

Effect of Water Drag on Diffusion of Drifting Polarons in DNA

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It has been shown, theoretically and experimentally, that a hole or an excess electron on a DNA molecule in solution forms a delocalized wave function, a polaron. For an all-adenine (A) sequence or a mixed sequence of guanines (G's) and A's, calculations taking into account the polarization of the solution give the wave function spread over approximately four bases, which appears to be in agreement with experiment. The polaron may move by hopping or by drift. Drift can take place in a region with all the same bases, for example, A's, by the polaron dropping an A on the trailing edge and picking up an A on the leading edge. For drift that is not too rapid, the necessity of the polarization changing as the polaron moves exerts a drag on the polaron. We calculate the drag by using a model introduced earlier to describe the polaron. We find the drag to be proportional to the velocity of the polaron and to the orientational relaxation time of the water molecules. The drag is also a function of the Coulomb interactions of the fractional charges on the bases constituting the polaron, as modified by the polarization charge induced in the solution. The diffusion rate and mobility for all A polarons, calculated taking into account the drag, are $8 \times 10^{-5} \text{ cm}^2/\text{s}$ and $3 \times 10^{-3} \text{ cm}^2/(\text{V s})$, respectively. We believe that in the experimental studies that have been carried out on hole propagation in a series of A's it was drift being observed rather than the hopping of a localized hole between adjacent A's, as was assumed to be the case.

Introduction

Calculations show that a hole or an excess electron on a DNA molecule lowers its energy substantially by polarizing its surroundings, particularly water.^{1–5} It was found that if a hole is in a sequence of four or more A's, or A's and G's, its wave function is spread over approximately four bases, constituting a polaron.^{1–3,6} This is in agreement with experiments that have shown that the wave function of a hole on DNA in solution is delocalized⁷ and other experiments suggesting that the delocalization is over approximately four bases for an all-A sequence.^{3,8}

Somewhat less direct evidence for the delocalization of the hole wave function comes from the experiments of Schuster and colleagues that tracked the motion of holes injected into various sequences.⁹

The polaron may move by hopping or by drift. Drift motion requires a sequence of all the same bases, for example, A's, and is accomplished by an A at the trailing edge of the polaron being dropped off while an A at the leading edge is incorporated. Hopping may take place between two regions in which the bases in the sequence are all the same or are different. For either type of motion to be reasonably probable, the bases and water molecules in the final region must be aligned similarly to those in the initial region (conformationally gated transport⁸). This is clearly a more difficult condition to satisfy for hopping than for drift, making hopping a much slower process.

Motion of a hole injected into a DNA sequence consisting of a G followed by a number of A's was first studied extensively by Giese and co-workers, who concluded initially that hole transport consists of hopping between G's.¹⁰ After the group

extended their experiments to more than three A's following the G, they interpreted the results as showing tunneling of the hole through the first three A's, after which the hole acquired sufficient energy to jump onto the bridge of A's.^{11,12} The motion of the hole beyond the first three A's differed in that it showed much smaller attenuation. It was postulated by Giese to be hopping of the hole, localized on a single A, between neighboring A's,^{11,12} called A-hopping. A serious difficulty with this explanation, however, is that it is not possible to account for both the strong attenuation at the first three A's and the weak attenuation when the hole traverses further A's.¹³ It was suggested by Bixon and Jortner that the results could be accounted for if back-recombination of the holes were greatly decreased after three A's.^{13,14}

These difficulties can be resolved with the introduction of polarons. In the presence of a fourth A following the initial G, a polaron can be formed. Because the binding energy of the polaron is $\sim 0.5 \text{ eV}$,¹ polaron formation lowers the energy of the hole sufficiently so that the G is no longer an effective hole trap.^{2,3} Thus, back-recombination is greatly decreased by the introduction of a fourth A and if there are further A's, the hole polaron can move on with relatively little attenuation.

Subsequent studies of hole motion in a series of A's have been carried out by many groups. Typically, holes are created by optical excitation of a suitable electron acceptor attached to a series of A's, which then accepts an electron from an adjacent A. The hole thus created moves down the series of A's toward a hole acceptor. In the discussions of A-hopping, it is assumed that the hole is localized on one site (base) and that each hop is one base in length.^{11,12} In the case of a polaron, although it is delocalized over a number of sites, it can, like the localized hole, move only one site at a time in a sequence of all A's. If the motion is pure diffusion, either the localized hole or the

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polaron would diffuse in time τ over a distance $L = (2D\tau)^{1/2}$, where D is the appropriate diffusion coefficient. Using $L = Na$, where N is the number of sites advanced due to diffusion in time τ_{diff} and a is the distance between sites, we obtain the well-known relationship between the time of diffusion and the number of sites advanced:¹⁵

$$\tau_{\text{diff}} = (a^2/2D)N^2 \quad (1)$$

If the hole motion were pure drift in a constant field of strength E , the relation between the time of drift, τ_{drift} , and the distance covered in that time would be linear, that is,

$$\tau_{\text{drift}} = (a/\mu E)N \quad (2)$$

where μ is the mobility, assumed to be field-independent. More generally, it has been shown that, for the case of diffusion in the presence of a bias,

$$\tau \propto N^\eta \quad (3)$$

where $1 \leq \eta \leq 2$ for a bias toward the hole acceptor and $\eta \geq 2$ for a bias toward the hole donor provided the difference between the rate of forward motion and the rate of backward motion is not too large.¹⁵ The relation (eq 3) would, of course, be true for either the polaron or the localized hole.

Clearly, η depends on the relative amounts of drift and diffusion. We note that, although τ_{drift} is inversely proportional to μ , η may depend little on μ . The ratio $\tau_{\text{diff}}/\tau_{\text{drift}}$ depends on μ/D . However, μ and D satisfy the Einstein relation $D = \mu kT/e$. The result is $(\tau_{\text{diff}}/\tau_{\text{drift}}) = aeEN/2kT$. Thus, the ratio depends on E and linearly on N but not on μ .

To test the N -dependence, experimental studies of hole hopping in a series of A's were carried out by Kawai et al.¹⁶ and Takada et al.¹⁷ In these experiments, the holes were generated by a laser flash on a suitable electron acceptor molecule, naphthalendiimide (NDI), linked to the first A, and propagated through bridges of N A's to a hole acceptor, phenothiazine (PTZ). They interpreted their results as demonstrating η values of -1.5^{16} and -1.7^{17} . To determine η , they used the measurement of the yield of holes at PTZ in both cases, making some simplifying assumptions about the relationship between yield and η . However, as they state, the yield in their experiments is determined primarily by the amount of back-recombination between NDI^- and the ionized A's rather than N or the bias, which means that the η values they obtained are not those defined in eq 3. Indeed, Takada et al. gave the yield as 2.1% or less for $N = 4-8$.¹⁷ The bias dependence will be discussed further in a later section.

The Model

To calculate the diffusion constant D , it is convenient to calculate the drift velocity in an electric field and then use the Einstein relation to obtain D . Earlier, we calculated the drift velocity v in an electric field of DNA polarons arising from chain distortion, that is, nonuniform spacing of the bases.¹⁹ For polarons stabilized by distortion, v is kept finite by the elastic properties attributed to the chain. In our previous calculation of polaron drift velocity,¹⁹ we did not consider the effect of the surrounding medium. We later found that, even if the calculated distortions did occur, they would have much less effect on the polaron properties than would the polarization of the water.¹ Thus, we simplified further calculations by neglecting the possible distortion of the polaron. Additional justification for this neglect is given by the calculations of Gervasio et al.,⁴ who

showed that chain distortion does not contribute to stabilization of the hole. Both Gervasio et al.⁴ and Barnett et al.⁵ found that changes in the solvation shell make the big contributions to stabilization. The Barnett et al. investigation was carried out on a duplex with the sequence (AAGG)₃AA on one chain, with the complementary sequence on the other chain, and with Na^+ ions and a large number of water molecules surrounding it. Their calculations gave the hole wave function mainly localized on a GG pair, in agreement with our earlier calculations for a polaron in water on an AGGA sequence.⁶ They found that the most significant structural changes were "reorientations of water molecules within a radius of 6–8 Å of the DNA..., which maximizes the interaction between the negative end (the oxygen lone-pairs) of the H_2O molecules with the (positive) hole", in other words, polarization.

For the calculation of the drift velocity of the polaron, we use the model setup in ref 1. The bases are considered to be inside a cylindrical cavity, otherwise empty because of the hydrophobicity of the bases, with a diameter equal to that of the double helix. A hole put on the base stack polarizes the water and ions outside the cavity. The water is treated as a continuum. The base structure is simplified by assuming it to be a single stack of bases at the center of the cavity. We allow the hole on the base stack to be delocalized over a number of bases. The energy of the hole is affected by the charge it induces in the water and ions outside the cavity.

As simple as this model is, it led to results in agreement, as noted earlier, with an experimental determination of the extent of the polaron in an all-A sequence and with the binding energy of the polaron obtained in the much more realistic calculations of Barnett et al.⁵ In that reference, the configurations of the system—DNA oligomer plus water and counterions—were generated by molecular dynamics simulations over 10 ns intervals. From these, a set was chosen, with relatively long residence times being the principal selection criterion. An electron was removed from each of these configurations, and the ones with the lowest vertical ionization potentials were chosen for further relaxation. Subsequent structural relaxation of the selected ionized DNA configurations gave an energy lowering of 0.4–0.5 eV, comparable to the 0.5 eV lowering that we found for the model described above.¹

To calculate the drift velocity in this model, we start with consideration of the electrostatic energy of a stationary charge in the model. This leads to the expression for the hole energy:¹

$$H(\psi_n, \psi_n^*) = H_0(\psi_n, \psi_n^*) + \frac{1}{2} \sum_{n,n'} g_{n-n'} |\psi_n|^2 |\psi_{n'}|^2 \quad (4)$$

where $e|\psi_n|^2$ represents the charge on the n th base and

$$H_0(\psi_n, \psi_n^*) = -t_0 \sum_n (\psi_n \psi_{n+1}^* + \psi_n^* \psi_{n+1}) \quad (5)$$

where t_0 represents the transfer integral. The $g_{n-n'}$ values were calculated in ref 1 for a stack of A's that were assumed to be at the center of the helix. A table of these values is provided in ref 1. With the $g_{n-n'}$ values, the energy and dimensions of a stationary polaron on the stack were determined using eqs 4 and 5 in the Schrodinger equation. The polarization of the water was found, as noted earlier, to give a hole binding energy of ~ 0.5 eV, specifically for a sequence of all A's and when $t_0 = 0.1$ or 0.2 eV.¹ In later calculations,⁶ we used $t_0 = 0.03$ eV, the value calculated by Voityuk et al.²⁰ and Senthilkumar et al.,²¹ for the transfer integral of a pair of A's and obtained a binding energy $\sim 10\%$ higher than that in ref 1.

When the polaron is moving, the necessity to reorient the water dipoles and reposition the ions as it moves gives rise to

a drag that tends to decrease its velocity. In this connection, an important quantity is the orientational relaxation time τ for water. A measure of the relaxation time is given by the solvation response time, which has been studied for water both theoretically and experimentally. Computer simulations have shown that the solvent response to a change in solute charge distribution is strongly bimodal.²² For water, there is an initial response for atomic solutes on a time scale of ~ 20 – 50 fs.²² The response at longer times, and thus at lower frequencies, has been studied by Kaatz through measurements of the frequency variation of complex permittivity ϵ .²³ For frequencies up to 100 GHz, he finds that the room-temperature data are well fitted by the Debye relation:

$$\epsilon(\omega) = \epsilon(\infty) + [\epsilon(0) - \epsilon(\infty)]/[1 + i\omega\tau]$$

where ω is the angular frequency, and $\tau = 8.3$ ps. According to the experiments of Takada et al. discussed earlier, the rate of hole motion in their sample is ≈ 1 base/ns.¹⁷ It is then reasonable that the hole motion would be affected by solvent changes at the rate of less than 100 GHz (10^{11} /s), where the Kaatz analysis holds, but not by changes at the rate of 10^{13} /s or 10^{14} /s. It can be concluded that the relaxation time appropriate for the description of polaron drift in a series of A's is 8.3 ps. This is much shorter than the relaxation time for repositioning ions, such as Na^+ or K^+ , as the hole moves. That relaxation time, given by $\epsilon/4\pi\sigma$, where σ is the conductivity, is 650 ps for a 0.1 M solution of NaCl ²⁴ and should be ineffective in causing drag.

Calculation of the Drag and the Diffusion Constant

To describe the effect of the polaron motion on the water, we introduce a screening charge around each base, to be denoted Q_n for the n th base. When the polaron is moving, Q_n changes with time. The equation of motion for the screening charge describes relaxation to the equilibrium value, Q_n^{eq} , which we take to be the value for a stationary polaron. Thus,

$$(dQ_n/dt) = -(Q_n - Q_n^{\text{eq}})/\tau \quad (6)$$

where τ is the rotational relaxation time. We set up a Hamiltonian to represent the coupling of Q_n to the hole motion:¹

$$H(\psi_n, \psi_n^*) = H_0(\psi_n, \psi_n^*) + \sum_{n,n'} \lambda_{n-n'} Q_n |\psi_{n'}|^2 + (\kappa/2) \sum_n Q_n^2 \quad (7)$$

where H_0 is given by eq 5. The second term on the right-hand side of eq 7 represents the Coulomb interaction between Q_n and the charges on the bases. The third term, increasing as Q_n^2 , is introduced to keep the charges, Q_n^{eq} , finite. κ may be thought of as a kind of elastic constant. The Hamiltonian in eq 7 must also be applicable for stationary, equilibrium polarons. By setting $(\partial H/\partial Q_n) = 0$, we obtain the following for the static case:

$$Q_n^{\text{eq}} = -\sum_{n'} (\lambda_{n-n'}/\kappa) |\psi_{n'}|^2 \quad (8)$$

From the Hamiltonian in eq 7 we can also obtain an expression for the rate of energy loss, $(d\epsilon/dt)_w$, of the drifting polaron to water. From the second and third terms on the right of eq 7, making use of eq 8, we find

$$(d\epsilon/dt)_w = -\kappa\tau \sum_n (dQ_n/dt)^2 \quad (9)$$

The energy loss constitutes a drag on the polaron. In the steady state, with the polaron propagating with constant velocity v ,

the drag force is given by

$$F_{\text{drag}} = -(\kappa\tau/v) \sum_n (dQ_n/dt)^2 \quad (10)$$

Now, we limit consideration to the case of slow motion of the polaron, specifically $v \ll$ length of the polaron divided by the orientational relaxation time and, thus, $v \ll 10^4$ cm/s. This condition is well satisfied in the samples studied by Takada et al.,¹⁷ where, as mentioned earlier, $v \approx 1$ base/ns and, thus, $v \approx 34$ cm/s. Of course, it could always be satisfied by keeping the bias low enough. To satisfy this condition with the mobility that will be obtained by the present calculations, 3×10^{-3} cm²/V s, the bias or equivalent electric field E must be much less than 4×10^6 V/cm. Satisfying this condition means that (dQ_n/dt) may be replaced by (dQ_n^{eq}/dt) , which may be obtained from eq 8. When Q_n is replaced by Q_n^{eq} in the Hamiltonian in eq 7, the resulting Hamiltonian must describe the stationary polaron; that is, it must be equal to the Hamiltonian in eq 4. Equating the two (eqs 7 and 4) sets up a relation between $g_{n-n'}$ and $\lambda_{n-n'}$, making it possible to express Q_n^{eq} in terms of the already evaluated $g_{n-n'}$:

$$\sum_n (dQ_n^{\text{eq}}/dt)^2 = \sum_{n,n'} (g_{n-n'}/\kappa) (d|\psi_n|^2/dt)(d|\psi_{n'}|^2/dt) \quad (11)$$

For slow motion of the polaron, we can neglect any change in shape, which would give a correction of higher order in v . We may then take $|\psi_n(t)|^2 = f(n - vt/a)$, with a being the spacing of the bases and $f(\xi)$ being a continuous function. With these quantities and eq 11, we may write eq 10:

$$F_{\text{drag}} = (\tau v/a^2) \sum_{n,n'} g_{n-n'} f'(n) f'(n') \quad (12)$$

where $f'(\xi) = df/d\xi$. It is seen that the drag force is linear in v , as it is for an object moving slowly in a viscous fluid.²⁵

Steady drift motion against this drag can be maintained by application of an electric field of intensity E , such that $F_{\text{drag}} = eE$. We can then obtain from eq 12 the drift velocity:

$$v = ea^2 E/\tau \sum_{n,n'} g_{n-n'} f'(n) f'(n') \quad (13)$$

Thus, the drift velocity is linear in field intensity for fields that are not too large. To complete the calculation of v , we may evaluate $f'(n)$ using $|\psi_n|^2$ obtained for the stationary polaron because, as noted above, the shape should not change under slow motion. The only parameter required is t_0 , the transfer integral. In ref 1, we used t_0 values of 0.2 and 0.1 eV and found the polaron shape to be quite similar for the two values. In the current calculations, we use t_0 values of 0.08 and 0.03 eV.^{20,21} We obtained good fits to the numerically evaluated $|\psi_n|^2$,¹ for both t_0 values with a Gaussian. For $t_0 = 0.08$ eV, $|\psi_n|^2$ was fitted by $f(x) = \alpha \exp[(-x/c)^2]$ with $\alpha = 0.36$ and $c = 1.559$, while, for $t_0 = 0.03$ eV, it was fitted by the same function with $\alpha = 0.49$ and $c = 1.14$. With these values and the $g_{n-n'}$ values from ref 1, the mobility μ , defined as v/E , was found to be 3.1×10^{-3} cm²/V s for $t_0 = 0.08$ eV and 2.7×10^{-3} cm²/V s for $t_0 = 0.03$ eV. Note that the mobility is smaller when t_0 is smaller because the effect of the water is greater. With these numbers, the diffusion rate, D , of the polaron obtained from the Einstein relation, $D = \mu kT/e$, is 8×10^{-5} cm²/s.

Unfortunately, it will not be easy to compare the theory with experimental results, such as those in ref 17. As noted earlier, holes were formed in the experiments as a result of a laser flash on the electron acceptor (NDI) bonded to one end of the series of A's. The holes were drawn to a hole acceptor, PTZ, by the difference in the oxidation potentials of A and PTZ, which can

be thought of as giving rise to an electric field. The oxidation potential of A is difficult to determine. The values quoted in the literature range from 1.0 to 1.7 V vs SCE. There is also a range of values for PTZ in the literature, 0.65–0.9 V vs SCE. To obtain a rough idea of the resulting electric field, we use the difference between the average values in the respective ranges, 0.6 V. If this difference were to be manifested as a uniform electric field over, for example, 8 A's, the field intensity would be 2×10^6 V/cm. If the field were this large, drift could dominate over diffusion. Of course, the field is not likely to be uniform. In addition, there is an opposing field that is due to the ionized electron acceptors at the other end of the sample, and this field is clearly nonuniform. If the nonuniformity of the total field were to give rise to a region of quite small fields, the time required for diffusion in this small-field region might dominate, and the N -dependence would look like that for diffusion in a weak field. The situation is obviously complex.

Conclusions

A polaron in a DNA molecule that is made up of a series of the same base pairs can drift in either a concentration gradient or a bias due to an electric field or a difference in the oxidation potentials of donor and acceptor molecules at the ends of the DNA. We believe it is this drift, rather than "A-hopping", that has been observed in experiments, such as those in refs 16 and 17, where the hole has been created by optical excitation. The delocalization of the polaron and its large binding energy suggest that random fluctuations of the bases are less important than the drag effect of the water in limiting the mobility or rate of diffusion of a slowly drifting polaron. In any case, the drag sets up an upper limit for μ or D of a drifting polaron. (Random fluctuations might, on the other hand, increase the hopping rate.) We find the drag force to be proportional to the velocity of the polaron and the orientational relaxation time of the water molecules. It also depends on how the charge is distributed among the bases constituting the polaron.

The comparison of experiment with theory for experiments such as those in refs 16 and 17 will not be easy because, with the bias being important, it will be necessary to know how the bias varies along the series of A's. It might be easier to determine the mobility by performing an electrochemical experiment. It is difficult to directly introduce holes into DNA electrochemically, but they could be introduced by attaching to the free end of the DNA, in the usual electrochemical cell setup for studying electrons in DNA, an electron acceptor that can be excited by light. This was accomplished by Okamoto et al., using anthraquinone as the acceptor.²⁶ An electrochemical experiment to determine mobility could also be carried out for electrons. The calculations carried out above are also valid for electron polarons, provided that protonation and deprotonation are avoided, which could be achieved by injecting electrons into DNA consisting of a series of A/T's.²⁷ The only parameter involved is t_0 , and it is likely to be in the range that we have used in calculating for holes. The major difficulty in doing the experiment electrochemically would be the determination of the voltage drop across the linker and the contacts.

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