Interaction between Covalent DNA Gels and a Cationic Surfactant

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The interaction of covalently cross-linked double-stranded (ds) DNA gels and cetyltrimethylammonium bromide (CTAB) is investigated. The volume transition of the gels that follows the absorption of the oppositely charged surfactant from aqueous solution is studied. As do other polyelectrolyte networks, DNA networks form complexes with oppositely charged surfactant micelles at surfactant concentrations far below the critical micelle concentration (cmc) of the polymer-free solution. The size of the absorbed surfactant aggregates is determined from time-resolved fluorescence quenching (TRFQ). At low surfactant concentrations, small discrete micelles ($160 < N < 210$) are found, whereas large micelles ($N > 500$) form at surfactant concentrations of 1 mM. When the DNA is in excess of the surfactant, the surfactant binding is essentially quantitative. The gel volume decreases by 90% when the surfactant to DNA charge ratio, β, increases from 0 to 1.

1. Introduction

The association between polyions and oppositely charged macroions is very favorable and has strong effects on phase stability and polyion conformations.[1−3] For instance, the binding of charged proteins, surfactant micelles, multivalent ions, and multivalent polyamines such as spermidine or spermine is known to condense large DNA coils,[4−6] resulting in (associative) phase separation in sufficiently concentrated solutions. Phase diagrams of mixed systems of DNA and cationic surfactants show a strongly associative phase separation.[7] Also, a phase map has been drawn for the aqueous system of DNA and positively charged vesicles, composed of SOS (sodium octyl sulfate) and CTAB (cetyltrimethylammonium bromide), and showed, as expected, a strongly associative phase behavior with the formation of a precipitate.[8] DNA also compacts on the surface of thermodynamically stable catanionic vesicles with a net positive charge.[8] DNA is adsorbed onto the surface of the vesicles in a collapsed globular form but expands on addition of an anionic surfactant.[7] Studies by fluorescence microscopy in solutions of both cationic and anionic surfactants reveal a compaction/decompaction process that is apparently reversible.[8,9] Melnikov and co-workers demonstrated,[10] using fluorescence microscopy, that large single DNA coils (circular T4 plasmids) respond to the binding of surfactant in an all-or-none fashion; that is, each chain was either in a swollen or in a collapsed state. The discrete volume transition took place in a narrow range of surfactant concentration, where the coexistence of coils and compact globules was observed. At this point the chains were seen to fluctuate between the two states.

Discrete transitions take place also in covalent polymer gels.[11,12] In this case the transition involves the concerted collapse (or expansion) of a large number of cross-linked chains, and therefore no fluctuations are observed.

Amiya and Tanaka[13] found a discrete volume transition for covalently cross-linked DNA gels at a certain composition of water/acetone mixtures. At about the same composition, the coexistence of DNA coils and globules was observed by others.[14]

Discrete volume transitions in gels are referred to as first-order transitions, as they show some resemblance to liquid−vapor transitions. However, the cross-linked gels show effects not present in fluids. For instance, temperature-sensitive gels are characterized by different critical temperatures for collapse and swelling.[15] The reason for this hysteresis appears to be the following. A gel behaves as a single elastic body due to long-range interactions mediated by the network.[16] The formation of a new phase is associated with a coexistence cost in network deformation energy.[17] In spherical gels the new phase always appears at the gel surface, where it forms more easily.[14] Due to geometry, the network of the collapsed phase is anisotropically deformed, but it cannot relax without deforming the coexisting phase. Therefore, during both swelling and collapse the growth of the new phase is hindered by the presence of the other phase. This shifts the transition temperature relative to that in a non-cross-linked system, but in different directions for swelling and collapse transitions.[18]

Complexes of polyelectrolyte gels with oppositely charged surfactants were intensively studied in the past decade[19−31] due to their interesting practical applications in biology, medicine/pharmacy (delivery systems), and industry.

Phase coexistence has been observed during volume transitions of polyelectrolyte gels following the uptake of surfactant ions from the solution.[30−34] The transition to the collapsed state is promoted by the favorable electrostatic interaction between the polyion and surfactant micelles. The gels studied so far have

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been made up from highly flexible polyions, that is, systems where the polyion chain has a possibility to adapt to the curvature of surfactant aggregates. The present study on DNA gives new information on a cross-linked system where the polyion lacks that possibility (the persistence length of dsDNA exceeds by far the diameter of CTAB micelles).

Recent investigations[31] show that oppositely charged pairs of polyion and surfactant form insoluble but swelling phases in the absence of salt (including their counterions), in general showing liquid crystalline order. The interaction weakens in the presence of salt, but the same type of complexation takes place once the surfactant concentration is larger than the critical association concentration (cac). No important differences between the ordered micelle structures formed with cross-linked and linear polyions have been reported so far. However, the structure and stability of the phases have important consequences for swelling and volume transition dynamics in gels. DNA has been found to form similar types of "complex salts" together with oppositely charged lipids and surfactants.[35−37] Novel phases with unique properties have been observed after mixing of such complexes (free from simple counterions) with water and oil.[38]

Phases of hexagonal (normal and inverted) and lamellar structure have been found, by small-angle X-ray scattering (SAXS), in the precipitated phase of mixtures of DNA and cationic surfactants and lipids.[39] Interestingly, micellar cubic phases, observed in a number of other systems,[30,33,34] appear to be less common with long DNA chains and have not yet been reported in the literature. One explanation for the difficulty in forming cubic phases may be that the rigid backbone of DNA is more compatible with rodlike micelles or bilayers. However, recent observations indicate that under certain conditions cubic phases can be also formed (unpublished work).

In the present paper we report for the first time on the complex formation between *covalently* cross-linked DNA and an oppositely charged surfactant, cetyltrimethylammonium bromide (CTAB). The critical aggregation concentration (cac) was found to be much lower than the critical micelle concentration (cmc) of CTAB in aqueous solution. By means of fluorescence quenching measurements we show that, depending on the conditions, either small discrete or "infinitely" large micelles (rods or bilayers) form in the gels. The DNA network−surfactant complex may constitute a possibility for many uses in medicine as drug delivery systems and for drug control during administration. Also, future development in the use of covalent DNA gels in separation seems to be a great challenge. Furthermore, these gels could be useful for separation purposes and also as a tool for investigating DNA−cosolute interactions by simply monitoring volume changes; this approach has been found to be very powerful for other polymer gels.[31,40,41]

2. Materials and Methods

Materials. Cetyltrimethylammonium bromide (CTAB) from Serva, *N*-cetylpyridinium chloride (CPC) from Merck, and pyrene from Janssen (99%+) were of analytical grade and used as supplied. Deoxyribonucleic acid (DNA) (from salmon testes, sodium salt; ∼1000 base pairs), *N*,*N*,*N*′,*N*′,-tetramethylethylenediamine (TEMED), sodium hydroxide (NaOH), and sodium bromide (NaBr), all from Sigma, and ethylene glycol diglycidyl ether (EGDE) from Aldrich, were used as supplied. All solutions were prepared with nitrogen-purged Millipore water. Single-stranded DNA from salmon testes was purchased from Sigma. This DNA is ethanol-precipitated and sonicated to produce single-stranded fragments.

Preparation of Gels. Double-stranded DNA, from salmon testes, was dissolved in water containing 3.7 mM NaBr, with a DNA concentration of 9 wt %. After the sample was mixed overnight at 35 °C, the cross-linker (EGDE) was added and the solution was vortexed for 45 min. After addition of 1 M NaOH and TEMED, the sample was mixed for another 10 min and then transferred to test tubes and incubated for 2 h in a water bath at 30 °C. Gels with 1% and 3% cross-linker were prepared in the same way. Freshly synthesized gels were neutralized and rinsed with large amounts of 1 mM NaOH solution. The DNA gels swelled considerably in the NaOH solution, and due to this fact the DNA concentration in gels is lowered. The concentration of DNA in gels equilibrated with 1 mM NaOH (reference state) was obtained by weighing gels before and after freeze-drying. A decrease in the DNA concentration from 9 wt %, at preparation time, to around 1 wt %, after immersion of the gels in the NaOH solution, was observed. The swelling characteristics of gels in surfactant-free solutions were investigated by placing gels in 1, 5, 10, 20, 50, and 100 mM NaBr solutions containing 1 mM NaOH. All samples were equilibrated in sealed containers for 1 week at 25 °C and shaken slowly during that time. CTAB/gel samples were prepared by placing cylindrical gel pieces of known mass (1−3 g) into 0.1 or 0.5 mM solutions of CTAB containing 1 mM NaOH. Different charge ratios (CR) (0.4, 0.8, 1, and 1.2) of surfactant to DNA in the system were obtained by using the appropriate volume of the solution. All samples were equilibrated in sealed containers for 4 weeks at 25 °C and shaken slowly several times during that period of time.

For fluorescence measurements with ethidium bromide, two different types of samples were prepared. In one case ethidium bromide was added to a 9 wt % DNA solution and then cross-linker and TEMED were added. The procedure of gel formation, described above, was followed and we succeeded in preparing DNA networks in the presence of ethidium bromide. In the other case, the DNA gels were synthesized following the procedure described above and then ethidium bromide was added.

Surfactant Binding and Gel Swelling. Gel pieces (ca. 1 g) were immersed in 0.50 mM CTAB solutions of volumes in the range from 38 to 90 mL, corresponding to surfactant-to-DNA charge ratios from 0.4 to 1.2. After 1 month the concentration in equilibrium with the gels was determined by use of a surfactant-sensitive electrode, as described in detail elsewhere.[42] The binding ratio β in the gels was obtained by subtracting the number of moles of surfactant in the solution from the initial amount added to the solution and then dividing by the number of moles of fixed charges in the gel. The mass of gels was determined by weighing. The relative volume change was calculated by assuming a constant gel density and expressed as V/V_0, where V_0 is the volume of the gel in pure water.

Static Fluorescence. For luminescence spectral measurements, a Spex Fluorolog 111 was used in 90° configuration. Emission spectra for the system of ethidium bromide and DNA were obtained with the monochromator set at appropriate wavelengths.

Time-Resolved Fluorescence Quenching. Fluorescence decay curves from DNA/CTAB gels containing small amounts of a fluorescent probe (pyrene) and a quencher (cetylpyridinium chloride, CPC) were recorded with the single-photon counting technique. The method and setup used have been described in detail elsewhere.[43] Gel pieces mounted vertically on the inner surface of a regular 1 cm quartz cuvette were illuminated by a pulsed laser beam ($\lambda_{ex} = 320$ nm, pulse frequency = 0.4 MHz, pulse width <1 ns). The emission from the probe, selected with an interference filter ($\lambda_{em} = 390 \pm 5$ nm), was detected front-face through the wall of the cuvette, at a low photon counting rate (<3 kHz) to avoid pile-up effects. Small amounts of the solution in equilibrium with the gel were present in the sealed cuvettes, to prevent dehydration of the gels during measurements. For each gel composition studied, one sample with and one without quencher were prepared. Both probe and quencher were mixed with CTAB prior to addition of the gel to the solution. The quencher-to-surfactant ratio was 0.010 in all samples. The pyrene to CTAB ratio was 3.7×10^{-5}. In other respects the samples were prepared in the same way as for the binding study.

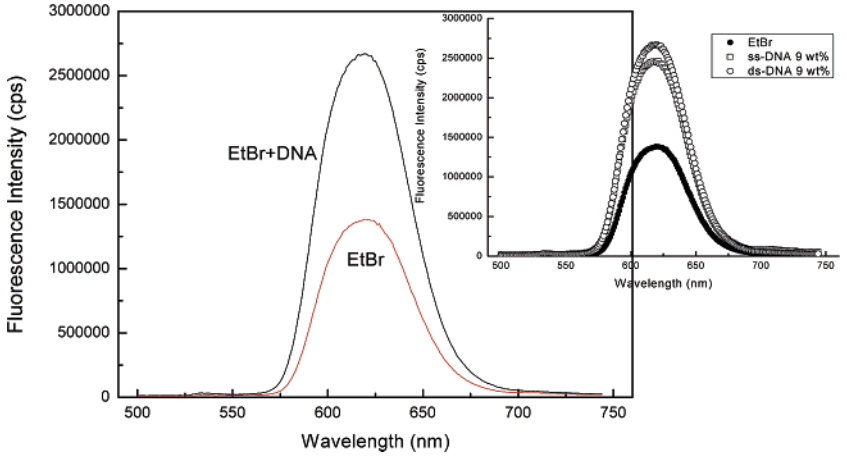

Figure 1. Fluorescence spectra of ethidium bromide in the absence and presence of DNA gel (1% cross-linker density), and in the presence of reference solutions of ds-DNA 9% and ss-DNA 9% (inset).

The fluorescence lifetime (τ_0) was measured for samples in the absence of quencher. For all samples investigated, the amounts of probe and quencher present in the aqueous subphase in the gels were negligible in comparison with that in surfactant aggregates. Furthermore, the probe was present at very low concentration to avoid self-quenching. For CPC/CTAB mixtures in the studied range of compositions, the mole fraction of quencher in the surfactant aggregates are the same as the average value (X_Q) for the whole system (gel + solution).[33,44] When discrete surfactant aggregates are at hand, this allows the aggregation number (N) to be obtained:[45]

$$N = \frac{\langle n \rangle}{X_Q} \tag{1}$$

where $\langle n \rangle$ is the average number of quenchers per micelle, determined from the decay curve. At long times after the excitation event, when the intramicellar quenching process is over, only probes in quencher-free micelles contribute to the fluorescence intensity. By assuming a Poisson distribution of the quencher among the micelles the fraction of quencher-free micelles is equal to $e^{-\langle n \rangle}$.[46] This is a very good approximation to the binominal distribution expected for mixed micelles of CPC and CTAB.[47,48] Thus, the decay curves have a characteristic single-exponential "tail" described by

$$F_{t\to\infty}(t) = F(0)e^{-\langle n \rangle}e^{-t/\tau_0} \tag{2}$$

where $F(0)$ is the amplitude of the decay curve. Importantly, eq 2 does not depend on kinetic models of the quenching process. Therefore, as long as the tail of the decay curve is single-exponential, $\langle n \rangle$ and thus N can be unambiguously determined. A conventional way to present the data is to divide the recorded decays by the function $\exp(-t/\tau_0)$ and use a logarithmic scale on the ordinate axis.[45] In this way curves with horizontal tails prove the existence of discrete micelles in the system. All quenched curves presented in this paper were treated in this way.

3. Results and Discussion

Shape and Visual Appearance of the DNA Gels. We succeeded in preparing DNA networks by cross-linking DNA, from salmon testes, with ethylene glycol diglycidyl ether (EGDE), which is a bifunctional cross-linker. As shown by another group,[49] epoxides covalently bind to the guanine bases of the DNA molecule. To these compounds, we added TEMED as an initiator of the reaction. Gels with different cross-linking densities (1% and 3%) were prepared followed the normal procedure of the gel formation described above. The experiments reported were carried out with cylindrical gel pieces of known mass (1−3 g) with a cross-linking density of 1%.

All cross-linked DNA gels in their swollen state, in equilibrium with 1 mM NaOH, were clear and transparent and had the same refractive index as water. When the gels came into contact with a cationic surfactant solution, a cloudy layer formed on the surface of the gel, and water was expelled to the bulk solution. The boundary between the collapsed surface layer and the highly swollen interior of the gel was sharp. However, the final state depended on both the concentration and the total amount of surfactant available in the solution, as will be discussed in further detail below. This type of behavior will be subsequently referred to as "regular shrinking". These observations have been made earlier by Khandurina et al.,[32] working on the reaction of cross-linked polyacrylate gels with alkyltrimethylammonium bromides, and Hansson et al.,[34] who also study the interaction of slightly cross-linked sodium polyacrylate (cl-NaPA) with cetyltrimethylammonium bromide (CTAB). Additionally, in this work, we observed that the DNA gels shrink in an irregular fashion when the surfactant concentration is higher than 0.02 mM.

Fluorescence Measurements: DNA Conformation in the Gels. Information about the conformation of the DNA molecules in the gels was obtained by fluorescence measurements with ethidium bromide. Figure 1 shows the fluorescence spectrum of ethidium bromide in the presence of the DNA gel for a DNA concentration of 9 wt %; as reference and for the same concentration, its spectrum is represented in the absence of the DNA gel. In the inset of this figure, the spectrum of ethidium bromide in aqueous solution and in aqueous solutions of double-stranded and single-stranded DNA, at the same concentration as in the gel (9 wt %), are shown. When EtBr is bound to nucleic acids, a marked enhancement in its fluorescence is observed; however, this increase depends on the configuration of the DNA. Double-stranded DNA leads to a higher increase in ethidium fluorescence intensity than single-stranded does.[50] Ethidium bromide is a dye that binds to double-stranded DNA by intercalation between the base pairs. It has been shown that ethidium bromide could form at least three types of complexes with ds-DNA and two types with ss-DNA. The strong binding of EtBr with ds-DNA corresponds to an intercalation mechanism of interaction and is characterized by a high quantum yield of fluorescence.[51] As ethidium bromide in the presence of DNA gels presents the same fluorescence intensity as in the double-stranded DNA solution, we can assume that ethidium binds to a DNA gel in the same way as it binds to ds-DNA. We conclude

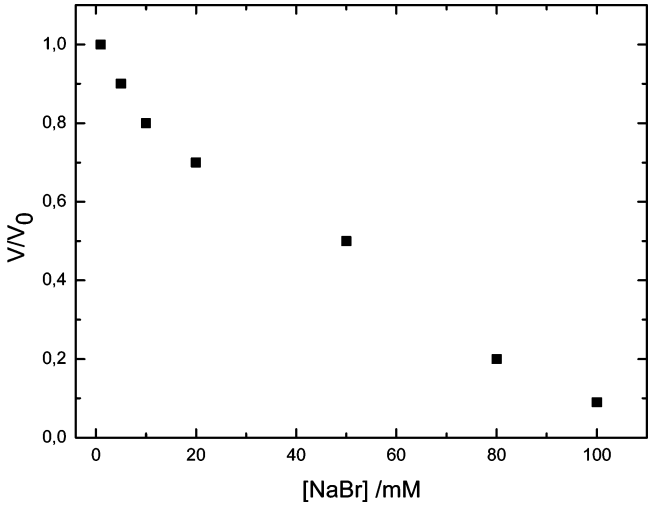

Figure 2. Dependence of relative volume (V/V_0) of DNA gels (1% cross-linker density) on NaBr concentration.

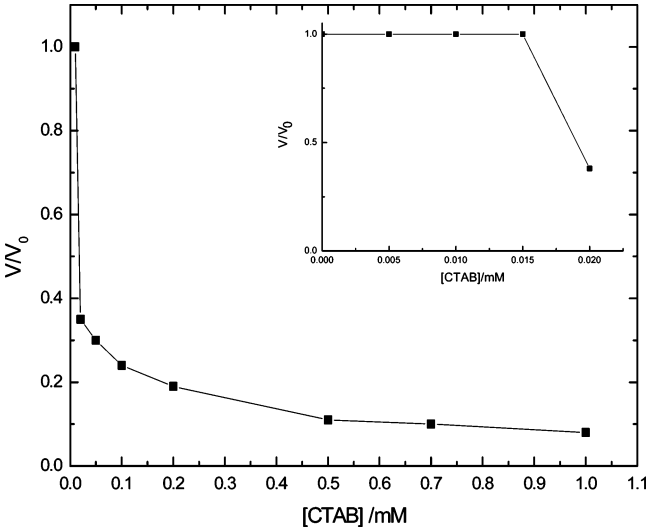

Figure 3. Dependence of relative volume (V/V_0) of DNA gels (1% cross-linker density) on CTAB concentration. The plateau from [CTAB] = 0 mM to [CTAB] = 0.02 mM (=cac) is also represented in detail (see inset).

that, for our gels, DNA molecules are in their double-stranded conformation. This was also observed for the two different samples of DNA gels prepared, described in the Experimental Section.

Gel Volume and Surfactant Binding. The DNA gels (1% cross-linker density) are highly swollen due to the osmotic pressure arising from the counterions, which are confined to the gel. On addition of an electrolyte there is a progressive contraction of the gels, as exemplified in Figure 2. Figure 2 shows the volume of the gels in the presence of salt (V), relative to the volume in pure water (V_0), as a function of NaBr concentration. When gels preswollen in 1 mM NaOH are placed into NaBr solutions at different concentrations, they shrink due to the screening effect of the salt. Contraction of the gel was observed, but here changes in volume are less drastic than in the CTAB/DNA gel system described below. It is evident that the monovalent salt NaBr must be present at considerably larger concentrations to produce the same degree of shrinking as CTAB.

The binding of a cationic surfactant results in a much more pronounced deswelling of the DNA gels. After the immersion of the swollen DNA gel in the solution of the oppositely charged surfactant cetyltrimethylammonium bromide (CTAB), the surfactant ions migrate into the network and replace the network counterions, which are released. This process is extremely favorable from the point of view of translational entropy of the counterions.[52] Adsorption of a considerable amount of CTAB ions leads to a transition of the swollen network to the collapsed state. The main reason for this transition consists of the aggregation of surfactant ions within the DNA gel due to hydrophobic interactions between their hydrocarbon chains. As a consequence of this, the mobile counterion concentration in the network decreases, leading to a significant decrease in the internal osmotic pressure in the gel. Furthermore, the surfactant aggregates will act as multivalent counterions and by ion correlation effects contribute to the contraction of the gel.[53,54] The swelling behavior was investigated in two ways. In one experiment, gels were placed in bulk solutions, that is, in solutions where the surfactant concentration was essentially the same prior to and after binding. The results are summarized in Figure 3, showing V/V_0, the volume of the gels in the presence of surfactant relative to the volume in pure water, as a function of CTAB concentration. No volume change is observed for CTAB concentrations below 0.02 mM. Above this concentration, there is a drastic decrease in the size of the gels in a very narrow concentration range. The same type of volume transition has been observed in other gel−surfactant systems.[55] Above the collapse concentration, which we interpret as the critical aggregation concentration (cac), the gels have a homogeneous composition, but the degree of swelling decreases gradually with increasing concentration in the solution. The aggregation of CTAB in the DNA network starts at a concentration that is much lower than the cmc of the surfactant in water (0.9 mM).[56] This is because normal micellization involves counterion binding to neutralize the charge of the micelle, while binding of surfactant to the DNA network involves the release of counterions. In accordance with this, a cac of 0.02 mM was found and this is in excellent agreement with cac values for CTAB in solution with DNA as obtained by other methods.[57−59]

In the other type of experiments, gels were placed in solutions with a limited amount of surfactant. In this case, the final gel volume decreases gradually as the amount of surfactant taken up by the gel increases. This is shown in Figure 4, where the volume of the gels in the presence of surfactant (V) relative to the volume in pure water (V_0) is given as a function of the degree of surfactant binding, β. Notably, no macroscopic separation of collapsed and swollen regions is observed at intermediate degrees of binding, suggesting that CTAB aggregates are evenly distributed in the gels. (Only the gel with the largest β appeared to have core/shell structure.) The behavior is in sharp contrast to that observed for CTAB−polyacrylate (PA) gels. Data for the latter system, obtained earlier under the same conditions[34] are included in Figure 4 for comparison. In this case, a dense surfactant-rich surface phase (skin) is found to coexist with a swollen core network for all gels with $\beta < 0.9$. It was recently demonstrated that the rubber elasticity of the skin contributes significantly to the deswelling of the surfactant-free core, with the result that the gels are fully collapsed already at $\beta \approx 0.8$.[34] Furthermore, from a comparison between two different surfactants interacting with the same type of gel, one distributing evenly and the other forming a dense surface phase (at a given β), it has been concluded that the gel volume is smaller in the latter than in the former case.[60] The swelling behavior displayed by DNA and PA gels, respectively, in Figure 4 may thus, to some extent, be reflective of the way CTAB is distributed in them. At the same time, the latter observation raises the question as to what determines the distribution of the aggregates in the

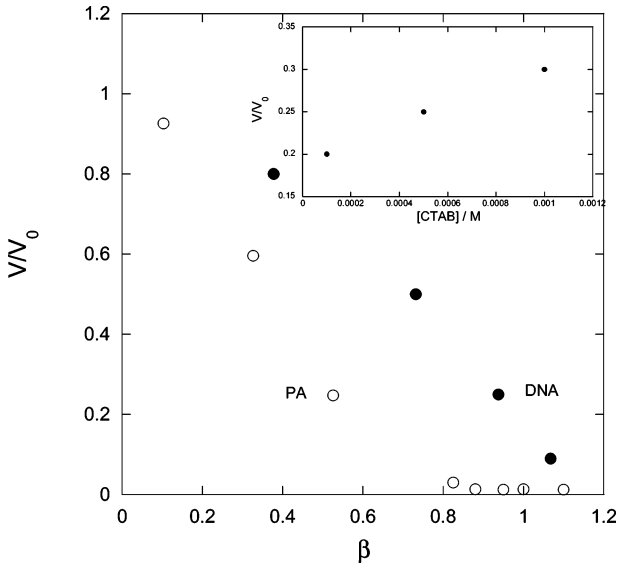

Figure 4. Dependence of relative volume (V/V_0) of DNA gels (1% cross-linker density) on degree of surfactant binding (β). All gels were equilibrated in 0.50 mM CTAB solutions of different volume. Shown for reference are data for 1% cross-linked sodium polyacrylate gels/CTAB (open symbols). Inset shows V/V_0 as a function of initial CTAB concentration in the solution for samples with charge ratio = 1.0.

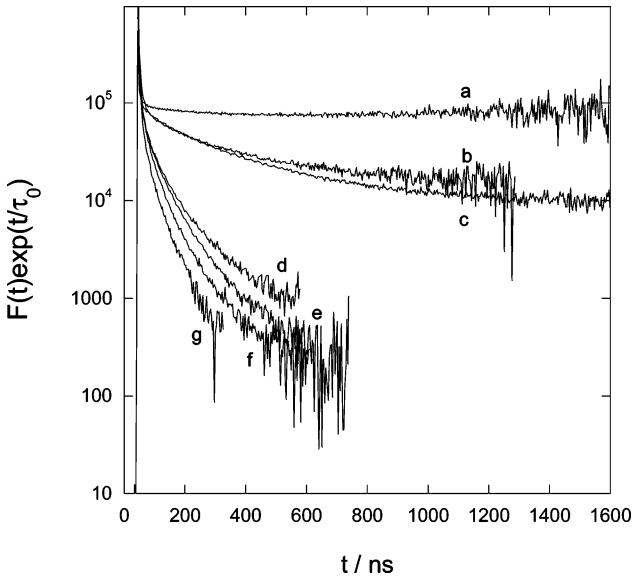

Figure 5. Fluorescence decay curves from pyrene in DNA/CTAB gels (1% cross-linker density) obtained in the absence (a) and presence (b−g) of CPC as quencher ($X_Q = 0.010$). From top to bottom: (b) $\beta = 0.8$, [CTAB] = 0.5 mM, $\tau_0 = 130$ ns; (c) $\beta = 1.2$, [CTAB] = 0.1, $\tau_0 = 184$ ns; (d) $\beta = 1.2$, [CTAB] = 1.0, $\tau_0 = 147$ ns; (e) $\beta = 1.0$, [CTAB] = 1.0, $\tau_0 = 133$ ns; (f) $\beta = 0.4$, [CTAB] = 1.0, $\tau_0 = 174$ ns; (g) $\beta = 0.8$, [CTAB] = 1.0, $\tau_0 = 153$ ns. All curves have been multiplied by $\exp(t/\tau_0)$ to better display the two types of quenching behavior.

respective case. For CTAB−PA the stability of the surface phase appearing at intermediate β is expected from the phase behavior of CTAB−linear PA, from which it is known that concentrated polyion−micelle phases (near 1:1 charge stoichiometry) are stable against dissolution when in contact with dilute solutions of the polyion. Thus, the motive for the formation of the surface is the same as for the volume transition observed in bulk solutions above the cac, but in the former case the amount of surfactant available is not enough to collapse the entire network. It is intriguing, therefore, that CTAB distributes evenly in the gels, in Figure 4, despite the fact it brings about a volume transition of DNA gels in bulk solutions (Figure 3). As pointed out elsewhere,[34] the network in a collapsed surface phase is nonuniformly deformed. Thus, in the direction parallel to the gel surface it is stretched out to the same extent as the swollen core network, and in the direction perpendicular to that it is compressed to an extent depending on how collapsed the phase is. One explanation, as to the absence of a surface phase at low and intermediate β in DNA gels, can thus be that the formation of a strongly collapsed skin is associated with a too-large deformation energy for the compression of the very stiff DNA chains in the direction perpendicular to the gel surface. The formation of a very concentrated phase may not be critical for the interaction between DNA and CTAB. However, an even distribution of surfactant in the gel is a better alternative for the system as a whole than no surfactant binding.

The inset in Figure 4 shows the volume of (partially) collapsed gels (CR = 1.0) as a function of the initial concentration of CTAB in the solution. Here V_0 is the volume of (partially) collapsed gels and V is the volume of the gels in the presence of surfactant. The volume increase may result from an incorporation of bromide ions into the DNA/CTA^+ complexes. A change of the stoichiometry of the complexes, to give them a weak net charge, is expected to cause an osmotic swelling of the complexes.[34]

Time-Resolved Fluorescence Quenching Results. Figure 5 shows representative fluorescence decay curves recorded for DNA gels collapsed by CTAB. To highlight the photophysics of the quenching produced by CPC, the contribution from the natural decay rate of the probe in the gels has been removed as described in the Experimental Section.[45] This means that the recorded intensity $F(t)$ has been multiplied by the function $\exp(t/\tau_0)$, where τ_0 is the lifetime recorded in the absence of quencher. The lifetime (τ_0) for each sample is given in the caption to Figure 5. In such a representation, a curve recorded in the absence of quencher (top) should ideally be a horizontal line. The additional fast decay observed during the first nanosecond of the curve in Figure 5 is an artifact due to the reflection of the laser beam from the gel surface. This perturbation is difficult to avoid, even with a band-pass filter in front of the detector or by optimizing the position and angle of the sample with respect to the direction of the beam. Fortunately, since it is very short-lived compared to the time range for the quenching process, the influence on the remaining part of the curves is negligible, and the qualitative interpretation of the results is not affected.

As can be seen, the quenched decays can be divided into two groups. The two uppermost curves, obtained for gels placed in solutions of low CTAB concentrations, are less quenched than the other ones. Furthermore, at long times the slope of the curves is essentially zero. This proves that the micelles are discrete, as explained in the Experimental Section. The other curves, obtained from gels placed in solutions of higher CTAB concentrations, are all heavily quenched and never become horizontal. For the samples corresponding to the lower decay curves, a quenching in "infinitely" large surfactant assemblies, for example, cylinder micelles or bilayers, is expected.[45] In this case we obtained aggregation numbers higher than 500 ($N > 500$). The observed growth from globular to "infinite" micelles with increasing initial CTAB concentration in the solution is expected if the amount of bromide ions incorporated into the complexes increases as mentioned above. This was found to be the case for CTAB/polyacrylate gels.[34]

For the gel samples with discrete micelles it is possible to estimate the surfactant aggregation number. Using eqs 1 and 2,

with $X_Q = 0.010$, we obtain 160 and 210 for the upper and the lower curve, respectively. Both values are quite reasonable for CTAB, considering the high concentration of surfactant and polymer in the gels. Previously, values between 110 and 160 were found for CTAB in polyacrylate gels.[34] To the best of our knowledge this is the first evidence of small CTAB micelles in complexes with DNA reported in the literature.

In principle it should be possible to distinguish between the cylinder micelles and bilayers by fitting models to the decays. This requires very good quality of the data, typically obtained after extending the time window of the experiment by measuring for extended times on deaerated samples. Therefore, we make no attempt at this point to analyze these data any further. Preliminary experiments with SAXS seem to reveal hexagonal microstructures in gel samples made under the same conditions, suggesting that the large micelles are rodlike. In principle, however less likely, an inverted hexagonal structure cannot be ruled out from the present investigation. Hexagonal and cubic structures have been found in cetyltrimethylammonium (CTA^+) aggregates in the complex with a polyacrylate network.[34]

Conclusions

The double-stranded DNA gels prepared offer a novel opportunity for monitoring DNA−cosolute interactions by simply following the change in gel volume. While sodium bromide addition gives a very gradual gel shrinkage with increasing concentration, addition of a cationic surfactant gives a dramatic shrinking due to the association of self-assembled surfactant with DNA. A value of 0.02 mM was found for the cac, which is much lower than the typical cmc of CTAB in aqueous solution. For the DNA gel placed in the most concentrated CTAB solution (1 mM; $\beta = 0.84$; CR = 1.0), a dense surfactant-rich surface phase was formed. The surfactant self-assemblies were examined with time-resolved fluorescence quenching, which showed that depending on the conditions there are either small globular micelles or long rodlike structures.

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