THERMOELECTRIC MEASUREMENTS OF SHARK GEL AND POLYELECTROLYTES IN SALT SOLUTIONS

by

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This work is dedicated to Alexis, Kevin, Pankaj, Utkarsha, Violet, and Phil who patiently put up with my daily worries, passions, failures, and of course, triumphs.

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Thermoelectric Measurements of Shark Gel and Polyelectrolytes in Salt Solutions

Abstract

By

CRAIG ADAM SNOEYINK

Measurements of the Seebeck coefficient of shark gel as well as functionally similar polyelectrolytes in salt solutions were performed to determine the mechanisms responsible for the enhanced Seebeck coefficient of shark gel over its main constituent, sea water. A systematic experiment in which the concentration of the synthetic materials varied relative to the concentration of salt ions in solution was also conducted. The resulting relationship of thermopower to relative concentration of functional groups suggests that the gel strongly raises the ionic concentration within the solution. The Seebeck coefficient for the resulting solution is raised by the same mechanism which raises the thermopower of simple salt solutions as the salt concentration is increased. It is postulated that the gel serves as an effective means by which a strong ionic concentration, and hence high Seebeck coefficient, is maintained within the electro-sensing pores of the shark.

Introduction:

Thermoelectric devices such as Peltier elements and thermoelectric generators currently have limited use in the marketplace. They are relegated to specialty uses such as active cooling of electronic devices and power generation in sail-boats or space-craft where normal refrigeration and power cycles can not be scaled down or used. The lure of such devices is their compact nature, lack of moving parts, and environmentally benign nature. Unfortunately, the coefficient of performance, a measure of efficiency, of current thermoelectric materials in a refrigeration use is far below that of a typical vapor-compression cycle refrigerator, typically 1 to 2 compared to 2 to 9 for the latter. As a result, in addition to moving heat from a cold to hot body they also generate a significant amount of heat.

Cheap efficient thermoelectric devices could find many uses in addition to the cooling of microelectronics. However, the obstacle is increasing the thermoelectric efficiency of these devices. A parameter that gives a measure of the thermoelectric capabilities of a device is called the figure of merit and is given below:

$$ZT = \frac{S^2\sigma}{k} \tag{1.1}$$

Where ZT is the figure of merit, S is the Seebeck coefficient, is the electrical conductivity, and k is the thermal conductivity. The Seebeck coefficient, the voltage produced by a thermal gradient, is a measure of the ability of the material to convert a thermal energy gradient into electrical energy. The electrical conductivity and thermal conductivity provide a measure of the efficiency of the device. If the material has a high thermal conductivity then too much of the heat is lost as it is conducted through the device. Conversely, a high electrical conductivity decreases the energy that is lost to Joule heating as the electrical current passes through the device. The thermoelectric capabilities of a material can be improved by manipulating any one of these properties; although, because it is to the second power, focus is usually directed towards the Seebeck coefficient.

Thermoelectricity, as a field, does not appear to lend itself towards inspiration from biological examples. There does not appear to be many examples where the conversion of a temperature gradient into an electric field is advantageous for the organism. Despite this difficulty two examples of thermoelectric materials in nature have been discovered. The first, several different related materials produced by hornets, is believed to allow these insects to survive in the extremely hot desert environment that they live in [1, 2]. A second material was found in the electro-sensing pores of sharks and related animals. It was reasoned that the electro-sensing pores, already very sensitive to electrical fields, could easily detect the voltage produced by the gel as a result of the temperature difference between the body of the shark and the ambient sea water. The pattern of these voltages about the body of the shark could then be interpreted to give knowledge of the surrounding temperature gradients. This assists the shark in finding the areas of the ocean where cold water wells up and meets the warm surface water, bringing with it nutrients that attract fish. Some of the claims made in the research on the chitin shell of hornets appeared to violate the second law of thermodynamics, casting some doubt as to the validity of the subject in general. As a result, the shark gel appeared to be the better candidate for investigation.

The shark gel is a very poor thermoelectric material. Since the main constituent is water the method of electrical conduction is ionic so it has a high electrical resistance. Additionally, the thermal conductivity of water is fairly high leading to further inefficiencies. These are largely the reason for the poor figure of merit of 0.001. Where the shark gel is unique is in it's Seebeck coefficient. As a liquid ionic conductor the shark gel has a much higher Seebeck coefficient then it's main constituent, sea water, as well as most other ionic solutions of similar salt concentration.

The possibility of a new mechanism to enhance the thermoelectric capabilities of ionic materials as well as a second look at a thermoelectric phenomenon in light of present day capabilities and technologies motivates this thesis and the topics covered within. Towards this goal, measurements of the Seebeck coefficients and the theory of the thermoelectricity of shark gel and related materials will be covered.

The Gel:

The biological material studied, shark gel, is obtained from the ampullae of Lorenzini found in the skin of sharks and their relatives. The ampullae of Lorenzini are exquisitely sensitive organs primarily used

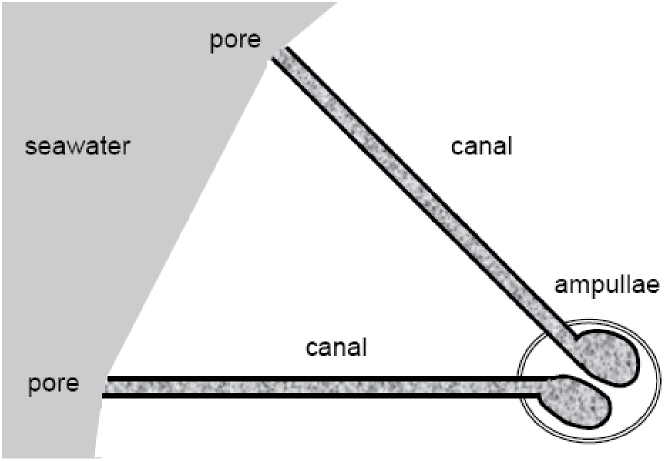


Fig. 1 Sketch of two electrosensitive organs. Sensing nerve cells are located in the bulbs at the base of the canals. The gel studied fills canals and bulbs. Reproduced from Brown, 2004.

to sense the electrical signals of other fish. [3] As can be seen in figure 1, the electrosensors are comprised of nerves set into the end of a long pore open to sea water. The gel studied fills this pore and serves to protect the nerve and conduct electrical signals from the sea water [3].

The gel itself is a rather unique substance. Comprised of 97% water by mass, the remaining 3% solid mass consists of large highly sulfated glycoproteins and salts in approximately the same concentration and composition as found in sea water. The exception to this is a higher concentration of potassium ions [3]. The higher concentration of potassium ions is consistent with the gel being in contact with dendrites of sensing nerve cells. The cell membrane of nerve cells is relatively permeable to potassium ions. In addition, a relatively high concentration of potassium ions must be maintained in the extra cellular fluid in order for the action potential caused by a sensory input to be initiated and transmitted properly. So, the nerve cells must continually leak potassium into the surrounding fluid where it slowly diffuses throughout.

The glycoprotein found in the shark gel consists of a long central protein to which many shorter carbohydrate chains are attached. The weight of this molecule can be greater then two hundred kilo Daltons, or two hundred thousand hydrogen atoms[3]. These carbohydrate chains are functionalized, giving the glycoprotein its properties. For the shark gel, each of the sugar molecules on the carbohydrate chains is functionalized with a sulfate group giving each sugar molecule an effective charge of -1 when in solution. This effective charge causes the carbohydrate chains to electrostatically repel each other and attract a layer of water molecules called a hydration shell. This gives the entire molecule the appearance of a pipe cleaner when hydrated in solution [Fig 2].

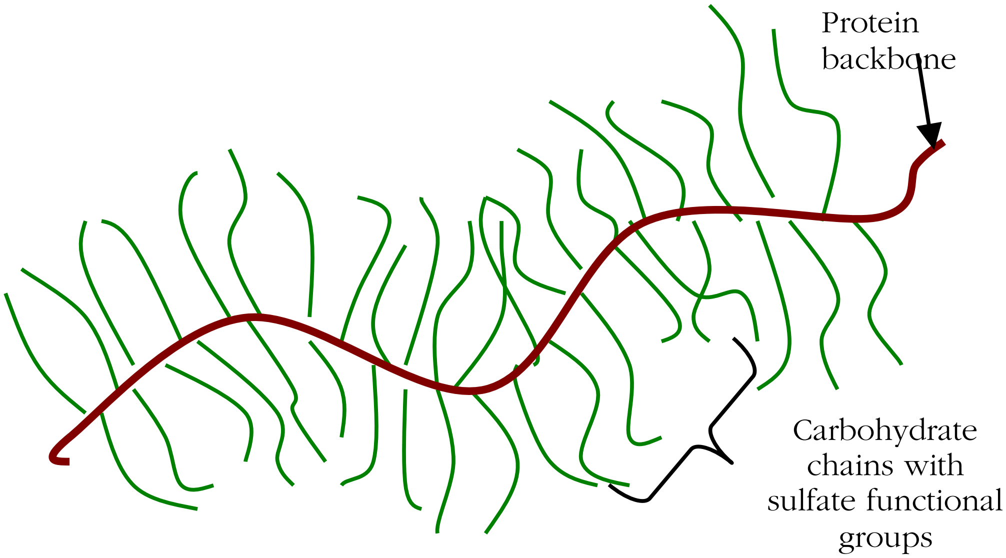


Fig. 2 Sulfated Glycoprotein in solution. The glycoprotein is uncoiled with its carbohydrate chains radiating outward, somewhat like a pipe cleaner.

The glycoprotein that gives the gel its structure and properties is functionally very similar to other hydrogels found in the human body. For example, both the vitreous humor of the eye and synovial fluid found in joints and tendons consist of large negatively charged glycoprotein. Like the shark gel, these gels are nearly all water and yet rather stiff as a result of the carbohydrate chains absorbing water molecules into its structure. In the body these gels can be used as springs. When compressed, the gels will shrink and lose some of their water content, regaining it and returning to their hydrated size when the pressure is reduced.

The gel used in our experiments was obtained by our collaborator Dr. Brandon Brown of the University of San Francisco. A metal paddle was applied to the skin of a shark *post-mortem* forcing a certain amount of gel from the pores in the shark's skin.[3] This gel was then dried in a vacuum for transport to our facilities.

The dried samples were then kept in a cool dry place surrounded by a desiccant until use. Our method for re-hydrating the samples will be described later in the methods section.

Owing to the small amount of gel we possessed, lack of knowledge of its exact composition, and an urge to generalize our results, the majority of our experiments were performed on ion exchange gels, a type of polyelectrolyte. The synthetic gels mimicked the shark gel in that they consist of a polystyrene backbone upon which charged functional groups are attached [Fig 3].

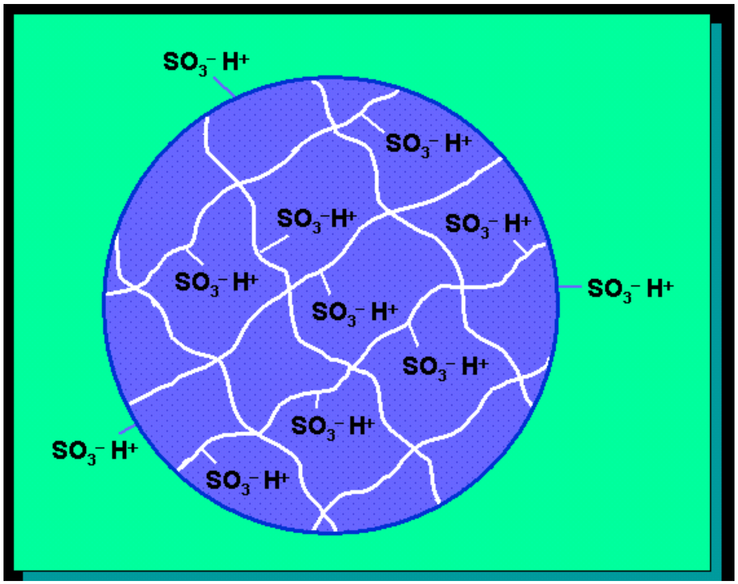


Fig. 3 Polystyrenesulfonate. White lines indicate polystyrene backbone off of which the sulfate functional groups are attached. Polymer cross linked and forms a solid which is typically porous.
From: http://separationprocesses.com/Adsorption/IE_Fig001.htm *11/4/04*

It is possible to purchase ion exchange gels with many different types of functional groups including sulfate groups. A cross-linked polystyrene network with sulfate groups is functionally very similar to the glycoprotein found in shark gel. Also studied were ion exchange gels with ammonium functional groups that give the polystyrene a positive charge when hydrated.

Nature is, however, much more effective at constructing these structures and can achieve a much higher charge density then is possible in man made polyelectrolytes. Further decreasing the effectiveness of the ion exchange gel with respect to the glycoprotein is the processing necessary to make them useable. Within the ion exchange gel the polymer strands are cross linked and the polymer is formed into beads several hundred microns in diameter. This allows the gel to be easily transported and removed from solutions. Despite the porous nature of the beads, the functional groups within the balls have comparatively little access to the solution and must rely on a tortuous diffusion path for access to mobile ions. The net result is that for a certain amount of sulfated glycoprotein a much larger amount of ion exchange gel must be used to provide an equal number of accessible functional groups.

Previous Work:

Our interest in this topic began while looking for biological examples of thermoelectric materials. Many other fields have learned from nature's vast experience and it was hoped that a new approach to creating thermoelectric materials could be found. Only two materials were discovered: the chitin and nest material of a certain species of wasp, and gel from the electrosensing pores of sharks. Of the two, shark gel appeared the most promising.

Dr. Brandon Brown of the University of San Francisco performed the original, as well as follow up measurements, of the shark gel's Seebeck coefficient [4, 5]. For the measurements, the shark gel was placed in a quartz container into which two platinum electrodes were inserted [Fig 4].

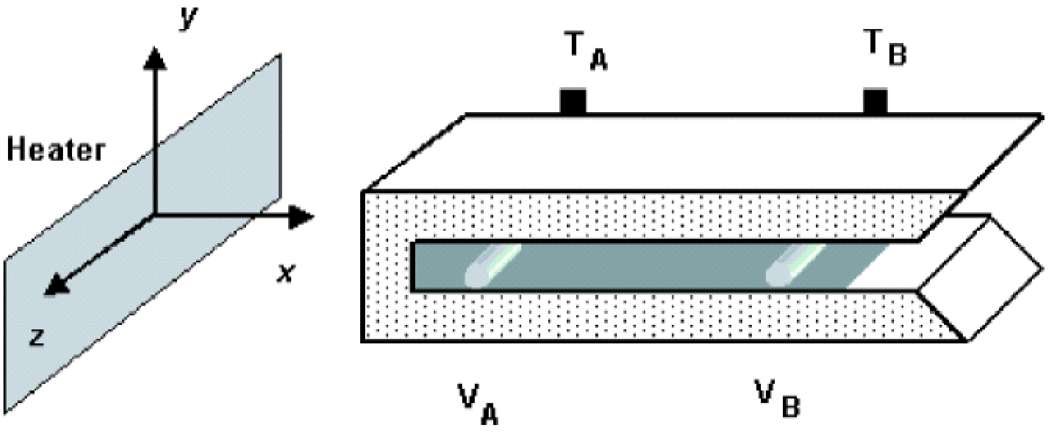


Fig. 4 Schematic of device to measure Seebeck coefficient of shark gel. Gel sample is shown in gray. Two platinum RTD's are attached via thermal grease to the thin sides of the cuvet, and two braided metallic leads run into the cuvet to sit adjacent the

The device was then pulse heated from one end with the temperature difference across the electrodes being measured by platinum resistance temperature detectors (RTDs). The voltage was then measured as a function of time and this was correlated to the temperature measurement from the RTDs. This data was plotted with the voltage difference measured as a function of the temperature difference between the two RTD's. The resulting slope of this line is the Seebeck coefficient for the sample. Using this technique, a Seebeck coefficient of 290 ± 70 μV/K was reported [5].

Several problems arise from this experimental setup. Given the placement of the electrodes and the material chosen to house the gel, a dynamic temperature measurement may not give an accurate estimate of the temperature difference across the two electrodes. Since the thermal diffusivity of quartz is approximately an order of magnitude greater then that of water, the thermal wave would not be expected to propagate evenly through the device. Additionally, the use of bare metal platinum electrodes could introduce many unknown electrochemical reactions between the electrodes and the solution. Each reaction would produce a voltage that is dependent upon the temperature of the electrodes. So, uncertainty is introduced as to whether the voltage measured is a result of the thermoelectric action of the gel and/or unwanted electrochemical reactions at the electrode surfaces. This last issue was addressed in the second paper, although many problems still remain [4]. A Keithley 2182 Nanovoltmeter was used to measure the voltage between the two braided platinum leads. This machine releases a small amount of current, called pumpout current, into the system after every measurement. Since the circuit used was a closed loop, the only path for this current is though the sample. For a current to be carried in such a manner there must be charge transfer between the solution and the electrodes in the form of chemical reactions between the metal and ions in solution. Simply measuring the voltage across the solution necessitates chemical reactions at the electrodes and the unknown voltages they produce.

Thermoelectricity of Dilute Ionic Solutions: Qualitative

The mechanism behind the thermopower of ionic solutions is fundamentally the same as that for other materials. A mobile charge carrier finds it energetically favorable to move under a temperature gradient. What makes the thermopower of ionic solutions different and interesting is that there are many different possible charge carriers present of different polarity, charge, and mobility. Each of these properties will effect the movement of the ion when under a temperature gradient.

When an ion is solvated in a polar solvent there exist three zones of structure[6]. The first zone, nearest to the atom, consists of solvent molecules tightly bound to the ion. While the attraction is purely coulombic, there is little or no exchange of these molecules with the surrounding bulk solvent. The second layer consists of solvent molecules not directly interacting with the ion but still influenced by the electric field. The third layer goes to infinity and consists of the bulk fluid. This model is accurate for dilute solutions up to about 0.01 M. Above these concentrations there are not enough solvent molecules to fill all of the shells requiring solvent to be shared between hydration shells of different ions. At this stage the theory becomes very complex and no treatment of it was found. Continuing with the dilute solution model will give a good understanding of the thermoelectric mechanism of ions in solution that can be interpreted under the conditions of higher concentrations.

In a solution, solvent molecules are constantly in flux, entering and leaving the second hydration shell of the ion. As the solvent molecules enter and leave they undergo what can be considered a chemical reaction with a corresponding change in free energy. Now, if the ion is arbitrarily dragged through the solution, the solvent can be forced to pass through the hydration shell. As they enter and leave, the solvent molecules will absorb or liberate a certain amount of heat equal to the change of free energy for that change in state. Figure 4 demonstrates the hydration shell along with the changing sphere of influence.

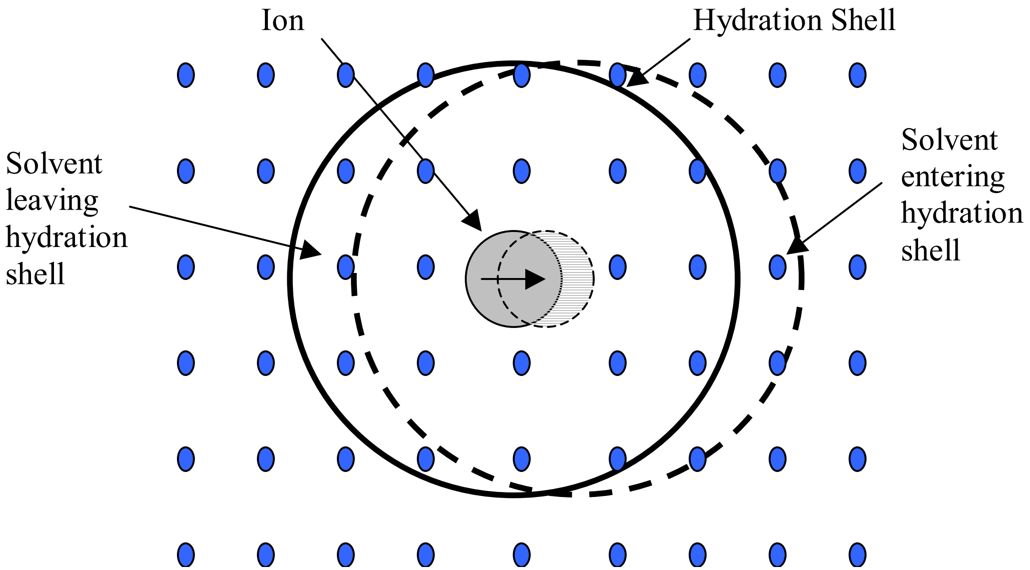


Fig. 4 Ion in solution with an arbitrary number of solvent molecules inside of hydration shell. As the ion moves through the solution, solvent molecules enter and leave the hydration shell releasing or absorbing energy corresponding to

From this figure a general equation describing the reaction involving the solvent molecules as they enter or leave the hydration shell can be written:

$$\Delta E + A \rightleftharpoons B \tag{1.2}$$

Where ΔE is the change in free energy between the bulk and hydration shell states, A is the state of the solvent molecule while in the hydration shell, and B is the solvent molecule in the bulk solution. With the application of a temperature gradient water molecules on the hot side will tend to have more thermal energy then those on the cold side. Le Chatelier's principle suggests that the equation will shift towards A, the bound solvent, on one side of the ion and shift towards B, the bulk solvent, on the other. For example, if a solvent molecule tends to absorb heat when entering the shell and liberate heat when leaving then bound solvent molecules will tend towards a greater concentration on the hot side then on the cold side. Functionally this is achieved by the ion moving through the solution as described in figure 4. In this manner the ion travels up the thermal gradient transporting heat across itself. The ability of the ion to migrate will thus depend on the change in free energy of the solvent molecules and the mobility of the ion. This corresponds to a force on an ion and it's resistance to movement[7][8].

An alternate way of visualizing this phenomenon that deals with the forces on the ions in solution and focuses on the difference in thermal energy of the ions on either side of the ion. Drawing a control volume around the hydration shell of the ion and using conservation of mass shows that the number of molecules in the hydration shell is fixed. If, on the hot side, the molecules have a greater propensity to enter relative to the cold side then molecules will tend to enter on that side and leave on the cold side keeping the total number of molecules constant. Since there is no fixed body from which a force can be applied to accelerate these molecules, the ion itself must be moving through the solvent. In reality, solvent molecules will enter and leave both sides of the ion. It is only because hot solvent molecules will have a slightly greater tendency to enter the hydration shell than cold solvent molecules that, over time, there is a net mass flux.

From this model it is now clear why the Seebeck coefficient of an ion would depend on the change in free energy of the molecules. A greater difference in free energy change for molecules entering the hydration shell will result in a more efficient selection of hot molecules over cold ones. With more of the molecules entering and leaving the hydration shell entering from the hot side and leaving from the cold side the time average results in a greater momentum impulse on the ion. Since the flux of ions into and out of the hydration shell is still mostly random, typical solvent – ion interactions will still play a role in determining the degree to which the ion moves.

Similarly, the temperature of the solution will greatly affect the thermopower of the ions. If the solution is at a higher average temperature there will be more exchange between the bulk solution and the hydration shell. If the same percentage of the solvent molecules entering the hot side migrate around and exit the back side then increasing the rate at which molecules enter will increase the number of molecules migrating. A greater mass flux through the control volume will result in a greater apparent velocity of the solvent and hence a greater velocity of the ion. Additionally, the free energy of solvent molecules in the bulk solvent and in the hydration shell will change.

A salt solution, such as NaCl, will always contain at least two species of ions of opposite charge. As can be seen from the previous explanation, the direction of motion is independent of the sign of the charge so two ions of roughly equal size and magnitude of charge will tend to move in the same direction. One will invariably move faster initially then the other causing a charge separation to develop. The electric field caused by the charge separation will tend to speed up the slower ion and drag on the faster ion until equilibrium is reached. Once the solution is at equilibrium both ions are traveling at the same rate. It is this electric field that is sensed as the thermopower of a solution. While macroscale migration of ions towards the electrodes occurs, the time scale for this movement is on the order of a day. The phenomenon of steady state equilibrium distribution of the ions under a thermal gradient is called Soret diffusion. Like the Seebeck coefficient, the Soret diffusion coefficient is dependent on the heat of transfer, which is the quantity of energy released as one mole of a particular component of a solution is moved across an imaginary plane dividing a solution in half. It is stipulated that (a) the net amount of other components crossing the plane is zero; (b) there is no change in pressure at any point; and (c) there is no change in temperature at any point. (a) and (b) can be satisfied by acting on the components with a suitably chosen force and moving the reference frame relative to the containment vessel. For (c) to be satisfied there must be some transfer of heat to or from the surroundings. The heat transferred to each side in order to keep each half of the solution isothermal is the heat of transport. For many ionic solutions it is easier to measure the Soret diffusion coefficient and use that quantity to get the heats of transfer. Non-electrical methods exist for measuring the steady state concentration differences that such as changes in index of refraction.

The result of the ions possessing two different polarities is that any ionic solution will have a net thermopower that is significantly less then the thermopower of the individual ions. The oppositely charged ions will mask the other with only the difference in thermopowers expressed in the bulk solution. This effect is most prominent in solutions of potassium chloride where the ions are similar enough in size and charge that they almost completely cancel the other out, leaving a solution with an effective Seebeck coefficient of almost zero.

Thermoelectricity of Dilute Ionic Solutions: Quantitative

The previous model of ionic thermopower does not lend itself easily to mathematical expression in terms of quantities that can be measured. To do so, one must first take a more abstract look at the processes at work.

Agar, following Eastman's initial work, derives the following formula for the EMF of a non isothermal infinitely dilute salt solution[8]:

$$F\frac{\partial\varphi}{\partial x} = -\left[\frac{t_1}{z_1}\hat{S}_1 + \frac{t_2}{z_2}\hat{S}_2\right]\frac{\partial T}{\partial x} \tag{1.3}$$

Where F is Faraday constant, t_n are the Hittorf transport numbers, z_n are the valences of the respective ions, $\hat{S}_n$ are the Eastman entropy of transport, T is the temperature, and   is the electrical potential. The Faraday constant gives the amount of charge carried by one mole of ions, while the Hittorf numbers give the relative amounts of current carried by each ion. As such, $t_1 + t_2 = 1$, but $t_1 \bullet t_2$ because each of the different ionic species will have a different mobility and therefore carry proportionally more of the current. For example, when an electric current is passed through a solution of NaCl, the sodium ions carry forty percent of the current while the chlorine ions carry sixty percent of the current. Their Hittorf numbers are then 0.4 and 0.6 respectively. For NaCl, the valence numbers are +1 and -1 for Na and Cl respectively. Since Eastman's initial work on the subject it has become much more favorable to speak in terms of heat of transport as opposed to energy of transport. The two are related through the expression:

$$\hat{S}_i = \frac{\hat{Q}_i}{T} \tag{1.4}$$

Where $\hat{Q}_i$ is the heat of transport for ionic species *i*. Making this substitution and some further simplification results in:

$$S = \frac{\partial \varphi}{\partial T} = -\frac{1}{F}\left[\frac{t_1}{z_1}\frac{\hat{Q}_1}{T} + \frac{t_2}{z_2}\frac{\hat{Q}_2}{T}\right] \tag{1.5}$$

The term on the left, S or $\frac{d\varphi}{dT}$ is the Seebeck coefficient for the solution. The heats of transport, as discussed earlier, are for individual ionic species and are also measurable through the Soret Effect in which they also play a part. The Soret effect concerns the long term steady state distribution of ions in a solution under a temperature gradient. At equilibrium a balance is achieved between diffusion, which tends to decrease concentration gradients, and thermal diffusion, which drives the formation of the concentration gradient[9].

It should be noted that the assumptions which are made in the derivation are clearly not applicable to the environment of the shark gel. The salt concentrations of sea water are far greater than that considered dilute. In addition, the severe ordering of the solvent molecules by the gel as they are incorporated into its structure will drastically alter the properties of the bulk solution. This will affect the heats of transport as well as the diffusion coefficients, and hence the Hittorf transport numbers, of the participating ions. Since nearly all of these problems are not theoretically accessible and have not been experimentally studied a qualitative approach to analyzing the mechanism behind the high Seebeck coefficient of the gel will be taken.

Polyelectrolytes in Solution:

With the addition of polyelectrolytes, charged polymers similar to shark gel, the situation gets much more complex. Much of this complexity arises from the interactions between the bound charges on the macroions, themselves, and free ions in solutions. These interactions are not equivalent to free ion interactions at similar concentrations because the charges on the macroions are highly limited in mobility and essentially fixed in concentration. Thus, while a solution of free ions will tend to diffuse and homogenize, a polyelectrolyte solution will have regions of relatively immobile and concentrated ionic charge[10].

A polyelectrolyte consists of a very large molecule with functional groups attached to it that disassociate when the polyelectrolyte is dissolved in water as shown in figure 5. Typically these functional groups are similar in nature to organic acids and bases where the group consists of a large base molecule and a smaller hydrogen ion or hydroxide group. In a polyelectrolyte, the large base molecule stays attached to the polymer while the smaller ion disassociates and diffuses into the solvent.

For sulfate groups, essentially a strong acid, this dissociation is complete and so occurs for every functional group on the polyelectrolyte. However, these counter-ions are not always free to diffuse equally throughout the solution. Depending on the concentration of the polyelectrolyte, the counter-ions can be considered significantly localized in the vicinity of the macroion. This effect is not well understood but is considered to be a result of it being more energetically favorable for counter-ions to be removed out of solution to screen the electric field in the vicinity of the macroion [10, 11]. For the sodium salt of poly-styrenesulfonate, the ion exchange gel used in this experiment, the fraction of counter-ions that are apparently bound can range from as high as seventy percent at dilute concentrations to a limit of about fifty percent as the concentration of the polyelectrolyte increases[12]. Additionally, evidence of large amounts of apparent ion binding were concluded to be behind much of the electrical behavior of the shark gel, although, the degree of ion localization was not discussed.[13]

As can be imagined, if some amount of counter-ions are apparently bound up within the macroion then the apparent mobility or self diffusion coefficient of the counter-ion must also be affected. Also hindering the motion of counter ions is the non-uniform distribution of the electric field around the macroion[14]. Beyond this simple description, the diffusion coefficients behave in a highly complex manner that is dependent on many aspects of the solution such as ion concentration, macroion concentration, solvent properties, and the nature of other ions in solution. The diffusion coefficients of salt ions in solutions of chondroitin sulfate, a proteoglycand similar to shark gel but with partially ionized functional groups, have been studied. At concentrations similar to that of the shark gel, both sodium and chloride ions have their diffusion coefficients decreased by increasing the concentration of the gel[15]. The source also mentions that the diffusivities were relatively independent of the ionic strength at medium to high concentrations of added salt. Results based on polystyrenesulfonate show conflicting results. They report that increasing the concentration will increase the diffusion coefficient for the counter-ions[11, 16]. It is likely that the latter is more applicable owing to the possible influence of partially ionized functional groups on the chondroitin sulfate. In the presence of changing concentration, the degree of ionization of this macroion will change, possibly leading to changes in the fraction of apparently bound counter-ions as well as diffusivities. In addition, earlier it was shown that the fraction of apparently free ions increases with increasing polyelectrolyte concentration[12]. Since the degree of screening supplied by the condensed counter-ions is less at higher concentrations it is highly possible that the macroions are partially screening each other through interactions with the highly polarizable solvent[10]. Both suggest a decreasing macroion influence upon the counter-ions as the concentration of the polyelectrolyte increases.

The diffusivities of the macroions themselves are as poorly understood. The diffusion coefficients for these molecules are typically an order of magnitude less then that of their counter-ions and apparently also dependent upon the concentration of the polyelectrolyte, charge density of the macroion, and valency of the counter-ion[11].

Polyelectrolytes in Solution With Added Salt:

The behavior of polelectrolytes in a solution with added salt is fundamentally the same as that for salt free solutions. Greater amounts of free counter-ions tend only to act as increasingly effective screens for the charge of the macroion[10, 11] While the increased concentration of the counter-ions does not increase the number of apparently bound counter-ions, it does decrease the mean distance between the apparently bound counter-ions and the macroions.

The increased screening of the macroion leads to a decreased diffusion coefficient. This result is expected given that a neutral polymer of similar chemistry, mass, and length will diffuse many time slower then the equivalent macroion [10]. It follows that the diffusion coefficient for the macroions will approach that of a neutral polymer for high concentrations of added salt.

Another phenomena related to the screening caused by added salt is a swelling of the shark gel with dialysis as reported by Brown in his work characterizing the electrical properties of the gel [3]. As mentioned earlier, the gel swells by incorporating water molecules into its structure through interactions with their dipole. The stronger the apparent charge of the macroion the stronger the response of the polar solvent. In the case of the shark gel sample after dialysis, most of the extra salt ions were removed allowing the charge on the macroion to be more fully expressed, attracting the polar water molecules more strongly.

Overall, a fairly complex picture of the shark gel is emerging. Indeed, very little research has gone into measuring such physical properties as the Seebeck coefficient of polyelectrolytes because of the difficulties in finding meaning in the results. With much to be investigated of the basics of polyelectrolyte solutions, especially those with added salt, there is little reason to move ahead to overly complex situations. A rough and particularly qualitative attempt at this will be undertaken in the next section.

Thermopower of Polyelectrolytes:

The thermopower of ions in a polar solvent is fundamentally dependent on three things: the change in free energy of molecules as they enter the sphere of influence of the ion, the mobility of the ion, and the effective surface area of the ion. Of these, the addition of a large amount of fixed charge into the solution will predominantly change the former two. As was described in the previous section, the chemistry of a polyelectrolyte solution with excess salt is highly complex and does not lend itself to theoretical or experimental analysis. In order to determine the mechanism behind the improved Seebeck coefficient of the gel, a very qualitative approach will be used to narrow the possibilities.

If the macroions in solution are manipulating the properties of the solution in such a way as to change the free energy of the solvent molecules then there are several behavioral characteristics that should be found. The nature of these changes will be similar to what occurs in simple ionic solutions of higher concentration. In both of these solutions, the simple and the polyelectrolyte, the large amount of charge is going to significantly affect the order of the solution and the spheres of influence of each ion will overlap with their neighbor. Data on the effects of increased concentration on heats of transfer of ions in solutions, essentially a measure of the change of free energy, is sparse but suggests a minimum at concentrations of roughly 0.25 M after which the heat of transfer significantly increases with increasing concentration [Fig. 5][8].

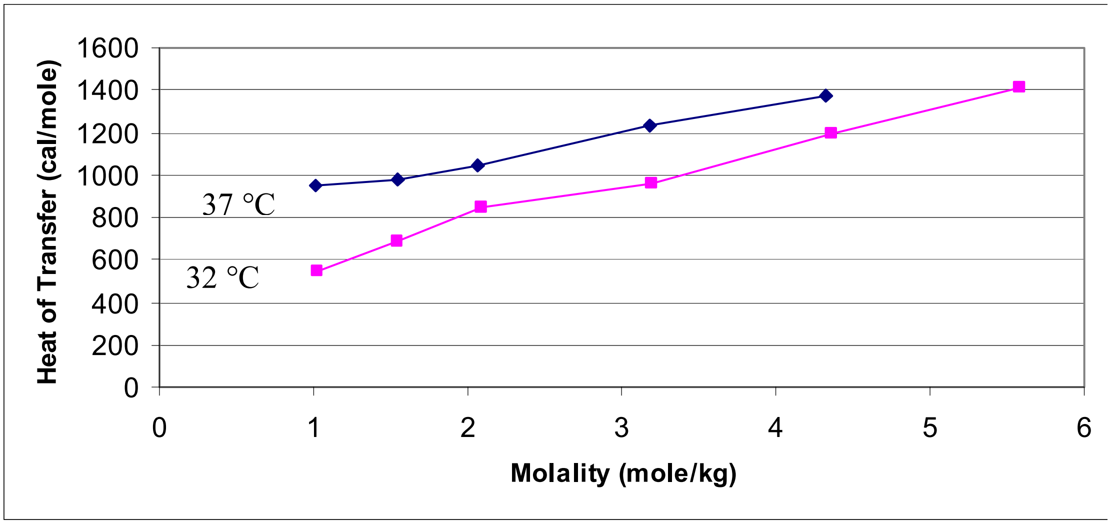


Fig. 5 Plot of Heats of Transfer of aqueous NaCl as a function of molality of solution. Note how the Heat of Transfer increases with increasing concentration. Data from Tyrrell's *Diffusion and Heat Flow in Fluids* [22]

Using equation (1.5), the Heat of Transfer for aqueous NaCl at 32 °C corresponds to a Seebeck coefficient of approximately 202 μV/K at 5.59 Molality. This value is nearly seven times the magnitude found for dilute solutions. Note that increasing the concentration does not cause the sign of the Seebeck coefficient to change. Similar data exists for potassium chloride solutions and is shown in figure 6.

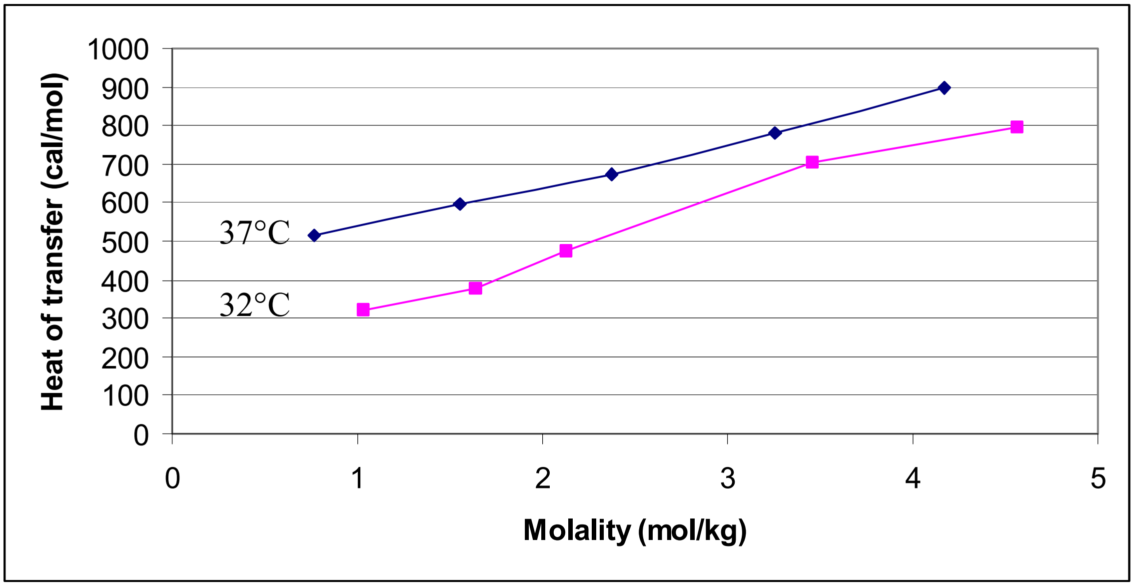


Fig. 6 Plot of Heats of Transfer of aqueous KCl as a function of molality of solution.
Note how the Heat of Transfer increases with increasing concentration.
Data from Tyrrell's *Diffusion and Heat Flow in Fluids* [22]

Both the potassium chloride solutions and the sodium chloride solutions show a strong positive relationship with concentration and temperature.

The second mode through which the macroions could influence the bulk Seebeck coefficient is through impeding the movement of the smaller mobile ions in solution. Very little hard data can be found on this topic owing to the difficulty of determining the different diffusion coefficients for components of a polyelectrolyte. However, some inferences can be drawn. It is known that the diffusion coefficients for both polarities of ions will be impeded through purely steric action of the macroion[11]. This means that, neglecting for the moment any coulombic interaction, the presence of the macroions will create a more tortuous and elongated path for the ions to follow. What is less certain is if coulombic interactions will selectively hinder the motion of one species of ion. If this is the case, then the Hittrof transport numbers mentioned in eq. (1.5) will no longer be close to equal. If the Hittrof transport numbers are sufficiently unbalanced then the thermopower of one ion would no longer be mostly canceled by the actions of the other.

A third possibility is that the macroions possess a significant thermopower unto themselves. The heat of transport for these macroions is dependent upon the length of the polymer chain but is significantly greater then that of a small ion. This follows from the large amount of surface area these molecules have and thus their ability to exchange large numbers of solvent molecules with their environment. However, the change in free energy for these solvent molecules will be the same for the macroions as for small mobile ions. Because of the large surface area, macroions have many more of these ions entering and leaving their sphere of influence at any moment. This leads to a heat of transport several orders of magnitude greater then the equivalent charged monomer in solution [17]. However, when the heat of transfer is divided by the number of monomers the heat of transfer per monomer is found to be nearly equal to that of the free monomer in solution [17]. If the heat of transfer per charge for a macroion is small then by equation (1.5) it can be seen that the Seebeck coefficient for such a solution would be dependent upon the transference numbers. Data on the transference numbers for macroions or charged colloidal particles in a salt solution could not be found. Related to this phenomenon is electrophoresis, or the movement of particles and molecules under an electric field. On this topic it was found that while the diffusion coefficient increased slightly with increasing salt concentration, the electrophoretic mobility strongly decreased [18] This is a result of condensation of counter-ions on the macro-molecule lowering its effective charge and the force it feels under an electric field. It can be speculated that the condensation of counter-ions will lower the charge to mass or volume ratio of the macroions decreasing the transference number and heat of transfer per unit charge.

Hypothesis:

It is believed that while all of the previous mechanisms are likely present and active in the shark gel as well as the polyelectrolyte solution, one will dominate the overall behavior. Besides the three phenomena mentioned previously (i.e. 1. Manipulating the properties of the bulk solution 2. Selectively impeding the movement of one ion 3. Thermoelectric contribution of the macroions and/or counter-ions), other factors non-thermoelectric in nature and inherent in electrochemical measurements could be present and contributing to the thermoelectric voltages. These factors include liquid junction potentials at the interface between the sample solution and the reference electrode solution as well as reactions occurring at the metal leads within reference electrodes. Since the voltage produced by the reactions at the metal electrodes is dependent upon the temperature, a net voltage between the two electrodes could develop due to the temperature difference imposed on the system. Previously, it was demonstrated that it is unlikely for the polyions in solution to be contributing to the thermopower in any direct way. While they have very large heats of transfer, the heat of transfer per unit charge is average and the transference numbers for macro-ions should be quite low. A low heat of transfer per charge combined with a small transference number will lead to a small contribution to the Seebeck coefficient. As a result, if the systematic errors of the system can be shown not to be a factor one of the remaining two mechanisms can be expected to dominate the behavior of the system.

If the macro-ions are changing the free energy of the solvent molecules and thus the heat of transfer of the small ions in solution, then an increase in the concentration of macro-ions should affect the solution in the same way as increasing the concentration of the simple salt solution. Increasing the number of macro-ions in solution will severely change the free energy of the solvent molecules as more of the solvent molecules are taken up in the hydration shell. At higher concentrations the hydration shells of the ions in solution begin to overlap and they begin to share solvent molecules. This occurs irrespective of the nature of the charge being introduced into solution. So, qualitatively, an increase in concentration of macro-ions, regardless of the macro-ion polarity, will affect the Seebeck coefficient in much the same way as simply increasing the concentration of the base salt solution.

If the macro-ions are impeding the movement of counter-ions then quite different behavior will be expected. Since the Seebeck coefficient of the solution is the sum of the constituents it was shown that often times the ions of one charge will tend to negate the effects of the other. If the movement of only one ion is severely effected then the transference number will decrease with respect to the other ions in solution. If the solution is chosen well, increasing the concentration of macro-ions in solution may hinder the motion of one species of ion to such a degree as to change the sign of the Seebeck coefficient of the solution.

There is now a criterion for choosing a solution with which to test which mechanism is dominating the behavior of the solution. The solution of NaCl depicted in figure 5 has a total heat of transfer that increases with concentration. The Seebeck Coefficient will also increase with increasing concentration of ions in solution. A solution of NaCl is also ideal because the thermoelectric contribution of the sodium ion is greater then that of the chloride ion. If we choose a negatively charged polyelectrolyte to add to the solution then if the macro ions hinder the motion of the counter ions we can expect that at a certain concentration the contribution of the chloride ions will become greater then that of the sodium. Increasing the number of macro-ions in solution will increase the available surface area to hinder the counter-ions and decreasing their effective transference number. From equation (1.3), decreasing the transference number on the positively charged sodium ions and increasing the transference number for the negatively charged chlorine ions will cause the Seebeck Coefficient to decrease, reach zero, and start increasing but with the opposite sign. Adding a positively charged polyelectrolyte will have the opposite effect of hindering the negatively charged ions. This allows the positive ions to be more fully expressed and increasing the thermopower of the system in the negative direction.

Comparing the results of the two solutions of macro-ions will show if the macro-ions are simply creating an environment for the ions similar to that found in solutions with greater salt concentrations. If, as the concentration of macro-ions increases, the two solutions behave the same then it is likely this mechanism is dominating the thermoelectric behavior of salt solutions with added polyelectrolyes.

Experiment Design:

Experiment Plan:

For this investigation, measurements of the Seebeck coefficient of shark gel and the Seebeck coefficients of several different solutions of polyelectrolytes are required. A value for the Seebeck coefficient of shark gel is needed to compare our measurement setup with that of our collaborators and to verify their results. As such, the conditions of this measurement should closely approximate that of previous work for such variables as the mean temperature of the experiment and the temperature difference across the sample.

In order to discern the mechanism behind the large Seebeck coefficient of the shark gel, measurements on different solutions of polyelectrolyts will be performed to ascertain which mechanism discussed earlier is dominant. Towards this goal, measurements of the Seebeck coefficient of a reference solution of NaCl with increasing concentrations of polyelectrolyte will be made. Additional measurements of a KCl reference solution with polyelectrolytes of differing concentrations and functional group charge will also be made to investigate the influence of different systematic errors such as liquid junction potentials. Further measurements of varying concentrations of NaCl will be compared to previous data to estimate the accuracy of the experimental setup.

Measurement Setup:

When measuring the Seebeck coefficient of a material there are two quantities that must be recorded: the voltage and temperature difference across the sample.

However, given the nature of the shark gel there are special constraints upon the measurement setup. The primary constraint is to minimize the amount of sample needed in order to conserve the quantity of shark gel that was given to us by our collaborator. Taking into account possible future work as well as contaminated or otherwise ruined samples it was decided that a maximum of 80 μL of gel be used. To maximize the temperature difference across the sample an aspect ratio of 10 was chosen giving a sample of rectangular cross-section the dimensions of 0.2 cm by 0.2 cm by 2 cm. These dimensions worked well with the electrodes chosen but caused some difficulty with the temperature measurement.

Temperature:

Due to the small cross-section of the gel, some care was needed in choosing a method of measuring the temperature. Platinum RTD's offered adequate accuracy, but were large and took the temperature as an average over the entire body of the device. Thermistors offered a smaller, but slightly less accurate possibility. Though much smaller, they were still the same size as the width of the sample. Thermocouples offered superior spatial resolution but lacked the necessary accuracy. To compensate for the thermocouple's weakness, several were combined in series to make a thermopile. By adding the voltages of each thermocouple, the small temperature differences could be more accurately measured. Ideally, the accuracy of the thermocouples is increased by a factor proportional to the number of thermocouples used. In practice, increased noise and increased thermal conduction by the thermocouple wires decreases the advantage gained. If the voltage developed by the thermocouple is given by:

$$E = N\alpha\left(\Delta T\right) \tag{1.6}$$

Where E is the voltage output of the thermopile, N is the number of thermocouples, is the thermocouple's effective thermopower, and T is the temperature difference across the two junctions. The thermal noise of the system will be essentially that of a metal resistor which is given by:

$$E_n = \sqrt{4kTBR} \tag{1.7}$$

Where E_n is the electrical noise, k is Boltzmann constant, T is the absolute temperature of the metal, B is the noise bandwidth, and R is the total series resistance of the thermopile. This series resistance can be expressed as:

$$R = rN \tag{1.8}$$

Where r is the resistance of each thermocouple unit and N is again the number of thermocouples used. Substituting this into the previous equation and taking the ratio of the signal to the noise the following relationship develops:

$$\frac{E_s}{E_n} \approx C\frac{N}{\sqrt{N}} \propto \sqrt{N}, C = \frac{\alpha\Delta T}{\sqrt{4kTBr}} \tag{1.9}$$

Where C is a constant representing everything not affected by the number of thermocouples. As can be seen, the effective signal to noise ratio is proportional to the square root of the number of thermocouples used. The thermopile constructed for this experiment consists of four differential thermocouples hooked in series indicating a signal to noise ratio that is approximately twice that of a single thermocouple [19].

The temperature measurement itself was to be taken under steady state conditions to improve the accuracy. While effort was made to place the junctions of the thermopile as close to the electrode interface as possible some distance was necessary. Since the materials of the device had similar, if lower, thermal conductivities then the samples a steady state measurement would provide good estimate of the temperature at that cross sectional plane of the device. Additionally, any difference in thermal diffusivity between different components is no longer a factor further increasing our confidence in the temperature measurement.

Voltage:

The electrodes for this experiment were selected with the help of James Burgess Ph.D. of the Chemistry Department at Case Western Reserve University. The electrodes selected are Ag/AgCl reference electrodes commonly used in electrochemistry experiments. The advantage of these electrodes over a simple metal electrode is that reactions and the voltages they produce at the electrode-solution interface are well characterized. Reference electrodes are based on placing a known, reference electrolyte between the solution to be measured and the metal electrode. In the case of a Ag/AgCl electrode the known electrolyte is commonly 4 M KCl. If the temperature at the electrode is known, typically the voltages created by this reaction can be calculated. Additionally, a concentrated solution of KCl has a Seebeck coefficient of nearly zero. Reference electrodes therefore offer the advantage of known reactions at the metal electrode and a nearly zero thermopower for the intermediate electrolyte. While reference electrodes reduce the effect of reactions at the metal-solution interface, they introduce voltages created by liquid junction potentials. These are not as well known, and unlike the previous two, cannot be measured.

Liquid junction potentials occur anywhere two solutions of differing ion concentrations meet. As the ions diffuse between the two solutions at different rates, a concentration gradient builds and a voltage develops as a result of the separation of charge. Typically, the voltage caused by one electrode will directly oppose the voltage of its partner. However, if the system is not isothermal, the rates of diffusion at the two electrodes will not be equal. The two liquid junction potentials will therefore no longer directly oppose and cancel each other out. It is impossible to directly measure this effect, but there have been some estimates as to its magnitude. Below is the equation for the potential caused by an ion species in dilute solution:

$$E_j = \frac{-RT}{F} \frac{\sum u\left(C_2 - C_1\right)}{\sum uz\left(C_2 - C_1\right)} \ln \frac{\sum uzC_2}{\sum uzC_1} \tag{1.10}$$

Where R is the ideal gas constant, T is the absolute temperature of the system, F is Faraday's constant, u is the mobility of a specific ion, C_i is the concentration of the ion in solution i, and z is the effective charge per ion [20]. Z is -1 for Chloride, +2 for Calcium ions, etc. In a measurement, the net liquid junction potential is expressed as the sum of the liquid junction potentials at each electrode.

$$E_{jTotal} = E_{j1} - E_{j2} \tag{1.11}$$

Since the properties of the solutions at each electrode are assumed to be the same with the exception of the temperature, equations 1 and 2 can be combined into:

$$E_{jTotal} = A\left(T_{j1} - T_{j2}\right) \tag{1.12}$$

Where A is a coefficient equal to:

$$A = \frac{-R}{F} \frac{\sum u\left(C_2 - C_1\right)}{\sum uz\left(C_2 - C_1\right)} \ln \frac{\sum uxC_2}{\sum uzC_1} \tag{1.13}$$

Estimates of the liquid junction potential range as high as 5 mV at 300 K [21]. Using this as a maximum, the magnitude of *A* can be estimated for 300 K or about the temperature where the thermopower measurements will be taken. If this value for *A* is then used in equation 1.10 with a temperature difference of 1 K, a net liquid junction potential of 15 μV is developed. This is well within the voltage requirement. With the high concentration of ions that is expected in the shark gel, along with very large highly charged macromolecules, the situation could be much different. Additionally, measurements of other polyelectrolytes will be of the charged polymers in colloidal solution. However, a error contribution of approximately 15 μV/K is a good estimate.

A related problem created by imposing a temperature gradient across the measurement setup is unequal rates of reactions at the reference electrode metal/solution interface. As mentioned before, the reference electrode serves to isolate the metal electrode from unwanted chemical species in solution. What remains are well known and characterized reactions between the metal and the reference electrolyte. For the Ag/AgCl reference electrode this reaction is: $Ag_{(aq)}^{+} + Cl^{-}_{(aq)} \rightleftharpoons AgCl_{solid}$. Associated with this reaction is a half cell voltage like that which occurs at one terminal within a battery. Again, in an iso-thermal system these voltages at each electrode would oppose each other and have no effect on the measurement. However, in the non-isothermal system in which the electrodes are at two different temperatures the voltages will have different magnitudes resulting in a net voltage. Under a changing temperature gradient this net voltage will also change appearing very similar to a thermoelectric effect. The metal leads within the reference electrodes were moved as far away from the sample as possible to minimize possible temperature changes. This is shown in figure 7.

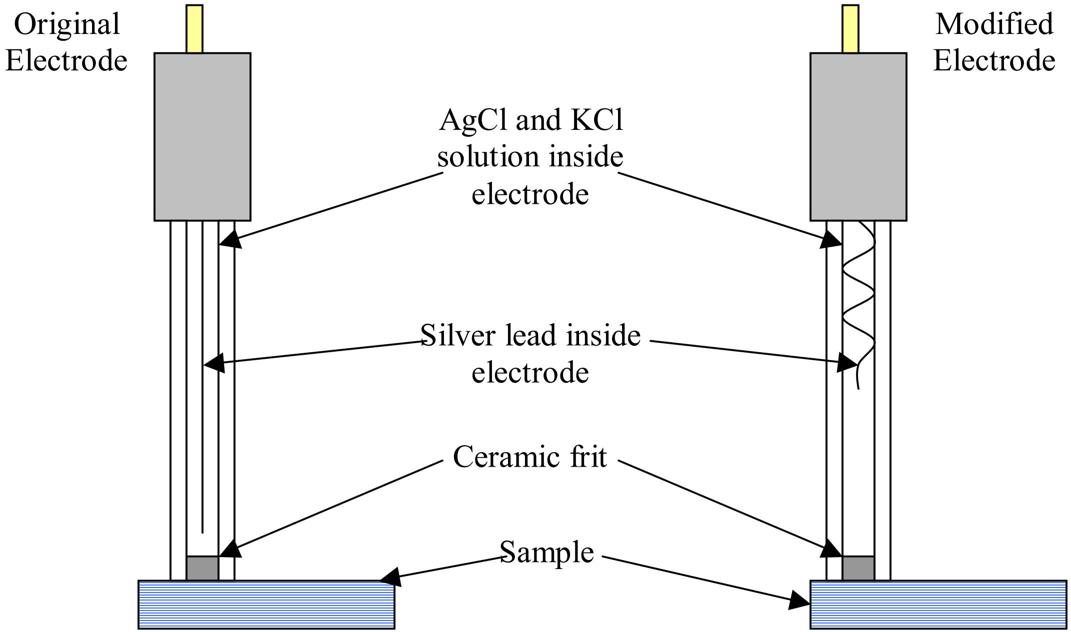


Fig. 7 Schematic of modified electrode. Silver lead inside electrode is coiled up increasing its distance from the sample.

Increasing the distance through which the current must travel will increase the total resistance through the electrode-sample-electrode series but it was found that this increase was not significant. It is likely that the majority of the resistance through the system is localized at the ceramic frits used to separate the reference electrode solution from the sample.

The instrument chosen to measure the voltage across the sample was a Keithley 2182 Nanovoltmeter. The nanovoltmeter provided the necessary accuracy to observe Seebeck coefficients of tens of microvolts per degree Kelvin but was ill suited to deal with the high resistance of the electrochemical system. Pumpout current, an unavoidable small amount of current injected into the system by switching transistors within the nanovoltmeter can cause a significant voltage bias across a high resistance sample. Since the total resistance of the system was never more then 20 k ,giving a voltage bias of only about 6 μV, this could not have caused the large variations in voltages recorded. The voltage difference measured would vary over a range on the order of magnitude of 1 mV with an average period of from several minutes to an hour. Since the length of time required for the system to achieve a steady state value fell within the time span given, little could be done to separate the thermoelectric effects from the errors present. Efforts to minimize the pumpout current were mildly successful in improving the quality of the data but not sufficient.

In response, an alternative measurement setup in which the nanovoltmeter would not be directly measuring the voltage across the sample was implemented. A reference resistor of comparable or smaller resistance was placed in parallel to the sample and electrodes. A current of known magnitude is then briefly passed through the resistor-sample network and the voltage across the reference resistor is measured. The convention of Tyrrell and Agar is used in which the hot electrode is considered positive [8, 22]. An electrical schematic of the set up is provided in figure 8.

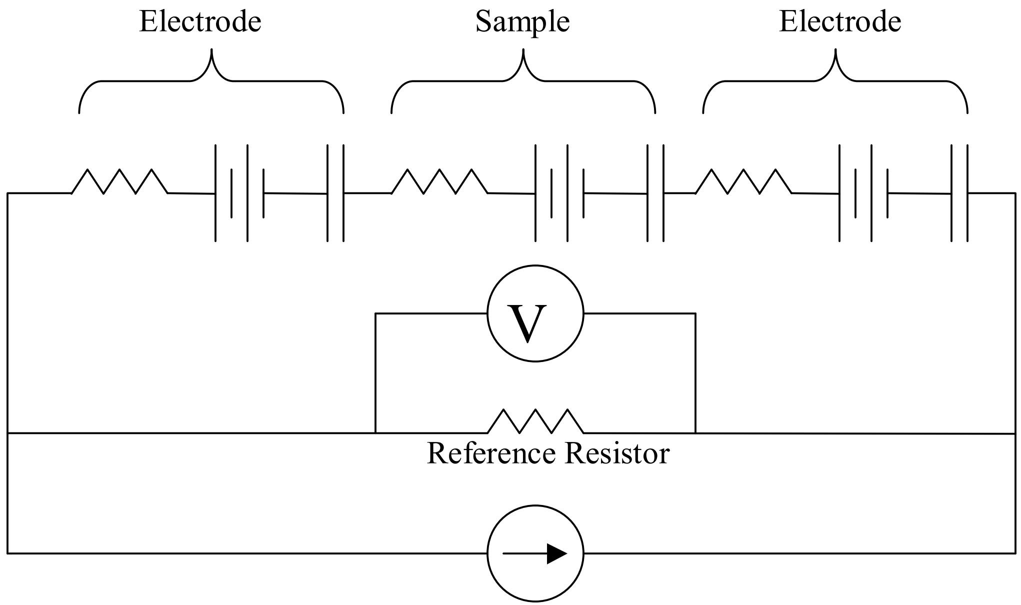


Fig. 8 Electrical model of voltage measurement setup. Each cell, the sample and the electrodes, as a corresponding resistance, voltage it produces, and capacitance caused by the separation and then relaxation of charge in

At this point several assumptions are made to simplify the circuit. The first assumption is that neither of the electrodes produces a significant voltage. Since both are filled with 4 M KCl, which has a negligible Seebeck coefficient, this is a reasonable assumption. A second assumption made is that the total capacitance of the system can be neglected. The capacitance of the electrode-sample-electrode series was empirically found to be about 1000 μF while the resistance of the series was about 10 k . This gives a time constant for the system of about 10 seconds. Current is passed through the system for about a quarter of a second giving the resistance-capacitor series little time to charge. Although a fixed current is used, the reference resistor and current source act as a norton equivalent source producing a voltage across the sample and electrodes. Additionally, the current is chosen to produce a voltage across the reference resistor exactly equal in magnitude and sign as the estimated voltage produced by the gel. In this way, all of the current will pass through the reference resistor with a minimum passing through the sample branch of the circuit. A second current is passed through the system exactly one half the magnitude of the first for reasons discussed later. This obviously does not produce a voltage across the gel directly opposing the thermoelectric voltage. In this case, the charging voltage is then roughly half of the thermoelectric voltage of the sample. Given the time constant of the gel, the short time period over which it is charged, and the voltage which it is charged with, an estimate can be made of the voltage across the capacitor at the end of the measurement. This voltage is approximately 2% of the thermoelectric voltage of the sample and thus negligible. Removing these components and simplifying the circuit results in the following model of the system:

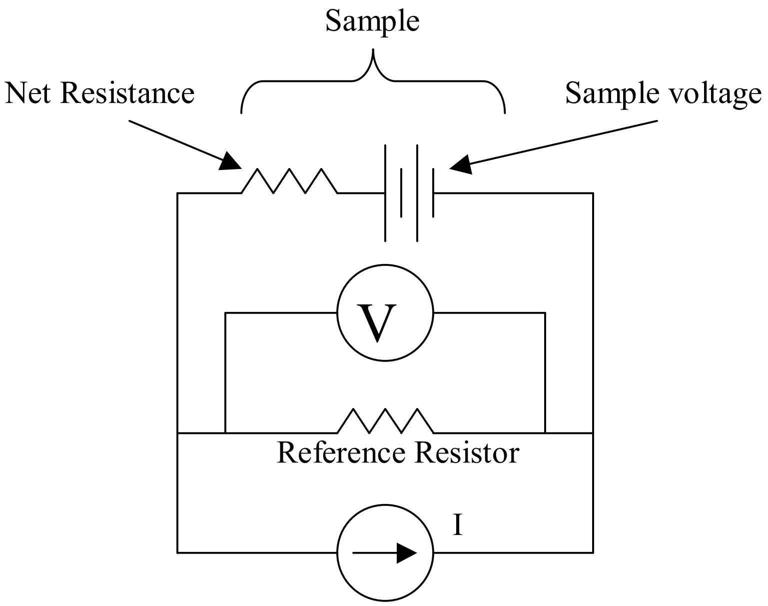


Fig. 9 Simplified model of voltage measurement setup. There are two unknowns, net resistance and sample voltage. The rest of the parameters of

The circuit has two unknown quantities, the net resistance of the sample-electrode series and the voltage produced by the sample. Using mesh current analysis the following equation relating the voltage measured, source current, reference resistor, net resistance, and sample voltage can be found:

$$0 = V_{meas} + V_{sample} + R_{net}\left(I - \frac{V_{meas}}{R_{ref}} \right) \tag{1.14}$$

Where V_{meas} is the voltage measured across the reference resistor, V_{sample} is the voltage produced by the sample, R_{net} is the net resistance of the sample and electrodes, I is the measured source current, and R_{ref} is the reference resistor. If a different current, I', is used a second equation can be obtained:

$$0 = V'_{meas} + V_{sample} + R_{net}\left(I' - \frac{V'_{meas}}{R_{ref}} \right) \tag{1.15}$$

Using these two equations and solving for V_{sample} leads to:

$$V_{sample} = \frac{IV'_{meas} - I'V_{meas}}{I' - I + \frac{V_{meas}}{R_{ref}} - \frac{V'_{meas}}{R_{ref}}} \tag{1.16}$$

Using a 10 k resistor with a Keithley 2400 Sourcemeter which is capable of sourcing currents down to 50 pA and the Keithley 2182 Nanovoltmeter to sense V_{meas} the theoretical minimum V_{sample} is about 100 nV. This is well within error added by the liquid junction potentials. The process of communicating with the nanovoltmeter and source meter for the voltage measurement consumes a significant amount of the 1.5 s cycle time.

To prevent the gradual buildup of charge in the sample-electrode series, the system is forcibly discharged after every current sourcing. Using the calculated voltage produced by the sample an estimate is made of the voltage seen across the capacitors in figure 8. A current is then sourced to produce a voltage equal in magnitude but opposite in sign to the voltage produced by the initial measurement current. If applied for the same amount of time this effectively returns the voltage across the capacitor to zero. This added significantly to the measurement cycle time but resulted in improvements in stability.

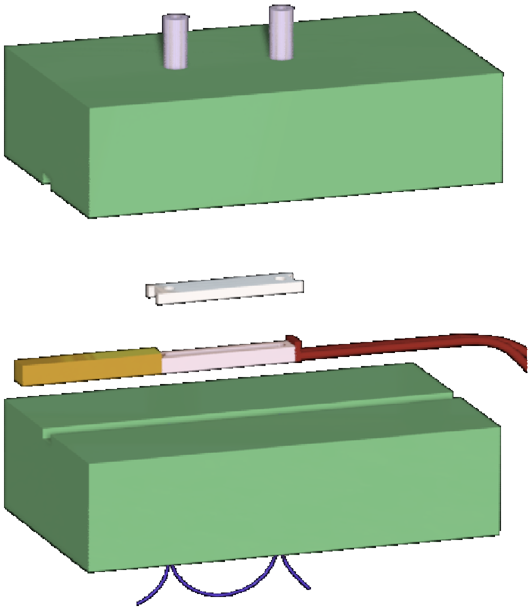
Heating Cycle:

Each measurement consists of a voltage reading at one temperature difference, changing the power supplied to the heater, allowing the temperature to reach steady state, and recording the new voltage across the sample. The time it takes for the temperature to reach an acceptable steady state value was found empirically to be about 25 minutes. The energy is supplied to the system using a resistor placed at one end of the sample container. This resistor is powered using a Lakeshore 331 Temperature Controller which is controlled through LabView. The power output is chosen such as to produce a temperature difference across the sample of about 1 K. In practice this temperature difference is greater then 1 K so that a change in temperature difference between the high and low power output of 1 K can be achieved. Prior to cycling the heater, the measurement system is run at the low power output for a period of about an hour. This allows the system to come to equilibrium, electrically and thermally, prior to measurements.

The Device:

An exploded view of the device design is shown in figure 10.

Fig. 10 Exploded view of final design. Sample container is shown as white, heat sink as orange, and heater as red. Note the plastic tubes that pass through the top half of foam to provide access for electrodes to the gel. The thermopile used to measure temperature difference



The device consists of a hollow plastic container shown in white bonded on one end to a copper heat sink shown in orange and on the other to a heater shown as red. The whole assembly is encased in foam to both minimize and stabilize heat loss to the surroundings. The Ag/AgCl reference electrodes will be guided down to the sample container by the plastic tubes shown in the top half of the green foam. Two holes in the top of the sample container cap allow access by the electrodes to the gel. The temperature difference is measured using a thermopile shown in blue at the bottom of the figure. The thermocouple wires are run up through plastic tubes in the bottom half of the green foam into holes cut in the bottom of the sample container. More drawings, photographs, and dimensions can be found in appendix A.

Procedure:

Sample Preparation:

Shark Gel:

The gel samples were obtained from our collaborator Dr. Brown of the University of San Francisco. The samples were shipped in a dehydrated state in order to prevent contamination from biological growth. To re-hydrate the shark gel a sample of the dried material is weighed out corresponding to the percent solid mass of a 80 μL hydrated sample. Then 80 μL of distilled water is added to the dried shark gel and it is ultrasonicated for at least one day to homogenize the sample.

Polyelectrolyte solutions:

Reference solutions of 0.912 M NaCl and 4.00 M KCl were prepared and served as the base solutions to which the polyelectrolyts were added. The polyelectrolytes used were Amberlite® IR-120 Plus-Na and IRA-402-Cl ion exchange resins. Both resins come in the form of beads ranging in diameter from 0.5 mm to 1 mm. Since the effect of the charged macromolecules on the bulk solution is the interest of the study, the small amount of surface area presented by the beads proved to be a problem. Consequently, the beads were dried in a vacuum and then crushed using a mortar and pestle to a fine powder to increase the effective surface area. Varying amounts of this powder were then weighted using an Adventurer microbalance from Ohaus. The polyelectrolyte powder was then placed in the sample container and one of the reference salt solutions was added in sufficient quantities with a 10 microliter syringe to fill the container. The amount of salt solution necessary was recorded.

Heating Cycle:

Once the sample is in place and the measusurement system is running properly the heating cycle is started. For a period of one hour the system is heated at low power, typically 5 % of the medium heater power output for the Lakeshore 331 Temperature controller. This allows the system to reach equilibrium before the measurements start. After one hour the system is heated at high power, typically 90% of the medium heater output, for a period of 30 minutes. A 30 minute time period is enough for the temperature to reach a steady state value and provides sufficient time at this temperature difference to collect data. At the end of this time period the system is brought back down to low power for an additional 30 minutes. This cycle continues until the measurements have ceased.

Data Analysis:

Measurements for both the voltage difference and the temperature difference across the sample are recorded for every measurement cycle. A representative plot of this data is shown in figure 11.

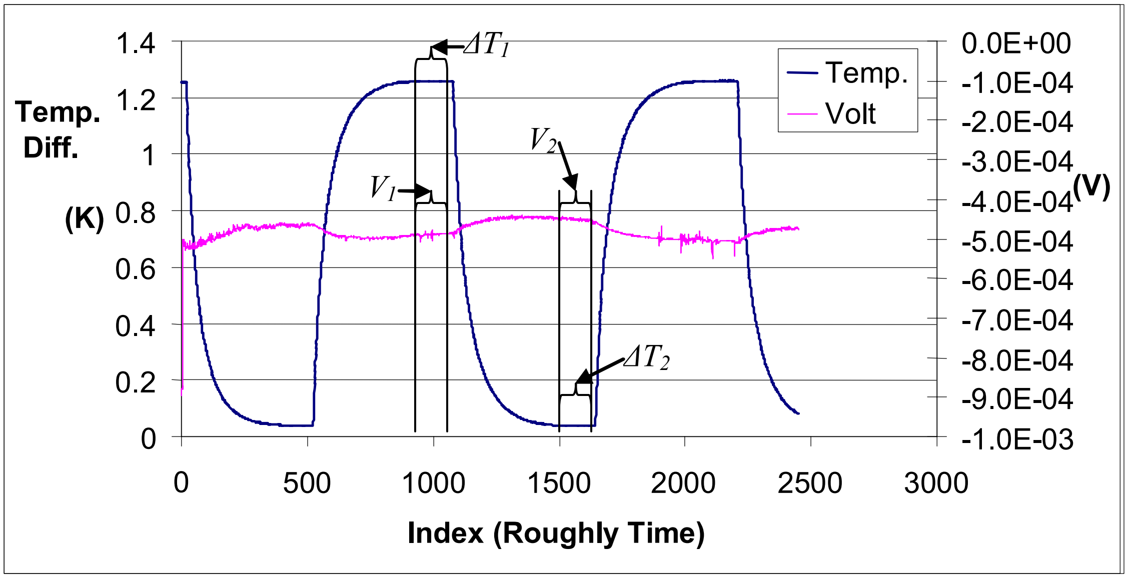


Fig. 11 Plot of data recorded over several heating cycles. Temperature difference is in blue and voltage difference is in pink. Data is plotted vs. its index.

The temperature difference across the sample is plotted in blue while the voltage difference across the sample is plotted in pink. As can be seen, the temperature difference cycles between a high and low value corresponding to the high and low power supplied to the heater. At the end of each heating cycle there is a period of time for which the temperature difference is relatively constant. The voltage and the temperature are both averaged over this time period. The thermopower is then found through the following equation:

$$S = \frac{V_2 - V_1}{\Delta T_2 - \Delta T_1} \tag{1.17}$$

Where S is the Seebeck coefficient, V_1 and T_1 are the averages of the voltage and temperature measurements during the first steady state time period, and V_2 and T_2 are the same during the following steady state time period. The period over which each of these values is averaged is labeled in figure 11. Each change in temperature difference can thus yield a value for the Seebeck coefficient of the sample.

Data as clean as that shown in figure 11 was not common. Of the data sets taken only about half had usable data and it was rare for more then half of the temperature difference changes within a data set to yield useful data. The criterion used to judge the quality of the data was based on two tests: the voltage must be monotonic over one period of heat change, and if the voltage is drifting the change must be a closely linear and there must exist a region of linear voltage change during the previous period of steady state temperature difference. The region of linear voltage change is used to find the rate of change of voltage with time which is subtracted from the heating cycle following it. For example, figure

12 demonstrates data which while not ideal is acceptable while figure 13 shows data that does not meet the acceptable criterion.

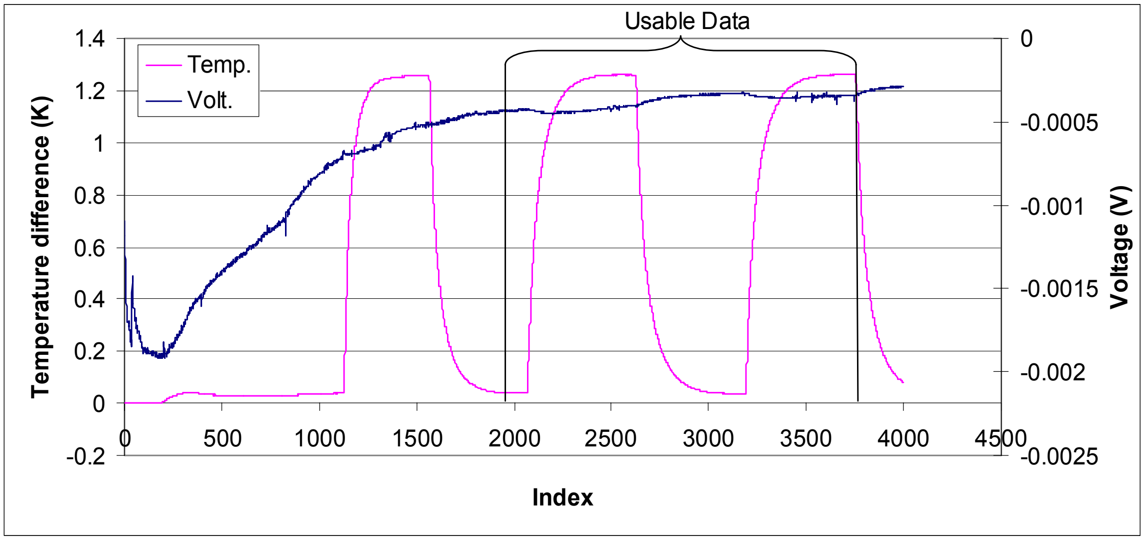


Fig. 12 Non-ideal but usable data. Note how voltage is increasing with time through the usable section but in a linear fashion. Prior to the usable section lies data that is changing but not linearly and so is unacceptable.

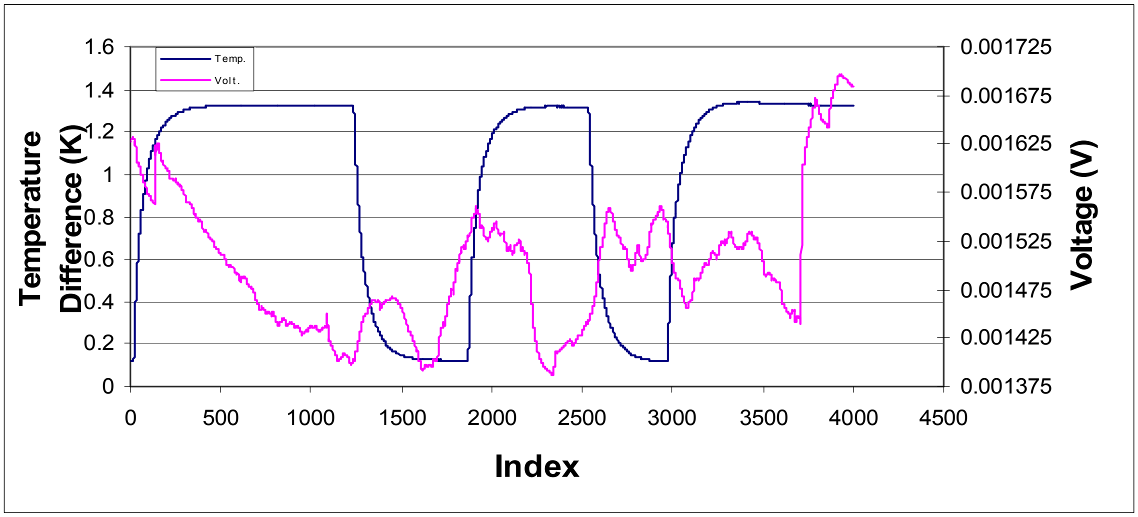


Fig. 13 Unusable data. Note how the voltage data is not monotonic over a period of temperature change.

Results:

Validation of Experimental Setup:

Using data on the heats of transfer for sodium chloride as a function of molality predictions can be made as to the approximate Seebeck coefficient measured at each concentration. This data, from figure 5, is analyzed using equation (1.5) and given in table 1:

Seebeck coefficient for NaCl at 32°C

Molality (mol/kg)	Seebeck (μV/K)
1.02	80
1.55	100
2.09	120
3.2	140
4.37	180
5.59	200

Seebeck Coefficient for NaCl at 37 °C

Molality (mol/kg)	Seebeck (μV/K)
1.01	140
1.54	140
2.07	150
3.18	180
4.23	200
-	-

Table 1. Seebeck coefficients for NaCl at 32°C and 37°C. Note that for a given concentration a 5 degree change in temperature can nearly double the Seebeck coefficient. There is some uncertainty in the second position. Data from Tyrrell's

These Seebeck coefficients provide a guideline for which to test the experimental setup. Unfortunately, the experimental setup as designed can not achieve mean temperatures of 32 °C so some inference is required. Also, equation (1.5) is based upon many assumptions that no longer apply such as infinitely dilute solutions. Regardless, at present this is the best data with which to compare results too. Included in table 2 is data collected on several different concentrations of NaCl.

Seebeck coefficient for solutions of NaCl at approximately 24°C

Molality (mol/kg)	Seebeck (μV/K)
0.91	27 ± 16
2.00	-26 ± 20
4.00	-26 ± 10

Table 2. Measured Seebeck coefficient for NaCl solutions.

For increasing concentration of NaCl in aqueous solution the Seebeck coefficient increases in the negative direction as would be expected. It should be noted that it is not clear from the sources used if equation (1.5) is applicable to the data obtained on heats of transfer for salt solutions at different concentrations. The equation is based upon assumptions not applicable to concentrated solutions. It is likely that the heats of transfer given are obtained from measurements of the Soret diffusion coefficient for which the transference numbers of the ion species play no part. It can not be ruled out that while the heats of transfer increase with increasing concentration so do the Hittorf transference numbers [eq. (1.5)]. It is quite possible that the transference number for the negative ion species to increase relative to the positive ions and flip the sign of the Seebeck coefficient irrespective of changes occurring in the heats of transfer.

Polyelectrolyte solutions in 0.914 M NaCl salt solution:

The purpose of measuring the Seebeck coefficient of polyelectrolyte solutions at various concentrations is to attempt to narrow down the possible mechanisms behind the relatively large thermopower of shark gel. Since polystyrenesulfonate is particularly similar to the sulfated glycoprotein found in the shark gel in terms of functional groups and structure, it served as a good substitute in these experiments. A plot of the measured data is presented in figure 14. All data shown in the following graphs is also tabulated in appendix B.

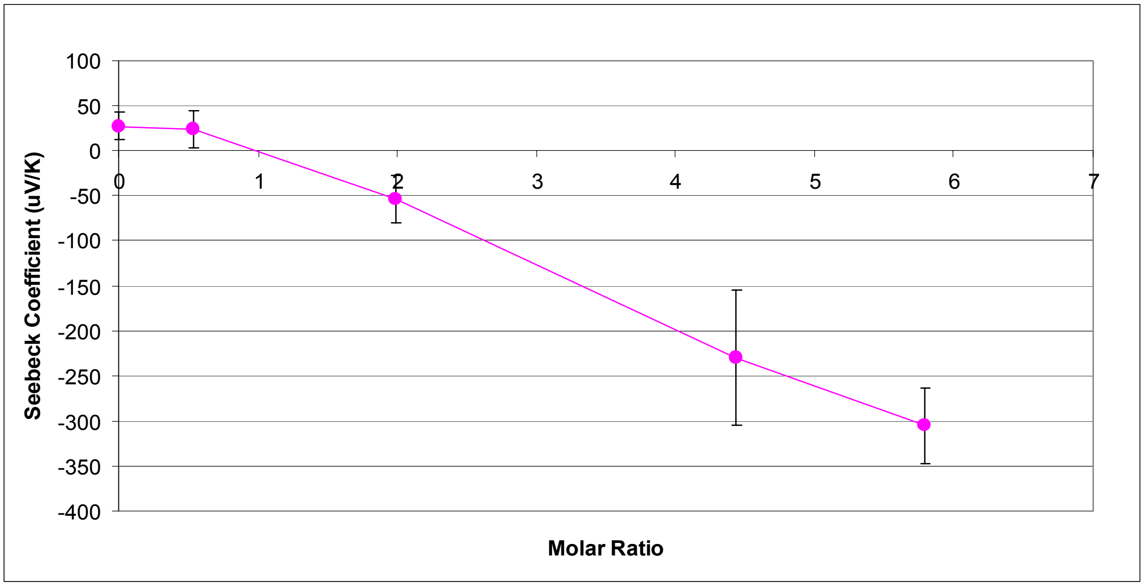


Fig. 14 Plot of Seebeck coefficient as a function of the molar ratio of salt to functional groups. Data is taken from varying amounts of polystyrenesulfonate added to 0.91 M

The data is plotted with Seebeck coefficient as a function of the molar ratio of functional groups in the polyelectrolyte to the number of moles of salt in the solution. Since the concentration of the salt solution was the same for all trials, this is equivalent to plotting as a function of the base molar concentration of the polyelelctrolyte. However, since the amount of accessible functional sites is unknown, either scale is sufficient.

The Seebeck coefficient for the solutions starts at 27 ± 16 μV/K with no polyelectrolyte added and ranges to nearly -300 ± 40 μV/K. As the concentration of polyelelctrolyte increases the thermopower first decreases, becomes zero, and then continues increasing in a linear fashion but with the opposite polarity as the simple NaCl salt solution. If the increased charge associated with the polystyrenesulfonate along with the sodium counter-ions added to the solution acted in the same manner as simply increasing the concentration of salt then an increase in Seebeck coefficient away from zero would be expected. However, Seebeck coefficients recorded do not start high enough above zero to be confident that this is occuring.

Since in a dried state the polyelectrolyte must be neutral, the functional groups in polystyrenesulphonate are ironically bonded to sodium ions. When the polystyrenesulfonate is added to the solution the ionic bond disassociates and the sodium ions diffuse throughout. This keeps the total charge of the solution neutral and leads to an increase in the concentration of sodium in the solution. The increase in sodium ions can possibly have two effects: the first is to increase the magnitude of the liquid junction potential; the second is to increase the Seebeck coefficient by greatly outnumbering the chlorine ions in solution. For the Seebeck coefficient, this will increase the transference number of the sodium relative to the chlorine species and magnifying the sodium ions effect in equation (1.5). For the liquid junction potential, as given in equation (1.12), an increase in concentration of sodium ions in the sample will increase the magnitude of the coefficient but not change its sign. That is solely dependent upon the charge of the ionic species. In both cases, the result is a positive increase in the thermopower of the solution. This effectively rules out either of these mechanisms.

Other possible mechanisms remaining include a thermopower contribution of the charged colloidal polyelectrolyte particles, their influence on the liquid junction potential, and their selective hindrance of the motion of ions with opposite charge. As mentioned before, the condensation of counter-ions around the macroions in solution would appear to mitigate the first two possibilities and bolster the third.

The degree to which this will occur is uncertain and so must be further investigated.

A second polyelectrolyte, polystyrene with quaternary ammonium functional groups, was also examined with the 0.91 M NaCl base solution. The behavior of this polyelectrolyte was unexpected. Instead of monotonically increasing with increasing molar ratio, it appears to decrease in much the same manner as when the negatively charged polystyrenesulfonate is added to the solution. This data is shown in figure 15 plotted alongside the results for polystyrenesulfonate in NaCl.

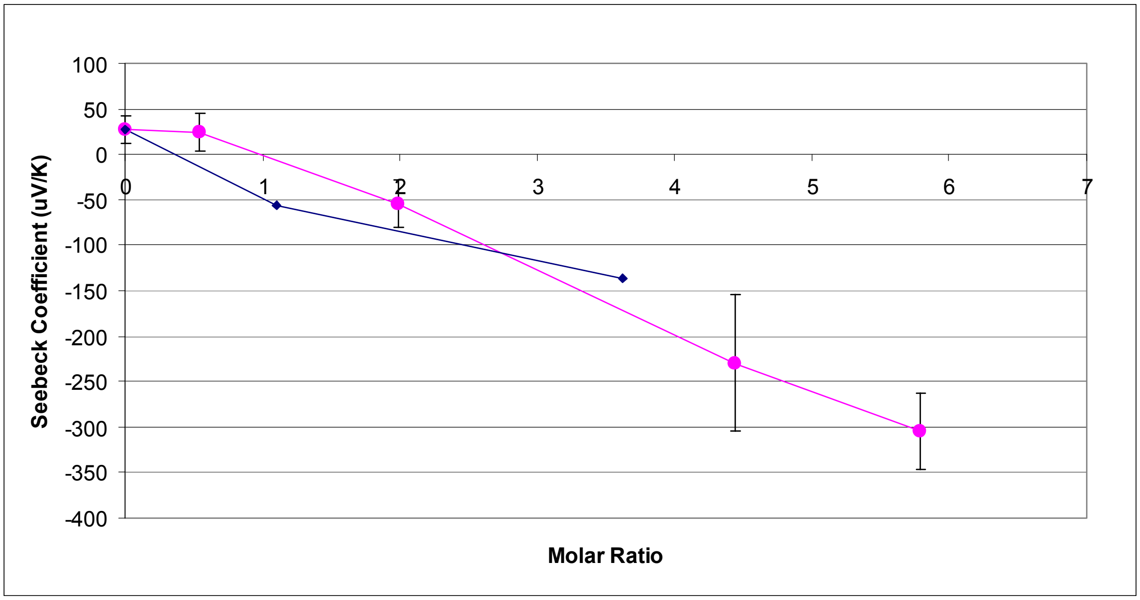


Fig. 15 Plot of 0.91 M NaCl and increasing concentrations of polystyrenesulfonate (pink) and polystyrene with ammonium groups (blue). Both solutions trend downward with increasing polyelectrolyte concentration.

This data suggests that the mechanism increasing the Seebeck coefficient with increasing concentration of polyelectrolyte is independent polyelectrolyte charge. Of the possibilities discussed in the section titled *Thermopower of Polyelectrolytes*, the only mechanism independent of the charge of the polyelectrolyte involves manipulating the properties of the solvent surrounding the ion thus changing the effective heat of transfer of the ion pair. In other words, the polyelectrolyte increases the degree to which water molecules are shared between hydration shells. Since it is more likely that a positive and negative ion will be near each other then the converse, it is probable that moving between hydration shells of different polarity involves a greater difference in energy then moving to and from the neutral bulk solution.

Polyelectrolytes in 4.0 M KCl salt solution:

Further experiments were performed using a base salt solution of 4.0 M KCl. The purpose of these experiments was to investigate the influence of liquid junction potentials on the measurements. Results for polystyrenesulfonate are shown in figure 16.

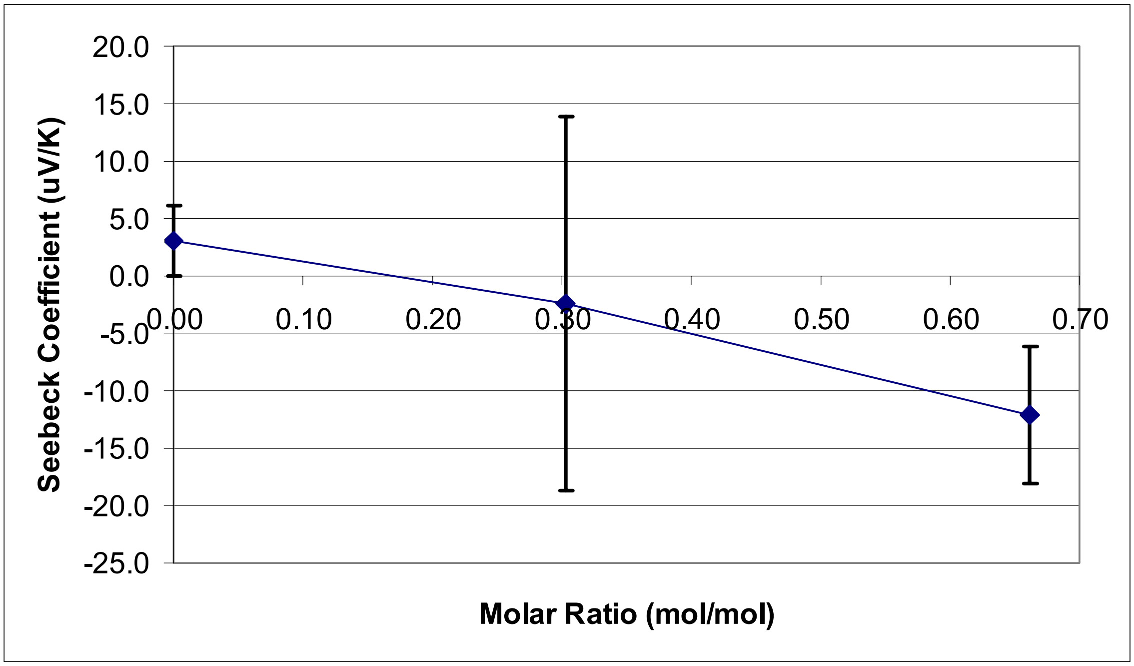


Fig. 16 Polystyrenesulfonate in 4.0 M KCl solution. The Seebeck coefficient at zero added polyelectrolyte is much smaller then for NaCl and the trend is downward with increasing amounts of polyelectrolyte.

The purpose of this measurement was to test a base salt solution with the same ion composition and concentration as the reference solutions within the electrodes. Since the solutions on both sides of the liquid junction are nearly identical, the error producing liquid junction potentials should be at a minimum. Additionally, since the Seebeck Coefficient for this solution is expected to be nearly zero, other error producing reactions such as different temperatures at the silver electrode-reference solution interface will show up.

As can be seen in figure 16, the Seebeck coefficient for 4.0 M KCl is nearly zero as expected. The magnitude of the Seebeck coefficient measured can not be determined due to the large errors involved in this measurement and lack of sufficient data, but it is intriguing that the average should fall about where the real, though ideal, Seebeck coefficient exists. Since no change in voltage with temperature could be detected, side effect voltages can be ruled out.

Since the base salt solution had a molarity of 4.0 it was difficult to obtain large molar ratios given the fixed size of the container and the limited amount of polyelectrolyte it is capable of containing. Despite this fact, a clear downward trend can be seen similar to that found with the sodium chloride solutions. Although, over the molar ratio range shown in figure 14, very little change occurs in the sodium chloride solution. This can be attributed to the comparatively greater stability and ease of measurement that resulted from using a base salt solution of similar ion content to that of the electrodes. It is possible that experimental errors obscured this decent in the sodium chloride solutions for small molar ratios.

Presented in figure 17 is a plot of data using polystyrene with quaternary ammonium functional groups as the polyelectrolyte added to the base 4.0 M KCl solution. The ammonium groups give the polyelectrolyte a positive charge when disassociated in water from its counter ion.

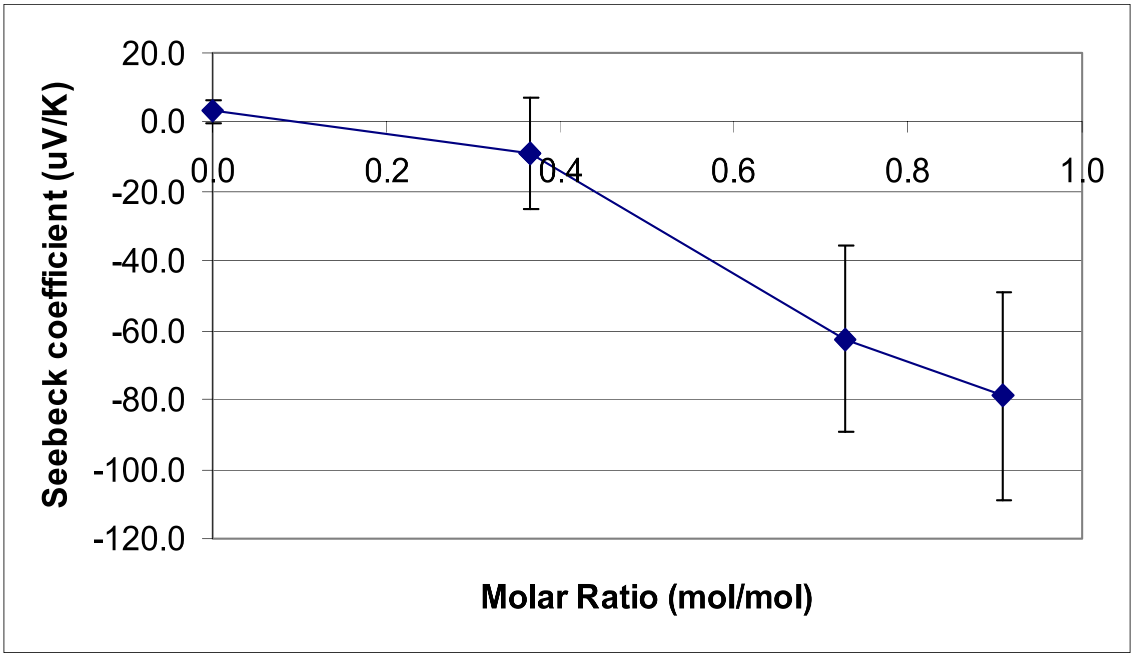


Fig. 17 Polystyrene with quaternary ammonium functional groups.

Contrary to expectations, the Seebeck coefficient trends downward with increasing molar ratio. Since the polyelectrolyte added is the opposite of the polystyrenesulfonate in terms of charge it might be expected that the Seebeck coefficient would behave in the opposite manner, increasing with increasing polyelectrolyte concentration. This behavior was also noticed in solutions of polystyrene with ammonium functional groups and a base salt solution of NaCl. It is believe this also occurs as a result of the increased amount of charge brought into the system by the polyelectrolyte. The degree to which the water molecules are now shared between hydration shells is increased. Since at higher concentrations the tendency is to form ion pairs, a negative and positive ion closely orbiting each other, it is likely that the water molecules are shared between oppositely charged ions. The energy corresponding to a shift from one hydration shell to another in such a situation could be greater then that required to shift from a neutral bulk solution to the hydration shell. As a result, there is a greater tendency to preferentially select hot water molecules to enter the hydration shell then cold ones (equation 1.2). This would tend to increase the Seebeck coefficient of the ion.

Shark Gel:

Seebeck coefficients of the shark gel proved more difficult to obtain then the synthetic polyelectrolyte samples previously measured. During the measurement, while the voltage across the gel appeared to be strongly influenced by temperature, the noise in the system made interpretation of the data difficult. Much of this noise is attributed to the non-homogeneous ion and gel concentration in the re-hydrated shark gel. After treatment in the ultrasonic bath the quality of the data improved to where a Seebeck coefficient of -60 ± 30 μV/K was observed. The uncertainty in this value is high due to the small number of measurements obtained.

When compared, it can be seen that the presented measured Seebeck coefficient for shark gel is nearly a fifth of that obtained by previous researchers. As noted before, the Seebeck coefficient for salt solutions with and without polyelectrolytes is highly dependent upon the concentration. It is likely that the re-hydration process did not perfectly preserve the absolute and relative concentrations of the shark gel glycoprotein and salt species. This could result in a significantly different result. However, as expected from the results obtained on ion exchange gel in salt solutions, the gel has a negative Seebeck coefficient.

Summary of Results:

The experimental setup, while not rigorously validated, appears to produce consistent results of correct magnitude and behavior for ionic solutions. Since no theory exists which can accurately predict the thermopower of complex solutions such as polyelectrolytes, analysis is restricted to general trends for which the experimental setup is adequate.

Measurements involving a solution of potassium chloride of identical concentration to that in the electrodes were performed to investigate other possible forms of systematic error. Since the solutions on both sides of the frits used in the electrodes were isotonic the liquid junction potentials usually involved in such a measurement were eliminated. The potassium chloride solution itself is known to have minimal thermopower, a fact born out by the measurements performed. By removing these sources of voltage it is possible to sense the contribution of error producing signals like non-isothermal conditions at the surfaces of the two electrodes used. The lack of any measured thermopower for the potassium chloride solution adds confidence in the abilities of the experimental setup.

Based on trials involving two different polyelectrolytes of opposite polarity, polystyrenesulfonate and polystyrene with ammonium functional groups, several different possible mechanisms behind the high thermopower of the shark gel were able to be eliminated. Both types of polyelectrolytes, which have opposite charge when in solution, behaved the same under increasing molar ratios of functional groups to moles of salt in solution. Contributions from liquid junction potentials, as well as thermopower contributions from the polyelectrolytes themselves, could be ruled out due to their dependence on the polarity of the ions added to the solution. Likewise, the mechanism of the macroions selectively impeding the path of the counter-ions in solution will show different behavior using the oppositely charged polyelectrolytes. Each will selectively impede the progress of ions of opposite charge allowing ions of similar charge to be more fully expressed. Thus, a negatively charged polyelectrolyte will lead to a more negative Seebeck coefficient while a positively charged polyelectrolyte will give a more positive Seebeck coefficient. This was not observed so it too can be dismissed as a possible mechanism for increasing the thermopower of the shark gel.

From the results obtained several general conjectures can be made regarding the nature of the Seebeck effect in shark gel and related polyelectrolytes.   The similar behavior of a wide variety of different solutions and mixtures over a range of concentrations suggests that that the increased Seebeck effect is dominated by a single mechanism common to all the solutions. The only mechanism that acts independent of the charge of the added polyelectrolyte operates through changing the structure and free energy of the bulk solvent. Simply adding more ions to solution decreases the number of solvent molecules per hydration shell requiring some overlap. The overlapping potential energy wells from the electric fields of the ions as well as the changed structure of the water will alter the difference in free energy as the solvent molecules move from one hydration shell to another.

The increase in Seebeck effect is likely a result of a large change in free energy occurring between the hydration shells of positive and negative ions in solution. Regardless of the reason, it is apparent that the sulfated glycoprotein found in the shark gel is having a similar affect upon the base sea water solution.

The shark gel is likely much more efficient at this process since it has a higher charge density and is not cross-linked. As a result, the shark gel has more charged functional groups that are more accessible to the bulk solution then the polystyrene. Measurements of the shark gel itself were attempted unsuccessfully many times. The final results obtained, while sparse, gave an average Seebeck coefficient of -60 ± 30 μV/K. This is significantly smaller then results previously published on the material. Likely reasons for this discrepancy include errors and difficulties in re-hydrating the gel. Previous data as well as results obtained in this study demonstrate a significant dependence between the Seebeck coefficient of ionic solutions and ionic concentration. A small change in concentration or relative concentration of ions in solution could have magnified effects on the resulting Seebeck coefficient.

Future work:

Before further progress can be made, the capabilities of the experimental setup need to be quantitatively determined. No published results have been found as of yet regarding the Seebeck coefficient of salt solutions of sufficient concentration to allow them to be tested with the current setup. While an exhaustive literature search was undertaken to find such a value, much of the research in this field was completed prior to the middle 1980's, meaning many of the journal articles pertaining to this subject are not listed in an online database. It is quite possible that many papers were overlooked. It is of note that J.N. Agar, who in 1963 wrote the seminal chapter on the theory of thermoelectricity in ionic solutions, also attempted polyelectrolyte solutions in 1975 [8, 17]. In the latter paper the theory is extended to discuss the heats of transport of polyelectrolytes but state nothing of the thermoelectric properties of such a system. Further articles in this line of study were implied but none were found.

The difficulties and disappointing results associated with the measured Seebeck coefficients obtained from re-hydrated shark gel warrant considering obtaining unprocessed shark gel. However, given the difficulties in obtaining samples of the shark gel it is unlikely that this will occur. If this is the case, different methods of re-hydrating the gel and or experiments varying the concentration of water in the rehydrated gel need to be investigated before further measurements can take place.

Additional measurements of salt solutions with neutral crushed polystyrene should also be undertaken for completeness.

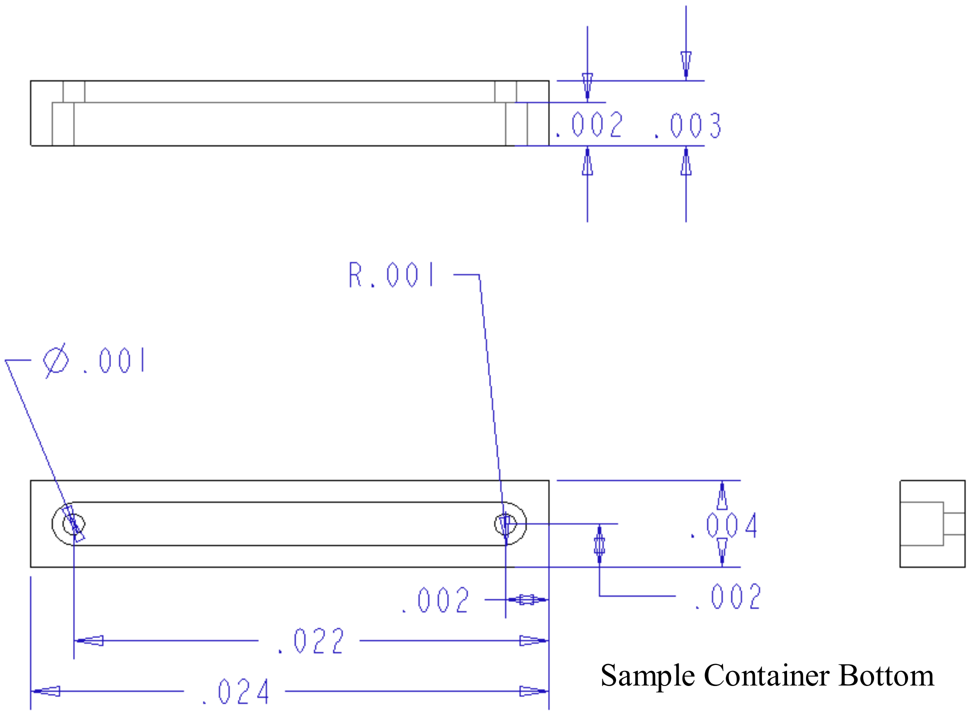
Further effort can be directed towards other materials with a mind towards practical sensors or other technologies. Promising areas include functionalized zeolites. Zeolytes are ceramic like materials with a regularly repeating internal structure. In some cases this structure has been manipulated to create long nanochannels that repeat within the crystal-like structure. The inside of these channels can then be functionalized by attaching tailored functional groups to the walls of the channels. The enormous surface area and small dimensions offered by such materials can possibly mimic the structure and function of shark gel. Since the zeolites are a solid, the charge density and concentration can be precisely and uniformly controlled which may not be the case with macro-ions in solution. This would give stable and reproducible behavior.

Since the time period during which much of the theory of this subject was developed many advances in technology have occurred. A focus on a physical understanding of thermoelectric phenomena was stressed in this paper because it is believed that current abilities in nanotechnology can capitalize upon this mindset. By describing the mechanisms in terms of changes in state, it becomes possible to think of other ways in which a localized change in state of a fluid can be achieved. Nanochannels, for example, have been shown to order the fluids within them in much the same way as the solvent is ordered around the ion. If a temperature gradient is placed across the length of the channel, a flow of fluid, like that around the ion, may develop. The resulting pressure gradient can then be used to perform useful work. Likewise, the system could be forced in reverse to serve as a refrigeration device.

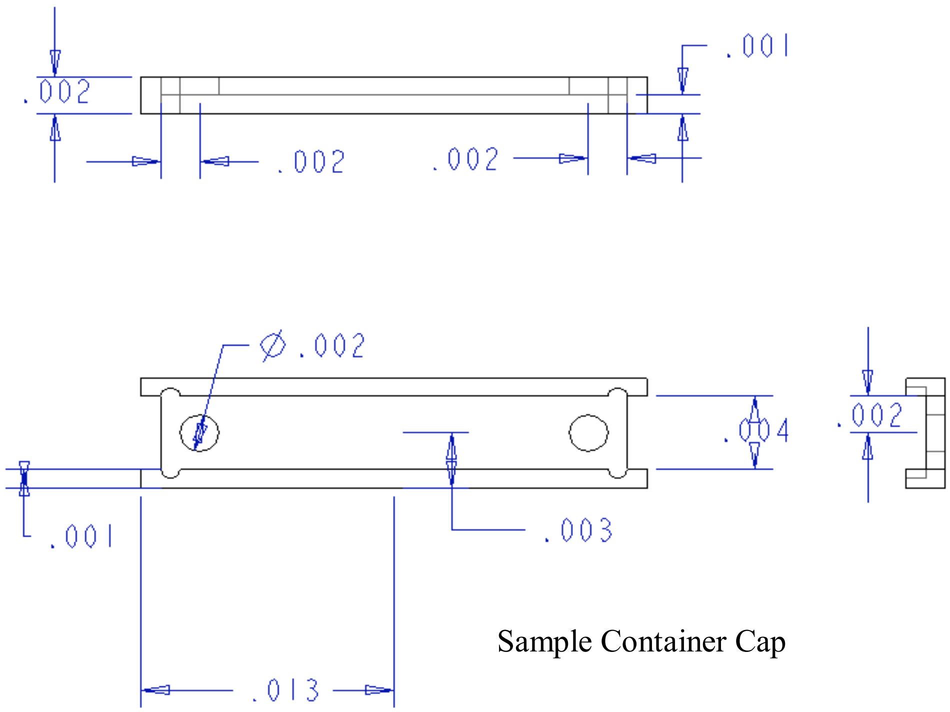
A similar yet more easily measured phenomenon would be to incorporate this mechanism into a nano-scale motor that utilizes the flow of fluid to propel itself through the solution. This motor, though possibly nanometers in dimension, could be tagged and its movements tracked. Since it may be possible to have the device move up a thermal gradient, merely watching it do so would be confirmation of this theory. A possible device could include an uncapped carbon nanotube tagged with a florescent dye. The physical characteristics of the inner surface as well as the diameter of the nanotube are important variables in determining the properties of the water within and as a result the energy difference between it and the bulk solution.

Appendix A

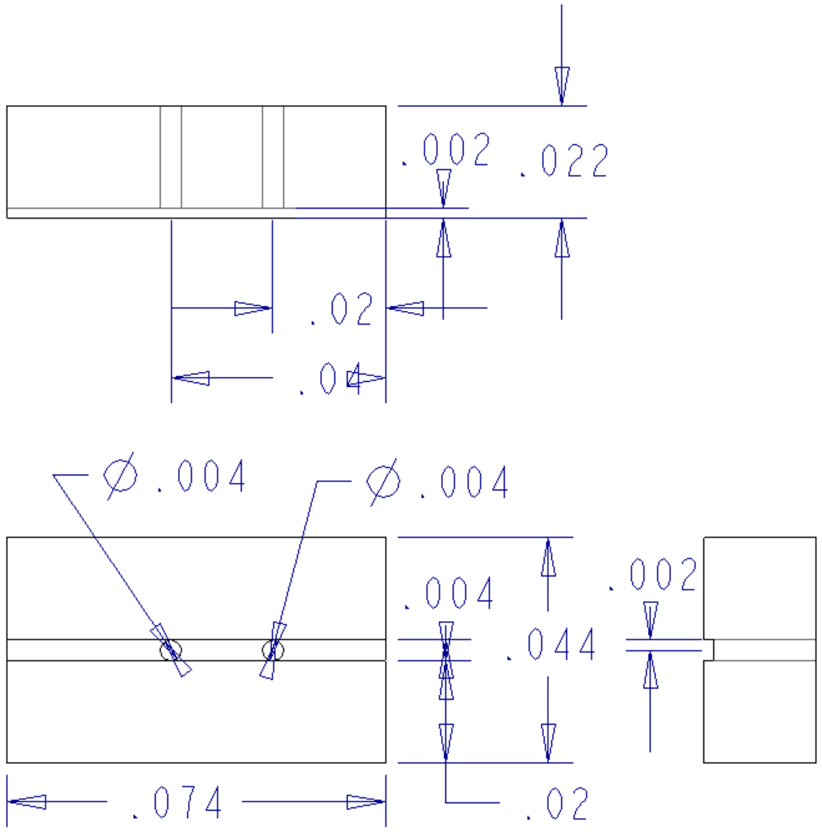
Dimensions of Parts



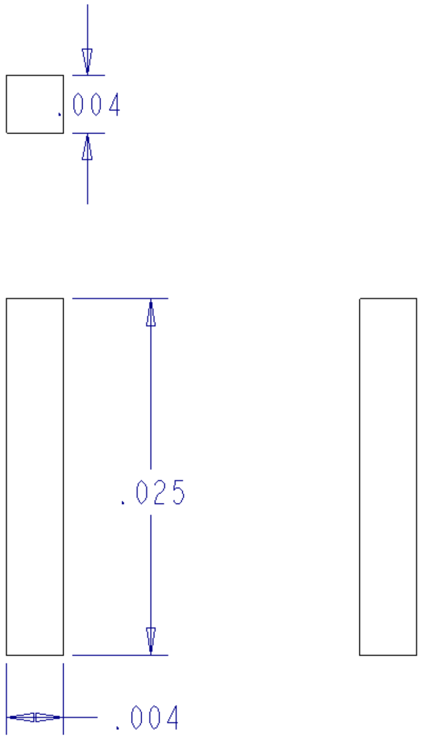
Sample Container Bottom



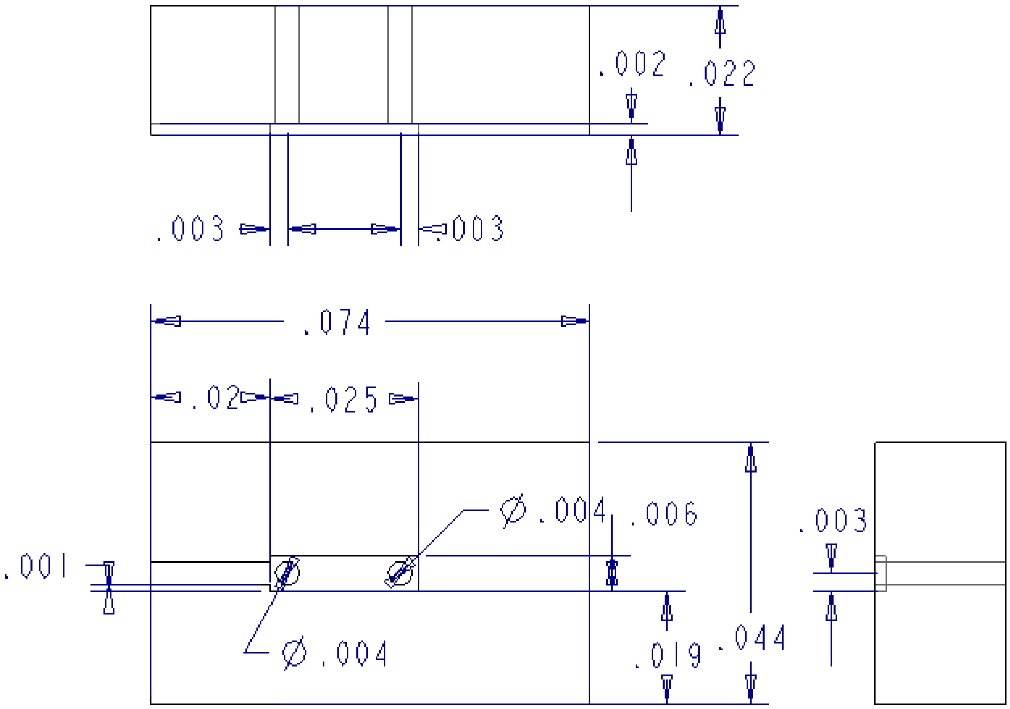
Sample Container Cap



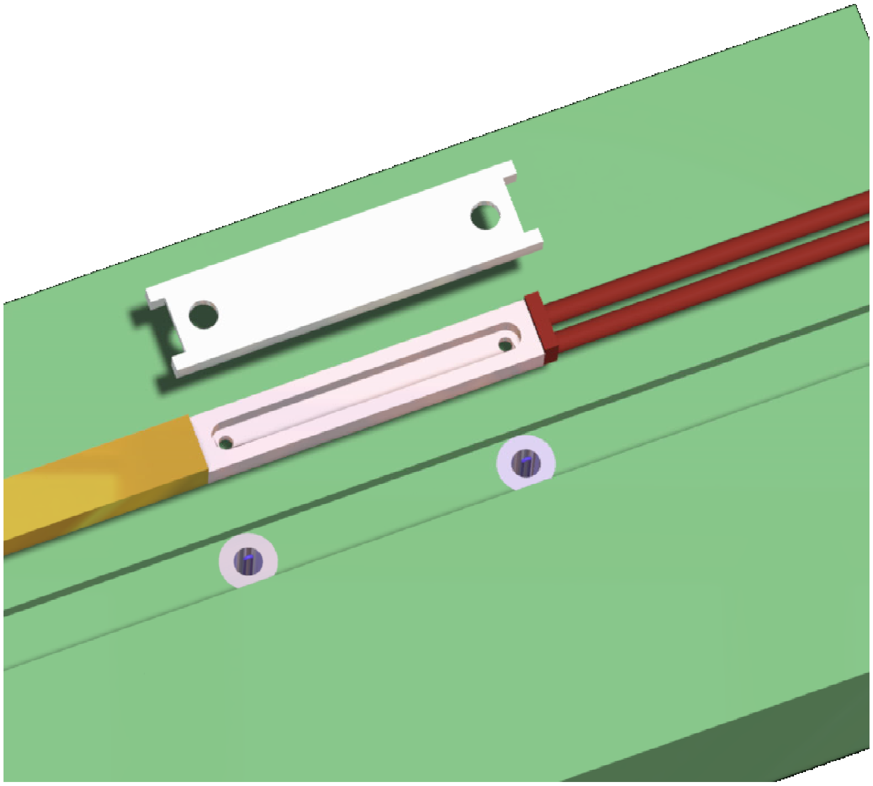
Foam Insulation Bottom Half



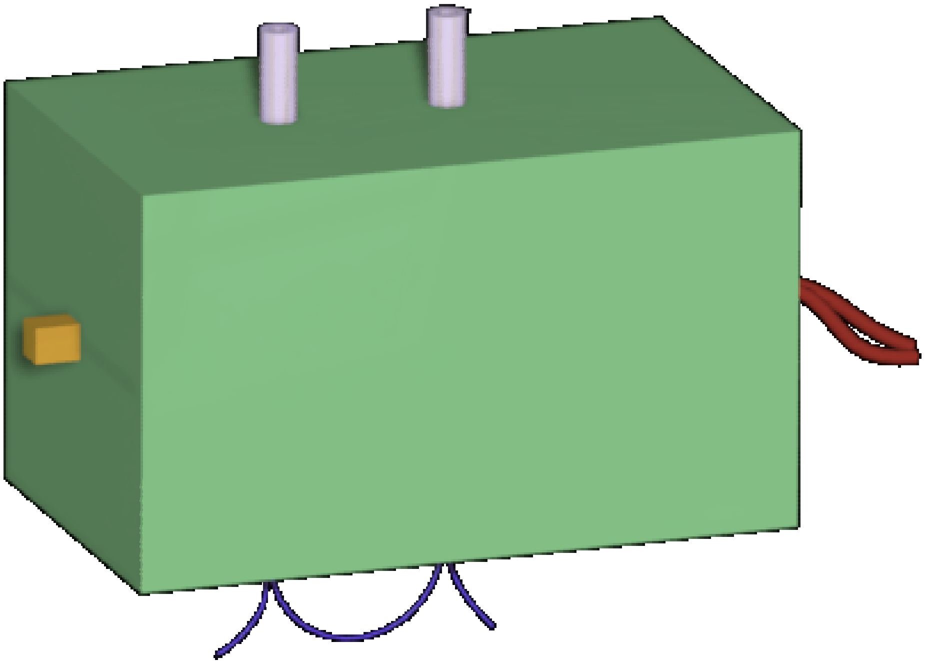
Copper Heat Sink



Sample Container Bottom



Rendered Drawin
Close up of heate
sample container, h
sink assembly show
location of holes f
electrodes in cap a
thermopile in
container.



Rendered Drawing: Total assembly.

Appendix B

Seebeck coefficients of 0.91 M aqueous NaCl with added polystyrenesulfonate

Molar ratio (mol/mol)	**Seebeck coefficient (µV/K)**
0.0	27 ± 15
0.5	24 ± 20
2.0	-54 ± 30
4.4	-230 ± 70
5.8	-305 ± 80

Table 3. Seebeck coefficients of 0.91 M aqueous NaCl with added polystyrenesulfonate

Seebeck coefficients of 0.91 M aqueous NaCl with added polystyrene with ammonium functional groups

Molar ratio (mol/mol)	**Seebeck coefficient (µV/K)**
0.0	30
1.1	60
3.6	140

Table 4. Seebeck coefficients of 0.91 M aqueous NaCl with added polystyrene with ammonium functional groups. Each coefficient consists of 3 measurements. Uncertainty is given by significant digits.

Seebeck coefficients of 4.0 M aqueous KCl with added polystyrenesulfonate

Molar ratio (mol/mol)	**Seebeck coefficient (µV/K)**
0.0	3
0.3	-2
0.7	-10

Table 5. Seebeck coefficients of 4.0 M aqueous KCl with added polystyrenesulfonate. Each coefficient consists of about 3 measurements. Uncertainty is given by significant digits.

Seebeck coefficients of 4.0 M aqueous KCl with added polystyrene with ammonium functional groups

Molar ratio (mol/mol)	**Seebeck coefficient (µV/K)**
0.0	3
0.4	-10
0.7	-60
0.9	-80

Table 6. Seebeck coefficients of 0.91 M aqueous NaCl with added polystyrene with ammonium functional groups. Each coefficient consists of 3 measurements. Uncertainty is given by significant digits.

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