Isothermal Titration Calorimetry of the Polyelectrolyte/Water Interaction and Binding of Ca^{2+}: Effects Determining the Quality of Polymeric Scale Inhibitors

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ABSTRACT: The interaction of poly(sodium acrylate) (NaPAA) and poly(sodium styrenesulfonate) (NaPSS) with water over a broad range of concentrations was followed by isothermal titration calorimetry (ITC) and compared to the corresponding low molecular weight salts, sodium acetate and sodium sulfate. Astonishingly, the backbone of NaPSS, known to be more hydrophobic, remains unseen in the dilution enthalpy, and NaPAA and NaPSS show very similar and close to ideal dilution curves. The NaPSS dilution is even more exothermic than Na_2SO_4. This is related to the specific structure of water screening the hydrophobic polystyrene backbone. Counterintuitively, binding of Ca^{2+} ions to PAA, a spontaneous process, shows to be highly endothermic; i.e., the binding is solely driven by entropy. This suggests that not Coulomb interactions, but liberation of water molecules from the hydration shells of the components is the driving energy source for the binding of multivalent ions onto polyelectrolytes. Analysis of binding titrations of Ca^{2+} to three different industrial scale inhibitors (poly(acrylic acid), poly(aspartic acid), poly(acrylic-*co*-maleic acid) (Sokolan)) allows to qualify their performance. The experiments underline that the understanding of polyelectrolytes and counterion condensation on the basis of Coulomb descriptions, i.e., ions as point charges and water as a homogeneous dielectric media, is at least misleading, as it disregards the predominant thermodynamic effects, the chemical specificity of the components in response to the structure of water.

Introduction

Polyelectrolytes receive an increasing attention with regard both to technological applications and to biological studies. Despite their importance, the understanding of their behavior is still limited (for a recommendable and critical review, see ref 1). For an experimentalist, it is particularly disappointing that the rich hydration chemistry and the structure of water are often not considered. Hydrogen bonding influences the dielectric properties of solutions while ion hydration ascribes distinct specificity to ions. Despite these well-known facts, water is mostly still treated as an unstructured medium with a dielectric constant independent of distance and time scale, while the diverse ions are described as Coulombic point charges. Thus, very often the richness and complexity of observed system responses are lost.

Let us consider two vivid examples illustrating the significance of this problem: the Hofmeister series and the variation of the dielectric constant of water solutions. First, the observation that different salts influence the solubility of proteins in a different fashion, the Hofmeister effect, is still unexplained. It was originally reported by Lewith in 1888.[2] The various ions in the series have been defined as chaotropic ("water structure breaker") or cosmotropic ("water structure maker"). However, it is not yet clearly understood if the effect of the ions can be ascribed to their direct interaction with the proteins or to their influence on water structure. For a review on ion specific effects in water and the Hofmeister series, two articles reviewing more than 1200 original papers on peculiar water ion effects are recommended, including folding of proteins, gelatin melting, macromolecular conformation, and phase transitions of lipid and surfactant structures.[3,4]

Second, related to our own work on synthetic polyelectrolytes, dielectric measurements on dilute poly(vinylpyridinium bromide) solutions revealed that their dielectric constant, ϵ, at room temperature is about 55 (instead of 81), increasing local field strengths by about a factor of 2.[5] Obviously, addition of the polyelectrolyte has influence on the structure of water equivalent to increasing the temperature to the boiling point. This is nicely supported by numerical Poisson−Boltzmann methods where ϵ values of 30 in the proximity of protein molecules and DNA strands (slowly decreasing to the bulk value with increasing distance) had to be assumed to adjust the numerical description to the experimentally determined ion distributions.[6] Strong electrostatic potential gradients due to the lateral modulation of ϵ close to surfaces would indeed represent an exciting new mechanism for electrostatic guiding of ions and for self-assembly processes.

The objective of this work is consequently rather simple: it is intended to investigate the interaction of two model polyelectrolytes (NaPAA as a "weak" and NaPSS as a "strong" polyelectrolyte) with water. We study their heat of dilution using high-precision calorimetric measurements. The tool is isothermal titration calorimetry (ITC), which has become very popular for studying heats of reactions.[7−13]

In addition, we examine the calorimetric effects of the specific counterion binding of Ca^{2+} ions onto NaPAA and two technical scale inhibitors, poly(sodium aspartate) and Sokolan, to learn about the competition of electrostatic and hydration forces in these technologically relevant cases.

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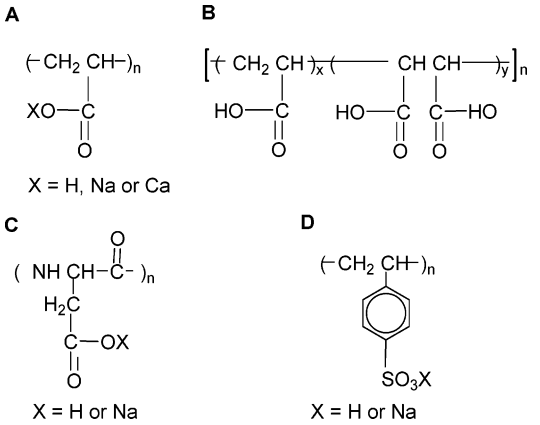
Chart 1. Chemical Structure of the Used Polymers[a]



[a] A: PAA, NaPAA1, NaPAA2, CaPAA, NaPAA3. B: Sokolan; $x/y = 1$. C: PAsp, NaPAsp. D: PSS, NaPSS.

Experimental Section

Materials. Sodium sulfate, Na_2SO_4, and sodium acetate, CH_3COONa (NaAc), were purchased from Aldrich (Germany). Three poly(sodium acrylates) (NaPAA) of different degrees of polymerization (DP_n) were used. NaPAA1 and NaPAA2 used for the dilution measurements were purchased from Fluka (Germany). Their weight-averaged molecular weights, M_w, are 2.1×10^3 g/mol for NaPAA1 and 5.1×10^3 g/mol for NaPAA2 with a DP_w of about 22 and 53, respectively. NaPAA3 used for the titration experiments was prepared from PAA (Aldrich, Germany, $M_w \approx 100 \times 10^3$ g/mol, $DP_w \approx 1040$) by adjusting the pH to 7 using NaOH (Merck, Germany). The poly(acrylic-*co*-maleic acid) (Sokolan) and poly(aspartic acid) (PAsp) with $M_w \approx 70 \times 10^3$ g/mol and $M_w \approx 20 \times 10^3$ g/mol, respectively, were purchased from BASF (Germany). The solutions of Sokolan and PAsp used for the titration experiments were adjusted to pH 7 using NaOH. PAsp at pH 7 will be further denoted as NaPAsp. $CaCl_2$ was purchased from Merck (Germany). NaPSS was a commercial standard supplied by Polymer Standard Service (Mainz, Germany) with $M_w \approx 8 \times 10^3$ g/mol, corresponding to a DP_n of about 40. A ^1H NMR spectrum indicated a monomer purity of about 95%.

Because poly(calcium acrylate) is a byproduct of the process of calcium binding, we studied the dilution of the polymer in water. However, poly(calcium acrylate) is insoluble in water. Therefore, we analyzed the heat of dilution of a modified NaPAA2 salt where the sodium was partially exchanged with Ca^{2+} ions (this product will be further denoted as CaPAA). To determine the critical exchange limit at which CaPAA gives a homogeneous solution, we prepared solutions of different molar concentration ratios of Ca^{2+} to NaPAA2. For a fixed monomer concentration the molar ratio was increased from 0.20 in steps of 0.02 up to 0.30. The solutions were prepared by mixing of 0.4 M NaPAA2 solution with a certain amount of CaO (purchased from Aldrich), giving the desired concentration ratio. The solutions were shaken to obtain good mixing of the reactants and stirred for 3 days to ensure complete equilibration of the reaction. The maximum ratio (or the critical exchange limit) at which CaO fully dissolved in the NaPAA2 solution was found to be about 20 mol %, corresponding to a neutralization of 40% of all acrylate sites. (Note that the critical exchange limit depends on both the polymer concentration and the pH of the system.)

All solutions were prepared using deionized water from an Elix Milli-Q Millipore system with a TOC of less than 15 ppb and a resistivity of 18 MΩ cm. Chart 1 displays the chemical structure of the different polymers used here. The molecular weights, the degree of polymerization, and the concentration ranges of the solutions used in the various experiments are given in Table 1.

Methods. We have used three different techniques to investigate the interaction of several polyelectrolytes with water and to study the counterion binding of Ca^{2+}. The microcalorimetry measurements with the ITC were used to determine the heat of dilution of the polymers and the enthalpy associated with the calcium binding to the polymers. With the Ca^{2+} ion selective electrode the amount of free and bound to the polymer calcium was measured. To prevent precipitation in the ITC cell, turbidity measurements were used to determine the critical molar ratio of Ca^{2+} to polymer at which precipitation occurs.

Table 1. Weight-Averaged Molecular Weight, Degree of Polymerization, and Concentration Range of the Polymer and Salt Solutions Used in This Work[a]

polymer/salt	degree of polymerization, DP_w	mol wt, $\bar{M}_w$, g/mol	concn range, N
NaAc		82	0.03−1
Na_2SO_4		142	0.12−1
NaPAA1	22	2.1×10^3	0.03−0.88
NaPAA2	53	5.1×10^3	0.03−1
NaPAA3	1040	100×10^3	0.08−0.4
NaPSS	40	8×10^3	0.03−0.5
CaPAA	55	5×10^3	0.06−0.64
Sokolan	740	70×10^3	0.105
PAsp	145	20×10^3	0.037

[a] The polymers are technical samples and possess polydispersities between 2 and 4.

a. Microcalorimetry. Isothermal titration calorimetry (ITC) is a technique that measures the released or absorbed heat upon mixing of two solutions. The instrument used in this work is a VP-ITC microcalorimeter from MicroCal (Northhampton, MA). Two identical spherical cells, a reference cell and a sample cell, both with a volume of 1.442 mL, are enclosed in an adiabatic jacket. The working cell is filled with the sample solution, and the reference cell is filled with the solvent or buffer used to prepare the sample solution. The titrant is injected stepwise into the working cell with a syringe of total volume of 288 μL. The sample cell is constantly stirred. For the experiments reported here the stirring rate was 310 rpm. The measurement is performed at constant temperature. The data in this work were acquired at 25 °C. Small aliquots of titrant (typically 10 μL) are successively injected into the solution of the working cell. The first injection is usually set to a volume of 2 μL. (Because of possible dilution during the equilibration time preceding the measurement, the first injection was ignored in the analysis of the data.) Each injection produces a characteristic peak in the heat flow (J/s) due to released or absorbed heat (see Figure 1A). In the analysis, a baseline is subsequently subtracted from the data. It corresponds to the signal between consecutive injections when no change in the heat flow is detected. An exothermic reaction yields a negative peak signal because the released heat in the sample cell is no longer required from the resistive heater of the instrument. Similarly, endothermic reactions cause a positive peak. Integrating each of the peaks provides the heat per injection. The data analysis was performed using the Origin software provided by MicroCal.

b. Determination of Ca^{2+} Binding to Polymers Using Ca^{2+} Ion Selective Electrode. Binding isotherms where measured by using a Ca^{2+} ion selective electrode from Mettler Toledo, Switzerland. The electrode measures the potential difference between a solution and a reference electrode which is proportional to the logarithm of the Ca^{2+} concentration in the solution. The precision of the instrument is better than ±4% of the measured Ca^{2+} concentration. The calibration of the electrode was carried out with $CaCl_2$ solutions with concentrations in the range 1×10^{-6}−5×10^{-2} M. The calibration curve of measured voltage vs $CaCl_2$ concentration was consequently used to determine the concentration of free calcium ions in the polymer solutions.

c. Turbidity Measurements. Above certain concentration ratios $CaCl_2$ causes precipitation of the polymers. To determine the corresponding precipitation limits of the different polymers, turbidity measurements where performed with a UV−vis spectrophotometer Helios Gamma from Thermo Spectronic, Great Britain. The instrument measures the absorbance of a

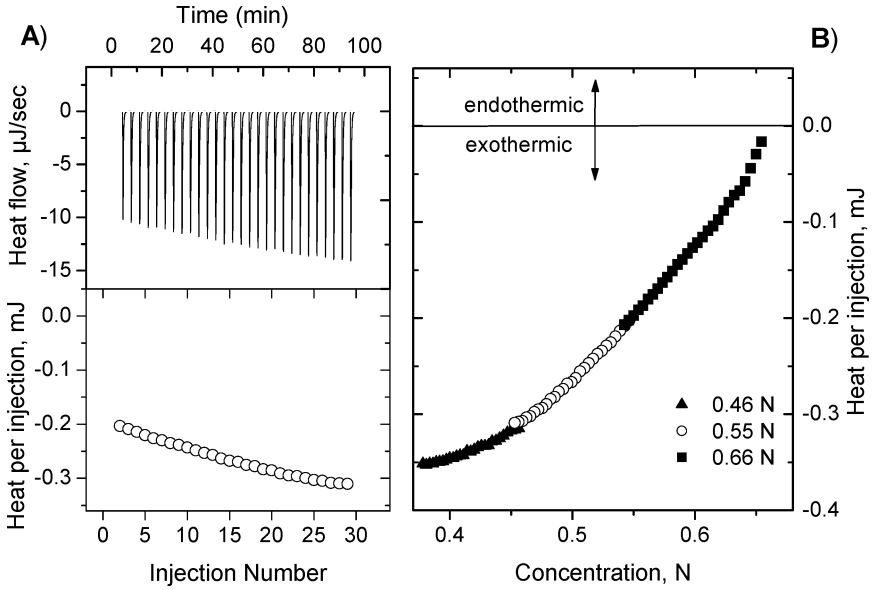


Figure 1. Dilution measurements. (A) Raw ITC data from injecting water (10 μL aliquots) into 0.55 N NaPAA1 (upper panel) with subtracted baseline. Heat per injection (lower panel) obtained from integrating the heat flow over time. (B) Three separate dilution measurements at different initial concentration of NaPAA1 in the working cell. The open circles correspond to the data in (A).

sample as a function of the wavelength with respect to a reference.

The pH of PAA, Sokolan, and PAsp solutions of concentrations 0.08, 0.105, and 0.037 N, respectively, was adjusted to 7 using NaOH. Small aliquots of a 0.2 N $CaCl_2$ solution were injected into the polymer solutions until the measured absorbance increased significantly at the onset of precipitation. To avoid contributions to the signal from formation of precipitate, all the titration measurements were performed at concentration ratios below the measured precipitation limits.

Results and Discussion

Three different types of ITC experiments were performed. (i) In the *dilution experiments* water was injected into a solution of salt or polymer. (ii) In the *binding titrations* we injected a solution of $CaCl_2$ into polymer solutions. (iii) To eliminate possible contribution to the signal from diluting the calcium salt, we also measured the *dilution of $CaCl_2$ into water* by injecting a solution of the salt into water. In the analysis we subtracted this signal from the binding titration curves.

Figure 1 represents an example of a dilution measurement. Figure 1A shows the raw data of one dilution experiment of NaPAA1 with initial concentration of 0.55 N. The upper panel shows the heat flow (μJ s^{-1}) caused by the consecutive injection of 10 μL aliquots of water into the solution of NaPAA1. Integrating the heat flow peaks yields the heat of each injection (lower panel). Because of the small volume of the syringe (288 μL) compared to the volume of the working cell (1442 μL), only a narrow interval of concentrations can be covered by one titration measurement. To span a larger concentration range, we performed a series of dilution measurements with different initial concentrations of the polymer in the working cell. Of course, for covering a larger concentration interval we could have performed the inversed measurement, i.e., injecting the polymer solution in water. However, plotting the resulting molar heat of several measurements on a master curve would not be possible due to inadequacy of the starting and final solution volumes of two consecutive measurements. Figure 1B shows three separate dilution experiments of NaPAA1 solutions of 0.46, 0.55, and 0.66 N. The upward and downward arrows indicate the direction of the peaks for an endothermic and an exothermic signal, respectively. Note that in the course of a dilution measurement the polymer concentration in the working cell decreases; therefore, the slope of the heat dependence in Figure 1B is inversed compared to the one in the lower panel of Figure 1A. For lucidity, in the following figures of dilution series we will indicate only 3−6 evenly spaced data points from each separate titration measurement.

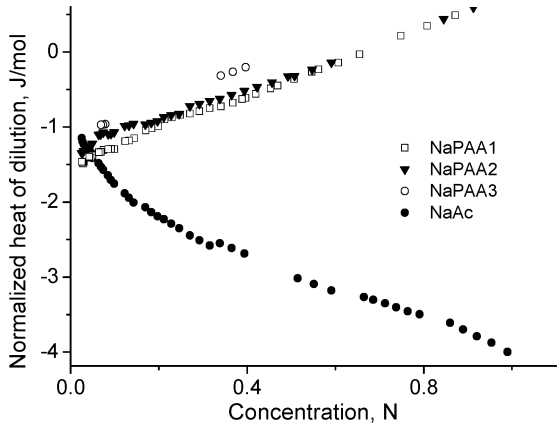


Figure 2. Experimental heats of dilution for NaAc, NaPAA1, NaPAA2, and NaPAA3. The heat is normalized by the moles Na^+ present in the system.

In attempt to characterize the role of the backbone of the polymer and its hydrophobicity on its interaction with water, we performed dilution measurements with the polymers and with their corresponding low molecular weight salts. NaPAA1, NaPAA2, NaPAA3, and NaAc were titrated with water at different starting concentrations of the chemicals in the cell. Several sets of ITC experiments are presented in Figure 2. The released heat is normalized by the moles Na^+ in each system.

The dilution of NaAc is exothermic over the whole examined range of concentrations. The magnitude of the signal increases with concentration. The released heat

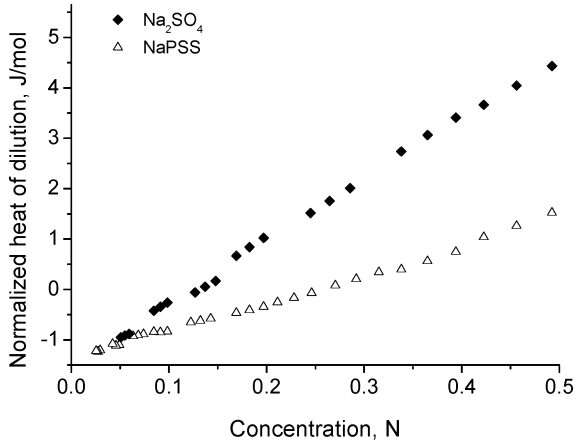


Figure 3. Experimental heats of dilution for NaPSS and Na_2SO_4. The heat is normalized by the moles of Na^+ present in the system.

cannot be explained with change in the pH of the system[14] but rather suggests a local exothermic binding and rearrangement of water molecules around the acetate anion. NaPAA, on the contrary, is only weakly exothermic and shows nearly ideal behavior over the whole examined concentration range up to 1 N solutions. Within the whole concentration range the heat of dilution of the three NaPAA samples with different molecular weights is within 2 J/mol, indicating that the heat of dilution depends only weakly on molecular weight, at least in the examined range. It is worth mentioning that NaPAA shows no solution limit or mixing gap with water; i.e., the free energy of mixing is negative in the whole composition range. It is interesting to note that in the low concentration limit both the low molecular salt and the polymers yield similar heats of dilution. One may speculate that in this regime the two compounds are indistinguishable from the point of view of the water molecules; i.e., the presence of the hydrophobic backbone of the polymer has no influence in this range and is not seen by the majority of rather distant water molecules. However, this proximity in the dilution heats could also be due to compensating contributions.

In a similar way we compare the dilution of NaPSS and its low molecular equivalent Na_2SO_4 (see Figure 3). At small concentrations of Na_2SO_4, the signal is slightly exothermic but turns strongly endothermic at higher concentrations. This is consistent with the thermal effects occurring throughout the crystallization of Na_2SO_4 from water solutions. The enthalpy turn from exo- to endothermic behavior corresponds to a favorable effect of the SO_4^{2-} on the long-range structure of water, whereas the short-range contributions (observed predominantly at higher concentrations) are strictly heat-consuming.

The curve of NaPSS starts exothermic but turns only to slight endothermic behavior and is overall closer to the ideal athermal behavior. This, at first glance, is somewhat counterintuitive. NaPSS is definitely more hydrophobic than Na_2SO_4 but gives a less endothermic signal. This implies that appropriate fit of the molecules to the water structure is more important than the usually overestimated backbone "hydrophobicity". The data are also in agreement with dilution data of sodium dodecyl sulfate in water at 25 °C[15] where close to athermal dilution was demonstrated as well and is interpreted to be coherent with the general knowledge coined as "the hydrophobic effect".[16,17]

Comparison of the data of NaPAA and NaPSS (Figures 2 and 3) shows that the dilution of PSS is slightly more endothermic. However, both polymers show similar, nearly ideal behavior, making both systems the ideal model systems they are known for. It is worth noting that the described effects are in this case of the order of 0.001 kJ/mol, i.e., indeed very tiny, and only revealed by the very high sensitivity of the setup. Again, the similarity is somewhat surprising as both polyelectrolytes differ significantly in their chemical composition and in the polarizability of their charges.

Because we are interested in the thermodynamics of the specific interaction of those polyelectrolytes with Ca^{2+}, we also have to analyze the heat of dilution of CaPAA. This was studied only in the concentration range of 0.06 N up to 0.64 N, which is the limit set by the solubility of the polymer. It is very interesting to note that, just like NaPAA, CaPAA also shows practically athermal behavior. Dilution measurements with CaPAA (data not shown) revealed that the heat of dilution in the examined concentration range is small and almost constant, equal to ~ -0.6 J/mol. This value is close to the signal obtained from diluting NaPAA, which suggests that when part of the Na^+ counterions are replaced by Ca^{2+}, the dilution of the polymer is effectively unchanged. This is consistent with the general observation that water is more influenced by the anions than by the cations,[3] but it does not mean that the close-distance hydration of both species is similar.

As the heats of dilution for both NaPAA and CaPAA are close to zero, the binding heat of Ca^{2+}onto NaPAA can simply be determined by titrating a dilute $CaCl_2$ solution into NaPAA. Any measured heat can then be ascribed to the sum of the heat of dilution of $CaCl_2$ and the desired binding of Ca^{2+} onto the polymer. These experiments essentially follow earlier experiments on Ca^{2+} binding onto NaPAA.[18,19]

We use NaPAA3 for these experiments because it has the highest molecular weight among the three samples which allowed us to measure the amount of bound calcium with the Ca^{2+} electrode. In contrast, NaPAA1 and NaPAA2 are not usable for the Ca^{2+} electrode due to their small size, generating unexpected secondary electrode signals which can be stronger than the signal generated by Ca^{2+} (see Figure 5). Furthermore, since the molecular weight of NaPAA3 is similar to that of Sokolan, we are able to compare those two polymers free of molecular weight effects.

To prevent precipitation in the sample cell, the initial concentration of the polymer solution was chosen so that the binding of Ca^{2+} to the carboxyl groups of the polymer does not lead to a complete neutralization and resulting precipitation. The critical ratio, *r*, which is defined as the minimum molar ratio of added Ca^{2+} to carboxylate binding sites at which precipitation occurs, was determined by following the turbidity of the solution. *r* was measured to be 0.31 for the titration of a 0.2 N $CaCl_2$ solution into a 0.08 N NaPAA3 solution, and the initial NaPAA3 concentration was consequently set to 0.08 N.

The measured molar enthalpy change following the stepwise addition of 8 μL aliquots of a 0.2 N $CaCl_2$ solution into an 0.08 N solution of NaPAA3 is shown in Figure 4. To determine the enthalpy associated with the counterion binding, the dilution enthalpy of a 0.2 N $CaCl_2$ solution into pure deionized water was measured

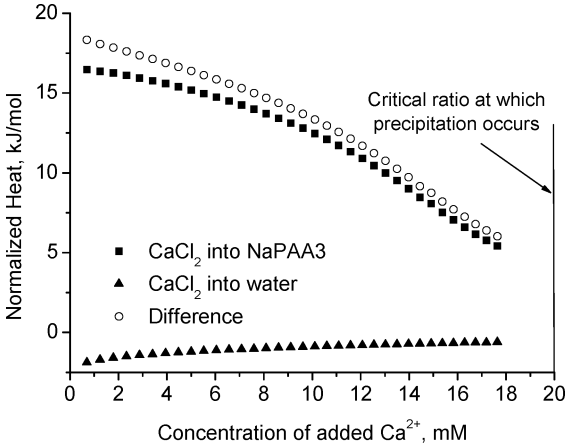


Figure 4. Titration of 0.08 N NaPAA3 solution at pH 7 and water with 0.2 N $CaCl_2$. The difference of the two signals is the heat associated with the interaction of Ca^{2+} with the polymer chain (the heat of dilution of NaPAA3 is negligible). The heat is normalized by the moles of injected Ca^{2+}.

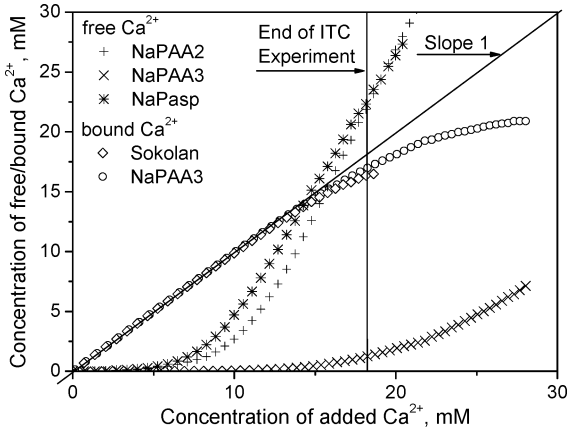


Figure 5. Calcium electrode isotherms. 0.2 N solution of $CaCl_2$ is titrated into 0.06 N NaPAA2, 0.08 N NaPAA3, 0.037 N NaPAsp, and 0.105 N Sokolan (pH 7). Free (measured) and bound calcium (see legend) are plotted as a function of added Ca^{2+}. The line indicated with "slope 1" represents the case of 100% binding. The unrealistic excess of the apparent concentration of free calcium for the measurements with NaPAA2 and NaPAsp is presumably due to additional signal of the polymers passing through the calcium electrode glass membrane (see text for details).

and subtracted from the total enthalpy. The measurements illustrate that the dilution enthalpy of the $CaCl_2$ solution is negative, but also much smaller in magnitude than the complexation enthalpy. The heat of dilution of the NaPAA3 solution in this concentration region is almost constant (~ -0.1 mJ) and can be neglected compared to the heat of the titration of $CaCl_2$ into NaPAA3, which varies from 5.2 to 17 mJ.

The interaction of Ca^{2+} ions with the NaPAA3 solution is contrary to expectations based on Coulombic pair potentials, a strongly endothermic process, as previously already observed by Pochard et al.[18] As there is no doubt that Ca^{2+} binds deliberately onto NaPAA and that the free energy of binding is negative, the driving force of the reaction is an increase in the entropy, which is believed to be primarily due to the liberation of water molecules. The total amount of released water molecules is given by the dehydration of Ca^{2+} and COO^- minus the rehydration of Na^+.

The decrease of the reaction enthalpy with increasing concentration of added calcium could be caused by two effects: The enthalpy drops either because the amount of Ca^{2+} bound to the polymer decreases or because the heat per bound Ca^{2+} falls. Both effects could also occur simultaneously. The answer to this question was studied by using a calcium electrode to determine the binding isotherm.

In Figure 5, the concentration of free and bound Ca^{2+} for different polymer solutions (0.06 N NaPAA2, 0.08 N NaPAA3, 0.037 N NaPAsp, and 0.105 N Sokolan (pH 7)) following the stepwise addition of an 0.2 N $CaCl_2$ solution is plotted as a function of the concentration of added Ca^{2+}. The amount of bound Ca^{2+} was determined by measuring the concentration of free calcium in the polymer solution after each injection with the Ca^{2+} electrode and subtracting this value from the concentration of added calcium. The line indicated with "slope 1" represents the case of 100% binding of the added Ca^{2+}. In the case of NaPAA2 and NaPAsp, the apparent concentration of free Ca^{2+} "exceeds" the concentration of added Ca^{2+} above $\sim$15 mM. This unrealistic artifact can be explained by a continuous decrease in the radius of gyration of the polymers upon the formation of Ca−PAsp and Ca−PAA2. The latter eventually become small enough to pass through the ion selective porous membrane and contribute to the measured electrochemical potential difference. We just present this very special artifact to alert other groups to take care that low molecular weight fractions in the polymers may seriously counterfeit the outcome of binding measurements. Hence, the binding isotherm could not be measured for NaPAsp, NaPAA2, and NaPAA1.

The binding isotherm of NaPAA3 presented in Figure 5 shows that almost all of the added Ca^{2+} ions bind to the polymer while only a few remain free in the bulk solution. Combining these results with the microcalorimetric experiments, we find that the enthalpy of binding of Ca^{2+} to PAA is continuously linearly decreasing with the Ca loading (up to 40%). This is contrary to other observations reported in the literature[18] (this study was performed for lower calcium concentrations).

Just before the precipitation limit ($r = 0.31$), the amount of free calcium increases. Fitting the whole curve with a bimolecular binding equilibrium reveals an equilibrium constant of ca. 150 000, with deviations from the ideal binding when approaching the precipitation limit. Above this limit, CaPAA precipitates and forms a hydrophobic, not water-swollen, phase. The decreasing ability of the polymer to bind calcium is therefore presumably due to the approaching phase transition and the coupled conformational changes and progressing collapse of the CaPAA, burying the remaining binding sites for Ca^{2+} in the interior of the hydrophobic coils. The calcium-induced shrinking of polyacrylate chains and the coupled transformation of a Gaussian coil into some globular structure with increasing Ca loading was nicely quantified by Huber et al.,[20−22] supporting this interpretation.

On the basis of the equilibrium constant (and the underlying binding model), a free energy of binding of $\Delta G_{Ca-bind} = -29.6$ kJ/mol is calculated. Taking the binding enthalpy $\Delta H_{Ca-bind} = 17$ kJ/mol (for the first Ca^{2+} to bind), we obtain a binding entropy of $\Delta S_{Ca-bind} = 19R$, R being the gas constant. This corresponds to the liberation of ca. 10 water molecules and 2 sodium ions per bound Ca^{2+}.

The fact that the endothermic character of binding enthalpy is decreasing while the binding on the contrary

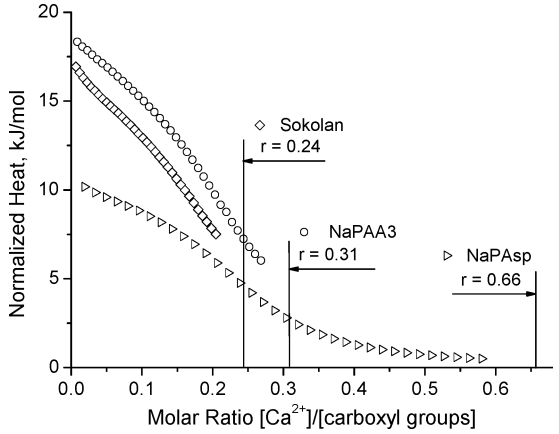


Figure 6. Binding titration of NaPAA3, Sokolan, and NaPAsp. The heat is normalized by moles Ca^{2+} injected into the system. Straight lines indicate the critical ratio *r*, at which precipitation occurs.

is, at most, slightly weakened indicates that also the binding entropy changes with concentration in an appropriate fashion. This effect is well-known for many thermodynamic phenomena in water and was coined as "enthalpy−entropy compensation".[16,17] It strongly supports our view that the endothermic character of binding is coming from the water structure and not from the ion binding process itself. Similar measurements were also performed at elevated temperatures (45 °C) but did reveal a very similar behavior. This is why we omitted the presentation of those data in the present context.

It is also interesting to compare the calorimetric binding curve of the NaPAA3 with two other technical scale inhibitors, NaPAsp and Sokolan, as presented in Figure 6. Similarly to NaPAA3, the heats of dilution of these polymers are negligible. The initial concentrations of the polymer solutions were again chosen so that the complexation of Ca^{2+} with the carboxyl groups of the polymers does not lead to precipitation in the working cell. *r* was measured to be 0.24 for Sokolan and 0.66 for NaPAsp. Correspondingly, the working concentrations of the polymers were selected to be 0.105 and 0.037 N, respectively.

We observe that the NaPAsp (a natural scale modifier) precipitates at much higher Ca loads. The value of $r = 0.66$ is beyond stoichiometric equivalence (considering that each Ca^{2+} binds two carboxylic groups) and implies lower ion sensitive solubility. Obviously, the nature of Ca^{2+} binding to NaPAsp is more elaborated involving collapse and stability. For this polymer, the binding is also less endothermic than for the other two examples, but it saturates at about the same levels of binding. For Sokolan, the Ca^{2+} electrode was used to determine the amount of bound calcium in the course of the titration experiment, revealing similar curves as for PAA3 (see Figure 5). As mentioned above, the Ca^{2+} electrode cannot be used for NaPAsp due to its small size.

In the context of the present experiments, we can only speculate about the nature of the unexpected endothermic binding character and its dependence on the chemical constitution of the polymer backbone. Obviously, both PAA and Sokolan fit well to the water structure, whereas the complexes with Ca^{2+} do not and require major, enthalpically unfavorable rearrangements of the water, which leads to dehydration and finally precipitation of a hydrophobic complex. This is much less the case for polyaspartate where the amide bonds in the backbone ensure higher hydrophilicity which keeps the Ca complex in solution. The lowered heat flow value suggests that the amide structure must also influence the hydrophobicity of the neighboring carboxylic acid sites, potentially via some type of amphiphilicity allowing lower polarity gradients or "molecular surface tensions". We have to conclude that nature has developed more elaborated principles for Ca^{2+} binding and stabilization than technology.

Discussion and Conclusion

In a first set of experiments, we have determined the heat of dilution of two standard polyelectrolytes poly(sodium acrylate) and poly(sodium styrenesulfonate). Unexpectedly, but in good agreement with the so-called hydrophobic effect, the higher hydrophobicity of the poly(styrenesulfonate) backbone remained unseen up to rather high polymer concentrations. As the dilution of PSS and PAA are practically athermal, this justifies their use as the model polyelectrolytes.

Afterward, we characterized the enthalpic effects of counterion exchange of Na^+ with Ca^{2+} for three carboxylate carrying polymers. Contrary to simple expectations, the heat of exchange is strongly endothermic. Because heat can be regarded as liberated potential energy, it becomes obvious that the description of the Ca^{2+} binding to polyelectrolytes by screened Coulomb potentials is simply wrong (as this would always lead to an exothermic process). Instead, binding has to be described as a counterion exchange, which is at best *energetically neutral* with respect to the electrostatic forces involved. The real reason for the stronger binding of multivalent ions onto polyelectrolytes is therefore not the stronger electrostatic force, but it is simply due to entropic effects, which keep the free energy of this process negative (as it occurs spontaneously) but which remain unseen in calorimetric experiments. This is in good agreement with the binding of ions onto other colloidal objects, such as the binding of earth alkaline ions and La^{3+} onto lipid vesicles,[23,24] or the binding of earth alkaline cations onto low molecular weight compounds. Therefore, the observed effects seem to be the rule rather than the exception.

The total amount of released water molecules is given by the dehydration of Ca^{2+} and COO^- minus the partial rehydration of Na^+. As the final product, Ca−PAA, precipitates from water as a hydrophobic liquid (i.e., the hydration is very low), this process easily generates the minimal number of six water molecules required to counterbalance the endothermic binding heat. A quantitative estimate on the base of the binding measurements with the Ca^{2+}-sensitive electrode revealed the equivalent of 10 ± 2 water molecules, leaving enough gain of free energy for strong and spontaneous binding. As the heat of dilution of all involved species is about athermal, we can exclude a relevance of long-range water structure effects onto the binding process.

This scenario also implies seriously altered target structures for the development of optimized scale inhibitors: it is in the very end not the charge or charge density which is decisive, but the induction of a transition from a very hydrated to a rather unhydrated polymer state by ion binding. It is the very special charm of this model that one can now easily prescibe additional features like ion selectivity of binding, which is found in a number of cases, but cannot be explained by electrostatic models.

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References and Notes

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