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Determination and correlation of heat of mixing of the carbon dioxide + *tert*-butyl methyl ether system at 298.15 and 303.15 K and 5.0–7.0 MPa

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ABSTRACT

The heat of mixing (ΔH^M) of the carbon dioxide + *tert*-butyl methyl ether system was measured near the critical point of carbon dioxide using a flow-type isothermal microcalorimeter at 298.15 and 303.15 K and 5.0–7.0 MPa. The mixtures showed strong exothermic behavior in these regions. The maximum absolute value of ΔH^M (maximum exothermic value) was about 7.9 kJ mol^{-1} at 298.15 K and 5.0 MPa. A two-phase region, where ΔH^M varied linearly with composition, was found in the CO_2 rich region at all temperatures and pressures except at 298.15 K and 7.0 MPa.

1. Introduction

Many researchers have measured the heat of mixing (ΔH^M) of mixtures containing carbon dioxide (CO_2) and an organic solvent near the critical point of CO_2 (T_c = 304.2 K, P_c = 7.376 MPa [1]) [2–17]. Our research group has also measured ΔH^M for binary systems of CO_2 + alcohol (methanol [18,19], 2-propanol [20], 2-butanol [20], and 2-methyl-1-propanol [21]), + ester (dimethyl carbonate (DMC) [22], diethyl carbonate (DEC) [23], ethyl acetate [24]), + ether (diisopropyl ether (DIPE) [25]), and the ternary system CO_2 + ethanol + water [21]. The CO_2 + ester and + ether systems showed extremely large exothermic behavior in their ΔH^M data. This large heat effect is expected to be applicable to the development of a new energy supply system [26].

The objective of the present work was to identify a solvent that can be combined with CO_2 to produce a large heat effect for the development of an efficient energy supply system. In this work, we selected the *tert*-butyl methyl ether (MTBE) as the organic solvent to be mixed with CO_2. The ΔH^M data for this mixture have not been reported previously in the literature. Thus, measurement of ΔH^M for the CO_2 + MTBE system was carried out at 298.15, 303.15 K and 5.0–7.0 MPa using a flow-type isothermal microcalorimeter. The mixtures showed exothermic behavior in these regions. A two-phase region in which ΔH^M varies linearly with composition was found in the CO_2-rich region except under the condition 298.15 K and 7.0 MPa. The experimental ΔH^M data within the one-phase region were correlated with the modeified Redlich–Kister (mRK) equation proposed by Myers and Scott [27], and the Peng–Robinson (PR) equation of state [28] coupled with the van der Waals one fluid mixing rule. ΔH^M data reduction was also carried out using the linear expression for the mole fraction of CO_2 in the two-phase region.

2. Experimental

2.1. Materials

The chemicals used in this work are summarized in Table 1. First-grade pure reagent MTBE (Wako Pure Chemical Industry Ltd., Japan) was used after the removal of trace water with a 3 A molecular sieve. The mole purity of the MTBE was confirmed to be >99.9% by gas chromatography. The volume fraction purity of the CO_2 was 99.99% (Showa Carbonic Acid Company Ltd., Japan). The CO_2 was filtered through a 0.5-μm inline filter (Nupro Company, Japan) before use.

Flow rates measured in cm^3 min^{-1} at a constant temperature of

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Table 1
Chemicals used in this work.

Chemical name	Source	Purification method	Final purity	Analysis method
Carbon dioxide	Showa Carbonic Acid Company Limited, Japan	none	0.9999[a]	–
tert-Butyl methyl ether	Wako Pure Chemical Industry Limited, Japan	3 A molecular sieves	0.999[b]	Gas chromatography

[a] Volume fraction.
[b] Mass fraction.

283.15 K were converted to mole min^{-1} and then to mole fractions using the densities of the pure materials, which were estimated as follows. The density of CO_2 at 283.15 K and the pressures studied was calculated using the equation of state (EOS) for CO_2 proposed by Span and Wagner [29,30]. The density of MTBE at 283.15 K and the pressures studied was obtained by interpolating the literature values of Ihmels et al. [31]. The estimated densities of the pure components are given in Table 2. The uncertainty of the calculated mole fraction was ±0.001.

2.2. Apparatus and procedure

A high-pressure, flow-type isothermal microcalorimeter (Calorimetry Sciences Corporation, UT, USA) was used to measure ΔH^M. The apparatus consisted of a mixing unit, constant temperature water bath, two high-pressure ISCO syringe pumps for sample supply, cooling circulation system for the syringe, pressure-adjustment device, degassing unit, and a personal computer for signal collection and data processing. Measurements could be made from 233 K to 353 K and from 0.1 MPa to 20 MPa. The details of the experimental apparatus and procedure have been described elsewhere [18–20,32]. The temperature stability of the water bath was within ±0.0005 K. The pressure was also kept within 0.01 MPa during the ΔH^M measurements. The uncertainty of our experimental ΔH^M data could be estimated to within ±1.0% (maximum absolute error of 8 J mol^{-1}). This uncertainty was caused primarily by the high sensitivity of ΔH^M to small changes in temperature and pressure. The total flow rate was varied from 0.05 cm^3 min^{-1} to 0.20 cm^3 min^{-1}, and the effect of the total flow rate on the measurement of ΔH^M was taken into consideration. The optimal total flow rate was 0.08 cm^3 min^{-1} for all cases.

Each pure component was charged into an ISCO syringe after degassing. The temperatures of the syringes and their contents were kept constant with a water thermostat. The supply of the pure components to the mixing unit was carried out at a constant temperature of 283.15 K (about −20 K lower than the critical temperature of CO_2) to prevent variations in the density caused by slight changes in temperature and pressure.

3. Results and discussion

ΔH^M was measured for the CO_2 + MTBE system over the entire composition range of 298.15, 303.15 K under pressures of 5.0–7.0 MPa. The experimental results of ΔH^M are summarized in Table 3. Figs. 1 and 2 show the ΔH^M vs. x_1 (mole fraction of CO_2) isobars obtained at 298.15, and 303.15 K, respectively. The mixtures showed large exothermic mixing throughout the region studied. The maximum absolute value (i.e., maximum exothermic value $|\Delta H^M|_{max}$) at each temperature and pressure was about 5.4–7.9 kJ mol^{-1}, except at the condition 298.15 K and 7.0 MPa. The mole fraction of CO_2 at which $|\Delta H^M|_{max}$ appeared was also shifted to the CO_2-rich side with increasing pressure. These tendencies are

Table 2
Densities ρ of the pure components at 283.15 K.

P (MPa)	ρ (kg m^{-3})	
	CO_2[a]	*tert*-Butyl methyl ether[b]
5.00	868.63	755.82
5.50	875.48	756.32
6.00	881.78	756.82
7.00	893.11	757.82

[a] Span and Wagner [29,30].
[b] Ihmels et al. [31].

Table 3
Experimental heats of mixing ΔH^M at temperature T of 298.15 and 303.15 K, pressure P from 5.0 to 7.0 MPa, and mole fraction x_1 for the system CO_2 (1) + *tert*-butyl methyl ether (2).[a]

x_1	ΔH^M (J mol^{-1})	x_1	ΔH^M (J mol^{-1})	x_1	ΔH^M (J mol^{-1})
298.15 K, 5.00 MPa					
0.100	−1150	0.600	−6280	0.870[b]	−6273
0.200	−2164	0.700	−7102	0.900[b]	−4405
0.299	−3311	0.770	−7648	0.950[b]	−1503
0.400	−4362	0.799	−7812		
0.500	−5332	0.850[b]	−7302		
298.15 K, 5.50 MPa					
0.100	−1030	0.600	−5881	0.900	−7825
0.200	−2067	0.700	−6649	0.920[b]	−6377
0.300	−3155	0.799	−7353	0.930[b]	−5121
0.400	−4109	0.850	−7635	0.950[b]	−2948
0.500	−5012	0.880	−7769		
298.15 K, 6.00 MPa					
0.100	−1011	0.600	−5443	0.930[b]	−7107
0.200	−2029	0.700	−6132	0.950[b]	−4838
0.300	−2926	0.799	−6735	0.960[b]	−3251
0.399	−3813	0.850	−7023		
0.500	−4673	0.900	−7153		
298.15 K, 7.00 MPa					
0.100	−279	0.500	−1009	0.850	−867
0.200	−527	0.600	−1069	0.900	−681
0.299	−737	0.700	−1045	0.929	−532
0.400	−900	0.800	−960	0.950	−389
303.15 K, 5.00 MPa					
0.100	−1149	0.500	−5351	0.750	−7357
0.200	−2253	0.600	−6234	0.850[b]	−5022
0.300	−3332	0.700	−7049	0.900[b]	−3356
0.400	−4384	0.720	−7240	0.950[b]	−1295
303.15 K, 5.50 MPa					
0.200	−2151	0.700	−6784	0.900[b]	−5274
0.300	−3210	0.750	−7126	0.920[b]	−3948
0.400	−4170	0.799	−7470	0.950[b]	−2304
0.500	−5111	0.819	−7532	0.979[b]	−499
0.600	−6027	0.849	−7719		
303.15 K, 6.00 MPa					
0.100	−1042	0.600	−5675	0.930[b]	−5099
0.200	−2118	0.700	−6377	0.950[b]	−3478
0.300	−3056	0.800	−6966	0.980[b]	−506
0.400	−3990	0.850	−7268		
0.500	−4863	0.900	−7345		
303.15 K, 7.00 MPa					
0.100	−827	0.600	−4474	0.960[b]	−5199
0.200	−1665	0.700	−5049	0.970[b]	−2788
0.299	−2402	0.800	−5396	0.979[b]	−447
0.400	−3196	0.850	−5545		
0.500	−3828	0.950	−5385		

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(p) = 0.01$ MPa, $u(x) = 0.001$, and the combined expanded uncertainty U_c is $U_c(\Delta H^M) = 1.0\%$.
[b] Two-phase region.