

List of abbreviations

The following abbreviations are used:

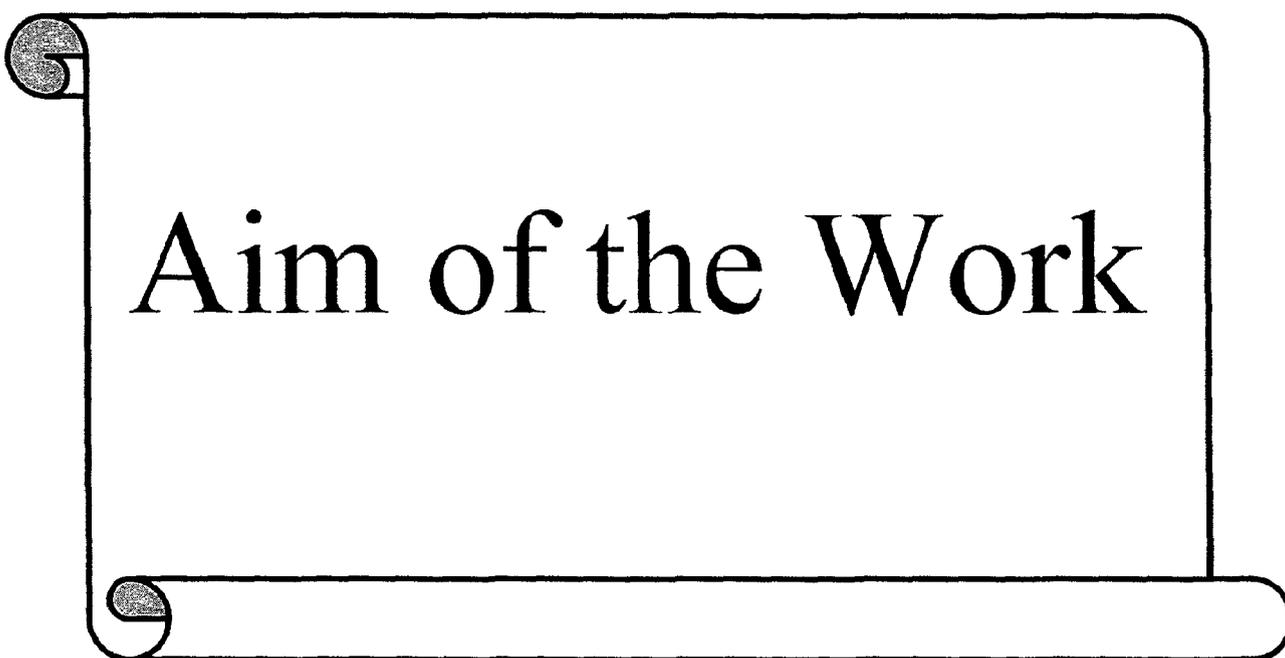
DEDIABr	N,N,N,N-decyldimethylisopropylammonium bromide
DODIABr	N,N,N,N-dodecyldimethylisopropylammonium bromide
HEDIABr	N,N,N,N-hexadecyldimethylisopropylammonium bromide
DEDIAOH	N,N,N,N-decyldimethylisopropylammonium hydroxide
DODIAOH	N,N,N,N-dodecyldimethylisopropylammonium hydroxide
HEDIAOH	N,N,N,N-hexadecyldimethylisopropylammonium hydroxide
E(54)	Ethoxylated N,N,N,N-dodecyldimethylammonium bromide benzoic acid with 54 units
E(64)	Ethoxylated N,N,N,N-dodecyldimethylammonium bromide benzoic acid with 64 units
E(74)	Ethoxylated N,N,N,N-dodecyldimethylammonium bromide benzoic acid with 74 units
E(84)	Ethoxylated N,N,N,N-dodecyldimethylammonium bromide benzoic acid with 84 units
DMSO	Dimethylsulfoxide
FT-IR	Fourier transform-Infra red
¹ HNMR	H-proton nuclear magnetic resonance
SEM	Scanning electron microscopy
γ	Surface tension of surfactants
CMC	Critical micelle concentration

Abbreviations

Π_{CMC}	The effectiveness of the surfactant solution
γ_0	Surface tensions of pure water
γ_{CMC}	Surface tension of surfactants at CMC
Γ_{max}	The maximum surface excess concentration of surfactant ions
C	The concentration of surfactant
R	The gas constant
T	The absolute temperature
A_{min}	The minimum surface area per adsorbed molecule
N_A	The Avogadro's number
K	The specific conductivity of surfactants
β	The degree of counter ion dissociation of surfactants
ΔG_m^0	The standard free energy of micelle formation
W	The average weight loss of three parallel carbon steel sheets
S	The total area of the specimen
t	The immersion time of specimen in solution
η_w	The corrosion inhibition efficiency
θ	The surface coverage of inhibitor on carbon steel
W_{corr}	The weight loss of carbon steel in absence of the inhibitors
$W_{\text{corr}}(\text{inh})$	The weight loss of carbon steel in presence of the inhibitors
$i_{\text{corr}}(\text{inh})$	The corrosion current density values with inhibitor
i_{corr}	The corrosion current density values without inhibitor
E_{corr}	The corrosion potentials
β_a	The anodic Tafel slope
β_c	The cathodic Tafel slope
k	The corrosion rate
E_a	The activation energy of the metal dissolution reaction

Abbreviations

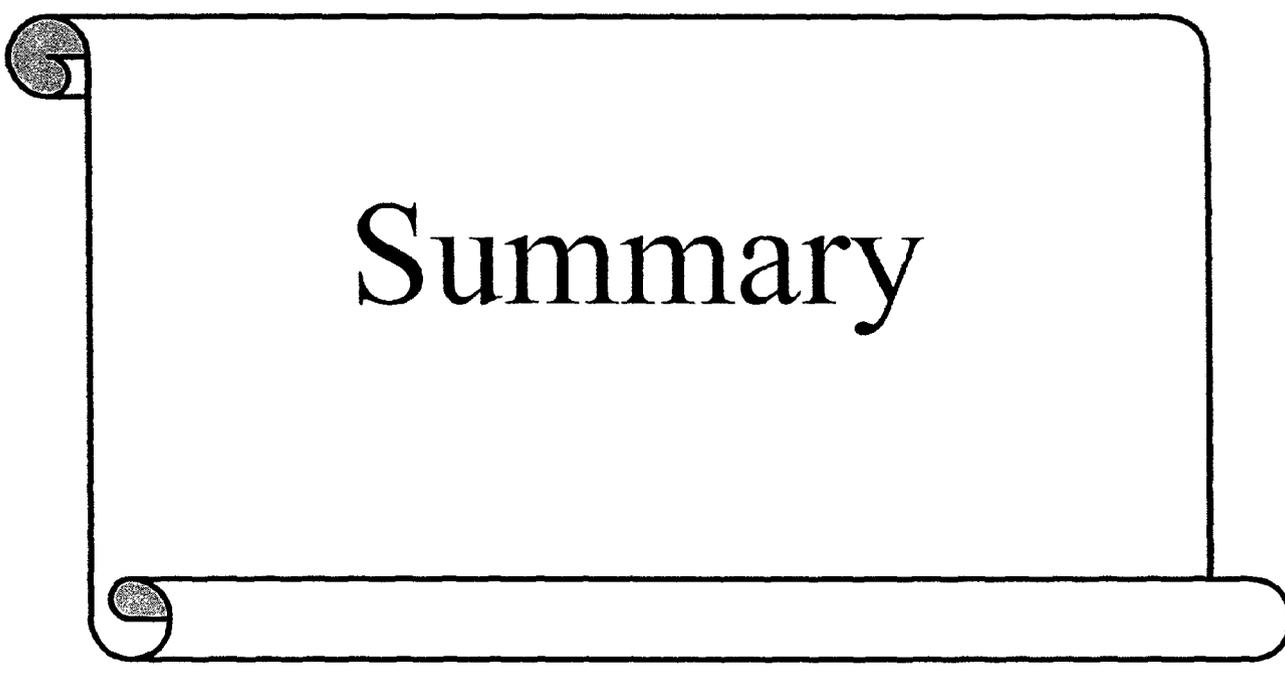
A	Arrhenius constant
K_{ads}	The equilibrium constant for adsorption desorption process
ΔG_{ads}	The free energy of adsorption process
ΔH_{ads}	The enthalpy of adsorption process
ΔS_{ads}	The entropy of adsorption process
SRB	Sulfate reducing bacteria



Aim of the Work

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- 1- Preparation of some cationic surfactants as following:
 - a) The reaction between different alkyl halides (decyl-,dodecyl-and hexadecyl bromide) with N,N-dimethylisopropyl amine.
 - b) The reaction between different ethylene oxide units with p-N,N-dimethylaminobenzoic acid and quaternization with alkyl halide.
 - 2- Confirmation of the structure of the prepared cationic surfactants using different spectroscopic techniques mainly:
 - a) FT-IR spectroscopy
 - b) ¹HNMR spectroscopy
 - 3- Determination of critical micelle concentration (CMC).
 - 4- Determination of thermodynamic parameters such standard free energy (ΔG_m), of the micelle formation.
 - 5- Evaluation of the prepared surfactants as corrosion inhibitor of steel.
 - 6- Determination of corrosion parameters, inhibition efficiency and surface coverage.
 - 7- Determination of activation energy (ΔE_a) of the prepared surfactants.
 - 8- Determination of thermodynamic parameters such standard free energy (ΔG_{ads}), enthalpy (ΔH_{ads}), and entropy (ΔS_{ads}) of the surfactants adsorption for the prepared surfactants.
 - 9- Evaluation of the prepared surfactants as biocide for sulfate reducing bacteria.
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Summary

SUMMARY

Cationic surfactants were prepared by reaction between different alkyl halides (decyl-, dodecyl- and hexadecyl bromide) with N,N-dimethylisopropyl amine to give N,N,N,N-alkyldimethylisopropylammonium bromide. Then, refluxed with potassium hydroxide pellets to give N,N,N,N-alkyldimethylisopropylammonium hydroxide.

Ethoxylated-cationic surfactants were prepared by reaction between different ethylene oxide units with p-dimethylaminobenzoic acid then refluxed with dodecyl bromide to give the corresponding ethoxylated N,N,N,N-dodecyldimethylammonium bromide benzoic acid with 54, 64, 74, 84 units.

The chemical structure of the prepared compounds was confirmed using FT-IR and ^1H NMR spectroscopes.

The surface properties of the prepared surfactants were determined by measuring the surface tension. Results have showed that, linear decrease in surface tension was observed with the increase of for all surfactant concentrations. For cationic surfactants, a comparison among CMC for homologous series of surfactant, demonstrates that, increasing the length of the hydrocarbon chain has the tendency of lowering the concentration, at which aggregation is initiated. For ethoxylated-cationic surfactants, it can be observed that an increase in the ethoxylation degree from 54 to 84 EO reduces the CMC value.

Specific conductivity (K) measurements were performed for the prepared surfactants at 30 °C in order to evaluate the CMC and the degree of counter ion dissociation, β . Results showed that, for cationic surfactants, the degree of dissociation of surfactants increase by increasing carbon chain length and for ethoxylated-cationic surfactants, the dissociation

degree of surfactants increase by increasing ethoxylation degree from 54 to 84 EO units.

Standard free energy (ΔG_m), of the micelle formation was determined. and showed that, for cationic surfactants, ΔG_m° values increase in the negative value as the carbon chain length of the prepared surfactants increase and for ethoxylated-cationic surfactants, ΔG_m° values increase as ethoxylation degree from 54 to 84 EO units increase.

The prepared compounds were investigated as corrosion inhibitors using three techniques.

From gravimetric measurements, results were showed that the inhibition efficiency for all prepared surfactants was increase with increasing the concentration. The maximum inhibition efficiency approached 98.8 % in the presence of 1×10^{-2} M of the corrosion inhibitor HEDIABr. The corrosion inhibition efficiency decreases with increasing the temperatures. For cationic surfactants, the corrosion inhibition efficiency was increase with increasing alkyl chain in surfactants and for ethoxylated-cationic surfactants, the corrosion inhibition efficiency was increase as ethoxylation degree from 54 to 84 EO units increase.

From potentiodynamic polarization measurements, all prepared surfactants shifted the corrosion potential (E_{corr}) in the cathodic direction and the cathodic Tafel slopes (β_c) and anodic Tafel slopes (β_a) values were changed when compared with those values obtained in the reference solutions, which confirms that surfactants act as cathodic inhibitor. The gravimetric measurements are in good agreement with those obtained from potentiodynamic polarization method.

The values of activation energy (E_a) of carbon steel dissolution in 1M HCl were calculated in absence and presence of each corrosion inhibitor. Results showed that, the activation energy increase in presence of corrosion inhibitor which indicates that physical adsorption (electrostatic)

occurs in the first stage. The concentration of inhibitors is playing an important role in increasing the activation energy value, thereby indicating a more efficient inhibiting effect. The increase in the activation energy, E_a , can correlate to the thickening of the electrical double layer.

The adsorption of the corrosion inhibitors on carbon steel obeys the langmuir adsorption isotherm. The values of equilibrium constant were decrease with increasing temperature and indicating that the adsorption type of the prepared corrosion inhibitors on the steel surface is physical adsorption. The high values of the adsorption equilibrium constant reflect the high adsorption ability of this inhibitor on carbon steel surface.

Thermodynamic parameters such as standard free energy (ΔG_{ads}), enthalpy (ΔH_{ads}), and entropy (ΔS_{ads}) for the prepared surfactants were determined. Results showed that, cationic surfactants with absolute values of ΔG_{ads} less than -40 kJ mol^{-1} indicate the electrostatic interaction between the charged inhibitor molecules and the charged metal surface (physical adsorption), where as ethoxylated-cationic surfactants with absolute values of ΔG_{ads} were more negative than -40 kJ mol^{-1} and involve charge sharing or its transfer from the inhibitor molecules to the metal surface to form co-ordinate type of bond (chemisorption).

All prepared surfactants have negative sign of ΔH_{ads} , indicating that the adsorption of the prepared surfactants on the carbon steel surface in 1M HCl solution is an exothermic process.

All prepared surfactants have positive value of ΔS_{ads} , attributed to the increase of disorder due to the adsorption of only one surfactant molecule by desorption of more water molecules.

Scanning electron microscopy (SEM) of the prepared corrosion inhibitors reveals that, the surface was strongly damaged in absence of corrosion inhibitors, where the surface in presence of corrosion inhibitors is free from pits and it is smooth which indicates a good protective film present

on the steel surface and also confirms the highest inhibition efficiency of the prepared surfactants at 1×10^{-2} M concentration.

Evaluating of the prepared surfactants as biocide against sulfate reducing bacteria, results showed that the synthesized cationic surfactants have antimicrobial activity against the tested microorganisms (SRB) and their activities depend on their chemical structures (mainly the hydrophobic chain length). The action mode of such cationic biocides on the bacterial strain is explained as an electrostatic interaction and physical disruption. However, ethoxylated-cationic surfactants showed weak antimicrobial activity against the tested microorganisms (SRB).