

# Solubility of 4,4'-Methylene Diphenyl Diisocyanate in Supercritical Carbon Dioxide

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**Abstract** The solubility of 4,4'-methylene diphenyl diisocyanate (MDI) in supercritical carbon dioxide were tested at temperatures from 313 K to 353 K and pressures over the range of 9.6 MPa to 16.3 MPa. The density-based correlation models proposed by Bartle and Chrastil were used to correlate the solubility data. The correlation results showed good consistency between the experimental and calculated data, and values of the average absolute relative deviation (AARD) were between 4.56% and 10.68% for Bartle model, and 10.79% for Chrastil model, respectively. Finally, the partial molar volume  $\bar{V}_2$  of MDI were calculated in supercritical CO<sub>2</sub> according to the Kumar and Johnston theory.

**Keywords** 4,4'-methylene diphenyl diisocyanate; supercritical carbon dioxide; solubility; Bartle and Chrastil models; partial molar volume

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## 4,4'-二异氰酸酯二苯甲烷在超临界 CO<sub>2</sub> 中溶解行为研究

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**摘要** 测定了温度为 313~353 K、压力为 9.6~16.3 MPa 条件下 4,4'-二异氰酸酯二苯甲烷(MDI)在超临界 CO<sub>2</sub> 中的溶解度,运用 Bartle 和 Chrastil 半经验模型对溶解度数据进行了关联分析。结果表明:实验数据和理论数据吻合良好,平均值绝对相关偏差对 Bartle 模型在 4.56%~10.68%,Chrastil 模型为 10.79%。根据 Kumar 和 Johnston 的理论算得 MDI 在该条件下的超临界 CO<sub>2</sub> 中的偏摩尔体积  $\bar{V}_2$ 。

**关键词** 4,4'-二异氰酸酯二苯甲烷;超临界 CO<sub>2</sub>;溶解度;Bartle 和 Chrastil 模型;偏摩尔体积

In the past decades, supercritical carbon dioxide (SF-CO<sub>2</sub>) as a significant supercritical fluids (SCFs), has been arousing increasing interest for its versatile properties, such as nontoxicity, nonflammability, low cost and especially for its moderate critical values<sup>[1-2]</sup>. Besides, unlike traditional solvents, its properties such as density, dielectric constant, diffusion coefficient, and solubility parameter can be continuously tuned just by changing the pressure or temperature at the supercritical condition, especially in the near-critical region. Hence SF-CO<sub>2</sub> has the potentials to take the place of many traditional organic solvents for various industrial

applications<sup>[3-5]</sup>.

Nowadays 4,4'-methylene diphenyl diisocyanate (MDI), despite its toxicity<sup>[6]</sup>, has been the most important resource for the synthesis of polyurethane, which is mainly applied as an excellent industrial adhesive<sup>[7]</sup>. However, a typical polymerization procedure of MDI is conducted in a traditional solvent such as water or organic solvent, where high concentration of residual isocyanate can be detected after polymerization. Isocyanate is very hard to be separated from the traditional solvent and is considered very harmful to the environment regarding the toxicity of anion NCO<sup>-</sup>.

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Consequently, developing a polymerization process by using green solvent such as supercritical CO<sub>2</sub> is of great significance. Before developing a polymerization process the solubility data of MDI in supercritical CO<sub>2</sub> would be interesting and useful.

To the best of our knowledge, solubility data of MDI in SF-CO<sub>2</sub> have never been reported. Hence in our present work the solubility of MDI were studied at the temperature ranging from 313 to 353 K and pressure over the range of 9.6 to 16.3 MPa. The tested results were correlated by two density-based correlations (Bartle and Chrastil models). Finally the solubility data were utilized to calculate partial molar volumes of MDI at various temperatures in SF-CO<sub>2</sub> based on Kumar and Johnston theory.

## 1 Experimental

### 1.1 Chemicals and Apparatus

CO<sub>2</sub> was purchased from Wuhan Steel Co. (mass fraction purity of 99.99%), and 4,4'-methylene diphenyl diisocyanate (mass fraction purity of 99.5%) was supplied by Shanghai Darui Co. and directly used without further purification. The apparatuses of supercritical CO<sub>2</sub> were bought from JASCO Corporation (Hachioji Japan): PU-1580-CO<sub>2</sub> CO<sub>2</sub> Delivery Pump and BP-1580-81 Back Pressure Regulator.

### 1.2 Procedure for Solubility Test in Supercritical CO<sub>2</sub>

A certain amount of MDI were added into the cell (7.11 mL) with two sapphire windows, then the cell was sealed immediately after the replacement of air by CO<sub>2</sub>. The solute was stirred and the temperature was controlled by using a temperature controller jacket with a circulator. CO<sub>2</sub> was gradually compressed into the cell (0.2 mL · min<sup>-1</sup>) again by delivery pump after the system was heated to the set temperature<sup>[8]</sup>. When the compound disappeared and the system in the cell became transparent single phase, stirring was stopped and the state was kept for 5 h to fix the equilibria. The pressure was recorded and defined as dissolution pressure if the transparent single phase was still stable, and the experiment was repeated at least three times. The uncertainty of the dissolution pressure was ± 0.2

MPa and the uncertainty for the dissolution temperature was ± 0.1 °C<sup>[9]</sup>.

## 2 Results and Discussion

### 2.1 Solubility results

The solubilities of MDI in supercritical CO<sub>2</sub> were determined at 313 K, 323 K, 333 K, 343 K, 353 K and the pressure range of 9.6 to 16.3 MPa. The experimental results are shown in Fig. 1. The mole fraction of MDI in SF-CO<sub>2</sub> could reach as high as 3.61% at 11 MPa and 313 K, and all the mole fraction was reproducible within ± 2%. The solubilities of MDI increased with the increase of pressure at the same temperature, and the solubilities decreased with the increase of temperature at the same pressure.

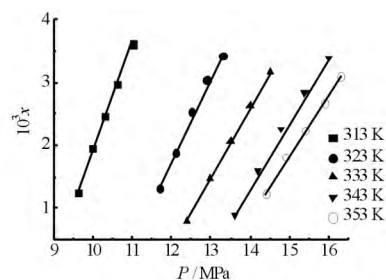


Fig. 1 Solubility of MDI in supercritical CO<sub>2</sub> at various temperatures

图1 不同温度下 MDI 在超临界 CO<sub>2</sub> 中的溶解度

### 2.2 Bartle model

The experimental solubility data of MDI were correlated according to the following equation<sup>[10]</sup>:

$$\ln(xP/P_{\text{ref}}) = A + C(\rho - \rho_{\text{ref}}) \quad (1)$$

$$A = a + b/T \quad (2)$$

where  $x$  is the mole fraction of MDI;  $P$  is the pressure;  $P_{\text{ref}}$  is 0.1 MPa;  $\rho$  is the density of pure CO<sub>2</sub> under experimental conditions;  $\rho_{\text{ref}}$  is 700 kg · m<sup>-3</sup>; and  $A$ ,  $C$ ,  $a$  and  $b$  are constants.

In order to predict the solubility of MDI, the values of  $a$ ,  $b$  and  $C$  are required to be calculated by using Eq. (1) and Eq. (2). Consequently, the first step was to obtain the values of  $C$  parameter at five temperatures (313 to 353 K), which could be achieved by plotting  $\ln(xP/P_{\text{ref}})$  against  $(\rho - \rho_{\text{ref}})$  (Fig. 2) and regarding the corresponding slopes as  $C$ . Then the five slopes were averaged to gain  $A$  parameters at different temperatures by using Eq. (1). Secondly, according to Eq. (2), we fitted the plots of  $A$  versus  $1/T$  into a

straight line to get the intercept  $a$  and slope  $b$  ( Fig. 3) , and the relevant values of  $a$  ,  $b$  and  $C$  were shown in Tab. 1. In Bartle model ,  $b$  depends on the enthalpy of sublimation of MDI  $\Delta_{\text{sub}}H$  , and their relationship can be expressed as  $\Delta_{\text{sub}}H = -Rb$  , where  $R$  is the gas constant.

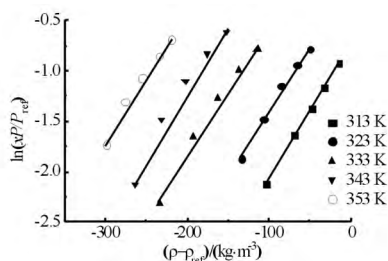


Fig.2 Plots of  $\ln(xP/P_{\text{ref}})$  vs  $(\rho - \rho_{\text{ref}})$  for MDI at various temperatures  
 图 2 MDI 在不同温度下关联的  $\ln(xP/P_{\text{ref}})$  对  $(\rho - \rho_{\text{ref}})$  拟合数据

$x$ : mole fraction of compound;  $P$ : CO<sub>2</sub> pressure;  $P_{\text{ref}}$ : 0.1MPa;  
 $\rho$ : density of pure CO<sub>2</sub>;  $\rho_{\text{ref}}$ : 700 kg · m<sup>-3</sup>

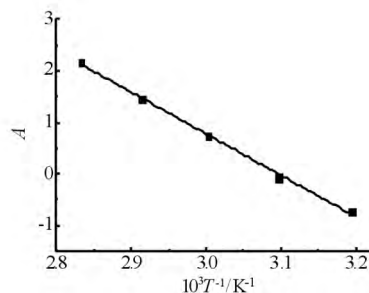


Fig. 3 Plots of  $A$  vs  $1/T$  for MDI at various temperatures by Bartle model

图 3 不同温度下关联的  $A$  对  $1/T$  Bartle 模型拟合数据

Finally ,the AARD from experimental data was used to test the correlation results and calculated with the following Eq. ( 3 ) :

$$\text{AARD} = 1/n \sum | (x_{i \text{ calc}} - x_{i \text{ expt}}) / x_{i \text{ expt}} | \times 100 \% , \quad (3)$$

where  $n$  is the number of experimental points and  $x_{i \text{ calc}}$  and  $x_{i \text{ expt}}$  are the calculated and experimental data ,respectively. The values of AARD were in the range of 4.56% to 10.68 % .

Tab. 1 Results of the solubility data correlation by Bartle and Chrastil model

表 1 由 Bartle 和 Chrastil 模型拟合溶解度数据结果

model	$n$	$a$	$k$	$b/K$	$\alpha/K$	$C/(m^3 \cdot kg^{-1})$	$\beta$	$\sigma^2$	$\Delta_{\text{sub}}H/(kJ \cdot mol^{-1})$	AARD/%
Bartle	25	24.95	-	-8054.6	-	0.01309	-	-	66.97	4.56 ~ 10.68
Chrastil	25	-	-6.71	-	-5710.3	-	-23.14	0.98	47.48	10.79

$n$ : number of data points used in the correlation;  $a$  ,  $b$  and  $C$ : parameters of Bartle model ;  $\Delta_{\text{sub}}H$ : the enthalpy of sublimation of the solid solute; - : undone data

### 2.3 Chrastil model

As one of the most frequently-used and traditional density-based models ,the Chrastil<sup>[11]</sup> model relates the solute solubility ( $S$  g · L<sup>-1</sup>) in SF-CO<sub>2</sub> ,the density of SF-CO<sub>2</sub> ( $\rho$  g · L<sup>-1</sup>) ,and temperature ( $T$  K) . Chrastil suggested a hypothesis that when solute A has just been completely dissolved in SF ,one of its molecule is attached with  $k$  molecules of solvent B and this causes a phase equilibrium between the resulting solvate-complex AB <sub>$k$</sub>  and the system<sup>[12-44]</sup> . Therefore ,the experimental solubility of the solute can be correlated by studying the relationship between the solubility of the solute and the density of the supercritical solvent ,and it can be specified as Eq. ( 4 ) :

$$\ln S = k \ln \rho + (\alpha / T) + \beta , \quad (4)$$

where  $\rho$  ( kg · m<sup>-3</sup>) is the density of pure CO<sub>2</sub>

obtained from NIST<sup>[18]</sup>;  $T$  is the experimental temperature;  $k$  is the association number of CO<sub>2</sub>;  $\alpha$  is a constant defined as  $-\Delta H/R$  ( where  $\Delta H$  is the sum of the enthalpies of vaporization and salvation of the solute and  $R$  is the gas constant) and  $\beta$  depends on the molecular weights of the solute and solvent.  $S$  is the solubility of the solute ( g · L<sup>-1</sup>) ,which could be calculated by Eq. ( 5 ) :

$$S = (\rho M_2 x) / [M_1 (1 - x) ] , \quad (5)$$

where  $x$  is the molar fraction of MDI;  $M_1$  and  $M_2$  are the molecular weights of CO<sub>2</sub> and MDI , respectively. The values of constants  $\alpha$  ,  $\beta$  and  $k$  are estimated via conducting a multiple linear regression on the experimental solubility data in Fig. 4.

Consequently ,parameters for the Chrastil equation were listed in Tab. 1. Evidently ,the AARD between experimental data and correlated results indicated that

good consistency between them was observed by using the Chrastil equation.

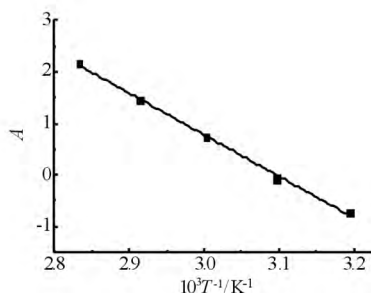


Fig. 4 Plots of  $\ln S$  vs  $\ln \rho_r$  for MDI at various temperatures

图4 MDI在不同温度下  $\ln S$  对  $\ln \rho_r$  曲线

## 2.4 Estimation of the partial molar volumes of the solutes

Normally at the given temperature and pressure, adding a certain amount of solute into a solvent would lead to a variety in the system's volume, which is called partial molar volume and considered very essential for the evaluation of the solute's solubility. Despite the fact that the values of MDI's partial molar volumes are not accessible from other works, it will still be referential for other future solubility researches. Thus, the partial molar volumes of MDI were estimated in accordance with Kumar and Johnston's theory<sup>[12-15]</sup>. To study this, the relationship between the solute's solubility and partial molar volume was investigated in the vicinity of the critical density of SF-CO<sub>2</sub>, and it can be shown as the Eq. (6):

$$\ln y = -C_1 + \ln\left(\frac{P_2^{VP}}{\rho_c RT}\right) + \left(\frac{PV_2^S}{RT}\right) + \left(\frac{\bar{V}_2}{RT\kappa_T}\right)_{\rho_r=1} \ln \rho_r, \quad (6)$$

where  $y$  represents the equilibrium mole fraction of the solute in the SF-CO<sub>2</sub>;  $V_2^S$  and  $V_2^S$  are the vapor pressure and molar volume of the solid solute, respectively;  $R$  is the gas constant;  $\bar{V}_2$  is the partial molar volume of the solute in the SCF phase;  $\kappa_T = [(1/\rho)(\partial\rho/\partial P)_{T,y}]$  and  $\rho_r = \rho/\rho_c$  are the isothermal compressibility and reduced density of the phase, respectively;  $T$  is the operating temperature.

The partial molar volumes of the solute in the SCFs phase ( $\bar{V}_2$ ) are much larger than the molar volume of the solute. The third term in Eq. (6) is considered to be constant in the region of interest. Eq. (6) may thus be simplified as:

$$\ln y = C_0 - \left(\frac{\bar{V}_2}{KT\kappa_T}\right)_{\rho_r=1} \ln \rho_r, \quad (7)$$

In order to estimate  $\bar{V}_2$  it is necessary to plot the log of  $y$  versus the log of  $\rho_r$  to obtain the slope, which is thought to be the ratio of the partial molar volume of the solute to the isothermal compressibility of the fluid phase. It can be also inferred from Eq. (7) that this ratio remains constant in the approximate density interval  $0.5 \leq \rho_r \leq 2.0$  and is irrelevant with  $\rho_r$ , which allows the estimation of  $\bar{V}_2$  with the value of  $\kappa_T$  under given  $P-T$  conditions. As demonstrated in Fig. 5, the investigated systems exhibited good linearity by plotting  $\ln y$  versus  $\ln \rho_r$ , which agreed well with previous Eq. (7). Then the slopes for five temperatures were calculated via a linear squares fit for the MDI + SF-CO<sub>2</sub> system, so the values of partial molar volumes, which were not experimentally available, were then worked out according to these five slopes and the values of  $\kappa_T$  under given  $P-T$  conditions.

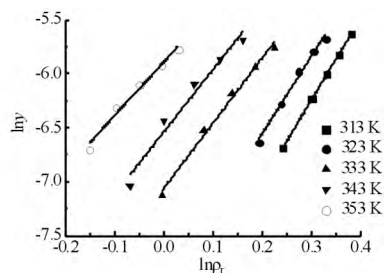


Fig. 5 Plots of  $\ln y$  vs  $\ln \rho_r$  for MDI at various temperatures

图5 MDI在不同温度下  $\ln y$  对  $\ln \rho_r$  曲线

Finally, the quality of the linear correlation is conveyed in the term of  $\sigma^2$  and all the results are summarized in Tab. 2. As shown in Tab. 2, the partial molar volume of MDI decrease when temperature goes up, which agree with Kumar and Johnston's theory.

Tab. 2 Slopes and partial molar volumes for MDP at different temperatures

表2 不同温度下的MDI的偏摩尔体积和相关参数

compound	$T/K$	slope at $\rho_r = 1$	$\sigma^2$	$\bar{V}_2$
MDI	313	2.776	0.9969	-4519.11
	323	2.542	0.9972	-1665.65
	333	2.668	0.9912	-1096.61
	343	2.513	0.9966	-748.98
	353	2.185	0.9930	-510.20

### 3 Conclusion

The solubilities of MDI were measured in supercritical CO<sub>2</sub> and high solubility was obtained at easily available temperatures and pressures. Good correlation consistency is obtained between the experimental and calculated data, and the AARD is in the range of 4.56% to 10.68% for Bartle model and 10.79% for Chrastil model. Solubility data are employed to calculate the partial molar volume  $\bar{V}_2$  of MDI in SF-CO<sub>2</sub> according to Kumar and Johnston theory.

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