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Saida Asfour
Hebron University, saidaasfour2020@gmail.com

Ahmed Ayyad
Hebron University, ahmadh@hebron.edu

Fahed Takrori
Hebron University, fahedt@hebron.edu

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

Saida Asfour, Ahmed Ayyad and Fahed Takrori
Department of Chemistry, Faculty of Science and Technology, Hebron University, Palestine.
saidaasfour2020@gmail.com, ahmadh@hebron.edu, fahedt@hebron.edu,

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Abstract:

The conductivity of sodium (polystyrene sulfonate) (NaPSS) aqueous solutions as a function of NaPSS concentration 0.15 g – 2.0 g NaPSS in 100 mL of distilled water, sodium chloride concentration (NaCl) in the range of 0.1 M - 0.4 M and in temperature range of 278 K – 328 K have been studied. The study found that conductivity increases with increasing NaPSS concentration both in pure water and in salt solution. It is also found that conductivity increases with increasing either NaCl concentration or temperature. The interesting finding here is that 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 only holds at low NaPSS concentration and deviates at high NaPSS concentration. 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. This latter behaviour is only found at high NaPSS concentration while it is inverted at low NaPSS concentration. These findings will certainly contribute to the understanding of the complex behaviour of the conductivity of polyelectrolytes solutions.

Keywords: Surface Tension, Polyelectrolytes, Temperature Effects

دراسة تأثير درجة الحراره واضافة أملاح على موصلية البواليترولويت متعدد سلفونات الصوديوم

سائده فوزي عصفور، احمد حسن عياد، فهد ماجد تكروري، جامعه الخليل، فلسطين

saidaasfour2020@gmail.com, ahmadh@hebron.edu, fahedt@hebron.edu,

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الملخص:

تم في هذا البحث دراسة الموصلية الكهربائية للمحاليل المائية لمركب بوليستايرين سلفونات الصوديوم (NaPSS) عند تراكيز مختلفة من هذا المركب البولي إلكترولايتي تتراوح بين 0.15 –2.0 غم/100 ملليتر من الماء النقي، وفي محاليل ملحية من كلوريد الصوديوم ذات تراكيز تتراوح بين 0.1 الى 0.4 مول/لتر وعند درجات حرارة تتراوح بين 278 الى 328 كلفن، ووجد أنَّ هذه الموصلية تزداد مع زيادة تركيز NaPSS في كل من الماء النقي والمحلول الملحي، كما وجد أنَّ الموصلية تزداد مع زيادة تراكيز كلوريد الصوديوم أو درجات الحرارة، ومن النتائج اللافتة للاهتمام في هذا البحث أنَّ قاعدة الإضافة، التي تعني مجموع الموصلية للبولي إلكترولايت (k_{ps}) في محلول ملحي هي مجموع الموصلية في الماء النقي (k_p) إضافة إلى موصلية الملح (k_s) تكون سارية فقط عند تراكيز منخفضة من NaPSS، لكنها تنحرف عن هذه القاعدة عند زيادة هذه التراكيز، كما أنَّ انطباق هذه القاعدة يكون أفضل كلما ارتفعت درجة الحرارة وزاد تركيز الملح المضاف، ومما يثير الاهتمام ايضا في هذه النتائج أنَّ مساهمة NaPSS في موصلية المحاليل تكون أعلى في الماء النقي منها في المحلول الملحي، وتم ملاحظة هذا السلوك فقط عندما تكون تراكيز مركب NaPSS مرتفعة، بينما ينعكس هذا السلوك عندما تكون التراكيز منخفضة، ويُؤمل أنَّ تساهم هذه النتائج في فهم السلوك المعقد للموصلية الكهربائية لمحاليل المركبات البولي إلكترولايتي.

الكلمات المفتاحية: التوتر السطحي، متعدد البولي إلكتروليت، تاثير درجه الحراره.

Introduction

Polyelectrolytes are charged polymers that dissociate in aqueous solution into a macro ions and counter ions (Hara, 1993, Dautzenberg, et al., 1994, Schmitz 1993). These charged polymers are soluble in water because of the presence of charges on the backbone of the polymer. Another reason for their solubility is entropy gain when counter ions are released into water. This makes these polymers of fundamental interest in the physics and chemistry of soft condensed matter (Likos, 2001, p.348, Gelbert, 1996, p.100) and in biological systems (Bloomfield, and Carpenter, 1993, p.77). Due to their conducting ability, these charged polymers are employed for technological applications (Barrat, and Joanny, 1993, p.1). To understand the transport properties of aqueous solutions of polyelectrolytes, electrical conductivity is employed and in turn is a matter of current interest (Ray, and Das, 2015, p.54890, Santra, et al., 2022, p.131292). It has been found theoretically that the transport properties of these systems are governed by the linear charge density ξ and depend on the degree of dissociation α of the polyelectrolyte (Vink, 1981, p.2439, Vink, 1982, p.2273, Manning, 1969, p.924).

In the last few decades, these charged polymers have attracted much attention due to their unusual properties (Cametti, 2014, p.1207). The dynamical properties and the structure of these polyelectrolytes are 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 thermodynamics and the transport properties of solutions of these charged polymers are largely influenced by counter ion condensation. Conductivity is the key parameter to study and understand the coupling between counter ions condensation and chain conformation. When the electrical conductivity of these systems is studied as a function of polyion concentration, in the absence or presence of added salt, the outcome of these studies may provide a better understanding of the chain mobility and of the coupling.

The conductivity of polyelectrolytes in pure water and with the addition of salt, has been studied by a number of authors. (Vink. et al., 1982. P.2273) studied the conductivity of poly (methacry1ic acid), carboxymethylcellulose, poly (vinyl sulfonates), and poly (styrene su1fonates) solutions, and the limiting equivalent conductivity Λ^o was determined from their work. A rapid increase in conductivity was found in diluted solutions and this was explained by a decrease in counterion binding. (Rios. et al., 1990, p.505) investigated the electrical conductivity of dilute solutions of four prepared cationic polyelectrolytes. From their experimental data, the distances between neighbouring charges were determined and found to be in good agreement with those calculated according to Manning’s model (Manninings, 1972, p.117).

Recently, (De. et al., 2015, p.54890) studied aqueous solutions of sodium (polystyrene sulfonate) in the presence of NaCl by electrical conductivity. The study was meant to understand the interaction between counter-ions and the polyion. By taking the scaling description for the conformation of a polyion chain in consideration they developed an equation by which they analysed the specific conductivity versus polyelectrolyte concentration. In addition to that, they investigated the influence of added salt, polyelectrolyte concentration, temperature and molecular weight on conductivity of the polyelectrolyte. Both the concentration of the polyelectrolyte and its molecular weight were found to greatly influence counter-ion condensation. However, their study has been carried out in a much lower NaPSS and NaCl concentrations and only at three different temperatures namely, 298 K, 308 K and 318 K. Moreover, there was no mention of the dialysis of NaPSS samples they used. This dialysis process for NaPSS prior to any measurement was found to have a significant effect on the conductivity behaviour of this polyelectrolyte (Sen, and Juvekar, 2012, p.1).

In this work, the conductivity of NaPSS aqueous solutions as a function of the polyelectrolyte concentration in a wider range of 0.15g -2.0 g NaPSS in 100 mL of distilled water, as a function of NaCl concentration of 0.1 M – 0.4 M and at different temperatures in the range of 278 K-328 K was investigated. The NaPSS sample used in this work was pre-dialysed by the producer. In this manner, the work here is different from that of (De. et al., 2015, p.54890). These types of studies will certainly contribute to a better understanding of the complex behaviour of polyelectrolytes' conductivity in solutions.

Experiment

All glassware used were cleaned by immersing in distilled water to boiling temperature for at least 2 hours. This method of cleaning proved to yield good results. NaPSS was supplied by Sigma- Aldrich, with weight average molar mass of M_w = 70000 g/mol. This NaPSS sample was pre-dialysed by the producer. Solutions were prepared using distilled water from a stock solution by successive dilution. The latter method was used to minimize errors and proven to be an effective one. A refrigerated circulating water bath from VWR company was used for temperature control. It has an accuracy of 0.1 K. The NaCl salt was of analytical grade with a purity that exceeds 99% supplied by Sigma- Aldrich. Conductivity measurements were carried out by a modern Orion Star A212 conductivity Benchtop Meter (Thermo Scientific^{TM}) with high precision. The cell constant of the conductivity meter is 0.460 cm^{-1}. Calibration of the cell was done with 0.02 M potassium chloride. The uncertainty of the measurement was 0.01%. Measurements were carried out in a test tube that was placed in the water bath until the temperature in question was reached. Distilled water conductivity was measured to be of the order of 10^{-6} S/cm at 298 K.

Results and discussion

Figure 1 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. The obtained data is in excellent agreement with that reported by Hervas et al and the comparison is important to ensure the reproducibility of the experiment (Hervas. Et al., 2006). As can be seen from figure 1, the conductivity of NaCl increases with increasing NaCl concentration and this is a result of an increase in the number of ions in the solution.

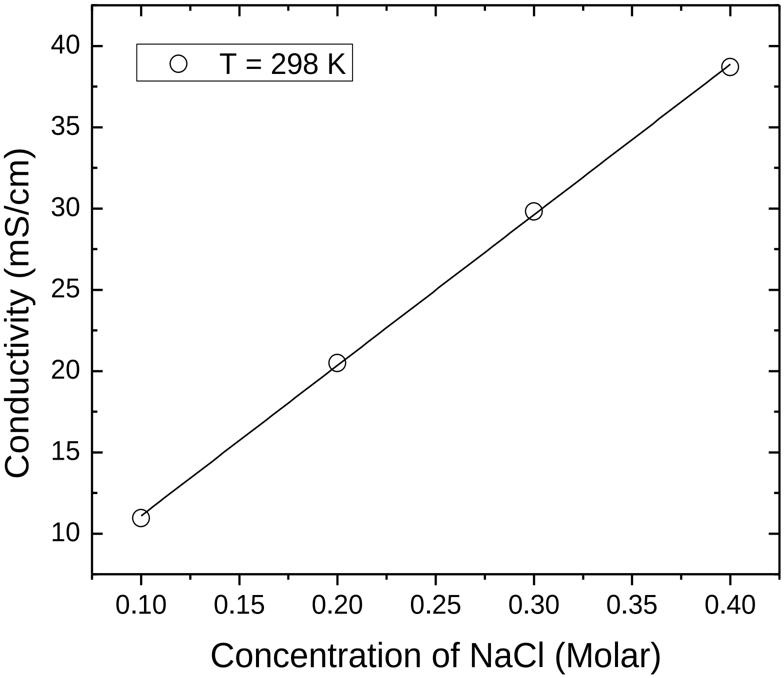

Figure 1. Conductivity of NaCl aqueous solutions as a function of NaCl concentration at 298 K. Open circles are experimental data and the solid line is a linear fit to the data.

The effect of temperature on the conductivity of NaCl aqueous solution is shown in figure 2.

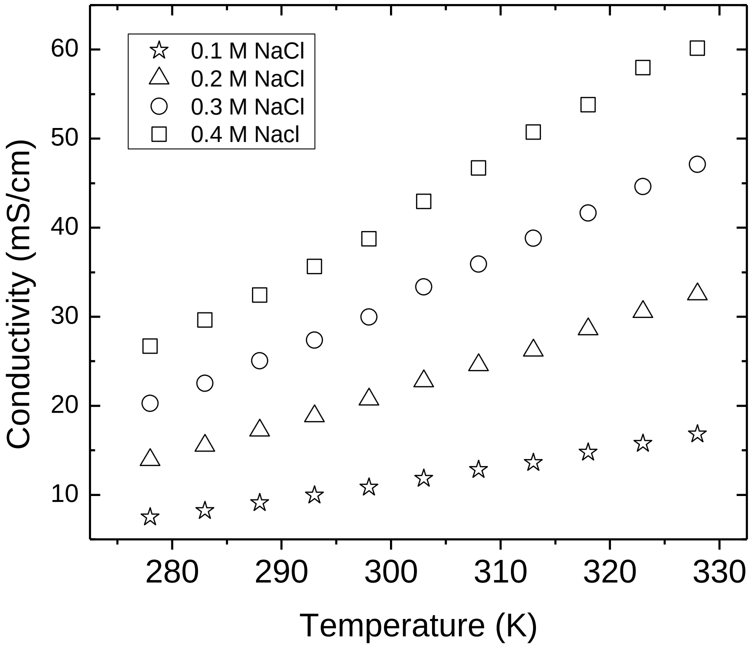

Figure 2. Temperature dependence of the conductivity of NaCl aqueous solutions.

There is an increase in conductivity with increasing temperature, and this is due to a number of factors. First of all, there is an increase in ion mobility and a decrease in solution viscosity. Second of all, as temperature increases, the energy gained by the molecules in the medium (electrolyte) increases and hence the ions are in a higher energy state. This energy will be converted into kinetic energy means an increase in the mobility of these ions. The effect of temperature on NaPSS conductivity at different concentrations in pure water is shown in figure 3.

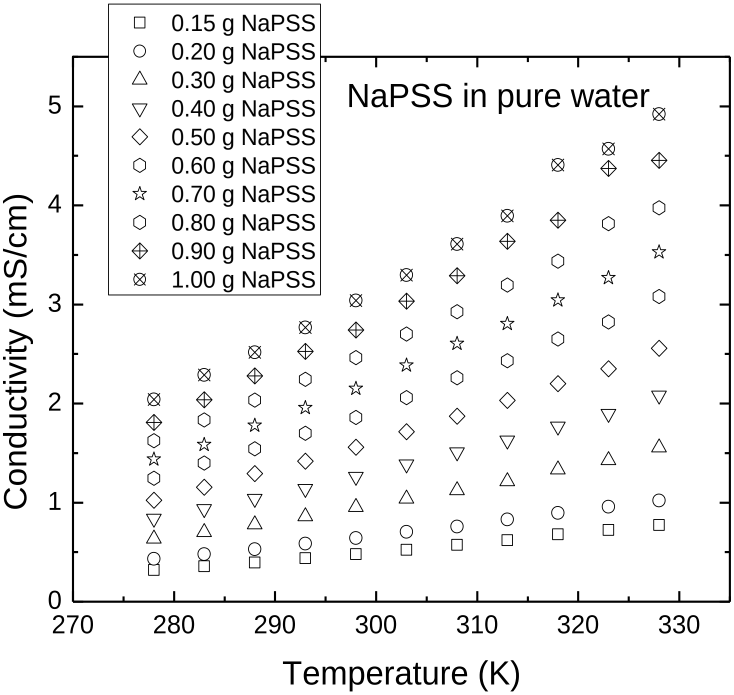

Figure 3. Temperature dependence of the NaPSS conductivity in pure water. The concentration range is 0.15 g NaPSS/100 mL water – 1.0 g NaPSS/100 mL water from top to bottom in the figure. The temperature range is 287 K - 328 K.

The concentration range is 0.15 g NaPSS/100 mL – 1.0 g NaPSS /100 mL of distilled water and the temperature range is 278 – 328 K. As can be seen in the figure, the conductivity increases with increasing temperature, and this can be explained by the same main reasons given above for conductivity of NaCl solution. Since an immense amount of data similar to that shown in figure 3 were obtained in this study, these results were summarized by plotting the conductivity per gram NaPSS as a function of NaPSS concentration in pure water and in different NaCl solutions at 298 K shown in figure 4.

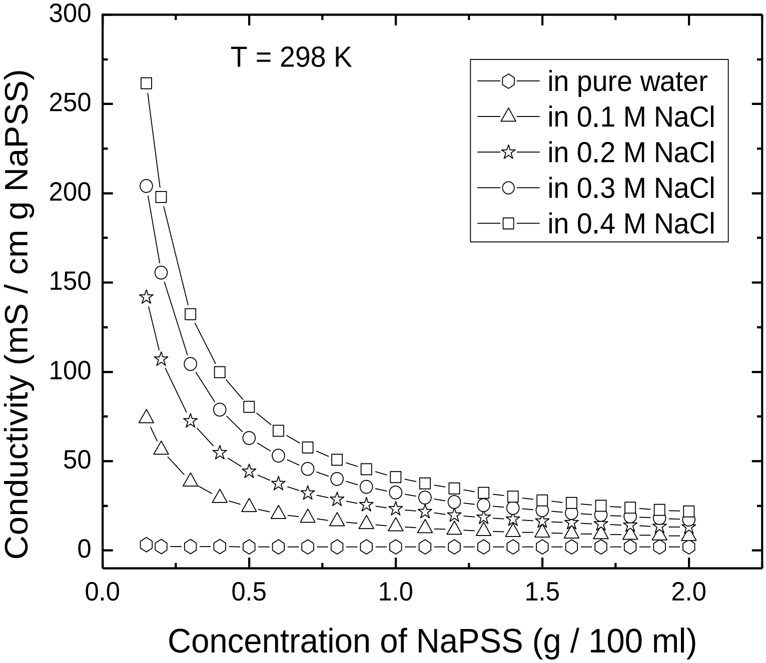

Figure 4. Conductivity per gram of NaPSS versus NaPSS concentration in pure water and at different NaCl concentrations as indicated in the figure and at 298 K.

This figure makes it easier to compare the experimental data obtained in this work with that of De et al [8]. Although the conductivity behavior of the polyelectrolyte in the two works is similar, the curves in this work are much steeper and saturated at high NaPSS concentrations. An exact comparison cannot be made because the NaCl concentration in this work is much higher, and this is probably what makes the difference between this work and that of De et al. Nevertheless, when looking at figure 4, it can be seen that the NaPSS conductivity per gram decreases with increasing NaPSS concentration rapidly at low concentration and then flattens at high concentrations. It can also be noted that the conductivity per gram of NaPSS is more in salt solution than in pure water and that it is higher the higher the NaCl concentration.

The additivity rule [9] assumes that the conductivity of the polyelectrolyte in salt solution k_{ps} is the sum of its conductivity in pure water k_p and the conductivity of the salt solution k_s without NaPSS. To test this assumption, the conductivity of NaPSS solutions in water and the conductivity of 0.1 M NaCl solution without NaPSS and the conductivity of NaPSS in 0.1 M NaCl are plotted in figure 5 at two different temperatures.

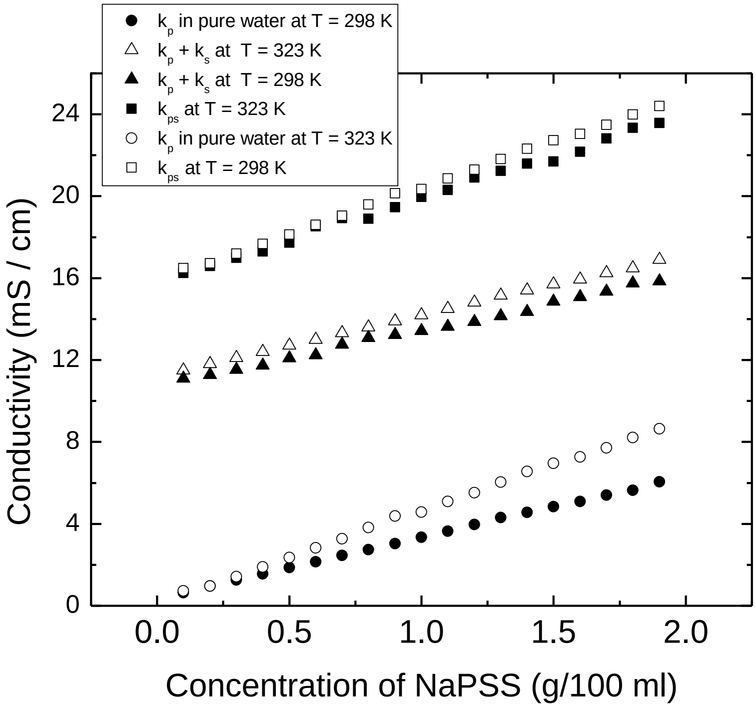

Figure 5. The conductivity of NaPSS solutions in pure water (k_p), conductivity of NaPSS plus the conductivity of the 0.1 M NaCl without NaPSS ($k_p + k_s$) and the conductivity of NaPSS in 0.1 M NaCl, (k_{ps}) at 298 K and 323 K.

The data confirms this assumption only at low NaPSS, yet deviation from this rule was found at high polyelectrolyte concentration as is clearly seen in figure 5. The data in this work adds to the existing data in the literature that the higher the temperature and polyelectrolyte concentration, the less the deviation from simple additivity rule. Accordingly, as the temperature increases the difference between the conductivity of NaPSS solutions and that of the conductivity of NaPSS plus the conductivity of the 0.1 M NaCl becomes smaller. It is also interesting to note in figure 5 that the conductivity of NaPSS solutions in pure water increases with temperature only when NaPSS concentrations are high. It has to be mentioned here that the uncertainty (0.01%) of the conductivity meter and thus the conductivity measurement is much less than the difference presented in figure 5.

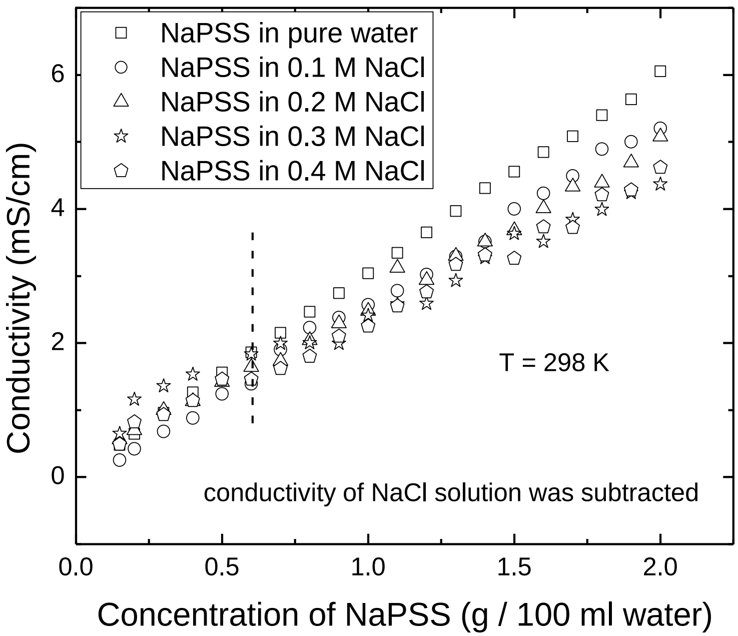

Figure 6. The conductivity of NaPSS in pure water and in different NaCl concentrations where the conductivity of the NaCl salt was subtracted at 298 K

Figure 6 shows the conductivity of NaPSS in pure water and in different NaCl concentrations where the conductivity of the NaCl salt was subtracted. The results presented in figure 6 indicate that the transport of charge by the polyelectrolyte in salt free environment is more in comparison to its ability in saline environment. This means that in pure water, the conformation of the polyion substantially differs from its conformation in salt solutions. In pure water, the polyion is expected to display extended conformation due to charge-charge repulsion on its backbone, while this repulsion is screened in the presence of salt. 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 play very important role in charge transport phenomena of polyelectrolyte solutions. It is also interesting to note in figure 6 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 aforementioned figure. Based on these results, it is possible to claim that the higher the salt concentration the higher the polyion-salt interaction and the more of this crippling effect. Note that in figure 6 that when one compares the open circles and open stars below the vertical dashed line at low NaPSS concentration an opposite effect is observed. 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 only when the polyelectrolyte concentration is very low. At this stage, it is necessary to comment in more details on the behaviour of NaPSS as a function of its concentration, the NaCl concentration and temperature. As mentioned before, the conductivity of NaPSS increases with increasing temperature due to the decrease in the solution viscosity and increase in ion mobility. Another factor may be added here related to the decrease in the fraction of free counter-ions. As temperature changes, there will be alteration in counter-ion condensation accompanied by a variation of hydration of these ions. At a higher temperature, there will be a lower degree of counter-ion condensation. More counter-ion condensation is driven by (1) a gradual dehydration of the counter-ions (2) the dissociated sites on the polyion chain as there will be greater electrostatic attraction between the dehydrated ionic species with higher surface charge densities.

Increasing polyion concentration will cause an increase in the dielectric constant and this will cause a reduction in Bjerrum length. Such increase in the dielectric constant of the medium will lower counter-ion condensation. It has to be mentioned here that the length scale for the separation between the dissociated sites on the polyion chain is set by Bjerrum length. At higher concentration of the polyion, this effect becomes more important. Moreover, it is found here that as the added salt increases, the polyion conductivity increases. There would probably be more counter-ion condensation as the salt concentration increases, and less effective charge on the monomer.

Conclusions

In this work the conductivity of NaPSS solutions was studied as a function of temperature, NaPSS concentration and NaCl salt concentration. The following conclusions can be drawn:

1. Conductivity of NaPSS increases with increasing temperature.
2. The conductivity increases with increasing NaPSS concentration. Obviously, this effect becomes more important at higher polyelectrolyte concentrations.
3. The polyion conductivity is found to increase as the concentration of the added salt increases.
4. The contribution of the polyion to the solution conductivity is more in pure water 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 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 negligible.

Data Availability Statement: the data used to generate the results in the paper are not available.

Conflict of Interest

The authors declare that there is no conflict of interest.

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