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Vapor−Liquid Equilibria of Binary Carbon Dioxide + Alkyl Carbonate Mixture Systems

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We measured binary vapor liquid equilibrium data of the carbon dioxide + dimethyl carbonate system and the carbon dioxide + diethyl carbonate system at temperatures from 310 K to 340 K. A circulating type apparatus with on-line gas chromatography was used in this study. The measured data were correlated well by the Peng−Robinson equation of state using van der Waals one fluid mixing rules.

Introduction

Dimethyl carbonate (DMC) is a good nontoxic substitute for corrosive and toxic dimethyl sulfate, methyl halide, and phosgene in methylation and carbonylation reactions, respectively.[1−3] As a nonaqueous electrolyte component, it is applied to lithium rechargeable batteries.[4] It is used as an intermediate for preparing the carbamates, isocyanates, and polycarbonates,[3,4] and it is also used as a fuel additive[5] and solvent.[3]

The phosgenation of methanol was an important method to synthesize DMC until the 1980s. This process had the disadvantage of using or generating toxic and corrosive chemicals, such as phosgene and hydrogen chloride. At present DMC is synthesized mainly by oxidative carbonylation of methanol.[1−3] In the past decade, many research groups have made a study of the direct synthesis of DMC starting from carbon dioxide (CO_2)[6−10] and its industrial manufacturing process.[11,12] This method is attractive due to various advantages. Unlike other methods using or producing toxic or corrosive chemicals, it uses CO_2 and methanol as raw materials and produces DMC and water. CO_2 is an environmentally benign and thermodynamically stable compound. Moreover, it is nontoxic, nonflammable, and cheap, and its reactivity in the supercritical region is dramatically increased. Besides, separation from the reaction mixture is relatively easy.

Phase equilibrium data are essential to design the new process and to find the optimum operating conditions for the separation and reaction processes. There are a few vapor liquid equilibrium data for the above process (binary DMC + water,[12] CO_2 + water,[13−15] CO_2 + methanol,[16−19] water + methanol,[20,21] and DMC + methanol[22−25]), but the data for the CO_2 + DMC system[12] are scarce. Therefore, we measured the binary vapor liquid equilibria of CO_2 + DMC at temperatures from 310.23 K to 340.27 K. The binary vapor liquid equilibria of CO_2 + diethyl carbonate (DEC) at temperatures from 320.31 K to 340.28 K were also measured to study the phase behavior of alkyl carbonates in CO_2 media.

Experimental Section

Chemicals. CO_2 of 99.99% purity was supplied by Korean industrial gases. DMC of minimum 99+% (HPLC grade) purity was supplied by Aldrich. DEC of minimum 99+% (HPLC grade) purity was supplied by Aldrich. All components were used without further purification in these experiments.

Apparatus. Details of this apparatus were given in our previous studies.[26] An equilibrium cell was made of type-316 stainless steel, and its internal volume was approximately 320 mL. Two magnetic pumps were used to circulate the vapor and liquid phases separately to attain eqilibrium conditions quickly, and two sampling loops were also used. The cell had two reinforced glass windows of 19 mm thickness on both sides of the cell, through which the phase boundary could be observed. We used a gas booster pump for charging CO_2 into the cell, and a liquid pump for alkyl carbonates. The temperature of the system was monitored with a 100 Ω platinum resistance thermometer (PRT), model 5627 by Hart Scientific Co., with an accuracy of 0.05 K, and a 1502A digital indicator by Hart Scientific Co. The PRT was calibrated to the international temperature scale of 1990 (ITS-90), and it is traceable to the National Institute of Standards and Technology (NIST). A model Super TJE (<1500 psia) pressure transducer by Sensotec Co. connected to a model L20010WM1 digital indicator by Laurel was used to measure the pressure of the system. The estimated accuracy of the digital pressure gauge is 0.05%. An on-line gas chromatograph with a thermal conductivity detector (TCD) was used to analyze the vapor and liquid phase compositions. A Rheodyne 7413 valve with a 0.5 μL sampling loop and a Rheodyne 7010 valve with a 10 μL sampling loop were used to trap liquid and vapor samples, separately. A packed column with OV17 packing material (length, 6 m; mesh size, 80/100; 1/8 in. stainless steel; from Restek) was used, and we used helium gas as a carrier. To calibrate DMC, DEC, and CO_2, a Hamilton microliter syringe with a 0.5 μL volume for liquids and a Hamilton gastight syringe (500 μL) were used.

Experimental Procedure. After the cell was evacuated, an alkyl carbonate was injected into the cell, and then CO_2 was charged. Two magnetic pumps were turned on to circulate vapor and liquid phases. When equilibrium was

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Table 1. Physical Properties

	CO_2	$C_3H_6O_3$	$C_5H_{10}O_3$
T_c/K	304.12[a]	557.0[a]	576.0[b]
P_c/bar	73.74[a]	48.0[a]	33.9[b]
ω	0.225[a]	0.336[a]	0.485[b]

[a] Reference 28. [b] These properties are estimated by using Lydersen's method.[29]

Table 2. Measured Vapor−Liquid Equilibrium Data of the CO_2 + DMC System

P/bar	x_1	y_1	P/bar	x_1	y_1
		T = 310.27 K			
8.63	0.1431	0.9525	43.80	0.6273	0.9917
18.97	0.3019	0.9818	55.47	0.7648	0.9930
25.56	0.3919	0.9885	67.14	0.8867	0.9931
31.90	0.4809	0.9879	72.46	0.9290	0.9934
37.18	0.5473	0.9907			
		T = 320.36 K			
8.27	0.1140	0.9388	57.57	0.6820	0.9885
16.64	0.2250	0.9699	70.84	0.8162	0.9888
25.53	0.3356	0.9778	76.97	0.8597	0.9879
32.19	0.4144	0.9850	81.40	0.8950	0.9866
42.50	0.5269	0.9881			
		T = 330.30 K			
12.37	0.1477	0.9587	52.18	0.5565	0.9842
25.09	0.2914	0.9755	74.03	0.7490	0.9829
34.38	0.3876	0.9812	85.30	0.8307	0.9813
42.99	0.4707	0.9828	92.56	0.8954	0.9741
61.36	0.6397	0.9844			
		T = 340.27 K			
10.19	0.1076	0.9276	70.82	0.6412	0.9787
24.03	0.2450	0.9645	82.69	0.7353	0.9776
36.84	0.3616	0.9741	94.13	0.8141	0.9727
48.66	0.4667	0.9773	99.96	0.8569	0.9630
58.52	0.5445	0.9786			

Table 3. Measured Vapor−Liquid Equilibrium Data of the CO_2 + DEC System

P/bar	x_1	y_1	P/bar	x_1	y_1
		T = 320.32 K			
7.15	0.1194	0.9743	44.41	0.5835	0.9949
19.02	0.2961	0.9894	60.79	0.7370	0.9953
26.60	0.3903	0.9923	73.65	0.8460	0.9945
33.51	0.4706	0.9941	84.11	0.9426	0.9906
		T = 330.33 K			
7.46	0.1095	0.9689	46.10	0.5374	0.9930
17.15	0.2367	0.9854	60.69	0.6554	0.9936
24.34	0.3204	0.9906	71.75	0.7438	0.9932
34.58	0.4301	0.9922	83.30	0.8227	0.9916
		T = 340.29 K			
11.83	0.1490	0.9762	55.57	0.5587	0.9910
21.47	0.2566	0.9848	67.47	0.6439	0.9910
32.28	0.3625	0.9885	77.61	0.7138	0.9903
40.58	0.4357	0.9900	90.08	0.7960	0.9878

reached, the vapor and liquid samples were taken into the gas chromatograph to measure the vapor and liquid compositions.

Results and Discussion

Vapor liquid equilibrium data for the CO_2 + DMC system at (340.27, 330.30, 320.36, and 310.27) K and the CO_2 + DEC system at (340.29, 330.33, and 320.32) K are given in Tables 2 and 3, respectively. Comparisons between experimental and calculated results are shown in Figures 1 and 2.

The experimental data were correlated with the Peng−Robinson equation of state (EOS)[27] with van der Waals one fluid mixing rules.

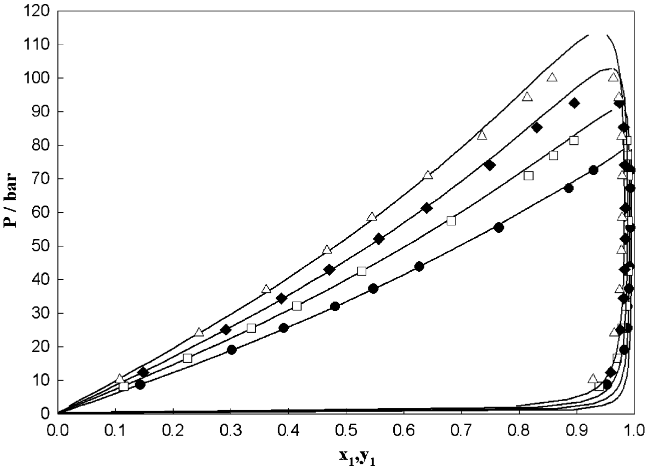

Figure 1. Vapor−liquid equilibria of the CO_2 (1) + DMC (2) system: (—) P−R EOS; experimental data at (△) T = 340.27 K; (◆) 330.30 K; (□) 320.36 K; (●) 310.27 K.

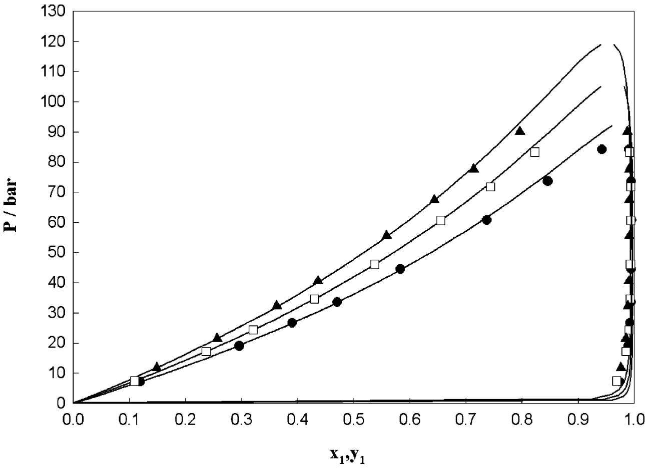

Figure 2. Vapor−liquid equilibria of the CO_2 (1) + DEC (2) system: (—) P−R EOS; experimental data at (▲) T = 340.29 K; (□), 330.33 K; (●) 320.32 K.

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{1}$$

$$a(T_c) = 0.45724\frac{R^2 T_c^{\,2}}{P_c} \tag{2}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{4}$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{5}$$

where

$$a_{ij} = (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \tag{6}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - \eta_{ij}) \tag{7}$$

Table 4. Interaction Parameters and AADs for the CO_2 + DMC and CO_2 + DEC Systems

CO_2 + DMC				CO_2 + DEC			
T/K	k_{12}	η_{12}	AAD[a]/%	T/K	k_{12}	η_{12}	AAD[a]/%
310.27	−0.0187	−0.0052	0.67	320.32	−0.0147	0.0057	1.64
320.36	−0.0172	−0.0067	1.09	330.33	−0.0150	0.0073	0.70
330.30	−0.0272	−0.0133	1.44	340.29	−0.0192	0.0045	0.92
340.27	−0.0313	−0.0170	1.94	overall	−0.0184	0.0035	1.20
overall	−0.0245	−0.0112	1.46				

[a] AAD/% = $(100/N)\sum_i^N |P_{i(\mathrm{exp})} - P_{i(\mathrm{cal})}|/P_{i(\mathrm{exp})}$.

The binary interaction parameters (k_{ij} and η_{ij}) and the Marquardt algorithm were used to minimize the objective function,

$$\mathrm{OF} = \sum_i^N \left|\frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}}\right| \qquad (8)$$

where N is the number of experimental data points and P_{exp} and P_{cal} are the experimental and the calculated pressures, respectively. The physical properties of each component are listed in Table 1. The binary interaction parameters for the CO_2 + DMC system and the CO_2 + DEC system are listed in Table 4.

As can be seen in Figures 1 and 2, the solubility of CO_2 in DMC and DEC decreases with increasing temperature and decreasing pressure. Although the calculated pressures are higher than the experimental data when approaching the critical region, the agreement is satisfactory with an absolute average deviation less than 2% for both systems.

Conclusions

Isothermal vapor−liquid data of the binary CO_2 + DMC system and the CO_2 + DEC system were obtained at various temperatures from subcritical to the near-critical region. A circulation type apparatus was used in this study. The measured data were correlated well by the Peng−Robinson EOS using the van der Waals one fluid mixing rule with two adjustable parameters.

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