



Hebron University
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Chemistry Department

**Effect of Temperature and Salt Addition on the Conductivity of
Sodium (polystyrene sulfonate) Aqueous Solutions**

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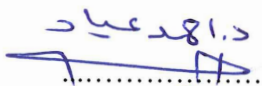

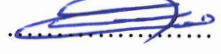

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Dedicate

Dedicated to the soul of my dear father Fawzy, may God have mercy on him, and make this humble

research in the balance of his good deeds, to my dear mother, may God give her long life, and to my dear husband Mousa, companion of the path and life partner and to my lovely children Baraa Mai and Qassam, may God bless them all.

Abstract

In this work I have studied the conductivity of sodium (polystyrene sulfonate) (NaPSS) aqueous solutions as a function of NaPSS concentration in the range 0.15 g – 2.0 g NaPSS in 100 ml of distilled water and in sodium chloride solutions at concentrations in the range of 0.1 M - 0.4 M and temperature in the range of 278 K – 328 K. The conductivity is found to increase with increasing NaPSS concentration both in pure water and in salt solutions. It is also found that the conductivity increases with increasing either NaCl concentration or temperature. The interesting findings here is the additivity rule: that the conductivity of the polyelectrolyte (k_{ps}) in the salt solution is the sum of its conductivity (k_p) in pure water plus the conductivity of the salt (k_s) holds only at low NaPSS concentration and deviates at higher NaPSS concentrations. This additivity rule holds better the higher the temperature and the higher the salt concentration. What is more interesting is that the contribution of NaPSS to the conductivity of the solution is more in pure water than in salt solution and that its contribution is higher the lower the NaCl concentration in salt solutions. This latter behaviour is only found at high NaPSS concentration while it is inverted at low NaPSS concentration. These findings will certainly contribute to a better understanding of the complex behaviour of the conductivity of polyelectrolytes in aqueous solutions.

نبذة مختصره

تم في هذا البحث دراسة الموصلية الكهربائية للمحاليل المائية للمركب الألكتروليتي المسمى متعدد ستايرين سلفونات الصوديوم (NaPSS)، عند تراكيز ودرجات حرارة مختلفة إضافة إلى إجراء ذات القياسات بوجود تراكيز مختلفة من كلوريد الصوديوم، وقد وجد أن هناك زيادة في قيم الموصلية الكهربائية مع زيادة تركيز مركب NaPSS سواء المحاليل التي احتوت على المركب الألكتروليتي لوحده أو يوجد ملح كلوريد الصوديوم، كما أن هذه الموصلية شهدت زيادة في قيمها مع رفع درجات الحرارة وهو أمر مرتبط بزيادة حركة الأيونات نتيجة لهذه الزيادة إضافة إلى انخفاض لزوجة المحاليل مما يعزز حركة هذه الجزيئات، لكن اللافت في هذه النتائج أن مقدار الزيادة في هذه الموصلية لم يكن مقدارا جمعيا لكلا المركبين عند كافة التراكيز تم دراستها، فعند التراكيز المنخفضة لمركب NaPSS كانت خاصية الإضافة (additivity rule) صالحة لكن حدث انحراف واضح في هذه الخاصية مع الزيادة المضطردة في تراكيز NaPSS، أما في الحالات التي تم فيها زيادة درجات الحرارة أو تركيز ملح كلوريد الصوديوم فإن خاصية الإضافة كانت أكثر صلاحية وانطباقا، أما النتائج الأكثر لفتا للانتباه فهي أن إجراء عملية طرح لقيم مساهمة الملح للموصلية تبين أن موصلية أيونات NaPSS لها موصلية أعلى في حال وجودها في الماء النقي مقارنة مع وجودها في المحاليل الملحية وأن هذه المساهمة تكون أعلى عند تراكيز منخفضة من الملح وعالية NaPSS، ويمكن أن يتم تفسير هذا السلوك بقيام أيونات الملح المضافة عند التركيز العالية بإعاقة حركة جزيئات NaPSS وبالتالي التقليل من الموصلية الكهربائية الناتجة عنها.

Chapter 1

1.1. Introduction

1.1.1. Polyelectrolytes

Polyelectrolytes are polymers have repeating units that are dissociating groups. They are either polycation, polyanions and polysalts [1-2]. They dissociated in aqueous solutions, when the solvent is water just like ordinary electrolytes (acids, bases and salts), and carry one or more charges depending on the pH value. As polyelectrolytes carry dual properties that are similar to both electrolytes and polymers they are called polyelectrolytes [3]. Poly-salts are the products of a monomeric base with polyacids (polyanions) and vice versa. In solution, they are electrically conducting like regular salts and their viscosity, like polymers, depends strongly on their polymer concentration and molecular weight [4].

Carboxylate ($-\text{COO}^-$), phosphonate ($-\text{PO}_3\text{H}^-$, $-\text{PO}_3^{2-}$), and sulfonate ($-\text{SO}_3^-$) are the most common anionic groups for anionic polyelectrolytes. For cationic polyelectrolytes; primary, secondary and quaternary ammonium ($-\text{NH}_3^+$, $=\text{NH}_2^+$ & $\equiv\text{N}^+$) are the common groups that one encounters. The properties of a polyelectrolyte are determined by the structure of its repeating units, the counter ions it carries and its ionic group. These properties include their solubility in polar and hydrogen-bonding solvents, solution viscosity and their transport properties and their conductivity. These properties are also strongly dependent on the type of salt added and the pH of their solution. In this case, they have different properties than their counterpart neutral polymers [5].

Chemical crosslinking of polyelectrolytes molecules is achieved by incorporating a small amount of the right crosslinking agent. Cross-linked polyelectrolytes form three-dimensional structures that when dissolved in water swell rather than dissolving in it [6]. Through hydrogen bond formation with water molecules, they can retain extremely large amounts of liquid relative to their own mass. In this cross-linked form they are so to speak hydrogels or superabsorbent polyelectrolytes. These superabsorbent hydrogels can absorb water up to 500 times their weight and from 30 to 60 times their own volume. Therefore, a hydrogel may contain more than 99%

liquid. The type and amounts of crosslinks in their structure controls their total absorbency and swelling capacity of these superabsorbent materials.

Synthetic and non-synthetic polyelectrolytes are produced and manufactured on large scale. Polygalacturonic acid (pectin), alginic acid or alginates, polypeptides and carboxymethyl cellulose are examples of natural polyelectrolytes. Polystyrene sulfonate, polyallylamine, polyacrylic acid and their salts are examples of synthetic polyelectrolytes. Examples of these polyelectrolytes with their chemical structures are shown in figure 1.

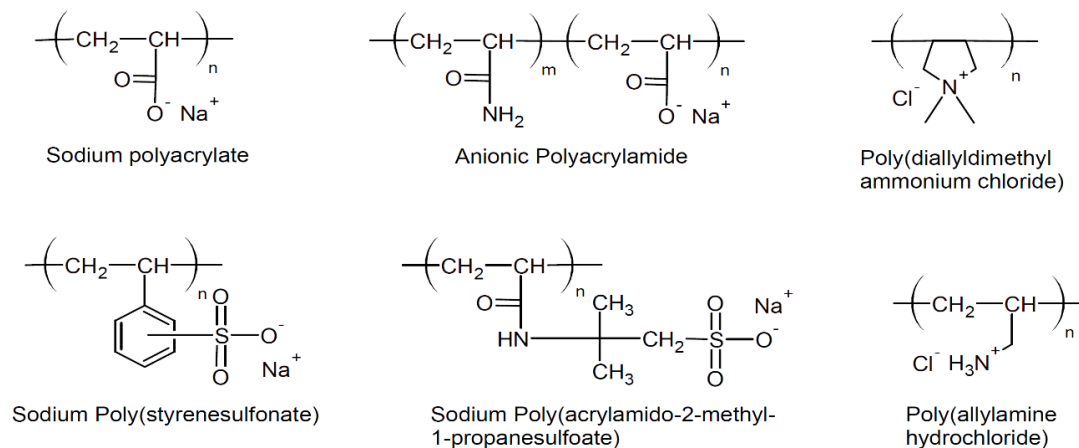
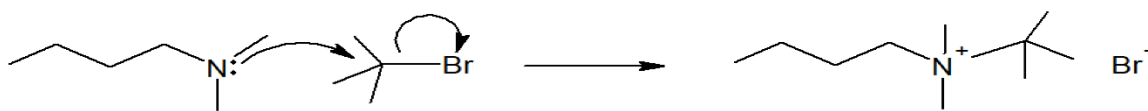


Figure 1. Names and chemical structure of some polyelectrolytes.

Some polyelectrolytes contain ionizable groups in their backbone instead of carrying them as side groups. These kinds of polyelectrolytes are called polyionenes. Quaternary ammonium group is the most common charged group in their backbone. Through Menshutkin reaction of ditertiary amines and alkyl dihalides these ionic polyamines or polyionenes are typically synthesized. This reaction mechanism is shown below:



The commercial availability of a large number of dihalides and ditertiary enables the synthesis of a large number of well-defined polyionenes. These starting materials are cheap and in combination with the simple synthesis route; these special type of polyelectrolytes can be synthesised. Polyelectrolytes with different molecular weights and different charge densities (ionic spacing on the polymer) backbone can be easily synthesis. Furthermore, different functional groups can be incorporated. This allows for tailoring the physical and mechanical properties and crosslinking. Chemical structures of some amine polyelectrolytes are shown in figure 2 below.

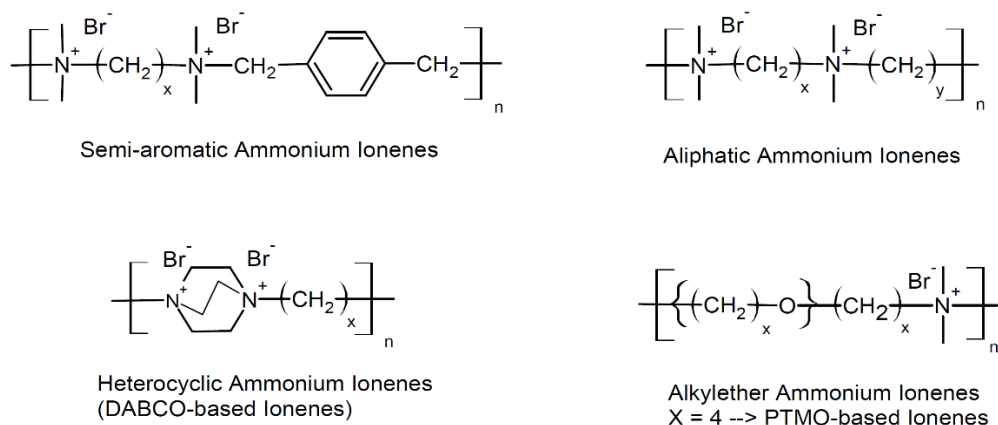


Figure 2. Chemical structure of some amine polyelectrolytes

1.1.2. Physicochemical Properties

The properties of polyelectrolytes in a solution is determined by the electrostatic interaction between the charged groups in the chain and the low molecular weight ions in the solution. These charges in the polyelectrolyte generate a strong electrostatic field that has a significant effect on molecule structure. It substantially alters the macromolecular conformations. With increasing dissociation, the effective size of the chains (e.g. hydrodynamic radius, distance from end to end) increases, and the coiled molecules straighten out reaching an almost linear, rod-like shape at high degrees of polyelectrolyte dissociation[59].

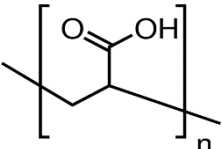
The physicochemical properties are significantly altered with a changing degree of dissociation. For example: the viscosity of the solution will increase by a factor of a hundred or even more depending on polyelectrolyte concentration, degree of dissociation, and free ion (salt) concentration (low molecular weight ions in the solution).[59]

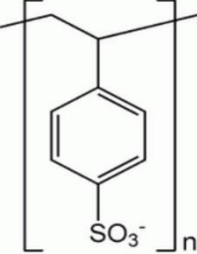
The theory established for solutions of low molecular weight electrolytes is not valid for polyelectrolyte solutions. A diffuse counter-ion cloud around the oppositely charged surface of the polymers is created, by the low molecular weight ions appearing during the dissociation of polar groups of the polyelectrolytes. The composition (solvation) and size of this diffuse counter-ion cloud affects the structure and dynamics of the polyelectrolytes in the solution and also the swelling capacity and the visco-elastic response of polyelectrolyte gels.

There is a considerable effect on the structure, stability and interactions of various (biological) molecular assemblies by the charged molecular chains that are commonly present in systems of soft matter. The theoretical approaches which goal is to describe the statistical properties of these assemblies are totally different from the approaches used to describe their electrically neutral counterparts. Many of existing biological molecules are polyelectrolytes, for example polypeptides and DNA.

1.1.3. Commercial Polyelectrolytes

Commercial grade polyelectrolytes (PAA's) can be obtained from Rohm & Haas (Acusol™, Acumer™), BASF (Dispex®, Magnafloc®), Dow Chemical (Duramax, Tamol™, Romax™, Dowex), and Arkema company (Rheoslove™, Terrablend).

Polyelectrolyte	Structure of Repeat Unit	Trade Name
Polyacrylic acid (PAA)		Acusol (copolymer), Acumer, Acrysol, Alcosperse

Polyelectrolyte	Structure of Repeat Unit	Trade Name
Polystyrene sulfonate		Resonium, Sorbisterit, Resikali

1.1.4. Applications

There are many applications of polyelectrolytes. Most are related to flow modification and the improvement of the stability of aqueous colloids and gels, or for inducing agglomeration. For example, they are used for destabilization of colloidal suspensions and for initiating flocculation and precipitation. Another use case is for imparting a surface charge to neutral particles, so that they can be dispersed in aqueous solutions. For that reason, they are often used as dispersant agents, thickeners, emulsifiers, conditioners, ion-exchanger and clarifying agents. For instance: in water treatment [6-7] they are used as flocculation agents [8], in ceramic slurries as stabilizing agents [10] and in concrete mixtures as superplasticizers. Polyelectrolytes can be found in many cosmetic products, shampoos and soaps. Some polyelectrolytes are used in food products, for instance as coatings or release agents [11]. Some examples are alginate (alginic acid), pectin (polygalacturonic acid), and carboxymethyl cellulose.

Sodium polyacrylate co-polymers of slightly cross-linked which are called hydrogels are used as superabsorbent. Baby diapers and other personal disposable hygiene products such as adult protective underwear and sanitary napkins form the largest use of these superabsorbent polyelectrolytes.

1.1.5. Conductivity of Polyelectrolytes

When dissolved in water polyelectrolytes dissociate into a macro ion and counter ions [12-14]. When counter-ions are released in aqueous solutions there is gain in entropy. The latter effect in combination with the presence of charged monomers along the polymer chain make polyelectrolytes systems of fundamental interest in the physical chemistry of soft condensed matter [15, 16] as well as in biological systems [17]. Due to their conducting properties, they are

largely used for technological applications [18]. Of current interest is understanding the transport properties of these systems. Electrical conductivity of their solutions is the key for understanding their transport properties [19]. The transport properties of these systems is fundamentally governed by their linear charge density ξ [20-22] and therefore depend on the degree of dissociation α of the polyelectrolyte.

In the last decades, these charged polymers have attracted much attention [23]. This is due to charge distribution which creates long range electrostatic interaction and this introduces a new length scale and new time scale. Thus, these systems have unusual properties. The dynamical properties and the structure of these is governed by the balance between attractive hydrophobic interactions and repulsive electrostatic interactions. When the ionisable groups along the chain are dissociated, the counter ions are partially released into the solution. This results in an effective charge of the polymer that is lower than its bare structural charge. This makes these charged polymers of important properties. The interplay between electrostatic attraction of counter ions with the polymer chain creates such phenomenon. In addition to that, this phenomenon is also caused by the loss of their conformational entropy. The thermodynamics and the transport properties of solutions of these charged polymers are largely influenced by counter ion condensation. To study and understand the coupling between counter ions condensation and chain conformation, conductivity is the key parameter. Biological functions of biological polyelectrolytes are influenced by the chain conformation, which makes the previous mentioned coupling of particular importance. When the electrical conductivity of these systems is studied as a function of polyion concentration, in absence or presence of added salt, the outcome of these studies may provide better understanding of the chain mobility and of the coupling [23].

In order to understand how the conductivity of a polyelectrolyte solution differ from the conductivity of small electrolyte, it is inevitable to introduce the theory of polyelectrolytes conductivity. The origin of the electrical conductivity σ of an aqueous solution of polyelectrolytes is the movement of any charged entity. This movement is made in response to an external applied electric field. This in turn depends on three contributions, the charge carriers of type i , the numerical concentration n_i , their electrical charge ($z_i e$) and their mobility u_i , according to the relationship [23]:

$$\sigma = \sum_i (|z_i| e) n_i u_i \quad (1)$$

the charge mobility u is defined as the ratio of the average velocity of the charged carrier to an applied electric field of unit strength. The usual definition of the conductivity σ , from an experimental point of view, is given by the linear relationship [23]:

$$\langle \vec{J} \rangle = \sigma \vec{E} \quad (2)$$

where $\langle \vec{J} \rangle$ is the volume averaged current density and \vec{E} is the measured electrical field. If one expresses the numerical concentration by the molar concentration C_i ($n_i = N_A C_i$) of the polyelectrolyte, equation (1) can be written in a more usual way through the molar concentration, where N_A is the Avogadro number and the mobility u_i through the equivalent conductance λ_i ($u_i = \frac{\lambda_i}{F}$) (where $F = eN_A$ is the Faraday constant). We obtain:

$$\sigma = \sum_i (|z_i|) C_i \lambda_i \quad (3)$$

The whole transport process is actually given by equation 3 which also forms the basis of any theoretical description of polyelectrolytes conductivity. It depends on the concentration C_i and the equivalent conductance λ_i of each charge carrier. The partial dissociation of the polyelectrolyte actually drives charge and equation 3 can be written as:

$$\sigma = |z_i| C_1 \lambda_1 + |z_p| C_p \lambda_p \quad (4)$$

where the subscripts “1” and “p” refer to counter ions and polyions, respectively. Because of the counter ion condensation effect, the following relationships hold: $C_i = \nu_1 N f C_p$ and $Z_1 = z_i$, $Z_p = N f z_p$ and equation 3 can be written as:[23]:

$$\sigma = N f C_p (\nu_i |z_1| \lambda_1 + |z_p| \lambda_p) \quad (5)$$

The equivalent conductance λ_1 differs from the value λ_1^o of the counter ion in the absence of the polyelectrolyte and this is given by:

$$\lambda_1 = \lambda_1^o \frac{D_1^u}{D_1^o} - \lambda_p \left(1 - \frac{D_1^u}{D_1^o} \right) \quad (6)$$

where D_1^u and D_1^o are the diffusion coefficients of counter ions in the limit of infinite dilution and in the presence of polyions, respectively. Now, substituting equation 6 in equation 5 one gets:

$$\sigma = \nu_1 |z_1| N f C_p \frac{D_1^u}{D_1^o} (\lambda_1^o + \lambda_p) \quad (7)$$

The electrical conductivity of polyelectrolytes solution is defined by the following parameters: the polyion concentration (C_p), the fraction f of free un-condensed counter ions, the equivalent conductance (λ_p) of the polyion chain and the degree of polymerization (N) [23].

1.1.6. Literature Review on Polyelectrolytes Conductivity

The conductivity of polyelectrolytes solutions in pure water and with the addition of salts had been studied by a number of authors. Vink et al [21] studied the conductivity of the polyelectrolytes poly (methacrylic acid), carboxymethylcellulose, poly(vinylsulfonates) and poly(styrenesulfonates). The conductivity as a function of polyelectrolyte concentration was measured to determine the limiting equivalent conductivity (Λ^0). According to their work with dilute solutions, a rapid increase of the conductivity with increasing concentration was observed. This behaviour was explained by a decreased counterion binding. RiOS [24] investigated the electrical conductivity of dilute solutions of four prepared cationic polyelectrolytes. They calculated the distances between neighbouring charges from their experimental data and found a good agreement with those calculated according to Manning's model [25]. Highly charged strong polymers in dilute and semi-dilute solutions were studied theoretically by Wandrey [26] and the electrical conductivity was calculated. Their study was the first one to consider the influence of the charge density, polyelectrolytes concentration, the ionic strength and concentration of added salts. He found that the equivalent conductivity increases with decreasing polyelectrolyte concentration. He also found out that the effect of molar mass above the overlap concentration (c^*) is weak. A strong increase of the equivalent conductivity with decreasing polyelectrolytes below this overlap concentration was also found. With an additional change of the interaction parameter and using the Manning's theory, the conductivity was explained qualitatively. He derived an empirical dependence of the interaction parameter on the ratio of the Debye length to the contour length. He also identified three concentration regimes differing in the polyelectrolyte-counter-ion interaction. Solutions of these polymers without added salt as well as solutions with any ratio of polyelectrolyte to salt concentration was considered. Zhiyong Hu et al [27] studied three different polyacrylamides with three different amination degrees by conductometric measurements. Their results show that with increasing amination degree of polyvinylamine value (a measure of electrostatic interactions of neighbouring groups on the

chains) the electrostatic interaction parameter increased. They also found out that the pK_a value of these polyelectrolytes θ decrease with increasing amination degree. Finally, they found a gradual decrease of the equivalent conductivity with increasing concentration of the polymer and the conductivity was enhanced with increasing degree of amination.

The electrical conductivities of aqueous solutions of sodium i-carrageenan, sodium heparin, and sodium dextran sulfate in NaCl and Na₂SO₄ solutions at room temperature was studied by Douglas et al [28]. They found anomalous behaviour for sodium dextran sulfate. They discussed the correlation between the Manning law with their experimental results. They found theoretical justification using a modified model for the additivity of simple salt and polyelectrolyte conductivities. Their theoretical equations for the conductivity were developed for salt-containing polyelectrolyte solution and for the case where the charge density of the polyelectrolyte is less than the critical charge density. The variation of mobilities of the counterions in aqueous solutions of sodium polystyrenesulfonic acid over a wide concentration range was studied at room temperature by Fernandez et al [29]. They attributed the enhancement of mobilities to an increase in the degree of apparent dissociation due to purely electrostatic interactions among neighbouring chains. They found out that this interaction should be accompanied by short-range interactions which would produce entanglements among neighbouring chains. This was evident as concentration increased and chains approached each other. They found that this may be responsible for the appearance of a maximum in mobilities as the concentration increased. In addition, they found out that the counterions Cs⁺ had a slightly larger degree of association than Na⁺. They explained the behaviour of Ca⁺⁺ by the very strong association due to its double charge and for silver as partially due to the presence of complexes. Different salts of polystyrenesulfonic acid in salt-free aqueous solutions were studied by Szymczak et al [30]. They determined the conductivities in salt-free aqueous solutions in the concentration range from 0.003-0.02 N. The conductivity was found to increase with dilution, gradually at first, followed by a rapid increase at higher dilutions. The order of change in conductivity was found to be Li⁺ < Na⁺ < K⁺ = NH₄⁺ < Rb⁺ = Cs⁺. Good agreement was found when they compared their experimental data with that of Manning's rod like polyelectrolytes model.

Benmansour et al [31] determined the conductivities of poly[N-(3,6,9-trioxadecyl)-4-vinylpyridinium] bromide and its chlorate and tosylate derivatives. Their method of preparation gives a grafted polyelectrolyte having a positive charge on each pyridinic moiety on the backbone. The polyelectrolyte concentration range in the aqueous solution was 10^{-4} to 10^{-2} M at 25 °C. A typical polyelectrolytes behaviour of the conductivity versus concentration was found. They also found out that the polyelectrolyte conductivity increases with the ion size. They showed in their analysis that big ions are weakly or not associated to the backbone. They suggested that counter-ion mobility is mainly influenced by steric effect. Values of the conductivity predicted from Manning rod-like polyelectrolyte model were compared with their experimental results and good agreements was found.

Rios [32] studied the interaction of alkaline ions with an anionic dicarboxylic polyelectrolyte by means of electrical conductivity measurements. His results show that lithium, sodium and potassium counter-ions interact in a very different way with this polyelectrolyte. He found out that the Kohlrausch plots bend downwards in the high-dilution zone. He determined the limiting equivalent conductivities of these polymers according to Vink's method using a polynomial adjustment of his data. He also found out that although the dissociation order follows the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, the trend in equivalent conductivity follows the reverse order. This is mainly determined by the equivalent conductivity of the counter-ions. He determined the interaction parameter using the Manning theory for the limiting equivalent conductivity of the polyion species. His values of the latter parameters, the average distance between charges agreed well with that calculated from simple geometrical calculations for a mesomeric configuration. He used an alternative method to obtain the relative interaction parameter as a function of polymer concentration. He explained the results in terms of the hydration parameters and the limiting equivalent conductivities of the counter-ions.

Rios et al [33] studied the intermolecular association of amphipathic polyelectrolytes using fluorescence and conductivity methods. In their study, as the polyelectrolytes chain increases in length there is a decrease in the average distances between charges. As a consequence, the degree of dissociation and the linear charge density are modified. They calculated the average

distances with the Manning counter-ion condensation theory for the conductivity of polyelectrolyte solutions. Their calculated distances were found to vary with polyelectrolyte concentration. Their values of the conductivity were also found to depend on the size of the side chain of the polyelectrolyte. They explained the experimental behaviour of the solution electrical conductivity of polyelectrolytes, which increase drastically with dilution, as a continuous change in the average distances between charges which produce conformational changes.

Vuletic et al [34] studied the Manning free, uncondensed, counter-ions fraction θ for dilute aqueous solutions of rodlike polyions: 150 bp DNA fragments, in the presence of a very low concentration of monovalent salt for concentration < 0.05 mM. They measured the conductivity of these solutions for DNA base pair concentration range 0.015-8 mM. Their conductivity values were complemented by fluorescence correlation spectroscopy (FCS) measurements of the DNA polyion diffusion coefficient. They observed a crossover in the normalized conductivity that nearly halved across the $c = 0.05$ –1 mM range. Through analysis of their data they extracted $\theta(c) = 0.30$ –0.45. By taking the Manning asymmetry field effect on polyelectrolyte conductivity into account they got $\theta(c) = 0.40$ –0.60. They related the $\theta(c)$ variation to gradual DNA denaturation occurring, in the very low salt environment, with the decrease in DNA concentration itself. They found out that the extremes of the experimental $\theta(c)$ range occur toward the highest, above 1 mM, and the lowest, below 0.05 mM, DNA concentrations and correspond to the theoretical θ values for dsDNA and ssDNA, respectively. They confirmed Manning condensation and conductivity models to be valuable in description of dilute solutions of rodlike polyions.

The electro-kinetic properties of carboxymethyl-dextran, a soft and anionic polysaccharide, in aqueous NaNO_3 solutions were analysed through measurements of the electrical conductivity of the suspensions by Jean-Pierre et al [35]. Their results actually furnish new experimental support for the structure of soft polysaccharides in electrolyte solution. They showed that the polyion concentration governs the conductance behaviour of the suspension as the ionic strength decreases. They found out that this is particularly evident for large polymer concentrations, for which electrical double layer overlap is more likely. They found that the electrical conductivity of the suspension at high ionic strength reduces to the contribution of the ions in solution, as

screening of the polyion charges is more efficient in such conditions. They examined applicability of Ohshima's general conductivity expression to these electrical conductivity measurements, and observed a major discrepancy against the theory. Their calculated values of the electrical conductivity deduced on the basis of this theory were found to be lower than the experimental ones. They discussed the possible reasons for this discrepancy and found out that a numerical model, based on the use of a cell approach to account for hydrodynamic and electrical interactions between particles, to be a good description of the experimental electrokinetic data.

The conductance of poly (anetholesulfonic acid) and its lithium, sodium and caesium salts in the concentration range of 0.001-0.20 mmol/L and in the temperature range of 278 – 308 K were studied by Irna et al [36]. They found that the Walden's rule to be reasonably satisfied for the alkaline salts of the polyelectrolytes but not for the polyacid itself. They determined the concentration dependence of the polyion transference number at 298 K. From their measurements they calculated the fraction of the free sodium ions in the solution. They also compared their results with the existing ones for poly (styrenesulfonic acid). They found out that the conductivities of the studied polyion and its salts are higher than that of the poly (styrenesulfonic acid). They explained this difference by a smaller fraction of free conducting counter ions. They found out that their findings are consistent with thermodynamic data for these solutions.

Nagy [37] measured the conductivity of dilute, salt free solutions of poly (vinyl alcohol) (PVA) and poly(vinyl alcohol, vinyl sulphate ester) copolymer salts in order to get information on transition from a neutral to charged macromolecules. He found out that with increasing linear charge density from a very low value to a moderate one a non-linear dependence of polyelectrolyte effect on copolymer composition. He also found out that there is a close analogy between the expansion of polyanions and swelling of polyelectrolyte networks at comparable linear charge density range. He revealed by the electric conductance measurements that the transition from a neutral to charged macromolecules could be a very complex one calling for a new and more detailed theoretical consideration of polyelectrolyte solutions.

Bratko et al [38] studied the effect of the temperature on the electrolytic conductivity of aqueous poly (styrenesulfonate) solutions. The molar conductivities of the poly (styrenesulfonic acid) (poly [1-(4-sulfophenylethylene)]) (HPSS) and its sodium (NaPSS) and magnesium salts (MgPSS) were determined as functions of the concentration at different temperatures ranging from 0 to 40 °C. The Walden rule was shown to apply approximately to the overall conductivity of the two polysalts as well as to the molar conductivity of the polyion. They found out that the estimated relaxation effect on the conductivity, presumably mainly determined by the equilibrium structure of the polyelectrolyte found not to depend on the temperature within the accuracy attained.

Bhattacharai [39] measured the specific conductance for sodium polystyrene sulfonate in water and methanol-water mixture. The equivalent conductivity data against concentration were evaluated by scaling concept. He calculated the effects of the solvent composition and the polyelectrolyte concentration on the fractions of uncondensed counterions, the polyion conductivities, the standard state free energies of counterion association, and the polyion transference number. The charge density of sodium polystyrene sulfonate was used for the research article to see the variation of the critical aggregation concentration of cetyltrimethyl ammonium bromide in sodium polystyrene sulfonate against the charge density of sodium polystyrene sulfonate.

Recently, Ranjit De [57] studied aqueous solutions of sodium polystyrenesulfonate in the presence of NaCl by electrical conductivity. The study meant to understand the interaction between counter-ions with the polyion. By an equation developed by them and by considering the scaling description for the conformation of a polyion chain, they analysed the specific conductivity versus polyelectrolyte concentration. They investigated the influences of added salt, polyelectrolyte concentration, temperature and molecular weight. Both, the concentration of the polyelectrolyte and its molecular weight were found to greatly influence counter-ion condensation.

1.1.7. Sodium (Polystyrene sulfonate) and its Uses

Sodium polystyrene sulfonate is an organic compound, light amber liquid, odourless. It is a water-soluble polymer with a unique effect, used in: reactive emulsifiers [40], water-soluble polymers (coagulants, dispersants, container cleaning agents and cosmetics), water treatment

agents (dispersion Chemicals, flocculants), sulfur exchange resins (membrane), photographic agents (membrane), semiconductors, imaging films and heat conduction products [40]. It is well known that Sodium polystyrene sulfonate (PSS) has strong hydrophilic properties. It is used to prepare adsorption ultrafiltration membranes and is also used to treat heavy metal water pollution. It will migrate to the surface of particles when it is gelled with water. In these cases, it will be mainly fixed on the surface of the particles or the surface of the pore channels. It is used in the preparation of ultrafiltration membrane that on not only removes water, macromolecules, colloids and other substances, but is capable of can simultaneously removing various toxic and harmful cations in the water [41].

1.1.8. Synthesis of NaPSS

The sodium salt of the polyelectrolyte polystyrene sulfonate can be prepared using an aqueous reversible-deactivation radical polymerization (RDRP) approach to synthesize directly from functionalized monomers to give uniformly and completely sulfonated materials. This was done by Balding et al [42, 43]. Under simple one pot reaction conditions, reproducible gram scale syntheses are achieved. In addition, full monomer conversions are achieved within approximately 3 h. They found out that reaction variables such as pH, sodium chloride concentration, and methanol co-solvent have a significant effect on the molecular weights obtained by gel permeation chromatography coupled with multi angle light scattering. A parametric optimization, rather than direct variation of the monomer to initiator ratio, resulted in some of the highest molecular weight polymers. Linear progression between number average molar mass and monomer conversion occurs at a neutral reaction pH, which results in narrow polymer molecular weight distributions, along with high end-group fidelity as demonstrated with chain extension reactions. This is an up to date method of NaPSS synthesis.

1.1.9. Importance of the study

Despite the previously mentioned studies, the effect of different salt concentrations and wide temperature range on the conductivity of sodium (polystyrene sulfonate) aqueous solutions have never been thoroughly investigated. The scientific contribution of this work is obtaining the electrical conductivity of NaPSS solutions in wide range of concentrations of NaCl added salts at different temperatures. The effect of temperature on the conductivity of this polyion has been studied only by one author and up to 40°C in pure water [38]. It has to be noted here that only

few studies on the conductivity of this polyion have been carried out. However, the only study that directly measured the conductivity of this polyion was in water as a solvent and this study was indeed an old one [38]. Conductivity measurements are extremely important for the understanding of the dynamics and ion mobilities of this polyion in particular and of polyelectrolytes in general. Knowledge of the conductivity of NaPSS deepen our understanding of its behaviour and could lead to new applications of NaPSS. Through measurement of electrical conductivity, challenges for the existing theories are provided. So in this thesis work, I have studied the effect of NaCl addition in the concentration range of 0.1- 0.4 M and the effect of temperature in the range of 5 – 55 °C on the electrical conductivity of the polyion Sodium (polystyrenesulfonate) (NaPSS). To our knowledge, such a study has never been conducted so far and will certainly contribute to the field of interest.

Chapter 2

2.1. Experimental Part

2.1.1. Materials

NaPSS was supplied by Sigma- Aldrich, with purity of 99.8% and a weight average molar mass of $M_w = 70000$ g/mol. It is an organic compound with the molecular formula $(C_8H_7NaO_3S)_n$. The anionic polyelectrolyte is a white to light yellow crystal. This NaPSS sample was pre-dialysed by the producer.

NaCl from Sigma-Aldrich with purity that exceeds 99% and molar mass of 58.44 gm/mol.

2.1.2. Conductivity Meter

Conductivity measurements were carried out by a modern Orion Star A212 Conductivity Benchtop Meter (Thermo Scientific™) with high precision. The uncertainty of the measurement was 0.01%.

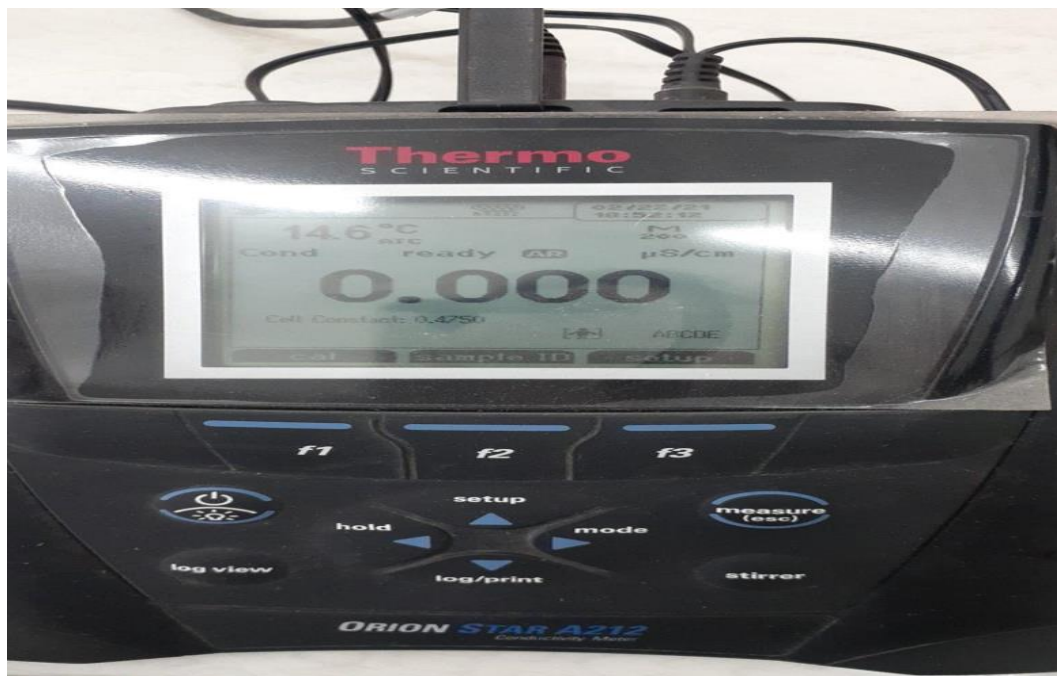


Figure 2.1. Orion Star A212 Conductivity Benchtop Meter (Thermo Scientific™) with high precision. The uncertainty of the measurement was 0.01%.

Measurements were carried out in a test tube that was immersed in the water bath until the temperature in question was reached.

2.1.3. Furnace

A Lab furnace manufactured by CM Furnaces and has a maximum operating temperature up to 2000 K was used for drying salts. The furnace shown in the figure below has sealed designs that support atmosphere control necessary for advanced processes including heat treating, sintering, annealing, glass or ceramic firing.



Figure 2.2. A Lab furnace by CM Furnaces with heating temperature up to 2000 K.

2.1.4 Preparation of Solution

In this work, preparation of different concentrations of solutions was carried out either by direct weighing or by successive dilution. In both cases, solutions give us the same conductivity reading exactly. Measurement of each sample was repeated three times and the average value was tabulated. The solutions were prepared and then left them to the next day to made the conductivity measurments.

To control the temperature of the sample, it was putted in a refrigerated circulating water bath and its temperature was measured manually with a thermometer to check it.

NaCl used is a hygroscopic salt, so it was putted in the furnace for two hours to drying and then waited until it cooled to use.

All glassware (beakers, volumetric flasks, test tubes) were carefully cleaned by filling them with hot distilled water for several hours and then rinsed thoroughly with distilled. Freshly prepared distilled water that was used to prepare solutions throughout this work was tested repeatedly for the values of conductivity to ensure its purity. Distilled water conductivity was measured to be of the order of 10^{-6} S/cm at 298 K. This method of cleaning proved to yield good results.



Figure 2.3. Refrigerated circulating water bath with temperature controller that has an accuracy of $\pm 0.1^{\circ}\text{C}$.

Chapter 3

3.1. Results and Discussions

3.1.1. Conductivity Results of NaCl in Pure Water

Figure 3.1a. shows the conductivity of NaCl aqueous solutions, as a function of NaCl concentration at 298 K. Open circles are the experimental points while the solid line is a linear fit to the data. Figure 3.1b. shows the conductivity of NaCl aqueous solutions as a function of NaCl concentration reported by Hervas et al. [43]. The experimental data of this work is in excellent agreement with that of Hervas et al. As can be seen from figure 3.1a, the conductivity of NaCl increases.

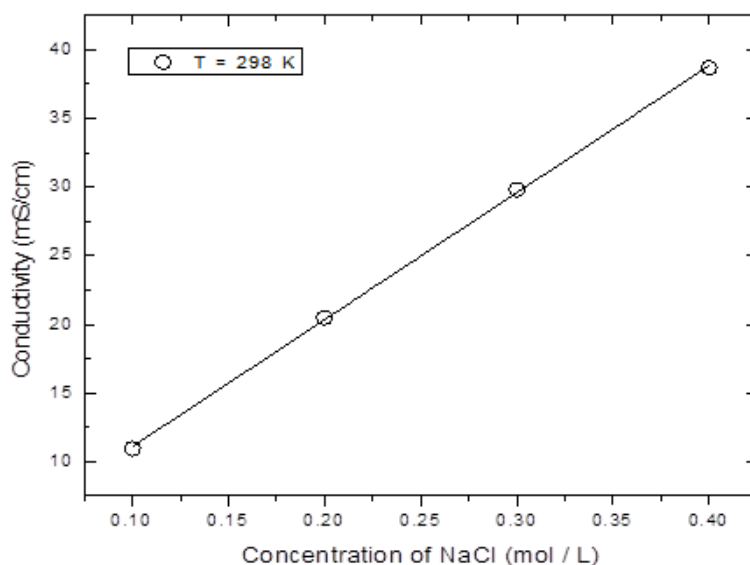


Figure 3.1a. Conductivity of NaCl aqueous solutions as a function of NaCl concentration at 298 K. Open circles are experimental data and the solid line is a linear fit to the data.

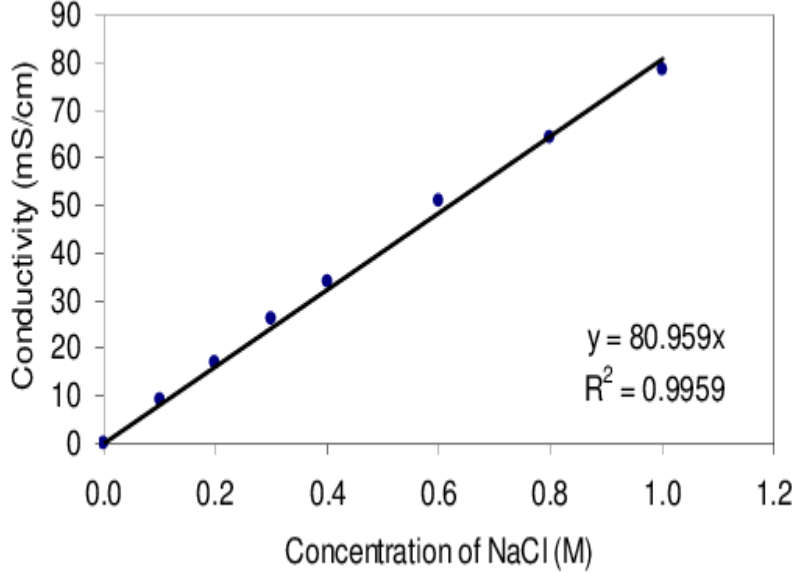


Figure 3.1b. Conductivity of NaCl aqueous solutions as a function of NaCl concentration at 298 K taken from ref [43].

with increasing NaCl concentration. The presence of ions in the solution cause the conducting properties of electrolyte solutions. The greater the concentration, the greater the number of ions in solution and the greater is the conductance. Figure 3.2 shows the molar conductivity Λ_m of NaCl aqueous solutions as a function of the square root of the concentration of NaCl. The molar conductivity decreases with increasing concentration according to the well-known Kohrausch's law for the conductivity of strong electrolytes:

$$\Lambda_m = \Lambda_m^o - k\sqrt{conc} \quad (8)$$

$$\text{Conductivity(L)} = \text{Conductance} \times \text{cell constant} \quad (9)$$

$$\Lambda_m = L/\text{concentration} \quad (10)$$

where Λ_m and Λ_m^o are the molar conductivities at a given concentration and at infinite dilution respectively and k is a constant. The molar conductivities decrease as a result of increasing concentration of the electrolytes, compared to what it was at infinite dilution. Chemically, what this means is that the ion-ion interaction increases as the concentration of salt in solution increases. The decrease in the molar conductivity comes from different contributions: first the ion-solvent and second the solvent-solvent interactions of the electrolytic solution. It has to be

mentioned here that there is no contradiction between figures 3.1a. and figure 3.2 because the conductivity of a solution is the conductance of one-unit volume of the solution, but molar conductivity is the conductance of that volume solution containing one mole of electrolyte. So the conductivity increases with increasing concentration while the molar conductivity decreases with increasing concentration.

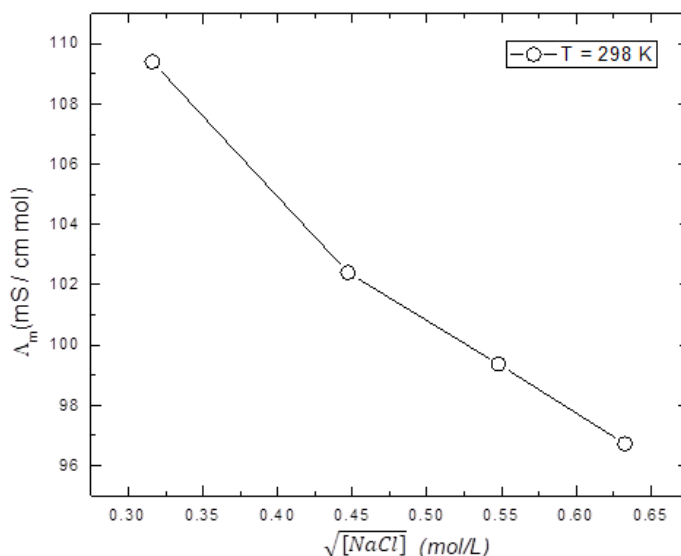


Figure 3.2. The molar conductivity of NaCl aqueous solutions as a function of the square root of the NaCl concentration. The open circles are the experimental data and the solid line is drawn just to guide the eye.

The temperature dependence of the conductivity of NaCl aqueous solution is shown in figure 3.3. As indicated in the figure, open stars, open triangle, open circles and open squares are for 0.1, 0.2 0.3 and 0.4 Molar of NaCl, respectively. As can be seen from figure 3.3, the conductivity increases with increasing the temperature. This is due to a number of factors. First of all, there is decrease in the viscosity of the solution and an increase in the mobility of the ions in solution. Secondly, there is gain in energy by the molecules of the electrolyte (ions), as temperature increases. This leads the ions to have higher energy and to be in higher state of energy. The mobility of the ions increases as the energy gained by them is converted to kinetic energy. As the ion mobility increase so the conductivity of the solution increases. The previous concentration measurements and the explanation provided is already known in the literature and presented in chemistry text books. The object here is to prove that our experimental set up has produced data that is consistent with the published and known.

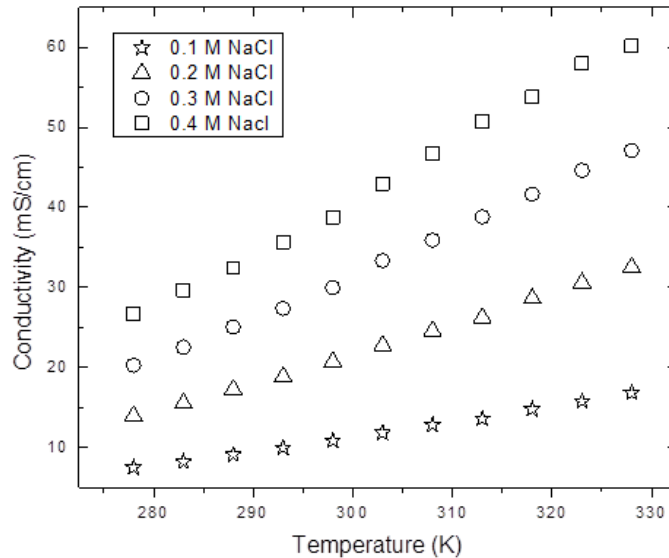


Figure 3.3. Temperature dependence of the conductivity of NaCl aqueous solutions in different concentrations.

3.1.2. Results for NaPSS in Pure Water

Temperature dependence of NaPSS conductivity at different concentrations of NaCl in pure water is shown in figure 3.4(a+b). The concentration range is 0.15 g NaPSS/100ml – 2.0 g NaPSS / 100 ml distilled water and the temperature range is 278 K – 328 K. As can be seen in the figure, the conductivity increases with increasing temperature. This could primarily be explained as mentioned above for Pure NaCl which is due to viscosity decrease with increasing temperature and due to increase in energy that these ions have acquired due to temperature increase. In order to compare with limited available data in the literature(Szymczak), the conductivity per gram NaPSS as a function of NaPSS concentration at 298 K was plotted in figure 3.5. It is seen in the figure that the conductivity of NaPSS in pure water increases slightly in the beginning with increasing dilution or decreasing polyelectrolyte concentration and then rapidly increases at high dilution.

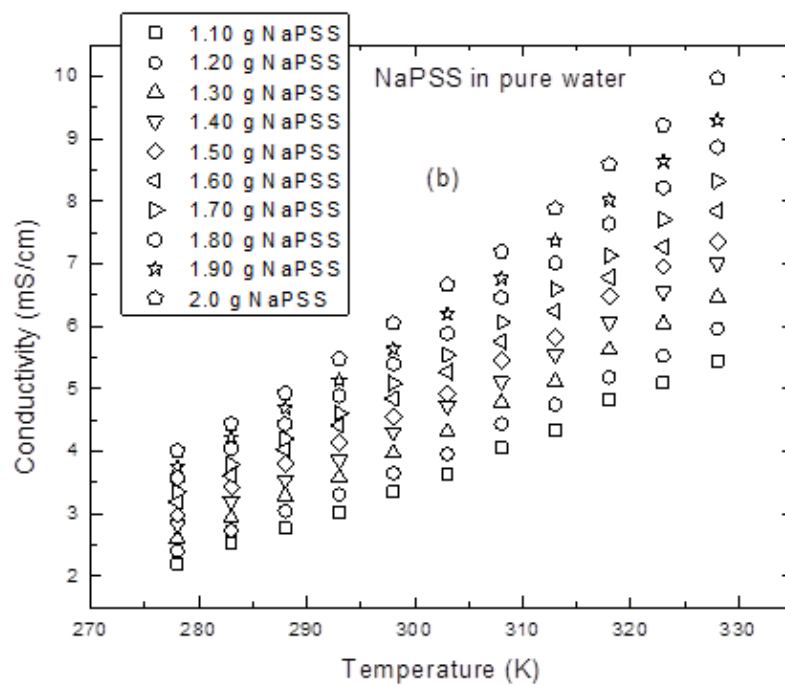
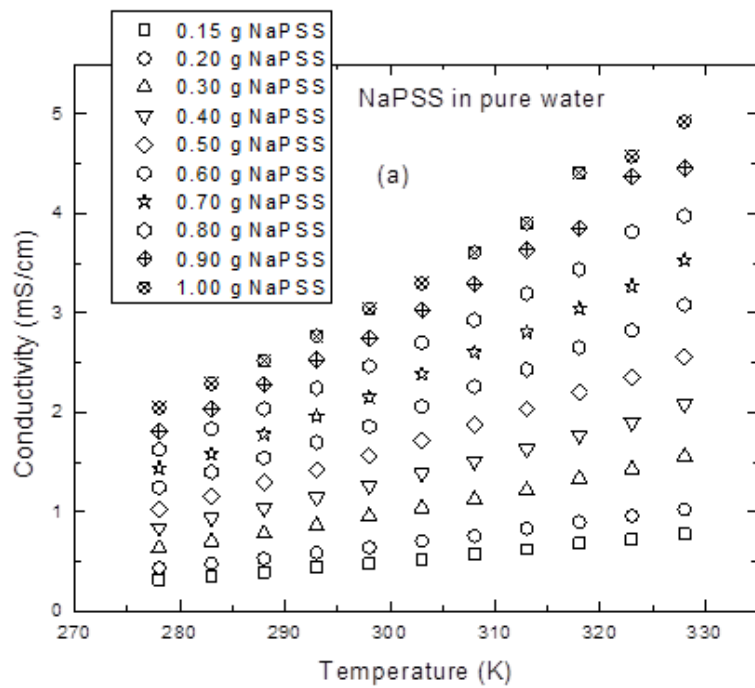


Figure 3.4(a+b). The NaPSS conductivity as a function of temperature

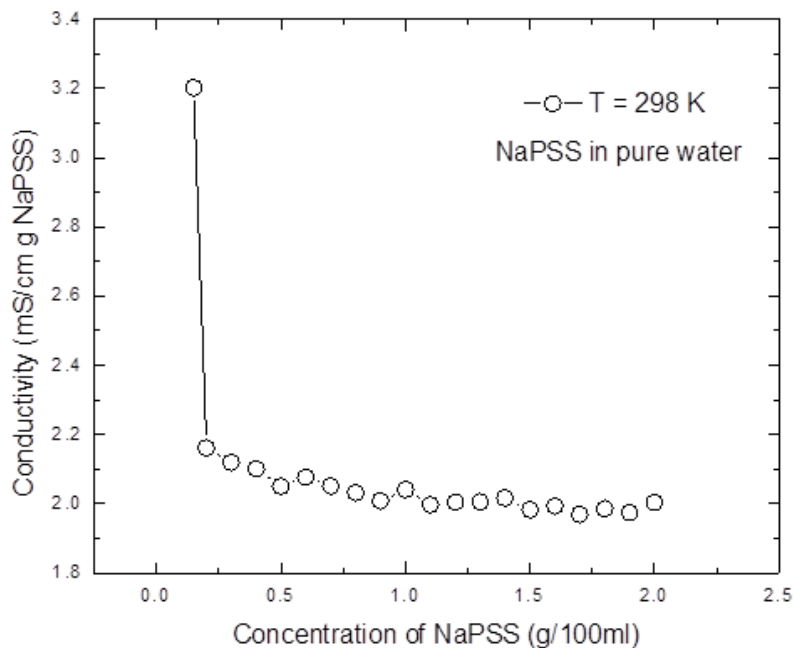


Figure 3.5. Concentration dependence of the conductivity per gram of NaPSS in pure water at 298. Open circle are experimental data and solid line is just drawn to guide the eye.

Szymczak et al [30] measured the conductivity of NaPSS in pure water at 298 K and found a similar behavior. However, their NaPSS has been prepared from polystyrene sulfonic acid. So in this case the behavior of conductivity per gram NaPSS can be compared rather than the exact conductivity values. The same order of magnitude of conductivity was found here as those found by Szymczak. The behavior of polyelectrolyte conductivity as a function of polyelectrolyte concentration cannot be explained as those of simple salt. In the absence of added salt, the electrical conductivities of dilute aqueous solutions of polyelectrolyte salts increase with decreasing polyelectrolyte concentration, slightly first followed by a rapid increase at higher dilutions. The increase in ionization of the polyelectrolytes with dilution of the solution by itself cannot explain the behaviour of the conductivity. But rather a well-defined charge fraction parameter that is independent on the concentration (the ratio of the number of counter-ions moving in the opposite direction in an electric field to the total number of counter-ions resulted from the dissociation of the polyelectrolyte) that plays a decisive role of the transport properties and thus conductivity of polyelectrolytes solutions [44]. A positive deviation from the limiting

law was found by Szymczak comparing theory with experiment. This behaviour was found even at low concentration. Manning [45] mentioned that the degree of coiling of the polyelectrolytes could have a huge effect on the polyelectrolytes. This is due to the influence of the frictional constant of the polyelectrolyte. At higher polyelectrolyte concentration there is coiling of the polyion which, might be responsible for the increase in the counter-ion mobility with increasing concentration [46]. It has been mentioned here that due to the strong electrostatic interactions between counter-ions in solution and charged groups on the polyelectrolyte chain, electrical transport properties of aqueous polyelectrolyte solutions, differ from their neutral polymer solutions and those of simple electrolytes [47-55].

The increase in NaPSS conductivity with temperature is definitely not simple to interpret. The contribution of the non-Coulombic forces to the thermodynamic quantities have been revealed by temperature effects and this have been observed in calorimetric studies of the same system [56]. Due to the temperature dependence of the viscosity of water, which is usually the solvent in most studies, significant influence of the temperature is to be expected and indeed have been found in the case of the transport properties in these systems. This also determines the ionic mobilities and hydrodynamic interactions, among ions [38].

3.1.3. Results for NaPSS in Salt Solutions

Temperature dependence of NaPSS conductivity in 0.1 M, 0.2 M, 0.3 M and 0.4 M NaCl solutions is shown in figures 3.6(a+b) – 3.9(a+b), respectively. These figures are also at different NaPSS concentration ranging from 0.15 g – 2.0 g NaPSS in 100 ml of distilled water. Also here the conductivity is seen to increase with increasing temperature, NaPSS concentration and the concentration of NaCl. The interaction between different polyelectrolytes, polycation and polyanion and sodium chloride in aqueous solutions have been investigated using electrical conductivity. The conductivity data in these studies was coupled with a developed model using the scaling description for the conformation of a polyion chain. It has been found that high level of counter-ion condensation takes place with decreasing polyelectrolyte concentration. The same trend was found for increasing temperature and increasing addition simple salt concentration. An increase in the dielectric constant of the solvent was caused by an increase in the concentration of the polyelectrolyte accompanied by a reduction in counter-ion condensation. Higher counter-ion condensation and dehydration of the counter-ions was found with increasing the temperature.

The role of the monomer size and its effective charge explained the variations of polyion equivalent conductivity with salt concentration, polyelectrolyte concentration and temperature.

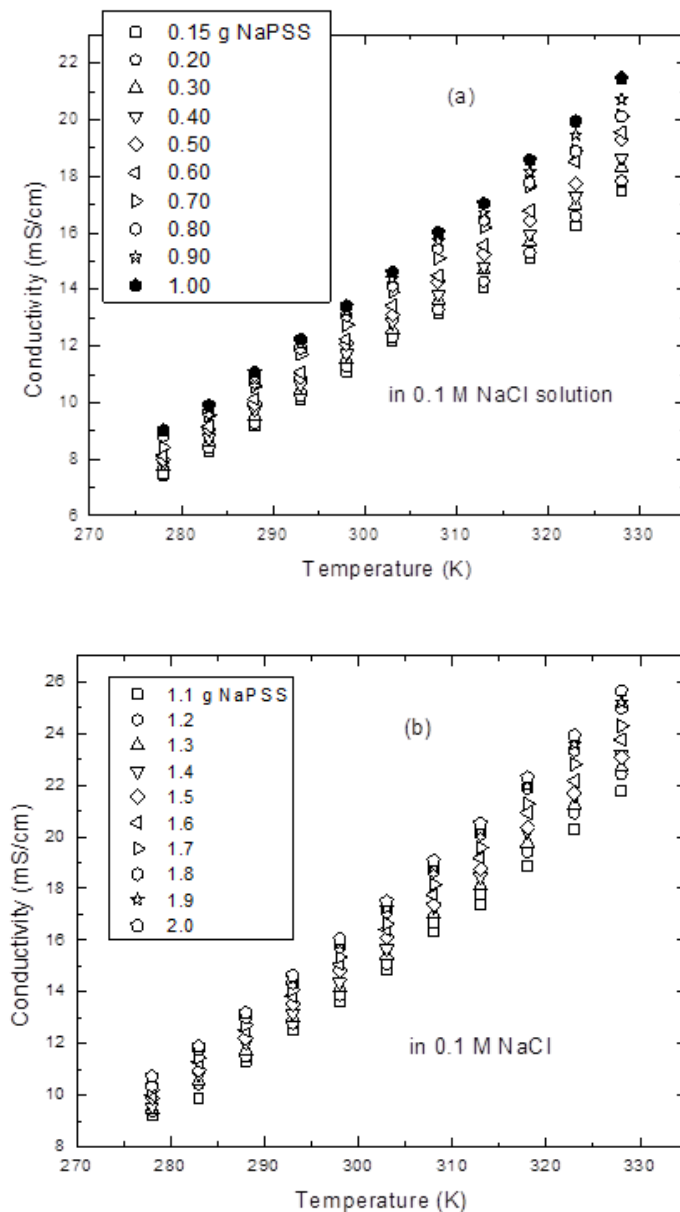


Figure 3.6. (a) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (0.15g – 1.0g NaPSS) in 0,1 M NaCl solutions. (b) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (1.0g – 2.0g NaPSS) in 0.1 M NaCl solutions.

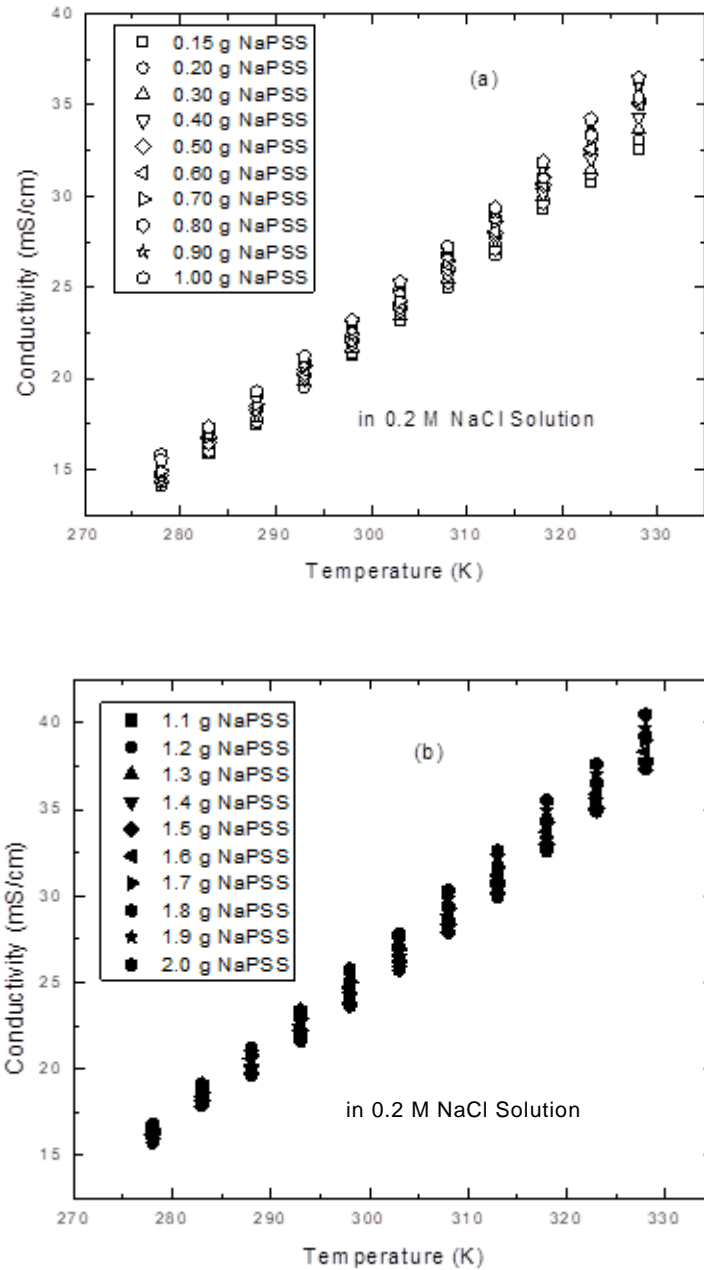


Figure 3.7. (a) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (0.15 g – 1.0 g NaPSS) in 0.2 M NaCl solutions. (b) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (1.0 g – 2.0 g NaPSS) in 0.2 M NaCl solutions.

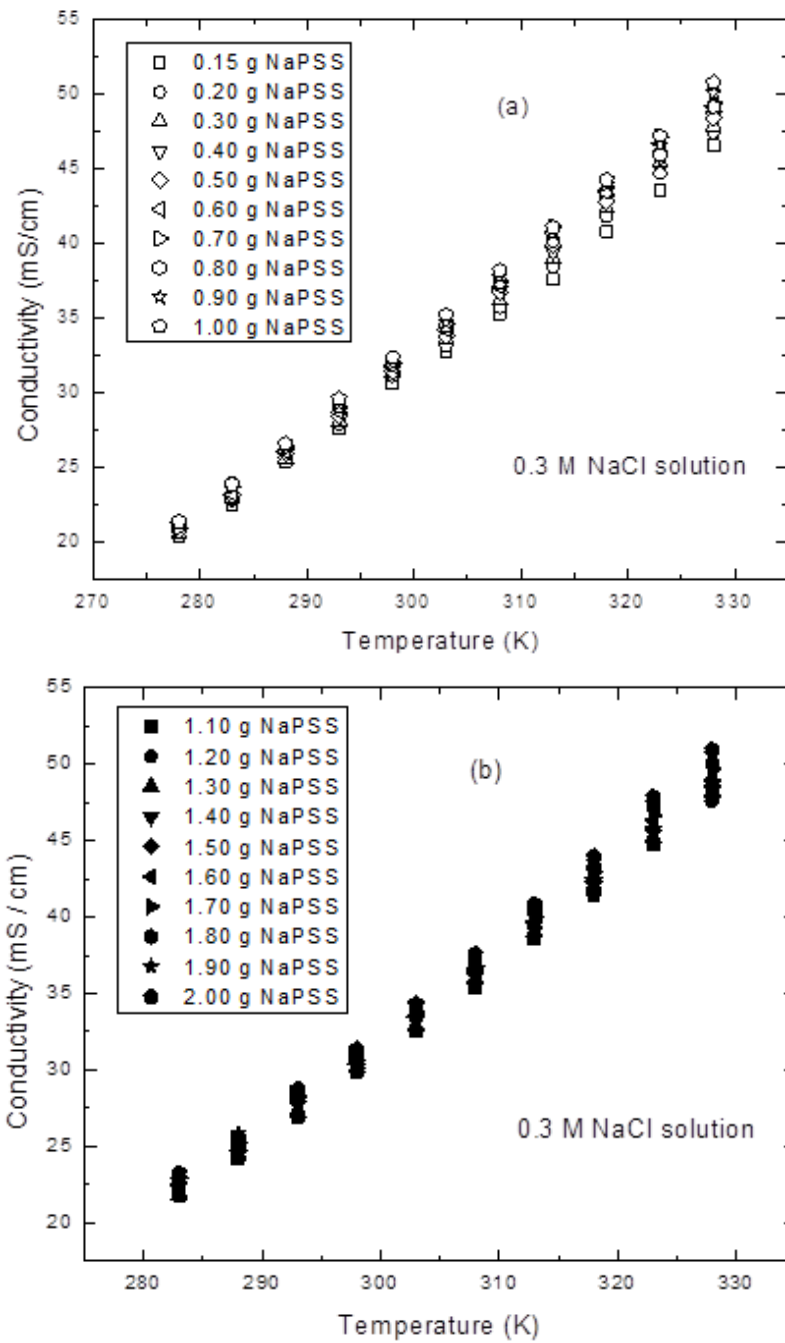


Figure 3.8. (a) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (0.15 g – 1.0 g NaPSS) in 0.3 M NaCl solutions. (b) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (1.0 g – 2.0 g NaPSS) in 0.3 M NaCl solutions.

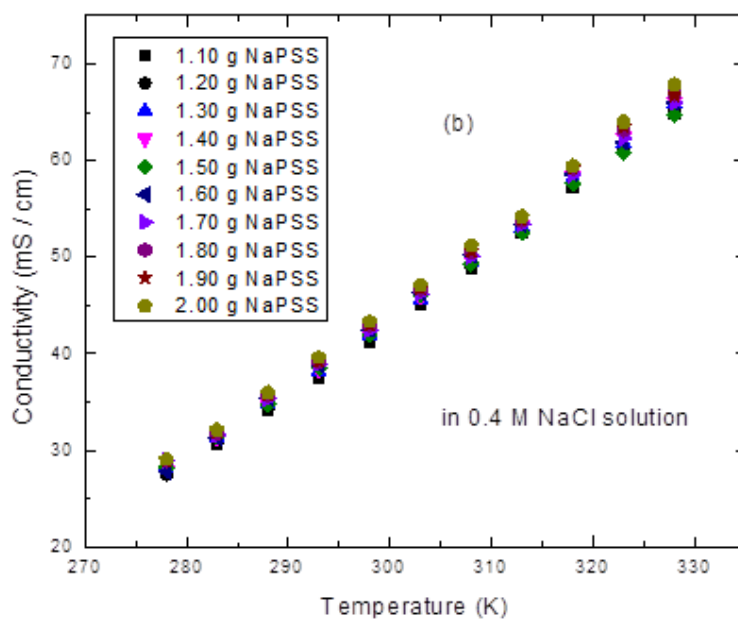
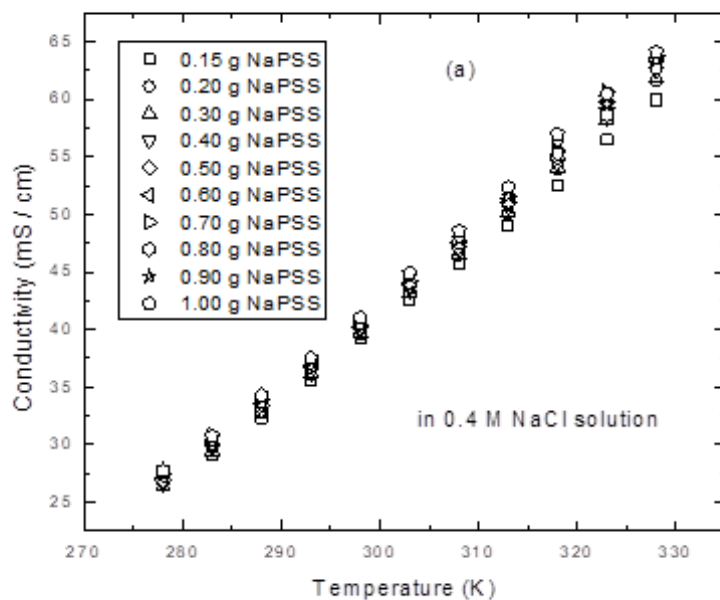


Figure 3.9. (a) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (0.15 g – 1.0 g NaPSS) in 0.4 M NaCl solutions. (b) Temperature dependence of NaPSS conductivity at different NaPSS concentrations (1.0 g – 2.0 g NaPSS) in 0.4 M NaCl solutions

In these systems, the charge effects govern the variation of the polyelectrolyte conductivity with the concentration of simple added salt. On the other hand, the size effect governs the variation of the polyelectrolyte conductivity with the concentration of the polyelectrolyte. Recently, Ranjit De [57] studied aqueous solutions of sodium polystyrene sulfonate in the presence of NaCl by electrical conductivity. The study meant to understand the interaction between counter-ions with the polyion. By an equation developed by them and by considering the scaling description for the conformation of a polyion chain, they analysed the specific conductivity versus polyelectrolyte concentration. They investigated the influences of added salt, polyelectrolyte concentration, temperature and molecular weight. Both, the concentration of the polyelectrolyte and its molecular weight were found to greatly influence counter-ion condensation. The molecular weight and the concentration of the polyelectrolyte was found to influence the extent of the counter-ion condensation. From Ranjit De study, information on the importance of the size and charge of the polyelectrolyte were provided by the conductivity measurements coupled with their derived friction coefficient (between the polyion monomer units and the solvent). The overall results have been elucidated taking the medium dielectric constant, the hydration behaviour of the counter-ions, and the coiling behaviour of the polyion chains into account. However, Ranjit De study has been carried out at only three different temperatures, namely at 298 K, 308 K and 318 K and at much lower NaCl concentrations namely, 0.0001 M, 0.001 M and 0.01 M NaCl. The work presented in this thesis work has extended the study to a wider NaPSS concentration, wider temperature ranges and more concentrated NaCl salt solution.

Going back to figures (3.6), (3.9), one can see that the difference in conductivity with increasing NaCl concentration becomes smaller with increasing NaPSS concentration. Figure 3.10 shows the NaPSS solutions conductivities as a function of temperature at different NaCl concentration for constant NaPSS concentration of 2.0 g NaPSS/100 ml solution. It is clearly seen that the conductivity increases with both temperature and increasing NaCl solution. Of course there is large contribution to the conductivity due to the presence of the salts. The reason for these effect can be explained by the same arguments mentioned above. This figure is presented to clarify the behaviour of conductivity with temperature and NaCl concentration.

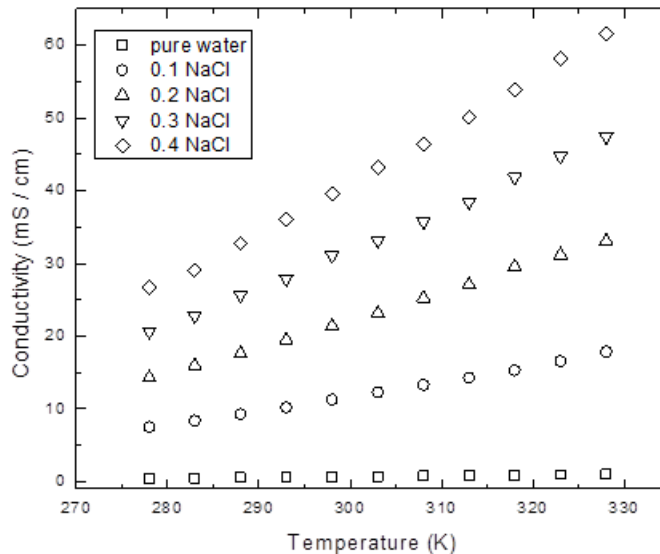


Figure 3.10. Temperature dependence of NaPSS solution conductivity at different NaCl concentration for a constant NaPSS concentration of 2.0 g NaPSS / 100 ml of distilled water.

Figure 3.11 shows the conductivity per gram of NaPSS as a function of NaPSS concentration at 298 K for NaPSS in pure water and in 0.1 M, 0.2 M, 0.3 M and 0.4 M NaCl as is indicated in the figure. The conductivity presented in this work is similar to the equivalent conductivity presented by Ranjit De [57]. The authors found the same trend of the conductivity as a function of polyanion concentration, though they carried out their measurements only at three different temperatures and at lower NaCl concentrations. Nevertheless, the general behaviour is the same in both cases and our conductivity behaviour is in consistent with their data. The general behaviour which talked about here is the following: in the beginning the conductivity decreases rapidly with increasing NaPSS concentration and then settles down and almost becomes constant at large concentration of NaPSS. However, our data show a more significant decrease in conductivity per gram NaCl than those presents by Ranijt De. Our conductivity curve is steeper than that of Ranijt. This is probably due to much higher NaCl concentration used in this work. Figure 3.12 shows NaPSS conductivity as a function of NaPSS concentration in pure water and in different NaCl solutions as is indicated in the figure at 298K.

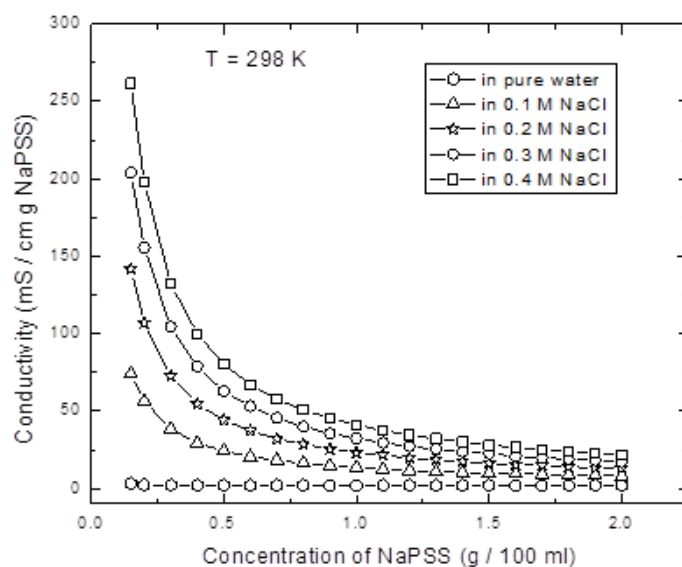


Figure 3.11. Conductivity per gram of NaPSS versus NaPSS concentration at different NaCl concentrations as indicated in the figure and at 298 K.

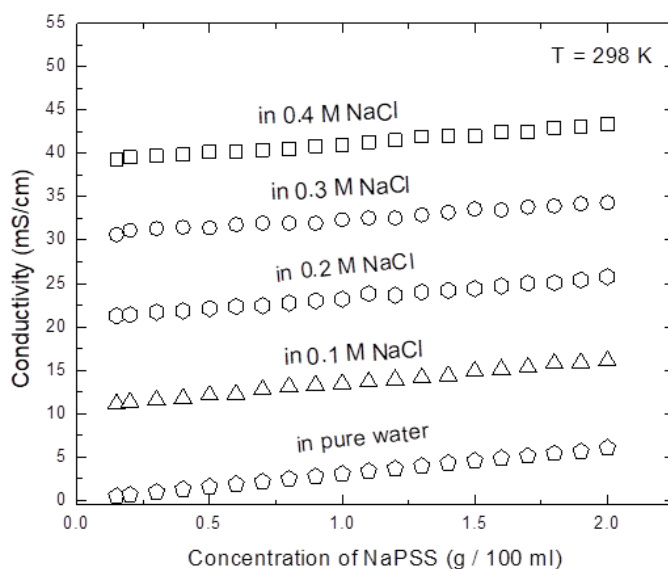


Figure 3.12. NaPSS conductivity as a function of NaPSS concentration in pure water and in different NaCl solutions as is indicated in the figure at 298 K. (zoom in view of fig 3.11).

As can be seen from the figure the presence of salt has a significant influence on the conductivity of NaPSS solutions as conductivity increases largely with increasing NaCl concentration. Polyelectrolyte conformation and polyelectrolyte-counter-ion interaction change when a salt is added. The previous effect will lead to a different degree of counter ion-condensation. In salt media, the dissociation of the counter-ions was found to be significantly reduced. Reduction of the counter-ion dissociation was found to occur at different temperatures. An observation was noticed through different studies on the polyelectrolytes solutions that the higher the temperature the higher the reduction in counter-ion dissociations. Through different studies mentioned in this thesis the polyelectrolyte-counter-ion interactions was largely influenced by the charge density along the polyelectrolyte chain. The charge density is greatly affected by the presence of added salt [58]. It has been claimed that the simple additivity given by:

$$k_{PS} = k_P + k_S \quad (6.1)$$

where k_{PS} is the conductivity of the polyelectrolyte in the presence of a salt, k_P is the conductivity of the polyelectrolyte in the absence of a salt and k_S is the conductivity of the salt without the polyelectrolyte, does not hold and therefore modification has to be applied [58]. This modification is given by:

$$k_{PS} = k_P + k_S \left(\frac{D_s}{D_s^0} \right) \quad (6.2)$$

where D_s is the diffusion coefficient of the co-ion in polyelectrolyte salt solution and D_s^0 is that in a salt solution as the salt concentration approaches zero. My data confirm this assumption and is represented by figure 3.13 which shows the conductivity of NaPSS solutions in pure water and that in pure water plus the conductivity of 0.1 M NaCl solution without NaPSS and the conductivity of NaPSS in 0.1 M NaCl. In fact, the additivity rule is valid at low polyelectrolyte solution and deviates at high polyelectrolyte concentration. My data result adds to the existing data in the literature that the higher the temperature and the higher the polyelectrolyte concentration the less the deviation from simple additivity rule. This is shown in figure 3.14 which shows the conductivity of NaPSS solutions in pure water and the conductivity of NaPSS in pure water plus the conductivity of 0.1 M NaCl without the NaPSS, at two temperatures of 298 K and 323 K, respectively. It is clearly seen that as the temperature increases the difference between the conductivity of NaPSS solutions and that of the conductivity of NaPSS + the

conductivity of the 0.1 M NaCl becomes smaller. It is also interesting to note (in figure 3.14) that the conductivity of NaPSS solutions in pure water increases as temperature increases at higher NaPSS concentrations. This is represented in figure 3.14 by the solid and open circles.

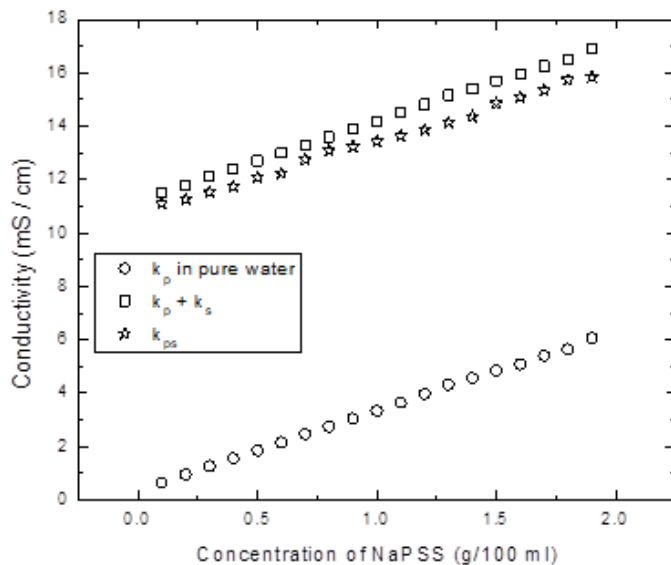


Figure 3.13. The conductivity of NaPSS solutions in pure water (k_p), conductivity of NaPSS + the conductivity of the 0.1 M NaCl in pure water ($k_p + k_s$) and the conductivity of NaPSS in 0.1 M NaCl at 298K.

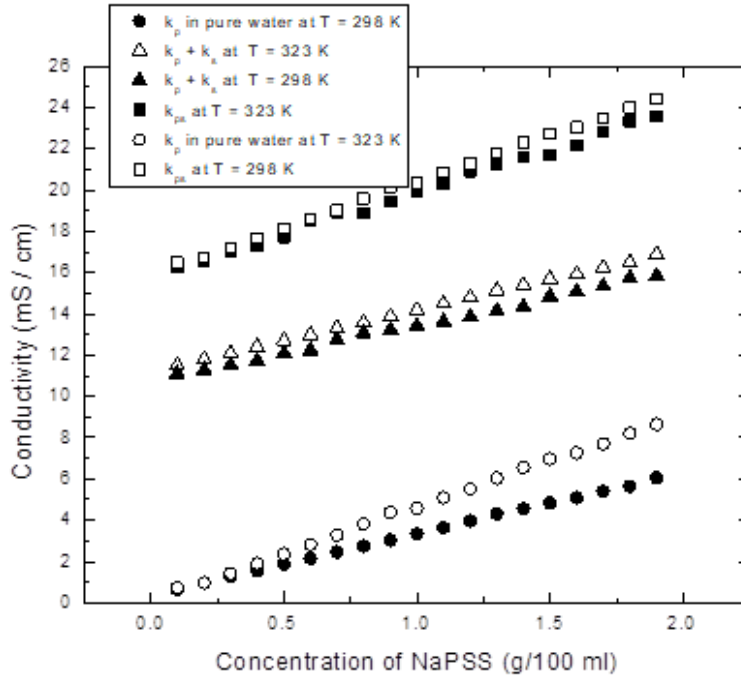


Figure 3.14. The conductivity of NaPSS solutions in pure water (k_p), conductivity of NaPSS + the conductivity of the 0.1 M NaCl without NaPSS ($k_p + k_s$) and the conductivity of NaPSS in 0.1 M NaCl, (k_{ps}) at 298 K and 323 K.

One of the interesting results in this thesis work are the results shown in figure 3.15 which shows the conductivity of NaPSS in pure water and in different NaCl concentration where the conductivity of the NaCl salt was subtracted. This figure is different from figure 3.14 and in fact summarises our results in this thesis work. In this figure what is drawn is the pure contribution of the conductivity due to the presence of the polyelectrolyte only. That is, this figure gives an indication of the transport of charge by the polyelectrolyte in salt free environment in comparison to its ability in presence of salt.

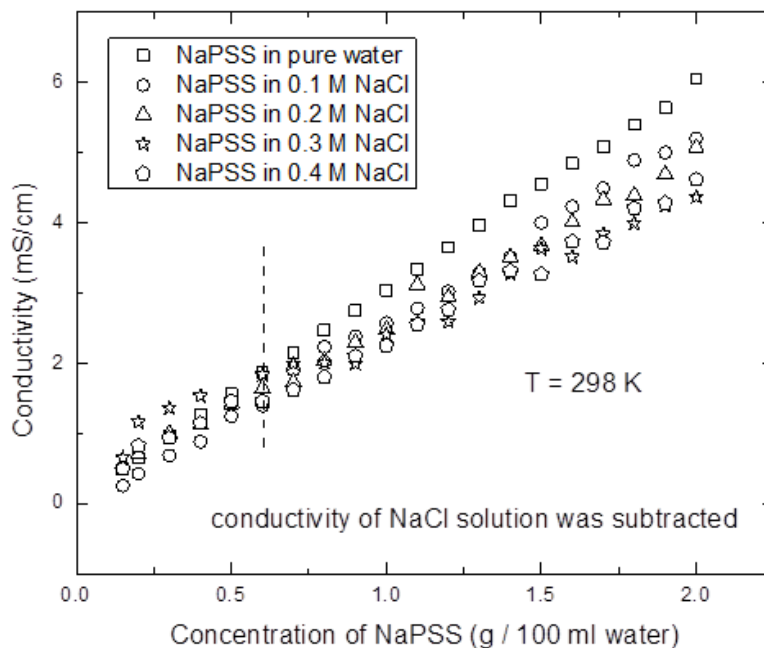


Figure 3.15. The conductivity of NaPSS in pure water and in different NaCl concentrations where the conductivity of the NaCl salt was subtracted at 298 K.

This interesting result shows that NaPSS is better able to transport charge when no salt is present. That is in pure water. The conformation of the polyion in pure water differs substantially from its conformation in salt solutions. In pure water it has an extended conformation due to charge-charge repulsion on its back bone while in the presence of salt this repulsion is screened. It seems that the salt hinders the ability of the polyion in transporting charges while this crippling effect does not exist in pure water. In addition, it seems that the polyion-salt interactions plays very important role in charge transport phenomena of polyelectrolyte solutions. What is also interesting to note in figure 3.15 is that the higher the salt concentration the lower the ability of the polyion to transport charges. This is clearly seen when comparing open stars with open circles in the figure. To add more to this interesting result, we claim that the higher the salt concentration the higher the polyion-salt interaction and the more of this crippling effect. It is also interesting to note in figure 3.15 is that when one compares the open circles and open stars below the vertical dashed line at low NaPSS concentration then an opposite effect is observed. That is at low NaPSS concentration the contribution of NaPSS to the conductivity of the solution

is higher in the salt solution than in salt free solution and that this contribution increases with increasing salt concentration. To make things more clear let's compare values of the conductivity. Table 3.1 shows a comparison between conductivity values at two different NaPSS concentration of 0.3 g/100 ml and 2.0 g /100 ml and two different NaCl concentrations. This table confirms the previous discussion.

Table 3.1. Comparison of conductivity values at two different NaPSS concentrations and two NaCl Concentrations.

NaPSS concentration (g/100 ml)	0.3		2.0	
NaCl concentration (M)	0.10	0.30	0.10	0.30
Conductivity (mS/ cm)	0.66	1.34	5.20	4.36

It has to be remembered that the accuracy of the conductivity meter is very high and is less than 1% so the values of conductivity in table 3.1. reflect this accuracy.

4. Conclusions

In this thesis work the conductivity of NaPSS solutions was studied as a function of temperature, NaPSS concentration and NaCl salt concentration. It is found that:

1. Conductivity of NaPSS increases with increasing temperature. This increase can be explained by many factors. One is the decrease in the solution viscosity with increasing temperature, which lead to increase in mobility of the conducting species. The other is the increase in energy of the conducting species with increasing temperature which enhances the mobility of the conducting species. A third factor is the decrease in the fraction of free counter-ions. At higher temperatures, there will be a gradual dehydration of the counter-ions and more dissociated sites on the polyelectrolyte chain. These combined effects result in more counter-ion condensation. In addition, and as the temperature is raised there will be higher electrostatic attraction between the surface charges on the polyion

and the dehydrated. At higher temperatures, there will be lower degree of counter-ion condensation.

2. The conductivity increases with increasing NaPSS concentration. An increase in polyelectrolyte concentration will cause an increase in the dielectric constant of the solvent and this in turn will cause a decrease in the Bjerrum length. The length scale between the dissociated sites on the polyelectrolyte is set by the value of the Bjerrum length. This increase in the dielectric constant of the solvent will lead to lower counter-ion condensation. At higher polyion concentration this effect is more important.
3. The polyion conductivity is found to increase as the concentration of the added salt increases. Counter-ion condensation is higher as the salt concentration is higher and there will be also less effective charge on the monomer.
4. The contribution of the polyion to the solution conductivity is more in pure than in salt solution only at high NaPSS concentration. At very low NaPSS concentration its contribution is less in pure water and higher at higher NaCl concentration.
5. The additivity rule: that the conductivity of the polyelectrolyte in salt solution is equal to the sum of its conductivity in pure water plus the conductivity of the salt alone is not valid at high NaPSS while it is valid only at low NaPSS concentration.
6. The conductivity of NaPSS in water is higher at higher temperatures only at high NaPSS concentration. At very low NaPSS concentrations the temperature effect is weak.

5. References

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Table1. Conductivity of NaCl in Pure Water

% Error = The uncertainty of conductivity meter(0.01) × conductivity value

0.1 NaCl			0.2 NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	7.496	0.07496	278	13.92	0.1392
278	8.222	0.08222	278	15.51	0.1551
288	9.104	0.09104	288	17.23	0.1723
293	9.94	0.0994	293	18.84	0.1884
298	10.85	0.1085	298	20.7	0.207
303	11.84	0.1184	303	22.77	0.2277
308	12.82	0.1282	308	24.58	0.2458
313	13.59	0.1359	313	26.21	0.2621
318	14.78	0.1478	318	28.59	0.2859
323	15.77	0.1577	323	30.56	0.3056
328	16.83	0.1683	328	32.53	0.3253

0.3 NaCl			0.4 NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	20.28	0.2028	278	26.69	0.2669
278	22.52	0.2252	278	29.62	0.2962
288	25.05	0.2505	288	32.42	0.3252
293	27.37	0.2737	293	35.62	0.3562
298	29.95	0.2995	298	38.74	0.3874
303	33.36	0.3336	303	42.93	0.4293
308	35.92	0.3592	308	46.69	0.4669
313	38.8	0.388	313	50.74	0.5074
318	41.64	0.4164	318	53.8	0.538
323	44.63	0.4463	323	57.95	0.5795
328	47.09	0.4709	328	60.15	0.6015

Tables 2. Conductivity of NaPSS in Pure Water.

0.15gm NaPSS			0.2gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	318.8	3.188	278	432.2	4.322
278	356	3.56	278	479.3	4.793
288	395.4	3.954	288	528	5.28
293	438.3	4.383	293	584.4	5.844
298	480.4	4.804	298	642.4	6.424
303	523.6	5.236	303	703.5	7.035
308	573.2	5.732	308	756.6	7.566
313	618.8	6.188	313	828.9	8.289
318	678.4	6.784	318	896.4	8.964
323	722.1	7.221	323	958.1	9.581
328	772.5	7.725	328	1021	10.21

0.3gm NaPSS			0.4gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	635.8	6.358	278	840.4	8.404
278	702.5	7.025	278	936.6	9.366
288	780	7.8	288	1038	10.38
293	861.8	8.618	293	1140	11.4
298	955.8	9.558	298	1261	12.61
303	1038	10.38	303	1387	13.87
308	1125	11.25	308	1508	15.08
313	1214	12.14	313	1629	16.29
318	1334	13.34	318	1768	17.68
323	1427	14.27	323	1896	18.96
328	1555	15.55	328	2081	20.81

0.5gm NaPSS			0.6gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	1025	10.25	278	1246	12.46
278	1154	11.54	278	1399	13.99
288	1292	12.92	288	1543	15.43
293	1418	14.18	293	1699	16.99
298	1558	15.58	298	1858	18.58
303	1714	17.14	303	2061	20.61
308	1873	18.73	308	2259	22.59
313	2032	20.32	313	2431	24.31
318	2200	22	318	2651	26.51
323	2351	23.51	323	2825	28.25
328	2557	25.57	328	3079	30.79

0.7gm NaPSS			0.8gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	1436	14.36	278	1626	16.26
278	1585	15.85	278	1833	18.33
288	1778	17.78	288	2036	20.36
293	1957	19.57	293	2246	22.46
298	2149	21.49	298	2463	24.63
303	2384	23.84	303	2701	27.01
308	2604	26.04	308	2926	29.26
313	2805	28.05	313	3195	31.95
318	3043	30.43	318	3436	34.36
323	3268	32.68	323	3817	38.17
328	3528	35.28	328	3976	39.76

0.9gm NaPSS			1.0gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	1808	18.08	278	2041	20.41
278	2038	20.38	278	2287	22.87
288	2278	22.78	288	2517	25.17
293	2527	25.27	293	2766	27.66
298	2743	27.43	298	3040	30.4
303	3034	30.34	303	3297	32.97
308	3291	32.91	308	3610	36.1
313	3636	36.36	313	3895	38.95
318	3850	38.5	318	4407	44.07
323	4374	43.74	323	4570	45.7
328	4456	44.56	328	4921	49.21

1.1gm NaPSS			1.2gm NaPSS		
Temp(K)	Cond(μs)	% Error \pm	Temp(K)	Cond(μs)	% Error \pm
278	2197	21.97	278	2406	24.06
278	2520	25.2	278	2735	27.35
288	2772	27.72	288	3044	30.44
293	3031	30.31	293	3309	33.09
298	3342	33.42	298	3647	36.47
303	3631	36.31	303	3953	39.53
308	4049	40.49	308	4436	44.36
313	4340	43.4	313	4750	47.5
318	4828	48.28	318	5182	51.82
323	5091	50.91	323	5526	55.26
328	5441	54.41	328	5963	59.63

1.3gm NaPSS			1.4gm NaPSS		
Temp(K)	Cond(μ s)	% Error \pm	Temp(K)	Cond(μ s)	% Error \pm
278	2608	26.08	278	2824	28.24
278	2936	29.36	278	3201	32.01
288	3287	32.87	288	3543	35.43
293	3583	35.83	293	3857	38.57
298	3969	39.69	298	4308	43.08
303	4309	43.09	303	4726	47.26
308	4778	47.78	308	5109	51.09
313	5111	51.11	313	5539	55.39
318	5623	56.23	318	6063	60.63
323	6039	60.39	323	6551	65.51
328	6465	64.65	328	7004	70.04

1.5gm NaPSS			1.6gm NaPSS		
Temp(K)	Cond(μ s)	% Error \pm	Temp(K)	Cond(μ s)	% Error \pm
278	2974	29.74	278	3191	31.91
278	3432	34.32	278	3610	36.1
288	3799	37.99	288	4030	40.3
293	4140	41.4	293	4414	44.14
298	4557	45.57	298	4845	48.45
303	4922	49.22	303	5272	52.72
308	5456	54.56	308	5756	57.56
313	5829	58.29	313	6244	62.44
318	6478	64.78	318	6780	67.8
323	6956	69.56	323	7266	72.66
328	7350	73.5	328	7841	78.41

1.7gm NaPSS			1.8gm NaPSS		
Temp(K)	Cond(μ s)	% Error \pm	Temp(K)	Cond(μ s)	% Error \pm
278	3348	33.48	278	3575	35.75
278	3789	37.89	278	4042	40.42
288	4202	42.02	288	4433	44.33
293	4608	46.08	293	4893	48.93
298	5084	50.84	298	5396	53.96
303	5541	55.41	303	5883	58.83
308	6063	60.63	308	6456	64.56
313	6591	65.91	313	7011	70.11
318	7128	71.28	318	7642	76.42
323	7706	77.06	323	8220	82.2
328	8316	83.16	328	8866	88.66

1.9gm NaPSS			2.0gm NaPSS		
Temp(K)	Cond(μ s)	% Error \pm	Temp(K)	Cond(μ s)	% Error \pm
278	3753	37.53	278	4008	40.08
278	4222	42.22	278	4444	44.44
288	4688	46.88	288	4931	49.31
293	5128	51.28	293	5482	54.82
298	5635	56.35	298	6051	60.51
303	6196	61.96	303	6665	66.65
308	6763	67.63	308	7197	71.97
313	7364	73.64	313	7885	78.85
318	8018	80.18	318	8588	85.88
323	8637	86.37	323	9221	92.21
328	9293	92.93	328	9963	99.63

Tables 3. Conductivity of NaPSS in 0.1 NaCl

0.15 NaPSS\0.1NaCl			0.2 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	7.441	0.0744	278	7.484	0.0748
278	8.271	0.0827	278	8.392	0.0839
288	9.152	0.0915	288	9.284	0.0928
293	10.12	0.1012	293	10.24	0.1024
298	11.1	0.111	298	11.27	0.1127
303	12.16	0.1216	303	12.31	0.1231
308	13.13	0.1313	308	13.3	0.133
313	14.06	0.1406	313	14.28	0.1428
318	15.12	0.1512	318	15.31	0.1531
323	16.25	0.1625	323	16.59	0.1659
328	17.48	0.1748	328	17.84	0.1784

0.3 PSS\0.1NaCl			0.4 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	7.732	0.0773	278	7.859	0.0785
278	8.611	0.0861	278	8.752	0.0875
288	9.532	0.0953	288	9.744	0.0974
293	10.46	0.1046	293	10.63	0.1063
298	11.53	0.1153	298	11.73	0.1173
303	12.58	0.1258	303	12.84	0.1284
308	13.62	0.1362	308	13.82	0.1382
313	14.69	0.1469	313	14.83	0.1483
318	15.69	0.1569	318	15.98	0.1598
323	16.99	0.1699	323	17.3	0.173
328	18.34	0.1834	328	18.66	0.1866

0.5 PSS\0.1NaCl			0.6 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	7.99	0.0799	278	8.142	0.0814
278	9.031	0.0903	278	9.164	0.0916
288	9.967	0.0996	288	10.13	0.1013
293	10.9	0.109	293	11.07	0.1107
298	12.09	0.1209	298	12.24	0.1224
303	13.12	0.1312	303	13.43	0.1343
308	14.28	0.1428	308	14.5	0.145
313	15.26	0.1526	313	15.57	0.1557
318	16.44	0.1644	318	16.79	0.1679
323	17.73	0.1773	323	18.53	0.1853
328	19.3	0.193	328	19.57	0.1957

0.7 PSS\0.1NaCl			0.8 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	8.415	0.0841	278	8.811	0.0881
278	9.552	0.0955	278	9.643	0.0964
288	10.59	0.1059	288	10.72	0.1072
293	11.71	0.1171	293	11.92	0.1192
298	12.75	0.1275	298	13.08	0.1308
303	13.92	0.1392	303	14.14	0.1414
308	15.11	0.1511	308	15.46	0.1546
313	16.2	0.162	313	16.46	0.1646
318	17.66	0.1766	318	17.78	0.1778
323	18.92	0.1892	323	18.9	0.189
328	20.15	0.2015	328	20.14	0.2014

0.9 PSS\0.1NaCl			1.0 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	8.991	0.0899	278	9.029	0.0902
278	9.795	0.0979	278	9.905	0.099
288	10.82	0.1082	288	11.08	0.1108
293	12.09	0.1209	293	12.24	0.1224
298	13.23	0.1323	298	13.42	0.1342
303	14.39	0.1439	303	14.61	0.1461
308	15.72	0.1572	308	16.02	0.1602
313	16.72	0.1672	313	17.05	0.1705
318	18.16	0.1816	318	18.6	0.186
323	19.46	0.1946	323	19.96	0.1996
328	20.74	0.2074	328	21.48	0.2148

1.1 PSS\0.1NaCl			1.2 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	9.204	0.092	278	9.376	0.0937
278	9.879	0.0987	278	10.42	0.1042
288	11.31	0.1131	288	11.48	0.1148
293	12.51	0.1251	293	12.77	0.1277
298	13.63	0.1363	298	13.87	0.1387
303	14.85	0.1485	303	15.06	0.1506
308	16.31	0.1631	308	16.67	0.1667
313	17.38	0.1738	313	17.76	0.1776
318	18.88	0.1888	318	19.4	0.194
323	20.3	0.203	323	20.91	0.2091
328	21.77	0.2177	328	22.42	0.2242

1.3 PSS\0.1NaCl			1.4 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	9.443	0.0944	278	9.562	0.0956
278	10.52	0.1052	278	10.8	0.108
288	11.72	0.1172	288	12.03	0.1203
293	12.98	0.1298	293	13.16	0.1316
298	14.14	0.1414	298	14.36	0.1436
303	15.41	0.1541	303	15.66	0.1566
308	17	0.17	308	17.31	0.1731
313	18.11	0.1811	313	18.46	0.1846
318	19.77	0.1977	318	20.22	0.2022
323	21.24	0.2124	323	21.59	0.2159
328	22.68	0.2268	328	23.19	0.2319

1.5 PSS\0.1NaCl			1.6 PSS\0.1NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	9.896	0.0989	278	9.999	0.0999
278	10.96	0.1096	278	11.29	0.1129
288	12.21	0.1221	288	12.51	0.1251
293	13.53	0.1353	293	13.83	0.1383
298	14.85	0.1485	298	15.08	0.1508
303	16.1	0.161	303	16.41	0.1641
308	17.37	0.1737	308	17.75	0.1775
313	18.75	0.1875	313	19.18	0.1918
318	20.36	0.2036	318	20.93	0.2093
323	21.69	0.2169	323	22.17	0.2217
328	23.07	0.2307	328	23.77	0.2377

1.7 PSS\0.1NaCl			1.8 PSS\0.1NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	10.21	0.1021	278	10.37	0.1037
278	11.45	0.1145	278	11.77	0.1177
288	12.72	0.1272	288	13.02	0.1302
293	14.08	0.1408	293	14.35	0.1435
298	15.34	0.1534	298	15.74	0.1574
303	16.63	0.1663	303	17.09	0.1709
308	18.15	0.1815	308	18.67	0.1867
313	19.58	0.1958	313	20.11	0.2011
318	21.28	0.2128	318	21.88	0.2188
323	22.82	0.2282	323	23.34	0.2334
328	24.3	0.243	328	24.99	0.2499

1.9 PSS\0.1NaCl			2.0 PSS\0.1NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	10.68	0.1068	278	10.72	0.1072
278	11.85	0.1185	278	11.89	0.1189
288	13.17	0.1317	288	13.2	0.132
293	14.49	0.1449	293	14.64	0.1464
298	15.85	0.1585	298	16.05	0.1605
303	17.24	0.1724	303	17.49	0.1749
308	18.82	0.1882	308	19.08	0.1908
313	20.25	0.2025	313	20.52	0.2052
318	21.98	0.2198	318	22.3	0.223
323	23.58	0.2358	323	23.93	0.2393
328	25.21	0.2521	328	25.65	0.2565

Tables 4. Conductivity of NaPSS in 0.2 NaCl

0.1 PSS\0.2NaCl			0.2 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	14.15	0.1415	278	14.29	0.1429
278	15.88	0.1588	278	15.98	0.1598
288	17.48	0.1748	288	17.61	0.1761
293	19.6	0.196	293	19.5	0.195
298	21.26	0.2126	298	21.4	0.214
303	23.13	0.2313	303	23.17	0.2317
308	25	0.25	308	25.24	0.2524
313	26.81	0.2681	313	27.05	0.2705
318	29.29	0.2929	318	29.59	0.2959
323	30.81	0.3018	323	31.19	0.3119
328	32.57	0.3257	328	33.09	0.3309

0.3 PSS\0.2NaCl			0.4 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	14.52	0.1452	278	14.47	0.1447
278	16.34	0.1634	278	16.48	0.1648
288	17.89	0.1789	288	18.05	0.1805
293	19.81	0.1981	293	19.97	0.1997
298	21.7	0.217	298	21.83	0.2183
303	23.4	0.234	303	23.59	0.2359
308	25.46	0.2546	308	25.64	0.2564
313	27.49	0.2749	313	27.64	0.2764
318	29.99	0.2999	318	30.17	0.3017
323	31.43	0.3143	323	32.05	0.3205
328	33.64	0.3364	328	34.35	0.3435

0.5 PSS\0.2NaCl			0.6 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	14.68	0.1468	278	14.82	0.1482
278	16.44	0.1644	278	16.84	0.1684
288	18.31	0.1813	288	18.49	0.1849
293	20.25	0.2025	293	20.47	0.2047
298	22.12	0.2212	298	22.34	0.2234
303	23.9	0.239	303	24.12	0.2412
308	26.01	0.2601	308	26.25	0.2625
313	28	0.28	313	28.06	0.2806
318	30.63	0.3063	318	30.66	0.3066
323	32.57	0.3257	323	32.61	0.3261
328	35.11	0.3511	328	35.12	0.3512

0.7 PSS\0.2NaCl			0.8 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	14.92	0.1492	278	15.82	0.1582
278	16.81	0.1618	278	17.02	0.1702
288	18.55	0.1855	288	19.02	0.1902
293	20.65	0.2065	293	20.88	0.2088
298	22.43	0.2243	298	22.74	0.2274
303	24.26	0.2426	303	24.8	0.284
308	26.45	0.2645	308	26.76	0.2676
313	28.58	0.2858	313	28.83	0.2883
318	31.07	0.3107	318	31.03	0.3103
323	33.1	0.331	323	33.33	0.3333
328	35.29	0.3529	328	35.41	0.3541

0.9 PSS\0.2NaCl			1.0 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	15.38	0.1538	278	15.52	0.1552
278	17.2	0.172	278	17.33	0.1733
288	19.24	0.1924	288	19.28	0.1928
293	21.06	0.2106	293	21.2	0.212
298	22.99	0.2299	298	23.18	0.2318
303	25.05	0.2505	303	25.3	0.253
308	27.02	0.2702	308	27.24	0.2724
313	29.08	0.2908	313	29.36	0.2936
318	31.45	0.3145	318	31.89	0.3189
323	33.96	0.3396	323	34.22	0.3422
328	36.03	0.3603	328	36.5	0.365

1.1 PSS\0.2NaCl			1.2 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	15.85	0.1585	278	15.73	0.1573
278	18.05	0.1805	278	17.9	0.179
288	19.91	0.1991	288	19.63	0.1963
293	21.77	0.2177	293	21.6	0.216
298	23.82	0.2382	298	23.64	0.2364
303	25.96	0.2596	303	25.72	0.2572
308	28.07	0.2807	308	27.87	0.2787
313	30.14	0.3014	313	29.92	0.2992
318	32.86	0.3286	318	32.6	0.326
323	35.23	0.3523	323	34.87	0.3487
328	37.44	0.3744	328	37.34	0.3734

1.3 PSS\0.2NaCl			1.4 PSS\0.2NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	16.17	0.1617	278	16.33	0.1633
278	18.01	0.1801	278	18.13	0.1813
288	19.97	0.1997	288	20.06	0.2006
293	21.9	0.219	293	22.08	0.2208
298	24	0.24	298	24.21	0.2421
303	26.11	0.2611	303	26.34	0.2634
308	28.12	0.2812	308	28.42	0.2842
313	30.38	0.3038	313	30.63	0.3063
318	32.94	0.3294	318	33.27	0.3327
323	35.19	0.3519	323	35.47	0.3547
328	37.51	0.3751	328	37.7	0.377

1.5 PSS\0.2NaCl			1.6 PSS\0.2NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	16.23	0.1623	278	16.23	0.1623
278	18.17	0.1817	278	18.17	0.1817
288	20.13	0.2013	288	20.61	0.2061
293	22.23	0.2223	293	22.55	0.2255
298	24.38	0.2438	298	24.71	0.2471
303	26.21	0.2621	303	26.58	0.2658
308	28.36	0.2836	308	28.91	0.2891
313	30.63	0.3063	313	31.18	0.3118
318	32.99	0.3299	318	33.7	0.337
323	35.07	0.3507	323	35.88	0.3588
328	37.68	0.3768	328	38.34	0.3834

1.7 PSS\0.2NaCl			1.8 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	16.38	0.1638	278	16.44	0.1644
278	18.65	0.1865	278	18.52	0.1852
288	20.8	0.208	288	20.8	0.208
293	22.89	0.2289	293	22.99	0.2299
298	25.03	0.2503	298	25.09	0.2509
303	26.94	0.2694	303	27.03	0.2703
308	29.3	0.293	308	29.41	0.2941
313	31.62	0.3162	313	31.78	0.3178
318	34.3	0.343	318	34.36	0.3436
323	36.52	0.3652	323	36.53	0.3653
328	39.04	0.3904	328	39.28	0.3928

1.9 PSS\0.2NaCl			2.0 PSS\0.2NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	16.64	0.1664	278	16.8	0.168
278	18.72	0.1872	278	19.15	0.1915
288	20.93	0.2093	288	21.2	0.212
293	23.17	0.2317	293	23.41	0.2341
298	25.39	0.2539	298	25.78	0.2578
303	27.39	0.2739	303	27.82	0.2782
308	29.81	0.2981	308	30.32	0.3032
313	32.25	0.3225	313	32.63	0.3263
318	34.92	0.3492	318	35.53	0.3553
323	37.03	0.3703	323	37.62	0.3762
328	39.7	0.397	328	40.5	0.405

Tables 5. Conductivity of NaPSS in 0.3 NaCl

0.1 PSS\0.3NaCl			0.2 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	20.37	0.2037	278	20.67	0.2067
278	22.51	0.2251	278	22.81	0.2281
288	25.39	0.2539	288	25.63	0.2563
293	27.56	0.2756	293	27.9	0.279
298	30.6	0.306	298	31.11	0.3111
303	32.75	0.3275	303	33.15	0.3315
308	35.25	0.3525	308	35.73	0.3573
313	37.59	0.3759	313	38.46	0.3846
318	40.79	0.4079	318	41.82	0.4182
323	43.59	0.4359	323	44.7	0.447
328	46.53	0.4653	328	47.42	0.4742

0.3 PSS\0.3NaCl			0.4 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	20.53	0.2053	278	20.75	0.2075
278	22.89	0.2289	278	23.01	0.2301
288	25.56	0.2556	288	25.91	0.2591
293	28.09	0.2809	293	28.36	0.2836
298	31.31	0.3131	298	31.48	0.3148
303	33.53	0.3353	303	33.95	0.3395
308	36.18	0.3618	308	36.8	0.368
313	38.92	0.3892	313	39.44	0.3944
318	42.34	0.4234	318	42.94	0.4294
323	45.4	0.454	323	45.79	0.4579
328	47.85	0.4785	328	48.56	0.4856

0.5 PSS\0.3NaCl			0.6 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	20.73	0.2073	278	21.26	0.2126
278	23.16	0.2316	278	23.19	0.2319
288	25.9	0.259	288	26.03	0.2603
293	28.4	0.284	293	28.7	0.287
298	31.41	0.3141	298	31.78	0.3178
303	33.81	0.3381	303	34.21	0.3421
308	36.75	0.3675	308	37.09	0.3709
313	39.84	0.3984	313	40.69	0.4069
318	42.8	0.428	318	43.49	0.4349
323	46.09	0.4609	323	46.68	0.4668
328	48.37	0.4837	328	49.19	0.4919

0.7 PSS\0.3NaCl			0.8 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	20.94	0.2094	278	21.32	0.2132
278	23.74	0.2374	278	23.92	0.2392
288	26.41	0.2641	288	26.41	0.2641
293	29.05	0.2905	293	29.12	0.2912
298	31.94	0.3194	298	31.95	0.3195
303	34.57	0.3457	303	34.48	0.3448
308	37.45	0.3745	308	37.41	0.3741
313	41.09	0.4109	313	40.2	0.402
318	43.73	0.4373	318	43.52	0.4352
323	47.12	0.4712	323	45.95	0.4595
328	49.39	0.4939	328	49.15	0.4915

0.9 PSS\0.3NaCl			1.0 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	21.28	0.2128	278	21.38	0.2138
278	23.74	0.2374	278	23.88	0.2388
288	26.35	0.2635	288	26.58	0.2658
293	29.27	0.2927	293	29.61	0.2961
298	31.94	0.3194	298	32.36	0.3236
303	34.72	0.3472	303	35.22	0.3522
308	37.74	0.3774	308	38.19	0.3819
313	40.64	0.4064	313	41.08	0.4108
318	43.93	0.4393	318	44.27	0.4427
323	46.59	0.4659	323	47.19	0.4719
328	50.08	0.5008	328	50.77	0.5077

1.1 PSS\0.3NaCl			1.2 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	21.81	0.2181	278	21.74	0.2174
278	24.13	0.2413	278	24.22	0.2422
288	26.93	0.2693	288	27.12	0.2712
293	29.85	0.2985	293	29.86	0.2986
298	32.53	0.3253	298	32.54	0.3254
303	35.32	0.3532	303	35.54	0.3554
308	38.55	0.3855	308	38.71	0.3871
313	41.42	0.4142	313	41.48	0.4148
318	44.75	0.4475	318	44.84	0.4484
323	47.89	0.4789	323	47.58	0.4758
328	51.18	0.5118	328	51.28	0.5128

1.3 PSS\0.3NaCl			1.4 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	21.82	0.2182	278	22.68	0.2268
278	24.43	0.2443	278	24.75	0.2475
288	27.2	0.272	288	27.84	0.2784
293	30.13	0.3013	293	30.35	0.3035
298	32.88	0.3288	298	33.22	0.3322
303	35.98	0.3598	303	36.32	0.3632
308	39.04	0.3904	308	39.47	0.3947
313	42.03	0.4203	313	42.31	0.4231
318	45.22	0.4522	318	45.59	0.4559
323	48.17	0.4817	323	48.66	0.4866
328	51.95	0.5195	328	51.17	0.5117

1.5 PSS\0.3NaCl			1.6 PSS\0.3NaCl		
Temp(K)	Cond(mjs)	% Error ±	Temp(K)	Cond(mjs)	% Error ±
278	22.59	0.2259	278	22.38	0.2238
278	24.74	0.2474	278	24.76	0.2476
288	27.91	0.2791	288	28	0.28
293	30.39	0.3039	293	30.4	0.304
298	33.58	0.3358	298	33.46	0.3346
303	36.31	0.3631	303	36.49	0.3649
308	39.3	0.393	308	39.6	0.396
313	42.3	0.423	313	42.54	0.4254
318	45.68	0.4568	318	46.33	0.4633
323	48.55	0.4855	323	48.97	0.4897
328	51.81	0.5181	328	52.24	0.5224

1.7 PSS\0.3NaCl			1.8 PSS\0.3NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	22.95	0.2295	278	22.67	0.2267
278	25.27	0.2527	278	25.24	0.2524
288	28.28	0.2828	288	28.36	0.2836
293	30.09	0.3009	293	30.94	0.3094
298	33.79	0.3379	298	33.94	0.3394
303	36.78	0.3678	303	37.07	0.3707
308	39.99	0.3999	308	40.31	0.4031
313	42.98	0.4298	313	43.21	0.4321
318	46.66	0.4666	318	47.23	0.4723
323	49.69	0.4969	323	50.06	0.5006
328	53.01	0.5301	328	53.66	0.5366

1.9 PSS\0.3NaCl			2.0 PSS\0.3NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	23.12	0.2312	278	23.29	0.2329
278	25.82	0.2582	278	25.63	0.2563
288	28.67	0.2867	288	28.76	0.2876
293	31.15	0.3115	293	31.38	0.3138
298	34.19	0.3419	298	34.32	0.3432
303	37.33	0.3733	303	37.6	0.376
308	40.56	0.4056	308	40.84	0.4084
313	43.59	0.4359	313	43.97	0.4397
318	47.41	0.4741	318	47.88	0.4788
323	50.59	0.5059	323	50.94	0.5094
328	53.94	0.5394	328	54.56	0.5456

Tables 6. Conductivity of NaPSS in 0.4 NaCl

0.1 PSS\0.4NaCl			0.2 PSS\0.4NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	26.86	0.2686	278	26.74	0.2674
278	29.13	0.2913	278	29.13	0.2913
288	32.26	0.3226	288	32.78	0.3278
293	35.62	0.3562	293	36.04	0.3604
298	39.23	0.3923	298	39.56	0.3956
303	42.57	0.4257	303	43.23	0.4323
308	45.61	0.4561	308	46.45	0.4645
313	49.04	0.4904	313	50.07	0.5007
318	52.48	0.5248	318	53.9	0.539
323	56.47	0.5647	323	58.2	0.582
328	59.91	0.5991	328	61.58	0.6158

0.3 PSS\0.4NaCl			0.4 PSS\0.4NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	26.43	0.2643	278	26.6	0.266
278	29.41	0.2941	278	29.72	0.2972
288	32.8	0.328	288	32.94	0.3294
293	36.18	0.3618	293	36.32	0.3632
298	39.67	0.3967	298	39.88	0.3988
303	43.2	0.432	303	43.52	0.4352
308	46.52	0.4652	308	46.82	0.4682
313	50.18	0.5018	313	50.64	0.5064
318	54.06	0.5406	318	54.42	0.5442
323	58.2	0.582	323	58.86	0.5886
328	61.83	0.6183	328	62.42	0.6242

0.5PSS\0.4NaCl			0.6 PSS\0.4NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	26.92	0.2692	278	27.16	0.2716
278	29.95	0.2995	278	30.14	0.3014
288	33.42	0.3342	288	33.54	0.3354
293	36.75	0.3675	293	36.85	0.3685
298	40.2	0.402	298	40.2	0.402
303	43.78	0.4378	303	44.1	0.441
308	47.15	0.4715	308	47.56	0.4756
313	51.02	0.5102	313	51.32	0.5132
318	54.89	0.5489	318	55.16	0.5516
323	59.71	0.5971	323	60.3	0.603
328	63.36	0.6336	328	63.42	0.6342

0.7 PSS\0.4NaCl			0.8 PSS\0.4NaCl		
Temp(K)	Cond(mμs)	% Error \pm	Temp(K)	Cond(mμs)	% Error \pm
278	27.46	0.2746	278	27.64	0.2764
278	30.79	0.3079	278	30.17	0.3017
288	33.95	0.3395	288	33.75	0.3375
293	37.11	0.3711	293	37.13	0.3713
298	40.36	0.4036	298	40.54	0.4054
303	44.19	0.4419	303	44.07	0.4407
308	47.68	0.4768	308	47.49	0.4749
313	51.48	0.5148	313	51.09	0.5109
318	55.49	0.5549	318	55.28	0.5528
323	60.61	0.6061	323	58.61	0.5861
328	63.76	0.6376	328	62.68	0.6268

0.9 PSS\0.4NaCl			1.0 PSS\0.4NaCl		
Temp(K)	Cond(mS)	% Error ±	Temp(K)	Cond(mS)	% Error ±
278	27.9	0.279	278	27.69	0.2769
278	30.27	0.3027	278	30.74	0.3074
288	34.01	0.3401	288	34.28	0.3428
293	37.26	0.3726	293	37.5	0.375
298	40.84	0.4084	298	40.99	0.4099
303	44.51	0.4451	303	44.89	0.4489
308	47.79	0.4779	308	48.54	0.4854
313	51.54	0.5154	313	52.33	0.5233
318	56.15	0.5615	318	56.98	0.5698
323	59.51	0.5951	323	60.4	0.604
328	63.39	0.6339	328	64.09	0.6409

1.1 PSS\0.4NaCl			1.2 PSS\0.4NaCl		
Temp(K)	Cond(mS)	% Error ±	Temp(K)	Cond(mS)	% Error ±
278	27.7	0.277	278	27.52	0.2752
278	30.6	0.306	278	30.83	0.3083
288	34.12	0.3412	288	34.35	0.3435
293	37.59	0.3759	293	37.72	0.3772
298	41.29	0.4129	298	41.5	0.415
303	45.11	0.4511	303	45.17	0.4517
308	48.88	0.4888	308	49.06	0.4906
313	52.55	0.5255	313	52.69	0.5269
318	57.2	0.572	318	57.63	0.5763
323	61.06	0.6106	323	61.41	0.6141
328	64.83	0.6483	328	65.42	0.6542

1.3 PSS\0.4NaCl			1.4 PSS\0.4NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	28.3	0.283	278	27.99	0.2799
278	31.35	0.3135	278	31.31	0.3131
288	34.78	0.3478	288	34.75	0.3475
293	38.11	0.3811	293	38.34	0.3834
298	41.91	0.4191	298	42.05	0.4205
303	45.55	0.4555	303	45.91	0.4591
308	49.57	0.4957	308	49.75	0.4975
313	53.09	0.5309	313	53.23	0.5323
318	58.12	0.5812	318	58.49	0.5849
323	61.75	0.6175	323	62.46	0.6246
328	65.91	0.6591	328	66.11	0.6611

1.5 PSS\0.4NaCl			1.6 PSS\0.4NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	28.24	0.2824	278	27.78	0.2778
278	31.41	0.3141	278	31.28	0.3128
288	34.77	0.3477	288	35.42	0.3542
293	38.56	0.3856	293	38.86	0.3886
298	42	0.42	298	42.47	0.4247
303	46.09	0.4609	303	46.29	0.4629
308	49.34	0.4934	308	50.22	0.5022
313	52.53	0.5253	313	53.37	0.5337
318	57.6	0.576	318	58.59	0.5859
323	60.8	0.608	323	61.89	0.6189
328	64.77	0.6477	328	65.99	0.6599

1.7 PSS\0.4NaCl			1.8 PSS\0.4NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	28.98	0.2898	278	28.91	0.2891
278	31.58	0.3158	278	31.74	0.3174
288	35.33	0.3533	288	35.67	0.3567
293	38.94	0.3894	293	39.17	0.3917
298	42.46	0.4246	298	42.95	0.4295
303	46.24	0.4624	303	46.6	0.466
308	50.08	0.5008	308	50.48	0.5048
313	53.4	0.534	313	53.76	0.5376
318	58.54	0.5854	318	59.19	0.5919
323	62.32	0.6232	323	63.18	0.6318
328	65.99	0.6599	328	66.84	0.6684

1.9 PSS\0.4NaCl			2.0 PSS\0.4 NaCl		
Temp(K)	Cond(m μ s)	% Error \pm	Temp(K)	Cond(m μ s)	% Error \pm
278	28.9	0.289	278	29.07	0.2907
278	31.9	0.319	278	32.14	0.3214
288	35.68	0.3568	288	36.01	0.3601
293	39.18	0.3918	293	39.62	0.3962
298	43.02	0.4302	298	43.36	0.4336
303	46.75	0.4675	303	47.11	0.4711
308	50.62	0.5062	308	51.21	0.5121
313	53.88	0.5388	313	54.26	0.5426
318	59.2	0.592	318	59.46	0.5946
323	63.47	0.6347	323	64.04	0.6404
328	66.74	0.6674	328	67.88	0.6788