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A transient spherical source method to determine thermal conductivity of liquids and gels

ULRICH B. HOLESCHOVSKY,† GREGORY T. MARTIN‡ and JEFFERSON W. TESTER§||

† Department of Chemical Engineering, ‡ Department of Mechanical Engineering, § The Energy Laboratory, Massachusetts Institute of Technology, E40-455, Cambridge, MA 02139-4307, U.S.A.

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Abstract—A method developed for the measurement of tissue blood flow is modified to measure the thermal conductivity of liquids and silica gels. The method controls a thermistor temperature at a set point above the baseline and determines conductivity from the power as a function of time. Natural convection in the liquids is suppressed by reducing the measurement time to 10 s and by reducing the temperature step, thus decreasing the magnitude of buoyancy. Conductivities were measured in six aqueous liquids and in gels constituted from these liquids with various amounts of silica. The technique determined the conductivity with a 95% confidence interval to less than 1% in nearly all cases. It was found that conductivity varied 0.3% per 1% silica for gels made from a $CuSO_4$ solution and 1% per 1% silica for gels made from a $Cu(BF_4)_2$ solution.

1. INTRODUCTION

Our work to develop a simple and fast method for determining the thermal conductivity of liquids and gels was motivated by a need to characterize the performance of fuel cells and thermogalvanic converters [1, 2]. In these devices, a variety of aqueous electrolytes are used as the free fluid or used in fused silica gels. For the types of materials used and the temperature operating range, an accurate method for the measurement of thermal conductivity and blood flow in biological tissue has already been developed [3–5].

The method uses a spherical, self-heated thermistor bead mounted at the tip of a needle catheter and inserted into a medium. The thermistor bead, modeled as a sphere, is used as both a temperature sensor and a heat source. The power necessary to maintain the thermistor at a constant temperature step above the medium baseline depends on the thermal properties of the surrounding medium. The presence of fluid flow increases the thermal energy necessary to maintain the preset temperature difference between the thermistor bead and the surrounding medium. This change of the heat generation rate can be used to determine the fluid flow rate, i.e. the flow rate of blood through tissue. Chato [3] was first to model the heat transfer from a spherical source into a stagnant surrounding medium. He assumed the thermistor bead to be a spherical lumped thermal mass. His solution is only applicable for media with thermal conductivities much smaller than the thermal conductivity of the thermistor bead. Balasubramaniam and Bowman [4] improved the theoretical treatment by modeling the thermistor bead as a distributed thermal mass and solving for the coupled thermal response of both the bead and the medium. Their approach takes into account the temperature gradient that exists within the bead. The thermistor bead is treated as a sphere of radius a embedded in a homogeneous medium with no surface contact thermal resistance. The governing equations for the heat conduction in the medium and the thermistor are:

$$\frac{1}{\alpha_m}\frac{\partial T_m}{\partial t} = \nabla^2 T_m \qquad (1)$$

$$\frac{1}{\alpha_b}\frac{\partial T_b}{\partial t} = \nabla^2 T_b + \frac{Q}{k_b} \qquad (2)$$

where t is time; T_m is the medium temperature elevation above the baseline; α_m is the medium thermal diffusivity; T_b is the bead temperature elevation above the baseline; α_b is the bead thermal diffusivity; k_b is the bead thermal conductivity and Q is bead power dissipation per unit volume. The boundary conditions require that temperature everywhere is bounded, continuity of temperature and heat flux are maintained at the medium–bead interface and that temperature elevation approaches zero at infinite spatial extent. The heat generation rate, H, in the bead for times $t > 0$ is given by:

$$H = H_{ss} + B\frac{1}{t^{1/2}} \qquad (3)$$

|| Author to whom correspondence should be addressed.

NOMENCLATURE

a	effective thermistor bead radius [m]
B	constant dependent on thermal properties of the material [W $s^{1/2}$]
H	thermistor heat generation rate [W]
H_{ss}	thermistor heat generation rate at steady state [W]
k_b	thermistor bead thermal conductivity [W m^{-1} $°C^{-1}$]
k_m	medium thermal conductivity [W m^{-1} $°C^{-1}$]
Q	thermistor bead power dissipation per unit volume [W m^{-3}]
t	time [s]
T_b	temperature elevation of the bead above the baseline [°C]
T_m	temperature elevation of the medium above the baseline [°C].

Greek symbols

α_b	thermistor bead thermal diffusivity [m^2 s^{-1}]
α_m	medium thermal diffusivity [m^2 s^{-1}]
∇^2	Laplacian operator
$\theta_{b,avg}$	volumetric averaged bead temperature minus the baseline medium temperature [°C].

Subscripts and superscripts

b	relating to the thermistor bead
m	relating to the medium
ss	steady state.

where H_{ss} is the heat generation rate at steady state and B is a constant that depends on the thermal properties of the medium and the bead. The relationship of equation (3) is theoretically consistent with an instantaneous step change in temperature at time $t = 0$ yielding a heat flux into a finite spherical volume of uniform thermal properties varying inversely with $t^{1/2}$, e.g. see Carslaw and Jaeger [6]. According to Balasubramaniam and Bowman [4], the difference between the average bead temperature and the baseline temperature of the medium at steady state is given by:

$$\theta_{b,avg} = \frac{H_{ss}}{4\pi a k_b}\left[\frac{k_b}{k_m} + \frac{1}{5}\right] \qquad (4)$$

where k_m is the medium thermal conductivity.

The thermal conductivity of the medium, k_m, is determined by measuring H_{ss} where the effective bead radius a and k_b are known through calibration using two substances with known thermal properties. In biological tissue, the presence of a flow changes both the steady state and transient term of the heat generation function in equation (3). Valvano *et al.* [5] used this change in heat generation to determine the blood flow rate through perfused tissue.

The spherical source method can also be applied before steady state is reached. The steady state part of the heat generation function, H_{ss} in equation (3), can be obtained by extrapolation to infinite times in a heat generation vs $t^{-1/2}$ plot, (i.e. as $t^{-1/2}$ approaches 0).

A key aspect of this research was to investigate if the described spherical source method of Valvano *et al.* could be used to determine the thermal conductivity of liquids where the effects of natural (free) convection are important. There are two main concerns when dealing with natural convection. The first is that the necessary gradients which drive the flow take time to develop. Useful data may be obtained by measuring during the early time period before natural convection effects become significant. On the other hand, the time periods need to be sufficiently long to collect enough data points to allow reliable extrapolation of the steady state heat generation rate term in equation (3). The second concern is that the higher the temperature step, the earlier natural convection will set in and the more pronounced its effects will be on the measured conductivity. Accordingly, a small temperature step will decrease the onset time and reduce the magnitude of buoyancy driven flow. On the other hand, the temperature step needs to be sufficiently large to yield a measurable heat generation rate.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

The thermistor probe used was a TDP100 'Enhanced Thermal Diffusion Probe' supplied by Thermal Technologies Inc., Cambridge, MA. A portable computer was used to run the Control Software Version 1.3. The spherical probe has a diameter of about 1 mm and the instrument contains analog circuitry for the excitation and measurement of the thermistor based transducer, an analog-to-digital (A/D) converter and a dedicated microprocessor. The quantization error of the A/D converter gives the instrument a theoretical conductivity resolution of about 0.2% for a temperature step of 4°C. During the experiments, the probe was inserted into 60 ml plastic bottles containing about 30 ml of the liquid or gel to be measured. The sample bottles were positioned in a temperature controlled water bath (TU-16A, Techne, Inc., Princeton, NJ) and allowed to thermally equilibrate. All measurements were conducted at 37

($\pm$0.02)°C, since the thermistor probe was calibrated at this temperature. However, we also made measurements of the water conductivity at room temperature (approximately 22°C) yielding results of the same quality as at 37°C.

A set of experiments for each liquid or gel sample consisted of 10 consecutive measurement runs with 10 s of data collected during each run. The temperature step was varied between 1.5 and 4°C. Two minutes of cooling time between each experiment was found to be sufficient to eliminate heating interference from one experiment to the next. During each run, the power dissipation, H, was measured and recorded every 0.5 s yielding a minimum of 20 data points over a 10-s data window. The data were extrapolated to infinite times in a H vs $t^{-1/2}$ plot to determine H_{ss}. Measurement, recording and data analysis procedures were automated and controlled by the measurement software.

3. RESULTS AND DISCUSSION

As discussed in Section 1, the spherical source method based on the extrapolation of the heat generation transient is applicable for the thermal conductivity measurement of liquids by adjusting the temperature step and choosing appropriate time window. We experimented with temperature steps ranging from 1 to 4°C. The minimum necessary temperature step to permit experiments with satisfactory reproducibility was found to be around 2°C. Figure 1 shows an example of the data analysis procedure used for the liquids. The circular symbols in the left panel show the thermistor power dissipation as a function of time for measurements taken in water using the Thermal Diffusion Probe (TDP 100). In the initial 10 s, the heating rate H decreases, as expected from equation (3). After about 10 s, the onset of natural convection causes the heating rate to pass through a minimum since convection increases the heat removal rate. This requires a higher heating rate to maintain the temperature step at 2°C. In order to isolate the effects of conduction only, the initial 10 s of data are used in the fit to equation (3). The right panel plots the power dissipation as a function of $1/\sqrt{t}$. According to equation (3), the effect of conduction alone is described by a straight line fit and natural convection at later times causes deviation from this line. The solid lines in the left and right panels of Fig. 1 show the results of the fit when plotted in the appropriate manner for each abscissa. This method of data analysis was then subsequently used for all the liquid thermal conductivity measurements.

The average thermal conductivity of water based on ten experiments was 0.6167 W m^{-1} K^{-1} with a 95% confidence interval of 1.6% (see Table 1). This is in very good agreement (1%) with the literature value for water at 37°C of 0.623 W m^{-1} K^{-1}, (Keenan *et al.* [7]). These experimental results indicate that the Thermal Diffusion Probe can be used to accurately measure the thermal conductivity of liquids with a Prandtl number and a coefficient of thermal expansion (β) close to that of water. The results obtained for the conductivity of water were considered sufficiently accurate to proceed with the conductivity measurements of electrolyte liquids and gels of unknown conductivity. Table 1 summarizes the results as well as the literature values when available. The average conductivity value measured with glycerol, which is used for the calibration of the thermistor probe, was very

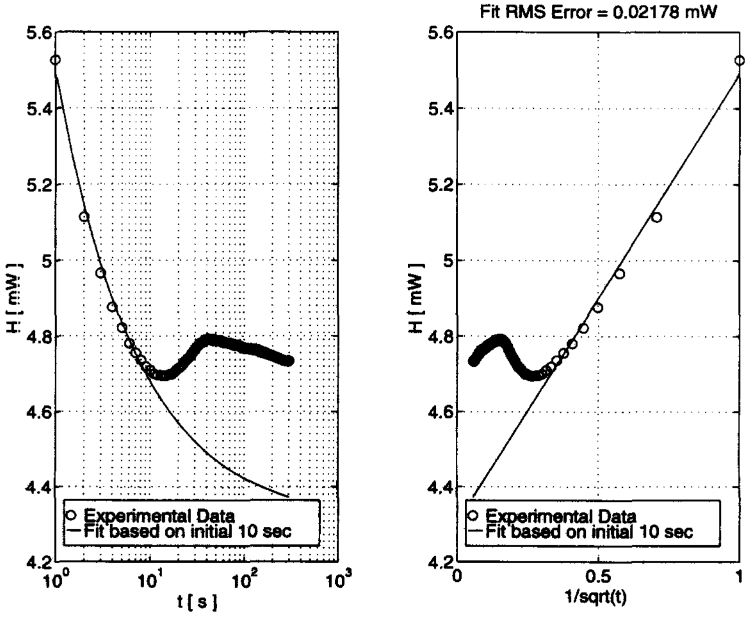

Fig. 1. Heat generation required to maintain a constant 2°C mean temperature elevation in a thermistor in water as a function of time (left panel) and the heat generation as a function of $1/t^{1/2}$ (right panel).

Table 1. Thermal conductivities of liquid and gelated electrolytes at 37°C (each based on 10 experiments with $t = 10$ s)

Material	k [W m^{-1} K^{-1}]	95% Conf. interval	ΔT [°C]	Literature values k [W m^{-1} K^{-1}]
Water (deionized)	0.6167	0.0096	2	0.623 Keenan *et al.* [7]
Glycerol	0.2834	0.0015	4	0.2855 Touloukian [9]
10% $CuSO_4$	0.5968	0.0081	2	0.6025 @ 32°C Jäger [10]
9.8% $CuSO_4$+2% SiO_2	0.5984	0.0025	4	—
9.6% $CuSO_4$+4% SiO_2	0.6047	0.0017	4	—
9.3% $CuSO_4$+7% SiO_2	0.6082	0.0047	4	—
45% $Cu(BF_4)_2$	0.4421	0.0037	2	—
44.1% $Cu(BF_4)_2$+2% SiO_2	0.4537	0.0045	4	—
43.3% $Cu(BF_4)_2$+4% SiO_2	0.4719	0.0020	4	—
41.9% $Cu(BF_4)_2$+7% SiO_2	0.4741	0.0022	4	—
7% $Cu(OOCCH_3)_2$	0.5525	0.026	1.5	—
7% $Cu(OOCCH_3)_2$	(0.602)	(0.105)	2	—
6.7% $Cu(OOCCH_3)_2$+7% SiO_2	0.5762	0.0064	4	—
45% $Cu(NO_3)_2$	0.5010	0.0052	2	—
41.9% $Cu(NO_3)_2$+7% SiO_2	0.5023	0.0024	4	—
45% $Cu(ClO_4)_2$	0.4942	0.0041	2	—
41.9% $Cu(ClO_4)_2$+7% SiO_2	0.4948	0.0028	4	—
1M $Fe(ClO_4)_2$+1M $Fe(ClO_4)_3$	0.4872	0.0050	2	—
2M $FeCl_2$+2M $FeCl_3$	0.4734	0.0027	2	—
2M $FeCl_2$+2M $FeCl_3$+7% SiO_2	0.4935	0.0024	4	—

precisely determined (0.2834 ± 0.0015 W m^{-1} K^{-1}) but still 0.5% lower than the value quoted in literature by Touloukian [9]. Most likely, the higher Prandtl number of glycerol (2400) as compared to water (4) contributed significantly to the suppression of natural convection and the smaller confidence interval.

The 95% confidence interval for 10 experiments with liquid water was very small, about 1.6%. We found that the temperature step for gelated electrolytes, in which natural convection is suppressed, could be increased to 4°C without adversely affecting the measurement. Since higher temperature steps increase the signal to noise ratio, we used a step of 4°C for the measurement with gels. The conductivity data for liquid electrolytes were determined with a step of 2°C. As a consequence, the confidence interval for the liquid electrolytes was 0.5–4 times higher than for the gelated electrolyte. In the case of copper acetate ($Cu(OOCCH_3)_2$), experiments with 2°C yielded relatively high thermal conductivities (see Table 1) with an untypically large confidence interval suggesting that natural convection was adversely affecting the measurement. Experiments with a 1.5°C step yielded lower thermal conductivity values which were more consistent with the results for the other electrolytes. Though the Prandtl number for the copper acetate solution is close to that of water, we suspect that the lower surface tension of an acetate–water solution of 7% accounts for the larger confidence interval. Gallant and Railey [11] have measured the surface tension of aqueous acetone and found that at about 37°C and for a 7% solution, the mixture surface tension is about 30% lower than that of pure water. Marquet *et al.* [12] have shown numerically that the surface tension affects the heat transfer from a hot wire immersed in a liquid. In any case, care should be taken to properly identify the onset of natural convection. This is clearly evident, for instance, in Fig. 1 where the minimum in thermistor power indicates the transition to natural convection dominated heat transfer.

The results given in Table 1 indicate that the addition of silica to gelate the electrolyte increases the thermal conductivity only marginally even though the intrinsic conductivity of silica is relatively high (1.3 W m^{-1} K^{-1} [8]. This is probably because the silica particles are finely dispersed in a liquid matrix of electrolyte. Figure 2 plots the conductivity of the $CuSO_4$ aqueous solution against increasing concentrations of SiO_2. The plot shows this modest increase in conductivity of about 0.3% per % concentration of SiO_2. Figure 3 plots the conductivity of the $Cu(BF_4)_2$ aqueous solution against increasing concentrations of SiO_2. This plot also shows a modest increase in conductivity, rising about 1% per % concentration of SiO_2.

4. CONCLUSIONS

A device designed to measure the thermal conductivity of perfused biological tissue was evaluated for its applicability to the measurement of thermal conductivities of liquids. The experimental results show that the device can be used to measure the thermal conductivity of liquids if the operating parameters are chosen properly to reduce the measurement artifact from the onset of natural convection. Using a measurement time of 10 s and temperature perturbation steps of approximately 2°C, the conductivity of water and a 10% $Cu(SO_4)$ solution at 37°C were measured to be within 1% of the values quoted in literature. This method yields very accurate results with short measurement times and low sample

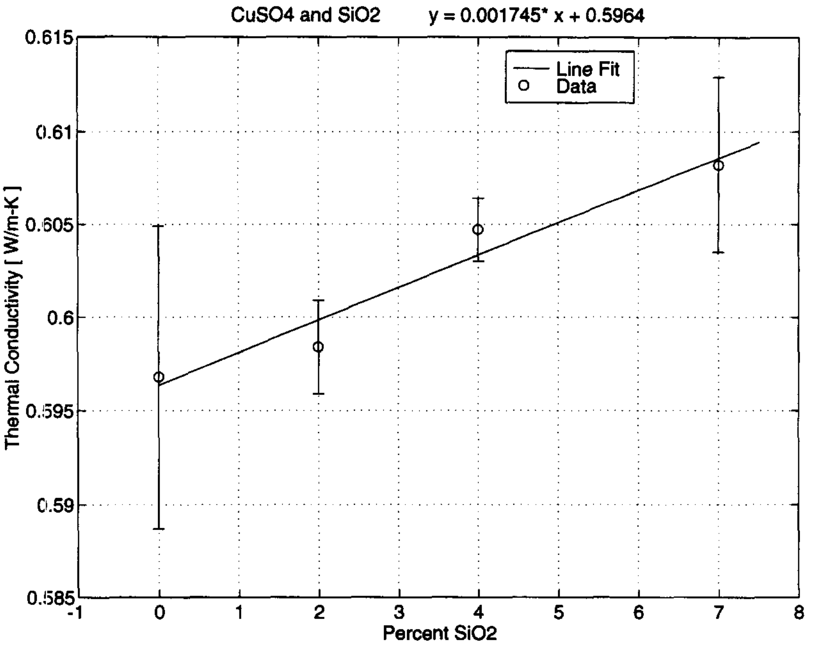

Fig. 2. Thermal conductivity of $CuSO_4$ aqueous solution as a function of SiO_2 concentration.

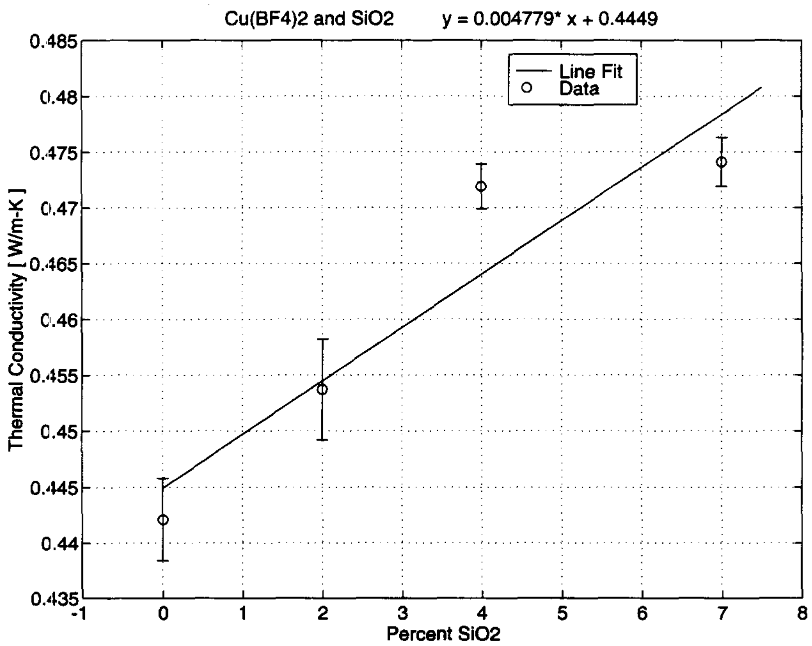

Fig. 3. Thermal conductivity of $Cu(BF_4)_2$ aqueous solution as a function of SiO_2 concentration.

volumes. Using the Thermal Diffusion Probe, we measured the thermal conductivities of four copper-salt electrolytes and two Fe^{2+}/Fe^{3+} electrolyte mixtures for which no previously reported data exist. We also measured the conductivities of electrolytes which were gelated by adding varying amounts of fumed silica. Each measurement was repeated 10 times resulting in confidence intervals of typically ±1.5% for the pure liquid electrolytes and about ±0.5% for the gelated electrolytes. Even though the intrinsic conductivity of silica is relatively high (1.3 $W\ m^{-1}\ K^{-1}$), the thermal conductivity of the gelated electrolyte was only slightly greater than liquid electrolyte of similar composition, probably because the silica particles are dispersed in a continuum matrix of liquid. In summary, the Thermal Diffusion Probe provides a high accuracy, repeatable and simple measurement of thermal conductivity for liquids and gel-like solids.

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