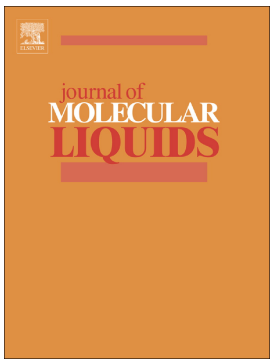

Micellar catalyzed hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene: Role of cationic head group–π interaction

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PII: S0167-7322(19)34902-5

DOI: https://doi.org/10.1016/j.molliq.2019.112429

Reference: MOLLIQ 112429

To appear in: *Journal of Molecular Liquids*

Received date: 2 September 2019

Revised date: 20 December 2019

Accepted date: 30 December 2019

Please cite this article as: A. Ravani, A. Shukla, N.V. Sastry, et al., Micellar catalyzed hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene: Role of cationic head group–π interaction, *Journal of Molecular Liquids*(2020), https://doi.org/10.1016/j.molliq.2019.112429

Micellar catalyzed hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene: Role of cationic head group–π interaction

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Abstract

The micellar catalysis of the hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene (DNTCB) with aqueous NaOH, to synthesize 2-chloro-4,6-dinitroresorcinol (CDNR), was studied using cationic, anionic and non-ionic surfactants at different concentrations to promote the reaction kinetics. The micellar catalysis using cationic surfactants at optimum concentrations was effective giving highest conversion of DNTCB (92–100%), which was ascribed to high solubilization capacity of the micellar solutions for DNTCB, surface positive charges of micelles increasing OH^- ions concentration near micellar surface, and the cation-π interaction of surfactant molecules (through cationic head group) with DNTCB molecules. The cation-π interaction plays important role in solubilization process, substrate activation and catalysis of the reaction. The higher surfactant concentrations retard the reaction owing to strong solubilization of DNTCB in micelles and reduced OH^- ions concentration around the

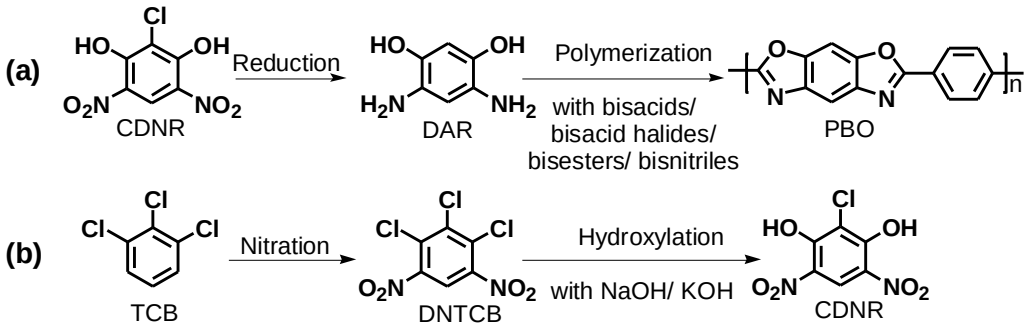
micelles. The cationic micellar solutions at optimum surfactant concentrations can be effective catalytic system for the aromatic nucleophilic substitution reactions.

Keywords: Cationic surfactants; micellar catalysis; cation–π interaction; aromatic nucleophilic substitution; 1,2,3-trichloro-4,6-dinitrobenzene; 2-chloro-4,6-dinitroresorcinol.

1. Introduction

The 2-chloro-4,6-dinitroresorcinol (CDNR) is an important chemical for the synthesis of 4,6-diaminoresorcinol (DAR), which is used as monomer to polymerize with bisacids, bisacid halides, bisesters or bisnitriles to synthesize various poly-*p*-phenylene-benzobisoxazoles (PBOs; **Scheme 1a**) [**1**]. The PBOs are fibers with high tensile strength and thermal stability, and are suitable for military, aerospace and high performance material applications [**2**]. The DAR monomer is synthesized from CDNR by reduction of its both nitro groups followed by dechlorination using hydrogen and Pd/C catalyst [**3**]. Alternatively, DAR has also been synthesized by reduction of 4,6-dinitroresorcinol obtained from nitration of resorcinol diacetate [**4**] and by hydroxylation of 2,4-dinitrochlorobenzene followed by reduction [**5**]. However, these processes suffer from low yield of DAR due to the formation of byproducts.

The 1,2,3-trichlorobenzene (TCB) is produced in significant amount as by-product in the benzene chlorination process to synthesize chlorobenzene and dichlorobenzene. TCB has been considered to be an organic waste creating serious environmental issue for the industries [**6**]. It is mainly used as solvent/ dye carrier by textile industries, however, this application is hazardous to the environment because of its toxic nature [**7**]. The use of TCB as starting material for the synthesis of valuable chemicals could be the appropriate way for its utilization and to solve its serious concerns. The nitration of TCB with nitric acid and sulfuric acid results to high yield of 4,6-dinitro-l,2,3-trichlorobenzene (DNTCB) [**8**], which is a suitable precursor for the synthesis of CDNR by hydroxylation reaction [**9**] (**Scheme 1b**). The synthesis of DAR from CDNR, which can be produced by hydroxylation of DNTCB obtained from TCB (as shown in **Scheme 1**), can provide a cost effective methodology for the synthesis of PBOs. Thus, the use of TCB as starting raw material for the synthesis of CDNR (from DNTCB) will be promising to utilize an industrial organic waste and to reduce the production cost of PBOs.



Scheme 1. (a) Synthesis of PBO fibers from DAR, which can be obtained from CDNR, and (b) synthesis of CDNR from DNTCB, obtained from nitration of TCB.

The synthesis of CDNR from DNTCB by treating with alkali (NaOH or KOH) in an alcohol (methanol, ethanol, *n*-propanol, etc.) has been reported [**9**]. However, the use of large amounts of expensive and flammable organic solvents (alcohols) with excess amount of alkali is not practicable at industrial scale. Therefore, there is need of an environmentally benign process, a Green Chemistry approach for the conversion of DNTCB into CDNR using optimum amount/ concentration of alkali and avoiding the use of organic solvents.

With an objective to have organic solvent free process for the synthesis of CDNR from DNTCB and to utilize TCB as raw chemical, we attempted hydroxylation of DNTCB with NaOH using water as solvent. The reaction of DNTCB and aqueous NaOH (under biphasic condition) was sluggish due to poor solubility of DNTCB (non-polar nature) in water. The organic-aqueous biphasic reactions have received much interest owing to the use of water as inexpensive and environmentally benign solvent [**10**], however, the immiscibility of non-polar organic compounds in water results to slow rate of reaction [**11**]. In recent years, micellar catalysis using aqueous solutions of cationic, anionic and non-ionic surfactants has received much attention to promote organic reactions (conversion rate as well as product selectivity) in water [**12**]. The micelles (aggregates of surfactant molecules) facilitate the reactions by dissolving non-polar reactant(s) in the core and thus increasing their solubility in aqueous phase [**13**]. The ionic surface of micelles concentrates water soluble ionic species

(reactant/ catalyst; *e.g.*, OH^- or H^+) near the micellar surface [**13**]. Thus, huge interface between aqueous and organic phase is created for interaction of water soluble and water insoluble reaction components. Furthermore, the disintegration and reformation of micelles due to extremely small life time of micelles (in msec) significantly contribute in generation of huge interfacial area during the reaction time interval. In addition, the favorable interactions between surfactant and substrate/ reactant molecules in micelles have also been observed to facilitate the reactions by bringing substrate molecules in activated form for the reaction [**14**]. The micellar catalysis enables convenient isolation of the product and the separation of water soluble catalysts from the reaction mass for reuse [**15**]. Therefore, we were interested in the use of aqueous solution of surfactants (micellar solutions) for hydroxylation of DNTCB with NaOH to develop an efficient, cost effective and organic solvent free process to synthesize CDNR utilizing TCB, an industrial organic waste. The reaction in water was studied under different conditions such as biphasic condition, phase transfer catalysis using a phase transfer agent, and micellar catalysis using different types of surfactants (cationic/ anionic/ non-ionic) at varied concentrations. The micellar catalysis using aqueous solution of cationic surfactants at optimum concentrations was found to be effective to promote the reaction kinetics. This was ascribed to cation-π interaction of surfactant molecules (through cationic head group) with DNTCB molecules, which played important role in solubilization process, substrate activation and catalysis of the reaction. To the best of our knowledge, there is no report on micellar catalysis of aromatic nucleophilic substitution reactions facilitated by cation-π interaction.

2. Experimental

2.1. Chemicals

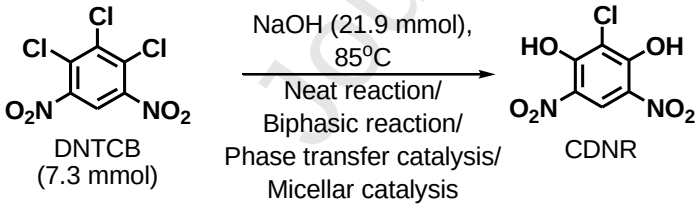
The 1,2,3-trichloro-4,6-dinitrobenzene (DNTCB; 99%) was synthesized by nitration of 1,2,3-trichlorobenzene (TCB; 98%, supplied by Kutch Chemicals Industries, Baroda, Gujarat,

India) with nitric acid using sulfuric acid as catalyst [**8**]. Sodium hydroxide (NaOH; 98%), concentrated hydrochloric acid (HCl; 35%), sodium chloride (NaCl; 98%) and ethyl acetate (99%) were procured from Merck, India. Cetyltrimethylammonium bromide (CTAB; 98%), cetylpyridinium chloride (CPC; 98%), sodium dodecyl sulfate (SDS; 98%), Triton X-100 (98%), methanol (98%) and toluene (99%) were from S. D. Fine Chemicals, India. Cetylpyridinium bromide (CPB; 98%) was from Sigma-Aldrich. The phase transfer agent, benzyltriethylammonium chloride (BTEA), was provided by Kutch Chemical Industries Limited, Baroda, India. All the chemicals were used without any further purification. All the aqueous and surfactant micellar solutions were prepared by using milli-pore deionized water.

2.2. General procedures for hydroxylation of DNTCB with NaOH under different conditions

The hydroxylation of DNTCB with NaOH was carried out under different conditions (**Scheme 2**) *viz.* under solvent free (neat) and biphasic conditions (*i.e.*, reactions in pure water), phase transfer catalysis (PTC; reactions in aqueous solution of BTEA), and micellar catalysis (reactions in aqueous solution of CTAB, CPC, CPB, SDS and TX-100). In a reaction tube of the reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK), DNTCB (7.3 mmol) was melted at 90°C and then the temperature was brought down to the reaction temperature (85°C; ±1°C). The NaOH flakes (21.9 mmol) were added in the molten DNTCB and heated under stirring (1200 rpm) at 85°C for the required period of time to carry out the reaction under neat condition. The biphasic reactions were carried out by adding the aqueous solution of NaOH (21.9 mmol; dissolved in 5 mL water) in the molten DNTCB and stirring (1200 rpm) at 85°C for the required period of time. In addition, the biphasic reaction was also carried out using toluene (2 mL) as solvent to dissolve DNTCB. For PTC and micellar catalysis of the reaction, the aqueous solutions of NaOH–BTEA (21.9 mmol NaOH dissolved in 5 mL aqueous solution of 1 mol% BTEA) and

NaOH–surfactant (21.9 mmol NaOH dissolved in 5 mL surfactant solution of required concentration), respectively, were added in the molten DNTCB and the reaction mixture was kept under stirring (1200 rpm) at 85°C for required period of time. After the completion of reaction, the reaction mixture was allowed to cool and to get phase separated. The aqueous phase was collected using separating funnel. The reaction product remains in aqueous phase and therefore, the aqueous phase was analyzed by using UV spectrophotometer (Agilent, Carry 5000 spectrometer at room temperature) to quantify the yield of the product. In addition, the organic phase extracted with ethyl acetate (12 mL), which contains un-reacted DNTCB, was also analyzed by using UV spectrophotometer to quantify the un-reacted DNTCB (*i.e.*, conversion of DNTCB). To study the progress of biphasic/ PTC/ micellar reactions (**Figure 1** and **Figure 2f**), the reactions were carried out in different reaction tubes (8 tubes) for 0.5 h to 12 h, *viz.* 0.5, 1, 1.5, 2, 3, 6, 9 and 12 h at 85°C. The reaction tubes were removed from the reaction station after different time period. The aqueous and organic phases of reaction mixtures were separated and analyzed by UV-vis spectrophotometer to measure the conversion of DNTCB. All the conversion values are within ±2% precision. The details of reaction conditions are also mentioned in footnote of tables and figures.



Scheme 2. Reaction of DNTCB with NaOH to synthesize CDNR under different conditions.

For the isolation of product, the aqueous phase was neutralized with HCl (8 mL) and extracted with ethyl acetate (12 mL). The solvent removal by evaporation under vacuum resulted to solid product. The DNTCB and the product (CDNR) were characterized (**ESI; Figure S1 & S2**) by ^{1}H and ^{13}C NMR spectra recorded on a FT-NMR spectrometer (Bruker UltraShield 400 MHz) in $CDCl_3$/ DMSO-d_6 solutions, FT-IR spectra recorded on a FT-IR

spectrophotometer (IRPrestige-21, Shimadzu), and LC-MS analysis using a Micromass Q-TOF micro™. The purity of product was analyzed by High Performance Liquid Chromatograph (HPLC; Dionex Ultimate 3000) with C18 column (Acclaim 120, 5 μm, 120Å, 4.6 mm × 250 mm) and using methanol-water (70:30) as mobile phase, flow rate of 1 mL/ min and 278 nm wave length of photodiode array detector at constant column temperature of 298 K.

2.3. **Characterization of micellar solutions**

The ^{1}H NMR analysis of DNTCB in micellar solutions and in pure D_2O was carried out by using a Bruker UltraShield 400 MHz. To prepare the DNTCB solutions in D_2O or in micellar media, the molten DNTCB (2.0 g) was stirred with 5 mL of D_2O or surfactant solution prepared in D_2O at 85°C for 2 h. The solution was allowed to cool and to get phase separated to obtain the aqueous phase for the ^{1}H NMR analysis. The number of acquisitions was 32 for each sample. The ^{1}H chemical shifts are reported in δ units (ppm) relative to that of tetramethylsilane (TMS) as external standard. The UV–vis spectra of DNTCB in water and in micellar solutions (of CTAB and CPC) were recorded on an Agilent, Carry 5000 spectrometer at room temperature using DNTCB solutions in water or in micellar solution. For this, the solutions of DNTCB in water and in micellar solutions were prepared by stirring the molten DNTCB (0.5 g) in 5 mL of water and surfactant solutions, respectively, at 85°C for 2 h. The solutions were allowed to cool and get phase separated, and the aqueous phase was analyzed by UV–vis spectrometer. It is to be noted the micellar solutions (5 mL) of CTAB and CPC treated with 2.0 g DNTCB, which is the condition used for reactions, resulted to very high dissolution of DNTCB, especially in micellar solutions, giving very high absorption in UV spectra. Therefore, to keep the absorption below 2.0 in the spectra, UV–vis analysis was performed by dissolving 0.5 g of DNTCB in micellar solutions (5 mL). The critical micellar concentrations (CMCs) of surfactants in pure water and in presence of

NaOH (21.9 mmol dissolved in 5 mL water) were obtained by conductivity method (**ESI; Figure S3 & S4**). The DNTCB-surfactant (CTAB and CPC at 0.5 mM) emulsion solutions were analyzed by a transmitted light optical microscope (Bristol, AS-4, 1687) under 10X objective lance magnification. A drop of solution was placed on a glass slide without a cover slip. The images were captured with a digital microscope imager (Celestron, Model No.: 44421) and processed by DDU 3D software. The surface charge on micelles in surfactant solutions was obtained by measuring zeta potential at 25°C using Zetasizer (Malvern). The dynamic surface tension (DST) of solutions were measured by using a bubble tensiometer (Biolin, model # BPA-800P) at 25°C using maximum bubble pressure method as a function of bubble lifetime.

3. Results and discussion

3.1. **Hydroxylation of DNTCB with NaOH in different reaction media**

The neat reaction of DNTCB and NaOH at 85°C (**Scheme 2**) did not give product (CDNR) even after 24 h of reaction, which may be due to insolubility of NaOH in molten DNTCB. To show the reactivity, NaOH may require the presence of water to produce OH^- ions (nucleophile) for the reaction. The biphasic reaction of DNTCB with aqueous NaOH solution was very slow giving ~60% conversion of DNTCB after 12 h (**Figure 1a**), which can be due to poor solubility of DNTCB in aqueous phase (3 mM; **ESI, Table S1**). Interestingly, the use of toluene, which was used as water immiscible organic solvent and to dissolve DNTCB, in a biphasic reaction facilitated the reaction giving faster conversion of DNTCB than toluene free biphasic reaction (**Figure 1b**). This enhancement in reaction rate was found to be attributed to increased solubility of DNTCB in water (30 mM; **ESI, Table S1**) in the presence of toluene. The DNTCB-toluene solution, being less viscous as compared to molten DNTCB, was easy to stir with aqueous NaOH solution enhancing the partitioning (solubility) of

DNTCB molecules in aqueous phase. However, in view of the hazardous effects of toluene, toluene cannot be considered to be an appropriate solvent for this reaction.

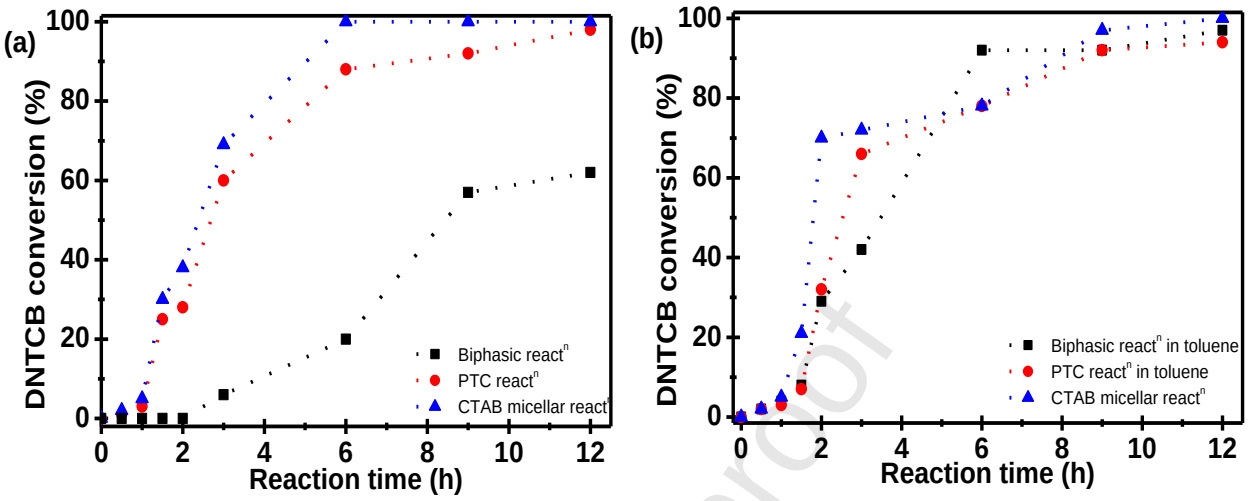


Figure 1. Progress of biphasic, PTC and CTAB micellar reactions of DNTCB and NaOH (a) in absence and (b) in presence of toluene as organic solvent [biphasic react^n (-■-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 5 mL water; PTC react^n (-●-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 5 mL aqueous solution of 1 mol% BTEA; CTAB micellar react^n (-▲-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 5 mL aqueous solution of CTAB at 15 mM concentration; 2 mL toluene was used in reactions carried out in the presence of toluene].

The phase-transfer catalyzed (PTC) reaction using BTEA, even without using toluene as solvent, was observed to be much faster than biphasic reactions (**Figure 1a**). The phase-transfer catalyst, being an organic molecule with a quaternary nitrogen center, has ability to get dissolved in both aqueous and organic phase. The BTEA molecules can enhance reaction rate by increasing the solubility of DNTCB in aqueous phase (10 mM; **ESI, Table S1**) by binding the DNTCB molecules (by hydrophobic interaction) and bringing them into aqueous phase. In addition, the reaction may also be facilitated by increased solubility of OH^- ions in oil phase (*i.e.*, in the molten DNTCB) by BTEA's cations, as they can bind OH^- ions by ionic interaction to bring them into the oil phase [**16**].

From above results, we learned that the conversion of DNTCB into CDNR can be improved by increasing the solubility of DNTCB in aqueous phase. The attractive features of

surfactants, particularly amphiphilic nature and ability of their micelles to solubilize the non-polar/ water insoluble compounds in water, motivated us to carry out this reaction in an aqueous surfactant solution. As the reaction involves the participation of OH^- ions, the aqueous solution of a cationic surfactant, having a quaternary ammonium head group, can be used to have positively charged micelles [**15**]. The hydrophobicity of cationic micelles can serve the purpose of solubilization of DNTCB in the micelles and the positively charged micellar surface can concentrate OH^- ions around the micelles. Therefore, the CTAB (a cationic surfactant) micellar solution at 15 mM was employed in the reaction and was found to be much effective giving fastest conversion of DNTCB (**Figure 1a**). Unlike toluene assisted biphasic reaction, the use of toluene in PTC or in micellar reactions was not much helpful (**Figure 1b**). It is to be noted that in PTC reaction, 1 mol% of BTEA (which corresponds to 10 M) was used, whereas in the micellar reaction, very dilute solution of CTAB (15 mM) was taken. This result clearly demonstrates that the CTAB, a quaternary ammonium head group containing surface active molecule, does not work like a phase transfer agent; it promotes the reaction with the help of micelles formed in the aqueous medium. In the PTC reaction, BTEA molecules bind OH^- ions and DNTCB molecules to bring them into organic and aqueous phase, respectively, for the reaction, and therefore huge quantity of BTEA, as compared to CTAB, is needed to make the reaction faster. This is also evident from the result showing increasing conversion of DNTCB (from 40% to 88% in 6 h) on increasing the amount of BTEA (from 0.25 mol% to 1 mol%; **ESI**, **Figure S5**). In the micellar catalysis, the small amount of CTAB (15 mM) promoted the reaction by producing numerous micelles in the aqueous medium. The micellar effect on the reaction has been discussed in detail in the following sections.

3.2. **Micellar catalyzed hydroxylation of DNTCB with NaOH in micellar solutions of different surfactants: Effect of surfactant's nature and concentration**

The results (**Figure 1**) clearly reveal that the hydroxylation of DNTCB with aqueous NaOH can be promoted by micellar catalysis using an aqueous solution of surfactant at nominal concentration. In addition to CTAB, different types of surfactants namely CPC and CPB (cationic surfactants with different nature of head group), SDS (anionic surfactant) and TX-100 (non-ionic surfactant), were also studied at similar concentration (15 mM) and reaction condition. The results (**Table 1**) suggest the highest activity of CTAB micellar solution giving highest conversion of DNTCB.

Table 1. Conversion (%) of DNTCB in different surfactant micellar solutions.

Sr. No.	Micellar solution	Conversion (%) of DNTCB
1	15 mM CTAB	100
2	15 mM CPC	63
3	15 mM CPB	78
4	15 mM SDS	20
5	15 mM TX-100	30

Reaction condition: 7.3 mmol DNTCB; 21.9 mmol NaOH; 85°C; 12 h; 5 mL aqueous solution of surfactant.

As these surfactants (CTAB, CPC, CPB, SDS and TX-100) have different alkyl chain, head group charge and size, and CMCs (0.97, 0.99, 0.85, 7.2 and 0.25 mM, respectively; **ESI; Figure S3**), therefore, 15 mM micellar solutions of these surfactants will have micelles with different characteristics (hydrophobicity, surface charge, intermolecular distance, *etc.*). To find out an appropriate surfactant and concentration providing optimum micro-environment for faster conversion of DNTCB, the reactions were carried out in the micellar solutions of these surfactants at different concentrations ranging from 0.125 mM to 150 mM and under similar reaction condition. The CMCs of CTAB, CPC, SDS and TX-100 in aqueous NaOH solution were found to be slightly decreased (0.89, 0.85, 0.80, 6.9 and 0.21 mM, respectively; **ESI; Figure S4**).

The results (**Figure 2a-e**) indicate that the nature of surfactant (cationic/ anionic/ non-ionic, and head group size) and the concentration significantly influence the reaction (*i.e.*, the conversion of DNTCB). The increase in surfactant concentrations initially increases the conversion up to certain concentration (optimum concentration), and further increase in surfactant concentration (above an optimum concentration) decreases the conversion. The cationic surfactants (CTAB, CPC and CPB) provide most effective micellar media to promote the reaction giving highest conversion (92-100%) at their optimum concentrations (15 mM, 0.5 mM and 1 mM, respectively). It is to be noted that as compared to CTAB, CPC and CPB provide equally efficient micellar medium at very less concentrations (0.5 mM and 1 mM, respectively) to give highest conversion of DNTCB. The nature of counter anion (Cl^-/ Br^-) present in cationic surfactants (CPC and CPB) does not show remarkable effect on activity of their solutions for DNTCB conversion. The TX-100 micellar solution also showed similar activity (92% conversion of DNTCB), however, a higher concentration of TX-100 (100 mM) was required. The SDS micellar solution was least in activity giving maximum ~37% conversion of DNTCB at 5 mM concentration. The **Figure 2f** shows the progress of reaction with time in biphasic and in different surfactants' micellar solutions at their optimum concentrations. The four surfactant solutions at their optimum concentrations, *viz.* 15 mM CTAB, 0.5 mM CPC, 1 mM CPB and 100 mM TX-100, exhibited almost similar activity giving complete conversion of DNTCB. However, the cationic surfactant solutions *i.e.*, 15 mM CTAB, 0.5 mM CPC and 1 mM CPB, are more appropriate for micellar catalysis of the reaction giving faster conversion of DNTCB at low concentrations. In several studies, CPC has been studied for comparison with CTAB to observe the effect of cationic head group size on micellar catalysis [**17**], therefore, CTAB and CPC micellar systems were investigated in detail. To explain the molecular mechanism for higher catalytic activity of cationic micellar solutions at their optimum surfactant concentrations, the characteristics of the DNTCB

solubilized micelles *viz.* molecular interactions, molecular packing, micellar surface charge, *etc.*, and the solubilization behavior of micellar solutions were studied.

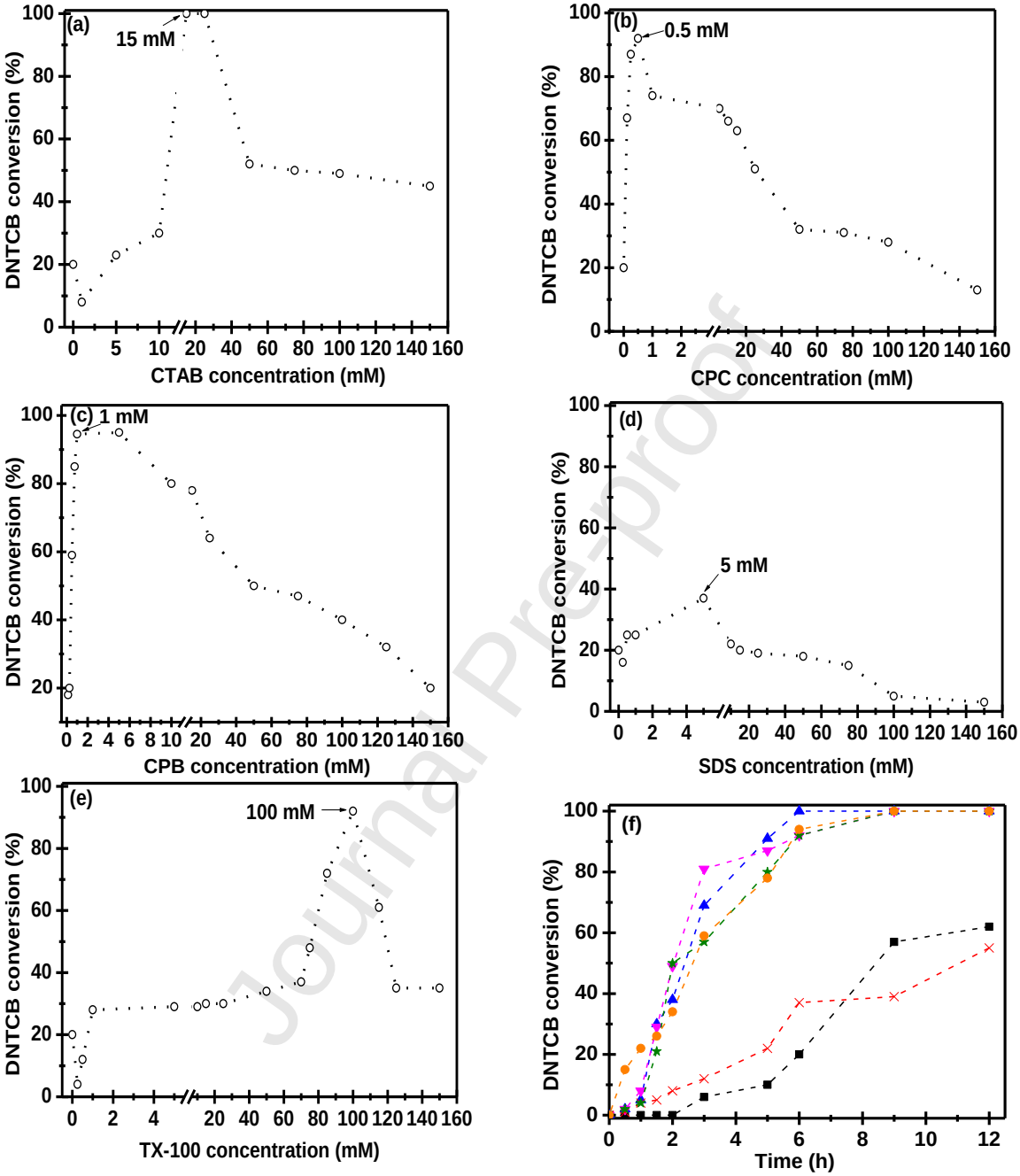
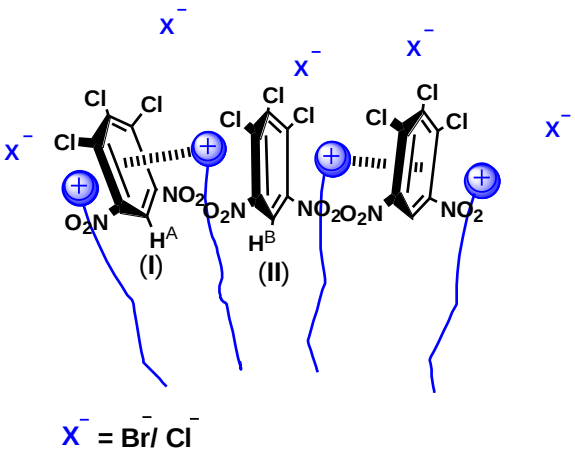


Figure 2. (a-e) Effect of surfactants' concentration on DNTCB conversion [7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of surfactant], and (f) Kinetics of biphasic and micellar reactions [biphasic react^n (-■-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL water; CTAB micellar react^n (-▲-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of CTAB at 15 mM; CPC micellar react^n (-▼-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of CPC at 0.5 mM; CPB micellar react^n (-●-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of CPB at 1 mM; SDS micellar react^n (-×-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of SDS at 5 mM; TX-100 micellar react^n (-★-): 7.3 mmol DNTCB, 21.9 mmol NaOH, 85°C, 6 h, 5 mL aqueous solution of TX-100 at 100 mM].

3.2.1. Molecular interactions and packing in the DNTCB solubilized micellar system

The ^{1}H NMR studies have been used to investigate the location, orientation and molecular interactions of organic molecules solubilized in the micelles by monitoring the changes in the chemical shifts of the surfactant and organic molecules [**18**]. The ^{1}H NMR analysis of DNTCB in micellar solutions of CTAB, CPC, SDS and TX-100 prepared in D_2O at different concentrations were carried out to investigate molecular interactions and packing in DNTCB solubilized micelles. There is an aromatic proton in DNTCB, which exhibits a chemical shift at 8.58 ppm in D_2O (without surfactant). The chemical shift of DNTCB (aromatic proton) was monitored in ^{1}H NMR studies of DNTCB-micellar solutions. The ^{1}H NMR spectra of DNTCB in the CTAB micellar solutions at different concentrations (**Figure 3a**) can be seen to exhibit two signals in the aromatic region, which are very distinct at 15 mM and above concentrations, indicating the presence of DNTCB in two different forms in CTAB micelles. The signal "***A***" represents DNTCB molecules (**structure I**; **Scheme 3**), which are involved in cation-π interaction with cationic head group of CTAB molecules in micelles. The signal "***B***" was assigned to DNTCB molecules (**structure II**; **Scheme 3**), which are hydrophobically solubilized in micelles, and are not involved in cation-π interaction. The cation π-interaction of DNTCB with cationic head group of CTAB will reduce the electron density over aromatic nucleus of DNTCB showing downfield shifting of its aromatic proton "***A***" as compared to aromatic proton of DNTCB (8.58 ppm) in pure D_2O. Ikeda and Sbinka [**19**] have shown two sets of signals in ^{1}H NMR spectra of 1,3-Alternate Calix[4]arenes-Ag^{+} and 1,3-Alternate Calix[4]arenes-K^{+} systems representing free 1,3-alternate Calix[4]arenes molecules and 1,3-Alternate Calix[4]arenes-metal complexes having cation-π interaction.



Scheme 3. DNTCB molecules in cation-π interaction with surfactant's cationic head group (structure **I**), and hydrophobically solubilized (structure **II**) in micellar phase of cationic (CTAB/ CPC) micelles.

The gradual downfield shifting of the signal "***A***" with CTAB concentration (**Figure 3a**) represents increasing cation-π interaction (strength of interaction) between solubilized DNTCB molecules (**I**) and CTAB molecules in micelles. The downfield chemical shift for the aromatic proton of **II** (signal "***B***") in 15 mM to 150 mM CTAB solutions as compared to the aromatic proton of DNTCB in pure D_2O (at 8.58 ppm) indicates that **II** reside in more ionic environment (than water; *i.e.*, in Stern layer) of micelles. Thus, from ^{1}H NMR study, the solubilization of DNTCB as **I** and **II** in the Stern layer of CTAB micelles is clearly evident. Similarly, the ^{1}H NMR spectra of DNTCB in CPC (**Figure 3b**) as well as in CPB (**ESI; Figure S6**) micellar solutions also exhibited "***A***" and "***B***" signals showing the cation π-interaction between DNTCB and head group and the existence of both types of DNTCB molecules (**I** and **II**) in the Stern layer of micelles.

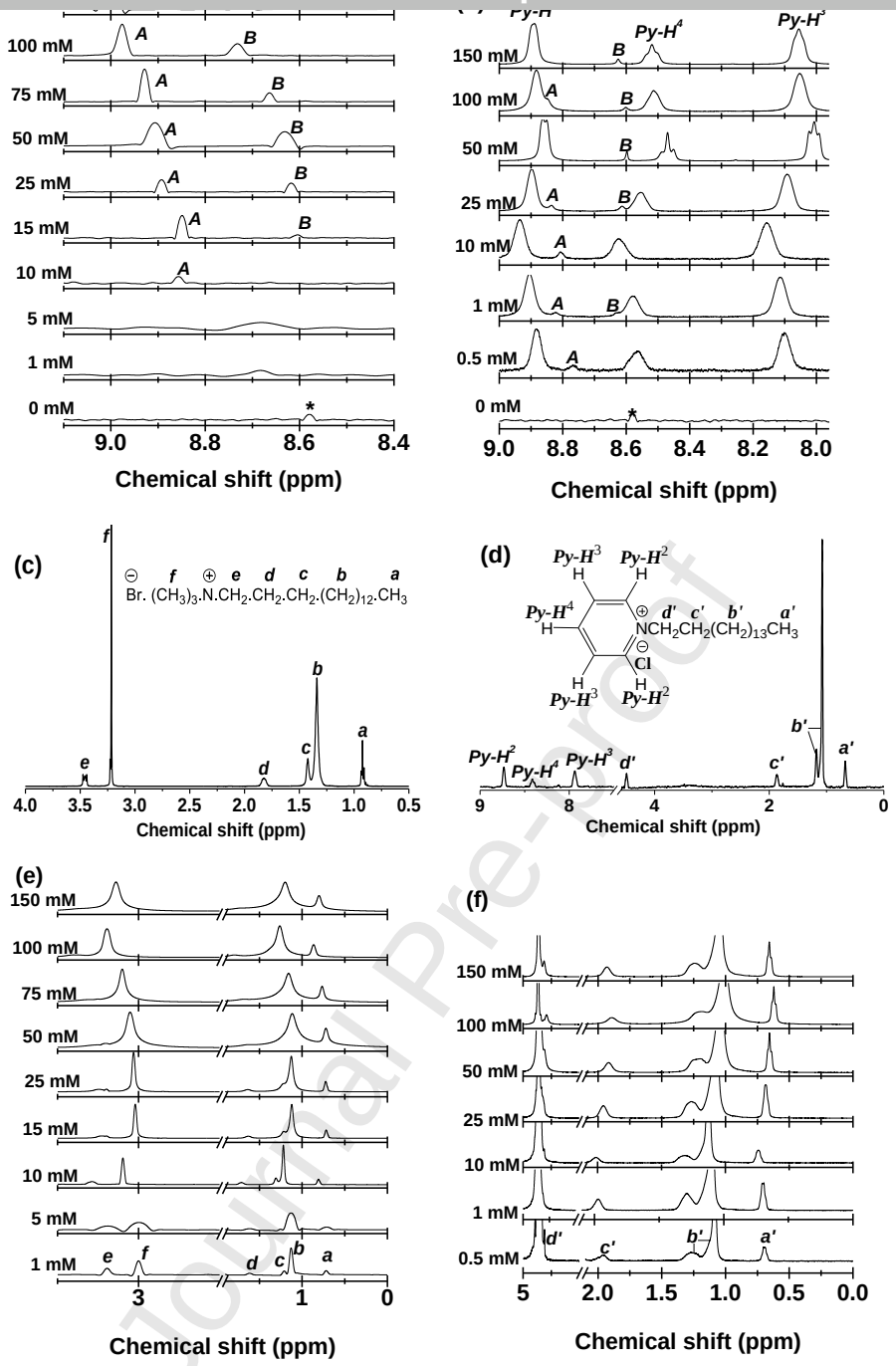


Figure 3. ^{1}H NMR spectra of (**a** & **b**) DNTCB in CTAB and CPC micellar solutions, respectively, at different surfactant concentrations showing chemical shift of aromatic proton, (**c** & **d**) CTAB and CPC micellar solutions, respectively, at different concentrations in presence of DNTCB, and (**e** & **f**) 0.5 mM CTAB and 0.5 mM CPC micellar solutions, respectively, in absence of DNTCB [*****: signal for aromatic proton of DNTCB in D_2O; ***A***: signal for aromatic proton of DNTCB molecules (**I**) involved in cation-π interaction with cationic head group (quaternary ammonium group) of cationic surfactants in micelles; ***B***: signal for aromatic proton of DNTCB molecules (**II**) solubilized in micelles of cationic surfactants by hydrophobic interaction; ***Py-H^2***, ***Py-H^3*** and ***Py-H^4***: signals for aromatic protons at 2nd, 3rd and 4th carbon atoms, respectively, of pyridinium group of CPC].

Figure 3c and **3d** are ^{1}H NMR spectra of CTAB and CPC solutions, respectively, (without DNTCB) at 0.5 mM concentration, *i.e.*, below their CMC and therefore, the spectra are presenting chemical shifts of surfactant molecules existing as monomers and submicellar aggregates. The changes in chemical shifts of protons of CTAB with increase in concentration and in the presence of DNTCB can be clearly seen (**Figure 3e**). On increasing the CTAB concentration, we noticed the increase in amount of solubilization of DNTCB in the CTAB micellar solution, which has been discussed in the following section. Therefore, the spectra (**Figure 3e**) are showing effect of surfactant as well as DNTCB concentrations on chemical shifts of CTAB. The downfield shifting of chemical shifts for various protons (which is much significant for "***f***" protons) of CTAB with increase in surfactant concentration and DNTCB solubilization (**Figure 3e**) indicates the location of solubilized DNTCB near the head groups of CTAB in micelles, *i.e.*, in the Stern layer. The downfield shifting of various protons of CTAB with surfactant and DNTCB concentration is indication of slight increase in the intermolecular distance between the molecules after inclusion of new molecules of surfactant and DNTCB in micelles. The increasing number of surfactant molecules and solubilization of DNTCB in Stern layer of CTAB micelles may elongate micelles orienting CTAB molecules parallel to each other showing increased intermolecular distance and downfield shifting of protons of CTAB. This shows that CTAB micelles get elongated with increase in concentrations and in the presence of DNTCB. In a previous work [**18a**], we noticed the downfield shifting for CTAB's protons above 75 mM (in absence of any solubilized organic molecules), which was ascribed to increased intermolecular distance between surfactant molecules due to transformation of spherical micelles to elongated micelles. On the contrary, the CPC molecules get tightly packed in DNTCB solubilized micelles on increasing CPC concentration. The slight upfield shifting of protons of CPC including aromatic ring protons (***Py-H^{2}***, ***Py-H^{3}*** and ***Py-H^{4}***; **Figure 3b & 3f**) with

concentration and in the presence of DNTCB is clear evidence of increasing closeness of CPC molecules in micelles.

The change in UV-vis spectra of DNTCB in CTAB and CPC micellar solutions at different concentrations as compared to the spectra of DNTCB in water (**ESI; Figure S7**) also revealed solubilization of DNTCB in micellar phase and the cation-π interaction of DNTCB molecules with surfactant's cationic head group showing blue shift of the characteristic band of DNTCB. The spectrum of DNTCB in water showed a weak band in the range of 300-350 nm, which was suppressed in the spectrum of DNTCB-CTAB and DNTCB-CPC micellar solutions, and a band at lower wavelength (< 300 nm) appeared. The band < 300 nm was ascribed to DNTCB molecules solubilized in micelles. The intensity of this band was observed to be increasing with increase in surfactant concentration from 5 mM to 75 mM due to the increasing concentration of DNTCB in micelles.

The ^{1}H NMR spectra of DNTCB in SDS micellar solutions at 1 mM to 150 mM showed the solubilization of DNTCB in the SDS micelles preferably in the Stern layer exhibiting slight downfield shifting for aromatic proton of DNTCB as compared to that in D_2O (**Figure S8a**). The solubilization of DNTCB in TX-100 micellar solutions is also evident from ^{1}H NMR spectra (**Figure S8b**). At 5 mM to 50 mM concentrations of TX-100, the DNTCB molecules were observed to be located in polar region (in shell) of micelles showing downfield shifting of DNTCB aromatic proton's signal. At higher concentrations of TX-100 (75 mM to 150 mM), DNTCB molecules seem to be residing slightly deeper in the shell towards the core of micelles exhibiting upfield shifting of aromatic proton of DNTCB. It has been shown in ^{1}H NMR experiments that at higher level of solubilization of cinnamic acid in TX-100 micellar solutions, the majority of cinnamic acid molecules reside at core–shell interface of TX-100 micelles [**20**]. The broadness of NMR peaks of various protons of TX-100 with increase in its

concentration and in the presence of DNTCB was observed (not shown in the spectra), which indicated the growth of micelles [**20**].

3.2.2. Solubilization behavior of micellar solutions for DNTCB

The solubilization capacity of four surfactant (CTAB, CPC, SDS and TX-100) micellar solutions at different concentrations (0.125 mM to 150 mM) for DNTCB was measured to study the solubilization behavior of micellar media for DNTCB (**see ESI**). The solubilization capacity of micellar solutions of all four surfactants was found to be increasing with increase in surfactant concentration (**Figure 4a**). The cationic (CTAB and CPC) surfactants' micellar solutions exhibited much higher solubilization capacity for DNTCB as compared to anionic (SDS) and non-ionic (TX-100) surfactants. The increasing intensity of yellow color of cationic micellar solutions with surfactant concentration indicates the increasing solubility of DNTCB (**Figure 4b-d**). The higher solubility of DNTCB in CTAB and CPC micellar solutions than SDS and TX-100 solutions is also evident from the intense yellow color of DNTCB-CTAB and DNTCB-CPC solutions at 15 mM and 100 mM surfactant concentrations (**Figure 4c** & **4d**).

The higher solubilization capacity of CTAB and CPC cationic surfactants than SDS and TX-100 can be ascribed to their tendency to make cation-π interaction, through cationic head group, with DNTCB molecules. The DNTCB-cationic surfactant π-complexed species will provide more hydrophobic environment to micelles for more solubilization of DNTCB. The smaller head group of CTAB as compared to that of CPC [**21**] may allow inclusion of more DNTCB molecules in the micelles showing higher solubilization capacity than CPC. In addition, the tendency of CTAB micelles to get elongated at higher concentrations, as evident from ^{1}H NMR study, can also increase the solubilization of DNTCB. On the contrary, the tightly packed CPC molecules in micelles and their bulky head group may hinder the further inclusion/ solubilization of DNTCB on increasing the CPC concentration and therefore, there

is not much enhancement in the solubilization of DNTCB with CPC concentration above its CMC (**Figure 4a**).

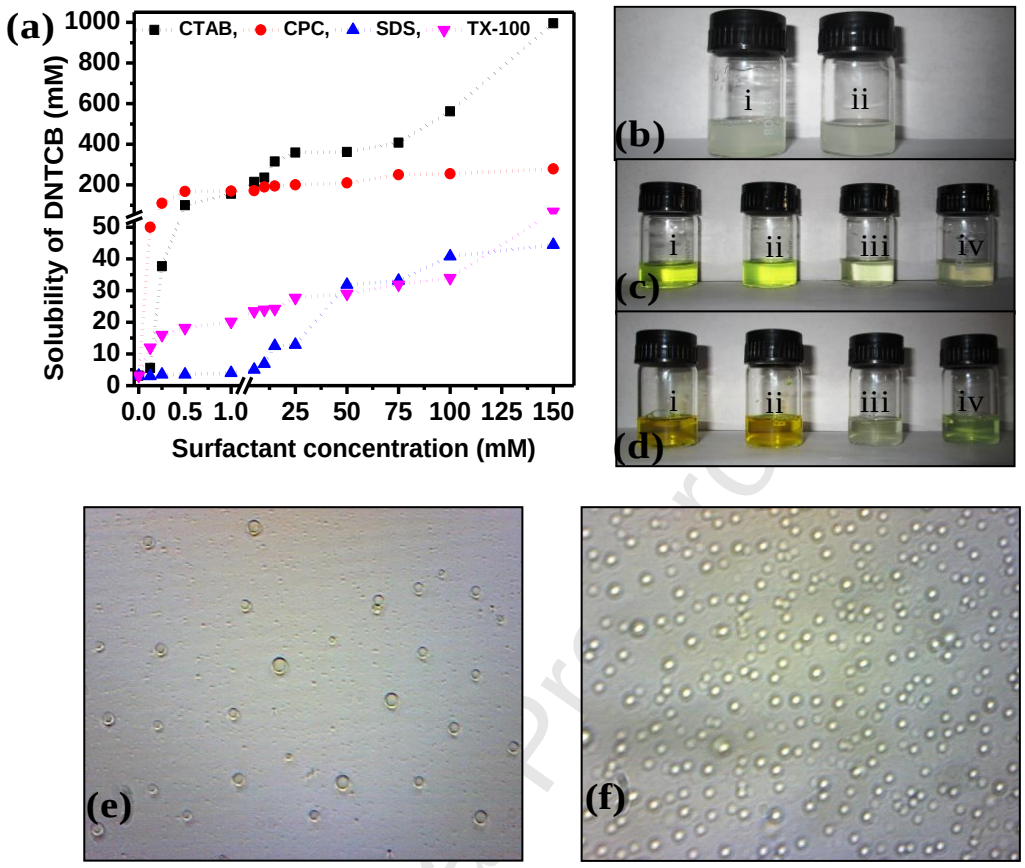


Figure 4. (a) Solubility of DNTCB in different micellar solutions, (b-d) Color of DNTCB solubilized micellar solutions [(b) 0.5 mM, (c) 15 mM, (d) 100 mM; i: CTAB, ii: CPC, iii: SDS, iv: TX-100], (e & f) optical microscope images of DNTCB-0.5 mM CPC and DNTCB-0.5 mM CTAB emulsion solutions, respectively.

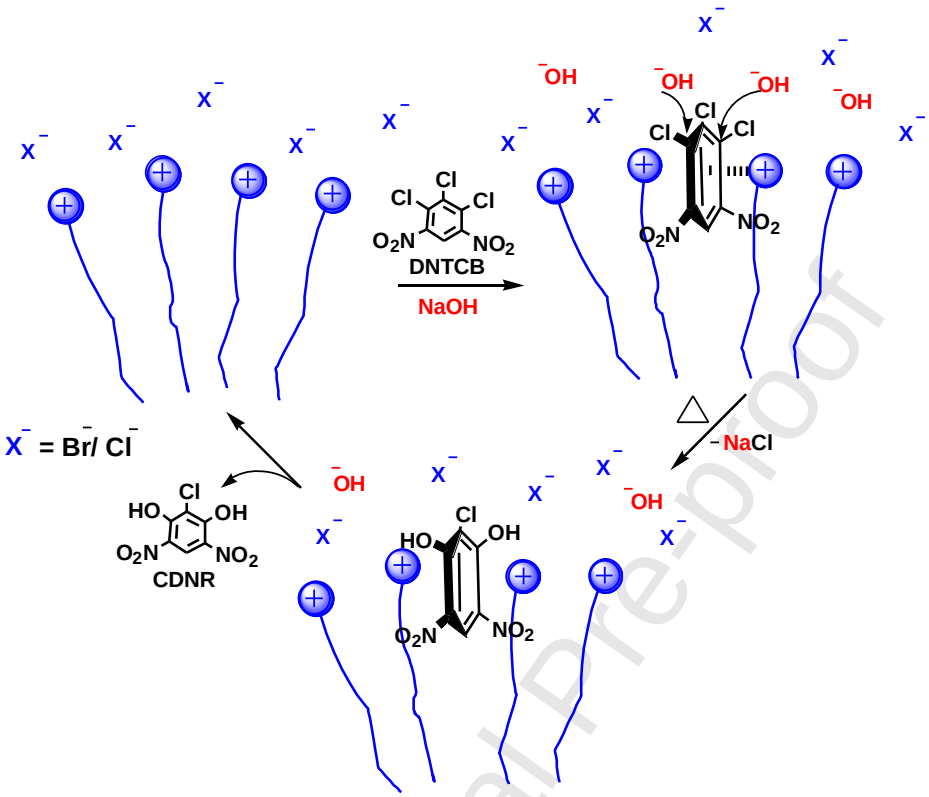
It is to be noted that there is significant solubility of DNTCB in CTAB and CPC solutions even at below CMC (*i.e.*, < 1.0 mM). For instance, at 0.5 mM concentration, the solubility of DNTCB in CTAB and CPC solutions is 96 mM and 166 mM, respectively (**Figure 4a**). In the solutions below CMC (also known as premicellar concentration; pre-CMC), very likely there are monomers and submicellar aggregates. The significant solubilization of DNTCB by both cationic surfactants at below CMC may be due to free surfactant monomers and the surfactant molecules released by disintegration of premicellar aggregates forming emulsified droplets of DNTCB. The presence of emulsion droplets of DNTCB in DNTCB-0.5 mM CTAB and

DNTCB-0.5 mM CPC solutions is evident from the turbidity of both the solutions (**Figure 4b**) and from their optical microscope images (**Figure 4e & 4f**). However, the optical micrograph of DNTCB-0.5 mM CPC solution shows the presence of significant amount of smaller droplets along with few large size droplets. The reason for the formation of smaller emulsion droplets of DNTCB in 0.5 mM CPC was investigated (**ESI; Figure S9**) and was found to be attributed to the DNTCB-CPC π-complex species formed in the solution by interaction (cationic head group-π interaction) of CPC and DNTCB molecules. The aromatic nature of pyridinium head group of CPC may provide better interaction (cation-π) with DNTCB molecules than CTAB molecules forming more number of DNTCB-CPC π-complex species. The DNTCB-CPC π-complex species, being more hydrophobic and surface active than CPC monomers, will efficiently emulsify DNTCB producing more number of smaller emulsion droplets and also solubilizing more amount of DNTCB than CTAB.

3.2.3. Molecular mechanism for efficient micellar catalysis in cationic surfactants' solutions

The higher efficiency of cationic micellar solutions (of CTAB and CPC at their optimum concentrations) in the hydroxylation of DNTCB than TX-100 and SDS micellar solutions can be related to higher solubilization capacity of CTAB and CPC micelles for DNTCB. The positive values of zeta potential for micelles of cationic surfactants in their aqueous solutions (*e.g.*, +14.9 mV and +20.5 mV, respectively, for CTAB and CPC at 15 mM; without DNTCB) indicate the positively charged surface of micelles. The positively charged micellar surface will increase the local surface pH, as compared to the pH of bulk solution, by attracting OH^- ions near micellar surface to facilitate the reaction [**22**]. With the help of micelles or emulsion droplets (in the case of 0.5 mM CPC), the cationic surfactants create

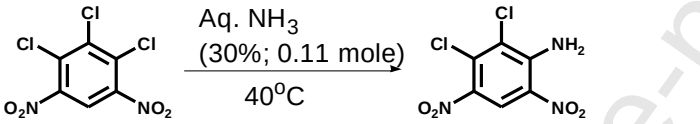
huge interface between organic (DNTCB) and aqueous (NaOH) phase and provide better interaction between DNTCB and OH^- ions to react with faster rate giving high conversion.



Scheme 4. Nucleophilic attack of OH^- ions on DNTCB molecule, interacting (by cation-π interaction) with cationic head group of a surfactant molecule in micellar phase of the micelle.

The cation-π interaction of cationic surfactant and DNTCB can reduce the electron density over aromatic nucleus of DNTCB molecules, which will make them more reactive towards nucleophilic attack of OH^- ions to replace Cl−atom (**Scheme 4**). In addition to creating high pH (OH^- ions/ nucleophile concentration) at micellar surface, the promotion of the reaction by cationic micelles can be greatly attributed to cation-π interaction, which helps in solubilization of large amount of DNTCB and activate them for aromatic nucleophilic substitution reaction. The major role of cation-π interaction in micellar catalysis was proved by carrying out a reaction of DNTCB with NH_3 (**Scheme 5**); in this reaction NH_3, a neutral nucleophile, will not be involved in electrostatic interaction with cationic micelles. The

biphasic reaction of DNTCB with aqueous NH_3 was very slow giving 75% conversion into a mono-amine derivative (DCDNA) after 48 h of reaction. The biphasic reaction (without surfactant) was observed to be fast in the presence of a base (0.5 mol% Na_2CO_3) giving 99% conversion of DNTCB after 5 h. In 15 mM CTAB and 0.5 mM CPC micellar catalyzed reactions, the highest conversion of DNTCB (99% and 75%, respectively) into the desired product was achieved within 5 h without use of the base. This result clearly demonstrates that the cationic head group of surfactant at optimum concentration plays important role through cation-π interaction in solubilization and in the catalysis of hydroxylation reaction (and aromatic nucleophilic substitution reactions).



DNTCB
(7.3 mmole)

2,3-dichloro-4,6-dinitro-aniline

Reaction condition	**Conversion (%)**
Biphasic, 48 h	75
Biphasic, 0.5 mol% Na_2CO_3, 5 h	91
15 mM CTAB, 5 h	99
0.5 mM CPC, 5 h	75
5 mM SDS	15

Scheme 5. Reaction of DNTCB with aqueous NH_3 under different conditions.

The negligible solubilization of CDNR in cationic micellar solutions measured by UV-vis analysis showed that the product (CDNR) was insoluble in micelles. Like DNTCB, CDNR molecules did not show any interaction (cation-π/ ionic/ hydrophobic) with surfactant molecules in the micelles, which was confirmed by ^{1}HNMR study. The CDNR, being insoluble in the micelles, comes out from micelles into aqueous medium, and gets crystallized upon cooling the reaction mixture.

The poor performance of SDS (**Figure 2d**) can be due to its poor solubilization capacity for DNTCB (**Figure 4a**) and the negatively charged micelles (zeta potential of SDS at 5 mM was

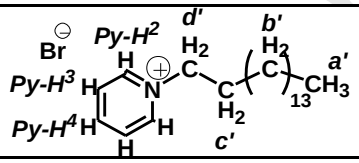
-21.0 mV) repelling the OH^- ions and reducing the pH (OH^- ion concentration) near micellar surface. Furthermore, unlike cationic micelles, there is no favorable interaction (like cation-π interaction) between SDS and DNTCB in micelles to facilitate the reaction. At lower concentrations (<100 mM), TX-100 solutions gave less conversion of DNTCB (**Figure 2e**), but at 100 mM concentration, there was highest conversion of DNTCB, which may be due to the formation of more number of micelles, at this concentration, solubilizing significant amount of DNTCB and populating sufficient number of OH^- ions (by hydrogen bonding with –OH groups of TX-100) at the micellar surface. The zeta potential of 100 mM TX-100 solution was -0.03 mV, which was found to be -30.7 mV in presence of NaOH (mmol) indicating the binding of OH^- ions with micelles, by hydrogen bonding through –OH groups of TX-100 molecules. At higher concentrations (>100 mM) of TX-100, again conversion of DNTCB is observed to be decreased (**Figure 2e**). This can be attributed to deeply resided DNTCB molecules in micelles at higher concentrations, which are not easily accessible by OH^- ions for reaction, and also to the dilution of OH^- ions around the micelles due to increased number of micelles. The study shows that 100 mM TX-100 solution provides sufficient number of micelles with optimum microenvironment for the solubilization and the reaction of DNTCB.

3.2.4. Efficiency of dilute CPC micellar solution in micellar catalysis

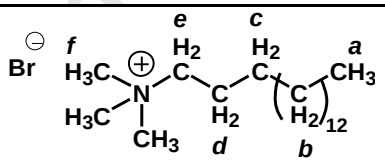
The better performance of CPC than CTAB for the hydroxylation of DNTCB is evident from the highest conversion of DNTCB (92%) obtained in a dilute solution of CPC (at 0.5 mM), which was very less (8% conversion of DNTCB) with 0.5 mM CTAB solution. The higher activity of CPC at 0.5 mM can be attributed to comparatively higher solubilization of DNTCB (166 mM; which was 96 mM in 0.5 mM CTAB) and the formation of smaller droplets of DNTCB (**Figure 4e & 4f**) providing huge interface for the reaction of DNTCB and OH^- ions. The chemical shifts for various protons of CPC molecules in 0.5 mM CPC

solution (in absence of DNTCB) were compared with chemical shifts of CPC in the presence of DNTCB, *i.e.*, in DNTCB-0.5 mM CPC emulsion solution (**Table 2**). The negative values of Δδ (downfield shifting for all chemical shifts) indicate increased intermolecular distance or loose molecular packing of CPC molecules at oil-water interface (*i.e.*, at the surface of emulsified DNTCB droplets; **Scheme 6a**) as compared to the CPC molecules existing as monomers and sub-micelles in 0.5 mM CPC solution. The loose molecular packing of CPC molecules at interface of emulsion droplet will enhance the accessibility of DNTCB molecules and OH^- ions to each other for reaction giving faster conversion of DNTCB.

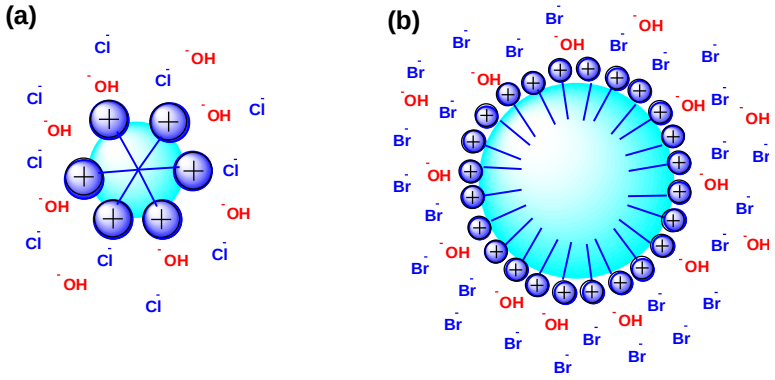
Table 2. Chemical shifts of various protons of CPC (0.5 mM) and CTAB (0.5 mM) in the absence and the presence of DNTCB.



Surfactant solution	Chemical shifts (δ; ppm) of different protons						
	g′	***f′***	***e′***	***d′***	***c′***	***b′***	***a′***
Pure CPC (0.5 mM)	8.41	7.93	8.73	4.49	1.86	1.07	0.67
DNTCB-CPC (0.5 mM)	8.56	8.10	8.88	4.62	1.96	1.09	0.69
Δδ (ppm)	-0.15	-0.17	-0.15	-0.13	-0.10	-0.02	-0.02



Surfactant solution	Chemical shifts (δ; ppm) of different protons					
	f	***e***	***d***	***c***	***b***	***a***
Pure CTAB (0.5 mM)	2.99	3.21	1.64	1.23	1.16	0.74
DNTCB-CTAB (0.5 mM)	2.94	3.11	1.59	1.18	1.10	0.70
Δδ (ppm)	0.05	0.10	0.05	0.05	0.06	0.04



Scheme 6. Molecular packing of (a) CPC and (b) CTAB molecules at oil-water interface of an emulsified droplet of DNTCB at 0.5 mM surfactant concentration.

On the contrary, the emulsion droplets of DNTCB in 0.5 mM CTAB solution have close molecular packing of CTAB molecules at interface (**Scheme 6b**), which is evident from the upfield shifting (positive values of Δδ; **Table 2**) of all the chemical shifts of CTAB molecules as compared to chemical shifts of CTAB (existing as monomers and sub-micelles) in 0.5 mM CTAB solution. The 0.5 mM CTAB micellar solution has significant solubilization of DNTCB (96 mM), however, the solution showed very poor activity (8% conversion). This can be ascribed to the formation of larger emulsion droplet size of DNTCB in 0.5 mM CTAB solution creating lesser interfacial area for the interaction of DNTCB and OH^- ions. In addition, the close molecular packing of CTAB molecules at oil-water interface of emulsion droplets will also inhibit the approach of OH^- ions to react with DNTCB slowing down the reaction. So, the higher efficiency of a dilute CPC micellar solution was because of its higher solubilization capacity for DNTCB, formation of smaller emulsion droplets of DNTCB and loose molecular packing of surfactant molecules at interface. The DST of pure surfactants (CTAB and CPC) and surfactant-DNTCB solutions at 0.5 mM concentration of surfactant were measured (**ESI; Figure S9**), which showed the presence of less number of free surfactant monomers in DNTCB-0.5 mM CTAB solution as compared to DNTCB-0.5 mM CPC solution. This indicates the involvement of more number of CTAB molecules in

emulsification of DNTCB droplets resulting into close packing of CTAB molecules at interface. The micellar catalytic behavior of CPC differs from CTAB due to planner structure and large size of its head group [**17a-c,23**]. In many reactions, especially where anionic substrates are involved in the reaction and form substrate-induced micelles, the CPC micellar solution performs better than CTAB solution at pre-CMC concentration [**17a-c**]. This has been attributed to loose molecular packing/ large intermolecular gaping of CPC molecules at micellar interface due to bigger size of pyridinium head group and less steric hindrance by planner pyridinium group in the reaction.

3.2.5. Reduced activity of cationic micellar solutions at higher (above optimum) concentrations

It was observed that the increase in CTAB concentration in micellar solution increases the solubility of DNTCB (**Figure 4a**), however, the conversion of DNTCB increases only up to optimum concentration (15 mM to 25 mM) and further increase in CTAB concentration decreases the conversion of DNTCB (**Figure 2a**). The increasing concentration of CTAB (up to optimum concentrations) in the solution increases the number of micelles, which increases the conversion of DNTCB by solubilizing more number of DNTCB molecules and providing huge oil-aqueous interface, high local pH effect near micellar surface and favorable (cation-π) interaction with DNTCB. The decreasing conversion with increase in CTAB concentration above 25 mM (**Figure 2a**) may be attributed to strong binding of DNTCB in the micelles by strong cation-π interaction and hydrophobicity of the micelles slowing down the reaction. The gradual downfield shifting of the signal "***A***" with CTAB concentration (**Figure 3a**) indicate the increasing cation-π interaction of solubilized DNTCB molecules (**I**) showing strong binding/ solubilization of DNTCB molecules in the micelles.

We also observed that the solubilization of DNTCB in CTAB micelles reduces the surface charge density of CTAB micelles due to neutralization of charges by cation-π interaction with DNTCB. The zeta potential for CTAB micelles at 150 mM was found to be +24.8 mV, which greatly decreased to -0.005 mV for DNTCB solubilized CTAB micelles. The decrease in surface charge for DNTAB solubilized CTAB micelles at 15 mM was also noticed; the zeta potential values of CTAB micelles before and after solubilization of DNTCB was +14.9 mV and +0.25 mV, respectively. The significant decrease in surface charge density of CTAB micelles at high concentrations after solubilization of DNTCB will reduce the concentration of OH^- ions around micelles. In addition, at higher surfactant concentrations, the increased number of micelles in unit volume will also reduce the OH^- ions concentration per micelle. Thus, the strong solubilization of DNTCB and the reduced OH^- ions concentration around the micelles at high CTAB concentrations are possible causes for slow reaction rate giving less conversion of DNTCB. The study shows that the CTAB micelles in the concentration range of 15 mM to 25 mM provide optimum characteristics/ microenvironment (strength of cation-π interaction with DNTCB, surface charge density and surface OH^- ions concentration) for the reaction giving highest conversion of DNTCB.

Similarly, the effect of CPC concentration on micellar catalysis was also noticed; however, at much lower concentration (1.0 mM), the conversion of DNTCB was significantly reduced (74%; **Figure 2b**). At this concentration, the CPC solution will have micelles to solubilize good amount of the DNTCB molecules (**Figure 4a**). However, the bulky head group of CPC than CTAB [**21**] and close packing of CPC molecules in the DNTCB solubilized micelles may slow down the reaction by hindering the approach of OH^- ions to react with solubilized DNTCB molecules and, therefore, the conversion was reduced at much lower concentration (1.0 mM). Further increase in concentration of CPC (>1.0 mM) greatly reduced the conversion of DNTCB, which can be ascribed to strong solubilization of DNTCB molecules

in the micelles because of strong cation-π interaction and enhanced hydrophobic environment. The downfield shifting of the signal "***A***" with CPC concentration in the ^{1}H NMR spectra (**Figure 3b**) is indication of increasing strength of cation-π interaction of DNTCB molecules with CPC molecules in the micelles. The upfield shifting of all the protons of CPC (pyridinium group and alkyl group; **Figure 3b** and **3f**) with concentration shows increasing hydrophobic environment inside the micelles. At higher CPC concentrations, the reduced OH^- ions concentration around the micelles, due to reduced surface charge density of micelles (the excessive cation-π interaction) and the increased number of micelles in unit volume, will also slow down the reaction. The reduction in conversion of DNTCB with increase in CPC concentrations was much higher in comparison of CTAB (above their optimum concentrations; **Figure 2a** and **2b**), which is the effect of closer molecular packing and larger head group of CPC molecules in the micelles hindering the approach of OH^- ions for the reaction. The reduced activity of CPC at CMC or higher concentrations in micellar catalysis has been reported [**17b**], which was ascribed to strong solubilization (ionic and/or polar and hydrophobic) of substrate molecules in the micelles, compact packing of CPC molecules (due to planner structure of CPC head group) at micellar interface and large pyridinium head group inhibiting the approach of water soluble species to react with solubilized substrate molecules.

3.3. **Effect of reaction temperature on the reactions**

While studying the effect of reaction temperature (at 75°C and 85°C) on the biphasic and cationic micellar catalyzed reactions, there was an interesting observation with CTAB micellar catalyzed reactions. We noticed that the micellar reactions in 15 mM CTAB was not influenced by the reaction temperature showing no change in DNTCB conversion rate on increasing the reaction temperature from 75°C to 85°C (**Figure 5**). However, the conversion

rate of DNTCB in CPC (0.5 mM) micellar reactions and biphasic reactions were found to be increasing on increasing the reaction temperature (**Figure 5**). This result was interpreted in terms of rigidity of CTAB micelles or close molecular packing in the micelles (at 15 mM concentration) after solubilization of DNTCB restricting the molecular motions, showing no effect of temperature on the reaction. The rigidity of DNTCB solubilized CTAB micelles may be resulted from the cation-π interaction between DNTCB and CTAB molecules. On the contrary, the DNTCB-0.5 mM CPC micellar solution have emulsion droplets stabilized by loosely packed CPC molecules (*i.e.*, DNTCB-CPC complex species), in which the molecular motion of bulk DNTCB can be affected by temperature showing effect on the reaction. Therefore, the increase in reaction temperature can enhance the molecular motion of DNTCB and the conversion rate. Similarly, in the biphasic systems (either in presence or absence of toluene), the molecules of DNTCB in the droplets are free to move showing effect of reaction temperature on the conversion. The rigidity of CTAB micelles in 15 mM solution and in the presence of solubilized DNTCB is also evident from ^{1}H NMR results (**Table 3**) showing upfield shifting of all the protons of CTAB as compared to that in the absence of DNTCB. The upfield shifting of all the protons of CTAB in the presence of DNTCB is indication of the increased molecular closeness (decreased intermolecular distance) in the micelles after DNTCB solubilization. For CPC's protons, we observed the downfield shifting of chemical shifts (**Table 2**) indicating the loose molecular packing (increased intermolecular distance) between CPC molecules at oil-water interface of emulsified droplets as compared to the CPC molecules existing as monomers and/or submicelles in 0.5 mM CPC solution. The study shows that CTAB micellar catalyzed hydroxylation of DNTCB can be carried out at a lower temperature (75 °C). Further decrease in the temperature (to 65°C) lowered the conversion rate showing 75 °C to be optimum temperature for reaction in CTAB solution.

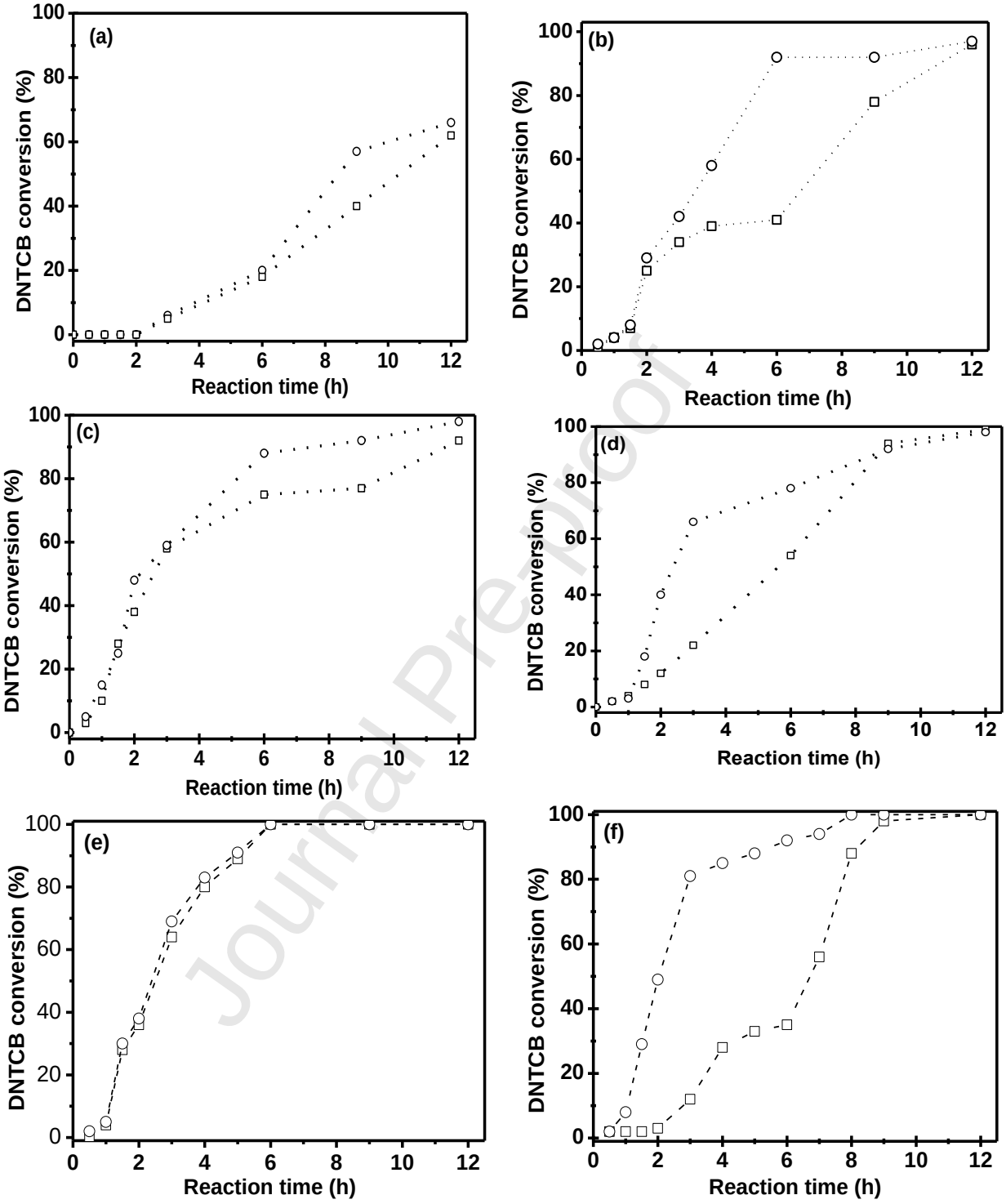
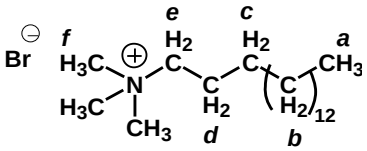


Figure 5. Reaction kinetics of (a) solvent free biphasic reactions, (b) biphasic reactions in toluene, (c) solvent free PTC reactions, (d) PTC reactions in toluene, (e) CTAB micellar reactions, and (f) CPC micellar reactions at 75°C (-□-) and 85°C (-○-) [Reaction condition: 7.3 mmol DNTCB, 21.9 mmol NaOH, 6 h; 1 mol% BTEA was taken in 5 mL water for PTC reactions; 5 mL pure water and 5 mL aqueous CTAB solution of 15 mM concentration were taken for biphasic and micellar reactions, respectively; 2 mL toluene was used in the reactions carried out in the presence of toluene].

Table 3. Chemical shifts of various protons of CTAB at 15 mM concentration in the pure micellar solution (without DNTCB) and in the presence of DNTCB.

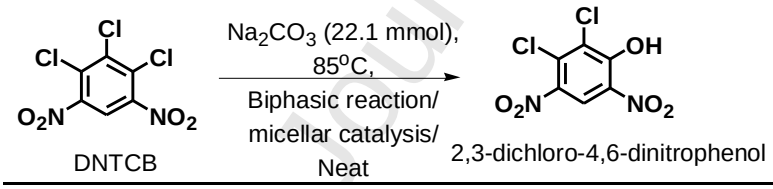


Surfactant solution	Chemical shifts (δ; ppm) of different protons					
	f	**e**	**d**	**c**	**b**	**a**
Pure CTAB (15 mM)	3.06	3.31	1.66	1.26	1.18	0.76
DNTCB-CTAB (15 mM)	3.02	3.22	1.63	1.21	1.12	0.72
Δδ (ppm)	0.04	0.09	0.03	0.05	0.06	0.04

3.4. Hydroxylation of DNTCB with Na_2CO_3 in micellar solution

In order to use a mild base (to replace NaOH) in hydroxylation of DNTCB, the reactions (neat, biphasic and micellar) were also carried out using Na_2CO_3 and $NaHCO_3$ under similar reaction condition and following the procedure discussed for hydroxylation using NaOH in experimental section. The Na_2CO_3 and $NaHCO_3$ react with water and produce OH^- ions, therefore, Na_2CO_3 and $NaHCO_3$ can be used as source of OH^- ions for hydroxylation of DNTCB.

Table 4. Hydroxylation of DNTCB with aqueous Na_2CO_3 under different reaction conditions.



Sr. No.	Reaction system	Conversion of DNTCB (%)
1	Neat reaction	1
2	Biphasic reaction (solvent free)	2
3	Biphasic reaction (in toluene)	4
4	15 mM CTAB	76
5	0.5 Mm CPC	63
6	5 mM SDS	21
7	100 mM TX-100	27

Reaction condition: 7.3 mmol DNTCB, 22.1 mmol Na_2CO_3, 5 mL surfactant solution (15 mM), 2 mL toluene, 85°C, 6 h.

There was no conversion of DNTCB in the reactions carried out using $NaHCO_3$ under neat, biphasic and micellar conditions. The neat or biphasic reactions of DNTCB with Na_2CO_3 gave very less amount of conversion (**Table 4**). The micellar solutions of cationic surfactants (15 M CTAB and 0.5 mM CPC) showed good activity in the reaction giving highest conversion of DNTCB (76% and 63% with CTAB and CPC micellar solutions, respectively). However, the product was found to be a mono-hydroxyl derivative (2,3-dichloro-4,-dinitrophenol). The result suggests that the Na_2CO_3-CTAB micellar system can be effective for mono-hydroxylation of DNTCB after optimization of the reaction conditions.

3.5. **Reuse study of spent micellar solution**

After completion of the reaction in 15 mM CTAB micellar solution, the reaction mixture was kept for complete crystallization of the product. The product crystals settled down at the bottom of the reaction tube. The spent CTAB micellar solution was obtained by filtration and was used for consecutive two reaction cycles under similar reaction condition. As the NaOH is used up in the reaction, therefore, the required amount of NaOH (21.9 mmol) along with DNTCB (7.3 mmol) are added in the spent micellar solution in each reaction cycle. The results (**Table 5**) show drastic decrease in conversion from 99% to 20% after 2nd cycle.

Table 5. Reuse study of spent CTAB (15 mM) micellar solutions.

Sr. No.	Reaction cycle	Conversion (%) of DNTCB
1	Fresh	99
2	1st	49
3	2nd	20

Reaction condition: 7.3 mmol DNTCB, 21.9 mmol NaOH, 5 mL CTAB micellar solution (15 mM), 85°C, 6 h.

The decreased conversion with spent micellar solution is possibly due to surfactant loss during the product separation and/ or NaCl co-product formed in the reaction. In previous work on micellar catalysis [**15**, **17b**], we observed marginal loss in activity of spent micellar solutions due to surfactant loss. So, the presence of NaCl in the spent micellar solution may

be the reason for the decreased activity of spent micellar solution. This was confirmed by adding 14.6 mmol of NaCl in micellar reactions (in 15 mM CTAB solution) assuming that the complete conversion of DNTCB produces ~ 14.6 mmol NaCl. The conversion of DNTCB in micellar solution containing NaCl was observed to be significantly decreased (32%) as compared to the conversion obtained with micellar reaction carried out without NaCl (99%). The solubility of DNTCB was measured in the spent micellar solution and in NaCl-CTAB micellar solution (5 mL, 15 mM CTAB + 14.6 mmol NaCl), and was found to be decreased to 132 mM and 135 mM, respectively, as compared to the fresh CTAB micellar solution (351 mM). This experiment clearly shows that the reduced conversion of DNTCB with the spent micellar solution is because of the decreased solubility of DNTCB in the presence of NaCl. The micelles are dynamic structures, which are continuously disintegrating and reassembling in the solution, and have two relaxation processes [**24**]. The first is a fast relaxation process (τ_1), which represents the exchange of monomers between micelles and the bulk, and the second relaxation time (τ_2; slow relaxation) denotes the formation and disintegration of micelle (*i.e.*, the stability of the micelle). The presence of salt in the micellar solutions has been observed to increase τ_1 and τ_2, *i.e.*, the stability of the micelles [**25**]. The presence of NaCl in the micellar solution of a cationic surfactant will increase the stability of the micelles, which will slow down the disintegration of the micelles reducing the solubilization of DNTCB. For the solubilization process, the micelles should frequently disintegrate to uptake the DNTCB molecules. The DST of 15 mM CTAB micellar solution was measured in the absence as well as in the presence of NaCl (14.6 mmol). The results (**Figure S10**) indicate increased DST of the solution in the presence of NaCl showing decreased rate of micellar disintegration (release of monomers), *i.e.*, increased stability of micelles. The DST of the spent micellar solution was also observed to be increased, as compared to fresh micellar solution, and the DST graph of the spent micellar solution resembled the DST graph of the

micellar solution in the presence of NaCl. Thus, the decreased conversion of DNTCB with the spent CTAB micellar solutions was mainly because of NaCl co-product produced during the reaction, which enhanced the stability of micelles and therefore, reduced the solubility of DNTCB in micellar medium resulting into a slow reaction.

4. Conclusions

The hydroxylation of DNTCB with aqueous NaOH under biphasic condition was found to be very slow. The micellar catalysis in micellar solutions of cationic surfactants at an optimum concentration was found to be effective promoting the reaction rate. The efficiency of cationic micellar solutions was ascribed to their high solubilization capacity for DNTCB, surface positive charges of micelles enhancing local surface pH, and cation-π interaction of cationic head group of surfactants with DNTCB molecules. The cation-π interaction in cationic surfactant solutions at optimum concentration plays important role in high solubilization of DNTCB and catalysis of the reaction by making DNTCB molecules more reactive for nucleophilic reaction with OH^- ions. As compared to CTAB, CPC is required in very low concentration (0.5 mM) to achieve highest conversion. At higher concentrations of cationic surfactants, the conversion of DNTCB was reduced owing to the strong solubilization of the DNTCB in micelles and the reduced OH^- ion concentration around micelles. The present work provides an efficient and environmental benign route for the synthesis of CDNR by micellar catalyzed hydroxylation of DNTCB utilizing an industrial organic waste, TCB as raw material. The cationic micellar solutions at optimum surfactant concentrations could also be an effective catalytic system to activate the aromatic substrates through cation-π interaction for various nucleophilic reactions.

Acknowledgement

The authors are thankful to Kutch Chemical Industries Limited, Baroda, India for providing financial support and to the Vice-chancellor, D.D. University, for providing valuable support to carry out this research work. Authors are also thankful to Department of Chemistry, S.P. University for support under CPEPA and CAS programs. Instrumental support for NMR analyses from Dr. M.J. Barot is acknowledged. We are also thankful to the reviewers of this manuscript for their valuable and constructive comments.

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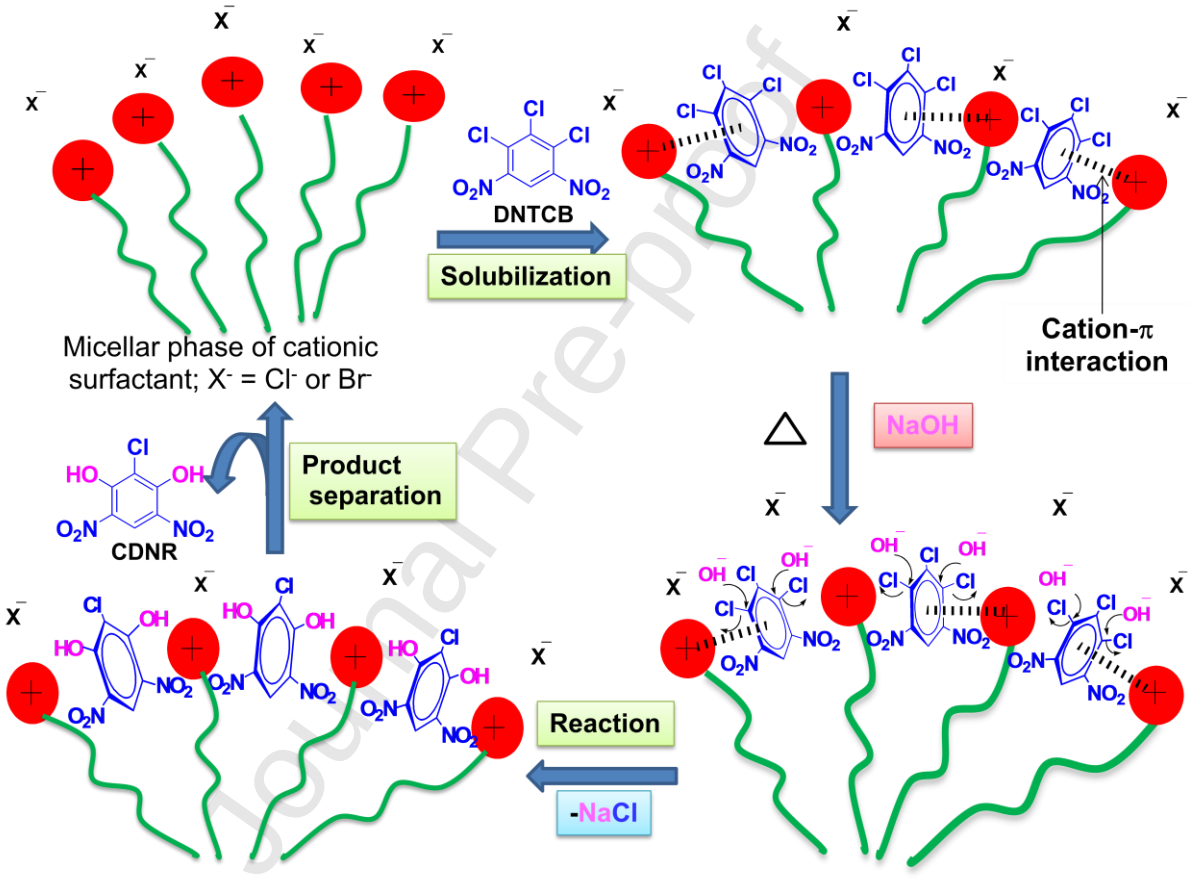
Declaration of interests

✓ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical Abstract

The hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene (DNTCB) with NaOH into 2-chloro-4,6-dinitroresorcinol (CDNR) was promoted in aqueous micellar solutions of cationic surfactants showing the role of cationic head group-π interaction with DNTCB molecules in catalysis.



Highlights

- Micellar catalysis of hydroxylation of 1,2,3-trichloro-4,6-dinitrobenzene with NaOH.
- Effect of surfactant's nature and concentration on the reaction.
- Promotion of reaction by cationic surfactants' head group-π interaction with substrate.
- Retardation of reaction at high surfactant at optimum concentrations.
- Effective catalytic system for the aromatic nucleophilic substitution reactions.