Absolute measurement of thermal conductivity of poly (acrylic acid) by transient hot wire technique

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Abstract The transient hot-wire method is considered the most accurate technique to measure the thermal conductivity of fluids. In this study, a transient hot wire instrument which employs 25.4-µm-diameter tantalum wire with an insulating tantalum pentoxide coating has been used. This hot-wire cell with a thin insulating layer is suitable for measurement of the thermal conductivity of electrically conducting and polar liquids. Measurements of the thermal conductivity of 50 wt% solution of PAA [poly (acrylic acid)] in water and PAA–Na in 50 wt% water are reported here. These measurements were obtained in the temperature range of 299–368 K at 1 atmospheric pressure. The measurement of thermal conductivity is estimated to be accurate within ±4%.

Keywords Anodic coating · Hot-wire · PAA ·
PAA–Na · Tantalum · Thermal conductivity

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Introduction

The thermophysical property of fluids such as thermal conductivity is of considerable significance for industrial applications, and several transient hot-wire instruments [1–12] have been developed for its accurate measurement. In these instruments, the thermal conductivity is determined from the transient temperature rise resulting from a step current through the wire which is submerged vertically in the test fluid. Thin bare wire (5–25-µm-diameter platinum wire) is used in these instruments for measurements of electrically non-conducting fluids. However, for electrically conducting fluids, the wire must be insulated to avoid current leakage into the test fluid. In this study, 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 of PAA [poly (acrylic acid)] solution and PAA with 0.5% Na (PAA–Na) solution. PAA is used in various technological applications such as drug delivery and as a medium for the synthesis of nanoparticles. PAA and PAA–Na are used to synthesize calcium silicates hydrates (C–S–H)-polymer nanocomposite (C–S–HPN) materials [13]. The nanomaterials consisting of inorganic nanolayers of C–S–H and organic polymers have evoked intense research interests recently because their unique characteristics create many potentially commercial applications [14]. Knowledge of the thermophysical properties of PAA is therefore vital and necessary. However, knowledge of the thermal conductivity of these materials is very limited at present.

In this article, experimental measurements of the thermal conductivity of PAA and PAA–Na in the temperature range of 298–368 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 change of 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. From the ideal mathematical model [15] for the transient temperature rise of the wire, the thermal conductivity of the fluid 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:

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

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

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

This results in the following solution for the temperature rise:

$$\Delta T_{\mathrm{w}}(a, t) = \left(\frac{q}{4\pi\lambda}\right)\ln\left(\frac{4kt}{a^2 C}\right) = \frac{q}{4\pi\lambda}\ln t + \frac{q}{4\pi\lambda}\ln\frac{4k}{a^2 C}$$
$$= G\ln t + A \tag{5a}$$

where

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

Here, 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 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. 5), 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.

Experimental

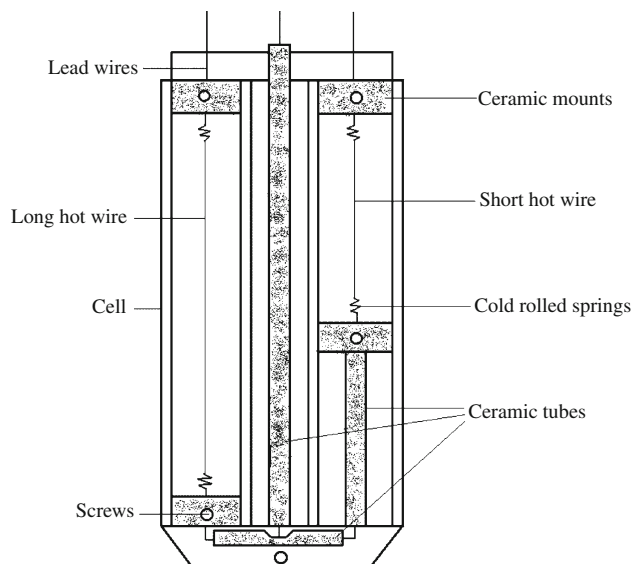A transient hot-wire cell (Fig. 1) was designed for measurement of thermal conductivity of electrically conducting liquids. The material of the body of the cell was Teflon. Two tantalum wires of different lengths, with a diameter of 25.4 µm coated with a layer of tantalum pentoxide were employed as heat sources.

Following the assembly of the 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, and were anodized by placing in 0.2 M solution of sulfuric acid solution in demineralized water. The layer of tantalum pentoxide on the surface of the wires was produced. The thickness of the coating was estimated to be about 170 nm. Hot wire specifications are listed in Table 1. The details of assembly and anodization of the cell are described elsewhere [16].

The electrical system (Fig. 2) includes a Hewlett Packard DC Power Supply (Model HP6625A), a Hewlett Packard Data Acquisition/Control Unit (Model HP3497A), a Hewlett Packard Multimeter (Model HP3458A), a Hewlett Packard System Voltmeter (Model HP3437A), and a C-MOS digital switch. The circuit consists of a calibrated 25 Ω standard resistance, R_{st}, four ballast resistance boxes, R_1, R_2, R_3, and R_4, a dummy resistance, R_{b}, and the two hot wires, R_1 and R_{s}. The details of the principle of measurement are described elsewhere [17].

The cell is immersed in a constant temperature oil bath (LAUDA, Model-KS-20D) 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.

Fig. 1 Experimental cell

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	180.948	441.893
Thermal conductivity/ W/m K	57.5	0.4
Specific heat/J/kg K	140	306
Density/kg/m^3	16400	8240

The hot wire was calibrated before the measurements to obtain the temperature coefficient of tantalum wire (Fig. 3). The calibration results are as follows:

For long wire

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

For short wire

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

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 was 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. Measurements for PAA solution (50 wt%) in water and PAA solution with 0.5% Na salt were obtained in the temperature range from ambient temperature to 368 K at atmospheric pressure.

Thermal conductivity measurement for water

Figure 4 shows the temperature rise versus the logarithm of time for 2 s at bath temperature of 328 K. Figure 5 shows the corresponding plot of the deviations of the corrected experimental temperature rise data from the linear fit. It can be seen that none of the data departs from the straight line by more than ±0.6%, and no systematic curvature was found in the deviation plot. This indicates the absence of radiation and convection. Furthermore, it also implies that the wire has been coated very well and no current leakage occurred in the test. The thermal conductivity of water was correlated with temperature as follows:

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

where λ is in W m^{-1} K^{-1} and T is in K.

Figure 6 shows the deviation of all the experimental data from Equation 8. It can be seen that the average deviation in
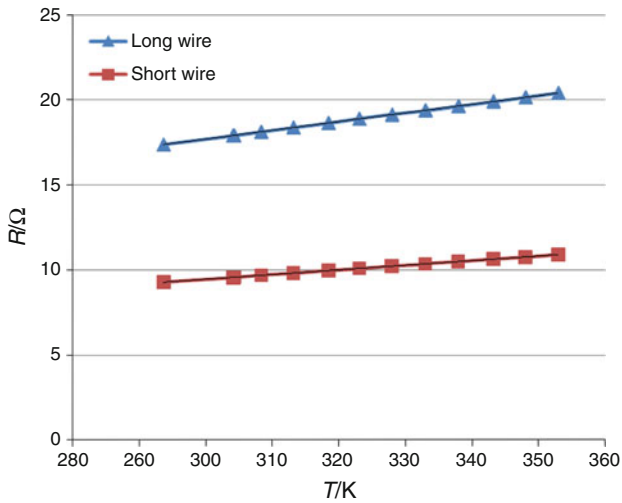

Fig. 2 Electrical and data acquisition system

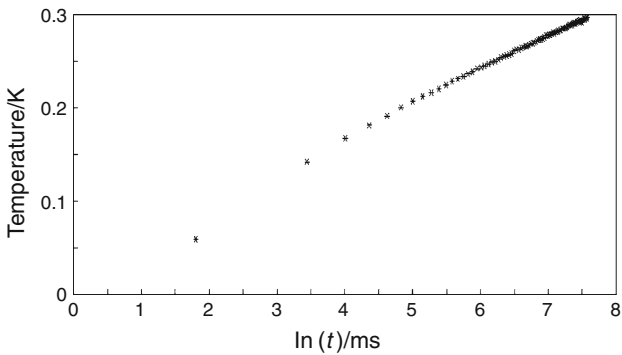**Fig. 3** Measured resistance of long and short hot wires versus temperature

Fig. 4 Temperature rise of the hot wire versus ln (t) for measurement on distilled water at 328 K
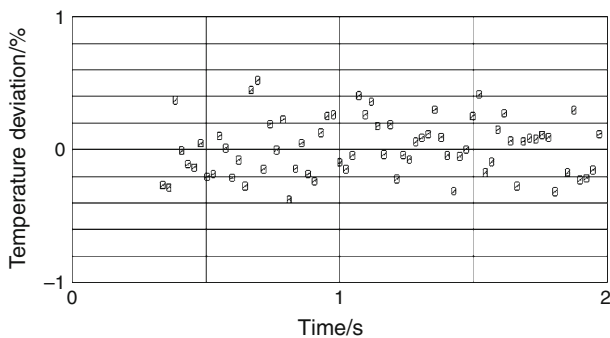

Fig. 5 Deviations of the temperature rise from the linear fit as a function of time for the measurement on distilled water at 328 K

the thermal conductivity of distilled water is about 1.8% with the maximum deviation being 7.6% at 343 K.

Figure 7 shows a comparison of the experimental values of thermal conductivity of water obtained by several earlier authors and this study with correlation recommended by
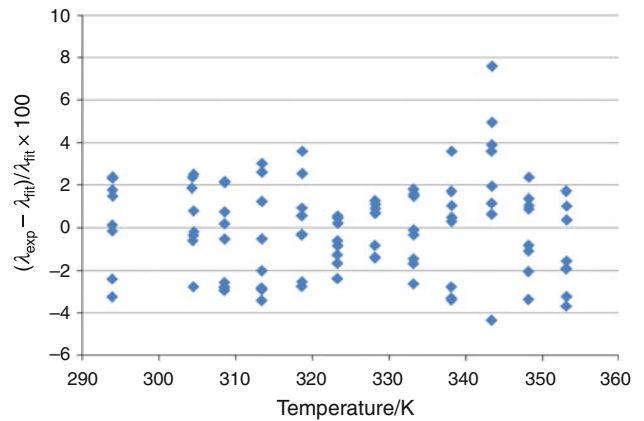

Fig. 6 Deviation of the thermal conductivity of distilled water from Eq. 8
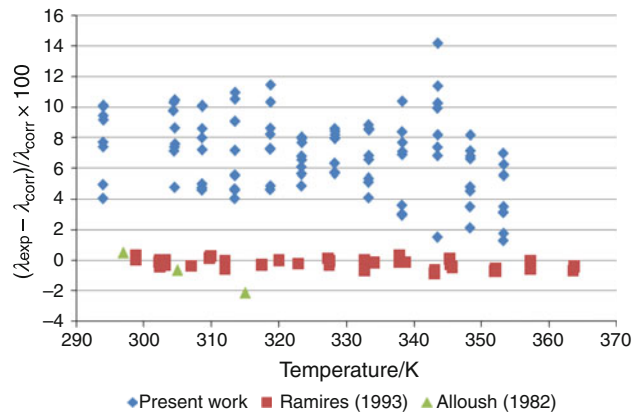

Fig. 7 Comparison of the experimental measurements of the thermal conductivity of water with the correlation recommended by IUPAC

IUPAC which claimed to be accurate within $\pm1.1\%$. It can be seen that the average deviation of this study from the correlation of IUPAC was 7% with a maximum deviation of 14%. Figure 8 compares the correlations of thermal conductivity of water obtained by other sources [18, 19] and this study. It can be seen that the absolute value of thermal conductivity of water obtained in present study was higher than those of IUPAC by 6% on average with a maximum of about 7.8% at 308 K and a minimum of 5.2% at 353 K.

Thermal conductivity measurement for PAA solution

A typical plot of the temperature rise of the hot wire as a function of the logarithm of time is shown in Fig. 9 for a test at 333 K with PAA. Figure 10 shows 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 correlation
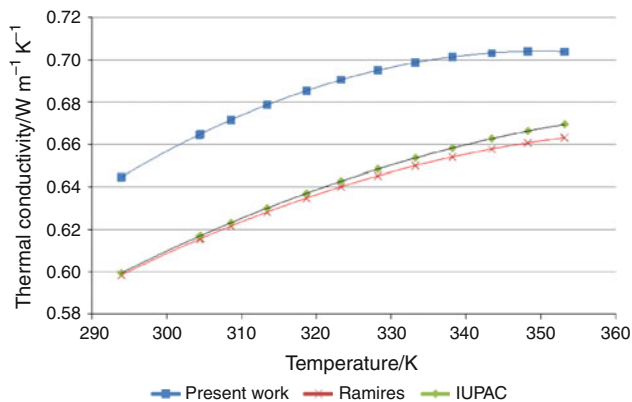
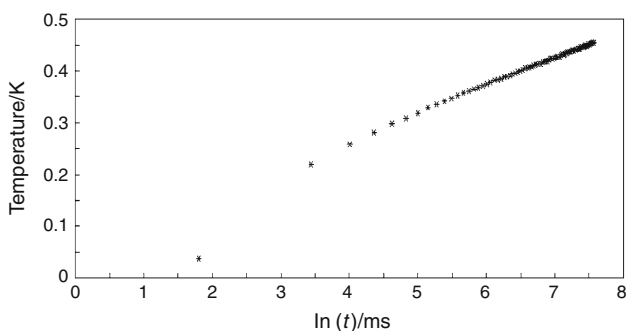Fig. 8 Comparison of the correlation of the thermal conductivity of water

Fig. 11 Deviation of the thermal conductivity of PAA from Eq. 10

Fig. 9 Temperature rise of the hot wire versus ln (t) for the measurement on PAA at 333 K

Fig. 12 Temperature rise of the hot wire versus ln (t) for the measurement on PAA–Na at 343 K

Thermal conductivity measurement for PAA–Na solution

The plots of the temperature rise versus logarithm of time for a measurement with PAA–Na solution at 343 K and the deviation of experimental data from the linear fit are shown in Figs. 12 and 13, respectively. The deviations are less than 0.4% and no systematic curvature appears. The correlation of the thermal conductivity and temperature was obtained as follows:

$$\lambda = 0.4498 + 0.001323\,(T - 273.15)$$
$$- 8.59 \times 10^{-6}\,(T - 273.15)^2 \tag{12}$$

where λ is in W m^{-1} K^{-1} and T is in K.

Figure 14 shows that the deviation of most of the experimental data from the correlation (Eq. 12) is within ±3% with a maximum deviation of ±4% at 343 K. The standard deviation of the experimental data from average value at each equilibrium temperature is about 2%.

Figure 15 shows the comparison between the correlations of the thermal conductivity of PAA with those of PAA–Na. It can be seen that the average value of PAA is
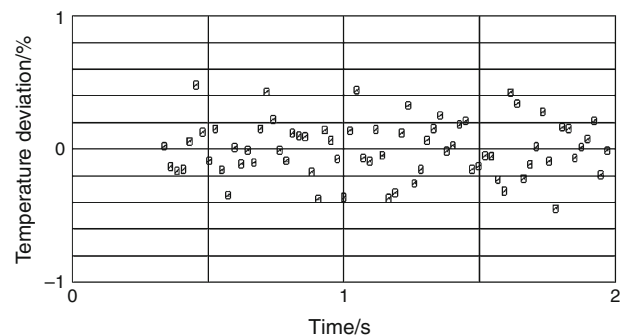

Fig. 10 Deviations of the temperature rise from the linear fit as a function of time for the measurement on PAA at 333 K

of thermal conductivity with temperature was obtained as follows:

$$\lambda = 0.4510 + 0.001804\,(T - 273.15)$$
$$- 1.35 \times 10^{-5}\,(T - 273.15)^2 \tag{10}$$

where λ is in W m^{-1} K^{-1} and T is in K.

Figure 11 shows plots of the deviation from the correlation expressed by Eq. 10. The average deviation is 1.3% with a maximum deviation of −4.8% at 323 K.
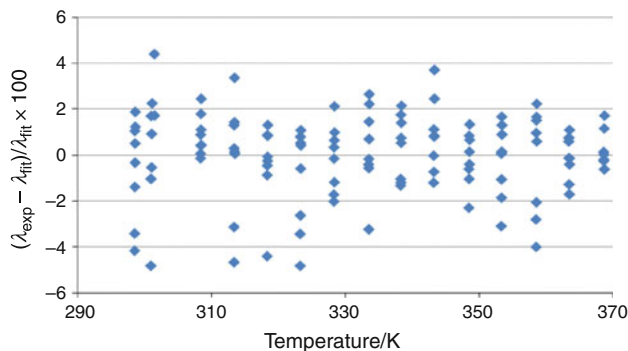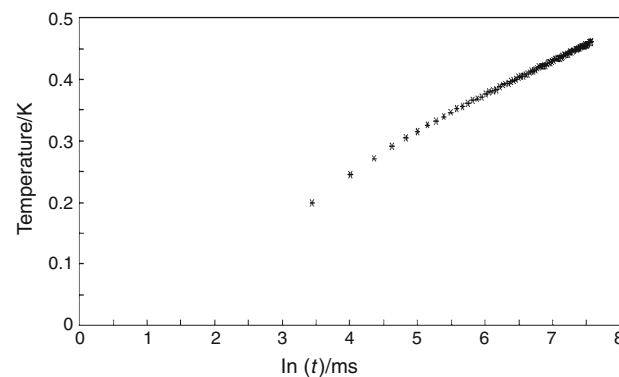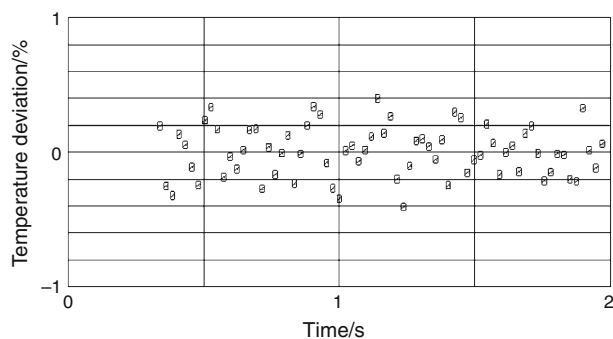
Fig. 13 Deviations of the temperature rise from the linear fit as a function of time for the measurement on PAA–Na at 343 K
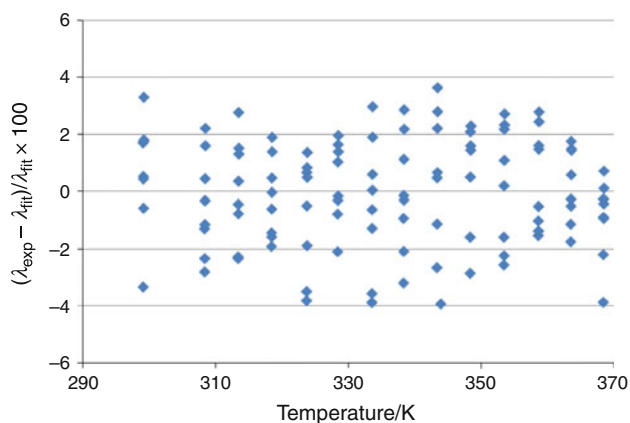

Fig. 14 Deviation of the thermal conductivity of PAA–Na from Eq. 12
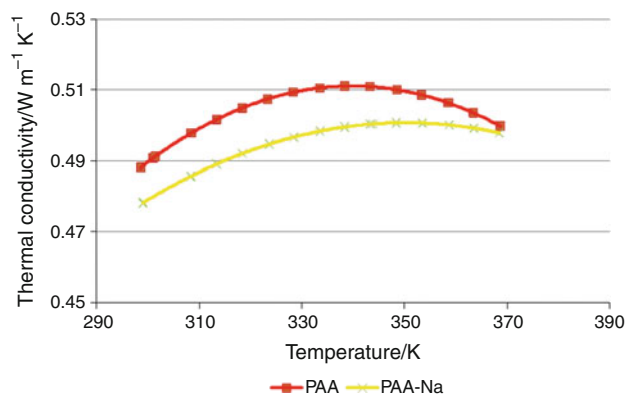

Fig. 15 Comparison of the correlation of thermal conductivity of PAA with PAA–Na

about 2% higher than that of PAA–Na for thermal conductivity.

The electrical resistivity of PAA and PAA–Na solutions were also measured at ambient temperature and 1 bar by an electrical conductivity meter (CAT. No. 4075). The resistivity is about 6.75 Ωm for PAA and 7.12 Ωm for PAA–Na.

This amounts to about 5% higher electrical conductivity of PAA solution with respect to PAA–Na solution. The trends shown by the electrical conductivity and the thermal conductivity appear to be similar. Additional measurements of the electrical conductivity values of PAA and PAA–Na solutions are needed over a range of temperature identical to those used for thermal conductivity measurements to further investigate this trend.

Conclusions

A new transient hot-wire instrument employing anodized tantalum wire for the measurement of the thermal conductivity of electrically conducting liquids has been constructed and used. The apparatus has been validated with the measurements of thermal conductivity of distilled water in the temperature range 290–353 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 $\pm 6\%$ for thermal conductivity. Experimental measurements of the thermal conductivity of PAA and PAA–Na solutions in the temperature range 299–368 K and their correlations have been reported. For PAA, the thermal conductivity correlation has an estimated uncertainty of $\pm 4\%$. The correlation for PAA–Na solution shows a similar uncertainty level of $\pm 4\%$ for thermal conductivity in the temperature range 299–368 K. Comparison of the present experimental data with others was not possible as there are no other experimental data available for thermal conductivity of PAA and PAA–Na solutions. This study clearly indicates the need for further refinement of the measurements to reduce high uncertainties. In addition, the difference between the measurements for PAA and PAA–Na solutions are of the same order as the uncertainties, and hence, the need for further investigation.

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