Supporting Text

Overview

The total scattering of the tethered DNA, $I(s)$, includes a contribution from the ion atmosphere surrounding the DNA. We extracted the signal corresponding to the tethered DNA scattering alone by applying an empirical correction factor for the ion atmosphere scattering. This factor was obtained from the ratio of the observed and predicted scattering of a control DNA duplex. Here, we theoretically predict this correction for individual tethered DNA conformations (Fig. 8) and estimate the systematic error incurred by assuming that the correction is constant for all DNA conformations and therefore obtainable from a control duplex measurement.

In the text, a Yukawa potential model between the pairwise phosphates was used to calculate the tethered DNA interhelical potential in varying conformations (Eqs. **1** and **2**). We show that this simple phenomonelogical model can reasonably reproduce the repulsive interhelical potentials between DNAs obtained from nonlinear Poisson Boltzmann treatments (Fig. 9), supporting the use of the simple model as a general form for electrostatic interactions between DNAs.

Fig. 10 shows scattering profiles for the different tethered duplexes in putrescine^{2+}, $Co[NH_3]_6^{3+}$, and spermine^{4+}.

Supporting Results

A constant ion atmosphere correction factor can be applied, as this factor is nearly independent of the tethered DNA conformation.

The total scattering profile $I(s)$ [$s = 2\sin(\theta/2)/\lambda$; θ is the scattering angle, λ is x-ray wavelength] includes contributions from the DNA itself and from the correlations between DNA and its surrounding ion atmosphere (refs. 1 and 2)

$$I(s) \propto b_D^{\,2} \cdot I_{DD}(s) + 2 \cdot b_D (n_I b_I) \cdot I_{DI}(s) \qquad [S1]$$

where b_D and b_I are the scattering factors (relative to solvent background) of hydrated DNA and a counterion, respectively, and n_I is the number of ions condensed onto each DNA. An additional scattering term from ion-ion correlations has a negligible effect on the data correction and was therefore not included in the treatment below (data not shown; ref. 2). Eq. **S1** can be rewritten as:

$$I(s) \propto I_{DD}(s) \cdot f_{ion}(s) \qquad [S2]$$

where

$$f_{ion}(s) = 1 + 2\frac{n_I b_I}{b_D} \cdot \frac{I_{DI}(s)}{I_{DD}(s)} \qquad [S3]$$

If the correction factor $f_{ion}(s)$, is independent of DNA conformation, the scattering profile from DNA scattering alone $I_{DD}(s)$ can be obtained by simply dividing the total observed scattering profile $I(s)$ by $f_{ion}(s)$ determined for a control DNA sample with a fixed conformation (i.e., a rigid duplex).

To test the assumption of constant $f_{ion}(s)$, we calculated this theoretical ion atmosphere correction factor for different DNA conformations in the presence of monovalent or divalent cations (Eq. **S3**). $I_{DD}(s)$ and $I_{DI}(s)$ were calculated with an ion atmosphere predicted by the nonlinear Poisson Boltzmann (NLPB) model, as described in refs. 2 and 3. The assumed numbers of Na^+ and Mg^{2+} ions in the vicinity of the tethered DNA (24 bp total), n_I , are 48 and 24, respectively.

The calculated theoretical correction factor $f_{ion}(s)$ for the *12/PEG9/12* tethered duplex in different conformational states and for a 24-bp DNA duplex in the presence of 1.2 M Na^+ and 0.6 M Mg^{2+} are shown in Fig. 8. The standard deviation of the correction factors due to the different conformations is less than 1% and is considerably smaller than the statistical error of the data at all scattering angles (Fig. 8) (see below). We conclude that the error incurred by using an ion atmosphere correction factor for the tethered duplex, determined by measurements on a control duplex, is negligible.

Note that the correction factors in higher charged multivalent cations (e.g., $Co[NH_3]_6^{3+}$, $spermine^{4+}$) were not evaluated theoretically because distributions of higher valence ions are not accurately predicted by the NLPB model (see ref. 6 and references therein) and are not implemented in Delphi. Nevertheless, the multivalent ions are expected to be more tightly bound to the DNA than monovalent ions, so their spatial distribution and scattering contributions should depend less on the DNA conformation.

The pairwise phosphate potential model can reproduce NLPB interhelical electrostatic energies for the tethered DNA

A simple pairwise phosphate potential model was used in the text to provide a quantitative estimate of the inter-helical potential of the tethered DNA (Eqs. **1** and **2**). Although the true physical potential may be fundamentally nonlinear, a pairwise-summed potential model may be an accurate phenomenological description of the potential. As a test of the model, we evaluate herein whether it reproduces the interhelical energy obtained from a well defined (and nonlinear) model, the repulsive potential between DNA double helices predicted by the NLPB model.

The electrostatic energies of the tethered DNA (*12/PEG9/12*) with 100 different conformations in four different ionic environments (0.02, 0.1, 0.6, and 1.2 M monovalent ions) were obtained by numerically solving the NLPB equation at atomic resolution in DelPhi (refs. 2-5). Self-energies of the individual duplexes were subtracted to obtain the interaction energy between the two helices. The pairwise phosphate potential model was

also applied to the tethered DNA conformations according to Eqs. **1** and **2**. Because the resulting energies depend on the values of two parameters, the amplitude of the repulsion energy $\Delta G_{P\text{-}P}$ and the repulsion range λ, we determined the values of these two parameters that allow the best agreement (least square deviation) between the energies calculated by the pairwise phosphate potential model and those obtained by NLPB. We found that the phenomonelogical model reproduces the NLPB calculations with appropriate parametrization of $\Delta G_{P\text{-}P}$ and λ, to a mean accuracy of ± 0.5 kT (Fig. 9). Furthermore, the best-fit range parameters λ were in good agreement with the Debye-Hückel screening lengths expected for the different salt conditions (Fig. 9).

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