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Surface active properties of gelatin and their effect on the electropolishing and corrosion behavior of steel in orthophosphoric acid



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 Steel

Abstract Electropolishing behavior of steel was studied in orthophosphoric acid in the presence of gelatin for improving the finish obtained. This was inspected by surface tension measurement and potentiodynamic polarization by measuring the limiting current in solutions containing different concentrations of gelatin. Gelatin addition to electropolishing solution results in a lower limiting current. The gelatin surface parameters were calculated from its surface tension. The parameters considered include critical micelle concentration (CMC), maximum surface excess (Γ_{\max}), minimum surface area (A_{\min}) and effectiveness (π_{CMC}). Thermodynamic parameters of micellization (ΔG_{mic} , ΔS_{mic}) for gelatin were also calculated. Gelatin records greatest reduction of surface tension (effectiveness, π_{cmc}) and higher minimum area (A_{\min}). This behavior agrees with the highest inhibition efficiency results obtained from a potentiodynamic method. Scanning electron microscope (SEM) was used to investigate steel surface after electropolishing in the absence and presence of gelatin. The addition of a higher concentration of gelatin was successful to enhance steel surface quality.

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1. Introduction

Steel has found a wide application in a broad spectrum of industries and machinery, but it has a tendency for corrosion, which is a fundamental industrial concern that has received a

considerable amount of attention [1]. Because of higher hardenability, better wear resistance, and suitable toughness, steel is widely used as the material for cutting tools, forging and punching dies.

A leveling and brightening surface can be achieved through anodic dissolution in a suitable electrolyte by electrochemical polishing [2–4]. The electropolishing was performed in the limiting-current plateau of the anodic polarization curve, in which anodic dissolution was under mass-transfer limitation. However, the species governing the mass-transfer limitation is appreciably dependent on both the metal electrode and electrolyte [5–7]. Two polishing mechanisms, the salt-film precipitation mechanism and the acceptor-limited of the species anion

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and water and/or their complexes mechanism were proposed [8–10].

The surface phenomena of electropolishing are generally classified into two processes: anodic leveling and anodic brightening. Anodic leveling results show a difference in the dissolution rate between peaks and valleys on a rough metal or alloy surface depending on the current circulation or mass-transport conditions [11–18]. On the other hand, anodic brightening was found to be achieved under the tertiary current distribution conditions only [2]. Since anodic brightening indicates the absence of crystallographic dissolution related to the metal microstructure [19–22], a shift in the dissolution mechanism from the surface-kinetic control of the diffusion control conditions [2] was proposed for the course of this microstructure-insensitive phenomenon.

In general, micro-finishing or surface refining of steels in industries through electropolishing is performed in a mixed electrolyte containing concentrated phosphoric and sulfuric acid [7] with the addition of glycerol [23,24] to suppress the influence of the metal microstructure on the dissolution rate. In general, two typical mechanisms of electropolishing have been proposed in the literature, which are mentioned above; the acceptor mechanism announced that the acceptors (water or water-related species) are the key factors starting the effective electropolishing process [25]. Based on this mechanism, the electrolyte, usually contained a small quantity of acceptor species, and the adsorbed ions would accumulate on the anode surface to form an absorbent layer. This layer increased the overpotential of metal dissolution and hindered the solvation of metal ions with acceptors. Theoretically, the mechanism of preferential adsorption of shielding molecules [26,27] is considered to involve the acceptor mechanism because the quantity of water in the electrolytes is small.

In this study, an attempt is extended to improve the surface quality by decreasing the etched pits and defects formed over the surface, consequently, the surface smoothness could be increased. Accordingly, the current work is aspired to study the effect of addition of gelatin to orthophosphoric acid solutions used as electrolytes for electropolishing of steel. The surface parameters of gelatin were calculated (from its surface tension profile) to correlate the inhibition efficiency of gelatin with their surface parameters.

Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from the skin, bones,

and connective tissues of animals such as domesticated cattle, chicken, pigs, and fish. Photographic and pharma grades of gelatin are generally made from beef bones, although some beef bone gelatin is used by the food industry. Gelatin forms a solution of high viscosity in water, thickening agent. The layer of adsorbed shielding molecules dominates the anodizing behavior in our system. The structure of the adsorbed shielding layer is determined by molecular interactions which are a complicated function of the molecular thermal motions and intermolecular forces, especially the strong hydrogen bonds and electrostatic forces. Thus, the bath temperature significantly influences the thermal motions of molecules and the gelatin content provides strong hydrogen bonds.

2. Experimental

2.1. Materials

Steel specimens [0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron] of dimensions 10.0 cm × 5.0 cm × 0.2 cm were degreased with trichloroethylene. 8 M orthophosphoric acid was prepared from annular grade H₃PO₄ (85%). Different concentrations of gelatin solutions with 8 M H₃PO₄ are used, ranging from 20 to 350 ppm. 160 bloom numbers, 50,000 g/mol gelatin (Fig. 1) of pure quality (>97%) was used, Medizen pharmaceutical industries (Barranquilla – Colombia). Doubly distilled de-ionized water with a measured resistivity > 18 MΩ/cm was used in the preparation of solutions.

2.2. Potentiodynamic polarization

The cell used in the present work consists of the rectangular container having the dimensions of 5 × 10 cm with electrodes fitting the whole cross section. The electrical circuit (Fig. 2) consisted of a 6 V D.C. power supply, a variable resistance and a multi range ammeter connected in a series with the cell. A high impedance voltmeter was connected in parallel with the cell to measure its potential. The steady state anode potential was measured against a reference electrode consisting of a steel piece immersed in a cup of lugging tube filled with orthophosphoric acid-organic solution similar to that in the cell. The tip of the lugging tube was placed 0.5–1 mm from anode wall. Polarization curves, from which the limiting current was

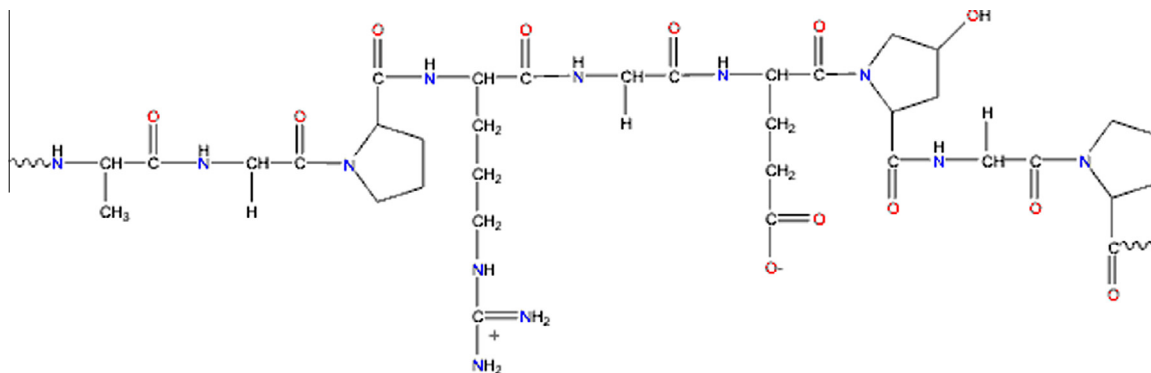


Figure 1 Gelatin structure.

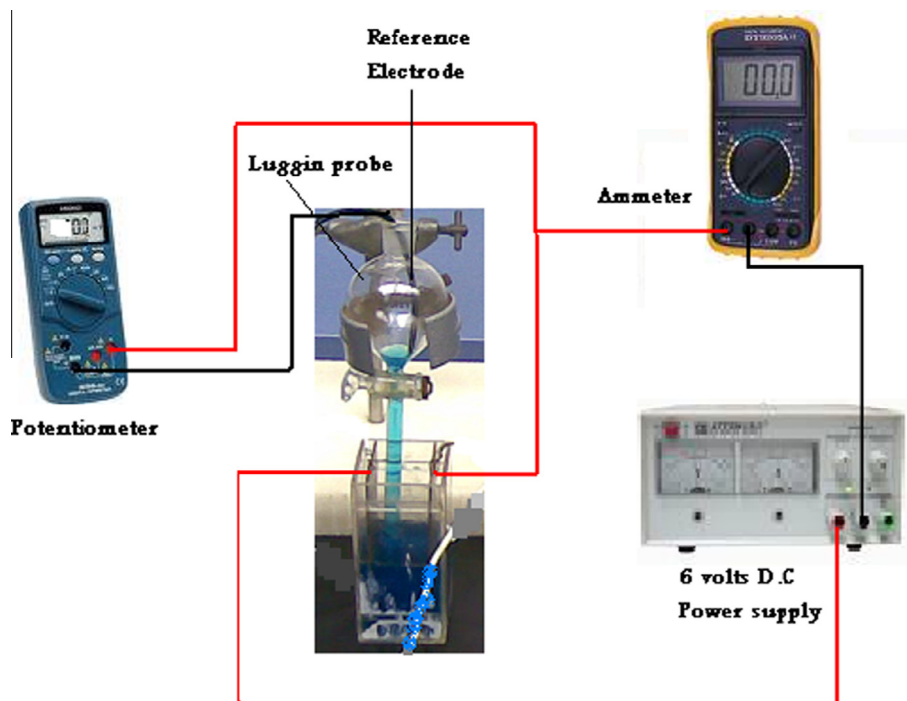


Figure 2 Electrical circuit.

determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady-state potential. Two minutes were allowed for reaching the steady state potential. Before each run, the grade of emery papers (800 grade) used for polishing the active surface of cathode and the back of anode was insulated with polystyrene lacquer and the working surface was degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. The temperature was regulated by placing the cell in thermostatic water bath (± 0.5 °C) at different temperatures (20, 30, 40 and 50 °C).

2.3. Surface tension measurements

The surface tension was measured at 20, 30, 40 and 50 °C using a Du Nouy tensiometer. The temperature (± 0.1 °C) was reserved constant by circulating the thermostated water through a jacketed vessel containing the solution. The concentration of the solution was varied by adding aliquots of stock solution of a known concentration to the known volume of the solution in the vessel. The reproducibility in the cmc was found to be $\pm 1\%$, calculated from the experimental cmc data from at least three runs.

2.4. Surface examination study

The scanning electron microscope images were taken using (JEOL, JSM-5300, scanning microscope, OXFORD instrument). For this purpose the steel sheet anode was (1 cm \times 1 cm).

3. Results and discussion

3.1. Surface active properties

3.1.1. Determination of the CMC of gelatin in water and gelatin in 8 M H_3PO_4

The main significance of the CMC consists of the fact, at this concentration, most of the physical and chemical properties of the surfactant solution present an unexpected variation [28]. The surface tension values (γ , mNm^{-1}) for the gelatin under investigation were plotted against the logarithm of the gelatin concentration ($\log C$, ppm) at different temperatures as shown in Fig. 3(a and b) for gelatin in water and gelatin in 8 M H_3PO_4 respectively. The critical micelle concentrations (CMCs) of the tested gelatin were determined from the point of intercept of the two linear portions obtained by the γ - $\log C$ plots.

It is clear that, the surface tension reduces with a raise in the concentration until CMC is reached, above which the surface tension is not affected by a further augment in the gelatin concentration. CMCs for gelatin in water are 1.2×10^{-5} , 1.8×10^{-5} , 3.0×10^{-5} and 8.0×10^{-5} at 20, 30, 40 and 50 °C respectively. While CMCs for gelatin in 8 M H_3PO_4 are 1.0×10^{-6} , 1.2×10^{-6} , 1.5×10^{-6} and 3.0×10^{-6} at 20, 30, 40 and 50 °C respectively.

From the above argument, we can assume that gelatin act as surfactants, for a characteristic property of surfactant is the ability to form aggregated molecules. It is clear that the value of the CMC of gelatin in water is greater than that in 8 M H_3PO_4 . The CMC is controlled by a number of factors

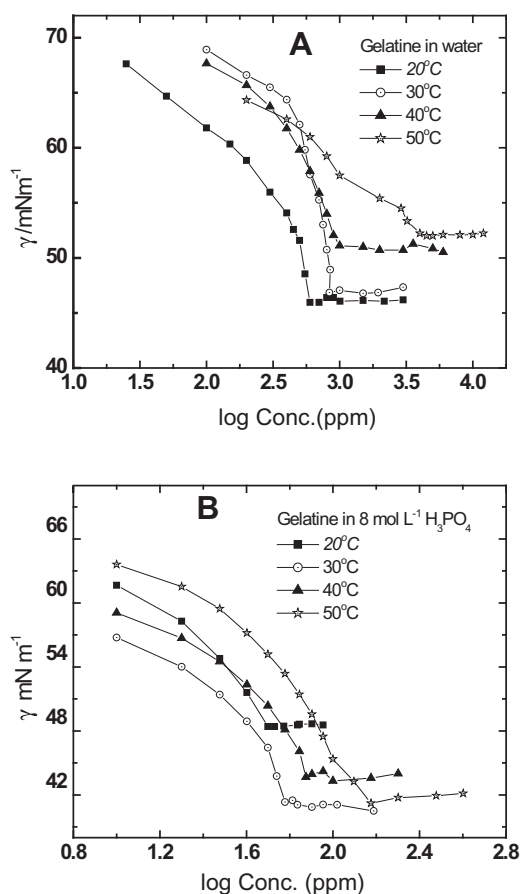
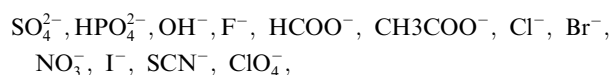


Figure 3 Variation in surface tension with concentration of gelatin (A) in water, (B) in 8 M H₃PO₄ at different temperatures.

that are dependent on the nature of surface active agent (SAS) and the aqueous environment. The company of HPO₄²⁻ in the present study is one of the influential factors being responsible for the shift of the CMC values with respect to their primary values in pure water.

These phenomena are related to the famous Hofmeister series, which is an empirical measure of ion hydration degree. The Hofmeister series orders ions with increased salting in potency from left to right, and is as follows:



HPO₄²⁻ which is located to the left of chloride ion (Cl⁻ represents in some way, a borderline with the Hofmeister series) acts as water structure makers (salting out ions) or (cosmotropic ions). The salting out effect is produced when HPO₄²⁻ 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 [29,30].

3.1.2. Effect of temperature on CMC values

The obtained CMC values show a rising trend with the mounting temperature (Table 1). The rising temperature causes a decrease in the hydration of the hydrophilic group (which favors micellization) or causes interruption of the structured water surrounding the hydrophobic group (an effect that disfavors micellization). The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. From the data in Table 1, it is clear that CMC increases by the rising temperature, which implies that the magnitude of two factors is disfavoring micellization thus CMC increases [31–33].

3.1.3. Surface active parameters

Surface pressure at C_{CMC} , (π_{cmc}), which is defined as the effectiveness of gelatin in reducing surface tension [34] was calculated from the following equation:

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

where γ_o is the surface tension calculated in pure water at the appropriate temperature and γ_{cmc} is the surface tension at CMC (mN/m). The greatest reduction in surface tension at CMC (effectiveness, π_{cmc}) achieved by gelatin is in good agreement with the high inhibition efficiency in the dissolution process [35–37].

- Maximum surface excess (Γ_{max}), is an effective measure of the surfactant adsorption at the air/solution interface. The concentration of the surfactant has been always higher at the surface phase than that in the bulk solution. The surface excess (Γ_{max}) was calculated by the Gibbs adsorption equation [38]:

Table 1 Surface active properties for the gelatin at different temperatures.

Gelatin	In H ₂ O				In 8 M H ₃ PO ₄			
	20	30	40	50	20	30	40	50
<i>Parameters</i>								
CMC, ppm	600	900	1500	4000	50	60	75	150
CMC, mol L ⁻¹	1.2×10^{-5}	1.8×10^{-5}	3.0×10^{-5}	8.0×10^{-5}	1.0×10^{-6}	1.2×10^{-6}	1.5×10^{-6}	3.0×10^{-6}
γ_{CMC} , mN m ⁻¹	45.96	46.60	50.98	52.22	55.86	46.34	43.68	41.23
$10^{10} \Gamma$, mol cm ⁻²	4.02	3.92	2.88	1.52	3.33	3.21	2.80	2.74
π_{cmc} , mN m ⁻¹	27.54	24.6	18.62	15.72	17.64	24.86	25.92	26.71
A_{min} , Å ²	41.30	42.35	57.65	109.23	49.85	51.72	59.30	60.59
$-\Delta G_{\text{mic}}$, kJ mol ⁻¹	27.60	27.52	27.10	25.33	33.65	34.34	34.90	34.15
ΔS_{mic} , kJ mol ⁻¹ K ⁻¹	0.094	0.091	0.087	0.078	0.114	0.113	0.111	0.106
$-\Delta G_{\text{ads}}$, kJ mol ⁻¹	28.28	28.14	27.74	26.36	34.18	35.11	35.82	35.12
ΔS_{ads} , kJ mol ⁻¹ K ⁻¹	0.097	0.093	0.088	0.082	0.117	0.116	0.114	0.109

$$\Gamma_{\max} = \frac{1}{2.303RT} \frac{-\delta\gamma}{\delta \log C} \quad (2)$$

(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 ($R = 8.314 \text{ J/mol K}$) and C is the concentration of surfactant in mol/l. A substance that lowers the surface energy is thus present in excess at or near the surface, i.e., when the surface tension diminishes with the growing activity of a surfactant. From Table 1, it is clear that the Γ_{\max} decreases with temperature.

- The minimum area per molecule (A_{\min}) was calculated using the Gibbs adsorption equation [38,39]:

$$A_{\min} = 10^{16} / [\Gamma_{\max} \cdot N_A] \quad (3)$$

N_A is the Avogadro's number (6.023×10^{23} molecule/mol). It was assumed that the head group area at the air/solution interface was the same as the equilibrium area per surfactant molecule at the supramolecule/solution interface [40,41]. Also, it is evident that A_{\min} increases with temperature. This is probably due to the increased thermal motion [35,36].

- The thermodynamic parameters of micellization expressed by standard free energy $\Delta G_{\text{mic}}^{\circ}$ and the entropy of micellization $\Delta S_{\text{mic}}^{\circ}$ are calculated from the equations:

$$\Delta G_{\text{mic}}^{\circ} = RT \ln \text{CMC} \quad (4)$$

$$\Delta S_{\text{mic}}^{\circ} = (-\delta \Delta S_{\text{mic}} / \delta T) \quad (5)$$

Analyzing thermodynamic parameters of micellization (Table 1), one may conclude that micellization process is a spontaneous process ($\Delta G_{\text{mic}}^{\circ} < 0$) [42]. The $\Delta G_{\text{mic}}^{\circ}$ for gelatin in 8 M H_3PO_4 is more negative than in water. This behavior shows that gelatin form micelle more easily in 8 M H_3PO_4 than in water, which confirms the values of CMC obtained, where CMC of gelatin in 8 M H_3PO_4 is less than that in water as mentioned above. Also, it is observed that $\Delta G_{\text{mic}}^{\circ}$ decreases with increasing temperature, which confirmed that the values of CMC increase with an increase in temperature [43].

We can observe that $\Delta S_{\text{mic}}^{\circ}$ values are positive (Table 1). The higher positive value recorded by gelatin in 8 M H_3PO_4 compared with its value in water, shows the increase in the randomness in the system upon the transformation of surfactant molecules into micelle.

The standard free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) of the surfactant at the air/solution interface was calculated by the equation

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{mic}}^{\circ} - [0.6022] \times [\pi_{\text{cmc}} \times A_{\min}] \quad (6)$$

$$\Delta S_{\text{ads}}^{\circ} = (-\delta \Delta G_{\text{ads}} / \delta T) \quad (7)$$

Investigation of the thermodynamic parameters of adsorption (Table 1) showed that;

- (1) $\Delta G_{\text{ads}}^{\circ}$ are negative values which are a sign of spontaneity the adsorption process.
- (2) The negative values of $\Delta G_{\text{ads}}^{\circ}$ are greater than $\Delta G_{\text{mic}}^{\circ}$ showing that surfactants favor adsorption rather than micellization.
- (3) Adsorption at an interface is associated with a diminish in the free energy of the system. These observations

agree with the data reported before [44] which indicate that the steric factors inhibit the micellization more than they affect adsorption at the air/aqueous interface.

Also, an examination of ΔS_{ads} values shows that the ΔS_{ads} values are all positive and greater than the ΔS_{mic} values reflecting the greater freedom of motion of the hydrocarbon chain at the planar/air, aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle [43].

3.2. Potentiodynamic measurements

Fig. 4 shows polarization curves for dissolution of steel in the presence of different concentrations of gelatin, from which limiting current (I_L) was obtained. It is characterized by an initial exponential increase in current with anode potential which is due to activation polarization. The current reaches a peak value then stabilizes at a plateau value that is relatively constant over a wide range of potential. The current peak results from super-saturation of the solution and precipitation of a salty film on the electrode surface for systems that exhibit the salt film mechanism of electropolishing. In case of electropolishing systems that follow acceptor mechanism, the salt film is not formed. Instead, there is a viscous layer close to the electrode surface. The peak could be because of a competition

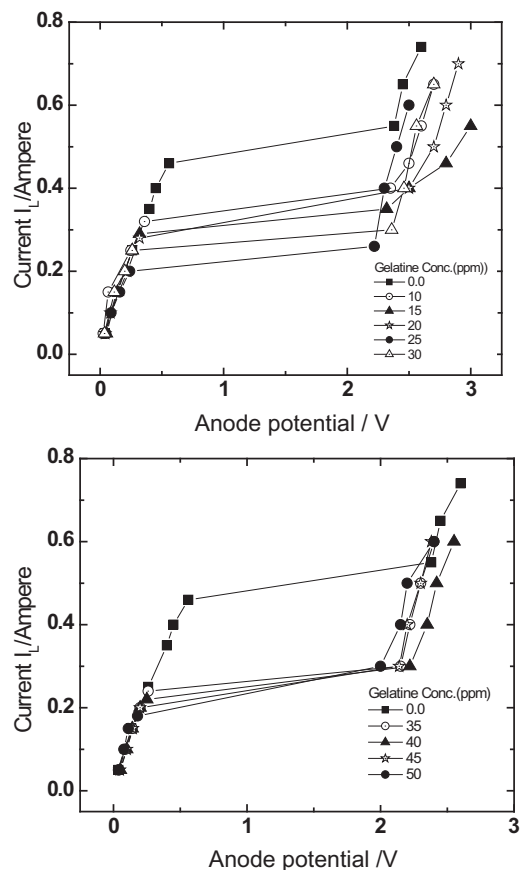


Figure 4 Typical polarization curves obtained for dissolution of vertical steel plate in 8 M H_3PO_4 in the presence of different concentrations of gelatin at 20 °C.

between the thickening viscous films and increasing transport rate of anions to the surface, an increasing the applied potential, the diffusion layer establishes a suitable thickness resulting in a constant plateau current density and the system is under mass transport control.

The dissolution rate (I_L values) and inhibition efficiency percentage (IE%) for the studied gelatin at a concentration range from 10 to 350 ppm and temperature range from 20 to 50 °C are given in Table 2. The inhibition efficiency percentage (IE%) was calculated according to the following equation:

$$IE\% = \frac{I_{L(\text{blank})} - I_{L(\text{gelatin})}}{I_{L(\text{blank})}} \times 100 \quad (8)$$

It is clear that the current decreases obviously with an increase in the concentration of gelatin up to CMC value in all temperature ranges studied (Table 2).

Dissolution retardation of steel in 8 M H_3PO_4 solutions by gelatin can be explained on the basis of molecular adsorption. Molecule adsorption of the gelatin on the metal surface should also be considered due to the interaction between the unshared electron pairs in the molecule and the metal. Adsorption on steel surface was occurring through ester group ($O-C=O$), π -electrons of aromatic ring and lone pair of electrons of oxygen atoms. The high performance of gelatin was attributed to the presence of many adsorption centers, large molecular sizes, and planarity of the compound. [45]. Gluten is a colloidal substance (Gel type). A colloidal substance has a high molecular weight and has the ability to form a film on the metal surface generally and thus interferes with the attack partly by hindering the replacement of acid and partly in other ways according to Ivanov et al. [46]; we can conclude that gelatin are believed to be generally molecularly adsorbed on the metal surface, these adsorbed layers characterized by high electrical resis-

tance are formed on the metal surface which may be responsible for the reduction in the rate of diffusion of ions necessary for the dissolution process and subsequently the rate of dissolution process decreases .i.e. limiting current I_L decreases.

3.2.1. The relation between dissolution inhibition and surface properties of gelatin

The Gibbs equation (Eq. (2)) was applied to calculate the area per surfactant molecule (A_{min}) at the air/liquid interface (Section 3.1.3, Table 1). This value was used to calculate the monolayer coverage of surfactant at the steel/electrolyte interface, assuming that the occupied area per surfactant molecule at the steel/electrolyte interface is the same as that at the air/liquid interface [47].

Surface active property data of surfactants (Table 1) show the greatest reduction of surface tension (effectiveness, π_{cmc}) was achieved by Gelatin. This is in good agreement with the inhibition efficiency results achieved by gelatin using potentiodynamic measurements (Table 2) [33].

3.3. SEM analysis

Fig. 5a–f, shows the surface morphology before and after EP in the absence of additives and in the presence of different concentrations of gelatin.

Raw sample (Fig. 5a) looked uneven and appeared to have potholes. A large number of pits with large size and high depth distributed over the surface are seen. But, after the EP in 8 M H_3PO_4 , only a slight difference was observed more than the raw sample, where some numbers of pits are still observed. The specimen surface was smooth to some extent, where leveling and brightening occur and some deep cavities were filled up (Fig. 5b).

Table 2 Values of limiting current, % inhibition for dissolution of steel in 8 M H_3PO_4 in the presence of different concentrations of Gelatin at different temperatures.

Temperature	20 °C		30 °C		40 °C			50 °C				
	Gelatin conc. (ppm)	I_L (A)	IE (%)	Gelatin conc. (ppm)	I_L (A)	IE (%)	Gelatin conc. (ppm)	I_L (A)	IE (%)	Gelatin conc. (ppm)	I_L (A)	IE (%)
	0.00	0.461	–	0.00	0.505	–	0.00	0.562	–		0.755	–
	10	0.322	30.15	10	0.462	8.51	10	0.535	4.80	10	0.582	22.91
	15	0.292	36.66	15	0.450	10.89	20	0.522	7.12	20	0.535	29.14
	20	0.281	39.05	20	0.442	12.48	25	0.510	9.25	30	0.515	31.79
	25	0.262	43.17	25	0.431	14.65	30	0.492	12.46	40	0.502	33.51
	30	0.250	45.77	30	0.420	16.83	35	0.482	14.23	50	0.492	34.83
	35	0.242	47.51	35	0.411	18.61	40	0.465	17.26	55	0.472	37.48
	40	0.222	51.84	40	0.382	24.36	45	0.450	19.93	60	0.452	40.13
	45	0.200	56.62	45	0.362	28.32	50	0.440	21.71	65	0.433	42.65
	50	0.182	60.52	50	0.350	30.69	55	0.432	23.13	70	0.415	45.03
	60	0.222	51.84	55	0.333	34.06	60	0.422	24.91	75	0.390	48.34
	70	0.222	51.84	60	0.322	36.24	70	0.400	28.83	80	0.377	50.07
	80	0.222	51.84	70	0.366	27.52	75	0.380	32.38	85	0.353	53.25
	90	0.222	51.84	80	0.366	27.52	80	0.444	21.00	90	0.341	54.41
	100	0.222	51.84	100	0.366	27.52	85	0.444	21.00	95	0.325	56.95
	150	0.222	51.84	150	0.366	27.52	90	0.444	21.00	100	0.312	58.68
	200	0.222	51.84	200	0.366	27.52	100	0.444	21.00	125	0.300	60.26
	250	0.222	51.84	250	0.366	27.52	150	0.444	21.00	150	0.282	62.64
	300	0.222	51.84	300	0.366	27.52	200	0.444	21.00	200	0.322	57.35
	350	0.222	51.84	350	0.366	27.52	250	0.444	21.00	250	0.322	57.35

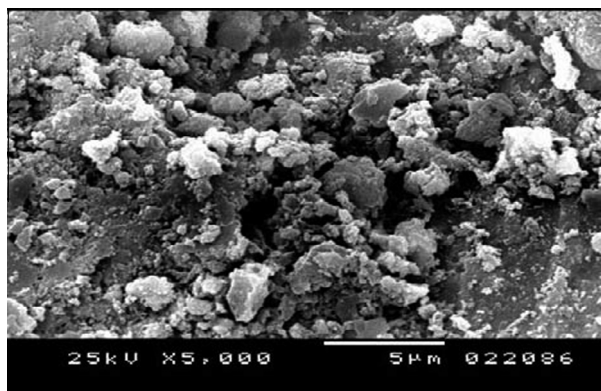


Figure 5a Raw sample before polishing.

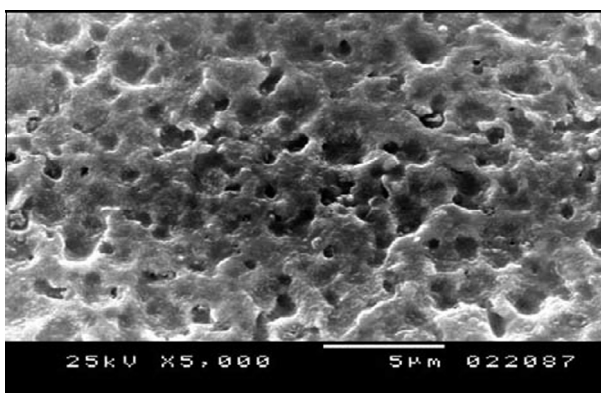


Figure 5b After electropolishing (blank) at 20 °C.

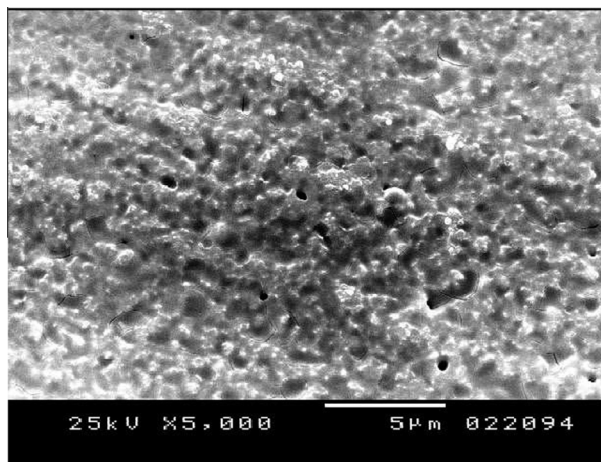


Figure 5c After EP + 10 ppm gelatin (before CMC).

The micrograph of the specimen in the presence of 10 ppm gelatin (below CMC) is shown in Fig. 5c, where leveling and brightening are occurring. Only a slight difference was observed compared to blank, where the pits decrease gradually and some protrusions are still represented on the surface of steel but it appears uniform more than blank.

In the presence of 30 ppm gelatin (below CMC) (Fig. 5d), the electropolished surface appears uniform, smooth and

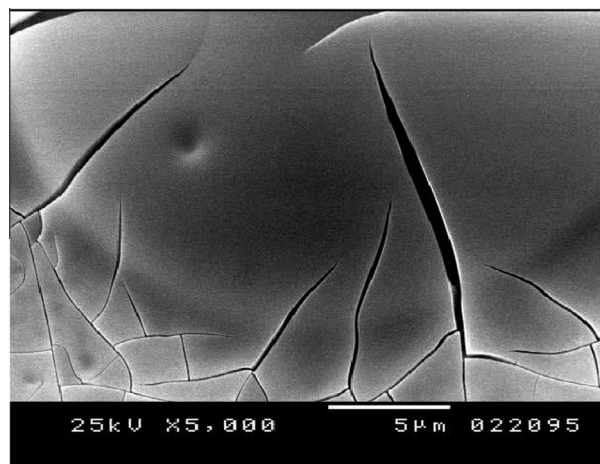


Figure 5d After EP + 30 ppm gelatin (before CMC).

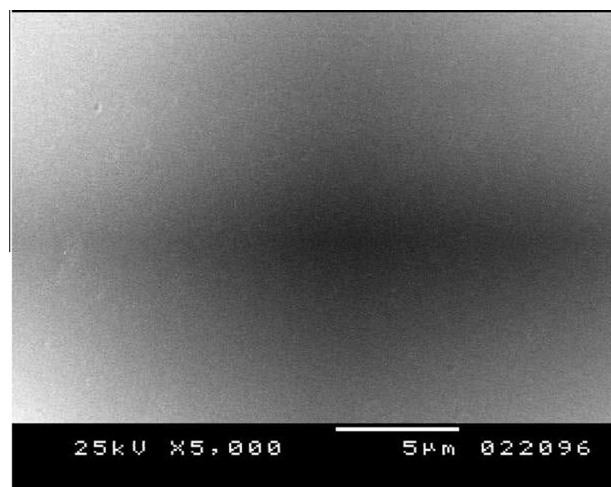


Figure 5e After EP + 50 ppm gelatin (at CMC).

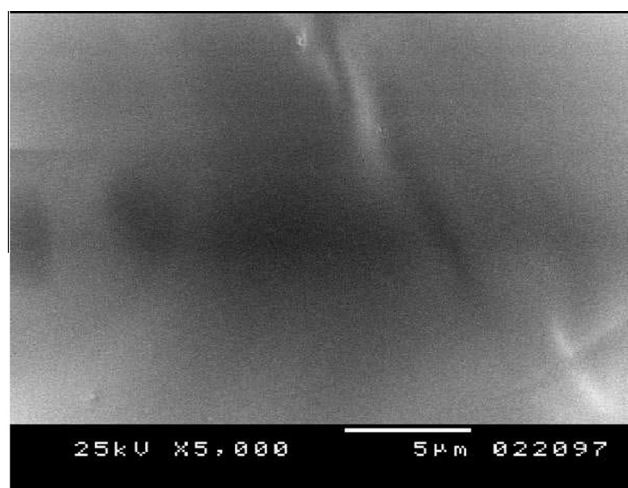


Figure 5f After EP + 100 ppm gelatin (after CMC).

bright more than Fig. 5c. There is enhanced in surface appearance to a great extent where the protrusions and pits are completely diminished. This is due to involvement of higher number gelatin molecules in the cavities of steel surface so appear more uniform, but some grain boundaries are represented evidently on the surface of steel.

In the presence of 50 ppm gelatin (at CMC) (Fig. 5e) and 100 ppm gelatin (after CMC) (Fig. 5f), the surface appears uniform, homogenous, compact and even grain boundary structures are completely diminished. The surface looked totally flat. This seems to be due to micelle formation; the solution is highly viscous and the adsorption of gelatin increases and consequently the grain boundaries are eliminated.

During the anodic dissolution, the dissolution rate of the anode is slowest and is the controlling factor. Therefore, the electrochemical reaction is under diffusive mechanism. Due to the diffusive mechanism, a viscous layer will be formed on the anode. With respect to the bulk of the electrolyte, this layer has a higher viscosity and greater electrical resistivity. The layer thickness differs from site to site: the film is thinner above protrusions than above valleys. Hence peaks dissolve more rapidly than valleys.

Gelatin form a solution of high viscosity in water, thickening agent. The layer of adsorbed shielding molecules dominates the anodizing behavior in our system.

It is probable that adsorption of gelatin on and close to the anode surface could help to control ion diffusion process in three ways, namely (i) filling up of surface cavities and depressions (ii) the looser packing of the adsorbed film at peaks facilitates the removal of the metal at a faster rate than losses from the valleys. Therefore surface leveling takes place because the passivation of crevices is more stable and it inhibits etching. Peaks are instead dissolving more rapidly. (iii) By replacement of water molecules in this region. This process may affect the dielectric constant of the medium and lower the number of water molecules available for solvation cations, hence lower the rate of diffusion of cations away from the anode surface [48].

4. Conclusions

- The studied gelatin revealed surface active properties and behave like surfactants.
- By increasing the concentration of the gelatin, the limiting current decreases and their inhibition efficiency due to their tendency toward adsorption.
- EP treatment of steel in a bath composition containing the gelatin could increase the ability of the bath to produce continuous polishing over an anode.
- Improvement produced an EP by the studied gelatin was due to the adsorption of such agents on the anode surface.
- Gelatin played the part of inhibitors, reducing the etching action of the acid, and increasing the brightness of the surface.
- In the presence of the gelatin, the solution appeared hopeful, and a distinct improvement in the finish was noted.

References

- [1] S. Pednehar, S. Smialowska, *Corrosion* 36 (1980) 565.
- [2] D. Landolt, *Electrochim. Acta* 32 (1987) 1.
- [3] J.R. Scully, R.G. Kelly, *Corrosion* 42 (1986) 537.
- [4] W.K. Kelly, R.N. Lyer, W. Pickering, *J. Electrochem. Soc.* 140 (11) (1993) 3134.
- [5] F.S. Shieu, Y.C. Sung, L.H. Cheng, J.H. Huang, G.P. Yu, *Corros. Sci.* 39 (1997) 893.
- [6] P. Chung, S.S. Smialowska, *Corrosion* 37 (1) (1981) 39.
- [7] S. Magaino, M. Matlosz, D. Landolt, *J. Electrochem. Soc.* 140 (5) (1993) 1365.
- [8] W.J. Mc.G. Tegart, *The Electrolytic and Chemical Polishing of Metals in Research and Industry*, Pergamon Press, 1959.
- [9] P.A. Jacquet, *Nature* 135 (1935) 1076.
- [10] W.D. Chandler, US Patent Number # 6,579,439, June, 2003.
- [11] T.P. Hoar, G.P. Rothwell, *Electrochim. Acta* 9 (1964) 135.
- [12] C. Wagner, *J. Electrochem. Soc.* 181 (1954) 225.
- [13] J.M. Fitzgerald, J.A. McGeough, *J. Inst. Math. Appl.* 5 (1969) 389.
- [14] P. Fedkiw, *J. Electrochem. Soc.* 127 (1980) 1304.
- [15] R. Sautebin, D. Landolt, *J. Electrochem. Soc.* 129 (1982) 946.
- [16] C. Clerc, D. Landolt, *Electrochim. Acta* 29 (1984) 787.
- [17] C. Clerc, D. Landolt, *Electrochim. Acta* 32 (1987) 1435.
- [18] M. Matlosz, D. Landolt, *J. Electrochem. Soc.* 136 (1989) 919.
- [19] R. Sautebin, H. Froidevaux, D. Landolt, *J. Electrochem. Soc.* 127 (1980) 1096.
- [20] C. Clerc, M. Datta, D. Landolt, *Electrochim. Acta* 29 (1984) 1477.
- [21] M. Datta, D. Landolt, *J. Electrochem. Soc.* 122 (1975) 1466.
- [22] M. Datta, D. Landolt, *Electrochim. Acta* 25 (1980) 1255.
- [23] M. Datta, L.T. Romankiw, *J. Electrochem. Soc.* 145 (1998) 3052.
- [24] M. Datta, J.C. Andreshak, L.T. Romankiw, L.F. Vega, U.S. Pat. 5,066,370, 1991.
- [25] M. Matlosz, *Electrochim. Acta* 40 (1995) 393.
- [26] V.V. Yuzhakov, H.C. Chang, A.E. Miller, *Phys. Rev. B* 56 (12) (1997) 12608.
- [27] S. Bandyopadhyay, A.E. Miller, H.C. Chang, G. Banerjee, V. Yuzhakov, D.F. Yue, R.E. Ricker, S. Jones, J.A. Eastman, E. Baugher, M. Chandrasekhar, *Nanotechnology* 7 (1996) 360.
- [28] A.M. El-Sabagh, N.S. Tantawy, N.M. Nasser, M.R. Mishrif, *J. Dispersion Sci. Technol.* 30 (2009) 1411.
- [29] R. Fuchs-Godec, *Electrochim. Acta* 54 (2009) 2171.
- [30] R. Fuchs-Godec, M.G. Pavlovic, *Corros. Sci.* 58 (2012) 192.
- [31] Z. Abdel Hamid, *Mater. Lett.* 57 (2003) 2558.
- [32] N. Tantawy, Evaluation of New Cationic Surfactant as Corrosion Inhibitor for Carbon Steel in a Metal Working Fluid, *Annals Of University "Dunarea De Jos" Of Galati Fascicle VIII*, 2005 (Issn 1221-4590 Tribology).
- [33] A.A. Taha, H.H. Abdel Rahman, F.M. Abouzeid, *Int. J. Electrochem. Sci.* 8 (2013) 6744.
- [34] M.J. Rosen, *Surfactant and Interfacial Phenomena*, third ed., John Wiley & sons, Hoboken, New Jersey, 2010 (p. 1).
- [35] M.A. Hegazy, *Corros. Sci.* 51 (11) (2009) 2610.
- [36] M.A. Migahed, E.M.S. Azzam, A.M. Al-Sabagh, *Mater. Chem. Phys.* 85 (2–3) (2004) 273.
- [37] M.J. Rosen, *Surfactants and Interfacial Phenomena*, second ed., John Wiley and Sons Inc., New York, 1989.
- [38] D.K. Chattoraj, K.S. Birdi, *Adsorption and the Gibbs Surface Excess*, Plenum, New York, 1984.
- [39] Q. Zhou, M.J. Rosen, *Langmuir* 19 (2003) 4555.
- [40] D. Jurasin, I. Habus, N. Filipovic-Vincekovic, *Colloid Surf. A: Physicochem. Eng. Aspects* 368 (1–3) (2010) 119.
- [41] H. Hoffmann, *Adv. Colloid Interface Sci.* 32 (1990) 123.

- [42] K. Szymczyk, B. Jańczuk, *Colloid Surf. A: Physicochem. Eng. Aspects* 293 (1–3) (2007) 39.
- [43] A.M. Al Sabagh, N.Gh. Kandil, A.M. Badawi, H. El-Sharkawy, *Colloid Surf. A: Physicochem. Eng. Aspects* 170 (2–3) (2000) 127.
- [44] A.M. Al-Sabagh, M.E. Abdul-Raouf, R. Abdel-Raheem, *Colloid Surf. A: Physicochem. Eng. Aspects* 251 (1–3) (2004) 167.
- [45] M.A. Hegazy, A.S. El-Tabei, H.M. Ahmed, *Corros. Sci.* 64 (2012) 115.
- [46] S. Ivanov, M. Rajcic-Vujasinovi, Z. Stevi, *J. Min. Metall.* 42B (2006) 33.
- [47] Z. Wei, P. Duby, P. Somasundaran, *J. Colloid Interface Sci.* 259 (2003) 97.
- [48] A.A. Taha, A.M. Ahmed, H.H. Abdel Rahman, F.M. Abouzeid, *Appl. Surf. Sci.* 277 (2013) 155.