A conductivity study and calorimetric analysis of dried poly(sodium 4-styrene sulfonate)/poly(diallyldimethylammonium chloride) polyelectrolyte complexes

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I. INTRODUCTION

The complexation of polyelectrolytes of opposite charge in aqueous solutions is a long-known phenomenon, often leading to the precipitation of ionic cross-linked polymer complexes.1–3 Recently, such polyelectrolyte complexes (PECs) have regained interest due to their similarity to polyelectrolyte multilayers (PEMs) formed by layer-by-layer self-assembly. PEM can be considered as a model system for PEC with similar short-range interactions: for example, by employing regions of stability at varying electrolyte conditions in phase diagrams, PEM and PEC systems are compared to each other.4,5 Furthermore, it was shown that the distance of positive and negative charges in either type of complex is identical.6 This implies that both structures have a similar complexation on a microscopic scale and, therefore, similar transport properties.

PECs and their multilayered alternative have been studied for practical applications such as, e.g., ultrafiltration membranes, molecular sieves or ion sieves for size-selective separation of neutral or charged aromatic compounds, respectively,7–10 for sensing unit in taste sensors,11 for battery charge separators,12 and for solid electrolyte membranes in fuel cells.13–15 The application of PEMs as polymer electrolyte membranes in battery applications appears to be promising, since ultrathin membranes of nanometer thickness can be fabricated. At the current stage, however, after a long controversy in the literature about the content of residual counterions in PEM, which could act as mobile charge carriers, still little is known about the ion transport properties in PEM. Several very recent papers have dealt with ionic conductivities in PEM,16–19 comparing combinations of different polyelectrolytes,17–19 presenting conductivity spectra of PEM,19 and systematically studying the influence of hydration.19 Except the conductivity studies during the 1960s, there are almost no extended conductivity studies for dried PEM reported in the literature.7 A reason for this vacancy might be connected to low dc conductivities of dry PEM and the necessity of applying sophisticated impedance spectroscopy devices for measuring the conductivity. The majority of the work on PEM is done on soluble complexes, for example, by light scattering20 or osmotic stress equilibration.21

In the work presented here, we show the first conductivity study of dried PEC where the temperature dependence of the dc conductivity is measured for PEC with various predefined polyanion to polycation fractions. Both PEC and PEM have their specific advantage in fundamental studies of transport mechanisms. PEM can be prepared as ultrathin films with thickness control on the order of nanometers. Their stoichiometry is given by the self-assembly process and, thus, the degree of intrinsic (polyion-polyion) versus extrinsic (polyion-counterion) charge compensation in the films is a priori unknown. In a few cases, the polyion...
stoichiometry and counterion content were investigated.\textsuperscript{22,23} PECs have the advantage of preparation of any desired polyanion to polycation ratio. Here, we make use of this possibility to systematically investigate the influence of the polion stoichiometry on the ionic transport properties. In addition, an advantage of PEC is the fact that large bulk amounts can be prepared, if needed for macroscopic measurements.

The PEC studied in this work was synthesized from poly(diallyldimethyl ammonium chloride) (PDADMAC) and poly(sodium 4-styrene sulfonate) (PSS). PSS presents a physically well-characterized flexible polyelectrolyte system. The cationic PDADMAC has also captured much scientific attention due to its application as flocculation agent. These polyelectrolytes form one of the most commonly employed physically well-characterized flexible polyelectrolyte system.

We present here a thermal analysis and an impedance spectroscopy study of a PSS/PDADMAC PEC series. To study the ion dynamics, the dc conductivity is investigated as a function of composition and temperature. The dc conductivities of samples with and without water and salt contents are compared and discussed. To the best of our knowledge, detailed thermal, dielectric, and/or ionic conductivity studies of the otherwise well-studied PSS/PDADMAC complex do not exist so far in the literature.

The transport of ions and their charge are studied by means of conductivity measurements. The dc conductivity of PEC cannot be directly measured by using conventional electron conducting electrodes such as gold or silver electrodes. These metallic electrodes are blocking the ion movements and, consequently, polarization effects at the sample-electrode interface prevent the buildup of a dc current. Conductivity measurements with alternating voltage can overcome this problem if a frequency is applied, which is large enough to avoid significant polarization effects.

### II. EXPERIMENTAL

#### A. Materials and sample preparation

PSS was purchased from Acrös Organics with an average molar weight of 70 000 g/mol. The solid PSS was added to ultrapure water (specific resistance of >18 MΩ/cm, Millipore), and a semipermeable membrane (Nadir dialysis hose, 2.5–3 nm, Carl Roth GmbH, Karlsruhe) was used to filter out the short PSS chains and other possible contaminations. The solutions were then freeze dried and kept in a desiccator until use.

PDADMAC was purchased from Aldrich as a 20 wt% aqueous solution with an average molar weight of 100 000–200 000 g/mol. The aqueous solution was then diluted with ultrapure water to obtain the desired concentration.

Appropriate amounts of 0.05M (molar) aqueous solutions of PSS and PDADMAC were added dropwise to ultrapure water by using a three-necked bottle. This solution was continuously stirred during the PSS/PDADMAC complexation. To remove the free salt developed during the PEC complexation, the solutions were dialyzed against ultrapure water (cutoff of 3 nm). The dialysis was continued until the conductivity of the exchange water dropped below 3 μS/cm. By this method, we have prepared 13 solutions of xPSS·(1−x)PDADMAC with monomer molar fractions x ranging from 0.30 to 0.70, in steps of 0.05 (see Table I). Afterwards, the PEC solutions were freeze dried by using an Alpha 1-2 LD freeze dryer (Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany).

Two regions and one specific stoichiometric composition can be distinguished in the investigated composition range, viz., x > 0.5, x < 0.5, and x = 0.5 for xPSS·(1−x)PDADMAC. For x > 0.5, the extrinsic charge carriers are predominantly the Na⁺ ions, for x < 0.5, the Cl⁻ ions are the majority extrinsic charge carriers, and for the stoichiometric composition with x = 0.5, no extrinsic charge compensation is theoretically expected. We find that for x ≥0.5, the PECs appear as cottonlike, white homogeneous solid substances. For PDADMAC-rich complexes (x < 0.5), we could distinguish two phases. One of these phases is a cottonlike phase similar to that of the PSS-rich compositions and the second one is a hard saltlike phase. The two-phase systems were milled and mixed before use. For conductivity measurements, about 1 mm thick cylindrical samples (with about 15 or 21 mm in diameter) were pressed by a Paul
Weber press from the powders by applying a pressure corresponding to 20 kg cm\(^{-2}\) for 2 min. After weighing the pressed samples, 100 nm thick gold contacts were sputtered on both opposite faces of the samples by a SCD 005 cool sputtering device (BAL-TEC, Tucson, AZ). The samples were stored in a desiccator filled with orange silica gel.

The dimensions and weight of the samples were measured before and after the impedance measurement and corresponding heat treatment, see below. From these values, we obtained the overall density of the pressed PEC samples. It was observed that, after heat treatment, the dimensions and also the weight of the samples were slightly smaller than before the heat treatment. These changes are due to evaporation of water that is still present in the freeze-dried PEC samples and resulted in a small (less than 10%) decrease in the mass density. The mass densities \(\rho\), as displayed in Table I, were calculated from masses and sample dimensions after completing the impedance measurements. Therefore, possible changes in both the mass and the dimension occurring during the drying process in the beginning of the heat treatment are taken into account.

The samples are designated as PEC\(X/(100-X)\), where \(X=100-x\) is the monomeric mol % of PSS and \((100-X)\) is the monomeric mol % of PDADMAC (see Table I). Supposing that all anionic polymer units have reacted with all available cationic polymer units, and that all the “free” NaCl was successfully removed during dialysis, \(A=2(X−50)\) gives the percentage of extrinsic charge carriers in the PEC in mol %. The sign of \(A\) displays whether the positive or the negative extrinsic charge compensating ions remain in PSS/PDADMAC complex.

**B. Measurement techniques**

Small amounts of freeze-dried PEC samples were used for thermal analysis. The thermal analysis of the samples has been performed by means of differential scanning calorimetry (DSC) using a 204 Phoenix (NETZSCH, Selb, Germany) apparatus. Subsequent DSC measurements were performed between \(-73\) and \(300 °C\) with a heating rate of \(10 °C/min\).

Complex impedance spectra of the samples were measured in a frequency range of \(10^{-2}–10^{6}\) Hz by using a Novocontrol \(\alpha\)-S high resolution dielectric analyzer equipped with a Quatro cryosystem and controlled by WINDETA software (Novocontrol, Hundsangen, Germany). During measurements, the samples were deposited in a chamber, where the temperature is controlled by a preheated flow of dry nitrogen. Impedance measurements were performed between \(-70\) and \(300 °C\) by using temperature steps of \(10 °C\). A heating and two cooling measurement series was applied. The Nyquist (also called complex impedance or Cole–Cole) plots of the impedance data were analyzed with a MATLAB fitting tool.

Figure 1 shows typical Nyquist plots, consisting of a depressed semicircle arc, which continues as an inclined straight line at small frequencies. This steep increase in the imaginary component of the complex impedance \(\hat{Z}\) with decreasing frequency is due to polarization effects at the PEC-Au contact interface. The bulk ionic dc conductivity was obtained by fitting a model equivalent circuit to the data. The best fit was obtained when the data due to polarization effects were removed and an equivalent circuit of a parallel connected constant phase element and an Ohmic resistance was used to describe the data. The complex impedance of such an equivalent circuit is

\[
\hat{Z} = \frac{R}{1 + RC(i\omega)^p},
\]

where \(R\) is the bulk resistance, \(C\) is the capacity, \(\omega\) is the angular frequency of the ac current, and \(p\) is the phase. The continuous lines in Fig. 1 show the best fits of Eq. (1) to the data. The ionic dc conductivity was obtained from the product of the reciprocal intercept resistance value of the semicircle and the cell constant.

The reproducibility of the conductivity results was investigated by comparing the conductivity and its temperature dependence of the individually prepared samples with the same composition. These studies reveal a maximal experimental error with a factor of 2 for the absolute values of conductivity and an error of 7% for the activation enthalpy.

**III. RESULTS AND DISCUSSION**

**A. Thermal analysis and glass transition**

Typical DSC thermograms of the samples are shown in Fig. 2. During the first run we observed a huge endothermic peak with an onset temperature \(T_1\) between 41 and 69 °C, depending on composition (see Table I). This peak was absent during the second and third runs. We, therefore, attribute this endothermic peak to the evaporation of water from the sample. The temperature where the thermogram starts to deviate from the linearity of pretransition baselines (at about \(20 °C\), marked in Fig. 2) is apparently close to room temperature. We think that this value is connected to the temperature at which the sample was previously equilibrated. Since before the DSC experiments, the samples were kept for a while in a desiccator at room temperature; the so-called
investigated in this work.

The specific heat capacity of the samples is calculated from the ratio of the DSC signal to the base line. Interestingly, the PEC50/50 complex has the lowest glass transition temperature among all samples, its value is similar when the subsequent heating runs are equivalent within an error of 10 °C. Inter- estingly, the PEC50/50 complex has the lowest glass transition temperature and apart from the two most asymmetric

temperatures that of during the first heating run. This is a remarkable result, since the transition temperature of PDADMAC was measured as a function of water content by Yeo and Eisenberg. The largest $T_g$ of 68 °C was reported for the dry PDADMAC (see the arrows with annotations). For pure PSS, we obtained a $T_g$ of about 180 °C in this study (see the arrows with annotations). This value is somewhat smaller than 211 °C, which was estimated for PSS in an earlier work. It is interesting to note that the $T_g$ values obtained for PSS/PDADMAC PEC are in between the glass transition temperatures of pure PDADMAC and pure PSS.

In PDADMAC/PSS water-saturated PEM capsules, Köhler et al. report a $T_g$ of about 35 °C. The discrepancy to the $T_g$ values of dry PEC can be attributed to the hydration water which is screening electrostatic interactions and, thus, enhancing the polymer mobility. In addition, surface effects may play a role in the case of PEM capsules.

B. Ionic conductivity

1. Kinetics

The conductivity of a material depends on charge, number density, and mobility of the charge carriers. In the case of PEC, the most important parameters which affect these quantities are the composition, the water content, the state of matter, the microstructure, and the density. Drying of the samples not only removes the water but also modifies the structure of the polyelectrolyte complex, which may have a significant impact on the concentration and mobility of the mobile charge carriers, for example, alkali ions. A structural rearrangement of the PEC network may also occur during an annealing above the glass transition temperature. This may significantly affect the mobility of the ionic species and, thus, the conductivity. The equilibration kinetics could, in principle, affect the experiment, if the changes are relevant
on the time scale needed for the data collection (about 25 min). Therefore, the magnitude of these changes has been studied for a representative sample and PEC60/40 sample by measuring the variation of the ionic conductivity during an isothermal heat treatment in the heating chamber of the impedance device at 200 and 300 °C, respectively. Figure 4 shows the ionic conductivity as a function of annealing time for two subsequent measurement series. The first series was carried out at a temperature of 200 °C and the second at 300 °C without cooling the sample to room temperature in between the measurement series.

The first measurement series shows an abrupt decrease in the conductivity by about 83% in the first 3 h. In the next 3 h, the decrease in conductivity is approximately 8.6% and only 1.1% in the last 3 h of the measurement. Since the acquisition time of any impedance spectrum was about 20 min, after a 3 h long preannealing at 200 °C, the changes in conductivity during recording a single spectrum was about 1%. After this measurement, the sample was directly heated to 300 °C. In the first 3 h of these second series, we observed a conductivity decrease of about 90%, and in the following 3 h this decrease was still about 30%. At this temperature, the decrease in the conductivity after 3 h of annealing is still significant. We continued this isothermal heat treatment for 7 h. This time was not sufficient to reach a constant conductivity but the results contain important information about equilibration at this high temperature. The decrease in the conductivity cannot be described with a single exponential function neither at 200 nor at 300 °C. For the dc conductivity kinetics at 200 °C, one can clearly distinguish two regimes. A fast regime in the first 2000 s and a much slower after this time. In these processes, both the evaporation of bound water and some structural relaxation of the PEC network can be involved. For PEMs, a slow equilibrium of the hydration taking several hours after a temperature jump had also been observed.27 There, it was attributed to slow chain rearrangement, which causes water evaporation even at long times in addition to a first initial water evaporation.

To achieve a good reproducibility of conductivity results, in the present study, a prolonged preannealing of about 6 h at high temperature measurement has been performed before the conductivities were recorded. The conductivity data obtained after such a preannealing are referred to as “conductivities of dried samples.”

2. Effect of drying

As described in the previous section, the conductivity of PEC depends on the annealing history. To investigate the conductivity as a function of the annealing history, we performed two series of conductivity measurements. In the first series, the sample is cooled down to about −90 °C. Then, the temperature is increased up to 200 °C in steps of 10 °C, while the complex ac conductivity is measured in the investigated frequency range. The samples were kept at 200 °C for about 3 h and then cooled down stepwise (10 °C) to the lowest temperature at which the conductivity could still be determined. We refer to these measurements as “first measurement series.” In a second conductivity measurement series, the sample was first heated to 300 °C and after a prolonged isothermal heat treatment of more than 6 h, the temperature dependence of the complex conductivity was measured by decreasing the temperature stepwise by 10 °C. Arrhenius plots of the ionic conductivity of PEC70/30 obtained from both first and second measurement series are shown in Fig. 5. The upper straight line shown in Fig. 5 corresponds to the conductivity of the sample before drying (starting the measurements at −90 °C). It obeys the Arrhenius law. A strong deviation from this Arrhenius fit starts above 25 °C. This temperature is consistent with the DSC data obtained on the first heating and attributed to a loss of water. The loss of water continues until 200 °C is reached.
The conductivity observed during cooling down from 200 °C is also Arrhenius-like; however, it is three orders of magnitude lower than the conductivity of the samples before drying. Arrhenius parameters determined from the first measurement series are listed in Table II. It is interesting to observe that in contrast to the huge discrepancy of the ionic conductivity values of “humid” and “dried” samples, the activation enthalpy of the conductivity is almost identical. Similar features have been observed for PEC65/35 and PEC60/40 too. The results of the second measurement series will be presented and compared with these data further below.

3. Stoichiometric PEC with and without salt

Two PEC50/50 batches have been prepared to investigate the effect of residual NaCl on the ionic conductivity. The batches were identically prepared, except that the dialysis step after complexation and before freeze drying was omitted for one of them. This sample, marked as PEC50/50+, contains a mixture of PEC and NaCl. Since the samples were dried for 3 h at a temperature of 300 °C, we may assume that the water content of the samples is practically zero. One expects a higher conductivity of this sample as compared to that prepared with dialysis, since the number of charge carriers might be larger in PEC50/50+ than in pure PEC50/50. Figure 6 shows the ionic conductivity of these samples. Indeed, the PEC50/50+ sample has a two orders of magnitude higher ionic conductivity than the sample without salt. However, the activation enthalpies of the conductivity of 1.40 eV for PEC50/50 and 1.35 eV for PEC50/50+ are practically identical. Is the higher conductivity of the salt-containing sample a consequence of a simple number concentration increase in the mobile charge carriers? It seems that the situation is not that simple because a convex deviation from the Arrhenius law showed as a solid line in Fig. 6 can be observed for the PEC50/50+ sample. This leads to the conclusion that in the PEC50/50+, more than one mobile species and/or transport mechanism are present.

4. Composition and temperature dependence

Figure 7 shows the ionic dc conductivity times temperature as a function of reciprocal temperature. The solid lines in the figure correspond to fits to the Arrhenius equation,

$$\sigma_n T = C \exp\left( -\frac{\Delta H}{k_B T} \right),$$

where $C$, $\Delta H$, and $k_B$ are the preexponential factor, the activation enthalpy, and the Boltzmann constant, respectively. Since the measured data obey the Arrhenius law, the temperature dependence of the conductivity of the present PEC, similarly to almost all solid materials, can be well described with a single exponential function. The preexponential factors and activation enthalpies are listed in Table III.
TABLE III. Activation enthalpies $\Delta H$ and preexponential factors of the dc conductivity times temperature, $C$, obtained after equilibration at 300 °C of PSS/PDADMAC PEC samples. Note that the index $^+$ is used for the PEC prepared without dialysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H$ (eV)</th>
<th>$C$ ((\Omega \text{ cm})^{-1} \text{ K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEC30/70</td>
<td>1.72</td>
<td>5.0 x 10^7</td>
</tr>
<tr>
<td>PEC35/65</td>
<td>1.59</td>
<td>4.5 x 10^6</td>
</tr>
<tr>
<td>PEC40/60</td>
<td>1.51</td>
<td>1.0 x 10^6</td>
</tr>
<tr>
<td>PEC45/55</td>
<td>1.50</td>
<td>3.2 x 10^6</td>
</tr>
<tr>
<td>PEC50/50</td>
<td>1.39</td>
<td>1.9 x 10^5</td>
</tr>
<tr>
<td>PEC50/50$^+$</td>
<td>1.35</td>
<td>3.1 x 10^6</td>
</tr>
<tr>
<td>PEC55/45</td>
<td>1.31</td>
<td>9.0 x 10^4</td>
</tr>
<tr>
<td>PEC60/40</td>
<td>0.96</td>
<td>6.4 x 10^3</td>
</tr>
<tr>
<td>PEC65/35</td>
<td>0.84</td>
<td>6.6 x 10^3</td>
</tr>
<tr>
<td>PEC70/30</td>
<td>0.80</td>
<td>1.0 x 10^4</td>
</tr>
</tbody>
</table>

For PEC70/30 and PEC65/35, the glass transition temperature falls in the temperature interval employed in the conductivity study. However, no significant change in the slope at the calorimetric glass transition temperature is seen in Fig. 7. Therefore, we conclude that the impact of the glass transition on ion transport properties is not significant for the PEC70/30 and PEC70/30. The dynamics of the matrix as probed by DSC seems to be not relevant for ion transport. Note that the glass transition temperature of other compositions lies outside the conductivity measurement range.

Figure 7 shows that at a given temperature, the conductivity of the xPSS-(1-x)PDADMAC complexes decreases with decreasing PSS molar fraction $x$. This decrease is much more pronounced for PSS-rich as well as for PDADMAC-rich compositions. Furthermore, we do not observe a minimum in ion conductivity for the PEC50/50 sample, while a minimum for the number concentration of the extrinsic charge carriers is predicted for this stoichiometric composition. These features of the $x$-dependent conductivity are even more obvious in Fig. 8, where the activation enthalpy (full circles, left $Y$ axis) and the dc conductivity (full squares, right $Y$ axis) measured at 290 °C are presented as a function of $x$. The upper $X$ axis in this figure displays the extrinsic charge concentration of the Cl$^-$ ions (left direction) or of the Na$^+$ ions (right direction), as calculated from $[2(1-x)]$ (see Sec. II). The asymmetric nature of the curves in Fig. 8 points to the conclusion that the transport mechanism in PDADMAC-rich PEC significantly differs from that in PSS-rich PEC. As pointed out in Sec. II A, after freeze drying of the PDADMAC-rich ($x<0.5$) PEC, we could distinguish two phases. The separation into two phases was more and more pronounced on decreasing $x$. In a stereo light microscope, the soft phase was visually similar to the single phase PSS-rich PSS/PDADMAC PEC. Therefore, we believe that the PDADMAC-rich PEC of this study may act according to the classical model by Michaels and Miekka, which suggests the formation of a 1:1 stoichiometric, physically cross-linked precipitate, and the excess polyelectrolyte will form a second phase. According to this model, in our case, this second phase should be a solid PDADMAC. This interpretation of the two phases is supported by a previous study of PDADMAC/PSS complexes in solution, where osmotic coefficients were measured and interpreted in terms of counterion binding to available charged sites in the complex. There, the PSS-rich complexes were behaving similar to an ideal mixture, where the counterion binding is controlled by the average distance of polyion excess charge in the homogeneous complex. On the other hand, the PDADMAC-rich complexes showed osmotic coefficients consistent with a microphase separation of excess PDADMAC from neutral complex. Here, we even macroscopically observe this phase separation. This phase separation might be responsible...
C. Ion dynamics

Interestingly, the activation enthalpies $\Delta H$ determined from the second measurement series (see Table III) are similar to $\Delta H_{11}$ and $\Delta H_{11}$ (see Table II). Therefore, the remarkable difference in conductivity of freeze-dried samples (which still contain some water) and samples dried at high temperature is mostly due to the variation of the preexponential factor. The higher conductivity of freeze-dried samples is, on the one hand, due to the fact that the water acts as a plasticizer and has a significant impact on the PEC network. The changes of the PEC network induced by water should influence the potential energy landscape in which the ions move and, thus, the mobility of the Na$^+$ ions. On the other hand, the higher conductivity of samples after freeze drying might be connected to a proton contribution, since these samples still contain some water. However, changes in potential landscape and a change from predominantly Na$^+$ ion conductivity to predominantly proton conductivity should have significant impact on the activation enthalpy of the conductivity. In contrast, our results display within experimental errors almost identical activation enthalpies for humid and dried samples. Regarding the microscopic ion dynamics, we may resolve this contradiction via a “modified random network model,” which allows a network of “percolation channels.” These percolation channels are the presumed pathways for ion migration. The ions move fast on pathways and are mostly immobilized elsewhere. Additionally, we should suppose that the energy landscape on these paths is not strongly influenced by the water content in PEC. However, the number density and cross-links of paths should significantly increase with water content. In this context, the water molecules may create “bridges,” where the continuity of the paths is otherwise broken. Thus, the increase in the conductivity might be attributed to an increase in the number density of paths with increasing water content of the PEC.

D. Comparison of the conductivity values

Last but not the least, it is interesting to compare the dc conductivity values determined here with those of similar materials in view of the limit of approximately $10^{-2} \Omega^{-1} \text{cm}^{-1}$ required for many applications. There is a great demand for stable solid electrolyte materials with such high ionic conductivity. In the dry state, the PEC70/30 sample, with about 40 mol % Na$^+$, has the highest conductivity among the investigated PECs. Its dc conductivity in a dry state is about $3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at $300 \degree C$. The room temperature ionic dc conductivity of the freeze-dried PEC70/30 sample is about $10^{-8} \Omega^{-1} \text{cm}^{-1}$. These conductivity values are far from the values needed for applications. However, one parameter that may be tuned to achieve a higher conductivity is the humidity. For example, Michaels has shown for the dc conductivity of PEC that the increase in the relative humidity from 0% to 50% results in a four orders of magnitude large increase in the dc conductivity. An exponential dependence of conductivity on relative humidity was recently reported for PSS/poly (allylamino hydrochloride) (PAH) PEMs. Supposing a similar increase in the conductivity of PSS/PDADMAC PEC, in a humid atmosphere of about 50% relative humidity, a conductivity of $10^{-4} \Omega^{-1} \text{cm}^{-1}$ can be reached. This would make the PSS/PDADMAC PEC promising for applications as a solid electrolyte even at room temperature.

Let us compare the room temperature conductivity values of the PEC70/30 with conductivities of similar PEMs at a higher relative humidity. The dc conductivity value for dried PEC70/30 is three orders of magnitude lower than that of a poly(ethyleneimine)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid) PEM measured at a relative humidity of 50%. On the other hand, the dc conductivity of the PEC70/30 sample is 1 decade higher than that obtained at a relative humidity of 50% for PSS/PAH PEMs.

In contrast to the PSS-rich samples, the PDADMAC-rich PEC samples have very low dc conductivities. The activation enthalpy increases and $\sigma_{dc,T}$ almost linearly decreases with increasing PDADMAC content. From these low conductivities, we conclude that the mobility of the negatively charged Cl$^-$ ions in PDADMAC-rich PEC is extremely low.

IV. SUMMARY AND CONCLUSIONS

In this paper, we have shown that PSS/PDADMAC complexes have distinct transport properties comparing the PSS-rich with PDADMAC-rich compositions. An increasing dc conductivity was observed with increasing PSS content up to a 70/30 relative molar ratio. This increase is mostly due to an increased Na$^+$ content and mobility. The Na$^+$ ions play the role of extrinsic charge carriers in PSS-rich PEC and relatively move easy through the PEC network. On the other hand, the PDADMAC-rich PSS/PDADMAC complexes show very low ionic conductivities, which are due to a low mobility of Cl$^-$ ions and probably a phase separation observed for PDADMAC-rich compositions. The DSC thermograms of dried samples display a reproducible endothermic peak in the temperature range of 90–143 °C (depending on PSS to PDADMAC fraction), which is attributed to a glass transition. This transition does not significantly affect the ionic conductivity. There is a three orders of magnitude large discrepancy between the conductivities of as-prepared and dried samples; nevertheless, the activation enthalpies are identical within experimental errors. The PEC50/50$^+$ sample with salt has a two orders of magnitude higher conductivity as compared to PEC50/50 without salt, but interestingly, the activation enthalpies are again similar. Thus, the conductivity and activation enthalpy values at a given temperature strongly depend on the PSS content of the complex. For a given composition, however, the activation enthalpy does not significantly change upon drying or salt addition. Within a modified random network model, this may imply that the overall energy landscape, where the fast ion conducting
paths evolve, is not strongly influenced by salt and water content, instead, only the number of paths accessible for ion transport changes.

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