



Binary Mixtures of Nonyl Phenol with Alkyl Substituted Anilines as Corrosion Inhibitors for Mild Steel in Acidic Medium

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Abstract: The present study deals with the evaluation of the corrosion inhibition effectiveness of the two binary mixtures of nonyl phenol (NPH) with 2, 4 dimethyl aniline (DMA) and 2 ethyl aniline (EA) at different concentration ratios (from 1:7 to 7:1) for mild steel in H_2SO_4 (pH=1) solution by weight loss and potentiodynamic polarization method. Corrosion inhibition ability of the compounds has been tested at different exposure periods (6 h to 24 h) and at different temperatures (303 K to 333 K). The binary mixture of NPH and EA (at 7:1 concentration ratio) has afforded maximum inhibition (IE% 93.5%) at 6 h exposure period and 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. Electrochemical impedance study suggests formation of an inhibition layer by the adsorption of the inhibitors on the metal surface. An adsorption model of the inhibitor molecules on the metal surface has been proposed after immersion test in the inhibited acid showed characteristic shift of N-H and O-H bond frequencies towards lower side compared to that of the respective pure samples which indicated the donation of electron pair through N and O atom 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.

Keywords: Substituted aniline, Isotherm, FTIR, Micrographs, Adsorption

Introduction

Acid solutions are widely used in industries for acid pickling, acid cleaning of boilers, descaling and oil well acidizing. Chemical cleaning and pickling processes are extensively used to remove corrosion scales from metallic surface in high concentrated acidic media at

elevated temperature. Sulfuric acid is generally the choice in the steel surface treatment basically due to its lower cost, minimal fumes and non-corrosive nature of the SO_4^{2-} ion^{1,4}. Mild steel is widely applied as constructional material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost⁵⁻⁷. However, its tendency to corrode makes it unsuitable for exposure to acids. The use of inhibitors is one of the most practical methods for the protection of mild steel against corrosion especially in acidic media⁸⁻¹⁰. In general, most of the efficient inhibitors in usage are organic compounds having π bonds and heteroatoms like nitrogen, sulphur and oxygen *etc.*, in their structures. Inhibition efficiency of an organic compound is mainly dependent on its ability to get adsorbed on the metal surface through the heteroatoms as well as aromatic ring in their structure¹¹⁻¹⁴. Most of the efficient acid inhibitors are expensive synthetic compounds and are limited for their specificity of action; hence combinations of inhibitors are more likely to provide the multiple services required for effective corrosion inhibition^{15,16}. The synergistic effect of ionic species mainly the halides and the metal cation with organic acid inhibitors have been studied more frequently¹⁷⁻²⁰. Mixed inhibition is an effective means to improve the inhibitive force of the individual inhibitor, to decrease the amount of usage, to diversify the application of inhibitor in acidic media^{21,22}.

In this paper two binary mixtures containing NPH with alkyl substituted anilines DMA and EA were taken in different concentration ratios for investigating corrosion inhibition behavior on mild steel in H_2SO_4 solution (pH=1). Thermodynamic parameters obtained from experimental data of the studies of the inhibition process at different temperatures. The inhibition action is satisfactorily explained by using both thermodynamic and kinetic parameters. FTIR study has been carried out to characterize the adsorbed compound on the metal surface after the test in presence of the binary inhibitor mixtures. Morphological study of corroded metal surface has been carried out by SEM technique.

Experimental

The composition of the mild steel used for corrosion studies was C (0.12%), S (0.02%), P (0.01%), Si (0.15%), Mn (0.57%), W (0.015%), Al (0.01%) and Fe the rest. Mild Steel coupons were cut into the sizes 4.4 x 2.2 x 0.15 cm with a small hole (2 mm diameter) at the upper edge of the rectangular panels. Triplicate sets of steel panels were used for weight loss experiments in pH=1 H_2SO_4 solution and the volume of the test solution was 500 mL. All the corrosion inhibitors tested were of AR grade chemical.

Test coupons were mechanically polished with different grades of emery papers, degreased with acetone, washed with distilled water and finally dried in hot air. A water circulated ultra thermostat was used for high temperature (303-333 K) experiments with an accuracy of ± 1.0 K. Potentiodynamic polarization measurements were carried out at static condition using a potentiostat (CH Instrument, Model 680 Amp Booster) at room temperature. A three electrode cell consisting square steel coupons (1 cm^2 area) working electrode, a platinum counter electrode (2 cm^2 area) and a saturated calomel reference electrode (SCE) were used for measurements. The details regarding calculation of thermodynamic parameters and corrosion studies are reported elsewhere²³⁻²⁵.

Fourier transform infrared spectroscopic analysis was performed with the surface products obtained from the steel surface after 6 h exposure in presence of the inhibitors at room temperature using Perkin Elmer FTIR spectrometer (Model 2000) by KBr pellet technique. Surface morphology of steel specimens was analyzed after exposure to acid solution in absence and presence of the inhibitors with the help of scanning electron microscopy (HITACHI, Model S3400N).

Results and Discussion

Weight loss studies

The gravimetric experiments for 6 h exposure period at room temperature (25 ± 1 °C) were carried out with different ratio of the single inhibitors. The effect of exposure period has been studied at room temperature with the optimum concentration ratio of the inhibitor mixtures. Experiments were carried out at different temperatures to understand temperature effect with the optimum concentration ratio of the inhibitor mixtures for 6 h exposure. The thermodynamical parameters have been calculated from the data obtained from the high temperature experiments.

Effect of inhibitor concentration

The corrosion experiments were carried out at different concentrations ratio of the single inhibitors (from 1:7 to 7:1) keeping the total concentration of the mixture same (80 mM) for 6 h of immersion period at room temperature. It has been found that all the inhibitor mixtures inhibit corrosion of mild steel in H_2SO_4 (pH=1) solution. The inhibition efficiency increases with the increase of concentration of NPH for both the inhibitor mixtures. The corrosion parameters for the inhibitor mixtures for the studied concentration ratios have been listed in Table 1.

Table 1. Corrosion parameters in presence of the mixtures of NPH and DMA at different concentration ratio

NPH		Conc., mM	IE%		Conc. (v/v%) in mM	NPH +	NPH +	Increase in IE% of NPH	
Conc, mM	IE%		DMA	EA		DMA	EA	(NPH+DMA)	(NPH+EA)
10	73.21	70	83.65	82.80	10+70	86.62	87.19	13.41	13.98
20	77.86	60	82.34	81.67	20+60	88.46	88.24	10.60	10.38
30	80.15	50	80.77	79.48	30+50	90.02	89.43	9.87	9.28
40	83.92	40	78.19	75.93	40+40	90.79	90.83	6.87	6.91
50	86.16	30	75.04	71.72	50+30	91.86	91.76	5.70	5.60
60	87.87	20	71.12	67.89	60+20	92.41	92.91	4.54	5.04
70	88.39	10	67.70	63.17	70+10	92.78	93.48	4.39	5.09

Inhibition efficiency offered by the binary mixture of NPH and DMA at the concentration ratio (1:7) was found to be 86.62% and it was 92.78% at the concentration ratio (7:1). NPH showed inhibition efficiency 73.21% and 88.39% at the concentration levels 10 mM and 70 mM respectively when used separately. DMA showed inhibition efficiency 67.70% and 83.65% at the concentration levels 10 mM and 70 mM respectively when used separately. In case of the binary mixture of NPH and EA inhibition efficiency was found to be 87.19% at the concentration ratio (1:7) and it was 93.48% at the concentration ratio (7:1). EA showed inhibition efficiency 63.17% and 82.80% at the concentration levels 10 mM and 70 mM respectively when used separately. The higher increment in the inhibition efficiency of NPH (~13%) in the binary mixture containing 10 mM of NPH and 70 mM of DMA has been observed while it was less (~5%) in the binary mixture containing 70 mM of NPH and 10 mM of DMA. In case of the mixture of NPH and EA the inhibition efficiency of NPH increased by ~14% in the binary mixture containing 10 mM of NPH and 70 mM of EA while it was ~5% for the binary mixture containing 70 mM of NPH and 10 mM of EA.

Effect of immersion time

The dissolution rate of the steel in presence of both the inhibitor mixtures has been found to decrease with the time. The corrosion rate, weight loss and percentage inhibition in absence and in presence of both the inhibitors for the tested exposure period (from 6 h to 24 h) have been listed in Table 2. Percentage inhibition efficiency of both the binary mixtures were found to decrease gradually with increase in exposure period. The inhibition efficiency offered by the binary mixtures containing NPH and DMA and the binary mixtures containing NPH and EA at the concentration ratio 7:1 (70 mM + 10 mM) was found to be 82.63% and 83.74% respectively at 24 hours exposure period.

Table 2. Corrosion parameters in absence and presence of inhibitors at different exposure period

Exposure Period, h	Blank		NPH + DMA			NPH + EA		
	Weight loss, mg	CR, mpy	Weight loss, mg	CR, mpy	PI	Weight loss, mg	CR, mpy	PI
6	134.4	359.70	9.70	25.96	92.78	9.18	24.56	93.17
12	276.9	370.61	31.32	41.91	88.69	28.91	28.91	89.56
18	440.1	392.42	65.66	58.58	85.08	61.04	61.04	86.13
24	629.5	421.27	109.34	73.16	82.63	102.36	102.36	83.74

Effect of temperature

Experiments were carried out at different temperatures (ambient to 333 K) with the inhibitor mixtures used at the optimum concentration ratio. Corrosion rate of the mild steel was found to increase steeply from 303 K to 333 K with rise in temperature in absence the inhibitor mixtures whereas in presence of the inhibitor mixtures the corrosion rate increases slowly (Figure 1). The results show that the inhibition efficiency offered by the binary mixture of NPH and DMA and the binary mixture of NPH and EA was 62.46% and 67.73% respectively at 333 K. The corrosion rates are much less (1088.92 mpy and 936.05 mpy for binary mixtures of NPH and DMA and NPH and EA at 7:1 (70 mM +10 mM) ratio at 333 K) compared to free acid (2900.68 mpy at 333 K) throughout the testing duration.

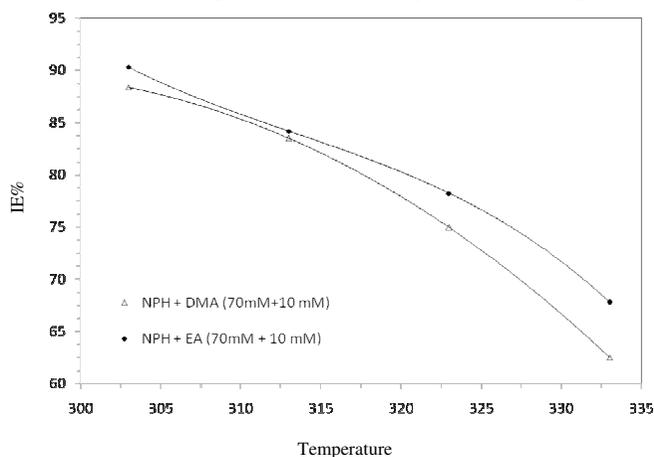


Figure 1. Variation of inhibition efficiency of the binary inhibitor mixtures with temperature at optimum concentration ratio

Table 3. Corrosion parameters in absence and presence of inhibitors at different temperatures

Temp, K	Blank	NPH+DMA		NPH+EA	
	CR, mpy	CR, mpy	IE%	CR, mpy	IE%
303	603.80	70.52	88.32	58.69	90.28
313	1215.89	201.23	83.45	192.72	84.15
323	2111.95	529.89	74.91	460.83	78.18
333	2900.68	1088.92	62.46	936.05	67.73

Kinetic study

Activation energy for the corrosion of mild steel in pH=1 H₂SO₄ acid solution in absence of inhibitor was found to be 45.72 KJ/mol (Table 4) and higher values were obtained in the presence of both the binary mixtures. The heats of adsorption for both the mixtures were ~76 kJ/mol. The mixture of NPH and EA shows slightly higher ΔG_{ads} (-40.47 kJ/mol) than mixture of NPH and DMA (-42.37 kJ/mol). The ΔS_{ads} values obtained were very low (for NPH and DMA mixture 177 J/mol and for NPH and EA mixture 175 J/mol).

Table 4. Thermodynamic parameters in absence and in presence of the inhibitors

Inhibitor	Heat of adsorption, kJ/mol	Heat of activation, kJ/mol	Average Free energy, kJ/mol	Entropy of adsorption, J/mol
Blank	-	45.72	-	-
NPH+DMA	75.86	78.50	-42.37	177
NPH+EA	75.76	78.41	-40.47	175

Potentiodynamic polarization studies

The electrochemical parameters for corrosion of the experimental steel in the acid containing the binary inhibitor mixtures are given in Table 5. The E_0 value in presence of the inhibitors slightly shifted towards positive side (-0.5490 V for NPH and DMA -0.5460 V for NPH and EA at 7:1 concentration ratio) compare to free acid (-0.5518 V). Both the tafel lines are shifted to more positive and negative side (Figure 2 and 3).

Table 5. Electrochemical parameters in absence and in presence of the binary mixtures

Conc of Inhibitor	E_0 (V)	I_0 (μ amp / sq. cm) (a)	Tafel Slopes		PI From (a)	PI From wt. Loss
			Cathodic (β_c) mV	Anodic (β_a) mV		
Blank	-0.5518	423	191.93	124.16	-	-
NPH + DMA						
10 mM + 70 mM	-0.5820	48.67	110.99	72.94	88.49	86.62
40 mM + 40 mM	-0.5781	37.42	107.50	88.35	91.15	90.79
70 mM + 10 mM	-0.5490	26.05	117.49	87.29	93.84	92.78
NPH + EA						
10 mM + 70 mM	-0.5661	44.31	109.30	82.10	89.52	87.19
40 mM + 40 mM	-0.5672	33.18	105.13	89.57	92.40	90.83
70 mM + 10 mM	-0.5460	25.75	123.38	101.56	93.91	93.48

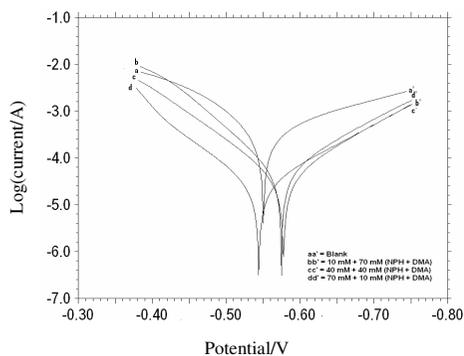


Figure 2. Potentiodynamic polarization curves in absence and in presence of the binary inhibitor mixtures of NPH and DMA at different concentration ratio

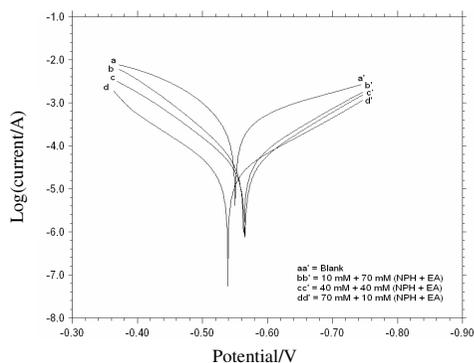


Figure 3. Potentiodynamic polarization curves in absence and in presence of the binary inhibitor mixtures of NPH and EA at different concentration ratio

AC impedance studies

Electrochemical impedance spectra for mild steel/ H_2SO_4 (pH=1) interface in absence and presence of binary inhibitor mixtures were recorded as Nyquist plot (Figure 4 & 5) and the impedance data obtained were summarized in Table 6.

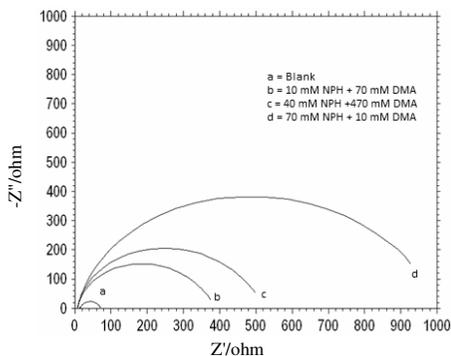


Figure 4. Electrochemical impedance plots in absence and in presence of NPH + DMA

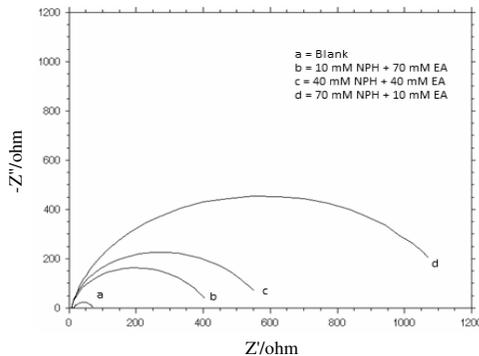


Figure 5. Electrochemical impedance plots in absence and in presence of NPH + EA

Table 6. Electrochemical impedance parameters in absence and in presence of the binary inhibitor mixtures

Inhibitor Conc.	$R_t, \Omega \text{ cm}^2$	$C_{dl}, \mu\text{Fcm}^{-2}$	%IE
Blank	58	121.32	-
NPH + DMA			
10 mM + 70 mM	382	2.73	84.81
40 mM + 40 mM	505	1.531	88.51
70 mM + 10 mM	990	0.421	94.14
NPH + EA			
10 mM + 70 mM	419.35	1.844	86.17
40 mM + 40 mM	584.67	1.789	90.08
70 mM + 10 mM	1139.49	0.308	94.91

FTIR studies of metal surface product

The FTIR spectra of the metal surface product in presence of the binary mixture NPH and DMA (70 mM + 10 mM) has been shown in Figure 6. The major peaks obtained from the spectral analysis have been listed in Table 7.

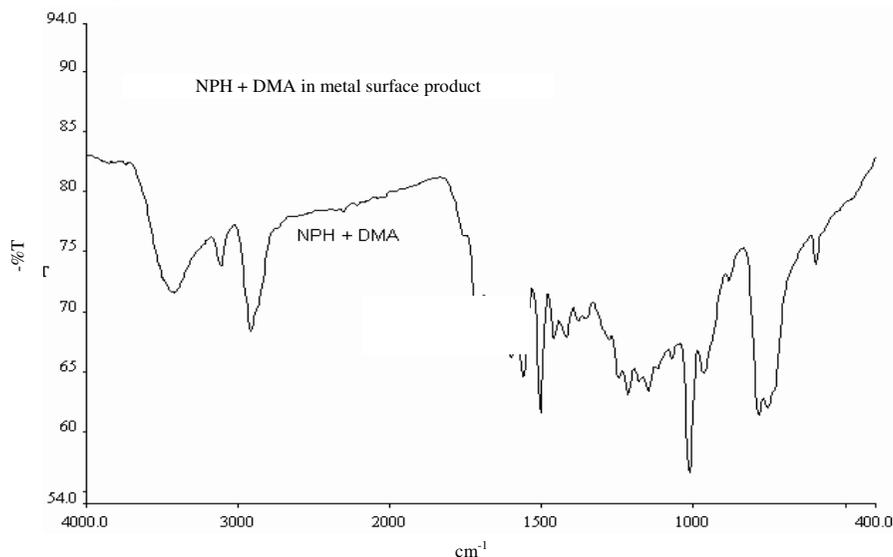


Figure 6. FTIR spectra of metal surface after immersion in the acid solution containing the binary mixture of NPH and DMA

Table 7. Spectral study of FTIR for surface product of binary mixture NPH and DMA

Pure		Metal surface product in presence of			Assignments
DMA	NPH	DMA	NPH	NPH + DMA	
3484	-	3394	-	-	N-H stretching
-	3376	-	3302	3392	O-H stretching
1653-1560	1600-1545	1652-1537	1624-1540	1632-1563	Ring mode
1025	-	1030	-	1040	C-N stretching
-	658	-	669	655	C-O stretching

Table 8. Spectral study of FTIR for surface product of binary mixture NPH and EA

Pure		Metal surface product in presence of			Assignments
EA	NPH	EA	NPH	NPH + EA	
3515	-	3414	-	-	N-H stretching
-	3376	-	3302	3392	O-H stretching
1626-1557	1600-1545	1635-1570	1624-1540	1652-1505	Ring mode
1072	-	1030	-	1021	C-N stretching
-	658	-	669	752	C-O stretching

Figure 7 has been shown the FTIR spectra of the metal surface product in presence of the binary mixture NPH and EA (70 mM + 10 mM). The major peaks obtained from the spectral analysis have been listed in Table 8.

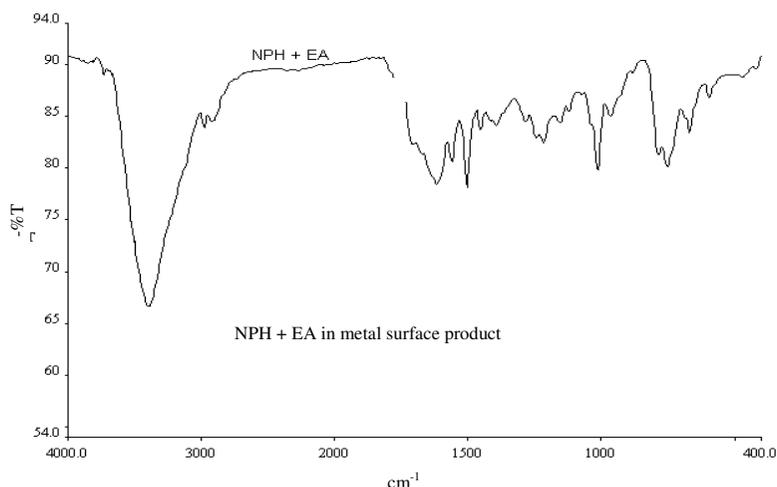


Figure 7. FTIR spectra of metal surface after immersion in the acid solution containing the binary mixture of NPH and EA

Morphological studies of metal surface

The scanning electron micrographs (Figure 8) of the steel surface in absence and in presence of the binary inhibitor mixtures have been taken at different magnifications. A uniform flake type is seen in case of the free acid (Figure 8a and 8b). In presence of the inhibitor mixtures the metal surface is covered (Figure 8c, d, e and f) with the inhibitor products. The flake type products were also present in presence of both the inhibitor mixtures and it was clearer at higher magnifications.

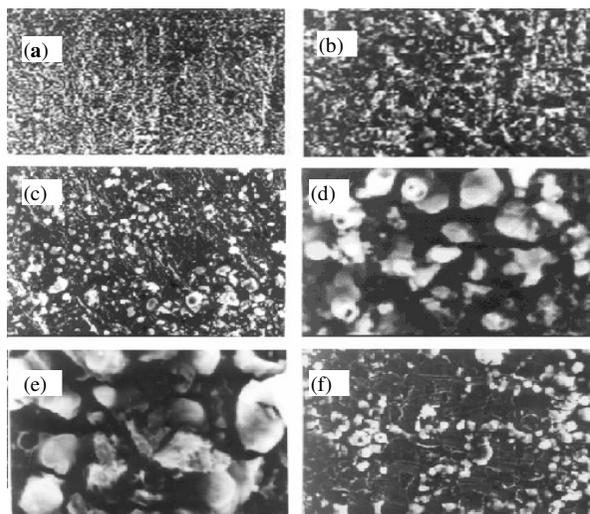


Figure 8. SEM Micrographs of the metal surface in absence and in presence of the binary inhibitor mixtures at different magnifications (a) Blank at 1000X; (b) Blank at 5000X; (c) NPH + DMA at 1000X; (d) NPH + DMA at 5000X; (e) NPH + EA at 1000X and (f) NPH + EA at 5000X (1000X and 5000X)

The results in the present study have shown synergistic effect for all the formulations for both the tested binary mixtures. The mixture containing 70 mM NPH with 10 mM DMA has shown a maximum efficiency 92.78% at room temperature among the tested combinations of this binary mixture. The inhibition efficiency of NPH increased in all the combinations and the highest increment (~13%) has been observed at 1:7 concentration (10 mM of NPH and 70 mM of DMA) ratios. In case of the binary mixture of NPH and EA the highest inhibition efficiency (93.48%) was also obtained at 7:1 concentration (70 mM of NPH and 10 mM of EA) ratio. The inhibition efficiency of NPH was increased in highest amount (~14%) at the 1:7 concentration (10 mM of NPH and 70 mM of EA) ratios. In many cases, a mixed type inhibitor is found to be more efficient than the single type inhibitor towards the inhibition of metal corrosion. The summation of protective properties of two inhibitors in a mixture can take place if the following requirements are fulfilled;

1. The inhibitors do not compete for the active sites
2. Efficiency depends on the extent of surface fraction screened by the inhibitor
3. The inhibitors do not interact either on the protected surface or in the solution

These conditions would be fulfilled absolutely in ideal solutions only and experimental results indicated both the binary mixtures might fulfill partially. The effect of exposure period on inhibition efficiency for NPH and EA mixture was less compared to the mixture of NPH and DMA. The binary mixture of NPH and EA offered 83.74% inhibition at 24 h exposure period while it was 80.51% in case of the NPH and DMA at 24 h exposure period. The decreasing trend in the inhibition efficiency and increasing trend in the corrosion rate with exposure period indicated that the formation of film by the components of the mixtures was not sustainable with time. This might be due to partial desorption of the inhibitor molecules responsible for the corrosion protection from the metal surface²⁶. The inhibition efficiency was found to be 67.7% for NPH and DMA and it was found to be 62.4% for NPH and EA mixture at 333 K. The lower inhibition efficiency in case of both the inhibitor mixtures at higher temperature may be due to higher desorption rate than adsorption at higher temperature. Higher values of E_a (~78 kJ/mol for both the binary mixtures) were obtained in presence of the studied inhibitor mixtures in comparison with that in the case of uninhibited acid solution (~46 kJ/mol) which indicates the physical adsorption by the formation of an adsorptive film of an electrostatic character²⁷. The negative values of ΔG_{ads} (~ 42 kJ/mol for NPH and DMA mixture and ~ 40 kJ/mol for NPH and EA mixture) suggest the spontaneous adsorption of the inhibitors on the metal surface for the inhibitors within tested temperature range. The positive values of ΔH_{ads} (~ 76 kJ/mol for both the mixtures) reflect the endothermic nature of the adsorption process and mean that the dissolution of steel is difficult. The lower positive values of ΔS_{ads} indicate the less orderliness of the transition state of 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 compare to water²⁸.

The inhibition efficiencies calculated from potentiodynamic polarization study are slightly different (Table 5) from that of the weight loss study. This may be due to the difference in experimental method. The results obtained from weight loss measurement are average values, while the results obtained from potentiodynamic measurement are instantaneous values. The R_t values increases with inhibitor concentration and this in turn leads to an increase in IE% and may be attributed to the formation of protective film on the metal–solution interface. The addition of inhibitor lowers the C_{dl} value, suggesting that the inhibition can be attributed to surface adsorption²⁹.

The infrared spectra obtained for the metal surface products in presence of both the inhibitor mixtures are found to be almost similar when compared with the spectrum of the respective pure compounds³⁰. The broad band obtained at 3372 cm^{-1} in the metal surface product in presence of the NPH and DMA mixture may be due to the N-H stretching vibration of anilines or due to the O-H stretching vibration of phenols. A few peaks observed in the range from $1632\text{--}1563\text{ cm}^{-1}$ were attributable for the ring mode (these were obtained in the range from $1652\text{--}1537\text{ cm}^{-1}$ for pure DMA and from $1600\text{--}1545\text{ cm}^{-1}$ for pure NPH). The peak observed at 1040 cm^{-1} may be due to C-N stretching of DMA. The peak observed at 655 cm^{-1} for the metal surface product may be due to the C-O stretching of NPH. In the spectra of the metal surface product in presence of NPH and EA mixture a broad band was obtained at 3392 cm^{-1} may be due to the N-H stretching vibration of anilines or due to the O-H stretching vibration of phenols. The peaks observed in the range from $1652\text{--}1505\text{ cm}^{-1}$ were attributable for the ring mode and for the pure EA these were obtained in the range from $1626\text{--}1537\text{ cm}^{-1}$ and for pure NPH these were obtained in the range from $1600\text{--}1545\text{ cm}^{-1}$. The peak due to C-N stretching of EA was observed at 1021 cm^{-1} for metal surface product. The peak observed at 752 cm^{-1} for the metal surface product may be due to the C-O stretching of NPH.

These results reveal the presence of all the individual component inhibitors of the binary mixtures in the film formed on metal surface after immersion in the acid solution containing the inhibitor mixtures. The broad band for the hydroxyl group and amine group in case of the metal surface products for both the inhibitor mixtures were shifted towards lower side in comparison to the respective pure compounds. The peak positions for the other characteristic bonds are remains almost unchanged for both the inhibitor mixtures compared to the respective pure compounds. It was a sign of the weakening of the O-H or N-H bond in the respective compounds indicating the adsorption of inhibitor molecules on the metal surface through the oxygen or nitrogen atom.

A uniform flake type corrosion product in case of the free acid (Figure 9a and 9b) may be metal oxides and metal hydroxides deposited on the metal surface have been seen in SEM micrographs³². Formation of a compact adsorption layer containing semi globular inhibitor species on metal surface is observed in presence of both the binary inhibitor mixtures. A more compact layer has been observed in case of the mixture of NPH and EA compared to that of the mixture of NPH and DMA. The compactness of the film formed on the metal surface is more prominent at higher magnifications.

Adsorption model

In acid solution these alkyl substituted aniline isomers undergo easy protonation through the N atom of the $-\text{NH}_2$ group and the NPH undergoes protonation through the O atom of $-\text{OH}$ group. The unprotonated and protonated species of the corresponding inhibitor molecules will be at a dynamic equilibrium. 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^{31,32} (Figure 9a and b and Figure 10a and b). At the same time electron donation from $-\text{OH}$ group of NPH towards anodic sites of the metal surface and the back donation of the electrons from the cathodic sites of the metal surface towards $-\text{O}^+\text{H}_2$ occur simultaneously. The metal dissolution from the anodic sites due to the corrosive attack by acid solution will be difficult and the hydrogen evolution rate decreased due to partial blocking of the cathodic sites by the inhibitor molecules. The potentiodynamic polarization study

indicated that these inhibitors are mixed type inhibitors predominantly act on cathodic areas. The electron density on the N atom will be higher in EA compared to DMA due to stronger +I effect of $-C_2H_5$ group in case of EA than +I effect $-CH_3$ group in DMA. The higher value of inhibition efficiency for the binary mixture of NPH and EA as compared to the binary mixture of NPH and DMA can be attributable to the higher electron density of the reacting centre ($-NH_2$ group) of EA compared to DMA. The contributory effect in the corrosion inhibition of NPH is common in both the mixtures. The phenyl ring of NPH, DMA and EA may also involve into this electronic interaction through its delocalized π -electron:

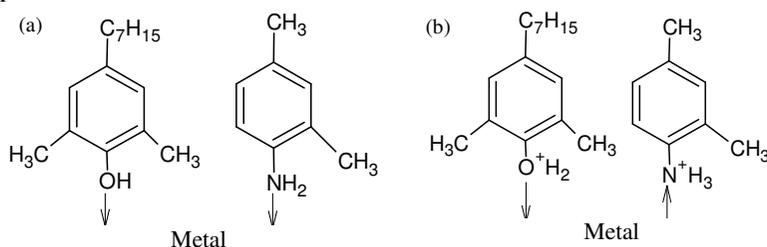


Figure 9. Adsorption model for the binary inhibitor on the metal surface (a) Unprotonated DMA and unprotonated NPH (b) Protonated DMA and protonated NPH

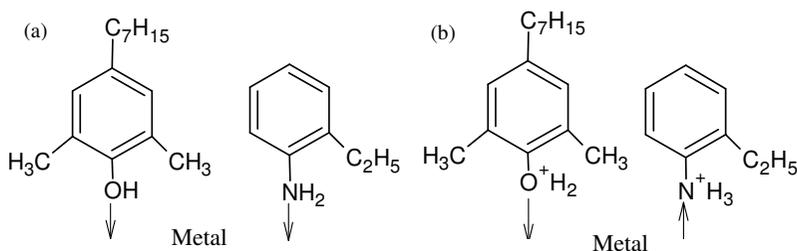


Figure 10. Adsorption model for the binary inhibitor mixtures on the metal surface (a) Unprotonated EA and unprotonated NPH (b) Protonated EA and protonated NPH

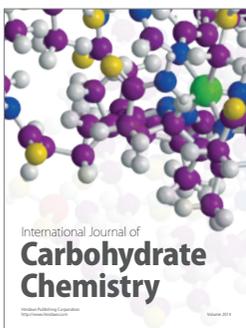
Conclusion

1. The maximum inhibition efficiencies were obtained at (70+10 mM) for both the binary mixtures (for NPH+DMA 92.78%; for NPH+EA 93.48%) at 6 h whereas at 24 h exposure NPH+DMA offered 82.63% and NPH+EA offered 83.74% inhibition. Among the inhibitors NPH+DMA attained 62.46% at 333K whereas it was 67.73% for NPH+EA.
2. The spontaneous adsorption of the inhibitors on the metal surface revealed by negative values of ΔG_{ads} . The endothermic nature of the adsorption process indicated by the positive ΔH_{ad} values. The lower positive values of ΔS_{ads} indicate the less orderliness of the transition state of the adsorption process.
3. The binary mixtures are found to be mixed type inhibitors active predominantly towards cathodic reactions.
4. The FTIR spectrum of the metal surface product revealed the presence of both phenol and substituted aniline molecules in the metal surface products. The characteristic shift of the peak obtained due to $-N-H$ stretching and $-O-H$ stretching indicated the electron donation through the $-NH_2$ and $-OH$ group of the respective inhibitor molecules.

5. The uniform flake type corrosion products have been seen in absence of the inhibitors whereas a compact layer of semi globular inhibitor products have been observed in presence of both the binary inhibitor mixture.

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