Measurement and Correlation of Excess Molar Enthalpies of CO_2 + CH_3OH System in the Vicinity of Critical Point of Carbon Dioxide

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The excess molar enthalpies of the carbon dioxide + methanol system were measured in the vicinity of the critical point of carbon dioxide using a flow-type isothermal microcalorimeter at temperatures 303.15 K and 308.15 K and pressures from 6.5 to 8.0 MPa. A strong dependence of H^E on pressure at this area was observed. The correlation of the excess molar enthalpies was made using a composition-dependent equation composed of two polynomial expressions. It worked successfully for the H^E-x curves including the region where there is a complicated change.

Introduction

Supercritical carbon dioxide has been widely used as a solvent in extraction processes. The chemical and petrochemical, food, and pharmaceutical industries have mostly benefited from these new extraction technologies. Supercritical carbon dioxide also can be used for the development of heat pumps and other energy-saving processes in heat exchange, heat transport, and heat storage. This is because under conditions exceeding the critical point of carbon dioxide, the excess molar enthalpy of binary systems often shows large deviations in comparison with the low-pressure behavior. The critical temperature of carbon dioxide is close to ambient temperature, and carbon dioxide has no smell or taste and is unburnable. In our previous paper (Dai et al., 1998a) we constructed a database for excess molar enthalpy data of binary systems containing a supercritical fluid, and some characteristic phenomena have been analyzed. In this study, we measured excess molar enthalpies of the carbon dioxide + methanol system in the vicinity of the critical point of carbon dioxide to examine the pressure dependence of its thermal behavior in detail. The measurement was carried out using a flow isothermal microcalorimeter at temperatures 303.15 K and 308.15 K and pressures from 6.5 to 8.0 MPa. For this binary system, the excess molar enthalpy data have also been measured by Christensen at temperatures from 308.15 to 573.15 K and pressures from 7.5 to 12.5 MPa (Christensen et al., 1988), by Hauser at temperatures 298.15 and 308.15 K and pressures from 7.5 to 12.6 MPa (Hauser et al., 1996), and by Massucci at temperatures from 448.2 to 548.2 K and pressures from 0.74 to 14.75 MPa under equimolar conditions (Massucci et al., 1995).

Experimental Section

Devices. The high-pressure flow isothermal microcalorimeter (Calorimetry Sciences Corp.) was used for the measurement. This apparatus has previously been shown (Dai et al., 1998b) and will only be reviewed here briefly. It mainly consists of a mixing unit, constant temperature water bath, two high-pressure ISCO syringe pumps for sample supply, cooling circulation system, pressure adjustment device, and personal computer for signal collection and data processing. Measurement is possible from 273 K to 473 K and from 0.1 MPa to 14 MPa.

The mixing unit of the calorimeter is a large aluminum heat sink incorporating two test wells. Heat that is produced or absorbed by any mixing process is completely exchanged with the heat sink so that the mixing cell is kept at a constant temperature. A heat change occurring in a sample will create a temperature difference between the sample and the heat sink. The thermoelectric sensors located between the sample and the aluminum block will generate a voltage, which is proportional to the temperature gradient being directly dependent on the heat flux. A reference cell is used to correct for electronic noise and any heat flux due to temperature fluctuations in the heat sink. The differential signal from the twin calorimeter test wells (sample and reference) corresponds to the rate of heat production from the sample itself. The mixing cell is a Y-shaped configuration where the two components come together in individual tubes and exit through a single tube. The orientation is a “Y” junction on its side, with one component entering on the top, the other component entering on the side, and the exit being out the bottom. After the “Y” junction there is a mixing wire inside the first 50 cm of tubing. To make it mix more perfectly, we run the denser component on top and the less dense component on the side. The differential heat conduction design in combination with the ultrastable environmental temperature control makes measurements as low as ±0.1 μW possible.

The temperature stability of water bath is ±0.001 K at a temperature of 303.15 K and 308.15 K. Temperature resettability is ±0.01 K, and the accuracy of the measuring unit is ±0.2% on a 100 μW signal. The flow rate accuracy of the high-pressure ISCO syringe pumps is ±0.5%, and the accuracy of the back-pressure regulator for pressure adjustment is 0.25%.

Methods. Two high-pressure ISCO syringe pumps supplied at a constant flow the two fluids to be mixed. All runs were made in the fixed composition mode. The verification of the measurement device and the measurement method was made by measuring the excess molar enthalpies of methanol + water (exothermic system) and hexane +

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Table 1. Densities of Materials Used in This Study To Convert Flow Rates from $cm^3\ min^{-1}$ to Mole Fractions

		ρ/g cm^{-3}	
T/K	*P*/MPa	carbon dioxide	methanol
293.15	6.5	0.7975	0.7976
	7.0	0.8092	0.7977
	7.5	0.8193	0.7981
	8.0	0.8283	0.7985

cyclohexane (endothermic system) at normal pressure and normal temperature. Results of the verification have been described in our previous paper (Dai et al., 1998b). For the methanol + water system, the maximum standard deviation of our data from the three data sets in the literature (Christensen et al., 1984; Gmehling and Holderbaum, 1991) was 12.4 J mol^{-1}. The standard deviations of the literature values (Marsh, 1987; Raal and Webley, 1987) for the hexane + cyclohexane system were 0.6 J mol^{-1} and 0.8 J mol^{-1}, respectively. Reproducibility of results was ±0.2% (absolute accuracy is 0.2 J mol^{-1}) or better over most of the mole fraction range ($0.2 < x < 0.8$). Experiments with changes in flow rate were also conducted, and it was confirmed that the suitable total flow rate for this apparatus was 0.05−0.20 $cm^3\ min^{-1}$.

In the present study, the reproducibility is within ±0.8% (absolute accuracy is 10 J mol^{-1}), the uncertainty being due primarily to the high sensitivity of the H^E values to small changes in temperature and pressure. The range of total flow rate was 0.05−0.20 $cm^3\ min^{-1}$ for all temperatures and pressures studied.

Materials. Methanol was special grade pure reagents (Wako Pure Chemical Industry, Ltd., Japan) and was used after removing trace water with molecular sieves. The purity of methanol was checked by gas chromatography and found to be better than 99.9 mol %. The purity of carbon dioxide was 99.99 vol % (Showa Carbonic Acid Company Ltd., Japan). Prior to use, the carbon dioxide was filtered through a 0.5 μm inline filter (NUPRO Company).

Flow rates measured in $cm^3\ min^{-1}$ at a constant temperature of 293.15 K were converted to mol min^{-1} and to mole fractions using the densities of the pure materials estimated as follows. The densities of carbon dioxide at 293.15 K and different pressures were from the values of the literature (NIST, 1998). The densities of methanol at 293.15 K and different pressures were obtained by interpolating the values of the literature (Kubota et al., 1987). The calculated densities of materials are given in Table 1.

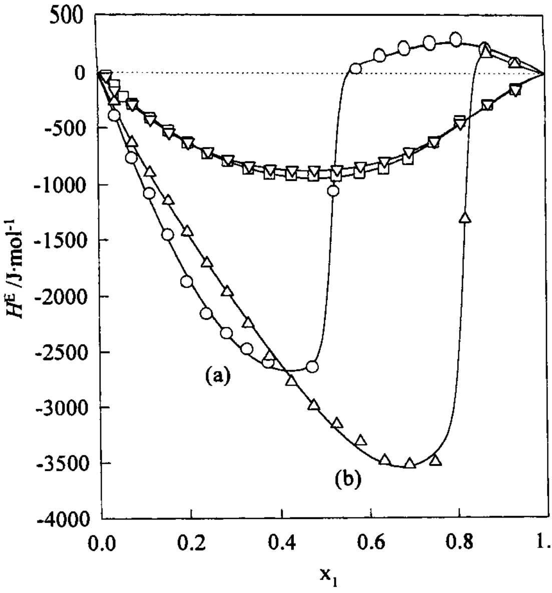

Figure 1. Experimental excess molar enthalpy data for the system carbon dioxide (1) + methanol (2) at 303.15 K: (○) 6.5 MPa, (△) 7.0 MPa, (□) 7.5 MPa, (▽) 8.0 MPa. Solid lines are correlated with eqs 1 and 2.

Results and Discussion

Excess molar enthalpies were determined for the CO_2 + CH_3OH system over the entire composition range at 303.15 K and 308.15 K under pressures from 6.5 MPa to 8.0 MPa. The experimental results are given in Table 2, and plots of H^E against x are shown in Figures 1 and 2 compared with the literature values (Christensen et al., 1988; Dai et al., 1998b; Hauser et al., 1996). The critical temperature and critical pressure of carbon dioxide are 304.2 K and 7.38 MPa (Reid et al., 1987), respectively. In Figures 1 and 2 the excess molar enthalpy shows large deviations from low-pressure behavior at the critical point of carbon dioxide. The large changes in H^E with temperature and pressure,

Table 2. Experimental Excess Molar Enthalpies of Carbon Dioxide (1) + Methanol (2) System

303.15 /K								308.15 /K	
6.5/MPa		7.0/MPa		7.5/MPa		8.0/MPa		7.0/MPa	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0369	−389	0.0374	−262	0.0188	−25	0.0190	−36	0.0374	−294
0.0748	−760	0.0758	−627	0.0378	−115	0.0382	−165	0.0759	−698
0.1138	−1079	0.1153	−895	0.0571	−220	0.0774	−288	0.1154	−1038
0.1540	−1453	0.1559	−1151	0.0767	−285	0.1176	−424	0.1559	−1384
0.1953	−1869	0.1975	−1430	0.1165	−409	0.1588	−540	0.1976	−1732
0.2378	−2154	0.2404	−1705	0.1574	−521	0.2011	−622	0.2405	−2051
0.2816	−2331	0.2845	−1963	0.1995	−623	0.2445	−702	0.2846	−2347
0.3267	−2475	0.3299	−2245	0.2426	−720	0.2891	−768	0.3300	−2669
0.3733	−2596	0.3767	−2540	0.2870	−788	0.3349	−829	0.3768	−2981
0.4718	−2636	0.4248	−2773	0.3326	−857	0.3819	−857	0.4249	−3229
0.5220	−1058	0.4744	−2990	0.3795	−902	0.4303	−868	0.4745	−3418
0.5748	46	0.5256	−3157	0.4277	−914	0.4800	−866	0.5257	−3628
0.6294	162	0.5783	−3315	0.4774	−917	0.5311	−863	0.5892	−3794
0.6859	220	0.6328	−3489	0.5286	−919	0.5838	−831	0.6329	−3779
0.7444	260	0.6890	−3524	0.5813	−893	0.6380	−785	0.7006	−3142
0.8048	287	0.7471	−3500	0.6356	−855	0.6938	−701	0.7472	−2572
0.8676	212	0.8194	−1313	0.6916	−770	0.7513	−610	0.8072	−1704
0.9326	109	0.8692	190	0.7494	−617	0.8106	−449	0.8195	−1408
		0.9335	94	0.8090	−429	0.8717	−270	0.8693	−721
				0.8706	−278	0.9349	−142	0.9335	91
				0.9342	−141				

Table 3. Parameters and Deviations of Correlation by Using Eqs 1 and 2[a]

	T/K = 308.15		*T*/K = 303.15			
P/MPa	7.0	7.5	6.5	7.0	7.5	8.0
A	5	5	50	50	5	5
B	0.745	0.850	0.519	0.819	0.946	0.756
a_1	−37952.5	−114651	−93.1175	3635.26	−30.1352	−5662.32
a_2	−48258	−208206	−2874.33	2446.69	24.5945	−4186.84
a_3		−180019				
b_1	−12295.1	−10088.6	−10301.1	−12396.1	−3796.15	−3313.59
b_2	2761.57	2123.49	−4936.55	8804.08	−138.476	−951.562
b_3			4851.26	−5513.45		
δ_1	38	36	26	27	14	8
δ_2	1.0	0.8	1.0	0.8	1.5	1.0

[a] δ_1: average absolute deviation = $\{\sum_{i=1}^{N}|(H^E_{cal} - H^E_{exp})_i|\}/N$ (J mol^{-1}), where *N* is the number of data sets. δ_2: average relative deviation = $\{\sum_{i=1}^{N}|(H^E_{cal} - H^E_{exp})_i/H^E_{(exp)max}| \times 100\%\}/N(\%)$, where *N* is the number of data sets.

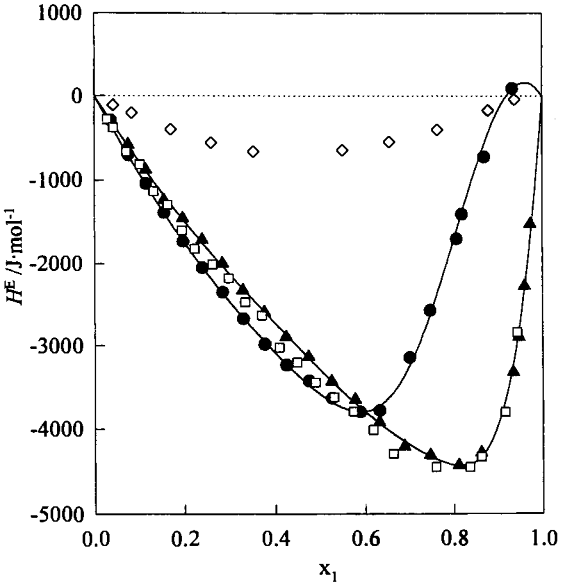

Figure 2. Experimental excess molar enthalpy data for the system carbon dioxide (1) + methanol (2) at 308.15 K under (●) 7.0 MPa, (▲) 7.5 MPa (Dai et al., 1998b), and (□) 7.5 MPa (Christensen et al., 1988) and at 298.15 K under (◇) 7.5 MPa (Hauser et al., 1996). Solid lines are correlated with eqs 1 and 2.

especially with pressure, were observed. If the system pressure falls, the measurement at a high concentration of carbon dioxide becomes difficult and the reproducibility also becomes poor. With respect to the particular behavior under pressures of 7.0 MPa and 6.5 MPa at a temperature of 303.15 K in Figure 1, it is difficult to estimate whether a two-phase (vapor−liquid) region appears or not. Then we checked the phase behavior around 7.0 and 6.5 MPa at a temperature of 303.15 K with reference to the literature values (Brunner, 1985; Brunner et al., 1987; Chang et al., 1997; Leu et al., 1991; Reighard et al., 1996; Suzuki et al., 1990; Yoon et al., 1993). As a result, it was concluded that there was no appearance of the two-phase region under such conditions.

Correlation

In this work, the experimental results of excess molar enthalpies H^E were correlated by a composition-dependent equation composed of two polynomial expression (Gruszkiewicz et al., 1993):

$$H^E\ (\text{J mol}^{-1}) = x(1-x)\{S\sum_{i=0}^{N-1}a_i(1-2x)^i + (1-S)\sum_{i=0}^{N-1}b_i(1-2x)^i\} \quad (1)$$

where a_i and b_i are adjustable parameters, *x* is the mole fraction of carbon dioxide, and *N* is the number of adjustable parameters a_i, b_i. In this work, *N* was set to 3. *S* is a switching function used to change from a polynomial fit at low mole fraction to a different polynomial fit at high mole fraction (Gruszkiewicz et al., 1993). To control the value of *S* to vary from 0 to 1, *S* is given as

$$S = 0.5[\tanh\{A(x - B)\} + 1] \quad (2)$$

where tanh is a hyperbolic tangent function, *A* is a parameter for characterizing the sharpness of the switch, and *B* is the value of *x* where the switch occurs. Thus, *A* can vary from 0 to infinity while *B* has a range from 0 to 1. The correlation result of the adjustable parameters *A*, *B*, a_i, b_i for the mixtures are shown in Table 3, and the plots of calculated results are shown in Figures 1 and 2. In this work, we set the value of *A* to 5 except for the case that includes the region where there is a complicated change appearing in the H^E-x curves (plots a and b in Figure 1), where A is 50 (see Table 3).

An algorithm suggested by Marquardt (Marquardt, 1963), based on an earlier suggestion of Levenberg (Levenberg, 1944), had been used in the data reduction. A suitable objective function to be minimized is

$$\text{OF} = \sum_{i=1}^{n}\left[\frac{(H^E_{cal} - H^E_{exp})_i}{\sigma}\right]^2 \quad (3)$$

where

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(H^E_{cal} - H^E_{exp})_i^2}{n}} \quad (4)$$

n is the point number of experimental data, and σ is the standard deviation.

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