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CAMEL'S URINE AS A NEW CLASS OF NONTOXIC INHIBITORS FOR MILD STEEL CORROSION IN HYDROCHLORIC ACID SOLUTIONS EFFECT OF TEMPERATURE

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ABSTRACT

The corrosion inhibition behavior of camel's urine (CU) on mild steel in 1.0 M HCl solutions were investigated at different temperatures. The effect of the inhibitor on the general corrosion of mild steel were examined by using gravimetric and electrochemical techniques. The inhibition efficiency increased with concentration of inhibitor but decreased with increase in temperature. The thermodynamic parameters of corrosion reaction for mild steel and adsorption process for CU were determined. Potentiodynamic polarization data suggest that CU acts as an inhibitor of mixed type, while impedance and SEM data reveal that as the inhibitor concentration increases a protective porous film is formed on the metal surface. Correlation between the inhibition characteristics of CU and its constituents was made.

Key words:- mild steel, hydrochloric acid, corrosion, inhibition, camel's urine, impedance and polarization.

INTRODUCTION

Numerous investigations on the corrosion inhibition of iron and iron alloys in different media and under various conditions were performed[1-6]. Inhibitors are used generally in several industrial processes to control the metal dissolution. Existing data show that most inhibitors act by adsorption on the metal surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte, and by the chemical structure of inhibitor[7]. Unfortunately, most corrosion inhibitors used in aqueous heating and cooling systems are health hazards[8]. Their toxic properties limit the field of their applications.

Camel's urine (CU) was never used as a corrosion inhibitor, but recent studies have proved the high efficiency of CU against a number of pathogenic microbes when compared with some antibiotics[9-11]. Usage of natural resources, such as CU as antimicrobial agents are usually safe, especially it is mentioned in the Muslim Sunni and as instructed by the Prophetic medicine. It is well known that drinking CU for therapeutic purposes was indicated by Prophet Mohammed Peace Be Upon Him.

Amer and Alhendi[12] gave details of the physical picture, the levels of urea (0.052 g 1^{-1}), uric acid (6.041 g 1^{-1}), creatinine (0.052 g 1^{-1}), chlorides (0.450 g 1^{-1}), phosphates (0.171 g 1^{-1}) and sulphates (7.760 g 1^{-1}) as well as the microscopic investigation of the urine. They found that its mean specific gravity was 1.056, and the pH value of most urine samples was slightly acidic. Microscopic

examination of urine shows that there were some chemical deposits such as calcium oxalate, calcium hydrogen phosphate, ammonium ureate and triple phosphate. The high contents of uric acid and chloride in urine of camel can also explain the higher specific gravity of CU than the other animals. The low concentration of urea in CU may be referred to the kidney function in camels'[3] and the presence of micro-organisms in the rumen of herbivores in which the urea is partially incorporated into microbial proteins in order to form amino acids[14]. The predominant occurrence of calcium oxalate, calcium hydrogen phosphate, triple phosphate and ammonium urate may reflect the calculogenic nature of the diet of the camel.

Accordingly, in the present work, the effect of the addition of CU, as a natural and nontoxic resource containing all the previous constituents, on the corrosion resistance of mild steel in 1.0 M HCI was examined at different temperatures using gravimetric and electrochemical techniques (electrochemical impedance spectroscopy [EIS] and potentiodynamic polarization measurements [PM]).

EXPERIMENTAL

Experiments were carried out in 1.0 M HCI solution in the absence and presence of different concentrations of CU. The urine sample is obtained from an apparently healthy male camel (one humped) with age around 5 years, slaughtered early in the evening in east Jeddah. Physically the urine sample appeared clear, urine- ferous, amber yellow and watery. All solutions were prepared from doubly distilled water and A.R. chemicals. Mild steel containing 0.02% P, 0.37% Mn, 0.03% S, 0.01% Mo, 0.039% Ni, 0.21% C and the remainder iron were used for the study. The influence of inhibitor on the corrosion of mild steel in 1 M HCI was monitored gravimetrically and electrochemically. The preparation of the specimens and electrodes for gravimetric and electrochemical measurements were described previously[15]. The weight loss was determined after 90 min. of immersion period in solutions of volume 100 cm^3 in absence and presence of different concentrations of CU (4.4 g 1^{-1}) to 125.1 g V^{-1}) at fixed temperatures in the range of 30°C to 60° C. The temperatures were adjusted by using an ultra thermostat (Julabo U3 No. 8311) at t° ±0.1 °C. For the electrochemical study, a standerd corrosion cell which was described previously[15] was used. The potentiodynamic and impedance measurements were run on ACM Gill AC connected to a Samsung computer (Bridge DVD ASUS 8X max.) at 30°C. The a.c. impedance measurements were performed at open circuit potential after 20 min. of immersion over a frequency range of 10 KHz - 0.1 Hz, with a signal amplitude perturbation of 10mV. The potentiodynamic polarization measurements were carried out, after the impedance test, at a sweep rate of 60 mV/min. All potentials were measured against silver/silver chloride / (3.0 M) KCI and the electrochemical measurements were done in deaerated solutions by using ultra pure nitrogen (99.999%). The morphology of mild steel surface after treatment in solutions was examined by a scanning electron microscope (Leitz METALLUX3 scanning microscope, WETZLAR, Germany).

RESULTS AND DISCUSSION

Gravimetric measurements at different temperatures :

The weight loss of mild steel specimen in 1.0 M HCI solutions in the absence and presence of different concentrations of CU at different temperatures were determined and the results are shown as general corrosion rate (R', g cm^2 min^1) in Figure 1. In all cases, increase in CU concentration leads to a decrease in the corrosion rate, indicating that the presence of CU retards the general corrosion of mild steel in 1.0 M HCI. This suggests that the inhibition of mild steel corrosion in the presence of CU occurs by adsorption at sites

on the metal surface. On the other hand, an increase in temperature from 30° to 60°C resulted in an increase in the corrosion rate, probably as a result of desorption of inhibitor molecules from the metal surface.

The percentage inhibition efficiencies (Inh.%) of CU were calculated by applying the following equation:

$$Inh.\% = (I-R'/R_0) \times 100 \quad (1)$$

where R_0 and R' are the corrosion rates in absence and presence of inhibitor, respectively. Figure 2 gives the variation of Inh.% with the logarithmic concentration of CU. As shown the Inh.% depends on the concentration of inhibitor and temperature and in all cases an S-shaped adsorption isotherm curves were obtained.

The apparent activation energy, enthalpy and entropy (E_a, $\Delta H°$, and $\Delta S°$, respectively) for the inhibition of mild steel in 1.0 M HCl were calculated from (a) Arrhenius-type equation[16]:

$$\log R = -E_a / 2.303\ RT + A \quad (2)$$

where A is the pre-exponential factor and R is universal gas constant, and from (b) the transition-state equation[16]:

$$\log R'/T = (\log R'/Nh + \Delta S°/R) - \Delta H°/2.303\ RT \quad (3)$$

where *h* is Plank's constant and N is Avogadro 's number. A plot of log R' against 1 / T gave straight lines, of slope $-E_a / 2.303$ R, as shown in Figure 3. E_a values for the corrosion reaction in the absence and presence of different concentrations of CU were estimated and presented in Table I. It was found that E_a value for mild steel corrosion obtained in free acid solution are of the same order of magnitude as those observed by other authors[17-19] for mild steel corrosion in some acid media. It is also of the order of activation energies

Table 1: Activation parameters for corrosion reaction of mild steel in 1.0 M HCl in the absence and presence of various concentrations of CU.

Cinh. gL^{-1}	Ea KJ mol^{-1}	AH^0 KJ mol^{-1}	AS^0 Jmol^K^{-1}
0.0	40.7	38.1	-191.7
4.4	50.1	46.8	-166.2
11.0	54.7	51.8	-152.6
21.7	62.9	60.2	-128.7
43.3	63.8	61.1	-129.7
65.0	68.1	64.9	-120.5
86.5	62.0	59.4	-138.5
125.3	58.1	55.4	-152.3

encountered for the hydrogen evolution reaction[20]. This is in accordance with the fact that the hydrogen evolution reaction in the absence of inhibitor is the rate-determining step for the overall corrosion reaction. However, the average value of E_a (60 KJ mol^{-1}) for the inhibited solutions is higher than that for the uninhibited solution (Table 2), indicating a strong adsorption of the inhibitor at the metal surface which leads to increase the energy barrier for the corrosion process. On the other hand, it is in the order of activation energies of diffusion processes[21]. The reaction between the metal and the acid may take place by diffusion of metal ions through the protective film formed on the metal surface.

A plot of log R'/T against 1 / T (Equation 3) also gave straight lines, as shown in Figure 4. The slopes of these lines is $-\Delta H^0 / 2.303$ R and the intercept is log R' / Nh + $\Delta S°$ / R, from which the values of $\Delta H°$ and ΔS^0 were deduced (Table 1). It is clear that the average value of $\Delta S°$ (-141.2 Jmol^{-1}K^{-1}) for the inhibited solutions has a less negative value from that recorded for the uninhibited solution (-191.7 JmoMK^{-1}). According to Antropoy[22] and Grigoryev[23] the presence of inhibitor leads the corrosion system to pass from less random to more orderly arrangements, and hence a less negative value of entropy is observed.

Adsorption isotherm at different temperatures

For the studied CU, it was found that the gravimetrically experimental data obtained at different temperatures fit a Langmuir type of adsorption isotherm (Figure 5), which is given by[5] :

$$C_{inh}./ 6 = 1 / K + Cinh \quad (4)$$

where C_{inh} is the concentration of the inhibitor, 9 is the surface coverage (9 = Inh.% /100) and K is the adsorption equilibrium constant. The linear regression between C_{inh}. **/** 6 and C_{inh} at the studied temperatures was obtained and the adsorption parameters were calculated and listed in Table 2. The equilibrium constant value (K) decreases with rising temperature which indicates that the adsorption process becomes much weaker at elevated temperatures. The standard free energy of adsorption ($\Delta G°_{ads}$.) can be calculated from the equation[24]:

$$K = 1 / 995.65 (\Delta G°_{ads} / RT) \quad (5)$$

where 995.65 is the concentration of water molecules at the electrode/electrolyte interface in g 1^{-1} Figure 6 gives the relation between the calculated $\Delta G°_{ads}$ and T according to the following equation[24]:

$$\Delta G°_{ads} = \Delta H°_{ads}. - T \Delta S°_{ads}. \quad (6)$$

A straight line plot of slope $-\Delta G_{ads}$ (121.5 $Jmol^{-1}K^{-1}$) and of intercept $\Delta H°_{ads}$ (-48.8K $Jmol^{-1}$) was obtained. The negative value of $\Delta H°_{ads}$ indicates that the adsorption process is exothermic and the inhibitor is physically adsorbed on the mild steel surface.

Electrochemical measurements at 30 °C :

The effect of CU on the anodic and cathodic polarization curves of mild steel in 1.0 M HCI solution at 30°C is shown in Figure 7. The presence of CU in the corrosive medium increases the anodic and cathodic overpotential and decreases the corrosion current density ($I_{corr.}$). This behavior supports the observed inhibition function of CU by gravimetric studies. Decrease of $I_{corr.}$ values was associated with a shift in the corrosion potential ($E_{corr.}$) to less negative values especially at higher concentrations. This suggests that although inhibition is of a mixed type, it is predominately anodic. The values of Inh.% were also determined from polarization measurements according to the following equation:

Table 2: **The adsorption parameters of** CU **at different temperatures**

Tempe-rature t (°C)	Liuear relation R %	Slope	Equili-brium constant K ($g^{-1}L$)	-AG°ads KJ mol^{-1}
30	99.9	1.03	0.110	11.83
40	99.6	1.04	0.070	11.08
50	98.9	0.94	0.037	9.67
60	96.4	0.74	0.020	8.25

$$Inh.\% = (1 - I_{corr}/I°_{corr} X\ 100 \quad (7)$$

where $I°_{corr}$ and I_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively, obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. The Inh.% values are included in Table 3, which indicate that the inhibition efficiency of CU increases with increasing its concentration.

The corrosion behavior of mild steel in 1.0 M HC1 in the absence and presence of various concentrations of CU, was investigated by the EIS method at 30°C. Nyquist plots for mild steel in inhibited and uninhibited acidic solutions are shown in Figure 8. All Nyquist plots show a high frequency capaci-tive loop, while at low frequencies a small inductive loop for the uninhibited solution and a diffusion tails for the inhibited solutions of high CU concentrations, were observed. The inductive loop is correlated with the

localized process of corrosion[25]. The diffusion tail indicates the existence of a protective porous film on the metal surface[26] in which the diameters of the pores control the diffusion of ions through the film. Accordingly, the mild steel dissolution in the presence of CU is diffusion controlled which supports the previous results obtained from the thermodynamic data. Figure 9 gives a schematic diagram of the metal surface covered by porous film and the simplified

Table 3: **Electrochemical parameters for mild steel in absence and presence of various concentrations of camel urine**

Electrochemical parameters				
$C_{inh.}$/g l^{-1}	0.0	21.7	43.3	86.5
$-E_{corr.}$	0.494	0.500	0.475	0.460
PM V				
$I_{corr.}$	30.51	16.82	12.13	8.95
$mAcm^{-2}$				
Inh. %	-	44.9	60.2	70.7
$I_{corr.}$	33.16	17.70	13.02	8.53
EIS $mAcm^{-2}$				
R_{ct}	0.787	1.533	2.003	3.057
Ωcm^{-2}				
Inh.%	-	48.7	60.6	74.3

equivalent model for the previous system. At low frequencies, the capacitive component no longer affects the total impedance value and the total impedance Z_t, can be presented as[27]:

$$Z_t = R_s + R_{ct} + Z_w \quad (8)$$

The Warburg impedance (Z_w) can be given by the following equation :

$$Z_w = Z_w = \sigma\,\omega^{-1/2} - \sigma\,\omega^{-1/2}\,j \quad (9)$$

where a is the Warburg coefficient ($\Omega cm^2\ s^{-1/2}$) and co = $2\pi f/(\text{rad}\ s^{-1})$. From equation (9), the imaginary portion, $-\sigma\,\omega^{-1/2}$ /, represents the information of diffusion process. Therefore in the Niquist plot at low frequency, where the diffusion tail shows up, the value of imag-axis presents the item $\sigma\omega^{-1/2}$, so that the Warburg impedance can be obtained by the value of Imag-axis at low frequency. Here, bf, which is defined as following equation, is qualitative represented as the Warburg impe-danee :

$$b_1 = -\sigma\omega^{-1/2} \quad (10)$$

Probably, the larger the value of bf, the less porous the inhibitor film, or the smaller the equivalent diameters of the pores, and hence it is more diffcult for the ions to diffuse through the pores within the inhibitor film.

Finally, Charge transfer resistance (R_{ct}) was estimated from the difference in impedance at lower and higher frequencies. Inhibition efficiency of corrosion of steel is calculated by R_{ct} as follows:

$$\text{Inh.\%} = (I - R^{-1}{}_{ct}/\ R^{-1}{}_{cto}) \times 100 \quad (11)$$

where $R^1{}_{cto}$to and $R"^1{}_{cto}$ are the charge transfer resistances in the absence and presence of inhibitor, respectively. Impedance parameters derived from these investigations are also given in Table 3. Good consistency between the results obtained from the polarization and impedance measurements was observed.

Scanning Electron microscopy :

SEM examination of steel surface, in 1.0 M HCI solution in absence and presence of low and high concentration of CU was carried out at 30°C. In absence of CU, general and pitting corrosion (deep and irregular pits) were detected on the metal surface (Figure 10a), while in the presence of low concentration of CU, the pits turn to distinct and spherical ones (Figure 10b). This indicates an improvement in the film quality as CU is added to the HCI solution. As the concentration increases, the micrograph shows the

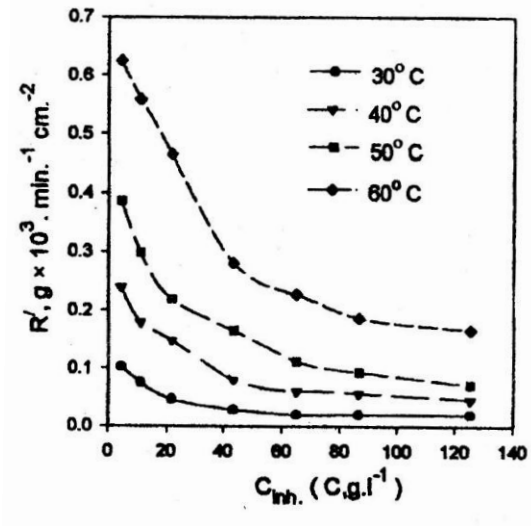

Fig. 1. Variation of corrosion rate with the concentrations of Cu for the mild steel in 1.0 M HCI at different temperatures.

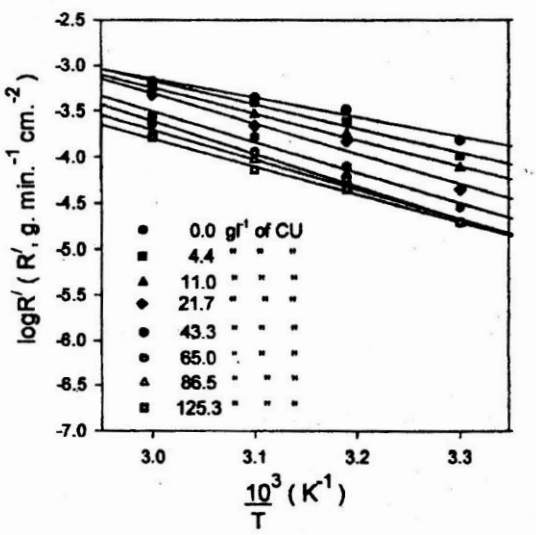

Fig. 3. Arrhenius plots of the corrosion rate for mild steel in 1.0 M HC1 in the absence and presence of different concentrations of CU.

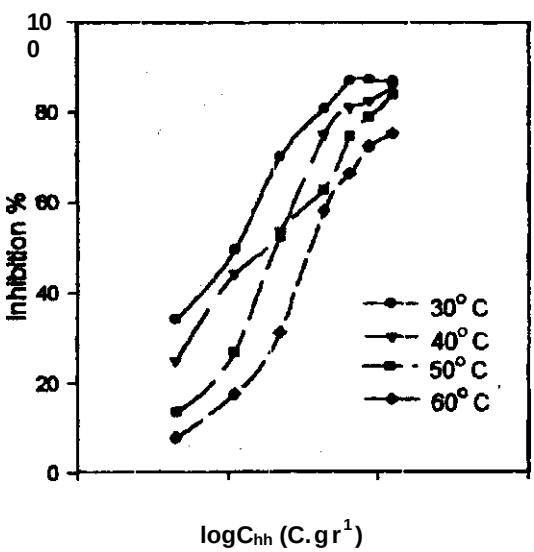

Fig. 2. Variation of the inhibition efficiency with the logarithmic concentrations of Cu at different temperatures.

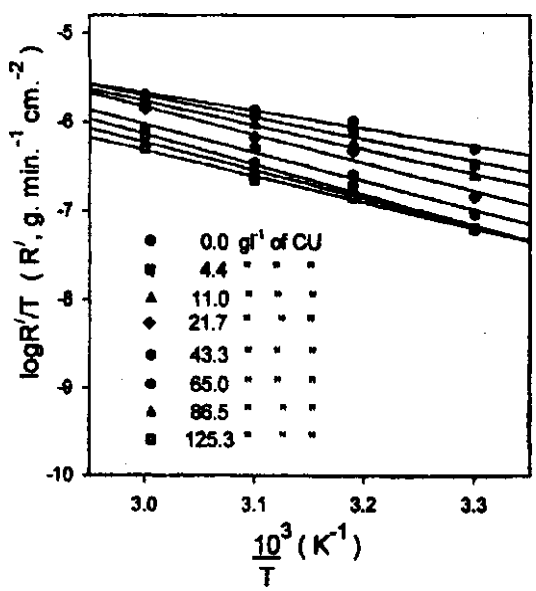

Fig. 4. Transition state plots of the corrosion rate for mild steel in 1.0 M HC1 in the absence and presence of different concentrations of CU.

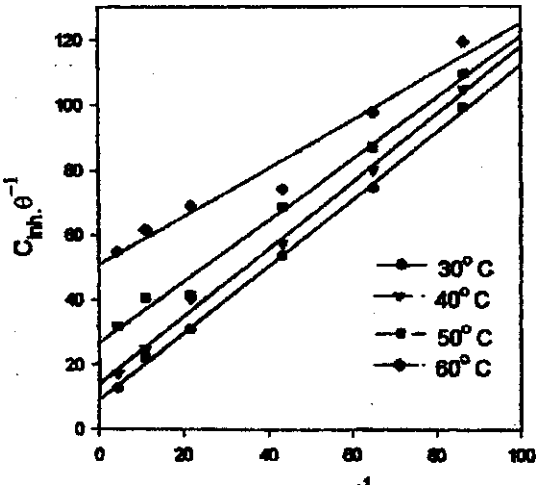

Fig. 5. Langmuir adsorption plots for mild steel in 1.0 M HCI containing different concentrations of CU at different temperatures.

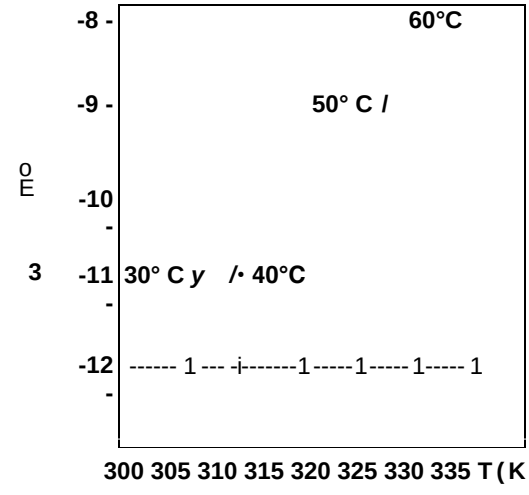

Fig. 6. The Relation between $\Delta G°_{ads}$ and T

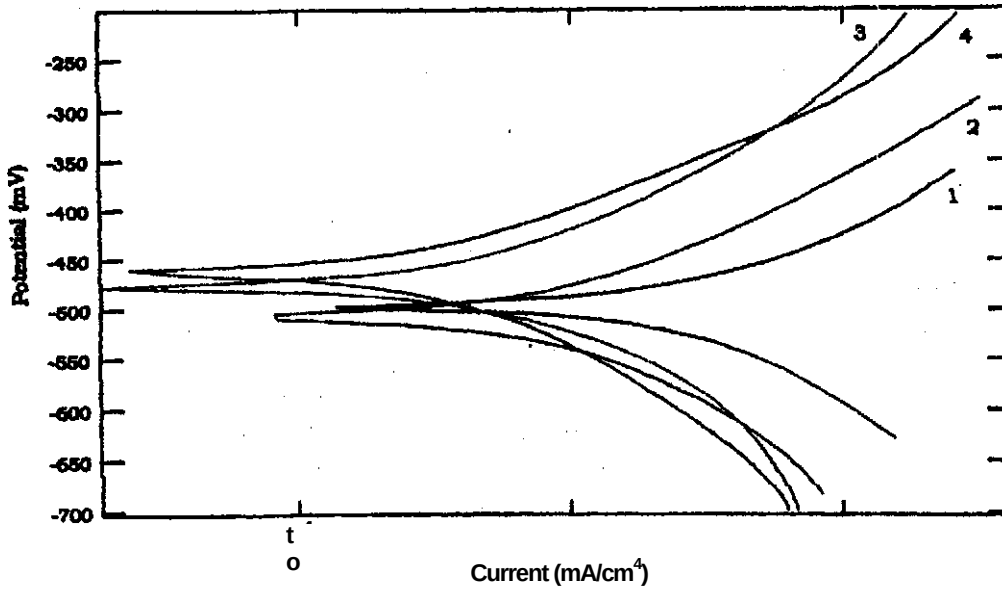

Fig 7. Polarization curves for mild steel in 1.0 M HCI in absence and presence of :
(1) 0.0 gl^{-1} of CU, (2) 21.7 gl^{-1} of CU, (3) 43.3 gl^{-1} of CU and (4) 86.5 gl^{-1} of CU.

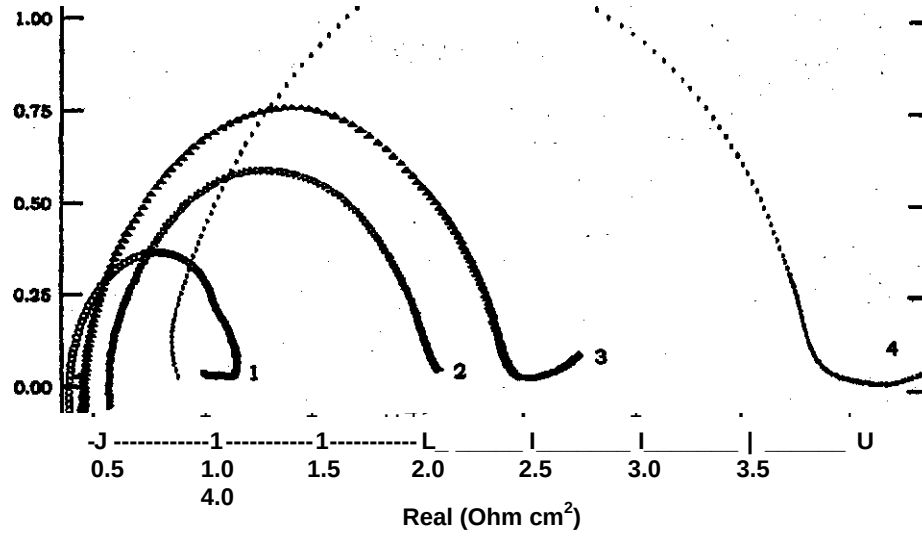

Fig. 8. Nyquist plots for mild steel in **1**.0 M HCI in absence and presence of: (1) 0.0 gl^{-1} of CU, (2) 21.7 gl^{-1} of CU, (3) 43.3 gl^{-1} of CU and (4) 86.5 gl^{-1} of CU.

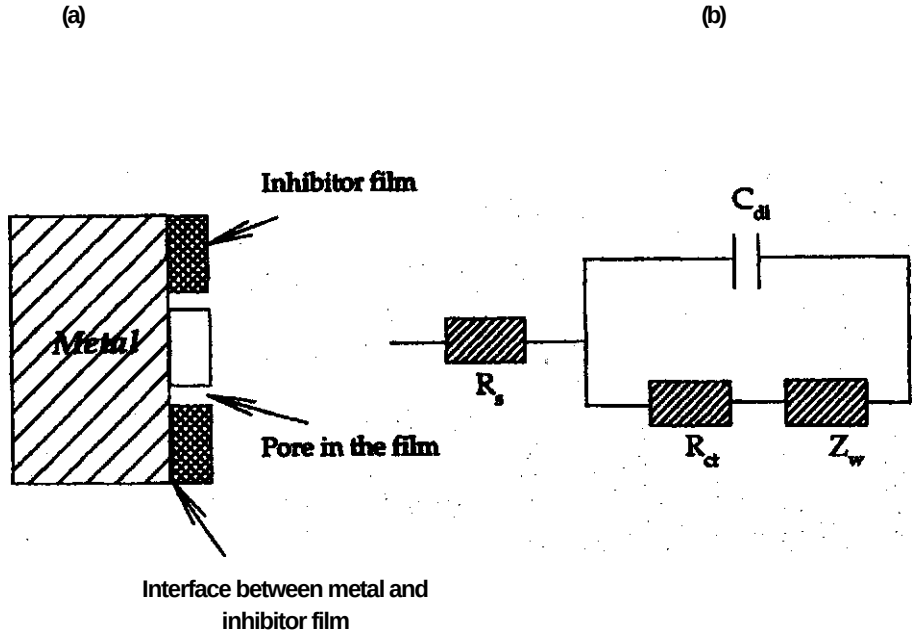

Fig. g. (a) A schematic diagram of metal covered by porous inhibitor film, **(b)** Simplified equivalent circuit for the metal covered by porous inhibitor film. R_s, solution resistance; R_ct, charge transfer resistance; Gdi, double layer capacitance; Z_w, Warburg impedance.

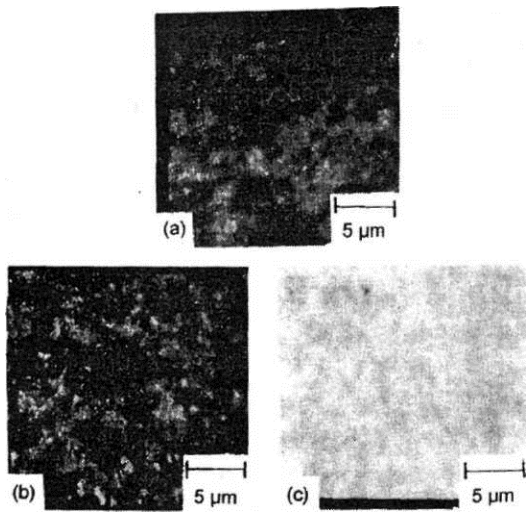

Fig. 10. Scanning electron micrographs of mild steel surface after 90 min. of immersion in 1 M HCI in the absence and presence of : (a) 0.0 g l^{-1} CU, (b) 21.7 g l^{-1} CU and (c) 86.5 g l^{-1} CU.

formation of a porous film on the metal surface with no evidence of pits on the metal surface (Figure 10c). This result is due to the adsorption of the inhibitor around the pits in the first stage of formation (initiation and propagation). These observations were in good agreement with those obtained from impedance measurements.

Correlation between the inhibition function of CU and its constituents :

The inhibition characteristic of CU may be referred to its constituents in combination. A recent study[28] revealed that urea acts as a corrosion inhibitor for mild steel in HCI solutions, and its inhibition ability depends on its concentration. At higher concentrations, it loses its inhibition efficiency and tends to act as an accelerator. This observation is not the case in CU in the present study. The results indicate that CU inhibits the steel corrosion in HCI solutions at all levels of studied concentrations and temperatures. This may be explained on the bases of: (i) the naturally low content of urea in CU and (ii) the expected synergistic effect between the protonated form of urea and the chloride ions naturally existing in the CU. The most interesting thing is that pure urea is a health hazard, whereas CU, which included urea, is used as a medicine as instructed by the Prophetic medicine without any side effects. Moreover, recent studies reported that oxalates[29], phosphates[30],[31] and sulphates[31] are passive species for mild steel corrosion. So, the existence of such species in CU may play an essential part in its inhibition function as a corrosion inhibitor.

CONCLUSION

► The inhibition efficiency of CU increases with increase in concentration but decreases with an increase in temperature.

► The thermodynamic data prove fhat the inhibitor is physically adsorbed on mild steel surface.

► SEM indicates that CU acts as inhibitor for pitting and general corrosion of mild steel in 1.0 M HCI.

► PM suggests that CU acts as a mixed -type inhibitor.

► EIS data reveals that the presence of inhibitor leads the mild steel dissolution to pass from charge transfer control to diffusion control in accordance with a protective porous filim formation mechanism.

► A good correlation between the inhibition function of CU and its constituents was carried out.

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