THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF POLY(ACRYLIC ACID) BY TRANSIENT HOT WIRE TECHNIQUE
Absolute measurement

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The paper describes a new transient hot wire instrument which employs 25.4 μm diameter tantalum wire with an insulating tantalum pentoxide coating. This hot-wire cell with a thin insulating layer is suitable for measurement of the thermal conductivity and the thermal diffusivity of electrically conducting and polar liquids. This instrument has been used for experimental measurement of the thermal conductivity and the thermal diffusivity of poly(acrylic acid) solution (50 mass%) in the temperature range of 299 to 368 K at atmospheric pressure. The thermal conductivity data is estimated to be accurate within ±4%. Thermal diffusivity measurements have a much higher uncertainty (±30%) and need further refinement.

Introduction

The thermophysical properties of fluids such as thermal conductivity and thermal diffusivity are of considerable significance for industrial applications. Several instruments have been developed to measure the thermal conductivity and thermal diffusivity [1–11]. Transient hot-wire instruments for measurement of electrically conducting liquids have also been described in many papers. In the present work, a hot-wire cell employing two tantalum wires 25.4 μm in diameter and anodized with an insulating coating of tantalum pentoxide has been used. The insulated hot-wire eliminates the leakage of electric current into electrically conducting liquids and thus closely approximates the ideal line source. This hot-wire cell has been used for the measurement of the thermal conductivity and thermal diffusivity of poly(acrylic acid) solution. Poly(acrylic acid), PAA is used in various technological applications such as drug delivery and as a medium for the synthesis of nanoparticles. They are also used in the cultural heritage conservation field as cleaning agents [12] and synthesis of calcium silicates hydrates (C–S–H)-polymer nanocomposite (C–S–HPN) materials [13, 14]. The knowledge of the thermal conductivity and the thermal diffusivity of poly(acrylic acid), though vital and necessary is, however, very limited at present.

In this paper, experimental measurement of the thermal conductivity and thermal diffusivity of PAA in the temperature range of 298 to 368 K at atmospheric pressure are reported.

Theory and the ideal line source technique

In the transient hot-wire technique, a thin wire is immersed in the test fluid and connected to the electrical circuit. The thin wire is used simultaneously as a heat source and a resistance temperature detector (RTD) to measure the resulting temperature rise. After a step voltage has been applied, the constant heat flux per unit length generated by the hot wire is dissipated into the fluid and a temperature rise history develops in both the wire and the fluid. According to the ideal mathematical model [15], the thermal conductivity and the thermal diffusivity can be obtained.

The basic governing equation is described by

$$\frac{\partial T}{\partial t} = k\nabla^2 T \tag{1}$$

with the boundary conditions:

$$\text{at } t \leq 0 \text{ and any } r, \ \Delta T(r,t)=0 \tag{2}$$

$$\text{at } r=0 \text{ and any } t \geq 0, \ \lim_{r \to 0}\left(r\frac{\partial T}{\partial r} \right)=-\frac{q}{2\pi\lambda} \tag{3}$$

at $r=\infty$ and any $t\geq0$, $\lim_{r\to\infty}\Delta T(r,t)=0$ (4)

This results in the following solution for the temperature rise:

$$\Delta T_w (a,t)=\left(\frac{q}{4\pi\lambda}\right)\ln\left(\frac{4kt}{a^2C}\right)$$

$$=\frac{q}{4\pi\lambda}\ln t+\frac{q}{4\pi\lambda}\ln\frac{4k}{a^2C}=G\ln t+A$$ (5a)

where

$$\Delta T=\Delta T_w (t)+\sum_{i=1}^{n}\delta T_i$$ (5b)

δT_i are appropriate corrections to the measured temperature rise, ΔT_w, λ is the thermal conductivity of the medium, k is the thermal diffusivity of the fluid medium, q is the heating power per unit length of the wire, a is the radius of the hot wire and C is the Euler's Constant. Based on the solution (Eq. (5a)), the thermal conductivity can be determined from the slope G of the linear relationship between the measured hot wire temperature rise and the logarithm of the elapsed time. At the same time, the thermal diffusivity can be derived from the intercept A of the linear relationship.

Experimental

A transient hot-wire cell (Fig. 1) was designed and constructed by the authors for measurement of both thermal conductivity and thermal diffusivity of electrically conducting liquids. The material of the cell was teflon. Two tantalum wires of different lengths, with a diameter of 25.4 μm coated with a layer of tantalum pentoxide were employed as heat sources. The long wire was 51.66 mm in length with a resistance of approximately 17.37 Ω at 20°C; the short wire was 27.18 mm in length with resistance of approximately 9.30 Ω at 20°C. The wires were spot welded to the springs and were held taut and straight by adjusting the springs.

Following the assembly of 25.4 μm diameter short and long Ta-wires in the teflon cell, the entire assembly (hot-wires, ceramics supports for the thick Ta-wires and Ta-springs) were chemically polished by immersing the cell in a mixture of 98% sulfuric acid, 70% nitric acid, and 40% hydrofluoric acid in the proportions of 10:4:3 respectively by volume for three seconds, then immediately leached in near boiling water for 15 min and then rinsed three times with distilled water.

In order to anodize all the components constructed with tantalum wire, the entire cell assembly was placed in 0.2 M solution of sulfuric acid in
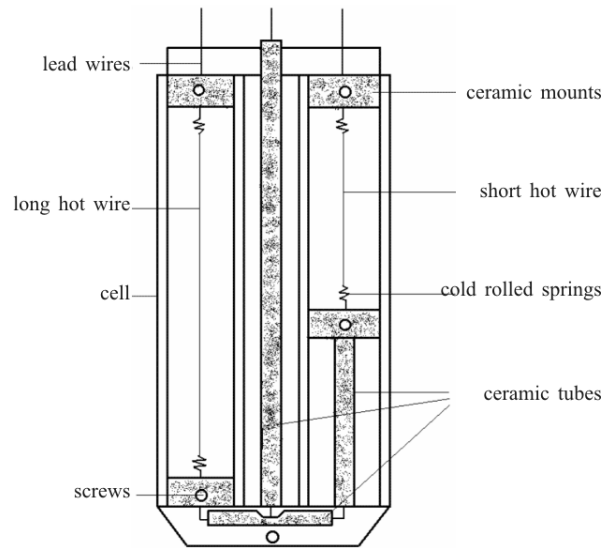

Fig. 1 Experimental cell

demineralized water. The tantalum wires were connected as anode while a platinum wire was used as a cathode. The voltage applied was 50 VDC and it was held constant until the current fell to approximately 0.015 mA. This procedure resulted in deposition of a layer of tantalum pentoxide on the surface of the wires. The thickness of the coating was estimated to be about 170 nm from scanning electron microscope (SEM) images of the cross section of the bare and coated wire. Hot wire specifications are listed in Table 1.

The electrical system (Fig. 2) includes a HP DC Power Supply (Model HP6625A), a HP Data Acquisition/Control Unit (Model HP3497A), a HP Multimeter (Model HP3458A) which provides integration from 0 to 16667 ms, a HP System Voltmeter (Model HP3437A) and a C-MOS digital

Table 1 Wire specifications

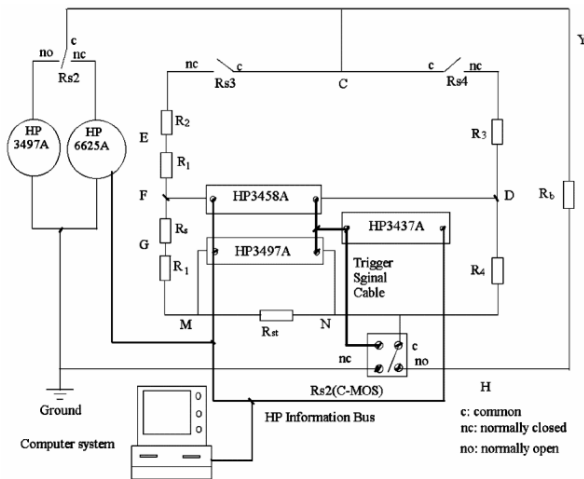| Parameter	Long wire	Short wire
Length/mm	51.66±0.36 (0.7%)	27.18±0.05 (0.18%)
Diameter/μm	25.43±0.04 (0.16%)	25.43±0.04 (0.16%)
Diameter after coating/μm	25.79±0.04 (0.15%)	25.79±0.04 (0.15%)
Material	Tantalum	Tantalum pentoxide
Symbol	Ta	Ta_2O_5
Molar mass/g mol^{-1}	180.948	441.893
Thermal conductivity/ W m^{-1} K^{-1}	57.5	0.4
Specific heat/J kg^{-1} K^{-1}	140	306
Density/kg m^{-3}	16400	8540

Fig. 2 Electrical and data acquisition system

switch used to switch from the 'dummy' to the 'measurement' circuit. HP3497A is used to provide digital switches for circuit connection and to provide a 1 mA constant current source to balance the measurement bridge. HP6625A, a programmable power supply, is used to provide the heating power during transient measurement under computer control. The circuit consists of a calibrated 25 Ω standard resistance, R_{st}, four ballast resistance boxes R_1, R_2, R_3, R_4 and a dummy resistance R_b and the two hot wires, R_l and R_s. The details of principle of the measurement are described elsewhere [16].

The cell is immersed in a constant temperature oil bath (LAUDA, Model-KS-20D, Brinkmann Instruments Ltd.) which uses a pressure pump to circulate oil to an external system, if required. Its operating range is from ambient to 523 K (250°C) and maintains a desired temperature within ±0.01 K.

The hot-wires were calibrated (Eqs (6) and (7)) before the measurements to obtain their temperature coefficients.

For long wire:

$$R_l = R_{l0}[1 + 3.2110 \cdot 10^{-3}(T - 273.15) - 7.4247 \cdot 10^{-7}(T - 279.15)^2] \quad (6)$$

For short wire:

$$R_s = R_{s0}[1 + 3.2343 \cdot 10^{-3}(T - 273.15) - 9.1717 \cdot 10^{-7}(T - 273.15)^2] \quad (7)$$

where R_{l0} (=16.2960 Ω) is the resistance of the long hot-wire and R_{s0} (=8.7225 Ω) is the resistance of the short wire at 273.15 K (0°C).

Results and discussion

First of all, the measurement of the thermal conductivity and the thermal diffusivity were obtained for distilled water over the temperature range from ambient temperature to 353 K at atmospheric pressure. Water was used as a reference fluid to test the instrument and the measurement system. Next, measurements for poly (acrylic) acid solution (50 mass%) in water were obtained in the temperature range from ambient temperature to 368 K at atmospheric pressure.

Measurements for water

Measurements of the thermal conductivity (λ) and the thermal diffusivity (κ) of water obtained by this system were correlated as follows:

$$\lambda(T) = 0.5927 + 0.002893(T - 273.15) - 1.88 \cdot 10^{-5}(T - 273.15)^2 \quad (8)$$

and

$$\kappa(T) = 9.76 \cdot 10^{-8} + 6.36 \cdot 10^{-9}(T - 273.15) - 5.98 \cdot 10^{-11}(T - 273.15)^2 \quad (9)$$

where λ is in W m^{-1} K^{-1}, κ is in m^2 s^{-1} and T is in K.

The average deviation of the correlation for thermal conductivity (Eq. (8)) water is about 1.8% with a maximum deviation of 7.6% at 343 K. For thermal diffusivity (Eq. (9)), the average deviation is about ±15% with a maximum deviation of ±35%.

Figure 3 compares the correlations of thermal conductivity of water obtained by other sources [17, 18] and present work. It can be seen that the absolute value of thermal conductivity of water obtained in present work was higher than those of IUPAC by 6% on average with a maximum of about 15% at 343 K and a minimum of 1% at 353 K.
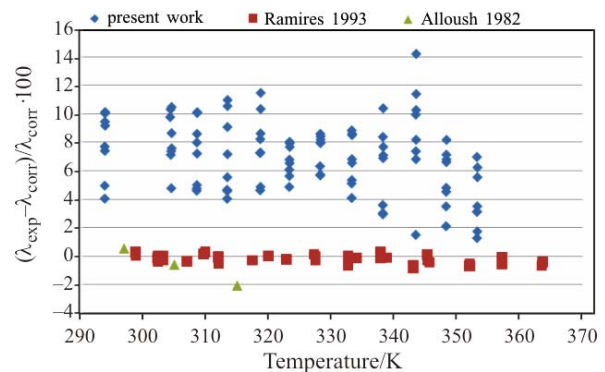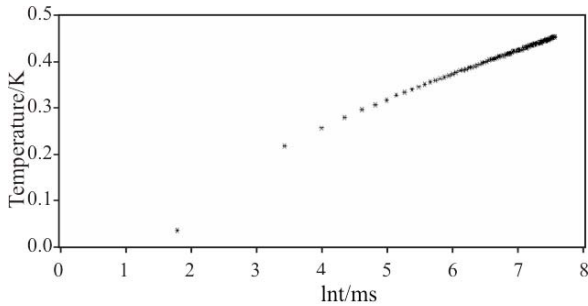

Fig. 3 Comparison of the experimental measurements of the thermal conductivity of water with the correlation recommended by IUPAC

*Measurements for PAA solution (50 mass%) in water*

A typical plot of the temperature rise of the hot wire as a function of the logarithm of time is shown in Fig. 4 for a measurement of PAA solution at 333 K. Figure 5 displays the plot of the deviations in the experimental data from the linear fit. It can be seen that the average deviation is 0.2%, with a few points showing a scatter as high as 0.5%, and there are no systematic curvatures in the deviation plot. The experimental results obtained for thermal conductivity and thermal diffusivity of PAA solution in the temperature range of 299 to 368 K are shown in Figs 6 and 7, respectively. Equations (10) and (11) show the correlations of the experimental data for thermal conductivity and thermal diffusivity, respectively.

$$\lambda(T)=0.4510+0.001804(T-273.15)- \\ -1.35\cdot10^{-5}(T-273.15)^2 \qquad (10)$$

and

$$\kappa(T)=1.43\cdot10^{-7}+6.3\cdot10^{-9}(T-273.15)- \\ -6.67\cdot10^{-11}(T-273.15)^2 \qquad (11)$$

where λ is in W m^{-1} K^{-1}, κ is in m^2 s^{-1} and T is in K.

Correlation (Eq. (10)) of the thermal conductivity has an average deviation of 1.3% with a

Fig. 4 Temperature rise of the hot wire *vs.* lnt for the measurement on PAA at 333 K
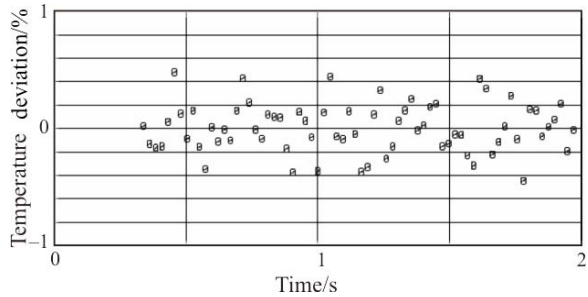
Fig. 5 Deviations of the temperature rise from the linear fit as a function of time for the measurement on PAA at 333 K
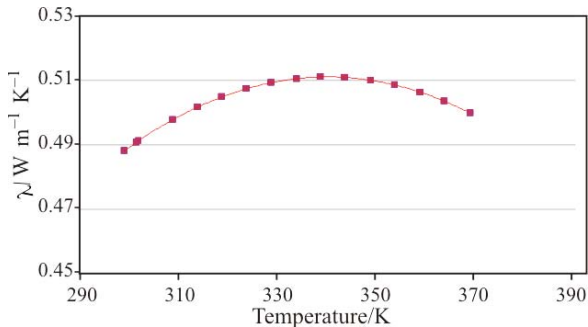
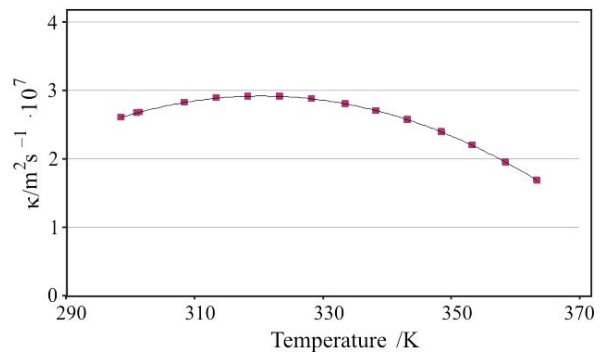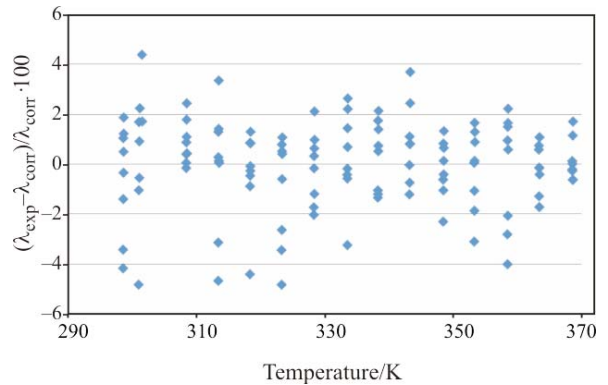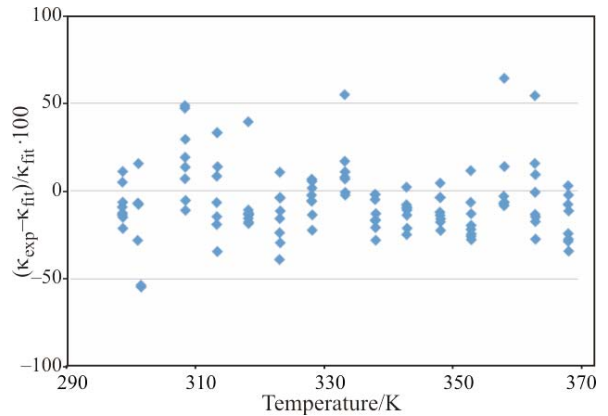**Fig. 6** Thermal conductivity of poly(acrylic acid) PAA

Fig. 7 Thermal diffusivity of poly(acrylic acid) PAA

Fig. 8 Deviation of the thermal conductivity of PAA from Eq. (10)

Fig. 9 Thermal diffusivity of PAA from Eq. (11)

maximum deviation of –4.8% (Fig. 8). For the correlation (Eq. (11)) for thermal diffusivity, the average deviation is within ±30% with maximum deviations of over ±50% for some data (Fig. 9). The average standard deviation of measurements at each equilibrium temperature is about 24% which contributes to the high uncertainty of the above correlation (Eq. (11)).

Conclusions

A new transient hot-wire instrument employing anodized tantalum wire for measurement of the thermal conductivity and the thermal diffusivity of electrically conducting liquids has been constructed. The apparatus has been validated with measurements of the thermal conductivity and thermal diffusivity of distilled water in the temperature range 290 to 353 K at atmospheric pressure. The present measurements were compared with other accurate measurements of water along the saturation line and show an average deviation of about ±2% for thermal conductivity and ±15% for thermal diffusivity. Experimental measurements of the thermal conductivity and the thermal diffusivity of PAA solution in the temperature range 299 to 368 K and their correlations have been reported. For PAA, the thermal conductivity and thermal diffusivity correlations have estimated average uncertainties of about ±5 and ±50% respectively. Comparison of the present experimental data with others was not possible as there is no other experimental data available for thermal conductivity and thermal diffusivity of PAA solution. The present work clearly indicates the need for further refinement of the measurements to reduce high uncertainties, especially for thermal diffusivity, hence, the need for further investigation.

Acknowledgements

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