Electrostatic Investigation of 4-Dicyanomethylene-2,6-dimethyl-4H-pyran (DDP) Dye with Amide Derivatives in Water

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Supporting Information

ABSTRACT: Cyclic voltammetry (CV) studies of 4-dicyanomethylene-2,6-4H-pyran (DDP) dye with alkyl-substituted amides were carried out in an aqueous solution. Formamide and substituted amide interaction with DDP dye were characterized by fluorescence spectral techniques in an aqueous solution, but the electrochemical nature and the interaction at the interface region between dye–amide remains largely unexplored. The introduction of formamide to DDP dye exhibits an increase in the peak current accompanied with potential values gradually shifting more toward a less positive region. A large variation in the current–potential characteristics is observed in alkyl-substituted amides. The cyclic voltammograms of alkyl amides are found to be entirely different from each other. The role of alkyl substitution in the amide molecular framework influences the reduction potential of the dye in an aqueous medium. The mode of interaction of the dye with alkyl-substituted amides is predominantly due to the electrostatic behavior, even though hydrogen-bonding interactions coexist throughout the aqueous phase. The binding constant parameter (K), free-energy changes (ΔG), and the variation in the potential behavior of the dye in the presence of formamide and alkyl amides authenticate that the nature of interaction operates by both hydrogen-bonding mode and electrostatic interactions. Electrochemical techniques when coupled with fluorescence methods provide an efficient method of determining the interaction at the bulk and the interface regions of a water-soluble dye with nonfluorophoric solutes.

INTRODUCTION

4-Dicyanomethylene-2,6-4H-pyran (DDP) dye belongs to the family of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) type dye. DDP dye is classified as intermolecular charge-transfer (ICT)-based dye. The structure of DDP dye has a strong acceptor group dicyanomethylene –C(CN)2 in the fourth position and a donor moiety (methyl) substituted in second and sixth positions, as shown in Figure 1. DDP dye possesses a striking advantage over DCM dye1−5 due to better solubility in water.

DCM dye has been widely employed as a fluorescent material in optoelectronic devices6 (high-performance organic electroluminescent devices). Further, the electroluminescent and photophysical properties are significantly enhanced7 by varying the structure of the electron-donating groups. The major disadvantage with DCM dye over DDP dye is attributed to its solubility in water. DDP dye has better solubility in water and it also serves as a light-emitter organic material. It also possesses the property of not crystalizing easily when coated upon polymeric surfaces, which portrays DDP dye as a useful probe molecule to study the electroluminescent properties in an aqueous solution.

The spectroscopic and electrochemical nature of many surface-bound fluorescent probes are found to be highly sensitive to the local microenvironment formed by the adlayer around the close vicinity, and the electronic interface provides valuable information on the electrochemical properties of these probes. Considering the high sensitivity of fluorescence and the salient structural information that it can provide, photophysical techniques are predominantly confined to the bulk region wherein the structure of the solvent and solvent-induced properties govern the absorption and emission phenomena. On the other hand, although redox reactions can be carried out in bulk solution, this technique provides very little control and idea about the processes taking place to a larger area. Cyclic voltammetry is an important analytical technique and also a powerful tool commonly employed to investigate the reduction and oxidation processes of molecular species. This technique also provides in depth information in studying and analyzing the electron transfer (ET)-initiated chemical reactions, which also includes catalysis. Electrochemistry provides a much easier and cleaner way to carry out...
redox reactions when the area of study is limited to a very small dimension. By monitoring the potential applied to a working electrode, it is possible to study the ET occurring between the electrode interface and dye in the presence of solute. Further, the kinetics of the reaction mechanisms involved could also be well established based on the current–potential characteristics. This technique, when coupled with spectroscopic outcomes provides better knowledge for understanding the nature of the interaction.

Electrochemical investigation and photophysical studies of a well-known water-soluble nonfluorophoric solute like guanidine hydrochloride (GuHCl) with DDP dye have been carried out in an aqueous phase wherein oxidation potential properties of DDP dye are largely governed by the solute and solute–solvent interactions. Like GuHCl, amides are classified as water-soluble hydrogen-bonding solutes, and a thorough investigation of the absorption, steady state emission, and time-resolved fluorescence lifetime properties of DDP dye interaction with amides was carried out in water but that of electrochemical aspects and the nature of the interaction at the interface of dye with amides was not carried out. The electrochemistry of amides has been explored in depth based on the carbonyl oxygen reduction electrochemically using lead and mercury cathodes in acidic catholytes, and several substituted amides (predominantly aromatic) were converted electrochemically into aldehydes and alcohols. The electrochemistry concerned with these amides depends upon the pH, nature of the electrolyte, and the substituent’s in the amide molecular framework.

In our present study, the possibility of DDP dye acting as an electroluminescent material in the presence of hydrogen-bonding solutes like formamide, dimethylformamide (DMF), and dimethylacetamide were investigated in water and the electrochemical studies were correlated to the fluorescence spectral studies, as reported in the literature. Soluble nonfluorescent solutes like amides can provide a basis for photoluminescence properties applicable in low-cost deposition in optoelectronic applications. DDP dye exhibits oxidation and reduction peaks in water, which provides a platform to understand the electrochemical properties in the presence of guest molecules. The combination of studies relating to the bulk and interface regions has a significant edge in establishing the influence of amides on the electrical and luminescent behavior in an aqueous solution in particular since very less information is available in the literature concerned. Further, the binding constant (K) and free-energy change (ΔG) obtained for DDP dye with formamide, acetamide (ACM), diethylformamide (DMF), and dimethylacetamide (DMAC) through cyclic voltammetry provides a better approach on the nature of interaction in comparison with fluorescence methods.

**RESULTS AND DISCUSSION**

**Cyclic Voltammograms of DDP Dye.** Cyclic voltammogram of DDP dye at a scan rate of 0.1 V s⁻¹ is shown in Figure 2 wherein Ag/AgCl is taken as the reference electrode and the supporting electrolyte used in the present study was 0.01 M KCl. The voltammogram recorded at various scan rates of DDP dye is shown in Figure 3. Cyclic potential sweeps that impose a current response on an electrode give information about the thermodynamics and kinetics of ET at the electrode–solution interface. The cyclic voltammograms of DDP dye exhibit a reduction and an oxidation peak. The anodic and cathodic peaks of DDP dye are almost similar to those observed for DCM dye, as reported in the literature.

The Randles–Sevcik equation generally provides a clear indication of whether an analyte is freely diffusing in a solution or not. A phenomenon of a diffusion or absorption process between free dye solution–electrode interface was obtained using the Randles–Sevcik equation (a plot of the peak current (I) versus the square root of the scan rate, ν¹/²), as provided in eq 1

\[ i_p = (2.69 \times 10^5)n^{3/2}A\text{C}_0D_0^{1/2}\nu^{1/2} \]

where \( i_p \) is the peak current (A), \( A \) is the surface area of the working electrode (cm²), \( \text{C}_0 \) is the bulk concentration (mol mL⁻¹) of the electroactive species (DDP dye), and \( D_0 \) is the diffusion coefficient (cm² s⁻¹). The number of electrons involved in the rate-determining step is given by \( n \) and \( \nu \) is the scan rate (V s⁻¹). The cyclic voltammogram of DDP dye (7.1 × 10⁻⁴ M) at different scan rates (from 0.10–0.5 mV s⁻¹) in a potential range between 1.5 and −1.6 V was recorded (Figure 3). With an increase in the scan rate, the peak current also increases with the cathodic peak potential shifting toward a more negative value and the anodic peak potential shifting toward a positive value. The shift in peak potential and increase in peak current provides information about the mode of interaction and nature of binding of DDP dye in an aqueous solution. With increase in large potential separation and the information ascertained based on the Randles–Sevcik plots (Figure 4), we authenticate that DDP dye exhibits an absorption-controlled quasi reversible behavior in the absence of hydrogen-bonding solutes. If the plot is completely

![Figure 2. Cyclic voltammogram of (7.1 × 10⁻⁴ M) DDP dye with Ag/AgCl as reference electrode and 0.01 M KCl as supporting electrolyte at scan rate of 0.1 V s⁻¹.](image)

![Figure 3. Cyclic voltammogram of (7.1 × 10⁻⁴ M) DDP dye at various scan rates.](image)
linear at any scan rate, we can authenticate that the adsorbed species vary linearly with the applied potential. However, we observe a slight deviation from linearity, which suggests that there could be either an electrochemical quasi reversibility or electron transfer phenomenon that may occur by surface adsorbed species. At different scan rates, it is evident that the peak separation shifts considerably, which suggests that DDP dye exhibits an electrochemically quasi reversible process rather than adsorbing on the electrode surface.

**Voltammetric Interaction of DDP Dye with Amides.**

Cyclic voltammogram of DDP dye with formamide and other alkyl-substituted amides was recorded at a scan rate of 0.1 V s\(^{-1}\). The phenomena of shift in peak potential values accompanied either with a decrease or increase in the peak current implies that there exists an interaction between DDP dye—amide at the electrode interface. This was correlated to an electrostatic interaction between DDP dye and amide. Interestingly, Carter and Bard\(^{16-18}\) studies on DNA complexes reveals that an electrostatic binding is more predominant if the potential shifts to a more negative value. On the contrary, if the potential had been shifted to a more positive value, the mode of interaction was found to be intercalational binding.

Amides were mostly used as a solvent for nonequilibrium medium, and to the best of our knowledge it was considered as a nonfluorophoric hydrogen-bonding solute only in the case of photophysical studies of certain photoinduced electron transfer-based dyes\(^ {19}\) and in the interaction of tryptophan residues in bovine serum albumin.\(^ {20}\) All amides used in the present investigation are liquids except ACM, which is a solid. These amides belong to an important class of solvents that are attributed to their large variation in their viscosity and dielectric constant. Further, the hydrogen-bonding acceptor and donor numbers are entirely different with alkyl group substitution in the amide molecular framework and these properties influence the microenvironment of the electroactive species and its close vicinity. Very recently amides and other urea derivatives were employed as hydrogen-bonding solutes to probe the photophysical properties of DDP in aqueous solutions wherein the presence of several hydrophobic moieties in combination with hydrogen-bonding interactions governs and influence the ground- and excited-state properties. Photophysical properties are completely categorized as a bulk phase phenomenon that has the presence of several forces and interactions. DDP dye exhibits a different current response behavior, which is predominantly occurring in a microenvironment, and how the presence of hydrophobic moieties (methyl group) and hydrophilic groups in the amide structural framework influences the current—potential curves is discussed in depth.

The cathodic peak potential of DDP dye shifts toward a negative value, and the peak current also increases gradually on the addition of formamide (Figure 5), which illustrates that the current flows through the electrode to the dye. The current passage increases with an increase in the concentration of formamide. The shift in the potential is attributed to the introduction of formamide such that the redox potential properties are influenced by the presence of solute molecules near the interface. Formamide as such does not exhibit any reduction or oxidation peak in the absence of DDP dye, which clearly reveals that the cathodic peak potential of the electroactive species (DDP dye) in an aqueous solution is governed and influenced by the number of formamide molecules. The cyclic voltammogram of formamide alone in water is provided in Supporting Information Figure S1.

The interface region in this regard is considered as a microenvironment compared with the bulk phase region (macroenvironment), which is found to be entirely different. Through ground state studies, a photophysical approach resulted in an isosbestic point, which was confined mainly to the bulk phase region properties only. The formation of an isosbestic point through absorption spectral studies implies a ground state complex formation, and this is completely a bulk phase phenomenon. This varies significantly from the electrode—dye interface region. The variation in the oxidation potential and current of DDP dye associated with amide is not as pronounced compared to that of the reduction potential. Addition of formamide results in a large variation in the microenvironment such that the reduction potential of the dye shifts gradually to a less positive value in a definite proportion, which is in accordance with the absorption spectral studies.\(^ {4}\) This signifies that the water molecules initially at the interface of dye—electrode are displaced on the addition of formamide such that formamide definitely involves in hydrogen bonding with water molecules. Apart from this, formamide also forms self-assemblies of chains/sheets or rings to form an extended hydrogen-bonding network and induces a hydrophobic environment throughout the bulk phase and presumably near the electrode region also. This results in a considerable variation in the presence of water and formamide molecules.
around DDP dye, resulting in a variation in the reduction potential values of dye.

Interestingly, the reduction potential of DDP dye increases drastically with a remarkable shift toward the less negative region on the addition of DMF and DMAC. Further addition of DMF and DMAC to DDP dye results in a decrease in the current, and the potential variation toward the positive side becomes predominant, and this pattern was not observed in formamide. The cyclic voltammograms of DDP dye with DMF and DMAC are provided in Figures 6 and 7 respectively.

Figure 6. Cyclic voltammogram of \((7.1 \times 10^{-4} \text{ M})\) DDP dye with DMF at a scan rate 0.1 V s\(^{-1}\). (1) DDP dye, (2) DDP dye + 2.0 M DMF, (3) DDP dye + 4.0 M DMF, (4) DDP dye + 6.0 M DMF, (5) DDP dye + 8.0 M DMF. Inset: Langmuir adsorption isotherm of 7.1 \(\times 10^{-4} \text{ M DDP}\). (x) DMF, 1.0 M \(\geq x \leq 8.0 \text{ M} \) from the relationship of \([\text{DMF}] \) M vs \(i_\text{pc}/\mu\text{A}\).

Figure 7. Cyclic voltammogram of \((7.1 \times 10^{-4} \text{ M})\) DDP dye with DMAC at a scan rate of 0.1 V s\(^{-1}\). (1) DDP dye, (2) DDP dye + 1.0 M DMAC, (3) DDP dye + 2.0 M DMAC, (4) DDP dye + 4.0 M DMAC, (5) DDP dye + 6.0 M DMAC, (6) DDP dye + 8.0 M DMAC. Inset: Langmuir adsorption isotherm of 7.1 \(\times 10^{-4} \text{ M DDP}\). (x) DMAC, 1.0 M \(\geq x \leq 8.0 \text{ M} \) from the relationship of \([\text{DMAC}] \) M vs \(i_\text{pc}/\mu\text{A}\).

Acetamide addition also results in a significant shift toward the less positive region similar to that of other alkyl amides. The cyclic voltammogram of DDP dye with acetamide is provided in the Supporting Information Figure S2.

The structure of DMF with water and DMAC with water hydrogen-bonding modes is found to be entirely different from that of hydrogen bonding of formamide with water. This phenomenon is presumed to be attributed to the absence of hydrogen-bonding donor sites in DMF and DMAC compared to that of formamide. On the initial addition of DMF, a steep increase in the current and shift in the reduction potential toward the negative region results and this is accompanied with an increase in the current and shift in the oxidation potential toward less positive values. Even though this shift in the reduction potential toward the negative potential was almost similar to that of formamide, no clear illustration on the behavior of the oxidation potential of DDP dye on the amides could be ascertained. Interestingly, the subsequent addition of DMF resulted in a decrease in the current (reduction potential), which was an entirely different phenomenon compared to that of formamide. This is presumably attributed to the variation in the properties of amide—water hydrogen bonding and the extent of hydrophobic influences near the interface. With an increase in the concentration of formamide, the peak current corresponding to the reduction potential increases gradually, which describes the adsorption process. The shift in the peak potential toward a negative value indicates electrostatic binding and no large effect of hydrophobic influences on the current—potential characteristics. A similar pattern of a nonsignificant shift in the emission spectra of DDP dye on the addition of formamide was observed through steady state emission spectral studies.\(^4\) The variation between formamide and DMF results from the unavailability of the N–H hydrogen in the amide framework such that the hydrophobic influences predominate over hydrogen-bonding interactions around the vicinity of the dye in the interface region in the case of alkyl-substituted amides. The current—potential characteristics of DDP dye vary significantly for formamide and DMF, and this provides an explanation that the nature of interaction and the functional groups involved in hydrogen-bonding with DDP dye and water molecules are entirely different. Interestingly, the current response becomes entirely different in the case DMAC (Figure 7) such that the reduction peak current of DDP dye decreases gradually on the addition of DMAC wherein no significant shift or characteristic change was observed in the peak potential values compared to that of formamide. Further, the oxidation potential diminishes and ceases to be insignificant on the introduction of DMAC molecules. This behavioral pattern was not observed in formamide and DMF. On the basis of the alkyl-substituted amides taken in the present study, the C=O oxygen atom readily forms hydrogen bonding with water and not with the dye molecule. If dye—amide direct hydrogen bonding would have been more predominant, a similar pattern on the electrochemical behavior of DDP dye would have been observed irrespective of the nature of amides, which was rather found to be strikingly different from each amide. The electrochemical behavior of DDP dye in host—guest interaction in an aqueous solution produces a new contemporary in the electrochemistry when various alkyl-substituted groups are present in the amide framework.

The cyclic voltammograms of DDP dye with DMF and DMAC reveal that the current response parameters of DDP dye are largely governed by the presence of methyl group substitution in the amide framework such that the microenvironment of DDP dye in the aqueous phase is completely disrupted such that several micro amide—water and amide—dye interactions operate that could not be quantified exactly. The peak current shift toward more negative and positive values illustrates that the microenvironment surrounding the dye changes based on the concentration of the amides, and the most predominant interaction is hydrogen bonding, which is competitive with the hydrophobic influences imparted by the methyl group substitution in the case of alkyl-substituted amides.
On the basis of the electrochemical nature of DDP dye in the presence of amides, we postulate that the shift in the peak current and peak potential toward a negative valve suggests the mode of interaction between DDP dye amides is presumably also through electrostatic interaction (at the interface region) apart from hydrogen bonding and hydrophobic interactions. The hydrogen-bonding arrangement of dye–water–amide is confined throughout the bulk region. The electrostatic force originates from hydrogen-bonding formation in DDP dye with amides and the methyl moieties impart an inductive effect in the amide molecular structure that results in a difference in the electrochemical behavior. The methyl group attached to carbonyl group of amide does show variation in current response when compared with hydrogen atom attached to carbonyl group in amides. The electrostatic binding with the adsorption process was observed with an increasing order of the hydrophobic nature of amides. Similarly, the pattern of fluorescence enhancement and the variation in the excited-state characteristics of DDP dye is of the order formamide < ACM < DMF < DMAC. DDP dye with amides shows an irreversible system of cathodic current response with shift toward a more negative value indicating electrostatic binding and hydrogen bonding.

**Binding Nature of DDP Dye with Amides.** For quantitative comparison of the binding constant \( K \) between DDP dye with amides, the Langmuir equation\(^{1,22} \) was used.

\[
\frac{1}{\Delta I_p} = \frac{1}{\Delta I_{p,max}} + K \frac{1}{[\text{amide}] M} \tag{2}
\]

From eq 2, we assume \( m = 1 \), \( \Delta I_p \) represents \( \Delta I_{p,max} \) where \( \Delta I_p = I_{p0} - I_p \) where \( I_{p0} \) and \( I_p \) represent the cathodic peak current of DDP dye in the absence and presence of amide, respectively. Figure 8 exhibits the plot of \( 1/[\text{formamide}] M \) vs \( 1/I_0 - I \) plot for determination of the binding constant \( K \). (\( I_0 \) and \( I \) are the difference in peak currents before and after addition of amide, respectively).

![Figure 8.](image)

**Table 1.** Binding Constant \((K)\) and the Free Energy \((-\Delta G)\) of \((7.1 \times 10^{-3} \text{ M})\) DDP Dye with Different Concentrations of Amides \(1.0 \text{ M} \geq x \leq 8.0 \text{ M} \) Arrived at from Cyclic Voltammetry

| S. no. | DDP–amide | \( K \times 10^4 \text{ (L mol}^{-1}\text{)} \) | \(-\Delta G \times 10^3 \text{ (kJ mol}^{-1}\text{)}\) |
|-------|------------|---------------------------------|---------------------------------|
| 1     | DDP–formamide | 1.7082                          | 12.12                           |
| 2     | DDP–DMF     | 2.1351                          | 15.41                           |
| 3     | DDP–DMAC    | 1.1581                          | 16.33                           |
| 4     | DDP–ACM     | 2.5456                          | 32.76                           |

**Binding Free Energy.** The free energy \((-\Delta G)\) was calculated from eq 3 to show the spontaneity of binding between DDP dye with amides in the aqueous phase, where \( R \) is the gas constant, \( T \) is the temperature in Kelvin, and \( K \) is the binding constant obtained from the binding plot, respectively.

\[ -\Delta G = RT \ln K \tag{3} \]

Binding free energy is calculated to check the spontaneity of the process between DDP dye–amide interaction. The calculated binding constant \((K)\) and free energy \((-\Delta G)\) from the cyclic voltammetry current response are shown in Table 1. The free-energy changes and the binding constant were almost similar in all amides except in the case of aceticamide. All amides except acetamide exhibit solvent-induced properties, like dipole moment, refractive index, viscosity, and induced polarity, and the redox properties of the dye varies in different medium. Cyclic voltammogram of DDP dye in acetonitrile also exhibits oxidation and reduction peaks as observed in water, but the shift in the potential and the peak current varies (Supporting Information Figure S5). Similar to photophysical properties that are governed by the nature of the solvent, the cathodic and anodic peaks are influenced by the presence of amides that exist as liquids. These properties influence the dye in aqueous medium, thereby resulting in a large variation in the microenvironment at the interface region, which is highly sensitive to the current—
potential characteristics compared with the bulk phase region. These factors could not be selectively ascertainment to the behavior of DDP dyes in the presence of amides in an aqueous phase, and this article provides a new outlook for the comparison of bulk characteristics that are predominantly solvent–solute governed compared with the changes at the microlevel around the close vicinity of the dye.

■ CONCLUSIONS

Cyclic voltammetric techniques were employed as an efficient tool in establishing the binding nature of DDP dye with formamide and alkyl amides. These techniques are used to evaluate the binding nature as well as the preferred mode of interaction of DDP dye in the presence of amide in an aqueous solution. The shift in the peak potential and peak current of the DDP dye decreases and increases with the increasing hydrophobic nature of amides. The calculated binding constant K and free energy −ΔG value help to conclude that the microenvironment surrounding the DDP dye molecule interaction with amides is due to hydrogen bonding. Moreover, we also observed that the interaction is also through electrostatic mode apart from hydrogen-bonding interaction. These investigations reveal that electrochemistry techniques certainly provide a convenient way to characterize both the binding mode and the electrostatic interaction of DDP dye with different concentrations of amides in an aqueous solution.

■ EXPERIMENTAL SECTION

Materials. Formamide, acetamide (ACM), dimethylformamide (DMF), dimethylacetamide (DMAC), 2,6-dimethyl-4-pyrone, malononitrile, acetic anhydride, and potassium chloride (KCl) were obtained from Merck chemicals and used as procured. DDP dye was synthesized as reported in the literature.6

Experimental Techniques. Cyclic voltammogram studies were recorded using a CH INSTRUMENT CHI604E electrochemical analyzer. A platinum electrode with surface area of 0.0314 cm² was employed as the working electrode and Ag/AgCl as the reference electrode. Platinum wire was employed as the auxiliary electrode. A supporting electrolyte (0.01 M KCl) was used in all our electrochemical experiments for recording voltammogram. The voltammograms of DDP dye (7.1 × 10⁻⁴ M) with varying concentration of amides (ranging from 1.0 to 8.0 M) were recorded at various scan rates (50 ≥ ν ≤ 500 mV s⁻¹). The solution of amides was prepared using triple distilled water. The bulk concentration of amides involved in our studies was used up to 10.0 M. The concentration of DDP dye was fixed at 7.1 × 10⁻⁴ M and was diluted with 1.0, 2.0, 4.0, 6.0, and 8.0 M amide solutions, respectively.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03427.

Cyclic voltammogram of formamide in the absence of DDP dye, DDP dye with ACM, binding constant of dye with DMF and DMAC, and that of dye in acetonitrile is provided in Figures S1–S5 (PDF)

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Notes
The authors declare no competing financial interest.

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