An NMR Self-Diffusion Study of the Interaction between Sodium Hyaluronate and Tetradecyltrimethylammonium Bromide

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ABSTRACT: A decrease of the NMR self-diffusion coefficient of sodium hyaluronate (NaHy) upon increasing tetradecyltrimethylammonium bromide (TTAB) concentration in 202 mM NaCl (just enough to attain single phase conditions irrespective of the TTAB concentration) is interpreted in terms of the formation of NaHy–TTAB complexes containing several NaHy chains. The complexes are judged to be induced by multiple-site electrostatic condensation of TTAB micelles onto the Hy chains. Thus, the TTAB micelles may act as bridging points between, and within, the NaHy chains. For a 1% wt NaHy solution, at 202 mM NaCl, the fraction of adsorbed TTAB has a maximum at 10 mM TTAB where an estimated 54% of all the added TTAB is bound. At 70 mM TTAB, the fraction of bound TTAB has decreased to 42%. The decrease of the binding constant with increasing TTAB concentration is attributed to a more efficient electrostatic screening; i.e., the ionic strength (due to uncondensed species) increases. The observed NaHy–TTAB complexes are likely to be precursors of the precipitated phase formed at lower salt concentrations.

Introduction

With the increased proliferation of detergents, the surfactant–polymer interaction is becoming an important aspect of everyday life.[1] In this study, we focus on the interactions between a natural, moderately charged, anionic polysaccharide, sodium hyaluronate (NaHy), and a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB). Adding TTAB to a NaHy solution causes precipitation unless a sufficient amount of excess inorganic salt (or surfactant) is present.[2–4] A number of recent investigations have been devoted to oppositely charged polyelectrolyte–surfactant systems.[5] In fact, precipitation is a well-known phenomenon in related systems and has been widely exploited in a number of practical applications, e.g., the purification of protein mixtures by selective precipitation induced by surfactants,[6–8] the precipitation of cations using polysaccharides,[9,10] waste-water treatment, etc. Since addition of excess inorganic salt "redissolves" the precipitate, it is convenient to define (for each TTAB concentration) a minimum critical electrolyte concentration, cec, where precipitation of NaHy is inhibited and single phase conditions are attained, and a maximum cec, $\mathrm{cec_{max}}$, where single phase conditions prevail irrespective of TTAB concentration. The strength of the interaction between the surfactant and the oppositely charged polyelectrolyte apparently decreases with increasing ionic strength. This is a clear indication that the interaction is of electrostatic nature.

From an electrostatic viewpoint (on the Poisson–Boltzmann level), a free surfactant ion, $\mathrm{TTA^+}$, behaves exactly as $\mathrm{Na^+}$ and a negatively charged polyelectrolyte would not show any preference for either of the two counterions. Nevertheless, the hydrophobicity (and size) of $\mathrm{TTA^+}$ leads to such a preference since its contact with water (excluded volume) is reduced in the vicinity of the polyelectrolyte. The consequent higher local concentration of $\mathrm{TTA^+}$ near the polyelectrolyte, as compared to the bulk, may exceed the critical micelle concentration, cmc. Micellar aggregates can therefore be induced by the presence of an oppositely charged polyelectrolyte, even at bulk surfactant concentrations below the (bulk) cmc, as suggested by the strongly cooperative binding isotherms for TTAB onto NaHy[11] and silica.[12] The presence of micelles induced by NaHy below the bulk cmc has also been suggested on the basis of results from time-resolved fluorescence quenching[11] and solubilization of hydrophobic dyes.[2,13] Since a micelle may be regarded as a multivalent counterion to the polyelectrolyte (and vice versa), the preference for surfactant counterions (in the form of aggregates) is greatly amplified by an electrostatic contribution.

The competition between counterions and the preference for multivalent counterions is adequately predicted within the context of the Poisson–Boltzmann cell model.[14–17] If the electrostatic potential near the polyelectrolyte is large, i.e., when the surface charge density is high and/or when the ionic strength is low, the concentration of multivalent counterions near the surface may be very much larger than the bulk concentration. (In the latter regime, the tractable counterion condensation theory presented by Manning[18] appropriately describes the situation.) When the electrostatic potential is zero, or very small, any preference may be neglected and the relative concentrations of counterions in the vicinity of the polyelectrolyte reflects the relative bulk concentrations (neglecting contributions of non-electrostatic origin). The decreased interaction between TTAB micelles and NaHy with increasing ionic strength can thus be understood as a decrease, or screening, of the electrostatic potential. However, a detailed theoretical treatment of these effects is beyond the scope of this paper and we shall content ourselves with a qualitative discussion in terms of the degree of TTAB micelle condensation onto NaHy or in terms of the "strength" of the interaction.

The present study concerns the effects on the NMR self-diffusion of NaHy and TTAB due to the electrostatic interaction that remains even under single phase condi-

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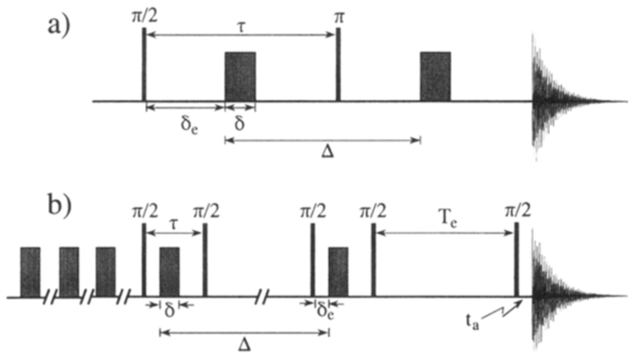

Figure 1. (a) Standard PGSE Hahn echo pulse sequence. (b) LED pulse sequence.

tions slightly above cec$_{\max}$. The same system has previously been investigated by rheology,[4] quasi-elastic light scattering (QELS),[13] and static light scattering (SLS).[19] The observed changes in rheology, QELS, and SLS, above cec$_{\max}$, also occur above the bulk cmc of TTAB (in the presence of additional salt), i.e., in a range where the concentration of nonassociated TTA$^+$ does not increase upon addition of more surfactant. This clearly indicates that the Hy chains primarily interact with TTAB micelles, rather than single surfactant ions. An advantage of NMR, as compared to QELS, is that the self-diffusion of each species may be followed separately (provided that the absorption bands do not overlap). It turns out that the NMR results presented here support the previous conclusions drawn from QELS (and SLS). Furthermore, the fraction of TTAB bound onto NaHy may be estimated.

Experimental Section

Materials. NaHy was kindly supplied by Pharmacia AB, Uppsala, Sweden. A sample with weight-average molecular weight, M_w, 440 000 was prepared by acid hydrolysis from an original sample with M_w 770 000, where both weight-average molecular weights were determined by low-angle laser light scattering. Size exclusion chromatography on the hydrolyzed NaHy (440) indicated a unimodal, very broad, molecular weight distribution.[20] TTAB (≈99%) was obtained from Sigma Chemical Co., St. Louis, MO. NaCl of analytical grade was purchased from Merck, Darmstadt, Germany, and ^2H_2O (99.9%) from Isotec Inc., Miamisburg, OH. All chemicals were used without further purification.

Solutions were prepared by weight from individual stock solutions of polyelectrolyte, surfactant, and salt in ^2H_2O. Once prepared, the solutions were stirred overnight or longer to ensure homogeneity. The total hyaluronate concentration in each sample was approximately 1% wt, which corresponds to a concentration of 25 mM of the monovalently charged repeating disaccharide. The NaCl concentration was 202 mM which is slightly above cec$_{\max}$, i.e., the minimum amount required to suppress precipitation of the NaHy–TTAB complex irrespective of TTAB concentration.[4]

NMR Self-Diffusion Measurements. Self-diffusion coefficients (D_s) of TTAB and NaHy were measured at 298 K using the Fourier-transform pulsed-gradient spin-echo (FT-PGSE) NMR technique.[21] In the case of TTAB, the measurements were performed on a JEOL FX-90 spectrometer with a 5 mm ^{1}H probe and an internal field/frequency lock provided by the deuterons in the ^2H_2O solvent. The standard PGSE Hahn echo pulse sequence (Figure 1a) was used. The radio frequency pulse interval was fixed (τ = 140 ms) in order to keep the effects of transverse relaxation constant. In the case of TTAB diffusion measurements the magnitude of the gradient pulse (G) was 0.025 T/m, as calibrated by the use of the known D_s of water in $H_2O/^2H_2O$ mixtures at 298 K.[22] The gradient pulse interval (Δ) was kept equal to τ and the gradient delay was $\delta_e = (\Delta - \delta)/2$. The attenuation of the amplitude of the half-echo of the N-methyl band (3.3 ppm) was monitored while the duration of the applied gradient pulses (δ) was varied from 20 to 110 ms in 10 ms intervals.

At the above conditions, spin echoes deriving from hyaluronate protons are invisible due to their very rapid transverse relaxation. An elegant method, which permits the observation of these echoes and alleviates the difficulties due to the strong gradient pulses required for slow-moving species, is the *l*ongitudinal *e*ddy-current *d*elay (LED) pulse sequence (Figure 1b).[23] It is essentially an extension of the stimulated-echo (STE) technique,[24] and the principal advantage with regard to macromolecular and colloid systems is that the period of transverse relaxation can be kept very short. Since the longitudinal relaxation time (T_1) for polymers in general is significantly longer than the transversal relaxation time (T_2), and much less dependent on the molecular weight, using the STE or LED sequences is therefore recommended practice when polydisperse macromolecular samples are studied.[25] (It should also be noted that the extensive transversal relaxation in polymers, such as NaHy, operates in a non-first-order J-coupled spin system.) Such measurements on Hy were performed on a Bruker MSL 200 spectrometer using a gradient pulse strength (G) of 1.74 T/m. The interval of transverse evolution (τ) was kept to a small, fixed, value (=10 ms), whereas the interval between the gradient pulses was large (Δ = 400 ms). The gradient delay (δ_e) was 2 ms, the eddy-current delay (T_e) was 40 ms, and the acquisition delay (t_a) was 0.125 ms. The attenuation of the amplitude of the half-echo of the 2.2 ppm band was monitored while the duration of the applied gradient pulses (δ) was varied from 0.2 to 6.4 ms in 0.2 ms intervals.

For molecules undergoing unhindered isotropic Brownian motion, an exponential decay of the echo amplitude is observed with increasing δ,

$$A(t) = A_0 e^{-kD_s} \qquad (1)$$

where A_0 is the amplitude in the absence of an applied gradient and the time function $k = (\gamma G\delta)^2(\Delta - \delta/3)$ depends on the experimental variables and the proton magnetogyric ratio (γ). For the standard PGSE Hahn echo pulse sequence (Figure 1a) $t = 2\tau$ and $A_{0,\text{Hahn}}$ is[21]

$$A_{0,\text{Hahn}} = A(0)\exp(-2\tau/T_2) \qquad (2)$$

whereas for the LED pulse sequence (Figure 1b) $t = \Delta + \tau + T_e + t_a$ and $A_{0,\text{LED}}$ is given by

$$A_{0,\text{LED}} = 0.5A(0)\exp(-[2\tau + t_a]/T_2 - [\Delta - \tau + T_e]/T_1) \qquad (3)$$

With the above experimental parameters, $A_{0,\text{LED}} > A_{0,\text{Hahn}}$ approximately when $1/T_1 + 1.6 < 0.6/T_2$ (with T_1 and T_2 expressed in seconds).

Data Treatment. Due to the inherent polydispersity of NaHy, and to the known NaHy–TTAB complex formation, the decay of the echo amplitudes will be more involved than the single exponential decay suggested by eq 1. For TTAB a rapid exchange between its different states (i.e., between single surfactant ions, surfactants in micellar aggregates not associated with NaHy, and surfactants in micellar aggregates associated with NaHy) is expected. The echo amplitude then decays exponentially, according to eq 1, but with a $D_{s,\text{obs}}$ that is a weighted average over the D_s of the states (see Discussion below).[26] For NaHy, on the other hand, the polydispersity and the expected slow exchange of molecules between states leads to a multi-exponential decay of the echo amplitude. As mentioned above, the use of the LED sequence minimizes the problems with unequal weights of signal amplitudes due to unequal transverse relaxation times in polydisperse samples. LED ensures that the decay of the echo amplitude primarily is due to diffusion and is equally weighted for all components.[25] In principle, the distribution of self-diffusion coefficients present in the sample may be extracted by applying an inverse Laplace transformation (ILT) to the attenuation function. In spite of the difficulties associated with the application of ILT to experimental data, there is a widely distributed computer algorithm, CONTIN, supplied for this purpose.[27,28] CONTIN has previously been applied to PGSE-NMR data, and the problems associated with this particular application have been discussed in considerable detail.[29,30] In short, the problem is that several different sets of self-diffusion coefficients may fit the inherently noisy experimental attenuation function to a comparable statistical quality. The selected set of self-diffusion coefficients and the intensities of their contribution to the attenuation function are not unique and are sensitive to *how* the time function (k) is sampled, i.e. to the number and separation of the data points, as well as the time window itself. Nevertheless, the distributions extracted by the ILT provide a valuable insight into complex dynamic systems, and provided that the data are consistently treated, useful comparisons can be made. In the present measurements, the NaHy attenuation functions as a function of TTAB concentration were identically sampled, as described above, and the echo amplitudes were normalized to the first point in the decay. The CONTIN analyses were performed using identical time windows and the same number of logarithmically spaced points. In addition, the obtained distributions were normalized to unit area, by dividing each intensity with the total area under the curve (as estimated by the sum of the areas of the trapezoids formed by the logarithmically spaced points), to further visualize the observed trends.

In view of the problems with ILT, it is illuminating to characterize the distributions by other means.[31] An attempt to account for the polydispersity of the diffusing species is to use the stretched exponential model, which has the same form as the Kohlrausch–Williams–Watts equation,[32]

$$A(t) = A_0 \exp(-[kD_{\mathrm{s,app}}]^{\beta}) \tag{4}$$

where the phenomenological parameter β describes the width of the distribution ($0 < \beta \leq 1$). The average self-diffusion coefficient is obtained by

$$D_{\mathrm{s,av}} = \beta D_{\mathrm{s,app}} / \Gamma(1/\beta) \tag{5}$$

where Γ is the gamma function. For a monodisperse sample β equals unity and eq 4 simplifies to eq 1. The main drawback of the stretched exponential is the implicit assumption of a unimodal distribution. A bimodal distribution may be estimated by fitting the attenuation function to a double exponential decay with a fast and a slow component, $D_{\mathrm{s,fast}}$ and $D_{\mathrm{s,slow}}$, respectively.

Results

A typical NaHy echo amplitude attenuation function may be represented by the data for the 30 mM TTAB case shown in Figure 2. The upward concavity of the data, when plotted in the form of eq 1, indicates a multiexponential decay, and a fit to eq 1 is unsuccessful. In view of the data quality, the CONTIN, stretched exponential, and double exponential fits are equally good. The inset in Figure 2 shows that the error of the CONTIN fit is in between the errors of the stretched and double exponential fits. The last two models can therefore be seen as extreme cases for the CONTIN fits.

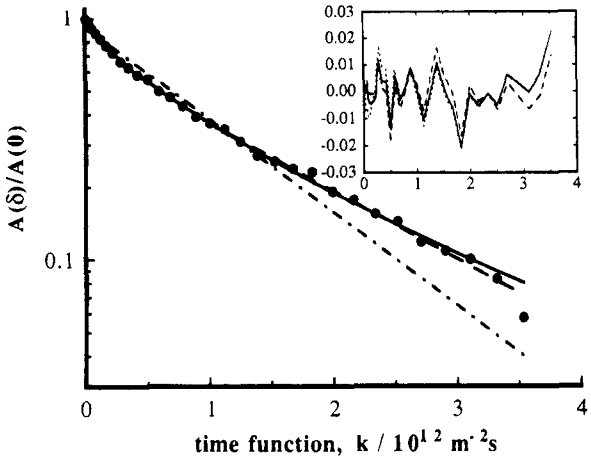

Figure 2. Experimental attenuation function of the NaHy 2.2 ppm band for the LED sequence with 1% NaHy, 30 mM TTAB, and 202 mM NaCl. Also shown are the CONTIN (solid line), stretched exponential (dashed line), double exponential (dotted line), and single exponential (dash-dotted line) fits. (Note that the CONTIN, stretched exponential, and double exponential fits virtually coincide.) The inset shows the error of the fits excluding the single exponential fit.

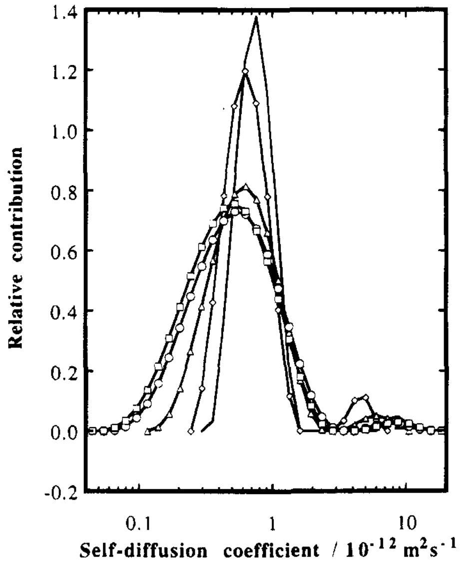

Figure 3. Area-normalized CONTIN analysis of the self-diffusion coefficient distribution of 1% wt NaHy in 202 mM NaCl as a function of TTAB concentration: 0 mM (solid line), 20 mM (open diamonds), 30 mM (open triangles), 50 mM (open circles), and 70 mM (open squares).

Table 1. Parameter Fits to the Stretched and the Double Exponential Models

[TTAB], nM	β	$10^{12} D_{\mathrm{s,app}}$, $\mathrm{m^2\,s^{-1}}$	$10^{12} D_{\mathrm{s,av}}$, $\mathrm{m^2\,s^{-1}}$	$10^{12} D_{\mathrm{s,slow}}$, $\mathrm{m^2\,s^{-1}}$	P_{fast}	$10^{12} D_{\mathrm{s,fast}}$, $\mathrm{m^2\,s^{-1}}$
0	0.79	0.99	0.86	0.76	0.19	7.12
20	0.72	1.04	0.84	0.65	0.30	4.42
30	0.72	1.05	0.84	0.65	0.30	4.35
50	0.70	0.99	0.78	0.62	0.29	4.72
70	0.67	0.96	0.73	0.59	0.29	5.46

The CONTIN D_{s} distributions for NaHy as a function of TTAB concentration are summarized in Figure 3. The parameter fits for the stretched and double exponential models to the same data are gathered in Table 1. The distributions extracted by CONTIN are bimodal with a major band of slower components. With increasing TTAB content, the major band broadens and the self-diffusion becomes slower on average. Reassuringly, the parameter fits in Table 1 do support this general trend. The slower self-diffusion for the hyaluronate with an increasing number of TTAB micelles is indicated by the decreasing $D_{\mathrm{s,slow}}$ and $D_{\mathrm{s,av}}$ for the double and the stretched exponential models, respectively. The broadening of the major band is phenomenologically represented by the decrease in the fitted β for the stretched exponential model. Given the sensitivity and resolution problems of CONTIN, the trends for the minor band of faster components should be interpreted with caution. In fact, in view of the unimodality found by SEC, even the bimodality may be questioned. Nevertheless, the double exponential model gives good fits to the 0, 20, and 30 mM TTAB cases. The extracted slower self-

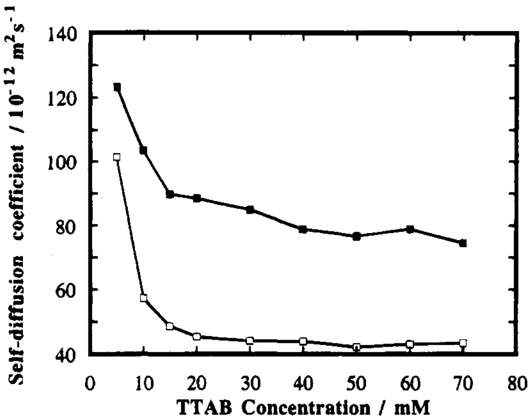

Figure 4. Self-diffusion coefficient for TTAB in 202 mM NaCl with (open squares) and without (filled squares) 1% wt NaHy present as a function of TTAB concentration.

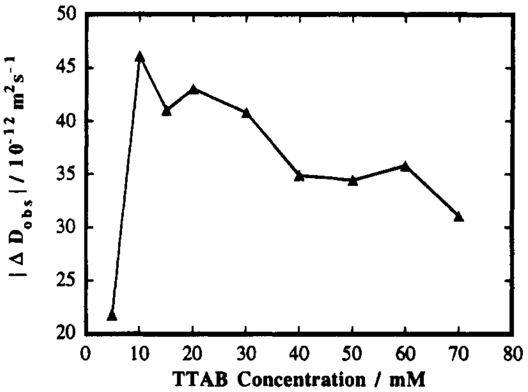

Figure 5. Absolute value of the difference between the observed self-diffusion coefficients for TTAB in 202 mM NaCl with and without 1% wt NaHy present as a function of TTAB concentration.

diffusion of the fast components for the 20 and 30 mM cases may reflect a real process.

The $D_{s,obs}$ for TTAB as a function of TTAB concentration in 202 mM NaCl with, or without, the presence of 1% wt NaHy is shown in Figure 4. The distinct decrease of the observed self-diffusion coefficient indicates that TTAB binds onto NaHy even below 10 mM. However, the interpretation is clouded by the fact that $D_{s,obs}$ decrease also in the absence of NaHy. The fraction of TTAB bound onto NaHy must, nevertheless, be related to the absolute value of the difference between the observed self-diffusion coefficients, $|\Delta D_{s,obs}|$, displayed in Figure 5 (vide infra).

Discussion

Using a few approximations, $|\Delta D_{s,obs}|$ may yield a useful estimate of the fraction of bound TTAB as a function of the TTAB concentration. Since the cmc for TTAB in the presence of 202 mM NaCl occurs already at approximately 0.5 mM,[4] most TTAB resides in micellar aggregates for the concentration range used. If a rapid exchange between free and self-associated surfactants is assumed, a two-state model for the observed self-diffusion coefficient,[26] $D_{s,obs}$, may be used in the absence of NaHy

$$D_{s,obs} = P_f D_f + P_m D_m \tag{6}$$

where P_f and P_m are the fractions of TTAB in the free and micellar state, respectively, and D_f and D_m are the corresponding self-diffusion coefficients. In the presence of NaHy, a three-state model may be used[33]

$$D'_{s,obs} = P'_f D'_f + P'_m D'_m + P'_b D'_b \tag{7}$$

where the prime denotes the presence of NaHy and where the fraction of TTAB in micelles bound onto NaHy and their corresponding self-diffusion coefficient are P_b and D_b, respectively. The proposed three-state model, where only micellar aggregates bind to the polyelectrolyte, is strongly supported (see also Introduction) by the fact that the observed changes occur above cmc, i.e., in a range where the concentration of free surfactant does not increase upon addition of more surfactant.

We may assume that the concentration of free TTAB is unaffected by the presence of NaHy at 202 mM NaCl, as indicated by surface tension measurements in the absence and in the presence of 0.1% wt NaHy.[4] If we further assume that the diffusion coefficients of free TTAB and TTAB micelles also are unaffected (vide infra), i.e., $D_f = D'_f$ and $D_m = D'_m$ then the fraction of TTAB in bound micelles is given by

$$P'_b = \frac{|\Delta D_{s,obs}|}{|D'_b - D'_m|} \approx \frac{|\Delta D_{s,obs}|}{D'_m} \tag{8}$$

where the latter equality holds if $D'_b \ll D'_m$. Using QELS, the diffusion coefficient of a TTAB micelle has been estimated to be $\approx 8.5 \times 10^{-11}$ m^2 s^{-1} (a diameter of 5 nm).[13] This is in good agreement with the measured (NMR) D'_m for concentrations greater than 20 mM TTAB in Figure 4. (At low TTAB concentrations, the contribution to the average $D_{s,obs}$ from the fast diffusion of the free surfactant cannot be neglected.) Thus, the TTAB micelle, D'_m, and the NaHy diffusion coefficient, D'_b (on the order of 1×10^{-12} m^2 s^{-1} according to Figure 3), differ by a factor of 85 and the latter equality holds. Equation 8 states that since P_b is proportional to $|\Delta D_{s,obs}|$, the maximum shown in Figure 5 corresponds to a maximum in the fraction of bound micelles. Using $D'_m = 8.5 \times 10^{-11}$ m^2 s^{-1} (from QELS), the maximum at 10 mM corresponds to 54% of bound TTAB. At 70 mM TTAB, now using the measured $D'_m = 7.5 \times 10^{-11}$ m^2 s^{-1}, the fraction of bound TTAB has decreased to 42%. If we do account for the expected decrease of the self-diffusion coefficients due to the presence of the polyelectrolyte (15% in a 2% wt NaHy solution as determined by Thalberg *et al.*[2]), it may be noted that eq 8 underestimates P_b for low and overestimates P_b for high TTAB concentrations. Consequently, the real effects are in fact larger than those predicted using eq 8.

Upon binding of the TTAB micelles onto NaHy, a fraction of the univalent counterions both on the polysaccharide chains and on the micelles are released to the bulk since the micelles may act as multivalent counterions to the polysaccharide chains, and vice versa. It is well-known that higher valence counterions are preferentially condensed as compared to lesser valence counterions and that this trend may be reversed by addition of an excess of the latter.[34] This competition and preference for higher valence counterions is adequately described on the Poisson–Boltzmann level,[14–17] but may be qualitatively understood simply by considering the increase in counterion mixing entropy as condensed low-valence counterions are replaced (and released to the bulk) by a smaller number of higher valence counterions. In view of the electrostatic nature of the interaction between the TTAB micelles and the

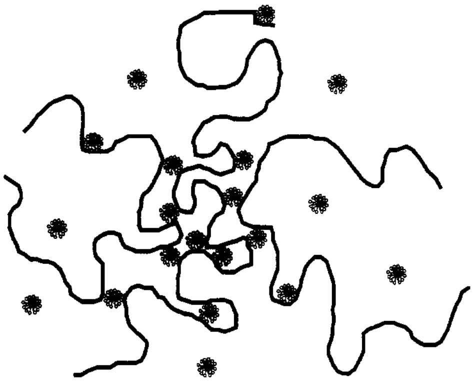

Figure 6. Schematic two-dimensional picture of a NaHy–TTAB complex containing three NaHy chains.

oppositely charged polyelectrolyte chains, the decrease of P_b as a function of TTAB concentration may be rationalized in terms of an increase of the ionic strength due to the increasing concentration of noncondensed TTAB micelles.

Due to the NaHy chain stiffness[35,36] (a persistence length estimated to be 5 nm), it is improbable that a bound TTAB micelle is completely charge-neutralized by adjacent charges on a Hy chain. The local net charge is therefore positive and sufficiently large so that a bound micelle also may condense onto another charged site on the same, or another, NaHy chain, thereby acting as a bridging point. Intramolecular bridging is expected to give a faster D_s for NaHy due to a contraction of the polyelectrolyte coil, whereas intermolecular bridging would give a slower D_s. Thus, the decreasing average D_s for NaHy shown in Figure 3 and Table 1 indicates that bridges primarily form between different NaHy chains, giving NaHy–TTAB complexes where each one contains several NaHy chains (see Figure 6). The observed broadening, on the other hand, may be due to a combination of inter- and intrachain bridging. The predicted aggregation of NaHy induced by TTAB is further supported by the decreasing diffusion coefficient and the increasing apparent molecular weight determined (both using 0.1% wt NaHy) by QELS[13] and SLS,[19] respectively. The decrease of the average self-diffusion coefficient observed by NMR for a 1% wt NaHy solution is smaller than the approximately 2-fold decrease observed by QELS in a 0.1% wt solution.

An important consideration is the critical entanglement concentration, c^*, of NaHy. For a comparable sample of NaHy (M_w 850 000 in 200 mM NaCl), Wik and Comper[37] estimate c^* to be 1.56% wt by intrinsic viscosity, but argue that an analysis of the mutual diffusion coefficient data for NaHy indicate a lower value of c^*. It should also be noted that c^* is not likely to be a distinct value for a polydisperse sample. We have assumed that a 1% wt NaHy solution with 202 mM NaCl is below c^* in the above interpretations.

The NaHy–TTAB complexes observed by us slightly above cec_{max} are obviously precursors to the precipitated phase obtained at lower salt concentrations. The solubility of the NaHy–TTAB complex in aqueous solution is lower than the solubility of NaHy itself since the adsorbed TTAB micelles decrease the effective charge and increase the hydrophobicity (micelles do expose hydrophobic parts in between the headgroups). The solubility of a complex is thus governed directly by the degree of binding of TTAB micelles onto NaHy and indirectly by the total molecular weight of the complex. Even though the condensation of TTAB micelles onto NaHy induces precipitation, the micelles are only members of the diffuse counterion atmosphere of NaHy according to the arguments above. This proposed mechanism for the precipitation is supported by the rheological measurements of the precipitated phase, performed by Thalberg *et al.*,[38,39] demonstrating that the precipitate behaves simply as a concentrated NaHy solution. The Hy chain does not penetrate into the interior of the induced micelles and binding is primarily of electrostatic nature.[11] The electrostatic bridging is of course weakened by an increasing ionic strength and this is the origin of the redissolution of the precipitate by addition of excess monovalent salt and/or excess surfactant.[3,4] The composition of the supernatant phase suggests that a binding saturation level is reached at approximately 50 mM TTAB with no NaCl added.[3] At 202 mM NaCl, just enough to achieve single phase conditions, the maximum fraction of bound TTAB (54%) occurs already at 10 mM TTAB. The proximity to the unstable system may thus indicate that 54% is a maximum allowed degree of TTAB binding while preserving single phase conditions.

Conclusions

NMR self-diffusion is a convenient method for study of the interaction between the negatively charged (pH = 7) polysaccharide NaHy and the oppositely charged surfactant TTAB. Even at salt concentrations sufficient to suppress precipitation, the electrostatic condensation of TTAB micelles onto NaHy is substantial. For a 1% wt NaHy solution, at 202 mM NaCl, the fraction of adsorbed TTAB has a maximum at 10 mM TTAB where an estimated 54% of all the added TTAB is bound. At 70 mM TTAB, the fraction of bound TTAB has decreased to 42%. The decrease of the binding constant with increasing TTAB concentration is attributed to a more efficient electrostatic screening; i.e., the ionic strength (due to uncondensed species) increases. We propose multiple-site condensation of micelles (rather than single-site condensation leading to the formation of a "pearl necklace") onto separate NaHy chains and attribute the slower average self-diffusion of NaHy to a formation of multichain NaHy–TTAB complexes. We conjecture that this is a general phenomenon in these systems of oppositely charged surfactant and polyelectrolyte. The complexes formed at single phase conditions may be viewed as precursors to the precipitated phase appearing at lower NaCl concentrations.

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