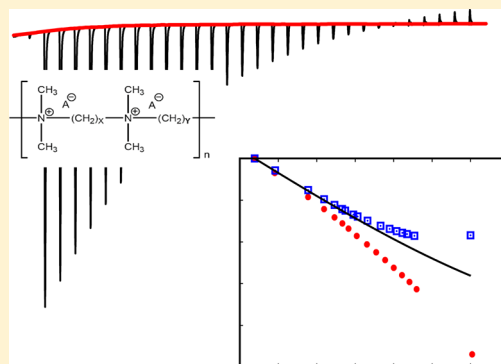# Presence of Hydrophobic Groups May Modify the Specific Ion Effect in Aqueous Polyelectrolyte Solutions

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Ⓢ *Supporting Information*

ABSTRACT: Enthalpies of dilution of aqueous solutions of aliphatic 6,12- and 12,12-ionene bromides and fluorides and enthalpies of mixing with low molecular-weight salts, such as sodium fluoride and bromide, are determined. In the second part of the study, the various x,y-ionenes (x, y are numbers of methylene groups between the adjacent charges) with fluoride, bromide, and iodide counterions are mixed with aqueous sodium sulfate solution. The polyelectrolytes examined in this part of the work are 3,3-, 6,9-, 6,12-, and 12,12-ionenes. A comparison with theoretical results, based on the Poisson–Boltzmann cell model, is presented. The theory predicts for the enthalpy of dilution to be exothermic and the enthalpy of mixing endothermic, while experiments show that signs of the heat effects depend on the nature of the counterion of the added salt, as also on the hydrophobicity (numbers x, y of methylene groups) of the ionene. We show that the salts when ordered by heat effects produced by mixing of NaF and NaBr with 3,3-, 6,9-, or 6,12-ionene fluorides and bromides follow the opposite ordering than in the case when the same alkali halide salts are mixed with more hydrophobic 12,12-ionene salts. The results for the enthalpy of mixing of ionenes under study with Na_2SO_4 follow the same order as obtained for monovalent salts.

1. INTRODUCTION

Biologically important macromolecules contain charges as also the non-polar (hydrophobic) groups. The presence of such groups may modify the solvation of embedded charges and influence the potential of the mean force between them and ions in the solution.[1] Here we study aliphatic x,y-ionenes,[2,3] that is, cationic polyelectrolytes with the repeating unit $-\overset{+}{N}(CH_3)_2-(CH_2)_x-\overset{+}{N}(CH_3)_2-(CH_2)_y-$, where integers x and y denote the number of methylene groups between the adjacent nitrogen atoms. Because the number of CH_2 groups can be varied during the synthesis, we can prepare ionenes of different charge densities, what makes them suitable to examine the effect of the hydrophobicity on the ion–polyion interactions.

Physicochemical properties of aqueous ionene solutions have been a subject of considerable interest.[4–17] The experimental results indicate strong deviations from the theoretical predictions based on the classical[18–21] continuum solvent models of polyelectrolyte solutions. The deviations depend on charge density, that is, on the x,y values (number of methylene groups) of the ionene macromolecule, and the nature of counterion in solution. Such discrepancies were noticed for conductivity,[14] activity,[8] osmotic pressure measurements,[11] and most notably for the enthalpy of dilution, $\Delta_{dil}H$, measurements.[10,15] To understand these effects on the molecular level, the 3,3- and 6,6-ionene oligoions were studied by the explicit water molecular dynamics simulations.[16,22,23]

In the recent articles,[16,17] we studied interaction of 3,3- and 6,6-ionenes with +1:−1 electrolyte. For this purpose, the isothermal titration calorimetry was applied. Theory and simulations, performed within the framework of the continuum solvent model, suggested that enthalpy of mixing, $\Delta_{mix}H$, should be a positive quantity. In contrast to this, our experiments yield the conclusion that $\Delta_{mix}H$ can also be exothermic, depending on the counterion in solution. For example, mixing the 3,3- or 6,6-ionene fluorides in water with NaF yields an endothermic effect in close agreement with the theory,[16] while $\Delta_{mix}H$ is negative upon mixing of ionene bromides with NaBr. In general, the enthalpy of mixing depends on the hydrophobicity of the aliphatic ionene, and on the nature of the added electrolyte as well.

One of the most interesting findings of our recent work[16] is the fact that the enthalpy of mixing of 3,3- and of 6,6-ionene fluorides with sodium halides can be expressed as a linear function of the enthalpy of hydration, $\Delta_{hyd}H$, of the halide counterions. The sequence follows the direct Hofmeister series.[24] A strong (though not always linear) correlation between the enthalpy of mixing and $\Delta_{hyd}H$ of the counterion species applies also to salts containing polyatomic ions,[17] as well as to other polyelectrolytes.[25]

In the present contribution, the calorimetric investigation is extended to more hydrophobic 6,12- and 12,12-ionene salts in water, as also to salts with divalent counterions. In the first part of the manuscript, we present the results for enthalpy of

dilution of newly synthesized 6,12- and 12,12-ionenes with fluoride and bromide counterions. The latter one is the most hydrophobic aliphatic ionene studied so far. The purpose of our work is to investigate how the increasing number of methylene groups influences the interaction between the x,y-ionene and different counterions in the solution. In the second part of the study, we report the enthalpy changes for 3,3-, 6,9-, 6,12-, and 12,12-ionene fluorides, bromides, and iodides, when mixed with sodium sulfate solution. To our best knowledge, there are no prior studies of the ionene interaction with divalent counterions. In this work, we therefore extend our previous investigations to more hydrophobic polyelectrolytes, and to solutions with divalent counterions as well. An important goal of the study is to examine a possible influence of hydrophobicity of the polyion chain on the specific ion effect.

2. EXPERIMENTAL SECTION

2.1. Materials. N,N,N',N'-Tetramethyl-1,3-propanediamine ($\geq$99%), N,N,N',N'-tetramethyl-1,6-hexanediamine (99%), 1,3-dibromopropane (99%), 1,9-dibromononane (97%), and 1,12-dibromododecane (98%) were purchased from Sigma-Aldrich and used as received. Dimethylamine hydrochloride (99%), tetrahydrofuran ($\geq$99.9%), methanol (99.8%), and diethyl ether (99.8%) were also purchased from Sigma-Aldrich and used without further purification. NaF, NaBr, NaI, and Na_2SO_4 salts were purchased from Merck.

Preparation of Dimethylamine Aqueous Solution. Dimethylamine hydrochloride (86.0 g, 1.05 mol) was transferred into a two-necked, 500 mL round-bottom flask equipped with a magnetic stirrer. One neck was connected to a 50 mL dropping and separating funnel containing NaOH aqueous solution (50 mL, 23 M, 1.15 mol) and the other one to the tube immersed in ice-cold water (18 mL). NaOH solution was slowly added to dimethylamine hydrochloride (DMA) while stirring in a thermostat (10 °C). The mixture was warmed to its initial boiling point (55 °C) and then slowly further on up to 90 °C. Vapors of DMA were condensed/dissolved while passing through the ice-cold water. The procedure yielded aqueous solution (65%, 55.5 g, 0.80 mol) of DMA.

Synthesis of N,N,N',N'-Tetramethyl-1,12-dodecanediamine. 1,12-Dibromododecane (8.35 g, 25 mmol) was dissolved in tetrahydrofuran (70 mL) in a 250 mL round-bottom flask, and the solution was cooled to −78 °C. Aqueous solution (65%, 35.0 g, 0.50 mol) of DMA was added to the flask, and the solution was magnetically stirred for 1 h. The solution was allowed to warm to room temperature and stir for an additional 48 h. Volatile components were removed under reduced pressure, and the resulting white residue was dissolved in the 2 M NaOH aqueous solution (200 mL). In the next step, the liquid–liquid extraction with diethyl ether was repeated several times. The organic phase was collected and concentrated to obtain "yellow oil". The crude product was purified via vacuum distillation (100 °C and 1 mbar) from CaH_2 to provide a clear colorless product (yield 5.45 g, 85%).

Synthesis of 12,12-Ionene Bromide. 1,12-Dibromododecane (6.70 g, 20.0 mmol), methanol (55 mL), and N,N,N',N'-tetramethyl-1,12-dodecanediamine (5.13 g, 20.0 mmol) were transferred in a 100 mL flask equipped with a magnetic stirrer. The flask was closed with a stopper, and the reaction was allowed to proceed for 3 days at 30 °C. The reaction mixture was then concentrated and the product precipitated with diethyl ether. The liquid phase was decanted and the product

dissolved in water. The yield (90%) was determined by the potentiometric titration with $AgNO_3$.

Synthesis of 6,12-, 6,9-, and 3,3-Ionene Bromides. These ionenes were prepared as described for 12,12-ionene bromide. In the case of 3,3-ionene bromide, small amounts of water were added into the reaction mixture, after it became white and very viscous, to ensure the solubility of all components. The procedure was repeated until the reaction mixture stopped being white and viscous.

Purification, Ion-Exchange, and Sample Preparation. Dialysis tubes (Sigma-Aldrich, MWCO = 12 000 g mol^{-1}) were filled with 0.025 M solution of ionene bromide (100 mL) and dialyzed (2 times for 24 h) first against 0.05 M NaBr solution (900 mL) and then 10 times for 24 h against deionized water (900 mL). During the dialysis process, we lost from 10 to 20% of sample, so we estimated that the molar mass of the remaining ionene is considerably above the MWCO (12 kDa) of dialysis tubes. For poly-addition reactions, it is hard to achieve high molar mass,[7] and we estimated the molar mass to be between 20 and 100 kDa. The estimate is consistent with the independent chromatographic determination for 3,3- and 6,6-ionene bromides synthesized and dialyzed by us, which are 37 and 30 kDa, respectively. In the chromatographic experiments, PEG was used as a standard, while the mobile phase was H_2O/MeOH (23%)/acetic acid (23%). The polymeric character of the samples can also be seen from the concentration dependence of the osmotic coefficient measurements, and from agreement of enthalpy of dilution with the Poisson–Boltzmann cell model calculations at low concentrations[15] (see also Figure 1 of this paper).
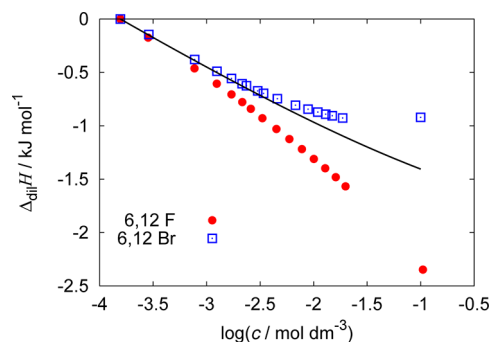

Figure 1. Enthalpy of dilution of aqueous 6,12-ionene fluoride and bromide solutions as a function of the polyelectrolyte concentration c. The line shows prediction of the Poisson–Boltzmann cell model; $c_f = 1.6 \times 10^{-4}$ M.

Ionene fluorides and iodides were prepared from bromide salts by an ion exchange during extensive dialysis (10 dialysis for 24 h each), using 0.05 M NaF and NaI solution, respectively, and further dialyzed against deionized water (again 10 times for 24 h). Solutions of sodium salts (NaF, NaBr, and Na_2SO_4) were after drying at 150 °C prepared gravimetrically. Concentrations of ionene salts were determined by potentiometric titration with standard solutions of $LaCl_3$ for fluoride ions and $AgNO_3$ for bromide and iodide ions. For this purpose, the ion selective electrodes (Merck) were used. The saturated mercury sulfate electrode served as the reference electrode in all cases.

2.2. Measurements. Heat effects upon adding an ionene solution to a measuring cell containing water at 25 °C were determined by the isothermal titration calorimetry. A VP-ITC

isothermal titration calorimeter (Microcal Inc., Northampton, MA) with a cell volume equal to 1.3862 cm^3 was used for this purpose. In the case of 6,12-ionene bromide and fluoride, two such experiments were combined, and in the case of 12,12-ionene bromide and fluoride salts, three such experiments were performed to obtain the average presented in figures.

Enthalpies of mixing (again at 25 °C) were determined using the same ITC instrument as above by adding sodium salt (0.1 M of anion) to a measuring cell containing ionene solution at a concentration of 0.01 M. By subtraction of the enthalpy change, resulting from titration in the absence of ionene (pure water), we obtained the enthalpy corresponding to the ionene–salt interaction upon mixing, which is confronted to the theoretical values in Figures 3–5.

The results are plotted as a function of the parameter x, defined as

$$x = \frac{c_s}{c} \tag{1}$$

where c_s and c denote the salt and ionene monomer concentrations, respectively. Upon addition of the low–molecular electrolyte with concentration c_s, the monomer concentration of ionene in the measuring cell changes as

$$c = \frac{c^0}{1 + \frac{x}{X}} \tag{2}$$

where X is defined as a ratio between the concentration of the electrolyte in the syringe, c_s^0, and the initial concentration of the ionene in the cell, c^0,

$$X = \frac{c_s^0}{c^0} \tag{3}$$

The concentration of the electrolyte in the syringe, c_s^0, was 100 mM, and the initial concentration of the ionene in the cell was 10 mM, so X is 10 in the case of 6,12- and 12,12-ionenes.

3. THEORETICAL PART

A simple approach to calculate Coulomb contribution to properties of polyelectrolyte solutions was proposed by Manning.[19,20] According to this approach, the polyelectrolyte is pictured as an infinitely long charged line, while the ions are treated as point charges. The theory is valid in the limit of infinite dilution with respect to the macromolecular component.

In the present study, we are interested in the concentration dependence of calculated properties, so we choose to analyze our experimental results within the framework of the Poisson–Boltzmann cell model.[18,21,26] In this model, the polyelectrolyte solution is depicted as an assembly of independent and electroneutral cylindrical cells. The cells are identical; each of them is of radius R and length $h \gg R$. A rigid cylindrical polyion with radius (or the distance of closest approach between ion and polyion) a and length h is placed along the z-axis of the cell. The radius R of the cell is determined by the polyelectrolyte concentration, c, expressed in monomer molar units (mol of monovalent counterions/dm^3 in our case),

$$c^{-1} = \pi R^2 N_A b \tag{4}$$

where b is the length of the monomer unit, while the length of the polyion is $h = Nb$ (N being the number of monomer units) and N_A is the Avogadro number. In this approach, the

dimension-less charge density parameter λ ($\equiv \xi$ in Manning's theory) is the main parameter.

$$\lambda = e_0^2 / 4\pi\epsilon_0\epsilon_r k_B T b \tag{5}$$

In the expression above, e_0 is an elementary charge, ϵ_0 is the permittivity of a vacuum, and ϵ_r is the relative permittivity of a solvent. As usual, k_B is Boltzmann's constant and T is the absolute temperature.

In our case, charges on the polyion are monovalent (one elementary charge per monomer unit) and uniformly distributed over the surface. Small ions present in the solution are distributed according to the Boltzmann distribution. The resulting Poisson–Boltzmann equation (for details, see the Supporting Information) has to be in such a case solved numerically. Once the electrostatic potential ψ is known, the quantities of interest can be calculated using the standard statistical–mechanical equations.[26−29]

In the enthalpy ($\Delta_{dil}H$ and $\Delta_{mix}H$) calculations, we assumed that $H^e \approx U^e$, where the latter quantity is the excess (electrostatic) internal energy of the system. The relevant expression for U^e reads[29]

$$U^e = \frac{1}{2}\epsilon_0\epsilon_r\left(1 + \frac{d \ln \epsilon_r}{d \ln T}\right)\int_a^R (\nabla\psi)^2 \, dV \tag{6}$$

where $\nabla\psi(r)$ is the gradient of the electrostatic potential at position r and the integration is extended over the volume of the cylindrical cell, V,

$$V = \pi(R^2 - a^2)h \tag{7}$$

and

$$dV = 2\pi r dr h$$

The term

$$\frac{d \ln \epsilon_r}{d \ln T} \tag{8}$$

equals −0.37 for pure water at 25 °C and normal pressure.

Two different quantities are of interest of us. One is the enthalpy (calculated as the excess energy) of dilution, $\Delta_{dil}H$, between the initial and final concentrations, and the other is the enthalpy of mixing, where a certain amount of +1:−1 or +1:−2 electrolyte is mixed with the ionene in water. The two experimental quantities have been previously studied theoretically by the Manning theory and the Monte Carlo method.[16,26]

To obtain the enthalpy of dilution, we apply eq 6 between the final (diluted, $c = c_f$) and initial (concentrated, $c = c_i$) states. No additional (low-molecular weight; $c_s = 0$) electrolyte is present in these experiments, so the concentration of co-ions is zero. In the enthalpy of mixing calculations, the concentrations of polyelectrolyte c and added low-molecular weight electrolyte c_s can vary arbitrarily, and they define the initial and final conditions (at constant T) in a unique way

$$\Delta_{mix}H = H^e(c_f, c_s) - H^e(c_i, c_s = 0) \tag{9}$$

where $H^e(c_f, c_s)$ is the excess enthalpy of the final and $H^e(c_i, c_s = 0)$ that of the initial state. Notice that the theory as presented here cannot account for the specific ion effects. We expect for measurements to approach the theoretical results in the low concentration limit, where the nature of a counterion does not play a significant role.

4. RESULTS AND DISCUSSION

All the results presented here apply to aqueous solutions at 25 °C. Notice that, for 6,12- and 12,12-ionenes, the charge density parameter $\lambda \equiv \xi$ assumes values of 0.572 and 0.440, which is below the threshold for the Manning's counterion condensation for monovalent counterions, and for 12,12-ionenes also for divalent counterions.

4.1. Enthalpies of Dilution of 6,12- and 12,12-Ionenes with Fluoride and Bromide Counterions. Results for the enthalpy of dilution of 6,12-ionene fluoride and bromide solutions are shown in Figure 1, and those for 12,12-ionene fluoride and bromide solutions, in Figure 2. Notice that the
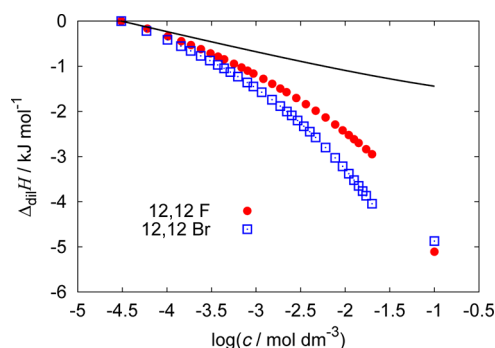

Figure 2. Enthalpy of dilution of 12,12-ionene fluoride and bromide solutions as a function of the polyelectrolyte concentration c. The line shows prediction of the Poisson−Boltzmann cell model; $c_f = 3.2 \times 10^{-5}$ M.

final (diluted) concentration is $c_f = 0.156$ mM in the case of 6,12-ionenes and 0.031 mM in the case of 12,12-ionenes. Theoretical results, obtained by the Poisson−Boltzmann cell model calculations, are given in the same plots.

The major competing effects, leading to either positive or negative values of enthalpy of dilution (see also ref 15), are the following: (i) First, there is a non-specific (Coulomb) effect, being dominant for dilute electrolyte or polyelectrolyte solutions. This term is correctly accounted for by the Debye−Hückel theory for simple electrolytes, or the Manning and Poisson−Boltzmann theories in the case of polyelectrolyte solutions. The non-specific effect suggests that, in dilute solutions, the process of further dilution must be exothermic. There is ample experimental evidence for electrolyte and polyelectrolyte solutions proving that these (continuum solvent) theories become asymptotically correct, when the concentration of (poly)electrolyte solution approaches zero. In the case of polyelectrolyte solutions, this is for 3,3-ionene fluorides demonstrated in Figure 3 of ref 15. This kind of result, $\Delta_{dil}H < 0$, is generally obtained for highly charged polyions with strongly hydrated counterions. Well known examples are poly(styrene) sulfonic acid and its lithium and sodium salts[30] or lithium and sodium salts of the poly(anethole)sulfonic acid.[31] A characteristic for these counterions is that they do not change appreciably their hydration "state" between the initial and final concentrations.

(ii) For moderate polyelectrolyte concentrations, the effect upon dilution may become endothermic. Examples are cesium salt of the poly(styrene)sulfonic acid[30] at low temperature and, as mentioned before, solutions of x,y-ionene chlorides, bromides, and iodides.[10,15] These anions are only "weakly" solvated, and the interaction with ammonium group on the

ionene may be accompanied with the release of some hydration water. A certain analogy with the cation−anion pair formation in solutions of low molecular weight electrolytes applies. This effect, in the literature called specific short-range interaction[32] or "site binding",[33,34] is also seen in the explicit water molecular dynamics simulations of 3,3-ionene iodides.[16,22,23] The dilution process is therefore accompanied by gradual release of the counterions ("unbinding") into the bulk solution, where they become fully solvated. This effect yields a positive contribution to $\Delta_{dil}H$.

(iii) In polyelectrolyte (or protein) solutions, in addition to charges, the hydrophobic groups are present. As discussed in refs 35 and 36, an introduction of the hydrophobic group such as methyl or methylene into water is associated with the release of heat; the effect has therefore the same sign as the Coulomb interaction upon dilution. This explains an apparent paradox that more hydrophobic 6,6-, 6,9-, 6,12-, and 12,12-ionene bromides (chlorides, iodides) behave at least qualitatively consistent with the continuum solvent theories, while the more highly charged 3,3-ionene salts do not.

We shall start the analysis of experimental results with data for ionene fluorides. Previously published results for the heats of dilution of 3,3-, 4,5-, 6,6-, and 6,9-ionene fluorides[10] and comparison with the Poisson−Boltzmann cell model (see Figure 3 of ref 15) indicated that the effect is exothermic and standard polyelectrolyte theories are in semi-quantitative agreement with experiments. The deviations between the calculations and experimental data increase with an increasing hydrophobicity of the x,y-ionene. The experimentally determined enthalpies of dilution are for 6,6- and 6,9-ionene fluorides more exothermic than theoretically predicted. These findings are, for even more hydrophobic 6,12- and 12,12-ionenes, confirmed in Figures 1 and 2, respectively. Agreement with the Poisson−Boltzmann cell model results is good in the case of dilute solutions of 6,12-ionene fluorides. The heats of dilution presented here apply to considerably lower polyelectrolyte concentrations (see figure captions) than those published in ref 15. Despite this, we cannot be completely sure for the 12,12-ionene fluoride results to follow the Poisson−Boltzmann cell model results (Figure 2) at high dilution. The measurements at still lower concentrations are, unfortunately, not accurate enough. The $\Delta_{dil}H$ values are considerably more negative for 12,12-ionene fluorides than in the case of the equivalent 6,12-ionene salt.

The enthalpy of dilution data for ionene solutions with bromide ions require a separate discussion. First, we wish to bring into the reader's attention the $\Delta_{dil}H$ results for 3,3-, 4,5-, 6,6-, and 6,9-ionenes. The measurements performed by Arh and Pohar[10] prove that dilution of ionene bromides, in contrast with electrostatic theories,[10,15] yielded either an exothermic or endothermic effect. For 3,3- and 4,5-ionene bromides, the dilution effects are endothermic, while, for 6,6- and 6,9-ionene bromides, they are exothermic in the low concentration regime, and become endothermic for more concentrated solutions. The increasing number of methylene groups between the two quaternary ammonium groups (decrease of the linear charge density parameter λ) makes the dilution effect more exothermic. As already mentioned, the measurements of Arh and Pohar[10] apply to much higher final concentrations than those, which yield our Figures 1 and 2. For this reason, their $\Delta_{dil}H$ values do not follow the Poisson−Boltzmann limiting result; the final concentrations upon dilution are too high.
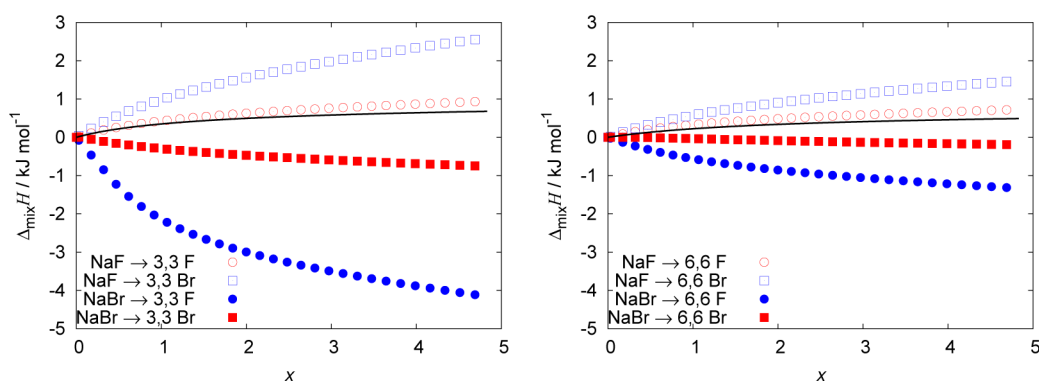
Figure 3. Enthalpy of mixing of 3,3- and 6,6-ionene fluoride and bromide salts with NaF and NaBr (expressed in kJ/mol of charged groups on the ionene) solutions in water, as a function of the ratio x (eq 1). The initial concentration of the ionene in the measuring cell was 5 mM, and that of the titrant was 100 mM. Previously published data[16,17] are combined into the new figures and supplemented with the Poisson−Boltzmann cell model results (lines).
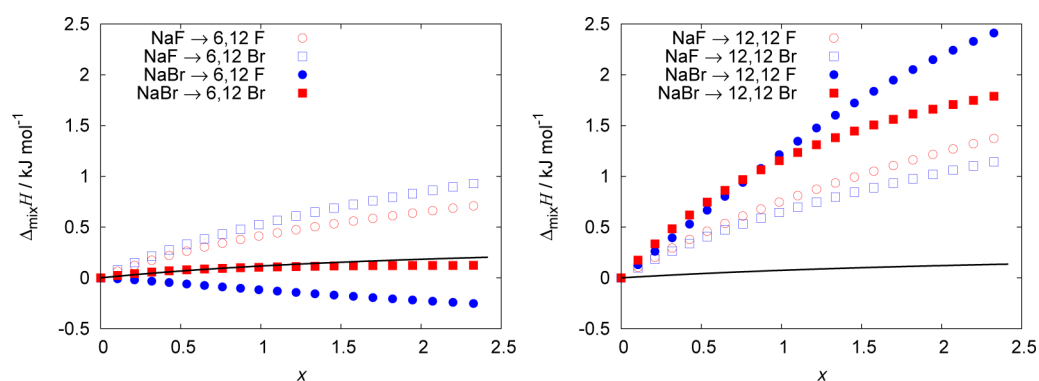

Figure 4. Enthalpy of mixing of 6,12- and 12,12-ionene fluoride and bromide salts (expressed in kJ/mol of charged groups on the ionene) with NaF and NaBr dissolved in water, as a function of the ratio x (eq 1). The Poisson−Boltzmann cell model predictions are shown by lines. The initial concentration of the ionene in the measuring cell was 10 mM (twice larger than for the preceding figure), and that of titrant was 100 mM.

Apart from this, the results of Arh and Pohar[10] are consistent with our discussion at the beginning of this section.

The $\Delta_{dil}H$ results obtained for 6,12- and 12,12-ionene bromides are shown in Figures 1 and 2. The enthalpies are exothermic and for 6,12-ionene salt in agreement with the Poisson−Boltzmann cell model theory. This result confirms that the ion specific effect vanishes for highly diluted solutions. The positive deviations of the bromide salt results from the Poisson−Boltzmann calculations, shown in Figure 1, resemble the results for the sodium, potassium, and cesium salts of the poly(styrene)sulfonic acid.[30]

There are qualitative and quantitative differences in dilution behavior of bromide salts for the 6,12- and 12,12-ionenes. In Figure 1, we see positive deviations from the Poisson−Boltzmann results for the 6,12-salt (less exothermic), while, in contrast to this, the 12,12-ionene bromide shows negative deviation from theory, i.e., a quite strong exothermic effect. We may say that 12,12-ionene bromides exhibit different behavior upon dilution than their more highly charged analogues.[10,15] A comparison of the results shown in Figures 1 and 2 indicates that for 6,12-ionene bromides the enthalpy of dilution is less exothermic (plotted above the fluoride salt), while for the 12,12-ionenes exactly the opposite is true. These results show unambiguously that additions of extra methylene groups (transition from 6,12- to 12,12-ionene) affect solutions with different counterions differently.

4.2. Enthalpies of Mixing of 6,12- and 12,12-Ionene Fluorides and Bromides with NaF and NaBr. The heat released or consumed upon the polyelectrolyte−electrolyte mixing, $\Delta_{mix}H$, is correlated with the enthalpy of dilution results. The two processes are namely related: in dilution we add water and accordingly we may increase the hydration of solute species, while in the process of mixing the number of available water molecules per ion is reduced. This is why the sign of the $\Delta_{mix}H$ in our measurements is opposite to the sign of the $\Delta_{dil}H$.

For the sake of comparison, and to make the discussion easier to follow, we combined some of the $\Delta_{mix}H$ data for 3,3- and 6,6-ionenes published in refs 16 and 17 into Figure 3. The newly composed figure contains also the Poisson−Boltzmann results not shown before. The results for titration of NaF into the 3,3- and 6,6-ionene fluoride solutions are in fair agreement with the predictions based on the Poisson−Boltzmann cell model. This was, as already discussed,[16,17] somewhat expected, because the fluoride ion is strongly ("rigidly") hydrated, and its hydration shell seems to remain intact during the mixing process and interaction with the ionene polyion. Remember that enthalpies of dilution of 3,3- and 6,6-ionene fluorides are also in fair agreement with the Poisson−Boltzmann cell model calculations.[15]

The results for the enthalpy of mixing, $\Delta_{mix}H$, of 6,12- and 12,12-ionene fluorides and bromides with NaF and NaBr salt solutions are shown in Figure 4. Obviously, the situation is more complicated (in comparison with the one shown in Figure 3) when hydrophobic aliphatic ionenes are in question. First, in titration of NaF into the ionene fluoride solution,
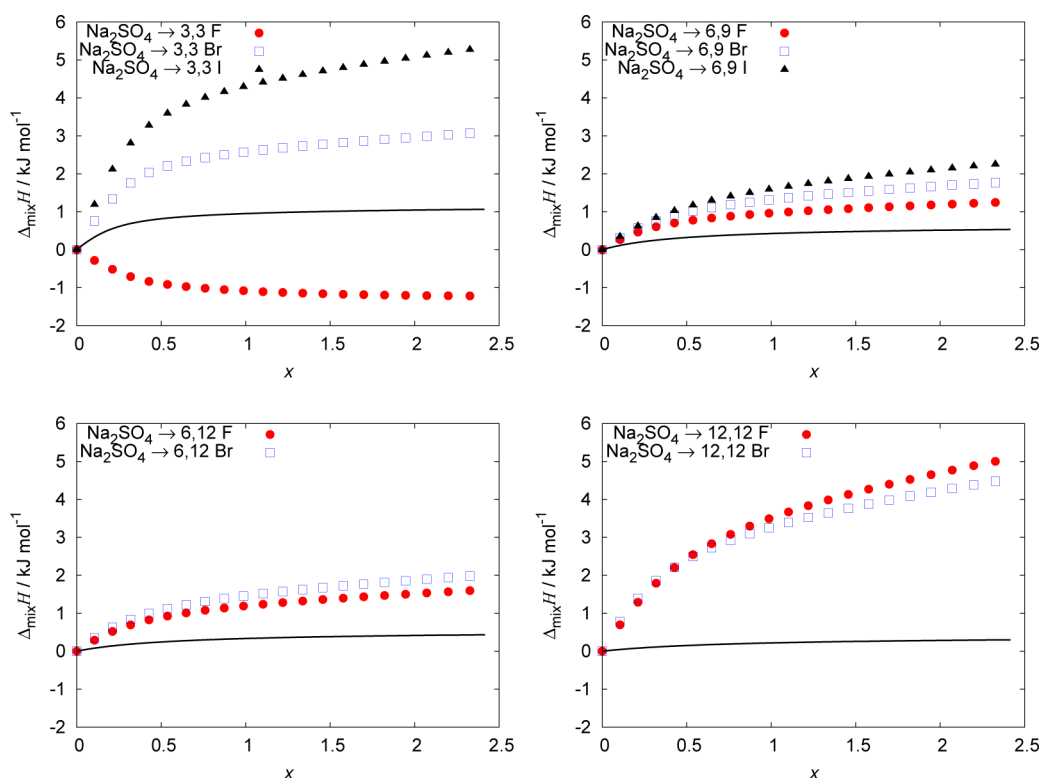
Figure 5. Enthalpy of mixing of the various x,y-ionene salts with Na_2SO_4 (expressed in kJ/mol of charged groups on the ionene), as a function of the ratio x (eq 1), with Poisson−Boltzmann cell model predictions (continuous line). The initial concentration of the ionene in the measuring cell was 10 mM, and that of the titrant was 100 mM.

noticeable deviations from the cell model calculation appear in the case of 6,12-ionenes. The deviations strongly amplify for 12,12-ionene salt. Second, there is a striking difference in the order of the enthalpy of mixing effect between the 6,12- (or other more highly charged ionenes) and 12,12-ionenes when mixed with NaF and NaBr. $\Delta_{mix}H$ values for 3,3-, 6,6-, and 6,12-ionenes follow the order (NaF → ionene Br) > (NaF → ionene F) > (NaBr → ionene Br) > (NaBr → ionene F). The ordering is (for $x > 1$) altogether inverted in the case of the more hydrophobic 12,12-ionenes. Introduction of the hydrophobic groups (transition from 6,12- to 12,12-ionenes) has a relatively small heat effect when fluoride ions are present as counterions. In contrast to this, the effect is large for 12,12-ionene solutions with bromide counterions. The results are consistent with the enthalpy of dilution data for equivalent ionene fluorides and bromides; see Figures 1 and 2 of the present contribution.

4.3. Mixing of the x,y-Ionene Salts with Na_2SO_4 in Water. Results for the enthalpy of mixing of water-soluble 3,3-, 6,9-, 6,12-, and 12,12-ionene fluorides and bromides (and iodides in two cases) with Na_2SO_4 are shown in Figure 5. For 6,12- and 12,12-ionene iodides, we found that these salts are not water-soluble. This is simply another confirmation of strong interaction of iodide ion with a quaternary ammonium group.

Before discussing these results, we wish to mention some previous measurements available in the literature. The enthalpy of mixing data for polyelectrolyte solutions with divalent counterions are not in abundance. Quite recently, Požar and co-workers[25] performed calorimetric titration of sodium salt of polystyrenesulfonic acid with magnesium and strontium chlorates in water. They found the effect of mixing to be small and endothermic for both salts. This is in contrast with the results for monovalent counterions (see Figures 1 and 3 of

ref 25), where heat could be either consumed or released, depending on the nature of the salt added.

In our study, the ordering of $\Delta_{mix}H$ for titration with Na_2SO_4 is for 3,3-, 6,9-, and 6,12-ionenes equal to that found for titrations with sodium fluoride or sodium bromide: (Na_2SO_4 → ionene I) > (Na_2SO_4 → ionene Br) > (Na_2SO_4 → ionene F). Again, as in Figure 4, this ordering is inverted for 12,12-ionene salts. A rather surprising finding of this section is an exothermic effect upon mixing Na_2SO_4 with 3,3-ionene fluoride. Sulfate ion is assumed to be strongly hydrated; its hydration enthalpy is much lower than that of the fluoride ion. Because of its charge, however, it is easy for sulfate ion to replace fluoride in the vicinity of the polyion and bind rather strongly (probably with some release of water) to the quaternary ammonium groups. In the case of 3,3-ionene, electrostatic attraction between two adjacent charges on the backbone and the divalent sulfate ion seems to be strong enough for this to happen. This kind of a process can explain negative values of $\Delta_{mix}H$.

It remains to be answered why the effects observed upon titration for other ionene salts are endothermic, i.e., in qualitative agreement with theoretical considerations. In our view, the reasons are two. For weakly charged 6,9-, 6,12-, and 12,12-ionenes, the electrostatic attractive contribution is weak and only a small amount of the hydration water on the ammonium group can be displaced. In the case of 3,3-bromides and iodides, the reason is different. These two counterions, strongly interacting with the ionene charges, are not replaced by the sulfate ions to such degree as are the (strongly hydrated) fluoride ions (left top panel of Figure 5).

5. CONCLUSIONS

New experimental results for the enthalpies of dilution and mixing of the aliphatic x,z ionenes with alkali halides are presented. Enthalpies, previously measured for 3,3-, 4,5-, 6,6-, and 6,9-ionene salts, are complemented with measurements for 6,12- and 12,12-ionene fluorides, bromides, and sulphates. The results for 12,12-ionene fluorides and bromides clearly show important differences to the less hydrophobic 6,12- (3,3-, 4,5-, 6,6-, and 6,9-) ionene salts with the same counterions. An important piece of information represents the fact that iodide salts of the 6,12- and 12,12-ionenes are not soluble. This indicates that, despite the small charge densities of these polyions, the "site binding" effect is still important.

As expected, an increased hydrophobicity of the polymer chain (larger numbers x,y of the methylene groups) yields a more exothermic effect upon dilution, and more heat consumed when polyelectrolyte is mixed with the alkali halide solutions. Hydrophobic hydration is exothermic, as reported in several previous articles, and as generally believed, the effect is primarily due to changes in water structure, and perhaps to a small degree also to the van der Waals water−solute interaction. The results presented here prove that this effect depends on the nature of the counterion present in the solution. For the first time, also the results for mixing of the various x,y-ionenes with the salt having a divalent anion are presented. The results are consistent with previous measurements for +1:−1 electrolytes, but the effect of the doubly charged anion is clearly visible.

From the thermodynamic measurements presented here, the molecular mechanism behind the results cannot be unambiguously determined. Changes of conformation upon dilution and in particular mixing with low molecular weight may play some role too. Previous studies of hydrophobic 10,10-ionene bromides performed by Izumrudov and his group[6] indicated that such polyions are even in dilute (salt-free) solutions far from being extended. They estimated for experimentally determined mean-charge spacing to be about 35% of the theoretical value and only weakly dependent on the degree of polymerization. Unfortunately, there are no results for ionene fluorides published yet. Additional experimental (for example, heat capacity, viscosity, and SANS measurements) and theoretical work, in particular the molecular dynamics simulations[37] of 12,12-ionene solutions with different counterions, is planned to understand better the effect of hydrophobic groups on the polyelectrolyte−small ion interaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Poisson−Boltzmann equation and boundary conditions for the cylindrical cell model. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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