

Excess molar enthalpies for binary carbon dioxide + diethyl carbonate system at 298.15–308.15 K and 5.0–6.5 MPa

Hiroyuki Matsuda, Shigetaka Yoshii, Akinori Nagashima, Kiyofumi Kurihara, Kenji Ochi*

Department of Materials and Applied Chemistry, Nihon University, 1-8 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

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Abstract

The excess molar enthalpies of the carbon dioxide + diethyl carbonate system were determined using a flow-type isothermal microcalorimeter at temperatures from 298.15 to 308.15 K and pressures from 5.0 to 6.5 MPa. Mixtures shows strong exothermic behavior in these regions. In addition, a strong pressure dependency of the excess molar enthalpies was observed, and the excess molar enthalpy values decreased with increasing pressure. The experimental results were correlated using a composition-dependent equation and the Peng–Robinson equation of state with the conventional mixing rule. Finally, the prediction of excess molar enthalpies using three mixing rules (MHV1, MHV2, and Wong–Sandler) was also tested on the basis of the vapor–liquid equilibrium data.

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1. Introduction

Recently, rapid progress has been made in some studies on environmentally benign processes using supercritical fluids. In particular, the large heat effect of a mixture containing supercritical carbon dioxide (CO₂) is expected to be applied to new energy cycle systems, such as heat pumps. In the development of these energy-saving processes, the excess enthalpy (H^E) data in the vicinity of the critical point of CO₂ and in the supercritical region are important. Many researchers have studied these H^E data, especially Christensen et al., who have made detailed measurements of binary mixtures containing supercritical CO₂ [1–4]. Previously, our group also measured four binary CO₂ and alcohol systems (methanol [5,6], 2-propanol [7], 2-butanol [7], and 2-methyl-1-propanol [8]), and the ternary CO₂ + ethanol + water system [8]. From those experimental results, we found that the H^E data near the critical point of CO₂ often shows a large deviation in comparison to its behavior at low pressure, exhibiting a dramatic change in H^E with a small change in pressure. In

addition, recently, we focused on dimethyl carbonate (DMC) as one of dialkyl carbonate, in order to find the fluid, which is environmentally benign and can be expected the larger heat effect, and the H^E of CO₂ + DMC system was measured at the temperatures 298–308 K, and the pressures 5.0–7.5 MPa. This mixture shows large exothermic behavior, and the maximum value of the exothermic was about 8900 J mol⁻¹ [9].

As an extension of that work, we investigated the diethyl carbonate (DEC) as the solvent for mixing with CO₂, in order to search the solvent that the larger heat effect is obtained. Detailed measurements of the H^E data for the CO₂ + DEC system were made 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 conventional mixing rule. Furthermore, an attempt was made to predict the H^E data of this mixture by using three equation of state excess Gibbs energy (EOS- G^E) models: MHV1, MHV2, and Wong–Sandler (WS), with parameters obtained from the vapor–liquid equilibrium (VLE) data, and the prediction accuracy was considered.

* Corresponding author. Tel.: +81 3 3259 0793; fax: +81 3 3293 7572.
E-mail address: ochi@chem.cst.nihon-u.ac.jp (K. Ochi).

2. Experimental

2.1. Apparatus and procedure

A high-pressure flow-type isothermal microcalorimeter (Calorimetry Sciences Corporation) 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 [5–10]. In this study, a modified model of the mixing cell as described in the previous paper by Nagashima and co-workers was used [9,10]. In the improved mixing cell, both a mixing wire and concentric tubes were used, in order to enhance the mixing of various compounds.

Table 1
Densities of the pure components at 283.15 K

P (MPa)	Density (g cm ⁻³)	
	CO ₂ ^a	DEC ^b
5.0	0.86863	0.99011
5.5	0.87548	0.99052
6.0	0.88178	0.99092
6.5	0.88763	0.99133

^a NIST [11].

^b Lugo et al. [12].

Degassing of liquids was carried out by combining a vacuum line and an ultrasonic wave unit. The temperature stability of the water bath is within 0.0005 K. The reproducibility of our measurements can be estimated to be within $\pm 1.0\%$ (maximum absolute accuracy is 8 J mol⁻¹), the uncertainty being due primarily to the high sensitivity of H^E values to small changes in temperature and pressure. In this study, the total

Table 2
Experimental excess molar enthalpies for the system CO₂ (1) + DEC (2) at different temperatures

x_1^a	H^E (J mol ⁻¹)	x_1^a	H^E (J mol ⁻¹)	x_1^a	H^E (J mol ⁻¹)
298.15 K, 5.0 MPa					
0.2074	-2384	0.6583	-7460	0.8760 ^b	-7377
0.2936	-3414	0.7019	-7890	0.9040 ^b	-5673
0.3706	-4299	0.7421	-8240	0.9303 ^b	-4174
0.4398	-5086	0.7794	-8556	0.9549 ^b	-2668
0.5023	-5850	0.8139	-8788	0.9781 ^b	-1290
0.5591	-6397	0.8460	-8973		
0.6109	-6894	0.8522 ^b	-8670		
298.15 K, 5.5 MPa					
0.1110	-1256	0.6600	-7019	0.9047	-8652
0.2086	-2388	0.7035	-7326	0.9100	-8655
0.2951	-3366	0.7436	-7680	0.9153 ^b	-8536
0.3723	-4161	0.7806	-7988	0.9205 ^b	-8138
0.4416	-4847	0.8150	-8213	0.9308 ^b	-7089
0.5041	-5538	0.8470	-8392	0.9553 ^b	-4498
0.5609	-6032	0.8768	-8516	0.9783 ^b	-2084
303.15 K, 5.0 MPa					
0.1103	-1252	0.6109	-7004	0.8139 ^b	-7772
0.2074	-2413	0.6583	-7509	0.8460 ^b	-6335
0.2936	-3409	0.7019	-7903	0.8760 ^b	-5078
0.3706	-4417	0.7421	-8264	0.9040 ^b	-3859
0.4398	-5189	0.7794	-8483	0.9303 ^b	-3022
0.5023	-5850	0.7935	-8562	0.9549 ^b	-1837
0.5591	-6491	0.8004 ^b	-8295	0.9781 ^b	-870
303.15 K, 5.5 MPa					
0.1110	-1270	0.6600	-7160	0.8470 ^b	-8056
0.2086	-2401	0.7035	-7483	0.8768 ^b	-6357
0.2951	-3355	0.7436	-7762	0.9047 ^b	-5053
0.3723	-4193	0.7806	-8100	0.9308 ^b	-3659
0.4416	-4906	0.8150	-8398	0.9553 ^b	-2361
0.5041	-5540	0.8281	-8498	0.9783 ^b	-1107
0.5609	-6112	0.8345	-8508		
0.6126	-6678	0.8408 ^b	-8502		
308.15 K, 5.0 MPa					
0.1103	-1401	0.6109	-7050	0.7421 ^b	-7583
0.2074	-2623	0.6583	-7536	0.7794 ^b	-6424
0.2936	-3484	0.7019	-7952	0.8460 ^b	-4456
0.3706	-4442	0.7184	-8125	0.9040 ^b	-2720

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