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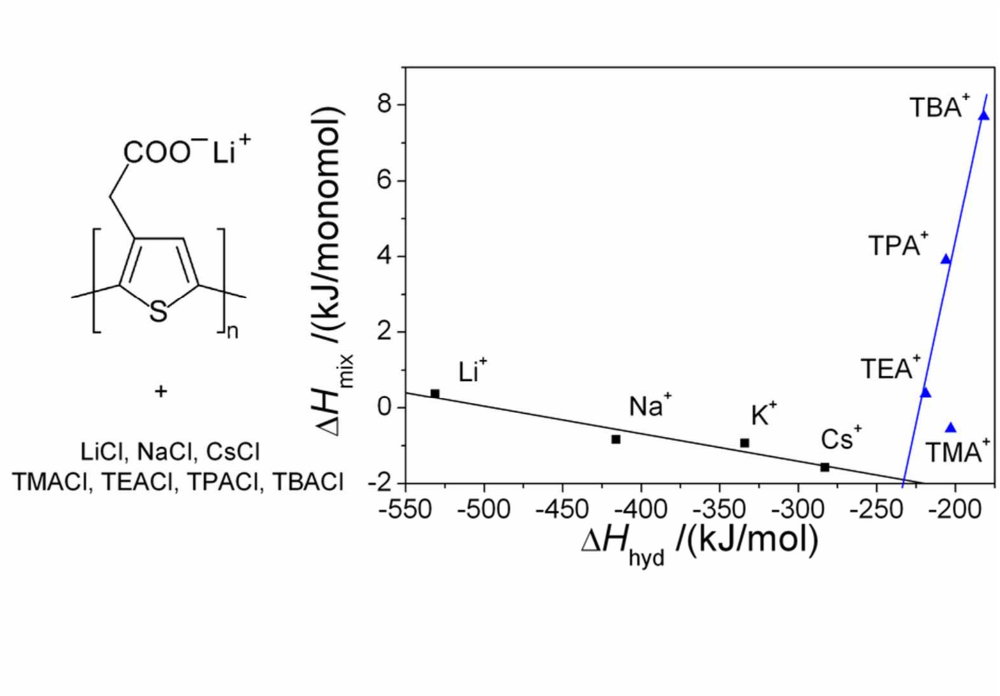

Differences in hydration of counterions are blamed for strong salt-specific effects upon dilution and mixing of poly(thiophene-3-ylacetic acid) salts with simple salts
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Differences in hydration of counterions are blamed for strong salt-specific effects upon dilution and mixing of poly(thiophene-3-ylacetic acid) salts with simple salts

Salt-specific effects observed in calorimetric studies of alkali and tetraalkylammonium salt solutions of poly(thiophen-3-ylacetic acid)†

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The enthalpies of dilution ΔH_{dil} of aqueous solutions of conjugated polyelectrolyte, poly(thiophen-3-ylacetic acid), neutralized by lithium, sodium, cesium, tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium hydroxides, were determined in the concentration range from $c_{\mathrm{p}} = 2\cdot10^{-3}$ to $1\cdot10^{-1}$ monomol/dm^3 and for T=278.15, 298.15, and 318.15 K. At low concentrations the dilution of the alkali PTAA salts yields an endothermic effect, which is in part a consequence of the hydrolysis. An exception is PTALi at 278.15 K, where $\Delta H_{\mathrm{dil}} < 0$. In case of tetraalkylammonium salts the enthalpies of dilution increase in the order TBA<TPA<TEA<TMA. Only the TBA salt of PTAA yields exothermic effect upon dilution in the whole temperature range. In the second part of the study we measured the enthalpies of mixing, ΔH_{mix}, of various salts of poly(thiophen-3-ylacetic acid) with LiCl, NaCl, KCl, and CsCl solutions in water. When lithium salt of PTAA is mixed with LiCl the ΔH_{mix} is positive. For mixing experiments with other alkali chlorides the effect is exothermic. In addition, the enthalpies of mixing of PTALi with tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium chloride were measured at T=278.15 K, 298.15 K, and 318.15 K. Popular polyelectrolyte theories, such as Manning's limiting law, predict for the heat to be released upon dilution, and consumed upon mixing; the agreement between this purely electrostatic theory and experiments is at best qualitative. The ΔH_{mix} values are correlated with the enthalpies of hydration of the cations of the low molecular mass salts added to solution.

1 Introduction

Polyelectrolytes with conjugated main chains[1,2] are currently attracting lots of research interest. This attention is stimulated by the application potential of these materials, most notably in the fields of optoelectronics and sensors[3–17]. Several important studies pointed out that properties of conjugated polyelectrolytes (CPEs) in solution correlate with their properties in multilayers[11,18,19]; for example, performance of the cationic conjugated polymer in Light Emitting Diodes can be controlled by the choice of the counterion species[11]. Even so, the number of papers in which the solution properties of conjugated polyelectrolytes are systematically examined is small, in particular the studies of thermodynamic properties of these solutes when dissolved in water are largely missing.

Conjugated polyelectrolyte being in focus of our study is poly(thiophen-3-ylacetic acid) (PTAA). This polyacid upon neutralization with a base forms a salt, which is soluble in water. Previous studies of salts of this weak polyacid are due to Kim et al[20–23] and Vallat and coworkers[24,25]. In our recent papers[26,27] we published the UV/Vis spectroscopic investigation of aqueous solutions of regio-irregular poly(thiophen-3-ylacetic acid) with and without methyl-ester groups in presence of sodium and lithium ions as counterions. More recently[28], we examined the electric transport and ion–binding in aqueous solutions of poly(thiophen-3-ylacetic acid) neutralized with LiOH, NaOH, and CsOH. In addition, the transport numbers of polyion constituent for these salts were determined at 298.15 K. For polyelectrolyte concentrations from $c_{\mathrm{p}} = 0.02$ to 0.08 monomol/dm^3 we determined the osmotic coefficients of these solutions, using the vapor pressure osmometry (at 313.15 K), and cryoscopic method. Fraction of "free" counterions, determined from the transport measurements and from osmotic pressure data were in good agreement; both experimental methods predicted for about one half of the counterions to be "associated" with polyions.

In the present paper, complementary to the preceding study[28], we present the measurements of heat effects in aqueous solutions of salts of poly(thiophen-3-ylacetic acid) upon dilution and mixing with various low molecular mass salts. The main purpose of the study is to investigate the specific ion effects in these solutions. First, the enthalpy of dilu-

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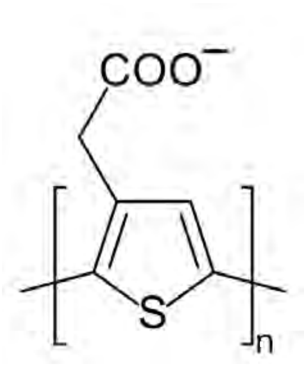

Fig. 1 Structural formula of PTAA monomeric unit.

tion, ΔH_{dil}, of lithium, sodium, cesium, tetramethyl (TMA), tetraethyl (TEA), tetrapropyl (TPA), and tetrabutyl (TBA) salts of the poly(thiophen-3-ylacetic acid) is determined at 278.15, 298.15, and 318.15 K. The effect produced by hydrolysis of the weak polyacid is estimated. In the second part of the work we measure the enthalpy of mixing, ΔH_{mix}, of these polysalts with LiCl, NaCl, CsCl, TMACl, TEACl, TPACl, and TBACl salt respectively, in the same temperature and concentration range as above. We show that ΔH_{mix} values correlate with the enthalpies of hydration of the cations of the low molecular mass salts added to solution.

By comparison with the measurements performed for other polyanions containing carboxyl groups we show that the results for the enthalpy of dilution do not depend only on the nature of the counterion and the group on the polyion, but also on the details of the polymer backbone. The results are discussed in view of the popular polyelectrolyte theories. We show that the theories, treating solvent as continuous dielectric, in many cases fail to reproduce the sign of the effect produced upon dilution or mixing. The contribution of hydrolysis to the enthalpy of dilution and its temperature dependence is estimated.

To put the present study in a more general context we stress, that carboxyl group is a part of many important molecules, most notably proteins and is as such of great importance for biology and technology. Studies of interactions between the cations and (poly)anions carrying carboxyl group are therefore of general interest.[29–31] The ion–specific effects in micellar and polyelectrolyte solutions, including those containing carboxyl group were reviewed by Kunz and coworkers[32,33]. The role of the carboxylate side chain in the cation Hofmeister series was recently examined also by Kherb and coworkers[34].

2 Experimental Part

2.1 Synthesis and sample preparation.

Description of synthesis, purification and preparation of different PTAA salts is given in our previous papers[26,28] and only the most important details are repeated here. PTAA precursor, poly(methyl thiophen-3-ylacetate) abbreviated PTAMe, was synthesized by oxidative polymerization of methyl thiophen-3-ylacetate. The resulting polymer was fractionated on the basis of molar mass–dependent solubility. In the work reported here the fraction with M_{w} = 13.4 kDa (M_{n} = 7.2 kDa), determined by the size exclusion chromatography with polyethylene glycol calibration, was used. For details see Ref.[28].

To introduce the desired counterion the solid PTAA sample was first dissolved in 0.1 mol/dm^3 alkali hydroxide (LiOH, NaOH or CsOH), filtered through the cellulose nitrate filter (pore size 1.2 μm, Sartorius AG, Göttingen, Germany), precipitated by HCl and isolated by centrifugation. The sample was finally dissolved in the desired alkali hydroxide, and filtered through cellulose nitrate filter (pore size 0.45 μm, Sartorius AG, Göttingen, Germany); upon this procedure the pH value was decreased to 5.1 by HCl addition. This solution was used to fill the dialysis tubes (Spectra/Por 3, relative molecular mass cut-off 3.5 kDa) and dialyzed against triply distilled water for about one month. Finally the level of neutralization of PTAA was adjusted to about 97 %. Tetraalkylammonium counterions were introduced into the solution by ion exchange. Four 3 ml columns were filled with cation exchange resin (Amberlite 200C) and saturated with TMA$^+$, TEA$^+$, TPA$^+$, and TBA$^+$ ions, respectively. 6 ml of 0.081 monomol/dm^3 PTANa stock solution was let to pass through each column. The presence of Na$^+$ was tested by the flame test. Test was in all cases negative indicating that sodium ions had been successfully substituted by tetraalkylammonium ions. Finally the degree of neutralization of these solutions was adjusted to about 97 %.

2.2 Measurements

Concentration determination. Concentration of the polyacid, c_{p} in moles of ionized monomer units per dm^3 (also denoted as monomol/dm^3), was determined by combination of potentiometric titration and atomic absorption spectroscopy.[27,28] Concentrations of low molecular weight salts (LiCl, NaCl, KCl, CsCl, TMACl, TEACl, TPACl, and TBACl) were determined at 298.15 K using the 736 GP Titrino automatic titrator. Standard AgNO$_3$ solution was used as a titrant, Metrohm chloride sensitive electrode (6.0502.120) as indicator electrode and mercury(I) sulfate electrode as the reference electrode. Concentrations of tetraalkylammonium salts of PTAA were determined by the UV/vis spectroscopy at 311 nm.[26] Absorption coefficient is not sensitive to the counterion species at this wavelength.

Enthalpies of dilution and mixing measurements. The enthalpies of dilution ΔH_{dil} and mixing ΔH_{mix} were obtained using the VP-ITC isothermal titration calorimeter (Microcal Inc., Northampton, MA, USA), having the cell volume equal to 1.3862 cm^3 and the syringe volume 0.3 cm^3. The measurements were performed at 278.15, 298.15, and 318.15 K. Few additional ΔH_{dil} values were obtained with a LKB 10700-1 flow microcalorimeter using the flow–mix method[35].

For ΔH_{dil} determination syringe was filled with stock solution of PTAA salts (0.074 monomol/dm^3 PTALi, 0.081 monomol/dm^3 PTANa, 0.063 monomol/dm^3 PTACs, 0.097 monomol/dm^3 PTATMA, 0.116 monomol/dm^3 PTATEA, 0.110 monomol/dm^3 PTATPA, and 0.125 monomol/dm^3 PTATBA, respectively) while the cell was filled with distilled water. The enthalpy change was obtained from the area under the peak, resulting from an injection of a titrant.

For ΔH_{mix} measurements the cell was filled with 0.005 monomol/dm^3 solution of corresponding salt of PTAA and titrated with 0.15 mol/dm^3 aqueous solution of low molecular mass salt. The enthalpy of mixing was obtained by subtracting the enthalpy of titration of pure water with the corresponding simple electrolyte.

3 Theoretical Part

3.1 Coulomb effects – the Manning theory

An elegant approach to evaluate the Coulomb contribution to properties of polyelectrolyte solutions was proposed by Manning.[36–38] According to his theory the polyion is pictured as 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. Based on these assumptions, Manning derived the expression for the enthalpy changes upon dilution (or mixing) in the form[36–38]

$$\Delta H = -\frac{RT}{2\xi}\left[1+\frac{\mathrm{d}\ln\varepsilon_{\mathrm{r}}}{\mathrm{d}\ln T}\right]\ln\left(\frac{c_{\mathrm{p}}^{\mathrm{f}}+2\xi c_{\mathrm{s}}^{\mathrm{f}}}{c_{\mathrm{p}}^{\mathrm{i}}+2\xi c_{\mathrm{s}}^{\mathrm{i}}}\right) \tag{1}$$

where c_{p} and c_{s} denote the molar concentrations of the monomeric units and of the low molecular weight salt and superscripts "*i*" and "*f*" designate the initial and final state. As usual, R stands for the gas constant and T for absolute temperature. Further, the parameter of linear charge density of the polyion, ξ, is for univalent groups on polyion and monovalent counterions defined as

$$\xi = \frac{e^2}{4\pi k_{\mathrm{B}} T \varepsilon_0 \varepsilon_{\mathrm{r}} b} \tag{2}$$

where k_{B} is the Boltzmann's constant, b the length of the polyelectrolyte unit carrying one (in our case negative) charge, e the proton charge, and ε_0 and ε_{r} the vacuum and relative permittivity of the solvent. Equation (1) is valid for $\xi > 1$. Notice that ξ=1.89 in case of completely neutralized aqueous solution of PTAA at T=298.15 K. The derivative below, determining the sign of heat effect

$$\left[1+\frac{\mathrm{d}\ln\varepsilon_{\mathrm{r}}}{\mathrm{d}\ln T}\right] \tag{3}$$

equals -0.368 for pure water at 298.15 K and normal pressure. The other values of ξ and temperature coefficients needed to calculate Eq. 1 are collected in Table 1.[39]

T /K	ξ	ε_{r}	d ln ε_{r}/d ln T
278.15	1.84	85.897	-1.279
298.15	1.89	78.358	-1.368
318.15	1.93	71.496	-1.456

Table 1 Temperature dependence of the linear charge density parameter ξ, relative permittivity ε_{r}, and the derivative d ln ε_{r}/d ln T.

Importance of the derivative given in Eq. (3), first pointed out by Bjerrum[40], is discussed in Ref.[41]. An alternative method often used to predict heat effects in polyelectrolyte solutions is based on the cylindrical cell model (see for example[41–46]). In this model the polyelectrolyte solution is depicted as an assembly of independent, identical, infinitely long and electroneutral cylindrical cells. Rigid cylindrical polyion with length equal to the length of the concentric cell is placed along the z–axis of the cell. In few cases we have also solved the Poisson–Boltzmann equation in the cylindrical symmetry to calculate the ΔH_{dil} and ΔH_{mix} values for the system of interest. For the dilute solutions studied here, the results obtained from the two approaches are very close to each other, so merely the results of the Manning's theory, which is easier to apply, are presented.

3.2 Heat effects upon hydrolysis

According to Manning's theory negative values of enthalpy of dilution, ΔH_{dil}, are expected at low concentrations. This holds true for many polyelectrolytes carrying the charged groups which do not hydrolyze[41,43–46]. However, the poly(thiophen-3-ylacetic acid) is a weak polycarboxylic acid whose salts can undergo hydrolysis during a dilution. The hydrolysis provokes an endothermic effect that may at low concentrations prevail over the exothermic (Coulomb) contribution.[47–50] The contribution of hydrolysis to the total enthalpy change upon dilution has been accounted for semi-quantitatively, as described in detail in the Electronic Supplementary Information (ESI).

4 Results and Discussion

4.1 Enthalpies of dilution

The term enthalpy (or heat) of dilution, ΔH_{dil}, is used to denote the cumulative enthalpy change, calculated per one mole of ionized charge group on the polyion, occurred upon the dilution of polyelectrolyte solution from an initial to the given final concentration. The results are sometimes presented as intermediate heats of dilution, which usually denote the enthalpy changes upon halving the initial concentration[49].

According to literature the effects influencing the enthalpy of dilution of polyelectrolyte solution are the following: (i) Coulomb (non-specific) effect, being dominant for dilute electrolyte or polyelectrolyte solutions. This term yields an exothermic contribution and is correctly accounted for by the Manning theory. (ii) For moderate polyelectrolyte concentrations, the heat effect upon dilution may become endothermic. This result[51–53], specific to the particular ionic species, is related to the hydration–dehydration equilibrium of the interacting group on the polyion and counterions in the solution. (iii) In polyelectrolyte solutions in addition to charges often also the hydrophobic groups are present. The presence of hydrophobic groups is usually manifested by the release of heat. (iv) Finally, for dilute solutions of weak polyelectrolytes such as ours, the effect of hydrolysis must be included into the picture.[47,50]

Before we present the results for salts of PTAA we wish to discuss some ΔH_{dil} data obtained for other polyelectrolytes carrying carboxyl group. Effect of the cation size on the enthalpies of dilution of aqueous solutions of alkali metal and tetramethylammonium salts of the polyacrylic, polymethacrylic, and polyethacrylic acids has been probably first studied by Daoust and Chabot[49]. For dilute solutions the effect upon further dilution is endothermic; it is the strongest for cesium and the weakest for sodium counterion. The authors[49] ascribe the effect, at least in part, to hydrolysis being stronger in the diluted regime[48]. In the concentrated range (more concentrated than studied here), the intermediate heats of dilution are endothermic for sodium, but exothermic for cesium salt of the first two polyacids. The TMA salts yield exothermic heats of dilution in this concentration range.

Hales and Pass[54] studied the effect of the nature of counterion in solutions of alkali–metal salts of carboxymethylcelulose at 298.15 K. They found for the integral enthalpies of dilution to be negative (exothermic effect) and to follow the order: $\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+ \approx \mathrm{NH}_4^+ \approx \mathrm{Cs}^+$. Comparison with the corresponding series of salts of poly(styrenesulfonic acid) and poly(anetholesulfonic acid) shows interesting similarities.[43,46] Enthalpies of dilution for aqueous solutions of lithium, sodium, and cesium salts of fullerenehexamalonic acid, $\mathrm{C}_{66}(\mathrm{COOH})_{12}$, were for 298.15 K published in Ref.[50].

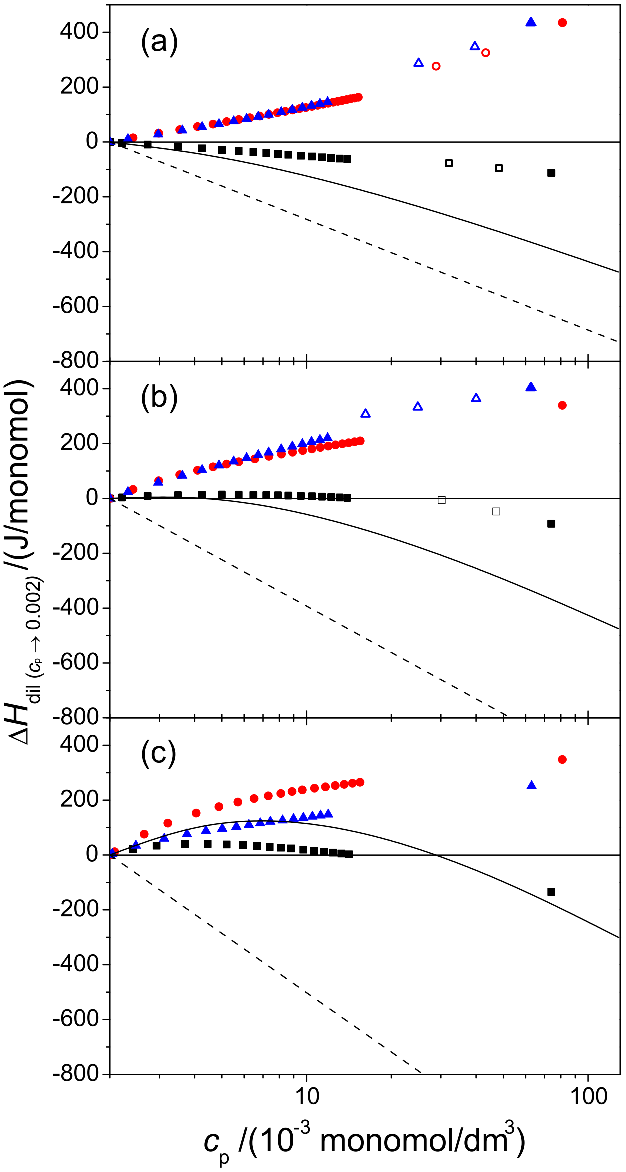

Fig. 2 Enthalpy of dilution from c_p^i=c_p to c_p^f =0.002 monomol/dm^3 (in Joule per mole of monomer units) for different alkali salts of PTAA at a) 278.15, b) 298.15 K, and c) 318.15 K, as a function of the logarithm of the polyelectrolyte concentration. Legend: lithium salt (black squares), sodium salt (red circles), cesium salt (blue triangles up). Dashed lines are obtained by Manning's theory[36], the solid lines include the correction due to hydrolysis, calculated for dissociation constant $K_a = 4 \cdot 10^{-8}$ as described in the Electronic Supplementary Information to this paper.

These results showed that lithium salt is the most and cesium the least exothermic among the three alkali halide salts. The enthalpies of dilution were ordered as: $\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{Cs}^+$. The results were obtained for polyelectrolyte concentrations

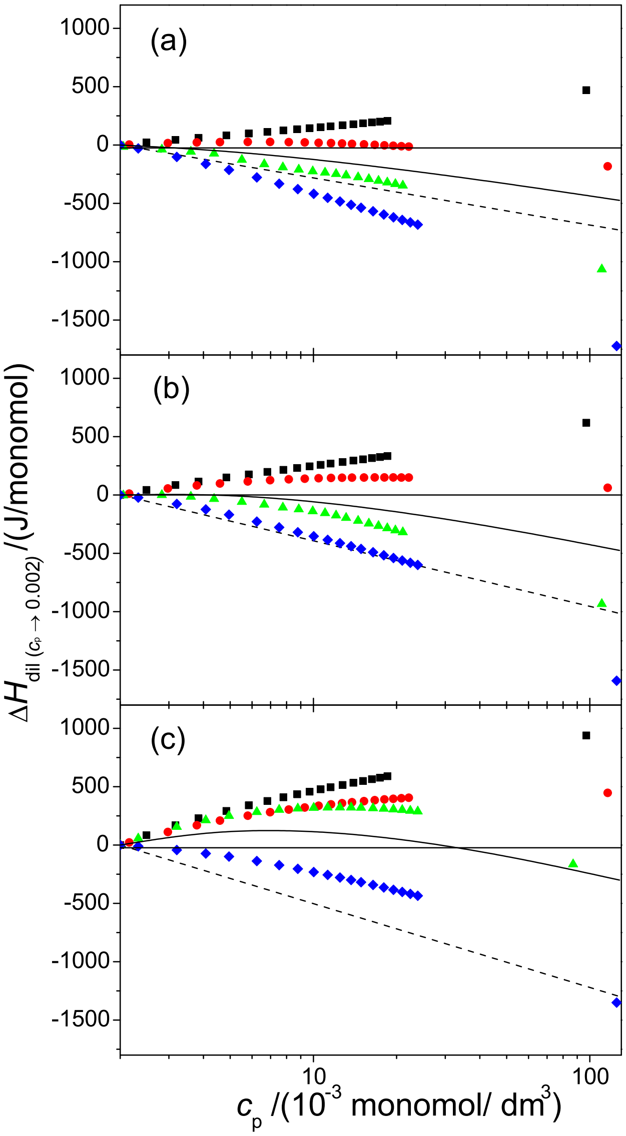

Fig. 3 Enthalpy of dilution for different salts of PTAA at a) 278.15, b) 298.15, and c) 318.15 K; tetramethylammonium salt (black squares), tetraethylammonium salt (red circles), tetrapropylammonium salt (green triangles up), and tetrabutylammonium salt (blue diamonds). Notation as for Fig. 2.

above 0.01 monomol/dm^3, where the hydrolysis effects are expected to be less important.

In Fig. 2a-c, we present measurements of the enthalpy of dilution, ΔH_{dil}, for the lithium, sodium, and cesium salts of poly(thiophen-3-ylacetic acid) at 278.15, 298.15, and 318.15 K, plotted as a function of the logarithm of the initial polyelectrolyte concentration, $c_p^i = c_p$. The lowest (the final, c_p^f) concentration for the reported heats of dilution, is 0.002 monomol/dm^3. The experimental results are shown by symbols, while the calculations are presented by lines. The experimental data represent a combination of two different type of measurements: the ITC results are shown by filled and the results obtained by the flow calorimeter by empty symbols.

From graphs on Fig. 2a-c we see that alkali salts of PTAA, with an exception of lithium salt at 278.15 K, yield an endothermic effect upon dilution. This is not what is expected on the basis of the electrostatic theory, which predicts for the heats of dilution (broken line shows results of the Manning theory) to be negative. A lack of quantitative and qualitative agreement between the results calculated by the Manning theory or the Poisson–Boltzmann cylindrical cell model approach, has also been noticed for other polyelectrolytes[43,46,51–53,55]. The enthalpies of dilution are ordered as: $\mathrm{Li}^+ < \mathrm{Na}^+ \approx \mathrm{Cs}^+$ in case of T=278.15 and 298.15 K. For T=318.15 K the series modifies to $\mathrm{Li}^+ < \mathrm{Cs}^+ < \mathrm{Na}^+$. Strong ion–specific effects, observed for polyanions carrying carboxyl groups, have been documented in several previous papers.[49,50,54,56].

Salts of poly(thiophene-3-ylacetic acid) are prone to hydrolyze. Hydrolysis is, in comparison with other contributions, relatively more important at high dilutions and yields endothermic effect[47,48]. Similar result was found before for alkali salts of fullerenehexamalonic acid[50]. The fact that lithium salts of polycarboxylic acids have the most exothermic (or the least endothermic) heats of dilution has already been observed before[56].

An important information is provided by the temperature dependence of ΔH_{dil}. Manning's theory suggests for heats of dilution to become more exothermic with an increase of temperature, what is confirmed by some experiments[54,56]. In Fig. 2a-c we observe an opposite effect, our ΔH_{dil} values become more positive. The hydrolysis is blamed for such behavior. We have estimated the magnitude of the contribution of hydrolysis to the enthalpy of dilution by a simplified approach, which is explained in the Electronic Supplementary Information (ESI). Corrections to the Manning theory due to hydrolysis are on Fig. 2a-c plotted by continuous lines. It is clear that, if this effect is included in theoretical consideration, the agreement between theory and experiments improves.

From calculations presented in the ESI we learned that the contribution of hydrolysis depends strongly on temperature. The effect becomes, in agreement with experimental data, stronger at higher temperatures as a consequence of the increase of ionization constant of water (K_w) with the increase of temperature.

At this point we need to mention that in addition to hydrolysis there is another positive contribution to the ΔH_{dil}. This contribution is ion specific and ascribed[51–53] to the gradual release of the counterions, "site–bound" to the polyion, into the bulk solution upon dilution. We shall discuss this effect in more detail in relation with the enthalpy of mixing measurements below.

It can be expected that tetraalkylammonium salts, in view of possesing hydrophobic groups, will show somehow different features than alkali salts studied above. From experience with other polyelectrolyte solutions[35,49,57] we know that presence of the hydrophobic groups makes the enthalpies of dilution more negative. This effect is clearly seen on Fig. 3a-c (note the scale), the most exothermic effect during the dilution is found for TBA salt. Enthalpies of dilution increase in the order TBA<TPA<TEA<TMA. The dilution of the tetrabutylammonium salt is an exothermic process at all temperatures. Our results are consistent with measurements of Tsuge et al.[55] who studied tetraalkylammonium polyacrylates and tetraalkylammonium chondroitin 4-sulfates. These authors also observed increasingly more exothermic effect with an increase of the carbon number in R_4N^+ cation. The enthalpies of dilution of tetraalkylammonium salts exhibit stronger temperature dependence than alkali salts. The orientation and distribution of water molecules near the hydrophobic groups is suggested to be sensitive to the temperature variations[58], what may cause the strong temperature dependence observed in Fig. 3a-c.

4.2 Enthalpies of mixing

From Manning's theory, Eq. 1, it follows that the same general equation can be used to calculate the enthalpy of dilution ΔH_{dil} and the enthalpy of mixing ΔH_{mix} of a polyelectrolyte with a solution of simple salt. It is easy to see that an addition of electrolyte to polyelectrolyte solution should yield – contrary to the dilution – an endothermic process, providing that concentration of polyelectrolyte solution does not change too much. The expressions for ΔH_{dil} and ΔH_{mix} namely differ only in the term which includes concentration of added low molecular mass salt[38].

Hales and Pass[59] measured ΔH_{mix} of sodium carboxymethyl cellulose solution in water upon mixing with aqueous lithium, sodium, and potassium chloride solutions. They found for the enthalpies of mixing to be endothermic in qualitative agreement with Manning's theory (Eq. 1). They concluded that mixtures containing lithium and sodium ions give an additional (with respect to the Manning theory) positive and the mixtures containing potassium and sodium ions additional negative contribution to the heat of mixing.

In Fig. 4 our results for the enthalpy of mixing of PTALi with LiCl, NaCl, and CsCl at 278.15, 298.15, and 318.15 K are presented as a function of molar ratio "*r*" between added low molecular mass electrolyte (LiCl, NaCl or CsCl) and polyelectrolyte (PTALi) monomeric units. Agreement between the predictions of Eq. 1 and experimental results is poor – only the enthalpies of mixing of PTALi with LiCl can be qualitatively explained by the Manning theory – while additions of NaCl and CsCl cause exothermic effects. We explain this results as follows: lithium ions are strongly hydrated and partially "expelled" from the vicinity of the carboxylate groups by the cations having less negative free energy of hydration. This causes changes in structure of the electric double–layer around the polyion. We ascribe the differences between calcu-

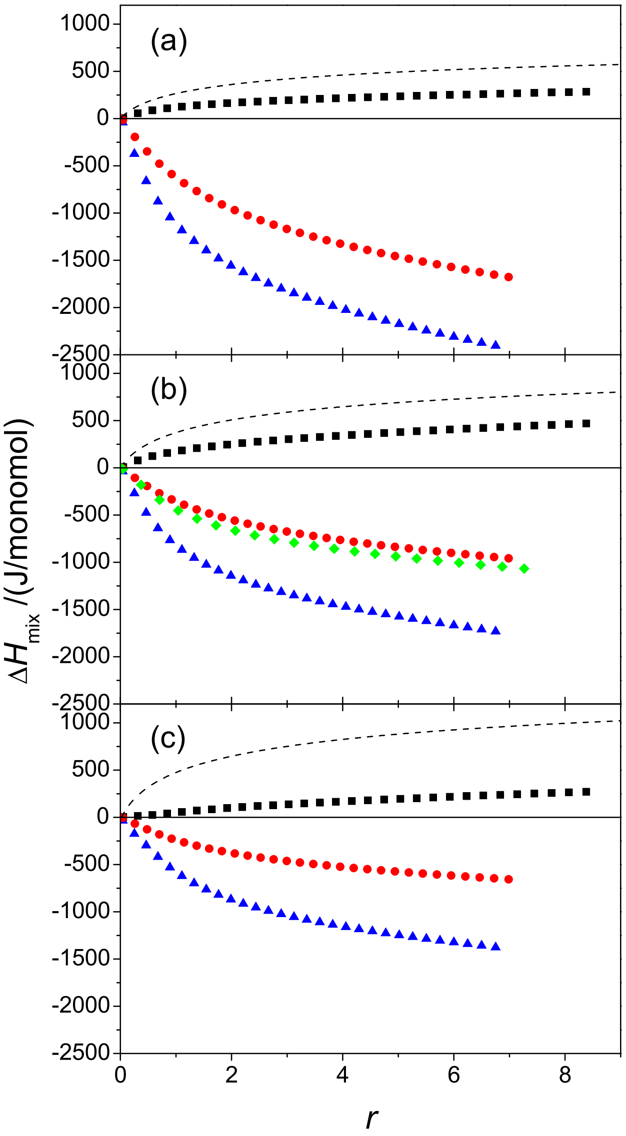

Fig. 4 Enthalpies of mixing of PTALi with LiCl, NaCl, and CsCl at a) 278.15, b) 298.15, and c) 318.15 K. Legend: lithium salt (black squares), sodium salt (red circles), and cesium salt (blue triangles up). For *T*=298.15 K also the values of mixing enthalpies with KCl (green diamonds) are shown. "*r*" is the molar ratio between added low molecular mass electrolyte and polyelectrolyte monomeric units. Broken line is calculated using Manning's theory.

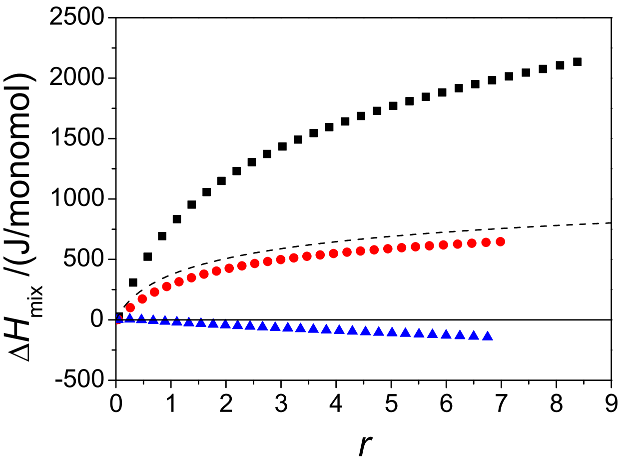

Fig. 5 Enthalpies of mixing of PTACs with LiCl, NaCl, and CsCl at 298.15 K. Notation as for Fig. 4.

lated and measured enthalpies of mixing of PTALi with NaCl (or CsCl) to the release of some hydrated water into the bulk (energetically more favorable environment), caused by strong sodium– or cesium–polyion interaction[51,52]. The ion–specific effects are stronger at lower temperatures[60] where water is more ordered[61].

To support this explanation we measured the ΔH_{mix} for PTACs when mixed with LiCl, NaCl and CsCl solutions. The measurements presented in Fig. 5 were performed at 298.15 K. As we see an addition of cesium chloride solution yields practically no heat effect under these conditions, while the titration with lithium salt causes rather strong endothermic effect. An addition of NaCl to PTACs yields fortuitously good agreement between theory and experiment. These results (Fig. 5) are fully consistent with those presented in Fig. 4 and will be further discussed later in the text.

The fact that an addition of low molecular mass salts containing less strongly hydrated counterions – an appropriate measure seems to be the free energy (or enthalpy) of hydration – than originally present in polyelectrolyte solution leads to less endothermic (or to even exothermic) effects upon mixing has been noticed before[54,62]. In contrast to this, an addition of salt containing the counterion with the more negative free energy (or enthalpy) of solvation may lead to the more endothermic effects than predicted by the theory. Such patterns have also been observed and explained in our recent measurements of enthalpy of mixing of x,y–ionene salts with various low molecular mass electrolytes[51,52].

In the next figure, Fig. 6, we present the ΔH_{mix} results for the case when tetraalkylammonium chloride solutions are added to the 0.005 monomol/dm^3 PTALi solution. In comparison with the previous figure we notice that the heat effects are much larger than in case of mixing with alkali chloride solutions in water. The enthalpy of mixing is (similarly as the heat of dilution) the largest when TBA$^+$ is present as the competing counterion. The ΔH_{mix} is for all temperatures decreasing in sequence TBA$^+$ > TPA$^+$ > TEA$^+$ > TMA$^+$. Mixing of TMACl with PTALi is an exothermic process while TEACl is the border case: the process is endothermic at 278.15 K and 298.15 K, but at 318.15 K it becomes exothermic. Požar and coworkers[62] (see Fig. 6 of their paper) found the ΔH_{mix}

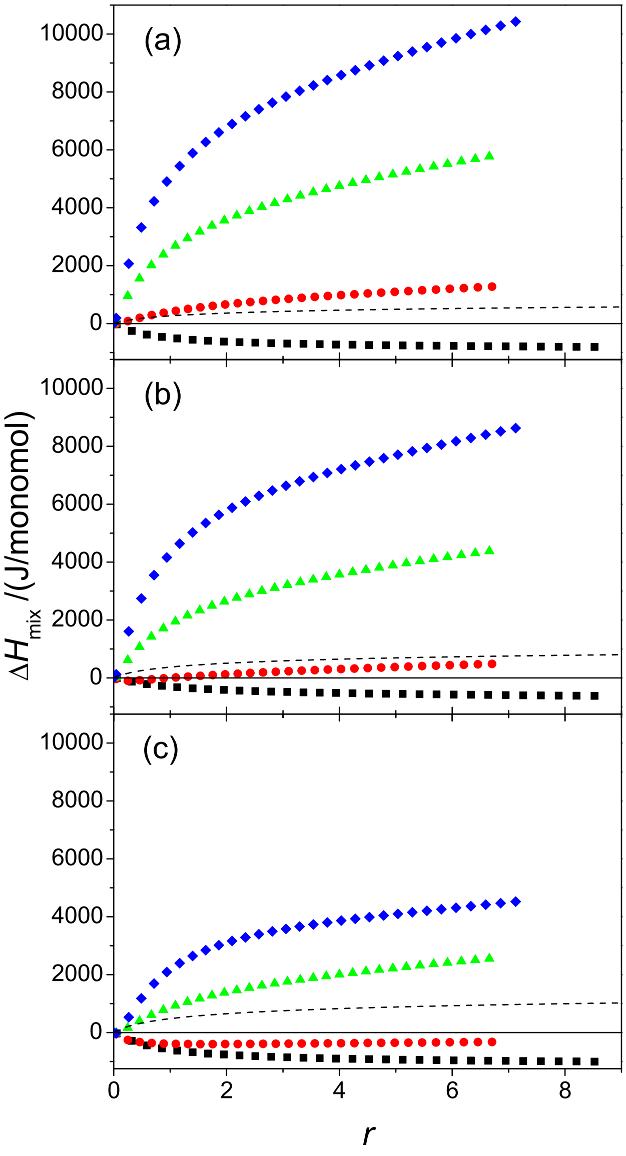

Fig. 6 Enthalpies of mixing of PTALi with TMACl (black squares), TEACl (red circles), TPACl (green triangles up), and TBACl (blue diamonds) at a) 278.15, b) 298.15, and c) 318.15 K. Other as for Fig. 4.

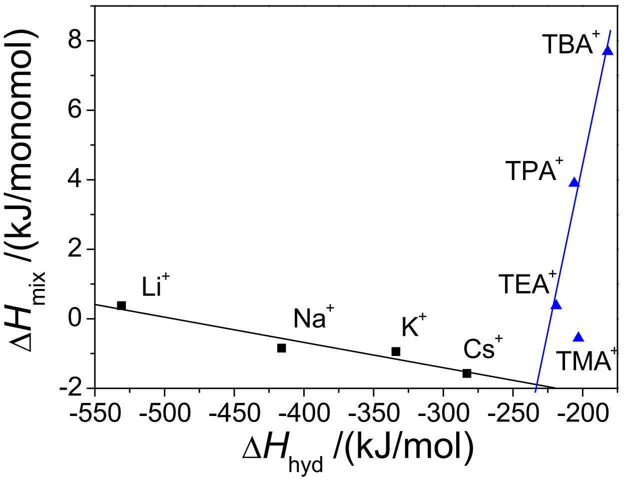

Fig. 7 Enthalpies of mixing, ΔH_{mix}, of PTALi with various low molecular mass salts at $r = 5$ as a function of the enthalpy of hydration of the salt cation; T=298.15 K. Lines are used to guide the eyes.

values of sodium polystyrenesulfonates with TMA and TEA negative – no results for more hydrophobic TPA or TBA salts are reported in their work.

Positive ΔH_{mix} values obtained upon mixing of PTALi with some tetraalkylammonium salts are consistent with the ΔH_{dil} measurements shown in Fig. 3a-c, and as such come as no surprise. What is surprising is the magnitude of the effect. While the heats of dilution of PTATBA and PTATPA are still comparable to the values predicted by theory, or exhibited by PTALi salt, this is clearly not the case when enthalpies of mixing are in question. In our case upon the mixing of PTALi with TBACl at 278.15 K and 298.15 K more than one order of magnitude larger amount of heat is absorbed than predicted by the Manning theory. The possible effect of hydrolysis is assumed to be small here, taken that the dilution is minimal. Unusually strong temperature dependence of enthalpies of mixing exhibited for adding TPACl and TBACl to PTALi has probably the same origin as in case of heats of dilution discussed in the previous subsection.

An important finding of this study, summarizing our heat of mixing results, is presented in Fig. 7. Here the correlation of ΔH_{mix} with the enthalpy of hydration[63,64] of various counterions is presented. We found an almost perfect linear dependence between the two quantities in case of alkali counterions studied here. The trend is in our view a consequence of the fact that "weakly" hydrated ions replace the more "strongly" (large negative enthalpy of hydration, ΔH_{hyd}) solvated ones in the vicinity of polyions. Some dehydration of the charged groups and counterions (this is in polyelectrolyte literature called "site–binding") takes place upon such processes. Linear correlation of ΔH_{mix} with ΔH_{hyd} of counterion species has also been found for cationic polyelectrolytes named ionenes[51–53] and for the alkali salts of polystyrenesulfonic acid[62]. As stressed above, the dependence of ΔH_{mix} on ΔH_{hyd} shows a different trend when aqueous solution of PTALi is titrated with tetraalkylammonium chlorides (TMACl, TEACl, TPACl, and TBACl). The results for TBA and TPA counterions presented in Fig. 7 seem to reflect the hydrophobic nature of these cations. This view is supported by the results of Yamakata and coworkers[65–67], who observed the displacement of water molecules (drying) from the region between tetrabutylammonium ion and oppositely charged hydrophobic surface.

5 Conclusions

The enthalpies of dilution of aqueous solutions of poly(thiophen-3-ylacetic acid) neutralized with LiOH, NaOH, and CsOH are measured in a concentration range from $c_{\mathrm{p}} = 2{\cdot}10^{-3}$ to $1{\cdot}10^{-1}$ monomol/dm^3 and for T=278.15, 298.15, and 318.15 K. The ΔH_{dil} data are complemented with the results for the heat effect caused by mixing of the alkali salts of the poly(thiophen-3-ylacetic acid) with LiCl, NaCl, KCl, CsCl, TMACl, TEACl, TPACl, and TBACl solutions in water.

Our experimental results yield the following conclusions: (i) Manning's theory, treating water as continuous dielectric in most cases fails to predict correct sign of the enthalpies of dilution and mixing. (ii) The comparison with other polyelectrolytes containing carboxyl group indicates that for alkali salts the heat effects upon dilution generally follow the series $\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{Cs}^+$, but the magnitude and even the sign of the effect vary with the nature of the polyion species. The ΔH_{dil} values for tetraalkylammonium salts follow the sequence: TBA<TPA<TEA<TMA. (iii) For the poly(thiophen-3-ylacetic acid) salts studied here, the ΔH_{dil} and ΔH_{mix} measurements are qualitatively consistent with each other. (iv) In case that alkali halide salts are added to the PTALi solution the ΔH_{mix} is a linear function of the enthalpy of hydration of the cation of added salt. The enthalpy of mixing decreases with an increasing crystal size of the cation from added alkali salt. (v) When tetraalkylammonium salts are added to the PTALi solution, an opposite effect is observed: the enthalpy of mixing increases with an increase of the size of the cation from added salt. The reason for this difference may lie in interaction of the hydrophobic tetraalkylammonium ions with thienyl groups of the polyelectrolyte backbone. We plan to explore this hypothesis in more detail using the combination of UV/Vis spectrum and NMR measurements.

The conclusions above are in line with recent experimental[53] and theoretical findings. For example, Čebašek et al.[53] observed experimentally that presence of hydrophobic groups on the polycation may reverse the ordering of the Hofmeister series. Specific short–range interactions and Hofmeister series have also been studied by the all–atom molecular dynamics approach.[31,68–71] In view of the differences between the various polyelectrolytes, having carboxyl group attached to the backbone, the paper of Sulatha et al[69] is of interest for us. These authors studied hydration behavior of poly(acrylic) and poly(metacrylic) acid in dilute aqueous solutions. They predict that upon neutralization with NaOH the poly(metacrylic) acid shows stronger correlation with sodium ions in comparison with poly(acrylic) acid under similar conditions. This is another indication that a solvation of the carboxyl group may be affected by the nature of the neighboring groups on the polyelectrolyte backbone. Experimental work presented in this paper confirms the conclusions of Paterová and coworkers[71] who stated that an explanation of the Hofmeister series on the basis of the bulk hydration properties of ions (or ionic groups) may not be adequate.

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