

Alkyl Substituted Anilines as Corrosion Inhibitor for N80 Steel in Hydrochloric Acid Medium

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(Received: 14 March 2011;

Accepted: 29 July 2011)

AJC-10226

The effect of 2-ethyl aniline and 2,4-dimethyl aniline as corrosion inhibitor for N80 steel in 15 % hydrochloric acid has been investigated by means of weight loss measurements and potentiodynamic polarization measurements. Corrosion inhibition ability of the compounds has been tested at different exposure periods (6 to 24 h) and at different temperatures (303 to 333 K and at 383 K). 2-Ethyl aniline has afforded maximum inhibition (88.3 %) at 6 h exposure period at room temperature. The adsorption of both the inhibitors is found to accord with Temkin adsorption isotherm. Potentiodynamic polarization study reveals that the tested inhibitors are mixed type inhibitor and preferentially act on cathodic areas. The characteristic shift of N-H and C-O bond frequencies towards lower side compared to that of the respective pure samples has been observed from FTIR studies which indicated the donation of electron pair through N atom and involvement of phenyl ring of the inhibitor molecule in the surface adsorption phenomena. SEM study has revealed formation of semi-globular inhibitor products on the metal surface. The comparisons of the protection efficiencies of these compounds according to their relative electron density on the adsorption centre and projected molecular area of the inhibitor molecules have been made.

Key Words: Substituted aniline, Isotherm, FTIR, Micrographs, Adsorption.

INTRODUCTION

Hydrochloric acid is the economically cheap acid among the other mineral acids those are used in oil wells for acidization operations and it leaves no insoluble products^{1,2} in the reaction medium. The corrosion of drill pipes is a common and very serious problem in industry, which often results in severe damage to pipes and equipment³. Most of the efficient acid corrosion inhibitors used in industry is organic compounds, which mainly contain nitrogen and sulfur atoms and multiple bonds in the molecules through which they are adsorbed on the metal surface⁴⁻⁷. Aromatic amines are well known corrosion inhibitors for iron and its alloys in acid medium⁸⁻¹¹. The relatively high water solubility of low molecular weight amines is an advantage for their use as corrosion inhibitors^{9,12-14}. In petroleum industry the nitrogen containing corrosion inhibitors are mostly used, which usually adsorb onto the metallic surface and can block the active sites or can create a physical barrier to reduce the corrosive attack. El-Sobki *et al.*¹⁵ and Ride *et al.*¹⁶ proposed that the aromatic amines are physically adsorbed on the cathodic region along with the direct adsorption and covering at the anodic sites. Hackerman and Makrides¹⁷ have found the better inhibition by introduction of alkyl groups on the benzene ring of aniline due to decrease of solubility and increase of electron density on the nitrogen atom.

In this present investigation, alkyl substituted isomeric aniline compounds; 2,4-dimethyl aniline (DMA) and 2-ethyl

aniline (EA) have been tested as corrosion inhibitor for N80 steel in 15 % HCl solution. The contributory effects of the structure, electron availability and the kinetics of adsorption have been explained. Studies were carried out on the variation of corrosion rate due to the metal corrodibility as functions of time, temperature together with analyses of the metal surface products for a better understanding of the inhibition mechanism. A plausible adsorption model for the inhibitor molecules on the metal surface in acid solution has also been proposed.

EXPERIMENTAL

The N80 steel sample (supplied by ONGC) used for the study was analyzed in MET-CHEM Laboratories, Boroda, India and found to have the composition C; 0.310 %, S; 0.008 %, P; 0.010 %, Si; 0.190 %, Mn; 0.920 %, Cr; 0.200 % and Fe the rest. The steel coupons used for weight studies were 6 cm × 2.0 cm × 0.3 cm in size. The steel surface was cleaned mechanically and polished with increasingly finer grades of emery papers and then degreased with acetone, washed and finally dried in a stream of warm air. In the present study, corrosion experiments were performed in 15 % HCl solution and for weight loss measurements 500 mL HCl solution was used and for the potentiodynamic polarization measurements 200 mL solution was used. Polarization curves were recorded at a scan rate 10 mV/sec at different inhibitor concentrations with the N80 steel electrode (area 1 cm²) as working electrode,

TABLE-1
CORROSION PARAMETERS IN PRESENCE OF 2,4-DIMETHYL ANILINE (DMA)
AND 2-ETHYL ANILINE (EA) AT DIFFERENT EXPOSURE PERIOD

Exposure period (h)	Blank		2,4-Dimethyl aniline			2-Ethyl aniline		
	Weight loss (mg)	CR (mmpy)	Weight loss (mg)	CR (mmpy)	PI	Weight loss (mg)	CR (mmpy)	PI
6	167.0	27.6	37.9	2.16	77.3	36.2	2.07	78.3
12	121.8	20.1	35.9	2.05	70.5	34.3	1.96	71.8
18	92.6	14.3	33.0	1.88	64.4	30.1	1.71	67.5
24	80.7	13.4	30.7	1.76	62.0	28.5	1.63	64.7

saturated calomel electrode as reference electrode and platinum as counter electrode with the help of a potentiostat (Amel, Model 2053, Italy). The surface morphology of the exposed steel surface in absence and in presence of the optimum inhibitor concentration was studied with the help of Scanning Electron Microscope (SEM Jeol JSM-5800) at different magnifications. The details about the experimental procedures have been discussed elsewhere¹⁸⁻²⁰.

RESULTS AND DISCUSSION

The effect of concentration on corrosion inhibition efficiency has been studied gravimetrically for 6 h exposure period at room temperature. Both the inhibitors inhibit corrosion at all the studied concentrations and the inhibition efficiency was found to increase (Fig. 1) with the inhibitor concentration up to 95 mM (DMA, 77.3 %; EA, 78.3 %) and then tends to a constant value (DMA, 77.1 %; EA, 78.2 % at 105 mM). The inhibition efficiency of 2,4-dimethyl aniline and 2-ethyl aniline were 51.3 and 44.3 % respectively at 5 mM.

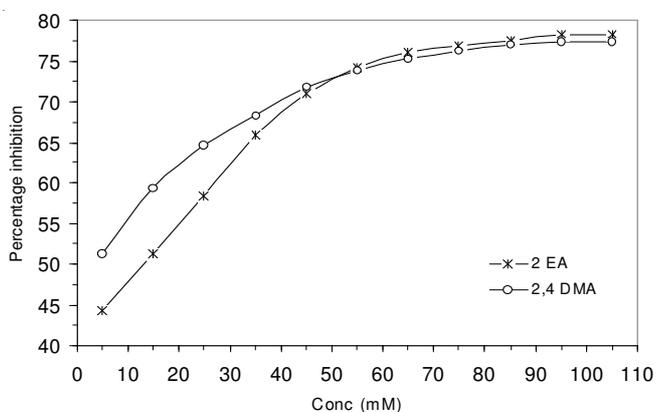


Fig. 1. Variation of percentage inhibition with the inhibitor concentration

The corrosion inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the metal surface. The adsorption isotherm can provide important information about the electrochemical interaction of the inhibitors with the metal surface. In the present study degree of surface coverage (θ) was tested graphically for fitting a suitable adsorption isotherm and straight lines were obtained from the plot of θ against $\log C$ for different concentrations of the inhibitors revealed the Temkin isotherm. Talati *et al.*²¹ and Sathiyarayanan *et al.*²² observed same type of adsorption characteristic for corrosion inhibition of steel in hydrochloric acid medium for aniline and its derivatives.

The corrosion rate, weight loss and percentage inhibition in presence and in absence of optimum inhibitors concentration

for the tested exposure periods (from 6 to 24 h) have been listed in Table-1. It is clear that both the inhibitors showed a gradual decrease in percentage inhibition with exposure period. Inhibition efficiency at 24 h has been found to be less (DMA-62 %; EA-65 %) for both the inhibitors. In case of these inhibitors the weight loss values were much less (DMA, 0.29 mg/inch²/h; EA, 0.26 mg/inch²/h; at 24 h exposure) compared to that of the free acid (0.75 mg/inch²/h 24 h exposure) throughout the testing duration.

The corrosion experiments were carried out at high temperatures (ambient to 333 K for 6 h exposure period) with the optimum inhibitor concentration to understand the effect of temperature. The corrosion parameters in absence and in presence of the inhibitors in the temperature range 303 to 333 K and at 383 K have been summarized in Table-2. The results show that the inhibition efficiency offered by 2,4-dimethyl aniline and 2-ethyl aniline was 51.7 and 62.1 % respectively at 333 K. The inhibition efficiency was 48.9 % for 2-ethyl aniline and 44.7 % for 2,4-dimethyl aniline at 383 K. The corrosion rates were much less (DMA, 23.64 mmpy; EA, 18.54 mmpy; at 333 K) compared to free acid (48.93 mmpy at 333 K) at all the tested temperatures. The lower inhibition efficiency at higher temperature in case of both the inhibitors may be due to higher desorption rate than the adsorption at high temperature^{23,24}. The percentage inhibition offered by 2,4-dimethyl aniline and 2-ethyl aniline were much better compared to that of the aniline itself in the same conditions²⁵. Increasing effect of the alkyl substituents on inhibition efficiency might be due to higher electron density on the N atom of -NH₂ group of inhibitor molecules for +I effect of the respective alkyl substituents present in the inhibitor molecules.

TABLE-2
CORROSION PARAMETERS IN PRESENCE OF 2,4-DIMETHYL ANILINE (DMA) AND 2-ETHYL ANILINE (EA) AT DIFFERENT TEMPERATURES

Temperature (K)	Blank		DMA		EA	
	CR (mmpy)	PI	CR (mmpy)	PI	CR (mmpy)	PI
303	12.16	-	2.77	77.2	2.66	78.1
313	19.26	-	4.95	74.3	4.68	75.7
323	30.43	-	9.89	67.5	8.34	72.6
333	48.93	-	23.64	51.7	18.54	62.1
383*	680.79	-	376.48	44.7	347.88	48.9

*At 17 psi pressure; Exposure period = 1 h

The activation energy has been calculated from the Arrhenius rate equation^{26,27} as:

$$K = Ae^{-E_a/RT}$$

where, K = corrosion rate, R = universal gas constant, T = absolute temperature, A = frequency factor. By plotting $\log k$ versus $1/T$, the values of activation energy (E_a) has been calculated from the slope ($E_a = -(\text{Slope}) \times 2.303 \times R$) of the obtained straight lines for both in case of free acid and in presence of inhibitors.

K_{eq} is related to the standard free energy of adsorptions (ΔG_{ads}) by the equation:

$$K_{eq} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

The equilibrium constant (K_{eq}) has been replaced by the equation:

$$\left[K_{eq} = \frac{\theta}{(1-\theta)C} \right]$$

By plotting $\log K_{eq}$ versus $1/T$ and the value ΔG_{ads} has been calculated from the slope ($\Delta G_{ads} = -2.303 \times R \times \text{Slope}$) of the straight line obtained. Enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption have been calculated from an alternative formulation of Arrhenius equation of transition state equation:

$$K = RT/N h e^{(\Delta S_{ads}/R)} e^{(-\Delta H_{ads}/RT)}$$

where, K is the corrosion rate, N is the Avogadro number, h is Planck's constant, ΔH_{ads} is the enthalpy of adsorption and ΔS_{ads} is the entropy of adsorption, respectively. From the plot of $\log(K/T)$ against $1/T$; ΔH_{ads} and ΔS_{ads} have been calculated from the intercept ($\log R/N h + \Delta S_{ads}/2.303 R$) and from the slope ($-\Delta H_{ads}/2.303 R$), respectively.

The E_a value (-38 kJ/mol) for dissolution of N80 steel in 15 % hydrochloric acid in absence of inhibitor has been reported²⁰. Higher values of E_a were obtained in presence of the studied inhibitors (DMA, -60 kJ/mol; EA, -98 kJ/mol) compared to that of uninhibited acid solution indicated the formation of an adsorptive film of an electrostatic character²⁸⁻³⁰. Among these inhibitors 2,4-dimethyl aniline showed higher ΔG_{ads} value (-31.478 kJ/mol) compared to that of the 2-ethyl aniline (-20.736 kJ/mol). The negative values of ΔG_{ads} suggested the spontaneous adsorption of the inhibitors on the metal surface^{24,25}. The negative values of ΔH_{ads} (DMA, -56.944 kJ/mol; EA, -50.912 kJ/mol) revealed the exothermic and physical adsorption of the inhibitors on the metal surface causes the dissolution of steel is difficult³¹. Positive values of ΔS_{ads} were observed for both the inhibitors (DMA, -86 J/mol; EA, -66 J/mol) may be due to involvement of less ordered transition state in the adsorption process. The adsorption of the inhibitor molecules occur after desorption of water molecules initially adsorbed on metal surface due to stronger attraction between the metal surface and inhibitors molecules compared to water^{32,33}.

Fig. 2 represents the potentiodynamic polarization curves for the steel in absence and in presence of the inhibitors at different concentrations. The electrochemical parameters for corrosion of the experimental steel in the acid containing 2,4-dimethyl aniline and 2-ethyl aniline are summarized in Table-3. The E_0 value in presence of the inhibitors was found to shift slightly towards more negative side (DMA, -0.5061 V; EA, -0.5224 V) compared to that of the free acid (-0.4992 V). The values of corrosion current, I_{corr} decreased from 189.89 $\mu\text{A}/\text{cm}^2$ in the case of the free acid to 37.79 $\mu\text{A}/\text{cm}^2$ and 36.65

$\mu\text{A}/\text{cm}^2$ in the presence of 95 mM 2,4-dimethyl aniline and 2-ethyl aniline respectively. The significant reduction (DMA, -152 $\mu\text{A}/\text{cm}^2$; EA, -153 $\mu\text{A}/\text{cm}^2$) in corrosion current at higher concentration level (95 mM) indicated more adsorption of the inhibitors and better inhibition performance. Variations in values of both the Tafel slopes were observed in the presence of these inhibitors. Significant increase in the values of cathodic Tafel slopes (β_c) (49 mV, DMA; 33 mV, EA). The anodic Tafel slopes remains almost unchanged (β_a) (6 mV, DMA; 11 mV, EA) in the presence of both the inhibitors at 95 mM concentration level. It is clear from the Tafel slopes that the cathode is more polarized ($\beta_c > \beta_a$), when external current is applied for each of the inhibitors indicated cathodic control in presence of both the inhibitors. The inhibition efficiency calculated from potentiodynamic polarization study was slightly different (Table-3) from that of the weight loss study. This may be explain as the results obtained from the weight loss measurement were average values, while the results obtained from potentiodynamic measurement were instantaneous values^{32,34}.

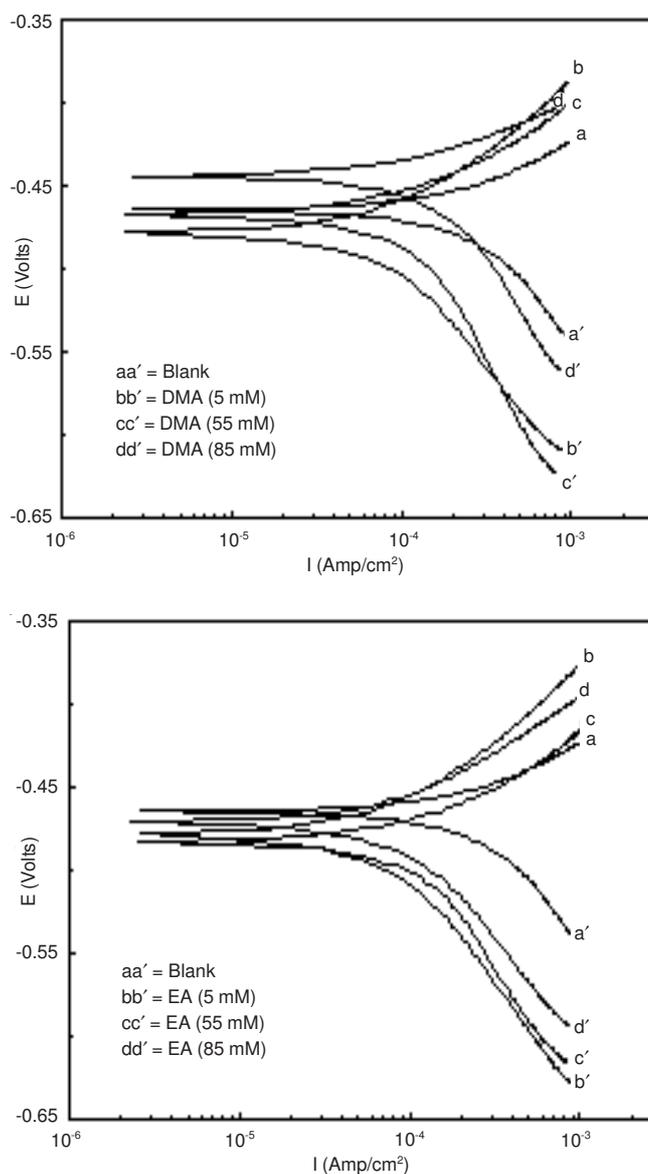


Fig. 2. Potentiodynamic polarization curves in presence of the inhibitors

TABLE-3
ELECTROCHEMICAL CORROSION PARAMETERS IN PRESENCE OF 2,4-DIMETHYL ANILINE (DMA) AND ETHYL ANILINE (EA)

Concentration of inhibitor	E_0 (V)	I_0 ($\mu\text{A}/\text{cm}^2$) (a)	Tafel Slopes		PI from (a)	PI from wt. loss
			Anodic (β_a) (mV)	Cathodic (β_c) (mV)		
Blank	-0.4992	189.890	178.61	86.16	-	-
DMA						
5 mM	-0.5032	83.13	155.01	103.78	56.2	51.3
55 mM	-0.4866	47.47	169.34	117.34	75.0	73.8
95 mM	-0.5061	37.79	171.24	133.12	80.1	77.3
EA						
5 mM	-0.5169	92.05	160.42	104.23	51.5	44.3
55 mM	-0.5125	45.38	171.32	115.65	76.1	74.2
95 mM	-0.5224	36.65	167.75	119.08	80.7	78.3

The infrared spectra obtained for the metal surface products in presence of both the inhibitors were matched well with that of the respective pure compounds. FTIR spectra of pure 2,4-dimethyl aniline and the spectra obtained with the metal surface products after the corrosion inhibition test in presence of 95 mM 2,4-dimethyl aniline has shown in Fig. 3.

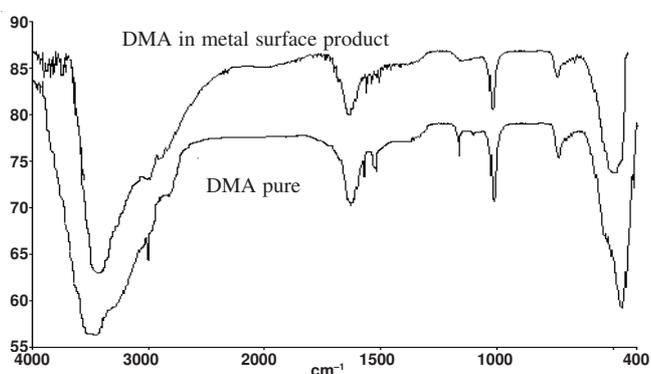


Fig. 3. FTIR spectra of 2,4-dimethyl aniline and in metal surface product

A broad band at 3394 cm^{-1} was observed in the IR spectra of metal surface product in presence of 2,4-dimethyl aniline whereas it was at 3484 cm^{-1} for the pure compound indicated N-H stretching vibration of anilines^{16,17}. A few peaks were observed in the range from 1653 to 1560 cm^{-1} (1652 - 1537 cm^{-1} for pure DMA) for 2,4-dimethyl aniline for the metal surface product was attributable for the ring mode. The peak was observed at 1030 cm^{-1} in case of metal surface product whereas it was almost at the same position (1025 cm^{-1}) for the pure sample may be due to C-N stretching in 2,4-dimethyl aniline. A broad band observed at 3414 cm^{-1} (Fig. 4) for the metal surface product in presence of 2-ethyl aniline (broad band at 3515 cm^{-1} for pure compound) indicated N-H stretching vibration of anilines. The peaks were obtained for the ring mode in the range from 1635 to 1570 cm^{-1} (1626 - 1537 cm^{-1} for pure 2-ethyl aniline) for 2-ethyl aniline in the metal surface product. The peak observed at 1030 cm^{-1} for 2-ethyl aniline in metal surface product and it was at 1072 cm^{-1} in pure compound may be due to C-N stretching of aniline moiety.

These results revealed the presence of the inhibitor molecules in the metal surface product obtained after immersion in the inhibited acid solution. The broad band observed for N-H stretching in metal surface products in presence of both the inhibitors was found to shift towards lower side compared to that of the pure compound. It indicated the weakening of the

-N-H bond in both the compounds may be due to the electron donation during the adsorption of inhibitor molecules on the metal surface through the N atom³⁵.

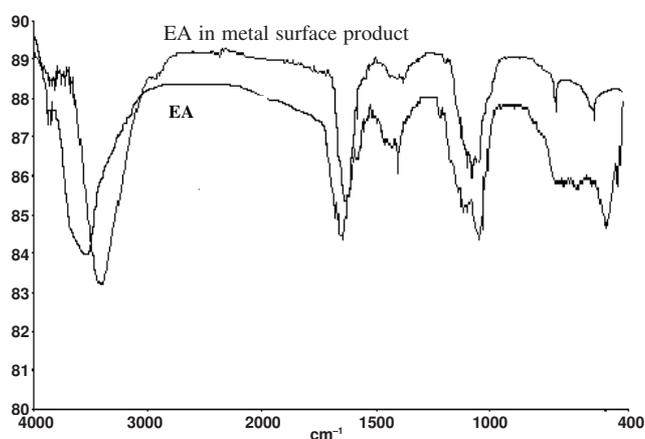


Fig. 4. FTIR spectra of 2-ethyl aniline and in metal surface product

Fig. 5 showed the SEM micrographs of the steel surface at different magnifications (1000X and 5000X). A uniform flake type corrosion product was seen in case of the free acid (Fig. 5 A and 5 B). In presence of the inhibitors the metal surface is covered (Fig. 5 C, D, E and F) with quasi globular inhibitor products. The flake type products were also present in presence of both the inhibitors and it was clearer at higher magnifications. The SEM micrographs also revealed presence of the quasi globular inhibitor products on the metal surface along with flake type deposition of metal oxides and metal hydroxides^{36,37}.

Proposed adsorption model : The effect of the molecular structure of this alkyl substituted anilines on their corrosion protective properties in acid may be dependent on the electron density of the N atom present in the inhibitor molecule. In acid solution these compounds undergo easy protonation through the N atom of the $-\text{NH}_2$ group. The unprotonated ($-\text{NH}_2$) and protonated species ($-\text{N}^+\text{H}_3$) may be at a dynamic equilibrium in the acid solution. Hence the electron donation from these inhibitor molecules through $-\text{NH}_2$ group towards anodic sites of the metal surface and the back donation of the electrons from the cathodic sites of the metal surface towards $-\text{N}^+\text{H}_3$ may occur simultaneously (Fig. 6)^{35,38}. The metal dissolution from the anodic sites will be difficult and the hydrogen evolution rate will decrease due to partial blocking of the cathodic sites by the protonated inhibitor molecules.

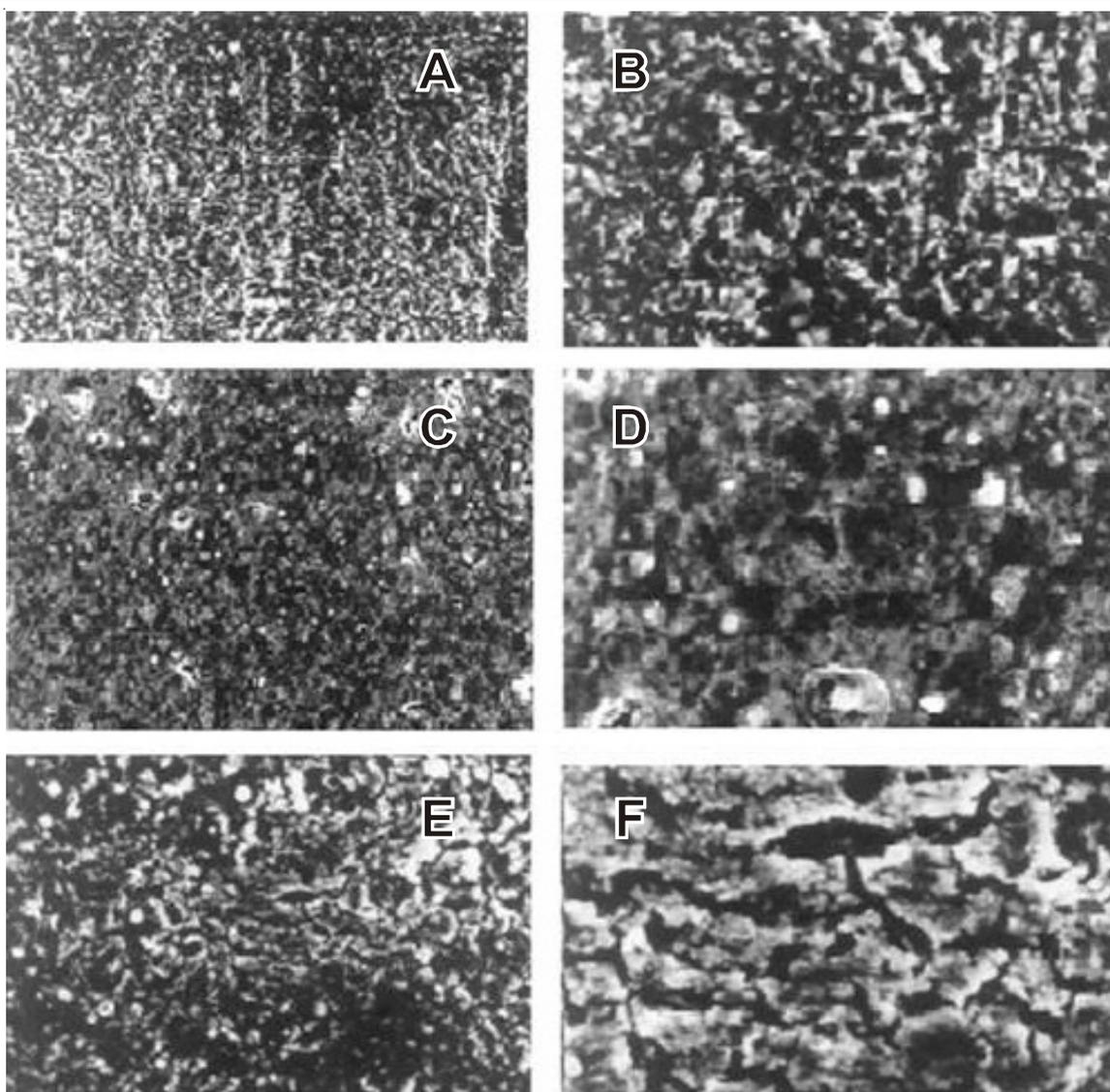


Fig. 5. SEM Micrographs of the metal surface in absence and in presence of the inhibitors (A) Blank at 1000X, (B) Blank at 5000X, (C) 2,4-dimethyl aniline at 1000X, (D) 2,4-dimethyl aniline at 5000X, (E) 2-ethyl aniline at 1000X and (F) 2-ethyl aniline at 5000X

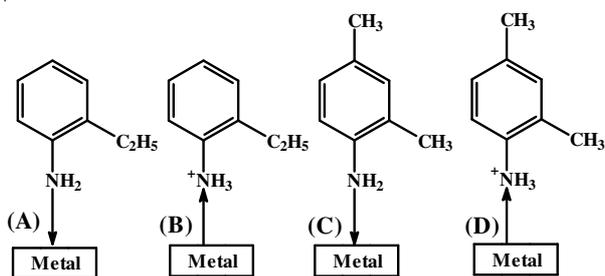


Fig. 6. Adsorption model of substituted anilines on the metal surface (A) Unprotonated 2-ethyl aniline (B) Protonated 2-ethyl aniline (C) Unprotonated 2,4-dimethyl aniline and (D) Protonated 2,4-dimethyl aniline

The mixed type of inhibition offered by both the inhibitors *i.e.*, retardation of both the anodic and cathodic reactions of the metal surface has been revealed by the potentiodynamic polarization study. The electron density on the N atom will be higher in 2-ethyl aniline compared to 2,4-dimethyl aniline due to stronger +I effect of $-C_2H_5$ group in case of 2-ethyl aniline

than +I effect of one $-CH_3$ group in 2,4-dimethyl aniline. The higher value of inhibition efficiency for 2-ethyl aniline as compared to 2,4-dimethyl aniline can be attributable to the higher electron density of the reacting centre ($-NH_2$ group) of 2-ethyl aniline compared to 2,4-dimethyl aniline. The phenyl ring of the inhibitor molecules may also involve into this electronic interaction with the metal surface atoms through its delocalized π -electron^{39,40}.

Conclusion

The maximum inhibition efficiencies for both the inhibitors were obtained at 95 mM (DMA, -78%; 2-ethyl aniline, -77 %) for 6 h exposure period. Inhibition efficiency at 24 h exposure was -62 and -66 % for 2,4-dimethyl aniline and 2-ethyl aniline respectively. Both the alkyl substituted aniline isomers follow Temkin adsorption isotherm. The spontaneous adsorption of the inhibitors on the metal surface revealed by negative values of ΔG_{ads} . The lower negative ΔH_{ads} values were obtained which indicated physisorption of the inhibitors on the metal surface. The positive values of ΔS_{ads} indicate the less orderliness of the

transition state of the adsorption process. 2-Ethyl aniline offered higher inhibition efficiency (-62 %) compared to that of 2,4-dimethyl aniline (-52 %) at 333 K. The inhibition efficiency was found to be -49 and -45 % for 2,4-dimethyl aniline and 2-ethyl aniline respectively at 383 K.

The potentiodynamic study suggested the mixed type inhibition and preferentially cathodic control in case of both the inhibitors. The characteristic shift of the FTIR peak obtained for metal surface product in presence of 2,4-dimethyl aniline and 2-ethyl aniline in comparison with that of the pure compound due to -N-H stretching indicated the involvement of the -NH₂ group of the compound in the adsorption of the inhibitor molecules on the metal surface. SEM study revealed that the metal surface was partially covered with the quasi globular inhibitor products in presence of both the inhibitors.

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