Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

DETERMINATION OF HEAT OF MIXING AND HEAT OF VAPORIZATION WITH A DIFFERENTIAL SCANNING CALORIMETER

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(Received October 12th, 1970)

ABSTRACT

A simple method is presented for measuring the heat of mixing and the heat of vaporization of volatile liquids at temperatures below their boiling point. It consists in introducing liquids by a microsyringe into a nearly closed cell of the DSC. The relative standard deviation for 4 to 5 runs is *ca.* 5% for heat of mixing and *ca.* 2% for heat of vaporization.

INTRODUCTION

The differential scanning calorimeter (DSC) is a calorimeter designed mainly to carry out temperature scans. It can also be used, however, as an isothermal calorimeter. This has been demonstrated by our work on the use of DSC for the determination of the rate of exothermic reactions at constant temperature[1-4]. Heat of mixing is determined accurately by any proper calorimeter. But our method, which consists in the successive addition of solute into solvent in a nearly closed cell of the DSC, affords very easily a cumulative heat of mixing using very small quantities of samples in a very short time. As for the heat of vaporization of a volatile liquid at its boiling point, Farritor and Tao[5] reported recently an improved method for measuring it with the DSC. Our purpose was to measure it at a temperature below the boiling point of the liquid. Our method, which also consists in a simple addition of the liquid into a pored cell at a constant temperature, is less accurate but much simpler than theirs.

EXPERIMENTAL

A Perkin–Elmer Model-1 DSC was used isothermally. For easy addition of liquid into a sample cell, the metallic cover of the apparatus was replaced by a glass cover with a glass tube at its center. The glass tube is designed so as to hold a microsyringe containing liquid sample (Fig. 1). By this device, the liquid sample can easily be introduced into the cell without any disturbance of the inner temperature.

A flat cylindrical closed cell with two holes on its surface was used to measure the heat of mixing. It was made of two standard open aluminum pans, bonded face to face by a heat-resistant adhesive (Fig. 1). The hole at the center of the cell is as small as possible but large enough to permit the needle of the microsyringe to pass without

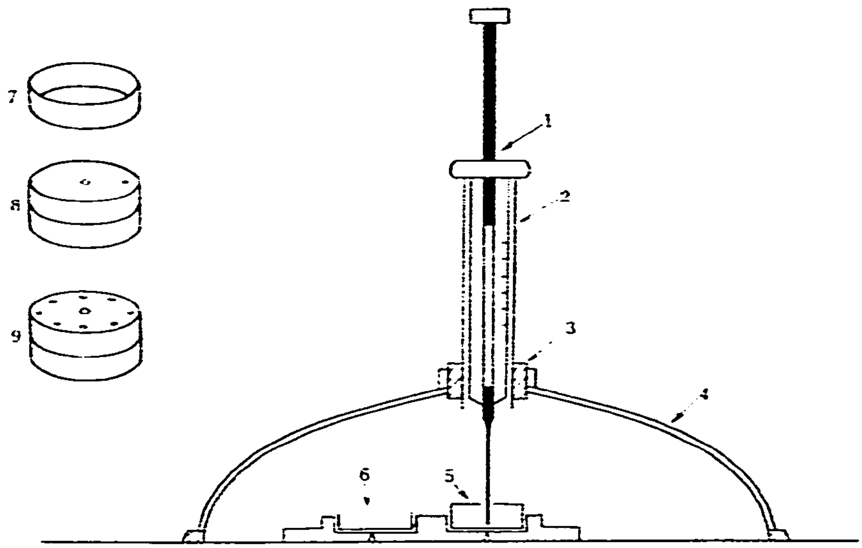

Fig. 1. Modified DSC mount and cells: 1, microsyringe; 2, glass tube; 3, rubber stopper; 4, glass cover; 5, sample cell; 6, reference cell; 7, standard open cell; 8, cell for the determination of heat of mixing; 9, cell for the determination of heat of vaporization.

contact with the cell. The other near periphery is a pin hole for the escape of air. When a cell with a single hole was used, a part of the liquid was often rejected through the clearance of the hole due to the increase in the inner pressure at the moment of addition. By the use of the above cell, vaporization of the liquid could be largely suppressed but not completely as will be discussed later. A known quantity (20–50 μl) of solvent, kept at an experimental temperature, was injected into the cell through the center hole by a microsyringe. After a temperature equilibrium was reached, a small quantity of solute (2–5 μl) was added by another microsyringe in the same manner, and the heat evolved or absorbed was registered on a chart. The heat evolution or absorption was complete within less than one minute. Then the same operation was repeated several times until the liquid in the microsyringe was exhausted.

A closed cell with many holes on its surface was used for the determination of the heat of vaporization. An open cell was also used for comparison. It was easy to control the rate of vaporization by the number and size of the holes. Volatile liquid was injected into the cell by means of a microsyringe at a desired temperature lower than the boiling point of the liquid and the heat absorbed was recorded.

The conversion factor relating the peak area on the chart to calories was obtained by a calibration using ten organic compounds with known heats of melting or heats of transition[1].

RESULTS AND DISCUSSION

Heat of mixing

A benzene–ethanol system was studied as a model for a endothermic mixing. Fig. 2 shows thermograms obtained by each successive addition of 2 or 4 μl of alcohol

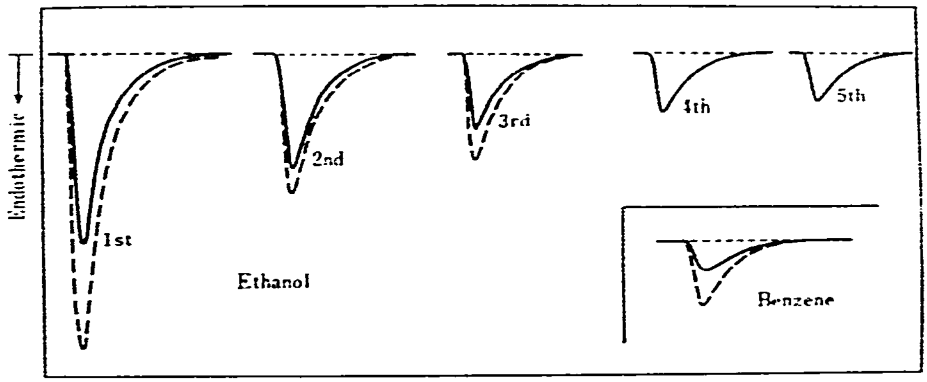

Fig. 2. Thermograms for mixing of ethanol with benzene at 40 °C. Solvent: benzene, 40 μl. ———, addition of 2 μl of ethanol; — — — —, addition of 4 μl of ethanol; lower right, addition of 2 μl of benzene.

to 40 μl of benzene. It is clearly evident that the higher the alcohol concentration in benzene, the smaller the heat of mixing for addition of an equal quantity of alcohol. Reproducibility of the experiments is rather good and the relative standard deviation for each area of the thermogram at different concentrations is within about 5%. Some examples of the data are given in Table I.

TABLE I

REPRODUCIBILITY OF HEAT OF MIXING

Figures in mcal; solvent: benzene 40 μl; temperature: 40 °C.

Run	*Successive addition of 2 μl of ethanol*					*Addition of 2 μl of benzene*
	1st	*2nd*	*3rd*	*4th*	*5th*	
1	5.50	3.38	2.62	2.11	1.78	1.11
2	5.90	3.15	2.61	2.23	1.90	1.02
3	5.60	3.41	2.40	2.03	1.67	1.18
4	5.96	3.52	2.72	2.10	1.93	1.14
Mean	5.74	3.37	2.59	2.12	1.82	1.11
Standard deviation	0.12	0.135	0.12	0.073	0.10	0.059
Relative standard deviation (%)	2.5	4.0	4.5	3.6	5.6	5.3

But unfortunately, vaporization of a very small quantity of solvent cannot be avoided. When benzene, instead of alcohol, is added to the cell already filled with benzene, a endothermic peak is observed which would not be present if the vaporization of a part of the benzene did not occur. The weight of benzene vaporized is too small (less than 0.5%) to affect the concentration. But because its molar heat of vaporization is rather large as compared with the heat of mixing, the effect of vaporization of solvent on the calorimetry cannot be ignored (Fig. 1 and Table I). The vaporization occurs only at the moment of addition, at which time the liquid is agitated. The stationary vaporization is sufficiently slow. As a consequence, the true heat of mixing is calculated by subtraction of the quantity from the apparent heat of mixing. It was confirmed that the calories due to vaporization are always the same provided that the same sample cell is used and the quantity of the added liquid is the same.

A cumulative heat of mixing of alcohol with benzene is easily obtained by summing up the heats of mixing at each successive addition. This is shown in Fig. 3. The plots of the cumulative heats of mixing obtained by the addition of 2, 3 and 4 μl of alcohol at each mixing lie on a same curve. This shows the reliability of the method. The data are converted to molar heats of mixing $\Delta H^M = \Delta H_{exp}/(n_1+n_2)$ where n_1 and n_2 are moles of solute and solvent. The latter two are plotted against the molar fraction of alcohol and compared with literature data[6] (Fig. 4). Our data at 40°C fall well between those at 35 and 45°C. The agreement is satisfactory.

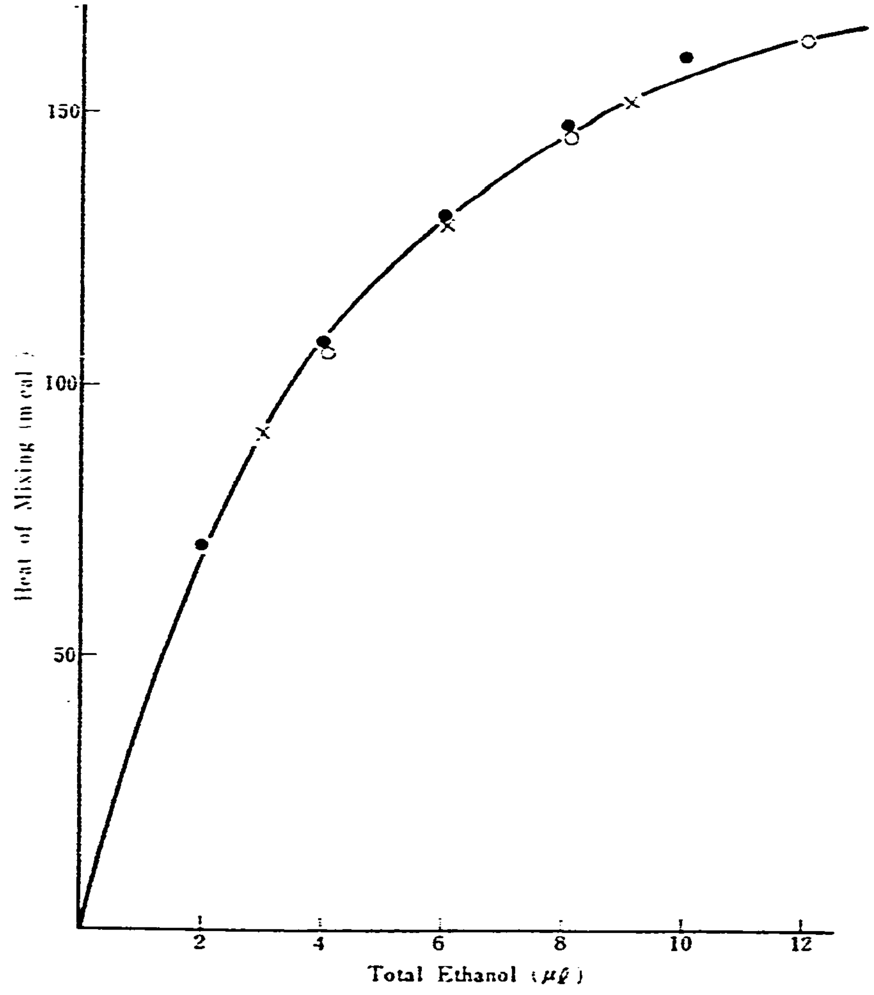

Fig. 3. Cumulative heat of mixing of ethanol with benzene (40 μl) at 40°C. Ethanol added at each mixing: ●, 2 μl; ×, 3 μl; O, 4 μl.

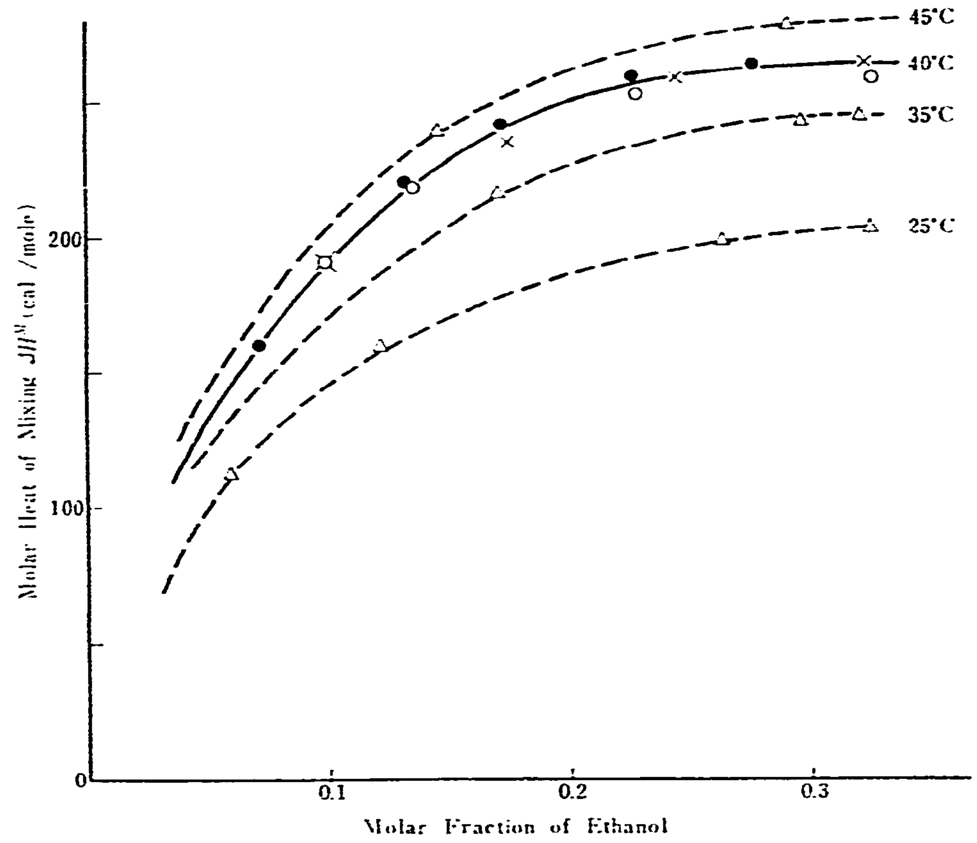

Fig. 4. Molar heat of mixing of ethanol with benzene. ———, this work: — — —, literature values.

As a model for exothermic mixing, pyridine was added to acetic acid. Its thermograms are given in Fig. 5. In this case also, the vaporization of some acetic acid cannot be avoided. By a nearly identical procedure, the heats of mixing per mole of

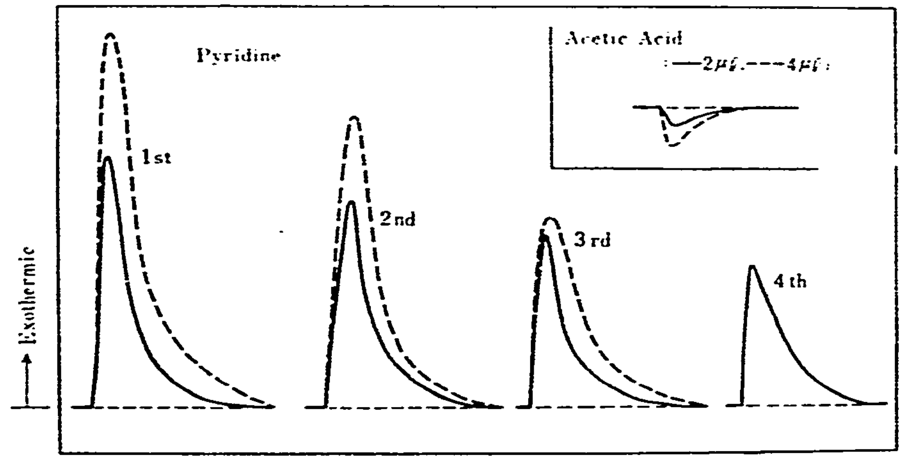

Fig. 5. Thermograms for mixing of pyridine with acetic acid at 40 °C. Solvent: acetic acid. ———, addition of 2 μl of pyridine; — — — — —, addition of 4 μl of pyridine.

solute $\Delta H^{M} = \Delta H_{exp}/n_1$ was calculated and plotted against the molar fraction of pyridine (Fig. 6). Extrapolation of the line to the ordinate affords a heat of mixing per mole of solute at infinite dilution which is 6.6 kcal/mole and in good agreement with a literature value of 6.5 kcal/mole[7].

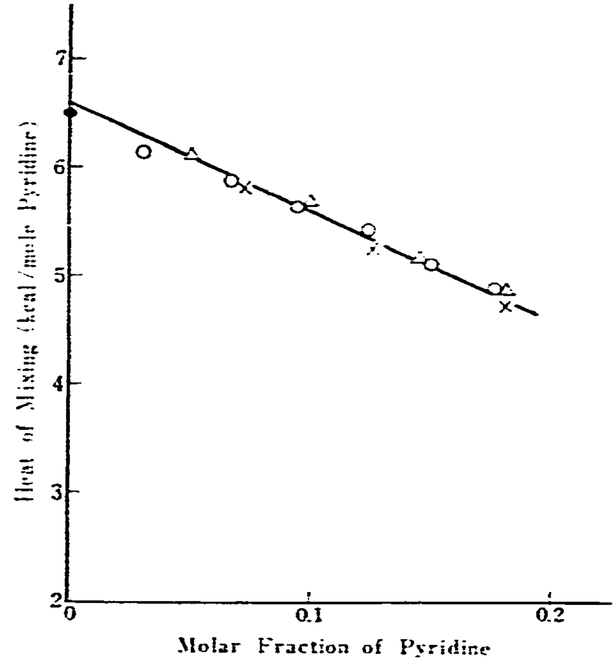

Fig. 6. Heat of mixing per mole of pyridine in acetic acid at 40 °C. Pyridine added at each mixing O, 2 μl; ×, 3 μl; △, 4 μl; ●, literature value.

Heat of vaporization

Fig. 7 shows thermograms for vaporization of benzene. When benzene is injected by a microsyringe into a pored cell, vaporization starts immediately and, as is seen in the figure, a peak due to a higher vaporization rate before the end of the flow is observed. Then a stationary vaporization follows. The rate of vaporization of this stationary period, expressed as the deflection from the base line, is nearly identical, irrespective of the sample quantity as long as the temperature is the same. At a higher temperature, the rate of vaporization is too high to be stationary. Even at 40 °C, when an open cell is used instead of a pored cell, the stationary vaporization cannot be observed (dotted line in the figure). The thermograms such as given may be used in studies on the kinetics of vaporization.

Reproducibility of the calorimetry for the heat of vaporization is better than that for the heat of mixing and the relative standard deviation for five runs remains within *ca.* 2%. The data are given in Table II. There is no systematic deviation with the quantity of the liquid used. Literature values are 7.83, 7.58[8], and 7.35[9] kcal/mole at 40, 60 and 80.1 °C (boiling point), respectively. At higher temperatures, our values

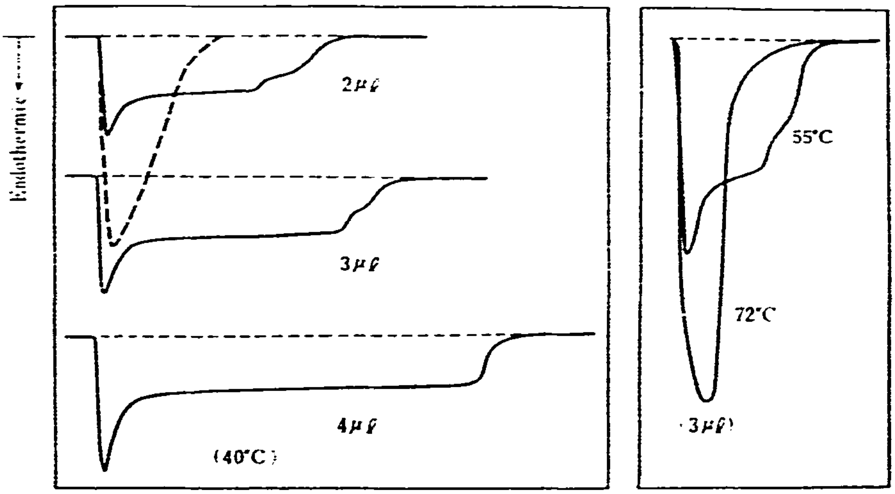

Fig. 7. Thermograms for vaporization of benzene. ———, pored cell; — — — —, open cell.

seem a little higher than these values. But as a whole the agreement between them is rather good.

TABLE II

HEAT OF VAPORIZATION OF BENZENE

Temperature (°C)	*Sample quantity (μl)*	*Heat of vaporization, mean value (kcal/mole)*	*Standard deviation (kcal/mole)*	*Relative standard deviation (%)*	*Number of runs*
	2	7.81	0.18	2.3	6
40	3	7.72	0.14	1.8	5
	4	7.90	0.10	1.3	5
	2	7.67	0.10	1.4	5
55	3	7.78	0.08	1.0	6
	4	7.88	0.12	1.5	5
	2	7.62	0.15	2.0	6
72	3	7.68	0.15	1.9	5
	4	7.48	0.09	1.2	5

Our method cannot be applied to directly measure the heat of vaporization of a liquid at its boiling point. This is not our purpose. But temperature dependence of the heat of vaporization is not very large. Consequently its value at the boiling point is estimated by extrapolation of the data at several temperatures to the boiling point. The value thus obtained is 7.5 kcal/mole for benzene which is 2% higher than the literature value. This is much better than the values obtained by a programmed temperature method or an isothermal miniputter method as mentioned by Farritor and Tao[5]. Their improved method is far better than ours, but it necessitates a special device. We think that our method is useful also for rough estimation of the heat of vaporization of a liquid at its boiling point.

It is seen from the above results that the heat of mixing and heat of vaporization can be determined by isothermal use of DSC within several % of relative standard deviation. The method is very simple and rapid, though the accuracy is not completely satisfactory. As for the heat of mixing, another advantage of the method is that a cumulative heat of mixing is obtained easily and a shortcoming is the unavoidable vaporization of the solvent at the moment of mixing. This point must be further elaborated.

Heats of mixing with solvents and heats of vaporization of some aldehydes were determined by this method. They have been used for the discussion of the polymerizability of aldehydes[10,11].

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