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Charge Transfer Kinetics and Solvatochromism of 1-(9-Anthryl)-3-(4-dimethylaniline) Propane in 1,4-Dioxane: Nonideal Quadrupolar Charge Distribution and the Origin of the Dioxane Anomaly†

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The solvent 1,4-dioxane behaves like a polar solvent even though its dielectric constant is small. This excess polarity is referred to as the “dioxane anomaly”. Several explanations of this anomaly have been offered in the literature including hydrogen bonding, conformational polarity, and quadrupolar interactions. We have investigated the origins of this anomaly by employing the unique photochemical properties of the ADMA (1-(9-anthryl)-3-(4-dimethylaniline) propane) molecule. ADMA forms an intramolecular exciplex in the excited state. Solvent polarity governs the mechanism of exciplex formation. In nonpolar solvents the decay of the locally excited-state population is monoexponential, while in polar solvents ($\epsilon > 5.4$) the decay of the locally excited-state population is biexponential. Although dioxane has a dielectric constant of 2.2, ADMA dissolved in dioxane exhibits biexponential kinetics. From this result and from the solvatochromic shift of the ADMA exciplex peak in dioxane, we have concluded that the large nonideal quadrupolar charge distribution of 1,4-dioxane is responsible for its anomalous polarity.

I. Introduction

1,4-Dioxane (dioxane, for brevity) has a dielectric constant of 2.2,[1] but many experimental results indicate that dioxane is polar. For example, dioxane has a much higher miscibility with water than do ethers with a comparable molecular weight, although the ethers have larger dielectric constants.[2] Solvatochromic shifts of dipolar chromophores dissolved in dioxane offer another example of the anomalous behavior. Solvatochromism is generally interpreted in the context of dielectric continuum models, which correlate spectroscopic peak shifts with the solvent reaction field. The field results from the response of the dipolar solvent, characterized by dielectric constant and refractive index, to the presence of a dipolar solute.[3,4] However, many researchers have observed solvatochromic shifts of dipolar chromophores dissolved in dioxane that exceed dielectric continuum theory predictions.[4−13] This observed phenomenon is often referred to as the “dioxane anomaly”.[4]

Several arguments have been invoked over the years to explain the dioxane anomaly. Perichet et al. suggest that the excess polarity is due to the hydrogen bonding ability of the dioxane oxygen atoms.[14] Suppan argues against this suggestion by demonstrating that the effective polarity observed by chromophores dissolved in dioxane is independent of the chromophore’s hydrogen bonding ability.[6] He has suggested that conformational polarity may be responsible for dioxane’s anomalous behavior.[5,6] He points out that dioxane has three conformers (chair, boat1, and boat2), and the boat conformations have finite dipole moments. Suppan has suggested that a dipolar solute can organize the nearby solvent molecules into boat conformations, resulting in stabilization of the solute that exceeds dielectric continuum predictions by virtue of an increased local dielectric constant. However, the boat conformation of dioxane has not been observed experimentally, and other factors may also explain its anomalous behavior, such as its unusual charge distribution.[4,9] Though the chair conformation of dioxane has no net dipole moment, its electron density varies widely as a result of the widely separated oxygen atoms. Dioxane’s quadrupole moment is not axially symmetric,[13] but its charge distribution can be approximated as a typical, nonideal quadrupole constructed from two dipoles of finite length having equal magnitude and opposite direction separated by a small distance. Just as a dipolar charge distribution has higher order moments that become important at short distances, it is also understood that this typical quadrupolar charge distribution will have higher order moments that will be significant with respect to solvent−solute interactions. Throughout this paper we use the quadrupolar terminology in this spirit, and we quantify the influence of the higher order moments of dioxane’s charge distribution in the discussion.

Recently, Reynolds et al. attempted to elucidate the contribution of the solvent quadrupole moment to the solvation energy of dipoles in nondipolar solvents.[15] Their results exhibit a correlation between the magnitude of the quadrupole moment and the excess solvation energy (i.e., the solvatochromic shift in excess of dielectric continuum predictions) observed in quadrupolar solvents. A rigorous theoretical treatment of the solvation energy of a dipole immersed in an ideal quadrupolar solvent (i.e., a solvent characterized by an axially symmetric point quadrupole at the center of a cavity) has been performed by Matyushov et al. (MV theory).[16,17] The theory indicates that the quadrupolar contribution to the solvation energy depends on the square of the magnitude of the effective quadrupole moment and on the solvent and solute sizes. We have demonstrated that the excess solvation energy of the charge transfer excited state of ADMA [1-(9-anthryl)-3-(4-dimethylaniline) propane, see Figure 1] in axially symmetric quadrupolar solvents is properly predicted by MV theory.[13] In the same paper we also pointed out that dioxane cannot be approximated as an

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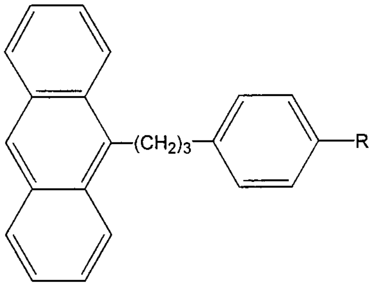

Figure 1. Structure of ADMA (R=$N(CH_3)_2$) and APP (R=H).

axially symmetric quadrupole, and therefore MV theory does not apply to dioxane. Thus, the static spectra of the ADMA exciplex in dioxane offers only qualitative evidence that its large solvatochromic shift can be attributed to its quadrupolar charge distribution.

The conformational polarity argument attributes dioxane's anomalous polarity to a subset of dioxane conformations with large dipole moments. As we shall demonstrate below, this subset represents only a very small fraction of the solvent molecules at equilibrium. If the conformational polarity argument is correct, dioxane's excess polarity must result from either preferential solvation of a solute by the dipolar subset of solvent molecules or solute-driven conformational interconversion. In either case, the solute dipole induces dioxane's anomalous polarity.

In this work we investigate the origin of the dioxane anomaly by employing the unique photochemistry of ADMA. The ADMA molecule forms an intramolecular charge transfer exciplex following photon absorption, thus quenching the emission from the locally excited state. The charge transfer reaction occurs in both polar and nonpolar solvents, and the mechanism of the reaction depends on the solvent polarity. In nonpolar solvents the locally excited-state emission exhibits single-exponential behavior, whereas multiexponential behavior is observed in "polar" solvents ($\epsilon > 5.5$). As a result, the fluorescence decay profile of ADMA can offer insight into the nature of solvent–solute interactions in dioxane. We demonstrate that ADMA dissolved in dioxane exhibits multiexponential quenching kinetics, indicating that it behaves like a polar solvent with respect to eletron transfer in ADMA. Because the locally excited state of ADMA is nonpolar, dipolar conformations of the 1,4-dioxane are not driven to preferentially solvate the solute before the charge-transfer reaction occurs. Therefore, data concerning the mechanism of charge transfer in 1,4-dioxane can be analyzed under the assumption that the composition of the solvation sphere mimics the bulk composition of the liquid. Employing both steady-state and time-resolved fluorescence from ADMA, we demonstrate that the nonideal quadrupolar charge distribution of dioxane is responsible for its anomalous polarity.

II. Experimental Section

ADMA and APP (1-(9-anthryl)-3-phenylpropane), shown in Figure 1, were synthesized according to the method outlined previously.[13,18] The solvents were obtained in the purest commercially available form, degassed with argon, and used without further purification. All measurements were made on 10^{-5} M samples thermostated at 25 °C. Steady-state fluorescence spectra were collected in a home-built scanning T-format fluorometer. The dispersed emission spectrum was collected through a monochromator in one arm of the instrument, and the fluorescence at a fixed wavelength was collected synchronously and simultaneously through the other arm to correct for fluctuations in the emission intensity due to sample and instrumental conditions. The emission slit widths were set at 1.5 nm, giving 3 nm resolution.

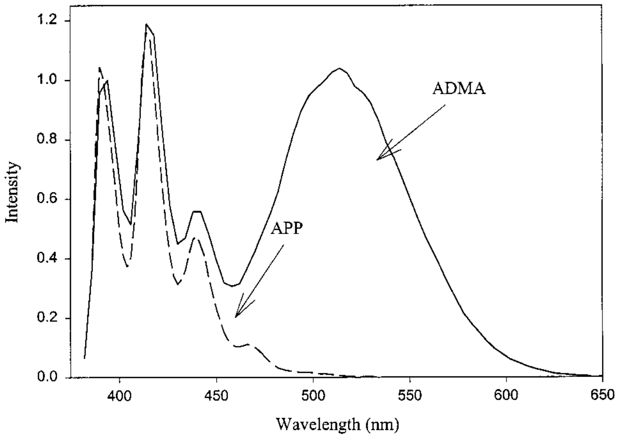

Figure 2. Fluorescence spectra of ADMA and APP in 1,4-dioxane, illustrating their similarity in the 400–480 nm region. The broad structureless emission observed at wavelengths greater than 490 nm is due to the ADMA SH exciplex emission.

Time-correlated photon counting was performed utilizing a mode-locked diode pumped Nd:YAG laser coupled to a dye laser. The dye laser was cavity dumped at 4 MHz. A β-BaB_2O_4 (BBO) crystal combined a 1064 nm IR beam with a 606 nm beam from the dye laser in order to obtain a 386 nm beam for exciting the sample. The excitation beam was vertically polarized and the emission was collected at the magic angle. The emission wavelength was selected with a band-pass filter (10 nm band-pass), and was collected by a micro channel plate PMT (Hamamatsu, R 3809U-50). The timing electronics have been described proviously.[19] A typical instrument function has a 70 ps full-width at half-maximum. The data were analyzed by the iterative reconvolution method using software of our own design that utilizes the Marquardt–Levenberg algorithm to minimize chi-square.

III. Spectroscopy and Solvatochromism of ADMA

ADMA undergoes a charge-transfer reaction in the excited electronic state in both polar and nonpolar solvents.[18,20–24] Figure 2 shows the fluorescence spectrum of ADMA in dioxane, along with the spectrum of APP, a structurally similar molecule that does not undergo charge transfer. Two distinct spectral features can be observed in the ADMA spectrum. Anthracene-like emission at wavelengths below 450 nm are observed in both ADMA and APP spectra. This region of the spectrum has been assigned to emission from the nonpolar locally excited (LE) state of ADMA.[25] The broad emission in the 450–600 nm range is observed only in the ADMA spectrum and has been assigned to emission from the "sandwich heteroexcimer" (SH).[26] The folded SH conformation is obtained following electron transfer from the dimethylaniline moiety to the excited anthracene moiety, and the kinetics of the charge-transfer reaction is described in section IV. The SH state of ADMA is long-lived and dipolar, and therefore exhibits solvatochromism.

Previously,[27] we have demonstrated that the ADMA SH peak energies in dipolar solvents are linearly correlated with the Lippert–Mataga polarity function

$$F = \frac{2(\epsilon-1)}{2\epsilon+1} - \frac{n^2-1}{2n^2+1} \qquad (1)$$

demonstrating that continuum models adequately describe

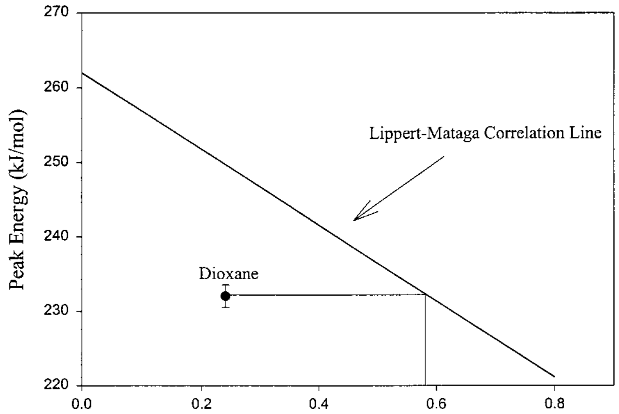

Figure 3. The ADMA SH peak energy measured in dioxane compared with prediction based on the Lippert−Mataga theory. The theory has been corroborated for dipolar solvents. The deviation from the correlation line is due to the excess stabilization energy from solute dipole-solvent quadrupole interactions.

TABLE 1: Fluorescence Decay Parameters of ADMA Dissolved in Intermediate Polarity Solvents[a]

solvent	e	B	τ_1(ns) 420 nm	C	τ_2(ns) 420 nm	peak energy (kJ/mol)
cyclohexane	2.02	...	2.52			252
dibutyl ether	3.06	...	2.16			243
tert-amylalcohol	5.82	0.987	0.71	0.013	3.73	231
dioxane	2.21	0.975	0.36	0.025	5.28	232
n-butyl chloride	7.09	0.953	0.29	0.047	3.34	235
tetrahydrofuran	7.58	0.989	0.02	0.011	6.46	228
dichloromethane	9.00	0.996	0.003	0.004	7.40	227

[a] When the dielectric constant exceeds 5.5, a transition from monoexponential to biexponential behavior occurs. Biexponential behavior indicates the formation of the loose heteroexcimer. From these results, it appears that dioxane can support the loose heteroexcimer.

solvation of the SH state of ADMA in these solvents. The correlation between *F* and peak energy is described by

$$E_p(\text{kJ/mol}) = -51.104[F] + 262 \tag{2}$$

Figure 3 presents the predicted dependence of the peak energy on *F* along with the observed peak energy of ADMA dissolved in dioxane. Correlation between peak energy and dielectric constant can also be seen in Table 1 for a series of solvents spanning the intermediate polarity range. The observed peak energy is comparable to that of ADMA in a dipolar solvent with a dielectric constant of 6.51. We refer to this value as the "effective dielectric constant" of dioxane with respect to the ADMA SH peak energy. The deviation from continuum model predictions is also observed in other solvents, which have very small dipole moments but large quadrupole moments. Following Reynolds et al., we refer to these solvents as nondipolar in order to distinguish them from low-dielectric nonpolar solvents such as alkanes.[15] In previous work,[13] we have demonstrated that the excess solvation energy (i.e., the excess solvatochromic shift observed relative to the Lippert−Mataga correlation line) of ADMA in nondipolar solvents follows the prediction of MV theory.[16,17] From this observation we have concluded that the excess solvation energy is due to the solvent quadrupole-solute dipole interaction.

As noted in the Introduction, MV theory has been developed for axially symmetric quadrupoles, and therefore cannot be applied to dioxane.[13] This fact distinguishes dioxane from other nondipolar solvents such as benzene, toluene, and supercritical CO_2. In a recent molecular dynamics simulation, Geerlings et al.[12] model the dioxane molecule as two separate point dipoles located on the oxygens of the two ether moieties pointing toward the molecular center of mass. Their simulations indicate that a dipole immersed in dioxane has a strong interaction with the closer dipole, and consequently the solute dipole experiences a reaction field that is comparable to that of a solvent having a dielectric constant between 6.4 and 7.7. This suggests that solvation of the ADMA SH exciplex in dioxane should be very similar to solvation in tetrahydrofuran. As noted above, the effective dielectric constant of dioxane with respect to the ADMA SH peak shift is 6.5, in excellent agreement with the conclusions of Geerlings et al. However, this does not rule out conformational polarization as a contributor to solvation of the exciplex in dioxane, because the SH state of ADMA is dipolar and may therefore induce preferential solvation by the dipolar conformations of the solvent. In the following section we examine the charge transfer mechanism of ADMA and demonstrate that dioxane behaves as a polar solvent with respect to the kinetics of the CT reaction, even though the reactant (i.e., the ADMA locally excited state) is nonpolar.

IV. Kinetics of Charge Transfer in ADMA

The kinetics of the excited state intramolecular charge transfer reaction of ADMA have been extensively studied by Eisenthal and co-workers,[23,24,26] and Mataga and co-workers.[22,25,28−30] Upon excitation, the anthracene moiety (A*) becomes an electron acceptor and charge transfer from the dimethylaniline moiety (DMA) can occur, forming an exciplex. The charge transfer occurs when the two moieties are in close proximity to one another, and the probability for electron transfer at a particular distance depends on the electrostatic properties (e.g., dielectric constant) of the solvent. In nonpolar solvents the molecule must fold in order to bring the A* and DMA moieties close enough to one another for charge transfer to occur, and as a result the charge-transfer reaction is viscosity dependent. The charge transfer in nonpolar solvents is irreversible, therefore the decay of the LE state population (and therefore the time-resolved fluorescence) is monoexponential,

$$[\text{LE}]_{\text{nonpolar}} = A\text{e}^{-t/\tau} \tag{3}$$

where *A* is a constant and τ is the lifetime of the locally excited (LE) state.[23,24,26] On the other hand, polar solvents support longer-range charge-transfer such that an extended charge-transfer intermediate (the "loose heteroexcimer " (LH)) is first formed, but in most cases (when ϵ < 20) the resulting extended charge-separated species is drawn to the folded configuration by Coulombic attraction.[22,28] According to the Mataga mechanism, the formation of the SH state from the LE state in polar solvents is a two-step consecutive process and the LE⇔LH reaction is reversible.[22,28] The decay of the LE state population is biexponential,

$$[\text{LE}] = B\text{e}^{-t/\tau_1} + C\text{e}^{-t/\tau_2} \tag{4}$$

where *B*, *C*, τ_1, and τ_2 are functions containing numerous rate constants and cannot be assigned to elementary steps in the overall reaction mechanism. When ϵ < 20 ADMA eventually assumes the SH configuration, the resulting "sandwich heteroexcimer" (SH) is fluorescent. The extended charge-transfer configuration, or "loose heteroexcimer" (LH) has a low fluorescence quantum yield. Thus the mechanism of charge-transfer that leads to exciplex formation is polarity dependent, and the kinetics of the reaction provides information about the polarity experienced by the LE state.

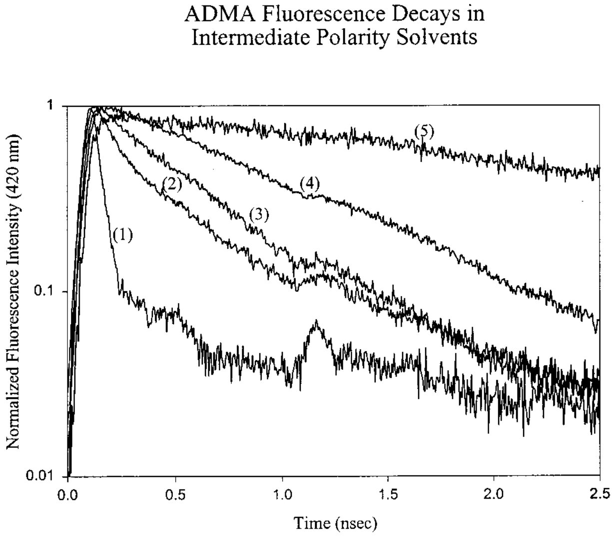

Figure 4. ADMA fluorescence decays measured in intermediate solvents. The 420 nm emission reflects the population of the LE state. The solvents are: (1) THF, (2) *n*-butyl chloride, (3) 1,4-dioxane, (4) *tert*-amylalcohol, (5) cyclohexane. The decays exhibit biexponential behavior in dipolar solvents when $\epsilon > 5.4$. ADMA dissolved in dioxane ($\epsilon = 2.2$) also exhibits biexponential behavior.

Figure 4 shows the solvent dependence of the decay profile of ADMA collected at 420 nm, which monitors the locally excited-state concentration. The solvents under study are cyclohexane, *tert*-amylalcohol, dioxane, *n*-butyl chloride, and tetrahydrofuran. We have fit these decays to biexponential model functions, and the fitting parameters are given in Table 1 along with the solvent dielectric constants. The decay is monoexponential in cyclohexane and biexponential in the other solvents. A biexponential decay indicates the excimer forms via the polar charge transfer mechanism. The polar mechanism requires the solvent to be sufficiently polar that it can stabilize the large dipole moment of the LH form of ADMA. In fact, studies that we have performed upon ADMA dissolved in other dipolar solvents indicate that the transition to the polar mechanism occurs at a dielectric constant near 5.4. The biexponential fluorescence decay of ADMA in dioxane observed in Figure 4 demonstrates that dioxane behaves like a solvent having a polarity between *tert*-amylalcohol and *n*-butyl chloride, even though the reactant is nonpolar.

V. Discussion

The chair conformation of dioxane, with a dipole moment of zero, is much more stable than the other conformations having dipole moments of 2.4 D and 1.4 D (see Figure 5).[31,32] Suppan postulates that when a dipole is dissolved in dioxane, the dipolar solute–solvent interactions perturb the nearby solvent molecules such that the boat conformations are favored over the chair conformation in the near vicinity of the solute. This causes the stabilization energy experienced by a dipole dissolved in dioxane to exceed that predicted from its dielectric constant. We evaluate this argument quantitatively below by first estimating the number of polar solvent molecules required to support the polar mechanism for charge transfer in ADMA and then examining the equilibrium composition of dioxane in the ADMA solvation sphere.

To estimate the number of dipolar solvent molecules required to support the polar mechanism, we consider our previous study of the preferential solvation of ADMA in ethanol-hexane mixtures.[27] The onset of biexponential behavior in these mixtures occurs between 0.20 and 0.30 mole fraction ethanol, which corresponds to a dielectric constant between 4 and 6, consistent with our observations in other dipolar solvents. The number of solvent molecules in the first solvation shell of ADMA is ~25,[13] and about 6 ethanol molecules are present in the first solvation shell of ADMA at the onset of biexponential behavior, neglecting preferential solvation. Based on the solubility of the nonpolar ground state of ADMA and the fact that the LE state of ADMA is also nonpolar, we anticipate preferential solvation of ADMA by the nonpolar solvent component. Thus it is possible that the number of polar molecules in the ADMA solvation sphere is somewhat diminished with respect to the bulk composition in hexane/ethanol mixtures, and we estimate that at least three polar solvent molecules are necessary in this solute's first solvation shell in order to support the polar charge-transfer mechanism.

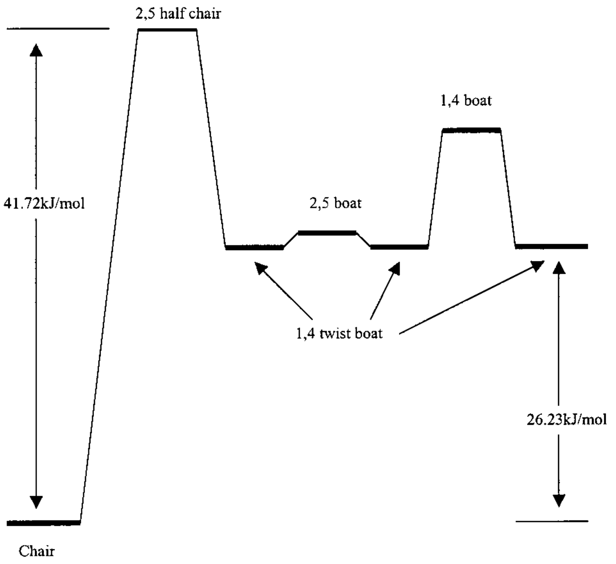

Figure 5. Energy levels of the different conformations of dioxane as calculated by Chapman and Hester.[32] The barrier for interconversion between the conformers is quite high.

Chapman and Hester[32] have performed an ab initio conformational analysis of 1,4-dioxane, and their results can be used to characterize the bulk equilibrium distribution of dioxane conformers. The energy levels of the different conformers of dioxane are depicted in Figure 5. The energy difference between the chair conformation and the other stable conformations is approximately 26 kJ/mol, and therefore the equilibrium constant of the reaction chair $\Leftrightarrow$ boat is on the order of 10^{-5} at room temperature. It is highly unlikely that the nonpolar LE state can have a significant influence on this equilibrium since a shift in excess of a factor of 10^3 is required to result in a single boat conformer in the ADMA solvation sphere. The ab initio analysis also indicates that the dipolar boat conformers are transition states rather than energy minima, which further diminishes the influence of conformational polarity on the solute. Preferential solvation of the LE state remains as a possible mechanism to increase the solvent polarity in the ADMA solvation sphere, but once again a 1000-fold increase of the polar component is required. Our analysis of preferential solvation of the dipolar ADMA exciplex in hexane/ethanol mixtures indicates that a two-fold increase in the polar component is reasonable when the solute is dipolar,[27] but this magnitude of preferential solvation is inadequate to have a significant influence on the conformational composition of dioxane in the ADMA solvation sphere. This analysis demonstrates that conformational polarity plays an insignificant role in solvation by dioxane, and we now turn

TABLE 2: Contribution of Multipole Moments of a Nonideal Quadrupole to the Total Electric Potential[a]

	$\boldsymbol{r} = 1.6$ Å				$r = 10.2$ Å			
	θ_=_0	θ_=_40	θ_=_60	θ_=_90	θ_=_0	θ_=_40	θ_=_60	θ_=_90
total potential of the quadrupole charge distribution	−21.82	0.07	0.86	0.96	−0.02	−0.01	∼0.00	∼0.00
quadrupole term	−3.69	−3.04	−2.31	−0.92	−0.01	−0.01	∼0.00	∼0.00
octupole term	−3.87	0.10	1.67	0.00	∼0.00	∼0.00	∼0.00	∼0.00
unsextapole term	−3.69	1.17	1.07	−1.38	∼0.00	∼0.00	∼0.00	∼0.00
total potential of the dipolar charge distribution	−22.32	−0.44	0.33	0.48	−0.04	−0.03	−0.01	∼0.00

[a] The charge distribution is an approximate model for dioxane. Potentials are given for specific values of r (field point distance relative to the center of charge of the distribution) and θ, the azimuthal angle relative to the symmetry axis of the charge distribution. The exact potential is also given, as well as the exact potential calculated for a dipolar charge distribution composed of the half of the quadrupolar distribution that is closest to the field point. All values are expressed in volts. $\theta = 0$ corresponds to the most negative potential for all distributions, whereas the most positive potential occurs near 90°, 60°, and 40° for the quadrupolar, octupolar, and unsextapolar moments, respectively.

our attention to dioxane's charge distribution and its dynamic influence on ADMA charge-transfer kinetics.

As we have remarked earlier, the dioxane quadrupole is nonideal and is devoid of axial symmetry,[13] but for the purpose of illustration we will approximate it as an axially symmetric, nonideal quadrupolar charge distribution. Using the oxygen partial charge and the dipole moment (∼1.2 D) of each half of the charge distribution estimated by Geerlings et al.,[12] we model the dioxane charge distribution in center of mass coordinates with positive charges of 0.35e located at +0.71 Å and −0.71 Å and negative charges of 0.35e located at +1.42 Å and −1.42 Å. We have calculated the electric potential for this charge distribution at the ADMA-dioxane contact distance (approximately 1.6 Å) and at 10.2 Å (the sum of the dioxane radius and the ADMA diameter) at several azimuthal angles, and the results are given in Table 2. The exact potential of the charge distribution is compared with the contributions for the first three nonzero moments of its multipole expansion, and with a dipolar charge distribution composed of the half of the quadrupolar charge distribution located nearest to the field point. We derive three conclusions from Table 2. First, at the contact distance the contribution of higher order moments are as significant as the quadrupole moment term, while as the distance increases the quadrupole moment term becomes dominant. Second, at the contact distance and $\theta = 0$, the exact potential of the quadrupolar charge distribution is nearly identical to that of a dipolar charge distribution composed of the two charges that are located closest to the field point, the latter being representative of a dipolar solvent such as tetrahydrofuran (THF). This observation is consistent with the conclusions drawn by Geerlings et al.,[12] and highlights the shielding of the most distant dipole from a solute in this geometry. Finally, orientational motion of dioxane can result in significant field fluctuations, and the fluctuations of the quadrupolar charge distribution will be of the same order of magnitude as the fluctuations of a dipolar charge distribution composed of one-half of the quadrupolar distribution. By inference, the fluctuations experienced by a solute dissolved in dioxane should be very similar to the fluctuations experienced by a solute dissolved in THF. The importance of the last observation is discussed below.

In the context of Marcus theory, solvent can influence the ADMA charge-transfer process in two ways.[33,34] First, stabilization of the charge transfer state by a polar solvent changes the position of curve crossing with regard to the solute nuclear coordinates, resulting in a crossing point that occurs in a more extended geometry. We have demonstrated that dioxane stabilizes the charge transfer state of ADMA through solvatochromic studies of the SH emission, and that the stabilization is anomalously large. Second, as the solvent becomes more polar, the magnitude of the electric field fluctuations experienced by the solute resulting from solvent motion increases, thereby assisting the ADMA in its trajectory over the barrier into the charge transfer state well. Both of these processes facilitate the formation of the loose heteroexcimer in sufficiently polar solvents, in contrast with nonpolar solvents that cannot support long-range charge transfer. Our time-resolved experiments in ordinary dipolar solvents demonstrate that the loose heteroexcimer can form in solvents that have a dielectric constant greater than 5. This reflects the fact that the static dielectric constant serves to characterize the magnitude of fluctuations in the local field experienced by the solute as a result of orientational fluctuations of solvent molecules in the first solvation shell.

For dioxane, two kinds of fluctuations are possible: reorientation of the dioxane quadrupole or a change in the dioxane conformation. The thermodynamic arguments above indicate that the boat-to-chair conformational change involves a large energy barrier for both the forward and reverse reactions. The probability of the occurrence of conformational changes is quite low, and it is highly unlikely that these changes occur with a high enough frequency to facilitate long-range charge transfer in ADMA. Orientational fluctuations on the other hand are thermally activated in liquids and occur over a range of time scales from 10^{-14} to 10^{-10} seconds. As the calculations of Geerlings et al. suggest,[12] a dipolar solute dissolved in dioxane primarily interacts with the closest ether moiety, causing a solute dissolved in dioxane to experience a THF-like environment. By analogy, just as the orientational fluctuations of the THF dipole facilitates the formation of the LH state in THF, the orientational fluctuations of the nonideal quadrupole charge distribution of dioxane are responsible for the formation of the loose heteroexcimer in dioxane.

Our experimental evidence indicates that the unique charge distribution of dioxane is responsible for its anomalous polarity. Dioxane differs from other "typical" nondipolar solvents (e.g., benzene) in two regards. First, it is not axially symmetric, this prohibits characterization of its polarity by a scalar effective quadrupole moment. Second the charge separation in the dioxane molecule is such that the quadrupole moment term in the multipole expansion does not become dominant until relatively large distances. This also prevents the quadrupole moment from being the characteristic parameter for solvent−solute interactions, even if dioxane were axially symmetric. This fact answers Suppan's criticism regarding the fact the dioxane anomaly is much more pronounced in dioxane than in other solvents with high quadrupole moments.[4]

As mentioned previously, there has been some attempt to ascribe the excess polarity of dioxane to the donor properties of the oxygen moieties.[14] Our spectroscopic evidence confirms Suppan's suspicions concerning the influence of specific interactions on solvation properties of dioxane. We have previously demonstrated[27] that the ADMA SH exciplex is insensitive to specific interactions (i.e., hydrogen bonding). The fact that the ADMA SH exciplex demonstrates excess stability when it is dissolved in dioxane demonstrates that the origin of this stability is nonspecific.

In conclusion, we have investigated the origins of the "dioxane anomaly". We have demonstrated that neither specific interactions nor the conformational polarity concept provide an adequate explanation for the excess solvation energy observed in dioxane. We have demonstrated that the origin of the "anomaly" lies in the unique charge distribution of the solvent. This property distinguishes dioxane from other nondipolar solvents.

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