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SHORT COMMUNICATION

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Anomalous electrophoretic mobility of microgel particles in buffer solutions

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Abstract The electrophoretic mobility (μ) of tunable surface charge poly(*N*-isopropylacrylamide) microgel particles (PNIPAM) was measured vs pH, using different anionic buffers. Two minima, just at the buffers' p*K* values, were found for the μ-pH curve. The preferential penetration of the small counterions into the soft-charged shell explains the electrokinetic charge reduction. For pH values higher than the p*K*, the charge screening leads to electrostatic repulsions among coions. It pushes them towards the particles; thus, balancing the global ionic distribution.

Keywords Electrophoretic mobility · Microgel particles · Buffer solutions

Introduction

Microgels are polymeric colloids with particles showing properties of individual mesoscopic gels [1]. Such materials are promising candidates for the development of biomedical applications, controlled release systems [2], rheological control, surface coating, wastewater treatment [3], and molecular imprinting [4]. It is well known that poly (*N*-isopropylacrylamide) microgel particles (PNIPAM particles) show a swollen state at low temperature due to the high polymer solubility, and it undergoes a drastic shrinking above 32 °C, favored by the elastic contribution coming from the mesh cross-linking [5]. In a recent paper [6], we have studied PNIPAM microgels cross-linked with *N*-*N*′-methylenebisacrylamide, finding that particles consist of a nondraining core covered by an ion-permeable charged layer. The presence of the soft-charged polyelectrolyte shell introduces interesting differences compared to "standard" hard particles.

On the other hand, the use of buffers to fix the sample pH has shown to not affect the mobility of hard particles, except when specific ion adsorption becomes apparent [7, 8]. The aim of the present work is to check the effect of the extra ions in the scramble coming from a specific buffer for a core-shell microgel with pH-variable surface charge. We performed electrophoretic mobility measurements for different pH values. In addition, the particle size was determined by dynamic light scattering (DLS) to check any possible direct influence on the particle mobility. The great size difference between the buffer counterions and coions

causes an anomalous behavior on the microgel mobility, becoming apparent two remarkable minima directly connected to the soft character of the microgel particles.

The outline of the papers is as follow. "Materials and methods" section describes the experimental system and the techniques employed in this study. The "Results and discussion" section presents the experimental results and the discussions. Finally, the conclusions are summarized in the "Conclusions" section.

Materials and methods

Experimental system

Spherical and highly monodisperse thermosensitive microgel particles with variable surface charge were used in this study (Fig. 1a). Details about particle preparation can be found elsewhere [9]. The synthesis is based on *N*-isopropylacrylamide (NIPAM) cross-linked with *N*-*N*′-methylenebisacrylamide (BIS, 0.5%). Sodium persulfate was employed as initiator, which introduces fully ionized sulfate groups. To generate pH-dependent charge, the reaction time was extended to facilitate the Kolthoff's reaction [10], in which the sulfate groups are hydrolyzed to carboxyl group. Any strong acid group was detected by conductimetric titration [6], confirming that all strong sulfate groups were transformed to weak carboxyl groups. A detailed analysis of the titrated charge [6] revealed that it cannot fit on the particle surface, implying that this charge must be distributed in a surface shell. The consequences of this core-shell morphology on the swelling and electrokinetic behavior are discussed in the referred paper [6]. In addition, potentiometric titrations were carried out to obtain the charge pH dependence. A cell supporting the pH or conductivity electrode, a nitrogen-inlet tube and a sodium hydroxide or hydrochloric acid feed tube, controlled with a dispenser of ±1 μl sensitivity. Gentle stirring was maintained during the experiments. Figure 1b shows the inverse potentiometric titration of microgel particles and the reference curve corresponding to NaOH solution. It is of interest to note that the reference and microgel data coincide for acid pHs, indicating the excess of H^+ ions. The charging–discharging of the carboxyl groups take place at the region where both curves are different: charging and discharging processes occur when the medium pH increases or decreases, respectively. From the difference between the microgel and reference curves, the charge density is extracted (see Fig. 1c). The surface charge increases as the pH increases due to the ionization of the carboxyl groups. Although at pH values close to 4 the microgel particles are completely discharged, the colloidal dispersion is stable due to the steric barrier and the low Van der Waals attraction for soft particles [11].

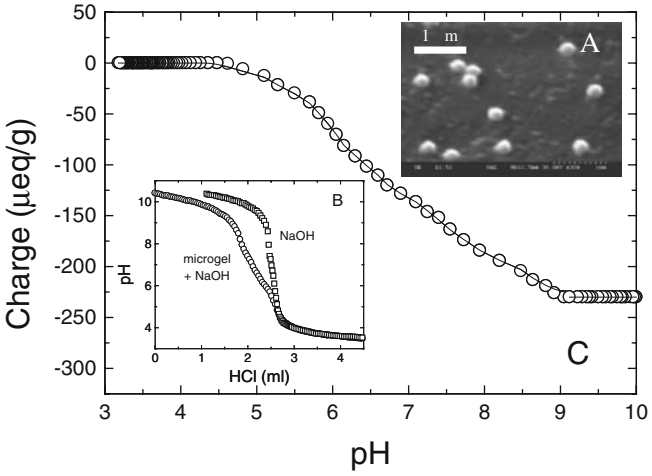

Fig. 1 **a** Scanning electron microscopy picture of the microgel particles. **b** Potentiometric inverse titration of the microgel particles and the reference curve (NaOH). **c** Charge of microgel particles vs pH

Experimental methods

DLS was employed to determine the microgel particle size, using a Malvern *4700* system with a He–Ne laser operating at 632.8 nm wavelength. The time correlation function of the scattered intensity $\langle I(0)I(\tau)\rangle$ was recorded at fixed scattering angle (θ=40°), wherefrom the mean hydrodynamic diameter was calculated by standard cumulant analysis. Sample temperature was set for 20 min before every measurement.

Electrophoretic mobility measurements were performed with a Zetasizer-Z (Malvern Instruments). This technique is based on the comparative phase analysis of the light scattered from the colloidal dispersion (scattering angle, θ=17°) and a well-known frequency reference beam [12]. The phase difference rate of change is related to the particle velocity and, therefore, to the electrophoretic mobility. To guarantee simple scattering conditions, the scattered intensity I was measured for different particle concentrations (Fig. 2). The maximum probability of multiple scattering is reached for maximum refraction index contrast. Thus, the experimental conditions were established for collapsed particles. A linear relation between scattered intensity and particle concentration guarantees single scattering. In this study, a working concentration of 0.02 %wt was set for all experiments.

Results and discussion

The electrophoretic mobility of a spherical polyelectrolyte-coated particle results from the competition between electrostatic and frictional forces [13]. An increase of the electrostatic force or a decrease of the friction coefficient reverts on higher particle mobility. Figure 3 plots the mean

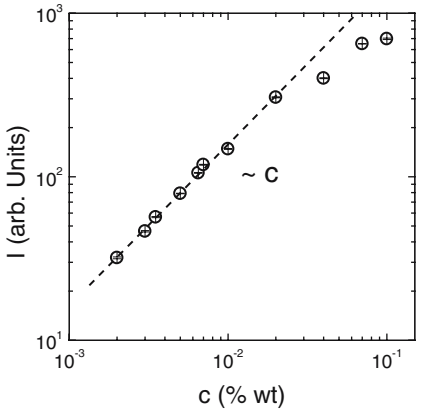

Fig. 2 Particle concentration dependence of the scattered intensity for microgel at deswollen state (T=45°C). The linear dependence under simple-scattering conditions is shown

particle size vs pH. The pH was fixed with buffers (open symbols) and in the absence of them (solid symbols). Anionic buffers were chosen to avoid extra electrostatic components. Measurements were performed at T=20 °C (swollen state) and T=45 °C (collapsed state). Any systematic pH dependence was detected, concluding that any hydrodynamic effect can be attributed to particle size changes.

Figure 4 plots the electrophoretic mobility of microgel particles vs pH, for the collapsed (A) and the swollen (B) states. The pH was fixed using several buffers (open symbols): (1) AcH/AcNa for 4<pH<6 (region I), (2) $NaH_2PO_4/NaHPO_4$ for 6<pH<8 (region II), and (3) $H_3BO_3/NaB(OH)_4$ for 8<pH<10.5 (region III). Additionally, the experiments were conducted without any buffer (solid symbols), using strong acid and bases to set the pH. The total ionic strength was the same in both cases, with and without buffer. It was carefully maintained constant by the addition of NaCl.

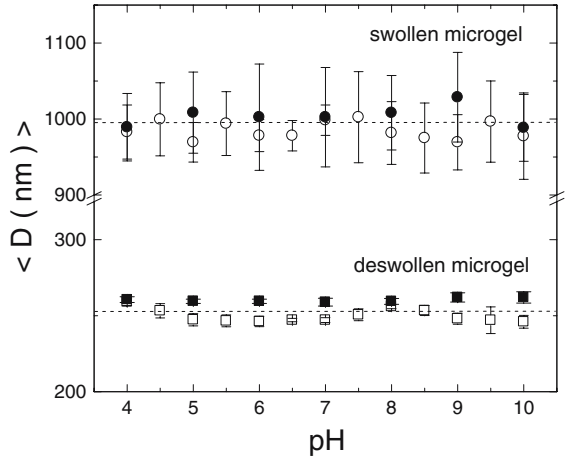

Fig. 3 Mean particle diameter vs pH for microgel particles at the swollen and deswollen states. The pH was fixed with buffers (*open symbols*) and without them (*solid symbols*)

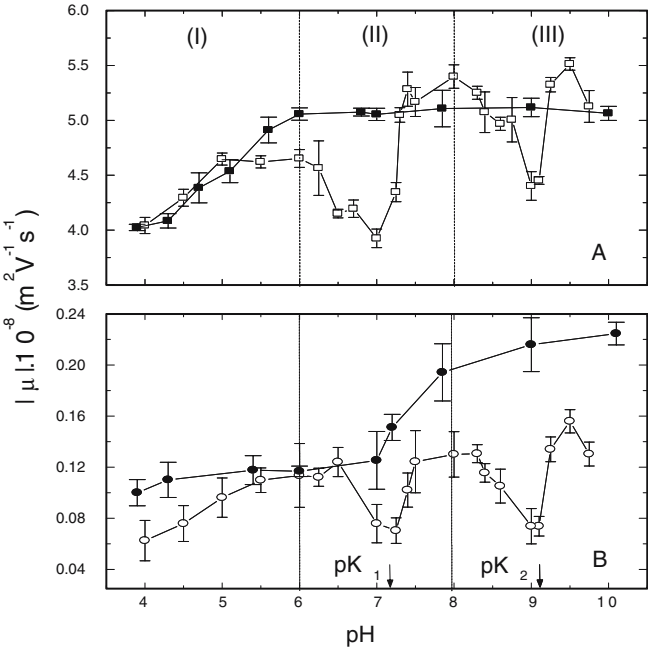

Fig. 4 Electrophoretic mobility μ vs pH for microgel particles at deswollen (**a**) and swollen states (**b**). The pH was fixed with buffers (*open symbols*) and without them (*solid symbols*). The minima account for the buffer effect and display its minimum value at the corresponding buffer pK

In the absence of buffers, μ raises monotonically as a consequence of the increasing surface charge provoked by the ionization of the carboxyl groups. Although the general trend of both swollen and collapsed curves is similar, a shift between them of around 2.5 pH units becomes apparent. The balance between electrostatic and frictional forces is responsible for this effect. The pH should increase to guarantee the charge effect to dominate over the frictional force. Consequently, the mobility should increase. This displacement can be also affected by the temperature effect on the carboxyl pKa value.

The observed behavior is similar for both states because the particle morphology remains unchanged, a nondraining core surrounded by a polyelectrolyte shell [6]. The only difference is a scale factor for the absolute μ values, extremely small for swollen microgels. Two factors contribute to this scale factor: (1) at the swollen state, the charge density is low; (2) the nondraining character of the PNIPAM microgel network provokes an increasing frictional force when particles deswell.

On the other hand, three regions are defined in Fig. 4 in presence of buffers. In region I, the particle mobility increases with the pH, while in regions II and III, two remarkable minima appear. In both cases, for low pH (region I), the buffer does not introduce any significant additional effect. This fact is a consequence of the low surface charge density exerting a weak electrostatic interaction over counterions. In region I, the μ–pH

behavior is controlled by the electrostatic force arising from the carboxyl groups ionization [14] because any relevant change of the frictional force was detected (Fig. 3).

In regions II and III, two well-defined minima are observed, corresponding to the pK value of the buffer used for each pH range:

$$(II) H_2PO_4^- \leftrightarrow HPO_4^{-2} + H^+ pK_1 = 7.2$$
$$(III) B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ pK_2 = 9.2$$

Both minima are somewhat unexpected because the electrophoretic mobility should increase or remain constant (depending on the microgel state) according to the charge variation against the pH. Each minimum is analyzed by dividing it in two zones, below and above the pK, in which the mobility decreases and increases, respectively. The observed behavior coincides with the buffer capacity, which reaches a maximum value at pH=pK. The buffer capacity keeps low salt concentrations, Na_2HPO_4 (II) and $NaB(OH)_4$ (III) below the pKs, while when pH≥pKs the concentration is higher (the salt concentration rises with the pH).

At pH<pKs, we propose that small counterions (Na^+) coming from the salt dissociation access to the shell region where large coions $\left(HPO_4^{-2} \text{ or } B(OH)_4^-\right)$ do not penetrate. This fact causes a partial charge screening and consequently, the effective surface charge reduces. The absolute μ value should decrease as observed in Fig. 4 for pH<pKs. This mechanism is induced by the soft character of the polyelectrolyte shell and the large size difference between counter and coions. Two arguments support this explanation: (1) the effect disappears in the absence of buffer (solid symbols) and (2) buffers do not introduce any anomalous effect on, for instance, polystyrene suspensions surrounded by nonionic surfactant layers [7] or bare polystyrene particles [8].

The complete screening of the fixed charge by an increasing concentration of counterions inside the polyelectrolyte shell is not possible because of the equilibrium of the penetrable ions in between inner and outer regions of the polymer shell. According to this picture, screening occurs mainly at the inner zones of the polyelectrolyte layer, although the counterions should be partially located at the mesh pores and at the diffuse layer. The screening effect is maximum at pH=pKs, where the counterion concentration (controlled by the buffer capacity) is large enough to saturate the polyelectrolyte layer.

For pH>pKs, the charge screening allows coions to be pushed towards the surface by electrostatic repulsions. When coions approach to the particle surface, counterions are spelled from the surface due to the coion excluded volume (where counterions cannot penetrate). The negative surface charge becomes exposed and the coions are repelled, leading the particle charge to be recovered. According to this mechanism, the electrophoretic mobility must increase as observed in Fig. 4 for pH>pKs. This mechanism is even more relevant for increasing pH because the increase of the buffer salt concentration reinforces the electrostatic repulsion of coions. Figure 4b shows that at the swollen state, μ does not reach the μ value expected in absence of buffer. This fact indicates that particle charge is not completely recovered. This effect can be a consequence of the large extent of the shell, making less effective the counterions repulsion by coion excluded volume effect.

Conclusions

The effect caused by buffer solutions on the electrophoretic mobility of PNIPAM microgel particles is discussed. The anomalies are associated to the soft character of the polyelectrolyte shell together with the large-size difference between counter and coions. This fact induces an electrophoretic mobility reduction for pH<pKs, followed by a further increase for pH>pKs. The minimum value is achieved when pH=pKs, just when the buffer salt concentration is high enough. Two different mechanisms have been proposed to explain such behaviors. Below the pKs, the small counterions penetrate into the charged shell causing a partial charge screening, which induces μ reduction. Above the pK values, the ionic distribution is balanced by coions approaching towards the particle surface. This leads the particle charge and, hence, the mobility to be recovered.

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