Thermal Conductivity Measurements of Ionic Liquids

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1 Abstract

Absorption refrigeration, sometimes called gas refrigeration, is an alternative to the standard vapor refrigeration cycle. The differences in the two refrigeration cycles originate from the compressor in a vapor system being replaced with an absorber and generator in the absorption refrigeration cycle. This cycle involves the use of a refrigerant and an absorbent, most commonly ammonia and water. However, there are problems with these refrigerants which are currently on the market for reasons such as the damage they cause to the environment. This project will examine the possibility of the refrigerants that are currently on the market for the absorption cycle being replaced by an ionic liquid. In this application, the ionic liquid would be the absorbent and carbon dioxide or possibly water would be the refrigerant. In order for the ionic liquid to be marketable, various properties must be determined in order to decide if it will work for the absorption refrigeration application. This section of the project will focus on determining a process to find the thermal conductivity of the ionic liquid in question.

2 Introduction

Before examining the ionic liquid, it may be conducive to first examine the absorption refrigeration cycle. A simplified version of the cycle contains four main components; an absorber, a generator, a condenser, and an evaporator. The vaporized refrigerant enters the absorber and results in a solution as it is absorbed by the absorbent, in addition to heat rejection. The solution is next sent through a pump where the pressure is increased. The solution then goes to the generator where heat is added from an outside source. The heat causes the refrigerant, now vaporized at a high pressure, to follow the standard refrigeration cycle while the absorbent returns to the absorber. The refrigerant is next condensed to a liquid in the condenser and heat is given off to the surroundings. The liquid is next sent to
the evaporator where it is evaporated as it absorbs heat from the source to be cooled, in this case the inside of the refrigerator. The vaporized refrigerant returns to the absorber and the cycle starts over [7]. A simplified version of the cycle may be seen in Figure (1), containing the main components of the absorption refrigeration cycle.

![Absorption Refrigeration Cycle Diagram](image-url)

**Figure 1: Absorption Refrigeration Cycle**
2.1 Working Fluids

The most common working fluids for an absorption refrigeration cycle are those of water, \( H_2O \), as the absorbent and ammonia, \( NH_3 \), as the refrigerant. These fluids are typically used for temperatures below 32 °F. The working fluids that are generally used for temperatures above 32 °F are lithium bromide, \( LiBr \), as the absorbent and water as the refrigerant [8]. The use of these refrigerants presents several problems. In the case of the water and lithium bromide mixture there is an issue with it being corrosive to materials and also having a rather high viscosity, which increases the work required to pump the mixture. The ammonia water mixture also has problems because if there is a leak in the refrigeration system because ammonia is harmful to the environment, and leads to the breaking apart of ozone.

2.2 Applications

Absorption refrigeration is used for a wide variety of applications, similarly to a standard vapor refrigeration system. Some of these applications include domestic refrigerators, refrigerators contained in recreational vehicles, air conditioners, and in rural locations. Absorption refrigeration is especially useful for industrial applications where low grade waste heat is a by-product that is currently being unused. A specific application where this is true is in that of power generation, where waste heat is often let out into the atmosphere. Using an absorption refrigeration system with the waste heat from the plant would help to increase efficiencies. In addition to low grade waste heat from industrial applications, absorption systems may utilize heat in the form of solar energy.

2.3 Advantages and Disadvantages

The main advantage of the aborption refrigeration cycle over the standard refrigeration cycle is that it requires less work input. The work needed is essentially proportional to the electricity required, therefore less work leads to a lower electrical requirement. In the
vapor compression cycle, for example, the work that is required is to compress a vapor. This requires more than that of an absorption cycle because in an absorption cycle the work is done on the fluid leaving the absorber, which is in a liquid state. For a reversible process the work required, \( W \), is shown in Equation (1) below where the variable \( v \) is the volume and the variable \( P \) is the pressure[7].

\[
W = - \int v \, dP
\]  

(1)

Therefore, because a liquid has a much less volume than a vapor, not as much work is required for this step in the absorption process. Another important advantage of absorption refrigeration, as mentioned above, is that it may be used in industrial applications where low grade waste heat is an available by-product. Therefore, it may be incorporated into existing applications. This may be a disadvantage over the standard vapor compression cycle in applications where no heat is available. Another advantage is in the coefficient of performance, which may be double that of a regular refrigerant cycle. The coefficient of performance is an important factor because it measures the efficiency of the cycle, or the benefit received for what that benefit costs. Disadvantages involved with absorption refrigeration when compared with a conventional refrigeration cycle is that there is more equipment involved, and thus the risk of having equipment malfunction is higher. Another disadvantage lies in the need for a heat source, which may be difficult to obtain for some applications.

2.4 Ionic Liquids

Ionic liquids are salts that are liquid at room temperature, which makes them ideal for a refrigerant system. Ionic liquids also have a rather low melting point, stay liquid over a wide range of temperatures, and are thermally stable. All of these qualities that them good solvents for the absorption refrigeration applications. [10]. Ionic liquids have another advantage over standard absorbents because they do not harm the environment. Ionic liquids
would be a good choice of working fluids for absorption refrigeration systems for all of
the above reasons. When compared to the standard solutions being used today of water
lithium bromide and ammonia water, ionic liquids have an advantage over these two fluids.
The advantage over water lithium bromide is that ionic liquids are non-corrosive, and the
advantage over ammonia water is that ionic liquids are not harmful to the environment.
Therefore, properties of the ionic liquids must be determined to further investigate their
usefulness as working fluids in refrigeration cycles.

3 Thermodynamic Properties

This section will be used to define and explain basic thermodynamic properties that are ap-
pllicable with respect to the absorption refrigeration cycle. Some important properties with
respect to ionic liquids that will be used in the cycle are density, viscosity, glass transition
temperature, thermal stability, emperical solvent parameters, absorption, toxicity, and dis-
posal. Another key property is the focus of this paper, the thermal conductivity of the ionic
liquid. This will be covered in the next section.

3.1 Pure Substances

A pure substance is comprised of just one substance, which may be an element or a com-
 pound. It has uniform composition throughout the substance [8]. The thermodynamic
equations of state may be used to relate properties for such pure substances. For example,
the thermal equation of state for an ideal gas is defined in Equation (2).

\[ P_v = RT \]  \hspace{1cm} (2)

For a real gas, the equations of state would be defined in graphical or chart form[7].
3.2 Mixtures

A mixture is a combination of more than one substance. In thermodynamic applications, mixtures are treated differently than pure substances and often involve a more complex analysis. For example, the pressure of a mixture is determined by summing the partial pressures of all the substances present in the mixture. For gas mixtures, the total mass, $m$, of the mixture is equal to the sum of the masses of each gas present, as shown in Equation (3).

$$m = m_1 + m_2 + \ldots + m_N = \sum m_i$$

Similarly, the total number of moles, $n$, in a gas mixture is equal to the summation of the number of moles in each gas present, shown in Equation (4)

$$n = n_1 + n_2 + \ldots + n_N = \sum n_i$$

The mass fraction for a specific gas contained in the mixture is defined as the following in Equation (5).

$$c_i \equiv \frac{m_i}{m}$$

The mole fraction for a specific gas contained in the mixture is defined as the following in Equation (6).

$$y_i \equiv \frac{n_i}{n}$$

The partial pressure of a substance is the mixture pressure times the mole fraction of the substance. The following sections define properties specific to mixtures with respect to thermodynamics[7].

3.2.1 Henry’s Law

Henry’s Law concerns the solubility of a gas in a liquid with respect to the partial pressure of the gas. Therefore, the concentration of the gas in the liquid depends on the pressure of
the gas at a state of equilibrium. This relationship is modeled by the following Equation (7).

\[ e^P = e^{kC} \]  

(7)

\( P= \) partial pressure of the gas
\( k= \) Henry’s law constant
\( C= \) concentration of the dissolved gas in the liquid

By taking the absolute value of Henry’s Law the following Equation (8) is obtained.

\[ P = kC \]  

(8)

The Henry’s Law constant is a function of temperature, pressure, and the substance which serves as the solvent in the mixture. Similarly to how gases deviate from the ideal gas law at high temperatures and pressures, Henry’s law becomes less accurate as temperatures and pressures increase[3].

3.2.2 Chemical Potential and Gibbs Free Energy

A useful equation in thermodynamics is Gibbs Free Energy, \( G \), defined in the next equation, Equation (9).

\[ G = U + PV - TS \]  

(9)

\( U= \) internal energy of the system
\( P= \) pressure of the system
\( V= \) volume of the system
\( T= \) temperature of the system
\( S= \) entropy of the system

The Gibbs Free Energy is used to derive relations between properties. It is related to the chemical potential of the system. The chemical potential, \( \mu \), is equivalent to the partial
molar Gibbs function, $\tilde{G}$. The partial molar Gibbs function is determined by taking the derivative of the Gibbs Free Energy Equation with respect to temperature, pressure, and the mass of the mixture constituents, $n_A$ and $n_B$. This relationship is shown in the next Equation (10)[7].

$$\mu_A = \tilde{G}_A = \left( \frac{\partial G}{\partial n_A} \right)_{T,P,N_B}$$

In Equation (10) the partial derivative is taken holding temperature, pressure, and the moles in substance B constant.

$$\mu_B = \tilde{G}_B = \left( \frac{\partial G}{\partial n_B} \right)_{T,P,N_A}$$

In Equation (11) the partial derivative is taken holding temperature, pressure, and the moles in substance A constant. The next equation, Equation (12), models the derivative with respect to $n_i$ at a constant temperature, pressure and $n_j$[5].

$$\left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} = \left( \frac{\partial u}{\partial n_i} \right)_{T,P,n_j} + P \left( \frac{\partial v}{\partial n_i} \right)_{T,P,n_j} - T \left( \frac{\partial s}{\partial n_i} \right)_{T,P,n_j}$$

The chemical potential represents a potential for various properties of the mixture, such as temperature and pressure, to be changed through a chemical reaction.

### 3.2.3 Phase and Chemical Equilibrium

Phase Equilibrium is determined by by the Gibbs free energy change. A change in the Gibbs free energy, as stated above, leads to a chemical potential difference. This difference drives the diffusion function which in turn leads to a phase equilibrium. Thus, phase equilibrium is reached when the Gibbs free energy change is zero. Chemical equilibrium is defined in the same manner as phase equilibrium. For chemical equilibrium to be reached, the summation of the chemical potential times the volume of each component present, as shown in the equation below, must also be zero[5].

$$\sum \mu_i v_i = 0$$
3.2.4 Heat of Formation

The heat of formation of a system is equal to the energy which must be transferred in the form of heat out of a system in order to keep the temperature and pressure of the system constant. This is related to the heat of reaction, $\Delta H^o$, or the heat transfer out of a system during a reaction[8]. The heat of reaction is an affect of an isothermal, or constant temperature, chemical reaction. The heat of reaction is shown in the equation below, Equation (14). [5].

$$\Delta H^o = \sum_{\text{products}} n_i \Delta H_i^f - \sum_{\text{reactants}} n_j \Delta H_j^f$$  \hspace{1cm} (14)

As can be seen in this equation, the heat of reaction is equal to the enthalpy change of the system after the chemical reaction.

4 Thermal Conductivity

Thermal conductivity, represented in this application by $\lambda$, is the ability of a substance to conduct heat. The units for thermal conductivity are Watts per meter-Kelvin, or W/mK. The thermal conductivity is equal to the heat flux, $q$, divided by the temperature gradient, $dT/dx$, as shown in the following equation.

$$\lambda = \frac{q}{dT/dx}$$  \hspace{1cm} (15)

This equation is valid only if the heat flux does not change over time. The heat flux is the heat flow across a given area for a specified time. The temperature gradient is the change of temperature over the change in distance[9]. A local heat flux is something which is difficult to measure, therefore, the above Equation (15) is not useful in actually determining the thermal conductivity of a substance, and a different form of the equation must be used.
4.1 Methods of Measuring Thermal Conductivity

In this application a method to measure the thermal conductivity of an ionic liquid is desired. Since these ionic liquids are indeed liquid at room temperature, as well as the operating temperatures of an absorption refrigeration cycle, it is necessary to develop a method to measure the thermal conductivity of a liquid. There are several considerations that become problems when attempting to measure the thermal conductivity. The first is that if you are transferring heat through a fluid there is the possibility that the heat will be transferred not only through conduction, but also through convection. To obtain an accurate measurement, it is necessary to try to eliminate all heat transfer through convection. Insulation is another important consideration, because it must be certain that all heat being applied is being applied to the fluid and not being dissipated to the surrounding elements. With caution applied toward the problems involved with measuring thermal conductivity, several methods are highlighted in the following sections. The methods may be divided into two main categories; non steady-state, or transient, and steady-state[2].

4.1.1 Non Steady-State Techniques

The non-steady state techniques for measuring thermal conductivity are time-dependent. The result comes from the measure of the fluid temperature with respect to time. A heat flux is generally applied to the fluid by a thin wire inserted in the fluid. The wire is usually cylindrical in shape and the heat flux is applied through electricity conducted through the wire. The primary non steady-state technique that is used is referred to as the transient hot-wire method[2].

Transient Hot-Wire Method

The theory of the transient hot-wire method is based on the ideal that there is an infinitely long wire inserted into an infinitely long cylinder of fluid. The thermal conductivity, density,
and specific heat with a constant pressure are all assumed to be constant in this method. 
The wire is the heat source and it is assumed that heat is only lost through conduction in 
the liquid. Therefore, the affects of convection are ignored, introducing the possibility for 
error. The formula for non-steady conduction is represented by the following two equations,
Equation (16) and Equation (17).

\[
\frac{\partial T}{\partial t} = \kappa \nabla^2 T
\]  
(16)

\[
\Delta T(r, t) = T(R, t) - T_o
\]  
(17)

\[\kappa = \text{thermal diffusivity}\]

\[r = \text{radius of cylinder}\]

\[T_o = \text{equilibrium temperature of the fluid}\]

By applying boundary conditions to Equation (16) and Equation (17), then the temperature 
rise in the fluid, \(\Delta T\), is given by the following equation, Equation (18).

\[
\Delta T = \left(\frac{q}{4\pi \lambda}\right) \ln \left(\frac{4\kappa t}{a^2 C}\right)
\]  
(18)

\[a = \text{wire radius}\]

\[C = \text{a constant}\]

As can be seen from Equation (18), the relationship between the temperature difference 
and the natural log value is linear, therefore, the thermal conductivity may be determined 
from the slope of the line obtained by plotting the temperature difference and the natural log.

More information regarding these measurements may be seen in Section 4.2.3.

To actually conduct the measurements for thermal conductivity, a heat flux is generated 
through an electric current passed through the wire. There are two potential taps located 
at the top and bottom of the wire, and the temperature rise in the wire is determined by
the increase in the potential difference in the potential taps that is measured by a digital voltmeter[2].

**Advantages of the Transient Hot-Wire Method**

A key advantage of the transient hot-wire method is that the effects of convection in the heat transfer through the fluid may be avoided for the most part. This is because the experiment may be done for very short periods of time, therefore, the convection forces are not given enough time to begin movement. Consequently, the effects of convection in this method may be considered nearly negligible. Another advantage of the transient hot-wire method is that the potential taps on the wire may be placed strategically so that they only include the middle of the wire. This makes the measurements more accurate because the wire supports do not affect conduction in the middle[2].

**Disadvantages of the Transient Hot-Wire Method**

A disadvantage of the transiente hot-wire method is related to the fact that the accuracy of the measurements improve with the less time the measurement is being conducted. This is because the longer a heat flux is applied to the fluid from the wire, the longer time that convective currents have to form. These currents make the measurements less accurate, therefore, it is better to conduct the exercise in as short amount of time as possible[2].

**Example of the Measuring Thermal Conductivity of Ionic Liquids Using the Transient Hot-Wire Method**

In this example, a device was built to measure thermodynamic properties of ionic liquids using the transient hot-wire method. This study focused on the use of three different ionic liquids, 1-methyl-3-ethylimidazolium tetrafluoroborate ([EMIM][BF4]), 1-methyl-3-
butylimidazolium tetrafluoroborate ([BMIM][BF4]), and 1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide ([DMPI]Im), chosen for their commercial availability. For simplicity, these ionic liquids will be referred to as EMIM, BMIM, and DMPI, respectively.

To measure thermal conductivity, a thermal conductivity cell was constructed. First, tantalum wire was welded to silver leads that were placed in two parallel glass tubes. These were then sealed with epoxy and the two tubes were cemented together. To measure the thermal conductivity, this cell is placed into another tube containing the ionic liquid which is to be measured. A current is run through the wire for 1-2 seconds by a potentiostat/galvanostat, and therefore the potential as a function of time may be determined as the voltage is recorded every 25 milliseconds. The recorded voltage is then converted to resistance and the temperature may be calculated using a resistivity-temperature plot for the wire material. The thermal conductivity is then determined using the equation for ΔT, Equation (18) defined in the Transient Hot-Wire Method section and using the plot of ΔT versus ln(t).

To determine the accuracy of the measurements, the thermal conductivity of water was tested in the device. The average deviation of the results of the tests from standard thermal conductivity values of water was 0.3 %. The measured thermal conductivities, in W/mK, at 298 K for EMIM, BMIM, and DMPI, were 0.200±0.003, 0.186±0.001, and 0.131±0.001, respectively[6].

A Second Example of the Measuring Thermal Conductivity of a Liquid Using the Transient Hot-Wire Method

Another experiment was done measuring the thermal conductivity of liquids, specifically the liquid toluene, using the transient hot-wire method. The measuring technique was estimated to have an accuracy of ±0.5% when compared with earlier studies. The thermal conductivity
cell is set up similarly to the preceding experiment measuring the thermal conductivity of ionic liquids, designed for pressures up to 50 MPa and 130°C. This experiment was done in a range from 0°C to 80°C while the pressure was atmospheric. The measuring time of the experiment was at the most 4 seconds. The results were that the thermal conductivity of the toluene went down as the thermopareture increased. The thermal conductivity at 1.43°C was 0.1374 W/mK and at 81.73°C was 0.1140 W/mK[11].

4.1.2 Steady-State Techniques

The steady-state techniques depend on conduction of the fluid based on geometry and do not rely on time. The steady-state techniques for measuring thermal conductivity are based on Fourier’s Law. This law can be seen in the following equation, Equation (19).

\[
Q = \frac{\lambda A \Delta T}{d}
\]

(19)

\(A=\text{area of parallel surfaces}\)
\(d=\text{distance between the parallel plates}\)

There are two steady-state methods that differ mainly on geometry. The primary method that is used most often in experiments is the parallel plate method. The other method is called the concentric cylinder method. They will both be examined in detail in the following sections.

Parallel Plate Technique

The parallel plate technique uses Fourier’s law, as written above in Equation (19) to determine the thermal conductivity of a fluid through the knowledge of the energy input, the temperature difference, and the dimensions. In this technique, there are two parallel plates separating a fluid. Heat is applied to the top plate, and the temperature difference between the two plates is measured after a sufficient amount of time has passed[2]. A simple schematic
of the parallel plate technique is shown in Figure (2) below. This figure shows the parallel plates along with a guard plate situated above the plates. The liquid in which the thermal conductivity is being measured is contained between the two parallel plates.

![Parallel Plate Schematic](image)

Figure 2: Parallel Plate Schematic

**Advantages of the Parallel Plate Technique**

Advantages of the parallel plate technique lie in its seemingly simplistic analysis. The applied heat, geometry of the plates, and temperature differences are all the information that needs to be known to find the thermal conductivity. The devices also seem simpler to build than perhaps the device for the transient wire method[2].

**Disadvantages of the Parallel Plate Technique**

A disadvantage of the parallel plate method is that although there is insulation present, there
is a possibility of heat escaping the fluid region. This would lead to an inaccurate measurement of thermal conductivity because some of the applied heat would not be accounted for in the analysis. This is a disadvantage of the parallel plate technique that may be improved with insulation but probably not completely prevented. Another disadvantage of the parallel plate technique is that there exists the possibility for errors due to heat transfer caused by convection of the fluid. Without the influence of convection, theoretically the thermal conductivity should not vary with plate distance or temperature difference. However, the results of convection can be seen with varying values of thermal conductivity based on those two varying parameters. This is difficult to prevent, therefore, the apparatus must be designed so that the affects of convection are within an acceptable error for the thermal conductivity[2].

An Example of Measuring Thermal Conductivity of a Liquid Using a Parallel Plate Apparatus

In this experiment, the thermal conductivity of H₂O and C₆Cl₂ solutions were determined using the parallel plate method. The temperature range in this case was 293 K to 473 K. The pressure range was 0.1 MPa to 100 MPa. In the end, the uncertainty in the value of the thermal conductivity of the liquid was ±1.6%.

The apparatus was constructed using a thermal conductivity cell (consisting of a guard plate and an upper and lower plate), a high-pressure vessel, a liquid thermostat, a dead-weight pressure gauge, a water-to-oil separator, a contained for degased water and a container for solution, and a backing pump. The cell was placed in a cylinder and was surrounded by the fluid being tested, with the upper and lower plates being separated by a layer of fluid. Heat is emitted from the upper plate and the temperature difference between the plates is measured to determine the thermal conductivity[1].
Concentric Cylinder Method

The concentric cylinder method for measuring thermal conductivity is similar to the parallel plate technique described above. To find the thermal conductivity, Fourier’s Law is integrated as shown in the equation below, Equation (20), where $a$ is the inner cylinder radius and $b$ is the outer cylinder radius.

$$q = \frac{2\pi \lambda (T_1 - T_2)}{\ln (b/a)}$$  \hspace{1cm} (20)

There are two methods of inducing a heat flux within the concentric cylinders. The first is to have a wire for the inner cylinder that is subjected to an electrical current. The second is to heat the inner cylinder by an electrical winding[2].

4.2 Final Design Recommended for Thermal Conductivity Measurements

The design recommended for conducting the thermal conductivity measurements of ionic liquids is modelled after the 2004 experiments conducted by Valkenburg, Vaughn, Williams, and Wilkes[6]. This was chosen because the experiment was done on ionic liquids rather than a different liquid. It may be advantageous to perform an experiment that has already been proved to work specifically for ionic liquids. Overall, a method using the transient hot-wire technique was deemed appropriate for its potential accuracy. The recommended design will now be discussed in detail in the following sections.

4.2.1 Thermal Conductivity Cell

The construction of the thermal conductivity cell is relatively simple. A picture of the cell may be seen in Figure (3).

The thermal conductivity cell consists of two glass tubes, two silver leads with a diameter
of 1.0 μm, one tantalum wire where the exposed portion is 2.53 cm by .052 μm, and epoxy. The tantalum wire is first welded to the silver leads. The second silver lead is bend at a 90° angle near the bottom, as shown in the figure above. The wire is then placed into glass tubes which are sealed at the bottom with epoxy. The tantalum wire, attached to both silver leads, is exposed to the solution. The tubes are then cemented together such that the tantalum wire is kept taut.
In the thermal conductivity cell, only the tantalum wire and the outside of the glass tubes are exposed to the ionic liquid. Silver leads are used rather than using tantalum because the tantalum is being measured and should not be otherwise affected. Silver is a good conductor, therefore, is a good material to be used in the glass tubes. Tantalum is used as the material to be submerged in the ionic liquid because it is a good conductor and would not corrode or rust, such as a material like copper would. It also has the possibility of being drawn into very thin wire, which is ideal for this application.

### 4.2.2 Assembly of a Thermal Conductivity Device

The entire thermal conductivity cell is placed in a tube containing the ionic liquid. This tube is then placed in a temperature-controlled silicone oil bath.

### 4.2.3 Analysis of Data to Obtain a Thermal Conductivity Measurement

The equation used to determine the thermal conductivity is the following Equation (21)[2].

\[
\Delta T = \left( \frac{q}{4\pi\lambda} \right) \ln\left( \frac{4\kappa t}{a^2C} \right)
\]  

\(\Delta T\) = change in temperature
\(q\) = heat flux
\(\lambda\) = thermal conductivity
\(\kappa\) = thermal diffusivity
\(t\) = time
\(a\) = wire radius
\(C\) = numerical constant

21
The derivation of this Equation (21) is as follows. The differential equation used to model the conduction of heat through an instantaneous point source is Equation (22).

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\kappa} \frac{\partial T}{\partial t}
\]  

(22)

The solution to Equation (22) is the following, Equation (23).

\[
\Delta T = \frac{q}{8\pi \kappa t} e^{-(x-x')^2+(y-y')^2+(z-z')^2/4\kappa t}
\]  

(23)

Now the source of the heat flux is assumed to be a line source that is parallel to the z-axis and passes through the point \((x', y')\). The previous Equation (23) is integrated as follows.

\[
\Delta T = \frac{q}{8\pi \kappa t} \int_{-\infty}^{\infty} dz' e^{-(x-x')^2+(y-y')^2+(z-z')^2/4\kappa t}
\]  

(24)

\[
\Delta T = \frac{q}{4\pi \kappa t} e^{-(x-x')^2+(y-y')^2/4\kappa t}
\]  

(25)

Thus, the \(z\) terms are eliminated from Equation (23). The case of a continuous line source is now considered because that will best model the wire, which is assumed to be infinitely long. The wire is heated at a rate per unit time per unit length once again parallel to the \(z\)-axis and through the point \((x', y')\). Making these assumptions yields Equation (26), when \(a^2=(x-x')^2+(y-y')^2\) and \(\phi\) is a heat rate.

\[
T = \frac{1}{4\pi \kappa} \int_{t}^{0} \phi(t') e^{-a^2/4\kappa(t-t')} \frac{dt'}{t-t'}
\]  

(26)

Next assume that \(\phi\) is constant. The equation then becomes as follows.

\[
T = \frac{q}{4\pi \kappa} \int_{\infty}^{a^2/4\kappa t} e^{u} du \frac{d}{u}
\]  

(27)

If

\[
\int_{\infty}^{z} \frac{e^{-u}}{u} du = -Ei(-x)
\]  

(28)
then the following equation arises.

\[ T = \frac{q}{4\pi\kappa} - Ei\left(-\frac{a^2}{4\kappa t}\right) \]  

(29)

Then, the integral in Equation (29) equals the following.

\[ Ei(-z) = \gamma + \ln x - x + \frac{1}{4}x^2 + O(x^3) \]  

(30)

The following equation, Equation(31) is determined when the value for the time is assumed to be large[4].

\[ T = \frac{q}{4\pi\kappa} \ln \frac{4\kappa t}{a^2} - \frac{\gamma q}{4\pi\kappa} \]  

(31)

The common term of \( q/4\pi\kappa \) is factored out in Equation (31).

\[ T = \frac{q}{4\pi\kappa} \left( \ln \frac{4\kappa t}{a^2} - \gamma \right) \]  

(32)

Using the definition of \( \gamma = \ln C \), the following Equation (33).

\[ T = \frac{q}{4\pi\kappa} \left( \ln \frac{4\kappa t}{a^2} - \ln C \right) \]  

(33)

Now with using the identities of the natural log, the following equation is obtained.

\[ T = \frac{q}{4\pi\kappa} \ln \frac{4\kappa t}{a^2 C} \]  

(34)

**Determining the \( \Delta T \) Term**

The change in temperature, or \( \Delta T \), is determined by measuring the temperature rise of the wire with time. This is determined through using Equation (35) and Equation (36).

\[ R = R_0[1 + \alpha(T - T_o)] \]  

(35)

\[ \Delta T = T - T_o \]  

(36)
\[ R = \text{Resistance} \]
\[ \alpha = \text{temperature coefficient} \]

The values for \( R \) and \( R_\alpha \) are determined through the following Equation (37).

\[
R = \frac{V}{i} \tag{37}
\]

\( V = \text{Voltage} \)
\( i = \text{current} \)

The values for the current and the voltage are primary quantities that are measured directly. By knowing these values for these two variables and using Equation (35), Equation (36), and Equation (37) it is possible to determine the temperature difference in the wire.

**Determining the \( q \) Term**

The variable \( q \) is defined as the heat flux, or the heat generation per unit length of the wire[11], and is given by the following Equation (38).

\[
q = Vi \tag{38}
\]

The values for the voltage and the current are the same as discussed in the previous section, and are known directly through the experiment.

**Determining the \( \kappa \) term**

The thermal diffusivity of the ionic liquid is represented by \( \kappa \). It may be determined by the definition of the thermal diffusivity, shown in Equation (39).

\[
\kappa = \frac{\lambda}{\rho c_p} \tag{39}
\]

\( \rho = \text{density of the fluid} \)
\( c_p = \text{specific heat capacity of the fluid} \)

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Determining the t term
The variable t, time, is known by the time that progresses in the experiment.

Determining the a term
The variable a, the wire radius, is another known constant.

Determining the C term
The variable C is determined by Euler’s Constant, \( \gamma \), which is equal to 0.5772.

\[
C = e^{\gamma}
\]  
(40)

Thus, the ability to determine all of the above terms makes it possible to solve for the thermal conductivity of the ionic liquid in question through the method described above.

4.3 Manufactured Devices to Measure Thermal Conductivity

A web search was conducted to find manufacturers that make instruments to find the thermal conductivity of liquids. When considering possible instruments, a small sample size and a temperature range including room temperature was considered. A list of instruments that could possibly satisfy the requirements is included below.

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>WEBSITE</th>
<th>PRODUCT NAME</th>
<th>T RANGE</th>
<th>SAMPLE SIZE</th>
<th>POSSIBLE MATERIALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auber</td>
<td><a href="http://www.auber.com">www.auber.com</a></td>
<td>Uniform 2022</td>
<td>-20 – 300 °C</td>
<td>1”-2” d</td>
<td>solids, pastes, liquids</td>
</tr>
<tr>
<td>Netsch</td>
<td>www Netsch.com</td>
<td>LFA 457 Microflash</td>
<td>-100 – 500 °C</td>
<td>.01-.052 mm d</td>
<td>solids, powders, liquids</td>
</tr>
<tr>
<td>P.A. Hillebrand Ltd.</td>
<td><a href="http://www.p-ar.hillebrand.co.uk">www.p-ar.hillebrand.co.uk</a></td>
<td>H471</td>
<td>unknown</td>
<td>.09 mm d</td>
<td>liquids and gases</td>
</tr>
<tr>
<td>Int. Thermal Instrument Corp.</td>
<td><a href="http://www.thermalinstrument.com">www.thermalinstrument.com</a></td>
<td>C-600-L</td>
<td>-30 – 250 °F</td>
<td>4”</td>
<td>liquids and gases</td>
</tr>
<tr>
<td>Linney</td>
<td><a href="http://www.linney.com">www.linney.com</a></td>
<td>TC 7000</td>
<td>-50 – 1500 °C</td>
<td>unknown</td>
<td>solids, powders, liquids</td>
</tr>
<tr>
<td>ThermTest Inc.</td>
<td><a href="http://www.thermtest.com">www.thermtest.com</a></td>
<td>ASTM C177, etc.</td>
<td>-100 – 1000 °C</td>
<td>unknown</td>
<td>solids, liquids, pastes, powders</td>
</tr>
</tbody>
</table>

REFERENCES


