7 Diethylaminocoumarin (DEAC) 레이저 염료의 광물리적 파라미터, 광분해, 형광 소광 및 Convolutive Voltammetry

S. A. El-Daly and I. S. El-Hallag*
Chemistry Department, Faculty of Science, Tanta University, Tanta, 31527, Egypt
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Photophysical Parameters, Photodecomposition, Fluorescence Quenching and Convolutive Voltammetry of 7-Diethylaminocoumarin (DEAC) Laser Dye

S. A. El-Daly and I. S. El-Hallag*
Chemistry Department, Faculty of Science, Tanta University, Tanta, 31527, Egypt
*E-mail: ielhallag@yahoo.co.uk
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INTRODUCTION

Derivatives of 1,2-benzopyrone, commonly known as the coumarine dyes, are well-known laser dyes for the blue-green region. Among these dyes, the ones having different amino groups at 7-position (commonly known as 7-aminocoumarins) are of special significations. The fluorescence quantum yield ($\phi_f$) of these dyes is usually very high, often close to unity. These dyes undergo substantial changes in their dipole moment upon excitation, causing large Stokes shifts between their absorption and fluorescence spectra. Which are very sensitive to solvent polarities. Because of these properties, the 7-aminocoumarin dyes have been widely used as probes in a variety of investigation, namely, in the study of solvatochromic properties, determination of polarities in microenvironments, measurements of solvent relaxation times. In the literature, it is reported that the coumarin dyes with 7-dialkylamino groups behave unusually in higher polar solvents, showing drastic reduction in their fluorescence quantum yield and fluorescence lifetime values. Twisted intramolecular charge transfer (TICT)
states have been invoked to explain these results in higher polarity solvents.

On the other hand, study of the electrochemical reduction of coumarin has been started by Harle and Capka. Zuman have reported the half-wave potential and substituent effects for coumarin derivatives and Gourley have obtained the result that coumarin derivative becomes dihydrocoumarins by the electrochemical reduction in the presence of tertiary amine coumarin. Reddy have suggested a polarographic reaction mechanism of 3-acetyl coumarin and Partridge, Bond have explained a phenomenon that coumarin becomes adsorbed to mercury electrode. Helin have reported the electrochemiluminescence of 4-methyl coumarin derivatives induced by hot electrons into aqueous electrolyte solution. Diez have surveyed the voltammetric determination in coumarin in the emulsified media and Wang have done a differential pulse voltammetric determination with 7-hydroxy coumarin of human urine. Wang have made an amperometric biosensor by modifying antibody of 7-hydroxy coumarin with glassy carbon electrode, and have investigated antibody specificity and antibody-antigen interaction kinetic. 7-hydroxy coumarins were studied using cyclic voltammetry, differential pulse voltammetry and chronocoulometry. The results showed that the coumarins undergo a pH-dependent, irreversible oxidation with product adsorption.

In the present work, photophysical properties, laser parameters, fluorescence quenching and photoreactivity of DEAC have been investigated. Also, in this article, we have studied the electrochemical reduction of DEAC laser dye by cyclic voltammetry (CV), convolutive voltammetry combined with digital simulation technique.

**EXPERIMENTAL DETAILS**

Laser-grade DEAC dye was obtained from Fluka and used without further purification. The organic solvents used were of spectroscopic grade. Picric acid (Aldrich) was recrystallized from ethanol, TCNE and TCNQ (Aldrich) was purified by sublimation, sodium dodecyl sulphate (SDS, Fluka) was used to prepare anionic micelles and cetyltrimethylammonium chloride (CTAC, Fluka) to prepare cationic micelles. UV-Visible electronic absorption spectra were recorded on a Shimadzu UV-160 A spectrophotometer and the steady state fluorescence spectra were measured using Shimadzu RF 510 spectrofluorophotometer. The fluorescence spectra were corrected for the mirror response using 10^5 mol L^-1 anthracene solution in benzene. The fluorescence quantum yield (Φ) was measured relative to 9,10-diphenylanthracene, according to the following equation:

\[ Φ(λ) = Φ(λ_{max}) \frac{D}{R} \frac{A_s}{A_r} \frac{λ_{max}^2}{n_s^2} \]

Where D represents the corrected fluorescence peak area, A is the absorbance at excitation wavelengh, and n is the refractive index of solvent used. The subscripts 's' and 'r' refer to sample and reference, respectively. All measurements were made at very low concentration of dye (< 1 × 10^-5 mol L^-1) to avoid re-absorption of emitted photons. The photochemical quantum yields were calculated using method that was described in details previously. The light intensity was measured by using ferrioxalate actinometry. The laser action of DEAC using GL-302 dye laser, pumped by a nitrogen laser (GL-3300 nitrogen laser, PTI). The pump laser (λ = 337.1 nm) was operated at repetition of 3 Hz with a pulse energy of 1.48 mJ and pulse duration rate of 800 ps. The narrow-band output of the dye laser was measured with pyroelectric Joule meter (ED 200, Gen-Tec Inc.).

Cyclic voltammetry measurements are made using a conventional three electrode cell configuration linked to an EG & G model 170 PAR apparatus. The platinum electrode surface was 1 × 10^-5 m^2 as a working electrode, silver-silver chloride as a reference electrode, coiled platinum wire as a counter electrode and 0.1 mol L^-1 tetrabutyl ammonium perchlorate (TBAP) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and iR compensation to minimize double-layer charging current and solution resistance. The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rates ranging from 0.02 to 5 V s^-1 in non-aqueous media at 22 ± 2 °C. Digital simulation of the data for cyclic voltammetric experiments were carried out on a PC computer using EG & G condesim package. Convolution-deconvolution voltammetry was performed using EG & G condecon software package. All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

**RESULTS AND DISCUSSION**

**Solvent polarity effect on absorption and fluorescence spectra**

Absorption and fluorescence spectra of DEAC dye are strongly dependent on solvent polarities (Fig. 1). Table 1 lists the photophysical parameters such as λabs (max), λem (max), and fluorescence quantum yield along with solvent polarity function (∆f). The spectral shifts in absorption are generally found to be smaller than those found in fluorescence emission implying a greater dipole moment (polarity) of the dye in the excited state compared to that in the ground state. This is also in agreement with π,π' nature of the lowest singlet excited state of DEAC. The marginal deviation in data points for alcoholic solvents are assigned to solute-solvent hydrogen bonding
interaction, which causes an extra red shift in the observed spectra. Analysis of the solvatochromic behavior allows to estimate the difference in the dipole moment between the excited singlet and the ground state (Δμα - Δμβ). This was achieved by applying the simplified Lippert-Mataga equation.

\[
\Delta \mu = \frac{2(\mu_e - \mu_a)}{\hbar c a^2} \Delta f
\]

\[
\Delta f = \frac{\epsilon - 1}{2\epsilon + 2} - \frac{n^2 - 1}{2n^2 + 1}
\]

Table 1. Photophysical properties of DEAC in different solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Δf</th>
<th>λα (nm)</th>
<th>λem (nm)</th>
<th>Δν (cm⁻¹)</th>
<th>Φf</th>
<th>Ma (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>0.0</td>
<td>353</td>
<td>392</td>
<td>2817</td>
<td>0.85</td>
<td>10.8</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.0002</td>
<td>352</td>
<td>390</td>
<td>2768</td>
<td>0.85</td>
<td>10.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0052</td>
<td>355</td>
<td>395</td>
<td>2853</td>
<td>0.83</td>
<td>10.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0133</td>
<td>369</td>
<td>418</td>
<td>3177</td>
<td>0.83</td>
<td>10.3</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.166</td>
<td>359</td>
<td>405</td>
<td>3164</td>
<td>0.80</td>
<td>10.5</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0.008</td>
<td>360</td>
<td>412</td>
<td>3505</td>
<td>---</td>
<td>10.2</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>0.233</td>
<td>375</td>
<td>435</td>
<td>3677</td>
<td>0.62</td>
<td>9.6</td>
</tr>
<tr>
<td>DMF</td>
<td>0.274</td>
<td>379</td>
<td>440</td>
<td>3657</td>
<td>0.56</td>
<td>9.4</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>0.277</td>
<td>379</td>
<td>442</td>
<td>3760</td>
<td>0.52</td>
<td>8.85</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.284</td>
<td>370</td>
<td>430</td>
<td>3771</td>
<td>0.55</td>
<td>10.7</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.290</td>
<td>380</td>
<td>443</td>
<td>3742</td>
<td>0.39</td>
<td>8.6</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.309</td>
<td>381</td>
<td>445</td>
<td>3775</td>
<td>0.27</td>
<td>8.62</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.30</td>
<td>381</td>
<td>445</td>
<td>3775</td>
<td>0.25</td>
<td>---</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.263</td>
<td>379</td>
<td>442</td>
<td>3376</td>
<td>0.47</td>
<td>---</td>
</tr>
</tbody>
</table>

Where Δνα is the Stokes-shift (in cm⁻¹), which increases with increasing solvent polarity pointing to stronger stabilization of excited state in polar solvents, h is the Planck's constant, c is the velocity of light and α is the Onsager cavity radius, e and n are the dielectric constant and refractive index of the solvent, respectively. The Onsager cavity radius α was calculated from the energy minimized structures obtained with the AM1 calculation. It defined as the radius of the spherical cavity surrounding the molecular van der Waals radius. The maximum distance where charge separation can occur across the molecule must be considered, rather than the actual molecular axis of the molecule. For DEAC this distance lies between the average coordinates of the nitrogen atoms on one side of the molecule and the oxygen atom in the other side of the molecules it was estimated to 9.0 Å, the cavity radius α was taken as half of this distance that is 4.5 Å. Fig. 2 shows the plot of Stokes shift versus the orientation polarization (Δf). The change of dipole moment upon excitation which was calculated from slope of the plot and the cavity radius is 4.76 Debye, indicating the polar nature of the fluorescent states. We assign this state to be of intramolecular charge transfer (ICT) character. In the earlier work, a similar ICT character was assigned to the fluorescent states of 7-amino coumarin derivatives.

The fluorescence quantum yield (Φf) values of DEAC were estimated in different solvents at room temperature and listed in Table 1. Fig. 3 shows the plot of Φf versus Δf. The interesting point from this plot is that the Φf values reduce in higher polarity solvents, having Δf > 0.2. In lower medium polarity solvent region (Δf<0.2), however, Φf reduces only marginally with Δf following apparently a linear correlation indicated that the dye exist in ICT structure in these solvents. Thus the drastic reduction in the Φf values above Δf ≅ 0.2 clearly indicates that in the higher polarity solvents, the excited state of the dye undergoes...
a fast non-radiative deexcitation process due to stabilization of twisting intramolecular charge transfer (TICT) non-emissive state, which is absent in lower medium polarity of solvents.45

The transition dipole moment ($M_a$) of DEAC from ground to excited state was calculated in different solvents from the absorption spectrum using the simplified expression$^{40,47,48}$

$$M_a = 0.0958 \left( \varepsilon_{\text{max}} \Delta \nu_{a}^{1/2} \nu_{a} \right)^{0.5}$$

Where $\varepsilon_{\text{max}}$ is the maximum value of molar absorption coefficient of the absorption band with a maximum at $\nu_{a}$ and full width at half maximum of $\Delta \nu_{a}^{1/2}$, the values of $M_a$ are listed in Table 1.

The emission spectrum of $1 \times 10^{-5}$ mol L$^{-1}$ of DEAC has also been measured in CTAC and SDS micelles media, as shown in Fig. 4. The emission intensity of dye increases as the concentration of surfactants increase, an abrupt change in the fluorescence intensity is observed at surfactant concentration of $1 \times 10^{-4}$ and $8 \times 10^{-3}$ mol L$^{-1}$ which is very close to the critical micelle concentration of CTAC and SDS, respectively.49,50

**Laser parameters of DEAC**

DEAC has high fluorescence quantum yield, high molar absorptivity and high photostability in most organic solvents. In addition, the dye is free from molecular aggregation both in ground and in the excited state since the emission spectrum suffers no shift as the concentration is raised up to $5 \times 10^{-3}$ mol L$^{-1}$. Solution of $2 \times 10^{-5}$ mol L$^{-1}$ in different solvents namely acetone, dioxane, DMF and ethanol give laser emission upon pumping by nitrogen laser ($\lambda_{\text{ex}} = 337.1$ nm) of 800 ps duration rate and 1.48 mJ pulse energy. The dye solution was taken in oscillator and amplifier cuvetts of 10 mm path length. The output energy of laser dye was measured as a function of wavelength to determine the lasing range in different solvents. The gain coefficient $\alpha (\lambda)$ of laser emission of DEAC was calculated by measuring the intensity of laser emission from the entire cell length and that from the cell half-length ($I_{L}$ and $I_{L/2}$, respectively) according to the following relation:51

$$\alpha (\lambda) = \frac{2}{L} \ln \left[ \frac{I_{L}}{I_{L/2}} - 1 \right]$$

The cross section for stimulated laser emission $\sigma_e$ was calculated at laser emission maximum according to the equation:51

$$\sigma_e = \frac{\lambda^4 E(\lambda) \Phi_f}{8 \pi n^2 \tau_f}$$

Where $\sigma_e$ is the emission wavelength, $n$ is the refractive index of solution, $c$ is the velocity of light and $E (\lambda)$ is the normalized fluorescence line-shape function. This is correlated with fluorescence quantum yield by the equation:52

$$\int E(\lambda) d\lambda = \Phi_f$$

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Table 2. Laser parameters of DEAC laser dye

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Lasing range (nm)</th>
<th>λ (max) (nm)</th>
<th>α (cm⁻¹)</th>
<th>σₑ × 10¹⁶ cm²</th>
<th>E₁/₂ J/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>415-451</td>
<td>430</td>
<td>2.2</td>
<td>1.6</td>
<td>7400</td>
</tr>
<tr>
<td>Dioxane</td>
<td>405-450</td>
<td>425</td>
<td>1.8</td>
<td>1.45</td>
<td>13333</td>
</tr>
<tr>
<td>EtOH</td>
<td>425-465</td>
<td>440</td>
<td>1.74</td>
<td>1.5</td>
<td>14800</td>
</tr>
<tr>
<td>DMF</td>
<td>420-45</td>
<td>438</td>
<td>2.4</td>
<td>1.65</td>
<td>15564</td>
</tr>
</tbody>
</table>

E (λ) is obtained from solution whose absorbance is low to avoid reabsorption processes (optical density at absorption maximum < 0.1).

The values of α (λ) and σₑ at maximum laser emission are listed in Table 2. The photochemical stability of DEAC laser dye was determined as half-life energy (E₁/₂) which is the amount of total absorbed pump energy until the dye laser energy has dropped to 50% of its output initial value. By knowing the concentration of the laser dye and photon energy of nitrogen laser used the E₁/₂ value was calculated in term of Joule per liter of solution (Table 2).

Photoreactivity of DEAC in carbon tetrachloride solvent

The photoreactivity of DEAC has been studied in carbon tetrachloride (CCl₄) upon irradiation of 2 × 10⁻⁵ mol L⁻¹ solution of DEAC by 366 nm light (I₀ = 3.6 × 10⁻⁶ Ein/min). The absorbance of DEAC decreases with increasing the radiation time and two isobestic points appear at 325 and 385 nm indicating the presence of two photoproducts. The two new absorption peaks appear at 410 nm and 280 nm corresponding to the absorption of contact ion pair which has large dipole moment and to the absorption of trichloromethyl radical as shown in Fig. 5. The net photochemical quantum yield (φₗ) of the underlying reaction was calculated as 0.054. The formation of photoproduct is a one photon process and represented by the following scheme as reported earlier for some aliphatic and aromatic amine and also for aromatic hydrocarbon such as anthracene and perylene derivatives.

DEAC + hν → ¹(DEAC)* absorption of light ····················· 1
¹(DEAC)* → DEAC + hν fluorescence ····························· 2
¹(DEAC)* + CCl₄ → ¹[DEAC⁺ + δCCl₄]- exciplex ··· 3
¹[DEAC⁺ + δCCl₄]- → DEAC⁺ + .Cl + .CCl₃ ····························· 4

It was proposed that the electron transfer from excited singlet DEAC⁺ to CCl₄ within transient excited charge transfer complex is the main primary photochemical process (step 3). It leads to the DEAC radical cation, a chloride ion and a trichloromethyl radical in solvent cage (step 4). The formation of a contact ion pair [DEAC⁻ + Cl⁻] usually occurs by electron transfer from excited donor molecule to acceptor. In order to such compound to be formed a low ionization potential of donor and high electron affinity of acceptor are necessary.

The rate constant of photodecomposition of DEAC was calculated by applying the simple first order rate equation as follow:

\[ \ln \frac{A_0 - A_t}{A_t - A_\infty} = kt \]

Where A₀, Aₜ, and A∞ are the initial absorbance, absorbance at time (t) and infinity, respectively. k is the rate constant. The rate constant was found to be 0.067 min⁻¹.

It worthwhile to mention that the DEAC is highly photostable in polar solvents.

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Fig. 5. (a) effect of irradiation on electronic absorption spectrum of 2 × 10⁻⁵ mol dm⁻³ of DEAC (λₑₓ = 365nm, I₀ = 3.6 ×10⁻⁶ Ein/min). The irradiation times at decreasing absorption are 0.0, 3, 7, 10, 15, 20, 26, 32, 40, 45, and 50 min.

Fig. 6. Emission spectrum of 1 × 10⁻⁵ mol dm⁻³ of DEAC in absence (-x--) and presence (...) of 1.4 × 10⁻⁴ mol dm⁻³ of picric acid (λₑₓ = 337 nm).
Fluorescence quenching by organic acceptors

The fluorescence quenching of $1 \times 10^{-5}$ mol L$^{-1}$ DEAC are also studied in acetonitril solvent using organic acceptors such as picric acid (PA, $E_a = 0.7$ eV), TCNE ($E_a = 1.7$ eV) and TCNQ ($E_a = 2.2$ eV). It was observed that the absorption spectrum when taken with increasing concentration of acceptor does not show any shift in wavelength. There is no additionally peak appearing, hence there could not be any ground state interaction between DEAC and acceptors. The emission spectrum of DEAC shows (i) no change in fluorescence spectra other than diminishing fluorescence intensity with increasing quencher concentration, (ii) no appearances of any new band at longer wavelength as shown in Fig. 6, this shows the absence of emissive exciplex and (iii) the Stern-Volmer plot for the fluorescence quenching of DEAC by organic acceptor is linear (Fig. 7). The Stern-Volmer equation is given by:

$$\frac{I_0}{I} = 1 + k_{sv}[Q]$$

Where $I_0$ and $I$ are the fluorescence intensities in the absence and presence of the quencher $[Q]$, $K_{sv}$ is the Stern-Volmer rate constant obtained from the slope. For dynamic quenching $K_{sv} = k_q \tau_f$ where $k_q$ is the bimolecular quenching rate constant ($M^{-1} s^{-1}$) and $\tau_f$ is the excited singlet lifetime of fluorophore in the absence of quencher. For DEAC $\tau_f$ is 2.25 ns, the bimolecular quenching rate constants $k_q$ were calculated as $5.3 \times 10^{12}$, $8.8 \times 10^{12}$ and $1.5 \times 10^{13}$ $M^{-1} s^{-1}$ for PA, TCNE and TCNQ, respectively, indicating that the fluorescence quenching rate constant increases with increasing the electron affinity of acceptor. The effect of temperature of fluorescence quenching of DEAC by picric acid was also studied in the range 25 - 60 °C. The activation energy $E_a$ associated with $k_q$ was calculated assuming the Arrhenius equation to be valid for $k_q$:

$$k_q = A \exp\left(- \frac{E_a}{RT}\right)$$

The value obtained is 9.8 kJ mol$^{-1}$, which is very close to the activation energy associated with solvent viscosity ($E_\eta = 10 - 13$ kJ mol$^{-1}$), indicating a diffusion mechanism for fluorescence quenching (dynamic quenching mechanism). Thus, we infer that quenching of DEAC by organic acceptor proceed predominantly via a non-emissive exciplex with charge transfer occurring from the excited fluorophore to acceptor according to the following scheme.

$$D^* \ldots A \leftrightarrow D^*A \rightarrow [DA]^* \rightarrow D^+A^- \rightarrow D^+ \ldots A^- \rightarrow D^+ + A^-$$

Cyclic Voltammetry study

Cyclic voltammetry of the reductive process of the laser dye compound, DEAC, was measured in CH$_2$CN, solvent, at scan rates ranging from 0.02 - 5 V s$^{-1}$. The cyclic voltammogram shown in Fig. 8 exhibited two reductive peaks coupled with
Table 3. Electrochemical parameters of the reduction process of DEAC laser dye

<table>
<thead>
<tr>
<th>Technique</th>
<th>-E1 o V</th>
<th>-E2 o V</th>
<th>ks1 x 10^5 m s^-1</th>
<th>ks2 x 10^5 m s^-1</th>
<th>D1 x 10^10 m s^-1</th>
<th>D2 x 10^10 m s^-1</th>
<th>α1</th>
<th>α2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>1.520</td>
<td>1.680</td>
<td>2.30</td>
<td>1.50</td>
<td>4.50</td>
<td>4.85</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>Conv</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>4.60</td>
<td>4.79</td>
<td>---</td>
</tr>
<tr>
<td>Decon</td>
<td>1.510</td>
<td>1.690</td>
<td>---</td>
<td>---</td>
<td>4.46</td>
<td>4.46</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sim</td>
<td>1.513</td>
<td>1.675</td>
<td>---</td>
<td>---</td>
<td>3.23</td>
<td>3.54</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Fig. 8. Cyclic voltammogram of DEAC at sweep rate of 0.1 Vs^-1.

Two anodic peaks. It was found that the peak currents increase with increasing the scan rate, while the cathodic peak potentials of the reduction process are dependent on the scan rate. From cyclic voltammetric investigation, it was found that, the cathodic reduction process of the investigated DEAC laser dye proceeded as a simple moderate fast charge transfer at all sweep rates. This behaviour demonstrates that the first charge transfer of the first peak produces a radical anion which gains another electron to form a dianion in the second peak. Fig. 8. Gives an example of the cyclic voltammogram at sweep rate of 0.1 Vs^-1 of the compound DEAC. It was observed that the forward peak potentials (E_p) shift to more negative potential with increasing the sweep rate confirming the moderate rate of electron transfer. In the selected media, the first and the second reductive peaks were coupled with the oxidative peaks in the reverse scan. The ratio of the backward peak to the forward peak (i_bp/i_fp) equals to one for the two peaks, confirming the absence of chemical step, i.e., the electrode reaction behaves as EE scheme.

The reduction peak current, after elimination of the background current, is proportional to the square root of the scan rate (v^(1/2)) and the difference between the forward and backward peak potentials, ΔE_p, is dependent on the value of the scan rate (v) used. The measured values of peak width E_p - E_0 = 76.5 mV ± 2 and 81 mV ± 2 at scan rate of 0.1 Vs^-1 for the first and the second peak respectively demonstrate the quasi-reversible behaviour of the system, where E_p, E_0 and n are the peak potential, the half peak potential and the number of electrons respectively. At scan rate of 0.2 Vs^-1 the peak separation ΔE_p of the first charge transfers was found to be 110 mV while for the second peak is 115 mV confirming the moderate fast of charge transfer in 0.1 mol L^-1 TBAP/CH3CN. The redox potential (E') was determined from the mean position of the peak potentials (Table 3). The standard heterogeneous rate constant (k_s) was extracted from the cyclic voltammograms via peak separation using a table of ΔE_p values vs. heterogeneous rate constants. In this case, the peak current i_p is governed by the Randle-Sevcik relationship. From the plot of i_p vs. √(v), the diffusion coefficient (D) of the electroactive species was determined. The calculated values of D are cited in Table 3. A direct test of the experimental electrochemical parameters was verified via matching of the generated cyclic voltammograms with the experimental one using the average experimentally determined values of k_s, D and E' cited in Table 3 for a symmetry coefficient (α) of 0.32 ± 0.01 which determined from digital simulation. The results given in Fig. 9 employ the experimental and theoretical voltammograms of the compound DEAC, which demonstrate good agreement between the captured and the simulated data.

Fig. 9. Matching between experimental (---) and simulated (-----) voltammograms of DEAC at sweep rate of 0.1 Vs^-1.

Convolutive voltammetry has been successfully applied to analysis of mechanism of several electrochemical processes. Convolution of the current with an inverse square root of time function was defined as.
Table 4. Peak characteristics of the first peak of DEAC laser dye extracted from cyclic, deconvolution transforms voltammetry and digital simulation techniques at 0.1 V s\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>(E_p-E_{p/2}) mV</th>
<th>(W_p) mV</th>
<th>(\Delta E_{p\text{-deconv}}) mV</th>
<th>(\alpha_{p/\text{deconv}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>76.5(^a)</td>
<td>112(^b)</td>
<td>74(^b)</td>
<td>1.0(^b)</td>
</tr>
<tr>
<td></td>
<td>76.7(^a)</td>
<td>111.8(^c)</td>
<td>85(^c)</td>
<td>1.0(^c)</td>
</tr>
</tbody>
</table>

\(^a\)Values determined from CV. \(^b\)Values determined from deconvolution. \(^c\)Values determined from digital simulation.

where \(i_p\) is the peak current, and the other parameters have their usual meanings. The \(I_1\) convolution of the investigated system illustrated in Fig. 10 shows a distinct separation between the forward and reverse sweep and clearly indicates the sluggishness of electron transfer of the reduction process. At all sweep rates, the reverse sweep of the \(I_1\) convolution return to zero due to the absence of chemical reaction at time scale of the experiments. Values of the diffusion coefficient \(D\) evaluated via Eqs 6 & 7 are listed in Table 3.

The deconvolution transforms gives a rapid assessment of either the electron transfer regime or value of \(E^\circ\). Also, as shown in Fig. 11, the equality of peak heights of the forward and backward sweep of deconvoluted current \((e_{p/\text{deconv}})\) gives strong evidence for the simple electron transfer scheme. The mean values of the cathodic \((E_{p\text{-deconv}}^\circ)\) and the anodic \((E_{p\text{+deconv}}^\circ)\) peak potentials were taken as the redox potentials \((E^\circ)\) of the system under consideration. The estimated values of \(E^\circ\) is given in Table 3.

The cathodic half-peak width \((w^\circ)\) was taken as a route for knowing the nature of electron transfer. The values of \(w^\circ\) shown in Table 4 confirm the quasi-reversibility of the system under consideration.

The diffusion coefficient was also determined from deconvolution transforms using Eq. 8\(^{64}\)

\[
e_p = \frac{an^2 F^2 v CD^{1/2}}{3.367 RT}
\]

where \(e_p\) is the peak height (in Ampere) of the forward deconvolution sweep and the remaining terms have their usual meanings. Values of the diffusion coefficient estimated from this method are given in Table 3.

Also from combination between convolution and deconvolution transforms the following relationship was deduced:

\[
I_1 = \frac{1}{(2\pi)^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du
\]

where \(I_1\) is the convoluted current at the total elapsed time \((t)\), \(i(u)\) is the experimental current at time \(u\). The diffusion coefficient of the investigated complex was determined, after applying background subtraction and correction for uncompensated resistance, from Eq. 6\(^{69}\)

\[
I_{lim} = nFSD^{1/2}C^b
\]

Where \(I_{lim}\) is the limiting value achieved for \(I_1\) when the potential is driven to a sufficiently extreme value past the peak, and the other terms have their usual meanings. The diffusion coefficient was also determined from a simple and accurate method via combination between the definition of both limiting convoluted current and peak current of the cyclic voltammogram using Eq. 7\(^{65}\)

\[
I_{lim} = \frac{i_p}{3.099 (anv)^{1/2}}
\]
where $n$ is the number of electrons consumed in electrode reaction, the other symbols have their usual definitions. From Eq. 9 the number of electrons was calculated and found to be $1.1 \pm 1.0$ for the first peak and $1.03 \pm 1.0$ for the second one. As shown the number of electrons was determined without knowing the electrode surface area which considers a good, precise and simple method for determination of the number of electrons involved in the electrode reaction via convolution-deconvolution voltammetry.

**CONCLUSION**

From our study we concluded that DEAC has high photostable in non-chlorinated solvents, undergoes solubilization in cationic and anionic micelles. DEAC displays formation of non-emissive exciplex with some organic acceptors.

DEAC was studied electrochemically via cyclic voltammetry, convolutive voltammetry combined with digital simulation. It was found that, the electroreduction of DEAC in 0.1 mol L$^{-1}$ TBAP/CH$_3$CN proceeds as EE mechanism. The first charge transfer produces monoanion radical while the second charge transfer produces dianion. Digital simulation was used to confirm the electrochemical parameters and the electrode nature of the investigated system.

**REFERENCES**