

Ternary excess molar enthalpies of chloroform + acetone + cyclohexane mixtures at 298.15 K

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Abstract

Excess molar enthalpies of ternary mixtures formed by chloroform, acetone and cyclohexane were measured using a flow microcalorimeter. The calorimeter used was the same as that designed by Ogawa and Murakami. The performance of the calorimeter was examined by comparing experimental excess molar enthalpies of benzene + cyclohexane at 298.15 K with literature values. Agreement between our results and the literature values was within $\pm 0.5\%$.

LIST OF SYMBOLS

$A_{n,ij}$	coefficients in eqn. (1)
B_i	coefficients in eqn. (3)
H_m^E, H_{ij}^E	excess molar enthalpies
R	gas constant
T	absolute temperature
x	mole fraction

Greek letters

Δ	ternary function defined by eqn. (3)
δH_m^E	deviation between experimental and calculated values
$ \delta H_m^E $	absolute arithmetic mean deviation
$ \delta H_m^E/H_m^E $	absolute relative mean deviation
σ	standard deviation

Subscript

123	ternary mixture
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INTRODUCTION

We have been studying binary and ternary excess molar enthalpies of mixtures containing hydrogen-bonded molecules. Flow microcalorimeters for measuring excess molar enthalpies of fluid mixtures have been widely used, and we have constructed a flow microcalorimeter similar to that of Ogawa and Murakami [1]. The performance of the calorimeter is examined by comparing our experimental values for benzene + cyclohexane at 298.15 K with literature values [2–5] measured with various calorimeters. In this work, we have measured the ternary excess molar enthalpies of chloroform + acetone + cyclohexane mixtures and compared them with those of Lark et al. [6]. The excess molar enthalpies at 298.15 K for the three binaries constituting the ternary mixture have been reported: chloroform + acetone [7], chloroform + cyclohexane [8], and acetone + cyclohexane [9, 10].

EXPERIMENTAL

Materials

All chemicals were purchased from Wako Pure Chemical Ind. Ltd. Cyclohexane (A.R.) was used without further purifications. Benzene (C.P.) was purified by recrystallization three times. Acetone (C.P.) was treated with dry potassium carbonate and then fractionally distilled in a packed column (Shibata Sci. Tech. Ltd., HP9000B). Chloroform (A.R.) was washed with pure water after shaking with concentrated sulfuric acid to remove alcohol, and then distilled after drying over potassium carbonate. Densities of the substance measured with a densimeter (Anton Paar DMA40) were in good agreement with literature values [11]. All the compounds were degassed before use.

Apparatus

The flow microcalorimeter used in this work was the same as that described by Ogawa and Murakami [1] except for a few modifications, as follows. A spiral stainless-steel wire inserted into the flow mixing tube improved completeness of mixing in the mixing tube. A personal computer monitoring the heat flux of mixing as a function of time and voltage changes was connected to the calorimeter. A schematic diagram of the flow calorimeter is shown in Fig. 1. The piston displacement pumps A (Yuasa Co., SP-01) propel the flow of the first and the second components through inlet tubes into the flow mixing cell installed in the brass container B. The pure liquid flows out when the stainless-steel piston J is inserted through the tight Teflon seal K into the glass cylinder L with thermostated water jacket M. The piston is moved by the screw shaft N

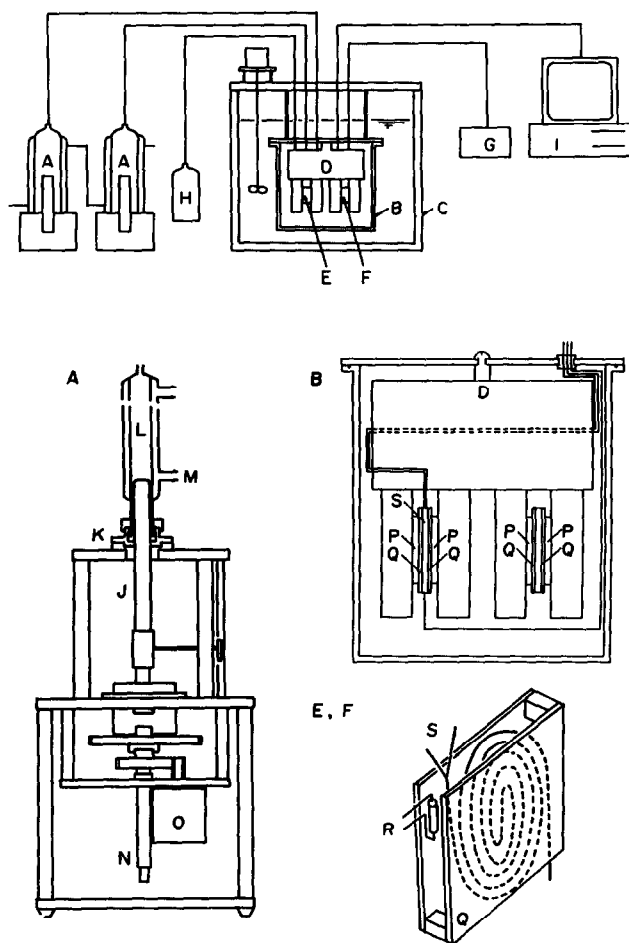


Fig. 1. Schematic diagram of flow calorimeter: A, piston displacement pump; B, brass container; C, thermostated water bath; D, aluminum heat sink block; E, flow mixing cell; F, reference cell; G, d.c. power supply; H, waste reservoir; I, computer; J, stainless-steel piston; K, Teflon seal; L, glass cylinder; M, thermostated water jacket; N, precise screw shaft; O, stepping motor; P, thermomodule; Q, copper plate; R, metal film heater; S, 1 m long stainless-steel tube.

together with gearing which is rotated by the stepping motor O (Nippon Servo, KP6M2-001). The pumps regulate the flow rates of the liquids, fluctuations of which between 0.5 and 5 ml min^{-1} are less than $\pm 0.5\%$. The total volumetric flow of the mixtures was fixed at 5 ml min^{-1} for all measurements. The ratio of the flow rate of each pure liquid gives the composition of the liquid mixture. The inaccuracies of the composition of the mixtures were estimated to be less than 1×10^{-4} in mole fraction terms.

The brass container was immersed in the thermostated water bath C having temperature stability within 1 mK . The aluminum heat sink block

D had two identical compartments for the flow mixing cell E and the reference cell F. These cells were mounted between two pairs of thermomodules P (Netsu Denshi Ind. Co., CP1.4-127-06L). Both the flow mixing cell and the reference cell were made of two copper plates Q and had the same dimensions of 50 mm × 50 mm × 5 mm; they included a calibrated metal film heater R (0.25 W, resistance about 1 kΩ) connected to the d.c. power supply G and a 1 m long stainless-steel tube S (1 mm i.d.) with a spiral stainless-steel wire (60 μm o.d.) inserted. Fused alloy was introduced into openings between the copper plates and these components for good thermal contact.

Mixing occurs at the union of the two inlet tubes in the flow mixing cell. The mixtures pass through the flow mixing tube and then flow out of the cell into the waste reservoir H. The thermomodule detects differences of heat flux between these two cells and converts them to thermomodule voltages. The voltages are fed to a digital voltmeter (Keithley DVM196) via an amplifier (Ohkura AM1001) and then recorded by the computer I (NEC PC-9801VX) fitted with a GP-IB interface board. After equilibrium voltages are established, excess molar enthalpies are calculated from the voltages using the calibration constants of the thermomodule. The thermomodule calibration constants, which are determined by supplying a known amount of direct current to the heater in the flow mixing cell at several flow rates of the pure components, are obtained from preliminary experiments. Further details of the description and procedure for this type of calorimeter are given elsewhere [1, 3].

RESULTS

Test on benzene + cyclohexane mixture

The excess molar enthalpies of binary mixtures for benzene(1) + cyclohexane(2) at 298.15 K were measured for comparison with literature values obtained with different types of calorimeter. Table 1 lists our experimental results, along with the deviations $\delta H_m^E (= H_m^E - H_{ij}^E)$ calculated from an equation of the form

$$H_{ij}^E = x_i x_j \sum_{n=1}^m A_{n,ij} (x_i - x_j)^{n-1} \quad (1)$$

Table 2 gives the coefficients $A_{n,ij}$ and the absolute arithmetic mean deviation and standard deviation obtained by an equally weighted least mean squares method. Figure 2 illustrates the deviations δH_m^E between our results for the benzene(1) + cyclohexane(2) mixture and the published values [2–5]. The points in Fig. 2 show the deviations of our

TABLE 1

Experimental binary excess molar enthalpies at 298.15 K

x_1	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x_1	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)	x_1	H_m^E (J mol ⁻¹)	δH_m^E (J mol ⁻¹)
<i>Benzene(1) + cyclohexane(2)</i>								
0.0500	164.5	0.5	0.4000	764.0	2.3	0.7500	624.9	2.3
0.1000	277.5	-0.7	0.4500	790.6	1.6	0.8000	535.8	-1.1
0.1500	395.4	-0.8	0.5000	801.1	0.3	0.8500	432.8	-0.1
0.2000	498.6	-0.9	0.5500	794.7	-2.4	0.9000	309.7	-0.0
0.2500	586.9	-0.9	0.6000	776.4	-1.4	0.9500	166.0	0.1
0.3000	662.0	0.9	0.6500	742.5	0.0			
0.3500	720.0	1.0	0.7000	690.1	-0.8			
<i>Acetone(1) + cyclohexane(2)</i>								
0.1000	744.2	0.4	0.4000	1591.7	0.2	0.7000	1363.2	0.5
0.1500	986.9	-4.2	0.4500	1619.8	2.2	0.7500	1228.0	-1.1
0.2000	1189.8	4.7	0.5000	1619.7	2.4	0.8000	1058.0	-2.6
0.2500	1340.6	3.5	0.5500	1592.9	1.2	0.8500	852.2	-0.8
0.3000	1449.6	-3.8	0.6000	1540.9	-0.6	0.9000	610.5	6.3
0.3500	1534.3	-3.1	0.6500	1466.0	0.3			

experimental results from the values calculated by eqn. (1). The solid lines represent the deviations between our results calculated by eqn. (1) and the smoothed results of other workers [2–5]. The broken lines indicate $\pm 0.5\%$ of the excess molar enthalpies of the benzene + cyclohexane mixture. Agreement between our results and the literature values was virtually within $\pm 0.5\%$. The reproducibility of the measurements was 0.1%.

Mixtures of chloroform + acetone + benzene

The experimental binary excess molar enthalpies of the acetone(1) + cyclohexane(2) mixture at 298.15 K and atmospheric pressure are listed in Table 1. The binary coefficients of eqn. (1) and the absolute arithmetic mean deviation and standard deviation are given in Table 2. Figure 3 compares our results with the literature values [9, 10]. Our values are about 40 J mol⁻¹ higher than those in the literature for the equimolar mixture. Table 3 lists the experimental ternary excess molar enthalpies of chloroform(1) + acetone(2) + cyclohexane (3) at 298.15 K and atmospheric pressure, together with the results calculated from a polynomial equation

$$H_{m,123}^E = H_{12}^E + H_{13}^E + H_{23}^E + \Delta_{123}x_1x_2(1 - x_1 - x_2) \quad (2)$$

where the binary excess molar enthalpies H_{ij}^E are evaluated from eqn. (1) with the coefficients given in Table 2 and the additional term for the

TABLE 2
Binary coefficients of eqn. (1) and deviations

System (<i>i</i> + <i>j</i>)	No. of data points	$A_{1,ij}$ (J mol ⁻¹)	$A_{2,ij}$ (J mol ⁻¹)	$A_{3,ij}$ (J mol ⁻¹)	$A_{4,ij}$ (J mol ⁻¹)	$A_{5,ij}$ (J mol ⁻¹)	$A_{6,ij}$ (J mol ⁻¹)	$ \delta H_m^E $ (J mol ⁻¹)	σ (J mol ⁻¹)	Ref.
Benzene + cyclohexane	19	3203.2	164.0	98.4	85.6			1.0	1.4	This work
Chloroform + acetone	21	-7560.6	-2396.6	923.6	877.6			1.4	2.0	7
Chloroform + cyclohexane	19	2566.0	-109.3	-43.3				1.7	2.4	8
Acetone + cyclohexane	17	6469.3	-524.4	1433.8	105.2	249.3	-1252.1	2.2	3.5	This work

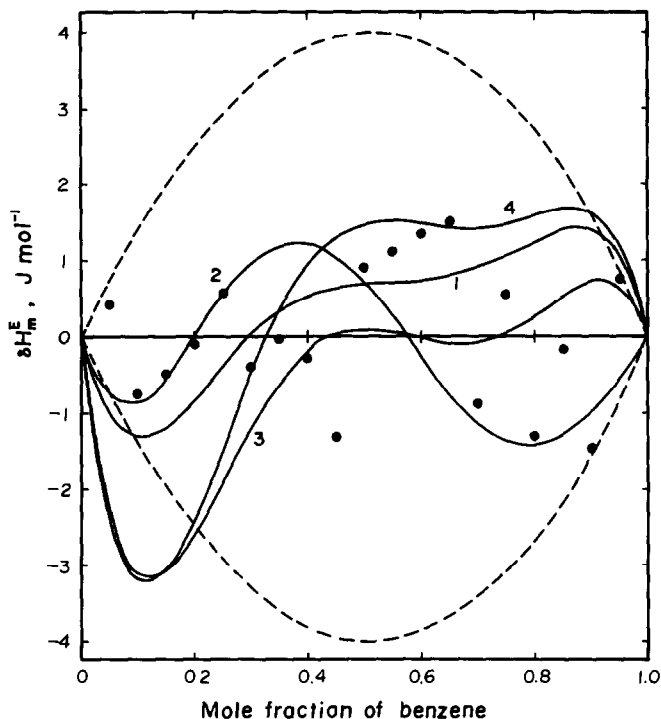


Fig. 2. Comparisons of excess molar enthalpies for benzene(1) + cyclohexane(2) at 298.15 K: ●, this work; 1, Nagata and Kazuma [2]; 2, Tanaka et al. [3]; Tanaka et al. [4]; 4, Stokes et al. [5]. Broken lines represent $\pm 0.5\%$ of the excess molar enthalpies for the benzene + cyclohexane mixture.

ternary mixture is

$$\Delta_{123}/RT = B_1 - B_2x_1 - B_3x_2 - B_4x_1^2 - B_5x_2^2 - B_6x_1x_2 \quad (3)$$

The ternary parameters B_i of eqn. (3) were calculated using the least-squares method. Table 4 gives the parameters and the absolute arithmetic mean deviations and standard deviations for the ternary mixture, together with the results calculated from the experimental values of Lark et al. [6] using eqns. (2) and (3). Lines of constant values of the ternary excess molar enthalpies of chloroform(1) + acetone(2) + cyclohexane (3) mixtures calculated from eqns. (2) and (3) with the coefficients presented in Tables 2 and 4 are plotted in Fig. 4 for the comparison of our results with those of Lark et al. Agreement between our results and Lark's values was not good. The absolute relative mean deviation $|\delta H_m^E/H_m^E|$ of the ternary excess molar enthalpies between the results of Lark et al. and our values calculated from eqns. (3) and (4) was 24.8%.

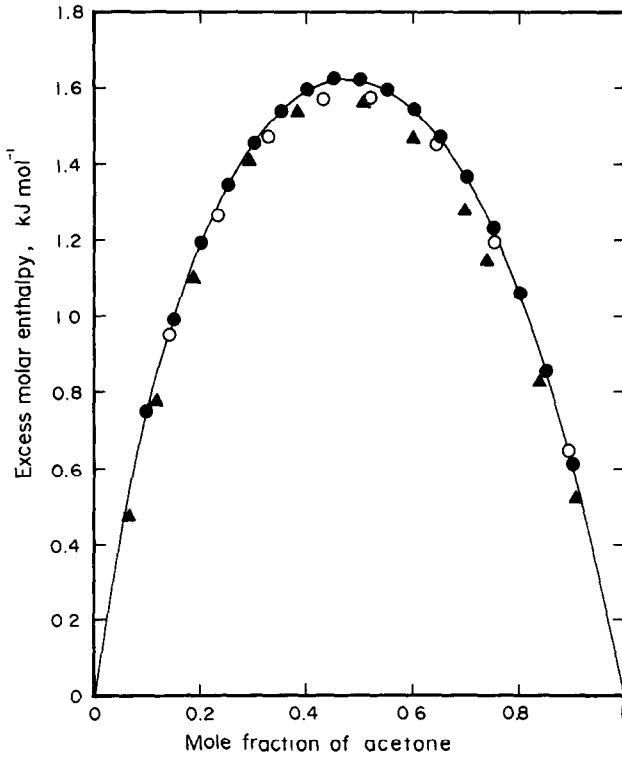


Fig. 3. Binary excess molar enthalpies for acetone(1) + cyclohexane(2) mixture at 298.15 K: ●, this work; ○, Handa and Fenby [9]; ▲, Marongiu [10]; —, calculated from eqn. (1).

TABLE 3

Experimental ternary results for chloroform(1) + acetone(2) + cyclohexane(3) mixture at 298.15 K

x_1	x_2	H_m^E (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)
$x_2' = 0.2524^a$			
0.0500	0.2398	1092.8	1089.9
0.1000	0.2271	853.8	856.8
0.1500	0.2145	644.7	649.9
0.2000	0.2019	470.6	472.1
0.2500	0.1823	322.3	329.7
0.3000	0.1767	210.2	207.0
0.3500	0.1640	129.6	118.0
0.4000	0.1514	71.7	54.5
0.4500	0.1388	32.1	12.9
0.5000	0.1262	-1.9	-10.8
0.5500	0.1136	-21.0	-20.9
0.6000	0.1010	-26.2	-21.8
0.6500	0.0883	-30.5	-16.9
0.7000	0.0757	-27.8	-10.9

TABLE 3 (continued)

x_1	x_2	H_m^E (J mol ⁻¹)	$H_{m,123}^E$ (J mol ⁻¹)
0.7500	0.0631	-23.5	-6.0
0.8000	0.0505	-17.6	-3.8
0.8500	0.0379	-13.1	-4.5
0.9000	0.0252	-7.0	-5.9
0.9500	0.0126	-2.2	-6.5
$x_2' = 0.5023^a$			
0.0500	0.4771	1375.6	1376.0
0.1000	0.4520	1074.9	1085.7
0.1500	0.4269	748.0	775.4
0.2000	0.4018	444.0	468.4
0.2500	0.3767	173.3	182.4
0.3000	0.3516	-63.5	-70.4
0.3500	0.3265	-253.6	-281.8
0.4000	0.3013	-403.2	-447.6
0.4500	0.2762	-515.2	-567.5
0.5000	0.2511	-599.3	-643.1
0.5500	0.2260	-641.3	-678.2
0.6000	0.2009	-659.9	-678.0
0.6500	0.1758	-647.1	-648.6
0.7000	0.1507	-613.9	-596.1
0.7500	0.1256	-546.4	-526.2
0.8000	0.1005	-459.3	-443.3
0.8500	0.0753	-355.0	-349.5
0.9000	0.0502	-245.3	-247.0
0.9500	0.0251	-119.6	-132.5
$x_2' = 0.7529^a$			
0.0500	0.7152	1044.3	1059.6
0.1000	0.6776	784.3	804.2
0.1500	0.6400	481.0	493.7
0.2000	0.6023	157.4	160.4
0.2500	0.5647	-166.7	-170.5
0.3000	0.5270	-456.7	-478.5
0.3500	0.4894	-705.6	-749.6
0.4000	0.4517	-909.6	-972.9
0.4500	0.4141	-1073.5	-1143.3
0.5000	0.3764	-1195.8	-1257.3
0.5500	0.3388	-1272.9	-1316.1
0.6000	0.3012	-1307.7	-1321.6
0.6500	0.2635	-1283.0	-1277.4
0.7000	0.2259	-1205.4	-1189.7
0.7500	0.1882	-1090.4	-1062.7
0.8000	0.1506	-929.4	-903.4
0.8500	0.1129	-736.2	-714.5
0.9000	0.0753	-515.7	-501.3
0.9500	0.0376	-266.4	-262.8

^aTernary mixtures were obtained by mixing pure chloroform with [x_2' acetone + (1 - x_2')cyclohexane].

TABLE 4
Ternary additional parameters and deviations fitting eqns. (2) and (3) to the ternary chloroform + acetone + cyclohexane mixture

No. of data points	B_1	B_2	B_3	B_4	B_5	B_6	$ \delta H_m^E $ (J mol ⁻¹)	σ (J mol ⁻¹)	Ref.
57	-12.2138	-12.4549	-26.2531	-3.7962	-2.4225	49.3522	18.0	25.6	This work
30	4.8430	15.0485	26.3494	-14.0110	-23.3239	-35.6347	6.7	9.2	6

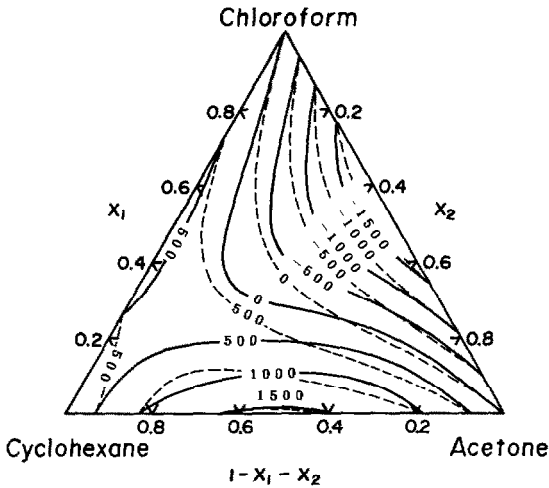


Fig. 4. Contours of ternary excess molar enthalpies of chloroform(1) + acetone(2) + cyclohexane(3) mixture at 298.15 K; —, calculated from eqns. (2) and (3); - - - - -, from Lark et al. [6].

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