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Effects of Hofmeister anions on the flocculation behavior of temperature-responsive poly(*N*-isopropylacrylamide) microgels

**Shirin Fanaian · Nodar Al-Manasir · Kaizheng Zhu ·
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Abstract Effects of some sodium salts (NaCl, NaClO₃, and NaSCN) in the Hofmeister series on deswelling and temperature-induced aggregation behavior of microgels of poly(*N*-isopropylacrylamide) (PNIPAAM) and PNIPAAM-*co*-PAA with attached poly(acrylic acid) moieties were investigated with the aid of turbidimetry and dynamic light scattering. Addition of salt in the concentration range 0.1–0.5 M generated aggregation of the PNIPAAM microgel particles at elevated temperatures, but it was no distinct difference between chaotropic and kosmotropic anions. In contrast, the flocculation behavior at high temperatures for PNIPAAM-*co*-PAA revealed a prominent influence of salinity and type of anion on the formation of aggregates. The aggregation transition was shifted to the highest temperature for the most chaotropic anion (SCN⁻), and the aggregation transition at the same salt concentration is consistent with the typical Hofmeister series. The turbidity results from the PNIPAAM-*co*-PAA microgels disclosed a two-step transition for the considered anions, and both a low and high temperature change in the turbidity data was observed. The high-temperature transition followed the Hofmeister series.

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Introduction

Specific salt effects are ubiquitous in chemistry and biology, and salinity may influence phenomena such as protein stability, enzyme activity, macromolecule crystallization, as well as protein and polymer folding [1–6]. Many years ago, it was noted that the aptitude of salts to precipitate certain proteins from an aqueous solution follows a recurring trend called Hofmeister series [7, 8], which is generally more pronounced for anions than for cations. The typical order of the anion series is:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_3PO_4^- > F^- > Cl^-$$
$$> Br^- \approx NO_3^- > ClO_3^- > I^- > ClO_4^- > SCN^-$$
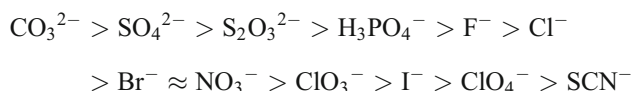
In this series, the ions on the left side are referred to as kosmotropes consisting of small ions with high charge density, and they are considered as "water making structure" with a thick hydration shell, whereas the species on the right side of the Hofmeister series are called chaotropes, which are large ions with small charge density and high polarizability, and they are considered as "water breaking structure" with a thin hydration layer. For aqueous solutions of proteins or polymers, the presence of the former group of ions frequently lead to higher surface tension, lower solubility of the macromolecules, and salting-out effects (aggregation of molecules) [6]. For macromolecules or proteins in the presence of the latter group of ions, the effect is usually reduced surface tension and enhanced macromolecular

solubility and salting-in (improved solvency) effects. Poly (N-isopropylacrylamide) (PNIPAAM) is an amphiphilic polymer that has attracted a great deal of interest in recent years partly because it has been described as a model system for the cold denaturation of peptides and proteins [9]. This polymer is also the subject of the present work.

In the past, effects of various types of salt on aqueous solutions of the temperature-responsive polymer PNI-PAAM have been reported [4, 10–12]. PNIPAAM bears both hydrophilic (amide) and hydrophobic (isopropyl) groups, and in aqueous solutions, PNIPAAM behaves as a thermoresponsive polymer that exhibits phase separation above its lower critical solution temperature (LCST is about 32 °C [13]) It has been clearly shown [4] that addition of kosmotropes lowered the cloud point strongly, while the effect is much weaker for chaotropes. In another study [10], it was shown that a high concentration of kosmotropic anions leads to a two-step phase transition of high molecular weights PNIPAAM, where the first step was sensitive to the polymer's molecular weight and solution concentration, whereas the second step was not. It has been argued [12] that the shift of cloud point for PNIPAAM systems is not correlated to either solubility or hydrophobicity of the additive but rather the chemical structure of the cosolute plays a major role. Effect of salt addition on microgels of PNIPAAM (chemically cross-linked particles of PNIPAAM) is a topic that is reminiscent of that of the homopolymer, and it has attracted a great deal of interest [14–19]. Microgels of N-isopropylacrylamide and acrylic acid is swollen at room temperature as a result of the internal electrostatic repulsion between the negative charge sites, but when moderate levels of salt is added, shrinking was shown [14] to occur due to screening of the electrostatic interactions. Due to the pH-responsive nature of the acrylic acid groups, the electrostatic interactions of this kind of microgels can also be modulated by changing the pH of the suspensions [20].

In this study, we have prepared PNIPAAM microgels, both with (PNIPAAM-co-PAA) and without charged acrylic acid units, and various concentrations of salts from the Hofmeister series have been added to the suspensions of particles of different charge densities. The aim of this work is to investigate effects of addition of different types of salt on the association behavior of these microgels over an extended temperature domain. The idea is to obtain a more detailed picture of direct interactions between the ions and microgels when various amounts of sodium salts from the Hofmeister series are added to the suspensions of particles. It will be shown that the interparticle aggregation, especially for the PNIPAAM-co-PAA microgels, is affected by the type and concentration of salt, temperature, and electrostatic interactions, which probably are of minor importance in this study because the salt concentrations are

fairly high (from 0.1 to 0.5 M). It is important to be able to control these parameters when microgels are used for, e.g., enhanced oil recovery.

Experimental

Materials and preparation of samples

N-Isopropylacrylamide (NIPAAM; Acros) was recrystallized from a toluene/hexane mixture solvent and dried at room temperature under vacuum prior to use. N, N′-Methylenebis (acrylamide) (BIS), ammonium persulfate, and acrylic acid (AA was utilized in the preparation of the microgel samples) and all chemicals were purchased from Sigma-Aldrich, Norway AS and used as received. The salts, NaCl, NaClO₃, and NaSCN, used in this study were purchased from Sigma-Aldrich and Fluka and used as received. The water employed in this investigation was purified with a Millipore Milli-Q system, and the resistivity was approximately 18 MΩ cm.

Microgel synthesis

A detailed route for preparation of micro- or nanogels by free radical precipitation polymerization has been described previously [21, 22]. The details of the synthesis and characterization of the microgels employed in this work have been reported recently [20].

Table 1 shows that the particles have the same degree of cross-linking and the NIPAAM contents are almost the same. As frequently reported, the free radical precipitation polymerization produces nearly monodisperse spherical particles in the sub-micron size range [21, 23]. One type of particles (PNIPAAM) was synthesized from a mixture of only NIPAAM and the cross-linker (BIS), and these microgels consist of only cross-linked NIPAAM chains without incorporated acrylic acid groups and the other sample (PNIPAAM-co-PAA) has 6 mol % acrylic acid groups. We note that the microgels have different zeta potentials with a higher value for the sample with acrylic acid groups. This suggests that the PNIPAAM-co-PAA spheres have the highest capacity to resist aggregation, whereas flocculation is

Table 1 Characteristic data of PNIPAAM and PNIPAAM-co-PAA microgel samples at a temperature of 25 °C

Sample name	NIPAAM (mol%)	BIS (mol%)	AA (mol%)	Zeta potential (mV)
PNIPAAM-co-PAA	92	2	6	−25±2
PNIPAAM	98	2	0	−12±2

more feasible for the PNIPAAM spheres at elevated temperatures and low salinity.

Turbidimetry

Effects of temperature and salinity on the transmittance of aqueous suspensions of the studied microgel systems were measured with a temperature-controlled Helios Gamma (Thermo Spectronic, Cambridge, UK) spectrophotometer at a wavelength of 500 nm. The apparatus is equipped with a temperature unit (Peltier plate) that gives a good temperature control over an extended time. In this work, the heating rate was set to 0.2 °C/min. The heating rate of the spectrophotometer was controlled by a PC that was interfaced to the apparatus and equipped with homemade software that gives the possibility of performing both temperature and wavelength scans with user-defined protocols.

The turbidity τ of the samples can be determined from the following relationship: $\tau = (-1/L) \ln (I_t/I_0)$ where L is the light path length in the cell (1 cm), I_t is the transmitted light intensity, and I_0 is the incident light intensity. The results from the spectrophotometer measurements will be presented in terms of turbidity.

Dynamic light scattering

In this study, dynamic light scattering (DLS) experiments were performed by means of an ALV/CGS-8 F multi-detector version compact goniometer system, with eight fiber-optical detection units, from ALV-GmbH., Langen, Germany. The beam from a Uniphase cylindrical 22-mW HeNe laser, operating at a wavelength of 632.8 nm with vertically polarized light, was focused on the sample cell (10-mm NMR tubes, Wilmad Glass Co., of highest quality) through a temperature-controlled cylindrical quartz container (with two plane-parallel windows), which is filled with a refractive index matching liquid (cis-decalin). The temperature in the container is controlled to within ±0.01 °C with a heating/cooling circulator. The polymer solutions were filtered in an atmosphere of filtered air through a 5-μm filter (Millipore) directly into precleaned NMR tubes. The DLS experiments were performed with a temperature gradient (0.2 °C/min) as for the turbidity measurements.

In the dilute suspensions of these nanogels, the experimentally recorded intensity autocorrelation function $g^2(q,t)$ (where q is wave vector of magnitude $q = (4\pi n/\lambda) \sin(\theta/2)$, λ is the wavelength of the incident light in a vacuum, θ is the scattering angle, and n is the refractive index of the medium) is directly linked to the theoretically amenable first-order electric field autocorrelation $g^1(q,t)$ through the Siegert [24] relationship $g^2(q,t) = 1 + B|g^1(q,t)|^2$, where B (≤ 1) is an instrumental parameter.

Analyses of the correlation functions revealed for all systems that the decays can be described by a single stretched exponential (Eq. (1))

$$g^1(q,t) = \exp[-(t/\tau_e)^{\beta}] \tag{1}$$

The variable τ_e is an effective relaxation time, and β ($0 < \beta \leq 1$) is a measure of the width of the distributions of relaxation times. The mean relaxation times are given by

$$\tau = \frac{\tau_e}{\beta} \Gamma\left(\frac{1}{\beta}\right) \tag{1a}$$

The correlation functions were analyzed with a nonlinear fitting algorithm to obtain best-fit values of the parameters τ_{se} and β appearing on the right-hand side of Eq. (1). The value of β was always larger than 0.97, which suggests that the size distribution is rather narrow. A fit was considered satisfactory if there was no systematic deviation in the plot of the residuals of the fitted curve. The nonsystematic residuals observed at all scattering angles and β values close to one confirm that only one relaxation mode is present in the system. Previous studies have shown that this method is capable of detecting the presence of two relaxation modes in the correlation functions even when methods based on regularized inverse Laplace transformation (such as CONTIN) only exhibits one mode [25, 26].

The relaxation mode is always diffusive (q^2-dependent). Since the relaxation mode is diffusive, it is possible via the Stokes–Einstein relationship to calculate an apparent hydrodynamic radius R_h and thereby estimate the sizes of the species

$$R_h = \frac{k_B T}{6\pi \eta D} \tag{2}$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium, and the mutual diffusion coefficient $D = 1/(\tau q^2)$. The measurements were routinely carried out at eight scattering angles simultaneously, with an accumulation time of 3 min, and the q-dependences of the relaxation times were checked continuously. For some of the measurements, the values obtained for R_h were in the region where $qR_h > 1$. At these conditions, the sizes are too large to be accurately determined by the DLS experiments. However, we have chosen to represent the data in this region by an apparent hydrodynamic radius, since the size changes are still expected to reflect the general trends of the systems.

Results

Dynamic light scattering results

The apparent hydrodynamic radius R_h can be used to monitor swelling and contraction of nano- or microgel particles

under the influence of temperature. In this work, effects of temperature, salinity, and type of salt on R_h for suspensions (0.02 wt.%) of PNIPAAM and PNIPAAM-co-PAA microgels (see Table 1) are discussed in detail. The impact of salinity and type of salt (Hofmeister series) on the size of microgels with and without charged groups is analyzed.

In Fig. 1, the apparent hydrodynamic radii are plotted as a function of temperature for microgels without PAA groups (Fig. 1a) and with PAA groups (Fig. 1b) for suspensions with various levels of salt addition and with different types of salt in the Hofmeister series. Let us first discuss the results for the PNIPAAM microgels without attached PAA groups. At low temperatures, it is evident that the microgels are compressed upon addition of all types of salt, and it seems that a salt concentration of 0.1 M is sufficient to screen most of the electrostatic interactions. However, for 0.1 M concentration of NaSCN (the most chaotropic salt), the shrinking effect is less pronounced. This suggests that this salt is less efficient to screen the electrostatic interactions, or a more efficient binding of the anion to the amide group of PNIPAAM (vide infra). At temperatures below the aggregate growth transition, the microgels without and with added cosolute shrink as the hydrogen bonds in the microgels are disrupted and the isopropyl groups associate.

At temperatures close to the transition, the particles become sticky and aggregates are formed, which leads to a drastic increase of R_h. A close inspection of the data reveals that a higher salt concentration of a given salt shifts the

aggregate transition to lower temperatures, and addition of a salt with a more chaotropic anion in the Hofmeister series shifts the transition to higher temperatures. It should be mentioned that in the presence of 0.5 M NaCl, very large aggregates were formed at early times and the gravitational force caused them to sediment. This prevented measurements at this high salinity with NaCl.

For the microgels with attached PAA groups (Fig. 1b), a clearer picture emerges when it comes to the effects of salt concentration and types of salt. Again, addition of salt results in contraction of the microgels at low temperatures and virtually all R_h data condense onto a single curve. In the presence of NaCl, no aggregation transition is observed at elevated temperatures for the lowest (0.1 M) salinity, but at higher levels of NaCl addition strong transitions are detected at a higher or a lower temperature, depending on the salt concentration. Upon addition of NaClO$_3$, marked transitions are only found for the higher two salt concentrations, but these transitions are shifted to higher temperatures than for the corresponding NaCl concentrations as predicted by the Hofmeister series. In the case of NaSCN addition (the most chaotropic anion), no transition of R_h occurs for the lower two salt concentrations in the considered temperature domain, but a significant transition is registered for the highest salinity; the transition is shifted to the highest temperature compared to the corresponding salt concentration of the other salts.

Turbidimetry results

Turbidimetry is a frequently utilized technique to detect the growth of large association structures or flocs in polymer solutions or suspensions. The effects of temperature, salt concentration, and type of salt on the turbidity for suspensions of PNIPAAM (0.02 wt.%) are depicted in Fig. 2a. At low temperatures, the suspensions that exhibit the strongest deswelling (cf. Fig. 1a) give rise to the lowest turbidity values. In the transition zone, the turbidity rises strongly and low salinity and more chaotropic anions promote shift of the turbidity to higher temperatures. As is evident from Fig. 1a, the apparent hydrodynamic radius falls off monotonously over the considered temperature range for the suspension without added salt, but in spite of this trend, the pattern of turbidity behavior is reminiscent of the turbidity features of the other suspensions with added salt, which all show flocculation tendency at elevated temperatures. These features can be rationalized in the theoretical approaches [27, 28] elaborated for spherical colloidal particles. The following expression was derived [28] for the turbidity $\tau = 3cQ_{ext}/(2d\rho)$, where c is the mass concentration (grams per cubic centimeters), Q_{ext} is the Mie extinction efficiency, d is the particle diameter, and ρ is the density of the particles. If we assume that the mass m of the spherical particles is constant,
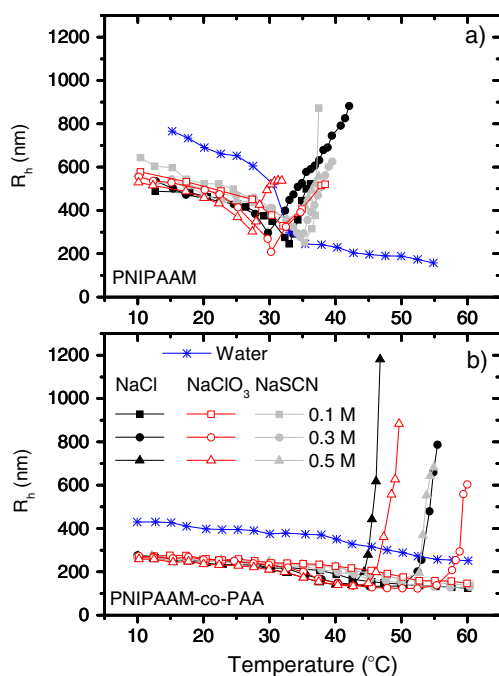

Fig. 1 Plot of the apparent hydrodynamic radius as a function of temperature for 0.02 wt.% suspensions of PNIPAAM (**a**) and PNIPAAM-co-PAA (**b**), with the salt concentrations and types of salt indicated
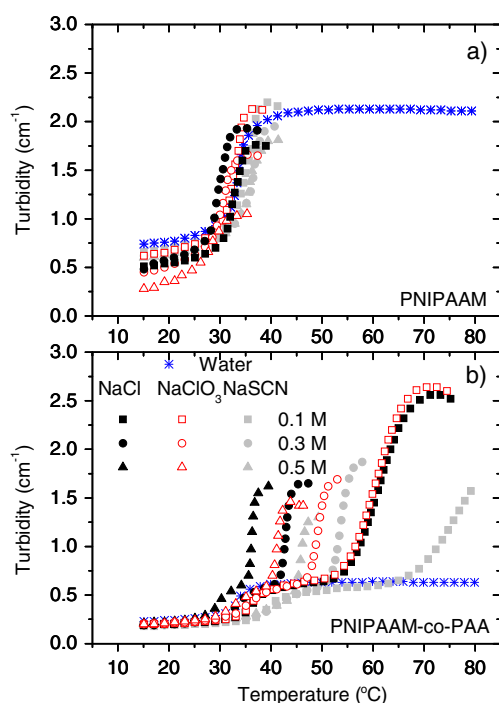
Fig. 2 Plot of the turbidity as a function of temperature for 0.02 wt.% microgel suspensions of PNIPAAM (**a**) and PNIPAAM-*co*-PAA (**b**), with the salt concentrations and types of salt indicated

the turbidity relation may be rewritten [20] on the form $\tau = cQ_{ext}\pi d^2/4m$. This relation readily explains the mentioned turbidity trend of the suspensions at low temperatures on the basis of changes of the particle size. However, the pronounced turbidity transition in the temperature region 15–40 °C (Fig. 2a) observed for the PNIPAAM microgel suspension without added salt is accompanied by compression of the particles from about 800 to 200 nm (Fig. 1a). This behavior is more intricate to interpret on the basis of the above equation because it is necessary to argue that the value of Q_{ext} should increase with increasing temperature because c and m for a given suspension should be constant. The quantity Q_{ext} is difficult to determine experimentally, but its value is a function of the relative refractive index n_p/n_0 (n_p is the refractive index of the spherical particle and n_0 is the refractive index of the solvent), and the value of Q_{ext} increases with increasing value of n_p/n_0. It is reasonable to assume that the refractive index of the particle is augmented when the particles are exposed to this very strong contraction. This means that the value of the relative refractive index rises, and this leads to an increase of Q_{ext} and the turbidity. This effect has been elucidated in detail for temperature-induced shrinking of PNIPAAM microgels in a previously work [20]. Changes of the refractive index of PNIPAAM particles upon compression have recently been discussed [20]. In the presence of salt, the DLS data for all samples indicate flocculation of the PNIPAAM microgels at elevated temperatures. The turbidity

curves in Fig. 2a illustrate the combined effect of contraction and flocculation of the particles. The transition zones for turbidity and DLS are both located in the approximate temperature interval from 30 to 40 °C, but it is complicated to separate the aggregation and compression effect from each other in the turbidity curves.

Figure 2b shows the turbidity as a function of temperature for suspensions of PNIPAAM-*co*-PAA microgels in the presence of different types of salt and salinities. For the suspension in water without salt, the profile of the turbidity curve is similar to the curve representing the PNIPAAM suspension in the absence of salt, but in this case, the amplitude of the transition is much smaller than for the PNIPAAM sample because the temperature-induced particle contraction for PNIPAAM-*co*-PAA microgels is significantly less than for the PNIPAAM microgels. This trend is consistent with the theoretical approach described above. The general picture that emerges for all suspensions with added salt is that the marked transition zone is shifted to lower temperatures as the level of salt addition increases. The turbidity transition curves for the systems are shifted according to the Hofmeister series, i.e., the transitions for the suspensions with the added chaotropic salt NaSCN are displaced to significantly higher temperatures than the corresponding ones for the suspensions with the other salts. This finding, as well as the DLS results, suggests that higher salt concentrations are needed to induce flocculation in suspensions with added NaSCN.

An inspection of the turbidity curves for the PNIPAAM-*co*-PAA microgels (Fig. 2b) discloses a two-step transition that is detected for all anions, and both a low- and high-temperature change in the turbidity data is found. This finding was not observed for the PNIPAAM microgels (Fig. 2a) at any of the considered conditions, but a single-step transition appeared. This may indicate that the higher charge density and/or the attached PAA groups play an important role for the two-stage behavior. A two-step transition has recently been reported [4, 10] for aqueous salt solutions of the homopolymer PNIPAAM, where a two-step transition in the scattered intensity data was found beyond a certain salt concentration for various types of salt. Furthermore, it has been observed [10] that the two-step transition is dependent on the molecular weight of PNIPAAM; actually the two-step transition only occurred at a sufficiently high molecular weight of the PNIPAAM in 0.3 M Na_2SO_4 solutions. For anions such as Cl^- and SCN^-, only a single transition was detected, independent of the polymer's molecular weight or the salt concentration utilized. In this work, the two-step transition is visible for all three salts and the three levels of salt addition for the PNIPAAM-*co*-PAA microgel suspensions, but not for the PNIPAAM microgels.

Discussion

In the past, salt effects on the lower critical solution temperature of PNIPAAM have been reported and related to the Hofmeister series. Two interplaying mechanisms have been proposed [4, 6, 8] to cause the so-called salting-out effect. First, it has been argued that kosmotropic anions polarize water molecules that are involved in the hydrogen bonding to the amide groups. This effect weakens the hydrogen bonding of water with the polymer chains, thereby salting out the polymer. Second, as more salt is added to the suspension, the more costly it is to hydrate hydrophobic groups of PNIPAAM, and this should also lead to the salting-out effect. In contrast to kosmotropic anions, it has been claimed [4, 6, 11] that large chaotropic anions (e.g., SCN^-) bind directly to the amide groups on the backbone, leading to salting in of the polymer. It is argued that the specific ion effects on colloidal species usually become appreciable at relative high salinity (typically above 0.1 M). In theory, this occurs when Coulomb interactions are screened and dispersion forces responsible for ionic accumulation become important [6]. In this study, the salt concentration is ≥0.1 M suggesting that the electrostatic interactions should virtually be screened or very weak.

For PNIPAAM microgels without PAA groups, the DLS results (Fig. 1a) suggest that in the presence of salt, the particles shrink up to the phase transition, whereas at higher temperatures, strong aggregation is observed at all salinities and types of salt, and the flocculation transition is shifted to higher temperature with lower salt concentration and for more chaotropic anions. The deswelling feature at low temperatures upon addition of salt is due to screening of the electrostatic repulsive forces inside the microgels, and at higher salt concentrations, the hydrophobicity of the polymer segments may change depending on the type of salt and kosmotropic anions provoke a stronger compression of the microgels. This leads to lower values of the turbidity (cf. Fig. 2a) at low temperatures.

The flocculation behavior at elevated temperatures is due to absence of electrostatic stabilization when the salt concentration is sufficiently high. However, both the effects of salt concentration and the Hofmeister series are modest for the PNIPAAM microgels without attached PAA groups. In previous studies on PNIPAAM microgels, more pronounced Hofmeister effects have been reported [29]; however, these microgels were modified to carry a surface charge. It has recently been observed [18] that the phase diagrams in ternary systems of PNIPAAM/water/alcohol are strongly influenced by the Hofmeister effect at high salinity. In aqueous solutions of the homopolymer PNIPAAM, it has been shown [4] that both salinity and type of salt have a significant impact on the lower critical solution temperature over a wide salt concentration range. It has been argued [6]

that Hofmeister phenomena should be understood in terms of direct interactions between the salt ions and polymer chains, and less influence is expected from changes in bulk water structure upon addition of salt. In view of this, our hypothesis is that the interactions should be more efficient with linear PNIPAAM chains than for the chemically cross-linked microgels considered in this study. In the latter case, the amide moieties and isopropyl groups may be less accessible to interactions with the anions, and the rigid structure of the microgel particles make them less inclined to respond to ion interactions.

We notice that for suspensions of PNIPAAM with attached PAA groups, effects of Hofmeister anions on the apparent hydrodynamic radius (see Fig. 1b) and on the turbidity (see Fig. 2b) are well manifested in the displayed plots. At a salinity of 0.1 M, none of the considered anions induces aggregation while at 0.3 M salt concentration, flocculation is detected for both Cl^- and ClO_3^- anions, but not for the most chaotropic anion SCN^-. At 0.5 M salt concentration, growth of aggregates is observed for the three studied salts with flocculation transitions according to the Hofmeister series. It is clear that at sufficiently high salinity, both kosmotropic and chaotropic anions induce aggregation at elevated temperatures. In the model of Zhang and Cremer [6], it was claimed that salting out of PNIPAAM is due to two effects, namely that kosmotropic anions can polarize water molecules that are directly hydrogen-bonded with the amide groups of PNIPAAM and secondly both chaotropes and kosmotropes can interfere with the hydrophobic hydration of the polymer by increasing the surface tension of the cavity surrounding the backbone and the isopropyl side chains. In this scenario, salting in of the polymer is caused by chaotropic anions that can bind directly to the side-chain amide moieties. The phenomena leading to salting out depend linearly on salt concentration, whereas the salting in effect exhibits simple saturation behavior. For the cross-linked PNIPAAM-co-PAA microgel system, the conjecture is that kosmotropic anions can polarize water molecules that are directly hydrogen-bonded with the hydrophilic amide and/or carboxyl groups of PNIPAAM-co-PAA, and this effect is enhanced with increasing salt concentration. In addition, removal of the hydrophobic hydration waters from backbone, isopropyl groups, and acrylic moieties may occur, and this phenomenon is strengthened by increasing salinity. This lowers the cloud point by destabilizing the hydrophobic hydration of the polymer. Our conjecture is that the two salting-out effects play a major role for the flocculation feature observed for the PNIPAAM-co-PAA system at elevated temperatures, and since the Hofmeister effect is much weaker for PNIPAAM microgels, we suspect that interactions between anions and carboxyl and/or acrylic units may play an important role.

Let us now discuss the turbidity results for the PNIPAAM-*co*-PAA system (cf. Fig. 2b). In the absence of salt, a single-step transition is found for the temperature dependence of the turbidity, whereas in the presence of the studied salts and salinities, a two-step transition is observed for these anions, and both a low- and high-temperature change in the turbidity data is registered. The second step is more pronounced at lower salt concentration, and it follows the Hofmeister series. The second step is clearly shifted to lower temperature as the level of salt addition rises. This two-step feature has recently been reported [4] for PNI-PAAM chains in aqueous solutions with different salts. Only a single-step transition was observed at concentrations below ca. 0.1 M, but the two-stage transition was detected at higher salt concentrations. It has been observed [10] that the first stage of the two-step transition is sensitive to the PNIPAAM's molecular weight and solution concentration, whereas the second step is not. The first step was attributed to salting out of the amide group, and it was suggested that specific hydrogen bonds are being broken. The second step was ascribed to a salt-induced dehydration of the hydrophobic portions of the polymer, causing particle deswelling which becomes more pronounced with increasing electrolyte concentration. Even though the sizes of the microgels are still decreasing at the onset of the second step in the turbidity curves, it is reasonable to assume that the destabilization of the hydrophobic hydration, combined with the screening of the electrostatic repulsions, may induce an incipient aggregation of the microgels. However, since the microgels are also contracting, the overall size change is still declining. The turbidity data clearly reveal that the location of the transition of this stage is sensitive to both the salt concentration and type of anion.

Conclusions

Effects of salt concentration and type of anion on the specific ion interactions with microgels of PNIPAAM and PNIPAAM-*co*-PAA were investigated with the aid of turbidimetry and DLS. It was found that the effect of anions on the aggregation behavior of the PNIPAAM microgels was similar for the three salts and salinities, and only a modest difference between the systems could be traced, whereas at the corresponding conditions for PNIPAAM-*co*-PAA microgels, prominent differences were detected at different salt concentrations and type of anions. The trends followed the Hofmeister series prediction. It was speculated that the difference in flocculation behavior between the PNIPAAM and PNIPAAM-*co*-PAA microgels in the presence of various anions is attributed to the easier accessibility of these ions for direct interactions with the PAA moieties on the microgels. In the case of the most chaotropic anion (SCN^-), a high salinity (0.5 M) is needed to induce flocculation of the PNIPAAM-*co*-PAA microgels.

The turbidity results reveal a single transition behavior for the PNIPAAM microgels at all salinities and salt types, whereas for the PNIPAAM-*co*-PAA microgels, both a low- and high-temperature transition is observed for all anions and salt concentrations. Our conjecture is that in the first step, hydrogen bonds are broken, while the second step is associated with destabilization of the hydrophobic hydration of the polymer and this process is accompanied with aggregation of the microgels at elevated temperatures. This high-temperature stage of the turbidity is susceptible to the type of anion and salt concentration, and it follows the Hofmeister series. As a consequence, the transition is shifted to higher temperature as the anions become more chaotropic and the level of salt addition decreases.

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