Measurement of the Thermal Conductivities of Neopentylglycol, 1,1,1-Trihydroxymethylpropane, and Their Mixture in the Temperature Range from 20 °C to Their Supermelting Temperatures

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The thermal conductivities of neopentylglycol (NPG), 1,1,1-trihydroxymethylpropane (TMP), and their mixture (NPG + TMP, mole ratio 50:50) were measured in the temperature range from 20 °C to their supermelting temperatures, by means of a calorimeter equipped with a thermistor. The principles of the calorimetry and the calibration of the calorimeter were described in detail. The solid−solid transition and melting temperatures were found to be 40 °C and 133 °C for NPG and 40 °C and 120 °C for (NPG + TMP), and a melting temperature of 60 °C was found for TMP. The measured thermal conductivities of these substances were fitted in the temperature range from 20 °C to their supermelting temperatures to obtain the smoothed best-fit values. The uncertainties of the measured thermal conductivities were evaluated to be ±3.5, ±2.1, and ±2.4% for NPG, TMP, and (NPG + TMP), respectively.

Introduction

Some substances such as neopentylglycol (NPG), pentaerythritol (PE), and trihydroxymethylethane (PG) are being considered as potential candidates for the thermal storage of energy. Owing to the considerable enthalpy of a solid−solid transition in the temperature range from 20 °C to 200 °C, these substances have attracted both chemists and engineers. Murrill and Breed[1] reported on the transition parameters in the compounds $CR^1R^2R^3R^4$, where R^s are methyl, methylol, amino, and carboxy, by DSC. Zhang and Yang[2−4] measured the heat capacities and transition parameters for a series of polyalcohols having solid−solid transition, by an adiabatic calorimeter. However, the thermal conductivities of the potential materials for the thermal storage of energy do not appear to be in the literature. Therefore, we made a series of measurements of thermal conductivities on polyalcohols in the temperature range from 20 °C to 200 °C. Due to 1,1,1-trihydroxymethylpropane (TMP) being a most effective dopant for reducing the solid−solid transition temperatures of these substances, this compound was also included in the study although it does not exhibit a solid−solid transition in the temperature range from 20 °C to 200 °C. As the first part of the series of measurement of thermal conductivities, the paper will describe the apparatus used in the study and report the thermal conductivities of NPG, TMP, and (NPG + TMP) from 20 °C to the supermelting temperatures of the substances.

Principles

The thermal conductivity, λ, of any substance is defined by

$$\mathrm{d}Q/\mathrm{d}t = -\lambda S(\mathrm{d}T/\mathrm{d}x) \qquad (1)$$

where dQ is the heat transmitted in time dt along a temperature gradient, dT/dx, perpendicular to an area S. Since a direct experimental measurement of dQ is not easy, the resistance, R, of a thermal element, in general, is chosen as a directly measurable quantity. Papadopoulos[5] used a small thermistor bead to measure the thermal conductivity of a liquid, and the equation

$$\Delta R/I^2R = A/\lambda + B \qquad (2)$$

where ΔR is the change of the resistance of the thermistor, I^2R is the electric energy, and A and B are the constants of the thermal conductivity cell at a certain temperature, was derived. Since the conductivity is different for different materials, the rates of temperature change of thermistors placed in different materials are not the same. Thus, the rate of temperature change of the thermistor, dT/dt, may be chosen as a directly measurable quantity. For example, Eatough[6] found that dT/dt was a linear function of the thermal conductivity, λ, of the materials under investigation. Furthermore, dT/dt can be transformed into dV/dt, the voltage change of a bridge circuit with time. If the bridge circuit shown in Figure 1 is designed, the equation

$$V = E\left(\frac{R_1}{R_1 + R_3 + R_T} - \frac{R_2}{R_2 + R_4}\right) \qquad (3)$$

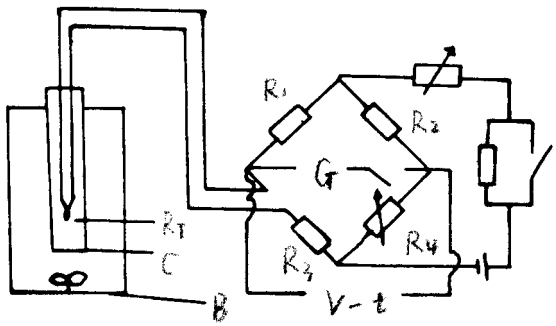

Figure 1. Schematic graph of the experimental apparatus: C, thermal conductivity cell; R_T, thermistor; R_1, R_2, R_3, standard resistances; R_4, adjustable resistance; B, thermostated oil bath; V−t, recorder.

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where V is the voltage of the bridge circuit and E is the stable dc main potential, can be derived. Since the relation

$$R_T = R_0 e^{B/T} \tag{4}$$

is valid for a thermistor, substituting eq 4 into eq 3 and differentiating it with respect to temperature gives the equation

$$dV/dT = EB\frac{R_1}{T^2}\frac{R_T}{(R_1 + R_3 + R_T)^2} \tag{5}$$

It can be seen from eq 5 that the dV/dT has a maximum value when R_T is about 3 KΩ and T is 298.15 K. When the temperature rise due to heating in the experiment is within 1 °C, the rate of voltage change of the bridge, dV/dT, can be considered as a constant; thus, the equation

$$dV/dt = dV/dT\ dT/dt = k\ dT/dt \tag{6}$$

can be obtained. It can be seen from eq 6 that dV/dt is proportional to dT/dt. Thus, dV/dt, an easily measurable quantity, will be a linear function of the thermal conductivity, λ, of the materials.

Experiment

Apparatus and Procedure. The apparatus is shown schematically in Figure 1. Basically, it is composed of a thermal conductivity cell, an electrical bridge circuit, and a thermostated oil bath. The thermal conductivity cell, C, is made of a 1 mm thick silica tube and is 40 mm long and 15 mm in inner diameter. A specially made small thermistor bead R_T fitted in the center of the cell is used as the heating and measuring element. The bridge circuit is composed of the three standard resistances R_1, R_2, and R_3, 1 KΩ each, the adjustable resistance R_4, and the thermistor R_T. A recorder (type LM20A-100 made by the Shanghai Dahua Factory) is used to record the voltage change of the bridge circuit, and a thermostated oil bath in which the cell is placed is used to obtain the constant temperature needed in the experiment.

Filling of the sample into the thermal conductivity cell is carried out at room temperature. A liquid sample is directly added into the cell. However, a solid sample is first melted in the cell and then cooled to room temperature. Putting the cell containing the sample and the thermistor into the thermostated oil bath, the thermistor is connected to the bridge circuit. Thus, a steady current of about 0.04 mA is passed through the bridge. Adjusting R_4 to keep the bridge balance, a heating current of about 1.00 mA is passed through the thermistor. Then dV/dt is measured. Since the time constant of the small thermistor bead placed in materials is less than 0.5 s, a measurement is completed within about 1 s.

Materials. Samples for this work were prepared in the following manner. NPG (No. l Reagent Manufactory, Shanghai) was sublimated twice. TMP (No. 1 Reagent Manufactory, Shanghai) was recrystallized from dry ether. The purities of the two samples were found to be 99.37 mol % and 99.12 mol %, respectively, from analysis of their equilibrium melting curves. To obtain the sample of (NPG + TMP), the two purified substances were mixed in a 50:50 mole ratio, heated to produce a clear liquid, and ground into a fine powder after the melted mixture was cooled to room temperature. Two chemically pure compounds, decanol and hexadecane, were purified by evaporation, and four analytically pure compounds, glycerol, heptane, 1,2-ethanediol, and toluene, were used as received from No. 1 Reagent Manufactory, Shanghai.

Calibration. Due to the wide temperature range needed in the study, two thermistors, one was 3 KΩ and the other was 30 kΩ at room temperature, were alternatively used in the apparatus. Thus, two sets of calibration of the conductivity cell were made. One was for the temperature range from 20 °C to 90 °C, and the other was for the temperature range from 90 °C to 200 °C. Four compounds, glycerol, 1,2-ethanediol, toluene, and heptane, were used as reference substances to calibrate the cell from 20 °C to 90 °C, and four compounds, glycerol, 1,2-ethanediol, decanol, and hexadecane, were used from 90 °C to 200 °C. The thermal conductivities for each of the six reference compounds used in this study were measured with an uncertainty of 2−5% by absolute method, for example, for glycerol by Venart and Krishnamurthy[7] and Rastorguev and Gazdiev,[8] for 1,2-ethanediol by Venart and Krishnamurthy[7] and Riedel,[9] for toluene by Rastorguev and Pugach[10] and Mani and Venar,[11] for heptane by Rastorguev et al.[12] and Pittman,[13] for hexadecane by Bogatov et al.[14] and Mukhamedzyanov et al.,[15] and for decanol by Ganiev[16] and Jobst.[17] The recommended thermal conductivities given by Orcharenko[18] for decanol were directly used in this study, while, for the five other compounds, we obtained the reference values from the literature values by the smoothed best-fit method. The relative standard deviations of the individual literature values from the smoothed best-fit values were evaluated to be 2.0%. Using these recommended and reference values, the relations of dV/dt to λ

$$\lambda = A - B\ dV/dt \tag{7}$$

where A and B were constants of the thermal conductivity cell at a certain temperature, were obtained at 10 °C intervals by the method of least squares. The A and B values obtained thus from 20 °C to 90 °C and from 90 °C to 200 °C are listed in Table 1 and Table 2, respectively.

Table 1. A and B,[a] Constants of the Cell, and Experimental and Reference Values of λ[b] for the Reference Compounds from 20 °C to 90 °C

	glycerol		1,2-ethanediol		toulene		heptane			
t/°C	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	A	B
20	287.9	285.2	251.3	254.6	135.5	135.3	121.3	120.8	626.3	60.21
30	285.9	286.0	255.8	255.7	132.8	132.9	117.6	117.6	623.5	60.57
40	286.0	286.8	257.8	256.9	130.3	130.4	114.9	114.4	620.2	60.82
50	286.3	287.6	259.7	258.1	127.7	127.9	111.1	111.2	616.7	61.14
60	286.4	288.4	261.7	259.3	125.2	125.5	107.9	108.0	613.0	61.48
70	286.5	289.2	263.6	260.5	122.7	123.1	104.8	104.8	608.9	61.62
80	286.6	290.0	265.6	261.7	120.2	120.6	101.5	101.6	604.9	61.84
90	286.7	290.8	267.5	262.9	117.7	118.2	98.4	98.4	600.7	62.04
σ	±2.65		±3.07		±0.33		±0.28			

[a] Units of 10^{-3} W m^{-1} K^{-1}. [b] Units of 10^{-3} W m^{-1} K^{-1}.

Table 2. *A* and *B*,[a] Constants of the Cell, and Experimental and Reference Values of λ[b] for the Reference Compounds from 90 °C to 200 °C

	glycerol		1,2-ethanediol		toluene		heptane			
t/°C	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	*A*	*B*
90	295.0	290.8	256.9	262.9	152.0	149.0	124.5	125.6	641.9	66.72
100	294.7	291.6	259.7	264.1	148.9	146.0	121.7	123.3	646.7	67.61
110	294.2	292.4	262.6	265.3	146.3	144.0	119.6	121.1	649.6	68.18
120	293.8	293.2	265.5	266.5	143.5	142.0	117.2	118.3	653.2	68.88
130	293.2	294.0	268.3	267.7	140.7	139.0	115.0	116.6	655.8	69.40
140	292.5	294.8	271.3	268.9	138.6	137.0	113.6	114.4	656.7	69.62
150	295.3	295.6	277.2	271.1	135.1	134.0	109.9	111.8	662.5	70.68
160	291.7	296.4	277.5	272.6	132.4	131.0	108.2	109.8	665.1	71.23
170	290.9	297.2	280.6	274.1	129.8	128.5	106.3	107.8	666.9	71.62
180	292.8	298.0	286.1	275.6	127.3	126.0	104.2	105.8	677.0	73.10
190	298.2	298.9			125.5	123.5	102.2	103.9	698.9	76.07
200	299.7	299.8			122.9	121.0	100.2	101.9	706.0	77.15
σ	±3.39		±5.61		±2.01		±1.57			

[a] Units of 10^{-3} W m^{-1} K^{-1}. [b] Units of 10^{-3} W m^{-1} K^{-1}.

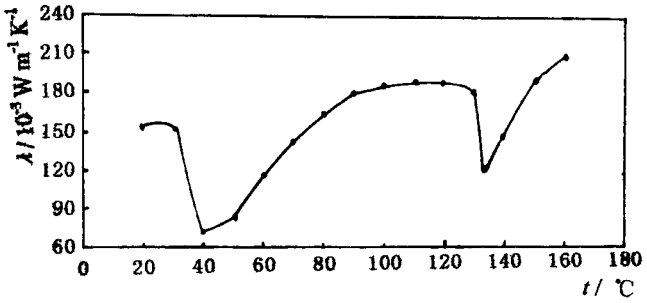

Figure 2. Thermal conductivity of NPG from 20 °C to 90 °C.

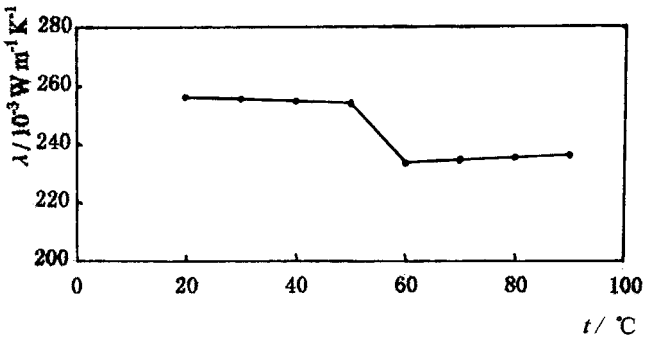

Figure 3. Thermal conductivity of TMP from 20 °C to 90 °C.

To illustrate the reliability of the apparatus and the calibration, the experimental and reference values of λ for the six reference substances are also listed in Table 1 from 20 °C to 90 °C and in Table 2 from 90 °C to 200 °C. The standard deviations, σ, given in Tables 1 and 2 were evaluated by the formula

$$\sigma = \pm\sqrt{\frac{(\lambda_{exp} - \lambda_{ref})^2}{n-1}}$$

in which n is the number of experimental temperature points.

Thermal Conductivities of NPG, TMP, and (NPG + TMP, Mole Ratio 50:50). The dV/dt values of NPG, TMP, and (NPG + TMP, mole ratio 50:50) were measured at 10 °C intervals from 20 °C to their supermelting temperatures. On the basis of these measured dV/dt values and the values of A and B, the constants of the cell at 10 °C intervals, the thermal conductivities of NPG, TMP, and (NPG + TMP) were determined and illustrated in Figures 2−4. From the figures, the solid−solid transition and melting temperatures were found to be 40 °C and 133 °C for NPG and 40 °C and 120 °C for (NPG + TMP), and the melting temperature was found to be 60 °C for TMP. The solid−solid transition and melting temperatures, obtained by this study, of NPG, TMP, and (NPG + TMP) agreed with the results given by Zhang and Yang[2,19] from the adiabatic calorimeter within 2 °C. The experimental thermal conductivities of NPG, TMP, and (NPG + TMP) were fitted in temperature to obtain the smoothed best-fit values. The experimental and smoothed λ values of these substances at 10 °C intervals are listed in Table 3. The relative standard deviations of the experimental λ values from the

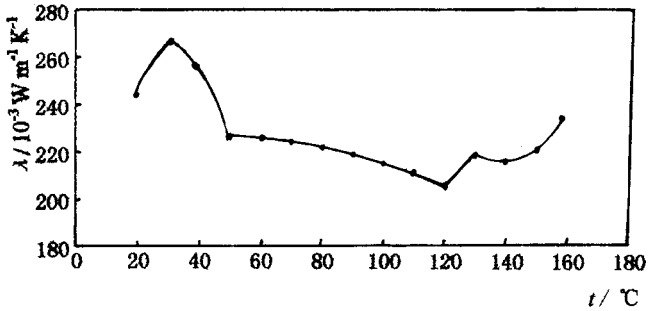

Figure 4. Thermal conductivity of (NPG + TMP, mole ratio 50:50) from 20 °C to 160 °C.

Table 3. Thermal Conductivities[a] of NPG, TMP, and (NPG + TMP, Mole Ratio 50:50)

	NPG		TMP		(NPG + TMP)	
t/°C	λ_{exp}	λ_{smo}	λ_{exp}	λ_{smo}	λ_{exp}	λ_{smo}
20	153.6	153.6	256.5	256.5	243.9	243.9
30	154.0	154.0	256.0	255.9	265.6	265.6
40	75.4[b]		255.2	255.2	257.1[b]	
50	84.5	83.8	254.6	254.5	228.1	227.6
60	112.5	115.9	234.4[b]		225.5	226.0
70	140.8	142.2	235.2	235.2	223.0	224.0
80	169.3	162.7	235.9	235.9	220.5	221.5
90	180.1	177.5	236.6	236.6	219.4	218.5
100	182.9	186.5			215.3	215.1
110	184.4	189.7			209.8	211.2
120	190.8	187.1			204.1[c]	
130	180.3	178.7			218.5	217.0
133	120.7[c]					
140	144.8	144.8			213.1	214.4
150	187.5	187.5			222.5	219.3
160	205.5	205.5			232.2	231.7
σ	±2.90		±0.17		±0.78	

[a] Units of 10^{-3} W m^{-1} K^{-1}. [b] Thermal conductivity at temperatures of transition. [c] Thermal conductivity at temperatures of fusion.

smoothed λ values are ±1.5, ±0.1, and ±0.4% for NPG, TMP, and (NPG + TMP), respectively.

Discussion

The experimental method applied in this study is a kind of relative method. Basically, the uncertainty of the thermal conductivities measured in the study depends on the accidental change in the experimental conditions and the uncertainty of the thermal conductivities of the reference substances used in the calibration of the apparatus. The former will result in the accidental uncertainty of the measurement, and the latter will bring the systematic uncertainty to the experimental results. The relative standard deviations of the experimental λ values from the smoothed λ values were evaluated to be ±1.5, ±0.1, and ±0.4% for NPG, TMP, and (NPG + TMP), respectively. Combining those values of uncertainty with the systematic uncertainty of ±2.0% resulted in the calibration of the apparatus; we evaluated that the uncertainty of the thermal conductivities measured in this study was ±3.5, ±2.1, and ±2.4% for NPG, TMP, and (NPG + TMP), respectively.

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