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DESIGN AND TESTING OF A MICROCALORIMETER WITH SEMICONDUCTOR THERMOPILES AS TEMPERATURE SENSOR AND STUDY OF THE INCLUSION OF Cu(II) WITH β-CYCLODEXTRIN *

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ABSTRACT

In this investigation, a microcalorimeter has been designed and tested which is primarily intended for studying heats of reaction in dilute solution at room temperature to 40 ° C. This microcalorimeter uses semiconductor thermopiles as the temperature difference sensor. Electrical calibration experiments and property testings indicate that the precision of the microcalorimeter is 0.3% for heat changes of about 2 J. The sensitivity is 170 μV mW^{-1}; the time constant is 260 sec.

The enthalpy of neutralization of TRIS with standard HCl solution has been measured. At 25 ° C, $\Delta H = -47.48 \pm 0.16$ kJ mol^{-1}, at 30 ° C, $\Delta H = -47.08 \pm 0.26$ kJ mol^{-1}: these results are in good agreement with values given in the literature. Using this microcalorimeter the enthalpy of the inclusion reaction of β-cyclodextrin with Cu(II) in dilute solution was measured and a value of $\Delta H = -184.2 \pm 0.7$ kJ mol^{-1} obtained at 30.0 ° C.

INTRODUCTION

In this work, a heat conduction microcalorimeter [1] has been designed and tested, at room temperature to 40 ° C. This microcalorimeter uses semiconductor thermopiles as the temperature difference sensor [2]. Heat evolved in the reaction vessel is conducted to a larger surrounding heatsink, all heat exchanges between the reaction vessel and heatsink being proportional to the voltage–time integral. The thermovoltage is directly sent to a CIR-B microprocessor. The semiconductor thermopiles used are a commercially available product designed for use in thermoelectric refrigerators and have a thermoelectric coefficient larger than that of metal thermopiles. The sensitivity of the microcalorimeter is 170 μV mW^{-1}. The reaction vessels are made from plastic material, and the volume is about 10 ml.

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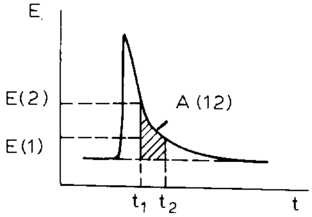

Fig. 1. Voltage–time curve.

PRINCIPLE

In this microcalorimeter, the reactants were contained in the two compartments of the batch reaction vessel, and the reaction was started by rotation of the microcalorimeter block. The total heat change of the reaction can be obtained by the Tian equation

$$Q=\frac{\gamma}{\lambda\alpha}\int_{t_1}^{t_2}E\,\mathrm{d}t+\frac{\mu}{\alpha}\int_{t_1}^{t_2}\mathrm{d}E$$

$$Q=K\times A(12)+\frac{\mu}{\alpha}[E(2)-E(1)]$$

where, γ is the thermal conductivity of the thermopile materials, μ is the effective heat capacity of the vessel and α is the thermoelectric coefficient of the materials. $A(12)$ is the integrated area of the voltage–time curve from $E(1)$ to $E(2)$ in Fig. 1, K is the electric calibration factor and λ is the fraction of the total heat conducted from the thermopiles.

ELECTRICAL CALIBRATION

In this microcalorimeter, the amount of heat evolved in the reaction vessel was calculated by integrating the area of the voltage–time curve. The calibration factors were obtained by a series of electrical calibration experi-

TABLE 1

Electrical calibration with different Q at 25 °C

Q (J)	Number of measurements	$(K\pm\sigma_a)\times10^6$ (J μV^{-1} s^{-1})	σ_a/K (%)
1.5	6	6.605 ± 0.021	0.3
2	7	6.426 ± 0.013	0.2
3	6	6.257 ± 0.009	0.17
5	5	6.169 ± 0.011	0.17

σ_a is the standard deviation of the mean.

TABLE 2

Electrical calibration with different wattage at 30.0 ° C

Power (mW)	EMF (μV)	$K \times 10^6$ (J μV^{-1} s^{-1})
0.1376	23.6	5.832
0.8216	140.4	5.833
3.989	683.6	5.832
4.854	832.1	5.832
6.852	1171	5.849
10.426	1782	5.849

ments at different temperatures and different wattages. All uncertainties are expressed as standard deviations of the mean.

Electrical calibration experiments indicated that the precision of the microcalorimeter is 0.3% when the heat change is about 2 J (see Table 1). The time constant is 260 s. The baseline was stable when the room temperature was controlled within ±1 ° C and the main block temperature varied less than ±0.05 ° C.

Electrical calibration showed that the factor K varied slightly with increasing amount of heat evolved. However, K basically remained constant with increasing wattage (see Table 2).

PROTONATION OF TRIS

The accuracy of the microcalorimeter was checked at 25.0 and 30.0 ° C by the standard reaction [3,4] of the protonation enthalpy change of TRIS (hydroxymethyl aminomethane, TRIS) buffer solution with hydrochloric acid solution (see Table 3).

The TRIS sample was of reagent grade (E. Merck) and was purified by recrystallization twice from CH_3OH. The sample was then passed through a 100 mesh screen and dried at 80 ° C for 6–8 h. Its purity was 99.98% by titration. The standard HCl solution was a 0.1 mol/1000 g solution prepared from constant boiling HCl solution; the TRIS buffer solution was a 0.1 mol/1000 g solution, pH = 8.

TABLE 3

Enthalpy results of protonation of TRIS

t (° C)	HCl (mol/1000 g)	TRIS (mol/1000 g)	Numbers of measurements	$-\Delta H$ (kJ mol^{-1})
25.0	0.009351	0.02	7	47.48 ± 0.16
30.0	0.001135	0.01	7	47.08 ± 0.26

TABLE 4

Comparison of the enthalpy of protonation of TRIS at 25.0 and 30.0 ° C

t (° C)		Method					
		Cal. [5]	EMF [6]	EMF [7]	Micro-cal. [2]	Cal. [8]	This work
25.0	$-\Delta H$ (kJ mol^{-1})	47.44	47.60	47.40	47.36	47.46	47.48
30.0	$-\Delta H$ (kJ mol^{-1})	47.11	47.27	–	–	47.11	47.08

In Table 4, results are summarized from the present measurements on TRIS together with results from the literature. It is shown that these results are in good agreement with values given in the literature and that the heat of a chemical reaction measured by this microcalorimeter is accurate and reliable.

INCLUSIONS OF Cu(II) WITH β-CYCLODEXTRIN

β-Cyclodextrin [9] is a cyclic oligosaccharide consisting of seven glucose units and can form inclusion compounds with smaller molecules which can go into its 8 Å cavity [10]. Inclusion compounds are widely utilized in the laboratory, in industry, in agriculture, in the home and so on. There are many papers [11] about the thermodynamics of the inclusion of organic molecules with cyclodextrin, but the thermodynamics of the inclusion of metal ions with cyclodextrin has not yet been reported. Using this microcalorimeter, the enthalpy of reaction of β-cyclodextrin with Cu(II) [12,13] in dilute solution at 30.0 ° C was measured, and a value of $\Delta H = -184.2 \pm 0.7$ kJ mol^{-1} obtained for the reaction

$$2\mathrm{Cu(OH)}_4^{2-} + \beta\text{-CD} = (\mathrm{C}_{42}\mathrm{H}_{66}\mathrm{O}_{35}\mathrm{Cu}_2)^{3-} + \mathrm{OH}^- + 5\mathrm{H}_2\mathrm{O}$$

The apparatus used was our microcalorimeter, a WT 80 SY NMR spectrograph, a 240 C elemental analyzer, a Beckmann DW-7 UV spectrophotometer, a "Rigard" D/MAX-IIA X-ray spectrograph, a Derivatograph thermal analyzer and a CDR-1 DSC. The β-CD (commercial product) was purified by recrystallization twice from water. Its specific rotation was 162.5 ± 0.5 °. Other reagents were of reagent grade without further purification. The β-CD with $\mathrm{CuSO_4}$ solution contained: Cu, 0.009637 mol/1000 g solution; β-CD, 0.006 mol/1000 g solution. The NaOH solution contained 0.26 mol/dm.

The two parts of the reaction vessel were filled with the two reaction solutions: by rotating the block, the enthalpy of the inclusion reaction was measured. Blank tests showed that the enthalpy of dilution of NaOH can be neglected. Using spectrophotometry, the equilibrium constant of the inclu-

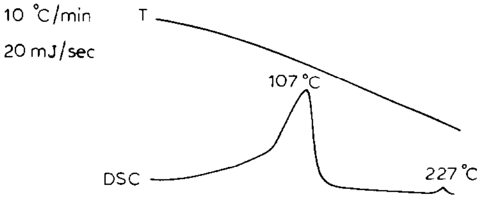

Fig. 2. DSC curve of β-CD.

sion reaction can be estimated. Crystalline inclusions have been obtained from the solution by adding known amounts of ethanol, and identified by NMR, DSC, TG–DTG–DTA–T (T = temperature curve of a sample) and X-ray diffraction.

RESULTS AND DISCUSSION

The enthalpy of the inclusion reaction was measured by microcalorimeter, giving $\Delta H = -184.2 \pm 0.7$ kJ mol^{-1} (seven experiments). The equilibrium constant of the inclusion reaction was estimated as 10^8 by spectrophotometry and iso-photodensitometry. Elemental analysis of the crystalline inclusion gave the same ratio of 2 : 1 for Cu(II) : β-CD as was found in solution.

The DSC, TG–DTG–DTA–T and X-ray diffraction results are shown in Figs 2–6.

From these results, the inclusion complex of β-CD with Cu(II) was identified. In NMR studies, it has been noted that the peaks for hydrogen within the cyclic structure were shifted slightly down-field after inclusion.

In general, it is thought that small molecules are included in cyclodextrin by van der Waals forces, hydrogen bonding and hydrophilic reactions, but in this case the enthalpy value was one order of magnitude larger than that of the inclusion of organic molecules, and this may indicate that chemical bonding is occurring in the inclusion reaction.

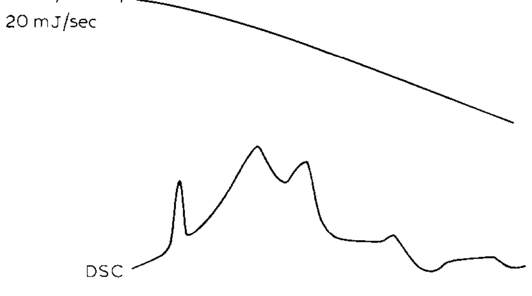

Fig. 3. DSC curve of β-CDCu$_2$(II).

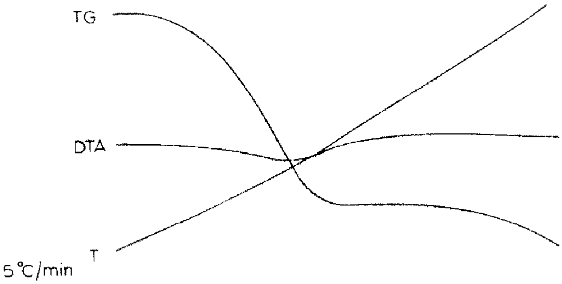

Fig. 4. TG–DTG–DTA–T curve of β-CDCu$_2$(II).

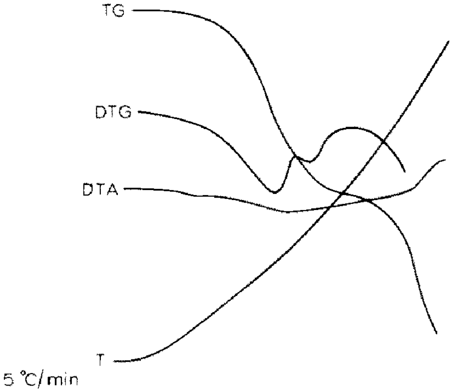

Fig. 5. TG–DTG–DTA–T curve of β-CD.

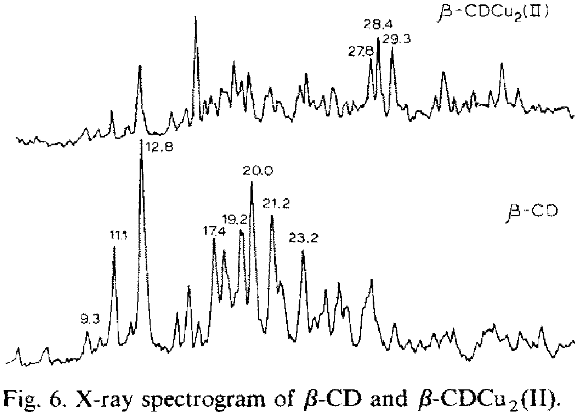

Fig. 6. X-ray spectrogram of β-CD and β-CDCu$_2$(II).

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