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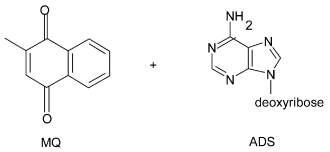

^{3}MQ +ADS $\rightarrow$ ^{3}MQ$^{\cdot-}$ +ADS$^{\cdot+}$ in acetonitrile

^{3}MQ +ADS $\rightarrow$ ^{3}MQH$^{\cdot}$ +ADS$^{\cdot}$ in SDS

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Medium-Dependent Electron and H Atom Transfer between 2′-Deoxyadenosine and Menadione: A Magnetic Field Effect Study

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Abstract: The interaction between 2′-deoxyadenosine and the model antitumor drug menadione has been studied in organic solvent and in micellar medium. The aim of the work is to elucidate the mechanism of this drug−nucleoside interaction and to determine the environmental effects. Laser flash photolysis and magnetic field effect are used to detect the transients and their spin states. The results indicate that H atom transfer and electron transfer are the operative mechanisms depending upon the medium.

Introduction

A very interesting recent problem is to find out the role of electron transfer in drug−DNA interaction[1] and H atom transfer in antioxidant−DNA interaction.[2] In this paper, we report the first observation of magnetic field effect (MFE) on the interaction between a nucleoside (2′-deoxyadenosine: ADS)/DNA base (adenine: ADE) and a model for quinone drugs used in cancer chemotherapy (2-methyl 1,4-naphthoquinone or menadione: MQ)[3] where H atom transfer is competitive with electron transfer. Over the past few decades, MFEs[4−6] have been extensively utilized to study primary photochemical processes, viz., the electron transfer and H atom transfer. However, only a few reports of MFE have been published on the biochemically important processes[7] or in biomolecular environments.[8] Photoinduced electron transfer or H atom abstraction produces a radical ion pair (RIP) or radical pair (RP) where the conversion between singlet (S) and triplet ($T_{\pm}$, T_0) states takes place by electron−nuclear hyperfine interaction.[4−6] An external magnetic field removes the degeneracy of the $T_{\pm}$ with S and T_0 thereby reducing the intersystem crossing. The overall effect is the increase in the population of the initial spin state. The model antitumor drug MQ has several other biological importances, and in a number of cases electron-transfer pathway was established to operate. Three distinct MQ reductases have been identified that reduce it in the hydroquinone form.[9] It is well-known that cell-mediated reduction of MQ produces reactive oxygen species and a dose-dependent increase in intracellular $[Ca^{2+}]$.[10] The latter increase is related to the oxidizing chemistry initiated by triplet MQ.

In living systems, the master molecule DNA has been found sensitive to UV radiation. The detrimental effect may be caused by two ways: (1) direct photoexcitation of the DNA which in the excited-state undergoes changes, e.g., formation of pyrimidine dimers,[11] and (2) DNA in the ground state interacts with another excited molecule.[12] The molecule MQ and its bisulfite were found to be efficient photosensitizers for cell killing when mammalian cells are exposed to near UV. The same authors reported that thymine is an important site for the photooxidation by MQ.[12] Single-strand breakage was also reported for the supercoiled DNA. Therefore, nucleic acids may be a site for lethal damage induced by photooxidation of MQ. However, Melvin et al.[13] reported photooxidation of ADS and DNA by MQ in aqueous medium that results in cross-linking and also strand breakage. The base damage caused by MQ was also reported by Douki and Cadet.[14] Extensive DNA damage was found for human leukemic cells exposed to MQ.[15] Therefore, it is a very important task to elucidate a possible mechanism for the interaction between this model drug and any nucleoside or DNA base. In our experiment, laser flash photolysis and MFE are utilized to rationalize the physical nature of this interaction in organic solvent and in micellar medium (sodium dodecyl

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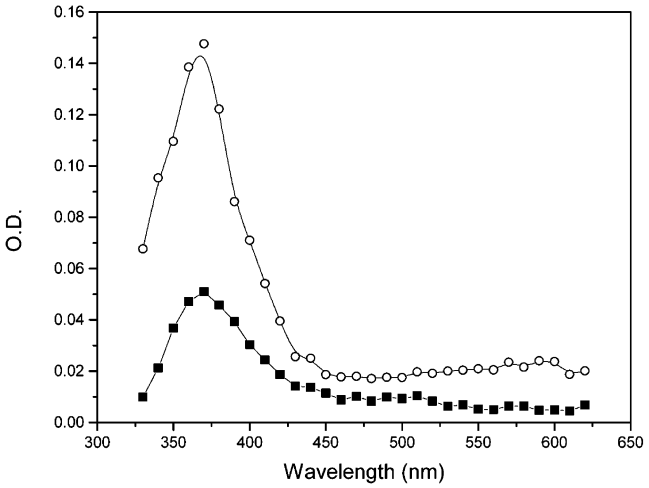

Figure 1. Transient absorption spectra generated by laser flash photolysis ($\lambda = 355$ nm, after 1 μs) of (1) MQ (0.1 mM), (■) and (2) MQ (0.1 mM) and ADS (2 mM) (○) in acetonitrile.

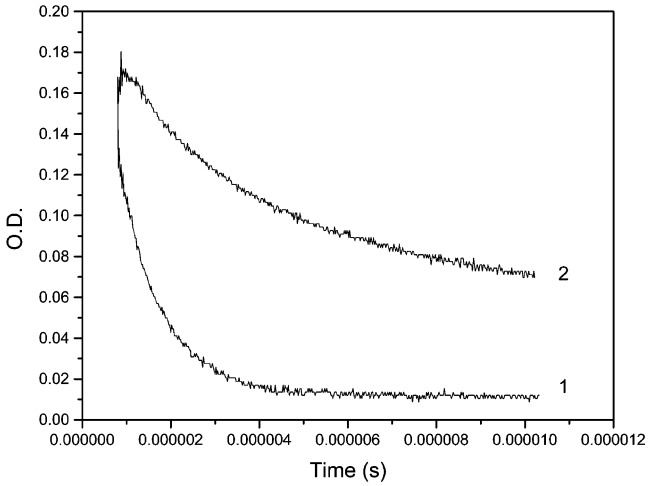

Figure 2. Normalized OD traces at 380 nm obtained by laser flash photolysis ($\lambda = 355$ nm) of (1) MQ (0.1 mM) and (2) MQ (0.1 mM) and ADS (2 mM) in acetonitrile

sulfate: SDS). We have compared our results with those obtained in aqueous solution.[13]

Experimental Section

The compounds MQ, ADS, and SDS were purchased from Sigma and ADE from Sisco Research Laboratory (India). Spectroscopic grade acetonitrile (AN), tetrahydrofuran (THF), and triple distilled water were used as solvents. All the solutions were deoxygenated by passing pure argon before experiment.

The nanosecond laser flash photolysis setup (Applied Photophysics) used (Nd:YAG laser, DCR 11, Spectra Physics) has been described elsewhere.[16] The samples were excited by a 355 nm laser pulse (fwhm = 8 ns). A pulsed xenon lamp (250 W) was used to record the absorption spectra of the transients produced. The signals were displayed by an oscilloscope (FLUKE PM3394B, 200 MHz). Subsequent data transfer to a computer was done by RS232 interface and analyzed by Fluke view Combiscope software (SW33W). The software Origin 5.0 was used to give curve fitting.

Results and Discussion

Laser Flash Photolysis in AN. Argon-saturated solutions of MQ and a mixture of MQ, ADS in AN are irradiated separately by a 355 nm laser pulse. The transient absorption spectra obtained are shown in Figure 1. The spectrum obtained from the excitation of MQ solution represents the T−T absorption of MQ. The maximum is at 370 nm with a hump at around 510 nm. The spectrum obtained by us is quite similar to that obtained for naphthoquinone (NPQ) in AN where the hump is absent.[17]

The transient absorption spectrum obtained from the flash photolysis of MQ in the presence of ADS shows a maximum in the same region, but the absorption is significantly enhanced (Figure 1). The spectrum is quite different in the region above 510 nm where a significant absorption appears in the presence of ADS. In contrast, T−T absorption of MQ is insignificant in this region. The results are similar to those obtained in the aqueous solution[13] but with a small blue shift in the maximum. This is attributed to the lower polarity of AN. The absorption at 370 nm emerges from the presence of $MQ^{\bullet-}$ formed by electron transfer. If electron transfer takes place, the radical cation $ADS^{\bullet+}$ should also be produced. Does the absorption above 510 nm result from this radical cation? The one-electron oxidation of ADE and its derivatives were studied earlier by using the powerful oxidant $SO_4^{\bullet-}$.[18] It was found that, with adenine nucleosides and nucleotides, $SO_4^{\bullet-}$ has a high preference for interaction with the base part rather than with the sugar unit. However, the $SO_4^{\bullet-}$ reaction produces one-electron oxidized and deprotonated species. The deprotonation was shown by the conductance measurements.[18,19] It was concluded that the primary product of one-electron oxidation (radical cation) has a very short lifetime in the aqueous solution and a very rapid deprotonation occurs. Melvin et al.[13] identified the absorption at 550 nm as a result of an N-6 deprotonated radical of ADS. The question arises whether the same arguments hold for the radical cation in AN. Deprotonation from the N-6 radical cation has been found to take place in single crystals even at 4 K.[18] This implies that the reaction has a very high intrinsic driving force. Therefore, the absorption above 510 nm in AN solution is also due to the N-6 deprotonated radical of ADS. This clearly establishes that an electron transfer has taken place between the ^{T}MQ and the ground-state ADS. The following reactions are believed to occur

$$MQ \rightarrow {}^1MQ^* \rightarrow {}^3MQ^*$$

$${}^3MQ^* + ADS \rightarrow MQ^{\bullet-} + ADS^{\bullet+}$$

$$ADS^{\bullet+} - H^+ \rightarrow ADS^{\bullet}$$

It was reported that the N-6, N-6-dimethyladenosine radical cation shows absorption in the same region as $ADS^{\bullet}$.[20] However, for ADS, N-6 deprotonation is possible as the N atom is linked with the H atom and not with the methyl group.

The traces of absorbance change with time are shown in Figure 2. For both wavelengths 380 and 550 nm, the presence of ADS slows the decay. This implies the formation of a longer lifetime species. The decay rate constants are shown in Table 1.

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Table 1. Decay Rate Constants at Two Different Wavelengths for MQ (0.1 mM), MQ (0.1 mM), and ADS (2 mM) in AN

wavelenth (nm)	rate constant (MQ) (s^{-1})	rate constant (MQ + ADS) (s^{-1})
380	1×10^6	2.8×10^5
550	8.6×10^5	3.5×10^5

The decay rate constants are not much different for 380 and 550 nm. This is probably due to the greater absorbance of $MQ^{\bullet-}$ so that its tail part remains in the region of $ADS^{\bullet}$ absorption. All the above results suggest that, in an environment of lesser polarity than water, MQ can interact with ADS by electron transfer. It was reported that in an aqueous medium electron transfer between DNA and ^{T}MQ yields a base radical cation and to a minor extent sugar phosphate radicals.[13] This encourages us to perform experiments separately with the DNA base ADE where the sugar unit is absent. The spectrum obtained for MQ and ADE is quite similar to that obtained for MQ and ADS (not shown). This proves that also, in AN, the major participant in electron transfer is the DNA base rather than the sugar unit.

Amada et al.[17] reported that, for NPQ, a small amount of H atom abstraction is possible from the solvent AN which is known as an inert solvent for substrate like benzophenone. For dimethylnaphthoquinone, no such H-atom abstraction was obvious. Becker and Natarajan[21] reported that H atom abstraction occurs in the triplet n,π^* state of quinones even from benzene. The radical $NPQH^{\bullet}$, produced by H atom abstraction, has the maximum almost in the same position as $NPQ^{\bullet-}$, but a small hump appears near 400 nm. However, for our system MQ, the hump is not as prominent as that for NPQ. It should be kept in mind that a small percentage of H atom abstraction is not impossible. However, in the presence of ADS, the major contributing pathway is electron transfer as the spectrum produced is more like that of $MQ^{\bullet-}$.

Laser Flash Photolysis in SDS. Having established an electron-transfer pathway between ^{T}MQ and ADS/ADE, we searched whether electron transfer is possible for these substrates in the micellar medium. Micellar media are unique in the sense that these provide a cage environment for the RPs/RIPs thus restricting their separation into free ions. We have carried out our experiments in 5% SDS. Micellar medium in this case brings a special situation, as it was shown by Sakaguchi and Hayashi that SDS transfers an H atom to MQ.[22] Later, the same research group observed electron/H atom transfer to MQ in SDS in the presence of another radical, 4-(lauroylamino) TEMPO.[23] It was our aim to study whether ADS or ADE can compete for electron transfer where the H atom transfer channel is open. Figure 3 shows the transient absorption spectra obtained by irradiating separately MQ in SDS, a mixture of MQ and ADS in SDS with a 355 nm laser pulse. The hump at 420 nm is a signature of the formation of $MQH^{\bullet}$. Since the absorption maximum of $MQH^{\bullet}$ is very close to that of the radical anion of $MQH^{\bullet-}$, it is not wise to identify the former only by the absorption maximum when there is a definite probability of the formation of the latter species. The presence of ADS not only enhances the maximum

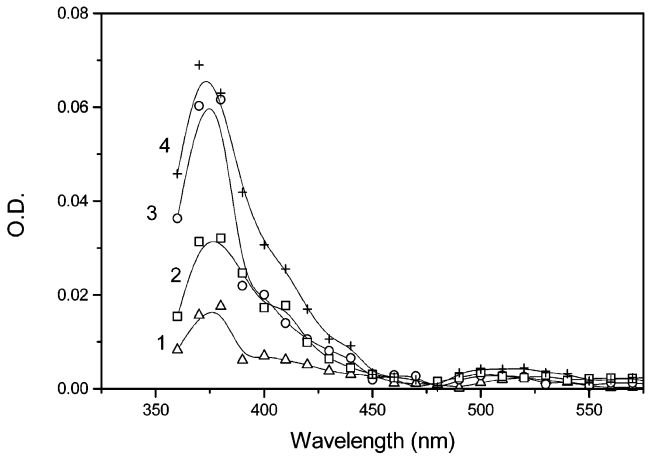

Figure 3. Transient absorption spectra generated by laser flash photolysis (λ = 355 nm, after 1 μs) in aqueous 5% SDS of (1) MQ (0.2 mM) at 0 T, (2) MQ (0.2 mM) and ADS (4 mM) at 0 T, (3) MQ (0.2 mM) at 0.08 T, and (4) MQ (0.2 mM) and ADS (4 mM) at 0.08 T magnetic field.

but also amplifies the hump. This implies that ADS enhances H atom abstraction more in SDS. The question arises why does ADS participate in H atom abstraction in micelle, while electron transfer is the dominating pathway in organic solvent and in water.[13] We feel that the contributing factors are more than one. In a polar solvent (AN or water), a radical ion (formed by electron transfer) is more stabilized than that in the hydrophobic interior of an SDS micelle. However, in the less polar solvent THF, neither electron transfer nor the H atom transfer was evident. The micellar environment is essential for H atom transfer. It was reported earlier that the interbase proton transfer could compete with the electron transfer along the DNA helix.[18] This was attributed to H bonding between the bases that brings the molecules in suitable geometry where a little displacement of the bridging proton leads to proton transfer. We feel that a similar mechanism is operative for H atom transfer between ADS and MQ. These molecules may form an H bond where the participating groups are NH_2 (ADS) and CO (MQ). It is well-known that two molecules forming an H bond in a less polar environment loses the strength of H bonding in an aqueous medium.[24] In aqueous solution, the solvent−MQ and solvent−ADS interaction predominate, and H bonding with the solvent is favored. Therefore, H atom transfer is not significant in water. The solvent AN is also polar where dipole−dipole interactions with MQ and ADS exist. This may reduce the possibility of H bonding between MQ and ADS. Nowick et al. found that the base pairing between adenine and thymine derivatives occurs in SDS due to H bonding and hydrophobicity.[25] In an aqueous medium, no such base pairing was evident. The micelle not only provides the nonpolar environment but also enhances the local concentration of MQ and ADS in its interior. It is quite plausible that the higher concentration makes possible the H bonding interaction and H atom transfer. In other words, the micellar environment forces MQ and ADS to form an H bond which breaks in polar and homogeneous environments due to solvent interaction and dilution. Moreover, it may happen that ADS transfers an H atom to MQ indirectly through SDS. The following reactions are believed to occur

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$$MQ \rightarrow {}^1MQ^* \rightarrow {}^3MQ^* \quad (1)$$

$${}^3MQ + RH\ (SDS) \rightarrow {}^3MQH^\bullet + R^\bullet \quad (2)$$

$${}^3MQ + ADS \rightarrow {}^3MQH^\bullet + ADS^\bullet \quad (3)$$

$$R^\bullet + ADS \rightarrow RH\ (SDS) + ADS^\bullet \quad (4)$$

$$RH + {}^3MQ \rightarrow \text{further reactions} \quad (5)$$

$${}^3(MQH^\bullet\ {}^\bullet ADS) \leftrightarrow {}^1(MQH^\bullet\ {}^\bullet ADS) \quad (6)$$

$${}^3(MQH^\bullet\ {}^\bullet R) \leftrightarrow {}^1(MQH^\bullet\ {}^\bullet R) \quad (7)$$

$${}^1(MQH^\bullet\ {}^\bullet ADS) \rightarrow \text{products} \quad (8)$$

$${}^1(MQH^\bullet\ {}^\bullet R) \rightarrow \text{products} \quad (9)$$

It is well-known that H bonding is a function of concentration of the participating molecules. Generally, intermolecular H bonding is reduced on dilution. To understand the role of H bonding in our system, we have carried out experiments in three different concentrations of ADS (10 mM, 4 mM, and 0.8 mM). At the lowest concentration (0.8 mM), absorbance of $MQH^\bullet$ (at 380 nm) is minimum. This result can be explained by the concept of H bonding; i.e., lowering of concentration reduces H bonding and the consequent H atom transfer. However, molecular recognition by hydrophobic interaction cannot be ruled out. It is possible that, at lower concentration, a lesser number of ADS molecules are available for the interaction with MQ reducing H atom transfer. The absence of H atom transfer or electron transfer in THF does not rule out the importance of hydrophobic interaction. The cage environment brings the molecules much closer (due to hydrophobic interaction) compared with that for the homogeneous solution thus increasing the probability of H atom transfer. It is known that electron transfer can take place over a long distance.[26] Therefore, in a homogeneous environment (AN or water), the model drug−nucleoside interaction can take place by electron transfer. We feel that both H bonding and hydrophobic interactions are responsible for molecular recognition in micelle and in fact, they are cooperative. The molecules MQ and ADS enter the micelle due to hydrophobic interaction where the closeness between them makes possible the H bond and H atom transfer.

Since, the sugar unit is present in ADS, it is quite plausible that the main source of H atom is the deoxyriobose moiety. However, it was reported that the quenching of triplet MQ with deoxyribose is relatively a slow process.[27] It should be kept in mind that this conclusion was drawn from the study in water and not in the micelle. It is possible that the cage environment of the SDS may enhance the H atom transfer rate from the sugar unit. If H atom transfer takes place from the deoxyribose unit, it would generate a sugar-centered radical. In reality, the transient absorption spectrum shows the presence of an N-6 centered radical. To realize the role of the adenine moiety, we performed an experiment with the DNA base ADE. Interestingly, in this case also, the H atom transfer is evident as the absorption of $MQH^\bullet$ is still detectable.

Magnetic Field Effect. In the presence of an external magnetic field, the decay of the transient at 380 nm becomes slower (Figure 4) accompanied by an enhanced absorption in the spectrum (Figure 3). The MFE is present also in the absence of ADS, which was reported by Sakaguchi and Hayashi.[22] The formation of a spin correlated radical pair ($^3MQH^\bullet\ R^\bullet$) (reaction 2) explains this MFE (reaction 7). However, the maximum MFE is observed in the presence of ADS. It is also noteworthy that the nature of decay profiles (at 380 nm) of $MQH^\bullet$ is quite different in the presence of ADS, particularly when a magnetic field is applied. This implies that the RP formed in the presence of ADS responds differently to an external magnetic field. For H atom transfer, $MQH^\bullet$ is formed irrespective of the presence of ADS. The latter not only opens another channel for its formation, but a different radical (N-6 centered adenosine) is formed simultaneously. It is possible that ADS transfers a H atom indirectly through SDS (reaction 4). However, the indirect way of $ADS^\bullet$ formation cannot explain the results as, in that case, it should have no spin correlation with $MQH^\bullet$. Moreover, the indirect mechanism should quench the MFE as the spin correlation between $R^\bullet$ and $MQH^\bullet$ is to be lost. Consequently MFE is not explainable with the idea of indirect transfer of a H atom. This suggests that the direct H atom transfer takes place from ADS to MQ (reaction 3). The decay of $MQH^\bullet$ depends on the spin evolution within the RP $^3(MQH^\bullet\ {}^\bullet ADS)$. In addition to this, MFE establishes the triplet spin state of these transients; i.e., H atom transfer takes place in the triplet state.[28]

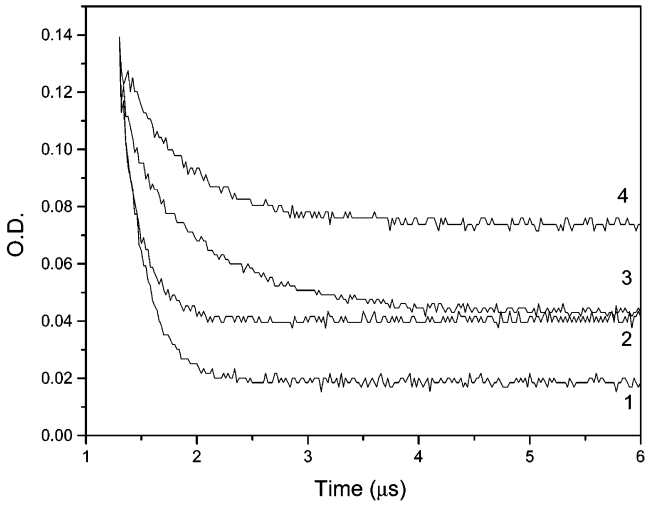

Figure 4. Normalized O. D. traces obtained by laser flash photolysis (λ = 355 nm) in aqueous 5% SDS of (1) MQ (0.2 mM) at 0 T, (2) MQ (0.2 mM) and ADS (4 mM) at 0 T, (3) MQ (0.2 mM) at 0.08 T, and (4) MQ (0.2 mM) and ADS (4 mM) at 0.08 T magnetic field.

In the presence of an external magnetic field, the decay of RP is expected to be biexponential,[29] i.e., the following equation is obeyed for the change in absorbance $A(t)$

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t)$$

where k_f and k_s are the respective rate constants for the fast and slow components of the decay profiles. The fast component of this equation corresponds to the RP decay in the micellar cage, while the slower one is due to the reaction of the escaped radicals. On giving a biexponential fit to curves 3 and 4 (Figure 4), the k_f values obtained are $3.2 \times 10^6\ s^{-1}$ and

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Table 2. Variation of Decay Rate Constant (k_f) and Relative Escape Radical Yield (at 380 nm) with Magnetic Field for Aqueous Micellar Solution (SDS) of MQ and ADS

magnetic field (tesla)	decay rate constant (k_f) $(s)^{-1}$	relative radical escape yield (after 5 μs)
0	3.8×10^6	1.0[a]
0.03	2.27×10^6	1.24
0.08	1.73×10^6	1.66

[a] Arbitrarily taken.

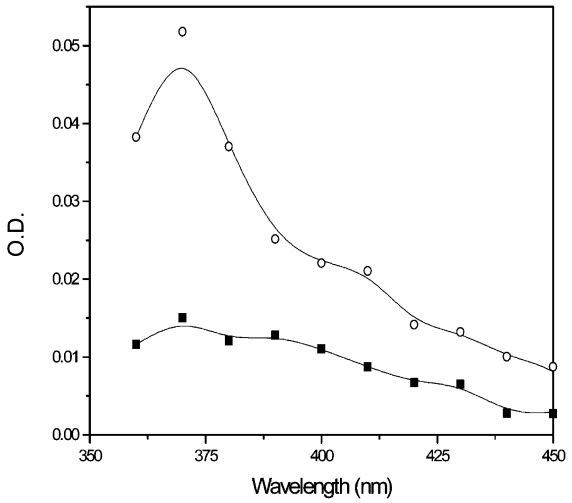

Figure 5. Transient absorption spectra generated by laser flash photolysis (λ = 355 nm, after 1 μs) in aqueous 5% SDS of (1) MQ (0.2 mM) and ADS (0.8 mM) at 0 T (■) and (2) MQ (0.2 mM) and ADS (0.8 mM) at 0.08 T magnetic field (○).

1.7×10^6 s^{-1}, respectively. This implies that the decay of the radical $MQH^•$ at 380 nm (within the micelle SDS) for MQ and ADS becomes 1.8 times slower than that for MQ alone at 0.08 T. Moreover, Table 2 depicts the effect of variation of magnetic field on k_f and relative radical escape yield for MQ and ADS in an SDS micelle. It shows that the k_f values decrease gradually with increasing magnetic field and simultaneously the relative radical escape yield is enhanced. This implies that the conversion of the T RP into the S state is retarded in the presence of a magnetic field. Therefore, the escape of the radicals is enhanced on application of a magnetic field. The escape yield is also higher for MQ and ADS (1.7 times) (curve 4) compared with MQ alone (curve 3) at 0.08 T which is consistent with the slower decay of a fast component for the former case.

Interestingly, the field induced change of absorbance of $MQH^•$ at 380 nm is maximum for the lowest concentration of ADS (0.8 mM) (Figure 5) and minimum for the highest concentration of it (10 mM). This implies that at higher concentration, all the events of MQ−ADS interaction do not respond to an external magnetic field. The observation of maximum MFE depends on the efficient separation of the RPs to a distance where the exchange interaction is negligible. At higher concentration, a greater number of ADS molecules makes the environment more crowded thereby hindering this separation. Consequently, the MFE is reduced at a higher concentration of ADS. Moreover, H atom exchange between ADS and $ADS^•$ in the micelle leads to loss of spin correlation and reduces MFE. Alternatively, at a higher concentration of ADS, some of the molecules reside in the aqueous phase where electron transfer is the dominant pathway. However, the processes occurring in the aqueous phase are not sensitive to the magnetic field. Since the absorption of radical anion $MQH^{•-}$ is very close to that for the radical $MQH^•$, it is not possible to identify a small amount of electron transfer.

Conclusion

We have demonstrated the dependence of model drug−nucleoside interaction (MQ−ADS) on environmental conditions. In polar and homogeneous media, electron transfer takes place while H atom transfer is evident only in an SDS micelle. The transient absorption spectrum and decay profiles prove that the drug−nucleoside interaction can be modulated by an external magnetic field. The slowness of the decay in the presence of a magnetic field suggests that H atom transfer takes place in the triplet state. All these results would stimulate future studies on drug−DNA interaction in the presence of an external magnetic field.

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