(REVIEW ARTICLE)

Surfactants in electrochemical applications: A review

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Abstract

Surfactants have been commonly used as corrosion inhibitors to protect metallic materials against corrosion. Also used as additives for electropolishing baths to improve surface texture. The amphiphilic nature of surfactant molecules creates an affinity for adsorption at interfaces such as metal/metal oxide–water interface. The adsorption of surfactants on metals and metal oxides creates a barrier that can inhibit corrosion. The surfactant's properties and the surfactant's interaction with metal or metal oxide and the surrounding solution environments determine the level of adsorption and corrosion inhibition.

1. Introduction

Surface active agents, surfactants naturally have a large impact on the chemistry of current interest. Their role in electrochemistry has been well-documented over the years. It can accumulate at the surface or interface. For surfactants to be surface active, these molecules' property is to adsorb at the interface between bulk phases, such as air and water, oil and water, or electrode and solution. Surfactants are usually amphiphilic organic compounds, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase into the air or the oil phase, while the water-soluble head group remains in the water phase [1]

Surfactants can modify and control the properties of electrode surfaces. The use of surfactant structures to alter or enhance reaction rates has been known for years. In the bulk aqueous phase, surfactants form aggregates, such as micelles, where the hydrophobic tails form the core of the aggregate, and the hydrophilic heads are in contact with the surrounding liquid. Other aggregates, such as spherical or cylindrical micelles or lipid bilayers, can also be formed. The shape of the aggregates depends on the chemical structure of the surfactants, namely the balance in size between the hydrophilic head and hydrophobic tail. A measure of this is the HLB, Hydrophilic-lipophilic balance. Surfactants reduce the surface tension of water by adsorbing at the liquid-air interface. The relation that links the surface tension and the surface excess is known as the Gibbs isotherm [2]

Recently, surfactant structures have been used to control reaction pathways. As early as the 1950s, there was evidence that surfactants could be used to control electrochemical reactions and solubilize organic compounds for electrochemical studies in water. A large fraction of the research in controlling electrochemical reactions with

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surfactants as well as aggregate characterization by electrochemical methods has been published within the past 20 years. They are found to control the electrochemical catalysis through their microstructures. Research since the late 1970s has demonstrated that columbic and hydrophobic interactions with surfactants can stabilize various electrochemically produced ion radicals [2]. Much early work was done on mercury electrodes, especially on dropping mercury electrodes (DME).part of the research in terms of inhibition of electron transfer and electrostatic interactions. More recent work concerning surfactants adsorbed from micelle solutions has focused on elucidating, or utilizing, aggregate structures formed on the electrode. Surfactant molecules generally adsorb at the interface between two bulk phases such as air and water, oil and water, or electrode and solution as pointed out earlier. Adsorption of surfactants on electrodes can have a profound influence on electrochemistry in fluids. [3]

2. Surfactant properties

2.1. Micelles & Critical micelle concentration

The term micelles refers to aggregates of surfactants. Above the critical micelle concentration (CMC), the soluble single surfactants aggregate. At very low concentrations surfactants do not associate themselves with form micelles. In water, the polar charged head groups face the water, and the hydrocarbon chains face the interior of the micelles. Reverse micelles are associations of surfactant molecules containing a water core, formed in an organic phase by the addition of surfactants. Critical micelle concentration is the concentration where sudden changes in physical properties such as conductivity and surface tension occur. The CMC is very characteristic for each surfactant, it is important to know the CMC value for the commonly employed surfactants for quantitative understanding of experimental data. [4]

2.2. Adsorption of surfactants at solid-liquid interface

In general, adsorption begins well below the surfactant's CMC, as evidenced, for example, by the low concentrations of Triton X-100, a nonionic surfactant (0.001–0.005%) employed for maximum suppression in polarography. Results above and just below the CMC for ionic surfactants on Pt. and Hg electrodes [4] agree with the formation of bilayers or hemi micelles (surface micelles).

2.3. Mechanism of surfactant adsorption

2.3.1. For ionic surfactant

Adsorption isotherm of charged surfactants on oppositely charged surfaces is illustrated in many papers [5] where the adsorption of negatively charged sodium dodecyl sulfate (SDS) on positively charged alumina is shown. This isotherm is characterized by four regions, attributed to four different dominant mechanisms being operative in each region. The mechanisms involved in these regions may be viewed as follows. Region I, which has a slope of unity under constant ionic strength conditions, is characterized by the existence of electrostatic interactions between the ionic surfactant and the oppositely charged solid surface. Region II is marked by a clear increase in adsorption which is attributed to the beginning of surfactant aggregation at the surface through lateral interaction between hydrocarbon chains [6]. Such colloidal aggregates are generically referred to as "solids". In the region, both electrostatic and lateral interaction forces are contributing to the adsorption. Region III exhibits a marked decrease in the slope of the isotherm, and this is ascribed to the increasing electrostatic hindrance to surfactant adsorption following interfacial charge reversal caused by the adsorption of the charged species in region III and beyond. Region IV and the plateau in it correspond to the maximum surface coverage as determined by micelle formation in the bulk or monolayer coverage, whichever is attained at the lowest surfactant concentration; further increase in surfactant concentration does not alter the adsorption density.

2.3.2. For non-ionic surfactant

The adsorption of non-ionic surfactants differs from that of ionic surfactants largely because of the absence of electrostatic interactions. Since hydrogen bonding is relatively weak in comparison with electrostatic and chemical bonding, the nature of the water structure at the solid-liquid interface will be of particular importance for the adsorption of nonionic. Adsorption of this type of surfactant depends on the length of the alkyl chain. A decrease in critical micelle concentration (CMC) with an increase in hydrocarbon chain length occurs [7].

2.3.3. For cationic surfactant

In literature, there are two conceptual structures of micelles. The first approach is based on packing parameters, in which the micelles are determined mostly by the volume of the surfactant tails. The approach implies that counter-ions and water can only penetrate the outer "shell" of micelles, which is dominated by the head-groups. The second approach is based on the hydration/ionic pairing interactions and is referred to as the "ion-pairing/hydration" model. This

approach designates a much smaller dry core, which contains only a few carbons, and originated from an observation of the high water content within the micelle [8]. It should be highlighted that the water molecules within the micelles contain non-hydrogen-bonded–OH groups, due to interaction with hydrophobic molecules. The existence of this water condition (hereafter referred to as "bound" water) has been confirmed at the air/water surface, alkane/ water interface, and in hydrophobic hydration shells of alkanols. The equilibrium between the bound water and "free" water (which has normal water-water H-bonds) has been validated for many aggregation systems. The hydration shells around halides and hydrophilic heads are also more rigid than the "free" water and constitute other types of hydration layers. A recent simulation showed that the structure of hydrophobic hydration is different from the water arrangement around ionic groups. Dielectric spectra of water have revealed that the water number of the hydration layer can be more than 10 for both anionic and cationic surfactants. The quantities of "bound" water would be a critical factor for the 2nd concept, as these water molecules affect the binding probability. In both structures, the micelles have fewer counter-ions than surfactants and form charged aggregates. Similar to other charged aggregates, the counter-ions are located within a thin electrical layer, the diffuse layer. The diffuse layer forms an inseparable counterpart of the micelle and plays a critical role in the experimental quantification of micellar structure [9].

2.3.4. Effect of functional group

The structure of the adsorbed layer depends on the packing of the molecules which in turn depends on the mutual repulsion and steric constraints among adsorbate species which affect the aggregation number (the number of molecules present in a micelle once the critical micelle concentration (CMC) has been reached [8].

2.4. Surface active properties

2.4.1. Determination of the CMC of the SAS in H_3PO_4

The main significance of the CMC consists of the fact, that at this Concentration, most of the physical and chemical properties of the surfactant solution present an unexpected variation [4]. The surface tension values (γ, mN/m) for the surface tension for the four SAS under investigation were plotted against the logarithm of the SAS concentration (log C) at different temperatures as shown in Fig 1, and values of the surface tension at every concentration of the four surface active agents at different temperatures
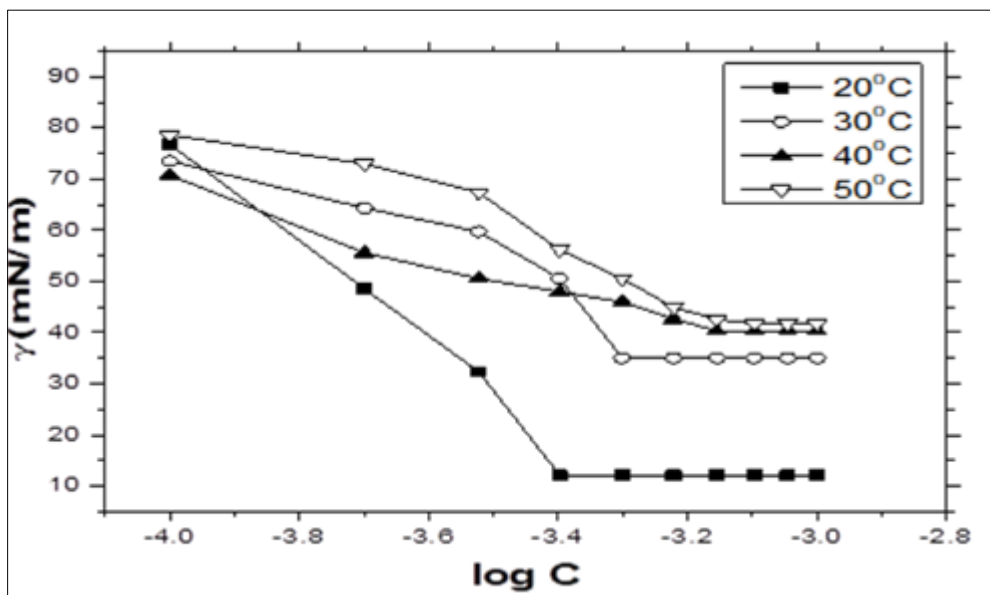
Figure 1 Relation between surface tension and log C at different temperatures

The critical micelle concentrations (CMCs) of the tested SAS were determined from the point of intercept of the two linear portions obtained by the γ –log C plots. The reproducibility of the surface tension versus concentration curve was checked by performing at least three separate experiments. It is obvious that the surface tension reduces with a rise in the concentration until CMC is reached, above which the surface tension is not affected by a further addition in the SAS concentration [9]

It was found that a decrease in surface tension is observed as the concentration of SAS increases and then remains constant at fixed points where further addition would not affect surface tension indicating the point at which CMC takes place at all temperatures.

In general(ionic surfactants), have higher CMC than (nonionic surfactants). This can be attributed to the fact that the free energy required to bring the polar heads of the surfactant together in the case of nonionic surfactant when the head group is uncharged the CMC is usually smaller than that when the heads are charged in ionic surfactant [10].

It was found that in case of ionic surfactants have the highest CMC at all temperatures that's can be explained as follows, for ionic surfactants with charged heads possess a higher CMC than that of nonionic surfactant as the head groups causes a steric repulsions between the similar charges of the surfactant so repulsion can be expected to increase as the number of positively charged nitrogen atom increases, and the higher CMC can be attributed to small hydrophobic alkyl tail of Benzalkonium chloride and the presence of the benzene ring and it's orientation were found to increases the CMC value in this study.[1]

For ionic surfactants have CMC higher than nonionic surfactants in this study due to the repulsion force between the similarly charged heads as mentioned before as well increasing the sulfate groups gives rise to an increase in the CMC as the head group size increases. For a given ethylene oxide chain length and an equilibrium packing parameter corresponding to spherical micelles, increasing the chain length of the surfactant tail will cause an increase in the aggregation number. [11]

For example Diisononyl phthalate possesses a higher CMC than that of n-oleil1.3diamino propane due to the presence of the benzene ring, diisononyl phthalate is considered a double tail surfactant If single-tail and double-tail surfactant molecules are compared, for the same equilibrium area per molecule, the double tail molecule will have an aggregation number twice as large as that of the single tail molecule. Therefore, the double-tail molecule can self-assemble to form bilayer vesicles whereas the corresponding single-tail molecule aggregates into only spherical micelles. [12] In addition to that the steric hindrance possessed by the benzene ring and its orientation will also have a great effect on the unexpected rise in its CMC and the ionic surfactants with ethylene oxide as the head group in di isononyl phthalat, the steric repulsions between the head groups can be expected to increase if the number of ethylene oxide units in a head group.

In general, comparing ionic and nonionic surfactants, the head group interaction will be larger for the ionic surfactants than for the nonionic surfactants because one has to also consider ionic repulsions between the head groups so compared to nonionic surfactants of the same tail length an increase in the CMC when ionic and nonionic surfactants of equal tail lengths are compared.

In the case, that there is no charged head group, surfactants manage to form micelles via the hydrophobic force and Vander Waals interaction. The strong interaction between water molecules repels the hydrocarbon chain out off the water bulk phase. [13]This forces the surfactants to aggregate forming micelle, where the hydrophilic head groups point to the water covering the hydrocarbon tail. Micelle formation is therefore expected to take place at lower concentrations for non-ionic surfactants in comparable with ionic surfactants. For ionic surfactants, high concentrations are necessary to get rid of the electrostatic repulsion between ionic-charged head groups during the micelle formation process.

2.4.2. Effect of electrolyte

The CMC is affected by some factors including the nature of SAS and the aqueous electrolyte used. The presence of HPO_4^{2-} in the electro-polishing cell is one of the major factors responsible for the alteration of the CMC values in comparison with their original values in pure water. These phenomena are related to the famous Hofmeister series, which is an empirical measure of the degree of ion hydration. The Hofmeister series orders ions with increased salting in potency from left to right, and is as follows:

$$SO_4^{-2}, HPO_4^{-2}, OH^-, HCOO^-, CH_3COO^-, Cl^-, Br^-, NO_3^-, I^-, SCN^-, ClO4^-,$$

HPO_4^{-2} is located to the left of chloride ion (Cl^- represents in some way, a borderline with the Hofmeister series) and acts as water structure makers (salting out ions) or (cosmotropic ions). The salting out effect occurs when HPO_4^{-2} competing with surfactant for hydration water, reduces the amount of water available in the micelles for polar chain hydration. Thus micelle formation will be produced at a lower surfactant concentration. [14]

2.4.3. Effect of temperature

Ionic liquids are considered a network of cations and anions interacting not only via electrostatic forces but also by forming extended hydrogen bond networks [15]. An addition of a surfactant to this supra-molecular structure results in solvent-solute interactions, and an increase in the temperature may result in some changes among the interactions affecting the final effect. What is more, the number of relatively weak hydrogen and van der Waals interactions between surfactant molecules becomes reduced. Thereby, the solvophobicity of surfactants in IL is increased, favoring the micellization process to occur at higher surfactant concentrations.

The obtained CMC values show an increasing trend with increasing temperature The raise in temperature causes a reduction in the hydration of the hydrophilic group (which favors micelles formation) or causes disturbance in the structural of water molecules surrounding the hydrophobic group (that effect that is not preferred micellization). The relative magnitude of these two opposite effects, so, determines if the CMC increases or decreases over a desired temperature range. The data in Table 2 indicates that CMC increases by increasing temperature which indicates that the magnitude of two factors does not prefer micelle formation so CMC increases [15].

2.4.4. Surface active parameters

The surface active properties of pure surfactant, effectiveness (π_{cmc}), maximum surface excess (Γ_{max}), and minimum area per molecule (A_{min}) were calculated using the following equations:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \quad ....Eq.\ (1)$$

$$\Gamma_{max\ =\ 1/303RT\ -\partial}\gamma\ /_{\partial\ Log}\ C \quad ....Eq.\ (2)$$

$$A_{min} = 10^{16}/[\Gamma_{max}.NA] \quad ....Eq.\ (3)$$

Where γ_o is the surface tension measured for pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC (mN/m). (Γ_{max}) is expressed as the concentration of surfactant molecules at the interface per unit area (mol cm^{-2}), T is the absolute temperature, R is the molar gas constant (R=8.314 J/mol.K), C is the concentration of surfactant in mol/l. NA is the Avogadros number (6.023×10^{23} molecule/mol)

The thermodynamic parameters of micellization expressed by standard free energy ΔG_{mic} and entropy of micellization ΔS_{mic} are calculated from the equations:

$$\Delta G_{mic} = RTln\ CMC \quad ....Eq.\ (4)$$

$$\Delta S_{mic} = (-\delta\Delta G_{mic}/\ \delta T) \quad ....Eq.\ (5)$$

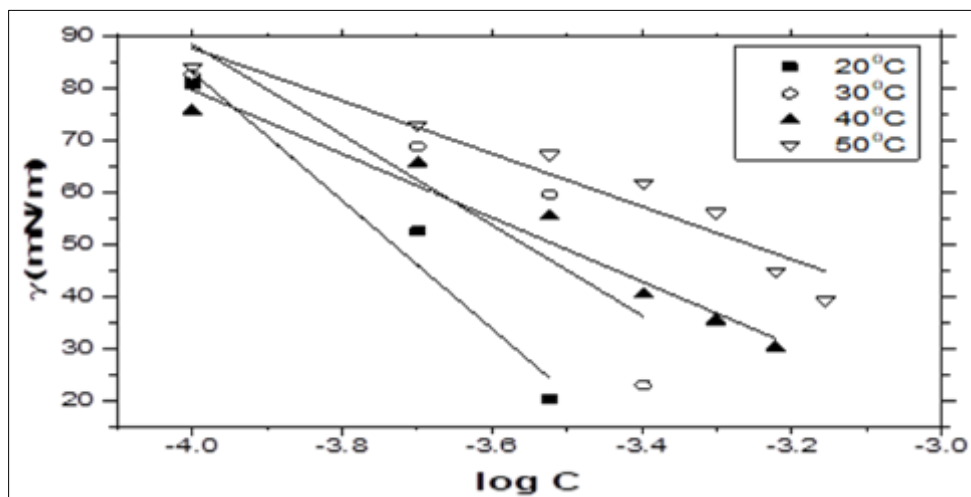Γ_{max} is calculated from the slop of γ –log C plots

Figure 2 γ –log C plots of at a different temperature

It is obvious that the lesser Γ_{max}, and the higher A_{min} is recorded for nonionic surfactants propane relative to ionic surfactants

A_{min} increases as the temperature increases. This may be attributed to the gradual increase in thermal motion.

The values of π_{cmc} indicate that the most surfactant effectiveness among the investigated surfactants due to the large decrease in surface tension which takes place at the CMC it has the largest inhibition efficiency on dissolution process

it`s apparent that from thermodynamic parameters of micelle formation we can deduce that micelle formation process is a spontaneous process ($\Delta G_{mic} < 0$) [17]. The ΔG_{mic} value is more negative indicating which surfactant can form micelle more easily than the others.

ΔS_{mic} possess a positive value indicating that the randomness of the system increases during the transformation of surfactant molecules into micelle.

2.5. Surfactant and electropolishing

Electropolishing is widely employed in industry for micro finishing and deburring of different metallic components. Electrolytic baths with different operating conditions and electrolyte compositions have been studied over the years [18]. Despite much advancement in the field of metals science and technology, the phenomenon of deterioration of metals remains a major concern to industries around the world. Electropolishing is the electrolytic metal finishing process currently widely used in several high applications such as cardiovascular and orthopedic body implants, and pharmaceutical and semiconductor installations.

Among others, the process provides a very clean, smooth layer, resistant surface. Currently, almost any metal, alloy, and intermetallic compound can be electropolished. [18]The importance of electropolishing on the surface of the metal process mainly is for the treatment of metals and alloys to enhance brilliant surface finishes with very low surface roughness values, no residual surface tensions, and improved steel resistance to deterioration

The enhancement of the surface morphology, topography, and brightness was achieved by addition of the three SAS to the electrolytic solution. The degree of brightness of the polished surface increases

Mechanistic studies of electropolishing have revealed that electropolishing is a diffusion-controlled reaction that takes place at the limiting current the limiting current is attained most probably when the diffusion layer becomes saturated with M^{+2} ions [18].

Therefore the value of the limiting current which determines the polishing rate depends on the rate of mass transfer of M^{+2} from the diffusion layer to the solution bulk. [19]The rate of steel polishing in the presence of phosphoric acid and organic additives in electro polishing process was studied by measuring the limiting current amount which represents the rate of electro-polishing. This rate decreases by increasing organic additives concentration with due to increasing solution viscosity.

This decrease was attributed to the presence of SAS particles deposited on the surface of the steel electrode, which acts as a protective layer and reduces the interaction between H_3PO_4 and the steel surface.

It is also clear that the inhibition increases with growth in concentration, which means that organic additives may be classed as corrosion inhibitors H_3PO_4. [20]. The anodic polarization behavior of metals is so sensitive to small concentrations of the selected surfactants. The decrease in limiting current with the addition of the studied SAS is consistent with a salt-film mechanism. When the surfactants were added, it is possible that adsorption occurred on and close to the anode helped to control the ion diffusion process in three ways namely:

2.6. Occupation of the surface cavities and depressions

The rate of electro-polishing over valleys is higher than that of cavities. That's why surface leveling takes place because the passivation of crevices is more stable and it inhibits etching.

Water molecules surrounding the anode become replaced. This replacement changes the dielectric constant of the medium and decreases the number of water molecules that solvate cations, hence decreasing the rate of diffusion of cations apart from the anode surface. [21] non-ionic surfactant composed of a polar hydrophilic and a hydrophobic part from.The decrease in on dissolution rate of metals can be attributed to two factors; molecular adsorption and the CMC

barrier conditions. Under CMC, the non-ionic surfactant exhibits the monolayer level on the surface of the electrode, and above the CMC adsorption of non-ionic surfactant may form multiple layers of physically adsorbed molecules. By increasing surfactant concentration after the CMC concentration, a gradual formation of multilayers that lead to a reduction in the rate of electro-polishing more than that estimated from the monolayer coverage resulted from concentrations lower than that of the CMC. In other meaning; the increase in thickness of multilayers and thus increasing surface barrier layer viscosity are the reason why an additional increase in dissolution inhibition above CMC takes place. [22]

For ionic surfactants, it was found that the anodic dissolution rate decreases with increasing concentrations of surfactant. It was found that, the dissolution inhibition action of ionic surfactant in H_3PO_4 results from physical (electrostatic interaction) adsorption of the two opposite charges of the metal ions from dissolution and charge on ionic surfactant forming a barrier on a metal surface. At low concentrations of anionic, the negative charge possessed by functional group adsorbed on the positive charges of M^{+2} on the electrode. By increasing the concentration of anionic, the barrier thickness consisting of sodium lauryl sulphate increases forming a hemi micelles as a result of the interaction between the oxygen atoms via Vander Waals forces. The barrier becomes stronger with adsorption of the highly negatively charged sodium lauryl sulfate micelle (when the surfactant concentration exceeds the CMC, the number of micelles increases but the free surfactant molecules remain constant at the CMC). So more decrease in limiting current and higher I% will happen after CMC of ionic surfactant [22].

The structure of a cationic surfactant consists of CnHmX+ and counter Y^-. cationic surfactant exhibits retardation behavior for dissolution of positively charged electrodes. This can be attributed to the adsorption of Y^- firstly at the electrode solution interface through the electrostatic attraction and creating excess negative charge toward the solution phase which favors more adsorption of positively charged CnHmX+ cation, so Y^- anion acts as an adsorption mediator of an adsorption composite film in which Y^- ions are sandwiched between the anode and positively charged part of cationic surfactant Taha et al, [4] investigated the electropolishing behavior of copper in orthophosphoric acid with Triton X-100, sodium dodecyl sulfate and cetyl pyridinium chloride as additives for improving the finish obtained on copper surface by measuring and comparing anode potential-limiting current relationships in solutions of gradually increasing concentration of surfactants. The addition of surfactants to the electro-polishing solution results in a lower limiting current. This confirms the mass transport of dissolved species from the anode surface to the bulk of the solution as the rate-determining step in the presence of three surfactants in all concentrations investigated. Scanning electron microscope (SEM), atomic force microscope (AFM), and measured brightness values were used to investigate the copper surface after electro-polishing, and the results were compared to polishing done in the absence of surfactants. According to SEM images and brightness values, the addition of Triton X-100 was effective in enhancing leveling and brightening more than sodium dodecyl sulfate and cetyl pyridinium chloride. AFM analysis showed that the roughness values (Ra) for an electro-polished copper surface, in the presence of surfactants, are significantly lower than in the absence of surfactants. Different reaction conditions and the physical properties of solutions are studied to obtain dimensionless correlation among all these parameters.

Abouzeid [1] Steel electro-dissolution performance was investigated in orthophosphoric acid in the presence of N-oleyl 1.3 Diaminopropane, Benzalkounuim chloride, Sodium Lauryl sulphate and Di-Isononyl phthalate as a surfactant using potentiodynamic polarization measurements. The retardation performance of these surfactants was examined. The surfactant surface active parameters were estimated based on surface tension measurements. The parameters calculated comprise the critical micelle concentration (CMC), maximum surface excess (Γmax), minimum surface area (Amin) and effectiveness (πCMC). The micellization thermodynamic parameters (ΔGmic, ΔSmic) for the estimated surfactants were also computed. Results obtained from surface active properties are comparable with those gained from galvanostatic polarization measurements. Temperature influence on the steel dissolution performance was examined in the 25 to 40 range. Steel kinetic study in orthophosphoric acid-free solution and orthophosphoric acid-containing surfactant was also examined. The dissolution kinetic and activated parameters were computed. Results based on microscopy measurement indicate that the addition of new four surfactants, resulting in the solution showing potential, discrete progress in the metal texture was monitored. Improvement produced in the electro-polishing bath by the investigated SAS owing to the adsorption of such surface active agents on the anode surface

Taha et al, [2], The effect of Triton x-100 (non-ionic surfactant), sodium dodecyl sulphate (anionic) and cetyl pyridinium chloride (cationic) on the corrosion rate of copper in 8 M H_3PO_4 was investigated using potentiodynamic polarization and surface tension measurements . The inhibition behavior of these surfactants was investigated. The surface parameters of each studied surfactant were calculated from its surface tension. The parameters studied include the critical micelle concentration (CMC), maximum surface excess (Γmax), minimum surface area (Amin) and effectiveness (πCMC).The thermodynamic parameters of micellization (ΔGmic, ΔSmic) for the studied surfactants were also calculated. The greatest reduction of surface tension (effectiveness, πcmc) and higher minimum area (Amin) were

achieved by Triton x-100 relative to the other two surfactants. This behavior agrees with the highest inhibition efficiency results achieved by Triton x- 100 obtained from potentiodynamic polarization method. The effect of temperature on the dissolution behavior of copper was studied at temperatures ranging from 25 to 40°C. A kinetic study of copper in uninhibited and inhibited acids was also discussed. The kinetic and activated parameters were calculated for the dissolution process .The adsorption of surfactants on copper surface in the acid solution was found to obey Kinetic-thermodynamic adsorption isotherm. The thermodynamic parameters were calculated.

Taha et al, [3], investigated the electropolishing behavior of copper was studied in orthophosphoric acid with Triton X-100, sodium dodecyl sulfate and cetyl pyridinium chloride as additives for improving the finish obtained on a copper surface. This was investigated by measuring and comparing anode potential-limiting current relationships in solutions of gradually increasing concentration of surfactants. Adding surfactants to the electropolishing solution results in a lower limiting current. This confirms the mass transport of dissolved species from the anode surface to the bulk of the solution as the rate-determining step in the presence of three surfactants in all concentrations investigated. Scanning electron microscope (SEM), atomic force microscope (AFM) and measured brightness values were used to investigate the copper surface after electropolishing and the results were compared to polishing done in the absence of surfactants

Taha et al, [4], The rotating cylinder electrode (RCE) and rotating disc electrode (RDE) are used for the investigation of dissolution behavior of copper in presence of surfactant (Triton x-100, SDS and CPC). The dissolution of copper was studied in 8M H_3PO_4 as a function of surfactant concentration (5×10^{-7} -1×10^{-2} M) at 25°C. Measurements were conducted based on the potentiodynamic polarization method. The inhibition behavior of low-cost surfactants compounds was inspected. The inhibition efficiency of these surfactants depended on their concentration and their chemical structure. The rotation speed of the RCE and RDE effects was explored. The adsorption of surfactants on copper surface was found to be not obeying Langmuir and followed the Kinetic-thermodynamic adsorption isotherm. Activation energy, the pre-exponential factor and adsorption-free energy $\Delta G°_{ads}$ are calculated and discussed

2.7. Surfactant and corrosion

Surfactants are a vast category of organic inhibitors used to obtain this protection. The ionic and nonionic surfactants were relevant to be great corrosion inhibitors for many metals and their alloys (iron, copper, aluminum, brass, zinc, magnesium, and carbon steel). Numerous studies proposed that most surfactant inhibitors are adsorbed on the electrode surface by moving water molecules from the surface and obtaining a compact and consolidated barrier film. The capacity of a surfactant molecule to adsorb is mainly directly connected to its property to aggregate and form micelles.

Recent research suggests that surfactants are reasonable choices for aqueous-phase corrosion inhibitors. The surfactant molecule contains a polar hydrophilic head and a nonpolar hydrophobic tail. The hydrophilic portion generally interacts with the metal surface, whereas the hydrophobic part is directed toward the solution side. The type of environment affects how they are aligned at the interface. For example, at the water-air and water-oil interfaces, hydrophilic heads point in the direction of the water. The carbon chain length is thought to impact the surfactant molecule's inhibitory potential significantly.

Theoretically, longer hydrocarbon chains should correlate with better inhibitory performance. This is undoubtedly accurate for surfactant molecules with the ideal size. However, a longer hydrocarbon chain has the reverse effect on how well it performs after a certain length [23-25].Their decreased solubility explains this. Most surfactant molecules demonstrate the best inhibition performance in the C8- C12 alkyl chain length.[23]

Industrial corrosion is a serious problem that causes severe economic losses because of the destruction of metal- and alloy-based processing equipment and the devaluation of industrial products. It has been reported that cationic-type surfactants are good inhibitors in certain acidic media [15]. Molecules of these compounds form a monomolecular hydrophobic protective layer at the metal surface that effectively prevents further attack by the corrosive media. In some corrosive systems especially in water–oil liquid systems certain compounds require hydrophilic groups or groups present on their structures for effectiveness as corrosion inhibitors. These groups affect the solubility behaviors of corrosion inhibitor compounds and are dispersible in such media.

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Adhikari et al [11] report a dataset for the scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), surfactant properties, thermokinetics, and corrosion inhibition activity of [[Co(HL) 2 .2H 2 O] Cl 2 .H 2 O]] (1) and [[Zn(HL) 2 .Cl] Cl.3H 2 O]] (2) complexes with surfactant-based Schiff base ligand (HL). It contains analyzed data related to thermokinetics, such as the activation energy (E ∗), entropy change (S ∗), enthalpy change (H ∗), and free energy change (G ∗) of HL and metal complexes. It also contains the SEM micrographs and EDX images of the studied ligand and metal complexes. A detailed analysis of the critical micelle concentration (CMC) data and figures illustrating the surfactant behavior of the synthesized complexes are presented in this article. The data for the corrosion inhibition activity of all synthesized compounds are also included. The dataset is related to the research article entitled "Bioinorganic inter-est on Co(II) and Zn(II) complexes of pyrrole-based surface- tant ligand: Synthesis, characterization, and in silico-ADME study.

Seyam et al [13], Two novel amido-amine-based cationic surfactants, namely, 3-decanamido-N,N,N-trimethylpropan-1-aminium methyl sulfate (DAMS) and N-(3-decanamidopropyl)-N,N-dimethylbutan-1-aminium bromide (DABB) were prepared and their chemicalstructures were elucidated via various spectroscopic tools. The surface activitiesof the targeted prepared surfactants were investigated. Utilizing potentiodynamicpolarization, hydrogen evolution, and weight loss methods, the inhibition impactof both synthesized surfactants on aluminum corrosion in solution with 0.5 M HClwas studied. The effect of raising both temperature and surfactant concentrationon the inhibition efficiency was studied and the thermodynamic functions werecalculated and clarified. Langmuir adsorption isotherm fitted widely with theempirical data. At all concentrations and temperatures, it was found that the inhi-bition efficiency for DAMS is greater than that of DABB

Attia et al [14]The gravimetric results showed maximum inhibition efficiency of ~ 77% when 50 ppm of Triton-X 100 used at 30 °C, while the potentiodynamic polarization measurements showed a maximum inhibition efficiency of ~ 63% when 20 ppm were used. The adsorption isotherms followed the Langmuir isotherm. The adsorption of TX-100 is a spontaneous process; accompanied by a decrease in entropy upon increasing the concentration of TX-100. Electrochemical polarization measurements support the finding of weight loss data. The results from this work can be useful to relevant industrial sectors using this surfactant as a corrosion inhibitor during acid cleaning.

3. Conclusion

Critical micelle concentration is regarded as a main factor in influencing the effectiveness of surfactants as corrosion retardation substances. The retardation mechanism is ascribed to the strong adsorption capability of the investigated surfactants on metal surfaces, forming an excellent protective film, that separates the surface from the destructive environment. Surfactants played the part of retardation, diminishing the acid etching action, and increasing the surface brightness. Surfactants make the electropolishing solution appear hopeful, and a distinctive development in the finish was observed. Improvement produced by electropolishing by surfactants was owing to their adsorption on the anode surface.

Compliance with ethical standards

Disclosure of conflict of interest

I am interested in water treatment and removal of heavy metals using environmentally friendly materials also low-cost materials and applied electrochemistry like electropolishing, electroplating, and corrosion

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