Vapor−Liquid Equilibria of CO_2 + 1-Octene + Polyethylene Glycol Systems

Xiaoyong Li,[†,‡] Minqiang Hou,[‡] Buxing Han,*[,‡] Xiaoling Wang,[†] Guanying Yang,[‡] and Lizhuang Zou*[,†]

School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), 100083, China, and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China

---

The vapor−liquid equilibria for CO_2 + 1-octene + polyethylene glycol (PEG) were determined at 308.15 K, 318.15 K, and 328.15 K at pressures up to 10 MPa, and the average molecular weights of PEGs were 200, 400, and 600, respectively. It was shown that CO_2 could considerably enhance the dissolution of 1-octene in PEGs under suitable conditions.

Introduction

Polyethylene glycol (PEG), which has a molecular formula of $HO-(CH_2CH_2O)_n-H$, has been used widely in pharmaceutical, cosmetics, and food industries. PEGs have some unusual properties, such as nonvolatility, nontoxicity, biodegradability, inexpensive, and wide availability. Their properties can be tuned by changing molecular weight.[1–3] Recently, PEGs have also been used as an environmentally benign solvent to replace volatile organic solvents in different processes, such as chemical reactions.[1,4–6] However, the miscibility of PEGs and nonpolar or weak polar organic compounds is usually poor, which limits application of PEGs to a certain extent. Organic cosolvents can be used to enhance the miscibility of PEGs and organic compounds, but they cause a separation problem and may result in cross contamination.

Compressed or supercritical CO_2 is another green solvent due to its favorable physical and chemical properties. Combination of PEGs and CO_2 is an interesting topic, and some research in this field has been carried out recently. For example, some chemical reactions have been carried out in the PEG + CO_2 system, and satisfactory results have been obtained.[7–9] It is well-known that the phase behaviors of the related systems are crucial for various applications. The solubility of CO_2 in PEGs has been studied extensively.[10–12] However, study of phase behaviors of PEG + CO_2 + organic compound systems is very limited.[13,14]

Conversion of olefins into different chemicals is a class of important reactions in the chemical industry. Some of the reactions may be more efficient if they are conducted in PEGs or PEG + CO_2 mixed solvents, and 1-octene may be among the most suitable ones. In this work, we studied the vapor−liquid equilibria of CO_2 + 1-octene + PEG systems under different conditions. It was demonstrated that CO_2 can enhance the dissolution of 1-octene in PEGs considerably under suitable conditions. This may be favorable to the chemical reaction of 1-octene in PEGs. We believe that CO_2 can also enhance the miscibility of PEGs and some other nonpolar substances.

Experimental

Materials. CO_2 with a purity of 99.995 % was supplied by Beijing Analytical Instrument Factory. 1-Octene with a purity of >99.5 % was supplied by Alfa Aesar. PEG200, PEG400, and PEG600, which had average molecular weights of 200, 400, and 600, respectively, were analytical grade produced by Beijing Chemical Reagent Plant. The chemicals were used as received.

Apparatus. The apparatus used was similar to that reported previously.[15] It consisted of a CO_2 cylinder, a computer-controlled metering syringe pump (DB-80, Beijing Satellite Manufacture Company), a constant-temperature water bath, a pressure gauge, a volume-variable view cell, a sample bomb, and a magnetic stirrer. The volume of the view cell could be changed in the range from 23 cm^3 to 50 cm^3 by moving the piston. The temperature of the constant-temperature water bath was controlled by a Haake-D8 temperature controller. The temperature was determined by accurate mercury thermometers with the uncertainty of ± 0.05 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT model 93) and an indicator. Its uncertainty was ± 0.025 MPa in the pressure range of (0 to 20) MPa.

Procedures. The experimental procedures were also similar to those reported previously.[15] As an example, we describe the procedures to determine the composition of the PEG-rich phase of the CO_2 + 1-octene + PEG200 system. In a typical experiment, the desired amounts of PEG200 and 1-octene were loaded into the cell using a syringe, and the air in the volume-variable view cell was replaced by CO_2. The cell was placed in the constant-temperature water bath, and CO_2 was charged into the system using the high-pressure pump until a suitable pressure was reached. The valve connected to the view cell was closed, and the system was stirred. If the pressure of the system was unchanged with time, it was considered that the system had reached equilibrium. The pressure of the system was recorded. Our experiments showed that 5 h was required for the system to reach equilibrium. The valve of the sample bomb for sampling the bottom liquid phase was opened slowly to collect some sample. At the same time, the volume of the view cell was adjusted to keep the pressure unchanged during the sampling process. The sampling valve was closed after enough liquid sample had been collected in the sample bomb which was then removed for composition analysis. All the experiments were carried out in the three-phase region, which was known from direct observation.

To analyze the composition of the sample, the mass of the sample bomb was first determined by an electronic balance (Mettler MP1200) with a resolution of 0.001 g. The mass of the sample was known from the masses of the sample bomb with and without sample. The sample bomb was placed in an

---

* Corresponding authors. E-mail: hanbx@iccas.ac.cn; zoulizhuang@263.net.
[†] China University of Mining & Technology (Beijing).
[‡] Chinese Academy of Sciences.

10.1021/je800025s CCC: $40.75

Table 1. Mass Fraction of CO_2 (w_1), 1-Octene (w_2), PEG (w_3), and $w_2' = w_2/(w_2 + w_3)$ in PEG-Rich Phase under Different Conditions

T/K	P/MPa	100 w_1	100 w_2	100 w_3	100 w_2'
			PEG200		
308.15 K	/	0^{a}	0.80^{a}	99.2^{a}	0.80^{a}
	1.24	3.00	1.40	95.6	1.44
	2.70	6.66	1.74	91.6	1.86
	4.14	9.57	2.03	88.4	2.24
	5.13	12.2	2.10	85.7	2.39
	7.09	16.9	1.80	81.3	2.17
	8.07	19.4	1.30	79.3	1.61
	9.55	22.5	0.80	76.7	1.03
318.15 K	/	0^{a}	1.20^{a}	98.8^{a}	1.20^{a}
	1.01	2.22	1.58	96.2	1.62
	2.49	5.28	2.02	92.7	2.13
	4.02	8.40	2.40	89.2	2.62
	5.47	11.3	2.50	86.2	2.82
	7.00	14.5	2.30	83.2	2.69
	8.08	17.4	1.90	80.7	2.30
	9.37	21.0	1.40	77.6	1.77
328.15 K	/	0^{a}	1.80^{a}	98.2^{a}	1.80^{a}
	1.05	1.84	2.06	96.1	2.10
	2.56	4.41	2.49	93.1	2.60
	3.97	6.76	2.84	90.4	3.05
	5.53	9.95	2.95	87.1	3.28
	7.08	12.5	2.80	84.7	3.20
	8.01	14.9	2.40	82.7	2.82
	9.61	18.8	1.80	79.4	2.22
			PEG400		
308.15 K	/	0^{a}	1.30^{a}	98.7^{a}	1.30^{a}
	1.27	3.17	1.73	95.1	1.79
	1.87	4.68	2.12	93.2	2.22
	3.52	8.78	2.91	88.3	3.19
	5.15	11.9	3.20	84.9	3.63
	5.95	14.0	3.20	82.8	3.72
	7.67	18.2	2.50	79.3	3.06
	9.17	23.0	1.70	75.3	2.21
318.15 K	/	0^{a}	1.90^{a}	98.1^{a}	1.90^{a}
	1.06	2.61	2.09	95.3	2.15
	2.55	5.64	2.96	91.4	3.14
	4.07	8.81	3.49	87.7	3.83
	5.66	11.9	3.60	84.5	4.09
	6.85	14.9	3.20	81.9	3.76
	8.30	18.3	2.60	79.1	3.18
	9.80	22.0	1.80	76.2	2.31
328.15 K	/	0^{a}	2.40^{a}	97.6^{a}	2.40^{a}
	1.22	2.42	2.68	94.9	2.75
	2.71	5.22	3.38	91.4	3.57
	4.22	8.03	3.87	88.1	4.21
	5.87	11.3	4.00	84.7	4.51
	7.21	13.9	3.60	82.5	4.18
	8.70	17.5	2.90	79.6	3.51
	9.45	19.6	2.50	77.9	3.11
			PEG600		
308.15 K	/	0^{a}	1.60^{a}	98.3^{a}	1.60^{a}
	1.21	3.57	2.13	94.3	2.21
	2.22	5.88	2.62	91.5	2.78
	3.44	8.87	3.43	87.8	3.76
	4.60	11.0	4.00	85.0	4.49
	5.48	13.2	4.20	82.6	4.84
	6.98	17.8	3.60	78.6	4.38
	7.96	20.8	3.00	76.2	3.79
	9.15	24.9	1.70	73.4	2.26
318.15 K	/	0^{a}	2.50^{a}	97.5^{a}	2.50^{a}
	1.17	3.21	2.79	94.0	2.88
	2.67	6.54	3.46	90.0	3.70
	4.15	9.65	4.25	86.1	4.70
	5.59	12.8	4.60	82.6	5.28
	7.11	16.8	4.40	78.8	5.29
	8.17	19.9	3.60	76.5	4.49
	9.12	22.3	3.10	74.6	3.99
328.15 K	/	0^{a}	3.30^{a}	96.7^{a}	3.30^{a}
	1.18	2.82	3.58	93.6	3.68
	2.64	6.04	4.06	89.9	4.32
	4.15	9.10	4.70	86.2	5.17
	5.91	12.7	5.00	82.3	5.73
	6.38	13.9	5.10	81.0	5.92
	7.14	15.6	4.90	79.5	5.81
	8.10	18.2	4.50	77.3	5.50
	9.13	20.8	3.90	75.3	4.92

[a] Without CO_2 in the system.

ice bath, and the CO_2 in the sample bomb was released slowly through a cold trap with *n*-heptane as the absorbent. The mass of CO_2 in the sample was obtained from the mass change of the sample bomb because the amount of PEG and 1-octene entrained by CO_2 was negligible compared with the amount of CO_2, as was confirmed by our simulation experiments by charging a known amount of PEG, 1-octene, and CO_2 in the sample bomb. The *n*-heptane in the cold trap was mixed with the liquid in the sample bomb, and the 1-octene was extracted into the *n*-heptane-rich phase. Then, the amount of the 1-octene was determined by gas chromatography (Agilent 6820) with *n*-decane as the internal standard. Our simulation experiment using known amounts of 1-octene and PEG200 showed that the uncertainty of the amount of 1-octene determined by this method was less than 1.5 %.

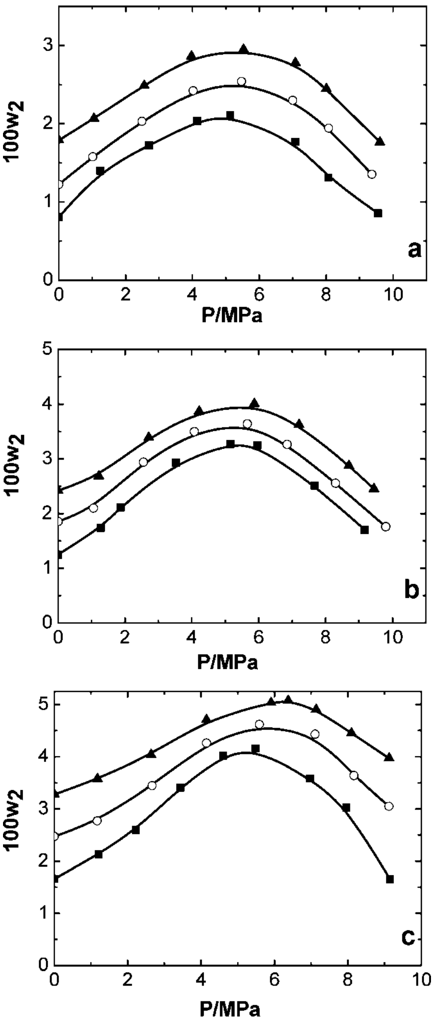

Figure 1. Mass fraction of 1-octene in the PEG-rich phase at different temperatures and pressures. (a) PEG200; (b) PEG400; (c) PEG600. ■, 308.15 K; ○, 318.15 K; ▲, 328.15 K; —, correlation.

Results and Discussion

As discussed above, all the experiments in this work were carried out in the three-phase region of the ternary systems; i.e., there was a CO_2-rich phase, a 1-octene-rich phase, and a PEG-rich phase in the system. It can be known from the phase rule that the compositions of all the three phases are fixed at fixed temperature and pressure. Our experiments showed that the solubility of PEGs in 1-octene and in CO_2 was extremely low. It can be deduced that the difference in compositions of the CO_2-rich phase and the 1-octene-rich phase in the ternary system and the CO_2 + 1-octene binary system should not be

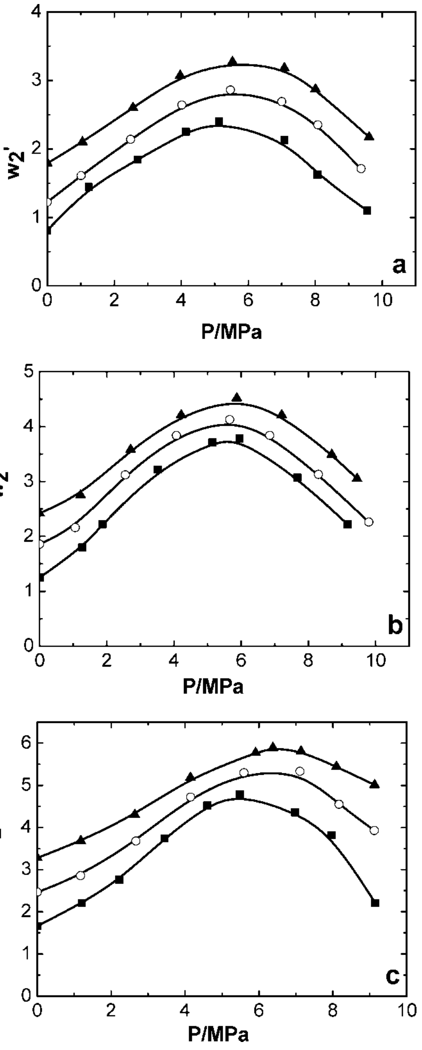

Figure 2. Effect of temperature and pressure on w_2' in the PEG-rich phase. (a) PEG200; (b) PEG400; (c) PEG600. ■, 308.15 K; ○, 318.15 K; ▲, 328.15 K; —, correlation.

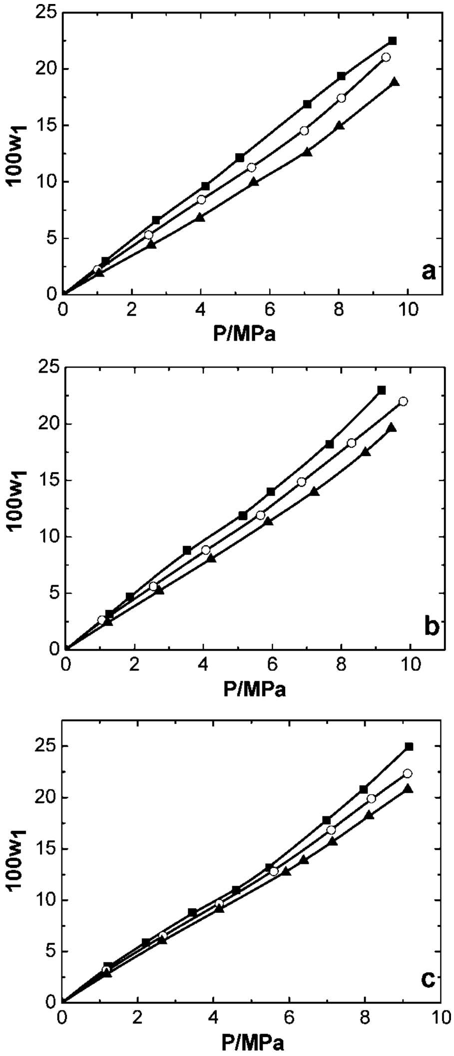

Figure 3. Mass fraction of CO_2 in the PEG-rich phase at different temperatures and pressures. (a) PEG200; (b) PEG400; (c) PEG600. ■, 308.15 K; ○, 318.15 K; ▲, 328.15 K; —, correlation.

considered at the same temperature and pressure. The vapor—liquid equilibria of the CO_2 + 1-octene system have been studied extensively by other authors. Therefore, we focused on the PEG-rich phase in this work.

Table 1 lists the composition of the PEG-rich phase in CO_2 + 1-octene + PEG200, CO_2 + 1-octene + PEG400, and CO_2 + 1-octene + PEG600 systems at 308.15 K, 318.15 K, and 328.15 K up to $P = 10$ MPa. In the table, w_1, w_2, and w_3 stand for mass fraction of CO_2, 1-octene, and PEG, respectively. It is estimated that the uncertainty of the data in the table is less than 2.0 %.

Figure 1 demonstrates the dependence of the mass fraction of 1-octene in the PEG-rich phase of the ternary systems. It is interesting that the mass fraction of 1-octene increased with increasing pressure in the low-pressure range and decreased with an increase in pressure in the high-pressure region; i.e., there is a maximum in each w_2 vs pressure curve. A reasonable explanation for this phenomenon is that pressure affects the mass fraction in two opposite ways. First, the increase of pressure should enhance the dissolution of 1-octene because CO_2 reduces the polarity of the PEGs, and the concentration of CO_2 in the PEG-rich phase increases with increasing pressure. Second, an increase in pressure results in an increase in the solvent power of CO_2 in the vapor phase, which is not favorable to the dissolution of 1-octene in the PEGs. The competition of the two factors results in the maxima in the curves.

As discussed above, the solubility of 1-octane in PEGs can be enhanced considerably by CO_2 at suitable pressures. PEGs can be used as a green solvent for chemical reactions of 1-octene, such as hydrogenation and oxidation reactions. The low solubility of the olefin in PEGs may lower reaction rates, reduce product yields, and cause the reaction to be mass-transfer limited. This disadvantage can be overcome to a certain degree by adding CO_2. Moreover, the viscosity of PEGs is relatively high. Dissolution of CO_2 may reduce the viscosity because dissolution of CO_2 can reduce the viscosity of other liquids significantly,[16] which may also enhance the reaction rates. Therefore, addition of CO_2 in the reaction system may be favorable to the chemical reaction. We believe that CO_2 can also enhance the solubility of some other hydrocarbon compounds in PEGs.

Figure 1 also shows that the mass fraction of 1-octene in the PEG-rich phase increased with increasing molecular weight of PEGs. The main reason is that the polarity of a PEG with larger molecular weight is lower, and 1-octene is nonpolar. We can also know from the figure that an increase in temperature resulted in an increase in mass fraction of 1-octene in the PEG-rich phase, which originated from the higher solubility of 1-octene in the PEGs at higher temperature.

The parameter $w_2/(w_2 + w_3)$ gives the 1-octene mass fraction in PEGs on a CO_2-free basis. The parameters of the systems under different conditions are given in Table 1 and shown in Figure 2. It can be known that the enhancement of dissolution of 1-octene by CO_2 is more pronounced on a CO_2-free basis.

The dependence of mass fraction of CO_2 in the PEG-rich phase on pressure is illustrated in Figure 3. As expected, the mass fraction of CO_2 increased continuously with increasing pressure. It can also be seen that the solubility of CO_2 in the PEG-rich phase decreased with increasing temperature at all the pressures. It can be known from Figure 3 that the mass fraction of CO_2 in the PEG-rich phase increased with the increase of molecular weight of PEG. This is probably due to the weaker polarity of larger PEG.

Conclusion

The vapor−liquid equilibria for CO_2 + 1-octene + PEG have been determined in the temperature range from 308.15 K to 328.15 K at pressures up to 10 MPa. It is shown that the mass fraction of 1-octene in the PEG-rich phase increases with increasing pressure in the low pressure range and then decreases after passing through a maximum. An increase in molecular weight of PEGs results in an increase in the mass fraction of the olefin in the PEG-rich phase. The solubility of the CO_2 can considerably enhance the dissolution of 1-octene in PEGs under suitable conditions. The mass fraction of CO_2 increases continuously with increasing pressure and decreases as temperature rises.

Literature Cited

(1) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem.* **2005**, *7*, 64–82.
(2) Chen, J.; Spear, S. K.; Huddleston, J. G.; Holbrey, J. H.; Swatloski, R. P.; Rogers, R. D. Application of poly(ethylene glycol)-based aqueous biphasic systems as reaction and reactive extraction media. *Ind. Eng. Chem. Res.* **2004**, *43*, 5358–5364.
(3) Leininger, N. F.; Gainer, J. L.; Kirwan, D. J. Effect of aqueous PEG or PPG solvents on reaction selectivity and Gibbs energies. *AIChE J.* **2004**, *50*, 511–517.
(4) Wang, L.; Zhang, Y. H.; Liu, L. F.; Wang, Y. G. Palladium-catalyzed homocoupling and cross-coupling reactions of aryl halides in poly(ethylene glycol). *J. Org. Chem.* **2006**, *71*, 1284–1287.
(5) Wang, J.; Cai, F.; Wang, E.; He, L. N. Supercritical carbon dioxide and poly(ethylene glycol): an environmentally benign biphasic solvent system for aerobic oxidation of styrene. *Green Chem.* **2007**, *9*, 882–887.
(6) Hou, Z. S.; Theyssen, N.; Brindmann, A.; Leitner, W. Biphasic aerobic oxidation of alcohols catalyzed by poly(ethylene glycol)-stabilized Palladium nanoparticles in supercritical carbon dioxide. *Angew. Chem., Int. Ed.* **2005**, *44*, 1346–1349.
(7) Heldebrant, D. J.; Jessop, P. G. Liquid poly(ethylene glycol) and supercritical carbon dioxide: a benign biphasic solvent system for use and recycling of homogeneous catalysts. *J. Am. Chem. Soc.* **2003**, *125*, 5600–5601.
(8) Komoto, I.; Kobayashi, S. Lewis acid catalysis in a supercritical carbon dioxide ($scCO_2$)-poly(ethylene glycol) derivatives (PEGs) system: remarkable effect of PEGS as additives on reactivity of $Ln(OTf)_3$-catalyzed Mannich and aldol reactions in $scCO_2$. *Chem. Commun.* **2001**, *18*, 1842–1843.
(9) Reetz, M. T.; Wiesenhofer, W. Liquid poly(ethylene glycol) and supercritical carbon dioxide as a biphasic solvent system for lipase-catalyzed esterification. *Chem. Commun.* **2004**, *23*, 2750–2751.
(10) Wiesmet, V.; Weidner, E.; Behme, S.; Sadowski, G.; Arlt, W. Measurement and modeling of high-pressure phase equilibria in the systems polyethyleneglycol (PEG)-propane, PEG-nitrogen and PEG-carbon dioxide. *J. Supercrit. Fluids* **2000**, *17*, 1–12.
(11) Lopes, J. A.; Gourgouillon, D.; Pereira, P. J.; Ramos, A. M.; Nunes da Ponte, M. On the effect of polymer fractionation on phase equilibrium in CO_2 + poly(ethylene glycol)s systems. *J. Supercrit. Fluids* **2000**, *16*, 261–267.
(12) Gourgouillon, D.; Nunes da Ponte, M. High pressure phase equilibria for poly(ethylene glycol)s + CO_2: experimental results and modeling. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5369–5375.
(13) Matsuyama, K.; Mishima, K. Phase behavior of CO_2 + polyethylene glycol + ethanol at pressures up to 20 MPa. *Fluid Phase Equilib.* **2006**, *249*, 173–178.
(14) Hou, M. Q.; Liang, S. G.; Zhang, Z. F.; Song, J. Y.; Jiang, T.; Han, B. X. Determination and modeling of solubility of CO_2 in PEG200 + 1-pentanol and PEG200 + 1-octanol mixtures. *Fluid Phase Equilib.* **2007**, *258*, 108–114.
(15) Zhang, Z. F.; Wu, W. Z.; Liu, Z. M.; Han, B. X.; Gao, H. X.; Jiang, T. A study of tri-phasic behavior of ionic liquid-methanol-CO_2 systems at elevated pressures. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2352–2357.
(16) Liu, Z. M.; Wu, W. Z.; Han, B. X.; Dong, Z. X.; Zhao, G. Y.; Wang, J. Q.; Jiang, T.; Yang, G. Y. Study on the Phase Behaviors, Viscosities, and thermodynamic properties of $CO_2/[C_4mim][PF_6]/$ methanol system at elevated pressures. *Chem.−Eur. J.* **2003**, *9*, 3897–3903.

Received for review January 09, 2008. Accepted March 10, 2008. This work was supported by the National Natural Science Foundation of China (20633080) and the National Key Basic Research Project of China (2006CB202504).

JE800025S