# REVIEW OF LITERATURE

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Mehta *et al.*, (2008) studied the aggregation behavior of cetylpyridinium chloride (CPyCl) in N,N-dimethylformamide (DMF)–water mixed solvents using both electrical conductivity and spectroscopic techniques. Micellar and thermodynamic parameters (ΔG^{o}_{m}, ΔH_{m}, ΔS_{m} and $\Delta_{m} C^{o}_{p}$) were obtained from the temperature dependence of critical micelle concentrations in various aqueous mixtures of DMF. The differences in the Gibbs energies of micellization of CPyCl between water and binary solvents were determined to evaluate the influence of the cosolvent. The effect of cosolvent on the Krafft temperature (K_{T}) and on the aggregation number was also analyzed. Micellar micropolarity was examined spectrophotometrically using two different probes, methyl orange (MO) and methylene blue (MB), and was found to increase with DMF addition, accompanied by an enhanced solvation. The mechanism of docking of surfactant and the probe molecules in the system were obtained by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy.

Bhasin *et al.*, (2008) studied the micellar behavior of aqueous solutions of dodecyldimethylethylammonium bromide (DDAB), dodecyltrimethylammonium chloride (DTAC) and tetradecyltrimethylammonium chloride (TDAC) in absence and presence of α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), hydroxypropyl-β-cyclodextrin (HPβ-CD) and γ-cyclodextrin (γ-CD) using conductivity, static fluorescence and ^{1}H-NMR measurements. The conductivity measurements were carried out at 298.15 K.

The influence of cyclodextrins on the micellar parameters, such as CMC (critical micellar concentration), β (degree of ionization) have been analyzed. Thermodynamics of the systems was discussed in terms of the change in standard free energy of micellization ΔG^{o}_{m}. Micellization was found to be less spontaneous in presence of cyclodextrins. The fluorescence intensity of the surfactant solutions is enhanced by the addition of cyclodextrins. The association constants obtained from conductivity and fluorescence data suggest the binding of γ-CD with the surfactants to be strongest among all the cyclodextrins used. ^{1}H-NMR chemical shift changes provide powerful means for probing the cyclodextrin–micellar interactions and inclusion of surfactant is shown by the change in the chemical shift of some of the guest and host protons in comparison with the chemical shifts of the same protons in the free compounds.
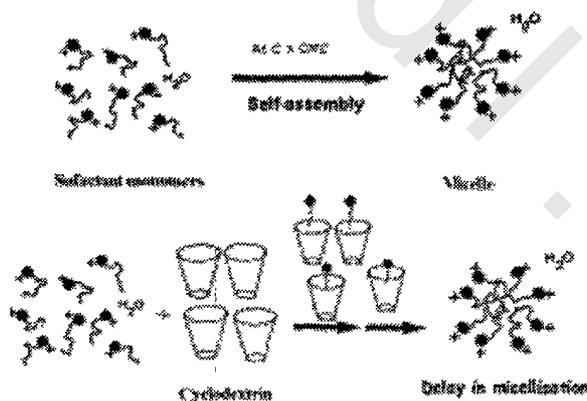

Wang *et al.*, **(2008)** prepared novel double-tailed cationic surfactant, N,N$'$-didodecylacetamidinium bicarbonate (Scheme 2), by reacting dimethylacetamide dimethyl acetal with dodecylamine, followed by reacting with dry ice. The surfactant reduced the surface tension of pure water to 24.7mNm^{-1}and its critical micelle

concentration was 8.75×10^{-5} M. Formation of vesicle was formed in an aqueous solution with ultrasonic bath.
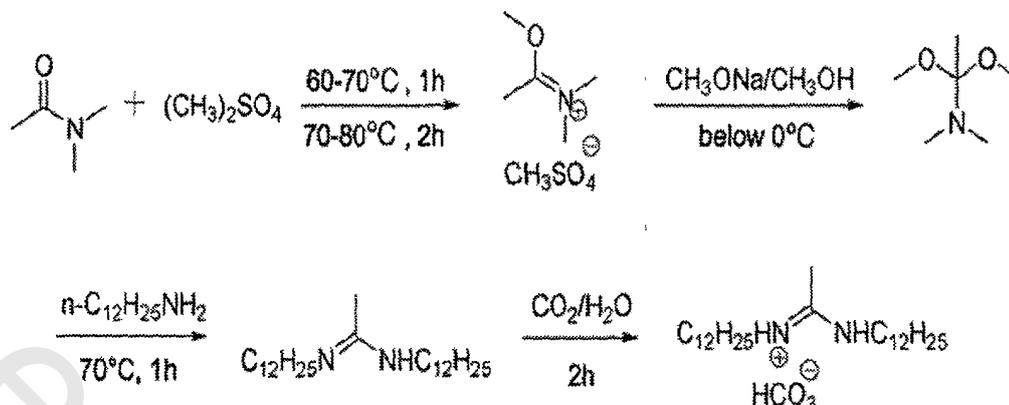
El Seoud et al., (2007) prepared a series of surface-active ionic liquids, by reaction of purified 1-methylimidazole and 1-chloroalkanes RCl, R = C10, C12, C14, and C16, respectively (Scheme 3). Adsorption and aggregation of these surfactants in water have been studied by surface tension measurement. Additionally, solution conductivity, electromotive force, fluorescence quenching of micelle-solubilized pyrene, and static light scattering have been employed to investigate micelle formation. The changes resulted from an increase in the length of R are an increase of micelle aggregation number and a decrease in minimum surface area of surfactant molecules at solution/air interface; critical micelle concentration, and degree of counter-ion dissociation. Theoretically-calculated aggregation numbers and those based on quenching of pyrene are in good agreement. Gibbs free energies of adsorption at solution/air interface, ΔG^{o}_{ads}, and micelle formation in water, ΔG^{o}_{mic}, were calculated.
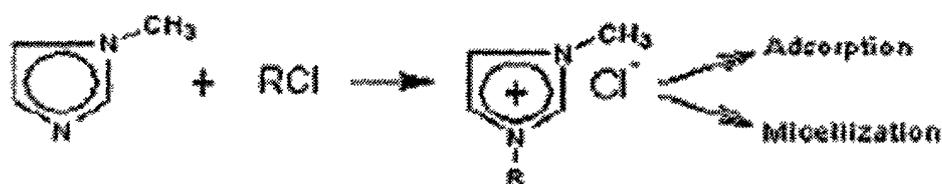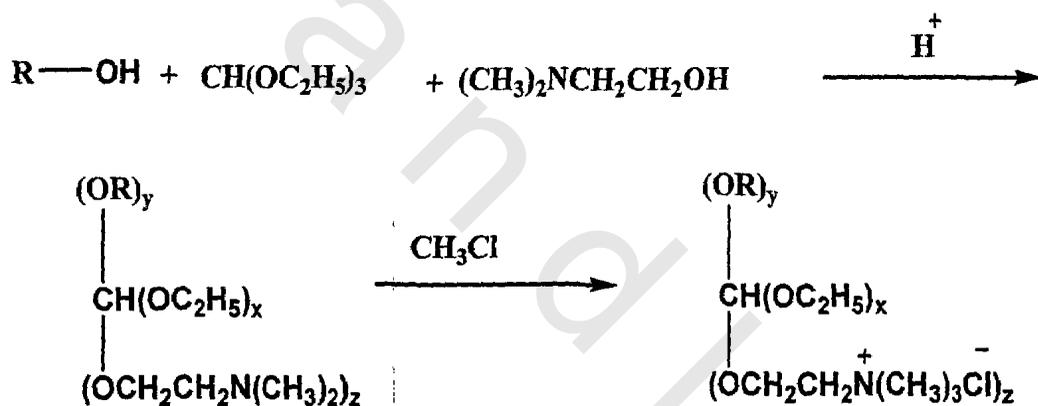
Scheme 3

Deyab (2007) studied corrosion behavior of carbon steel in formation water associated crude oil from Egyptian western desert at various concentrations of didecyl dimethyl ammonium chloride as a cationic surfactant. Polarization curves indicate that the prepared cationic surfactant has good inhibition efficiency for carbon steel in formation water and behaves as cathodic inhibitor. The inhibition efficiency was found to increase with increase the concentration until reaches a maximum constant value corresponding to the critical micelle concentration and decrease with increase in solution temperature. The adsorption of that surfactant follows the kinetic thermodynamic model and Flory–Huggins isotherm. Thermodynamic parameters obtained indicate that the presence of the didecyl dimethyl ammonium chloride increases the activation energy. Polarization and Impedance measurements indicate that the addition of KI has a significant synergistic effect with didecyl dimethyl ammonium chloride and results in increasing its inhibition efficiency in formation water.

Upadhyaya et al., (2007) studied the adsorption of anionic and cationic surfactant mixtures on charged metal oxide surfaces (i.e., alumina and silica). For an anionic-rich surfactant mixture below the CMC, the adsorption of anionic surfactant was found to substantially increase with the addition of low mole fractions of cationic surfactant. Two anionic surfactants (sodium dodecyl sulfate and sodium dihexyl sulfosuccinate) and two cationic surfactants (dodecylpyridinium chloride and benzethonium chloride) were studied to evaluate the effect of surfactant tail branching. While cationic surfactants were observed to co-

adsorb with anionic surfactants onto positively charged surfaces, the plateau level of anionic surfactant adsorption (i.e., at or above the CMC) did not change significantly for anionic–cationic surfactant mixtures. At the same time, the adsorption of anionic surfactants onto alumina was dramatically reduced when present in cationic-rich micelles and the adsorption of cationic surfactants on silica was substantially reduced in the presence of anionic-rich micelles. This demonstrates that mixed micelle formation can effectively reduce the activity of the highly adsorbing surfactant and thus inhibit the adsorption of the surfactant, especially when the highly adsorbing surfactant is present at a low mole fraction in the mixed surfactant system. Thus surfactant adsorption can be either enhanced or inhibited using mixed anionic–cationic surfactant systems by varying the concentration and composition.

Hellberg (2002) synthesized ortho ester amines with alkyl chain lengths from C8 to C16 from a short-chain ortho ester, a fatty alcohol, and an amino alcohol. The ortho ester amine was subsequently quaternized with methyl chloride, yielding a cationic surfactant (Scheme 4). The surface chemical properties were investigated by measuring both static and dynamic surface tensions. The results were compared to standard *n*-alkyl trimethyl ammonium bromides. The critical micelle concentrations were found to vary rather widely, whereas the surface tensions in some cases were comparatively low. The short alkyl chain ortho ester quaternaries were found to have low surface tensions at short surface ages and to induce rapid wetting of a hydrophobic surface in dynamic tests. Additionally, the new surfactants were found to hydrolyze rapidly under mild

acidic conditions, as measured by both titration and monitoring of the dynamic surface tension. Further, they showed excellent long-term stability at pH 10 in dilute aqueous solutions. The effect of added electrolyte on rate of hydrolysis was also investigated.

$$R\text{---}OH + CH(OC_2H_5)_3 + (CH_3)_2NCH_2CH_2OH \xrightarrow{\overset{+}{H}}$$

$$\begin{array}{c} (OR)_y \\ | \\ CH(OC_2H_5)_x \\ | \\ (OCH_2CH_2N(CH_3)_2)_z \end{array} \xrightarrow{CH_3Cl} \begin{array}{c} (OR)_y \\ | \\ CH(OC_2H_5)_x \\ | \\ (OCH_2CH_2\overset{+}{N}(CH_3)_3\overset{-}{Cl})_z \end{array}$$

x= 0-3, y= 0-3, z= 0-3

R= 2-ethylhexyl, n-C8, n-C10, , n-C12, n-C14, n-C16

Scheme 4

Bajpai *et al.*, (2008) prepared long chain dialkyldiamido imidazolines by the reaction of diethylenetriamine and several fatty acids under non-solvent microwave irradiation using calcium oxide as support. This synthesis required much less time in comparison to conventional thermal condensation and is carried out in an open vessel and the products obtained by this method were found to be in good yields and of high purity. Fatty imidazolines were then quaternized by using dimethyl sulfate as a quaternizing agent and isopropanol as a solvent, to produce cationic imidazolinium salts which were evaluated for yield and cationic content. This method produced imidazolines in the very low time of 5–10 min and gave a yield of 89–91% as compared to a very long time of 8–10 h and a lower yield of 75–80% by the conventional thermal condensation method.

Badawi *et al.*, (2007) concerned with the developments of bactericidal and fungicidal synthetic cationic surfactants by reacting decyl, dodecyl or tetradecyl amine with acetic or hydrochloric acid to produce a series of amine salts which consequently converted to copper or cobalt cationic complexes via complexing the first series compounds with copper (II) or cobalt (II) ions. Surface properties such as interfacial tension and emulsifying power of these surfactants were investigated. The surface parameters including critical micelle concentration (CMC), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) were studied. Free energy of micellization (ΔG^{o}_{mic}) and adsorption (ΔG^{o}_{ads}) were calculated. The antimicrobial activity was determined via the inhibition zone diameter of the prepared compounds.

Shehata et al., (2008) synthesized novel cationic surfactants from the quaternization of triethyl amine and various long chain alkyl halides. The physical properties of the synthesized surfactants including, electrical conductivity, critical micelle concentration, (CMC) and the degree of ionization of the micelle (β) were studied. The thermodynamic parameters of micelle formation, standard free energy ΔG^{o}_{m}, enthalpy ΔH^{o}_{m}, and entropy ΔS^{o}_{m} were calculated. The results of the surface parameter determination were correlated with their chemical structures. It was found that the hydrocarbon chain length is the main factor which has an effect on the value of the thermodynamic parameters.

El-Aila (2005) studied the effect of urea on micelle formation of zwitterionic surfactants by measuring conductivity, critical micelle concentration (CMC), relative viscosity, and the spectrophotometric shift in wavelength. And examined two zwitterionic surfactants, N,N-dimethyl dodecylamine N-oxide and N,N-dimethyl tetradecylamine N-oxide (DMTAO). The CMC values of the surfactants increased with the addition of urea. Also, the relative viscosity of the surfactant solutions decreased at higher concentrations of urea. The absorbance maxima of the surfactants decreased with increasing urea concentration.

Vora et al., (1999) measured the Critical micelle concentrations (CMC) from tensiometric studies on several binary surfactant mixtures (anionic-anionic, cationic-cationic, anionic-non-ionic, and cationic- non-ionic) in

water at different mole fractions (0–1). The composition of mixed micelles and the interaction parameter β, evaluated from the CMC data for different systems using Rubingh's theory, are discussed. Marked interaction is observed for ionic-non-ionic systems, whereas it is weak in the case of similarly charged surfactants. The influence of counter ion valence in the formation of mixed micelles was investigated, and results suggest that in similarly charged surfactant mixtures, the degree of counter ion binding does have a major role in deciding the extent of interactions. Salt addition reveals a weakening of interactions in ionic-non-ionic systems, and this is attributed to head group charge neutralization and dehydration of the ethylene oxide units of the non-ionic surfactants. Cloud point and viscosity data on these systems support the observation.

Tatsumi *et al.*, (2000) prepared Gemini cationic surfactants 1,3-bis[(acyloxyalkyl)dimethylammonio]-2-hydroxypropane dichloride, which possess hydrolyzable oxycarbonyl moieties in the lipophilic portions. These surfactants showed much better micelle-forming ability, ability to lower surface tension, foaming ability, and foam stability than corresponding single-chain surfactants. Their surface properties were largely influenced by changing the position of the oxycarbonyl group in the lipophilic moiety. The critical micelle concentration decreased with a decreasing number of methylene units in the linking moiety between the ammonio and the oxycarbonyl groups within the comparison of lipophilic chains of the same length. These cationic gemini surfactants also showed good biodegradability.

Kirk *et al.*, **(1998)** prepared a new type of cationic surfactant, 6-*O*-monoesters of 3-(trimethylammonio)propyl D-glucopyranoside, in high yield by a simple chemo enzymatic synthesis (Scheme 5). Surface-active properties of the compounds were found to be highly dependent on the fatty acyl chain length in the 6-*O*-position with the dodecanoyl and tetradecanoyl esters exhibiting the highest ability to lower surface tension as well as having the lowest critical micelle concentration values. Furthermore, the dodecanoyl ester had excellent foaming properties. The new surfactants also showed antimicrobial activity. Thus, the most potent compound, the dodecanoyl ester, was able to inhibit growth of both bacterial (Gram-positive as well as Gram-negative) and fungal test strains. The antimicrobial effect was somewhat weaker compared to benzalkonium chloride, one of the most frequently used cationic for topical disinfection. However, compared to benzalkonium chloride, the new cationic exhibit a highly improved compatibility with anionic surfactants, as no precipitation took place even in highly concentrated solutions thereby providing a much more robust antimicrobial system. Finally, the new surfactants are expected to be readily biodegradable because they are carbohydrate ester-based.
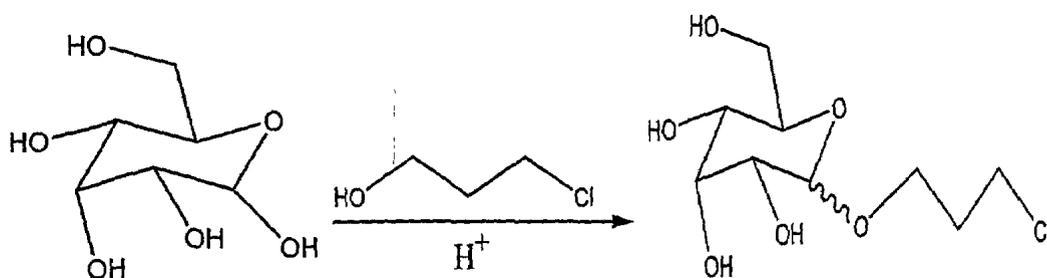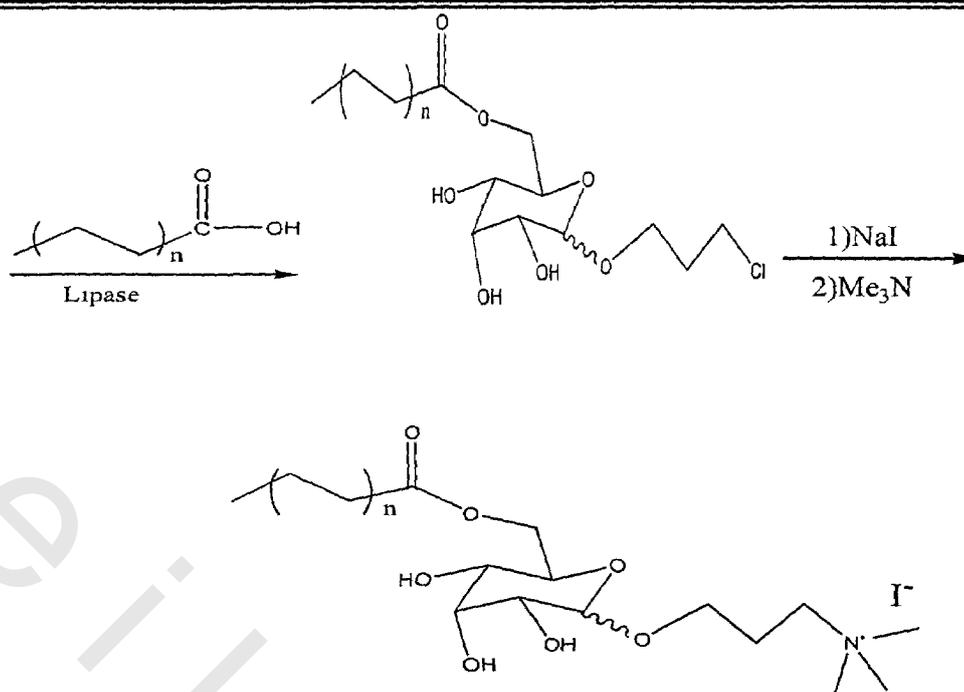
Scheme 5

Wegrzynska *et al.*, **(2006)** prepared a series of new cationic surfactants, bis-quaternary ammonium salts and tris-ammonium salts from N,N-dimethyldodecylamine and a product of the reaction of epichlorohydrin with ethyl-, propyl-, butyl-, pentyl-, hexyl-, and octylamine (in the case of bis-ammonium salts) or the hydrochloride of diethyl-, dipropyl-, dibutyl-, or dihexylamine (in the case of tris-ammonium salts). The obtained multiple salts were examined with respect to their surface-active properties: Critical micelle concentrations (CMC), effectiveness of surface tension reductions (γ_{CMC}), and adsorption efficiencies (PC_{20}) were measured. All these surfactants showed good water solubility and low CMC of more than one order of magnitude lower than those of corresponding monoalkylammonium salts. They also showed good foaming properties, but worse wetting capability. The obtained multiple salts showed excellent antielectrostatic properties.

Lunkenheimer *et al.*, **(2003)** made a new simple foam test, in which a well-controlled volume of gas is introduced into a definite volume of solution. Aqueous solutions of sodium dodecyl sulfate (SDS), *n*-octyl-β-D-glucopyranoside, cetyl trimethylammonium bromide (CTAB), and *n*-hexanol, i.e., four systems forming metastable and transient foams, were studied. The parameter R5, defined as the ratio of the height of the foam at 5 min after formation to the initial height, is proposed for the evaluation of foam stability. Foams having R5 values higher than 50% can be considered as metastable. Lower R5 values indicate low-stability foams. Changes of R5 values with concentration are similar to those of foam half-life with concentration. Thus, instead of measurements lasting hours for the foam half-life, one can obtain similar information from tests lasting only a few minutes. With this test also one can obtain information about the solution contents in foams. This parameter can be used as an additional criterion for the evaluation of foam stability. In the case of metastable foams formed by SDS, *n*-octyl- β-D-glucopyranoside, and CTAB the initial foam volume was almost equal to the volumes of the dispersed gas and the solution carried into the foam by the bubbles. This shows that there was practically no rupture of foam films at the stage of the foam formation.

Beard *et al.*, **(2002)** shown specific 1:1 ionic interaction between cationic alkyl quaternary surfactant molecules and the anionic sulfonate groups present on the hair surface by surface analysis using X-ray photoelectron spectroscopy (XPS). The primary driving force for the adsorption of alkyl quaternary amine molecules to the surface of the hair from aqueous solution is the ionic

interaction between quaternary groups and the surface SO3⁻ on the hair. Cationic quaternary molecules incorporating ester and alcohol functionalities (ester quaternaries) demonstrate a lower number of surface quaternary nitrogens per sulfonate group, indicating an altered surface interaction mechanism. For the ester quaternaries, a combination of electrostatic interaction modes exists in addition to the ionic $N^+/SO3^-$ interaction, specifically, H-bonding interactions of the –C–O, –C–OH, and –C(O)O⁻ polar groups with SO3⁻ and other polar groups on the hair. Surface coverage of the ester quaternaries is not reduced despite the decrease in ionic interaction at the surface. Both types of molecules orient their alkyl tails toward the surface. Molecular dynamics modeling of the surfactant/hair surface interaction indicates higher adsorption energies due to increased dipolar interactions for ester quaternary molecules.

Zhishen et al., (2001) prepared Chitosan derivatives with quaternary ammonium salt (Scheme 6), such as N,N,N-trimethyl chitosan, N-propyl-N,N-dimethyl chitosan and N-furfuryl-N,N-dimethyl chitosan using different 96% deacetylated chitin. Amino groups on chitosan react with aldehydes to from a Schiff base intermediate. Quaternized chitosan were obtained by reaction of a reduced Schiff base with methyl iodide. The degree of quaternization and water-solubility of quaternized chitosan were influenced by the molecular weight of the chitosan sample. The antibacterial activities of quaternized chitosan against *Escherichia coli* were explored by calculation of the minimum inhibitory concentration (MIC) and minimum bactericida concentration (MBC) in water, 0.25 and 0.50% acetic acid medium. Results show the antibacterial activities of
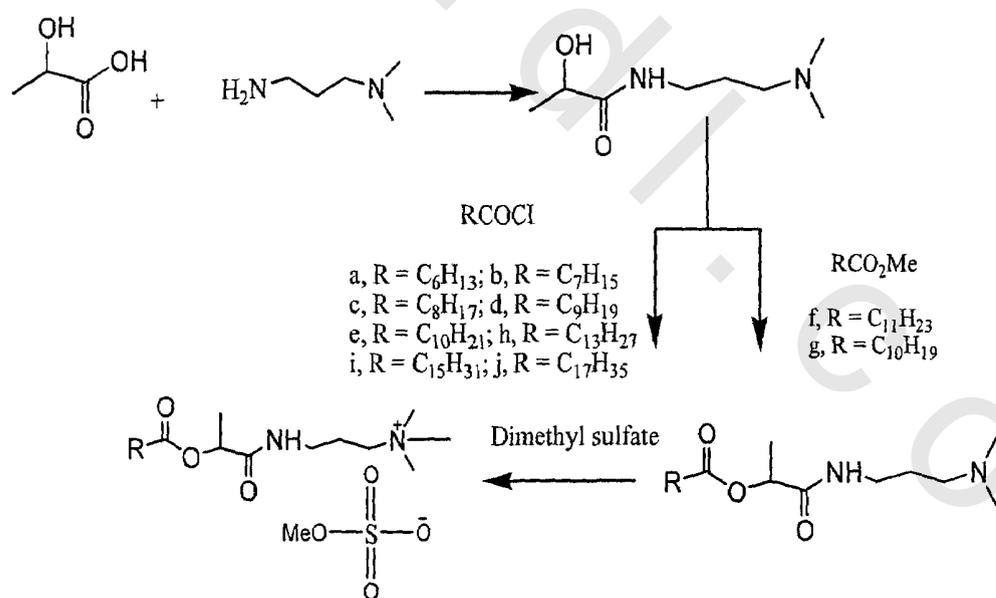
quaternized chitosan against *E. coli* are related to its molecular weight. Antibacterial activities of quaternized chitosan in acetic acid medium are stronger than that in water. Their antibacterial activities are increased as the concentration of acetic acid is increased. It was also found that the antibacterial activity of quaternized chitosan against *E. coli* is stronger than that of chitosan.

Quaternized *N*-alkyl chitosan
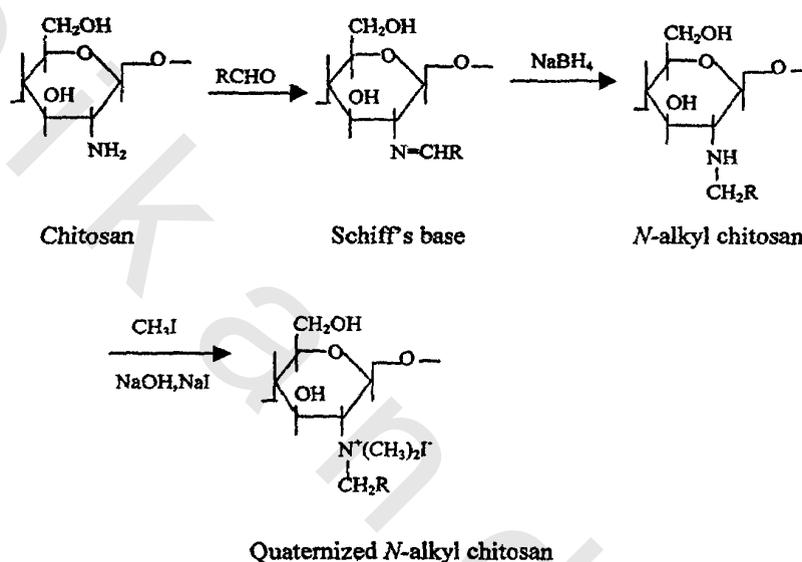
Negm *et al.*, **(2007)** prepared a series of cationic surfactants using economical raw materials. The synthesized surfactants were evaluated as oil-field protective additives. In this regard, several surface properties of the synthesized surfactants were studied including surface tension, critical micelle concentration, effectiveness, efficiency, maximum surface excess and minimum surface area. The results obtained from the surface activity measurements were correlated to their chemical structures. The emulsification power measurements for solutions of these surfactants showed their low emulsifying tendency towards paraffin and crude oil. The corrosion inhibition measurement of these surfactants for mild steel alloys in acidic media using

a weight loss technique showed good protection of mild steel alloys against acidic environments. These properties qualify the synthesized compounds as economical oil-field protective additives. The synthesized surfactants also exhibited high biocidal activity towards Gram-positive and Gram-negative bacteria and fungi. This activity was increased by increasing the hydrophobic chain length.

Anoune *et al.*, **(2000)** prepared a series of new cationic surfactants by condensation of lactic acid with N,N-dimethyl propylamine, followed successively by acetylation with acid chloride or ester and by quaternization with dimethylsulfate (Scheme 7). Critical micelle concentrations, contact angles, kinetics of drop spreading, and foam capacities were determined.

RCOCl

a, R = C_6H_{13}; b, R = C_7H_{15}
c, R = C_8H_{17}; d, R = C_9H_{19}
e, R = $C_{10}H_{21}$; h, R = $C_{13}H_{27}$
i, R = $C_{15}H_{31}$; j, R = $C_{17}H_{35}$

RCO$_2$Me

f, R = $C_{11}H_{23}$
g, R = $C_{10}H_{19}$

Dimethyl sulfate

Scheme 7

Abd El-Maksoud (2004) investigated the effect of hexadecyl- pyridinium bromide (HPB) and hexadecyltrimethyl ammonium bromide (HTAB) on the

corrosion behaviour of iron and copper in hydrochloric and sulfuric acid solutions by potentiodynamic polarization and Tafel extrapolation methods. The polarization curves indicate that the two compounds behave as mixed inhibitors. And the HPB is more effective than HTAB in both acids; this is explained on the basis of the charge located on the nitrogen atom on the two compounds. And the inhibition efficiency of the compounds investigated is more effective for iron and copper metals in HCl than in H_2SO_4, which is explained on the basis of the potential of zero charge of the metal surface and the adsorption ability of both Cl^- and SO_4^{2-} on the metal surface.

Mirghasem *et al.*, (2003) studied the inhibition effects on the corrosion of mild steel in sulfuric acid solution of sodium dodecylbenzenesulfonate (SDBS) and hexamethylenetetramine using weight loss technique, electrochemical impedance and Tafel polarisation measurements. And fond that hexamethylenetetramine show a continuous increase in inhibition efficiency is observed as a function of concentration but for SDBS, however, an optimum in the inhibition efficiency is observed for a concentration close to 250 ppm, which is ascribed to the formation of hemi-micellar aggregates which provide inhibitor desorption from the metal/solution interface at higher concentrations. Upon mixing SDBS and hexamethylenetetramine, concentration regions showing synergistic and antagonistic inhibition behaviour are identified, and it is concluded that electrostatic interactions between adsorbate ions are likely responsible for both phenomena. They tested Langmuir and Frumkin isotherms

for relevance in describing the adsorption behaviour of both hexamethylenetetramine and SDBS.

Soror *et al.,* **(2003)** studied the influence of cetyltrimethyl ammonium bromide (CTAB) on the corrosion of carbon steel in HCl and H_2SO_4 solutions using several techniques such as weight loss, Tafel polarization, linear polarization and open circuit potential. Inhibition efficiencies have been obtaining from weight loss measurement; the effect of temperature on corrosion inhibition and the effectiveness of the inhibitor at higher acid strength have been examined. Polarization studies reveal that the inhibitor behaves as an effective inhibitor in H_2SO_4 as well as in HCl solutions. Measurements of values of polarization resistance (Rp) have also been carried out. They found that the open circuit potential curves were shifted to less negative potential contrary to the blank.

González-Pérez *et al.,* **(2004)** measured the specific conductivity, κ, of decyldimethylbenzylammonium bromide in aqueous solution as a function of molality in the 5–50 °C temperature range at 1 °C intervals. The critical micelle concentration CMC, and ionization degree of the micelles β, were estimated from the conductivity measurements. Comparison with literature data indicates that the minimum on the CMC against temperature plots T* (minimum temperature at minimum CMC), is shifted to lower temperatures with increase in length of the alkyl chain of the surfactant and with increase in hydrophobicity of the counter ion.

Chauhan *et al.*, (2003) determined critical micelle concentrations (CMC) of sodium dodecyl sulfate (SDS) in aqueous mixtures of dimethylsulfoxide (DMSO) between 25 and 45 °C and at very low NaBr concentration range $(0.0025-0.03 \text{ mol dm}^{-3})$. The ability of NaBr to lower the CMC in water is inhibited by DMSO below ~0.014 mol dm^{-3} of NaBr. However, the contribution of DMSO in regard to its effect upon micellization process of SDS in aqueous electrolyte solutions have been discussed in terms of the observed behavior of thermodynamic properties, such as entropy (ΔS_m°), free energy (ΔG_m°) and enthalpy (ΔH_m°). In particular, they discuss counter ion binding as revealed by different experimental conditions. The data suggest mass action effect and salt-induced increase in micelle size with concomitant reduction in charge density of Stern-layer. These observations point to the counter ion solvation effect of DMSO in addition to the loss of hydrophobic interactions due to strong intermolecular interactions.

Negm *et al.*, (2008) prepared series of self-assembled non-ionic Schiff base amphiphiles (Scheme 8). The surface activities of these amphiphiles were determined based on the data of surface and interfacial tension, critical micelle concentration, effectiveness, efficiency, maximum surface excess and minimum surface area. Thermodynamics of adsorption and micellization processes of these amphiphiles in their solutions were also calculated. The surface and thermodynamic data showed their higher tendency towards adsorption at the interfaces. The synthesized amphiphiles were evaluated as corrosion inhibitors for aluminum (3SR) at different doses (10–400 ppm) in acidic medium (4N HCl) using weight loss and hydrogen evolution techniques. The

corrosion measurements showed that the synthesized non-ionic Schiff bases could serve as effective corrosion inhibitors. The surface and corrosion inhibition activities were correlated to the chemical structures of the inhibitors.

$$CH_3O-\bigcirc-\underset{\underset{H}{|}}{C}=N-\bigcirc-COO-[CH_2CH_2O]_n^-\!\!\!-R$$

SB - PEG - Alkanoate
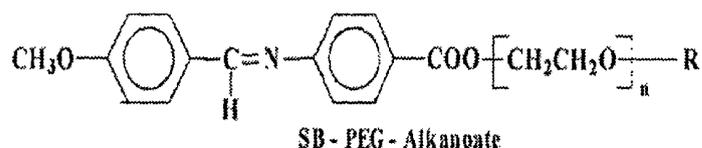
n = 9, 45 and 68 ethylene oxide units

R = decanoate, hexadecanoate, octadecanoate, oleate

El Achouri *et al.*, (2001) prepared three new gemini surfactants in the series of alkanediyl-α,ω-bis-(dimethylalkyl ammonium bromide) and tested as corrosion inhibitors of iron in hydrochloric acid medium using gravimetric, electrochemical polarisation and electrochemical impedance spectroscopy (EIS) measurements. Results obtained show that the surfactants studied are good cathodic inhibitors acting on the cathodic hydrogen reaction without modifying its mechanism. EIS results show that the changes in the impedance parameters (R_T and C_{dl}) with concentration of surfactants studied is indicative of the adsorption of molecules of surfactant leading to the formation of a protective layer on the surface of iron. The effect of the temperature on the iron corrosion in 1M HCl with addition of various concentrations of 1,2-ethane bis-(dimethyltetradecylammonium bromide) in the range of 20–60°C was studied. The associated apparent activation corrosion energy has been determined.

Migahed *et al.*, (2004) measured the surface tension at 298 K of prepared anionic surfactant [*p*-myristyloxy carbonyl methoxy-p'-sodium carboxylate-azobenzene]. The

critical micelle concentration (CMC) and some surface active parameters were calculated. The inhibition efficiency (η %) of this surfactant has been studied by both chemical and electrochemical techniques at 25°C. A significant decrease in the corrosion rate was observed in presence of the investigated inhibitor. The galvanostatic polarization curves showed that, the inhibitor behaves as mixed type but the cathodic effect is more pronounced. Tafel slopes are approximately constant and independent on the inhibitor concentration. The observed corrosion data indicate that, the inhibition of mild steel corrosion is due to the adsorption of the inhibitor molecules on the surface, which follow Langmuir adsorption isotherm. The surface morphology of mild steel samples in absence and presence of the inhibitor was examined using scanning electron microscopy.

Saleh (2006) studied the inhibiting action of hexadecylpyridinium bromide (HDPB) on mild steel in 0.5M H_2SO_4 solution in the temperature range of 30–60°C by using potentiodynamic technique and weight loss measurements. The collected polarization curves were used to study the effects of the inhibitor concentration and temperature on the corrosion behavior of mild steel. The inhibitor was found to be a mixed-type inhibitor. Maximum range of protection efficiency of HDPB was obtained at its critical micelle concentration (CMC). Weight loss measurements confirmed the above results. The inhibitor showed stronger influence on the anodic branch by shifting the free corrosion potential to more positive values. The surface coverage values were found to fit with Bockris–Swinkels isotherm with molecular ratio equal to 3. The apparent activation energy of corrosion, E_a is lower in

presence than in absence of the inhibitor. Also, higher negative values of the free energy of adsorption, ΔG°_{ads} and higher positive value of the enthalpy of adsorption, ΔH°_{ads} were obtained. The above results helped us to predict the mode and extent of adsorption of HDPB on the iron surface.

Infante *et al.*, **(2001)** synthesised some gemini surfactants in the series of 1,2-ethane bis(dimethyl alkyl (C_nH_{2n+1}) ammonium bromide) referred as n-2-n, where n = 10, 12 and 14. Their surface active properties at equilibrium in water at 25°C were determined. The inhibitive effect of these compounds, in the case of iron immersed in 1M HCl, was investigated through mass-loss, potentio-kinetic methods and electrochemical impedance spectroscopy. Polarisation data indicate that these compounds act as very good cathodic inhibitors of iron in 1M HCl. In the anodic range, the surfactants studied do not show an inhibition effect at iron electrode potential more positive than 100mV/Saturated Calomel Electrode. Impedance plots of iron in the presence of various concentrations of surfactants studied are similar to semicircles in the capacitive quadrant. The associated values of transfer resistances increase by increasing the additive concentrations. From all measurements performed, the variation of the inhibition effeciency versus concentration shows the same trend. The gemini surfactants appear to be adsorbed in the metal/liquid interface through the general adsorption mode following the Frumkin adsorption isotherm model. The electrochemical impedance spectroscopy shows that the maximum inhibition effeciency is attributed to a formation of an adsorbed layer at the iron surface. From tensiometric measurements, it was

found that the ability of gemini surfactants studied to adsorb at the interface air/water is concordant with their order of the inhibition effeciency of iron corrosion.

Fuchs-Godec (2006) measured the effectiveness of cationic surfactants of the N-alkyl quaternary ammonium salt type, i.e. myristyl trimethylammonium chloride (MTACl), cetyl dimethyl benzylammonium chloride (CDBACl), and trioctyl methylammonium chloride (TOMACl), as corrosion inhibitors for type X_4Cr_{13} ferritic stainless steel in 2M H_2SO_4 solution by electrochemical measurements. Potentiodynamic polarization measurements showed that these surfactants hinder both anodic and cathodic processes, i.e. act as mixed-type inhibitors. It was found that the adsorption of the N-alkyl ammonium ion in 2M H_2SO_4 solution follows the Langmuir adsorption isotherm. Plots of log $[\theta/ (1-\theta)]$ versus log c_{inh} yielded straight lines with a slope, which changed drastically at the critical micelle concentration (CMC) of the surfactants studied. Accordingly the CMC could be accurately determined from these measurements.

Akhter et al., (2002) determined the critical micelle concentration (CMC) of Cetyltrimethylammonium bromide (CTAB) micellar solution, containing methanol, ethanol, n-propanol, n-butanol and n-pentanol in N-methyl acetamide (NMA) and in N,N-dimethyl acetamide (DMA) using electrical conductivity and surface tension measurements at various temperatures. Both methods show that micelles are formed in NMA and in DMA solution in absence and presence of n-alkanols. Critical micelle concentrations have

also been measured as a function of the concentration of alcohol added. It was found that alcohol addition leads to an increase in NMA and in DMA penetration into the micellar interface which depends on the alcohol chain length. The results are discussed in terms of alcohol penetration of the micelles formed and solvent structuring. Thermodynamic parameters were evaluated for micellar systems in absence and in presence of n-alkanols to further explain the results.

Mata *et al.*, **(2004)** examined micellar behavior of sodium dodecyl sulfate (SDS) in the presence of tetrabutylammonium bromide by surface tension, viscosity, dynamic light scattering (DLS), dye solubilization, and cloud point measurements. They notes that SDS showed enhanced solubilization properties and a remarkable decrease in surface tension and critical micelle concentration (CMC) in presence of tetrabutylammonium bromide.

Schweinsberg *et al.*, **(1988)** prepared n-butyl, n-dodecyl, and n-hexadecyl ammonium iodides. The corrosion inhibition of the prepared compounds studied through potentiostatic polarization. The results of this study showed that each quaternary ammonium salt inhibits the corrosion of pure iorn in 0.5 M sulphoric acid at 30 °C. They found that the behaviour is similar to the corresponding bromides. The polarization curves indicate that the compounds behave as mixed inhibitors, each compounds exhibits Langmuirian behaviour and inhibition increases with increasing alkyl chain length. This is attributed to cohesive Van der Waals forces between the positive head

groups co-adsorbed with iodide ion on the positively charged iron surface.

Kang *et al.*, **(2001)** determined the critical micelle concentrations (CMCs) of anionic ammonium dodecyl sulfate (ADS) and cationic octadecyltrimethylammonium chloride (OTAC) at various temperatures using surface tention method. They found that the CMC decreased to a certain minimum and then increased with the temperature, displaying a U-shaped behavior. This behavior was analyzed using a power-law equation on the basis of reduced variables. Also, the U-shaped behavior is explained in terms of hydrophobic forces, as described by the thermodynamic potentials and parameters in the pseudo-phase separation model.

RESEARCH OBJECTIVE

2-RESEARCH OBJECTIVES

The objectives of this study are:

1- Preparation of some cationic surfactants such as:

    a- N-(4-methoxybenzylidene)-N-benzyldodecyliminium chloride.

    b- N-(4-methoxybenzylidene)-N-benzylhexadecyliminium chloride.

    c- N-(4-methoxybenzylidene)-N-benzyloctadecyliminium chloride.

    d- N-benzylidene-N-benzyldodecyliminium chloride.

    e- N-benzylidene-N-benzylhexadecyliminium chloride.

    f- N-benzylidene-N-benzyloctadecyliminiumchloride.

    g- N-butylidene-N-benzyldodecyliminium chloride.

    h- N-butylidene-N-benzylhexadecyliminium hloride.

    i- N-butylidene-N-benzyloctadecyliminium chloride.

2- Confirmation of structure of prepared cationic surfactants using the following spectroscopic techniques:

    a- FTIR

    b- ^{1}H-NMR

    c- Mass spectroscopy

3- Determination of critical micelle concentration (CMC), maximum surface excess (Γ_{max}), minimum surface area (A_{min}), efficiency (PC_{20}) and effectiveness (π_{CMC}).

4- Determination of thermodynamic parameters of micellization such standard free energy (ΔG^{o}_{mic}), enthalpy (ΔH_{mic}), and entropy (ΔS_{mic}).

5- Determination of thermodynamic parameters of adsorption such standard free energy (ΔG^{o}_{ads}), enthalpy (ΔH_{ads}), and entropy (ΔS_{ads}).

6- Evaluation of prepared surfactants as corrosion inhibitors for mild steel.

7- Evaluation of prepared surfactants as biocides for:
   a-   Pathogenic bacteria
   b-   Pathogenic fungi
   c-   Sulfur reducing bacteria