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ORIGINAL CONTRIBUTION

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The effect of electrolyte on the colloidal properties of poly(N-isopropylacrylamide-*co*-dimethylaminoethylmethacrylate) microgel latexes

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Abstract Monodisperse cationic thermosensitive latex microgels prepared by radical-initiated precipitation copolymerization of *N*-isopropylacrylamide (NIPAM), methylenebisacrylamide, and dimethylaminoethylmethacrylate (DMAEMA) have been reported (Zha LS, Hu JH, Wang CC, Fu SK, Elaissari A, Zhang Y 2002 *Colloid Polym Sci* 280:1) and we suggested (Zhang Y, Zha LS, Fu SK *J Appl Polym Sci*) that the polyelectrolyte chains are rich in their expanded shell layers. The effect of a range of electrolytes on several colloidal properties of these cationic latexes (such as particle size, zeta potential and colloidal stability) has been investigated. The ability of the anions to induce the particle deswelling and flocculation is related to their position in the Hofmeister series. Owing to the DMAEMA-rich layer on the latex particles, the ionic-strength dependence of the particle hydrodynamic size and the zeta potential become more profound with increasing amount of DMAEMA incorporated into the microgel. It is suggested that the effect of electrolytes on the colloidal properties of the copolymer microgel latexes is attributed to the dehydration of the poly(NIPAM) segment and the screening of the electrostatic interaction between the charged DMAEMA units induced by electrolytes.

Keywords Poly(*N*-isopropylacrylamide-*co*-dimethylaminoethylmethacrylate) microgel latex · Electrolyte · Deswelling · Zeta potential · Colloidal stability

Introduction

Hydrophilic microgel latexes are an interesting subset of polymer colloids owing to their properties in common with water-soluble polymers, water-swollen macrogels, and water-insoluble latex particles. Cosmetics, coatings, food, and industrial processing industries employ hydrophilic microgels to modify their rheological properties, to retain water, or for many other reasons [1, 2]. Hydrophilic microgels exhibit different equilibrium degrees of swelling and colloidal properties in response to various kinds of electrolytes as well as their concentrations, and this behavior attracted much attention from both scientific and technical viewpoints.

Poly(*N*-isopropylacrylamide) [poly(NIPAM)] is the most well-studied hydrophilic microgel system, and undergoes a temperature-induced, reversible-volume phase transition in water at about 32 °C (volume-phase transition temperature, VPTT) [3]. Although the amide group in the NIPAM unit prefers to be in water owing to strong hydrogen-bonding capacity with water molecules, the isopropyl group tends to pull away from water molecules. It is generally believed that this hydrophilic–hydrophobic push–pull is responsible for the volume phase transition behavior of poly(NIPAM) microgels in water. Below the VPTT hydrophilic forces dominate, the microgel remains in a water-swollen state; above this temperature, hydrophobic forces dominate, the microgel sheds water, and shrinks.

It has been recognized that neutral electrolytes can drastically alter the swelling property of poly(NIPAM) microgel particles. The magnitude of this change strongly depends on the nature of the individual ions and their concentrations. A recent study by Daly and Saunders [4] has shown that addition of structure-making anions, such as Cl^-, causes strong deswelling, whereas addition of structure-breaking anions, such as SCN^-, causes slight swelling. The swelling behavior of the microgel particle is dependent on the competition for water molecules by the polymer and the electrolyte added.

Poly(NIPAM) microgel dispersions have fascinating electrical properties owing to their thermal sensitivity. Pelton et al. [5] have proposed that the electrophoretic mobility of poly(NIPAM) micdrogel particles can be modelled using a combination of the Helmholtz and Smoluchowski formulae. This model assumes that all the charged groups are located near the hydrodynamic surface of the particle and provides a semiquantitative fit to the experimental data. A more extensive theoretical analysis of the electrophoretic mobility of the so-called "soft particle" has been proposed by Ohshima and coworkers[6, 7, 8, 9]. According to Ohshima's theory, the electrophoretic mobility of a particle bearing a shell of polyelectrolyte materials depends on the Donnan potential of the polyelectrolyte surface layer, the potential at the boundary between the surface layer and surrounding solution, the density of the fixed charges, and the friction parameter.

Colloidal stability depends upon the balance of van der Waals attraction, which causes aggregation, and steric or electrostatic forces, which oppose aggregation. Previous studies [10, 11, 12] have shown that below the VPTT poly(NIPAM) microgel latexes are stabilized by three factors: the chains on the exterior of the particles act as a steric stabilizer; charged groups from the initiator give electrostatic stabilization; and the van der Waal's attraction between the highly swollen particles will be low. By contrast, above the VPTT, only electrostatic forces stabilize the latex.

Previously [13], we reported the preparation of monodisperse cationic poly(NIPAM) microgel latexes by surfactant-free emulsion polymerization using dimethylaminoethylmethacrylate (DMAEMA) as a cationic monomer, and 2,2′-azobis(2-amidinopropane hydrochloride) (V50) as an initiator.

The poly(NEPAM-*co*-DNIAEMA) microgel particle size can be adjusted by the amount of the incorporated ionic monomer, and its VPTT was found to be around 32 °C and was slightly dependent on the ionic monomer concentration.

Our recent study [14] suggested that poly(NIPAM-*co*-DMAEMA) chains are mainly located in the expanded shell layer of the latex particle by analysing the DMAEMA content within the microgel using NMR measurements. It can be expected that the DMAEMA content plays a major role in the colloidal properties. In this work, the effect of a range of electrolytes on the swelling and electrical properties and colloidal stability of poly(NIPAM-*co*-DMAEMA) microgel latexes is investigated using quasielastic light scattering (QELS), electrophoretic mobility, and turbidity measurements.

Experimental

Materials

Sodium chloride, sodium bromide, sodium thiocyanate, sodium sulfate, and sodium citrate (Na_3Cit) were analytical reagents and were used as received for ionic strength variation. Water was well deionized before use.

Preparation and purification of microgel latexes

The cationic poly(NIPAM-*co*-DMAEMA) microgel latexes were synthesized by precipitation polymerization at 70 °C using methylenebisacrylamide (MBA) as a cross-linker and V50 as an initiator. A detailed preparation process of such a system has been described previously [12]. The samples used in this work and their particle sizes are listed in Table 1.

All the latexes were cleaned by repetitive cycles of centrifugation, decantation, and redispersion using deionized water, before any characterization study, in order to remove free electrolyte and water-soluble polymers.

Characterization of microgel latexes

Poly(NIPAM-*co*-DMAEMA) microgel latexes were characterized with respect to the ionic-strength dependence of the hydrodynamic diameter, D_H, the ζ potential, and the extent of particle aggregation, n. The data for D_H, ζ, and n obtained at different ionic strengths were obtained by diluting the latexes with various electrolyte solutions of the respective concentration.

Particle size determination

The latex particle size was determined by QELS as a function of ionic strength based on various kinds of electrolytes and

Table 1 Sample composition and particle size: dimethylaminoethylmethacrylate (*DMAEMA*), quasielastic light scattering (*QELS*), transmission electron microscopy (*TEM*)

Sample	DMAEMA%[a]	Particle size (nm)		
		QELS		TEM
		20 °C[b]	50 °C[c]	
MG-405	0.15	643	315	298
MG-420	0.60	378	213	197
MG-480	2.40	260	170	126

[a] The molar percent of DMAEMA to total monomers
[b] Measured by QELS at 20 °C under 10^{-4} M NaCl
[c] Measured by QELS at 50 °C under 10^{-4} M NaCl

temperature using an Autosizer 4700 instrument (Malvern) at a scattering angle of 90°. The mean hydrodynamic diameter was calculated from the diffusion coefficient measurement, which, in the high dilution with negligible particle–particle interactions, is calculated by the Stokes–Einstein equation [15]:

$$D = k_B T / (3\pi\eta D_H), \tag{1}$$

where D is the diffusion coefficient of the latex particle, η the viscosity of the medium, k_B the Boltzmann constant, and T the absolute temperature of the dispersion. The diameter D_H measured in this manner is usually known as the hydrodynamic diameter.

ζ potential

The ζ potential of the latex particles was measured with a ZetaSizer 3000HS (Malvern) as a function of pH and ionic strength. Each point was obtained by taking the average of at least three measurements. The ζ potential used in this work was calculated from electrophoretic mobility, u, using the Helmholtz–Smoluchowski equation [15]:

$$u = \varepsilon \zeta / \eta, \tag{2}$$

where ϵ is the dielectric constant of the medium.

Determination of n

The extent of particle aggregation in the dispersion was estimated from the wavelength dependence of the turbidity, τ, [16], i.e.,

$$n = -(\mathrm{d}\log\tau / \mathrm{d}\log\lambda). \tag{3}$$

The measurement of n was carried out using dispersions of 0.1% (wt/vol) microgel particles, containing various concentrations of the electrolytes. The samples were placed in a water bath at 25 °C and allowed to stand for 24 h. The turbidity variation versus the wavelength was obtained over the wavelength range 400–625 nm using an HS 3000 UV–vis spectrophotometer (Hitachi).

Results and discussion

The effect of electrolyte on the microgel particle swelling

Generally, neutral electrolytes can drastically alter the solution properties of macromolecules, such as solubility, precipitation temperature, viscosity, etc. The magnitude of this change strongly depends on the nature of the individual ions. The hydrodynamic diameter of poly(NIPAM-*co*-DMAEMA) microgel particles with three different DMAEMA contents is shown in Fig. 1 as a function of NaCl concentration or ionic strength. The hydrodynamic diameter is found to decrease with an increase in the ionic strength, and the ionic strength dependence of the diameter is more significant for the microgel with higher DMAEMA concentration. The analysis of the effect of electrolyte on the microgel hydrodynamic size should consider polymer–polymer, polymer–water, polymer–ion, and water–ion interactions, and the various possibilities in providing a satisfactory explanation for the effect of electrolyte on the swelling properties of poly(NIPAM-*co*-DMAEMA) microgels may be as follows:

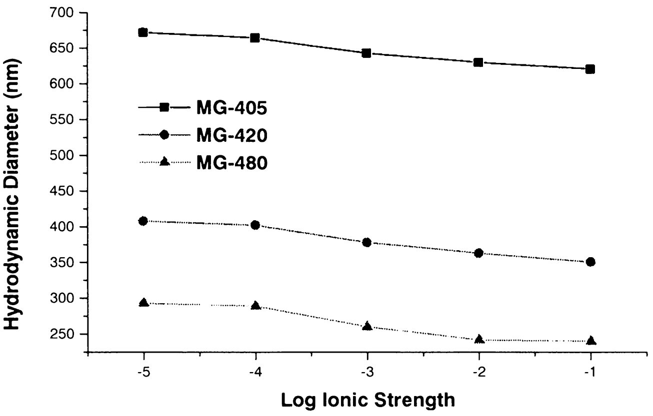

Fig. 1

1. Salts can change the structure of water and thus the free energy of interaction between the polymer and water. The change in the water structure may strongly affect the hydrophobic hydration [17] of the hydrophobic pendent isopropyl group. Accordingly, increasing the salt concentration reduced the solvency of the poly(NIPAM) segments in water (increase in the Flory–Huggins interaction parameter between the polymer and water) and deswelled the water-swollen microgel particle.
2. The tertiary amine groups in the DMAEMA units are protonated in pH 5 aqueous solutions (see the following discussion). The ionized DMAEMA units generate osmotic pressure within the particles, which facilitates the swelling of the particles, and the osmotic pressure is increased with DMAEMA content. In general, an increase in ionic strength decreases the osmotic swelling pressure because a higher salt concentration has the consequence that the NaCl concentration gradient between the inside and the outside of the microgel particles decreases.
3. The decrease in the hydrodynamic diameter upon increasing electrolyte concentrations can be partially attributed to a hairy particle model in which the polymer chains at the particle surface are polyelectrolytes. The interfacial polymers were immobilized in a complex conformation with tails and loops extending far into the surrounding solution. Added salt (NaCl) screens the electrostatic repulsion between the charged tertiary amine groups of inter- and intrapolyelectrolyte chains, leading to a decrease in the hydrodynamic volume of the corresponding

polyelectrolyte hairs as recently discussed by Seebergh and Berg [18]. The effect was enhanced with the increase in the ionic groups in the polyelectrolyte chains when a higher concentration of DMAEMA was used in the polymerization recipe, as reported in Table 1.

The variation in the hydrodynamic diameter at 25 °C as a function of ionic strength for MG-420 in the presence of NaCl, NaBr, NaSCN, Na_2SO_4, or Na_3Cit is shown in Fig. 2. As the cations are common (Na^+), the data allow comparison of the effects induced by the anions. The efficiency for the anions to deswell poly(NIPAM-*co*-DMAEMA) microgels decreases in the order $Cit^{3-} > SO_4^{2-} > Cl^- > Br^- > SCN^-$.

This order generally follows the classical Hofmeister series [19], which ranks various ions according to their ability to precipitate proteins from aqueous solutions. As illustrated in Fig. 2, Cit^{3-} is the most efficient in deswelling the particles, whereas SCN^- causes slight swelling in the concentration range from 10^{-5} to 10^{-3} M and deswelling at higher ionic strength. This is because Cit^{3-} is the most effective competitor for water molecules that hydrate the copolymer chains among the anions studied here; in contrast, SCN^- is helpful to hydration of the copolymer, but too high a concentration of Na^+ may contribute to the compression of the expanded shell layer.

Effect of pH on the ζ potential

Poly(NIPAM-*co*-DMAEMA) should have remarkable electrical properties owing to the presence of covalently bonded electrically charged groups originating from the cationic monomer (protonated DMAEMA) and the initiator (V50). The ζ-potential measurements were carried out as a function of pH in 10^{-5} M NaCl aqueous solution at 25 °C, and the results are shown in Fig. 3. The particles exhibit a positive ζ potential until pH 10.4 for all the latexes, and is representative of the positive surface charge density originating from the protonated functional monomer and the initiator. The ζ potential increases with DMAEMA concentration in poly(NIPAM-*co*-DMAEMA) microgel particles, reflecting the higher surface charge density imparted by more DMAEMA. As illustrated in Fig. 3, the ζ potential versus pH exhibits a marked maximum at pH 6. From our titration experiments, the pK_b of DMAEMA at 25 °C is 8.3, so the tertiary amino groups in the copolymer are likely to be completely protonated at pH 6. However, the reduction in the ζ potential with a decrease in pH is due to the increase in ionic strength induced by a higher concentration of HCl (see the following discussion). As the pH increases from 6 to 10.4, the ζ potential gradually decreases, revealing the partial neutralization of amidine and amine groups in this pH range. The pH of the solution determines the degree of protonation of amino groups on the polymer chains. The negative ζ potential observed above pH 10.4 is usually attributed to the presence of carboxylic groups originating from the hydrolysis of amidine groups [20] and ester groups from the initiator (V50) and the functional monomer (DMAEMA), respectively. It can be seen that the ζ potential becomes more negative when the DMAEMA concentration increases, corroborating the presence of hydrolysis of ester groups of DMAEMA under this condition. Note that the isoelectric points (IEP) for the three latexes are the same, i.e., 10.4, which is close to the IEP of amidine reported by Sauzedde et al. [21].

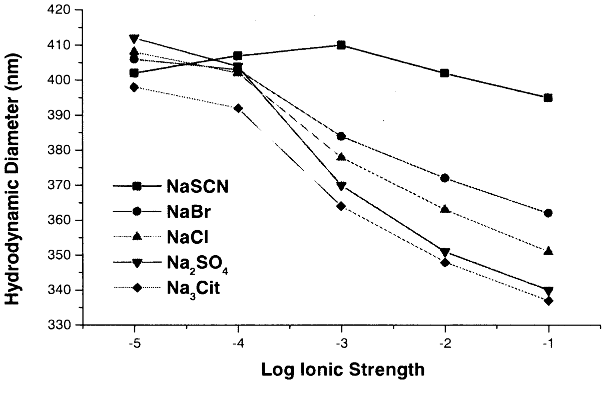

Fig. 2

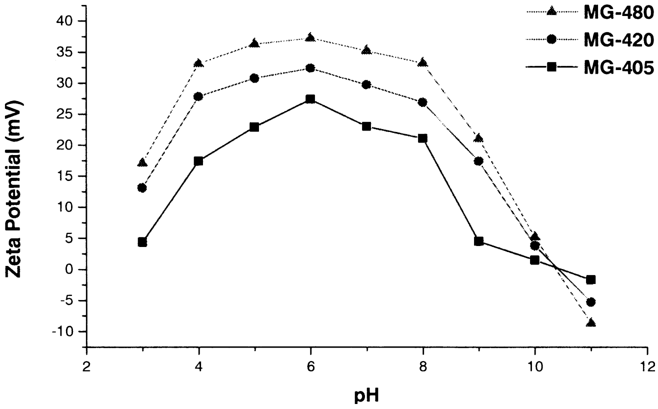

Fig. 3

Effect of ionic strength on the ζ potential

The effect of ionic strength on the ζ potential was investigated at 25 °C, and the results obtained for all the microgel latexes are shown in Fig. 4. The potential values for all the microgel latexes decrease upon increasing the ionic strength, and no maximum in the potential

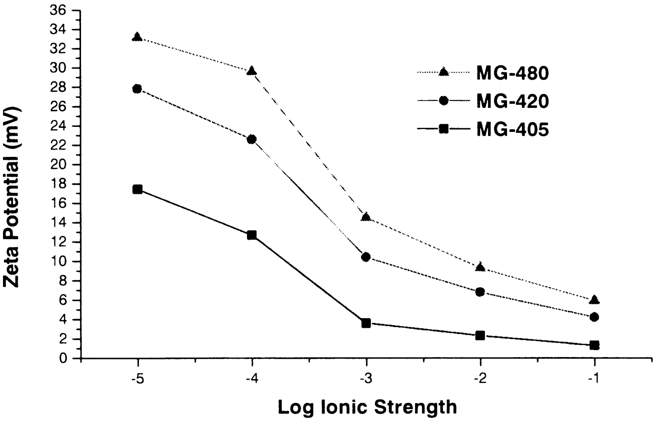

Fig. 4

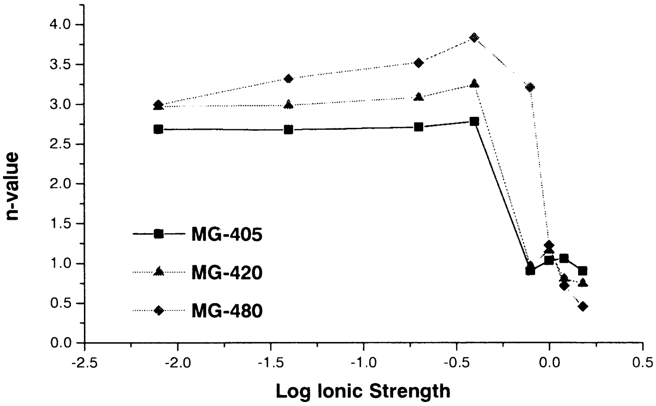

Fig. 5

versus NaCl concentration was observed, in contrast to other observations reported by Nabzar et al. [11] and Sauzedde et al. [21]. According to both the Helmoltz–Smoluchowski formula, the ζ potential may be related to the surface charge density, σ, and the D_H of the microgel particles through the following equations [22]:

$$\sigma = -Ne/\left(\pi D_H^2\right), \tag{5}$$

and

$$\xi = \sigma/(\varepsilon\kappa), \tag{6}$$

where κ is the reciprocal Debye length, N the number of charged groups, e the electron charge, and ϵ the permittivity of the medium. It is assumed that all the charged groups are located on the particle surface, and ζ is mainly influenced by D_H and κ. As already reported, an increase in the ionic strength led to a decrease in D_H, and then to an increase in σ and ζ. On the other hand, the thickness of the electrical double layer ($1/\kappa$) is heavily reduced upon increasing the ionic strength of the medium. The latter effect is dominant for the system studied here. The higher the DMAEMA concentration within the microgel, the thicker the electrical double layer and the more marked the influence of the ionic strength.

Effect of electrolyte on dispersion stability

Turbidity–wavelength measurement is a sensitive method for detecting aggregation in dispersions, and Daly and Saunders [3] have shown that the method is applicable to poly(NIPAM) microgel latexes. Flocculation is detected by a decrease in the magnitude of n. The value of n decreases abruptly when aggregation occurs. Poly(NIPAM) dispersions were colloidally stable when $n \approx 2.7$, and flocculated when n significantly decreased below this value. In this work, the poly(NIPAM-*co*-DMAEMA) microgel dispersion stability was investigated as the value of n versus ionic strength for various microgels with different DMAEMA concentrations and for various electrolytes, including NaCl, NaBr, NaSCN, Na_2SO_4, and Na_3Cit, as reported in Figs. 5 and 6, respectively. As shown in Fig. 5, the n values of poly(NIPAM-*co*-DMAEMA) microgel dispersions in the low-ionic-strength range remain constant and decrease at high ionic strength. The ionic strength at which the n value decreases sharply increases with the DMAEMA content of the microgel dispersions, indicating that DMAEMA serves to help colloidally stabilize the microgel dispersion. At high ionic strength two effects contribute to the destabilization of the copolymer microgel dispersions:

1. At low ionic strength the ζ potential of the poly(NIPAM-*co*-DMAEMA) microgels is relatively high, indicating that electrostatic stabilization is operative. High ionic strength induces coagulation because the electrostatic interaction is screened giving low electrostatic repulsion.

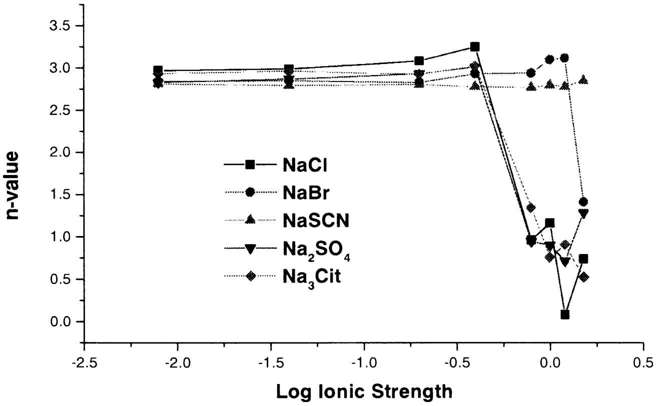

Fig. 6

2. Owing to the dehydration induced by anions such as Cl^-, poly(NIPAM) tails on the microgel surface will be partially collapsed and thus will not contribute to steric stabilization.

Figure 6 shows that Na_3Cit, Na_2SO_4, and NaCl are more effective at flocculating the poly(NIPAM-*co*-DMAEMA) microgel dispersion than NaBr and NaSCN, and NaSCN is the least effective among the electrolytes studied. The addition of highly charged and hydrated electrolytes, such as Na_3Cit, causes dehydration of the polymer and an increase in the value of the Hamaker constant, A, for the microgel particle as well as a corresponding decrease in the steric stabilization of the microgel leading to particle aggregation. The efficiency for anions to destabilize the microgel dispersion decreases in the order $Cit^{3-} \approx SO_4^{2-} \approx Cl^- > Br^- > SCN^-$, which is in agreement with the previous order for deswelling. As discussed by Dhara and Chatterji [23] in explaining the effect of salts on the phase transition of poly(NIPAM) in water, a small monovalent or polyvalent ion will be a structure-maker and a large monovalent ion should be structure-breaker. Structure-makers will enhance a hydrophobic interaction, thereby reducing the colloidal stability of poly(NIPAM) microgel latexes. On the other hand, structure-breakers should increase the colloidal stability by increasing the hydrophobic hydration. Among the anions studied here, Cit^{3-}, SO_4^{2-}, and Cl^- should be in the structure-maker series and be efficient in destabilizing poly(NIPAM-*co*-DMAEMA) microgel latexes, whereas SCN- is typically a structure-breaker and should induce minimum perturbation.

Conclusion

Cationic poly(NIPAM-*co*-DMAEMA) microgel latexes differing in the content of the cationic monomer (DMAEMA·HCl) used have been carefully characterized as regards particle size, ζ potential, and colloidal stability below their VPTT. At first, it was found that the hydrodynamic diameter of all the latex particles was found to decrease upon increasing the ionic strength of the dispersion medium, and the ability of the anions to deswell the copolymer microgel agrees with their position in the Hofmeister series. Owing to the DMAEMA-rich layer on the latex particle surface, the ionic-strength dependence of the particle deswelling and the electrical properties become more profound with increasing amount of DMAEMA incorporated into the microgel. Finally, the colloidal stability of the microgel latexes is increased upon raising the DMAEMA concentration, owing to the electrostatic interaction. Structure-making anions such as Cit^{3-}, SO_4^{2-}, and Cl^- have a remarkable effect in destabilizing the microgel dispersion, whereas structure-breaking anions such as SCN^- have virtually no effect.

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