

# Effect of High Pressure Carbon Dioxide on the Solubility and Diffusivity of Dichloromethane in Polyetherimide

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**ABSTRACT:** The high pressure inverse gas chromatography technique was used to study the effect of carbon dioxide on the solubility and diffusivity of dichloromethane in polyetherimide. CO<sub>2</sub> was used as the carrier gas with pressures from 0.7 to 3.5 MPa and temperatures between 100 and 175°C. Similar data were obtained for the dichloromethane-polyetherimide system using helium as the inert carrier gas. As a result of less favorable thermodynamic interactions between the polymer and solvent, the solubility of the dichloromethane was found to be decreased appreci-

ably in the presence of CO<sub>2</sub>. The increased free volume in the polymer provided by the dissolved CO<sub>2</sub> significantly increased the diffusion coefficient. When the temperature was increased the solubility was decreased while the diffusivity was increased. These behaviors have the potential to considerably improve devolatilization processes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2497–2501, 2009

**Key words:** chromatography; diffusion; phase separation; polyimides

## INTRODUCTION

The diffusion coefficient of polymer-solvent systems can be decreased several orders of magnitude as the solvent concentration approaches infinite dilution in the polymer. This solvent dilution effect can limit the mass transfer in polymer unit operations and, thus, result in longer processing times. To counteract this effect the polymer can be swelled or plasticized by using a high pressure cosolvent gas. In addition to the enhanced diffusivity, the cosolvent gas can alter the thermodynamic interactions between the polymer and solvent. These effects have the potential of enhancing devolatilization processes and allowing higher throughputs in the manufacture of films, insulating foams, bulk plastics, etc.

The phase equilibrium of many polymeric systems cannot be measured directly due to the complexities and physical state of the inherently immiscible systems and high viscosities. This is particularly difficult at high pressure. The high pressure inverse gas chromatography (HPIGC) technique can provide the needed data with relative ease.

Inverse gas chromatography (IGC) has been used to measure partition and diffusion coefficients in binary polymer-infinitely dilute solvent systems, and

to measure solubility and diffusion coefficients at finite concentrations of solvent in the polymer.<sup>1</sup> This technique has also been applied to measure diffusion and partition coefficients in ternary polymer-solvent-solvent systems<sup>2</sup> and in ternary polymer-solvent-high pressure, cosolvent gas systems.<sup>3–4</sup> A recent review by Voelkel et al.<sup>5</sup> discusses the use of IGC to determine physicochemical data.

In this work, HPIGC was used to study the influence of CO<sub>2</sub> on polymer-solvent mass transport and thermodynamic behavior in polyetherimide systems. The objective was to determine the effect of high pressure CO<sub>2</sub> on the solubility and diffusivity of dichloromethane in polyetherimide at different pressures and temperatures.

Polyetherimide (PEI) has the commercial name Ultem<sup>®</sup>, which is a registered trademark of Saudi Basic Industries Corporation. PEI is an amorphous thermoplastic polymer, which contains flexible ether linkages for good melt flow characteristics, and aromatic imide units for high heat resistance and mechanical properties. The high proportion of aromatic rings gives this polymer excellent thermal stability. Its glass transition temperature is 225°C. Moreover, the bisphenol group is symmetric, whereas the imide groups are asymmetric compared with the central group, which can give a specific dipole moment. The structure of PEI is shown in Figure 1. It is stable to acids, weak bases, and hot water hydrolysis; is flame retardant; withstands energetic radiation; is transparent to microwaves; and usable for food contact.<sup>6</sup>

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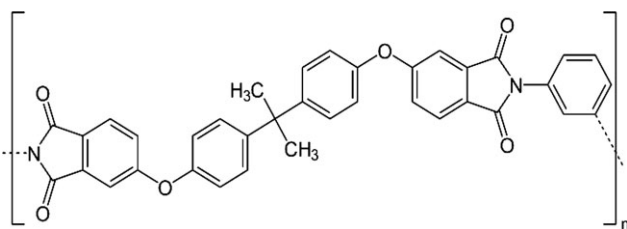


Figure 1 Structure of polyetherimide (PEI).

The study of dichloromethane (DCM) and PEI is of importance because while there is significant industrial interest, especially for devolatilization processes, there are essentially no published data.

### EXPERIMENTAL METHOD

The experimental equipment used in this study is detailed in the publication of Jones et al.<sup>3</sup> The main component of the HPIGC system was an HP 5890 gas chromatograph, equipped with a thermal conductivity detector. For either carrier gas, helium or CO<sub>2</sub>, the gas flowed through both the sample and reference sides of the TCD. The thermal conductivity of the dichloromethane was sufficiently different to obtain excellent peaks in all cases. A Tescom regulator with a maximum operating pressure of 27.6 MPa was used to control the pressure inside the column. The temperature controlled oven had a maximum operating temperature of 300°C. The pressure was monitored using a Heise pressure transducer rated up to 20.7 MPa. A standard Windows-based personal computer with Hewlett-Packard ChemStation was used for control of the TCD and GC temperature zones, as well for collection of the data. A Tylan model FC-260 mass flow controller along with a Tylan RO-28 controller module was used for delivery of gas to the reference line. Prior to carrying out an injection, the system was allowed to equilibrate for 30 min after any change in pressure or temperature so that equilibrium was reached between the carrier gas and polymer.

The PEI-coated column was made using the static coating technique as described by Grob.<sup>7</sup> The polymer is dissolved in a solvent and the capillary column is filled with a solution of the concentration needed to obtain the desired final film thickness in the capillary. One end of the column is sealed and the solvent is slowly evaporated by pulling a vacuum on the other end. The resulting 0.053 cm inner diameter column had a 1.0 μm-thick coating and a length of 30.5 m.

The DCM solvent was obtained from EMD Chemical (Gibbstown, NJ) and used without further purification. Helium and CO<sub>2</sub> gases were ultra high purity and bone dry, respectively.

### ANALYSIS OF DATA

The HPIGC technique depends upon a detailed analysis of the elution profile. The observed retention time on the chromatograph is related to the solubility (partition coefficient), and the spread of the peak is related to the diffusion coefficient. Therefore, different cosolvent gases can be applied to the polymer-solvent systems, and the diffusion and partition coefficients can be measured and compared with HPIGC.

The data analysis technique was based on the models developed by Macris<sup>8</sup> and Pawlisch et al.<sup>9-10</sup> Macris modeled the capillary column as a straight cylindrical tube with an annular film of polymer deposited on the inner wall. One of the assumptions was that a uniform coating existed. Pawlisch et al. modified the model developed by Macris for the elution profile in capillary columns. They developed the following expression for the concentration profile at the exit of the column in the Laplace domain.

$$\frac{\bar{C}L}{C_0v} = \exp\left[\frac{1}{2\gamma}\right] \exp\left[-\left(\frac{1}{4\gamma^2} + \frac{s}{\gamma} + \frac{2\sqrt{s}}{\alpha\beta\gamma} \tanh(\beta\sqrt{s})\right)^{1/2}\right] \quad (1)$$

$$\alpha = \frac{R}{K(1-y_1)\tau} \quad (2)$$

$$\beta^2 = \frac{\tau^2 v}{D_p L} \quad (3)$$

$$\gamma = \frac{D_g}{vL} \quad (4)$$

$\bar{C}$  is the eluent concentration,  $C_0$  is the initial concentration,  $L$  is the length of the capillary column,  $\tau$  is the thickness of polymer coating,  $R$  is the void radius of the capillary (radius of capillary column minus thickness of polymer coating),  $v$  is the velocity of the carrier gas,  $D_p$  is the mutual diffusion coefficient,  $K$  is the partition coefficient (concentration in the polymer divided by concentration in the vapor), and  $y_1$  is the concentration of solvent in the carrier gas.  $D_g$  is the diffusion coefficient of solvent in the carrier gas and was estimated using the method of Fuller et al.<sup>11</sup>

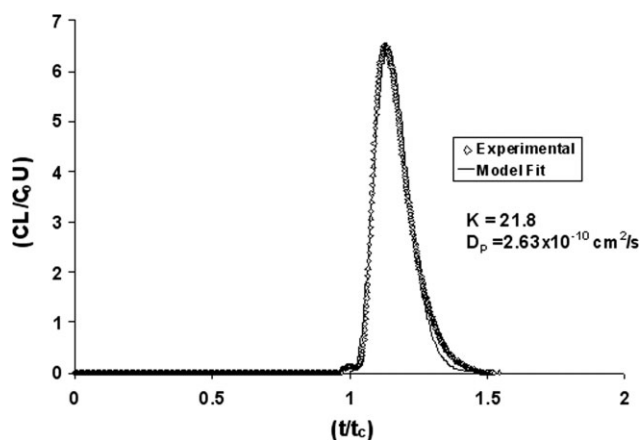
To obtain the model parameters the predicted elution profile was fit to the experimental data by minimizing the deviations in the time domain.<sup>12</sup> A fast Fourier inverse transform was used to invert the solution at the column exit from the Laplace domain to the time domain. A nonlinear regression routine was used with the input data to obtain  $\alpha$  and  $\beta$ . The partition and diffusion coefficients of the polymer-solvent system could then be determined.

**TABLE I**  
Summary of Partition and Diffusion Coefficients for DCM in PEI with Helium or CO<sub>2</sub> as the Carrier Gas

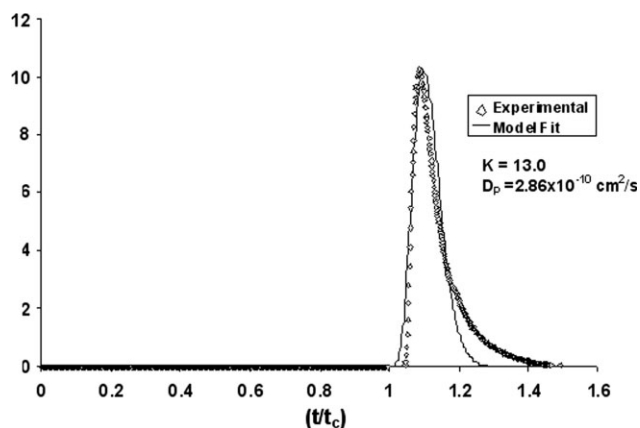
T (°C)	P (MPa)	Helium carrier		Carbon dioxide carrier	
		K	$D_p \times 10^{10}$ (cm <sup>2</sup> /s)	K	$D_p \times 10^{10}$ (cm <sup>2</sup> /s)
100	1.72	59.5	0.22	24.4	0.77
	3.45			15.0	1.75
125	0.72	39.3	1.01		
	1.72	48.1	0.83	13.0	2.86
150	3.45			9.70	7.00
	0.72	22.5	2.96		
175	1.72	21.8	2.63	8.80	6.57
	3.45				8.48
	0.72	10.7	7.87		
	1.72	10.2	7.84		

## RESULTS AND DISCUSSION

The solubility and diffusivity of DCM at infinite dilution on the PEI column were measured using helium or CO<sub>2</sub> as the carrier gas. A summary of the data that will be discussed is shown in Table I. As indicated only some temperature-pressure-carrier gas combinations were of interest or could be measured accurately. Results for an experimental elution profile and model fit observed for infinitely dilute DCM with inert helium as the carrier gas is shown in Figure 2. This essentially perfect fit was typical when helium was the carrier gas. When CO<sub>2</sub> was used as the carrier gas the model representation was not as good as when helium was used. The poorer fits are caused by significant asymmetry and tailing of the elution profile as shown in Figure 3. Figure 4 shows the case for a lower temperature where the solubility of the DCM is higher and thus the peak is spread over a much longer time and the mobile phase concentration is significantly reduced. In this



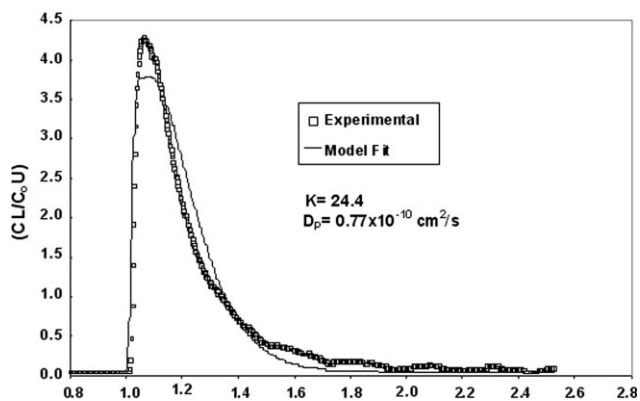
**Figure 2** Comparison between experimental and regressed elution profiles for DCM in PEI column at 1.72 MPa and 150°C with helium gas velocity of 2.87 cm/s.



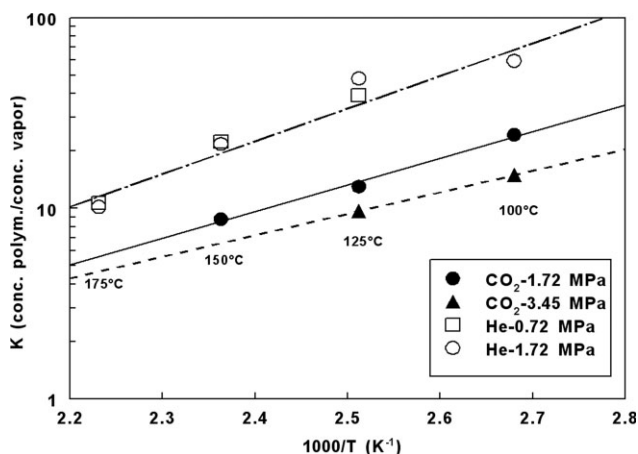
**Figure 3** Comparison between experimental and regressed elution profiles for DCM in PEI column at 1.72 MPa and 125°C with CO<sub>2</sub> gas velocity of 2.52 cm/s.

case a higher TCD sensitivity is needed and the noise in the output signal is more apparent.

Helium is not measurably soluble in the polymer and, thus, was not expected to have an influence on the partition coefficient of DCM in the polymer. The partition coefficient is defined as the DCM concentration in the polymer phase divided by the DCM concentration in the vapor phase. In the present experiments the measurements were in the infinitely dilute region of DCM. As shown in Figure 5 by the open symbols the solubility of the DCM decreased as the temperature increased but was not affected by the helium pressure. The solid symbols indicate the same decrease in solubility with increased temperature in the presence of CO<sub>2</sub>. As the CO<sub>2</sub> pressure increased at a set temperature more CO<sub>2</sub> was sorbed and the solubility of DCM was decreased. As with most polymer-solvent systems the log K increases linearly with reciprocal temperature. The K value for the DCM at 175°C with CO<sub>2</sub> as the carrier gas was too low to obtain reliable regressions of the elution



**Figure 4** Comparison between experimental and regressed elution profiles for DCM in PEI column at 1.72 MPa and 100°C with CO<sub>2</sub> gas velocity of 3.17 cm/s.



**Figure 5** Partition coefficients of DCM in PEI with either helium or CO<sub>2</sub> as the carrier gas.

profiles and, thus, no reliable  $K$  or  $D_p$  values could be obtained.

The diffusivity of DCM in PEI is shown in Figure 6. With both carrier gases the diffusivity increased with temperature. This is the expected response with the additional free volume provided by the thermal expansion. Increasing the pressure of the helium had no effect on the diffusivity. As all temperatures are considerably below the glass transition temperature of PEI (225°C), there are no basic structural changes in the PEI expected over the temperature range of the experiments.

The diffusivity increased as the CO<sub>2</sub> pressure increased from 1.72 to 3.45 MPa. This is the expected result since the additional CO<sub>2</sub> sorbed increases the free volume available to the DCM. Less expected was the lack of increase in the DCM diffusivity at 3.45 MPa. Jones et al.<sup>3</sup> and Zielinski et al.,<sup>4</sup> however, observed similar behavior for poly(vinyl acetate)-solvent systems at elevated helium carrier gas pressure. They suggested that the decreased diffusivity is due to the increased mass transfer resistance in the gas phase as more helium molecules are present to hinder the migration of the solvent molecules to the polymer at high pressure. There may also be some pressure effect due to the compression of the polymer. At the lower temperatures and pressures the log of  $D_p$  versus reciprocal temperature is linear as indicated by the lines in Figure 6. This is the behavior usually observed.

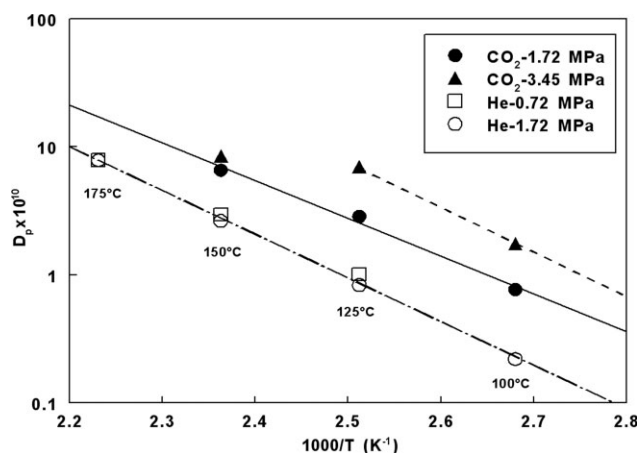
The more important observations are the effect of the CO<sub>2</sub> on the solubility and diffusivity of the DCM in the PEI compared to the results when helium was the carrier gas. The solubility was reduced in comparison to the helium carrier gas experiments (Fig. 5). When helium was the carrier gas there is essentially a binary system (DCM-PEI) in the polymer phase. When CO<sub>2</sub> was the carrier gas the polymer phase is a ternary system (DCM-PEI-CO<sub>2</sub>). The CO<sub>2</sub>

apparently has sufficient affinity for the polymer compared to the DCM that it displaces a portion of the DCM. As the pressure of the CO<sub>2</sub> was increased (and, thus, the concentration of CO<sub>2</sub> in the polymer) the amount of DCM displaced increased. This is, of course, a beneficial effect in terms of removing the solvent from the polymer.

The diffusivity is significantly higher in the ternary system than that in the binary system (Fig. 6). The mass transfer of the solvent molecules between the polymer and the gas phase was improved by the increased free volume provided by the CO<sub>2</sub> and the reduced thermodynamic affinity between the solvent molecules and the polymer. The degree of improvement decreased as one would expect as the temperature increased. This is because of the thermal expansion and free volume created by that mechanism. The point is reached where the additional free volume brought by the CO<sub>2</sub> becomes proportionally less as the thermal expansion increases.

It would be useful to have data for the solubility of CO<sub>2</sub> in the DCM. Unfortunately, the solubility cannot be measured with the present apparatus and no literature data could be found. Furthermore, no prediction methods were applicable because of a lack of one or more of the needed group contribution values.

The diffusivity of the DCM with CO<sub>2</sub> as the carrier gas at 3.45 MPa and 100°C ( $1.75 \times 10^{-10}$  cm<sup>2</sup>/s) is close to the value at 1.72 MPa and 125°C ( $2.86 \times 10^{-10}$  cm<sup>2</sup>/s). Zielinski et al.<sup>4</sup> observed similar results for vinyl acetate monomer and poly(vinyl acetate) system with high pressure CO<sub>2</sub> carrier gas. The temperature and pressure are two competing effects that influenced the total free volume within the system. The contribution of the CO<sub>2</sub> to the total free volume is reduced as the temperature decreases. The contribution of the CO<sub>2</sub>, however, to the total free volume increases as the pressure increases due



**Figure 6** Diffusion coefficients of DCM in PEI with either helium or CO<sub>2</sub> as the carrier gas.

to the increased sorption. Therefore, the plasticization effect of the increasing cosolvent gas can compensate for the temperature effect and lead to the observed result that the diffusion coefficient at a lower temperature was quite close to that at a higher temperature.

### CONCLUSION

The HPIGC study showed that the use of a high pressure cosolvent gas can affect the polymer-solvent devolatilization significantly. In this study, high pressure CO<sub>2</sub> was used as the cosolvent. Its effects on PEI-DCM system were studied, and it was found that the CO<sub>2</sub> cosolvent improves the polymer devolatilization in terms of both the mass transfer and thermodynamic aspects. This was confirmed by the measurements of the diffusion and partition coefficients.

The diffusion rate of the solvent in the polymer was increased as more CO<sub>2</sub> enters the polymer, i.e., at higher CO<sub>2</sub> pressures. Furthermore, the thermodynamic interactions between the polymer and solvent were less favorable in the presence of CO<sub>2</sub>, thus reducing the solubility of the solvent. The additional CO<sub>2</sub> in the polymer can be quickly removed by lowering the pressure: it has low solubility and a high diffusion coefficient.

Temperature also had significant effects on the solvent removal. The partition coefficient for the PEI-DCM system decreases as the temperature increases. At the same time the diffusion coefficient increases with the temperature. Both of these effects will enhance the devolatilization rate.

The limitations of the HPIGC measurement were the prominent effect of noise signals and asymmetric

elution profiles with high pressure carrier gas. The nature of the DCM becoming more like a non-solvent at higher temperatures was another limiting factor. This research work provides insights to the use of a high pressure gas to improve devolatilization applications. Further studies of the HPIGC method on other ternary systems with different solvents and cosolvent gases, such as chloroform and ethylene gas, would provide interesting and useful data.

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