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Humidity Dependence of the Ionic Conductivity of Polyelectrolyte Complexes

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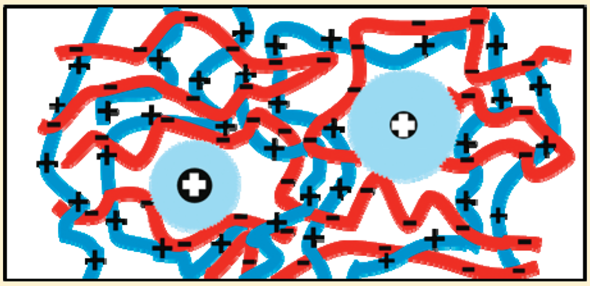

ABSTRACT: A series of polyelectrolyte complexes (PEC) of anionic poly(styrenesulfonate) (PSS) containing Na^+ or Cs^+ as counterions and cationic poly(diallyldimethylammonium chloride) (PDADMAC) were prepared as solid material at monomeric fractions X of PSS ranging from 50 to 75. The dc conductivity was measured as a function of relative humidity by impedance spectroscopy. The water content increases almost linearly with humidity, while the dc conductivity increases exponentially. This general behavior holds for all compositions and both types of cations and it is described by $\log(\sigma_{dc}) = a \cdot \mathrm{RH} + \text{constant}$. Comparing different compositions and counterions, we discuss the contributions of different charge carriers and conclude that alkali ions, transported in their hydrated state, are the major conducting species; the contribution from protons is negligible. In addition to properties of the cationic charge carriers, the water content and matrix properties such as the cross-linking density systematically influence the charge carrier mobility.

INTRODUCTION

The complexation of oppositely charged polyelectrolytes in solution, which often leads to the precipitation of ionically cross-linked polyelectrolyte complexes (PEC), is a well-known phenomenon.[1] Interpolyelectrolyte complexes are formed spontaneously by mixing of solutions of polyanions and polycations under release of the counterions. The main driving force of complex formation is the increase of entropy as a result of the liberation of the low molecular weight counterions. However, other interactions such as hydrogen bonding or hydrophobic interactions may also play an additional role.[2] PEC show interesting phase behavior and transport properties, for example, the formation of a coacervation complex in the vicinity of a charge stoichiometric complex.[3] For nonstoichiometric mixing of the polyelectrolyte charges, extrinsic charge compensation is required by excess counterions, their concentration depending on the mixing ratio of polyelectrolyte pairs. On the other hand, for stoichiometric mixing theoretically one would expect intrinsic charge compensation by polyion pairs leading to no residual counterions in PEC. However, there is also the possibility of a low extent of extrinsic charge compensation by cations and anions.

Recently, PEC have gained attention due to their similarities to the polyelectrolyte multilayers (PEM) as far as the microscopic structure is concerned.[4] In the other words, PEC can be considered as a model system for PEM with similar short-range interactions; i.e., both the systems have a similar complexation on a microscopic scale as well as similar transport properties.[5] Moreover, both PEC and PEM have similarities in various aspects in terms of their phase diagrams.[6] PEM have been studied for numerous practical applications such as ultrafiltration membranes, ion sieves or molecular sieves, or selective separation of charged or neutral aromatic compounds[7−9] and for solid electrolyte membranes in fuel cells.[10] At the current stage, in spite of a long controversy about the content of the residual counterions, very little is known about the ion transport properties in PEM. One of the major reasons is the lack of knowledge about the composition of the PEM, as they are prepared from self-assembly. Although from the entropic point of view intrinsic charge compensation between polyion pairs is favored, a number of PEM having unstoichiometric polyion combination is also reported in the literature.[11,12] In the early stages, the detection of small ions in PEM was attempted by XPS,[13] neutron reflectivity,[14] and radio analytical techniques,[15] but in general, these techniques have failed to detect the presence of small ions, which implies a very small ion concentration or no ions. However, at the later stage, Farhat et al. showed that small counterions can be contained in multilayers.[16] Moreover, since PEM are prepared by self-assembly the major disadvantage of PEM is that one cannot control the amount of incorporated ions. Therefore, PEM are materials of unknown stoichiometry. Because of this constraint, it is not possible to systematically investigate the role of ion content in PEM, if any. Recently, a few reports have been published regarding ionic conductivities at different humidity in PEM with different polyions.[17−19] A systematic study on the influence of hydration showed that in hydrated PEM conductivity is governed by protons as charge carriers.[20] Though doping with small counterions is feasible,[21] it is difficult to obtain PEM with tunable conductivity via incorporating different amounts of ions.

In contrast to PEM, PEC can be prepared from any desired polyanion to polycation ratio and therefore enable a systematic

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investigation of the influence of the polyion stoichiometry on the ionic transport properties by incorporating predefined amounts of ions. In spite of this advantage of known stoichiometry, no extended studies involving PEC were done for a long time. The majority of work done on PEC is performed on soluble complexes, for example by light scattering[22] or osmotic stress equilibration.[23] Recently, Imre et al. have published a few reports regarding the conductivity in dry PEC considering PEC as a bulk material,[24,25] where the thermal activation behavior was analyzed and the contribution of Na^+ counterions is shown to be dominant over that of Cl^- counterions. Nevertheless, the room temperature dc conductivity reported in these dry materials is far below from the limit required for use in practical applications.[24] Drawing an analogy from the humidity dependence of the conductivity in PEM, even for PEC, humidity seems to be an interesting parameter that can be employed to enhance the conductivity to the limit of the order of $10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. A larger effect of humidity as compared to temperature on PEM conductivity was already reported in the literature.[26] A systematic conductivity study on PEC as a function of humidity will not only help to understand structural issues of PEM but also help to establish the potential of PEC as an energy material for practical use such as in fuel cells.

Herein, we present humidity-dependent conductivity experiments of PEC with Na^+ and Cs^+ as counterions at different predefined compositions. We also present the variation of the water content in PEC as a function of the relative humidity of the environment and the influence of the absorbed water on the ion transport properties of PEC. The role of absorbed water molecules is also discussed by applying a recently established time—humidity superposition principle (THSP).[27] The polyelectrolyte components employed here are poly(diallyldimethylammonium chloride) (PDADMAC) and sodium poly(4-styrenesulfonate) (NaPSS) containing different types and concentrations of counterions (Na^+ and Cs^+, respectively). The experiments involve gravimetric analysis and impedance spectroscopy on the NaPSS/PDADMAC and CsPSS/PDADMAC PEC series, where the dc conductivity is investigated as a function of humidity.

■ MATERIALS AND METHODS

Materials. PDADMAC was purchased from Aldrich as a 20 wt % aqueous solutions having a molar mass of 100 000—200 000 g/mol. For aqueous solutions of PDADMAC and all other polymers ultrapure water with a specific resistivity >18 MΩ cm^{-1} prepared from a water purification system (Millipore) was used. NaPSS was purchased from Acros Organics with an average molecular weight of 70 000 g/mol. The solid powder was dissolved in ultrapure water and dialyzed against ultrapure water by a semipermeable membrane (Nadir dialysis hose, 2.5—3 nm, Carl Roth GmbH, Karlsruhe) in order to remove short chains as well as other possible contaminations. At the end of the dialysis the solutions are freeze-dried to obtain pure NaPSS.

CsPSS was prepared from NaPSS by an ion exchange process. First, Na^+ was removed by a cation exchange resin, which yields HPSS. Then an excess solution of CsOH and PSS was mixed in order to obtain CsPSS. The excess of OH^- was neutralized by dropwise addition of HCl. Pure CsPSS was obtained by means of dialysis and freeze-drying as described above.

Sample Preparation. For complex formation, appropriate amounts of 0.05 M aqueous solution of PDADMAC were added dropwise into 0.05 M aqueous solution of NaPSS or CsPSS, respectively. The solution was constantly stirred during the complexation reaction. Then, the solution was dialyzed against ultrapure water in order to get rid of the free salt formed during the complexation reactions. The dialysis was continued until the conductivity of the exchanged water fell below 2 μS/cm, and the remaining complexes in solution were freeze-dried. For conductivity measurements cylindrical pellets were prepared from ~0.05 g of powdered sample by applying a pressure of 12.5 kN/cm^2 for 2 min. The two opposite faces of the cylindrical pellets were sputtered with gold. Gold sputtered pellets were used for conductivity measurements by impedance spectroscopy.

Samples from a typical initial composition X MPSS$\cdot(100 - X)$ PDADMAC are designated as MPEC $X/(100 - X)$, where M^+ is the cationic counterpart of the complex (Na^+ or Cs^+), X is the monomeric mol % of PSS, and $(100 - X)$ is the monomeric mol % of PDADMAC in the initial complex.

Gravimetric Analysis. Gravimetric analysis (GA) was performed inside a glovebox. Pressed pellets of different compositions were first kept overnight at 100 °C in an oven. To remove water still present in the pellets, the samples were then put into a glovebox with a phosphorus pentoxide (P_2O_5) dried atmosphere for about 3 days. A hygrometer was used to check the relative humidity (RH) inside the gloves box. Pressed pellets were used in order to avoid any possible loss of material during the analysis. Under a dry atmosphere the weight (W_1) of the samples was determined by using a microbalance. Then, different constant relative humidity conditions (29—85%) were maintained in the glovebox using saturated salt solutions as described by Young.[28] The relative humidity measurement with the hygrometer showed an absolute error of ±2.5% RH. The weight (W_2) of the sample under each humidity was monitored until it was constant. Time-dependent experiments confirmed that an equilibration time of 5 days was sufficient. The water content in % is determined as $(W_2 - W_1)\cdot 100/W_2$.

Conductivity Measurements. Frequency-dependent conductivities are a valuable tool for studying the ion dynamics on different time scales. With the time window being given by the inverse angular frequency, conductivity spectroscopy allows to study elementary steps of the ion movements as well as macroscopic ion transport. In addition, the impedance spectroscopy technique employed in this study has the advantage that dc conductivies can be extracted from the measured spectra, even in the case when blocking electrodes are used.

In the present study, conductivity measurements were performed on gold sputtered pellets at ambient temperature inside a closed sample holder with an impedance analyzer (hp 4172, Hewlett-Packard) over a frequency range of 5 Hz—13 MHz. The real (σ') and the imaginary part (σ'') of the complex conductivity of the investigated materials were calculated from the experimentally determined frequency-dependent complex admittance, $Y^*(\nu)$. Here, ν stands for the experimental frequency; complex quantities are always denoted by the symbol $*$. The complex conductivity is obtained via $\sigma^*(\nu) = Y^*(\nu)d/A$, where A denotes the surface area of the gold electrodes and d is the sample thickness measured after sputtering. Note that the thickness of the gold electrodes was around 100 nm, which is negligible compared to the thickness of the sample (≈0.5 mm, measured before sputtering). The thickness measurements, required to calculate the conductivity value from the experimentally obtained admittance, were carried out prior to humidification, and the increase in thickness due to water uptake was neglected in the calculation of the conductivity. This approximation is justified, since the conductivity enhancement by humidity turned out to be much larger than any thickness changes.

Unlike in samples for gravimetric analysis, an equilibration time of a week was required to obtain constant conductivity values. Such a long equilibration time of the samples can be attributed to the fact that due to the electrodes covering the main pellet surfaces, only the radial surfaces of the sputtered pellets were exposed to the humid atmosphere for water uptake.

In the data analysis, the bulk resistance was obtained by fitting a model equivalent circuit consisting of a parallel connection of a constant phase element and an Ohmic resistance to the data. Data points at very

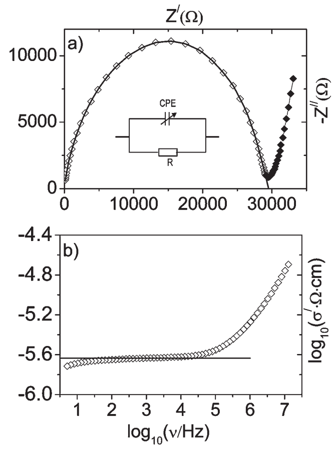

Figure 1. (a) Nyquist fit for extracting the bulk resistance for NaPEC 55/45 at 64% RH. Data points shown as full symbols are due to polarization effects. The inset shows the used equivalent circuit. (b) Corresponding conductivity spectrum of NaPEC 55/45 after equilibration at 64% RH. The dc conductivity determined from the Nyquist fit is included into the spectra as a straight line.

low frequencies, which were influenced by polarization effects due to the employed blocking electrodes, were removed before fitting (see Figure 1a, full symbols). The dc conductivity, σ_{dc}, was obtained by multiplying the cell constant with the inverse bulk resistance used in the fitting procedure. The dc conductivity so obtained is in all cases in excellent agreement with the conductivity value resulting from an extrapolation of the corresponding low-frequency conductivity plateau to $\nu = 0$ (see Figure 1b). In the following such data will, therefore, be termed "dc conductivity", although ac experiments were used for studying the ion transport. Like diffusion data, dc conductivities probe the macroscopic ion transport. The increase of the conductivity at higher frequencies (see Figure 1b) is due to the fact that the time window in which the ion dynamics is observed decreases with increasing frequencies. Therefore, also ion hops, which do not result in macroscopic ion transport, do contribute to the conductivity. The decrease of the experimental conductivity values at very low frequencies (see Figure 1b) is due polarization effects where ions accumulate at the blocking electrode surface. Such polarization effects are a natural consequence of the fact that blocking electrodes are used, and they will always occur. The onset of these effects on the frequency scale, however, strongly depends on the absolute value of the measured conductivity. The higher the conductivity, the higher is the frequency where polarization effects still can be detected. As shown in the following section, in our experimentally given frequency window, polarization effects are only significantly detectable at high relative humidity. Even there, they do not affect the determination of the dc conductivities which are evaluated in this work.

■ RESULTS

Conductivity Spectra. Figures 2a and 2b show a log−log plot of the real part of the conductivity spectra σ' against experimental frequency ν of NaPEC and CsPEC, respectively, at different RH ranging from 29% to 85%. At low relative humidity (29% and 46%) no appreciable electrode polarization effects are seen. However, with increasing RH, polarization effects move into the experimentally given frequency window and are detectable at low frequencies.

For both kinds of complexes (NaPEC and CsPEC) and over the entire humidity regime, we observe a well-defined low-frequency plateau, where the conductivity is independent of frequency. As outlined before, this plateau value can be identified with the dc conductivity. With increasing humidity the dc plateau moves toward higher conductivity values. At frequencies higher than those of the dc regime, the conductivity increases monotonously with frequency; this holds for each relative humidity. Moreover, the onset of this dispersion shifts toward higher frequency with increasing humidity. The onset of dispersion is characterized by the onset frequency ν^*, which is defined via $\sigma(\nu^*) = 2\sigma_{dc}$ and indicated by star symbols in Figure 2.

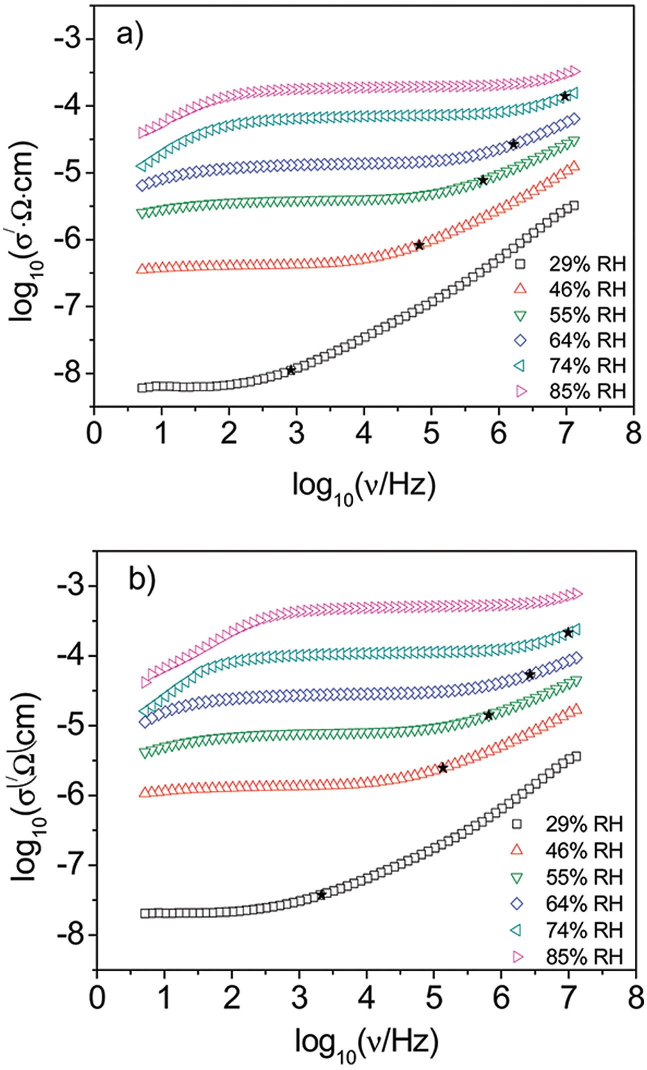

Figure 2. Conductivity spectra of (a) NaPEC 60/40 and (b) CsPEC 60/40 after equilibration at different relative humidity (RH) as given in the legend. The corresponding onset frequencies (ν^*) are marked with star symbols.

Though the sets of conductivity spectra of NaPEC and CsPEC show qualitatively the same dependence on frequency and on humidity, a major difference is that the conductivities are generally larger for CsPEC. Impedance spectra were taken in a similar way for a range of compositions, $X = 50$ to $X = 75$, and all of them show qualitatively the same shapes and dependences on frequency and humidity (data not shown).

Gravimetric Analysis. Figure 3 shows the results of the gravimetric analysis of (a) PEC 50/50 and PEC 70/30, respectively. The water content in % is plotted as a function of RH. For

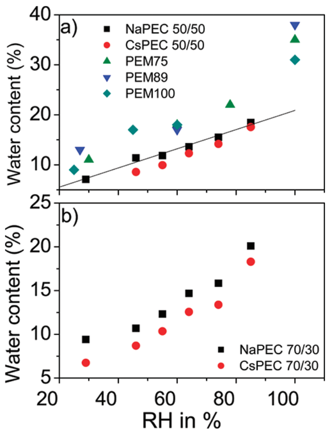

Figure 3. Plot of water content vs RH for (a) PEC 50/50 and PEC 70/30. In (a) the straight line was obtained by linear regression of the NaPEC 50/50 data. The data points for PEM 100, PEM 89, and PEM 75 (where the number indicates the degree of charge of PDADMAC in %) are extracted from Köhler et al.[29]

each composition, we observe an almost linear increase of the water content with RH at low and medium RH values. The water content for a particular system (NaPEC or CsPEC) at a fixed humidity is similar for all compositions (compare Figure 3a,b; other data not shown). However, over the entire humidity range NaPEC generally absorb a higher amount of water than CsPEC.

Swelling results of polyelectrolyte multilayers (PEM) reported in the literature show a slightly different behavior. Such data have been obtained by humidity-dependent thickness measurements, for example by neutron reflectivity. In PEM the thickness increases exponentially with humidity and at full hydration (100% RH) a thickness value of 130% of the dry thickness was reported.[30] In contrast, Köhler et al. reported two regions of swelling in PEM with a transition at about 60% RH:[29] The first region at low humidity was interpreted as a small volume expansion, while the region at high humidity was associated with a large volume increase. The major deviation of our results on PEC compared to the data of Köhler et al. for PEM is that in PEC we do not see such a sharp transition at 60% RH. Direct comparison at low humidity values shows that there is a somewhat lower water content in PEC compared to PEM made of the same polyelectrolytes (see data points in Figure 3a), and one would expect that this variation is consistent over the entire humidity regime. The lower water content in case of PEC compared to PEM can be attributed to the compact three-dimensional networks present in PEC.

σ_{dc}: Dependence on Relative Humidity. In Figures 4a and 4b $\log(\sigma_{dc})$ is plotted as a function of relative humidity for NaPEC and CsPEC, respectively, for different compositions.

For all compositions, a strong dependence of the dc conductivity on RH is observed, and the variation extends about 4 orders of magnitude. Moreover, $\log(\sigma_{dc})$ increases almost linearly with RH for NaPEC as well as for CsPEC for all compositions and can be described by the dependence: $\log(\sigma_{dc}) = a\cdot\mathrm{RH} + \mathrm{const}$. The straight lines in Figure 4 are obtained by linear regression. To the best of our knowledge, this behavior is seen for the first time in PEC, while it is a phenomenon already recently observed in PEM.[17,20]

σ_{dc}: Dependence on Type of Counterions. In order to investigate the dependence of the dc conductivity on the type of counterion (i.e., Na^+ or Cs^+), data for similar compositions of

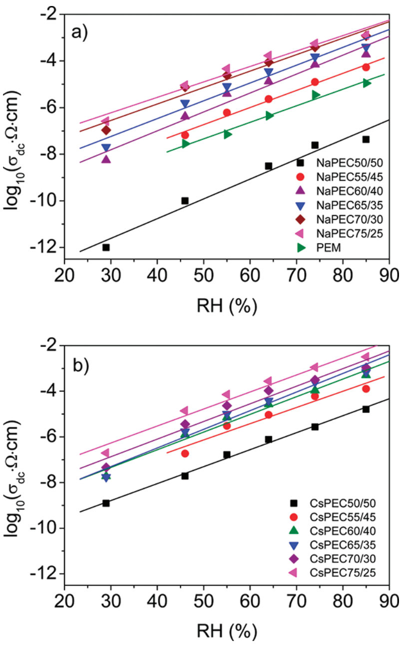

Figure 4. Plot of logarithm of σ_{dc} vs RH for (a) NaPEC and (b) CsPEC. Additionally, in the case of NaPEC (a), the conductivity of PEM composed of the same material is given for comparison; values are taken from ref 20.

NaPEC and CsPEC are plotted together in Figure 5, employing the data shown in Figure 4. The slope of the plot of $\log(\sigma_{dc})$ vs RH for different composition is 0.08 ± 0.01 and does not depend on the composition or the type of alkali cation. The slope values are in the range of the slope found for PEM composed of the same material as reported by Akgöl et al., which was 0.075 ± 0.015 (see ref 20).

The value of the slope indicates that conductivities of both NaPEC and CsPEC have the same dependence on humidity. In case of PEC 50/50, the conductivity of CsPEC, at a particular humidity, is almost 3 orders of magnitude higher as compared to the conductivity of NaPEC (see Figure 5, top left). However, the difference keeps on decreasing as one goes toward more PSS-rich compositions. At low PSS content, σ_{dc} for CsPEC is always higher over the entire humidity regime. For more PSS-rich compositions (e.g., PEC 65/35, PEC 70/30 and PEC 75/25) the conductivity of CsPEC and NaPEC are equal within the error limit.

σ_{dc} does not scale linearly with ion concentration. For example, the dc conductivity of NaPEC 70/30 is about 2 orders of magnitude higher as compared to NaPEC 55/45. Such an increase in conductivity with ion concentration cannot be explained by the increase of the charge carrier concentration itself, but a concentration-dependent mobility of the charge carriers has to be concluded. The dc conductivity in a system with only one type of charge carrier is given as a product of the charge q, the mobility μ, and the number density N, i.e.

$$\sigma_{dc} = q\mu N \qquad (1)$$

In many inorganic glasses, the change of mobility with charge density follows a power law.[31,32] Therefore, it is interesting to investigate the variation of the mobility with the number density at a particular humidity. A log−log type plot of (σ_{dc}/N) vs N therefore shows the dependence of ion mobility on ion number

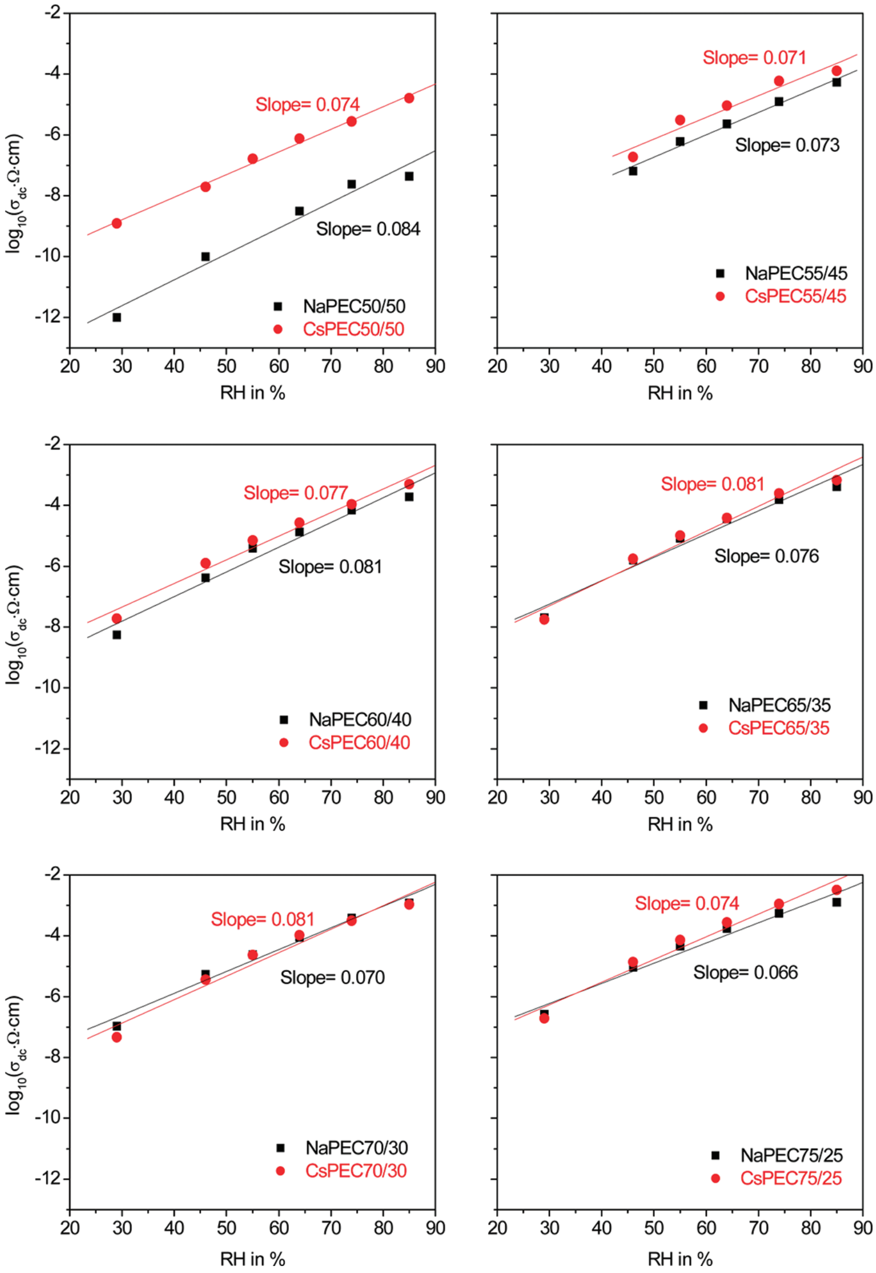

Figure 5. Plot of logarithm of σ_{dc} vs RH for similar compositions of NaPEC and CsPEC.

density N. In Figure 6 we see the variation of $\sigma_{dc}/N^{\%}$ as a function of $N^{\%}$, where $N^{\%}$ is the fraction of polyion charges that is not intrinsically compensated by oppositely charged polyion groups, but by an excess counterion. For example, in NaPEC 60/40, 80% of the total number of polyion charges undergo electrostatic cross-linking and 20% are compensated by small counterions, which we denote as $N^{\%} = 20\%$ (Table 1). Note that we assume here that the number density and $N^{\%}$ are proportional. This is a valid assumption because the PEC density is almost independent of composition.

The variation of $\log(\sigma_{dc}/N^{\%})$ with the counterion excess is linear irrespective of humidity, for both NaPEC (Figure 6a) and CsPEC (Figure 6b), which suggests that similar to many inorganic glasses the mobility of the ions follows a power law in dependence on their density. Note that we do not include the conductivity values of PEC50/50 in this consideration, as we do not know the exact stoichiometry, since $N^{\%}$ in this complex is close to zero and thus very sensitive to small errors in polymer composition and difficult to control.

■ DISCUSSION

Main Findings. The main observations we obtain on the basis of our systematic investigation of impedance spectra for PEC with different amounts of incorporated ions and different counterions are: (i) Over the entire humidity range the water content in PEC increases almost linearly with humidity and the water content in NaPEC is higher compared to CsPEC for similar composition. (ii) The conductivity of CsPEC is higher as compared to NaPEC at a given RH value

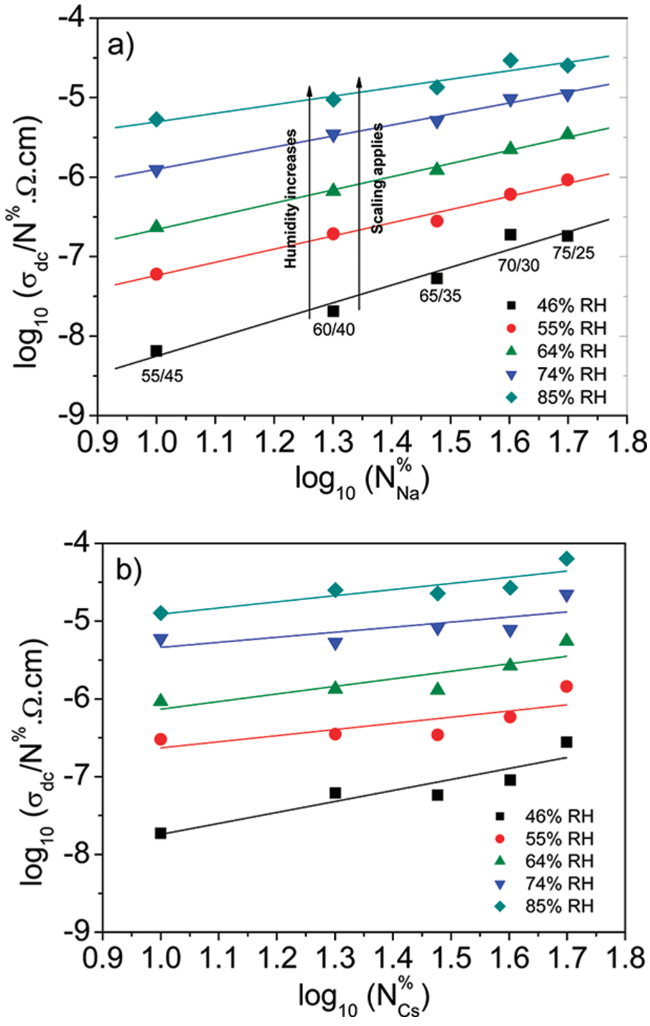

Figure 6. Plot of logarithm of $\sigma_{dc}/N^{\%}$ vs excess of counterions ($N^{\%}$) for (a) NaPEC and (b) CsPEC. The lines are obtained by linear regression.

for PEC with low or moderate ion content. However, at high ion contents both CsPEC and NaPEC show the same conductivity values within the error limits. (iii) The dc conductivity of all studied PEC increases exponentially with humidity and follows the linear dependence $\log(\sigma_{dc}) = a \cdot \mathrm{RH} + \mathrm{const.}$ As discussed in ref 27, the influence of RH on the conductivity is so strong that it cannot be simply traced back to a slight softening of the PEC matrix caused by the absorption of water. Instead, also the mobile cations and their local environment have to be considered. This will be discussed in the following section.

Conducting Species. Here we will discuss which implications the above observations have concerning the ion transport mechanisms in PEC and concerning the effect of RH and type of counterions on the conductivity. In case of dry PEC, Imre et al. have already shown that alkali ions are the major conducting species.[25] For humidified PEM it was shown that the dominant conducting species are protons.[20] This might be due to the low salt ion concentration in PEM as compared to PEC or due to a very high mobility of protons in hydrated samples. Thus, in humidified PEC investigated here, the charge carriers could either be protons as well, or incorporated small cations, or a combination of both.

Table 1. Compositions of the Samples and Their Conversion into the Fraction of Charge Carriers in Relation to the Number of Polyion Charges, $N^{\%}$

PEC composition (Na^+ or Cs^+)	theoretical extent of cross-linking (%)	theoretical content of small cations (%), $N^{\%}$
50/50	100	0
55/45	90	10
60/40	80	20
65/35	70	30
70/30	60	40
75/25	50	50

In PEC with $X = 50$ the number of incorporated small ions should be theoretically zero. However, in reality, the exact stoichiometry of PEC 50/50 is unknown and difficult to control. The number of alkali cations in such PEC is therefore not only unknown and very small, but it can also vary from sample to sample. In all other PEC compositions, however, the amount of alkali ions involved in extrinsic charge compensation is well-defined and determined by the ratio of polycations to polyanions. The number of Na^+ or Cs^+ ions is therefore known, and as displayed in Table 1, $N^{\%}$ ranges between 10% in the case of $X = 55$ and 50% in the case of $X = 75$. From this it follows that if protons were the dominant conducting species in humidified PEC, differences in conductivity between NaPEC and CsPEC with the same composition X would have to arise from differences in the water content. According to Figure 3, the water content in NaPEC is generally larger, while the conductivity (see Figure 5) is lower than or similar to the conductivity of CsPEC. These observations are the first indication speaking against proton conduction in humidified PEC.

Another argument against proton conduction in humidified PEC arises from recently published scaling relations of the conductivity spectra.[27] If protons were the dominant conducting species, for a given PEC composition, the number of mobile protons should increase with the number of absorbed water molecules and therefore with RH. This effect is, indeed, seen in humidified PEM and will be discussed in more detail in a forthcoming paper. However, scaling results for humidified PEC imply that the increase in conductivity with RH can be purely attributed to an enhancement in the mobility of the mobile ions, whereas their number density is not influenced by RH. On the basis of both arguments, we therefore conclude that in humidified PEC, protons are not the dominant conducting species.

As the situation in humid PEC differs from that of humid PEM, we may assume that, like in dry PEC, the alkali ions are the charge carriers dominating the ion transport in humidified PEC. However, if the alkali ions were the most mobile species, one would expect a higher conductivity for NaPEC as compared to CsPEC due to the larger size of the Cs^+ ions. This is indeed what is found in case of dry PEC[33] and will be discussed in more detail in a forthcoming paper.[34]

One could argue that the reversal of conductivity with respect to dry PEC might be due to a higher dissociation constant of the CsPSS compared to NaPSS under humidified atmosphere. However, if this was the case, the degree of dissociation of both NaPEC and CsPEC should depend upon humidity. This again speaks against the recently published scaling behavior of humidified PEC.[27] Moreover, the scaling results show that even for extreme nonstoichiometric compositions all ions are dissociated at humidity as low as 29%.

Therefore, we think that in a humid atmosphere neither protons nor bare alkali ions are determining the ion conductivity in PEC. Instead, hydrated alkali ions have to be considered. With the hydration shell, the relative ion size of sodium to cesium ions can be reversed. The effective size of a hydrated Na^+ ion is larger as compared to Cs^+ due to higher charge density (q/r, where q is the charge of the ion and r is the radius of the hydrated ions) of the former, causing a larger hydration shell. In fact, as outlined before, gravimetric analysis has shown higher water content for NaPEC as compared to CsPEC for similar composition, supporting the assumption of hydrated alkali ions as the predominant charge carriers. The conclusion is that the Na^+ ion is indeed surrounded by more water molecules, yielding a larger effective size. Thus, the mobility of hydrated Cs^+ is larger than that of hydrated Na^+, and the higher conductivity of CsPEC (see Figure 5) can be explained.

Only in the special case of PEC 50/50, the hydration argument cannot completely justify the large difference in the conductivities of NaPEC and CsPEC, respectively. As outlined before, these PEC are, however, very special due to the uncertainty in terms of extrinsic vs intrinsic charge compensation. This PEC composition will therefore not be considered here any further.

From all of the above arguments we conclude that the transport of solvated alkali ions constitutes the dominant contribution to the conductivity in humidified PEC, while that of the protons is negligible. The movements of alkali ions with their hydration shell result in a larger mobility for larger cations.

Composition Dependence. As shown in Figure 5, the difference in conductivity between NaPEC and CsPEC decreases as we move toward more PSS-rich compositions, and it ends up with almost similar values of the conductivity at high ion content. In general, PEC networks are formed by the Coulombic interactions between the polyion charges. The cross-linking density of the PEC network thus depends on the number of polyion groups involved in Coulombic interactions. PEC 50/50 are formed by mixing of equal molar amounts of either of the polyions and constitute the case of maximum cross-linking density. For PEM, a decrease of conductivity upon increasing the extent of cross-linking was already reported earlier.[26] If we transfer this observation to PEC, the motion of hydrated Na^+ ions in a compact network is hindered more strongly due to their larger effective size as compared to hydrated Cs^+. Thus, at a similar extent of extrinsic charge compensation, the conductivity of NaPEC should be lower than that of CsPEC. This argument holds for all compositions with X close to stoichiometric and explains the larger conductivity in CsPEC for compositions 55/45 and 60/40.

On the other hand, in strongly nonstoichiometric compositions ($X > 60$) we again expect a similar extent of extrinsic charge compensation by cations for similar compositions of NaPEC and CsPEC, i.e., similar charge carrier densities. However, here the conductivities do not differ any more for Na or Cs complexes (see Figure 5). As we move to more PSS-rich compositions, the cross-linking density decreases allowing ions to move faster even with large hydration shells. Therefore, with increasing PSS content, the ion mobility in both NaPEC as well as CsPEC increases. However, because of the higher effective size of the hydrated Na^+, we observe a higher increment in conductivity in case of Na^+ with increasingly PSS-rich compositions (compare Figure 5). Apparently, from $X = 65$ on the cross-linking density is low enough so that it does not restrict the transport of hydrated Na^+ or Cs^+ ions. Figure 6 shows the above trends as well, since it displays the mobility of the charge carriers: The slopes of the regression lines are larger for Na^+ (Figure 6a) as compared to Cs^+ (Figure 6b), indicating the stronger influence of the network density on the larger hydrated ion Na^+. In addition, this representation makes the influence of the water content on mobility evident, which is discussed in the next section.

Scaling Behavior and Effect of Absorbed Water. Generally, the contribution of a charged species i to the dc conductivity is given by

$$\sigma_{\mathrm{dc},\,i} = q_i \mu_i N_i \tag{2}$$

Therefore, it seems that the increase in conductivity with humidity for a fixed composition (see vertical arrows in Figure 6) is due to either an increase in mobility of the charged species or an increase of the number density of the charge carriers or a combination of both. One could argue that with increasing humidity the water content increases and fewer ions might be condensed, which results in an increasing number density and therefore increasing conductivity. However, the situation is somewhat different. In our recent work,[27] we have demonstrated that the shapes of spectra taken at different humidity can be completely superimposed when appropriately scaled. This finding was termed "time– humidity superposition principle"[27] in analogy to the well-known time–temperature superposition principle valid in many materials. Similar to Summerfield scaling[35] (valid for temperature-dependent conductivity), we find that the dc conductivity is proportional to the onset frequency ν^* over the entire humidity range. In other words, with this "Summerfield-type scaling" being valid, the slope in a plot of $\log(\sigma_{\mathrm{dc}})$ vs $\log(\nu^*)$ is unity over the entire humidity regime. This implies that the role of water molecules is only to speed up the ion hopping dynamics without altering the basic microscopic transport mechanism or the charge carrier density. Thus, we can say that for a fixed PEC composition the increase of conductivity with RH is solely due to an increase of the mobility of the charge carriers and not to an increase in the number density of mobile ions.[27]

Now the question is how water molecules influence the ion mobility. In order to answer this question, we again refer to Figure 6. For a fixed composition, humidity and thus water content increase along the line shown by the vertical arrow. In this direction Summerfield scaling applies; i.e., the charge carrier density is constant. The variation of the size of hydration shell cannot explain the mobility enhancement as it would rather cause a decrease in mobility with RH. Considering the fact that, even for the extreme PSS-rich composition (PEC75/25) all the cations are hydrated at RH as low as 29%,[27] we can discuss the influence of hydration water on the matrix: With increasing humidity, the number of water molecules not involved in hydration shells would then increase. We refer to them as "matrix water". So not only the hydration of the ion but also that of the polyelectrolytes plays a role yielding reduced polyion–polyion and polyion–cation interactions. All of these effects contribute to the overall increase of the ionic mobility. Microscopically, the matrix water leads to an enhancement of the ion mobilty on the basis of reduced potential barriers between different ionic sites. With increasing water content in PEC (Figure 3) the amount of matrix water molecules increases, which in turn provides a stronger effect of lowering the activation barrier for the ion transport. Therefore, we think that water molecules not only serve to hydrate the ions and polyions, but they also enhance ionic mobility by reduction of potential energy barriers.[27] Note that the vertical distance of data points in the logarithmic plot of Figure 6 is always the same. Thus, the mobility of any type of cation in any matrix composition is enhanced by the same factor. The same fact is also seen by the identical slopes of the humidity dependence shown in Figure 4. This effect of lowering is thus independent of composition and type of cation. One can further speculate which molecular processes might be involved. Certainly the hydration water screens the polyion charges and thus reduces the Coulombic interaction strength of a polyion charge—polyion charge bond. This would render the matrix more dynamic and flexible. In terms of the network density discussed above, the Coulomb screening might enable the network to dynamically open and close electrostatic bonds, such that for short times effectively larger network meshes are available for the transport of small cations.

■ CONCLUSIONS

In summary, a broad range of compositions of PEC containing Na^+ or Cs^+ as mobile ions are prepared and the conductivity is measured over a broad humidity range. σ_{dc} increases exponentially as a function of relative humidity for all compositions of NaPEC and CsPEC and follows the law $\log(\sigma_{dc}) = a \cdot \mathrm{RH} + \mathrm{const}$. At a given composition, higher conductivity values of CsPEC as compared to NaPEC indicate that hydrated ions are the charge carriers, even at relative humidity values as low as 29%. However, with increasing asymmetry in the compositions, the difference in conductivity of the CsPEC and NaPEC decreases due a lack of cross-linking between the polyions, which in turn results in more pathways for the ion transport. Furthermore, the mobility of the alkali ions increases with the PSS content, which is an effect of the reduced cross-linking density. Water molecules not only hydrate the ions but also play an important role via lowering the energy barrier of the ion transport which further facilitates the ionic mobility.

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