Published in final edited form as:

J Mol Liq. 2017 February ; 228: 126–132. doi:10.1016/j.molliq.2016.09.043.

Volumetric and calorimetric properties of aqueous ionene solutions

Miha Lukšič and Barbara Hribar-Lee

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

Abstract

The volumetric (partial and apparent molar volumes) and calorimetric properties (apparent heat capacities) of aqueous cationic polyelectrolyte solutions – ionenes – were studied using the oscillating tube densitometer and differential scanning calorimeter. The polyion's charge density and the counterion properties were considered as variables. The special attention was put to evaluate the contribution of electrostatic and hydrophobic effects to the properties studied. The contribution of the CH₂ group of the polyion's backbone to molar volumes and heat capacities was estimated. Synergistic effect between polyion and counterions was found.

Keywords

polyelectrolyte; aliphatic ionene; hydration; ion-specific effects; molar volume; heat capacity

1. Introduction

Over the bygone decades, vast research work has been performed in the field of physical chemistry of charged macromolecules in solutions. Besides academic motivation, interest in polyelectrolytes lies in the fact that these substances possess an indispensable role in a great variety of technological and industrial applications and are the key life driving molecules in living organisms [1–3]. Mechanisms of hydration of polar or ionic (hydrophilic) and non-polar (hydrophobic) solutes or solute's residues on molecular level is inevitable for all natural sciences dealing with physical, chemical or biological aspects of (bio)macromolecules. Studies of micelle or lipid membrane formation, protein folding or aggregation, molecular recognition etc. are only few examples of the biochemical processes for which knowledge of thermodynamics of hydration is crucial. Physico-chemical properties of synthetic and natural ionic macromolecules in solution (usually water) show complex interdependence of two basic characteristics of polyelectrolytes: *i)* the distribution of charges on the macroion, and *ii)* the chemical nature of the counterions (ions dissociated from the polyion) [4–7]. For linear type polyions usually the so-called linear charge density

parameter, $\xi = \lambda_B/b$, is used to characterize the effect of charged groups; $\lambda_B = e_0^2/4\pi\epsilon_0\epsilon k_B T$ is the Bjerrum's length (e_0 the elementary charge, ϵ_0 and ϵ the permittivity of vacuum and of solvent, respectively, k_B the Boltzmann constant, and T the absolute temperature) and b denotes the average length in-between two charged sites of the polyion. The larger the ξ the more charged (less hydrophobic) is the macroion. A methodical research of the two effects (charges plus ion-specificity) on thermodynamic and transport properties is of general interest.

Our laboratory has paid much attention to aqueous solutions of ionenes precisely because of the fact that these compounds enable one a *systematic* investigation of the two above-mentioned effects [8–15]. From chemical point of view, ionenes are synthetic polyelectrolytes with the repeating unit shown on Figure 1 [16]. The number of methylene groups (x and y) in-between charged nitrogens can be varied almost at will, preparing in this way analogues with varying charge density (hydrophobicity). Besides changing the structure of the polyion, ionenes with different counterions can be synthesized.

Thermodynamic and transport properties of ionenes have been investigated by our group both experimentally (osmotic and activity coefficients, heats of dilution, conductivity and transport numbers etc.) and theoretically [8–15, 18, 19]. It has been demonstrated that effects of charges and of the nature of the corresponding counterions are complex and interdependent. For analogues with counterions of the XVII. group of the periodic table (F^- , Cl^- , Br^- , I^-) the most striking differences are revealed in heats of dilution. For ionene fluorides they are exothermic (as predicted by well established electrostatic theories), while for chlorides and bromides they can be exo- or endothermic (depending on charge density and/or concentration), and for ionene iodides the values are endothermic for all investigated samples [8, 12]. The thermodynamic and transport properties, such as osmotic coefficients, heats of dilution, transport numbers, and conductivity, show strong dependence on the charge density of the polyelectrolyte's backbone as well. Interestingly, the spectroscopic methods, such as dielectric relaxation spectroscopy [18, 19], neutron scattering data and NMR [20–22], and ultra-fast optical Kerr effect [23], suggest that the ionenes studied, in spite their relatively low backbone charge density (linear charge density parameter ξ varying between 1.44 and 0.67; see Figure 1) show surprisingly hydrophilic character, an exception being 12,12-ionenes with $\xi = 0.43$ [20].

Two thermodynamic properties that are particularly sensitive to hydrophobic interactions are partial molar volumes [24–27] and heat capacities [28–32]. Both of these thermodynamic properties are helpful in the identification of solute-solvent, as well as the solvent-solvent interactions. In this paper we present and discuss the partial and apparent molar volumes and apparent molar heat capacities of aqueous x,y -ionene solutions as a function of the ionene's backbone charge density, as well as of the counterion type. Considering previous results on thermodynamic properties of these solutions described above, we focused only on ionene fluorides and bromides; it is known that these two ions have different hydration [33]: while fluoride ion interacts strongly with surrounding water molecules (kosmotrope), bromide ion does not (chaotrope). By applying the cell-model electrostatic theory, we wish to show that thermodynamic properties cannot be described by arguments of electrostatics alone.

The article is organized as follows: after the Introduction, we define all three quantities (partial and apparent molar volume, and apparent molar heat capacity). Next, we give Experimental details and proceed with Results and discussion section. Relevant observations are summarized in the Conclusions.

2. Definitions

2.1. Partial and apparent molar volumes

One of the thermodynamic quantities that is used to study the hydration of the polyion is the volume (density) of the solution, or more precisely the information on the partial, $\bar{V}_2$, or apparent molar volume, Φ_V , of the solute [24]. $\bar{V}_2$ is defined as the change in the volume of the solution (V) per unit of moles upon addition of an infinitesimal amount of the solute (n_2) at constant temperature, pressure, and composition, i. e. $\bar{V}_2 = (V/n_2)_{T,p,n_1}$. On the other hand, Φ_V represents the formal contribution of the solute to the total volume of the solute-solvent system. For a solution of n_2 moles of the solute in n_1 moles of the solvent, the total volume of the solution can be expressed as $V = n_1\bar{V}_1 + n_2\bar{V}_2 = n_1V_1^* + n_2\Phi_V$, where $\bar{V}_1$ and V_1^* denote the partial molar volume of the solvent and molar volume of the pure solvent, respectively.

The partial molar volumes of solutes contain contributions of both the intrinsic volume and volumetric effects due to solute-solvent interactions (hydration). The water molecules around the polyion rearrange under the influence of charged and hydrophobic groups. The charged groups strongly attract (electrostrict) the neighbouring water molecules, increasing the local density of the solvent, leading to the reduction in partial molar volumes of the polyelectrolyte [34, 35]. The electrostriction of water by the counterions should also be taken into account [25, 26]. Hydrophobic hydration usually leads to an increase in the partial molar volume of the solute [34]. Although Durchschlag and Zipper [36] or Gianni and Lepori [37] have used empirical procedures to account for partial molar volumes (all these authors give additivity rules to calculate partial molar volumes of solutes at infinite dilution), up to date, no theory of partial (apparent) molar volumes of polyelectrolyte solutions, capable of considering all types of interactions, exists.

2.2. Apparent molar heat capacity

Heat capacity is a thermodynamic property which depends directly on the chemical and physical structure of the solution under investigation. At constant pressure it is defined as $C_p = (H/T)_p$, where H denotes the enthalpy of the solution. For a particular binary solution, C_p can be written as a sum of the heat capacity contribution of the solvent and of the solute, i. e. $C_p = n_1\bar{C}_{p1} + n_2\bar{C}_{p2}$, where n_i is the number of moles of species i , and $\bar{C}_{pi}$ is the partial molar heat capacity of the species i in the solution [38]. Indices 1 and 2 stand for the solvent and the solute, respectively. Assuming the ideal behaviour of the solvent, i. e. $\bar{C}_{p1} = C_{p1}^*$ (molar heat capacity of pure solvent), we can write $C_p = n_1C_{p1}^* + n_2C_{p,\Phi}$, where $C_{p,\Phi}$ denotes the apparent molar heat capacity of the solute and represents a formal contribution of the solute to the total heat capacity of the solute-solvent system [38, 39].

The $C_{p,\Phi}$ measurements have been widely applied in the studies of aqueous solutions of simple solutes [40] and systems containing biopolymers [41]. Namely, hydrophobic interactions and changes in hydration cause large changes in the molar heat capacity of the solute. The heat capacity of hydration is positive for hydrophobic solvents and negative for hydrophilic ones [28, 30]. This is because the strong solute-water electrostatic interactions induce the distortion of the water structure around the solute and break hydrogen bonds, while the presence of a non-polar solute orders the hydration water [31, 42, 43]. Such picture is consistent with the results for the polyelectrolytes where $C_{p,\Phi}$ decreases with the increasing degree of ionization (increasing charge density) of polyacids [34, 38, 39]. Another classification was proposed by Makhataдзе and Privalov [29] who classified the amino acid side chains as hydrophobic or hydrophilic according to the sign of the temperature derivative of the apparent molar heat capacity (for hydrophobic amino acids, $C_{p,\Phi}/T < 0$, and for hydrophilic $C_{p,\Phi}/T > 0$).

Polyelectrolytes consist of a backbone with discrete charges and hydrophobic parts in-between. It is therefore convenient to split the apparent molar heat capacity into the electrostatic, $C_{p,\Phi}^e$, and non-electrostatic, $C_{p,\Phi}^n$, contribution [38], i. e. $C_{p,\Phi} = C_{p,\Phi}^e + C_{p,\Phi}^n$. While (as in the case of molar volumes) no theory yet permits to estimate the non-electrostatic part of the apparent molar heat capacity, the electrostatic contribution can be calculated within the existing cell-model theories of polyelectrolytes [38], and assuming that at low concentrations $\bar{C}_{p2}^e \approx C_{p,\Phi}^e$

$$C_{p,\Phi}^e = \frac{z_p R}{z_c \xi} \left\{ u \left(2 + 4 \frac{d \ln \varepsilon}{d \ln T} + \frac{T^2}{\varepsilon} \frac{d^2 \varepsilon}{dT^2} \right) + \left(1 + \frac{d \ln V}{d \ln T} \right) \left[\frac{1 + \beta^2}{2} \frac{d \ln V}{d \ln T} + \xi \left(1 + \frac{d \ln \varepsilon}{d \ln T} \right) \frac{1 - \xi^2 + \beta^2}{(1 - \xi)^2 - \beta^2} \right] \right\} + \frac{z_p R}{2 z_c \xi} \frac{d \ln V}{d \ln T} \left\{ v \left(2 + \frac{d \ln \varepsilon}{d \ln T} \right) + \frac{2 \xi e^{2\gamma}}{e^{2\gamma} - 1} \left[\left(1 + \frac{d \ln \varepsilon}{d \ln T} \right) + \frac{1}{e^{2\gamma} - 1} \frac{d \ln V}{d \ln T} \right] \right\} \quad (1)$$

where $u = (1 + \beta^2)\gamma + \ln\{[(1 - \xi)^2 - \beta^2]/(1 - \beta^2)\} + \xi$ and $v = 1 - \beta^2 - 2\xi e^{2\gamma}/(e^{2\gamma} - 1)$.

In equation (1) z_p and z_c are the charges of ionic group on the polyion and counterion (for ionenes $z_p = |z_c| = 1$), respectively, R is the gas constant, ε the dielectric constant of the solvent, V the volume of the solution, T the temperature, and ξ denotes the linear charge density parameter of the polyelectrolyte. γ is a concentration parameter, and β an integration constant related to γ and ξ [44, 45]

$$\gamma = -\frac{1}{2} \ln \left(\pi a^2 b N_A c \right) \quad (2)$$

$$\xi = \begin{cases} \frac{1-\beta^2}{1+\beta\coth\beta\gamma} & \xi < \frac{\gamma}{\gamma+1} \\ \frac{1+\beta^2}{1+\beta\cot\beta\gamma} & \xi > \frac{\gamma}{\gamma+1} \end{cases} \quad (3)$$

In the above equations, a denotes the radius of the poly-electrolyte cylinder (taken to be 3.35 Å for x,y -ionenes [9]), b the distance between neighbouring charges on the polyion, c the counterion concentration, and N_A the Avogadro's number. Equation (1) was first derived by Daust and co-workers [38] by differentiating the expression for the electrostatic enthalpy contribution to a polyelectrolyte solution [44]. It was assumed that $d \ln a / d \ln V$ and $d(d \ln V / d \ln T) / d T$ can be neglected and that $d\beta / dT = 0$ for $\xi > 1$ [38]. The authors showed that equation (1) fails for concentrations $> 0.1 \text{ mol dm}^{-3}$ [38].

3. Experimental

Ionenes were synthesized by a polyaddition reaction from the corresponding reactants. Details about the synthesis and sample preparation are given in Ref. [18]. All samples were thoroughly dialyzed as to remove the low molecular weight fractions. An estimate of the average degree of polymerization was 40 – 230, depending on the sample [18]. However, measurements of the osmotic coefficient revealed a characteristic polyelectrolytic behaviour for all ionenes under the investigation [9].

Densities, ρ , were measured with Anton Paar DMA 5000 oscillating tube densitometer.

Partial molar volumes of the solute, $\bar{V}_2$, at 25 °C were calculated *via* an intercept method from

$$\bar{V}_2 = \bar{V} + (1 - X_2) \left(\frac{\partial \bar{V}}{\partial X_2} \right) \quad (4)$$

where $\bar{V} = V / (n_1 + n_2) = (1 + m M_2) / (\rho [M_1^{-1} + m])$ is the molar volume and $X_2 = n_2 / (n_1 + n_2) = m / (M_1^{-1} + m)$ is the molar fraction of the solute. n_1 and n_2 represent moles of water and of the solute, respectively, M_1 and M_2 molar mass of water and of monomeric unit of the ionene, respectively, and m is the molality of the solution. $\bar{V}_2$ was calculated from equation (4) using least-squares fit of $\bar{V}$ vs. X_2 , since the intercept of this line at $X_2 = 1$ equals $\bar{V}_2$.

Apparent molar volumes, Φ_V , were calculated *via* equation

$$\Phi_V = \frac{1}{\rho} \left[M_2 - \frac{1}{m} \left(\frac{\rho - \rho_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \right) \right] \quad (5)$$

Apparent molar heat capacities, $C_{p,\Phi}$, of ionene solutions were determined with the differential scanning calorimeter (TA Instruments Nano DSC) in the temperature range from 5 to 55 °C. Heating and cooling rate, dT/dt , was set to 1 °C min⁻¹. Prior to DSC experiments, all samples were degassed for about 20–30 minutes using the ThermoVac degasser (MicroCal). The measured heat flow was corrected for the solvent contribution and normalized per monomole of the ionene in the measuring cell. The operation of the instrument was tested by first measuring a 0.1 mol dm⁻³ solution of sodium chloride and the $C_{p,\Phi}$ checked against the literature value.

Calculations of $\bar{V}_2$, Φ_V and $C_{p,\Phi}$ require the molecular mass of the monomeric unit as an input parameter. To be able to correlate $C_{p,\Phi}$ with theoretical calculations, $C_{p,\Phi}^e$, we redefined the repeating unit to consist of one quaternary nitrogen atom (bearing two methyl groups), a chain of methylene units (of length x or y) and one corresponding counterion. In the case of asymmetric 4,5 and 6,9-ionene the molecular mass was taken to be the arithmetic mean of the two monomer units having 4 and 5 or 6 and 9 CH₂ units. In contrast to the definition of the repeating unit given in Figure 1 the theory defines an average monomer unit, where the charged sites of the polyelectrolyte's backbone are separated by a distance b . In this case, the concentration of repeating units equals the stoichiometric concentration of counterions in the solution of the ionene, c .

4. Results and Discussion

4.1. Partial molar volumes of x,y-ionene solutions

We start our discussion with the partial molar volumes, $\bar{V}_2$, of selected x,y-ionene bromides and fluorides. All results apply to solutions at 25 °C. Figure 2a shows $\bar{V}_2$ for 3,3; 4,5; 6,6; and 6,9-ionene bromides (●) and fluorides (○) in water depending on their charge density parameter, ξ . ξ was calculated using $\lambda_B = 7.15$ Å and structural b values being 4.92, 6.85, 8.79, and 10.63 Å for 3,3; 4,5; 6,6; and 6,9-ionenes, respectively [9]. Numerical values of partial molar volumes for the ionenes studied are given in Table 1. We have established that $\bar{V}_2$ are independent of the concentration within the concentration range studied here (from 0.01 to 0.1 mol dm⁻³). In both cases of counterions (bromide, fluoride), the partial molar volumes decrease with the increasing linear charge density parameter, as observed already before for various polycarboxylates [24, 26, 35]. The polyelectrolytes with higher charge density electrostrict water to a higher degree and their partial molar volume is therefore lower.

At the same time we have to consider different “sizes” of the repeating unit (number of CH₂ groups). To separate the two effects, $\bar{V}_2$ normalized with respect to the length of the monomeric unit, i. e. $\bar{V}_2\xi \propto \bar{V}_2/b$, is shown in Figure 2b. While almost no effect of the charge density on $\bar{V}_2$ is observed in the case of ionene fluorides (○), the $\bar{V}_2\xi$ for ionene bromides (●) increases with the increasing charge density. The trends can be explained by taking into consideration also the fraction of “free” counterions. In the case of bromide salts, the “bound” counterions release some of their electrostricted water when coming into contact with the polyelectrolyte, increasing in this way the partial molar volume. The

fraction of “bound” bromide counterions decreases with decreasing charge density (see Refs. [18, 19]).

To examine the contribution of counterions to the partial molar volumes, the differences in $\bar{V}_2$ between bromide and fluoride samples of a given x,y -ionene, $\bar{V}_2 = \bar{V}_2(\text{Br}) - \bar{V}_2(\text{F})$, were calculated and compared with the difference in partial molar volumes between KBr and KF. $\bar{V}_2$ for the ionenes diminishes with decreasing charge density of the ionene backbone, and equals $\sim 30.3, 26.3, 24.9$ and $20.4 \text{ cm}^3 \text{ mol}^{-1}$ for 3,3; 4,5; 6,6; and 6,9-ionene, respectively (see Figure 2a and Table 1). The differences in $\bar{V}_2$ of ionene bromides and fluorides are of the same order as observed for Br^- and F^- in solutions of simple salts; it was established that in the case of simple salts partial molar volumes of bromide and fluoride ion at infinite dilution equal 30.2 and $4.3 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C , respectively [33], the difference amounting to $25.9 \text{ cm}^3 \text{ mol}^{-1}$. Certain deviations ($\sim 17\text{--}21\%$) from this value are seen for 3,3 and 6,9-ionene solutions, suggesting a certain cooperativity effect in the hydration of polyion and counterion that was previously observed by dielectric relaxation spectroscopy [15, 18, 19].

To further examine the interplay of hydrophobic and electrostatic contribution to the partial molar volume, we tried to estimate the contribution of the CH_2 functional group in the ionene's backbone to $\bar{V}_2$. Since the CH_2 groups that are attached to the nitrogen atom influence the water in the hydration shell differently than the CH_2 groups further away (so-called “hydrophobic” CH_2 groups) [27], this effects need to be separated. To extract just the contribution of the “hydrophobic” CH_2 groups, we calculated the differences in partial molar volume of the ionene in question (4,5; 6,6; and 6,9) and that of the 3,3-ionene. The result was divided by the number of excess “hydrophobic” CH_2 groups in the ionene in question. The values obtained are given in Table 2. The results (on average $17.1 \text{ cm}^3 \text{ mol}^{-1}$ for ionene bromides, and $19.4 \text{ cm}^3 \text{ mol}^{-1}$ for ionene fluorides) agree well with previous estimates for the CH_2 group contribution to $\bar{V}_2$ in aqueous solutions of carbohydrates, which vary between 15.7 and $16.0 \text{ cm}^3 \text{ mol}^{-1}$ [27, 46], suggesting the water around these parts of the ionene backbone is hydrophobically structured.

4.2. Apparent molar volumes of x,y -ionene solutions

To obtain a more direct comparison with the previous work on polyelectrolytes [25, 26, 47], the apparent molar volumes, Φ_V , of different ionene salt solutions studied were calculated at different concentrations and at 25°C . The results for Φ_V of 3,3; 4,5; 6,6; and 6,9-ionene fluorides (○) and bromides (●) are shown in Figure 3 and tabulated in Table 3. The apparent molar volumes of all the ionenes studied slightly increase with the increasing concentration. Such trend was observed also for salts of polyacrylic acid [26] and polystyrenesulfonic acid [25] in water. The fluoride salts have lower apparent molar volumes than corresponding bromide salts, which is also in agreement with previous observations: the polyelectrolytes with counterions that strongly electrostrict water (e. g. Li^+ , Mg^{2+}) show lower apparent molar volumes [25, 26].

The difference in the apparent molar volumes of ionene bromides and ionene fluorides, $\Phi_V = \Phi_V(\text{Br}) - \Phi_V(\text{F})$, does not depend much on concentration and equals $\sim 30.1, 25.8, 25.4$ and $20.4 \text{ cm}^3 \text{ mol}^{-1}$ for 3,3; 4,5; 6,6; and 6,9-ionene, respectively (see Figure 3 and Table

3). Again, this is approximately same as the difference between the apparent molar volume of KBr ($\sim 34 \text{ cm}^3 \text{ mol}^{-1}$ for 0.05 mol dm^{-3}) and KF ($\sim 8 \text{ cm}^3 \text{ mol}^{-1}$ for 0.05 mol dm^{-3}) in water at 25°C . Variances in the apparent molar volumes of ionene bromides and fluorides slightly diminish with decreasing charge density of the polyion.

As expected, the apparent molar volumes are the lowest for highly charged 3,3-ionenes and increase with decreasing charge density, suggesting that water molecules are strongly electrostricted by the charges of the 3,3-polyion, while this influence is diminished in the case of 6,9-ionene.

4.3. Apparent molar heat capacities of x,y -ionene solutions

The apparent molar heat capacities, $C_{p,\Phi}$, were for aqueous solutions of x,y -ionene fluorides and bromides measured as a function of temperature ($5 - 55^\circ\text{C}$) in the concentration range between 0.001 and 0.1 mol dm^{-3} . The results are for different concentrations and at 25°C given in Table 4, and for the case of $c = 0.01 \text{ mol dm}^{-3}$ presented in Figure 4 as a function of temperature. In all cases the apparent molar heat capacity slightly increases with concentration and depends very little on temperature, similarly as observed previously for poly(ethylene oxide) in water [39]. In all cases the heat capacities increase from 3,3 to 6,9-ionene, that is, with the decreasing charge density. The finding is in agreement with the previous results of polyelectrolytes [34, 38].

To examine the effect of the chemical nature of the counterion, we show in Figure 5 $C_{p,\Phi}$ at $c = 0.01 \text{ mol dm}^{-3}$ as a function of the linear charge density parameter ξ for both counterions. In the case of highly charged 3,3 and 4,5-ionenes, the apparent molar heat capacity of fluorides (○) is lower than that of bromides (●). The opposite holds true for the 6,9-ionenes. $C_{p,\Phi}$ are similar for both kind of ions in the cases of 6,6-ionenes.

In attempt to explain these effects, the electrostatic part to the apparent molar heat capacity was calculated according to equation (1). The effective values of ξ were considered for the consistency with previous results for these solutions (see Ref. [19]). The other parameters were for $T = 25^\circ\text{C}$ taken from the Refs. [38, 48]: $\epsilon = 78.32$, $d \ln \epsilon / d \ln T = -1.37$, $d^2 \epsilon / d T^2 = 0.00167$, and $d \ln V / d \ln T = 0.0768$. The results are for $c = 0.05$ and 0.01 mol dm^{-3} given in Table 5 and 6, respectively. As previously seen for sodium polyacrylate and sodium poly-L-glutamate [38] the electrostatic contribution is negative due to the electrostriction and slightly increases with increasing concentration and with decreasing charge density. The measured apparent molar heat capacities at 0.01 and 0.05 mol dm^{-3} are positive for all the x,y -ionene bromides and fluorides. This suggests that the non-electrostatic contribution to $C_{p,\Phi}$ needs to be taken into account.

Considering the fact that “free” counterions contribute to the heat capacity as well, we interpret the results of Figure 5 as follows: in the case of highly charged 3,3 and 4,5-ionenes a fraction of bromide ions release some of their hydration shell waters and condense on the polyion while, on the other hand, this is not the case for fluoride ions where water is electrostricted by charged groups on the polyion and independently hydrated fluoride ions. The resulting apparent molar heat capacity of 3,3 and 4,5-ionene is therefore lower for fluoride samples. With decreasing polyion's charge density the fraction of “free”

counterions increases (see Ref. [15]). Due to combined contribution of “free” counterions and polyion the heat capacities for the case of fluoride ions are similar to those of bromide counterions for 6,6-ionenes. In the case of 6,9-ionenes the amount of the electrostricted water is larger in the case of bromide ions. This can be explained by the electrostriction caused by the “free” counterions. As seen in the case of the conductivity [11, 15] the fraction of “free” bromide ions increases with decreasing charge density while the fraction of “free” fluoride counterions remains approximately constant.

Similar procedure as described above for the partial molar volumes was used to calculate the contribution of the “hydrophobic” CH₂ groups to the apparent molar heat capacity of the *x,y*-ionenes. The results are given in Table 7. In the case of 6,6 and 6,9-ionene fluorides the values are very close to the previously estimated for the hydrophobic CH₂ group, i. e. 87.5 J mol⁻¹ K⁻¹ [46], showing the hydrophobic contribution of the polyion backbone. The values for ionene bromides, however, are somehow lower suggesting that the microstructure of hydration water around polyion depends on the nature of the condensed counterions (synergistic effect). This was previously observed by dielectric relaxation spectroscopy measurements of ionene bromides in water [18, 19].

5. Conclusions

In this paper we presented the analysis of partial and apparent molar volumes, and apparent molar heat capacities of aqueous cationic polyelectrolyte solutions, the so-called *x,y*-ionenes, as a function of the polyion's charge density and concentration, as well as of the characteristic of the counterion (bromide, fluoride). The results show that both polyions and counterions are contributing to the structuring of the hydration water, reflecting the importance of the fraction of condensed counterions. It has been further shown, however, that the electrostatic contributions alone are not sufficient to explain the hydration of polyelectrolytes studied; the thermodynamic data suggest that the CH₂ groups that are not in the direct vicinity of the charged groups in the backbone, structure the surrounding water hydrophobically.

Acknowledgments

Support of the Slovenian Research Agency (ARRS) under the grant P1-0201 and National Institutes of Health (NIH) under the grant 2R01GM063592-14 is acknowledged. The calorimetric equipment was partially financed by the EU within the EN →FIST operation in 2011. We thank dr. I. Prislan for the help with the DSC measurements, and M. Seru nik for the help with the samples preparation. The authors thank Prof. V. Vlady for illuminating discussions on this and various other subjects.

References

1. Stuart MAC, Huck WTS, Genzer J, Muller M, Ober M, Stamm C, Sukhorukov GB, Szleifer I, Tsukruk VV, Urban M, Winnik F, Zauscher S, Luzinov I, Minko S. Emerging applications of stimuli-responsive polymer materials. *Nat Mater.* 2010; 9:101–113. [PubMed: 20094081]
2. Ortony JH, Chatterjee T, Garner LE, Chworoz A, Mikhailowsky A, Kramer EJ, Bazan GC. Self-assembly of an optically active conjugated oligoelectrolyte. *J Am Chem Soc.* 2011; 133:8380–8387. [PubMed: 21548560]
3. Materese CK, Savelyev A, Papoian GA. Counterion atmosphere and hydration patterns near a nucleosome core particle. *J Am Chem Soc.* 2009; 131:15005–15013. [PubMed: 19778017]

4. Kunz, W., editor. Specific Ion Effects. 1. World Scientific; Singapore: 2010.
5. Zhang Y, Creme PS. Interactions between macromolecules and ions: the Hofmeister series. *Curr Opin Chem Biol.* 2006; 10:658–663. [PubMed: 17035073]
6. Li LTS, Walker GC. Signature of hydrophobic hydration in a single polymer. *Proc Natl Acad Sci USA.* 2011; 108:16527–16532. [PubMed: 21911397]
7. Zhang YJ, Furry S, Bergbreiter DE, Cremer PS. Specific ion effects on the water solubility of macromolecules: PNIPAM and the Hofmeister series. *J Am Chem Soc.* 2005; 127:14505–14510. [PubMed: 16218647]
8. Arh K, Pohar C. Enthalpies of dilution of aqueous ionene solutions. *Acta Chim Slov.* 2001; 48:385–394.
9. Arh K, Pohar C, Vlady V. Osmotic properties of aqueous ionene solutions. *J Phys Chem B.* 2002; 106:9967–9973.
10. Bonina M, Lukši M, Serunik M, Vlady V. Thermodynamic analysis of the interaction of partially hydrophobic cationic polyelectrolytes with sodium halide salts in water. *Molecular Physics.* 2014; 112:1222–1229.
11. Rodi P, Bratuša M, Lukši M, Vlady V, Hribar-Lee B. Influence of the hydrophobic groups and the nature of counterions on ion-binding in aliphatic ionene solutions, Colloids and surfaces. A. Physicochemical and Engineering Aspects. 2013; 424:18–25.
12. ebašek S, Lukši M, Pohar C, Vlady V. Thermodynamics of dilution and the Hofmeister series in aqueous solutions of aliphatic ionenes with halide counterions. *J Chem Eng Data.* 2011; 56:1282–1292.
13. ebašek S, Serunik M, Vlady V. Presence of hydrophobic groups may modify the specific ion effect in aqueous polyelectrolyte solutions. *J Phys Chem B.* 2013; 117:3682–3688. [PubMed: 23472833]
14. Serunik M, Bonina M, Lukši M, Vlady V. Specific counter-ion and co-ion effects revealed in mixing of aqueous solutions of 3,3 and 6,6-ionenes with solutions of low molecular weight salts. *Phys Chem Chem Phys.* 2012; 14:6805–6811. [PubMed: 22491212]
15. Lukši M, Hribar-Lee B, Vlady V. Interplay of ion-specific and charge density effects in aqueous solutions of weakly charged ionenes as revealed by the electric transport measurements. *J Phys Chem B.* 2010; 114:10401–10408. [PubMed: 20701375]
16. Rembaum A, Baumgartner W, Eisenberg A. Aliphatic ionenes. *J Polym Sci, Polym Lett.* 1968; 6:159–171.
17. Nagaya J, Minakata A, Tanioka A. Conductance and counterion activity of ionene solutions. *Langmuir.* 1999; 15(12):4129–4134.
18. Lukši M, Buchner R, Hribar-Lee B, Vlady V. Dielectric relaxation spectroscopy of aliphatic ionene bromides and fluorides in water: The role of the polyions charge density and the nature of the counterions. *Macromolecules.* 2009; 42:4337–4342.
19. Lukši M, Hribar-Lee B, Buchner R, Vlady V. Modelling fast mode dielectric relaxation of counterions in aqueous solutions of ionene bromides and fluorides. *Phys Chem Chem Phys.* 2009; 11:10053–10058. [PubMed: 19865759]
20. Malikova N, Rollet AL, ebašek S, Tomši M, Vlady V. On the crossroads of current polyelectrolyte theory and counterion-specific effects. *Phys Chem Chem Phys.* 2015; 17:5650–5658. [PubMed: 25623061]
21. Malikova N, ebašek S, Glenisson V, Bhowmi D, Carro G, Vlady V. Aqueous solutions of ionenes: interactions and counterion specific effects as seen by neutron scattering. *Phys Chem Chem Phys.* 2012; 14:12898–12904. [PubMed: 22899253]
22. Druchok M, Malikova N, Rollet AL, Vlady V. Counter-ion binding and mobility in the presence of hydrophobic polyions - combining molecular dynamics simulations and nmr. *AIP Advances.* 2016; 6:1–15.
23. Palombo F, Heisler IA, Hribar-Lee B, Meech SR. Tuning the hydrophobic interaction: ultrafast optical Kerr effect study of aqueous ionene solutions. *J Phys Chem B.* 2015; 119:8900–8908. [PubMed: 25318075]
24. Ikegami A. Hydration of polyacids. *Biopolymers.* 1968; 6:431–440. [PubMed: 5641940]

25. Škerjanc J. Concentration dependence of the apparent molal volumes of polyelectrolytes. *J Phys Chem.* 1973; 77:2225–2228.
26. Tondre C, Zana R. Apparent molal volumes of polyelectrolytes in aqueous solutions. *J Phys Chem.* 1972; 76:3451–3459.
27. Shahidi F. Partial molar volumes of amino acid derivatives in water. *J Solut Chem.* 1983; 12:295–301.
28. Dill KA. The meaning of hydrophobicity. *Science.* 1990; 250:297298.
29. Makhatadze GI, Privalov PL. Heat capacity of proteins. I. Partial molar heat capacity of individual amino acid residues in aqueous solution: Hydration effect. *J Mol Biol.* 1990; 213:375–384. [PubMed: 2342113]
30. Kinoshita M, Yoshidome T. Molecular origin of the negative heat capacity in hydrophilic hydration. *J Chem Phys.* 2009; 130:144705. [PubMed: 19368463]
31. Sharp KA, Madan B. Hydrophobic effect, water structure, and heat capacity changes. *J Phys Chem B.* 1997; 101:4343–4348.
32. Prabhu NV, Sharp KA. Heat capacity in proteins. *Annu Rev Phys Chem.* 2005; 56:521–548. [PubMed: 15796710]
33. Marcus, Y. Ion properties. Marcel Dekker; New York: 1997.
34. Yamashita F, Kwak JCT. Heat capacity measurements in carboxylic polyelectrolyte solutions. *J Polym Sci B: Polym Phys.* 1987; 25:1395–1406.
35. Škerjanc J. Volume change on dilution and on protonation of polycarboxylates in aqueous solutions. *J Phys Chem.* 1978; 82:2313–2316.
36. Durchslag H, Zipper P. Calculation of the partial volume of organic compounds and polymers. *Prog Colloid Polym Sci.* 1994; 94:20–39.
37. Gianni P, Lepori L. Group contributions to the partial molar volume of ionic organic solutes in aqueous solution. *J Solution Chem.* 1996; 25:1–42.
38. Daoust H, Ferland P, St-Cyr D. Electrostatic contribution to heat capacity of polyelectrolyte solutions. *J Polym Sci: Polym Phys Ed.* 1983; 21:1563–1566.
39. Daoust H, St-Cyr D. Microcalorimetric study of poly(ethylene oxide) in water and in water–ethanol mixed solvent. *Macromolecules.* 1984; 17:596–601.
40. Desnoyers JE. Structural effects in aqueous solutions: a thermodynamic approach. *Pure Appl Chem.* 1982; 54:1469–1478.
41. Privalov PL, Potekhin SA. Scanning microcalorimetry in studying temperature-induced changes in proteins. *Methods in Enzymology.* 1986; 131:4–51. [PubMed: 3773768]
42. Madan B, Sharp KA. Heat capacity changes accompanying hydrophobic and ionic solvation: A monte carlo and random network model study. *J Phys Chem.* 1996; 100:7713–7721.
43. Sharp KA, Madan B, Manas E, Vanderkooi JM. Water structure changes induced by hydrophobic and polar solutes revealed by simulations and infrared spectroscopy. *J Chem Phys.* 2001; 114:1791–1796.
44. Škerjanc J, Dolar D, Leskovšek D. Heats of dilution of polyelectrolyte solutions. I. Polystyrenesulphonic acid and its sodium salt. *Z Phys Chemie.* 1967; 56:207–217.
45. Lifson S, Katchalsky A. The electrostatic free energy of polyelectrolyte solutions. II. Fully stretched macromolecules. *J Polymer Sci.* 1954; 13:43–55.
46. Cabani S, Gianni V, an Mollica P, Lepori L. Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J Solut Chem.* 1981; 10:563–595.
47. Jerman B, Breznik M, Kogej K, Paoletti S. Osmotic and volume properties of stereoregular poly(methacrylic acids) in aqueous solution: Role of intermolecular association. *J Phys Chem B.* 2007; 111:8435–8443. [PubMed: 17388472]
48. Buchner R, Barthel J, Stauber J. The dielectric relaxation of water between 0°C and 35°C. *Chem Phys Lett.* 1999; 306:57–63.

Highlights

- Volumetric and calorimetric properties of aqueous ionene solutions are analyzed.
- Partial molar volumes of ionenes in water increase with decreasing charge density of the polyion.
- Apparent molar heat capacities of these solutions show that hydrophobic hydration needs to be taken into account.
- The properties studied depend on the chemical nature of the counterions.

Figure 1.

Repeating unit of x,y -ionene and the structural values of the linear charge density parameter ξ for selected x and y [17]. Corresponding counterion(s) are not shown.

Figure 2. Partial molar volumes ($\bar{V}_2$, panel *a*) and normalized partial molar volumes ($\bar{V}_2\xi$, panel *b*) of *x,y*-ionene bromides (●) and fluorides (○) at 25 °C as a function of the linear charge density parameter ξ .

Figure 3.

Apparent molar volumes of ionene bromides (panel *a*) and fluorides (panel *b*) at 25 °C as a function of the concentration of the *x,y*-ionene. 3,3: (●), 4,5: (*), 6,6: (▲), and 6,9-ionene: (×).

Figure 4.

Apparent molar heat capacities of a 0.01 mol dm^{-3} solutions of x,y -ionene bromides (lines) and fluorides (lines decorated with symbols) as a function of temperature. 3,3: solid lines and (●), 4,5: dashed lines and (*), 6,6: dotted lines and (▲), 6,9-ionenes: dash-dotted lines and (x). (Color online.)

Figure 5. Apparent molar heat capacities of a 0.01 mol dm^{-3} solutions of x,y -ionene bromides (●) and fluorides (○) at 25°C as a function the linear charge density parameter ξ .

Table 1

Partial molar volumes, $\bar{V}_2$ (in $\text{cm}^3 \text{mol}^{-1}$), of 3,3; 4,5; 6,6; and 6,9-ionene bromides (Br) and fluorides (F) in water at 25 °C. $\bar{V}_2$ are not concentration depended in the concentration range of this study.

$x,y\text{-ionene}$	$\bar{V}_2(\text{Br})$	$\bar{V}_2(\text{F})$
3,3	99.02	68.68
4,5	124.97	98.67
6,6	152.55	127.64
6,9	172.38	151.93

Table 2

Contribution of the “hydrophobic” CH₂ group to the partial molar volumes, $\bar{V}_2$ (in cm³ mol⁻¹), for 4,5; 6,6; and 6,9-ionene bromides (Br) and fluorides (F) in water at 25 °C. On average, the contribution is 17.1 and 19.4 cm³ mol⁻¹ for ionene bromides and fluorides, respectively.

4,5-ionene		6,6-ionene		6,9-ionene	
(Br)	(F)	(Br)	(F)	(Br)	(F)
17.3	20.0	17.8	19.7	16.3	18.5

Table 3

Apparent molar volumes, Φ_V (in $\text{cm}^3 \text{mol}^{-1}$), of 3,3; 4,5; 6,6; and 6,9-ionene bromides (Br) and fluorides (F) as a function of the concentration, c , at 25 °C.

3,3-ionene			4,5-ionene	
$\approx c / \text{mol dm}^{-3}$	$\Phi_V(\text{Br})$	$\Phi_V(\text{F})$	$\Phi_V(\text{Br})$	$\Phi_V(\text{F})$
0.01	95.09	63.43	119.89	94.31
0.02	95.99	67.00	121.98	96.64
0.03	97.24	67.64	121.80	97.10
0.05	97.91	67.98	123.66	97.12
0.07	98.43	68.13	124.15	97.77
0.10	98.54	68.29	124.50	98.02

6,6-ionene		6,9-ionene		
$\approx c / \text{mol dm}^{-3}$	$\Phi_V(\text{Br})$	$\Phi_V(\text{F})$	$\Phi_V(\text{Br})$	$\Phi_V(\text{F})$
0.01	148.13	121.83	168.17	149.45
0.02	151.02	124.63	169.76	150.18
0.03	150.28	126.13	171.06	149.68
0.05	152.08	126.64	171.59	150.30
0.07	151.74	126.76	172.00	151.03
0.10	152.21	127.15	171.86	151.44

Table 4

Apparent molar heat capacities, $C_{p,\Phi}$ (in $\text{kJ mol}^{-1} \text{K}^{-1}$), of 3,3; 4,5; 6,6; and 6,9-ionene bromides (Br) and fluorides (F) as a function of the concentration at 25 °C.

3,3-ionene			4,5-ionene	
$\approx c / \text{mol dm}^{-3}$	$C_{p,\Phi}(\text{Br})$	$C_{p,\Phi}(\text{F})$	$C_{p,\Phi}(\text{Br})$	$C_{p,\Phi}(\text{F})$
0.001	0.07	-0.08	-0.01	0.06
0.005	0.08	0.04	0.16	0.09
0.01	0.10	0.05	0.18	0.12
0.05	0.11	0.04	0.18	0.14
0.10	0.11	0.07	0.19	0.14
6,6-ionene			6,9-ionene	
$\approx c / \text{mol dm}^{-3}$	$C_{p,\Phi}(\text{Br})$	$C_{p,\Phi}(\text{F})$	$C_{p,\Phi}(\text{Br})$	$C_{p,\Phi}(\text{F})$
0.001	0.19	0.19	0.37	0.47
0.005	0.28	0.28	0.39	0.41
0.01	0.28	0.29	0.36	0.43
0.05	0.30	0.29	0.41	0.48
0.10	0.30	0.30	0.43	0.43

Table 5

Effective values of ξ and the electrostatic contribution to the apparent molar heat capacity, $C_{p,\Phi}^e$ (in $\text{kJ mol}^{-1} \text{K}^{-1}$), calculated *via* equation (1) for $c = 0.05 \text{ mol dm}^{-3}$ x,y -ionene solutions at 25°C .

ionene	bromide		fluoride	
	ξ_{eff}	$C_{p,\Phi}^e \cdot 10^3$	ξ_{eff}	$C_{p,\Phi}^e \cdot 10^3$
3,3	2.1564	-17.95	1.8693	-15.86
4,5	1.7655	-15.02	1.4154	-12.22
6,6	1.6287	-13.89	1.5606	-13.35
6,9	1.3837	-12.01	1.5007	-12.84

Table 6

Same as in Table 5 but for $c = 0.01 \text{ mol dm}^{-3}$.

ionene	bromide		fluoride	
	ξ_{eff}	$C_p^e \cdot 10^3$	ξ_{eff}	$C_p^e \cdot 10^3$
3,3	1.9713	−22.34	1.7932	−21.05
4,5	1.6472	−19.83	1.4434	−18.07
6,6	1.5025	−18.58	1.4984	−18.54
6,9	1.2764	−16.90	1.5630	−19.12

Table 7

Contribution of the CH₂ group to the apparent molar heat capacity, $C_{p,\Phi}$ (in J mol⁻¹ K⁻¹), for 4,5; 6,6; and 6,9-ionene bromides (Br) and fluorides (F) at 25 °C and for $c = 0.01$ mol dm⁻³.

4,5-ionene		6,6-ionene		6,9-ionene	
(Br)	(F)	(Br)	(F)	(Br)	(F)
53.3	46.7	60.0	80.0	57.8	84.4