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Spectroscopic, computational and electrochemical studies on 2-(4-nitrophenyl)-1H-benzo[*d*]imidazole and its interaction with cationic surfactant cetyltrimethylammonium bromide

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ABSTRACT

2-(4-Nitrophenyl)-1H-benzo[*d*]imidazole (4-NBI) was prepared and characterized by experimental and computational methods. Electrochemical reduction of the compound was studied in dimethyl sulphoxide media which showed that the nitro group of the molecule undergoes quasireversible three-step reduction producing $-NH_2$ while the imidazole nitrogen bonded to hydrogen undergoes an irreversible one-electron reduction. The electronic spectra were studied by TDDFT computational method and compared with the experimental results which corroborated each other excellently. The interaction of 4-NBI with the cationic surfactant cetyltrimethylammonium bromide (CTAB) was investigated in aqueous solution at physiological pH (7.4) by UV–Vis spectroscopy. By using different nonlinear fitting methods binding parameters were evaluated for 4-NBI – CTAB micelles interaction. The results showed that the electrostatic interaction plays a major role over hydrophobic interaction in the binding of 4-NBI to CTAB micelles. The electrostatic interaction has also an important role in the distribution of 4-NBI between CTAB micelle–water phases. Gibbs free energy for the binding and distribution of 4-NBI between the bulk aqueous medium and surfactant micelles was calculated.

1. Introduction

Benzimidazole, its analogues and derivatives are a class of important nitrogen-containing heterocyclic compounds which has been used in biological and pharmaceutical chemistry for quite a long time. Imidazole nucleus plays many vital roles in human physiology in the form amino acid like histidine, vit-B12, nucleic acid bases, caffeine, biotin, etc. Several studies showed that these molecules are effective as antimicrobial, antihelminthic, antibacterial, anticonvulsant, anti-inflammatory, antiarrythmic, antioxidant, androgen receptor antagonist, antiprotozoal, antitumour, antiviral, antihypertensives, antihistaminics, antifolate, antifungal agents [1–18]. Their activity against several viruses such as HIV, herpes (HSV-1), influenza and human cytomegalovirus (HCMV) [19–21] draw an enormous attention of researchers to work in this field. Some established medicines such as astemizole, esomeprazole, albendazole, cimetidine, azomycin, metronidazole, etc., also consist of imidazole ring as the centre of drug action.

It is important to note that although some nitroimidazoles have been used successfully in treating various infections, some distinct toxicities of this class of molecules bind a limit of their use [22–24]. Previous studies have shown that the formation of radicals and/or anions being responsible for toxic side effects as well as for drug action is related with the electrochemical behavior of these molecules [25]. The electrochemical property of a molecule is further related to the electronic behavior as well chemical structure of the molecule. This makes the structural, spectroscopic and electrochemical studies on such molecules to be highly relevant to determine their structure–activity relationship.

Several studies explored that the mechanism of action of a biologically active molecule is related to its interaction with biological tissues through its binding to membranes at the molecular level. Several biological processes have been observed to happen at the ionizable surface of the biomembranes or along their hydrophobic area, leading to a comparative study on the interaction of such molecule with cationic, zwiterionic, anionic and neutral surfactants to be important [26–28]. This provides helpful information on the nature of drug–membrane interaction. This is why the studies on drug–surfactant interactions have been carried out by several researchers using various models and techniques owing to the extensive application of surfactants in the field pharmaceutical research. Earlier studies established that micellar systems have the ability to solubilize hydrophobic drugs [29–32] which increases their bioavailability and can be used as a model system for biomembrane, as well as drug carriers in various drug delivery and drug targeting systems [33–35]. The physicochemical interactions of a

Abbreviations: 4-NBI, 2-(4-nitrophenyl)-1H-benzo[*d*]imidazole; CTAB, cetyltrimethylammonium bromide.

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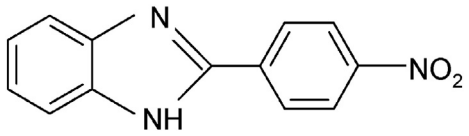


Scheme 1. Chemical structure of 2-(4-nitrophenyl)-1H-benzo[*d*]imidazole (4-NBI).

biologically active molecule with surfactant micelles may be envisaged as an estimate for their interactions with biomembranes. This provides an insight into complex biological processes such as passage of drugs through cell membranes. However, there are several studies on molecule–surfactant interactions were studied extensively with various types of drugs for quite a long time, there is a lack of research involving the interactions of benzimidazoles with surfactant micelles.

In the present study the structure, electronic properties and electrochemical behaviors of 2-(4-nitrophenyl)-1H-benzo[*d*]imidazole (4-NBI) (Scheme 1) were analyzed by theoretical and experimental techniques in order to enrich our knowledge in the area of physicochemical aspects of benzimidazole research. UV–Vis spectroscopy was employed to see whether 4-NBI has ability to penetrate in a biological membrane by using a model study with help of cationic surfactant, cetyltrimethylammoniumbromide (CTAB) (Scheme 1) as it is the most accepted model system for studying different aspects of molecule–membrane interactions. By using different non-linear fitting models binding constant, partition coefficient and binding stoichiometry were evaluated. The interaction of 4-NBI with CTAB micelles is of great interest from the standpoint of both drug development and biological point of view since it may hint about the biochemical activity of benzimidazole and this kind of study would definitely become a valuable addition in the area of benzimidazole research.

2. Experimental

2.1. Materials

2-(4-Nitrophenyl)-1H-benzo[*d*]imidazole (4-NBI) was prepared and characterized by the method described earlier [36]. Anhydrous dimethylsulfoxide (DMSO) was prepared from 99.0% DMSO (Spectrochem, India) by drying over fused $CaCl_2$ for 3–4 days, followed by decantation and distillation under reduced pressure [37]. The distilled DMSO was stored in a well stopper Jena bottle in desiccators and redistilled before use. A stock solution of 4-NBI of strength 1 mM was prepared by weighing an exact amount of it in anhydrous DMSO

Table 1
Structural parameters for the optimized molecular structure of 4-NBI at the B3LYP level.

(a) Bond length (Å)

Type of bond	Bond length (Å)	Type of bond	Bond length (Å)
N25-O27	1.231	C3-N11	1.380
N25-O26	1.231	C4-N12	1.380
C14-N12	1.384	N12-H13	1.006
C14-N11	1.318	C14-C15	1.464
C18-C25	1.468	C19-H23	1.082

(b) Bond angle (°)

Type of bond	Bond angle (°)	Type of bond	Bond angle (°)
O27-N25-O26	124.65	C15-C14-N11	124.15
C19-C18-25 N	118.96	C4-N12-C14	107.33
C17-C18-N25	119.23	C3-N11-C14	105.56
C15-C14-N12	123.61	C4-N12-H13	125.92

(Spectrochem, India). Acetonitrile (ACN) (99.8%, GR, Merck) was purified by refluxing with KOH (Merck) for several hours followed by fractional distillation and then again refluxing with CaH_2 (Merck) for several hours followed by fractional distillation [38]. Only the middle fraction was collected from each distillation, ensuring removal of all ammonia evolved during the alkali treatment. The solvent was stored as described above. CTAB (AR grade), purchased from Spectrochem, India was used without further purification. NaOH (AR grade), E-Merck, India was used in spectrometric titration. Phosphate buffer of ionic strength 0.05 M (pH 7.4) was used to maintain the pH in studying the interaction of the compound with the surfactant. In studying 4-NBI–CTAB interaction, 10% DMSO solutions of 4-NBI were used since the solubility of it is small in water. Tetrabutylammoniumbromide (TBAB) (AR, Spectrochem, India) was used as supporting electrolyte in the electrochemical measurements. All other reagents used were of AR grade. Aqueous solutions were prepared in triple distilled water.

2.2. Theoretical studies

The GAUSSIAN 03 [39] was used in the present study for all theoretical calculations. The structures of 4-NBI was optimized by using the Perdew–Wang 1991 exchange functional, as modified by Adamo and Barone and Perdew and Wang's 1991 gradient-corrected correlation functional [40] and 6-31 g (d,p) basis set [41–43]. The electronic absorption bands of the compound were evaluated by time dependent (TD-DFT) calculations.

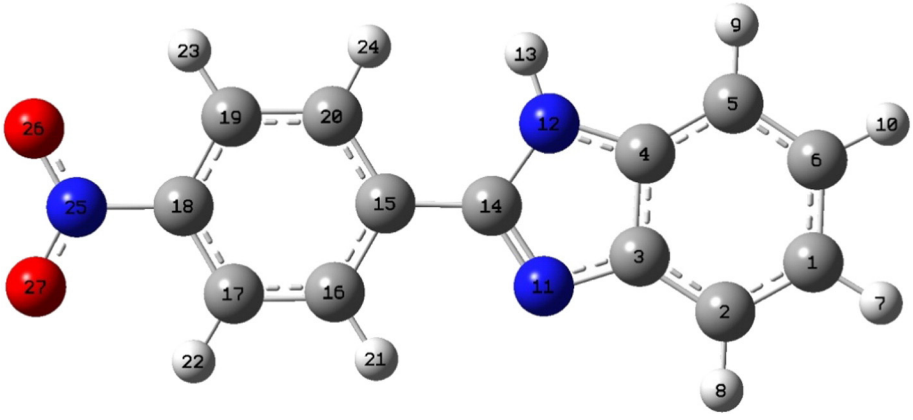


Fig. 1. The optimized geometry of 4-NBI and the atom numbering was used in the calculation.

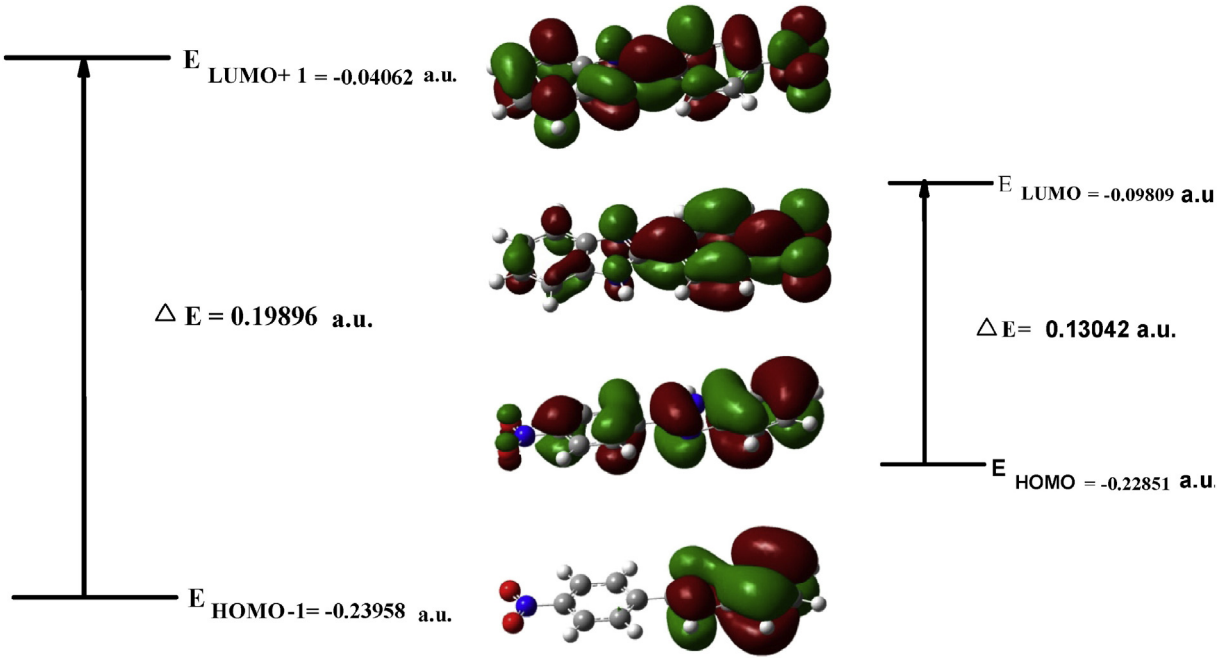


Fig. 2. Isodensity plot of HOMO, LUMO, HOMO −1 and LUMO +1 of 4-NBI.

2.3. Instrumentation

Electrochemical studies were carried out by using three-electrode system with *Digi-Ivy* Potentiostat (Model DY2312). During this measurement temperature was maintained at 298.15 K by a circulating water bath. A glassy carbon electrode having surface area of 0.07065 cm^2 was used as the working electrode, a platinum wire was used as the counter electrode and Ag/AgCl, saturated KCl was used as the reference electrode. The glassy carbon electrode surface was cleaned by following two successive steps such as abrasion with emery paper and polishing with alumina-water suspensions with particle size 0.5 μm. The electrode was washed with water carefully in between and after these steps. To make sure about the removal of adsorbed species from the electrode surface, the electrode was then washed with chloroform. Finally the activation of the glassy carbon electrode surface was made when the potential was cycled at intermediate scan rates (typically 0.1 V s^{-1}) in between a moderately negative potential and more positive potential (−0.5 and +1.50 V). To avoid the effects of dissolved oxygen, all experimental solutions were degassed for 45 min with highly pure argon gas, before any cyclic voltammetry measurement. Spectrophotometric studies were carried out using UV–Vis spectrophotometer, Model: MECASYS OPTIZEN POP, South Korea. Linear and nonlinear fitting of the experimental data was performed by using Grafit 3.0 software.

3. Results and discussion

3.1. Computational studies

The optimized molecular geometry of 4-NBI was calculated at the B3LYP level which is shown in Fig. 1 and the structural parameters are summarized in Table 1. From the structure it is interesting to note that C3–N11 and C4–N12 bond lengths are equal (1.380 Å) which means that the lone pair electron of N12 and N11 are delocalized over N12–C4 and N11–C3 bonds respectively.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) constitute the frontier molecular orbitals (FMO) of a molecule. A difference in energy of the FMO has been

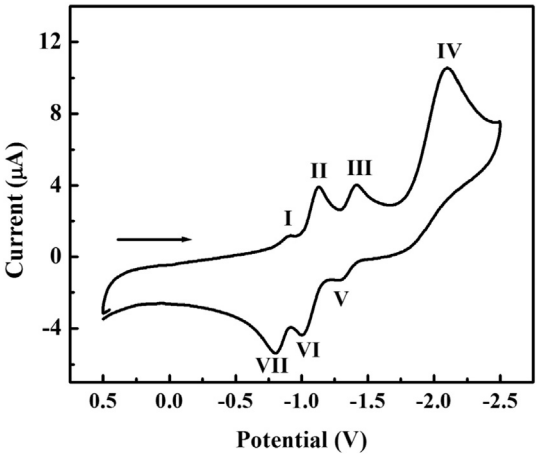


Fig. 3. Cyclic voltammogram of 4-NBI in anhydrous DMSO media. [4-NBI] = 1 mM, [TBAB] = 0.1 M, scan rate 0.100 V s^{-1}.

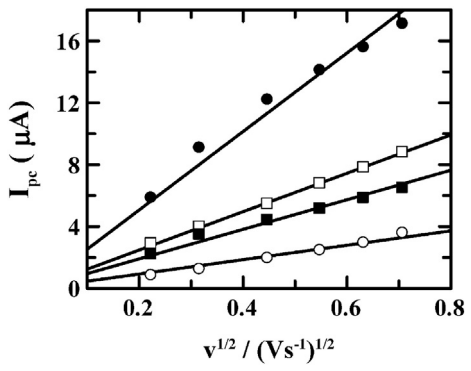
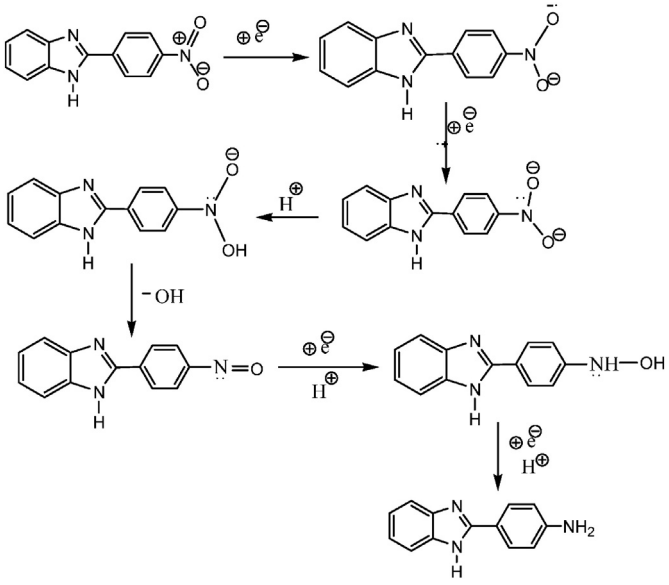


Fig. 4. A plot of cathodic peak current versus square root of the scan rate fitted according to Eq. (1) [Reduced chi squared = 0.5752 (●), =0.0055 (□), 0.2138 (■), 0.0377 (○)].



Scheme 2. Electrochemical reduction of aromatic NO_2 of 4-NBI in DMSO media.

observed to associate with the chemical reactivity of the molecule since a HOMO acts as an electron donor whereas a LUMO acts as an electron acceptor. In case of the present molecule the energy gap between the HOMO and LUMO was calculated as 0.13042 a.u. while the energy gap between HOMO −1 and LUMO +1 was found as 0.19896 a.u. An isodensity plot of the HOMO, LUMO, HOMO −1 and LUMO +1 is shown in Fig. 2. It is clear from Fig. 2 that HOMO and HOMO −1 are mainly delocalized over the benzoimidazole moiety which implied the oxidation processes, whereas LUMO, LUMO −1 are delocalized on the aromatic moiety implied the reduction processes, which is fully supported the experimental result (Section 3.2, Electrochemical Studies).

3.2. Electrochemical studies

The electrochemical behavior of 4-NBI was studied in anhydrous DMSO media in the presence of TBAB as supporting electrolyte by cyclic voltammetry. The cyclic voltammogram of the compound (Fig. 3) showed four reduction peaks (I–IV) at −0.915, −1.132, −1.420, and

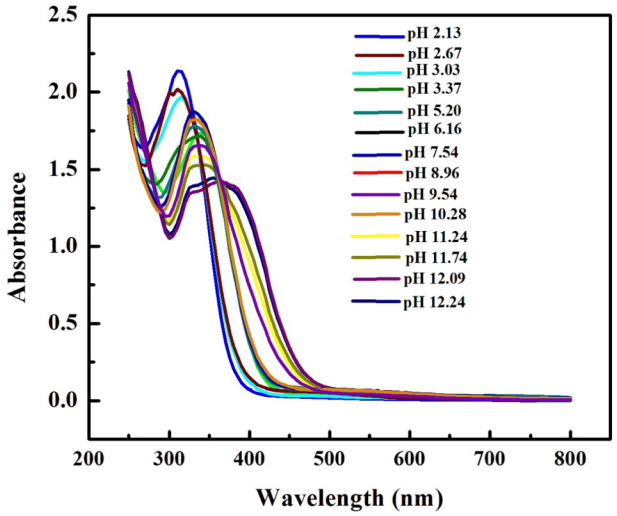


Fig. 5. UV–Vis spectra of 4-NBI at various pH. [4-NBI] = 100 μM, [NaCl] = 10 mM, 25 °C.

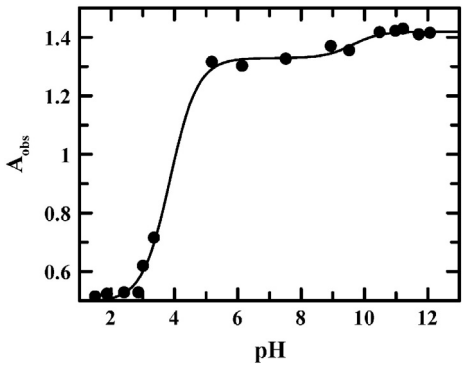


Fig. 6. Spectrophotometric titration of 4-NBI, shown by the variation of absorbance at 368 nm. [4-NBI] = 100 μM, [NaCl] = 10 mM, 25 °C.

−2.106 V at the scan rate 0.100 V s^{-1} in which first three (I–III) are quasireversible whereas the fourth (IV) is irreversible. The formal potential for these reductions were found as −0.858, −1.073, −1.357 and −2.106 V, respectively. A plot of cathodic peak current versus square root of the scan rate (Fig. 4) following Eq. (1) [44] for all these reductions showed a linear relationship which suggests that the reductions are totally diffusion controlled and there is no contribution of adsorption on the electrode surface during the reduction process. Comparing the present results with earlier [45] it may be said that the reductions I and II are due to the generation of a radical anion from the reduction of nitro group of 4-NBI which is then reduced to dianion and finally to nitroso group. This reduction requires a source of proton. Earlier studies [46,47] suggested that though DMSO is a polar aprotic solvent but it behaves as a weak acid. Thus in this case DMSO may act as proton source. In addition here there is another possibility that imidazole nitrogen of 4-NBI may act as a proton source in the experimental medium. The reductions III and IV involve the reduction of nitroso group to NHOH and finally NH_2 as shown in Scheme 2.

$$I_{pc} = \left(2.69 \times 10^5\right) n^{3/2} D_O{}^{1/2} A C v^{1/2} \quad (1)$$

where, I_{pc} = cathodic peak current (A), n = number of electron involved in the reduction, D_O = diffusion coefficient ($cm^2 s^{-1}$), A = area of the electrode (cm^2), C = concentration ($mol \cdot cm^{-3}$) and v = scan rate ($V \cdot s^{-1}$).

3.3. Determination of pKs of 4-NBI

In order to find the role of NH of 4-NBI and its effect during the interaction of 4-NBI with CTAB, it is necessary to determine its pK which was evaluated by spectrometric titration. At first 1×10^{-4} M aqueous solution of 4-NBI was acidified to pH 2.15 and it was then titrated slowly with 0.01 M NaOH solution keeping the concentration of 4-NBI constant and absorption spectra at various pH values were monitored. In such titration it was found that after pH 3.03 the peak at 312 nm starts to shift to 333 nm and it finally shifts to 368 nm at after pH (Fig. 5). Change in the absorbance at such wavelengths indicates the release of the NH proton in the pH range 3.03–12.24. The absorbance A_{obs} at 368 nm was fitted according to Eq. (2) [48] against pH of the solution (Fig. 6) and the pKs were determined as 3.86 and 9.61, respectively. At pH less than 3.86 the protonated N(2) of 4-NBI releases one proton while N(1)–H releases a proton at pH 9.61.

$$A_{obs} = \frac{A_1}{1 + 10^{(pH - pK_1)} + 10^{(pH - pK_2)}} + \frac{A_2}{1 + 10^{(pk_1 - pH)} + 10^{(pH - pK_2)}} + \frac{A_3}{1 + 10^{(pk_1 - pH)} + 10^{(pk_2 - pH)}} \quad (2)$$

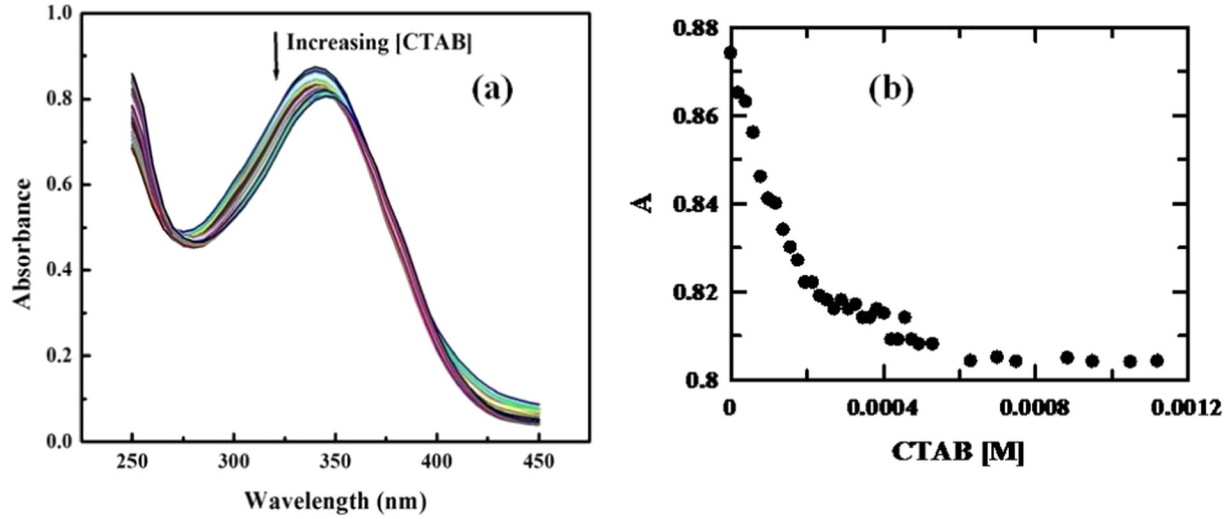


Fig. 7. (a) UV–Vis spectra of 4-NBI (10 μM) in the absence and presence of increasing CTAB concentrations: 0.02 mM to 0.584 mM; (b) Variation of the absorbance at 340 nm with CTAB concentration.

where, A_{obs} is the overall absorbance of the solution at 368 nm at different pH values while A_1, A_2 and A_3 refer to the absorbance of 4-NBIH$^+$, 4-NBI and 4-NBI$^-$, respectively.

3.4. Interaction of 4-NBI with CTAB

Interaction of 4-NBI with the cationic surfactant CTAB was studied by UV–Vis spectroscopy in the premicellar and micellar range of concentration at pH 7.4 in 0.05 M phosphate buffer. In the absence of surfactant, absorption spectrum of 4-NBI shows an absorption peak at 340 nm (Fig. 7a). The binding parameters for the interaction of 4-NBI with CTAB surfactant micelles was determined by monitoring the absorption peak at 340 nm for a series of solutions containing a constant concentration of 4-NBI and increasing concentrations of CTAB. The experimental measurements were made after 1 to 2 min from the mixing of CTAB with 4-NBI. The UV–Vis spectra of 4-NBI in the absence and in the presence of different concentrations of CTAB are shown in Fig. 5a. The critical micelle concentration (CMC) of CTAB, an indication about the beginning of micelle formation [50], in the presence of 4-NBI was determined by monitoring the change in absorption spectra of 4-NBI and it was evaluated as 1.77×10^{-4} M. Further measuring the absorbance of 4NBI - surfactant mixture as a function of surfactant concentration allows one to determine the CMC of the solution. It was observed that below the CMC, the solution absorbance falls rapidly with the increase in surfactant concentration while above CMC, the absorbance of the solution falls very slowly and reaches to saturation level. This produced the CMC value in the present study as 1.77×10^{-4} M. The observed CMC value is smaller than the CMC of CTAB in pure water (9.10×10^{-4} M) and in 0.1 M phosphate buffer (8.00×10^{-4} M) [51,52]. The lowering in CMC value is definitely due to the presence of different ions and molecules in the current study [53].

The variation of absorbance at 320 nm as a function of surfactant concentration is shown in Fig. 7b which shows that the absorbance decreases with the increase in CTAB concentration and reaches a saturation level after a certain concentration of CTAB. This may be assigned as the incorporation of 4-NBI molecules into CTAB micelles. The binding isotherm was analyzed by nonlinear fit by assuming 1:1 interaction between the 4-NBI and CTAB, with the help of Eq. (1) (Fig. 8). The binding constants was obtained as $K = (9.74 \pm 0.05) \times 10^3$ M^{-1} (Table 2) [50,53,54].

$$A = \frac{A_0 + A_\infty K[CTAB]}{1 + K[CTAB]} \quad (3)$$

where, A and A_0 are the measured absorbances at 340 nm of 4-NBI in the absence and presence of surfactant whereas A_∞ is the absorbance of 4-NBI bound to surfactant.

The Gibbs free energy for the binding of 4-NBI to the CTAB surfactant micelles was then evaluated by applying Eq. (4) [49,55].

$$\Delta G^0 = -RT \ln K \quad (4)$$

where R is the molar gas constant and T is the absolute temperature (298.15 K). The Gibbs free energy was found as −22.77 kJ/mol for interaction of the compound (4-NBI) to the surfactant (Table 2).

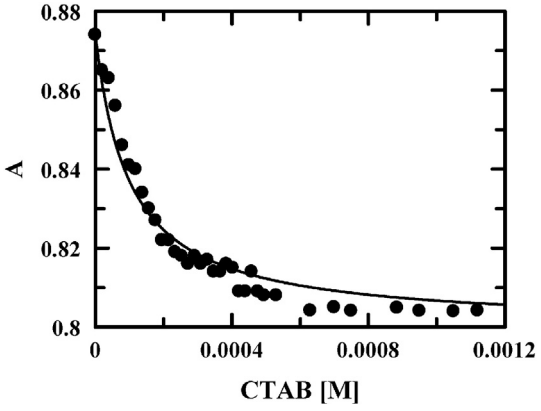


Fig. 8. Binding isotherm for the interaction of 4-NBI with CTAB micelles and the corresponding non-linear fit using Eq. (3) (reduced Chi squared = 1.61×10^{-5}).

Table 2
Binding constant (K_b), partition coefficient (K_X), the Gibbs free energy of binding (ΔG_b^0) and the standard free energy change for the transfer of 4-NBI from aqueous phase to micellar phase (ΔG_X^0) for the interaction of 4-NBI with CTAB micelles.

K	$(9.74 \pm 0.05) \times 10^3$
ΔG_b^0, kJ/mol	−22.77
K_X	$(4.26 \pm 0.06) \times 10^6$
ΔG_X^0, kJ/mol	−37.84

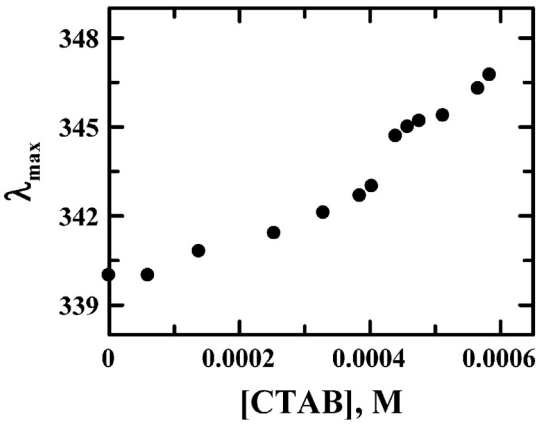


Fig. 9. Variation of the absorption maximum (λ_{max}) of 4-NBI with CTAB concentrations.

From the absorption spectra of 4-NBI in the absence and presence of CTAB, it is evident that in addition to hypochromic effect of the spectra with the increasing concentration of CTAB, a bathochroimic shift of about 7 nm (Fig. 7a) was observed which may provide an information about the mode of interaction of the molecule with surfactant micelles. The variation of the absorption maximum (λ_{max}) with CTAB concentration is shown in Fig. 9. In order to characterize such a mode, the absorption spectra of the compound were measured in three different solvents such as anhydrous acetonitrile, 90% ethanol and anhydrous dimethylsulphoxide (Fig. 10) having different dielectric constants. The observed values of λ_{max} and dielectric constants of the media are summarized in Table 3. The results clearly showed that the absorption spectrum of 4-NBI undergoes a bathochromic shift upon increase in the dielectric constant of the media. In other words it may be said that with the increase in polarity of the solvent, bathochromic effect increases. Considering this observation and comparing it with the results of 4-NBI - CTAB micelles interaction, it may be concluded that the electrostatic contribution plays a major role than hydrophobic contribution during the interaction of 4-NBI with CTAB micelles. Considering the pK values of 4-NBI one can say that at pH 7.4, only 0.61% of 4-NBI is ionized due to deprotonation of N(1)H. However, in all 4-NBI molecules at pH 7.4 oxygen of nitro group carries a negative charge which possibly interacts with the cationic CTAB.

Along with the measurement of binding constant and stoichiometry, the compound – surfactant interaction was further characterized by

Table 3
Dielectric constant of the solvent and wavelength maximum (λ_{max}) of the absorption spectra of 4-NBI.

Solvent	Dielectric constant	Wavelength maximum (λ_{max}), nm
Acetonitrile	37.50	335
90% ethanol	39.28	340
DMSO	46.70	355

partition coefficient (K_X) which is a thermodynamic parameter representing the affinity of a given compound to penetrate into the micellar phase from the aqueous phase. This is an important parameter elucidating the mechanism of solubilization of a drug molecule and definitely helps in understanding the biological phenomena like interaction between drugs and biological membranes. By applying the pseudo-phase model, [50,55–57] the partition coefficient was determined by using Eq. (5):

$$\frac{1}{\Delta A} = \frac{1}{\Delta A_\infty} + \frac{n_w}{K_X \Delta A_\infty ([CTAB] + C_T - CMC)} \quad (5)$$

where $\Delta A = (A - A_0)$; $\Delta A_\infty = (A_b - A_0)$ and $n_w = 55.5$ M is the molarity of water. The value of K_X was obtained from the slope of the plot of $1/\Delta A$ vs. $1/([CTAB] + C_T - CMC)$ (Fig. 11) and it is $(4.26 \pm 0.06) \times 10^6$. It is important to mention here that this linear relation holds good in a very high surfactant concentration region below which the curve tends to bend upwards with decreasing surfactant concentration. This deviation from the linearity was due to the approximation made in the evaluation of Eq. (5) [58].

The standard free energy change for the transfer of 4-NBI from the bulk aqueous phase to micellar phase was obtained as −37.84 kJ/mol by putting the value of K_X in Eq. (6) [48] and it is summarized in Table 2.

$$\Delta G_x^0 = -RT \ln K_X \quad (6)$$

A comparison of the partition coefficient (K_X) and corresponding free energy values of the present study with the values of other opposite charged molecule–surfactant interactions [26,50,58] clearly showed that the current results are significantly greater in magnitude which means that the interaction between 4-NBI and CTAB is predominantly electrostatic in nature. As the surface of biological membranes frequently presents a net charge, the binding properties of charged molecules such as drugs, as well as their membrane location are very important. Therefore the binding parameters determined for the 4-NBI–CTAB system in micellar and submicellar domain are also

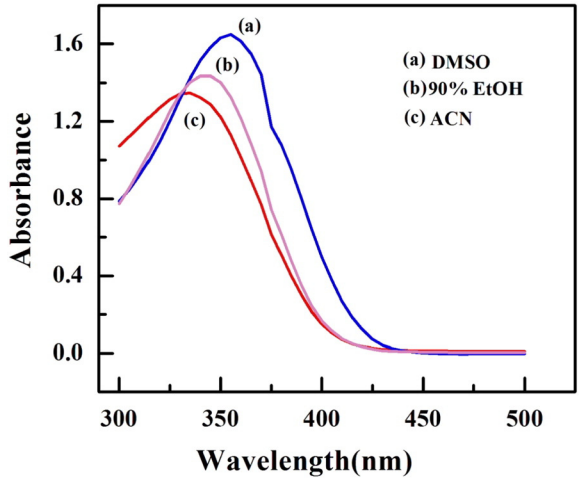


Fig. 10. Absorption spectra of 4-NBI in (a) anhydrous DMSO, (b) 90% ethanol (EtOH), and (c) anhydrous ACN.

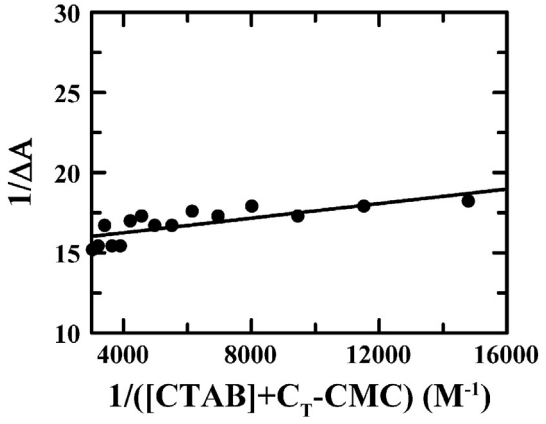


Fig. 11. A plot of $1/\Delta A$ vs. $1/([CTAB] + C_T - CMC)$ following Eq. (5) for 4-NBI in CTAB micelles at pH 7.4 (reduced Chi squared = 0.4351).

important for the understanding of the interaction of this molecule with biological membranes [58].

4. Conclusions

4-NBI was prepared and characterized by experimental and theoretical methods. In dimethyl sulphoxide media the nitro group of the molecule undergoes four- step reductions producing $-NH_2$. 4-NBI interacts with cationic surfactant cetyltrimethylammonium bromide (CTAB) micelles, which was studied in aqueous solution at physiological pH (7.4) by UV–Vis spectroscopy. The aspect of affinity of 4-NBI to cationic surfactant micelle, a model system for a biological membrane, are important in determining its biological action. Nonlinear fitting methods were used in this study to determine binding constant, partition coefficient and Gibbs free energy. It was observed that the electrostatic interaction plays a major role over hydrophobic interaction in the binding of 4-NBI with CTAB micelles. The electrostatic interaction also plays an important role in the distribution of 4-NBI between CTAB micelle–water phases. Gibbs free energy for the distribution of 4-NBI between the bulk aqueous medium and surfactant micelles was calculated.

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