table 3. Optimized Values of k_{ij} and l_{ij} from the PREOS

T/K	k_{ij}	l_{ij}	SSRD
323.2	0.0410	0.0029	0.0006
333.2	0.0356	−0.0003	0.0007

Optimized values of k_{ij} and l_{ij} from the correlation of the solubility data are shown in Table 3. It can be seen from Figure 2 that there is close agreement between the experimental data and the model. The average absolute relative deviations (AARDs) with respect to the calculated values of pressure are less than 1 % for the temperatures considered. The correlation of the data with the standard one-parameter model yields slightly less accurate results (AARDs < 2 %). The similarity of the correlation results for the two versions of the PREOS is attributed to the linearity of the $P-x$ data. The two-parameter model normally provides a significantly better fit for binary systems consisting of CO_2 and a polar solvent and for data obtained at pressures approaching the mixture critical point.[14,19]

The calculated composition of the vapor phase from the PREOS is generally greater than 99 mol % CO_2. The low concentration of butyl methacrylate in the vapor phase is highly desirable in the context of polymerization in CO_2-expanded monomers because it minimizes the loss of unreacted monomer from the liquid phase during the depressurization stage of the process.

Volumetric Expansion. Experimental data on the volumetric expansion of butyl methacrylate with CO_2 are shown in Figure 3. Each expansion isotherm represents the combination of two separate runs over the specified range of pressure. The values of E corresponding to the conditions used for measuring the solubility data are provided in Table 2. These values were obtained from interpolation of the experimental data shown in Figure 3. At constant pressure, E increases with decreasing temperature due to the increase in the solubility of CO_2 in the liquid phase. The data indicate that butyl methacrylate can be expanded with CO_2 to around three times its initial volume at pressures below 10 MPa. The solid curves in Figure 3 represent the volumetric expansions calculated with the PREOS and the optimized interaction parameters. In general, there is close agreement between the equation of state and the experimental data.

Kordikowski et al.[19] have investigated the relationship between volumetric expansion and the solubility of CO_2 in the liquid phase for several polar organic solvents. Their results suggest that the expansion isotherms for a given binary system coincide when plotted as a function of the solubility of CO_2.

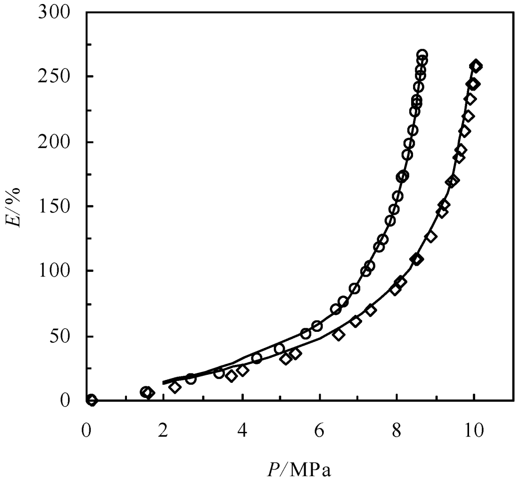

Figure 3. Volumetric expansion of butyl methacrylate with CO_2 as a function of temperature and pressure: ○, 323 K; ◇, 333 K. The solid lines represent the volumetric expansions calculated with the PREOS.

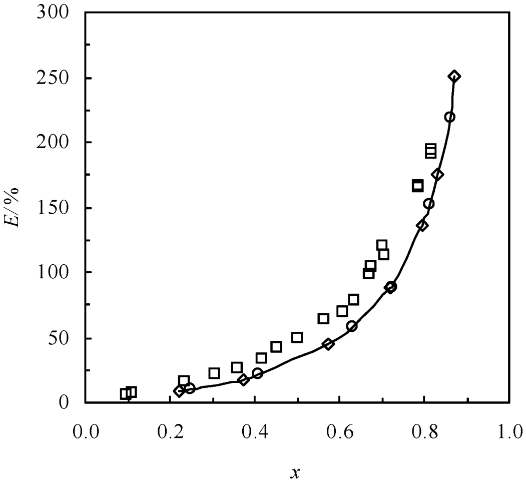

Figure 4. Relationship between volumetric expansion and liquid-phase composition: ○, BMA − 323 K; ◇, BMA − 333 K; □, MMA − (308 to 333) K.[12]

This feature is also evident in the data obtained for the CO_2− butyl methacrylate system, as shown in Figure 4. Some expansion data for methyl methacrylate with CO_2 are also presented in the figure. This set of data comprises measurements of the volumetric expansion at four different temperatures in the range of (308 to 333) K. The comparison between butyl methacrylate and methyl methacrylate suggests that the existence of a common expansion curve for methacrylates is unlikely.

Some further significance can be attached to the results in Figure 4. First, the construction of such a plot from experimental data at two different temperatures provides a means of estimating the liquid-phase composition at intermediate temperatures, simply from a knowledge of the volumetric expansion. Second, the amount of scatter in the plot provides an indication of the consistency of the experimental data. In the case of butyl methacrylate, the deviations for the liquid-phase composition are within the limits of experimental uncertainty and reinforce the consistency of the experimental data.

Conclusions

Solubilities of CO_2 in excess of 80 mol % can be attained in butyl methacrylate at pressures below 10 MPa and in the range of temperature used to polymerize the monomer. The corresponding measurements of the volumetric expansion indicate that the liquid phase is expanded by up to a factor of around 3. These characteristics indicate that butyl methacrylate is an appropriate choice for investigating the concept of polymerization in CO_2-expanded monomers.

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Received for review November 16, 2005. Accepted January 9, 2006. Financial support from the Australian Research Council is gratefully acknowledged.

JE0504820