Isothermal Titrination 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$_2$SO$_4$. 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, $\varepsilon$, 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 $\varepsilon$ 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 $\varepsilon$ 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.
A1H NMR spectrum

Experimental Section

Materials. Sodium sulfate, Na₂SO₄, and sodium acetate, CH₃COONa (NaAc), were purchased from Aldrich (Germany). Three polyelectrolytes (acrylates) (NaPAsp, NaPAA1, NaPAA2) used for the dilution measurements were purchased from Fluka (Germany), and for the titration experiments was prepared from PAA (Aldrich, USA). NaPAA3 used for the titration experiments were prepared from PAA (Aldrich, Germany, Mₘ ≈ 100 × 10³ g/mol, DPₘ ≈ 1040) by adjusting the pH to 7 using NaOH (Merck, Germany). The poly(acrylic-co-maleic) acid (Sokolan) and poly(aspartic acid) (PAsp) with Mₘ ≈ 70 × 10³ g/mol and Mₘ ≈ 20 × 10³ 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. CaCl₂ was purchased from Merck (Germany). NaPSS was a commercial standard supplied by Polymer Standard Service (Mainz, Germany) with Mₘ ≈ 8 × 10³ g/mol, corresponding to a DPₘ 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 Ca²⁺ 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 Ca²⁺ to polymer and measured the pH of the system.

Methods. We have used three different techniques to investigate the interaction of several polyelectrolytes with water and to study the counterion binding of Ca²⁺. 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 Ca²⁺ 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 Ca²⁺ to polymer at which precipitation of different polymers occurs.

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 (Northampton, 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 (q/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 Ca²⁺ Binding to Polymers Using Ca²⁺ Ion Selective Electrode. Binding isotherms where measured by using a Ca²⁺ 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 Ca²⁺ concentration in the solution. The precision of the instrument is better than ±4% of the measured Ca²⁺ concentration. The calibration of the electrode was carried out with CaCl₂ solutions with concentrations in the range 1 × 10⁻⁶ to 5 × 10⁻² M. The calibration curve of measured voltage vs CaCl₂ concentration was subsequently used to determine the concentration of free calcium ions in the polymer solutions.

c. Turbidity Measurements. Above a certain concentration ratio of CaCl₂ causes precipitation of the polymers. To determine the corresponding precipitation limits of the different polymers, turbidity measurements were performed with a UV–vis spectrophotometer Helios Gamma from Thermo Spectronic, Great Britain. The instrument measures the absorbance of a
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 CaCl₂ 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 CaCl₂ into polymer solutions. (iii) To eliminate possible contribution to the signal from diluting the calcium salt, we also measured the dilution of CaCl₂ 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 inverted 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.

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⁺ present in the system.

Figure 2. Experimental heats of dilution for NaAc, NaPAA1, NaPAA2, and NaPAA3. The heat is normalized by the moles Na⁺ present in the system.
but rather suggests a local exothermic binding cannot be explained with change in the pH of the
system but rather suggests a local exothermic binding
and rearrangement of water molecules around the
acetate anion. NaPAA, on the contrary, is only weakly
and its low molecular equivalent Na 2SO4 (see Figure
3). Experimental heats of dilution for NaPSS and Na2-
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 Na2SO4 (see Figure
3). At small concentrations of Na2SO4, the signal is
slightly exothermic but turns strongly endothermic at
higher concentrations. This is consistent with the
thermal effects occurring throughout the crystallization
of Na2SO4 from water solutions. The enthalpy turn from
exo- to endothermic behavior corresponds to a favorable
effect of the SO42- on the long-range structure of water,
whereas the short-range contributions (observed pre-
dominantly 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 Na2SO4 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 °C15 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 (Fig-
ures 2 and 3) shows that the dilution of PSS is slightly
more endothermic. However, both polymers show simi-
lar, 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 polyelec-
trolytes 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
Ca2+, 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 practi-
cally 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 Ca2+, 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 Ca2+ onto NaPAA
can simply be determined by titrating a dilute CaCl2
solution into NaPAA. Any measured heat can then be
ascribed to the sum of the heat of dilution of CaCl2 and
the desired binding of Ca2+ onto the polymer. These
experiments essentially follow earlier experiments on
Ca2+ 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 Ca2+ electrode. In contrast, NaPAA1
and NaPAA2 are not usable for the Ca2+ electrode due
to their small size, generating unexpected secondary
electrode signals which can be stronger than the signal
generated by Ca2+ (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 Ca2+ 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 Ca2+ to carboxylate
binding sites at which precipitation occurs, was deter-
mined by following the turbidity of the solution. r was
measured to be 0.31 for the titration of a 0.2 N CaCl2
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 CaCl2
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
CaCl2 solution into pure deionized water was measured

![Figure 3](image-url) Experimental heats of dilution for NaPSS and Na2-
SO4. The heat is normalized by the moles of Na+ present in
the system.
compared to the heat of the titration of CaCl$_2$ into 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 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 ~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$^{2+}$-PAA and Ca$^{2+}$-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 (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 $\Delta G_{Ca}^{\text{bind}} = -29.6$ kJ/mol is calculated. Taking the binding enthalpy $\Delta H_{Ca}^{\text{bind}} = 17$ kJ/mol (for the first Ca$^{2+}$ to bind), we obtain a binding entropy of $\Delta S_{Ca}^{\text{bind}} = 19$R, 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 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.

![Figure 4. Titrations 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$^{2+}$.](image)

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![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 of the added Ca$^{2+}$.](image)

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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. 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 dehydrogenation 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

[Diagram showing normalized heat of solution versus concentration of added Ca$^{2+}$ with data points and lines indicating different solutions and properties.]

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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, 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 basis 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 prescribe 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

(14) In the measuring concentration interval the pOH of the NaAc solution varies from 4.6 at 1 N to 5.4 at 0.03 N. The released heat associated with this change in the pOH is negligible compared to the measured signal. It can be calculated from the dissociation enthalpy of water, 57.6 kJ/mol. For the discussed concentration interval, we obtain value of the order of ~2 mJ, compared to the measured 0.9 kJ.

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