Measurement and Correlation of Excess Molar Enthalpies of Carbon Dioxide + 2-Butanol and 2-Propanol Systems at the Temperatures 303.15 K and 308.15 K and at Pressures from 7.0 to 8.5 MPa

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The excess molar enthalpies of carbon dioxide + 2-butanol and 2-propanol systems were measured in the vicinity of the critical point of carbon dioxide using a flow-type isothermal microcalorimeter at the temperatures 303.15 K and 308.15 K and at pressures from 7.0 to 8.5 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.

Introduction

In our previous paper, we constructed a database for excess molar enthalpy data of binary systems containing a supercritical fluid, and some characteristic phenomena have been analyzed (Dai et al., 1998a). Among several supercritical fluids, carbon dioxide has been widely used as a solvent in extraction processes. The chemical, 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 normal-pressure behavior. The critical temperature of carbon dioxide is close to ambient temperature, and carbon dioxide has no smell or taste and is unburnable. Therefore, we focused on the excess molar enthalpies of binary systems containing supercritical carbon dioxide. Some attempts were made to study the carbon dioxide + methanol system (Dai et al., 1998b; Dai et al., 1999). This work is a continuation of our previous studies.

In this study, we measured excess molar enthalpies of carbon dioxide + 2-butanol and + 2-propanol systems in the vicinity of the critical point of carbon dioxide to examine the pressure dependence of their thermal behavior in detail. The measurement was carried out using a flow isothermal microcalorimeter at the temperatures 303.15 K and 308.15 K and at pressures from 7.0 to 8.5 MPa. For those binary systems, there are no excess molar enthalpy data available in the literature. The high-pressure vapor−liquid equilibria for those binary systems have been measured by other authors (Stevens et al., 1997; Suzuki et al., 1991).

Experimental Section

The high-pressure flow isothermal microcalorimeter (Calorimetry Sciences Corp.) was used for the measurement. It mainly consists of a mixing unit, a constant-temperature water bath, two high-pressure ISCO syringe pumps for sample supply, a cooling circulation system, a pressure adjustment device, and a 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 experimental apparatus and procedure have been described in detail elsewhere (Dai et al., 1998b; Dai et al., 1999). 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.

Table 1. Densities of Materials Used in This Study To Convert Flow Rates from Cubic Centimeters per Minute to Mole Fractions

		ρ/g cm^{-3}		
T/K	*P*/MPa	carbon dioxide	2-butanol	2-propanol
293.15	7.0	0.7977	0.7911	0.8119
	7.5	0.7981	0.7914	0.8123
	8.0	0.7985	0.7918	0.8127
	8.5	0.7990	0.7922	0.8130

The 2-butanol and 2-propanol used in this study were special grade pure reagents (Wako Pure Chemical Industry, Ltd., Japan) and were used after removing trace water with molecular sieves. The purity of the 2-butanol and the 2-propanol was checked by gas chromatography and found to be better than 99.9 mol %. The purity of the 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 in-line filter (NUPRO Company).

Flow rates measured in cubic centimeters per minute at a constant temperature of 293.15 K were converted to moles per minute 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 2-butanol and 2-propanol 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.

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10.1021/je990175s CCC: $19.00

Table 2. Experimental Excess Molar Enthalpies of the Carbon Dioxide (1) + 2-Butanol (2) System

$P = 7.5$ MPa		$P = 8.0$ MPa		$P = 8.5$ MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
		$T = 303.15$ K			
0.0417	94	0.0422	105	0.0425	81
0.0821	247	0.0829	279	0.0836	253
0.1211	443	0.1222	442	0.1232	450
0.1588	548	0.1602	583	0.1614	663
0.2306	683	0.2325	752	0.2342	874
0.2981	791	0.3003	881	0.3022	958
0.3615	835	0.3640	948	0.3661	1021
0.4213	846	0.4239	988	0.4261	1047
0.4777	845	0.4803	984	0.4827	1052
0.5311	798	0.5337	959	0.5360	1033
0.5816	738	0.5841	910	0.5864	1000
0.6295	660	0.6319	853	0.6341	944
0.6749	580	0.6772	785	0.6793	875
0.7182	485	0.7203	697	0.7221	793
0.7593	359	0.7612	610	0.7629	702
0.7985	242	0.8002	514	0.8017	607
0.836	138	0.8374	418	0.8387	510
0.8717	17	0.8729	329	0.8739	423
0.9059	−74	0.9068	236	0.9076	328
0.9386	−175	0.9392	151	0.9397	231
0.9544	−164	0.9703	75	0.9705	107
0.9699	−125				
0.9851	−32				
		$T = 308.15$ K			
0.0821	−97	0.0422	132	0.0425	129
0.1588	−185	0.0829	280	0.0836	340
0.2306	−322	0.1222	407	0.1232	499
0.2981	−433	0.1602	485	0.1614	600
0.3615	−591	0.2325	565	0.2342	739
0.4213	−735	0.3003	616	0.3022	808
0.4777	−901	0.3640	637	0.3661	831
0.5311	−1064	0.4239	618	0.4261	833
0.5816	−1255	0.4803	571	0.4827	816
0.6295	−1435	0.5337	505	0.5360	766
0.6749	−1677	0.5841	419	0.5864	713
0.7182	−1929	0.6319	309	0.6341	633
0.7593	−2249	0.6772	199	0.6793	534
0.7985	−2607	0.7203	88	0.7221	444
0.836	−2899	0.7612	−29	0.7629	345
0.8717	−2895	0.8002	−165	0.8017	249
0.9059	−2530	0.8374	−267	0.8387	137
0.9386	−1381	0.8729	−408	0.8739	9
0.9596	−669	0.9068	−456	0.9076	−142
		0.9392	−420	0.9397	−134
				0.9553	−125
				0.9705	−71

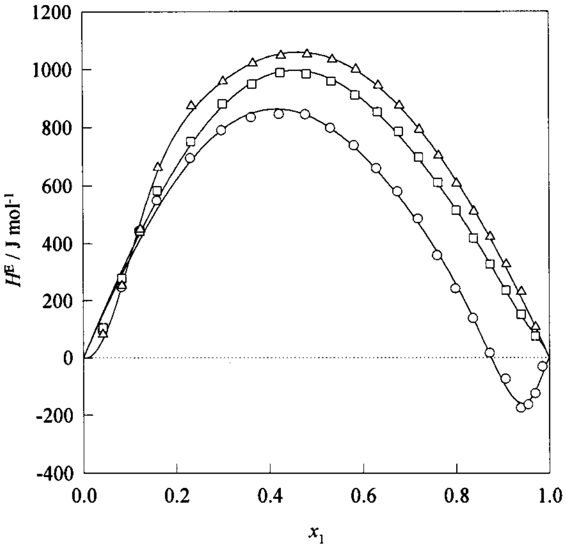

Figure 1. Experimental excess molar enthalpy data for the system carbon dioxide (1) + 2-butanol (2) at 303.15 K: (○) 7.5 MPa; (□) 8.0 MPa; (△) 8.5 MPa. Solid lines are correlated with eqs 2 and 3.

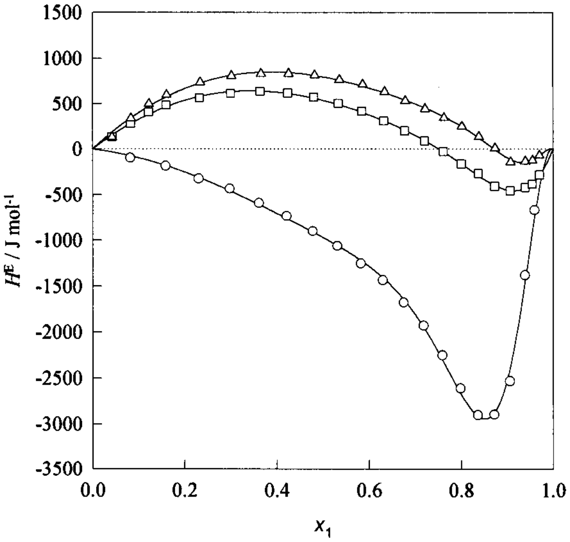

Figure 2. Experimental excess molar enthalpy data for the system carbon dioxide (1) + 2-butanol (2) at 308.15 K: (○) 7.5 MPa; (□) 8.0 MPa; (△) 8.5 MPa. Solid lines are correlated with eqs 2 and 3.

Results and Discussion

The experimental excess molar enthalpy data are listed in Tables 2 and 3. A graphical representation of the experimental H^E data is given in Figures 1−4. The critical temperature and critical pressure of carbon dioxide are 304.2 K and 7.38 MPa (Reid et al., 1987), respectively. As can be seen from different diagrams, large changes in H^E with temperature and pressure, especially with pressure, are observed. When the system pressure is decreased, the measurement of H^E becomes difficult at a high concentration of carbon dioxide and the reproducibility of H^E values also becomes poor.

The large changes in H^E near the critical region can be estimated by the changes in the heat capacity at constant pressure (C_P) of the components and the mixture in this region (Christensen et al., 1987). We examined the C_P of carbon dioxide near the critical point. Figure 5 is a C_P-T-P plot of carbon dioxide near the critical point which has been drawn from the available C_P data in the literature (Vargaftik, 1975). In Figure 5, it shows the maximum C_P values of carbon dioxide at the different temperatures and pressures (points A to G). As can be seen in Figure 5, the constant-pressure heat capacity changes sharply in the vicinity of the critical point, and it becomes infinite at the critical point A. We also made a ln(P_s) versus $1/T$ plot of carbon dioxide, shown in Figure 6, using the literature data (Vargaftik, 1975). The points A to G in Figure 6 correspond to the maximum values of the constant-pressure heat capacities in Figure 5. All of the points (A to G) are on the extension line of the vapor pressure curve of carbon dioxide beyond the critical point. It means that when temperature and pressure are on the vapor pressure curve or its extension line beyond the critical point, the value of C_P will change rapidly. At constant pressure, the excess molar enthalpy changes with the temperature can be expressed as eq 1.

$$\left(\frac{\partial H^E}{\partial T}\right)_P = C_P^E = C_P - (x_1 C_{P,1} + x_2 C_{P,2}) \qquad (1)$$

Table 3. Experimental Excess Molar Enthalpies of the Carbon Dioxide (1) + 2-Propanol (2) System

P = 7.0 MPa		P = 7.5 MPa		P = 8.0 MPa		P = 8.5 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}
			T = 303.15 K				
0.0819	−11	0.0693	36	0.0699	44	0.0705	93
0.1343	−57	0.1358	88	0.1370	112	0.1381	254
0.2101	−227	0.1997	133	0.2013	187	0.2028	368
0.2588	−372	0.2611	182	0.2631	247	0.2649	463
0.3745	−775	0.3203	222	0.3226	295	0.3246	526
0.4400	−1050	0.3773	240	0.3797	336	0.3819	573
0.4822	−1283	0.4322	251	0.4348	361	0.4370	601
0.5433	−1601	0.4852	244	0.4878	369	0.4901	614
0.5828	−1813	0.5363	211	0.5389	364	0.5412	611
0.6212	−2057	0.5857	178	0.5882	352	0.5904	597
0.6769	−2418	0.6334	123	0.6358	331	0.6379	571
0.7129	−2693	0.6795	70	0.6818	290	0.6838	539
0.7652	−1335	0.7242	15	0.7262	247	0.7281	488
0.7990	−3413	0.7674	−49	0.7692	206	0.7708	431
0.8482	−3835	0.8092	−115	0.8108	154	0.8122	381
0.8800	−4027	0.8497	−178	0.8511	105	0.8522	323
0.9263	−4186	0.8890	−223	0.8900	58	0.8909	255
0.9563	−4236	0.9271	−262	0.9278	17	0.9284	175
0.9856	−4141	0.9641	−223	0.9645	−38	0.9648	82
		0.9822	−145	0.9824	−37		
				0.9895	−26		
				0.9965	−6		
			T = 308.15 K				
		0.0693	−186	0.0699	−7	0.0215	6
		0.1358	−395	0.1370	−21	0.0705	34
		0.1997	−599	0.2013	−90	0.1381	74
		0.2611	−831	0.2631	−173	0.2028	110
		0.3203	−1063	0.3226	−255	0.2649	138
		0.3773	−1315	0.3797	−349	0.3248	157
		0.4322	−1594	0.4348	−450	0.3819	160
		0.4852	−1846	0.4878	−564	0.4370	146
		0.5363	−2132	0.5389	−667	0.4901	124
		0.5857	−2449	0.5882	−775	0.5412	96
		0.6334	−2746	0.6358	−871	0.5904	66
		0.675	−3074	0.6818	−987	0.6379	20
		0.7242	−3416	0.7262	−1111	0.6838	−42
		0.7674	−3698	0.7692	−1204	0.7281	−109
		0.8092	−3983	0.8108	−1272	0.7708	−181
		0.8497	−4066	0.8511	1325	0.8122	−252
		0.8890	−4059	0.8900	−1351	0.8522	−313
		0.9271	−3893	0.9278	−1332	0.8909	−352
		0.9641	−3240	0.9645	−1197	0.9284	−361
				0.9747	−1000	0.9648	−292
				0.9798	−878	0.9755	−242
				0.9849	−633	0.9825	−151
						0.9930	−17

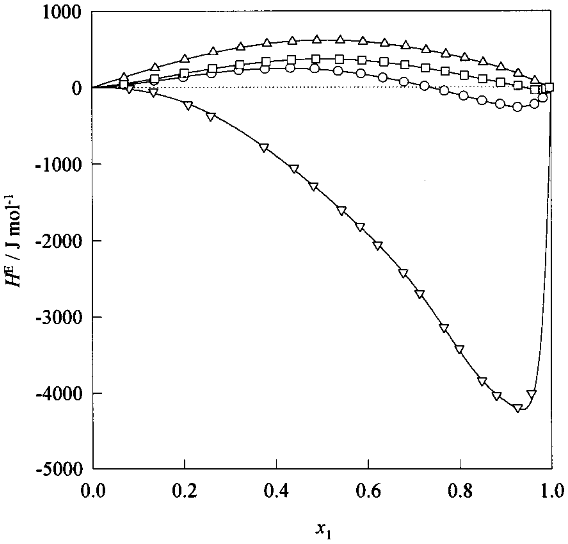

Figure 3. Experimental excess molar enthalpy data for the system carbon dioxide (1) + 2-propanol (2) at 303.15 K: (▽) 7.0 MPa; (○) 7.5 MPa; (□) 8.0 MPa; (△) 8.5 MPa. Solid lines are correlated with eqs 2 and 3.

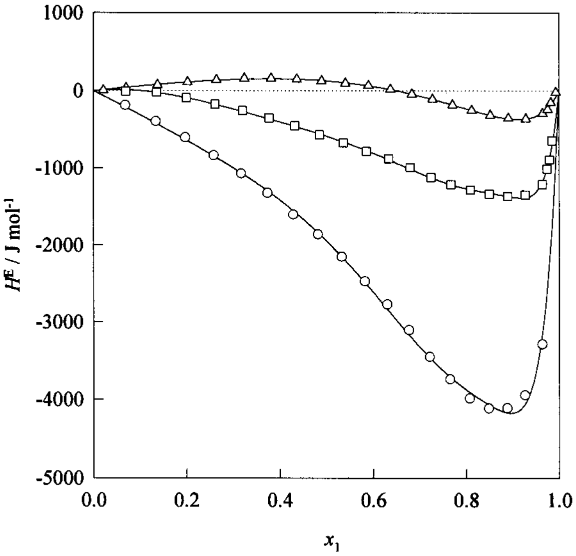

Figure 4. Experimental excess molar enthalpy data for the system carbon dioxide (1) + 2-propanol (2) at 308.15 K: (○) 7.5 MPa; (□) 8.0 MPa; (△) 8.5 MPa. Solid lines are correlated with eqs 2 and 3.

Table 4. Parameters and Deviations of Correlation by Using Eqs 2 and 3[a]

Carbon Dioxide + 2-Butanol

	T/K = 303.15			T/K = 308.15		
	$P^b = 7.5$	$P^b = 8.0$	$P^b = 8.5$	$P^b = 7.5$	$P^b = 8.0$	$P^b = 8.5$
a_1	2.89127×10^7	4.16512×10^7	7.05807×10^7	-1.2484×10^9	-1.31909×10^8	3.62844×10^7
a_2	9.92134×10^7	9.20847×10^7	1.45602×10^8	-2.41919×10^9	-2.28244×10^8	1.30952×10^8
a_3	6.89579×10^7	5.12848×10^7	7.63411×10^7	-1.16575×10^9	-1.01103×10^8	9.52039×10^7
b_1	3310.36	3941.37	4283.33	−3737.98	2170.41	3186.16
b_2	1662.13	934.621	904.786	4428.41	2444.43	1854.75
b_3	−1236.93	−1016.19	−1053.73	−1331.29	−765.066	−335.817
δ_1	16	10	8	36	10	13
δ_2	1.9	1.0	0.7	1.5	1.6	1.6

Carbon Dioxide + 2-Propanol

	T/K = 303.15				T/K = 308.15		
	$P^b = 7.0$	$P^b = 7.5$	$P^b = 8.0$	$P^b = 8.5$	$P^b = 7.5$	$P^b = 8.0$	$P^b = 8.5$
a_1	-1.26419×10^9	-4.04562×10^7	-1.87453×10^7	1.47014×10^7	-1.09362×10^9	-2.69217×10^8	-5.9184×10^7
a_2	-2.65297×10^9	-7.14283×10^7	-4.28111×10^7	2.43789×10^7	-2.27615×10^9	-5.43147×10^8	-9.36276×10^7
a_3	-1.48345×10^9	-3.49524×10^7	-2.5911×10^7	9.51481×10^6	-1.25155×10^9	-2.97161×10^8	-3.82568×10^7
b_1	−5351.70	927.875	1486.87	2741.46	−7830.19	−2365.41	500.746
b_2	9143.01	849.674	−22.1120	−63.8613	10640.30	4188.56	1084.54
b_3	−3704.48	−1601.12	−961.019	−494.999	−6544.86	−1976.02	−1315.98
δ_1	19	3	3	3	20	16	9
δ_2	0.4	1.8	0.8	0.8	0.8	1.2	2.5

[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 points. 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 points. [b] Units = MPa.

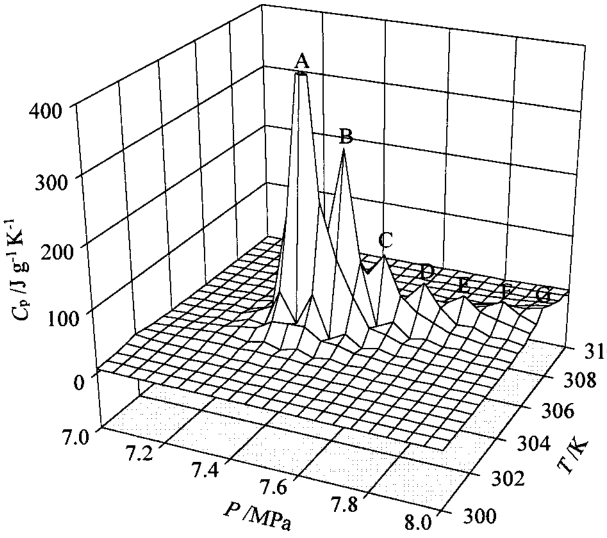

Figure 5. Plot of C_P−T−P for carbon dioxide near the critical point (P_c = 7.38 MPa, T_c = 304.2 K). C_P becomes infinite at the critical point A.

where H^E is the excess molar enthalpy, C_P^E is the excess molar heat capacity at constant pressure, C_P is the molar heat capacity at constant pressure of the mixture, $C_{P,i}$ is the molar heat capacity at constant pressure of pure component i, and x_i is the molar fraction of component i.

In eq 1, it is usually not so easy to find the data of C_P in the literature. Thus, for the behavior of H^E as shown in Figures 1 to 4, we estimated that the excess molar enthalpies of the mixture would be affected by the strong pressure dependency of the heat capacity at constant pressure (C_P, $C_{P,1}$, and $C_{P,2}$). We obtained the largest value of excess molar enthalpy at the conditions 308.15 K and 75 bar, which are closest to the critical point of carbon dioxide. When the temperature was reduced to 303.15 K, the maximum value of the excess molar enthalpy was obtained at 70 bar.

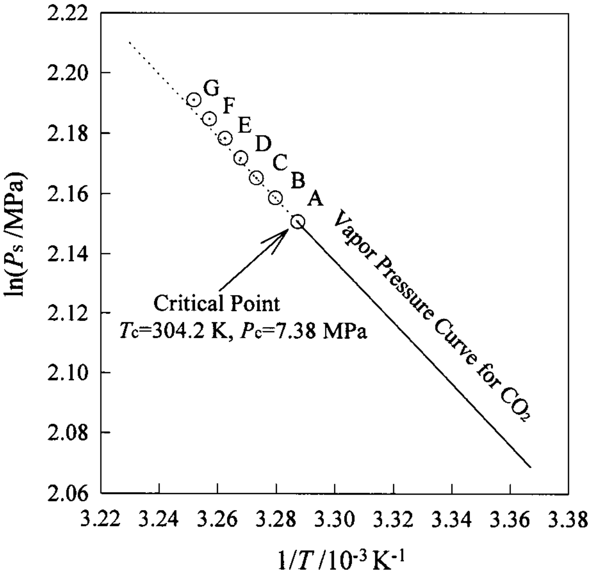

Figure 6. Vapor pressure curve for carbon dioxide extrapolated beyond the critical point. Circles indicate the temperature and pressure corresponding to the maximum values of C_P as determined from Figure 5.

Correlation

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

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

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

$$S = 0.5\left[\left(\frac{e^{y} - e^{-y}}{e^{y} + e^{-y}}\right) + 1\right] \tag{3}$$

where $y = 10(x - 1.3)$. The correlation results of the adjustable parameters a_i, b_i for the mixtures are shown in Table 4, and the plots of calculated results are shown in Figures 1 to 4.

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

$$\mathrm{OF} = \sum_{i=1}^{n}\left[\frac{(H^{\mathrm{E}}_{\mathrm{cal}} - H^{\mathrm{E}}_{\mathrm{exp}})_i}{\sigma}\right]^2 \tag{4}$$

where

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(H^{\mathrm{E}}_{\mathrm{cal}} - H^{\mathrm{E}}_{\mathrm{exp}})_i^{\,2}}{n}} \tag{5}$$

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

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Received for review July 2, 1999. Accepted September 13, 1999.

JE990175S