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A NEW CALORIMETER FOR MEASURING RAPIDLY THERMAL CONDUCTIVITIES OF THE ORGANIC LIQUIDS AND THE ELECTRICALLY CONDUCTING LIQUIDS

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Abstract

A new calorimeter for measuring thermal conductivity of liquids has been constructed. It is wholly automatic under the computer control. The time of measurement is 1 s and the temperature rise due to heating is within 1°C. Six organic liquids and six aqueous solutions of electrolytes were employed as reference standards. The instrument was calibrated at 25°C. Its accuracy is better then 1% with a precision of about 0.2%.

Keywords: calorimeter, electrically conducting liquids, thermal conductivity

Introduction

The measurement of thermal conductivity of liquids is very important to both practical applications and theoretical research. However, it is quite difficult to measure accurately the thermal conductivity of liquids, because of the presence of convection and radiation accompanying the measurement process.

Thermal conductivity (λ) of any substance is defined by Eq. (1).

$$dQ/dt = -\lambda A(dT/dx) \tag{1}$$

where dQ is the heat transmitted in time dt along a temperature gradient, dT/dx perpendicular to an area A. It is now known that, the convection and radiation caused by the temperature gradient and measurement time tend to make experimental values too high.

Mallan [1] have collected the experimental thermal conductivities of toluene at 20°C over the past 44 years. The experimental values have decreased, year by year, from 1923 to 1967. The decrease is due to improvements in the measuring method and experimental techniques. Reid [2] pointed out that many investigators have contributed notably to the measurement of λ of liquids, but the results of these investigations often do not agree well, with the deviations as large as 5

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to 10 percent. By reviewing, we conclude that the lower values are generally more acceptable.

The measuring of thermal conductivity of aqueous solutions of electrolytes is more difficult. The conventional 'hot wire' method is not applicable.

In order to overcome the effects of convection and radiation, the authors have constructed an experimental apparatus. The measuring time is 1 s, and the temperature rise due to heating is within 1°C.

Apparatus

The experimental apparatus is shown schematically in Fig. 1.

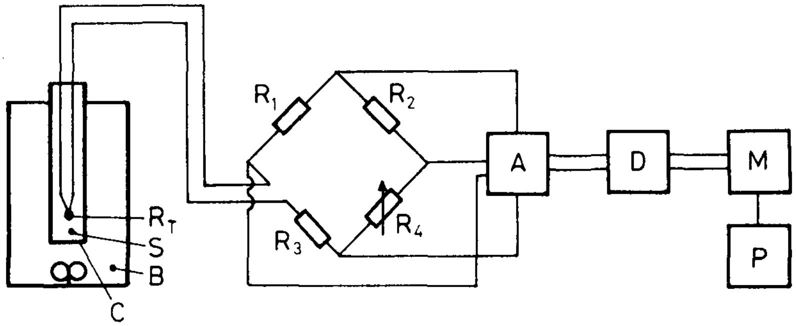

Fig. 1 Schematic graph of the experimental apparatus. *C*-thermal conductivity cell; *S*-liquid sample; R_T-thermistor; *B*-thermostatic water bath; R_1, R_2, R_3-standard resistance; R_4-adjust resistance; *A*-amplifier and d,c, mains; *D*-diskette and fixed disk system; *M*-computer; *P*-printer

The thermal conductivity cell is cylindrical in form, 40 mm in length and 15 mm inner diameter. A specially made small bead of glass thermistor is used as the heating element. It is immersed in the liquid to be investigated. The thermistor is connected to an electric circuit of an unbalance bridge. R_1, R_2 and R_3 are standard resistances, 1000 Ω each. R_T is resistance of the thermistor.

A steady current is passed through the thermistor immersed in the stationary liquid. Because the conductivity is different for different liquid, the rate of temperature change of the thermistor immersed in different liquid is not the same. It has been found that the rate of temperature change dT/dt is inversely proportional to the thermal conductivity λ of the liquid [3].

$$R_T = R_o e^{B/T} \tag{2}$$

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

where V is voltage of unbalance bridge, E is the stable d.c. main potential. Substituting Eq. (2) into Eq. (3) and differentiating it with respect to temperature T, we obtain:

$$\mathrm{d}V/\mathrm{d}T = \frac{EBR_1}{T^2}\left(\frac{R_T}{R_1 + R_3 + R_T}\right) \tag{4}$$

The $\mathrm{d}V/\mathrm{d}T$ is a function of temperature T and thermistor resistance R_T. E, R_1 and B are constants. The Eq. (4) shows that, if R_T is about 3 kΩ and T is 298. 15 K, then the $\mathrm{d}V/\mathrm{d}T$ is maximum value, and if the temperature rise due to heating in experiment is within 1°C, the $\mathrm{d}V/\mathrm{d}T$ can be considered as a constant.

$$S_i = \mathrm{d}V/\mathrm{d}t = \mathrm{d}V/\mathrm{d}T{\cdot}\mathrm{d}T/\mathrm{d}t = k\mathrm{d}T/\mathrm{d}t \tag{5}$$

The S_i is a rate of voltage change of the bridge and it is determined in experiment. Since $\mathrm{d}V/\mathrm{d}T$ is constant, the S_i will also be inversely proportional to thermal conductivity of the liquids [4, 5].

Experiment and results

Liquid sample is added into the thermal conductivity cell. A stable current 0.041 mA is passed through the thermistor bridge; R_4 is adjusted to keep bridge in balance. Then a heating current of 1.000 mA is passed through the thermistor. The time constant of small thermistor immersed in the liquids is less than 0.5 s. The S_i is measured 0.5 s after heating current circuit is closed, and the measuring time is 1 s.

The apparatus system is comprised of hardware wherein experimental controll, data acquisition and analysis are accomplished by a computer under soft-

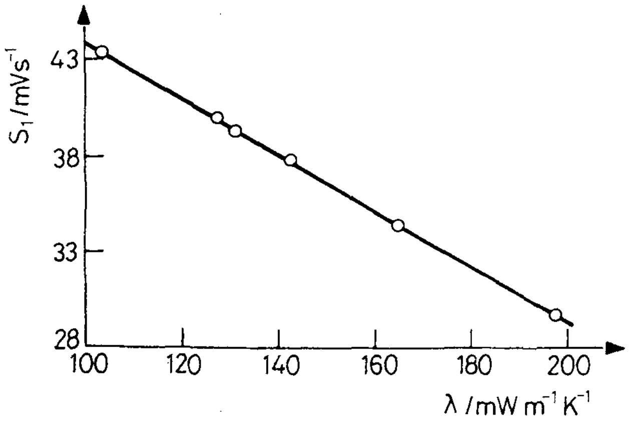

Fig. 2 The plot of λ *vs.* S_i for 6 reference liquids

ware control. In order to measure λ of organic liquids, six analytically pure liquids, methanol, ethanol, benzene, toluene, *n*-heptane and carbon tetrachloride, were taken as reference substances. The apparatus has been calibrated at 25°C by using these 6 liquids. Figures 2 shows a typical plot of λ *vs.* S_i.

The corresponding data have been calculated by means of least square. We obtained a calibration equation of the apparatus:

$$\lambda(\mathrm{mW/mK}) = 391.80 - 6.589S_i \tag{6}$$

Table 1 shows the comparison between predicted values by Eq. (6) and the corresponding literature values.

Table 1 The comparison of experiment λ_{exp}, and literature λ_{lit}

Sample	S_i/mV·S^{-1}	λ_{lit}/mW·mK^{-1}	λ_{exp}/mW·mK^{-1}	dev. / %
methanol	29.504	197.2$^{(6)}$	197.4	0.1
ethanol	34.528	164.2$^{(6)}$	164.3	0.1
benzene	37.928	142.1$^{(7)}$	141.9	0.1
toluene	39.445	131.6$^{(8)}$	131.9	0.2
n-heptane	40.280	127.5$^{(9)}$	126.4	0.8
carbon tetrachloride	43.800	102.5$^{(10)}$	103.2	0.7

The accuracy is better than 1%.

The S_i is mean value of six measurements, for toluene, and the S_i's six in Table 2.

Table 2 Six S_i and mean of toluene

No.	1	2	3	4	5	6	Mean
S_i/mV·S^{-1}	39.504	39.452	39.429	39.427	39.453	39.453	39.453

In order to measure λ of aqueous solutions of the electrolytes, six liquids, aqueous solution of 30% KOH, 25% H_2SO_4, 10% NaCl, 20% NaCl, 20% ethanol and water were taken as reference samples. As mentioned above, the apparatus has been calibrated. We obtained the calibration Eq. (7) and Table 3.

$$\lambda(\mathrm{mW/mK}) = 1381.3 - 49.9S_i \tag{7}$$

Discussion

Being a comparative method, the accuracy depends on the uncertainty of the thermal conductivity values of reference liquids. In order to maintain accuracy, six reference liquids were used to calibrate the apparatus and the corresponding data were calculated by means of least square.

Table 3 The comparison of λ_{exp} and λ_{lit}

Sample	S_i/mV·S^{-1}	λ_{exp}/mW·mK^{-1}	λ_{lit}/mW·mK^{-1}	dev./%
water	15.448	611.1	610$^{(11)}$	0.1
30% KOH	15.846	591.2	590$^{(11)}$	0.2
25% H_2SO_4	16.840	541.7	539$^{(12)}$	0.5
20% CH_3CH_2OH	18.178	475.0	476$^{(11)}$	0.2
10% NaCl	15.856	590.7	591$^{(13)}$	1.0
20% NaCl	15.946	586.3	584$^{(13)}$	0.4

The accuracy is better than 1%.

The measuring time is 1 s and the temperature rise is within 1°C, so that the effects of convection and radiation may be neglected.

The stability of this thermistor is not very good. The change in resistance is about 0.1% for one year. When obvious change in resistance is discovered, the apparatus will be calibrated once again.

From measured values of S_i of toluene (in Table 2), we find that the precision of measurement is better than 0.2%. Such as apparatus is also applicable for rapid compositional analysis.

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Zusammenfassung — Es wurde ein neues, vollständig rechnerkontrolliertes Kalorimeter zur Messung der Wärmeleitfähigkeit von Flüssigkeiten konstruiert. Die Meßzeit beträgt 1 s und die Temperaturerhöhung infolge des Erhitzens bleibt innerhalb 1°C. Als Bezugssubstanzen wurden sechs organische Flüssigkeiten und sechs wäßrige Lösungen von Elektrolyten verwendet. Das Gerät wurde bei 25°C kalibriert. Die Genauigkeit ist besser als 1%, der Meßfehler etwa 0.2%.