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Molecular mechanism of micellar catalysis of cross aldol reaction: Effect of surfactant chain length and surfactant concentration

Manu Vashishtha [a], Manish Mishra [a,*], Sachin Undre [b], Man Singh [b], Dinesh O. Shah [a,c]

[a] Department of Chemical Engineering & Shah-Schulman Center for Surface Science and Nanotechnology, Faculty of Technology, Dharmsinh Desai University, College Road, Nadiad 387 001, Gujarat, India
[b] School of Chemical Sciences, Central University of Gujarat, Sector-30, Gandhinagar 382030, India
[c] Department of Chemical Engineering and Department of Anesthesiology, University of Florida, Gainesville, FL 32608, USA

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ABSTRACT

The importance of alkyl chain length and concentration of quaternary ammonium surfactants (QAS) in the micellar catalysis of cross aldol reaction was investigated. The NaOH-micellar system catalyzed aldol reaction of benzaldehyde and cyclohexanone to α,α′-dibenzylidene cyclohexanone (di condensation/desired product) over mono condensation product was used as model reaction for this study. The C_{16}QAS micellar system (QAS with *n*-hexadecyl group) gave highest cyclohexanone conversion (90%) to desired product (82%) showing that C_{16}QAS micellar system possesses optimum properties and/or microenvironment for this reaction. Furthermore, the micellar system with high surfactant concentration (C_{16}QAS; >150 mM) made the reaction faster giving >99% conversion to selectively desired product (>99%) within 30 min The large interface created by C_{16}QAS micelles in the aqueous medium at high surfactant concentration makes the reaction faster by facilitating the interaction of hydrophobic reactants and water soluble catalyst (OH^- ions). The activation of benzaldehyde molecules, their localization preferably near the interface and stabilization of enolate ions (reactive intermediates) by micellar system at high surfactant concentration were observed to be promoting the cross reaction selectively to the desired product.

1. Introduction

The solvent-free and water mediated organic synthesis are in high demand to establish industrially viable ecofriendly processes for synthesis of chemicals. The water, being inexpensive and safe, is always preferred as green solvent in organic synthesis. Its great potential in promotion of many organic reactions under ambient reaction condition has been proven [1], which inspires the researchers to explore the use of water as solvent in organic synthesis. However, the limited solubility of organic reactants (hydrophobic) in water is the major constrain in water mediated synthesis especially when the other components (reactants and/or catalysts) of the reaction are water soluble resulting into very slow reaction. The less interfacial area between two phases (organic and aqueous) in such biphasic reactions reduces the residence time of water soluble and water insoluble components for their interaction. There are many organic compounds (e.g., aldehydes) which are sensitive toward water as they can undergo side reactions (like oxidation of aldehydes to acids) reducing the yield of desired product. The water can also be detrimental for some water sensitive catalysts causing the catalyst decomposition or deactivation and therefore cannot be reused. Therefore, the aqueous or biphasic reaction systems are required to be devised to overcome the above problems and to have the benefits of water in organic synthesis.

The surfactant micelles are aggregates of amphiphilic surfactant molecules in water having hydrophobic core and ionic surface. The micelles have been used for making hydrophobic compounds compatible with aqueous system by solubilization in the core to carry out the organic reactions in water [2]. The micelles facilitate the reactions in water by concentrating the hydrophobic compounds in the micelles and water soluble ionic species near micellar surface [3]. This promotional effect of micelles in the catalytic reactions is also known as micellar catalysis. The use of micellar system in catalysis can play a foremost role in the development of economical, energy efficient and environmentally benign processes avoiding the use of organic solvents, high temperature, decay of catalyst, side reactions, etc. In recent years, the use of surfactant micellar systems has been widely explored for promotion of various reactions in

* Corresponding author. Tel.: +91 268 2520502; fax: +91 268 2520501.
E-mail address: manishorgch@gmail.com (M. Mishra).

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water showing significant enhancement in reaction rate and product selectivity [4]. Recently we demonstrated the effectiveness and reusability of NaOH-cationic (quaternary ammonium surfactant: QAS) micellar system for equimolar aldol reaction of benzaldehyde and *n*-heptanal to cross aldol product (jasminaldehyde) giving its highest selectivity as compared to other heterogeneous catalysts reported till date [5]. We reported that the alkyl chain length and concentration of QAS play important role in micellar catalysis of cross aldol reaction of benzaldehyde and *n*-heptanal showing highest activity of C_{16}QAS (cetyltrimethylammonium bromide) micellar system at high concentration (200 mM).

In continuation of our work on micellar catalysis of cross aldol reactions, we did a detail study on NaOH-QAS micellar system catalyzed cross aldol condensation of benzaldehyde and cyclohexanone to α,α′-bisbenzylidene cyclohexanone (Scheme 1) as model reaction to investigate the importance of QAS's alkyl chain length and concentration on the cross aldol reactions. The α,α′-bis (substituted benzylidene) cycloketones are important precursors for the synthesis of bioactive pyrimidine derivatives, intermediates of perfumes, pharmaceuticals, and agrochemicals [6,7]. The mono condensation product (α-benzylidene cyclohexanone) is the co-product of the reaction, which is considered to be intermediate (it reacts with second molecule of benzaldehyde) of the di condensation product (α,α′-bisbenzylidene cyclohexanone). Incomplete conversion of mono condensation product to di condensation product reduces the selectivity or yield of α,α′-bisbenzylidene cyclohexanone. The synthesis of α,α′-bis (substituted benzylidene) cycloketones by cross aldol reaction of aromatic aldehydes with cyclic ketones using NaOH-cationic micellar (15 mM) system has already been reported by Janhavi et al. [8].

Supporting our previous observation this study also shows that the QAS's alkyl chain length and concentration are major factors in micellar system mediated cross aldol reaction of benzaldehyde and cyclohexanone influencing the reaction rate and product selectivity. The reaction in C_{16}QAS micellar system at high concentration (150 mM) gave complete conversion to >99% α,α′-bisbenzylidene cyclohexanone. Therefore, we were interested to investigate the role of surfactant's alkyl chain length and concentration in the promotion of cross aldol reactions. In the present study, by characterizing the reactants-micellar systems, we could explicate that C_{16}QAS micellar system (which possesses optimum properties and/or microenvironment for the reaction) at high concentration not only create large interface but also populates the reactants and reaction intermediates at interface for fast and selective conversion. It was also found that C_{16}QAS micellar aggregates activate the benzaldehyde molecules and stabilize the enolate ions of cyclohexanone and intermediate product (mono condensation product) for selective di-condensation reaction. The study revealed that NaOH-C_{16}QAS micellar system at high surfactant concentration is an efficient catalytic system for promotion of cross aldol reactions.

2. Materials and experimental methods

Benzaldehyde (>99%), cyclohexanone (99%), sodium hydroxide (NaOH; 97%), ethyl acetate (99%), concentrated hydrochloric acid (HCl; 35%) and sodium chloride (NaCl; 99%) were purchased from Merck, India. The quaternary ammonium surfactants (QASs) like decyl trimethyl ammonium bromide (C_{10}QAS; 98%) was from Spectrochem, India, dodecyl trimethyl ammonium bromide (C_{12}QAS; 98%), tetradecyl trimethyl ammonium bromide (C_{14}QAS; 98%) and hexadecyl trimethyl ammonium bromide (C_{16}QAS; 98%) were from s.d. Fine Chemicals, India and octadecyl trimethyl ammonium bromide (C_{18}QAS; 99%) was procured from Sigma–Aldrich. All the chemicals were used without any further purification. The millipore deionized water was used in preparation of all the solutions.

The cross aldol reaction of benzaldehyde (**1**) and cyclohexanone (**2**) (Scheme 1) was performed to evaluate the catalytic property of different NaOH-QAS micellar systems with varied alkyl chain length of surfactant and concentration studying their influence on the reaction (conversion and selectivity). For comparison biphasic reaction was also carried out in water (without QAS).

In a 50 mL reaction tube of reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK), 10 mL of QAS aqueous solution (of required concentration) or water (without surfactant) was taken and a mixture of benzaldehyde (10 mmol) and cyclohexanone (5 mmol) was added in the solution under stirring. The NaOH was dissolved in the solution and the reaction mixture was stirred at 60 °C for the required period of time. After the completion of reaction, the reaction mixture was neutralized with concentrated HCl and excess of saturated NaCl solution was added to reduce the surfactant concentration below the cmc. The organic phase was extracted with ethyl acetate (10 mL) and was analyzed by gas chromatography (Agilent 5975) having a HP-5 (60 m, 250 μm diameter) capillary column with a programmed oven temperature from 50 to 280 °C, at 1 mL min^{-1} flow rate of N_2 as carrier gas and FID detector. The conversion of cyclohexanone was calculated on the basis of its weight percent as follows:

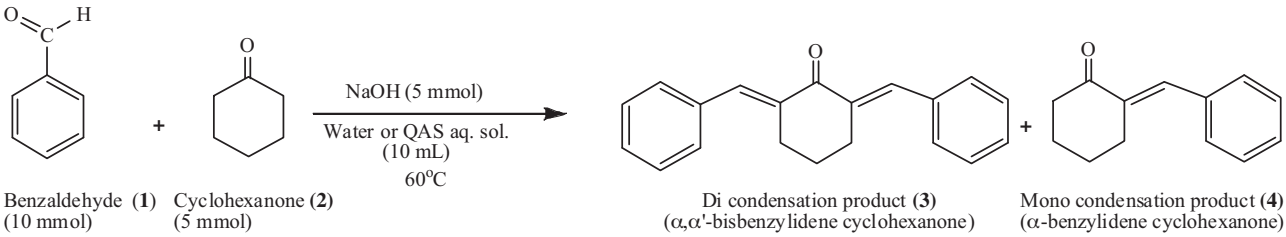
$$\text{conversion (wt.\%) of cyclohexanone} = 100 \times \frac{[\text{initial wt.\% of cyclohexanone} - \text{final wt.\% of cyclohexanone}]}{\text{initial wt.\% of cyclohexanone}}.$$

The selectivity of the products **3** and **4** was calculated as below:

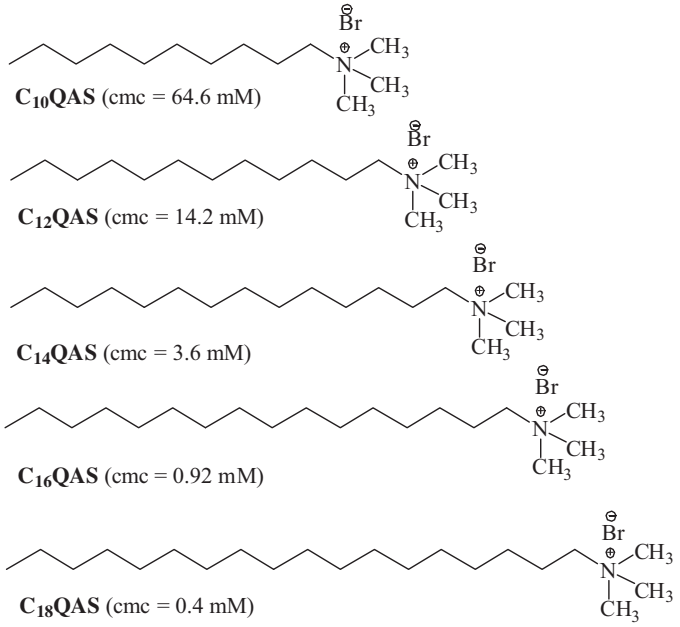
$$\text{selectivity (\%) of } \mathbf{3} \text{ or } \mathbf{4} = 100 \times \frac{\text{GC peak area\% of product } \mathbf{3} \text{ or } \mathbf{4}}{\sum \text{total peak area for all the products}}.$$

The di and mono condensation products were characterized by GC–MS analysis and the data were matched with those reported in the literature. GC–MS analysis was carried out using gas chromatograph mass spectrometer (Agilent 5975 GC/MSD with 7890A GC system) having HP-5 capillary column of 60 m length and 250 μm diameter with a programmed oven temperature from 50 to 280 °C, at 1 mL min^{-1} flow rate of He as carrier gas and ion source at 230 °C.

The aqueous solutions of reactants (**1** and **2** separately as well as their mixture) with and without QASs were analyzed using a Magnus light microscope (model-OLYMPUS CH 20iBIMF). A drop of solution was placed on a graduated glass slide (with least count 0.1 mm) without a cover slip. The images were captured with microscope fitted with a digital Sony color video camera (model-E413P) using TV home media software at 10× objective lance magnification. The UV–vis spectra of benzaldehyde and cyclohexanone in water and QAS aqueous solutions were performed on an Agilent, Carry 5000 spectrometer at room temperature. The path length of the quartz cell used in this experiment was 1 cm The UV absorptions of benzaldehyde and cyclohexanone in water and surfactant aqueous solutions were studied by using their separate solutions (benzaldehyde: 0.05 mM; cyclohexanone: 5 mM) in water and in surfactant solutions. This amount of benzaldehyde was completely soluble in the water and in QAS solutions giving a transparent solution, however, these concentrations of benzaldehyde and cyclohexanone were different from those used in the catalysis experiments. The ^{1}H NMR analysis of QASs solutions with and without reactants (benzaldehyde-cyclohexanone) mixture in D_2O was carried out using a Bruker Avance III 500 MHz spectrometer. The reactants mixture (benzaldehyde and cyclohexanone in 2:1 molar ratio; 10 μL) was solubilized in 1 mL D_2O or QAS solution in D_2O. The number of acquisitions was 32 for each sample. The



Scheme 1. Cross aldol reaction of benzaldehyde (**1**) and cyclohexanone (**2**) in NaOH-QAS solution/in water.



Scheme 2. Different QASs (and their CMC values in water at 25 °C [9]) used in cross aldol reaction of benzaldehyde and cyclohexanone in NaOH-QASs micellar solutions.

^{1}H chemical shifts are reported in δ units (ppm) relative to that of tetramethylsilane (TMS) as external standard.

3. Results and discussion

3.1. Cross aldol reaction of benzaldehyde and cyclohexanone in NaOH-QAS micellar systems of different surfactants with varied alkyl chain length

3.1.1. Conversion and product selectivity with different QAS micellar systems

The cross aldol reaction of benzaldehyde and cyclohexanone was first carried out in NaOH-QAS micellar systems (QAS concentration: 15 mM) of different surfactants with varied alkyl chain length (Scheme 2) to study the effect of alkyl chain length of QAS on the micellar catalysis of aldol reaction.

The reactions in NaOH-QAS micellar solutions (Fig. 1a) gave remarkably higher conversion of cyclohexanone (61–90%) than biphasic reaction (44% conversion) showing faster reaction rate in micellar media. There was no formation of di-condensation product (**3**) in biphasic reaction (i.e. without QAS), while di-condensation product was formed in good amount (17–82%) in NaOH-QAS micellar solutions. This is an interesting result that the presence of surfactant in reaction medium not only enhances the conversion rate but also promotes the di-condensation reaction. From Fig. 1a it is clearly evident that the alkyl chain length of QAS has significant influence over reaction rate as well as di-condensation reaction (i.e., selectivity to **3**). The C_{16}QAS micellar system showed highest activity giving highest cyclohexanone conversion (90%) and selectivity of **3** (82%) as compared to other QAS micellar systems. On increasing the alkyl chain length of QAS from C_{10} to C_{16}, the conversion and selectivity of **3** were gradually increased from 61% to 90% and 18% to 82%, respectively. With C_{18}QAS system, the conversion and the selectivity for **3** were reduced to 66% and 17%, respectively.

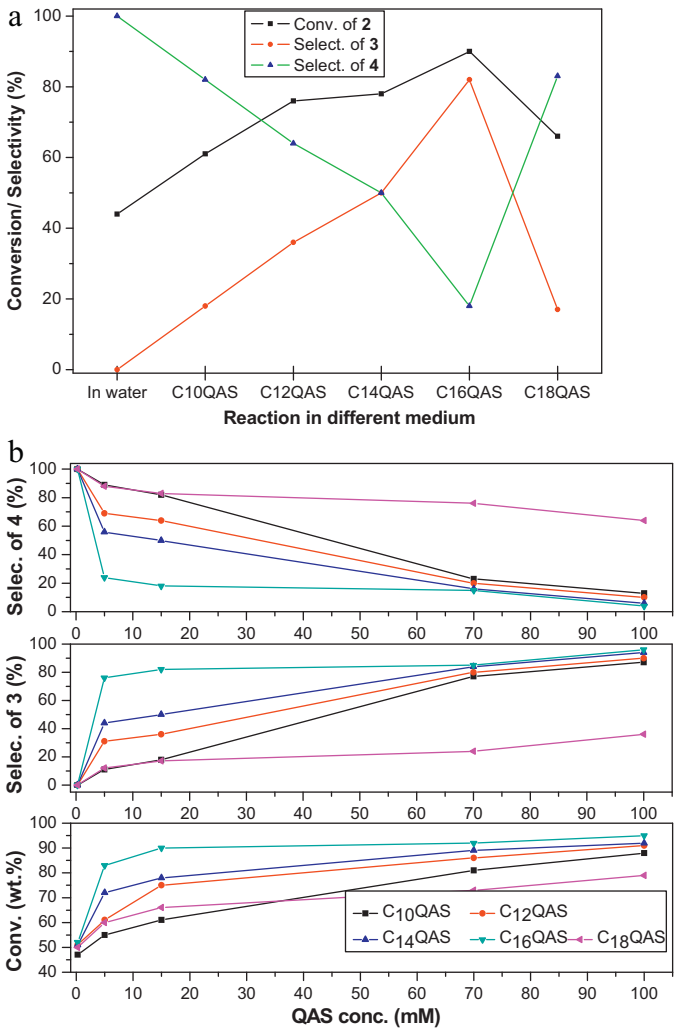


Fig. 1. (a) Conversion and selectivity of di (**3**) and mono (**4**) condensation products in NaOH base catalyzed cross aldol condensation of benzaldehyde and cyclohexanone in water and in different QAS micellar solutions [reaction condition: 10 mmol benzaldehyde, 5 mmol cyclohexanone, 5 mmol NaOH, 10 mL aqueous surfactant solution (15 mM), 60 °C, 30 min]. (b) Conversion and selectivity of di (**3**) and mono (**4**) condensation products in NaOH base catalyzed cross aldol condensation of benzaldehyde and cyclohexanone in QAS miceller solutions at different concentrations [reaction condition: 10 mmol benzaldehyde, 5 mmol cyclohexanone, 5 mmol NaOH, 10 mL aqueous surfactant solution (0.25 mM, 5 mM, 15 mM, 70 mM and 100 mM), 60 °C, 30 min].

The faster reaction rate in micellar media than pure water is attributed to large micellar interface generated in aqueous medium, which provides micellar surface as a platform for the interaction of hydrophobic and water soluble components. The positively charged micellar surface can have high OH^- ions concentration by attracting more OH^- ions due to Coulombic force increasing the local pHs (i.e. pH near the surface of the micelle) of the micellar surface than the pH of bulk solution [10,11]. The micelles will also concentrate the reactants by solubilizing within the micelles in required orientation [12]. The high OH^- ions concentration (high pH) at the micellar surface and concentrated reactants within the micelles can have better interaction giving faster conversion and preferred product in the reaction. The positively charged micellar surface may also assist in populating and stabilizing the reactants and intermediates (enolate ions) at the interface for their reaction [13,14].

It is well recognized that micelles are dynamic structures. They form and break at the time scale of milliseconds [15]. Thus at any time, there are submicellar fragments in equilibrium with micelles and monomers. By the same token, when micelles form, it is not abrupt phenomenon but as concentration increases toward Critical Micelle Concentration (CMC), the concentration of submicellar aggregate increases and at CMC, full micelles form and upon further addition of surfactant, the number of micelles increases, whereas the monomer concentration remains constant. Using filtration through nanoporous membranes, Smith et al. [16] have shown that sodium dodecyl sulfate micellar solutions are not only made up of micelles and monomers, but also contain a high concentration of sub-micellar aggregates and the concentration of sub-micellar aggregates decreases as the micellar stability increases. Thus, in the 15 mM C_{10}QAS solution, very likely there are monomers and submicellar aggregates as the concentration is less than CMC (64.6 mM). However, the increased cyclohexanone conversion (61%) and formation of **3** (18%) in 15 mM C_{10}QAS micellar solution (Fig. 1a) indicates the involvement of surfactant molecules, presumably in the form of submicellar aggregates, in catalysis of the reaction. This has been reported by several researchers that in the micellar mediated reactions below CMC, also known as premicellar concentration (pre-CMC), a small number of surfactant monomers may aggregate with a substrate molecule to form a catalytic micelle, which contributes in enhancement of the reaction rate [17–20]. Brinchi et al. [19], reported that didodecyldialkylammonium chloride and bromide accelerate the spontaneous decarboxylation reactions showing first-order rate constants, k_{obs}, maxima in very dilute surfactant solution. The phenomena were interpreted in terms of substrate-induced micellization, depletion of water at the reaction center and association of substrate and quaternary ammonium centers. In 15 mM C_{10}QAS solution, the reactant molecules may get associated with sub-micellar aggregates, which may catalyze the di-condensation reaction giving di-condensation product and enhancement in the reaction rate. Thus the reaction in 15 mM C_{10}QAS solution is due to presence of submicellar aggregates in the pre-CMC region.

The increasing cyclohexanone conversion with increasing alkyl chain length of QAS from C_{12} to C_{16} (15 mM solutions; Fig. 1a) might be a collective effect of important features of micellar system such as number of micelles and their size, stability of micelles, hydrophobicity, inter molecular distance of surfactant molecules in the micelles (molecular packing), surface charge density (surface pH), etc. These properties significantly change on varying the alkyl chain length of a surfactant [16,21–27]. With increasing chain length of QAS from C_{12} to C_{16} at same concentration (15 mM), the solubilization of reactant molecules by the micelles will increase due to increasing number of micelles (owing to decreasing CMC), micelle volume and hydrophobic nature of micelles [25]. In addition, the increasing number of micelles, on varying the chain length of QAS from C_{12} to C_{16} at same concentration, will also enhance the interfacial area in the micellar system. The increasing chain length of a surfactant increases the stability of micelles due to strong van der Waals forces as well as hydrophobic association between the alkyl chains [26], which can provide stable micellar interface (common platform) for better interaction of hydrophobic and water soluble reagents of the reaction. In addition to this, the strong interaction between surfactant molecules (close molecular packing) in the micelles also influences the surface charge [21,23]. As the quaternary ammonium group of QAS will come closer on increasing chain length due to close molecular packing in micelles, the surface pH (OH^- ion concentration) at micellar interface will be enhanced, which will accelerate the reaction rate. Thus the highest catalytic performance of C_{16}QAS micellar system in comparison of C_{12}QAS and C_{14}QAS systems can be attributed to more number of micelles, higher hydrophobicity of micelles, large interfacial area, stable micellar interface and high surface pH effect facilitating the solubilization of water insoluble components (reactants), enhancement of OH^-ion concentration at interface and the interaction of water soluble and water insoluble components. The C_{18}QAS system (15 mM solution) showed least activity giving low conversion and selectivity of **3**, which is due to very strong solubilization of the reactant molecules owing to compact molecular packing and high hydrophobicity, which restrict the diffusion of reactant molecules for interaction with OH^- ion at interface.

The reactions were also studied in C_{10} to C_{18}QAS solutions by using different concentrations covering their premicellar concentrations, CMC and higher concentrations (0.25–100 mM solutions; Fig. 1b). The results clearly reveal that C_{16}QAS micellar system possesses optimum properties and/or microenvironment for this reaction giving highest conversion and selectivity of **3** (at all concentrations) as compared to other QAS. At less concentrations (e.g., 10 and 15 mM), C_{16}QAS gave reasonably high conversion and selectivity of **3**. The lower QAS (C_{10}–C_{14}) also increased the conversion and selectivity of desired product, but at high concentrations (70 and 100 mM). The lower surfactants (C_{10}QAS, C_{12}QAS and C_{14}QAS) require high surfactant concentration to achieve the enhanced catalytic activity as C_{16}QAS micellar system possesses at less concentration (15 mM). The enhanced activity of C_{10} to C_{14}QAS micellar systems at higher concentrations can be attributed to enhanced number of micelles and increased interface, which facilitate the interaction of water soluble and water insoluble reagents by enhancing the solubilization of water insoluble reactants and populating more OH^- ions at interface. The C_{18}QAS systems (0.25–100 mM solutions) always give lower conversion and selectivity of **3** at all concentrations showing decreased activity of the C_{18}QAS systems in comparison of C_{16}QAS systems. In spite of higher number of micelles (less CMC) and huge interface in C_{18}QAS systems than other QAS systems, the lower conversion and selectivity of **3** clearly shows that very strong solubilization of the reactant molecules by micelles due to close packing of surfactant molecules might be reducing their availability at interface decreasing the reaction rate and selectivity to di-condensation reaction.

The formation of **3** in micellar systems (Fig. 1a and b) indicates that micelles might be concentrating benzaldehyde in sufficient amount and in proper orientation for di-condensation with cyclohexanone (i.e., its enolate ion). In addition, the formed mono condensation product (**4**) may also be retained by micelles, probably at micellar interface, for further condensation with second benzaldehyde molecule (i.e., di-condensation reaction). The hydrophobic nature of **4** and stabilization of its enolate ions by micellar interface (ionic interaction with ammonium group) may be the attributes for the localization of **4** at micellar interface for di-condensation reaction. The increasing selectivity of **3** with increasing alkyl chain length of QAS from C_{10} to C_{16} (Fig. 1a and b) can be attributed to increasing interface (due to increasing number

of micelles) and hydrophobicity, which help in stabilization of the intermediate product (**4**) at micellar interface for di-condensation reaction. The bis-alkylation of γ-phenylcyclohexanone with benzyl halides in two steps to bis-alkylation products in higher amount has been reported in cationic micellar system suggesting that the hydrophobic nature of intermediate and its stabilization by micellar aggregates facilitate di-alkylation reactions [13]. The less selectivity of **3** with C_{18}QAS systems may be due to less availability of benzaldehyde molecules at interface for di-condensation reaction with **4**, which may be due to very compact packing of surfactant molecules and their strong hydrophobicity, which restrict the diffusion of solubilized benzaldehyde molecules from bulk to interface. In addition, the strong solubilization of **4** within the micelles may also reduce its availability at interface for interaction with OH^- ions and reaction with benzaldehyde to form **3**.

In biphasic reaction, the reaction takes place at water–oil interface, where no surfactant molecules are available to hold the mono-condensation product to form its carbanions (with the help of OH^- ions) followed by reaction with second molecule of benzaldehyde. The mono-condensation product may go away from interface in bulk (probably in oil phase due to its hydrophobic nature) and may not be assessable to OH^- ions for carbanion formation and to react with benzaldehyde molecule. This may be the probable reason for no di-condensation reaction, when reaction is carried out in the pure water. The presence of surfactant molecules at interface not only speeds up the reaction, but it also helps in holding the intermediate product (mono-condensation product) at interface for di-condensation reaction.

It can be seen that the extremely high hydrophobicity of C_{18}QAS micellar system is unfavorable for the aldol reaction and di-condensation reaction. The very high hydrophobicity of C_{18}QAS micelles and tight packing of surfactant molecules in micelles may strongly solubilize the reactant(s) and/or intermediate product (**4**) within the micelles reducing their availability at interface, which will slow down the reaction rate as well as formation of di-condensation product (**3**). This indicates that C_{16}QAS micellar system possesses optimum properties for this reaction. We have reported the similar effect of QAS's alkyl chain length on the reaction rate of cross aldol reaction between benzaldehyde and *n*-heptanal, and selectivity to cross aldol product (jasminaldehyde) showing highest cross product selectivity with C_{16}QAS micellar system [5]. To investigate the role of alkyl chain length of QAS on the performance of micellar systems in cross aldol reaction, the micellar-reactants systems were characterized.

3.1.2. Optical microscopy analysis of reactants-QAS micellar systems

The benzaldehyde (10 mmol) and cyclohexanone (5 mmol) were separately mixed with water (10 mL) and QAS solutions (15 mM, 10 mL) to analyze their miscibility in both media by optical microscopy. The optical microscopy (Fig. 2a) analysis of benzaldehyde-water mixture indicates the existence of micron size droplets of benzaldehyde indicating that the benzaldehyde (the amount used in the reaction) is not completely miscible with water. Whereas cyclohexanone was found to be completely dissolved in water as no droplets were observed in optical microscopy analysis. The micellar-reactants systems can have micelles with solubilized molecules of reactants and emulsion droplets of different size. In QAS solutions (15 mM), the emulsion droplet size of benzaldehyde can be seen to be decreasing (Fig. 2b–f) with increasing QAS's alkyl chain length from C_{10} to C_{18}. The increase in alkyl chain length of QAS increases the hydrophobicity (solubilization capacity) of micelles [25,27]; this will cause depletion of benzaldehyde droplets solubilizing within the micelles and will form smaller emulsion droplets. On varying the chain length of QAS from C_{10} to C_{18}, the increasing chain-chain interaction within the micelles may also reduce the size of emulsion droplets. Gao et al. [25], demonstrated the higher solubilization capacity of C_{16}QAS micelles for polystyrene than C_{12}QAS due to higher hydrophobicity resulting into enhanced degree of chloromethylation of polystyrene in C_{16}QAS solution. The benzaldehyde emulsion droplets are of very small size in C_{18}QAS solution indicating very high solubilization of benzaldehyde in their micelles. The C_{10}QAS solution will have only monomers and submicellar aggregates as the concentration is below CMC (Scheme 2), therefore, benzaldehyde droplets in C_{10}QAS solution are not much changed as compare to the droplet size in water. The C_{10}QAS monomers and submicellar aggregates may emulsify the benzaldehyde droplets by getting adsorbed over droplets producing bigger size droplets. The droplet size of benzaldehyde-cyclohexanone mixture in water and QAS solutions were almost similar to that in water and QAS solutions.

The NaOH catalyzed aldol reaction of benzaldehyde and cyclohexanone in water is under biphasic condition (NaOH and cyclohexanone will be in aqueous phase), which has very limited interfacial area for interaction of hydrophobic and hydrophilic components giving less conversion to mono-condensation product. We observed that benzaldehyde-water mixture gets phase separated very quickly (within 30–40 s), however benzaldehyde-QASs solutions give comparatively stable emulsions. The benzaldehyde droplets are stabilized by QAS micelles and submicelles and the reaction in QAS solutions occurs at the interface of micelles or emulsion droplets. The optical microscopy results clearly support that the increasing substrate conversion with increasing alkyl chain length of QAS from C_{10} to C_{16} is attributed to huge interface created in the aqueous medium. From the optical microscopy results, it was expected that the C_{18}QAS giving smallest benzaldehyde droplets should be best micellar system providing high interfacial area for reaction. In spite of having smallest droplet size (high interfacial area) in the C_{18}QAS micellar system, its reduced performance in micellar catalysis can be attributed to close packing of surfactant molecules and very high hydrophobicity of the micelles resulting into strong solubilization of reactants and/or reaction intermediate reducing their availability at interface for reaction.

3.1.3. UV spectroscopic study of reactant-QAS micellar systems

In addition to creating huge interface by C_{16}QAS micelles in the aqueous medium, their optimum properties and/or microenvironment seems to be playing important role in promotion of the cross aldol reaction. To prove this, UV absorption characteristics of both the reactants (benzaldehyde and cyclohexanone) were separately studied in water and in different QAS micellar solutions (15 mM). The UV absorption spectrum of benzaldehyde in water (Fig. 3a) shows an intense band at 249.5 nm ascribed to $\pi \rightarrow \pi^*$ transition. This band does not show any shift in QAS solutions, however, the intensity of the band changes as the alkyl chain length of QAS is varied. In C_{10}QAS solution, the band intensity is decreased as compared to water. Whereas the band intensity gradually increases on varying the alkyl chain length of QAS from C_{12} to C_{16} and a very high increase in band intensity can be seen in C_{18}QAS solution. It indicates the increasing solubilization of benzaldehyde in micelles due to increasing hydrophobicity of QAS micelles. The decreased intensity of the band in C_{10}QAS solution may be due to encapsulation of benzaldehyde droplets with the help of C_{10}QAS molecules/submicelles (as the concentration is less than CMC). The greatly elevated intensity of the benzaldehyde band in C_{18}QAS system is indicative of very high solubilization of benzaldehyde due to very strong hydrophobicity of micelles i.e., strong interaction of benzaldehyde with hydrophobic core of C_{18}QAS micelles.

The major absorption band for cyclohexanone in water was occurred at 276 nm ($n \rightarrow \pi^*$). The band intensity was not much changed in the C_{12} to C_{18}QAS solutions as compared to water indicating no significant effect of increasing hydrophobicity of QAS

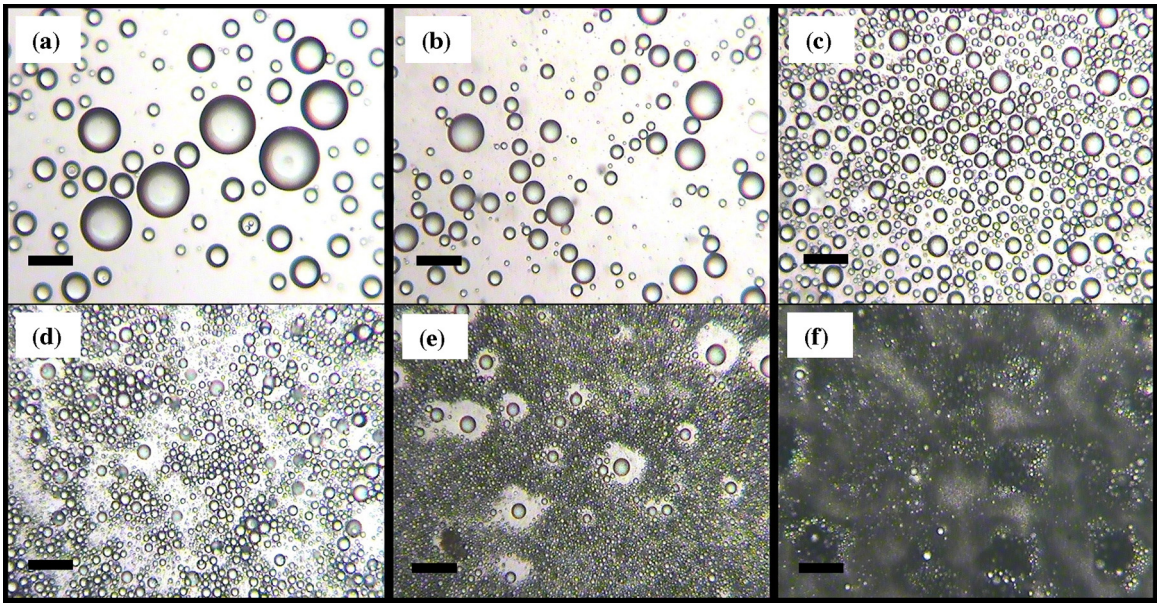


Fig. 2. Optical micrographs of benzaldehyde in (a) water, (b) C_{10}QAS, (c) C_{12}QAS, (d) C_{14}QAS, (e) C_{16}QAS and (f) C_{18}QAS solutions (conc.: 15 mM; the scale bar equals 200 μm).

on solubilization of cyclohexanone in the QAS micelles (Fig. 3b). However, the band intensity was observed to be increased in C_{10}QAS solution indicating the solubilization of cyclohexanone in their micelles, which may be due to association of cyclohexanone molecules with submicelles making their micellar aggregates. The lower band intensity with higher QAS (C_{12} to C_{18}QAS) indicates lesser solubilization of cyclohexanone in their micelles. The enhanced chain-chain interaction between QAS molecules on increasing alkyl chain length, structural incompatibility of cyclohexanone molecules in hydrophobic core and good solubility of cyclohexanone in water might be reducing the partitioning of cyclohexanone molecules into the micelles.

In spite of high solubilization of benzaldehyde in C_{18}QAS micelles, the reduced conversion and selectivity to di condensation product (**3**) is clearly indicating that the strong solubilization of benzaldehyde in the core of C_{18}QAS micelles slow down the reaction rate reducing the availability of reacting molecules at interface. The catalysis results and UV study revealed that C_{16}QAS micellar system possesses optimum properties and/or microenvironment sufficiently populating the benzaldehyde molecules at interface to facilitate the cross reaction. The free cyclohexanone molecules (which are not solubilized in micelles and are in aqueous medium) will form its enolate ions with the help of NaOH and can approach the positively charged micellar surface to react with benzaldehyde molecules solubilized in the micelles. The cationic micelles may also stabilize the enolate ions of cyclohexanone and mono-condensation product by interacting through quaternary ammonium group of surfactant. This has been reported that the cationic surfactants significantly enhance the acidity of aromatic ketones in micellar solution on account of a strong interaction of the enolate ions with the micellar aggregates [28].

3.2. Cross aldol reaction of benzaldehyde and cyclohexanone in NaOH-C_{16}QAS micellar systems with varied surfactant concentrations

3.2.1. Effect of surfactant concentration on conversion and product selectivity

The cross aldol reaction of benzaldehyde and cyclohexanone was carried out in C_{16}QAS micellar solutions of varied

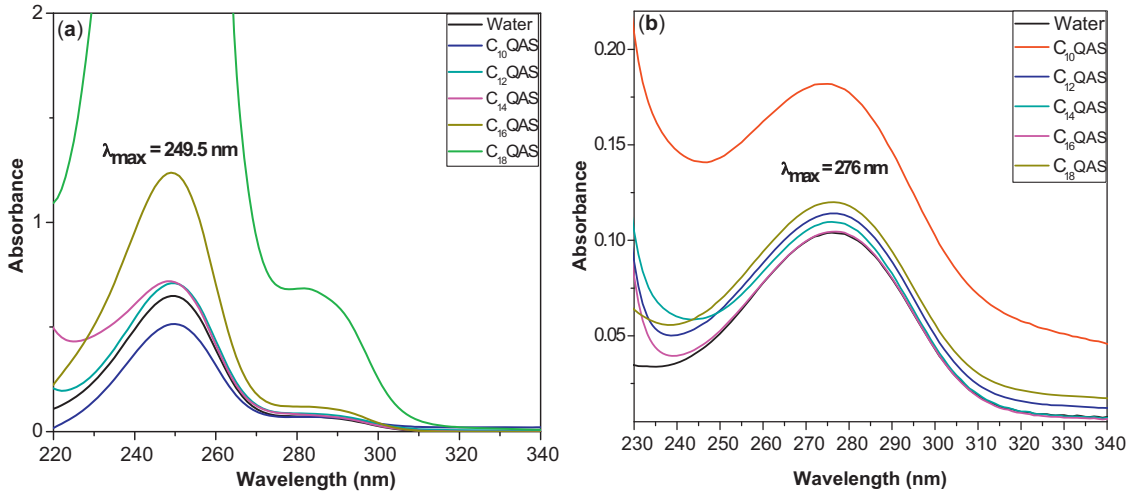


Fig. 3. UV absorption spectra of (a) benzaldehyde and (b) cyclohexanone in water and in aqueous solutions of different QASs (conc.: 15 mM).

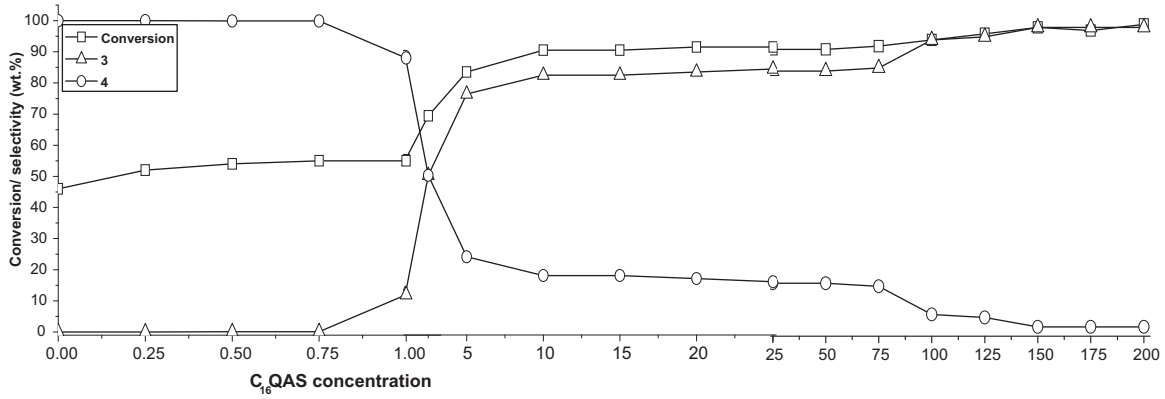


Fig. 4. Conversion and products selectivity in base catalyzed cross aldol condensation of benzaldehyde and cyclohexanone in NaOH-C_{16}QAS miceller solutions of different concentrations [reaction condition: 10 mmol benzaldehyde, 5 mmol cyclohexanone, 5 mmol NaOH, 10 mL aqueous surfactant solution, 60 °C, 30 min].

concentrations (from 1 mM to 200 mM) to study the effect of surfactant concentration on the reaction. The result (Fig. 4) shows that surfactant concentration has significant effect on the micellar catalyzed aldol reaction showing variation in cyclohexanone conversion and selectivity of products (**3** and **4**) with surfactant concentration.

The cyclohexanone conversion was slightly higher in the reactions using surfactant solutions with less than 1 mM concentration as compared to the biphasic reaction (surfactant free solution); and like biphasic reaction only mono-condensation product (**4**) was formed in these solutions showing that micelles are not involved in the catalysis of reaction. At 1 mM concentration of surfactant (which is CMC of pure C_{16}QAS in water), the conversion was not much changed but the di-condensation product (**3**) was started to be formed (12% selectivity) indicating the involvement of micelles in the catalysis of reaction facilitating di-condensation reaction. The increasing conversion and selectivity of **3** with increasing surfactant concentration from 1 mM to 10 mM is indicative of the important role of micelles in promotion of di-condensation reaction. Further increase in surfactant concentration from 10 mM to 75 mM shows very small rise in conversion and selectivity to **3** in the reactions. However, when the surfactant concentration was increased from 75 mM to 150 mM, significant increase in conversion and selectivity of **3** was observed (99% conversion with >99% selectivity to **3**). This study clearly shows the significance of increasing surfactant concentration for enhancement of reaction rate and selectivity of desired product in micellar catalyzed aldol reactions. For cross aldol reaction of benzaldehyde with *n*-heptanal, the highest cross product selectivity was also obtained in the reaction using 200 mM C_{16}QAS micellar system [5].

3.2.2. *Characterization of reactant-C_{16}QAS micellar systems*

In C_{16}QAS solutions of different concentrations (15 mM, 50 mM, 100 mM and 200 mM), the droplet size of benzaldehyde was seen to be decreasing (Fig. 5) with increasing surfactant concentration. The decrease in size of benzaldehyde droplets is attributed to increasing number of micelles in the solution on increasing surfactant concentration, which deplete the benzaldehyde droplets into smaller emulsion droplets. The repulsive force between the positively charged micelles at high surfactant concentration may reduce the size of micelles showing the decreased droplet size at high surfactant concentration [29]. From the optical microscopy results it was found that with increasing concentration of surfactant in solution, the increased number of micelles helps in splitting up bigger droplets of benzaldehyde in smaller size as well as create huge interfacial area for interaction of hydrophobic and water soluble components to undergo reaction giving enhanced conversion at high surfactant concentration.

The UV absorptions of benzaldehyde and cyclohexanone in water and in C_{16}QAS solutions of different concentrations (0, 5, 50, 100, 150 and 200 mM) were also measured by using their solutions. The gradually increasing intensity of characteristic UV bands of benzaldehyde and cyclohexanone (Fig. 6a and b) with increasing the surfactant concentration can be ascribed to their increasing solubilization or high localized concentration in the micelles. The solubility of aromatic aldehydes (benzaldehyde and *p*-methylbenzaldehyde) in aqueous solutions of non-ionic surfactants (polyoxyethylene glycol ethers) has been reported to be increasing with surfactant concentration [30]. The λ_{max} for benzaldehyde was observed to be slightly shifted to lower wavelength (i.e., blue shift) with increasing surfactant concentration. This shift is indicative of benzaldehyde molecule's interaction with C_{16}QAS molecules in the micelles; probably this interaction can be between functional groups of benzaldehyde (aldehydic group) and surfactant head group (ammonium group). The UV absorption study showed that on increasing the concentration of surfactant in solution, the increased solubility of reactants promotes the reaction giving high conversion at high surfactant concentration.

The ^{1}H NMR techniques have been widely used to investigate the location and orientation of the organic compounds as probe molecules in the micelles by studying the differences in chemical shifts of the probe molecules [31–33]. The ^{1}H NMR analysis of reactants (benzaldehyde and cyclohexanone) in C_{16}QAS solutions of different concentration revealed the location, orientation and interaction of reactant molecules within the micelles/emulsion droplets. The ^{1}H NMR spectra (Fig. 7) of benzaldehyde in 1 mM and 15 mM surfactant solutions show the shielding of aldehydic and aromatic protons indicating the location of solubilized benzaldehyde molecules in the core of micelles or emulsion. In the solutions with higher surfactant concentrations (50–250 mM), the benzaldehyde molecules seems to be located in hydrophilic zone/Stern layer of micelles showing the deshielding of aldehydic proton of benzaldehyde. At higher surfactant concentrations, the *ortho* protons of benzaldehyde are also slightly deshielded but *meta* and *para* protons are always observed to be shielded. The highest deshielding of aldehydic proton (—CHO) as compared to aromatic protons (*o*-, *p*- and *m*-^{1}Hs) with increasing surfactant concentration revealed that the —CHO group of benzaldehyde must be orientated toward interface and aromatic ring is embedded in the micelle. It is usually observed that a substituted aromatic molecule (with polar group) is solubilized in a micelle with an orientation such that the polar group directs toward the bulk water phase [12,32]. With

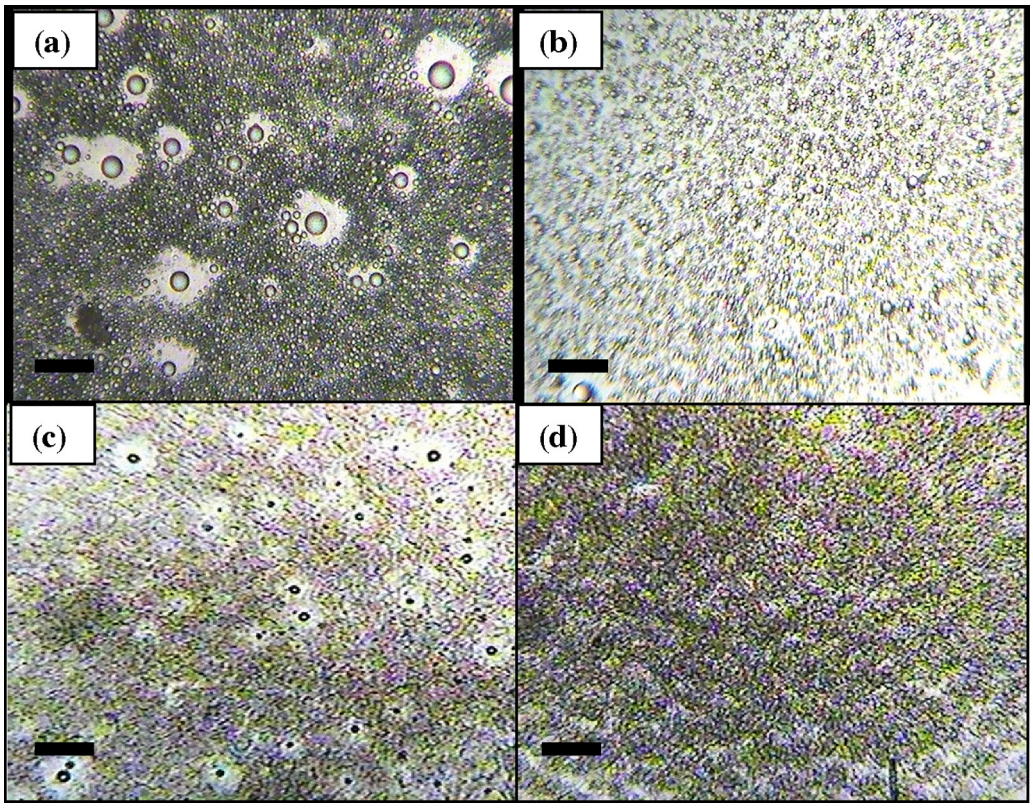


Fig. 5. Optical micrographs of benzaldehyde droplets in (a) 15 mM C_{16}QAS, (b) 50 mM C_{16}QAS, (c) 100 mM C_{16}QAS and (d) 200 mM C_{16}QAS micellar solutions (the scale bar equals 200 μm).

increasing the surfactant concentration from 50 mM to 250 mM, the gradually increasing deshielding of aldehydic proton of benzaldehyde indicates that benzaldehyde molecules are successively moving toward Stern layer. It shows that at very high surfactant concentrations, the benzaldehyde molecules are located in the Stern layer of micelles or at interface. The interaction of quaternary ammonium group of surfactant molecules with —CHO group of benzaldehyde may also cause the deshielding of aldehydic proton (Scheme 3i). The shift in UV band of benzaldehyde also shows the benzaldehyde molecule's interaction with C_{16}QAS molecules in the micelles. The similar interaction has been reported for solubilization of ketocyanine dyes in cationic surfactant micelles by interaction of carbonyl group of dye molecules and surfactant's head group [14].

Above 100 mM concentration, the *ortho* protons of benzaldehyde are also deshielded showing that *ortho* positions are also in hydrophilic zone at higher C_{16}QAS concentration. The *meta* and *para* protons of benzaldehyde molecules also show slight shielding and deshielding effect with variation in surfactant concentration showing interaction of *meta* and *para* protons with surfactants molecules. However, the *meta* and *para* protons always remain shielded which indicates that the *meta* and *para* positions are located in hydrophobic zone of micelles. The protons of cyclohexanone molecules were not much influenced by micellar system

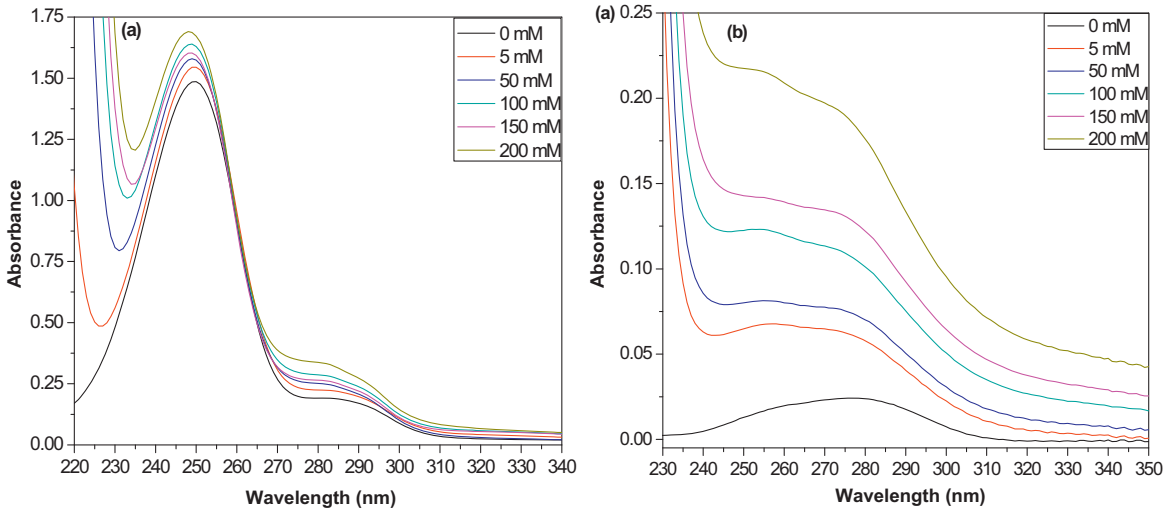


Fig. 6. UV absorption spectra of (a) benzaldehyde and (b) cyclohexanone in aqueous solutions of C_{16}QAS at different concentrations (0, 5, 50, 100, 150 and 200 mM).

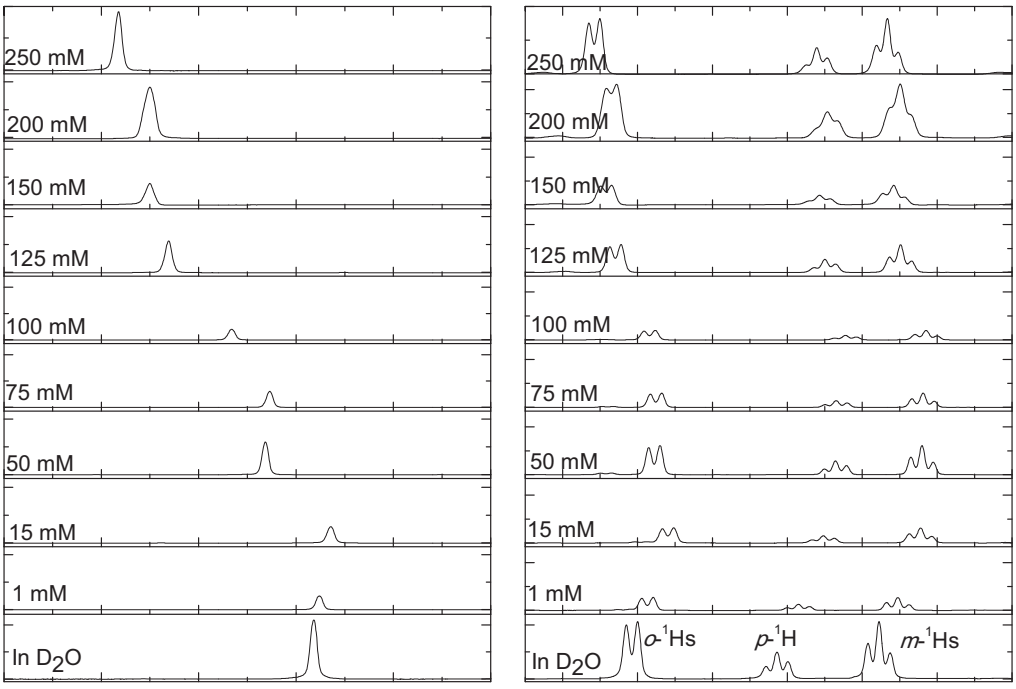
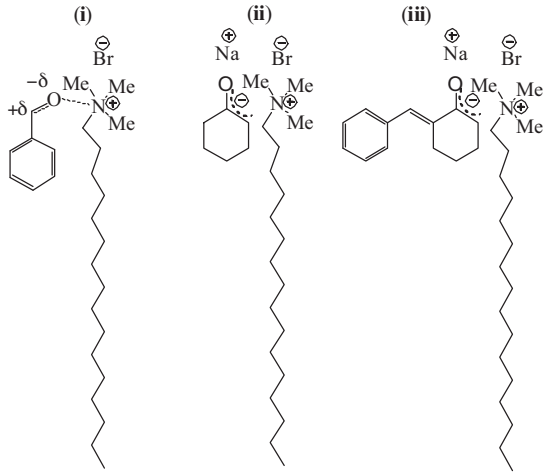


Fig. 7. ^{1}H NMR signals for aldehydic proton and aromatic protons of benzaldehyde in C_{16}QAS solutions of different concentrations.



Scheme 3. Interactions of (i) benzaldehyde, (ii) enolate ion of cyclohexanone and (iii) enolate ion of mono-condensation product (α-benzylidene cyclohexanone) with quaternary ammonium surfactant (C_{16}QAS) in the micellar system.

showing no significant change in chemical shifts of α, β and γ methylene protons of cyclohexanone molecules in ^{1}H NMR spectra (Fig. 8).

The weak intensity of the signals for the protons of benzaldehyde and cyclohexanone in the 1–150 mM surfactant solutions as compared to pure D_2O solution is indicative of tight packing of solubilized reactant molecules within the micelles. At higher concentrations (200 mm and 250 mm), the intensity of the signals again increased showing comparatively less tight packing of the reactant molecules in the micelles. This may be attributed to elongation of micelles at higher concentration [29], which will have loosely packed surfactant molecules with their parallel orientation within the micelles (See ESI; Scheme 4). The less compact molecular packing in these micelles can accommodate more number of reactant molecules at interface. The interaction of —CHO group of benzaldehyde molecules with surfactant molecules and parallel orientation of loosely packed surfactant molecules in the micelles at high surfactant concentrations might be forcing the benzaldehyde molecules to be located at the stern layer.

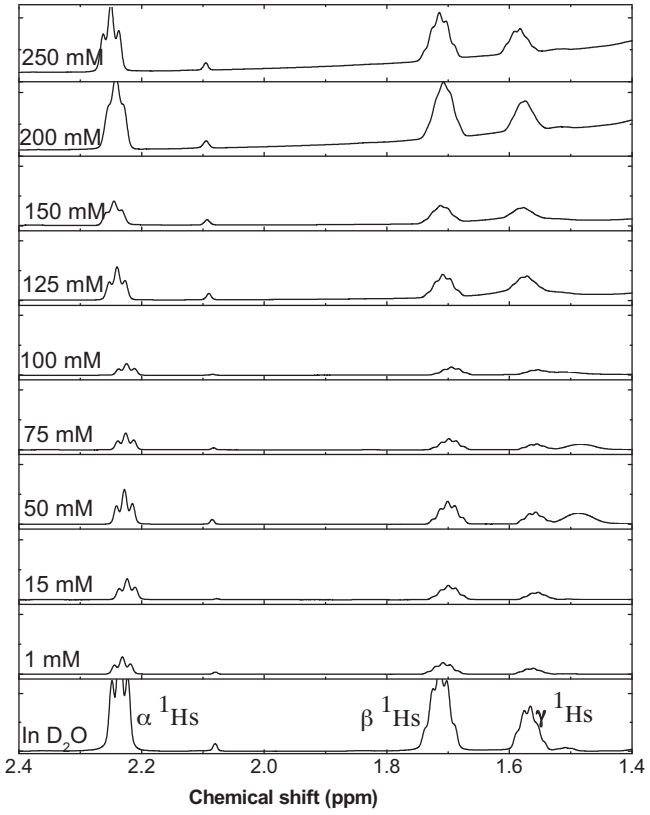
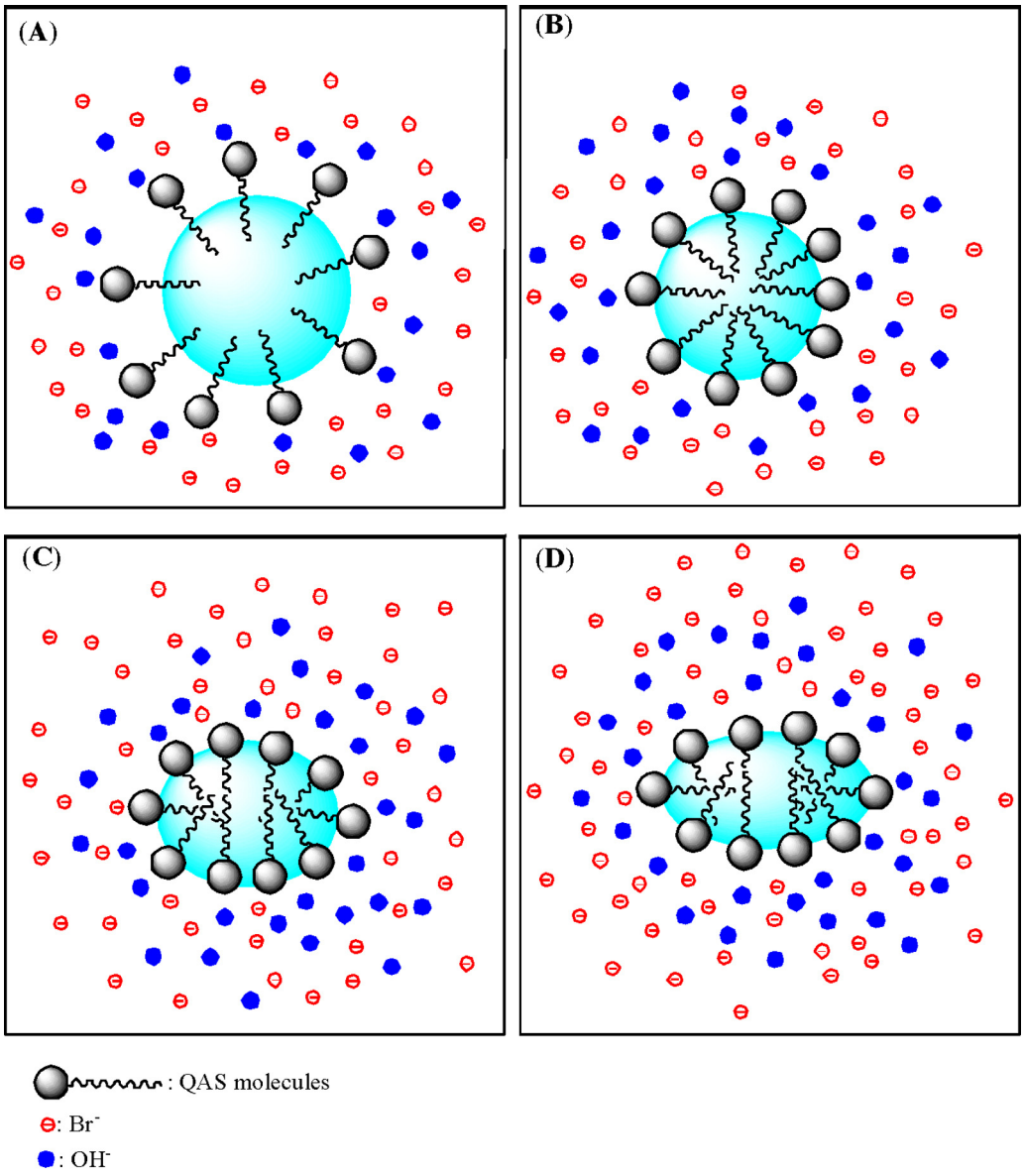


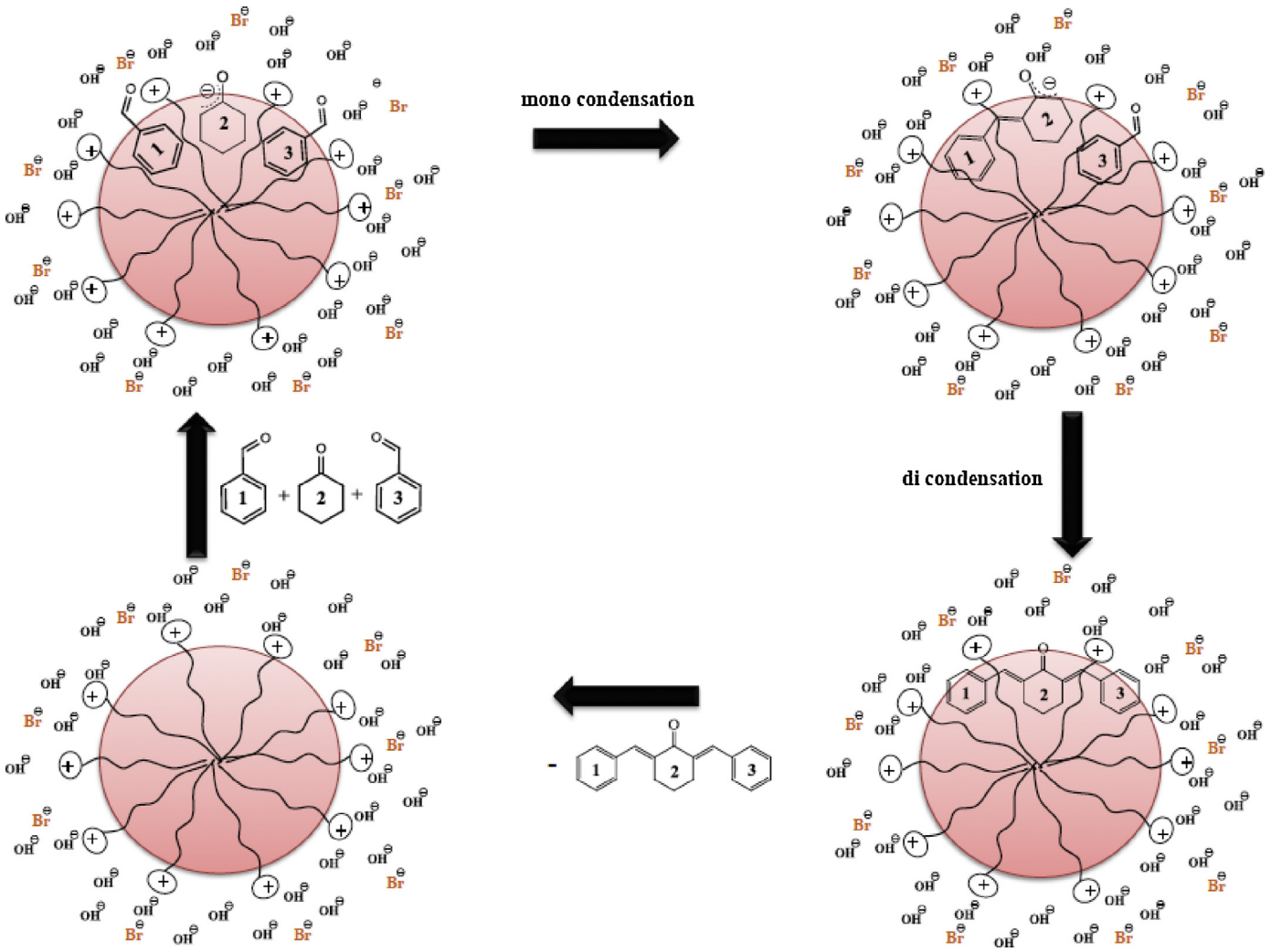
Fig. 8. ^{1}H NMR signals for different protons of cyclohexanone in C_{16}QAS solutions of different concentrations.

From the optical microscopy results it is evident that the fast conversion with C_{16}QAS micellar system at high concentration may be due to increased number of micelles, which will split up



Scheme 4. Schematic presentation for decreasing size of different C_{16}QAS micelles/emulsion droplets having solubilized reactants with increasing surfactant concentration (from A to D surfactant concentration gradually increases).

benzaldehyde phase into smaller droplets and create large interfacial area for interaction with water soluble components (cyclohexanone's enolate, OH^- ions, etc.) for reaction making the reaction faster. The UV and ^1H NMR studies revealed that higher surfactant concentration in the micellar solution not only creates large interface and solubilize the reactant molecules but also it helps in orienting the reactant molecules (e.g., benzaldehyde) in large proportion at interface or in Stern layer. The high solubilization of cyclohexanone in micelles at higher concentration of surfactant and stabilization of the cyclohexanone's enolate (Scheme 3ii) also enhance the rate of reaction. Furthermore, largely populated activated benzaldehyde molecules at interface may also promote the di-condensation of cyclohexanone giving highest selectivity of **3** at higher concentration of surfactant. The loosely packed surfactant molecules in elongated micellar system (at high surfactant concentration) can accommodate the reaction intermediate (**4**) at interface in its stabilized enolate form (Scheme 3iii) for further condensation with benzaldehyde. At lower surfactant concentration, cyclohexanone is less available with micelles (most of the cyclohexanone molecules are in aqueous medium) and the solubilized benzaldehyde molecules are also mostly located in the core of micelles, which reduces the benzaldehyde concentration at Stern layer/interface showing slow conversion with formation of significant amount of mono-condensation product. The very high deshielding of aldehydic proton at higher surfactant concentration, which may be due to interaction of carbonyl oxygen of benzaldehyde with quaternary ammonium group, indicates that the benzaldehyde molecules are in activated form (having more electrophilic carbonyl carbon) for electrophilic reaction with enolate of cyclohexanone. The plausible mechanism of micellar system catalyzed cross aldol reaction of benzaldehyde and cyclohexanone is shown in Scheme 5. The micellar system (micelles/emulsion) orients the benzaldehyde molecules and cyclohexanone/its enolate ions (either formed at interface from solubilized cyclohexanone or came from aqueous medium) at interface to form mono-condensation product, which remains at interface and further undergoes reaction (through its enolate ion) with second molecule of benzaldehyde to di-condensation product. The study shows that the micellar system with high surfactant concentration (>150 mM) is more appropriate medium for the aldol reaction. The similar



Scheme 5. Plausible mechanism of micellar catalysis of cross aldol reaction (selective di-condensation) of benzaldehyde and cyclohexanone to α,α′-bisbenzylidene cyclohexanone using NaOH-QAS micellar system.

observation was reported for cross aldol reaction of benzaldehyde and *n*-heptanal; the highest cross product (jasminaldehyde) selectivity was obtained with 200 mM C_{16}QAS micellar system [5]. It is evident from the present study that the highest cross product (jasminaldehyde) selectivity achieved at high C_{16}QAS concentration (200 mM) might also be attributed to presence of significantly more number of activated benzaldehyde molecules at Stern layer of micelles or interface of emulsion.

4. Conclusion

The quaternary ammonium surfactant chain length and concentration were found to be playing important role in the micellar catalysis of cross aldol reaction showing influence over reaction rate and products selectivity. The QAS surfactant micelles with C_{16} alkyl chain possess optimum properties and/or microenvironment for the reaction giving highest conversion rate and selectivity toward desired cross aldol product in NaOH-micellar catalyzed reaction of benzaldehyde and cyclohexanone. The C_{16}QAS micellar system with high surfactant concentration (>150 mM) made the reaction faster giving selectively complete conversion to desired product. The characterization of reactant molecules in micellar solutions of different concentrations by optical microscopy, UV–vis and ^{1}H NMR analyses revealed that large interface, high localization of reactant molecules in active form preferably near the interface at high surfactant concentration promote the reaction selectively to the desired product with faster rate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.09.023.

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