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Dielectric Relaxation Spectroscopy of Aliphatic Ionene Bromides and Fluorides in Water: The Role of the Polyion's Charge Density and the Nature of the Counterions

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1. Introduction

The electrolytic character of synthetic and bio-polyelectrolytes (proteins, nucleic acids) is a consequence of groups that ionize when exposed to polar solvents.[1,2] According to Oosawa,[3] the main features of the potential field produced by a rodlike polyion are deep potential holes at the charged groups and a cylindrical valley along the polyelectrolyte (PE) chain. Counterions distributed within the potential valley are considered "bound" ("localized" if in a potential hole and mobile if otherwise) whereas the counterions outside form a diffuse ionic atmosphere. These "bound" counterions cause the mutual perturbation of hydration layers, while on the other hand the transport and colligative properties of the PE solution are influenced by all counterions including those forming ionic atmosphere.[4−6] Decades ago Gross and Strauss[7] showed that the binding of counterions to polyions can be accompanied by the rearrangement of water molecules between the charges. The fraction of "bound" counterions estimated from their experiments is in good agreement with the fraction of "condensed" counterions predicted by the Manning theory.[8] Despite extensive research over the past decades, some truly fundamental questions of the chemistry and physics of polyelectrolytes (PEs) have yet to be answered.[9,10]

The generic name *ionene* is used for the group of cationic polymers having quarternized nitrogen atoms in their backbone. In what follows the term *x*,*y*-ionene bromide or fluoride will be used for the most basic aliphatic analogue with the monomeric unit shown in Figure 1. The character of ionene solutions depends on the charge density of the polyelectrolyte backbone as well as on the chemical nature of the counterions; both can be varied during the synthesis.[11,12] In the absence of added salts ionenes capture a relatively stiff (rodlike) configuration,[13−15] their charge density clearly depending on the values *x* and *y*. Following what has been said so far, ionenes represent ideal candidates for studying the simultaneous effect of charged and hydrophobic groups on the PE behavior in water. In addition, varying the counterion (by definition the ion dissociated from the polyion) species, one can investigate the influence of the very chemical nature of these ions on the solution characteristics.

While the thermodynamic and transport properties of ionene solutions have been reasonably well studied experimentally,[12−18] little is known about interactions in the immediate vicinity of the polyion. In this paper dielectric relaxation spectroscopy (DRS) has been chosen to "look" at what is "happening" next to the polyion. DRS seems to be suitable for the purpose, as this technique, which probes the complex permittivity, $\varepsilon^*(\nu)$, directly monitors fluctuations in the total dipole moment of the sample while exposed to an oscillating electrical field of frequency ν. As a result of such experiments, relaxation times and amplitudes can be obtained for dynamical processes associated with the solvent and the solute.[19−23] While information on solute hydration can be inferred from the water relaxation, the investigation of the solute-specific process can be used to study the interactions between the polyion and its counterions.

2. Experimental Section

2.1. Synthesis. Ionene bromides were synthesized from the corresponding equimolar amounts of *N*,*N*,*N'*,*N'*-tetramethyl-1,*x*-alkane and 1,*y*-dibromoalkane (Aldrich) by a polyaddition reaction in dimethylformamide at room temperature and under an argon atmosphere.[11,12] The crude product was washed with a large amount of acetone, filtered, and dried under vacuum for 48 h at 318 K. Conversion was checked by ^{1}H NMR. Dialysis tubes (Sigma, MWCO = 12 000) were filled with ≈ 0.02 M aqueous solutions of the reaction product and exhaustively dialyzed until the conductivity of the exchanging water solution remained < 2 μS/cm. Ionene fluorides were prepared from bromide salts by ion exchange during dialysis, using a 0.05 M NaF solution as the exchanging solution, and further dialyzed against water to remove sodium ions. The same conductivity criteria as in the case of bromide samples and a negative flame test for Na^+ were used to check completion of the purification procedure. The average molecular mass of the synthesized ionenes was estimated to be between 12 000 g/mol (characteristic of the dialysis tubes) and 40 000 g/mol,[13,14,24,25] which corresponds to an average degree of polymerization between 40 and 230 monomeric units. The polymeric character of the samples is clearly seen from the concentration dependence of the osmotic coefficients.[12]

2.2. Sample Preparation. Samples were prepared gravimetrically with Milipore water. The exact counterion concentrations were determined potentiometrically using bromide or fluoride ion selective electrodes and a saturated mercury sulfate electrode as the reference. Samples were titrated with standardized solutions of $AgNO_3$ and $LaCl_3$ for bromide and fluoride ionenes, respectively. If not stated otherwise, all concentrations, *c*, reported in this paper are given as moles of monovalent counterions per dm^3 (M).

2.3. Conductivity and Density. An arrangement of nine capillary cells of different cell constants, calibrated with KCl, was used to successively measure the resistance of nine ionene solutions.[26] A high-precision thermostat (Lauda UB 40J, WK 1400) was used to maintain the temperature with a

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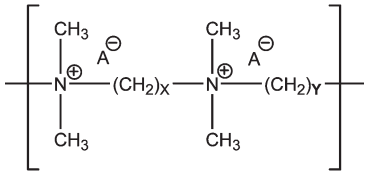

Figure 1. Monomeric unit of an *x*,*y*-ionene halide. *x*,*y* = 3,3; 4,5; 6,6; and 6,9; A^- = Br^- or F^-.

reproducibility better than ±0.003 K. DC conductivities, κ, obtained in this way[26] were used to correct the experimentally accessible total loss, $\eta''(\nu)$, of the DRS experiment according to eq 2.[27] A vibrating tube densimeter (Anton Paar DMA 60) was used to determine the solution densities, ρ, at 298.15 ± 0.05 K. This information was required to compute the analytical concentration of water. The data for κ and ρ are included in Tables S1 and S2 of the Supporting Information.

2.4. Dielectric Relaxation Spectroscopy. Dielectric spectra were recorded with a time-domain reflectometer (TDR) covering $0.05 \leq \nu/\mathrm{GHz} \lesssim 2$,[28] a frequency-domain reflectometer based on a vector network analyzer (VNA) for 0.2−20 GHz,[29] and a set of four frequency-domain waveguide interferometers (IFM) covering $8.5 \leq \nu/\mathrm{GHz} \leq 89$.[30] All the spectra were recorded at 298.15 ± 0.05 K and corrected for the Ohmic loss (cf. eq 2).[27] The uncertainty relative to the static permittivity, ε, of the sample was estimated to be less than 2% for ε' and η''; the precision was generally better than 0.5%. Typical experimental spectra and their fits are shown in Figure S3 of the Supporting Information.

3. Data Analysis

Dielectric spectroscopy records the total polarization, $\vec{P}(t)$, of a sample in a time-dependent electric field, $\vec{E}(t)$.[31] This response is usually expressed as a function of the field's frequency, ν, in terms of the complex permittivity, $\varepsilon^*(\nu)$

$$\varepsilon^*(\nu) = \varepsilon'(\nu) - \mathrm{i}\varepsilon''(\nu) \qquad (1)$$

The relative permittivity, $\varepsilon'(\nu)$, shows a dispersion from the static permittivity limit at low frequencies, ε, to the high-frequency limit, ε_∞. The dielectric loss, $\varepsilon''(\nu)$, expresses the energy dissipation within the sample, arising from the coupling of $\vec{E}(t)$ to dipole fluctuations. For electrically conducting samples of dc conductivity, κ, diffusive charge transport creates an additional Ohmic loss term. Since only the total loss, $\eta''(\nu)$, is experimentally accessible, the dielectric loss, $\varepsilon''(\nu)$, must be obtained by correcting for this effect

$$\varepsilon''(\nu) = \eta''(\nu) - \frac{\kappa}{2\pi\nu\varepsilon_0} \qquad (2)$$

Note that $\varepsilon^*(\nu)$ contains all contributions to $\vec{P}(t)$ that depend on frequency, irrespective of their rotational, vibrational, or translational character.

For the formal description of the spectra, various relaxation models based on the sum of n individual relaxation processes

$$\varepsilon^*(\nu) = \sum_{j=1}^{n} \frac{\varepsilon_j - \varepsilon_{j\infty}}{[1 + (\mathrm{i}2\pi\nu\tau_j)^{1-\alpha_j}]^{\beta_j}} + \varepsilon_\infty \qquad (3)$$

were tested using a nonlinear least-squares routine that simultaneously fitted $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$. In eq 3, $\varepsilon = \varepsilon_1$ is the static permittivity of the sample, $\varepsilon_{j\infty} = \varepsilon_{j+1}$, and $\varepsilon_{n\infty} = \varepsilon_\infty$. Each dispersion step j of amplitude $S_j = \varepsilon_j - \varepsilon_{j\infty}$ and relaxation time τ_j was modeled by a Havriliak−Negami equation with relaxation-time distribution parameters $0 \leq \alpha_j < 1$ and $0 < \beta_j \leq 1$. The simplified variants of this equation are the Cole−Davidson (CD, $\alpha_j = 0$), Cole−Cole (CC, $\beta_j = 1$), or Debye (D, $\alpha_j = 0, \beta_j = 1$) equations.[32] The fit quality was monitored by the value of the reduced error function, χ_r^2, which is normalized for the number of adjustable parameters and thus allows comparison of fit models with differing number of parameters.[27] Estimates for the uncertainties of the obtained fit parameters ε_i and τ_1 were obtained from the scatter of their fits vs concentration with simple equations (maximum three parameters; see lines included in Figure 3a).

3.1. Relaxation Model and Assignment of Modes. The dielectric relaxation of pure water (subscript "w") is dominated by a Debye process at ~18 GHz, corresponding to a relaxation time of $\tau_{w,c}$ = 8.38 ps at 298 K.[33] This mode is commonly associated with the cooperative ("c") dynamics of the hydrogen-bond network.[34,35] Additionally, a small high-frequency ("f") process, which is centered at ~400 GHz, can be detected and amounts to only ~3% of the total water dispersion.[35] The latter mode is commonly attributed to the reorientation of the mobile water molecules having no or only single H-bond within the network of H-bonded water molecules. Addition of electrolytes leads to a decrease of the water dispersion, $S_w(c) = S_{w,c} + S_{w,f}$, with increasing solute concentration, c, which generally exceeds the mere dilution effect because of ion hydration.[34,36] Analysis of $S_w(c)$ and comparison of the calculated apparent water concentration, c_w^{ap}, with the analytical solvent concentration, c_w, provides a route to define effective hydration numbers, since $c_w - c_w^{ap}$ gives the number of the water molecules that differ in their dynamics from (more or less) unperturbed bulk water.[36−39] Additionally, some shift of $\tau_{w,c}$ may be observed when changing the concentration of the solute.

The "fate" of the "bound" solvent depends on the nature and on the strength of their interactions with the solute.[36] Water dipoles hydrating cations with high surface-charge density (like Li^+ or Mg^{2+}) exhibit pronounced radial alignment due to the strong electrostatic ion−dipole interactions. The rotation and exchange dynamics of these "irrotationally" bound solvent molecules are so strongly reduced that they do not contribute to $\varepsilon^*(\nu)$ anymore. At the opposite end of the scale are most univalent anions, including Br^-. Their interaction with the hydrating water molecules is via hydrogen bonds of a strength similar to H_2O−H_2O interactions. As a consequence, only a shift of $\tau_{w,c}$ is observed but no irrotational bonding.[36] Intermediate is the effect of fluoride ion and of hydrophobic ions of sufficient size (tetrapropylammonium and larger),[37] including alkyltrimethylammonium halide micelles,[23] albeit for different reasons. Here the dynamics of the hydration water is slowed down (but not frozen), and the associated reduction of the bulk-water amplitude reappears as a new bound-water ("b") relaxation process with relaxation times of $\tau_b \approx$ 15−50 ps (loss peak frequency ~3−10 GHz). For F^- ion this retardation of the hydration water is almost certainly a combination of strong hydrogen-bonding and electrostatic interactions. On the other hand, the slow dynamics of the water surrounding hydrophobic solutes arises from the tendency of these water molecules to form hydrogen bonds with each other. The presence of the solute not only reduces the number of equivalent configurations but simultaneously shields this network against the defects ("fifth neighbors") catalyzing the cooperative water relaxation. As a consequence, the dynamics of the hydrating molecules is reduced.[36]

In addition, dielectric studies of PE solutions generally reveal the presence of two relaxations associated with the solute.[19−22] At least for high degrees of polymerization the conformation of PEs in aqueous solution can be understood as a chain of more or less loosely packed "beads" of the locally collapsed polymer chain, which can be mapped on a cylinder. The latter is surrounded and partly penetrated by counterions. It is commonly accepted that the slow relaxation in the 10−100 kHz region is associated with the fluctuations of the counterions in the ionic atmosphere along the cylinder axis.[19,20] For the fast PE relaxation, occurring in the region of several tens to hundreds of megahertz, two opposing interpretations can be found in the literature. According to Mandel and co-workers, this fast PE mode arises from the motion of "bound" counterions along some well-defined straight sections of the PE chains.[19,20] On the other hand, Ito et al. assume a radial motion of counterions in the ionic atmosphere[22] (called "loosely bound" by the authors). Specific quantities of both PE relaxations, irrespective of the model used for their description, are the mobility of counterions and their characteristic correlation length.

Based on the above information, a superposition of up to five dispersion steps may be anticipated for the present ionene solutions. However, the fast water relaxation at ~400 GHz is small and should thus be hardly detectable for the present $\varepsilon^*(\nu)$ restricted to $0.05 \le \nu/\text{GHz} \lesssim 89$. The 10−100 kHz relaxation of the PE is also outside the investigated frequency range. However, at least for the high degrees of polymerization studied so far,[20−22] the amplitude of this process is so large that it should show up in the present spectra.

The experimental $\varepsilon^*(\nu)$ of aqueous ionene solutions clearly show bimodal character (Figure 2 and Figures S3 and S4 in the Supporting Information). Indeed, all dielectric spectra of this investigation are best fitted by a low-frequency (~200 MHz) Cole−Cole mode and a Debye relaxation at high (~18 GHz) frequencies, i.e., by a CC + D relaxation model. The obtained parameters, limiting permittivities (ε, ε_2, ε_∞), relaxation times (τ_1, τ_2), and the width parameter (α_1) of the CC mode are summarized in Tables S1 and S2 of the Supporting Information, together with the corresponding values of the reduced error function, χ_r^2. Examples for the concentration dependence of the spectra and the derived parameters of the CC + D model are shown in Figures 2, 3, and 4 (and in Figures S3 and S4 of the Supporting Information). From the obtained data the assignment of the low-frequency relaxation ($S_1 = \varepsilon - \varepsilon_2$, τ_1, α_1) to the ionene and of the higher frequency mode ($S_2 = \varepsilon_2 - \varepsilon_\infty = S_{w,c}$, τ_2) to the cooperative water relaxation is straightforward.

Uncertainties, ΔX, of the obtained values for ε, ε_2, τ_1, and τ_2 were estimated from the standard errors of their fits vs concentration using simple equations of at maximum three parameters. This analysis yields $\Delta\varepsilon \approx 0.4$, $\Delta\tau_1/\tau_1 \approx 10{-}15\%$, $\Delta\varepsilon_2 \approx 0.1$, and $\Delta\tau_1/\tau_1 \approx 3\%$. The guidelines to the eye included in Figure 3a show such fits. This procedure allowed the identification of the outliers marked in Tables S1 and S2.

Attempts to fit the dielectric spectra with other variants of eq 3 failed except for a superposition of three Debye equations (D + D + D model), where a further intermediate relaxation at ~5−10 GHz was assumed. For D + D + D model the values of χ_r^2 obtained in trial fits with the intermediate relaxation time fixed to 17 and 30 ps were comparable to those of the CC + D model. However, the obtained parameters scattered too much to pursuit a meaningful interpretation. Note that a superposition of three relaxation processes would be expected in view of previous investigations of the dielectric relaxation of aqueous solutions of hydrophobic ions[23,37]and of alkali fluorides. Most likely our failure to unambiguously resolve the expected slow water relaxation was a combination of limited accuracy and low concentrations investigated.

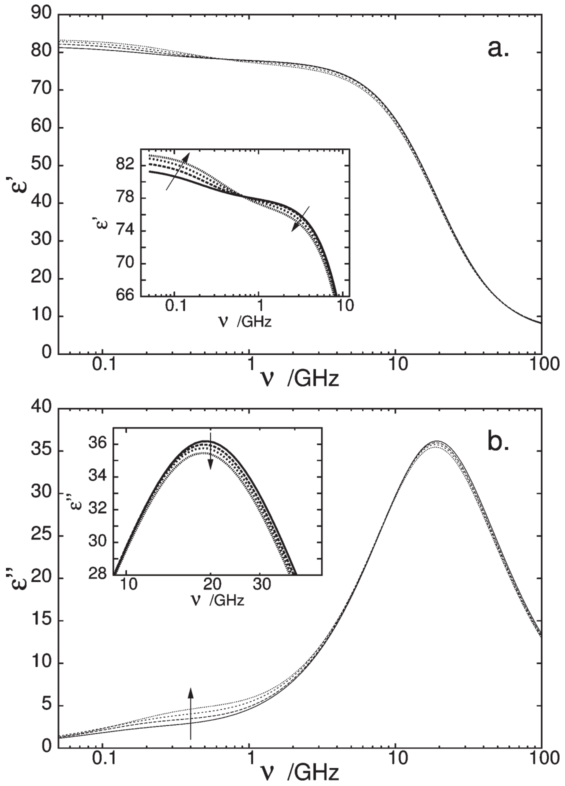

Figure 2. Concentration dependence of dielectric spectra of 6,6-ionene bromide solutions. Lines apply to the CC + D fit: (a) dielectric permittivity, $\varepsilon'(\nu)$; (b) dielectric loss, $\varepsilon''(\nu)$. Arrows indicate changes with increasing concentration of the ionene: 0.02, 0.03, 0.05, and 0.07 M. For clarity of presentation we omitted the experimental data.

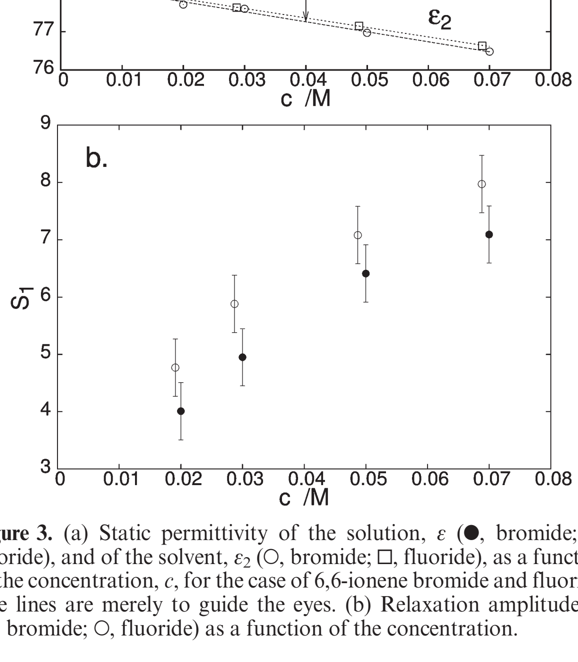

Figure 3. (a) Static permittivity of the solution, ε (●, bromide; ■, fluoride), and of the solvent, ε_2 (○, bromide; □, fluoride), as a function of the concentration, c, for the case of 6,6-ionene bromide and fluoride. The lines are merely to guide the eyes. (b) Relaxation amplitude S_1 (●, bromide; ○, fluoride) as a function of the concentration.

3.2. Water Relaxation and Polyelectrolyte Hydration. Within experimental error (~3%) the water relaxation time, τ_2, of 3,3- and 4,5-ionene bromide and fluoride solutions does not depend on concentration (Tables S1 and S2 of the Supporting Information) and equals the time constant for the cooperative H-bond rearrangement of pure water, $\tau_{w,c}$ = 8.38 ps.[33] For the 6,6- and 6,9-ionenes the data suggest a small increase. However, for all investigated PE solutions we can say that the dynamics of bulk water is practically unaffected. Clearly this is a consequence of large excess of water molecules (high dilution with respect to the PE component) present in the system.

Within experimental error ($\Delta\varepsilon_2 \approx 0.1$) the "water permittivity", $\varepsilon_2(c)$, of the solutions (Figure 3a) and thus the amplitude of the water dispersion, $S_w(c) = S_{w,c} + S_{w,f}$,[40] decrease linearly with increasing c. The magnitude of the slope, $dS_2(c)/dc$, significantly exceeds the value expected from the trivial dilution of the water dipoles by the added solute, indicating that a certain amount of water interacts sufficiently strongly with the solute to exhibit dynamics different from the bulk.[36] Analysis of the data along the lines described in detail previously[36,37] surprisingly reveals that, within the rather large error limits, the amount of water thus "bound" by the solute does neither depend on the ionene nor on the counterion. An effective PE hydration number of $Z = 14 \pm 4$ water molecules per repeat unit, that is, 7 ± 2 waters per ion pair, is obtained, which indicates strong interactions of the solute with water. Note that effective hydration numbers obtained from DRS incorporate packing requirements in the hydration shell and interaction strengths, with the latter usually dominating.[36] Thus, Z is generally different from the coordination numbers determined by scattering methods and computer simulations.

Since we failed to unambiguously resolve the "slow" water relaxation in the ~3− 10 GHz region (corresponding to $\tau_b \approx$ 15−50 ps), we have no specific information on the dynamics of this "bound" water. However, from the present ionic moieties it appears very unlikely that all water that has disappeared from $S_w(c)$ is irrotationally bound. A clear hint that some of this water relaxes with a time constant of ~20 ps is the possibility of fitting the D + D + D model to $\varepsilon^*(\nu)$. Unfortunately, the so-obtained parameters scatter too much to yield meaningful conclusions.

The interaction strengths of the anions with water is manifested by the effective hydration numbers of $Z(\mathrm{Br}^-) = 0$[36] (meaning that the water reorientation in the vicinity of Br^- and of other water molecules occurs on the same time scale) and $Z(\mathrm{F}^-) \approx 9$ obtained from the dielectric spectra of simple aqueous electrolytes. In view of these results one would expect that for a given x,y-ionene the effective hydration number, Z, of fluoride samples is systematically larger than that of the corresponding bromide salts (beyond the error of ±2 per ion pair!), which is not the case. This suggests that the same Z values for ionene bromides and fluorides, obtained in this study, arise from a compensation of contributions from the free anions, the polyions, and the "bound" counterions. Whereas the F^- counterion is expected to keep all the water for itself, the Br^- counterion (which in itself cannot "freeze" water[36]) seems to need the cooperation with the PE (which in itself also has not much effect on water) to "bind" approximately the same amount of water. Indeed, as discussed below, there are indications that F^- counterion keeps its hydration shell intact in interaction with ionene. On the other hand, the chaotropic Br^- ion seems to bind directly to the PE and, cooperatively with the ammonium groups of the polycation, appears to induce the formation of a well-defined hydration shell. Evidence for such a cooperative effect in the hydration of contact pairs between hydrophobic cations and halide anions was recently found with DRS of alkyltrimethylammonium halide micelles[23] and by a Car−Parrinello study of the ionic liquid 1-ethyl-3-methylimidazolium chloride in water.[41]

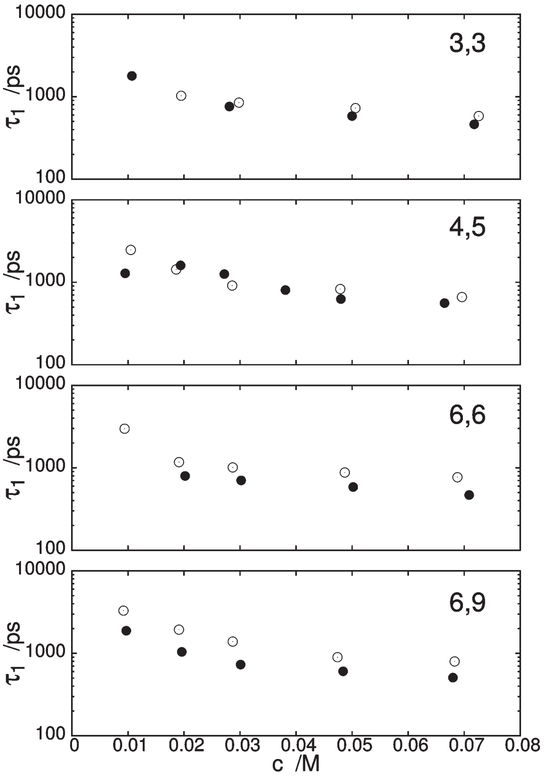

Figure 4. Relaxation times, τ_1, of ionene bromide (●) and fluoride (○) solutions as a function of concentration, c. The linear charge density of the ionene decreases from the top to bottom panels: 3,3-, 4,5-, 6,6-, and 6,9-ionene. Outlying data have been omitted from the plot (see Tables S1 and S2 of the Supporting Information). The size of the symbols exceeds the 10% error estimate.

3.3. Solute Relaxation. One may argue that due to the small degree of polymerization of the present polyions (which should lead to an essentially stretched conformation), the slow relaxation typical for long-chain PEs[20−22] does not appear, so that we have to deal only with the fast PE mode. The magnitude of the present relaxation times (Tables S1 and S2; Figure 4) is indeed comparable to the literature data for the fast PE mode.[20−22] However, a more likely reason for the observation of a single PE relaxation for the present ionene solutions is that the time scale for fluctuations of the ion cloud along the stretched PE chain approaches the relaxation time of the fast mode. Since, additionally, conflicting theories were put forward for the interpretation of the fast mode,[20,22] it is not straightforward to attribute the observed relaxation to "ionic atmosphere" or "bound (condensed)" counterions.

As indicated above, the parameters of the low-frequency relaxation, (S_1, τ_1), observed for the present ionene fluoride and bromide solutions (Tables S1 and S2, Figures 3 and 4) are compatible with an assignment of this mode at ~200 MHz to the fast PE relaxation arising through counterion fluctuations over a moderate length scale. Two opposing theories are commonly used to interpret the experimental data for (S_1, τ_1): The first, (i) developed by Ito et al.,[22] argues that the relaxation involves radial polarization over a characteristic length L_S of the diffuse cloud of counterions surrounding the polymer backbone (called "loosely bound" counterions by Ito). The second, (ii) based on the work of Mandel et al.,[19] assumes that the relaxation is due to polarization along (parallel) the chain's backbone, arising from the hopping of the condensed counterions along linear segments of certain length. Since the DRS results alone do not indicate whether the fluctuations of the counterions are transversal or longitudinal to the PE backbone and whether relaxation arises from the ions in the ionic atmosphere or from the "bound" counterions, the distinction between the Ito and Mandel model is virtually impossible.

Figure 4 shows relaxation times of counterions, τ_1, for 3,3-, 4,5-, 6,6-, and 6,9-ionene bromides (full symbols) and fluorides (open symbols) as a function of concentration. τ_1 decreases with increasing concentration of the ionene. While there are no obvious trends for differently charged ionene bromides, the relaxation times of fluoride samples decrease from 6,9- to 3,3-ionene for a given *c* (see Tables S1 and S2). The comparison between bromide and fluoride samples shows that τ_1 is lower in the case of bromide samples and that the differences become larger in the case of less charged 6,6- and 6,9-ionenes. These results could be explained within Ito's model by stronger electrostatic screening in more concentrated systems as the "radius" of the diffuse ion cloud is proportional to τ_1.[22] On the other hand, the interpretation within Mandel's model is also plausible. Here a shorter relaxation time also invokes a shorter hopping length and one might argue that this arises from increased PE−PE interactions.

What we have as a reliable information from the dielectric experiment is the different behavior in the ionene dependence of the solute relaxation time, τ_1, for fluorides and bromides at a given counterion concentration, *c*. For Br^- counterion τ_1 does not depend on the chosen type of *x*,*y*-ionene. This could be an indication that only the bulk mobility of the counterion is relevant and thus points at preferentially radial motion of Br^- counterions. On the other hand, τ_1 clearly increases from 3,3- to 6,9-ionene fluorides, that is in the direction of increasing charge separation, suggesting that for this anion the observed solute relaxation is dominated by the hopping of F^- counterions along the PE backbone.

4. Conclusions

Dielectric properties of ionene bromides and fluorides in water were studied. We showed that the best model for describing the experimental data in the range of frequencies $0.05 < \nu/\mathrm{GHz} < 89$ was the one that considered two relaxing species: (i) counterions and (ii) the bulk water.

From the reduction of the water amplitude, S_2, effective hydration numbers could be derived. Surprisingly, the value of $Z = 14 \pm 4$ per repeat unit was the same for all studied ionenes. Probably due to the lacking accuracy, we were unable to resolve the "slow water" relaxation ($\tau \approx 20$ ps) expected for waters hydrating fluoride counterions and hydrophobic moieties, preventing thus a closer look at the dynamic properties of the "bound" water. However, a hint for the existence of the "slow water" in the studied systems was the possibility to fit the dielectric spectra with a "forced" D + D + D model.

Relaxation times of counterions, τ_1, decreased with the increasing concentration, which was a consequence of stronger electrostatic screening in more concentrated solutions. The trends regarding the charge density of the polyion were in the case of fluoride salts 3,3- < 4,5- < 6,6- < 6,9-ionene, while the trends of τ_1 for bromide ionenes were not so clearly expressed. This different dependence of τ_1 for fluoride and bromide samples on charge density of ionenes was an indication that F^- counterions preferably moved along the polyelectrolyte backbone, whereas for Br^- counterions probably radial diffusion predominated. In addition, having in mind that F^- ions bind water molecules tightly and behave much like charged "hard spheres" with the hydrated radius could be taken as another argument for the longitudinal fluctuations of F^- counterions. However, the analysis of the solute relaxation (S_1, τ_1) did not allow us to make a firm conclusion whether the counterion dipole moment fluctuation corresponded exclusively to the Manning−Mandel or to the Ito model.

Water molecules hydrating Br^- counterions are rather "loosely" bound to it due to the chaotropic nature of this ion.[42] Thus, when approaching the polyion, Br^- counterions could release their hydration water molecules more easily than fluorides.[43] Being less strongly hydrated (again in comparison with fluoride ions), they can come to closer proximity of the polyion and may replace some of the "slow" water molecules hydrating the alkyl spacers of the polyelectrolyte. It appears even likely that the dimethyldialkylammonium groups of the ionene backbone and the intermittent condensed Br^- counterions exert a strong synergistic effect on the surrounding water molecules, as it would explain the surprisingly large effective hydration number found in this study. Such a synergism in hydration was suggested by dielectric studies of alkyltrimethylammonium halide micelles, where not only the "slow" water hydrating the bare hydrophobic micelle surface was found but surprisingly also a significant amount of "irrotationally" bound water. It is thought that the latter water fraction was so strongly reduced in its dynamics because it simultaneously interacted with the charged surfactant head groups and the condensed halide ions.[23,41]

The results presented in this contribution combined with insights from existing experimental and theoretical studies lead us to the conclusion that fluoride counterions were to a lesser extent affected by the polyion than bromide counterions. It seemed that charged sites of the polyions had a much grater influence on the F^- counterions than the chains of $-CH_2-$ units between them. This could be taken as an argument for the success of electrostatic theories in predicting the correct trends for the observed thermodynamic data (for example heats of dilution). For ionene bromides, however, the influence of polyion's charges and of hydrophobic parts of the backbone manifested itself in a more complex manner. High hydration numbers in the case of Br^- counterions as well as the insensitivity of τ_1 on the charge density of the polyion indicated that the role of the solvent could not be disregarded in these systems.

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Supporting Information Available: Tables S1 and S2: a CC + D model fit parameters (limiting permittivities (ε, ε_2, ε_∞), relaxation times (τ_1, τ_2), the Cole−Cole width parameter (α_1), the reduced error function (χ_r^2), together with conductivity and density of the ionene fluorides and bromides); Figure S3: dielectric permittivity, $\varepsilon'(\nu)$, and loss spectra, $\varepsilon''(\nu)$, of a 0.02 M aqueous solution of 6,6-ionene bromide and fluoride; Figure S4: identical as Figure 2 but for 6,6-ionene fluoride. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) $S_{\mathrm{w}}(c) = S_{\mathrm{w,c}} + S_{\mathrm{w,f}} = \varepsilon_2(c) - \varepsilon_\infty^{\mathrm{FIR}}(c)$. For the limiting permittivity of orientational polarization, $\varepsilon_\infty^{\mathrm{FIR}}(c)$,[35] reached in the far-infrared and thus outside the present frequency range, we may reasonably assume the value of pure water, $\varepsilon_\infty^{\mathrm{FIR}}(c) = \varepsilon_\infty^{\mathrm{FIR}}(0) = 3.48$.[35,37]
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