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Thermodynamics of Dilution and the Hofmeister Series in Aqueous Solutions of Aliphatic Ionenes with Halide Counterions

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Supporting Information

ABSTRACT: Enthalpies of dilution of aqueous solutions of aliphatic *x,y*-ionene fluorides and iodides, with *x,y* being equal to 3,3-, 4,5-, 6,6-, and 6,9-, were measured in the concentration range from 0.1 $\text{mol}\cdot\text{kg}^{-1}$ to 0.0016 $\text{mol}\cdot\text{kg}^{-1}$. The results were combined with previously obtained data for ionene chlorides and bromides to discuss the ion-specific and charge density effects in these solutions. The comparison with theoretical results, based on Manning's limiting law and cylindrical cell model founded on the solution of Poisson−Boltzmann's equation, is presented. These theories imply the enthalpy of dilution to be exothermic. Of all the solutions studied here, only those with fluoride ions as counterions agree with theoretical predictions. Solutions of 3,3-, 4,5-, and 6,6-ionene with bromide, chloride, and iodide counterions yield endothermic effect upon dilution. For the most hydrophobic 6,9-ionene, heat is released when adding water in the low concentration regime. Using the previously measured data for 3,3-, 4,5-, 6,6-, and 6,9-ionene bromides and chlorides, we calculated the Gibbs free energy and the entropy changes upon dilution. The non-Coulomb contributions to the Gibbs free energy, enthalpy, and entropy of dilution were estimated.

1. INTRODUCTION

Ions, both simple and complex, play important roles in diverse biochemical processes. Charged macromolecules (e.g., nucleic acids and proteins) are vital for living organisms. These molecules can be classified as polyelectrolytes because they are polymers bearing ionizable groups either in the polyion's backbone or on the side chains. Properties of polyelectrolytes dissolved in water are not a simple interpolation of the properties of solutions of uncharged polymers and low-molecular electrolytes, but they possess a new quality not seen in polymer and electrolyte solutions.[1−9] In this article, we will be concerned with solutions of poly[(dimethyliminio)-1,3-propanediylhalide], poly[(dimethyliminio)-1,4-butanediyl(dimethyliminio)-1,5-pentanediyldihalide], poly[(dimethyliminio)-1,6-hexanediylhalide] and poly[(dimethyliminio)-1,6-hexanediyl(dimethyliminio)-1,9-nonanediyldihalide], commonly named 3,3-, 4,5-, 6,6-, and 6,9-ionene halides.[10−15]

x,y-ionenes are polyelectrolytes with the following repeating unit: $-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_x-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_y-$. Integers x and y denote the number of methylene groups between the adjacent nitrogen atoms. For example, in 3,3-ionene the quaternary ammonium groups have three methylene groups on each side, while in the case of 6,6-ionene this number is six. Since the number of CH_2 groups can be different, depending on the components used in the synthesis, ionenes with different charge densities can be created. By changing the values x and y, the hydrophobic part of the polyion and accordingly the polyion's charge density can be controlled. This makes ionenes excellent materials for studying the interplay between the Coulomb and hydrophobic effects in the presence of various halide counterions in solution.

Aqueous ionene solutions have been characterized experimentally by several groups of researchers.[10−19] Minakata and coworkers[16,17] measured the electrical conductance and the activity coefficients of 3,3-, 4,5-, 6,6-, and 6,9-ionene solutions in mixtures with alkali halides, while enthalpies of dilution and osmotic coefficients of pure ionene halides (i.e., without added salt) were determined by Pohar and coworkers.[18,19] More recently, Lukšič et al.[20,21] examined the dielectric relaxation of counterions in aqueous solutions of ionene bromides and fluorides as also the transport numbers of ions in these systems.[22] The reported measurements indicated strong deviations from the theoretical predictions based on the continuum solvent models of the polyelectrolyte solution. The deviations were dependent on the ionene charge density (*x,y* values) and on the nature of the counterion.[16−22] Ion-specific effects were also noticed in conductivity measurements:[22] the conductivity of 3,3-ionene bromides was lower than the conductivity of fluoride analogues in the whole range of the investigated concentrations, while in the case of 6,9-ionenes the trend was reversed. Further, the measured activity[16] and osmotic coefficients[19] were much lower than theoretically predicted, and the deviations were stronger for (more hydrophobic) 6,6- and 6,9-ionenes. The 3,3- and 6,6-ionene oligoions in water were also studied with computer simulations. The explicit water molecular dynamics simulation results[23−26] are consistent with experimental data and prove to be helpful in explaining the deviations of the implicit solvent models[1−5] from experimental results.

Among various thermodynamic properties of polyelectrolyte solutions, the ion-specific effects are most clearly revealed in the enthalpy of dilution, $\Delta_{\text{dil}}H$.[27−37] This quantity reflects the amount of heat released or consumed upon diluting the sample

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from the initial to the final concentration. Classical implicit solvent theories of polyelectrolyte solutions, treating water as a dielectric continuum, such as the Manning's theory or the cylindrical cell model approach,[1−5,38] predict $\Delta_{\rm dil}H$ to be exothermic ($\Delta_{\rm dil}H < 0$) regardless of the solution's concentration or polyion's charge density. In many cases, however, experimental data for polyelectrolyte solutions reveal that heat is not released but rather consumed upon dilution.[18,31,32,35] For ionene solutions with chloride and bromide counterions, Arh and Pohar showed[18] that 3,3-, 4,5-, 6,6-, and 6,9-ionenes yield endothermic dilution effects, except for very dilute solutions of 6,6- and 6,9-ionenes, where the $\Delta_{\rm dil}H$ was established to be exothermic.

In dilute aqueous solutions of low-molecular electrolyte the negative sign of the enthalpy of dilution is due to the solvent effects.[39] This result is correctly reproduced by the Debye−Hückel limiting law.[39] At higher low-molecular electrolyte concentrations considerable deviations from the Debye−Hückel theory were noticed; in general the enthalpies of dilution became less exothermic. The extent of the deviations depends on the nature of the low-molecular salt. Such ion-specific effects are even more pronounced in polyelectrolyte systems.[18,27−37]

In view of the interesting results for $\Delta_{\rm dil}H$ reported by Arh and Pohar,[18] a more complete study of this quantity for ionene solutions seems to be warranted. In this paper we therefore report the measurements of enthalpies of dilution of 3,3-, 4,5-, 6,6-, and 6,9-ionene solutions with complete set of halide counterions. The measurements were compared with the results of the most popular polyelectrolyte theories, Manning's limiting law and Poisson−Boltzmann's cell model approach. Notice that these theories only account for the Coulomb forces and are a priori unable to describe the ion-specific effects. In addition to the previous $\Delta_{\rm dil}H$ measurements of *x,y*-ionenes with chloride and bromide solutions, which were in few cases repeated in this work, we also obtained the $\Delta_{\rm dil}H$ for solutions with fluoride and iodide counterions, which were not studied before. The interpretation of the experimental results was supplemented with the insights from recent explicit−water molecular dynamics simulations. From previously obtained results for the osmotic coefficients[19] and enthalpies of dilution of aqueous solutions of bromide and chloride ionenes,[18] we calculated the Gibbs free energy and entropy changes caused by the dilution of the samples with water. The Coulomb and non-Coulomb contributions of the chloride and bromide ions to these quantities were calculated and will be discussed in view of the solvation properties of these ions.

2. EXPERIMENTAL SECTION

2.1. Materials. Ionene bromides were synthesized from the corresponding equimolar amounts of *N,N,N*′,*N*′-tetramethyl-1,*x*-alkanediamine and 1,*y*-dibromoalkane (Sigma-Aldrich) by a polyaddition reaction in dimethylformamide at room temperature and under argon atmosphere.[10,11] The crude product was washed with a large amount of acetone and dried under vacuum for 48 h at 40 °C. The CAS numbers and purities of reagents are given in Supporting Information.

Ionene iodides were prepared by first converting bromide salts into hydroxy form with anion exchange resin (Dowex SBR LC NG (OH)). Ion conversion was checked potentiometrically using bromide selective electrode and saturated mercury sulfate electrode as the reference and the standardized solutions of $AgNO_3$ as the titrant reagent. The concentration of bromide ions was under the detection limit. The hydroxy form of the ionene was then titrated with hydroiodic acid to yield ionene iodide. Dialysis tubes (Sigma, MWCO = 12 000 $g\cdot mol^{-1}$) were filled with ∼0.02 $mol\cdot kg^{-1}$ solutions of the ionene and exhaustively dialyzed (4 weeks) until the conductivity of the exchanging water solution remained below 2 $\mu S\cdot cm^{-1}$.

Ionene fluorides were prepared from bromide salts by ion exchange during dialysis (3 weeks), using ∼0.05 $mol\cdot kg^{-1}$ NaF solution as the exchanging solution, and further dialyzed against water (3 weeks) to remove sodium ions. The same ion conversion test and conductivity criteria was applied as in the case of iodide samples and a negative flame test for Na^+ was used to check completion of the purification procedure.

All ionene solutions were prepared gravimetrically with the bidistilled water. The exact counterion concentrations were determined potentiometrically using iodide or fluoride selective electrodes and a saturated mercury sulfate electrode as the reference. Samples were titrated with standardized solutions of $AgNO_3$ and $LaCl_3$ for iodide and fluoride ionenes, respectively. All concentrations, *m*, reported in this article are given in moles of monovalent counterions per kilograms of water.

2.2. Measurements. Calorimetric measurements were performed at 25 °C with a LKB 10700-1 flow microcalorimeter using the flow−mix method. The solution and the distilled water were pumped simultaneously by means of two peristaltic pumps with an approximately equal, previously measured, flow rates (ca. 0.5 $cm^3\cdot min^{-1}$) into the calorimetric cell, where the incoming flows mixed. The diluted solution then traveled forward into a reference cell that was of equal dimensions as the measuring one, and it served to compensate the heat effects that were not due to the enthalpy of dilution. The temperature difference between these two cells is proportional to the enthalpy of dilution and was measured with a battery of thermocouples. To obtain the enthalpy of dilution, the electric calibration was performed with a heater located inside the measuring cell. The initial concentration of the solution was for each calorimetric measurement prepared in such a way as to match the concentration obtained in a previous dilution experiment. By summing up the intermediate enthalpies of dilution, the $\Delta_{\rm dil}H$ values over the presented concentration range were obtained.

3. THEORETICAL PART

The main parameter of polyelectrolyte theories is the charge density parameter λ, defined as

$$\lambda = \frac{|z_c z_p| e_0^2}{4\pi\varepsilon_0\varepsilon_r k_B T b} \tag{1}$$

where z_c and z_p are the charge numbers of the counterion and of the ionic group on the polyion, b is the average (in cases where $x \neq y$) length between two nitrogens on the polyion, that is, the length of the polyion per monovalent counterion, e_0 the elementary charge, k_B the Boltzmann's constant, T the absolute temperature, ε_0 the permittivity of the vacuum, and ε_r the relative permittivity of the solvent. In the examples studied in this publication, charged groups on the polyion and on the counterion in solution are monovalent (z_p = 1, z_c = −1). The values of b and λ are for the various *x,y*-ionenes provided in Table 1.[18]

3.1. Manning's Limiting Law. Manning's limiting law describes properties of very diluted polyelectrolyte solutions—strictly speaking, those at infinite dilution. It is based on the

Table 1. *x,y*-Ionenes[a]

x,y	*b*/nm	λ	$F(\lambda)$
3,3-	0.498	1.437	0.696
4,5-	0.685	1.045	0.957
6,6-	0.879	0.814	0.814
6,9-	1.063	0.673	0.673

[a] The first column gives the numbers of methylene groups (*x,y*) that successively appear between the quaternary nitrogens of the ionene's backbone. In the second column is the average structural distance between the adjacent nitrogens, *b*, given in nanometers. In the third column we report the charge density parameter λ (eq 1), and in the fourth one the value of $F(\lambda)$ for the particular ionene is given; λ and $F(\lambda)$ are given for T = 298.15 K.

following assumptions:[2,3] (i) the real polyelectrolyte chain is replaced by an infinitely long charged line of a given linear charge density, λ; (ii) interactions between polyions are neglected, (iii) relative permittivity, ε_r, of the solution is taken as that of the pure solvent; (iv) if $\lambda > 1$, sufficiently large fraction $(1 - \lambda^{-1})$ of counterions will "condense" on the polyion to lower the charge density parameter to the effective value 1; (v) the "uncondensed" ions are treated in the Debye−Hückel approximation.

According to this theory, the electrostatic (Coulomb) contribution to the enthalpy of dilution, $\Delta_{\text{dil}}H^{\text{c}}$, is[2,29]

$$\Delta_{\text{dil}}H^{\text{c}} = -\frac{1}{2}F(\lambda)RT\left(1+\frac{d\ln\varepsilon_r}{d\ln T}\right)\ln\left(\frac{m_f}{m}\right) \tag{2}$$

where m_f is the final (lower) and m the initial (higher) molal concentration. Notice again that concentrations reported in this article are given in moles of monovalent counterions per killigrams of water. Further, $F(\lambda) = \lambda$ for $\lambda < 1$, and $F(\lambda) = \lambda^{-1}$ for $\lambda > 1$. The derivative

$$\frac{d\ln\varepsilon_r}{d\ln T} \tag{3}$$

is for pure water at T = 298.15 K and 1 bar equal to −1.37.

It is quite clear that the calculated $\Delta_{\text{dil}}H^{\text{c}}$ values depend, besides on the final and initial concentrations, only on the value of the function $F(\lambda)$. In Table 1, we present $F(\lambda)$ values for various ionene analogues considered in this work: the first column provides an information about the numbers (*x,y*) of the methylene groups on both sides of the quaternary ammonium ion, the second column gives the average length of the monomer unit, *b*, the third one the charge density parameter λ, obtained from eq 1, and the fourth one the value of the function $F(\lambda)$ for the particular *x,y*-ionene. Notice that 3,3- and 4,5-ionenes have $\lambda > 1$ (λ above the critical value of Manning's theory), while the other two ionenes have $\lambda < 1$. It is interesting to observe that variations in *b* (and accordingly in λ) cause relatively small variations of $F(\lambda)$. In other words, the theory predicts for the limiting slope of $\Delta_{\text{dil}}H^{\text{c}}$ to be weakly sensitive on the charge density variations of the polyion in this interval of λ values.

3.2. Cylindrical Cell Model and Poisson−Boltzmann Results. In the cylindrical cell model, the polyelectrolyte solution is depicted as an assembly of identical, electroneutral, and infinitely long cylindrical cells of radius R_c (see, for example, refs 1 and 4). The cells are assumed to be mutually independent, so it is enough to treat only one such cell. The cylindrical polyion with radius *a* is placed along the *z*-axis of the cell's cylindrical coordinate system. In consistency with the previous Poisson−Boltzmann calculations,[18] the value of *a* was chosen to be 0.5 nm. Notice that small variations of this value did not affect the thermodynamic results appreciably. The radius R_c of the cell is determined by the polyelectrolyte concentration, *c*, expressed in monomer molar units (moles of monovalent counterions per dm^3 in our case)

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

N_A denotes Avogadro's number, while the values of *b* are given in Table 1. In the present work we consider polyelectrolyte solutions without added salt so in addition to the polyions only counterions and solvent molecules are present in solution. As in the Manning's theory described above, the solvent is treated as a dielectric continuum with the relative permittivity, ε_r, of pure water at T = 298.15 K. In our calculations it is taken to be 78.32.

From the solution of the Poisson−Boltzmann equation in the cylindrical symmetry, one obtains the expressions for the electrostatic contribution to the thermodynamic quantities.[5,27,32,33] For the range of values λ and $\gamma = \ln(R_c/a)$ where

$$0 \le \lambda \le \frac{\gamma}{1+\gamma} \tag{5}$$

β is real and assumes the values on the interval $1 \ge \beta \ge 0$. In this region we obtain

$$G^{\text{c}} = \frac{RT}{\lambda}\left[\lambda\ln\frac{(e^{2\gamma}-1)[(1-\lambda)^2-\beta^2]}{2\lambda} - (1+\beta^2)\gamma - \ln\frac{(1-\lambda)^2-\beta^2}{1-\beta^2} - \lambda\right] \tag{6}$$

$$H^{\text{c}} = \frac{RT}{\lambda}\left(1+\frac{d\ln\varepsilon_r}{d\ln T}\right)\left[\lambda + \gamma(1+\beta^2) + \ln\frac{(1-\lambda)^2-\beta^2}{1-\beta^2}\right] + \frac{RT}{2\lambda}\left[1-\beta^2-\frac{2\lambda e^{2\gamma}}{e^{2\gamma}-1}\right]\left[\frac{d\ln V}{d\ln T}-2\frac{d\ln a}{d\ln T}\right] \tag{7}$$

Here *R* is as usual the gas constant and β an integration constant calculated from the following equation

$$\lambda = \frac{1-\beta^2}{1+\beta\coth\beta\gamma} \tag{8}$$

For higher charge densities, where λ is out of the region defined above (see the nonequality 5), β becomes imaginary, and we need to replace β in eqs 6, 7, and 8 with $i\beta$ ($i = (-1)^{1/2}$), to obtain:

$$G^{\text{c}} = \frac{RT}{\lambda}\left[\lambda\ln\frac{(e^{2\gamma}-1)[(1-\lambda)^2+\beta^2]}{2\lambda} - (1-\beta^2)\gamma - \ln\frac{(1-\lambda)^2+\beta^2}{1+\beta^2} - \lambda\right] \tag{9}$$

$$H^{\text{c}} = \frac{RT}{\lambda}\left(1+\frac{d\ln\varepsilon_r}{d\ln T}\right)\left[\lambda + \gamma(1-\beta^2) + \ln\frac{(1-\lambda)^2+\beta^2}{1+\beta^2}\right] + \frac{RT}{2\lambda}\left[1+\beta^2-\frac{2\lambda e^{2\gamma}}{e^{2\gamma}-1}\right]\left[\frac{d\ln V}{d\ln T}-2\frac{d\ln a}{d\ln T}\right] \tag{10}$$

Table 2. Enthalpies of Dilution ($\Delta_{\mathrm{dil}}H$) for Fluoride Salts of *x*,*y*-Ionenes upon Dilution with Water from m to m_f at T = 298.15 K[a]

$10^3\ m \to 10^3\ m_f$ mol·kg^{-1}	$10^{-1}\ \Delta_{\mathrm{dil}}H$ J·mol^{-1}
	3,3-Ionene
$101 \to 50.3$	-16.3 ± 0.8
$50.3 \to 25.1$	-17 ± 1
$25.1 \to 12.5$	-18 ± 2
$12.5 \to 6.27$	-20 ± 3
$6.27 \to 3.14$	-21 ± 4
$3.14 \to 1.57$	-23 ± 7
	4,5-Ionene
$101 \to 50.7$	-14.2 ± 0.7
$50.7 \to 25.4$	-16 ± 1
$25.4 \to 12.7$	-18 ± 2
$12.7 \to 6.40$	-20 ± 3
$6.40 \to 3.22$	-22 ± 4
$3.22 \to 1.62$	-22 ± 7
	6,6-Ionene
$102 \to 50.7$	-16.5 ± 0.8
$50.7 \to 25.4$	-16 ± 1
$25.4 \to 12.7$	-20 ± 2
$12.7 \to 6.40$	-20 ± 3
$6.40 \to 3.22$	-22 ± 4
$3.22 \to 1.62$	-23 ± 7
	6,9-Ionene
$102 \to 50.5$	-18.9 ± 0.9
$50.5 \to 25.2$	-19 ± 1
$25.2 \to 12.6$	-20 ± 2
$12.6 \to 6.28$	-20 ± 3
$6.28 \to 3.14$	-21 ± 4
$3.14 \to 1.57$	-23 ± 7

[a] Concentration uncertainty is smaller than ± 0.5 %.

Table 3. Enthalpies of Dilution ($\Delta_{\mathrm{dil}}H$) for Iodide Salts of *x*,*y*-Ionenes upon Dilution with Water from m to m_f at T = 298.15 K[a]

$10^3\ m \to 10^3\ m_f$ mol·kg^{-1}	$10^{-1}\ \Delta_{\mathrm{dil}}H$ J·mol^{-1}
	3,3-Ionene
$96.8 \to 48.6$	54 ± 1
$48.6 \to 24.5$	46 ± 2
$24.5 \to 12.3$	40 ± 2
$12.3 \to 6.22$	35 ± 3
$6.22 \to 3.14$	35 ± 3
$3.14 \to 1.58$	29 ± 7
	4,5-Ionene
$97.2 \to 48.7$	56 ± 1
$48.7 \to 24.5$	45 ± 2
$24.5 \to 12.3$	37 ± 2
$12.3 \to 6.22$	28 ± 3
$6.22 \to 3.14$	23 ± 4
$3.14 \to 1.58$	18 ± 7
	6,6-Ionene
$97.3 \to 48.7$	50 ± 1
$48.7 \to 24.5$	36 ± 2
$24.5 \to 12.3$	24 ± 2
$12.3 \to 6.22$	18 ± 3
$6.22 \to 3.14$	14 ± 4
$3.14 \to 1.58$	10 ± 7
	6,9-Ionene
$97.5 \to 48.8$	52 ± 1
$48.8 \to 24.5$	33 ± 2
$24.5 \to 12.3$	21 ± 2
$12.3 \to 6.23$	7 ± 3
$6.23 \to 3.14$	-1 ± 4
$3.14 \to 1.58$	-6 ± 7

[a] Concentration uncertainty is smaller than ± 0.5 %.

and

$$\lambda = \frac{1 + \beta^2}{1 + \beta \cot \beta\gamma} \tag{11}$$

The derivative $\mathrm{d} \ln a / \mathrm{d} \ln T$ is small for dilute solutions and was in our calculations simply ignored. Further the term $\mathrm{d} \ln Va / \mathrm{d} \ln T$ is not known and is sometimes used as a fitting parameter.[18,19] For the present calculation it was set to zero.

4. RESULTS AND DISCUSSION

4.1. Measured $\Delta_{\mathrm{dil}}H$ for Solutions with Fluoride Counterions Agree with Theoretical Predictions. Experimental results for $\Delta_{\mathrm{dil}}H$ are shown in the next two figures and in Tables 2 and 3. First, in Figure 1 we present the results organized in such a way that panel a contains the results for fluoride, panel b for chloride, panel c for bromide, and panel d for iodide ions.

There are two immediate conclusions following from Figure 1: (i) In the case of fluoride counterions, all studied *x*,*y*-ionenes yield exothermic effect upon dilution ($\Delta_{\mathrm{dil}}H < 0$). (ii) In the investigated range of concentrations, there is little difference in $\Delta_{\mathrm{dil}}H$ values for the various ionene fluorides. In other words, the effect of the charge density (λ) variation is relatively small. Both conclusions are in agreement with theoretical predictions of Manning (see $F(\lambda)$ values in Table 1) and the Poisson–Boltzmann cell model theories.

For the other three panels of Figure 1, where the results for chloride (panel b), bromide (panel c), and iodide ions (panel d) are presented, we may say that only more hydrophobic (6,6- and 6,9-) ionenes exhibit a weak exothermic effect upon dilution at very low polyelectrolyte concentrations. For more strongly charged 3,3- and 4,5-ionenes with $\lambda > 1$ the measured $\Delta_{\mathrm{dil}}H$ are endothermic in the whole concentration range. The differences in enthalpies of dilution between various *x*,*y*-ionenes increase in the order from ionene fluorides, where they are small, over ionene chlorides and bromides to ionene iodides, where they are quite large.

The next figure (Figure 2) shows the same data but is organized differently. In panel a we present the results for $\Delta_{\mathrm{dil}}H$ of 3,3-ionene solutions with different halide counterions (fluoride, bromide, chloride, and iodide), while in panels b, c,

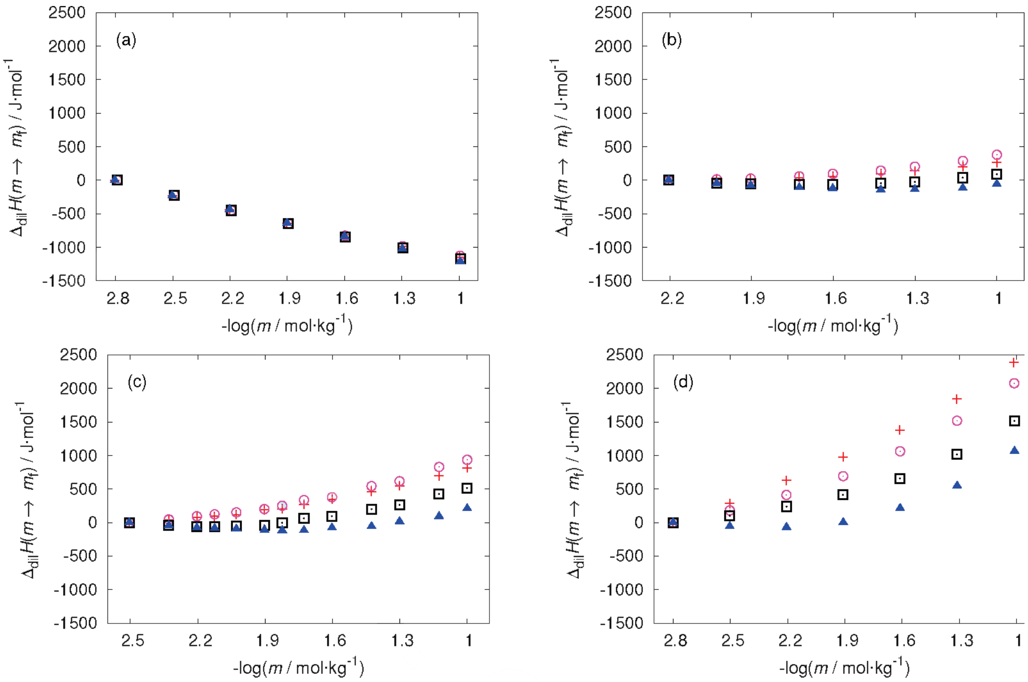

Figure 1. Enthalpy of dilution per mole of counterions as a function of the negative decadic logarithm of the counterion concentration. Panels (a) fluoride, (b) chloride, (c) bromide, (d) iodide counterion. Labeling: +, 3,3-; ⊙, 4,5-; □, 6,6-; and ▲, 6,9-. In all cases T = 298.15 K.

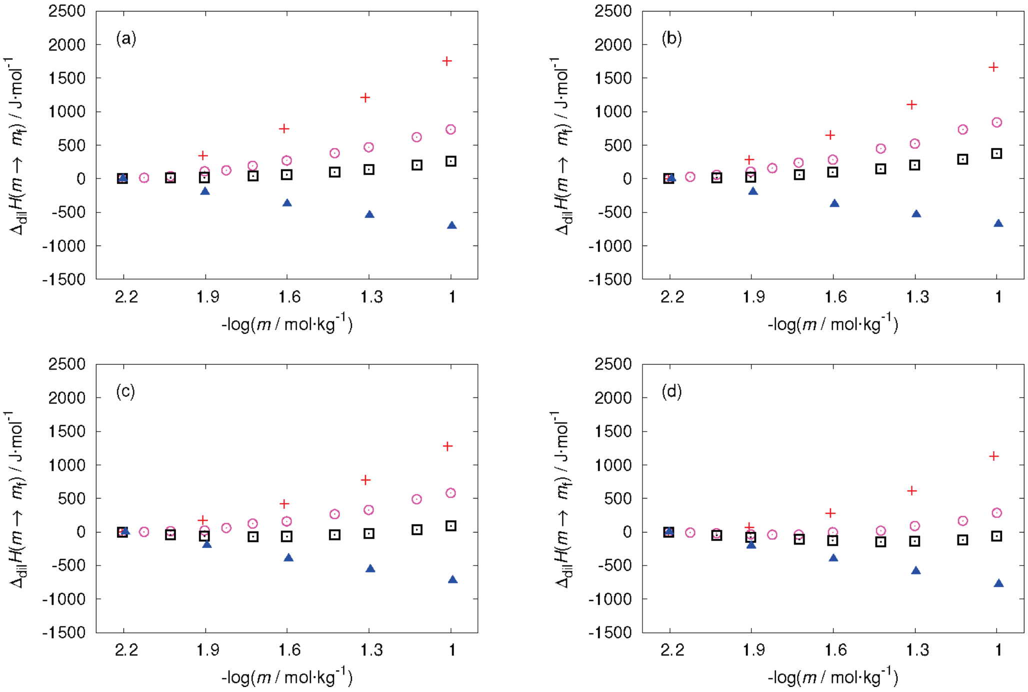

Figure 2. Enthalpy of dilution per mole of counterions as a function of the negative decadic logarithm of the counterion concentration. Panel (a) 3,3-ionenes, (b) 4,5-ionenes, (c) 6,6-ionenes, (d) 6,9-ionenes. Labeling: +, iodide; ⊙, bromide; □, chloride; and ▲, fluoride. In all cases T = 298.15 K.

and d, the same is shown for 4,5-, 6,6-, and 6,9-ionene halides, respectively. This figure allows us to better visualize the ion-specific effect, that is, the dependence of $\Delta_{\mathrm{dil}}H$ on the nature of the counterion in the solution of a particular *x,y*-ionene. It is clear that solutions with fluoride ions (strong kosmotrope) behave differently than solutions with other counterions; most notable is the distinction with ionene solutions having iodide counterions.

Finally, in Figure 3 we present the comparison between the theory and experiment for solutions of *x,y*-ionene fluorides. The experimental data are given by symbols, the Manning theory by dotted lines, and the Poisson−Boltzmann cell model results by continuous lines. An inspection of Figure 3 yields the conclusion that experimental data for 3,3-, 4,5- and 6,6-ionene fluorides are better described by the Poisson−Boltzmann cell model, while

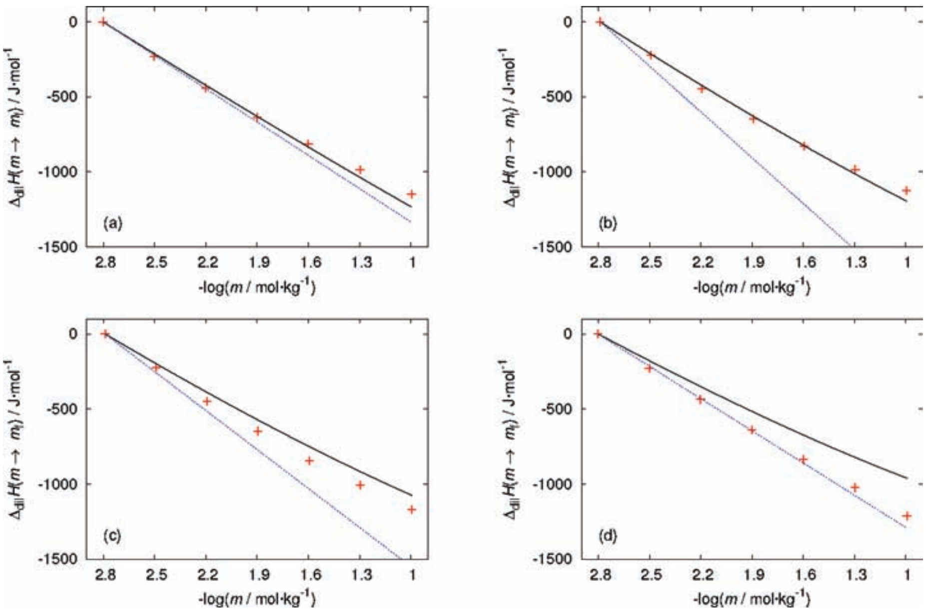

Figure 3. Enthalpy of dilution of *x,y*-ionene fluorides given per mole of counterions versus the negative decadic logarithm of the counterion concentration. Experimental data are denoted by symbols (+), while lines show predictions of the Manning (dotted line) and cell model (continuous line) theories. Panels: (a) 3,3-; (b) 4,5-; (c) 6,6-; and (d) 6,9-ionene. Experiment and calculations were performed at T = 298.15 K.

the Manning limiting law works better in the case of the 6,9-ionene solution. Notice, however, that here Manning's theory is applied out of the range of its validity. For solutions of ionene chlorides, bromides, and iodides both theories miss the sign in $\Delta_{dil}H$ (cf. Figure 1), and accordingly no comparison is presented for these cases.

4.2. Insights from the Molecular Dynamics Simulations. The ion-specific effects are currently one of the most studied topics in colloidal and (bio)physical chemistry. The progress in this area of research has been reviewed in several recent contributions.[40−44] Among the theoretical methods used to study the role of different salts in such systems, the explicit water molecular dynamics simulations seem to yield important insights.[45−47]

Recently, we performed a series of molecular dynamics simulations of a model 3,3- and 6,6-ionene oligoion in explicit water.[23−26] In these papers results for aqueous solutions of 3,3- and 6,6-ionene oligoions neutralized with fluoride, chloride, bromide, or iodide counterions were presented. In all cases, the sodium ions were present as co-ions. The oligoions mimicking ionene polyions were only six monomer units long, but it is not unreasonable to believe that the ion-specific effect, being of interest for us, behaves qualitatively the same as for much longer polyions. Results of these studies can be summarized as follows: (i) Fluoride ions, having strong affinity for water, hold their hydration waters tightly and as such do not approach close to the nitrogen of the ammonium group on the ionene. (ii) Quite the opposite is true for bromide, chloride, and most notably for iodide ions, which are loosely hydrated and can approach much closer to the positively charged nitrogen. The pair distribution function for iodide ions indicates high probability of finding this ion next to the ionene oligoion. The probabilities of finding an anion next to the ionene oligocation (measured by the height of the peak of the pair distribution function) follow the order: iodide > bromide > chloride > and fluoride ion. The consequences of different affinity of halogen ions for water are most clearly reflected in Figure 10 of ref 24 (see also Figure 3 of ref 25) where the coordination numbers of water oxygens within the arbitrary defined hydration shell around counterions are presented as a function of the distance between the counterion and the nearest nitrogen atom on the 3,3- and 6,6-ionene. It is clear from these simulations that counterions such as iodide (bromide, chloride) lose some of the hydration shell water when interacting with the ionene oligoion. This is not the case for fluoride counterions, which in interaction with nitrogens and carbons of the ionene behave as "rigidly" solvated particles.

The differences in the behavior of different counterions, seen in the pair distributions functions collected by the molecular dynamics simulations, help us to understand differences in the measured thermodynamic properties. In particular, a somewhat stronger "affinity" of bromide versus chloride counterions for 3,3-, 4,5-, 6,6-, and 6,9-ionenes indicated by the pair correlations is clearly reflected in the lower osmotic pressure of bromide salts.[19] Experimental data reveal that the ions such as fluoride in interaction with ionenes, or H^+ and Li^+ in solution with polyanions,[32] yield exothermic values for the enthalpy of dilution, quite often in quantitative agreement with the theoretical expressions given above (eqs 2 and 7 or 10). It seems that these ions in interaction with polyions behave as charged hard spheres, which justifies the application of the continuum solvent models and the derivative given by eq 3. Notice that this derivative, which applies to pure solvent at the temperature and pressure of observation, reflects an entropic contribution to the Gibbs free energy of interaction of two point-like ions when within a dielectric continuum media transferred from the infinity to some finite distance.[39,48] It seems that the term defined by eq 3, which is responsible for the negative sign of the theoretical values, becomes a much poorer approximation in cases where the rearrangement of water molecules between the interacting ions takes place.

4.3. Influence of Methylene Groups. The results for the enthalpy of dilution of more hydrophobic 6,6- and 6,9-ionenes with chloride, bromide, and iodide ions as counterions seem to request a separate analysis. In contrast to solutions of 3,3- and 4,5-ionenes, which yield endothermic effect upon dilution in the whole concentration range of this investigation, the intermediate values of $\Delta_{\rm dil}H$, given in Table 3 and in ref 18, are negative for very dilute solutions of 6,6- and 6,9-ionenes. The effect is quite small and cannot be explained by the electrostatic theories described in previous sections. Differences in $\Delta_{\rm dil}H$ between chloride, bromide, and iodide ionenes are small at low concentrations where the enthalpies of dilution are exothermic, but they amplify at concentrations higher than 0.02 mol·kg^{-1} where the dilution effect is endothermic.

An apparent paradox is that ionene polyions having low charge density (such as 6,6- and 6,9-ionenes) behave at least qualitatively consistent with the continuum solvent theories, while the more highly charged 3,3-ionene does not. In this relation it is important to mention the work of Daoust and Chabot[30] (cf. Figure 1 of their paper). These authors found the enthalpies of dilution of poly(acrylic) acid in water to be endothermic, whereas the poly(metacrylic) acid produced exothermic effect upon dilution. They have ascribed the result to the presence of an extra methyl group on the poly(metacrylic) acid chain. The transfer of a 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.

Additional information about the influence of hydrophobic groups comes from thermodynamic studies of the aqueous solutions of alkyltrimethylammonium (C_nTA) halides in the sub-micellar region. Birch and Hall[49] have systematically examined dilute aqueous solutions of alkyltrimethylammonium bromides, C_6TAB, C_8TAB, C_{10}TAB, and C_{12}TAB. They have proved that C_{10}TAB and C_{12}TAB show strong positive deviations from the Debye–Hückel law for the relative apparent molar enthalpy, which is just the negative of the enthalpy of dilution. In all cases examined in ref 49, as also in some other similar studies,[50] the heat of dilution decreases with an increased number of the methylene groups on the molecule. The results for aqueous solutions of dilute (below the critical micelle concentration) alkyltrimethylammonium bromides are therefore consistent with our measurements.

It seems that at sufficiently low polyelectrolyte concentrations the methylene groups present in 6,6- and 6,9-ionene have a decisive influence to the enthalpy of dilution, making it slightly exothermic. Differences in $\Delta_{\rm dil}H$ values between solutions of different ionenes shown in Figure 2 depend on the nature of the counterion and amplify at higher concentrations. This effect is especially large for solutions with iodide counterions, which are known to be strong chaotropes.

4.4. Thermodynamics of Dilution: Solutions with Chloride and Bromide Counterions. In this section we take advantage of previous measurements of enthalpies of dilution and osmotic coefficients of 3,3-, 4,5-, 6,6-, and 6,9-ionenes with chloride and bromide counterions[18,19] and calculate the Gibbs free energy ($\Delta_{\rm dil}G$) and entropy ($\Delta_{\rm dil}S$) changes upon dilution. In the present analysis we follow the approach of Vesnaver and Škerjanc[34] who calculated the entropies of dilution for aqueous alkali metal poly(styrenesulfonate) solutions. The Gibbs free energy upon dilution from the initial to the final ($m \rightarrow m_f$) concentration can formally be divided into three contributions

$$\Delta_{\rm dil}G(m \rightarrow m_{\rm f}) = \Delta_{\rm dil}G^{\rm id}(m \rightarrow m_{\rm f}) + \Delta_{\rm dil}G^{\rm c}(m \rightarrow m_{\rm f}) + \Delta_{\rm dil}G^{\rm n}(m \rightarrow m_{\rm f}) \qquad (12)$$

where $\Delta_{\rm dil}G^{\rm id}$ is the ideal part, while $\Delta_{\rm dil}G^{\rm c}$ and $\Delta_{\rm dil}G^{\rm n}$ are the respective Coulomb and non-Coulomb contributions during the process of dilution. Similar equations can be written for $\Delta_{\rm dil}H$ and $\Delta_{\rm dil}S$. In our analysis a well-known thermodynamic relation

$$\Delta_{\rm dil}G = \Delta_{\rm dil}H - T\Delta_{\rm dil}S \qquad (13)$$

is taken into account. In continuation, we assume that the number of ionic groups on the polyion, ν, is sufficiently large, that is, $\nu \gg 1$, so that in subsequent equations all terms multiplied with ν^{-1} can be ignored. To our estimate, this causes a difference, which is smaller than the experimental uncertainty in the determination of the osmotic coefficients (around ± 5 %). However, in no case does this approximation compromise the conclusions presented below.

$\Delta_{\rm dil}G$ can be expressed by the osmotic coefficient, Φ, as follows[34]

$$\Delta_{\rm dil}G(m \rightarrow m_{\rm f}) = RT \ln \frac{m_{\rm f}}{m} + RT \int_{m_{\rm f}}^{m} (1-\Phi) {\rm d} \ln m \qquad (14)$$

The corresponding expression for the ideal contribution can be obtained by setting $\Phi = 1$, i.e.

$$\Delta_{\rm dil}G^{\rm id}(m \rightarrow m_{\rm f}) = RT \ln \frac{m_{\rm f}}{m} \qquad (15)$$

Notice that $\Delta_{\rm dil}H^{\rm id}(m \rightarrow m_{\rm f}) = 0$. Combination of expressions 12, 14, and 15 yields

$$\Delta_{\rm dil}G^{\rm c}(m \rightarrow m_{\rm f}) + \Delta_{\rm dil}G^{\rm n}(m \rightarrow m_{\rm f}) = RT \int_{m_{\rm f}}^{m} (1-\Phi) {\rm d} \ln m \qquad (16)$$

The sum of the excess (Coulomb plus non-Coulomb) contributions to the entropy change upon dilution can be calculated from the next expression (see eqs 13 and 16)

$$T\Delta_{\rm dil}S^{\rm c}(m \rightarrow m_{\rm f}) + T\Delta_{\rm dil}S^{\rm n}(m \rightarrow m_{\rm f}) = \Delta_{\rm dil}H(m \rightarrow m_{\rm f}) - RT \int_{m_{\rm f}}^{m} (1-\Phi) {\rm d} \ln m \qquad (17)$$

Results for the thermodynamic functions are for *x,y*-ionene chlorides and bromides presented in the form of Tables 4 to 7. In Tables 4 and 5 we show the intermediate concentration values of $\Delta_{\rm dil}G$, $\Delta_{\rm dil}H$, and $T\Delta_{\rm dil}S$ for dilution from m to $m_{\rm f} = m/2$. The $\Delta_{\rm dil}G$ values are, as they should be for spontaneous processes, negative, but their absolute values increase in the direction from 3,3- (4,5-; 6,6-) to 6,9- ionenes. In addition, the $\Delta_{\rm dil}G$'s are more negative for chloride than for bromide salts.

The negative values of the $\Delta_{\rm dil}G$ are the consequence of the large $T\Delta_{\rm dil}S$ values, where the ideal part, given by eq 18, is dominant

$$T\Delta_{\rm dil}S^{\rm id}(m \rightarrow m_{\rm f}) = -\Delta_{\rm dil}G^{\rm id}(m \rightarrow m_{\rm f}) = RT \ln \frac{m}{m_{\rm f}} \qquad (18)$$

The intermediate $T\Delta_{\rm dil}S$ values are concentration-dependent and in the case of 3,3-, 4,5-, and partly for 6,6-, and 6,9-ionenes larger for solutions with bromide than with chloride counterions.

The intermediate values of the enthalpy of dilution, $\Delta_{\rm dil}H$, are positive at higher initial concentrations and become negative for dilute solutions of 6,6- and 6,9-ionene chlorides and 6,9-ionene bromides. Notice that positive values of $\Delta_{\rm dil}H$ do not contribute favorably to the $\Delta_{\rm dil}G$. Quite the opposite is true for *x,y*-ionenes with fluoride counterions for which the enthalpies of dilution are

Table 4. Changes of Gibbs Free Energy ($\Delta_{\text{dil}}G$), Enthalpy ($\Delta_{\text{dil}}H$),[18,19] and Entropy ($\Delta_{\text{dil}}S$) upon the Dilution of Chloride Salts of *x,y*-Ionenes from the Initial (m) to the Final Concentration (m_f) at T = 298.15 K

$10^3\ m \rightarrow 10^3\ m_f$	$10^{-1}\ \Delta_{\text{dil}}G$	$10^{-1}\ \Delta_{\text{dil}}H$	$10^{-1}\ T\Delta_{\text{dil}}S$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
		3,3-Ionene	
100→50	−65	12	77
50→25	−64	8	72
25→12.5	−64	4	68
12.5→6.25	−63	2	65
		4,5-Ionene	
100→50	−76	18	94
50→25	−75	11	86
25→12.5	−75	7	82
12.5→6.25	−74	3	77
		6,6-Ionene	
100→50	−87	11	98
50→25	−86	4	90
25→12.5	−86	−1	85
12.5→6.25	−85	−6	79
		6,9-Ionene	
100→50	−98	−2	96
50→25	−97	−5	92
25→12.5	−96	−7	89
12.5→6.25	−96	−8	88

Table 5. Changes of Gibbs Free Energy ($\Delta_{\text{dil}}G$), Enthalpy ($\Delta_{\text{dil}}H$),[18,19] and Entropy ($\Delta_{\text{dil}}S$) upon the Dilution of Bromide Salts of *x,y*-Ionenes from the Initial (m) to the Final Concentration (m_f) at T = 298.15 K

$10^3\ m \rightarrow 10^3\ m_f$	$10^{-1}\ \Delta_{\text{dil}}G$	$10^{-1}\ \Delta_{\text{dil}}H$	$10^{-1}\ T\Delta_{\text{dil}}S$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
		3,3-Ionene	
100→50	−62	27	89
50→25	−61	20	81
25→12.5	−60	16	76
12.5→6.25	−59	11	70
		4,5-Ionene	
100→50	−75	32	107
50→25	−73	24	97
25→12.5	−71	18	89
12.5→6.25	−69	11	80
		6,6-Ionene	
100→50	−80	25	105
50→25	−79	17	96
25→12.5	−77	13	90
12.5→6.25	−75	2	77
		6,9-Ionene	
100→50	−90	19	109
50→25	−88	10	98
25→12.5	−87	3	90
12.5→6.25	−85	−3	82

negative in all the concentration range studied here. On this basis, we may also speculate that fluoride salts of ionenes are more soluble in water than bromide (chloride, iodide) salts.

4.5. Estimates of the Non-Coulomb Contribution to Thermodynamics of Dilution. The Coulomb contributions to the thermodynamic functions of dilution (superscript c) were obtained from the Poisson−Boltzmann cylindrical cell model calculation with the help of eqs 6, 7, 9, and 10 for the $\Delta_{\text{dil}}G^{\text{c}}$ and $\Delta_{\text{dil}}H^{\text{c}}$ and for $T\Delta_{\text{dil}}S^{\text{c}}$ via eq 13. The reason lies in the fact that the validity of Manning's theory is restricted to very dilute solutions. However, qualitatively correct estimates are expected to be obtained also by the latter approach. The non-Coulomb contributions (denoted by superscript n) were obtained from eq 12 and from equivalent expressions for the other two thermodynamic quantities ($\Delta_{\text{dil}}H^{\text{n}}$ and $T\Delta_{\text{dil}}S^{\text{n}}$).

The results for $\Delta_{\text{dil}}G^{\text{n}}$, $\Delta_{\text{dil}}H^{\text{n}}$, and $T\Delta_{\text{dil}}S^{\text{n}}$ are collected in Tables 6 and 7 for ionene chlorides and bromides, respectively, which are organized similarly as Tables 4 and 5. We see that the values of $\Delta_{\text{dil}}G^{\text{n}}$ are positive, which means that the non-Coulomb term opposes the dilution. The values depend on the polyelectrolyte concentration, on the nature of the ionene as well as on the chemical nature of the counterion. The $\Delta_{\text{dil}}G^{\text{n}}$ values are larger for solutions with bromide than with chloride anions. The same pattern can be seen for the $\Delta_{\text{dil}}H^{\text{n}}$ term (> 0); again the contribution of bromide ion is larger. Probably the most interesting is the $T\Delta_{\text{dil}}S^{\text{n}}$ term. The non-Coulomb contribution to the entropy of dilution is positive in the case of the 3,3- and 4,5-ionenes and negative for the more hydrophobic 6,6- and 6,9-ionene solutions. The values therefore decrease in the direction from 3,3- to 6,9-ionenes and are concentration-dependent. The $T\Delta_{\text{dil}}S^{\text{n}}$ term is in most cases larger for solutions with bromide than with chloride counterions. The exceptions are values for 6,9-ionene at low dilution.

The approach, proposed by Vesnaver and Škerjanc,[34] used above is general and could be equally well applied to solutions with fluoride and iodide counterions. The only reason why this was not done is the fact that we do not possess all of the relevant information needed for such calculations. While the enthalpies of dilution are available (presented in this paper), there is no information about the osmotic coefficient of ionene iodides. Further, for solutions with fluoride ions only the preliminary measurements of the osmotic coefficient exist.[20,21] Yet, despite the missing information, it is still possible to speculate about the trends in the $T\Delta_{\text{dil}}S$ and $T\Delta_{\text{dil}}S^{\text{n}}$ contributions. The precise values of Φ do not seem to be extremely important here, because the enthalpy of dilution is negative for all fluoride salts presented in this article, and accordingly the $T\Delta_{\text{dil}}S$ values should be smaller than in the case of bromide and chloride salts. In other words, there seems to be less entropy increase upon dilution of *x,y*-ionene salts if the fluoride ion plays the role of the counterion. The result is consistent with our explicit water molecular dynamics simulations,[23−26] where it is shown that fluoride anions hold their waters tightly.

For ionene salts with iodide anion, one requires even more courage to predict the entropy changes upon dilution. The molecular dynamics simulations mentioned in the previous paragraph and in Section 4.2 suggest that the iodide ion is more strongly associated with the 3,3- and 6,6-ionenes than the other

Table 7. Values of Non-Coulomb Contributions of Gibbs Free Energy ($\Delta_{\mathrm{dil}}G^{\mathrm{n}}$), Enthalpy ($\Delta_{\mathrm{dil}}H^{\mathrm{n}}$), and Entropy ($\Delta_{\mathrm{dil}}S^{\mathrm{n}}$) to Dilution of Bromide Salts of *x,y*-Ionenes from the Initial (m) to the Final Concentration (m_{f}) at T = 298.15 K

$10^3\, m \rightarrow 10^3\, m_{\mathrm{f}}$	$10^{-1}\, \Delta_{\mathrm{dil}}G^{\mathrm{n}}$	$10^{-1}\, \Delta_{\mathrm{dil}}H^{\mathrm{n}}$	$10^{-1}\, T\Delta_{\mathrm{dil}}S^{\mathrm{n}}$
$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
		3,3-Ionene	
100→50	26	46	20
50→25	23	40	17
25→12.5	21	37	16
12.5→6.25	19	32	13
		4,5-Ionene	
100→50	32	50	18
50→25	30	43	13
25→12.5	28	37	9
12.5→6.25	27	31	4
		6,6-Ionene	
100→50	40	41	1
50→25	38	34	−4
25→12.5	36	31	−5
12.5→6.25	36	21	−15
		6,9-Ionene	
100→50	39	33	−6
50→25	37	24	−13
25→12.5	36	19	−17
12.5→6.25	35	13	−22

Table 6. Values of Non-Coulomb Contributions of Gibbs Free Energy ($\Delta_{\mathrm{dil}}G^{\mathrm{n}}$), Enthalpy ($\Delta_{\mathrm{dil}}H^{\mathrm{n}}$), and Entropy ($\Delta_{\mathrm{dil}}S^{\mathrm{n}}$) to Dilution of Chloride Salts of *x,y*-Ionenes from the Initial (m) to the Final Concentration (m_{f}) at T = 298.15 K

$10^3\, m \rightarrow 10^3\, m_{\mathrm{f}}$	$10^{-1}\, \Delta_{\mathrm{dil}}G^{\mathrm{n}}$	$10^{-1}\, \Delta_{\mathrm{dil}}H^{\mathrm{n}}$	$10^{-1}\, T\Delta_{\mathrm{dil}}S^{\mathrm{n}}$
$\mathrm{mol \cdot kg^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$
		3,3-Ionene	
100→50	23	32	9
50→25	20	28	8
25→12.5	17	25	8
12.5→6.25	15	23	8
		4,5-Ionene	
100→50	31	36	5
50→25	27	30	3
25→12.5	25	27	2
12.5→6.25	23	23	0
		6,6-Ionene	
100→50	33	27	−6
50→25	30	21	−9
25→12.5	28	17	−11
12.5→6.25	26	13	−13
		6,9-Ionene	
100→50	31	12	−19
50→25	28	10	−18
25→12.5	26	8	−18
12.5→6.25	25	9	−16

halide anions. This should in principle lead to the lowest osmotic coefficient (strong ion binding and high activity of water) for the ionene iodides in comparison with fluoride, chloride, and bromide salts. On the other hand, the measured enthalpies of dilution of the iodide salts are more positive than for the corresponding ionene solutions with other halide ions. It is therefore very likely that the $T\Delta_{\mathrm{dil}}S$ values (as also the $T\Delta_{\mathrm{dil}}S^{\mathrm{n}}$) shall be the largest for ionene salts with iodide counterions. Though such a result is consistent with the insights from the computer simulations of Druchok and coworkers,[23−26] accurate osmotic pressure measurements for *x,y*-ionene iodides are needed to confirm these speculations.

At this point it seems to be useful to compare our results with an analogous analysis performed by Vesnaver and Škerjanc for an anionic polyelectrolyte.[34] These authors determined the entropies of dilution of aqueous alkali metal poly(styrenesulfonate) solutions from the osmotic and enthalpy of dilution measurements. They found that the entropy of dilution was larger for cesium (chaotrope) than for lithium (strong kosmotrope) salt. Their finding is in complete agreement with ours.

5. CONCLUSIONS

Measurements of the enthalpy of dilution in aqueous solutions of aliphatic 3,3-, 4,5-, 6,6-, and 6,9-ionenes with halide counterions confirm a strong ion-specific effect which depends on the linear charge density of the *x,y*-ionene. The results are consistent with previous experimental studies of osmotic coefficients, transport quantities, as well as with the dielectric relaxation spectroscopy measurements. The enthalpies of dilution of *x,y*-ionenes with fluoride counterions are exothermic and in a good agreement with theoretical predictions based on the continuum solvent theories. These results only weakly depend on the type (charge density) of the ionene. In contrast to this, enthalpies of dilution of iodide salts are endothermic and depend quite strongly on the charge density of the ionene. The same holds true for the ionene salts neutralized with chloride or bromide counterions. If the ionene halides of a given charge density are ordered upon the $\Delta_{\mathrm{dil}}H$ effect that they produce in solution (beginning with the most exothermic and ending with the most endothermic) the following series is obtained: $\mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$. This is precisely the same ordering of anions as in the Hofmeister series for solubility of proteins. It is only in solutions of fluoride ionenes that enthalpies of dilution favorably contribute toward the Gibbs free energy of dilution. The non-Coulomb contributions to the thermodynamics of dilution, that is, to $\Delta_{\mathrm{dil}}G^{\mathrm{n}}$, $\Delta_{\mathrm{dil}}H^{\mathrm{n}}$, and $T\Delta_{\mathrm{dil}}S^{\mathrm{n}}$ were calculated for solutions with bromide and chloride counterions. The results indicate that the non-Coulomb contribution to $T\Delta_{\mathrm{dil}}S^{\mathrm{n}}$ varies from being positive for 3,3- and 4,5-ionenes to being negative for 6,6- and 6,9-ionenes. Unfortunately, no accurate osmotic pressure data for fluoride and iodide ionene salts exist, and accordingly, a similar analysis for these salts could not be performed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables with the CAS numbers and purities of the used chemicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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