JOURNAL OF CHEMICAL & ENGINEERING DATA

Solubilities of CO₂ in Poly(ethylene glycols) from (303.15 to 333.15) K

Jun Li, Yinmei Ye, Lifang Chen, and Zhiwen Qi*

State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

ABSTRACT: The solubilities of CO_2 in solvent poly-(ethylene glycols) (PEGs) with molecular weights of 150, 200, 300, and 400 were measured over the range of pressure from (100 to 1200) kPa and temperature from (303.15 to 333.15) K. Henry's constant was obtained by linear fitting of the experimental data, and thermodynamic properties of solutions were calculated from the correlation of Henry's constant. It indicates that the solubility of CO_2 increases with increasing molecular weights of PEGs. Henry's constant based on mole fraction and the molality of CO_2 in PEG400 vary from (4.78 to 7.09) MPa and (1.56 to 2.48) MPa·kg·mol⁻¹ from (303.15 to 333.15) K, respectively.

1. INTRODUCTION

The increasingly serious climate situation caused by greenhouse gases (GHGs) has raised public concern worldwide. CO₂ represents over 80 % of GHGs and is mainly produced by the combustion of fossil fuel.¹ To boost the CO₂ capture efficiency, three technological pathways to capture CO₂ by the coal-derived power generation have been developed: that is, postcombustion capture, precombustion capture, and oxycombustion.² Various technologies for these three pathways are under investigation, including absorption by solvents of amines^{3,4} and ionic liquids (ILs).^{5,6} However, it suffers from the drawbacks of high energy consumption and degradation of solvents when using amine-based solvents to capture CO₂ from flue gas.⁷ Unlike chemical absorption, physical solvents such as Rectisol and Selexol can be regenerated by pressure or temperature swings, leading to lower energy consumption. In practice, to prevent solvents from volatilizing and deteriorating, most of physical solvents are handled at low temperature as well as under high pressure and regenerated by the pressure swing process rather than the temperature swing process. The limited operation conditions inhibit the physical solvents applied to CO2 capture from flue gas under the conditions of high temperature and low pressure [(40 to 100) °C at ambient pressure].8 Hence, physical solvent operating at high temperatures without loss and degradation are desirable to absorb CO₂ from flue gas.⁹ ILs, the state of the art solvents developed for CO₂ capture from flue gas, show good solubility and high selectivity to CO₂. However, the high viscosity and price of ILs are the main barriers for large-scale industrial applications.¹⁰

Poly(ethylene glycol) (PEG) has the molecular structural formula of $H(OCH_2CH_2)_nOH$, where *n* is the number of ethylene oxide.¹¹ PEGs have similar excellent properties to ILs, such as negligible vapor pressure, chemical and thermal stability, and nontoxicity.¹² Moreover, PEGs are inexpensive and less viscous than ILs,¹³ which makes PEGs satisfy the



qualification of available physical solvents for gas separation processes even at high temperatures.¹⁴ In addition, due to the great choice of PEGs by varying the molecular weights, their properties may be tuned.¹⁵ Because of so many attractive advantages of PEGs, PEGs have been widely used in pharmaceutical, cosmetics, and food industries.^{16,17}

As polar solvents, PEGs also have high solubilities to CO_2 and good selectivities to mixtures of $(CO_2 + N_2)$ and $(CO_2 + H_2)$.^{18–20} Meanwhile, as cosolvents, PEGs have a good prospect to improve the CO_2 capture efficiency and reduce the regeneration energy consumption.^{12,21–23} However, in the open literature, the solubilities and thermodynamic properties of CO_2 in PEGs with low molecular weights are scarce. This contribution was aimed to determine the solubilities of CO_2 in PEGs with average molecular weights of 150, 200, 300, and 400 under the pressure of 1200 kPa and the temperature variations from (303.15 to 333.15) K in intervals of 10 K. Furthermore, the thermodynamic properties of CO_2 in PEGs were also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. Triethylene glycol (PEG150), poly(ethylene glycol) 200 (PEG200), and poly(ethylene glycol) 300 (PEG300) were obtained from Sinopharm Chemical Reagent Co., Ltd. in Shanghai. Poly(ethylene glycol) 400 (PEG400) was obtained from Aladdin Chemistry Co., Ltd. in Shanghai. Carbon dioxide (CO_2) with a mole fraction of 0.9999 was supplied by Shanghai Wetry Standard Reference Gas Co., Ltd. All substances were used as received. Some properties of these substances are listed in Table 1.

```
Received: November 9, 2011
Accepted: December 7, 2011
Published: December 29, 2011
```

Published: December 29, 2011

Table 1. Basic Physical Properties of PEGs (Data from Supplier)

component	PEG150	PEG200	PEG300	PEG400
MW	150.18	190-210	280-320	380-430
$M/g \cdot mo\Gamma^1$	150.18	200	300	400
$ \begin{array}{l} \beta/g \cdot cm^{-3} \\ (T = 293 \text{ K}) \end{array} $	1.123	1.127	1.127	1.1262 ^{<i>a</i>}
p/Pa	2005 ^b	9.9 ^c	1.5 ^c	
$\eta/\text{mPa·s}$ (T = 293 K)	47.80	63.96 ^d		115.95 ^d

^{*a*}Taken from ref 24. ^{*b*}Taken from supplier's data at 442 K. ^{*c*}Taken from ref 13 at 368 K. ^{*d*}Taken from ref 25.

2.2. Apparatus and Procedures. Figure 1 illustrates the schematic diagram of the apparatus in determining the



Figure 1. Schematic diagram of the apparatus. 1, CO_2 gas cylinder; 2, 3, water bath and magnetic stirrer; 4, CO_2 storage tank; 5, CO_2 absorption vessel; 6, cylindrical Teflon container; 7, pressure transducer; 8, computer.

solubility of CO₂ in PEGs. The apparatus mainly consists of a gas storage tank and a gas absorption vessel with volumes of 71.8 \pm 0.1 mL and 30.2 \pm 0.1 mL, respectively. They were placed in the water baths with thermostat heaters and magnetic stirrers. The temperature was controlled by a water bath with the accuracy of 0.1 K. A pressure transducer (Series 33X, Keller Co. in Swiss) with an accuracy of \pm 0.2 kPa was set up between the tank and the vessel for recording the pressure variation in intervals of 1 s and transmitting the data to the computer.

In a preliminary study, a leak test was performed. About 10 g of sample PEG in a cylindrical Teflon container was weighed on an electronic balance (Sartorius Co., Germany, ± 0.0001 g) and put into the absorption vessel. The system was controlled at the specific temperature with water baths and then evacuated with a vacuum pump to a pressure of <5 kPa for 1 h. The storage tank was charged with a specified amount of CO2 and held in the water bath until the pressure of the storage tank (P_s) was invariable. When the valve between the tank and the vessel was opened, the gas entered into the absorption vessel and was absorbed into the solvents. A magnetic stirrer was turned on at 15 r·min⁻¹ to accelerate absorption. After more than 2 h of absorption and the pressure value being invariable for another 1 h, the equilibrium can be considered to be reached. The pressure variation was recorded in the computer by the pressure transducer, and the equilibrium pressure (P_{e}) could be read from it. This method has also been applied to measuring solubilities of CO_2 in other kinds of solvents.^{26,2}

3. RESULTS AND DISCUSSION

3.1. Gas Solubilities in PEGs. Because of the negligible vapor pressure of PEGs,¹³ the gas phase was considered to be

Article

$$n_{\rm g} = n_1 - n_2 \tag{1}$$

where n_1 is the initial amount of CO₂ in the storage tank and n_2 is the amount of CO₂ in the gas phase at the equilibrium; both can be calculated by the Soave–Redlich–Kwong (SRK) equation of state from PVT data.

The mole quantity of solvent n_1 was calculated by the mass weight and average molar mass of PEGs (m_1, M) ; then the solubility of CO₂ in PEGs was obtained by the following equation:

$$x_{\rm CO_2} = \frac{n_g}{n_g + n_1} \tag{2}$$

$$m_{\rm CO_2} = \frac{n_{\rm g}}{m_{\rm l}} \tag{3}$$

where x_{CO_2} and m_{CO_2} are the mole fraction and the molality (mol·kg⁻¹) of CO₂ in solvent, respectively.

The expanded uncertainty of CO₂ solubility (U_c) in solvents with a level of confidence of approximately 95 % can be calculated by the following equations:^{14,26}

$$\frac{u_{\rm c}(x)}{x} = \sqrt{\frac{\sum_{i=1}^{2} u(n_i)}{n_{\rm g}^2} + \frac{\sum_{i=1}^{2} u(n_i) + u(n_1)^2}{(n_{\rm g} + n_1)}}$$
(4)

$$\frac{u_{\rm c}(m)}{m} = \sqrt{\frac{\sum u(n_i)}{n_{\rm g}^2} + \frac{u(m)^2}{m^2}}$$
(5)

$$u(n_i) = \frac{n_i}{R} \sqrt{\left(\frac{u(P_i)}{P_i}\right)^2 + \left(\frac{u(V_i)}{V_i}\right)^2 + \left(\frac{u(T_i)}{T_i}\right)^2} \tag{6}$$

$$u(n_1) = \frac{u(m)}{M} \tag{7}$$

$$U_{\rm c} = 2u_{\rm c}(x) \tag{8}$$

where $u_c(x)$ is the combined standard uncertainty of CO₂ solubility in solvents and *R* is the universal gas constant. The measurement uncertainties of pressure, volume, temperature, and mass are u(p) = 0.2 kPa, u(V) = 0.1 mL, u(T) = 0.1 K, and u(m) = 0.0001 g.

The solubilities of CO_2 in PEGs are listed in Tables 2 to 5 with the expanded uncertainties and plotted in Figures 2 to 5. Within the temperature and pressure regions investigated here, the equilibrium pressure linearly increases with the increase of CO_2 mole fraction at specific temperatures, which indicates that the absorption of CO_2 in PEGs is the typical physical process. Furthermore, with decreasing temperature and increasing molecular weights of PEGs, the solubilities of CO_2 in PEGs show an upward trend.

3.2. Henry's Constant. Henry's constant is frequently defined as:^{14,26,28,29}

Table 2. Experimental Values of Mole Fraction (x_{CO_2}) and Molality (m_{CO_2}) of CO₂ in PEG150 at Equilibrium Pressure (p) and Temperature (T)

Т	р		m _{CO2}
K	kPa	$x_{\rm CO_2}$	mol·kg ⁻¹
303.15	137.7	0.0103 ± 0.0001	0.0695 ± 0.0003
	264.2	0.0175 ± 0.0001	0.1188 ± 0.0005
	417.5	0.0300 ± 0.0001	0.2062 ± 0.0007
	558.0	0.0401 ± 0.0001	0.2780 ± 0.0009
	828.0	0.0614 ± 0.0002	0.4355 ± 0.0013
	1104.5	0.0850 ± 0.0003	0.6188 ± 0.0018
313.15	123.8	0.0071 ± 0.0001	0.0476 ± 0.0003
	167.6	0.0099 ± 0.0001	0.0664 ± 0.0003
	281.2	0.0169 ± 0.0001	0.1145 ± 0.0005
	418.0	0.0267 ± 0.0001	0.1828 ± 0.0007
	566.0	0.0339 ± 0.0001	0.2338 ± 0.0009
	853.4	0.0551 ± 0.0002	0.3880 ± 0.0013
	1134	0.0713 ± 0.0002	0.5114 ± 0.0017
323.15	117.9	0.0055 ± 0.0001	0.0370 ± 0.0003
	281.3	0.0152 ± 0.0001	0.1031 ± 0.0005
	346.3	0.0192 ± 0.0001	0.1304 ± 0.0005
	571.6	0.0304 ± 0.0001	0.2090 ± 0.0008
	867.8	0.0468 ± 0.0002	0.3272 ± 0.0013
	1143.5	0.0600 ± 0.0002	0.4249 ± 0.0017
333.15	164.8	0.0076 ± 0.0001	0.0471 ± 0.0003
	295.2	0.0137 ± 0.0001	0.0877 ± 0.0005
	436.5	0.0202 ± 0.0001	0.1298 ± 0.0006
	579.0	0.0268 ± 0.0001	0.1783 ± 0.0008
	856.5	0.0397 ± 0.0002	0.2726 ± 0.0012
	1130.0	0.0523 ± 0.0002	0.3705 ± 0.0016

$$H_{x}(T, P) = \lim_{x_{CO_{2}} \to 0} \frac{f_{CO_{2}}^{L}(T, P)}{x_{CO_{2}}}$$
$$= \lim_{x_{CO_{2}} \to 0} \frac{P\varphi_{CO_{2}}(T, P)}{x_{CO_{2}}}$$
$$\approx \frac{P_{e}}{x_{CO_{2}}}$$
(9)

where $H_x(T,P)$ is Henry's constant based on the mole fraction, x_{CO_2} is the mole fraction of CO₂ absorbed in liquid, $f_{CO_2}^L$ is the fugacity of CO₂, ϕ_{CO_2} is the fugacity coefficient, and P_e is the pressure of system at equilibrium. At the moderate pressure, we assume that $f_{CO_2}^L$ equals P_e here.

An analysis of CO₂ solubility carried on $H_x(T,P)$ alone would be inappropriate, because the reason for the increase in CO₂ mole fraction at isotonic conditions may be due to the increase of molecular weight of the solvent. Therefore, in this work, Henry's constant based on the molality ($H_b(T,P)$) was also applied to analysis the solubilities of CO₂ in PEGs. Similar to $H_x(T,P)$, $H_b(T,P)$ is defined as:

$$H_{\rm b}(T, P) = \lim_{m_{\rm CO_2} \to 0} \frac{f_{\rm CO_2}^{\rm L}(T, P)}{m_{\rm CO_2}} \approx \frac{P_{\rm e}}{m_{\rm CO_2}}$$
(10)

Henry's constant represents the linear relationship between gas concentration and pressure at finite dilution. Hence, Henry's constant can be obtained by calculating the linear

Т	р		$m_{\rm CO_2}$
К	kPa	$x_{\rm CO_2}$	mol·kg ⁻¹
303.15	140.8	0.0140 ± 0.0001	0.0711 ± 0.0003
	268.0	0.0303 ± 0.0001	0.1563 ± 0.0005
	398.3	0.0436 ± 0.0001	0.2282 ± 0.0007
	531.2	0.0586 ± 0.0002	0.3114 ± 0.0009
	832.5	0.0900 ± 0.0002	0.4944 ± 0.0014
	1102.5	0.1162 ± 0.0003	0.6571 ± 0.0018
313.15	72.2	0.0062 ± 0.0001	0.0312 ± 0.0003
	91.9	0.0077 ± 0.0001	0.0386 ± 0.0003
	154.8	0.0132 ± 0.0001	0.0669 ± 0.0003
	273.3	0.0242 ± 0.0001	0.1240 ± 0.0005
	497.3	0.0422 ± 0.0001	0.2205 ± 0.0008
	772.0	0.0676 ± 0.0003	0.3625 ± 0.0014
	1143.0	0.0994 ± 0.0003	0.5521 ± 0.0018
323.15	163.0	0.0116 ± 0.0001	0.0588 ± 0.0003
	286.1	0.0213 ± 0.0001	0.1087 ± 0.0005
	424.0	0.0323 ± 0.0001	0.1668 ± 0.0006
	551.2	0.0428 ± 0.0002	0.2236 ± 0.0008
	830.0	0.0625 ± 0.0002	0.3331 ± 0.0012
	1116.0	0.0833 ± 0.0003	0.4546 ± 0.0016
333.15	154.8	0.0092 ± 0.0001	0.0466 ± 0.0003
	292.6	0.0206 ± 0.0001	0.1052 ± 0.0005
	445.5	0.0298 ± 0.0001	0.1537 ± 0.0006
	580.0	0.0392 ± 0.0002	0.2042 ± 0.0008
	849.5	0.0600 ± 0.0002	0.3194 ± 0.0012
	1103.5	0.0756 ± 0.0003	0.4091 ± 0.0016

Table 3. Experimental Values of Mole Fraction (x_{CO_2}) and

Molality (m_{CO_2}) of CO₂ in PEG200 at Equilibrium Pressure

(p) and Temperature (T)

slope of pressure and molar fraction. Henry's constants at (303.15 to 333.15) K are presented in Tables 6 and 7 and shown in Figures 7 and 8. The uncertainty with a confidence of 95 % of Henry's constant is also given in Tables 6 and 7.

Figure 6 illustrates the measured Henry's constants of CO_2 in PEG150 compared with literature data, which verifies the reliability of the apparatus used in this study. As can be seen, this work is in good agreement with the data of Tan et al.,³⁰ and the absolute average deviation is 2.7 %. Compared to Jou et al.,³¹ the discrepancies may be caused by the different measurement conditions. Jou et al. mainly focused on the vapor–liquid–liquid equilibrium measurement at elevated pressure resulting in the considerable linear fit deviation of Henry's constant.

As depicted in Figures 7 and 8, H_r and H_h are enhanced as the temperature increases. At isothermal conditions, H_x increases dramatically with decreasing the molecular weight; that is, PEGs with higher molecular weights have higher CO₂ solubilities, and the solvency is ordered as: PEG400 > PEG300 > PEG200 > PEG150. The solubility difference is believed to derive from the strong interaction between CO₂ molecule and -O- groups in PEGs, that is, acid-base reactions of the acidic CO₂ with the electron-rich ether oxygen in the PEG molecule.³² Although the terminal -OH groups of PEGs have a higher affinity for CO_2 than -O- groups,¹⁸ the stronger interaction between solvent molecules cannot be neglected. The hydrogen bonds formed in solvents by -OH groups have negative effects on providing enough cavities to accommodate the CO₂ molecule in solvents, which means -OH groups would impede the CO₂ absorption.¹⁴ Consequently, PEG400

Table 4. Experimental Values of Mole Fraction (x_{CO_2}) and Molality (m_{CO_2}) of CO₂ in PEG300 at Equilibrium Pressure (p) and Temperature (T)

Т	р		$m_{\rm CO_2}$
K	kPa	$x_{\rm CO_2}$	mol·kg ⁻¹
303.15	148.3	0.0226 ± 0.0001	0.0772 ± 0.0003
	278.5	0.0483 ± 0.0001	0.1690 ± 0.0005
	424.2	0.0693 ± 0.0002	0.2482 ± 0.0007
	663.0	0.1045 ± 0.0003	0.3889 ± 0.0011
	804.0	0.1352 ± 0.0003	0.5213 ± 0.0013
	1066.0	0.1735 ± 0.0004	0.6995 ± 0.0018
313.15	156.5	0.0190 ± 0.0001	0.0644 ± 0.0003
	278.5	0.0363 ± 0.0001	0.1254 ± 0.0005
	419.0	0.0581 ± 0.0002	0.2058 ± 0.0007
	586.0	0.0764 ± 0.0003	0.2757 ± 0.0009
	835.0	0.1117 ± 0.0003	0.4193 ± 0.0013
	1102.0	0.1470 ± 0.0004	0.5745 ± 0.0017
323.15	141.3	0.0154 ± 0.0001	0.0520 ± 0.0003
	307.9	0.0321 ± 0.0001	0.1107 ± 0.0005
	421.6	0.0504 ± 0.0002	0.1768 ± 0.0006
	576.0	0.0672 ± 0.0002	0.2400 ± 0.0009
	840.5	0.0935 ± 0.0003	0.3438 ± 0.0012
	1107.0	0.1286 ± 0.0004	0.4918 ± 0.0016
333.15	155.2	0.0155 ± 0.0001	0.0525 ± 0.0003
	311.0	0.0312 ± 0.0001	0.1074 ± 0.0005
	437.0	0.0462 ± 0.0002	0.1615 ± 0.0006
	591.2	0.0605 ± 0.0002	0.2147 ± 0.0008
	880.5	0.0940 ± 0.0003	0.3457 ± 0.0013
	1130.5	0.1168 ± 0.0004	0.4406 ± 0.0016

Table 5. Experimental Values of Mole Fraction (x_{CO_2}) and Molality (m_{CO_2}) of CO₂ in PEG400 at Equilibrium Pressure (p) and Temperature (T)

Т	р		$m_{\rm CO_2}$
K	kPa	$x_{\rm CO_2}$	mol·kg ⁻¹
303.15	145.3	0.0319 ± 0.0001	0.0822 ± 0.0003
	282.2	0.0622 ± 0.0002	0.1660 ± 0.0005
	431.2	0.0897 ± 0.0003	0.2464 ± 0.0007
	561.5	0.1244 ± 0.0003	0.3553 ± 0.0009
	815.5	0.1684 ± 0.0004	0.5063 ± 0.0013
	1070.0	0.2220 ± 0.0006	0.7134 ± 0.0018
313.15	166.0	0.0279 ± 0.0001	0.0717 ± 0.0003
	300.5	0.0567 ± 0.0002	0.1504 ± 0.0005
	414.4	0.0759 ± 0.0002	0.2054 ± 0.0007
	578.0	0.1027 ± 0.0003	0.2861 ± 0.0009
	834.5	0.1467 ± 0.0004	0.4298 ± 0.0013
	1087.5	0.1905 ± 0.0006	0.5885 ± 0.0017
323.15	154.1	0.0237 ± 0.0001	0.0607 ± 0.0003
	217.4	0.0333 ± 0.0001	0.0861 ± 0.0004
	443.0	0.0690 ± 0.0003	0.1854 ± 0.0007
	564.0	0.0877 ± 0.0003	0.2404 ± 0.0008
	893.8	0.1362 ± 0.0004	0.3942 ± 0.0013
	1120.5	0.1701 ± 0.0006	0.5125 ± 0.0017
333.15	147.8	0.0213 ± 0.0001	0.0544 ± 0.0003
	282.9	0.0421 ± 0.0002	0.1099 ± 0.0004
	434.5	0.0625 ± 0.0002	0.1666 ± 0.0006
	557.2	0.0775 ± 0.0003	0.2099 ± 0.0008
	831.0	0.1184 ± 0.0004	0.3356 ± 0.0012
	1104.0	0.1545 ± 0.0005	0.4567 ± 0.0016



Figure 2. Solubilities of CO₂ in PEG150. ■, 303.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K; −, linear fit.



Figure 3. Solubilities of CO₂ in PEG200. ■, 303.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K; −, linear fit.



Figure 4. Solubilities of CO₂ in PEG300. ■, 303.15 K; ●, 313.15 K;
▲, 323.15 K; ▼, 333.15 K; −, linear fit.

with the highest density of free -O- groups and least density of -OH groups showed better absorbing capacity to CO_2 than other solvents. On the other hand, H_b shows the same tendency with H_{x} , while it varies a little with molecular weights, as shown in Figure 8, which is believed to originate from a similar number of -OH groups in PEG150, PEG200, PEG300, and PEG400. Moreover, the further increasing molecular weights of PEGs lead to high viscosity and thus make diffusion of CO_2 to



Figure 5. Solubilities of CO₂ in PEG400. ■, 303.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K; −, linear fit.

functional groups more difficult. This is in agreement with the findings by Aschenbrenner et al.,¹⁸ where the solubility of CO_2 in PEG600 was found to be lower than those in PEG200 and PEG300.

4. THERMODYNAMIC PROPERTIES

Thermodynamic properties of CO_2 absorbed in PEGs can be determined from the correlation of Henry's constant by the following equations:^{27,33}

$$\Delta_{\rm sol}G = RT \ln(H(T, P))/P^0 \tag{11}$$

$$\Delta_{\rm sol} H = R \left(\frac{\partial \ln(H(T, P)/P^0)}{\partial(1/T)} \right)_p \tag{12}$$

$$\Delta_{\rm sol}S = (\Delta_{\rm sol}H - \Delta_{\rm sol}G)/T \tag{13}$$

where $\Delta_{sol}G$, $\Delta_{sol}H$, and $\Delta_{sol}S$ are the solution Gibbs free energy, solution enthalpy, and solution entropy, respectively. P^0 refers to 0.1 MPa.

 $\Delta_{\rm sol}G$ is the chemical potential that is minimized when the gas–liquid system reaches equilibrium at constant pressure and temperature. $\Delta_{\rm sol}H$ indicates the strength of interaction between the CO₂ molecules and PEG molecules in the liquid, and $\Delta_{\rm sol}S$ shows the degree of ordering of the liquid/gas mixture.³⁴ The predicted values of $\Delta_{\rm sol}G$, $\Delta_{\rm sol}H$, and $\Delta_{\rm sol}S$ are listed in Table 8.

5. CONCLUSIONS

In this contribution, the solubilities of CO_2 in PEGs were determined. Henry's constants and thermodynamic properties of CO_2 in PEGs were evaluated from the experimental data. The results show that the solubilities of CO_2 in PEGs decrease with increasing temperature and decreasing pressure. Moreover,

Table 7. Henry's Constant (Based on Molality, H_b) of CO₂ in PEGs from (303.15 to 333.15) K

	$H_{\rm b}/{ m MPa}\cdot{ m kg}\cdot{ m mo}\Gamma^1$			
solution	303.15 K	313.15 K	323.15 K	333.15 K
CO ₂ + PEG150	1.86 ± 0.12	2.25 ± 0.08	2.69 ± 0.05	3.13 ± 0.12
CO ₂ + PEG200	1.69 ± 0.03	2.11 ± 0.06	2.48 ± 0.05	2.72 ± 0.10
CO ₂ + PEG300	1.57 ± 0.09	1.98 ± 0.10	2.34 ± 0.13	2.60 ± 0.10
CO ₂ + PEG400	1.56 ± 0.09	1.91 ± 0.09	2.25 ± 0.09	2.48 ± 0.10



Figure 6. Comparison of Henry's constant of CO_2 in PEG150 with the literature data. \blacksquare , this work; ●, Tan et al.;³⁰ ▲, Jou et al.³¹



Figure 7. Henry's constant (based on the mole fraction, H_x) of CO₂ in PEGs. \blacksquare , PEG150; \bullet , PEG200; \blacktriangle , PEG300; \blacktriangledown , PEG400; -, linear fit.

PEGs with higher molecular weights can enhance solubility

with CO_2 .

Table 6. Henry's Constant	: (Based on Mole	e Fraction, H_x) of	CO ₂ in PEGs from	(303.15 to 333.15)	K
---------------------------	------------------	------------------------	------------------------------	----------------------	---

	H_x/MPa			
solution	303.15 K	313.15 K	323.15 K	333.15 K
CO ₂ + PEG150	13.34 ± 0.51	15.89 ± 0.40	18.81 ± 0.39	21.59 ± 0.02
CO ₂ + PEG200	9.33 ± 0.22	11.50 ± 0.11	13.29 ± 0.22	14.51 ± 0.37
CO ₂ + PEG300	6.11 ± 0.17	7.50 ± 0.14	8.68 ± 0.29	9.60 ± 0.20
$CO_2 + PEG400$	4.78 ± 0.12	5.66 ± 0.12	6.54 ± 0.07	7.09 ± 0.12



Figure 8. Henry's constant (based on the molality scale, H_b) of CO₂ in PEGs. \blacksquare , PEG150; \blacklozenge , PEG200; \bigstar , PEG300; \blacktriangledown , PEG400.

Table 8. Thermodynamic Properties of Solutions for CO_2 in PEGs^a

	$\Delta_{sol}G^*$	$\Delta_{ m sol}H$	$\Delta_{sol}S^*$
solution	kJ·moΓ¹	kJ·mol ^{−1}	J·mol ^{−1} ·K ^{−1}
$CO_2 + PEG150$	12.31	-13.77	-86.03
$CO_2 + PEG200$	11.43	-12.40	-78.60
$CO_2 + PEG300$	10.37	-12.66	-75.94
$CO_2 + PEG400$	9.75	-11.18	-69.04

 ${}^a\Delta_{\rm sol}G^*$ and $\Delta_{\rm sol}S^*$ are the Gibbs free energy and entropy at 303.15 K, respectively.

Henry's constants and the thermodynamic properties of CO_2 in PEGs obtained will be important for developing processes of CO_2 capture from flue gas by PEGs. Moreover, these data are essential for the kinetic modeling of mixtures of PEGs, amines, and ILs.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zwqi@ecust.edu.cn. Fax: +86-21-6425 3528.

Funding

This research is supported by the Fundamental Research Funds for the Central Universities of China, Major State Basic Research Development Program of China (973 Program 2012CB720500), National Natural Science Foundation of China (NSFC 21076074, 21006029), Shanghai Pujiang Talents Program (10PJ1402400), Shanghai Natural Science Foundation (10ZR1407200), and the Program of Introducing Talents of Discipline to Universities (111 Project: B08021). Financial support by the Max Planck Partner Group Funding from the Max Planck Society, Germany, is greatly acknowledged.

REFERENCES

(1) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon dioxide capture: prospects for new materials. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058–6082.

(2) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Advances in CO_2 capture technology-The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenhouse Gas Control* **2008**, *2*, 9–20.

(3) Singh, P.; Brilman, D. W. F.; Groeneveld, M. J. Evaluation of CO_2 solubility in potential aqueous amine-based solvents at low CO_2 partial pressure. *Int. J. Greenhouse Gas Control* **2011**, *5*, 61–68.

(4) Rochelle, G. T. Amine scrubbing for CO_2 capture. Science 2009, 325, 1652–1654.

(5) Supasitmongkol, S.; Styring, P. High CO₂ solubility in ionic liquids and a tetraalkyl-ammonium-based poly(ionic liquid). *Energy Environ. Sci.* **2010**, *3*, 1961–1972.

(6) Gurkan, B. E.; de la Fuente, J. C.; Mindrup, E. M.; Ficke, L. E.; Goodrich, B. F.; Price, E. A.; Schneider, W. F.; Brennecke, J. F. Equimolar CO_2 absorption by anion-functionalized ionic liquids. *J. Am. Chem. Soc.* **2010**, *132*, 2116–2117.

(7) Chakma, A. CO₂ capture processes--Opportunities for improved energy efficiencies. *Energy Convers. Manage.* **1997**, *38*, S51–S56.

(8) Notz, R.; Tonnies, I.; McCann, N.; Scheffknecht, G.; Hasse, H. CO₂ capture for fossil fuel-fired power plants. *Chem. Eng. Technol.* **2011**, *34*, 163–172.

(9) Pennline, H. W.; Luebke, D. R.; Jones, K. L.; Myers, C. R.; Morsi, B. I.; Heintz, Y. J.; Ilconich, J. B. Progress in carbon dioxide capture and separation research for gasification-based power generation point sources. *Fuel Process. Technol.* **2008**, *89*, 897–907.

(10) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO_2 captured by a task-specific ionic liquid. *J. Am. Chem. Soc.* **2002**, 124, 926–927. (11) Hou, M.; Liang, S.; Zhang, Z.; Song, J.; Jiang, T.; Han, B. Determination and modeling of solubility of CO_2 in PEG200 + 1-pentanol and PEG200 + 1-octanol mixtures. *Fluid Phase Equilib.* **2007**, 258, 108–114.

(12) Li, X.; Hou, M.; Zhang, Z.; Han, B.; Yang, G.; Wang, X.; Zou, L. Absorption of CO_2 by ionic liquid/polyethylene glycol mixture and the thermodynamic parameters. *Green Chem.* **2008**, *10*, 879–884.

(13) Aschenbrenner, O.; Supasitmongkol, S.; Taylor, M.; Styring, P. Measurement of vapour pressures of ionic liquids and other low vapour pressure solvents. *Green Chem.* **2009**, *11*, 1217–1221.

(14) Gui, X.; Tang, Z.; Fei, W. Solubility of CO_2 in Alcohols, Glycols, Ethers, and Ketones at High Pressures from (288.15 to 318.15) K. J. Chem. Eng. Data 2011, 56, 2420–2429.

(15) Awwad, A. M.; Al-Dujaili, A. H.; Salman, H. E. Relative permittivities, densities, and refractive indices of the binary mixtures of sulfolane with ethylene glycol, diethylene glycol, and poly (ethylene glycol) at 303.15 K. J. Chem. Eng. Data 2002, 47, 421–424.

(16) Aionicesei, E.; Skerget, M.; Knez, Z. Measurement and modeling of the CO_2 solubility in poly(ethylene glycol) of different molecular weights. *J. Chem. Eng. Data* **2008**, *53*, 185–188.

(17) Wiesmet, V.; Weidner, E.; Behme, S.; Sadowski, G.; Arlt, W. Measurement and modelling of high-pressure phase equilibria in the systems polyethylene glycol (PEG)-propane, PEG-nitrogen and PEG-carbon dioxide. J. Supercrit. Fluids 2000, 17, 1–12.

(18) Aschenbrenner, O.; Styring, P. Comparative study of solvent properties for carbon dioxide absorption. *Energy Environ. Sci.* 2010, *3*, 1106–1113.

(19) Cong, H. L.; Yu, B. Aminosilane cross-linked PEG/PEPEG/PPEPG membranes for CO_2/N_2 and CO_2/H_2 separation. *Ind. Eng. Chem. Res.* **2010**, 49, 9363–9369.

(20) Amooghin, A. E.; Sanaeepur, H.; Moghadassi, A.; Kargari, A.; Ghanbari, D.; Mehrabadi, Z. S. Modification of ABS membrane by PEG for capturing carbon dioxide from CO_2/N_2 streams. *Sep. Sci. Technol.* **2010**, *45*, 1385–1394.

(21) Yang, Z. Z.; He, L. N.; Zhao, Y. N.; Li, B.; Yu, B. CO₂ capture and activation by superbase/polyethylene glycol and its subsequent conversion. *Energy Environ. Sci.* **2011**, *4*, 3971–3975.

(22) Rodriguez, H.; Rogers, R. D. Liquid mixtures of ionic liquids and polymers as solvent systems. *Fluid Phase Equilib.* 2010, 294, 7–14.
(23) Archane, A.; Furst, W.; Provost, E. Influence of Poly(ethylene oxide) 400 (PEG400) on the Absorption of CO₂ in Diethanolamine (DEA)/H₂O Systems. *J. Chem. Eng. Data* 2011, 56, 1852–1856.

(24) Davis, R. A.; Menbdez, R. E.; Sandall, O. C. Physical, thermodynamic, and transport properties for carbon dioxide and nitrous oxide in solutions of diethanolamine or di-2-propanolamine in polyethylene glycol. *J. Chem. Eng. Data* **1993**, *38*, 119–124.

(25) Trivedi, S.; Pandey, S. Interactions within a ionic liquid plus poly(ethylene glycol) mixture revealed by temperature-dependent

Journal of Chemical & Engineering Data

synergistic dynamic viscosity and probe-reported microviscosity. J. Phys. Chem. B 2011, 115, 7405-7416.

(26) Gui, X.; Tang, Z.; Fei, W. CO_2 capture with physical solvent dimethyl carbonate at high pressures. J. Chem. Eng. Data 2010, 55, 3736–3741.

(27) Kurnia, K. A.; Harris, F.; Wilfred, C. D.; Abdul Mutalib, M. I.; Murugesan, T. Thermodynamic properties of CO_2 absorption in hydroxyl ammonium ionic liquids at pressures of (100–1600) KPa. *J. Chem. Thermodyn.* **2009**, *41*, 1069–1073.

(28) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and thermodynamic properties of gases in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.

(29) Henni, A.; Tontiwachwuthikul, P.; Chakma, A. Solubilities of carbon dioxide in polyethylene glycol ethers. *Can. J. Chem. Eng.* **2005**, 83, 358–361.

(30) Tan, J.; Shao, H.; Xu, J.; Du, L.; Luo, G. Mixture absorption system of monoethanolamine triethylene glycol for CO_2 capture. *Ind. Eng. Chem. Res.* **2011**, *50*, 3966–3976.

(31) Jou, F. Y.; Deshmukh, R. D.; Otto, F. D.; Mather, A. E. Vapor liquid equilibria for acid gases and lower alkanes in triethylene glycol. *Fluid Phase Equilib.* **1987**, *36*, 121–140.

(32) Saha, S.; Chakma, A. Selective CO_2 separation from CO_2/C_2H_6 mixtures by immobilized diethanolamine/PEG membranes. *J. Membr. Sci.* **1995**, *98*, 157–171.

(33) Kamps, A. P.; Tuma, D.; Xia, J.; Maurer, G. Solubility of CO_2 in the ionic liquid [bmim][PF₆]. *J. Chem. Eng. Data* **2003**, *48*, 746–749.

(34) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. Anion effects on gas solubility in ionic liquids. *J. Phys. Chem. B* 2005, 109, 6366–6374.