Determination and Correlation of Excess Molar Enthalpies of the Binary Carbon Dioxide + Diisopropyl Ether (DIPE) System at Temperatures from (298.15 to 308.15) K and Pressures from (5.0 to 7.5) MPa

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The excess molar enthalpies (H^E) of the carbon dioxide + diisopropyl ether system were measured in the vicinity of the critical point of carbon dioxide using a flow-type isothermal microcalorimeter at temperatures from (298.15 to 308.15) K and pressures from (5.0 to 7.5) MPa. Mixtures showed strong exothermic behavior in these regions. The minimum negative value of H^E found in this study was about −7.8 kJ·mol^{-1} at 298.15 K and 5.0 MPa. The experimental results were represented using a composition-dependent equation and the Peng−Robinson equation of state with van der Waals one fluid mixing rules.

Introduction

When a carbon dioxide (CO_2) and an organic solvent are mixed in the vicinity of the critical point of CO_2 ($T_c = 304.12$ K, $P_c = 7.374$ MPa),[1] an exothermic behavior, that is, negative heats of mixing (excess molar enthalpy (H^E)), is observed. The exothermic value is extremely large in comparison with its behavior for mixing of normal liquids at low pressure. These heat effects have come to be recognized as a characteristic that may lead to the development of a new energy supply system,[2] for example, a heat pump. Therefore, many researchers have studied the H^E data, particularly Christensen et al., who have made detailed measurements of various binary mixtures containing supercritical CO_2[3–6] using a calorimeter for high pressures such that a precise measurement of H^E is possible. As an example of their results, they have measured the H^E of the CO_2 + toluene system at 308.15 K, and the lowest negative value of H^E, about −5.7 kJ·mol^{-1}, was found at 6.98 MPa.[5] In addition, the group of Zhao and Tremaine have determined the H^E of eight binary CO_2 + solvent (including *N*-methyl-2-pyrrolidone,[7] *N*-methyl-*ε*-caprolactam,[8] ethylene glycol dimethyl ether,[9] 2-methoxyethyl ether)[9] systems at temperatures (298.15 to 308.15) K and pressures (7.5 to 12.6) MPa, and their experimental results showed the minimum value of about −5.3 kJ·mol^{-1} in the CO_2 + ethylene glycol dimethyl ether system at 308.15 K and 7.5 MPa. Our group also measured four binary CO_2 and alcohol systems (methanol,[10,11] 2-propanol,[12] 2-butanol,[12] and 2-methyl-1-propanol[13]) and a ternary CO_2 + ethanol + water system,[13] and we found that the H^E data near the critical point of CO_2 often show a low negative deviation (about −4 kJ·mol^{-1}) in comparison with their behavior for mixing of normal liquids at low pressure. In addition, recently, we have selected two dialkyl carbonates (dimethyl carbonate (DMC)[14] and diethyl carbonate (DEC)[15]) that are environmentally benign solvents[16] to couple with CO_2, and the H^E data for these systems have been determined. As a result, an extremely low H^E value, that is, a maximum about −9.0 kJ·mol^{-1}, was obtained. This minimum negative value is about 1.6 times compared with that of the CO_2 + solvent systems reported previously in the literature. Such larger minimum behaviors of H^E have not been reported elsewhere.

With respect to the H^E in the critical region of CO_2 mentioned above, we have paid attention to the following points. First, the large heat effects can be obtained at ambient temperatures by mixing CO_2 and solvent, since the critical temperature of CO_2 is low (304.12 K). Second, when the heat cycle system is developed using these H^E, the design of the cycle for the mixing and separation of fluids will be possible because CO_2 (vapor phase) and solvent (liquid phase) can be easily separated. This separation of vapor and liquid phases is caused by reducing the pressure slightly from the vicinity of the critical pressure of CO_2. Moreover, natural refrigerants such as CO_2 have attracted attention as alternatives of the chlorofluorocarbon and hydrochlorofluorocarbons.[17,18] Therefore, using these features, the large heat effects obtained by mixing CO_2 with the environmental benign dialkyl carbonate could be applied to the environmentally benign heat supply system. Thus, we have designed an environmentally benign heat supply system using the H^E of the CO_2 + DEC system,[19] and an examination of the recovery of the heats of mixing was performed. As a result, a maximum of 5.6 kJ·mol^{-1} for the recovered heat, about 70 % of the maximum heat of mixing, could be obtained.[20]

The main aim of this study is to select a solvent for mixing with CO_2. Selection of the solvent is important for the determination of the operating conditions of this heat supply system. In this study, we investigated diisopropyl ether (DIPE) as the second component for mixing with CO_2, considering our previous results of the H^E data of the two esters, DMC and DEC. Zhao and Tremaine have also examined ethylene glycol dimethyl ether[9] and 2-methoxyethyl ether.[9] We have made detailed measurements of the H^E data for the CO_2 + DIPE system at temperatures from (298.15 to 308.15) K and pressures from (5.0 to 7.5) MPa, using a flow isothermal microcalorimeter. The experimental H^E data were correlated by the polynomial expression model and the Peng−Robinson (PR) equation of state (EOS) coupled with the van der Waals one fluid mixing rule. Literature data of H^E for this mixture have not been reported previously.

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Table 1. Densities ρ at $T = 283.15$ K of the Pure Components

P/MPa	ρ/kg·m^{-3}	
	CO_2[a]	DIPE[b]
5.0	868.63	739.41
5.5	875.48	739.95
6.0	881.78	740.49
6.5	887.63	741.02
7.0	893.11	741.54
7.5	898.26	742.07

[a] Span and Wagner.[22,23] [b] Ihmels et al.[24]

Experimental Section

Apparatus and Procedures. A high-pressure flow-type isothermal microcalorimeter (Calorimetry Sciences Corporation, Utah, USA) was used to measure H^E. It consists of a mixing unit, a constant temperature water bath, two high-pressure ISCO syringe pumps for sample supply, a cooling circulation system for the syringe, a pressure adjustment device, a degassing unit, and a personal computer for signal collection and data processing. Measurements can be made from (233 to 353) K and from (0.1 to 20) MPa. Details of the experimental apparatus and procedure have been described elsewhere.[10–12,21] The temperature stability of the water bath is within ± 0.0005 K. The reproducibility of our measurements can be estimated to be within ± 1.0 % (maximum absolute error is 8 J·mol^{-1}), with the uncertainty due primarily to the high sensitivity of H^E values to small changes in temperature and pressure. In this study, the total flow rate was varied from (0.05 to 0.20) cm^3·min^{-1}, and the dependence of the total flow rate for the measurement of H^E was considered. The optimum total flow rate was 0.10 cm^3·min^{-1} for all cases studied.

For our measurements, each pure component was charged into the ISCO syringe after degassing. The temperatures of the syringes and their contents were kept constant in a water thermostat. In this study, a supply of pure components was carried out at a constant temperature of 283.15 K, which is about 20 K lower than the critical temperature of CO_2, to prevent variations in the density resulting from slight changes in the temperature and pressure.

Materials. The DIPE used in this study was first grade pure reagent (Wako Pure Chemical Industry, Ltd., Japan) and was used after removing trace water with molecular sieves. The mole purity of DIPE was checked by gas chromatography and found to be above 99.9 %. The volume fraction purity of the CO_2 was 99.99 % (Showa Carbonic Acid Company, Ltd., Japan). Prior to use, the CO_2 was filtered through a 0.5 μm in-line filter (NUPRO Company).

Flow rates measured in cm^3·min^{-1} at a constant temperature of 283.15 K were converted to mol·min^{-1} and to mole fractions using the densities of the pure materials estimated as follows. The densities of CO_2 at 283.15 K and the pressures studied were calculated with the EOS for CO_2 proposed by Span and Wagner.[22,23] The densities of DIPE at 283.15 K and the pressures studied were obtained by interpolating the literature values of Ihmels et al.[24] The estimated densities of pure components are given in Table 1. The uncertainty of the calculated mole fraction is ± 0.0001.

Results and Discussion

The values of H^E were determined for the CO_2 + DIPE system over the entire composition range at temperatures from (298.15 to 308.15) K under pressures from (5.0 to 7.5) MPa. The experimental results of H^E are summarized in Table 2.

Table 2. Experimental Excess Molar Enthalpies for the System CO_2 (1) + DIPE (2) at Different Temperatures

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
		298.15 K, 5.0 MPa			
0.1255	−1169	0.6452	−6050	0.8642[a]	−6942
0.2326	−2203	0.6906	−6479	0.8911[a]	−5267
0.3249	−3069	0.7317	−6796	0.9160[a]	−3990
0.4054	−3822	0.7692	−7156	0.9392[a]	−2736
0.4762	−4493	0.8036	−7495	0.9609[a]	−1594
0.5389	−5026	0.8351	−7726	0.9811[a]	−573
0.5949	−5585	0.8470[a]	−7769		
		298.15 K, 5.5 MPa			
0.1263	−1158	0.6468	−5594	0.8918	−7621
0.2338	−2075	0.6921	−6050	0.9019	−7673
0.3265	−2853	0.7331	−6375	0.9166[a]	−7476
0.4071	−3603	0.7705	−6747	0.9396[a]	−5528
0.4780	−4147	0.8047	−6996	0.9611[a]	−3402
0.5407	−4746	0.8361	−7264		
0.5966	−5211	0.8650	−7436		
		298.15 K, 6.0 MPa			
0.1270	−972	0.6483	−4959	0.8924	−6806
0.2350	−1848	0.6934	−5311	0.9171	−6921
0.3279	−2597	0.7344	−5583	0.9310	−6837
0.4087	−3184	0.7716	−5843	0.9400	−6969
0.4796	−3723	0.8057	−6172	0.9614	−6872
0.5423	−4218	0.8370	−6370	0.9813	−6209
0.5982	−4575	0.8658	−6637		
		303.15 K, 5.0 MPa			
0.1255	−1050	0.6452	−6093	0.8911[a]	−3059
0.2326	−2199	0.6906	−6501	0.9160[a]	−2305
0.3249	−3100	0.7317	−6849	0.9392[a]	−1540
0.4054	−3859	0.7692[a]	−7074	0.9609[a]	−807
0.4762	−4513	0.8036[a]	−5924	0.9811[a]	−177
0.5389	−5120	0.8351[a]	−4923		
0.5949	−5647	0.8642[a]	−4076		
		303.15 K, 5.5 MPa			
0.1263	−1163	0.6468	−5773	0.8918[a]	−4819
0.2338	−2114	0.6921	−6177	0.9166[a]	−3714
0.3265	−2991	0.7331	−6529	0.9396[a]	−2337
0.4071	−3685	0.7705	−6845	0.9611[a]	−1390
0.4780	−4301	0.8047	−7083	0.9812[a]	−395
0.5407	−4861	0.8361[a]	−7287		
0.5966	−5353	0.8650[a]	−6000		
		303.15 K, 6.0 MPa			
0.1270	−1065	0.6483	−5507	0.8924	−7157
0.2350	−2006	0.6934	−5857	0.9171[a]	−5338
0.3279	−2826	0.7344	−6174	0.9400[a]	−3615
0.4087	−3512	0.7716	−6449	0.9614[a]	−2326
0.4796	−4073	0.8057	−6703	0.9813[a]	−749
0.5423	−4579	0.8370	−6956		
0.5982	−5042	0.8658	−7126		
		308.15 K, 5.0 MPa			
0.1255	−1226	0.6452	−6072	0.8911[a]	−2140
0.2326	−2218	0.6906	−6474	0.9160[a]	−1540
0.3249	−3118	0.7317[a]	−5928	0.9392[a]	−950
0.4054	−3865	0.7692[a]	−5100	0.9609[a]	−447
0.4762	−4562	0.8036[a]	−4249	0.9811[a]	47
0.5389	−5118	0.8351[a]	−3444		
0.5949	−5619	0.8642[a]	−2781		
		308.15 K, 5.5 MPa			
0.1263	−1150	0.6468	−5853	0.8918[a]	−2936
0.2338	−2195	0.6921	−6227	0.9166[a]	−2131
0.3265	−2967	0.7331	−6576	0.9396[a]	−1387
0.4071	−3730	0.7705[a]	−6814	0.9611[a]	−732
0.4780	−4358	0.8047[a]	−5612	0.9812[a]	−77
0.5407	−4921	0.8361[a]	−4713		
0.5966	−5397	0.8650[a]	−3767		
		308.15 K, 6.0 MPa			
0.1270	−1158	0.6483	−5611	0.8658[a]	−5245
0.2350	−2065	0.6934	−5941	0.8924[a]	−4154
0.3279	−2899	0.7344	−6230	0.9171[a]	−3085
0.4087	−3571	0.7716	−6528	0.9400[a]	−2027
0.4796	−4276	0.8057	−6728	0.9614[a]	−1118
0.5423	−4695	0.8248	−6851	0.9813[a]	−228
0.5982	−5115	0.8370[a]	−6567		
		308.15 K, 6.5 MPa			
0.1277	−1062	0.6496	−5184	0.8930[a]	−6497
0.2361	−1940	0.6947	−5547	0.9175[a]	−4870
0.3292	−2669	0.7355	−5804	0.9403[a]	−3052
0.4101	−3294	0.7727	−6056	0.9616[a]	−1792
0.4811	−3851	0.8066	−6267	0.9814[a]	−528
0.5438	−4340	0.8378	−6522		
0.5996	−4783	0.8665	−6705		
		308.15 K, 7.0 MPa			
0.1283	−970	0.6509	−4748	0.8935	−6098
0.2370	−1761	0.6958	−5077	0.9179	−6144
0.3304	−2458	0.7366	−5288	0.9406[a]	−5888
0.4114	−3046	0.7736	−5562	0.9618[a]	−3405
0.4824	−3587	0.8075	−5776	0.9815[a]	−1199
0.5451	−3976	0.8385	−5928		
0.6009	−4399	0.8671	−6020		
		308.15 K, 7.5 MPa			
0.1289	−836	0.6520	−4071	0.8940	−5358
0.2380	−1488	0.6969	−4364	0.9183	−5251
0.3315	−2041	0.7376	−4613	0.9409	−5174
0.4127	−2613	0.7745	−4798	0.9620	−4909
0.4837	−3043	0.8083	−4971	0.9700[a]	−2093
0.5464	−3428	0.8392	−5178	0.9816[a]	−1281
0.6021	−3781	0.8677	−5250	0.9891[a]	359

[a] Two-phase region.

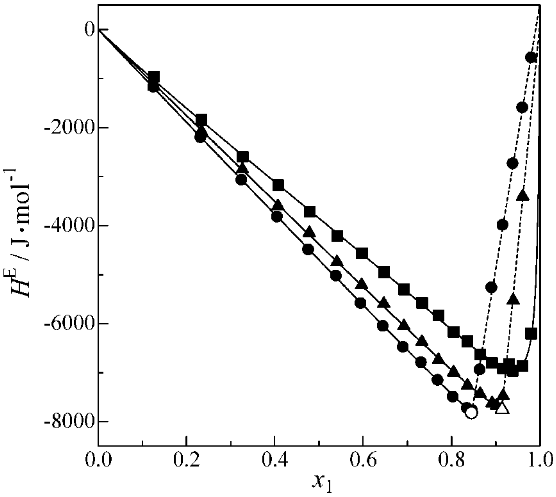

Figure 1. Experimental excess molar enthalpies for the system CO_2 (1) + DIPE (2) at 298.15 K. Determined herein: ●, 5.0 MPa; ▲, 5.5 MPa; ■, 6.0 MPa; —, eq 1; ---, eq 8. Calculated solubility limit points: ○, 5.0 MPa; △, 5.5 MPa.

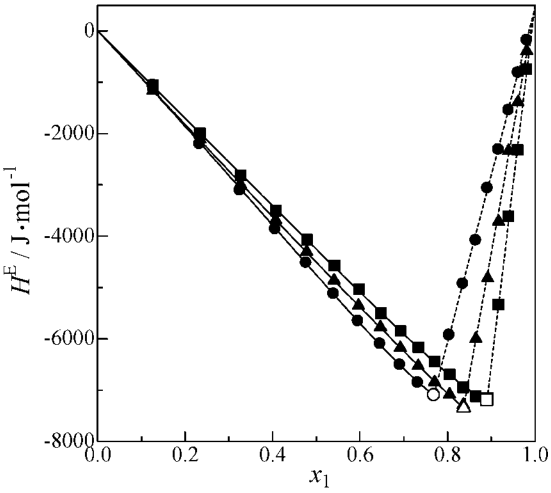

Figure 2. Experimental excess molar enthalpies for the system CO_2 (1) + DIPE (2) at 303.15 K. Determined herein: ●, 5.0 MPa; ▲, 5.5 MPa; ■, 6.0 MPa; —, eq 1; ---, eq 8. Calculated solubility limit points: ○, 5.0 MPa; △, 5.5 MPa; □, 6.0 MPa.

Figures 1 to 3 show the H^E vs CO_2mole fraction isobars studied at (298.15, 303.15, and 308.15) K, respectively. Mixtures in the region studied show large exothermic mixing. However, at (5.0 and 7.5) MPa and temperatures of 308.15 K, mixtures show a slight endothermic mixing in the extremely CO_2-rich region. The lowest negative value of H^E at each temperature and pressure is about (−5.4 to −7.8) kJ·mol^{-1}. The pressure which shows the lowest negative value of H^E is 5.0 MPa at 298.15 K, 5.5 MPa at 303.15 K, and 6.0 MPa at 308.15 K, respectively. Pressure dependency of this H^E value, $(\partial H^E_{\text{min}}/\partial P)_T$, is relatively small at (298 and 303) K. At 308 K, the value of $(\partial H^E_{\text{min}}/\partial P)_T$ somewhat increases at (7.0 and 7.5) MPa. These tendencies are similar to the mixtures of CO_2 + DMC and + DEC.[14,15] When these behaviors are compared with our previous experimental H^E data of CO_2 + alcohol systems at 308 K and (7.5 to 8.5) MPa,[10–13] the H^E sharply becomes less negative with a slight change of pressure, unlike the three mixtures mentioned above. At each temperature and pressure, the mole fraction of CO_2 at which the minimum negative value appears is shifted to the CO_2-rich side with an increase in the pressure. The minimum negative value of H^E found in this study was about −7.8 kJ·mol^{-1} at 298.15 K and 5.0 MPa. At all temperatures and pressures except 298.15 K and 6.0 MPa, the H^E values vary linearly with the composition in the CO_2-rich region, which corresponds to the two-phase region.

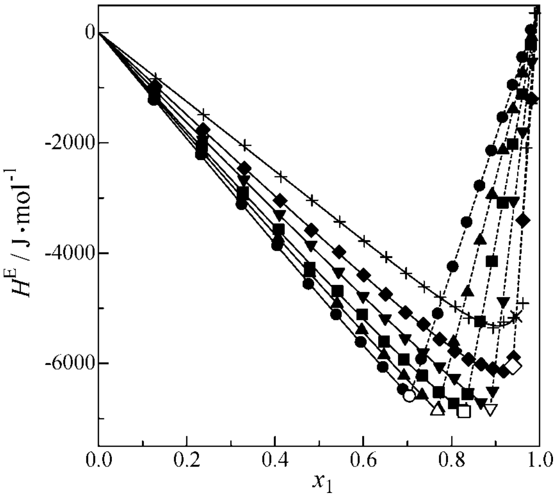

Figure 3. Experimental excess molar enthalpies for the system CO_2 (1) + DIPE (2) at 308.15 K. Determined herein: ●, 5.0 MPa; ▲, 5.5 MPa; ■, 6.0 MPa; ▼, 6.5 MPa; ◆, 7.0 MPa; +, 7.5 MPa; —, eq 1; ---, eq 8. Calculated solubility limit points: ○, 5.0 MPa; △, 5.5 MPa; □, 6.0 MPa; ▽, 6.5 MPa; ◇, 7.0 MPa; ×, 7.5 MPa.

Table 3. Pure Component Critical Data and Acetric Factor ω in the Calculations Using the PR EOS

component	T_c/K	P_c/MPa	ω
CO_2	304.12[a]	7.374[a]	0.225[a]
DIPE	500.0[b]	2.878[b]	0.338[b]

[a] Poling et al.[1] [b] DDB 2006.[29]

The lowest negative value of H^E obtained in this study is somewhat higher than that of H^E in the two binary systems CO_2 + DMC and + DEC, and the minimum behavior of H^E which falls below that of these two mixtures could not be obtained. However, the lowest negative value, about −7.8 kJ·mol^{-1}, is about 1.4 times compared with that reported previously. Detailed discussions concerning the extreme negative value of H^E containing supercritical fluids have been performed by several authors, including the research group of Christensen et al. using their experimental results of the mixtures CO_2 + pentane[3] and + toluene[4] and by the group of Renuncio et al. on the basis of four nitrous oxide + hydrocarbon mixtures.[25–28] They have discussed the behavior of H^E in the vicinity of the critical point or supercritical region of CO_2 or nitrous oxide in detail with regards to the state of the pure components and the mixture and the differences in the densities between CO_2 and the solvent. In this study, we also discuss the behavior of the large heat effect for the system containing CO_2 + DIPE.

Densities of CO_2 at the temperature and pressure ranges studied by the EOS by Span and Wagner[22] are about (131 to 273) kg·m^{-3}. On the other hand, those of DIPE calculated from the literature value by Ihmels et al.[24] are (715 to 726) kg·m^{-3}. When the densities of CO_2 and DIPE are compared, large differences in densities between CO_2 and DIPE are recognized, and the density of CO_2 is much lower than that of DIPE. The state of CO_2 is supercritical at 308.15 K and 7.5 MPa and vapor at the other temperatures and pressures. In contrast, that of DIPE is liquid at all temperatures and pressures since the temperature studied is far away from the critical temperature of DIPE (T_c = 500.0 K).[29] When two

Table 4. Determined Parameters and Deviations between Experimental and Calculated H^E for the System CO_2 (1) + DIPE (2) Using Equations 1 and 8

parameter	5.0 MPa	5.5 MPa	6.0 MPa	6.5 MPa	7.0 MPa	7.5 MPa
298.15 K, one-phase region						
k	0.9947	0.9924	0.9900			
a_0/J·mol^{-1}	$-1.8798 \cdot 10^4$	$-1.7527 \cdot 10^4$	$-1.53994 \cdot 10^4$			
a_1/J·mol^{-1}	$1.0273 \cdot 10^2$	$-5.3948 \cdot 10^1$	$3.79750 \cdot 10^2$			
a_2/J·mol^{-1}			$-1.00833 \cdot 10^3$			
Δ_1[a]/J·mol^{-1}	15	24	32			
Δ_2[b]/%	0.2	0.3	0.5			
298.15 K, two-phase region						
A/J·mol^{-1}	$-5.3606 \cdot 10^4$	$-9.1369 \cdot 10^4$				
B/J·mol^{-1}	$5.4125 \cdot 10^4$	$9.1471 \cdot 10^4$				
Δ_1[a]/J·mol^{-1}	53	70				
Δ_2[b]/%	0.7	0.9				
298.15 K, overall						
Δ_1[a]/J·mol^{-1}	29	31	32			
Δ_2[b]/%	0.4	0.4	0.5			
303.15 K, one-phase region						
k	0.9400	0.9915	0.9812			
a_0/J·mol^{-1}	$-1.9011 \cdot 10^4$	$-1.80314 \cdot 10^4$	$-1.70164 \cdot 10^4$			
a_1/J·mol^{-1}	$-1.3731 \cdot 10^3$	$2.51795 \cdot 10^2$	$-1.38266 \cdot 10^2$			
Δ_1[a]/J·mol^{-1}	26	11	22			
Δ_2[b]/%	0.4	0.2	0.3			
303.15 K, two-phase region						
A/J·mol^{-1}	$-3.2137 \cdot 10^4$	$-4.7408 \cdot 10^4$	$-6.9821 \cdot 10^4$			
B/J·mol^{-1}	$3.2580 \cdot 10^4$	$4.7864 \cdot 10^4$	$7.0334 \cdot 10^4$			
Δ_1[a]/J·mol^{-1}	25	78	72			
Δ_2[b]/%	0.4	1.1	1.0			
303.15 K, overall						
Δ_1[a]/J·mol^{-1}	26	36	32			
Δ_2[b]/%	0.4	0.5	0.4			
308.15 K, one-phase region						
k	0.9749	0.9910	0.9800	0.9919	0.9810	0.9773
a_0/J·mol^{-1}	$-1.9039 \cdot 10^4$	$-1.8219 \cdot 10^4$	$-1.7467 \cdot 10^4$	$-1.6063 \cdot 10^4$	$-1.4750 \cdot 10^4$	$-1.2559 \cdot 10^4$
a_1/J·mol^{-1}	$3.5659 \cdot 10^1$	$2.9348 \cdot 10^2$	$3.6042 \cdot 10^2$	$3.6791 \cdot 10^2$	$1.2211 \cdot 10^2$	$-3.1167 \cdot 10^2$
a_2/J·mol^{-1}						$-1.2375 \cdot 10^2$
Δ_1[a]/J·mol^{-1}	10	13	24	16	15	21
Δ_2[b]/%	0.2	0.2	0.4	0.2	0.2	0.4
308.15 K, two-phase region						
A/J·mol^{-1}	$-2.3580 \cdot 10^4$	$-3.1243 \cdot 10^4$	$-4.3180 \cdot 10^4$	$-6.7241 \cdot 10^4$	$-1.1374 \cdot 10^5$	$-1.2195 \cdot 10^5$
B/J·mol^{-1}	$2.4075 \cdot 10^4$	$3.1760 \cdot 10^4$	$4.3759 \cdot 10^4$	$6.8061 \cdot 10^4$	$1.1468 \cdot 10^5$	$1.2338 \cdot 10^5$
Δ_1[a]/J·mol^{-1}	18	21	23	77	23	296
Δ_2[b]/%	0.3	0.3	0.3	1.2	0.4	5.5
308.15 K, overall						
Δ_1[a]/J·mol^{-1}	14	17	24	32	16	60
Δ_2[b]/%	0.2	0.2	0.4	0.5	0.3	1.1

[a] $\Delta_1 = \Sigma_k |H^E_{\text{exptl}} - H^E_{\text{calcd}}|_k/\text{NDP}$, where NDP is the number of data points per a given data set. [b] $\Delta_2 = (100/\text{NDP})\ \Sigma_k |(H^E_{\text{exptl}} - H^E_{\text{calcd}})/H^E_{\text{exptl(max)}}|_k$, where $H^E_{\text{exptl(max)}}$ is the maximum experimental H^E data in a given data set.

pure components, such as CO_2 and DIPE, which have differing states and densities, are mixed together, CO_2 is dissolved to DIPE, and the state of CO_2 changes from that of low-density fluid (supercritical or vapor) to that of liquid. As a consequence, the resulting mixture is liquid. For this reason, the enthalpies of condensation of CO_2 are thought to contribute mainly to the large heat effects found in this study.

Correlation

In this work, the experimental results for H^E in the homogeneous phase were correlated using the following polynomial expression model for the composition

$$H^E/\text{J}\cdot\text{mol}^{-1} = x_1(1 - x_1)\sum_{i=0}^{N-1} a_i(2x_1 - 1)^i/\{1 - k(2x_1 - 1)\} \tag{1}$$

where a_i and k are adjustable parameters; x_i is the liquid mole fraction of component i; and N is the number of adjustable parameters a_i. The experimental data were also represented using the PR EOS[30]

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{2}$$

where P is the pressure; R is the gas constant; T is the temperature; V_m is the molar volume; a is the energy parameter; and b is the size parameter. These parameters for pure component i, a_{ii} and b_i, were calculated by the following equations

$$a_{ii}(T) = \frac{0.45724 R^2 T_{c,i}^2}{P_{c,i}}\left[1 + \kappa_i\left(1 - \sqrt{\frac{T}{T_{c,i}}}\right)\right] \tag{3}$$

$$\kappa_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2 \tag{4}$$

$$b_i = \frac{0.07780 R^2 T_{c,i}}{P_{c,i}} \tag{5}$$

where $T_{c,i}$ and $P_{c,i}$ are the critical temperature and the critical pressure of pure component i, respectively, and ω_i is the acentric factor. In this study, the following van der Waals one fluid mixing rules were used for the mixture energy parameter a and the size parameter b

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

where k_{ij} is a binary interaction parameter. Pure component parameters T_c, P_c, and ω, necessary for calculating the a and b values of the pure components of interest in this study, are shown in Table 3.[1,29]

At the region where the two phases form, the linear section of H^E values was expressed using the following equation

$$H^E/\mathrm{J \cdot mol^{-1}} = A + Bx_1 \tag{8}$$

where A and B are adjustable parameters.

Fitting parameters, a_i and k in eq 1, k_{ij} in the PR EOS, and A and B in eq 8, were estimated so that the following objective function (F_{obj}) was minimized for each system by means of the Marquardt algorithm[31]

$$F_{obj} = \sum_{k=1}^{NDP} (H^E_{exptl} - H^E_{calcd})^2_k \tag{9}$$

where NDP is the number of experimental data points and H^E_{exptl} and H^E_{calcd} are the experimental and calculated H^E, respectively.

The estimated parameters of eqs 1, 6, and 8 and the absolute and relative deviations between the experimental and correlated H^E data are given in Tables 4 and 5 for eqs 1, 6, and 8, respectively. The value of N in eq 1 was set to 1 to 3 at each temperature and pressure for the H^E data, considering the correlation accuracy in the polynomial expression model. With respect to the PR EOS, the binary parameter k_{12} was determined at each temperature independent of the pressure. Deviations listed in Tables 4 and 5 indicate that both models give reasonable correlated results at all temperatures and pressures in the one-phase region and that the results from the polynomial expression model are better than those from the PR EOS. The results correlated by the polynomial expression model are shown graphically in Figures 1 to 3.

Table 5. Determined Parameters and Deviations between Experimental and Calculated H^E for the System CO_2 (1) + DIPE (2) Using the PR EOS

parameter	5.0 MPa	5.5 MPa	6.0 MPa	6.5 MPa	7.0 MPa	7.5 MPa
298.15 K, one-phase region: $k_{12} = -3.276\cdot10^{-2}$						
$\Delta_1{}^a/\mathrm{J\cdot mol^{-1}}$	125	183	260			
$\Delta_2{}^b/\%$	1.6	2.4	3.7			
298.15 K, overall containing two-phase region						
$\Delta_1{}^a/\mathrm{J\cdot mol^{-1}}$	100	165	260			
$\Delta_2{}^b/\%$	1.3	2.2	3.7			
303.15 K, one-phase region: $k_{12} = -4.645\cdot10^{-2}$						
$\Delta_1{}^a/\mathrm{J\cdot mol^{-1}}$	93	110	168			
$\Delta_2{}^b/\%$	1.3	1.5	2.3			
303.15 K, overall containing two-phase region						
$\Delta_1{}^a/\ \mathrm{J\cdot mol^{-1}}$	61	98	148			
$\Delta_2{}^b/\%$	0.9	1.4	2.1			
308.15 K, one-phase region: $k_{12} = -4.496\cdot10^{-2}$						
$\Delta_1{}^a/\mathrm{J\cdot mol^{-1}}$	54	75	115	154	189	269
$\Delta_2{}^b/\%$	0.8	1.1	1.7	2.3	3.1	5.0
308.15 K, overall containing two-phase region						
$\Delta_1{}^a/\mathrm{J\cdot mol^{-1}}$	35	50	83	133	163	273
$\Delta_2{}^b/\%$	0.5	0.7	1.2	2.0	2.6	5.1

[a] $\Delta_1 = \Sigma_k|H^E_{exptl} - H^E_{calcd}|_k/\mathrm{NDP}$, where NDP is the number of data points per a given data set. [b] $\Delta_2 = (100/\mathrm{NDP})\Sigma_k|(H^E_{exptl} - H^E_{calcd})/H^E_{exptl(max)}|_k$, where $H^E_{exptl(max)}$ is the maximum experimental H^E data in a given data set.

Table 6. Solubility Limits from H^E for the System CO_2 (1) + DIPE (2)

P/MPa	x_1	$H^E/\mathrm{J\cdot mol^{-1}}$ (calculated)
	298.15 K	
5.0	0.8458	−7826
5.5	0.9142	−7749
	303.15 K	
5.0	0.7686	−7096
5.5	0.8370	−7346
6.0	0.8905	−7191
	308.15 K	
5.0	0.7055	−6595
5.5	0.7677	−6862
6.0	0.8295	−6880
6.5	0.8878	−6814
7.0	0.9390	−6048
7.5	0.9467	−5145

Finally, we determined the liquid composition of CO_2 in the vapor−liquid equilibrium (VLE) of this mixture at temperatures and pressures where a two-phase region was formed. This liquid composition was obtained by combining eqs 1 and 8. The determined liquid compositions of CO_2, x_1, and the corresponding H^E are summarized in Table 6 and illustrated in Figures 1 to 3. In this study, comparison of the determined x_1 with the literature values of VLE was not attempted because the literature VLE of this mixture has not been reported.

Conclusions

Excess molar enthalpies were determined for the CO_2 + DIPE system over the entire composition range at temperatures from (298.15 to 308.15) K and pressures from (5.0 to 7.5) MPa. From the experimental H^E data, this system showed exothermic behavior for all compositions at all of the temperatures and pressures studied, with the exception of being slightly endothermic in the extremely carbon dioxide rich region at (5.0 and 7.5) MPa and at the temperature of 308.15 K. The lowest negative value for each temperature and pressure is about (−5.4 to −7.8) kJ·mol⁻¹, and the pressure dependency of the H^E isotherm is relatively small, unlike those of the H^E data for the CO_2 + alcohol systems at 308 K measured by our group. The minimum negative value of the H^E data was about −7.8 $\mathrm{kJ\cdot mol^{-1}}$ at 298.15 K and 5.0 MPa. At all temperatures and pressures except 298.15 K and 6.0 MPa, a two-phase region, where H^E varies linearly with composition, was found in the CO_2-rich region. The experimental results were represented with the polynomial expression model and the PR EOS and with the linear expression for the mole fraction of CO_2 in the two-phase region. Reasonable correlation accuracy was yielded by using both models, while the polynomial expression model gave better results. The CO_2 liquid composition in the vapor−liquid equilibrium was also determined from the H^E data. The minimum value of H^E, about −7.8 $\mathrm{kJ\cdot mol^{-1}}$, is higher than that of the two binary systems CO_2 + dialkyl carbonate determined in our previous studies. However, this value is about 1.4 times compared with that reported previously. These results are thought to be an important conclusion of the search for the solvent coupled with CO_2, and the heats obtained would be enough to operate the heat cycle system based on the H^E data of the CO_2 + solvent system.

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