Control of Electron Transfer Rates in Liquid Crystalline Media

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Received: August 5, 2002; In Final Form: December 17, 2002

The solvent reorganization energy of electron-transfer reactions is calculated for a solvent undergoing a structural phase transition from the isotropic to nematic phase. The calculation is based on the response function of the solvent polarization fluctuations obtained from Monte Carlo simulations of a model fluid of hard dipolar spherocylinders in a range of densities covering both the isotropic and nematic phases. The reorganization energy shows a significant anisotropy with respect to the orientation of the donor−acceptor complex relative to the nematic director in the nematic phase. A possibility to control electron-transfer rates arising from solvation anisotropy is discussed.

1. Introduction

The biological environment for photosynthetic charge separation[1] and media employed for solar energy conversion[2] are highly dielectrically anisotropic. Liquid crystals present an excellent model solvent for studying electron transfer (ET) in anisotropic media[3] with a potential for technological applications.[2] The limited body of experimental evidence currently available points to quite dramatic changes in ET rates for some reactions occurring in the range of temperatures close to the point of isotropic−nematic (IN) phase transition of the solvent.[3] The existing experimental data do not allow an unambiguous assignment of the origin of observed changes to either retardation of solvent orientational motions in nematic mesogens (solvent dynamics effect) or to the variation in the reaction activation barrier. An understanding of the origin of the rate alteration and factors making the ET system sensitive to small changes in solvent parameters is important for clarifying the effect of anisotropy in biological systems and may help in designing molecular electronic devices with strong nonlinear response to an external action.[4] Measurements[5] and computer simulations[6] of the solvent dynamics in the IN transition region show that the local solvent dynamics is not substantially affected by the macroscopic orientational order in the solvent. These observations call for a thermodynamic explanation of the rate constant variation in terms of a change in the activation barrier of ET in the transition region. One can anticipate that solvation properties of the medium, represented by the solvent component of the ET driving force and the ET solvent reorganization energy λ_s,[7a] may experience substantial changes due to the structural phase transition. To understand the effect of solvent anisotropy on ET activation, we have performed Monte Carlo (MC) simulations of the distribution of microscopic fluctuations of the solvent polarization in a range of solvent densities covering both the isotropic and nematic phases. This paper presents our initial results focusing primarily on the solvent reorganization energy of ET.

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2. Model

We report here the first calculation of the solvent reorganization energy of ET in a solvent transforming from an isotropic to a nematic phase. The ET solvent reorganization energy λ_s is defined within the Marcus picture of ET either through the energy of vertical transition[7a] or through the width of Gaussian nuclear fluctuations of the donor−acceptor energy gap[7b] of the donor−acceptor complex (DAC). Within the linear response approximation used in the present paper, which is essentially equivalent to the assumption of the Gaussian statistics,[7c−e] the energy gap variance defines the solvation chemical potential and, therefore, the complete thermodynamics of solvent reorganization.[7f,g] The definition of λ_s in terms of the width of energy gap fluctuations is then equivalent to that in terms of the average vertical energy gap. In polar liquids, the donor−acceptor gap fluctuates because of thermal fluctuations of the nuclear solvent polarization **P** coupled to the difference in the vacuum electric field of the DAC, ΔE_0, in the final and initial states.[8] The correlation function of the polarization fluctuations $\delta\mathbf{P}$

$$\chi_{\alpha\beta}(\mathbf{r}',\mathbf{r}'') = (k_B T)^{-1} \langle \delta P_\alpha(\mathbf{r}')\delta P_\beta(\mathbf{r}'')\rangle \qquad (1)$$

in the vicinity of the DAC (the α and β subscripts stand for Cartesian components) then fully defines λ_s.[9] In eq 1, $\langle ... \rangle$ stands for the statistical average in the system containing both the solute and the solvent. The goal of the present paper is to obtain the polarization correlation function from computer simulations carried out on a model fluid undergoing the IN phase transition. This correlation function is then used to calculate λ_s. The function $\chi_{\alpha\beta}$ is obtained from the simulations of the pure solvent thus neglecting the component of λ_s originating from restructuring of the solute−solvent density profile[7c] (density reorganization energy,[9a] see below).

We have chosen a model fluid of hard spherocylinders (HSCs) with longitudinal point dipoles ($m^2/(\sigma^3 k_B T) = 1.0$, where m is the dipole moment, σ is the diameter, and the length/diameter aspect ratio is 5.0). This fluid is known to form a nematic phase[10] with increasing its packing fraction η (ratio of the volume occupied by the solvent molecules to the total volume of the liquid) at $\eta > 0.407$. Because the attraction forces affect

10.1021/jp026688e CCC: $25.00
Published on Web 02/06/2003

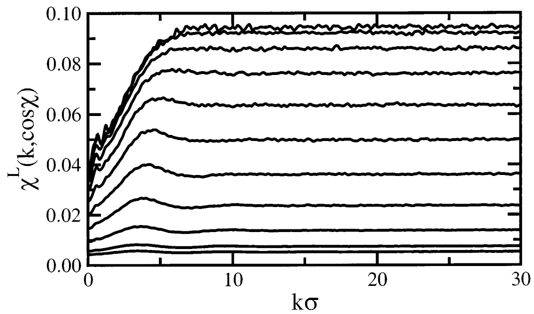

Figure 1. $\chi^L(k, \cos \chi)$ in the nematic phase. The curves are drawn with angles χ at equal intervals between 0° (upper curve) and 90° (lower curve); $\eta = 0.470$ and σ is the diameter of HSCs.

weakly the thermodynamic state of the fluid of HSCs,[10] changing the density is used here to drive the solvent from the isotropic to nematic phase. The choice of a relatively simple fluid of HSCs allowed us to run extensive MC simulations (0.6−0.8 million production cycles) with 800 solvent molecules and directly generate the Fourier transform of the polarization response function $\chi_{\alpha\beta}(\mathbf{k})$ (the details of the simulation procedure will be published elsewhere[11]). The polarization response function poorly converges in computer simulations,[12a] and it is hard to obtain for more complex model fluids.[12b,c,d] $\chi_{\alpha\beta}(\mathbf{k})$ is inaccessible experimentally and has been studied only theoretically for a few model isotropic fluids.[12,13] This is the first calculation of the polarization correlation function performed in a nematic solvent.

The response function obtained from computer simulations is used to calculate the solvent reorganization energy according to the equation[9]

$$\lambda_s = \int (d\mathbf{k}/16\pi^3)\, \chi^L(\mathbf{k}) |\Delta E_0(\mathbf{k})|^2 \tag{2}$$

In eq 2, $\chi^L(\mathbf{k}) = \sum_{\alpha,\beta} \hat{k}_\alpha \chi_{\alpha\beta} \hat{k}_\beta$ is the longitudinal response function ($\hat{k}_\alpha$ are the Cartesian components of the unit wave-vector $\hat{\mathbf{k}}$). $\chi^L(\mathbf{k})$ represents the solvent response to a spherically symmetric (longitudinal) solute field.[12,13] This type of the solute electric field is employed in the Marcus two-sphere configuration[7a] modeling the DAC as two spheres of radii R_D (donor) and R_A (acceptor) separated by the distance $R > R_D + R_A$ (intermolecular ET).[7a] The Marcus configuration with $R_A = R_D = 4$ Å and $R = 10$ Å is adopted here for the calculations of λ_s. For the explicit solvent used here, one has to specify the size of the solvent molecules. The calculations were carried out with the diameter of HSCs fixed at $\sigma = 4$ Å.

3. Results and Discussion

Because of the axial symmetry of the nematic solvent, $\chi^L(\mathbf{k})$ depends not only on the absolute value of the wave-vector $\mathbf{k}$ but also on the azimuthal angle χ between $\mathbf{k}$ and the nematic director. The function $\chi^L(k, \cos \chi)$ is shown in Figure 1 for the nematic phase formed by HSCs. The response function at large k is proportional to $1 + 2S_2P_2(\cos \chi)$, where S_2 is the nematic order parameter[14] and $P_2(\cos \chi)$ is the second-order Legendre polynomial. In our simulations, S_2 is close to zero in the isotropic phase ($\eta = 0.382$ in Figure 2) and is about 0.8 in the nematic phase ($\eta \geq 0.407$). The nematic phase is thus characterized by a substantial anisotropy of $\chi^L(\mathbf{k})$. This anisotropy is projected into the dependence of λ_s on the orientation of the DAC relative to the nematic director. Figure 2 shows the dependence of λ_s on the angle θ between a vector connecting the centers of the donor and acceptor and the director. There is no dependence of

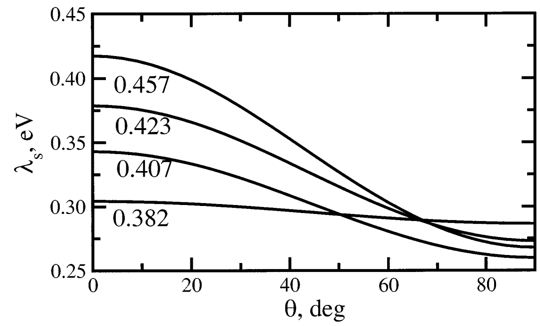

Figure 2. λ_s vs the angle θ between the nematic director and the vector pointing from the center of the donor to the center of acceptor at packing fractions of the solvent of HSCs shown in the plot. The DAC parameters are $R_D = R_A = 4$ Å and $R = 10$ Å.

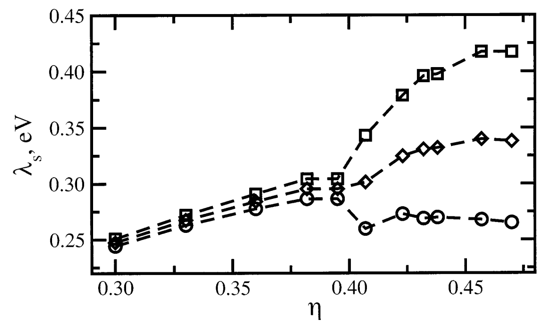

Figure 3. λ_s calculated according to eq 2 with the response functions from MC simulations. The points are obtained at different angles: $\theta = 0°$ (squares), $\theta = 45°$ (diamonds), and $\theta = 90°$ (circles). The parameters of the DAC are as in Figure 2. The dashed lines are drawn to guide the eye.

λ_s on θ in the isotropic phase ($\eta = 0.382$), and λ_s drops by about a factor of 2 when the DAC is rotated from a parallel alignment ($\theta = 0°$, superscript || in notation below) to a perpendicular alignment ($\theta = 90°$, superscript $\perp$) in the nematic phase with $\eta = 0.457$.

The dependence of λ_s on the solvent packing fraction is shown in Figure 3. The anisotropy of the response function results in a reorganization energy gap between the parallel and perpendicular orientations of the DAC in the nematic phase. The dielectric continuum limit of the Marcus theory[7a] follows from eq 2 by assuming $\chi^L(k) \simeq \chi^L(0)$[9a] when $R_{D,A} \gg \sigma$:

$$\lambda_s^{cont} = \frac{1}{3}\lambda_L + \frac{2}{3}\lambda_T + \lambda_A \tag{3}$$

Here, $\lambda_L = c_L g$, $\lambda_T = c_T g$, and the parallel, $c_L = \epsilon_{\infty,L}^{-1} - \epsilon_{s,L}^{-1}$, and perpendicular, $c_T = \epsilon_{\infty,T}^{-1} - \epsilon_{s,T}^{-1}$, Pekar factors are defined by the high-frequency, ϵ_∞, and static, ϵ_s, dielectric constants of the solvent at $\chi = 0°$ (L) and 90° (T), respectively. The geometric factor g is equal to $g = (e^2/2)(1/R_D + 1/R_A - 2/R)$ in the Marcus two-sphere configuration, where e is the elementary charge. The angular-dependent component

$$\lambda_A = e^2(c_L - c_T)P_2(\cos \theta)\, \frac{R^2 - {R_A}^2 - {R_D}^2}{3R^3} \tag{4}$$

accounts for the dependence of λ_s^{cont} on the angle between the DAC and the nematic director.

Figure 4 shows λ_s for $\theta = 0°$ (||) and $\theta = 90°$ ($\perp$) at varying size of the donor and acceptor units in a DAC with $R_D = R_A$ and $R/R_D = 2.5$. The reorganization energy obtained from structure factors (solid lines, eq 2) approaches the continuum

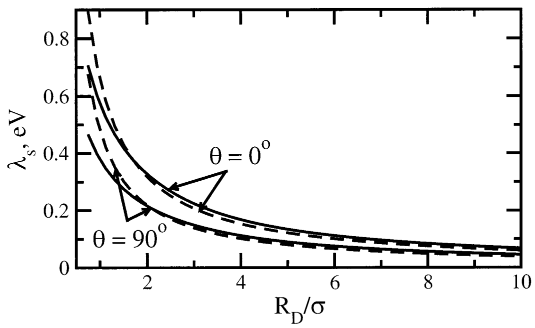

Figure 4. λ_s calculated from the structure factors (solid lines) and continuum estimates (dashed lines) vs R_D/σ at $\theta = 0°$ and 90°; $R_D = R_A$, $\eta = 0.457$, and $R/R_D = 2.5$.

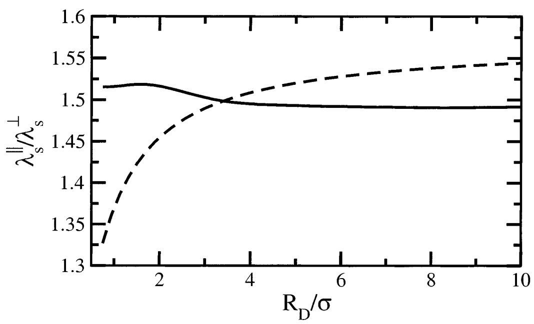

Figure 5. Reorganization energy anisotropy $\lambda_s^{||}/\lambda_s^{\perp}$ calculated from the structure factors (eq 2, solid line) and continuum estimates (eq 3, dashed line) vs R_D/σ at $R_D = R_A$, $\eta = 0.457$, and $R/R_D = 2.5$.

limit (dashed lines, eq 3) with increasing size of the DAC. The anisotropy of λ_s from eq 2 measured by the ratio $\lambda_s^{||}/\lambda_s^{\perp}$ (Figure 5) is noticeably higher than the continuum estimate (eq 3) for $R_{D,A}/\sigma \simeq 1$ commonly encountered in practical applications. The orientational reorganization energy considered here is the dominant part of λ_s for $R_{D,A} > \sigma$ in solvents of approximately spherical molecules.[9a] For smaller sizes, the magnitude of λ_s is noticeably affected by the reorganization component arising from the alteration of the local density profile (density reorganization energy[9a]). The observation that the reorganization energy anisotropy is nearly independent of the solute size (Figure 5) points to the stability of our conclusions for large solutes. The anisotropy of λ_s can be affected by the density reorganization for intermediate-size solutes. The calculation of the density reorganization energy within the linear response requires the density structure factor of the solvent as an input.[9a] Our present simulations do not allow us to calculate this property with sufficient accuracy because of limitations imposed by the finite size of the simulation box. Further studies with larger systems are necessary to resolve this problem.

A substantial dependence of the solvent reorganization energy on the orientation of the DAC relative to the nematic director opens the door to exercise external control over the ET rates. This possibility is based on the separation of characteristic time scale of microscopic molecular reorientations, which is not strongly modified by the IN transition (nanoseconds range),[5,6] and the time scale of director reorientation (milliseconds to seconds range).[15] To model the effect of solute orientation on ET kinetics, we consider here a model reaction of charge separation (CS) from a nonpolar state D−A to a polar state D^+-A^-. The backward reaction corresponds to charge recombination (CR). The change in the forward and backward activation barriers with the rotation of the DAC relative to the nematic director can be characterized by the reduced rate

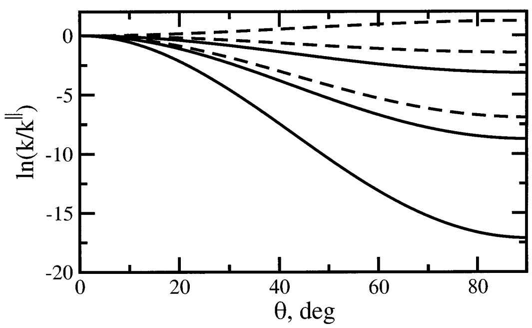

Figure 6. ln ($k_{CS}/k_{CS}^{||}$) (solid lines) and ln ($k_{CR}/k_{CR}^{||}$) (dashed lines) vs the angle between the direction of ET and the nematic director. The solid and dashed lines correspond to $\hbar\omega_{abs}^{||} = 0.6$ eV (upper curves), $\hbar\omega_{abs}^{||} = 1.0$ eV (middle curves), and $\hbar\omega_{abs}^{||} = 1.4$ eV (lower curves). The reorganization energy is calculated from simulated longitudinal polarization response function at $\eta = 0.457$, $R_D = R_A = 4$ Å, and $R = 10$ Å.

constants ln ($k_{CS}/k_{CS}^{||}$) and ln ($k_{CR}/k_{CR}^{||}$), where $k_{CS}^{||}$ and $k_{CR}^{||}$ refer to CS and CR at the parallel orientation ($\theta = 0°$). According to the Marcus relation,[7a,b] the change in the rate constant can be written as follows (assuming isotropic preexponential factor):

$$\ln \frac{k_{CS/CR}}{k_{CS/CR}^{||}} = -\frac{(\hbar\omega_{abs/em}(\theta))^2}{4k_B T\lambda_s(\theta)} + \frac{(\hbar\omega_{abs/em}^{||})^2}{4k_B T\lambda_s^{||}} \quad (5)$$

Here, $\omega_{abs}(\theta)$ and $\omega_{em}(\theta)$ are average vertical transition energies (first spectral moments) for CS and CR, respectively. Because we assume a neutral initial state for the DAC, $\omega_{abs}(\theta) = \omega_{abs}^{||}$ is independent of nuclear reorganization and $\hbar\omega_{em}(\theta) = \hbar\omega_{abs}^{||} - 2\lambda_s(\theta)$.

Figure 6 shows the dependence of the rate constant on the angle θ calculated according to eq 5 with $\lambda_s(\theta)$ from the upper curve in Figure 2. The angular variation of the reorganization energy is negative, $\delta\lambda(\theta) = \lambda_s(\theta) - \lambda_s^{||} < 0$ (Figure 2), and rotations out from the parallel alignment decrease the CS rate. The result for the CR rate constant depends on whether the reaction is in the normal or inverted region of ET. To illustrate the distinction between the normal and inverted regions for CR, we linearize eq 5 assuming that the angular variation of the solvent reorganization is relatively small, $|\delta\lambda(\theta)/\lambda_s^{||}| < 1$:

$$\ln(k_{CR}/k_{CR}^{||}) \simeq \frac{\hbar\omega_{em}^{||}\hbar\omega_{abs}^{||}}{4(\lambda_s^{||})^2}\frac{\delta\lambda(\theta)}{k_B T} \quad (6)$$

In the inverted region, $\hbar\omega_{em}^{||} = \hbar\omega_{abs}^{||} - 2\lambda_s^{||}$ is positive and the CR rate decays with θ similarly to the CS rate ($\hbar\omega_{abs}^{||} = 1.0$ and 1.4 eV in Figure 6). In the normal ET region, on the contrary, $\hbar\omega_{em}^{||}$ is negative, and rotations of the DAC out of the parallel alignment lead to higher CR rates (eq 6, $\hbar\omega_{abs}^{||} = 0.6$ in Figure 6).

For the reorganization energy shown in Figure 2 at $\eta = 0.457$ and $\hbar\omega_{abs}^{||} = 1.0$ eV, the ratio $k_{CS}^{\perp}/k_{CS}^{||}$ is about 10^{-4}. The rotation of the DAC from the parallel to the perpendicular orientation, which can be achieved by an external light pulse, then essentially shuts down the CS reaction. This property may be useful for an externally monitored switching function of ET systems.[4]

Acknowledgment. This research was supported by a Research Innovation Award (RI0748) by Research Corporation.

This is publication 510 from the ASU Center for the Study of Early Events in Photosynthesis.

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