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Micellar Catalysis Strategy of Cross-Condensation Reaction: The Effect of Polar Heads on the Catalytic Properties of Aminoalcohol-Based Surfactants

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Abstract

The effect of the polar head and the concentration of quaternary ammonium surfactants (C_{14}EtOH, C_{14}iPrOH, C_{14}PrOH, where, 14 = carbon number iPrOH = iso-propanol, EtOH = ethanol, PrOH = propanol) in micellar catalysis for the cross-condensation reaction (Claisen–Schmidt) was investigated. The reaction in the *Micellar-NaOH system* with different concentrations of surfactants above the critical micelle concentration from 15 to 30 mmol between benzaldehyde and acetophenone was used as a model of reaction for this study. The examination of the effectiveness of the catalytic activity reveals that the compound C_{14}EtOH has the best yield (80% of the desired product), followed by C_{14}iPrOH and C_{14}PrOH. The results were interpreted according to the solubilization capacity, droplet size analysis of reagents (benzaldehyde and acetophenone) in the micellar medium and stability of reaction intermediate (enolate) by the electrostatic interactions generated by positive charge of N^+ quaternary ammonium atom. Therefore, the quantum calculations carried out by DFT method for surfactants in the aqueous medium, show that electrophilicity degree and the reaction yield% for three cationic surfactants varies in the same following order: $C_{14}PrOH < C_{14}iPrOH < C_{14}EtOH$.

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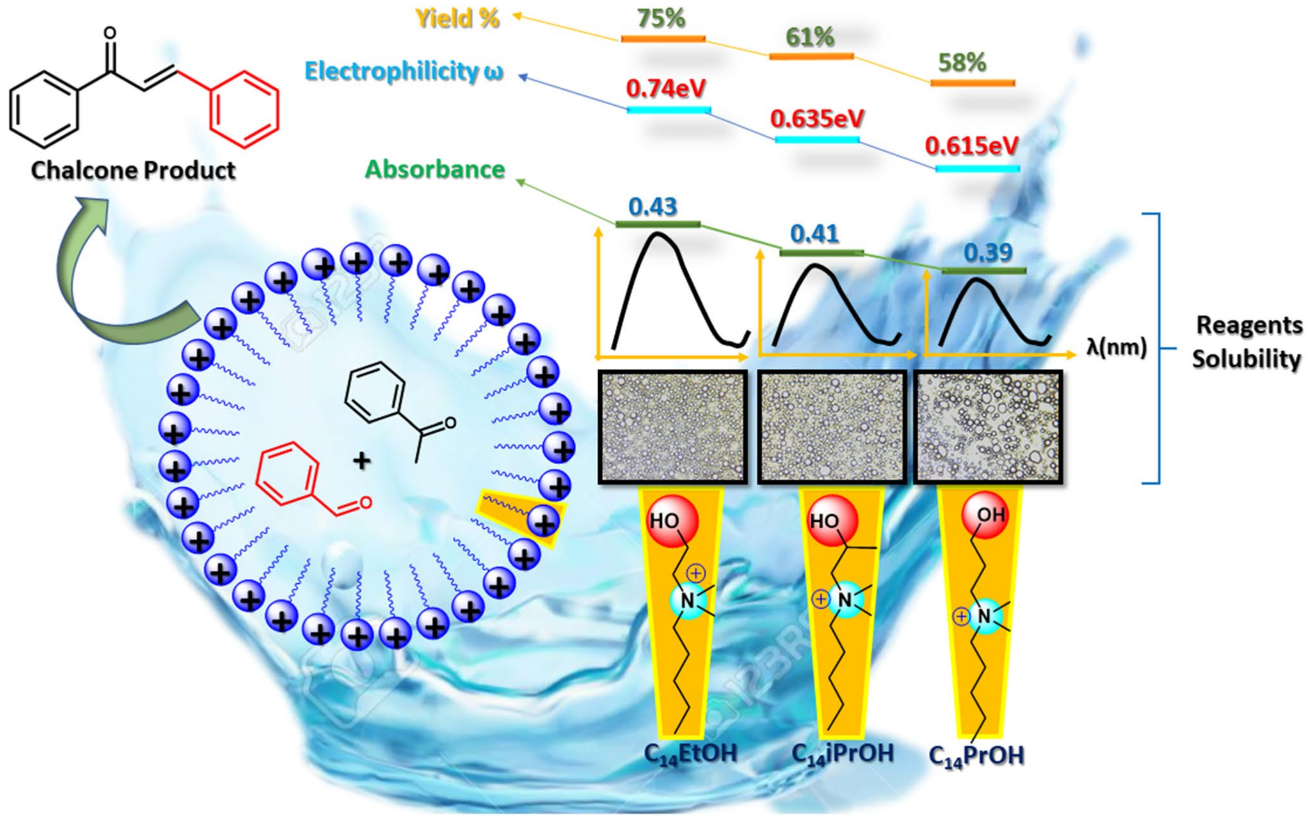
Graphic Abstract



Keywords Cationic surfactant · Micellar-catalysis · Claisen–Schmidt · Cross condensation · Electrophilicity

1 Introduction

The α, β-unsaturated ketones (Chalcones) are the class of compounds possessing different biological activities: antimicrobial, antimalarial, anti-inflammatory [1], anticancer [1, 2], antifungal, antibacterial [3] and inhibit leukotriene B4 [4]. They constitute an important precursor for the synthesis of heterocyclic compounds such as pyrimidines, pyrazolines, isoxazolines, flavonoids, isoflavonoids [5–8].

The Chalcones are commonly prepared via Claisen–Schmidt condensation between acetophenones, and aromatic aldehydes in an organic solvent under acidic or basic homogeneous conditions, or even using heterogeneous basic systems: alumina [9], zeolites [10], natural phosphates alone or activated with an ammonium salt [11]. However, most of this catalyst has several disadvantages including the use of toxic solvents, high-temperature reaction, and long reaction time, which limit their industrial applications.

The ecological procedure for organic synthesis is the replacement of volatile organic solvents by green reaction media. Volatile organic solvents are the major contributors to environmental pollution due to their abundant use (more than 85% of the total mass utilization of a chemical process) and incomplete recovery efficiency (50–80%) [12].

In this context, water is the most preferred solvent for an organic reaction, with several advantages such as its co-catalytic activity [13–15] nontoxic, abundant, nonflammable, and renewable. Furthermore, the use of water as a solvent accelerates the rates of the organic reaction and improves reaction selectivity, even when the reagents are poorly soluble or insoluble in this medium [16]. The use of surfactant molecules in an aqueous medium can solve the problem of the low solubility of organic reagents. The formation of micelles in aqueous media favors organic reactions by the concentration of organic compounds in micelles [17–19]. In micellar systems formed by cationic surfactants, the base-catalyzed condensation reactions show their efficiency compared to the biphasic system (absence of surfactants) [20–23]. Thus, surfactants with different types have sometimes been used for aldol condensation reaction [20, 24–27], the participation by which surfactants are involved in catalytic reactions is known as micellar catalysis [21, 28–30] or phase-transfer catalysis [31, 32].

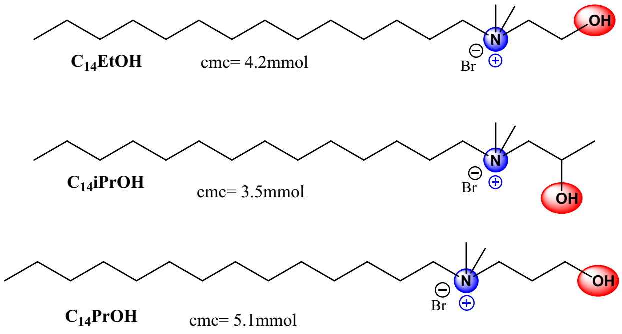
The catalyzed acid–base reactions are by far the most numerous, and well-studied reaction types [33–36], in which the organic functional groups undergo a series of different transformations with nucleophilic reagents in the presence of acids or bases as catalysts, among these types of reactions: the base-catalyzed (Claisen–Schmidt) condensation (Scheme 2) which generally involves the formation of the anion of acetophenone followed by its attack on the carbonyl group of benzaldehyde [37]. According to their required orientation in the micellar regions [37–40], the aromatic organic reagents (aldehydes and ketones) and the reaction intermediates (enol) undergo electrostatic interactions with the cationic polar head of the surfactants which remains among the factors responsible for the modification of the reaction rates [23, 38]. In the base-catalyzed condensation, reaction the positively charged micellar surface can increase the local pH in the micellar region because of the Colombian forces, allowing to attract more bases to the micellar interfaces [41, 42].

In this study, the cross-condensation reaction was made between acetophenone, and benzaldehyde as a model of reaction, in the Micellar catalysis-NaOH system for three new synthesized QAS with different polar heads (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH). The difference in the efficiency presented for the condensation reaction in the different micellar environment studied was discussed by comparing the surfactant capacity to solubilize the reagents in the reaction media, as well a microscopic study was introduced to distinguish the different texture of the dispersion (droplet size) of the reagents in the micellar media at different concentrations of surfactants. Furthermore, the study of the effect of the ionization degree (α) has been investigated to include the effect of the positive charge of the micelle to increase the local pH at the micellar interfaces. The electrostatic affinity between the positive heads N^+ of micelles with the solubilized substances (enolate intermediate, benzaldehyde, and acetophenone) in the micellar interface was estimated by the study of the degree of electrophilicity of the surfactant molecules in the aqueous medium. The calculation by the functional density theory, method associated with the non-local-Parr (B3LYP) was made in an aqueous medium for the two possible forms in which the catalytic support is presented in interaction with the counter-ion (Br^- and OH^-), in the reaction medium.

2 Experimental

2.1 Materials and Methods

4-Chlorobenzaldehyde, 4-methoxybenzaldehyde (99%), 4-methylbenzaldehyde (99%), benzaldehyde (99%), acetophenone (98%), sodium hydroxide (NaOH, 97%), Magnesium sulfate ($MgSO_4$, 95%), sodium chloride for analysis (NaCl, 99%), concentrated hydrochloric acid (35% HCl) were purchased from Sigma Aldrich. Solvents such as chloroform (99%), ethyl acetate (99%), dichloromethane (99%), hexane (99%) and ethanol absolute were obtained from Fluka. 3-(dimethylamino)propane-1-ol (> 99%), 1-(dimethylamino)propane-2-ol (> 99%) and 2-(dimethylamino)Ethan-1-ol (> 99%) were purchased from Fluka, the 1-bromododecane (> 97%), acetonitrile, dichloromethane, methanol, and sodium bromide, were purchased from Sigma Aldrich. All these chemicals were used without further purification.



Scheme 1 The three types of synthetic cationic surfactants, C_{14}EtOH, C_{14}iPrOH, and C_{14}PrOH

2.2 Preparation of Catalytic Support

The series of *N*-(*n*-hydroxyalkyl)-*N*, *N*-dimethyl *n*-alkyl ammonium bromide (Scheme 1) referred to as C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH (n = 14 carbons, EtOH = ethanol, PrOH = propanol, iPrOH = iso-propanol) were synthesized and characterized according to the procedure well detailed in our previous work [43]. The CMC values for synthetic cationic surfactants were determined in aqueous using the electrical conductivity (Fig. 1).

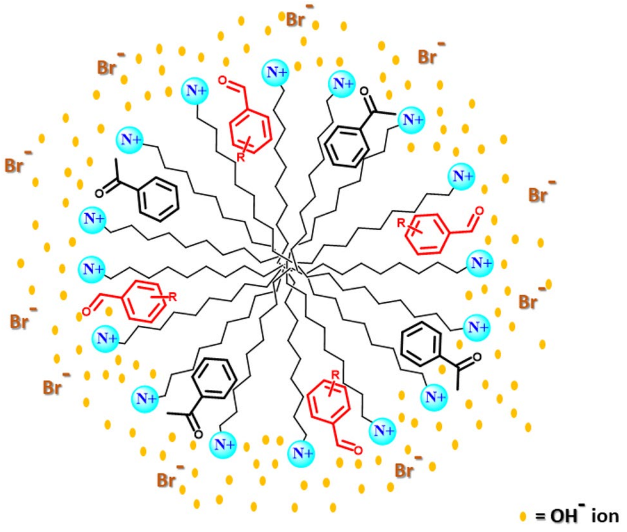
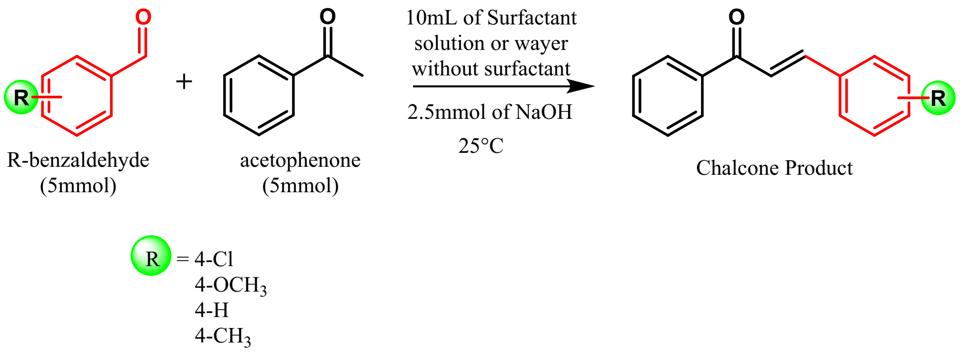


Fig. 1 Positively charged micelles of Cationic Surfactants having solubilized reactants within the micelles and surface OH^-ions

Scheme 2 Cross-condensation (Claisen–Schmidt reaction) of R-benzaldehyde (5 mmol) and acetophenone (5 mmol) in Micellar catalysis–NaOH/Water–NaOH



2.3 General Procedure for the Preparation of Chalcones in Micellar Systems NaOH-Surfactant

In a 50 ml flask, we have introduced 10 ml of aqueous solution surfactant at a required concentration above the (CMC) from 15 to 30 mmol, or water without surfactant. Then, a mixture of R-benzaldehyde (5 mmol) and acetophenone (5 mmol) (Scheme 2) was added. Likewise, an amount of NaOH (2.5 mmol) was dissolved in the reaction mixture with stirring at temperature t = 25 °C and for the required time. The progress of the reaction was monitored by TLC using a solvent system ethyl acetate: hexane (1:2, by vol), the spots were visualized under UV light. Once the reaction was completed, a saturated NaCl solution was added to the reaction mixture to reduce the surfactant concentration below the CMC and to release the maximum of synthesized products (Chalcone) from the micelles. The product formed undergoes neutralization under filtration with a concentrated solution of HCl. The product obtained was dissolved in 25 ml of dichloromethane to remove traces of water, using $MgSO_4$ desiccant. As soon as the traces of water are removed, evaporation under vacuum was carried out to remove the dichloromethane solvent. The dried product obtained was recrystallized in a volume of 5 ml of absolute ethanol. The structure of the Chalcone products after recrystallization was verified by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), recorded by using a Bruker spectrometer at 600 MHz (^{1}H) and 151 MHz (^{13}C) and Melting point.

2.4 Ionization Degree α

The ionization degree α is defined as the fraction of charge of the counter-ions not bound to the micelle. In other words, α makes it possible to quantify the proportion of counter-ions that are completely hydrated away from the micelle, respecting the set of counter-ions. α also allows determining the degree of bonds β which represents the fraction of dissociated counter-ions, sites on the micellar surface, which means that the fraction of the charges got neutralized on the micellar surface. For a surfactant with a single ionic head group, the degree of bonds is $\beta = 1 - \alpha$ [44].

The value of α, in reality, gives an idea of the size of the cloud of counter-ions around the charged micellar sphere which also gives an idea of the degree of electrostatic affinity between the counter-ion and the charged micellar surface.

The α can be determined by the potentiometric measurements, conductivity, electrophoretic mobility or by NMR [45].

In this current study the degree of ionization α is obtained by the conductivity (Fig. 2) method using the *Thermo Scientific Orion Star Conductor A212 Benchtop Conductivity Meter* of a constant cell K equal to 0.4750 cm^{-1}, the curve of the specific conductivity κ in (μS/cm), for cationic surfactant as a function of its concentration C in mol/L at pH 7 and t = 25 °C, represents two straight lines before, and after the CMC, the ratio of the slopes of these two lines S_1 and S_2 are

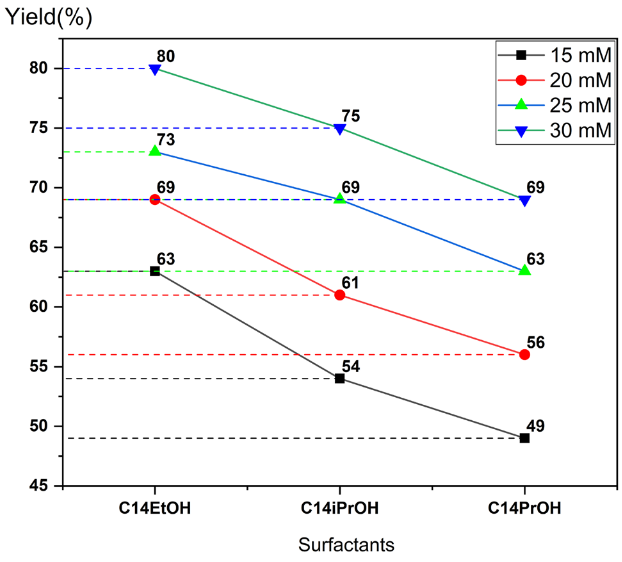


Fig. 2 The yield (%) of the condensation reaction (Claisen–Schmidt) between benzaldehyde and acetophenone as a function of surfactant concentration (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH) from 15 to 30 mmol in the Micellar catalysis–NaOH system (0.25 mmol of NaOH and at t = 25 °C)

used to calculate the value of α according to the following relation (Eq. 1) [46].

$$\alpha = \frac{S_2}{S_1} \tag{1}$$

2.5 Absorbance Measurements

The absorbance spectra of the benzaldehyde (0.05 mmol)—water and acetophenone (0.05 mmol)—water mixtures at different surfactant concentrations from 15 to 30 mmol were performed separately using a *Jasco V-630 UV–visible spectrophotometer* with quartz cups. The change in absorbance value from 200 to 400 nm in the presence of a surfactant was determined by using water as a reference.

2.6 Microscopic Analysis

The dispersed media of the aqueous solutions of the benzaldehyde (5 mmol) and acetophenone (5 mmol) in the presence and absence of surfactants at different concentrations from 15 to 30 mmol were analyzed separately by using an optical microscope. Images captured for the drops of the analyzed solutions were visualized at × 10 objective lance magnification.

2.7 Quantum Chemical Parameters Calculations

Quantum chemical methods and molecular modeling techniques help to define a large number of molecular descriptors characterizing the reactivity, the form and binding properties of a complete molecule as well as molecular fragments and substituents.

The use of the theoretical parameters makes it possible to characterize the compounds and their various fragments and substituents of their molecular structure and also to prove the mechanism proposed to be taken into consideration in terms of reactivity of the compounds studied [47]. The computational chemistry [the functional density theory (DFT)], was used, as a tool to know the availability in each case of N^+ as active sites with respect to the position of the OH alcoholic function for the three types of synthetic surfactants (C_{14}iPrOH, C_{14}EtOH, C_{14}PrOH). Calculations were performed with the non-local exchange–correlation function B3LYP [48], the solvent was treated with self-consistent reaction field theory (SCRF) [49], All quantum calculations were performed by using Gaussian software 09 [50] for Windows. Then, several quantum chemical parameters in terms of the descriptors in the aqueous phase have been determined, namely: Highest occupied molecular orbital energy (E_{HOMO}), low unoccupied orbital energy (E_{LUMO}), gap energy between E_{LUMO} and E_{HOMO} (ΔE). To complete the vision on the property of these molecules, other descriptors have been calculated as electronegativity (χ), the corresponding hardness (η), softness (σ) and electrophilicity (ω), of cationic surfactants molecules, are given using equations (Eq. 2) [51], (Eq. 3) [51, 52] and (Eq. 4). For electrophilic index (ω) it combines softness and chemical potential given by equation (Eq. 5) [48].

$$\chi = \frac{[E_{LUMO} + E_{HOMO}]}{2} \tag{2}$$

$$\eta = \frac{[E_{LUMO} - E_{HOMO}]}{2} \tag{3}$$

$$\sigma = \frac{1}{\eta} \tag{4}$$

$$\omega = \frac{\chi^2}{2\eta} \tag{5}$$

3 Results and Discussion

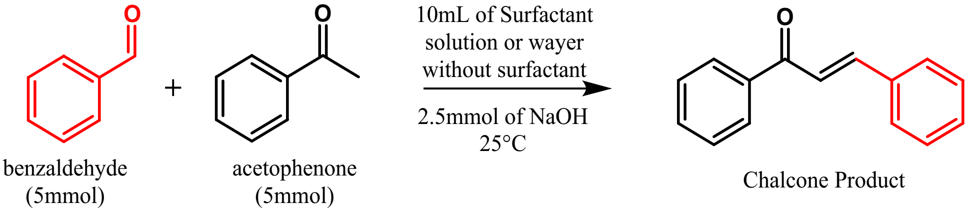
The Claisen–Schmidt reaction was first carried out between benzaldehyde and acetophenone (Table 1) at t = 25 °C in two systems*:* *Water–NaOH* and in the system *Micellar catalysis–NaOH* system (surfactants concentration = 15 mmol) for the three different surfactants with varied polar heads (Scheme 1).

From Table 1, in the biphasic system the absence of surfactants (*Water–NaOH* system) the reaction shows a low yield value (12%) for long periods (180 min) compared with the presence of surfactants (*Micellar catalysis–NaOH* system) who shows high efficiency between (49 and 63%) during a short period of time (55 min).

This necessity of high time for the reaction in the biphasic system can be attributed to the existence of a smaller interfacial surface between the aqueous, and organic phases available for an interaction between the reagents (acetophenone and benzaldehyde) and the hydroxyl anion OH^-, which causes a low probability of acetophenone to be attacked by OH^- to produce the carbanion (acetophenonate-ion) needed for the reactivity with benzaldehyde which will slow down the speed of the reaction in the Water–NaOH system.

The low efficiency of the reaction presented for the biphasic system (*Water–NaOH* system) can be attributed essentially to the formation of by-products during the condensation reaction, which has already been reported by several studies, include for example the work of Francesco et al. [53] in which, the authors show that the condensation reaction

Table 1 The isolated yields in (%) and the time in (min) for the condensation reaction between acetophenone and benzaldehyde (as a model of reaction) in two systems: Micellar catalysis–NaOH (15 mmol of surfactants–0.25 mmol of NaOH and) and in the Water–NaOH system (0.25 mmol of NaOH) at room temperatures (t = 25 °C)



Entry	Surfactants	Surfactants concentration	Reaction time (min)	Yield (%)
1	Water only	Neat	180	12
2	C_{14}EtOH	15 mmol	55	63
3	C_{14}iPrOH	15 mmol	55	54
4	C_{14}PrOH	15 mmol	55	49

between benzaldehyde and acetophenone in the aqueous medium (0.25 mol of NaOH) produces the by-products with a significant percentage of 37% of ketol compared to 8% of Chalcone dehydrated. Moreover, Vashishtha et al. [23] has found that the biphasic aldol condensation of benzaldehyde and n-heptanal in an aqueous solution of NaOH (pH 13.7) causes a decrease of the pH from 13.7 to 13.3. According to the authors, this decrease of pH was explained to the neutralization of NaOH fraction with by-products organic acids such as benzoic acid and n-heptanoic acid. Which were formed by oxidation of benzaldehyde and -heptanal, respectively in aqueous media.

On the other hand, the Claisen–Schmidt reaction in the *Micellar catalysis–NaOH* system with 15 mmol in surfactant (Table 1) shows a remarkable yield (%) between 49 and 63% depending on different surfactants (C_{14}EtOH, C_{14}iPrOH, and C_{14}PrOH). This presence of surfactant in the reaction medium does not only affect the yield but also the time of the reaction (55 min).

The rapidity (short duration) and the efficiency (high yield %) of the reaction in the micellar medium compared with lower yield (%) and longer duration (min) in aqueous media (*Water–NaOH* system) due to a large micellar surface provided by the *Micellar catalysis–NaOH* system that allows the reagents to be in interaction.

In the *Micellar Catalysis–NaOH* system with a high concentration of quaternary ammonium cationic surfactants, The positively charged micelles of the cationic surfactant molecules make it possible to concentrate the OH^- ions at the micellar interface, thus, increasing the local pH at the micellar interface [54, 55]. This favors the reagents according to their location as an aromatic compound in the polar region of the micelles [56] to be closer to the OH^- ion for the formation of acetophenonate-ion. This is why the increase in the surfactant concentration from 15 to 30 mmol in the solution for the three catalytic support (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH), causes according to Fig. 1 an improvement in the yield (%) for the reactions. This is due to the increased number of micelles and also to an increase in the micellar interface which facilitates the reactivity of the reagents (acetophenone and benzaldehyde) by the high concentration of OH^- ion in the micelle's polar region (Fig. 1).

The three catalytic supports used (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH) show different values of the yield (%) of the cross-condensation reaction. As observed in Table 1 and Fig. 2 the compound C_{14}EtOH has the best yield (%) of the condensation reaction in the *Micellar catalysis–NaOH* system at different concentrations from 15 to 30 mmol, following of C_{14}iPrOH and C_{14}PrOH respectively. This difference between the catalytic efficiency of the three surfactants used is mainly due to the existence of OH alcohol function in their polar head with different positions, which will cause a difference of the degree of steric hindrance at the polar head level, in addition to the existence of OH in the polar part can be contributed to the intramolecular electrostatic interactions Charge-Dipole type between the N^+ quaternary ammonium atom and the lone pair of the oxygen atom attached to the OH alcoholic function, reflecting as well the electrophilicity degree of micelles and the degree of steric hindrance of the polar head in the aqueous medium, which remains a very important factors, that are responsible for the increasing, and the decreasing the OH^- ion population in the micellar region.

The ionization degree α of the micelles can gives an idea of the free charge N^+ which does not contribute to the ionic bonds (electrostatic interaction) with the original counter-ion (Br^-) in aqueous solution, which gives another idea of the degree of electrophilicity of the micelles which remains a very important factor for the attraction of OH^- ions to

Table 2 The values of ionization degree (α) and bonding degree (β) calculated by equation Eq. 1

Surfactants	C_{14}EtOH	C_{14}iPrOH	C_{14}PrOH
Ionization degree α	0.32	0.29	0.33
Bonding degree β	0.68	0.71	0.67

the micellar region in the reaction medium. According to the results of α (Table 2) calculated from the slopes of the conductivity curve Fig. 3 as a function of surfactants concentration (mol/L).

It must be noted that the effect of the degree of electrophilicity of the micelle (α large) does not reflect the difference between the values of the condensation reaction yield (%) for the three catalytic supports (C_{14}EtOH, C_{14}iPrOH, C_{14}PrOH). This is why we observe according to Figs. 2 and 3 that the C_{14}PrOH which presents the high value of ionization degree $\alpha = 0.33$ (high electrophilicity of micelles), is the one that has lower reaction efficiency. On the contrary, the C_{14}iPrOH with a small $\alpha = 0.29$ value (low electrophilicity of micelles) is the one that presents an intermediate value of the reaction efficiency among the three cationic surfactants studied.

The α values presented in this work are very close, which prevents us to really draw a conclusion between the ionization degree and the efficiency of the Claisen–Schmidt condensation reaction. That is why we have introduced the comparison of the α values for a series of QAS with different alkyl chains from C_{10} to C_{16} carbon atoms with their catalytic efficiency via the cross-aldol reaction. According to Zana [46], the ionization degrees of quaternary ammonium surfactants in aqueous medium decreased from 0.27 to 0.16 depending on the increasing alkyl chain from C_{10} to C_{16}. From the work of Manu Vashishtha et al. [22], the conversion of the cross-aldol reaction increases from C_{10}QAS to C_{16}QAS which reveals that the ionization degree that's mean the degree of electrophilicity of the micelle does not reflect the OH^- ion population in the micellar polar region which does not give an idea about the difference in catalytic efficiency for different cationic surfactants.

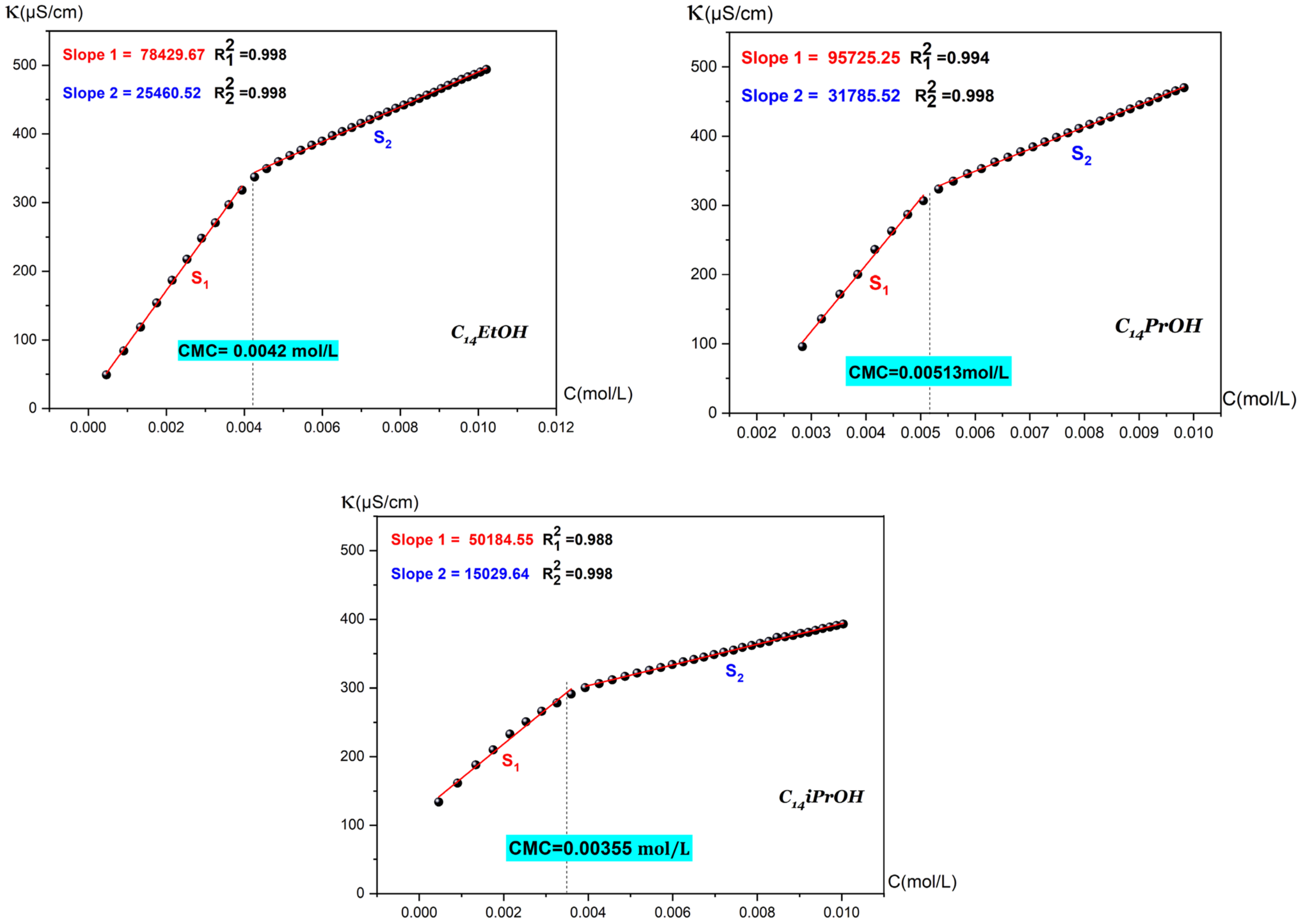


Fig. 3 The ionic conductivity in (μS/cm) for the three cationic surfactants (C_{14}EtOH, C_{14}IPrOH, C_{14}PrOH) in aqueous media as a function of their concentration in (mol/l) and the values of their slopes after (red) and before (blue) the CMC at pH 7 and T = 297.15 K

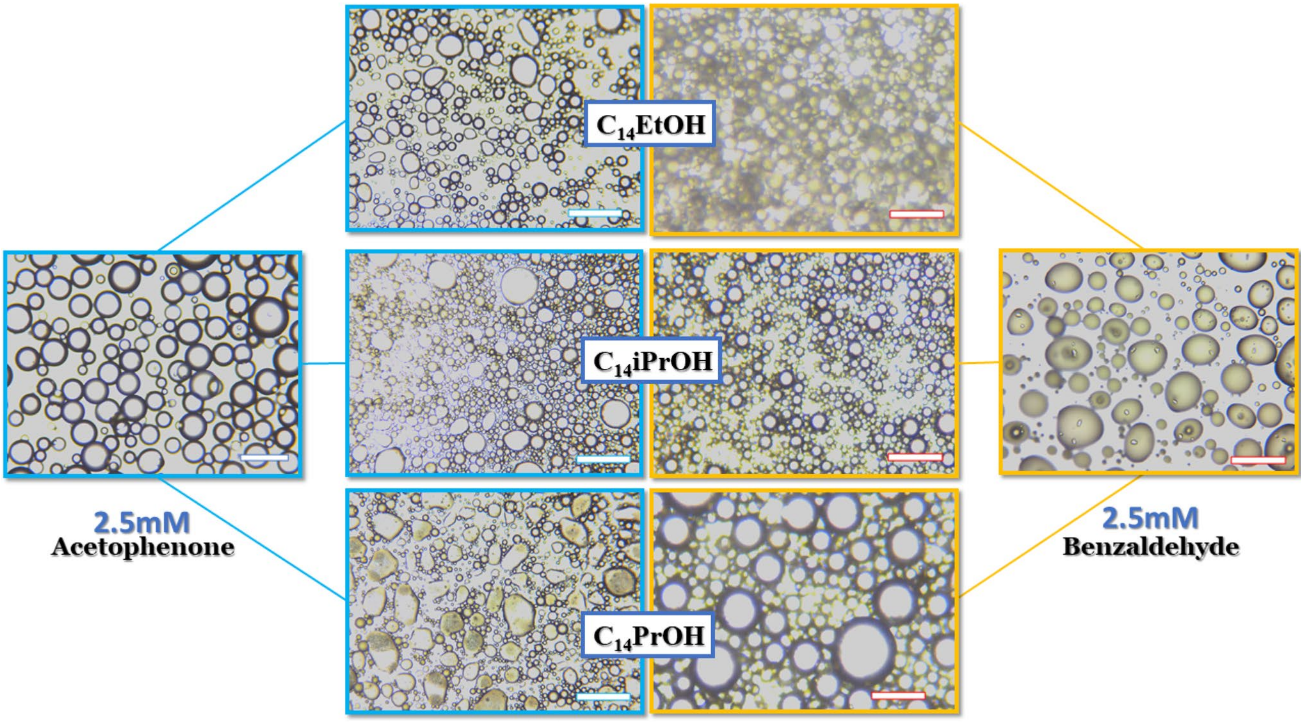


Fig. 4 Optical micrographs of benzaldehyde and acetophenone in water, and cationic surfactants solutions (C$_{14}$EtOH, C$_{14}$iPrOH, C$_{14}$PrOH) (conc.: 15 mmol; the scale bar equals 200 µm). 298.15 K

This discrepancy between the degree of electrophilicity of micelles and the yield (%) of the reaction in the Micellar catalysis–NaOH system for C$_{14}$EtOH, C$_{14}$iPrOH and C$_{14}$PrOH can be attributed to the degree of steric hindrance of the polar head which prevents OH$^-$ to integrate in the hydration region (Stern layer) for the reactivity with acetophenone. The Steric hindrance in micellar media for surfactants with different polar heads has been already mentioned in several works [20, 57, 58], as an example of the work of Sen et al. [59] who found that the planar structure of the pyridinium group of cetylpyridinium chloride provides less steric hindrance for the hydrolytic cleavage of phenyl salicylate in the Micellar–NaOH system among the three surfactants used [tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC)].

Furthermore, one of the most important properties of surfactants that are directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with the reduced thermodynamic activity of the solubilized material. Solubilization is distinguished from emulsification and miscibility (the dispersion of one liquid phase in another) [44, 60]. For a better understanding of the difference catalytic performance of the surfactants used, the miscibility of the reagents (benzaldehyde and acetophenone) in the micellar media (15 mmol of surfactants studies) was analyzed by optical microscope.

From Fig. 4 the benzaldehyde–water and acetophenone–water mixtures in the presence and the absence of surfactants (C$_{14}$EtOH, C$_{14}$iPrOH, C$_{14}$PrOH) indicates the existence of different droplet size reflecting as well the miscibility of benzaldehyde and acetophenone in water. The presence and absence of surfactants in the two reagents mixtures reflect the solubilizing and emulsifying capacities of surfactants, from Fig. 4 the optical micrographs of dispersion's textures of the reagents in the micellar media shows smaller emulsion droplets compared to those presented in the reagents-water system.

In micellar-reagent systems, the droplet size decreases from C$_{14}$PrOH > C$_{14}$iPrOH > C$_{14}$EtOH, the formed micelles allow the surfactant molecules to solubilize and emulsify the reagents in the form of droplets with different size. The increase in the surfactant concentration from 15 to 30 mmol in the micellar-reagent systems for the three catalytic support (C$_{14}$EtOH, C$_{14}$PrOH, C$_{14}$iPrOH) leads to an increase in the number of micelles in the solution, thus causing a decrease in the size of the benzaldehyde and acetophenone droplets (Fig. 5). Due to the repulsive electrostatic forces between the positively charged micelles, their size decreases at a higher concentration of surfactants, thus decreasing the

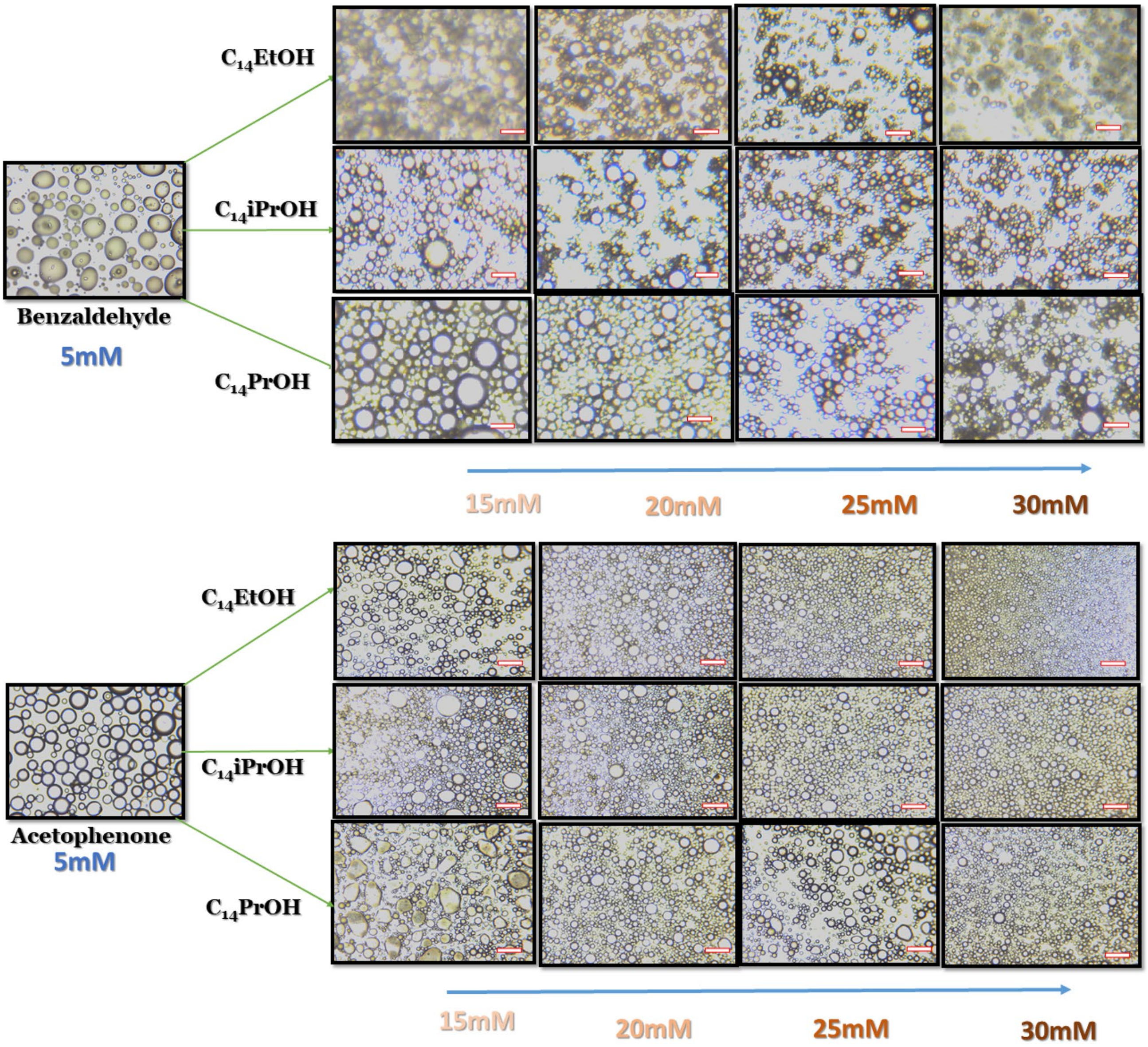


Fig. 5 Optical micrographs of benzaldehyde and acetophenone in water, and cationic surfactants solutions (C_{14}EtOH, C_{14}iPrOH, C_{14}PrOH) (conc.: 15 mmol to 30 mmol; the scale bar equals 200 µm)

size of the droplet of the reagents dispersed in aqueous solutions of surfactants with high concentrations [61].

For each surfactant, in the micellar media with different concentrations from 15 to 30 mmol, the droplet sizes of micelle-reagents vary according to the degree of miscibility between reagents and the aqueous environment from C_{14}EtOH to C_{14}PrOH thus reflecting the difference of miscibility and solubility capacities for each surfactant.

To prove this difference in solubility of the reactants with respect to the different micellar environments, the UV absorption characteristics of the reagents (benzaldehyde and acetophenone) were studied separately in water and in different micellar solutions of surfactants (C_{14}EtOH, C_{14}iPrOH, and C_{14}PrOH).

The UV absorption spectrum of benzaldehyde and acetophenone in water (Fig. 6) shows the maximum wavelength λ_{max} at 248 nm and 244 nm respectively, assigned to the transition $\pi \rightarrow \pi^*$. The absorbances bands λ_{max} of reagents in the presence of surfactants, do not present any hypsochromic or bathochromic offset. On the other hand, a hyperchromic shift with respect to the micellar environment was observed. In surfactant's solutions (15 mmol) the absorbance intensities of the reagents increase progressively as a function of the micellar environment which

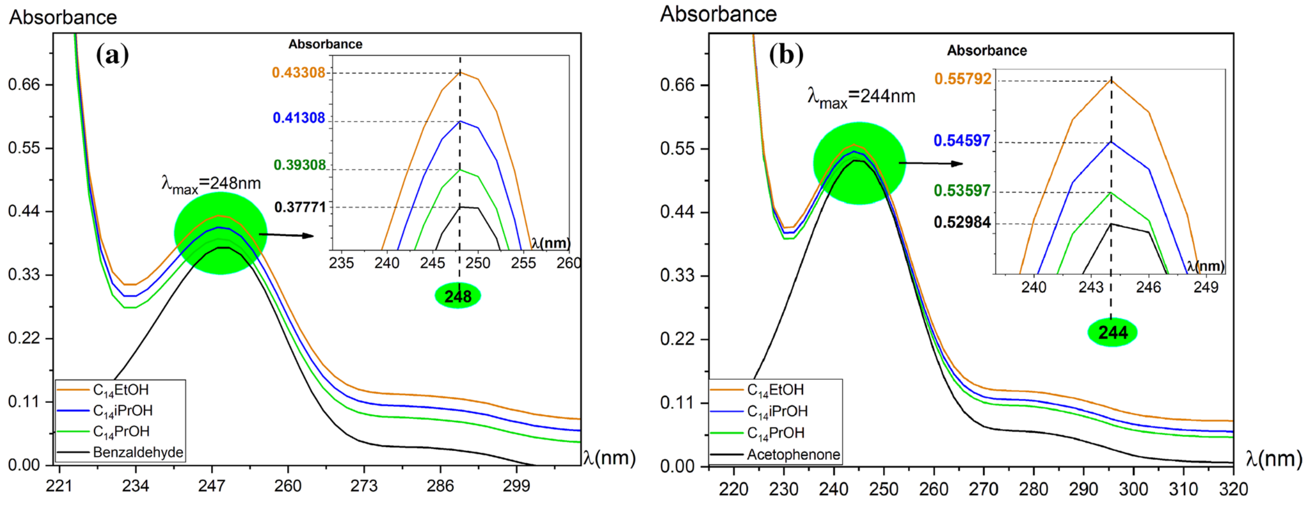


Fig. 6 UV absorption spectra of **a** benzaldehyde and **b** acetophenone in water and in aqueous solutions of different surfactants (C_{14}EtOH, C_{14}iPrOH, C_{14}PrOH) at 15 mmol of surfactants

indicates the increase of the solubilizing capacity of cationic surfactants from C_{14}PrOH to C_{14}EtOH.

In concentrated aqueous solutions of surfactants, although the shape of the micelles may be very different from that of a dilute solution, the solubilization site for a particular type of solubilizer appears to be similar to that of a dilute solution; that is, the polar molecules are mainly solubilized in the outer regions of the micellar structures, whereas the nonpolar solubilizers are contained in the inner portions.

The UV absorptions of benzaldehyde and acetophenone in the micellar solutions of C_{14}EtOH, C_{14}iPrOH and C_{14}PrOH at different concentrations from 15 mmol to 30 mmol were also studied according to Fig. 7.

The intensity of the maximum absorption bands shows an increase, as a function of the surfactant concentration in solution from 15 to 30 mmol. Thus, it's reflecting the increased solubility, which favors the cross-condensation reaction in the micellar environment in the following order: $C_{14}\text{PrOH} < C_{14}\text{iPrOH} < C_{14}\text{EtOH}$.

Several studies [38–40, 56], have been demonstrated that the polar group for substituted aromatic molecules is solubilized in a micelle with an orientation such that the polar group is directed to the aqueous phase. Vashishtha et al. [22] show using ^{1}H NMR that the benzaldehyde molecule appears to be located in the hydrophilic zone micelle (Stern layer) of cationic surfactants. The polarizability of the π-electron cloud of the aromatic nucleus and its ability to interact with the positively charged quaternary ammonium heads at the micelle-water interface may favor the adsorption of these aromatic hydrocarbons in the hydrophilic zone micelle.

In fact, the micellar surface positively charged by the polar heads of the cationic surfactants can help to populate and stabilize reagents (acetophenone and R-benzaldehyde) and intermediates such as enolate ions at the micellar interface, thus promoting the condensation reaction [62, 63].

However, the electrostatic and hydrophobic interaction between the reagents and the cationic surfactants will be discussed below, which represents a responsibility for the modification of the reaction rates [64].

The electrostatic interactions between the N^+ quaternary ammonium group and the carbonyl benzaldehyde group (Scheme 3a) could force the molecule of R-benzaldehyde to be located at the Stern layer [22], in the other hand the N^+ quaternary ammonium group can also participate in interaction with acetophenone (Scheme 3b) causing a decrease of electron density at the level of the carbonyl carbon to make it more electrophilic which favors the attack of OH^- anion.

For the enolate intermediate is a delocalized system, with a negative charge on both C and O atoms (oxyanion and carbanion) [65] its stability remains a very important factor for the formation of C–C and C–O bonds [62], the higher electrostatic affinity of the enolate with the quaternary ammonium group (Scheme 3c) justify the greatest reactivity in the presence of surfactants [66–68].

All interactions in which cationic surfactant molecules present (Scheme 3) are the attractive interactions between the positive charge carried by the N^+ quaternary ammonium group and the nucleophilic substances (enolate, benzaldehyde, and acetophenone).

For this reason, we have decided to study the electronic distribution for the three catalytic supports studied (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH) by the calculation DFT/B3LYP 6-31G (d) in the aqueous medium and according to their two possible states (Fig. 8): the cases of the formation of a pair of ions with Br^- anion ([cationic surfactant] [Br^-])

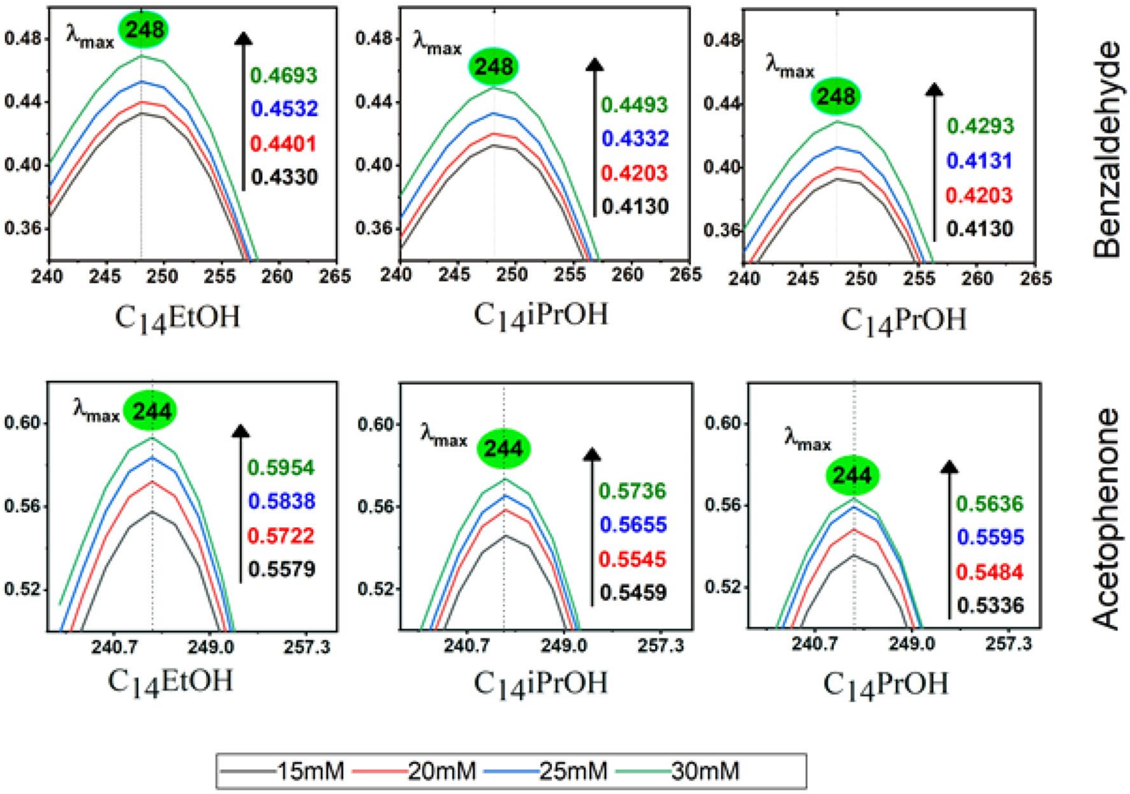
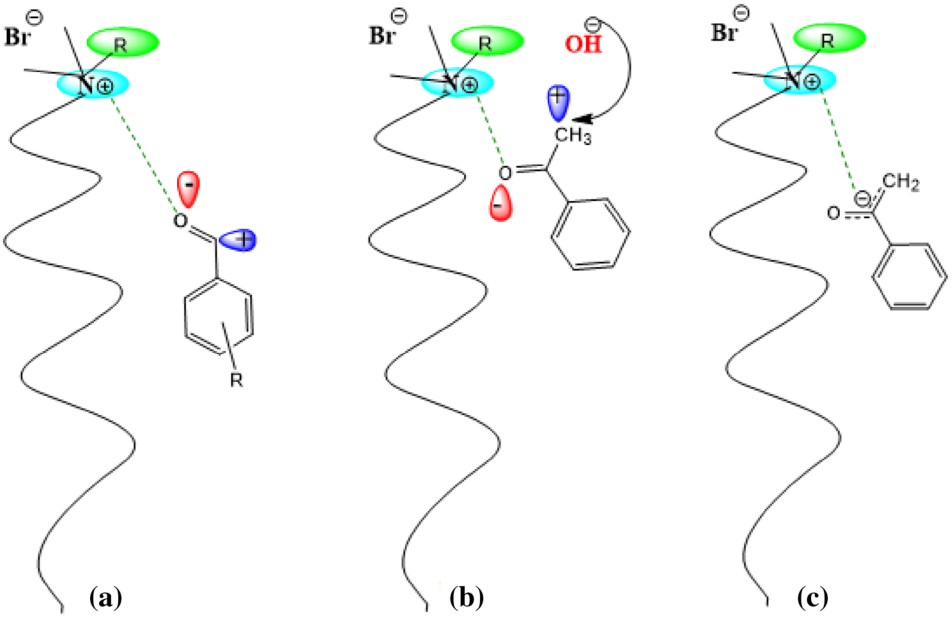


Fig. 7 UV absorption spectra of benzaldehyde and acetophenone in aqueous solutions of different surfactants (C_{14}EtOH, C_{14}iPrOH, C_{14}PrOH) with various concentrations from 15 to 30 mmol

Scheme 3 The electrostatic affinity between the cationic heads N^+ of the surfactants (R = ethanol, propanol and iso-propanol) with **a** R-benzaldehyde, **b** enolate intermediate and **c** acetophenone



and with the hydroxyl anion OH^- ([cationic surfactant][OH^-]) coming from the NaOH molecule.

The location of the alcoholic function OH with respect to the N^+ quaternary ammonium can influence the electrophilicity of the molecule, which plays an important role in the

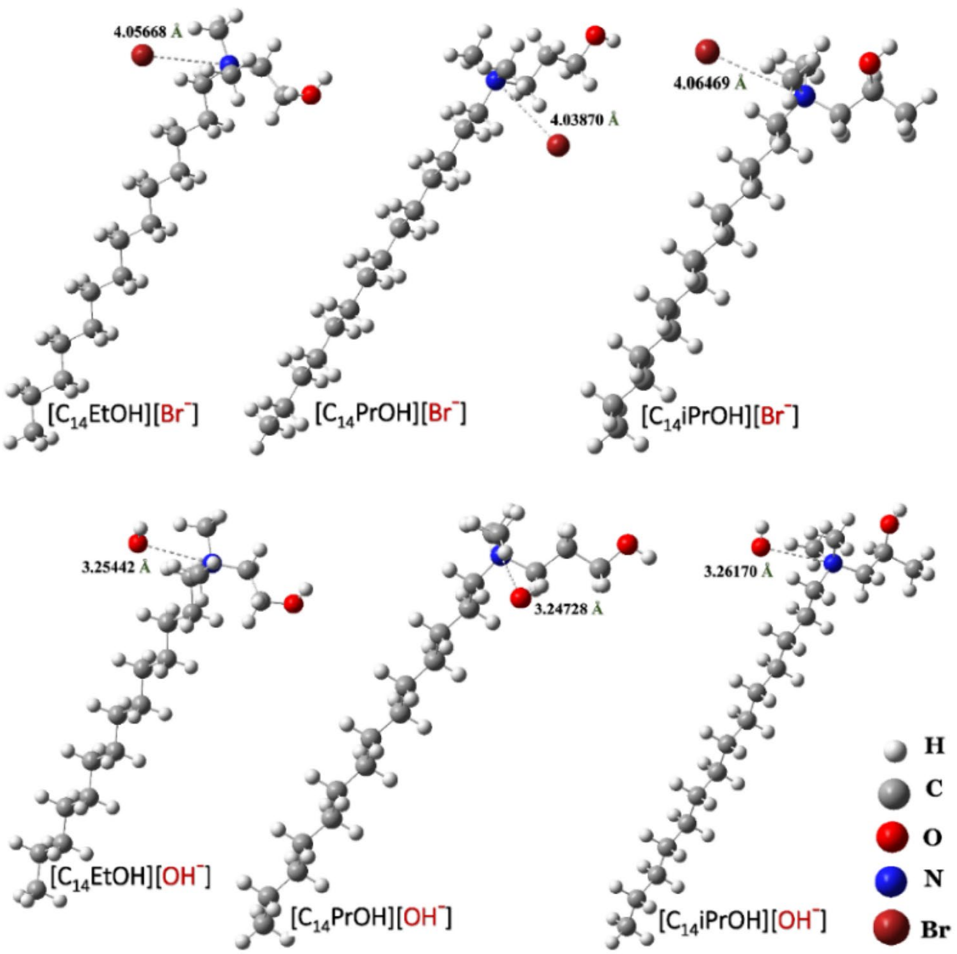


Fig. 8 Optimized geometric structures by DFT method for $C_{14}EtOH$, $C_{14}PrOH$, $C_{14}iPrOH$ according to their two possible form ([cationic surfactant] $[Br^-]$, [cationic surfactant] $[OH^-]$) in aqueous media obtained by DFT/B3LYP 6-31G (d) calculations

Table 3 Electronic parameters of studied surfactants $C_{14}EtOH$, $C_{14}PrOH$ and $C_{14}iPrOH$ according to their two possible form ([cationic surfactant] $[Br^-]$, [cationic surfactant] $[OH^-]$) in aqueous media obtained by DFT/B3LYP 6-31G(d) calculations

Surfactants	E_{HOMO} (eV)	E_{LUMO} (eV)	η (eV)	σ (eV)	ΔE (eV)	ω (eV)	χ (eV)
$[C_{14}EtOH][Br^-]$	− 5.808	1.239	3.524	0.283	7.048	0.74	2.284
$[C_{14}iPrOH][Br^-]$	− 5.777	1.481	3.629	0.275	7.259	0.635	2.148
$[C_{14}PrOH][Br^-]$	− 5.800	1.548	3.674	0.272	7.348	0.615	2.125
$[C_{14}EtOH][OH^-]$	− 4.298	1.563	2.930	0.341	5.862	0.3191	1.368
$[C_{14}iPrOH][OH^-]$	− 4.262	1.700	2.980	0.335	5.962	0.2752	1.281
$[C_{14}PrOH][OH^-]$	− 4.267	1.881	3.074	0.325	6.149	0.2315	1.193

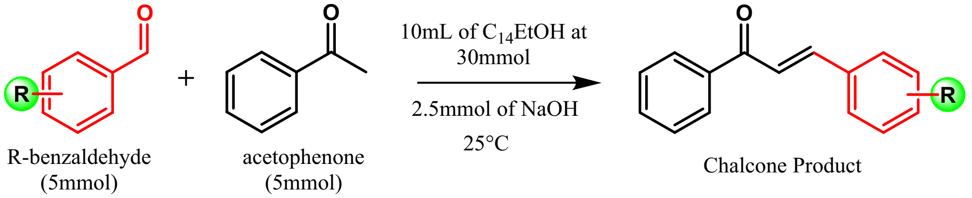
electrostatic affinity force between the different surfactants used and substances with nucleophilic character (enolate, benzaldehyde, and acetophenone) present in the reaction medium. Many calculated chemical descriptors are going to be the subject of the discussion above to correlate the cross-condensation reaction efficiency (yield %) and the molecular structure of surfactants.

The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the gap energy (ΔE), hardness (η), softness (σ), electrophilicity (ω) and electronegativity (χ), parameters are given in Table 3, for the three catalytic supports in two forms ($[C_{14}EtOH]$ $[Br^-]$, $[C_{14}PrOH]$ $[Br^-]$, $[C_{14}iPrOH]$ $[Br^-]$, $[C_{14}EtOH]$ $[OH^-]$, $[C_{14}PrOH]$ $[OH^-]$ and $[C_{14}iPrOH]$ $[OH^-]$.

The highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. According to the theory of molecular orbitals [69, 70], the formation of a transition state is due to an interaction between the border orbitals (HOMO and LUMO) of the reagents [71].

Therefore, the E_{HOMO} (higher energy) is often associated with the ability of the molecule to donate the electron and

Table 4 The isolated yields in (%) and the time in (min) for the condensation reaction between acetophenone and various substituted benzaldehyde (4-Cl, 4-OCH$_3$, 4-CH$_3$) in Micellar catalysis–NaOH systems (30 mmol of C$_{14}$EtOH) at 25 °C



Entry	R	Time (min)	Yield (%)	Chalcones pictures
1	4-Cl	35	91	
2	4-OCH$_3$	45	86	
3	4-CH$_3$	75	75	

the E$_{LUMO}$ (lowest energy) indicates the more probable the molecule would accept electron [72].

In Table 4 it is observed that the [cationic surfactant] [Br$^-$] form, has lower values of E$_{LUMO}$ compared to the values presented by the [cationic surfactant] [OH$^-$] form, for the three surfactants studied (C$_{14}$EtOH, C$_{14}$iPrOH, C$_{14}$PrOH). In both forms [cationic surfactant] [Br$^-$] and [cationic Surfactant] [OH$^-$], the HOMO energy has negative values for the three cationic surfactants studied, which indicates that these catalytic supports do not have the ability to donate electrons, likewise our interest it is to verify and examine their ability to accept the electrons earlier than give them, that is why we will examine the energy of LUMO which reveals that E$_{LUMO}$ decreases from C$_{14}$EtOH to C$_{14}$PrOH for both forms.

The energy of the gap $\Delta E = E_{LUMO} - E_{HOMO}$ reflects the polarizability and the reactivity of a molecule [73, 74], this parameter ΔE gap increases in order, C$_{14}$EtOH < C$_{14}$iPrOH < C$_{14}$PrOH, which indicated that the acceptance of the negative charge was easily made from C$_{14}$EtOH to C$_{14}$PrOH for both forms [cationic surfactant] [Br$^-$] and [cationic surfactant] [OH$^-$], which is in agreement with the results of the condensation reaction yield (%) shown in Table 1, therefore, the compound C$_{14}$EtOH has the best reaction efficiency, which means that C$_{14}$EtOH has a high capacity to accept a negative charge thus reflecting the electrostatic affinity force with the nucleophilic compounds (enolate, benzaldehyde, and acetophenone) following the C$_{14}$iPrOH and C$_{14}$PrOH respectively.

The Hard–Soft–Acid–Base theory (HSAB) classifies reactive species as relatively “hard” or “Soft”, based on polarizability, that is the ease with which electronic density can be displaced or delocalized to form new covalent bonds [75], the hard molecules are less reactive than the soft molecules because they require a higher energy for molecular excitation [76]. From Table 3, for two forms it was observed that the chemical hardness (η) decreases in the order of C$_{14}$PrOH > C$_{14}$iPrOH > C$_{14}$EtOH, the opposite trend is also observed for the chemical softness (σ) which explains the highest catalytic proprieties efficiency of C$_{14}$EtOH.

For other descriptors such as electrophilicity (ω) and electronegativity (χ), these are the indices allows to predict the reactivity of species to give or accept an electron, therefore the molecules have the lowest electronegativity values having the ability to easily give electrons and vice versa to molecules with high values of electronegativity [70].

As can be seen from Table 3 the two descriptors (ω) and (χ) present high values for the [cationic surfactant] [Br$^-$] form more than the form [cationic surfactant] [OH$^-$], moreover in both forms, the C$_{14}$EtOH remains the most species with the ability to accept a negative charge among the three surfactants studied because of these high values of

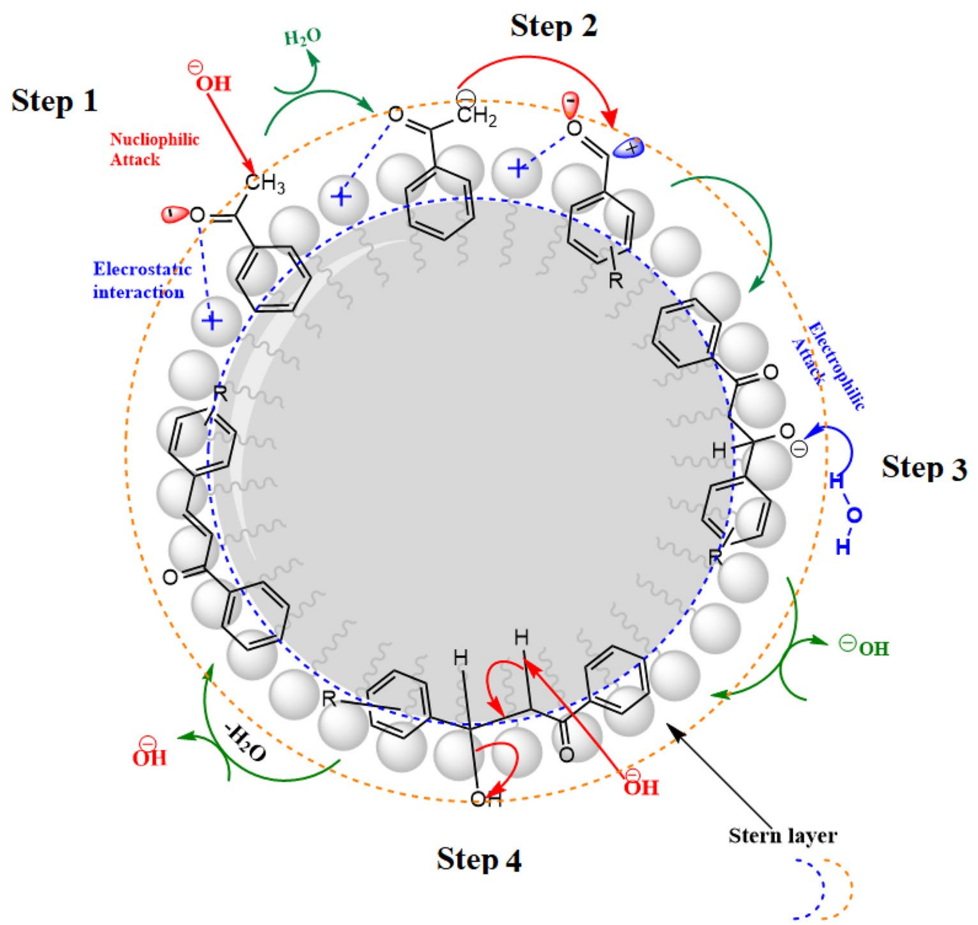


Fig. 9 The proposed mechanism of cross-condensation (Claisen–Schmidt reaction) in Micellar catalysis–NaOH/Water–NaOH

electronegativity (χ) thus following C_{14}iPrOH and C_{14}PrOH respectively.

This height acceptance capacity of negative charge for the species C_{14}EtOH in both forms ([cationic surfactant] [Br^-] and [cationic surfactant] [OH^-]) following respectively of C_{14}iPrOH and C_{14}PrOH, indicates the order of the electrostatic affinity ($C_{14}PrOH > C_{14}iPrOH > C_{14}EtOH$) between the positive charge carried by the quaternary ammonium atom N^+ and the substance with nucleophilic character present in the reaction medium (enolate, benzaldehyde and acetophenone), this also justifies the same order in which the cross-condensation reaction efficiency (yield(%)) with different substituted benzaldehyde increases from C_{14}PrOH to C_{14}EtOH.

with different R-benzaldehyde (R = 4-Cl, 4-OCH_3, 4-CH_3) the Claisen–Schmidt reaction was carried out in *Micellar catalysis–NaOH* of C_{14}EtOH surfactants at 30 mmol (Table 3). According to the mechanism proposed by Nayak and Rout [77, 78] in which the methyl group of acetophenone undergoes a nucleophilic attack by OH^- result an abstract of the proton thus forming the acetophenonate-ion this anion formed to attack the carbon atom of the carbonyl group in benzaldehyde, this step will be more favorable each time the carbon of the aldehyde is more electrophilic (poorer in electron). That is why it can be observed from the results that the effect of the donor and attractor group attached to the benzaldehyde molecule has an effect on the yields (%) and the time (min) of the condensation reaction (Table 1). This effect is due to the degree of nucleophilicity of the R group in the following order [79]: 4-Cl > 4-OCH_3 > 4-CH_3 which causes an influence on the electron density of the aldehyde carbon in order to make it more electrophile thus encouraging more the attack of the acetophenonate-ion. On the other hand, the reaction in the Micellar catalysis-NaOH system (15 mmol in surfactant) shows (Table 1 and Fig. 1) a remarkable yield (%) depending on the R-benzaldehyde (R = 4-Cl, 4-OCH_3, 4-CH_3) between 75 and 91%.

In this context, and with all these information's concerning the orientation of the reagents (acetophenone and R-benzaldehyde) and their reactivity in the Micellar catalysis–NaOH system we propose the following mechanism (Fig. 9).

4 Conclusions

The catalytic efficiency for the three cationic surfactants with different polar heads has been studied for the condensation reaction (Claisen–Schmidt) between benzaldehyde and acetophenone as a model of reaction. The comparison of the yield (%) in *Micellar catalysis–NaOH* system for (C_{14}EtOH, C_{14}PrOH, C_{14}iPrOH) reveals the following conclusions:

- As we have already mentioned above the positively charged micelles increase the local pH at the polar region of micelles by the Colombian attraction of the ion OH^- present in the reaction medium. The comparison of the ionization degree means that the degree of electrophilicity of the micelles shows a no-correlation between the yield (%) and the values of ionization degrees for the three surfactants. Another comparison of α with the yield (%) was included to highlight the no-correlation between the degree of ionization and the efficiency of the condensation reaction.
- The solubilization and the emulsification capacity for the various surfactants show, based on the spectroscopic UV–Vis and optical microscopic methods, that the miscibility of the benzaldehyde and acetophenone reagents has a significative effect on the yield (%) of the reaction.
- According to their positive charge, the cationic heads of the surfactants are contributed to the electrostatic interaction with the nucleophilic substance (benzaldehyde, acetophenone, and enolate). In the aqueous medium, the theoretical study with DFT shows that the degree of electrophilicity estimated, that is, the electrophilic character of the surfactants shows a correlation with the yield (%) of the reaction in the following order: C_{14}PrOH < C_{14}iPrOH < C_{14}EtOH.

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