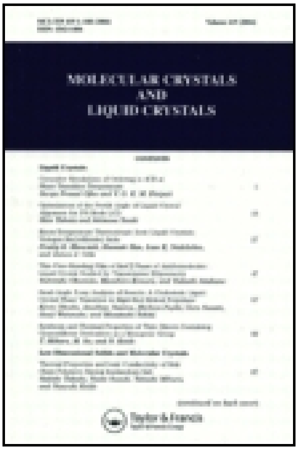

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Effect of Added Ions on the Self-Assembly of Guanosine

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EFFECT OF ADDED IONS ON THE SELF-ASSEMBLY OF GUANOSINE

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The dynamical behavior of deoxyguanosine 5′-monophosphate in the pretransitional region of the I-Ch phase transition was investigated by dynamic light scattering. Measurements reveal the presence of two diffusive modes: the slower mode is due to the motion of large globular aggregates while the faster mode is related to the motion of the self-assembled d(pG) columnar stacks. The behavior of the fast DLS mode is explained by the coupled mode theory, which relates the polyion motion with the dynamics of other ion species in the solution. The addition of 0.5 M KCl strongly promotes the self-assembly process resulting in a shift of the phase diagram towards lower d(pG) concentrations, while the properties of the two diffusive modes remain practically the same.

Keywords: lyotropic liquid crystals; self-assembly; polyelectrolytes

INTRODUCTION

It is known that from the four nucleic bases only guanosine shows liquid crystalline polymorphism [1]. This property is a consequence of its specific self-aggregation ability to form highly stable columnar stacks. The basic

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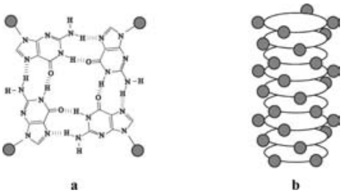

FIGURE 1 The self-assembly of guanosine molecules. (a) A tetramer of four hydrogen-bonded molecules. The gray spheres indicate the sugar-phosphate groups. (b) Stacking of the tetramers.

aggregation unit is a planar tetramer (Fig. 1(a)) formed by four hydrogen-bonded guanosine molecules [2]. Attractive π-π interactions between the aromatic planes induce vertical stacking of the tetramers and the formation of cylindrical columns (Fig. 1(b)). Highly concentrated aqueous solutions of guanosine exhibit a columnar lyotropic liquid crystalline polymorphism forming cholesteric (Ch) and hexagonal (H) phases at high and low water content, respectively [1].

The stacking process of guanosine molecules and column growth start already well below the I-Ch phase transition. Our recent investigations [3,4] of deoxyguanosine 5′-monophosphate by dynamic light scattering show that in this pretransitional region the dynamic behavior of the columnar stacks is dominated by their polyelectrolyte nature. To study these properties in more detail we investigate the effect of added KCl on the solution dynamics. Potassium ions are known to strongly promote the assembly process of different guanosine derivatives [5–10] and are also essential for the quadruplex DNA formation [11–13]. We therefore expected them to strongly influence also the dynamic processes of guanosine molecules in the solution that will be studied by dynamic light scattering.

EXPERIMENTAL

2′-deoxyguanosine 5′-monophosphate (d(pG)) in the form of sodium salt was purchased from Sigma (99% purity). The ammonium salt d(pG) was obtained by exchanging the cations using an Amberlite 200 ion exchange resin (Fluka) followed by subsequent lyophilization. Solutions of the required concentration were prepared by mixing the lyophylized material with distilled water or with a 0.5 M KCl solution. The concentrations of the investigated solutions ranged from 1 to 10 wt% (salt-free solutions) and from 1 to 6.25 wt% (with 0.5 M KCl). All the samples were examined with optical polarizing microscopy and were found to be isotropic.

Dynamic light scattering (DLS) experiments were performed using a digital correlator (model ALV 5000), a He-Ne laser ($\lambda = 632.8\,\text{nm}$) as a light source and a photomultiplier detector. The polarization of the detected scattered light was selected to be parallel (polarized scattering) to the incident polarization. The scattered light was detected at various scattering angles ϑ and the normalized homodyne intensity correlation function $g_2(t) = \langle I(0)I(t)\rangle/\langle I\rangle^2$ was measured. In the Gaussian approximation the normalized field correlation function $g_1(t)$ is related to $g_2(t)$ by the relation [14]

$$g_2(t) = 1 + \alpha|g_1(t)|^2 \tag{1}$$

where α is the spatial coherence factor depending on the apparatus. The field correlation function for scatterers with a polydisperze size distribution can be expressed by a Kohlrausch-Williams-Watts (KWW) function [15]

$$g_1(t) = \sum_i A_i \exp(-t/b_i)^{\beta_i} \tag{2}$$

where A_i is the amplitude of the i-th relaxation mode. The average relaxation time of the i-th mode is given by

$$\tau_i = \frac{b_i}{\beta_i}\Gamma(1/\beta_i) \tag{3}$$

where $\Gamma(1/\beta_i)$ is the gamma function. The KWW parameter β_i, constrained by $0 < \beta_i \leq 1$, is a measure of the width of the distribution of relaxation times. The translational diffusion coefficients of the modes were calculated as

$$D_i = 1/(\tau_i q^2) \tag{4}$$

where $q = (4\pi n/\lambda)\sin(\vartheta/2)$ is the scattering vector, n the refractive index of the solution, and λ the laser wavelength.

RESULTS

DLS time-correlation functions of isotropic d(pG) solutions in the I-Ch pretransitional region show two different relaxation modes. The slower mode is present in all d(pG) solutions with or without added salt. The corresponding diffusion coefficient D_{slow} calculated from Eq. (4) shows a slowing down of this mode with increasing the d(pG) concentration (Fig. 2).

The faster relaxation mode appears only above a certain concentration that is $c \geq 4\,\text{wt\%}$ in salt-free solutions and $c \geq 1\,\text{wt\%}$ in solutions with 0.5 M KCl. With increasing the d(pG) concentration the diffusion coeffi-

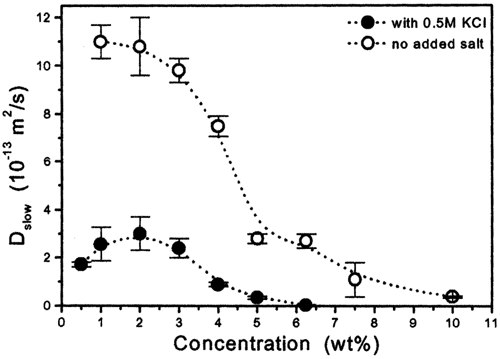

FIGURE 2 The concentration dependence of the slow diffusion coefficient for salt-free solutions and for solutions with 0.5 M KCl. The dotted lines are a guide to the eye.

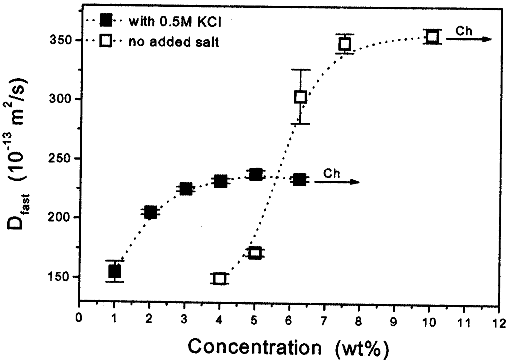

FIGURE 3 The concentration dependence of the fast diffusion coefficient for salt-free solutions and for solutions with 0.5 M KCl. The dotted lines are a guide to the eye.

cient D_{fast} increases until its value becomes saturated (Fig. 3). At higher d(pG) concentrations, i.e. above $c = 10$ wt% (salt-free solutions) and above $c = 6.25$ wt% (0.5 M KCl), the cholesteric phase is formed.

DISCUSSION

The slow DLS mode present in all investigated d(pG) solutions is related to the motion of large globular aggregates. These are spherical objects of about 100 nm in diameter, which existence was recently confirmed by freeze-fracture electron microscopy [4]. From the electron micrographs (EM), however, no information on the inner structure of the globules could be obtained. EM micrographs revealed also a tendency of the globules towards clustering and therefore some polydispersity is expected in the DLS response. Indeed, fitting the measured $g_2(t)$ functions to relations (1) and (2) yields a KWW parameter with an average value of $\beta_{slow} = 0.64 \pm 0.06$ in salt-free solutions, thus confirming the polydispersity of the scatterers. The addition of KCl results in an increase of the effective dimensions of the globules when compared to salt-free solutions. At the same time the aggregate size distribution becomes more polydisperse as seen from the decrease of the KWW parameter to $\beta_{slow} = 0.57 \pm 0.10$.

The presence of a slow DLS mode is a typical property of various polyelectrolyte systems [16–19], but its molecular origin is still a matter of controversy. Usually, the slow mode is interpreted as arising from ‘temporal aggregates’, but there is much speculation on forces that induce the formation of these aggregates [17,19–22]. In the case of d(pG), the slow mode has been observed also in sodium salt d(pG), which shows much weaker self-assembly [4]. We therefore conclude that the globular aggregates in d(pG) are presumably formed of monomers or tetramers rather than the d(pG) stacks.

The fast DLS mode is assigned to the translational diffusion of the d(pG) columnar stacks. The KWW parameters of this mode show that the polydispersity in column length is rather small: $\beta_{fast} = 0.92 \pm 0.05$ (salt-free) and $\beta_{fast} = 0.91 \pm 0.06$ (0.5 M KCl). However, to explain the dynamical behavior of the d(pG) stacks one must take into account also their ionization state. Each d(pG) molecule has a free phosphate end-group, and a tetrameric unit can therefore bear a total charge of $-8e_0$. In polyelectrolyte solutions the diffusion of the polyions is coupled to the dynamics of the counterions and can be qualitatively described by the coupled mode theory [15]. The simplest analytical expression for the zero angle limit of the polyion diffusion coefficient is given upon several assumptions: the added salt is a symmetric 1-1 electrolyte, it has common counterions with the polyion, and the charge and the diffusion coefficient of the counterion and the co-ion are the same.

$$D_{app}(q \to 0) = \frac{1}{2}[D_p(1-\Omega) + D_s(1+\Omega)] \tag{5}$$

with

$$\Omega = \frac{D_p Z_p - D_s[1 + (2c_s/Z_p c_p)]}{D_p Z_p + D_s[1 + (2c_s/Z_p c_p)]} \tag{6}$$

where D, Z, and c are the diffusion coefficient, charge, and molar concentration and indexes p and s refer to polyion and salt, respectively. The dependence of the polyion diffusion coefficient on the polyion

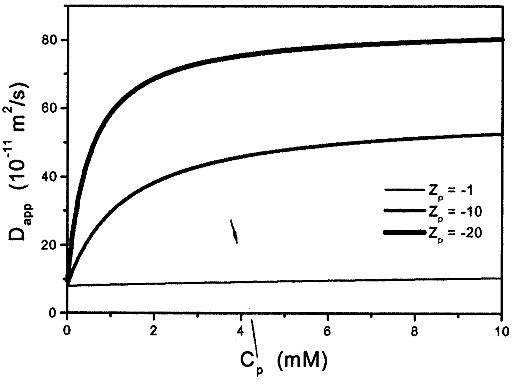

FIGURE 4 The dependence of the apparent polyion diffusion coefficient on the polyion concentration as predicted by the coupled mode theory (Eqs. (5) and (6)). The data are given for polyions with the values $D_p = 8.0 \cdot 10^{-11}$ m^2/s, $D_s = 160 \cdot 10^{-11}$ m^2/s, and $c_s = 10$ mM.

concentration as predicted by Eqs. (5) and (6) is presented in Figure 4. At low polyion concentrations the D_{app} value corresponds to the diffusion coefficient of the uncharged polyion, which depends only on the polyion dimensions. With an increase of the polyelectrolyte concentration the D_{app} value increases until a semidilute regime where polyions overlap is eventually reached and the D_{app} value remains constant. This saturation behavior predicted by the coupled mode theory is in very good agreement with our results presented in Figure 3. Also in most dilute solutions, with and without salt, the diffusion coefficients have the same value indicating that the dimensions of polyions in both cases are comparable.

The I-Ch phase transition and the appearance of the fast DLS mode in 0.5 M KCl solutions shift towards lower concentrations as compared to salt-free solutions. This indicates that potassium ions do not result only in screening of the polyions but stimulate at the same time the self-assembly of guanosine molecules, which is in agreement with NMR spectroscopy [6,7] and circular dichroism measurements [8]. The dynamic behavior of the d(pG) stacks in solutions with added KCl is therefore affected by both the electrostatic screening and the accelerated d(pG) aggregate growth. The distinct interplay of these two effects leads to very similar dynamic properties of solutions with added salt and salt-free solutions.

CONCLUSION

Dynamic light scattering in ammonium d(pG) solutions without added salt and with added 0.5 M KCl shows the presence of the same two relaxation modes in the vicinity of the I-Ch phase transition. The slow diffusive mode is related to the translational motion of large globular aggregates and the addition of 0.5 M KCl results only in an increase of the effective globular dimensions. The faster mode, on the other hand, is assigned to the motion of the charged d(pG) columnar stacks, which is coupled to the dynamics of the smaller counterions. The dependence of the fast diffusion coefficient on the d(pG) concentration can be explained by the coupled mode theory. Measurements with added 0.5 M KCl showed the ability of potassium ions to promote the self-assembly process of d(pG) molecules, which is reflected in a shift of the phase diagram towards lower concentrations in d(pG) solutions with added salt. The d(pG) concentration dependence of the fast diffusion coefficients in salt-free and 0.5 M KCl solutions show very similar behavior.

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