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DNA interaction with cis- and trans- isomers of photosensitive surfactant

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Abstract. Interaction between DNA and photosensitive cationic surfactant in a solution is studied. Studies were conducted to examine the impact of the surfactant in its cis-conformation on the size of DNA molecule and also to investigate the phase behavior of the system depending on DNA and surfactant concentration. We conclude that trans-isomer of surfactant requires its smaller concentration to reach the DNA compaction compared with cis-isomer received by UV radiation of solutions. Studies of DNA-surfactant systems were performed by means of spectrophotometry and viscometry. Variation of surfactant concentration enables us to determine the precipitation zone on phase diagram. From the viscosity study it can be indicated that precipitation zone is narrower for UV-radiated surfactant and it shifts to higher surfactant concentration. Also we examine the reversibility of DNA compaction in systems with the surfactant in its trans-form.

1. Introduction

In general, cationic surfactants are believed to be effective in terms of DNA compaction because of their self-assembly into micellar-type aggregates on the “surface” of the DNA molecules. Since DNA is a negatively charged polyelectrolyte, electrostatic interactions between oppositely charged DNA phosphate groups and cationic “heads” of surfactants are very important for the formation of complexes [1, 2]. Complex formation also depends on the length of surfactant hydrophobic alkyl chain [2, 3, 4]. The process of the surfactant binding to DNA starts at the concentrations below the surfactant critical micelle concentration, CMC [1, 2]. The longer chain causes lower surfactant concentration for DNA packaging [4]. The changes of DNA molecule conformation can be controlled by adding compacting or decompacting agent into the solution. The reversible compaction can be achieved without direct interference in the solution contents. It is possible if the photosensitive or pH-sensitive cationic surfactant is used [1].

Interaction of photosensitive cationic azobenzene containing surfactant Azo(C6)TAB (figure 1) with DNA in a solution was studied. It is well-known that azobenzene containing surfactants can change conformation form trans- to cis- form under UV irradiation (353 nm) [1, 5]. Reversible cis-trans transition can be induced by visible light (453 nm) or can be realized as a relaxing in a dark. This conformational transition can be checked with UV-spectroscopy as cis- and trans- isomers have typical absorption spectra including bands out of DNA absorption region. The influence of surfactant...
conformation on the size of DNA molecular coil in a solution was investigated. The phase behavior of the system depending on DNA and surfactant concentration was also regarded.

2. Materials and methods
Azo(C6)TAB (chemical formula CH3(CH2)3-C6H5N=NC6H5-O(CH2)6N(CH3)3Br) surfactant we used was synthesized according to the procedure described in [6]. Calf thymus DNA (CT-DNA) with \( M = 11 \times 10^6 \) Da by Sigma was used. Studies of DNA-surfactant solutions in 0.005 NaCl systems were performed by means of spectrophotometry and viscometry. Absorption spectra for DNA-surfactant systems were registered in 2 mm or 5 mm cells depending on components concentration. During the spectral studies we used SF-56 UV/Vis spectrophotometer (LOMO, Russian Federation). Viscosity measurements were carried out on a low-gradient original construction rotary viscometer of Zimm-Crothers type [7].

![Figure 1. Structure of Azo(C6)TAB](image)

3. Results and discussion

3.1. Viscosity studies
The relative viscosity of DNA solution \( \eta_r = \eta/\eta_0 \) (where \( \eta \) and \( \eta_0 \) are solution and solvent viscosities) at various surfactant concentrations \( C(Azo) \) was examined. Then the relative change of reduced viscosity \( (\eta_r - 1)/C(DNA) \) was plotted as a function of the ratio of surfactant concentration to DNA phosphate molar concentration \( z = C(Azo)/C(DNA) \). It is known that the change of reduced viscosity of DNA solution at constant \( C(DNA) \) reflects mainly change in the size of DNA molecular coil. Decrease in the viscosity of DNA solution in 0.005 M NaCl with \( z \) increase represents shrinkage of molecular coil induced by surfactant binding to DNA (at \( z > 0.2 \)). DNA packaging with the viscosity of a solution similar to the solvent viscosity at a definite \( C(Azo) \) was observed at \( z = 1 \) (figure 2). DNA precipitation as visible flakes in a solution is realized at \( z > 1 \). Interestingly, at \( z > 2 \) the solution becomes transparent again and DNA nanoparticles formation was observed instead of DNA precipitation [1].
Figure 2. The relative change in DNA solution reduced viscosity with z value in 0.005 M NaCl for trans- (black signs) and cis- (open signs) isomers. The precipitation zones for trans- and cis- isomers are framed.

So the variation of surfactant concentration in a solution at constant DNA concentration enables us to determine phase separation in the system – the appearance of the precipitation zone (see figure 2). It can be indicated from the viscometric data that the precipitation zone becomes narrower for UV-irradiated surfactant (cis- isomer). This zone also shifts to higher surfactant concentration. We conclude on the base of experimental results that more hydrophobic trans- isomer of surfactant provides more effective DNA packaging \([1, 8]\). It causes DNA precipitation at smaller concentration (more precisely, z value) compared to cis- isomer (which was received by 10 minutes-UV irradiation of surfactant solution before mixing with DNA). For the same DNA and surfactant concentrations DNA precipitation was observed for cis- isomer at \(z = 1.2\) up to \(z = 1.8\) instead \(z = 1\) and \(z = 2\) for trans- isomer respectively.

3.2. Spectral studies

During the experiment we check light-induced cis-trans isomerization with UV absorption spectra (figure 3). One can see the difference in absorption spectra for cis- and trans- isomers of surfactant in 0.005 M NaCl. We change surfactant conformation by 10 minutes UV irradiation at 353 nm for trans- to-cis isomerization (figure 3 spectra a and c). After that we use visible light illumination for cis-to-trans isomerization (b and d spectra). Two different surfactant solutions in 0.005 M NaCl (with \(C(Azo) = 2 \times 10^{-5}\) M below CMC (spectra a and b) and with \(C(Azo) = 3 \times 10^{-4}\) M above CMC (spectra c and d) were used. The spectrum of trans-isomer consists of two resolved bands with the shoulder at \(\lambda > 400\) nm. After trans-to-cis isomerization the main maximum shifts to the blue region with visible hypochromic effect, the short-wave band becomes wider and smaller and long-wave shoulder transforms into third band (spectra a and c). Visible light induces the returning of cis-conformation into trans-state again (spectra b and d). It is clear from figure 3 that at \(C(Azo) > CMC\) cis-to-trans transition also occurs, and micelle state for trans-isomers can be formed. Indeed, the most intensive band for trans-isomer has the tendency to the appearance of the second maximum at 345 nm typical for micelle with usual non-micellar maximum at 353 nm. This band for cis- isomer is not symmetric with the maximum at 325 nm. For \(C(Azo) < CMC\) the central band has one maximum at 353 nm for trans- and one maximum at 320 nm for cis- isomer. Nevertheless, surfactant state (micellar
or non-micellar) in a solution does not influence significantly on trans-to-cis and cis-to-trans transitions.

![Figure 3. Surfactant spectra after UV (a, c) and further visible (b, d) illumination for C(Azo) = 2 \times 10^{-5} \text{ M} (a, b) and C(Azo) = 3 \times 10^{-4} \text{ M} (c, d).](image)

After the mixing of DNA and surfactant solutions (for all systems C(Azo) < CMC) the spectrum of surfactant in trans- conformation out of DNA absorption band is similar to observed for micellar state. It was shown earlier that DNA as a template organizes micelle-like structure for bonded surfactants. After UV irradiation trans-to-cis transition is realized as it follows from spectral changes (figure 4a). The surfactant in these systems (spectra b’, c’, d’) was in cis- form as the systems were UV light illuminated (dashed lines). The precipitation does not exist for these systems. Two of these systems with surfactant in its trans- and cis- forms and its concentration C(Azo) = 2 \times 10^{-5} \text{ M} compared to the corresponding DNA-free surfactant solutions of the same C(Azo) are shown in figure 4b.

![Figure 4a. Spectra for DNA-surfactant systems with Z < 0.5: DNA control (a), z = 0.09 C(Azo) = 2 \times 10^{-5} \text{ M} before UV illumination (the surfactant in trans- form) (b), z = 0.13 C(Azo) = 2.8 \times 10^{-5} \text{ M} before UV illumination (c), z = 0.19 C(Azo) = 4 \times 10^{-5} \text{ M} before UV illumination (d), z = 0.09 C(Azo) = 2 \times 10^{-5} \text{ M} after UV illumination (the surfactant in cis- form) (a’), z = 0.13 C(Azo) = 2.8 \times 10^{-5} \text{ M} after UV illumination (b’), z = 0.13 C(Azo) = 2.8 \times 10^{-5} \text{ M} after UV illumination (c’), z = 0.19 C(Azo) = 4 \times 10^{-5} \text{ M} after UV illumination (d’).](image)
3.3. Reversibility of transition
The reversibility of surfactant-induced DNA compaction in a solution also has been examined. The system with DNA C(DNA) = 0.01 % (phosphate molar concentration $3 \times 10^{-4}$ M) after shrinkage and surfactant in trans- form at $z = 0.8$ was diluted with 0.005 M NaCl (scheme 1). The decompaction of DNA was indicated by the viscometric experiment (see table 1) via the comparison of examined system with the control solutions. Systems of $z = 0.8$ also can be compared with the system $z = 0.4$. It was shown earlier that the precipitation zone depends on C(DNA) \cite{9} so the system with C(DNA) = 0.01 % at $z = 0.8$ is closed to the border of this zone without any turbidity in solution. The tendency to the reversibility can be manifested for some of the systems.

Scheme 1. The preparation of systems for the viscometric experiment. Stock DNA solution with C(DNA) = 0.01 % ($3 \times 10^{-4}$ M) was diluted with 0.005 M NaCl (control 1) and with surfactant (control 2). DNA-surfactant solution after DNA shrinkage ($z = 0.8$) was diluted with 0.005 M NaCl for the measurements and checking the DNA decompaction. System $z = 0.4$ was also measured for comparison.
Table 1. The results of viscometry for DNA-surfactant solutions according to scheme 1.

<table>
<thead>
<tr>
<th>Syst. No.</th>
<th>C(DNA)</th>
<th>z</th>
<th>Definition</th>
<th>Reduced viscosity of DNA solutions (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01 %</td>
<td>0</td>
<td>initial</td>
<td>105±5</td>
</tr>
<tr>
<td>2</td>
<td>0.005 %</td>
<td>0</td>
<td>control 1</td>
<td>90±5</td>
</tr>
<tr>
<td>3</td>
<td>0.01 %</td>
<td>0.8</td>
<td>DNA shrinkage</td>
<td>20±5</td>
</tr>
<tr>
<td>4</td>
<td>0.005 %</td>
<td>0.8</td>
<td>control 2</td>
<td>74±5</td>
</tr>
<tr>
<td>5</td>
<td>0.005 %</td>
<td>0.8</td>
<td>checked</td>
<td>76±5</td>
</tr>
<tr>
<td>6</td>
<td>0.005 %</td>
<td>0.4</td>
<td>for comparison</td>
<td>84±5</td>
</tr>
</tbody>
</table>

4. Conclusion

It can be concluded that cis- isomers cause DNA shrinkage and DNA precipitation at higher z value than trans- isomers. This transition is reversible according to change in z value. The formation of DNA-surfactant complexes does not prevent cis-trans-cis isomerization in a solution.

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References