

FLOW MICROCALORIMETER FOR HEAT CAPACITIES OF SOLUTIONS

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ABSTRACT

A new type of flow microcalorimeter for measuring heat capacities at constant pressure of liquids and solutions was constructed. This calorimeter is similar in design to Picker's except for the flow system, which consists of two syringe type of pumps and two flowing paths in each flow cell. It was found that the magnitude of heat loss from cells depended on liquids themselves used and the flow rates of sample liquids. The molar heat capacities, C_p of benzene and ethanol were determined relative to those of cyclohexane and water, respectively. The excess molar heat capacities, $C_p(E)$ for the systems of benzene + cyclohexane and water + ethanol were also determined at 298.15K by the direct mixing method. An inaccuracy for $C_p(E)$ was estimated to be within $\pm 1\%$.

INTRODUCTION

The molar excess heat capacity measurement is of interest since it provides the information on the molecular interactions in solution. However, there is a paucity of the molar excess heat capacity data on the non-electrolyte solutions, because of the difficulty of the precise measurement.

Recently, $C_p(E)$ data of binary mixtures have been reported (ref.1) by the Picker flow microcalorimeter (ref.2), by which the volumetric heat capacity, C_p/V of sample liquid to the reference liquid can be determined precisely. We constructed a new type of the flow microcalorimeter for measuring the $C_p(E)$ of the binary mixtures accurately and examined the magnitude of heat loss from the flow cells. The purpose of this paper is to describe the outline of the new apparatus and the operating procedure.

APPARATUS

The new flow microcalorimeter constructed in this study has been described in detail elsewhere (ref.3) and then will be elaborated briefly on the outline of the apparatus. This apparatus consists of two pump systems, the thermostated water bath, the calorimetric unit, the thermal feedback circuit which is connected to the heaters in the both flow cells and controlled by the thermal detector, and the vacuum line. The thermal feedback circuit is similar in fashion to Picker's. However high precision operational

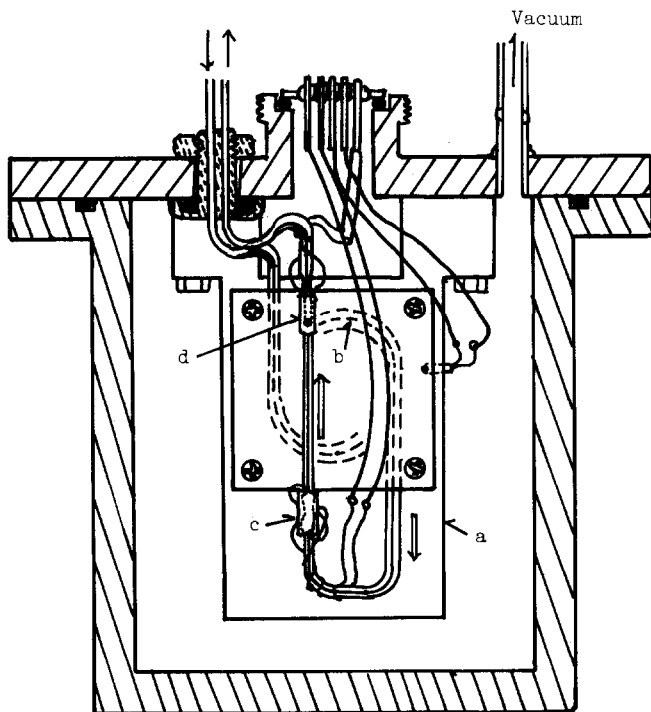


Fig. 1. Schematic diagram of calorimetric unit, a: brass block, b: heat exchanger (25cm long coiled stainless steel tube), c: heater, d: thermistor.

amplifiers (OP-05E, PMI) and 1/4W-metal film resistors as the heaters of the flow cells were used. The calorimetric unit is immersed in the water bath kept temperature within $\pm 3 \times 10^{-4}$ K, which illustrated in Fig. 1.

As shown in Fig. 1, the both cells, the sample cell and the reference cell, have two flowing paths, so that it is possible to use the calorimeter in various ways by combining with the pair of pumps, the mixing part and the delay loop shown in Fig. 2.

With Fig. 2(c), $C_p(E)$ can be directly determined without use of the delay loop, which is called the direct mixing mode.

CALCULATION OF HEAT CAPACITY

For the delay mode (Fig. 2(b)), volumetric heat capacities of sample liquids relative to the reference liquid were calculated from the equation by Fortier (ref.1) or Tanaka (ref.4). The estimation of the effective heating power P^* was described in detail elsewhere (ref.3). For the direct mixing mode, changes of flow in the two cells occur due to the volume change of mixing of the sample liquids, but total moles of liquids are equal

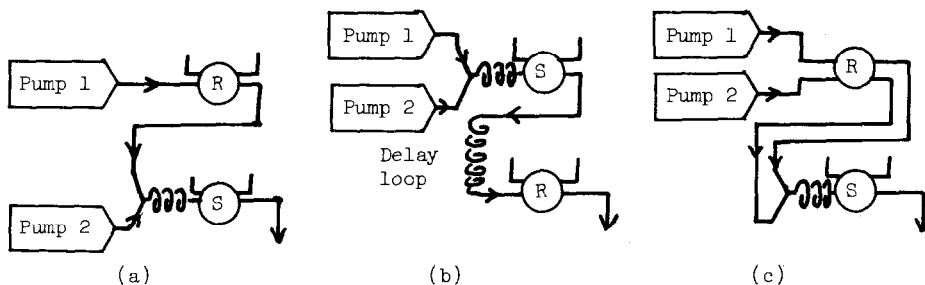


Fig. 2. Schematic diagram of flow system. S and R denote sample and reference cells, respectively. (a): mode for calibration of heat loss, (b): delay mode (Picker's normal mode), (c): direct mixing mode.

between before and after mixing. Therefore, the heating power for the each cell, P

$$P(R) = (n_1 \cdot C_{p,1} + n_2 \cdot C_{p,2}) \cdot \Delta T + H_L(S) - H_L(R) \quad (1)$$

$$P(S) = (n_1 + n_2) \cdot C_{p,s} \cdot \Delta T + H_L(S) \quad (2)$$

where S or R denotes the sample or reference cell, 1 or 2 stands for the pure component, $C_{p,i}$ is the molar heat capacity of the component i , ΔT is the change of temperature produced by electrical heating of the liquid, n_i is the moles of the component i . $H_L(S)$, which is heat loss of solution at the volume fraction ϕ , and $H_L(R)$, which is heat loss decrease of the reference cell relative to the sample cell at ϕ , are calculated from equations (3) and (4), respectively.

$$H_L(S) = \{ \phi \cdot C(HL)_1 + (1 - \phi) \cdot C(HL)_2 \} \cdot \Delta T \quad (3)$$

$$H_L(R) = \{ \phi \cdot R(HL)_1 + (1 - \phi) \cdot R(HL)_2 \} \cdot P(R) \quad (4)$$

where $C(HL)_i$ is heat loss at $\Delta T=1K$ of the component i and $R(HL)_i$ is heat loss decrease in the reference cell divided by heating power, which is estimated for the component i at ϕ .

From equations (1) and (2),

$$\frac{C_p(E)}{C_p(R)} = \frac{\Delta P - H_L(R)}{P(R) - H_L(S) + H_L(R)} \quad (5)$$

where $\Delta P = P(S) - P(R)$, $C_p(R) = x \cdot C_{p,1} + (1 - x) \cdot C_{p,2}$ and x is the mole

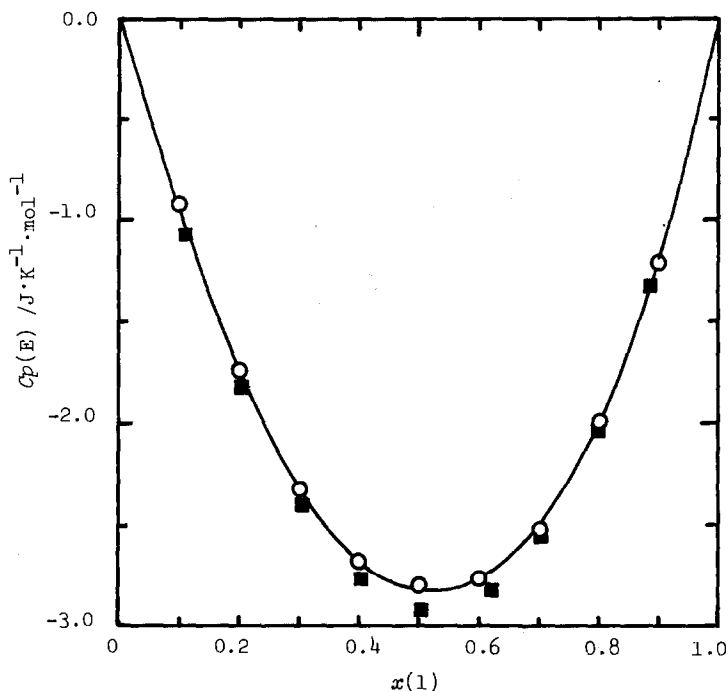


Fig. 3. Excess molar heat capacities for benzene (1) + cyclohexane (2) system at 298.15K. This work: ○, Tanaka (ref.4): ■.

fraction of the component i.

RESULTS AND DISCUSSION

The excellent linearity (less than $\pm 0.05\%$) of ΔT against P at the constant flow rate was obtained for water, benzene and cyclohexane, so that the heat losses in equations (1) and (2) were treated as the direct proportion to ΔT . In order to determine C_p accurately, the heat loss at $\Delta T=1K$ was determined for each sample. As shown in Table 1, the magnitude of the heat loss depends on the samples themselves and the flow rate.

Using the delay mode, C_p of ethanol and benzene were determined relative to C_p of water and cyclohexane, respectively. The results obtained were presented in Table 2 along with the literature values. $C_p(E)$ for the systems, benzene + cyclohexane and water + ethanol, were also determined by using the direct mixing mode. As shown in Fig. 3, $C_p(E)$ for the former case is in agreement with the literature values (ref.4) within 3.5%.

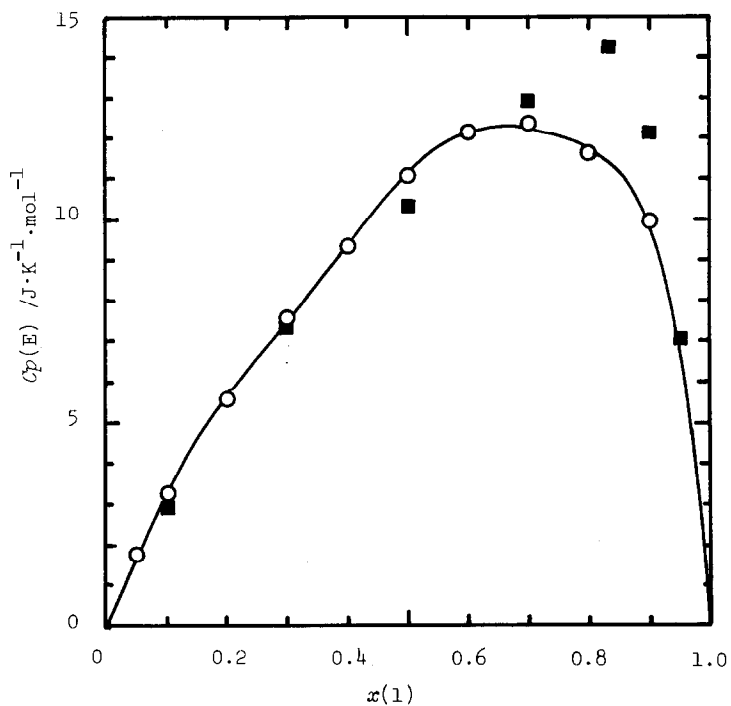


Fig. 4. Excess molar heat capacities for water (1) + ethanol (2) system at 298.15K. This work: —○—, Kiyohara *et al.* (ref.5): ■.

Table 1

Heat loss at $\Delta T=1K$ and its flow rate (fr) dependence for each samples.

Liquid	$10^3 \times C(HL) / J \cdot s^{-1} \cdot K^{-1}$			
	$fr / cm^3 \cdot s^{-1}$	5.5×10^{-3}	5.75×10^{-3}	6.0×10^{-3}
Water	1.182	1.153	-	-
Ethanol	1.884	1.824	-	-
Benzene	2.178	-	-	2.079
Cyclohexane	2.239	-	-	2.154

TABLE 2

Molar heat capacities at constant pressure of pure liquids at 298.15K.

Liquid	$C_p / J \cdot K^{-1} \cdot mol^{-1}$	Reference
Water	75.296 ^{b)}	6
Ethanol ^{a)}	110.51 ± 0.22	This work
	111.8	7
	112.34	1
Cyclohexane	155.4 ^{b)}	8
Benzene	136.06 ± 0.13	This work
	136.1	9
	135.74	4
	134.3	10

a): Ethanol (0.08 V/V % water)

b): Reference liquid

For the latter case, the dependence of $C_p(E)$ on the concentration differs remarkably from the result of Kiyohara *et al.* (ref.5) at $x=0.8$ as shown in Fig. 4. Further investigation will be required to clarify this difference.

Accuracy of the apparatus described here was found as follows; precision of the pumping rate: ± 0.05%, P : ± 0.01%, ΔP : ± 0.01% ± $3 \times 10^{-6} J \cdot s^{-1}$, stability of the thermistor bridge: ± $5 \times 10^{-5} K$, C_p : ± 0.1% (from the estimation of heat loss), $C_p(E)$: ± 1% for $C_p(E)/C_p=0.01$ (from the estimation of the stability of thermistor bridge against ΔT).

Reproducibility is believed to be better than accuracy mentioned above.

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