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Interaction of Monodisperse Poly(*N*-isopropylacrylamide) Microgel Particles with Sodium Dodecyl Sulfate in Aqueous Solution

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A thermodynamic analysis of ionic surfactant solutions in equilibrium with polymer solutions, polymer microgels, and macrogels is given. It is concluded that the surfactant binding isotherm cannot be exactly calculated only from the total and equilibrium surfactant concentrations. An additional trace probe electrolyte method is suggested for the determination of the binding isotherm. The interaction of sodium dodecyl sulfate with poly(*N*-isopropylacrylamide) microgel particles was investigated by dynamic light scattering, electrophoretic mobility, and surfactant binding isotherm measurements. The interaction of the surfactant with the microgel particles takes place in a two-step process. The surfactant binds above a critical surfactant concentration; then, after a plateau is reached a new binding step evolves in the isotherm. The hydrodynamic diameter of the particles also increases in a stepwise manner in correlation with the binding isotherm. The microgel−surfactant interaction is interpreted by means of polymer−surfactant interaction theories. The surfactant binds in the gel as small aggregates with different aggregation numbers in the two binding steps, which is a consequence of the inhomogeneous inner structure of the particles. The binding starts in an outer shell of the particles followed by surfactant binding in the particle core.

Introduction

Several studies have been reported in the past decade on stimuli-responsive hydrogels, which can change their swelling and shrinking in response to external stimuli. The discovery of a discontinuous volume phase transition in gels, which is often called a collapse transition, has rendered such soft materials technologically useful.[1−4] The stimuli that have been investigated to induce changes in polymer gels are diverse, and they include temperature, pH, solvent and ionic composition, electric field, light intensity, and an introduction of specific molecules such as surfactants.

Poly(*N*-isopropylacrylamide) hydrogel, abbreviated as PNIPAM gel, is one of the most frequently studied temperature-responsive hydrogels. PNIPAM gels have negative thermosensitivity resulting in a remarkable shrinking with increasing temperature. A noncontinuous collapse transition takes place around 34 °C. The interaction of surfactants (mainly sodium dodecyl sulfate, NaDS) with PNIPAM has been studied in polymer solutions,[5−10] in macrogels,[11−15] and in microgel latexes.[16−21] Ionic surfactants bind to the polymer (either it is in the form of polymer coils or cross-linked gel) above a critical concentration (cac) resulting in the formation of a polyelectrolyte type polymer−surfactant complex. The electrostatic interactions between the bound surfactant ions result in an increase of the hydrodynamic volume[5,7] and the cloud point[5] of the polymer as well as the swelling and the increase of the critical collapse temperature[16,18,19,21] of the gel.

One of the most important thermodynamic measurements is the determination of the binding isotherm of the surfactant on the gel or polymer. On one hand, this function is necessary to the interpretation of several physicochemical and scattering measurements. On the other hand, the isotherms provide general information about the way of binding (e.g., monomer binding or micellelike collective interaction) and the standard free energy change of the interaction.

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Surfactant binding measurements on gels are rare, and the results are contradictory.[17] Abuin et al.[18] studied the interaction between NaDS and PNIPAM microgel particles. Surface tension measurements indicated that the shape of the binding isotherm was similar to that of the polymer−surfactant systems. The interaction starts from a critical surfactant concentration (cac ≈ 1 mM), and there is no further surfactant binding above a second critical concentration as is the general experience in the case of surfactant−(free) polymer interaction.[22,23] However, Mears at al.[17] did not find a well-defined cac for the NaDS binding in PNIPAM microgel. Following a slight binding, the bound amount sharply increased above 3 mM equilibrium NaDS concentration. A further increase was experienced in the binding when the equilibrium surfactant concentration exceeded the critical micelle formation concentration (cmc).

Mylonas at al.[10] investigated the interaction between NaDS and PNIPAM polymer by the equilibrium dialysis method. They estimated a cac value that was similar to the one found previously in the case of PNIPAM microgel though this value seems to be adapted from ref 9 rather than determined from the dialysis experiments.

The discrepancies in these investigations can be attributed to different reasons. There may be a difference in the interaction depending on whether the polymer is in the form of free coils, macrogel, or microgel latex particles. The differences in the sample preparation, for example, the degree of cross-linkage and the type of the cross-linking monomer, may play a role as well. The sound base for the evaluation of the different experimental methods used to calculate the surfactant binding isotherm is also missing. The general route of calculating the bound surfactant amount as a difference of the total and equilibrium surfactant concentration seems to be trivial, but, as it will be shown in this work, is erroneous.

To investigate the role of the above-mentioned parameters, the first step is to give a consequent definition of the binding isotherm and an exact way to calculate it from experiments. In this work, an analysis is given to explore the relation of the bound surfactant amount to measurable quantities and the results are applied for studying the interaction of NaDS with PNIPAM microgels.

Experimental Section

Materials. For the preparation of the microgel, *N*-isopropylacrylamide (NIPAMM), methylenbisacrylamide (BA), ammonium persulfate (APS), and sodium dodecyl sulfate (NaDS) were used. These chemicals were provided by Aldrich and were used for the preparation without further purification. Our procedure was based on the method developed by Wu et al.[24] Fourteen grams of NIPAMM, 1.4 g of BA, and 94 mg of SDS were dissolved in 470 mL of distilled water. The temperature of the reactor was kept at 60 °C, and the solution was intensively stirred. To remove oxygen, nitrogen gas was purged through the solution for 30 min. Then, 0.28 g of APS dissolved in 30 mL of water was mixed to the solution and the reaction mixture was intensively stirred for 4 h. The PNIPAM latex was purified from unreacted monomers and surfactant by dialysis against distilled water for 4 weeks.

Determination of the Surfactant Binding Isotherm. A series of solutions with different SDS concentrations at a constant microgel concentration (10^{-2} g dry gel/cm^3) was prepared. After equilibrating the solutions, the microgel particles were separated by centrifugation at 20 000 rpm by means of a MOM (Hungary) ultracentrifuge. The surfactant concentration of the supernatant solution was determined by a two-phase titration with cetyltrimethylammonium bromide solution in the presence of bromophenol blue indicator. At the endpoint, the indicator can be extracted from the aqueous phase into chloroform. The standard error of the SDS concentration determined by the two-phase titration method is ±0.05 mM.

Trace Probe Electrolyte Measurements. NaI was used as an inert probe electrolyte[25] which does not bind to the polymer or to the surfactant. The electromotive force (emf) values of the following galvanic cell were determined by means of a Radelkis research pH meter at 25.0 ± 0.1 °C:

Na-glass | 10^{-4} M NaI, c NaDS,

c_p PNIPAM microgel | Ag | AgI

It was experimentally checked that the iodide ion electrode was not sensitive to the presence of the PNIPAM microgel and the surfactant ions.

The measured emf values can be given by the following equation:[25]

$$E(c_{\mathrm{NaDS}}) = E(\mathrm{cac}) + \frac{kT}{e} \ln \frac{c_{\mathrm{Tr,e}} c_{\mathrm{e}}}{\langle \mathrm{Tr} \rangle \mathrm{cac}}$$

where $c_{\mathrm{Tr,e}}$ is the equilibrium concentration, $\langle \mathrm{Tr} \rangle$ is the analytical concentration of the probe electrolyte, and c_e and cac are the equilibrium concentration and the critical aggregation concentration of the surfactant, respectively. Using this equation, the $\langle \mathrm{Tr} \rangle / c_{\mathrm{Tr,e}}$ values were calculated. The calculation of the binding isotherm from these measurements is discussed in the next section.

Static and Dynamic Light Scattering Measurements. Static and dynamic light scattering measurements were performed by means of Brookhaven dynamic light scattering equipment consisting of a BI-200SM goniometer and a BI-9000AT digital correlator. An argon-ion laser (Omnichrome, model 543AP) operating at 488 nm wavelength and emitting vertically polarized light was used as the light source. The signal analyzer was used in real-time "multi tau" mode. In this mode, the time axis was logarithmically spaced over a time interval ranging from 0.1 μs to 0.1 s and the correlator used 218 time channels. The pinhole was 100 μm.

Electrokinetic Measurements. The electrophoretic mobility of the microgel particles was determined by laser Doppler electrophoretic equipment (Malvern Zeta Sizer, version PCS). The PNIPAM microgel particles were found to be negatively charged. The electrophoretic mobility was $(-1.45 \pm 0.046) \times 10^{-4}$ cm^2 V^{-1} s^{-1} and $(-0.903 \pm 0.035) \times 10^{-4}$ cm^2 V^{-1} s^{-1} at 5×10^{-4} and 1×10^{-3} M ionic strength, respectively. The mobility of the ion-exchanged gel particles was -2.05×10^{-4} cm^2 V^{-1} s^{-1}. At 1×10^{-3} M NaCl concentration, practically the same mobility (-1.0×10^{-4} cm^2 V^{-1} s^{-1}) was measured by Snowden et al.[26] on PNIPAM latex particles prepared with carboxy initiator. The mobility of the gel particles was determined in the function of the NaDS concentration.

Determination of the Analytical Charge. The total analytical charge of the gel particles was determined by conductometric titration of the latex with NaOH solution. Prior to the titration, the microgel sample was purified by mixed bed anion−cation exchange,[27] by a similar method that has been used in the case of latex dispersions for the elimination of the ionic contaminants and to convert the latex into acidic form.

Binding Isotherm. In principle, a microgel latex can either be considered as a two-phase system (a gel phase in equilibrium with a solution phase) or as a one-phase system. For the thermodynamic description of the microgel, a gel-free solution in equilibrium with the latex can be used as a reference system (Figure 1).

The mass balance of the surfactant distributed in different molecular forms (as free monomers, polymer bound surfactants, and "free" micelles) in the microgel latex can be given as

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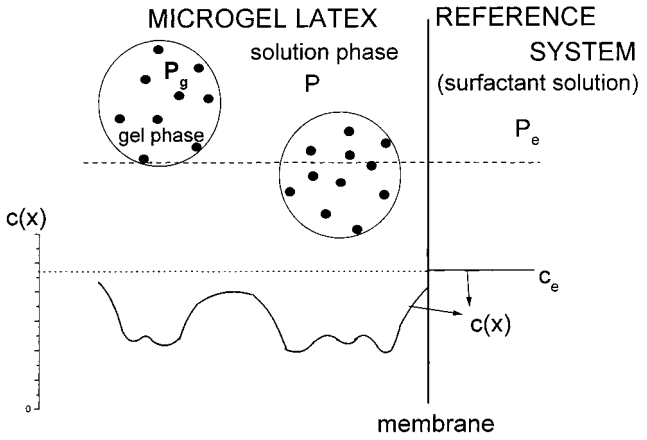

Figure 1. Scheme of the microgel latex−ionic surfactant system in equilibrium with a polymer-free reference solution. The solid spheres represent the surfactant aggregates bound in the microgel particles, and the $c(x)$ function denotes the local concentration of the free surfactant ions.

$$c_0 V = (\langle S \rangle + c_{mic})V + Bc_p V \tag{1}$$

where c_0 is the total (analytical) surfactant concentration, $\langle S \rangle$ is the volume average free surfactant monomer concentration, V is the volume of the system, c_{mic} is the concentration of the surfactant micelles, c_p is the polymer concentration (mass/volume), and B is moles of the bound surfactant per unit mass of polymer.

Equation 1 defines the bound surfactant amount B, but the quantity in brackets $\langle S \rangle$ cannot be measured. The experimentally available quantities are the mean surfactant activity in the microgel latex ($a_\pm$) and either the mean surfactant activity ($a_{\pm e}$) or the surfactant concentration (c) of the gel-free reference solution in equilibrium with the latex. In what follows, we discuss the relation between B and the measurable quantities.

The equilibrium condition is the invariance of the mean chemical potential of the surfactant electrolyte in the latex ($\mu_\pm$) and in the gel-free equilibrium solution ($\mu_{\pm e}$). The mean chemical potential of the surfactant electrolyte in the latex can be expressed as

$$\mu_\pm = \mu_\pm^\circ + kT \ln a_\pm \tag{2}$$

where $\mu_\pm^\circ$ is the standard state chemical potential defined at temperature T and pressure p. If the partial molar volume of the surfactant electrolyte ($\bar{V}_\pm$) does not depend on the pressure, then

$$\mu_{\pm e} = \mu_\pm^\circ + (p_e - p)\bar{V}_\pm + kT \ln a_{\pm e} \tag{3}$$

where p_e is the pressure in the reference system. It can be shown that the pressure term is negligible compared to the activity term in eq 3 because the pressure difference between the latex and its equilibrium solution is small (say less than 1 atm).

If the above neglect is justified, the equilibrium condition can be expressed as $a_\pm \cong a_{\pm e}$ and the mean activity can be given by means of the gel free solution as

$$a_{\pm e} = \gamma_{\pm e}(c_+ c_-)^{1/2} \approx c_e \tag{4}$$

where the symbols refer to a polymer-free surfactant solution in equilibrium with the gel−surfactant−solvent system. c_+ and c_- are the concentration of the surfactant monomer and its counterion, respectively. Using the notation $c_+ = c_- = c_e$ and taking into account that the equilibrium solution is a dilute surfactant solution ($\gamma_{\pm e} \approx 1$), the mean activity of the surfactant electrolyte can be approximated by c_e called equilibrium monomer concentration. Note that c_e is the surfactant monomer concentration and not the total surfactant concentration (c) of the equilibrium solution. This is important if the equilibrium concentration c exceeds the critical micelle formation concentration (cmc) in the gel-free reference system and micelles form. In this concentration range, $c = c_e + c_{mic,Ref} \approx$ cmc $+ c_{mic,Ref}$.

Taking into account only the electrostatic interactions, the relation between $\langle S \rangle$ and c_e can be formally expressed as

$$\langle S \rangle = \frac{c_e}{V}\int_V e^y \, dV' = c_e\langle e^y \rangle \tag{5}$$

where $y = e\psi/kT$ is the reduced electric potential with a reference potential chosen as $\psi = 0$ in the polymer-free reference system and V is the volume of the system concerned. y and the surfactant ion concentration are the local function of the space coordinates as it is schematically depicted in Figure 1. The concentration of the surfactant anions is smaller than c_e in the vicinity of the negatively charged surfactant aggregates due to the electrostatic repulsion. Consequently, $\langle e^y \rangle$ may be significantly smaller than unity. Rewriting eq 1 by means of eq 5, we get the following equation:

$$c_0 = c_e\langle e^y \rangle + c_{mic} + Bc_p \tag{6}$$

The binding isotherm is defined as the $B(c_e)$ function. As a route, B is generally calculated from the relation[10,17,18]

$$B = \frac{c_0 - c}{c_p} \tag{7}$$

and plotted against c, the total equilibrium surfactant concentration.

In a comparison of eq 7 to eq 6, the following can be stated: (i) the calculated B values can be accepted as an approximation if $c <$ cmc when $c \approx c_e$ (the error of B changes with the volume fraction of the gel and with the bound surfactant amount via the value of the $\langle e^y \rangle$ term); (ii) if $c >$ cmc, the calculated B is not the bound amount of the surfactant, since $c_{mic} \neq c_{mic,Ref}$; (iii) plotting B against c has no thermodynamic significance above the cmc because $c \neq c_e$.

The surfactant concentration of the equilibrium solution can be determined by analyzing the supernatant solution separated from the microgel particles by ultrafiltration, by ultracentrifugation[17] (supposing that the separation does not influence the equilibrium), or by the equilibrium dialysis method.[10] The separation of the microgel latex from the equilibrium solution is not necessary. Potentiometric measurements with two reversible electrodes for the surfactant ion and its counterion yield directly the mean surfactant activity (c_e) independently of the investigated concentration range. It is important to note that a surfactant-sensitive electrode cannot be applied against a reference electrode connected to the latex via a salt bridge because of the anomalous diffusion potential (the so-called suspension potential[28]) in the presence of colloid electrolytes.

To determine the binding isotherm, the $\langle e^y \rangle$ term in eq 6 must be determined from independent measurements. Recently, we have suggested a method for the determination of $\langle e^y \rangle$ from activity measurements on a probe electrolyte added to the system in a trace amount. If the probe electrolyte does not bind specifically to the polymer or to the surfactant and its concentration is negligible compared to that of the surfactant, we can write eq 5 for the anion of an added 1:1 probe electrolyte as $\langle \mathrm{Tr} \rangle = c_{e,\mathrm{Tr}}\langle e^y \rangle$, where $\langle \mathrm{Tr} \rangle$ and $c_{e,\mathrm{Tr}}$ are the total (analytical) and the equilibrium concentration of the probe anions, respectively. Using this equation, $\langle S \rangle$ can be given in the following form:

$$\langle S \rangle = \frac{c_e}{c_{e,\mathrm{Tr}}}\langle \mathrm{Tr} \rangle \tag{8}$$

This means that if in addition to the equilibrium surfactant concentration (c_e) we measure the equilibrium concentration of a probe electrolyte, the exact binding isotherm can be calculated.

Another possibility to calculate B from eq 6 is to perform the measurements in the presence of a large amount of inert electrolyte when $\langle e^y \rangle \approx 1$. However, in this case the investigated system is different from the salt-free one because the presence

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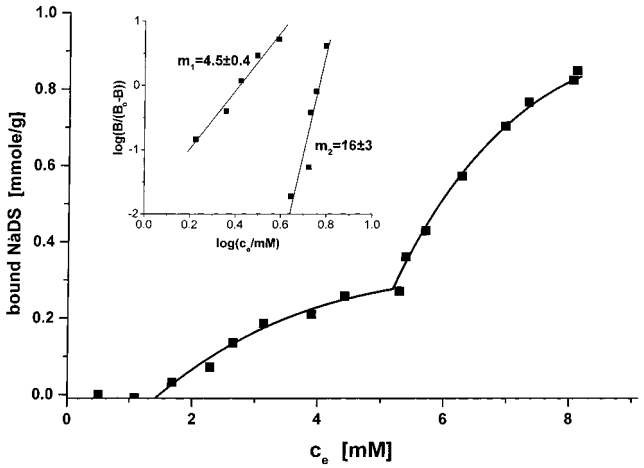

Figure 2. Binding of NaDS in PNIPAM microgel particles. In the inset, the binding isotherm is represented according to eq 9.

of a foreign electrolyte may influence the interaction between the polymer and surfactant.

The above discussion was restricted to the interaction of the ionic surfactants with electrically neutral gels (polymers). In the case of polyelectrolyte solutions or polyelectrolyte gels, an ion-exchange process must also be taken into account. In these cases, the determination of the binding isotherms requires further analysis. It should also be stressed that in eq 5 only electrostatic interactions were involved. However, the surfactant ions may be excluded from the vicinity of the polymer due to nonelectrostatic interactions (e.g., because of the preferential sorption of water). This exclusion theoretically results in negative B values at low surfactant concentrations where the surfactant does not bind to the polymer. Negative surfactant binding (exclusion of the surfactant) was detected below the critical interaction concentration for poly(vinyl alcohol) macrogel and alkyl sulfate systems.[29]

Results and Discussion

In Figure 2, the isotherm of the NaDS binding on a strongly cross-linked PNIPAM microgel is plotted. The bound amount of NaDS was calculated from eqs 1 and 8 in the concentration range $c_e <$ cmc when $c_{mic} \approx 0$. The difference between $\langle S \rangle$ and c_e was found to be significant (up to 50% depending on the bound surfactant amount). The correction of c_e influences only the numerical values of the bound amount but does not change the shape of the isotherm. The isotherm shows a stepwise surfactant binding. The surfactant starts to interact with the gel at around 1 mM equilibrium surfactant concentration (cac_1). A similar critical interaction concentration was found for the interaction between NaDS and PNIPAM polymer.[9] At 5 mM equilibrium surfactant concentration, the isotherm shows a second binding step (cac_2). Stepwise binding has not been reported for the NaDS−PNIPAM polymer or for the NaDS−PNIPAM microgel latex system in the literature.

The existence of the critical interaction concentration is thermodynamic evidence for the collective interaction of the surfactant molecules. Theoretically, stepwise surfactant binding can be predicted in the case of polymer mixtures or certain copolymers that contain two types of well-separated binding sites of different interaction energy[30] (e.g., in the case of block copolymers). Actually, as far as we know, a two-step isotherm has not been observed in the case of ordinary polymers. The PNIPAM microgel can be regarded as a copolymer in which the *N*-isopropylacrylamide monomer and the cross-links containing acrylamide units may represent two kind of binding sites. If the cross-links are statistically distributed in the microgel particles, one may expect homopolymer behavior with a mean interaction energy. However, polymerization kinetics[31,32] and structural investigations[33] on the microgel particles suggest that the segment distribution inside the particles is not homogeneous. The structure of the microgel particles can be represented with a core/shell architecture. The gel particles contain a less hydrophobic core with a higher cross-link density (rich in acrylamide monomers) and a loose, more hydrophobic shell (rich in isopropylacrylamide monomers). It is a general qualitative experience that the more hydrophobic the polymer the smaller the critical interaction concentration. It can be qualitatively predicted that the surfactant starts to interact in the more hydrophobic shell of the microgel particles at a similar critical concentration as in the case of PNIPAM polymer followed by the interaction in the core at a higher surfactant activity.

In what follows, we describe the interaction between the surfactant and the gel by means of recent theories of polymer−surfactant interaction (27):

$$\ln \frac{B}{B_0 - B} = -\overline{\Delta G^\circ_{aggr}}/kT + \bar{m} \ln x_e \qquad (9)$$

where B_0 is the saturated bound amount of the surfactant, $\overline{\Delta G^\circ_{aggr}} = \overline{G^\circ_{aggr}} - \bar{m}\mu^\circ$ is the standard free energy of the mean surfactant aggregate formation, $\bar{m}$ is the mean aggregation number, and x_e is the mole fraction of the surfactant monomers. As a first approximation, we treat $\bar{m}$ as a constant and neglect the change of the electrical free energy contribution in $\overline{\Delta G^\circ_{aggr}}$ with the ionic strength. By application of eq 9 for the first and second step of the binding process, the thermodynamic parameters of the interaction can be calculated. The B_0 value of the first binding step was estimated from the binding isotherm (as 0.25 mmol/g from the first plateau of the isotherm). This value was extracted from the total isotherm to get the second binding process. The B_0 value of the second binding process was calculated from the saturated bound amount near the cmc. In the inset of Figure 2, the representation of the isotherm according to eq 9 is given. The mean aggregation number can be estimated as $m_1 = 4-5$ with (-9.96 ± 0.05) kT standard free energy change per surfactant molecule for the first binding process. In the second binding step, the aggregation number is higher ($m_2 \approx 16$) with a smaller driving force (-9.16 ± 0.10) kT. The aggregation number of the polymer-bound surfactant is smaller than that of the free micelles ($m_{mic} = 56$)[34] according to the general experience.

Mears at al.[17] investigated the NaDS−PNIPAM microgel system with small-angle neutron scattering (SANS) at two surfactant concentrations. It was concluded that the bound surfactant existed as small aggregates of less than five monomer units in agreement with our result for the first binding step. Larger aggregates were not found, and the binding isotherm was monotonically increasing. However, the microgel samples cannot be compared because an important parameter, the amount of the cross-linking monomer, was not reported.

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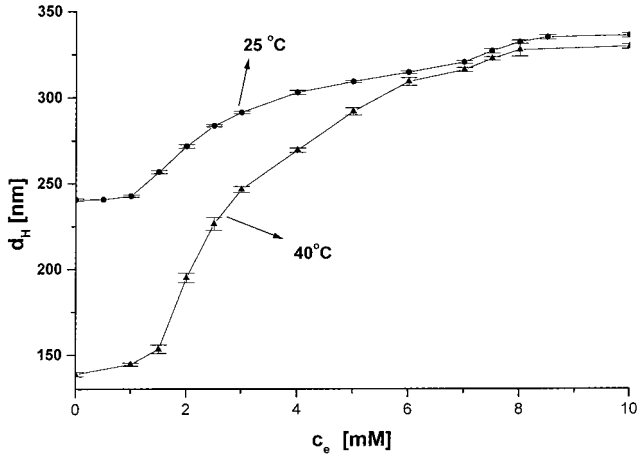

Figure 3. The hydrodynamic diameter of the microgel particles against the NaDS concentration above and below the collapse temperature of the microgel.

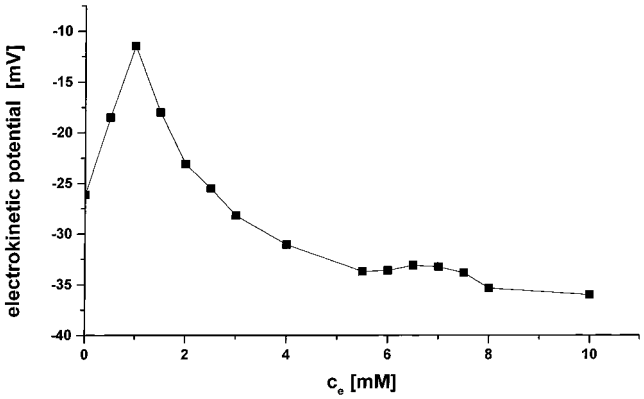

Figure 4. The electrokinetic potential of the microgel particles against the NaDS concentration.

Mylonas and Staikos[10] calculated the aggregation number of the NaDS bound on PNIPAM polymer from fluorescence-quenching measurements. The aggregation number was 7−8 in the concentration range from 2.5 to 6 mM (total surfactant concentration at 0.25% polymer concentration) and then increased up to 22 as the surfactant concentration was further increased. This result is similar to our finding, though we do not expect agreement between the polymer and the highly cross-linked microgel. The measured binding isotherm was interpreted as a monotonically increasing function.[10] Unfortunately, the isotherm was represented in a semi-logarithmic scale of the total surfactant concentration instead of a linear function of the equilibrium concentration. In this representation, the reported data may suggest a stepwise binding but a sound conclusion cannot be drawn.

In Figure 3, the hydrodynamic diameter of the gel particles is plotted against the surfactant concentration. The particles were found to be highly monodisperse (the cumulant analysis of the dynamic light scattering measurements yielded $p = 0.02 \pm 0.01$ for the second cumulant). The change of the particle size corresponds to the binding isotherm below (25 °C) and above (40 °C) the collapse temperature. The gel particles swell above the first critical aggregation concentration which can be explained by the increasing electrostatic interaction between the negatively charged bound surfactant aggregates. Around the second critical aggregation concentration, the swelling curve shows an inflection, and above the cmc (8.2 mM) the size of the particles remains constant.

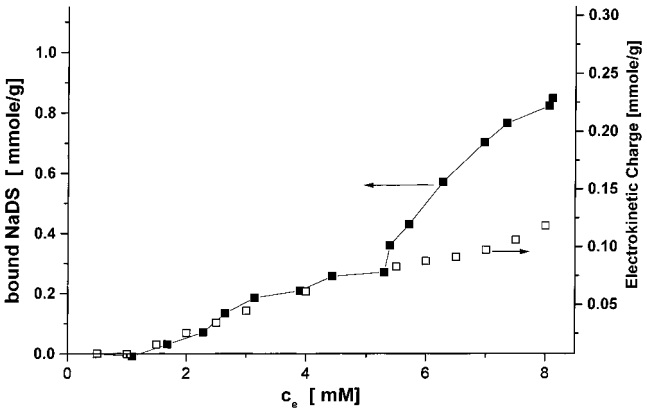

Figure 5. Comparison of the bound surfactant amount to the electrokinetic charge of the microgel particles.

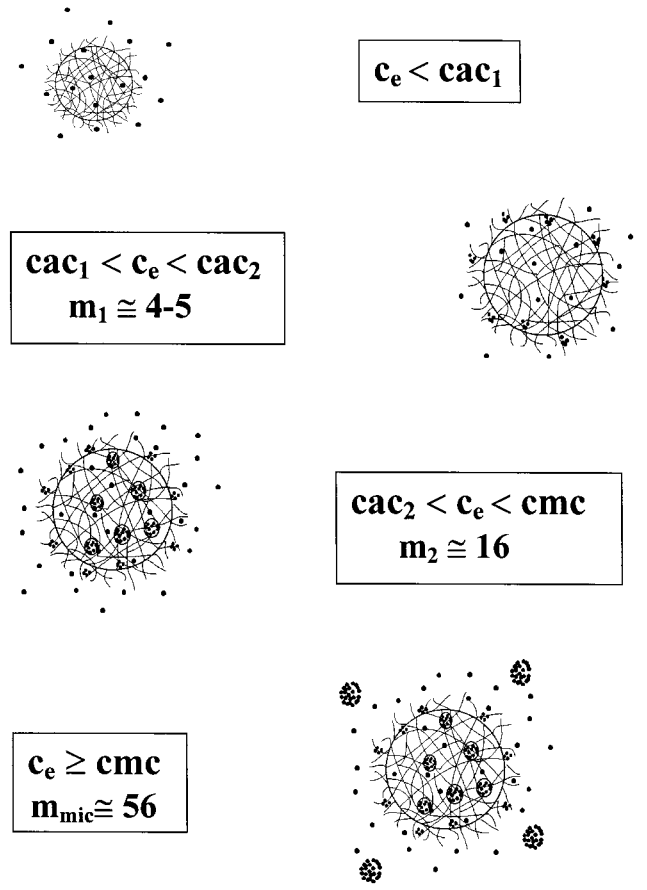

Figure 6. Schematic representation of the interaction between NaDS and PNIPAM microgel particles with increasing equilibrium surfactant concentration.

In Figure 4, the electrokinetic potential of the microgel particles is plotted against the surfactant concentration. The gel particles bear electric charges even without the addition of any surfactant. The total analytical charge of the microgel particles was found to be 1.6×10^{-6} mol negative charge per g dry gel from the conductometric titration. The charges originating from the initiator[35] are at the surface of the particles[33] likely on the terminal groups of the dangling polymer chains located in the surface layer. With increasing surfactant concentration, the absolute value of the ζ potential goes through a sharp minimum at the first critical interaction concentration.

(35) Pelton, R. H.; Pelton, H. M.; Morfesis, A. Rowell, R. L. *Langmuir* **1989**, *5*, 816.

The unusual change of the electrokinetic potential with the surfactant concentration can be interpreted by means of the relation between the surface charge density (σ) and the surface potential (ϕ_0). For small potentials,

$$\sigma = \frac{Q}{\pi d^2} = \epsilon\kappa\phi_0\left(1 + \frac{2}{\kappa d}\right) \tag{10}$$

where ϵ is the dielectric permittivity of the medium, Q is the electric charge, d is the diameter, and κ is the inverse Debye−Huckel screening length. If we apply eq 10 for the hydrodynamic particle, then $d/2$ means the hydrodynamic radius at which the potential is the electrokinetic potential and Q corresponds to the electrokinetic charge. When the surfactant concentration is below the first critical interaction concentration Q and d is constant and according to eq 10, the electrokinetic potential decreases since κ increases with the surfactant concentration. Above the critical concentration due to the binding of the surfactant anions, all of the parameters (Q, d, and κ) change resulting in an increase of the absolute value of the elecktrokinetic potential.

The electrokinetic charge of the microgel particles was calculated by means of eq 10 from the measured electrokinetic potentials and hydrodynamic diameters. The equilibrium surfactant concentration was taken as the ionic strength of the medium to calculate κ. In Figure 5, the binding isotherm is compared to the electrokinetic charge expressed in mol charge per g dry weight of the microgel particles. (The molecular weight of the latex particles was 5.8×10^8 determined from static light scattering measurements.) The electrokinetic charge starts to increase at the first critical concentration and changes in accordance with the bound surfactant amount during the first binding step. The observed net charge is about one-third of the bound surfactant amount. As can be expected, the major part of the counterions is located inside the particles and only a fraction of the bound surfactant charges are compensated in an electrical double layer around the hydrodynamic particles. However, above the second critical interaction concentration the particles electrically do not "feel" the strong increase in the bound surfactant amount. This is further evidence that the second binding process takes place in the core of the particles where the charges of the bound surfactant are screened by the counterions and practically do not affect the electrical double layer around the hydrodynamic particles.

Our results on the interaction between the PNIPAM microgel particles and sodium dodecyl sulfate are summarized in a scheme in Figure 6. Up to a critical surfactant concentration (cac_1), there is no interaction between the gel and the surfactant. Above the critical interaction concentration, the surfactant ions bind in the outer shell of the particles in the form of small aggregates resulting in the swelling of the gel particles. When the equilibrium surfactant concentration exceeds a second critical value (cac_2), the surfactant binds in the less hydrophobic core of the microgel particles with higher aggregation number. Finally, the formation of free micelles can be expected if the equilibrium surfactant concentration reaches the cmc.

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