Binding of Ion Pairs onto Polymer Gels via Dehydration Entropy: A New Mechanism for Ion Exchange

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Introduction

Desalination, the removal of ions from water, is usually performed by distillation or with desalination membranes.[1,2] For smaller quantities, consecutive application of polymeric cationic and anionic exchange resins is the typical solution.[3] All of these techniques however are fraught with different problems, and new effective options for the removal of ions from aqueous media are still highly relevant. Here we present a simple technique where polymer gels near to their critical solution temperature are used as "ion sponges". Both the anion and cation bind to the polymer gel ("ion pair binding"), driven by dehydration entropy.

In previous experiments we analyzed the ion binding of Ca^{2+} to negatively charged polymers by a combination of isothermal titration calorimetry (ITC) and ion selective electrodes (ISE). It was shown that this binding does not occur, as usually believed, by charge interactions, but it is essentially due to the entropy gain provided by a favorable change of the hydration shells of both polymer and ions.[4] As a general consequence, it was evidenced that ion binding onto polymers and colloidal surfaces does not rely on the presence of charges but should take place to large extents even onto neutral polymers with weakly bound hydration shells or water molecules.

Polymer gels which are able to undergo changes in hydration by changing temperature are ideal candidates to test this hypothesis and are known for more than 40 years. (For a review, see ref 5, with more than 300 references). These "intelligent gels" are used to generate motility, which was pioneered by Tanaka,[6,7] and are discussed as components of artificial soft machines (e.g, ref 8). In the present context, we are however only interested in the observation that the temperature of gel collapse also depends on salinity.[9] In addition, this shift is sensitive to the type of salt and follows for the involved anions the Hofmeister series.[10−12] This already indicates specific thermodynamic interactions between the salt and the electrically neutral gel.

Curiously, in all these examinations of critical gels it was not analyzed if the interaction of polymer with water and water with salt also leads to a mutual attraction of polymer and salt; i.e., it was always assumed that the ion concentration within the gels and outside the gels is the same. Considering the above-mentioned results on ion binding of polymers, we expect the opposite, as the ease to remove water from those structure supports entropy driven interactions of polymer and can lead to simultaneous binding of large amounts of salt and gel dehydration collapse.

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This is why we analyzed the binding of potassium chloride to microgels made of a standard temperature sensitive polymer, Poly(*N*-isopropylacrylamide) or PNIPAAM.

Experimental Section

Substances. Potassium chloride, KCl, was purchased from Sigma-Aldrich (Germany). The PNIPAAM microgels were made by cross-linking emulsion polymerization of NIPAAM monomer in the presence of methylene-bis-acrylamide (MBA, Sigma-Aldrich) as a cross-linker, potassium peroxodisulfate (KPS, Fluka Chemicals) as an initiator and sodiumdodecyl sulfate (SDS, Fluka Chemicals) as a surfactant. The obtained PNIPAAM particles were purified by precipitation in acetone. Poly(sodium)acrylate, sample code NaPAA3, was provided by Sigma-Aldrich (M_w = 100 000 g/mol, $M_w/M_n \approx 4$).

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 MΩcm.

Synthesis. The PNIPAAM microgels were made by cross-linking emulsion polymerization of NIPAAM monomer in the presence of methylenebis(acrylamide) (MBA, Sigma-Aldrich) as a cross-linker, potassium peroxodisulfate (KPS, Fluka Chemicals) as an initiator and sodiumdodecyl sulfate (SDS, Fluka Chemicals) as a surfactant. Before the synthesis, the NIPAAM was purified by recrystallization from a toluene/hexane mixture (1:3).

Microgel preparation was based on the procedure described by Kratz et al. and Pelton.[13] 6.75 g of NIPAAM (60 mmol), 0.5 g of SDS (1.7 mmol), and 0.1 g of MBA (0.65 mmol) were dissolved in 500 mL of double distilled water, degassed with nitrogen. The synthesis was carried out under nitrogen atmosphere to exclude oxygen. After heating the solution to 70 °C, 0.5 g of KPS (1.8 mmol) was added under rigorous stirring. The reaction mixture became turbid and the reaction proceeded for 4 h at constant temperature. The resulting latexes possess a diameter of ca. 80 nm, corresponding to a microgel weight of 160×10^6 g mol^{-1}.

The obtained PNIPAAM particles were purified by precipitation in acetone to remove the unreacted monomer and other low molecular weight impurities.

The particle sizes at high dilution were measured using a Nicomp particle sizer (model 370, PSS, Santa Barbara, CA) at a fixed scattering angle of 90°. Dynamic light scattering measurements at higher concentrations in near turbid solutions were performed with an ALV−NIBS/high performance particle sizer in backscattering mode at a fixed scattering angle of 173°. The polydispersity of the samples, as expressed with a Gaussian width of the radius, is below 5%, which is rather typical for the chosen pathway of precipitation polymerization.

Temperature-dependent measurement revealed a critical collapse temperature of 32.5 °C and a swelling ratio of Q = 43 at 20 °C, which goes well with the expectations based on a cross-linking density of 1/92 and data from the literature.[14]

Isothermal titration calorimetry was performed with 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 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 is 310 rpm. The measurement is performed at constant temperature, in this work 25 °C. Small aliquots of titrant (typically 10 μL) are successively injected into the solution of the working cell. Each injection produces a characteristic peak in the heat flow (J/s) due to released or absorbed heat. Integrating each of the peaks provides the heat per injection. The data analysis was performed using the Origin software provided By MicroCal.

A potassium ion selective electrode (Mettler Toledo, Switzerland) was used to measure binding isotherms at different temper-

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atures. The electrode measures the potential difference between a solution and a reference electrode which is proportional to the logarithm of the K^+ concentration in the solution. The precision of the instrument is better than ±2% of the measured of K^+ concentration. The calibration of the electrode was carried out with KCl solutions with concentrations in the range 10^{-5} to 5×10^{-3} M.

Ultracentrifugation was used to study the amount of potassium bound on PNIPAAM vs temperature with a preparative ultracentrifuge (Beckman-Coulter, L-70, 90 Ti fixed angle rotor). For the 4 °C samples, the centrifugation lasted 66 h with a speed of 60 000 rpm, whereas, for the 25 °C samples, it lasts 24 h at the same speed. The amount of free potassium in the supernatant was quantified by using potassium ion selective electrode.

After addition of milli-Q water on the centrifugation pellet, the samples were let at 45 °C during 24 h. After a centrifugation at 45 000 rpm, during 20 min, the supernatant was used to determine the released potassium

Results and Discussion

The ion binding was quantified by adding a 0.1 M solution of KCl to a 0.5 wt % microgel solution and determined the excess of bound KCl by a potassium selective electrode. In a parallel experiment, the change of calorimetric heat was followed by ITC. The experiments are performed at 25 °C, slightly below the temperature where the microgel collapses in pure water (32.5 °C).

The amount of bound potassium was determined with a calibration curve that was identical before and after the measurement. Thus, the polymer gel does not interact with the ion selective membrane. A typical result is shown in Figure 1A, where the amount of bound KCl is plotted against the amount of added KCl. The line indicated with "Slope 1" represents the case of 100% binding of the added K^+.

The PNIPAAM particles adsorb at lower salt concentrations practically all the salt added, that is they desalinate the solution very efficiently. Binding continues up to very high salt concentrations, until finally binding capacity is exhausted. This limiting ion binding capacity is not defined by stoichiometry but by the structural collapse of the microgels as the particles start to phase separate from water at this salt concentration. The real surprise is the extent of ion binding: each of monomer repeat unit binds 5 ion pairs of salt rather strongly and up to 15 units of salt more weakly, that is well beyond stoichiometry or the behavior of classical polymeric ion-exchange resins.

To characterize this binding further, we measured with ITC (Figure 1B) the molar binding enthalpy of small aliquots of 0.1 N KCl added into the 0.5 wt % microgel solution (pH 7). The heat associated with the interaction of KCl with the polymer gel was determined by subtracting the heats of dilution of the polymer and the salt solution. This binding enthalpy is endothermic, that is the salt is indeed not fixed by classical valences to the gel. A comparison with the charged poly(acrylic acid) (PAA), a classical ion binder, shows that this endothermic character is weaker for the uncharged polymer.[4] As binding of the ions to the gel occurs deliberately, the driving force of the reaction must be a gain of entropy, which is believed to be primarily due to the liberation of water molecules from the gel and the ions, leading also to the macroscopically observed salting out of the polymer gel.

This can be verified using dynamic light scattering (DLS) to determine the microgel size upon addition of two salts, KCl and NaCl. It is reminded that backscattering measurements do not reveal the absolute hydrodynamic radius (which is only obtained by extrapolating to zero scattering angle, but rather a relative quantity which however can be nicely compared with

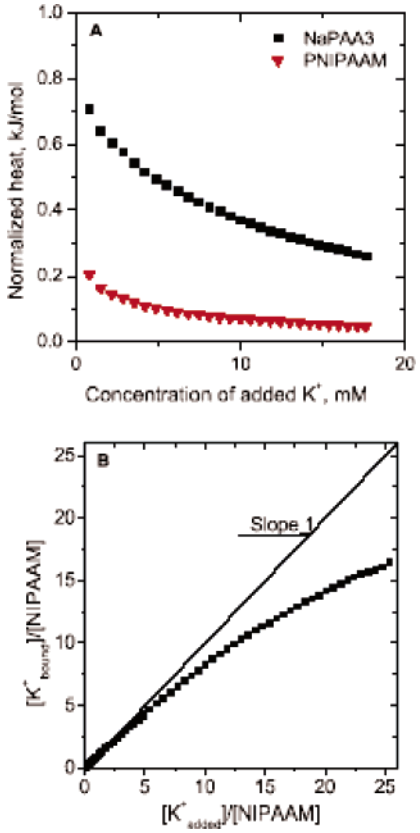

Figure 1. Binding isotherms. (A) Results of the ISE: molar ratio of bound K+ over monomer NIPAAM as a function of the molar ratio of added K+ over the monomer. The line indicated with "Slope 1" represents the case of 100% binding. (B) Molar binding enthalpies of 0.08 N NaPAA3 and 0.044 N PNIPAAM titrated with 0.1 N KCl, as determined by the ITC. The enthalpy associated with the binding of K+ was determined from the heat of injecting KCl into the polymer minus the dilution enthalpy of KCl minus the heat of dilution of the polymer. This heat is then normalized by the moles of added K^+.

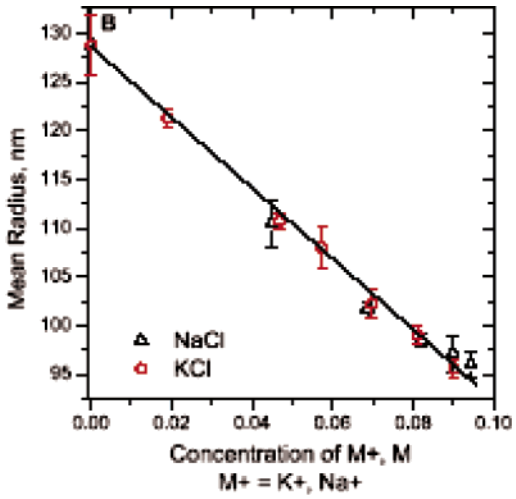

Figure 2. Hydrodynamic radius of the microgels as a function of concentration of added KCl and NaCl to a solution of 0.5 wt % PNIPAAM at 25 °C for a salt loading going up to 2 mol of salt per monomer unit. Error bars indicate reproducibility of three consecutive measurements. The line only guides the eye.

each other. This apparent radius of the microgel particles as a function of added concentration of NaCl and KCl for the titration of 0.044 m PNIPAAM is shown in Figure 2. Up to 0.1 m added salt (or two moles of salt per mole monomer units), all the changes of microgel size did not result in significant particle aggregation and flocculation, as indicated by the polydispersity

analysis of the DLS experiment which stays below 10% Gaussian width.

For both salts, we observe a linear decrease of the particle size similar for both ion pairs. From the known molecular volumes in the expanded and in the completely collapsed state, one can roughly estimate a molecular weight of each microgel and the swelling ratio, and one can translate the added molar amounts and deswelling ratios into a molecular picture for each microgel. On the back of the envelope, each microgel binds about 2.8×10^6 ion pairs, but simultaneously liberates about 177×10^6 water molecules, or the binding exchange occurs at a number ratio of molecules of about 30 for 1. According to simple thermodynamics, this is coupled to a sufficient entropy gain to counterbalance the measured endothermic binding enthalpy and to drive the observed reversible soft binding mode by entropy, only.

From another point of view, this shrinkage can also been described by the salt concentration dependent shift of the phase transition to lower temperatures, i.e., in the presence of 0.10 m KCl solution, the collapse point of the microgel is nearby 28 °C and therefore just slightly above the measuring temperature. This contraction with increasing salinity slightly below the lower critical solution temperature is well-known from many experimental observations,[9−12] the previously neglected point is that the salt concentration within the microgel is much higher than in the surrounding phase.

To proof the ability that such gels do not only immobilize ions, but also lead to macroscopic binding, we added 5 mL of a 3.5 wt % KCl solution (0.47 mol/L; "model seawater") to 5 mL of a 1.7 wt % microgel solution at 25 °C, then centrifuged off the microgels to form a separate bottom gel layer phase. The potassium concentration in the supernatant layer was determined to be 0.011 mol/L, that is the gel has indeed taken up 97.7% of the salt as ion pairs within the gel phase; this is twice its own weight. To our knowledge, this is by mass the most efficient chemical desalination process currently known.

A meaningful application of these gels also has to consider their potential regeneration. Again, one can favorably make use of the proximity of the critical behavior of the gel. The isolated bottom layer (the salt loaded gel) of the ultracentrifugation experiment is redispersed in another 5 mL of solution, and the whole system is brought to 40 °C to precipitate the polymer from this dispersion. Removal of the polymer at this temperature and determining the K^+ concentration in the liquid medium gave that more than 50% of the salt were released again. Obviously, at higher temperatures the polymer not only loses the option to bind water, but also the option to bind salt by water exchange. This underlines that the binding is merely entropic. We expect that the gel phase expels more salt throughout further heating, but did not apply higher temperatures to spare our ultracentrifugation setup.

It is interesting to note that the question of salt binding and salt specificity is also passionately discussed in context with biology, as many biological tissues bind salt which even seems to be potassium specific.[15] In this reference, Pollack also pointed to the relation of ion selectivity and the proximity of critical phase transitions in biological tissue. In this context, the present experiment can be regarded to be "biomimetic", and biological gels with similarly critical behavior, such as elastin gels, should show similar or even improved ion binding capacities.

Conclusion and Outlook

It was shown that neutral polymers with a weak hydration indeed can bind rather large amounts of salt as salt pairs, while the mechanism of ion binding is not electrostatic in nature, but mainly based on the liberation of solvent molecules and the coupled gain in entropy. ITC measurements indicated that this binding is even weakly endothermic. Current work is related to prove that this concept holds true for the wider class of polymers with a lower critical solution temperature. Another interesting option of the presented process is that it can be the source of chemical ion specificity: ions and molecules with a weak hydration shell would bind stronger than strongly hydrated ions. For that, competitive ion binding experiments are to be performed.

A further point to be analyzed is the role of anionic and cationic comonomers within the PNIPAAM system onto ion binding and colloidal stability, as recently discussed by Lopez-Leon et al.[16] Finally, so-called multiresponsive core−shell microgels, as described by Richtering et al.,[17] might result in directional ion gradients and deswelling effects, which can become the base of active transport and ion triggering systems.

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