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Surface modification of zinc by new organic compounds and its corrosion study

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ABSTRACT

The effect of a new organic compounds 4-benzylidene-5-methyl-2-phenylpyrazolidin-3-one (BMP) and (4Z)-4-[(4-methoxyphenyl)methylidene]-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (MMDP) on the corrosion behavior of zinc by surface modification was investigated. Electrochemical study of the surface modified zinc specimens were carried out in 0.1 M HCl and 3.5% NaCl solution using galvanostatic polarization and linear polarization method. The surface modification of zinc was achieved by immersion in solutions of different concentration of BMP and MMDP for different immersion time. MMDP shows more protection efficiency than BMP. The corrosion protection could be explained by the formation of a protective organometallic layer on the zinc surface due to the chelation reaction between zinc and organic compound. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) were applied to study formation of the protective layer.

Key words: organic compound, polarization, SEM, corrosion.

INTRODUCTION

Zinc is an active metal with numerous industrial applications and its coatings is largely used for the protection of steel. In humid atmosphere the zinc coated articles get corroded and thus the service life of articles gets reduced. To avoid the zinc corrosion generally a coating of passive layer is given to its surface. The chromation is one such method wherein the surface of zinc is exposed to chromate solution for few seconds. The chromate solutions have been applied successfully to protect zinc surface from white rust [1]. But the strict regulation on the environment restricts the use of chromate solution since chromium element being toxic in nature.

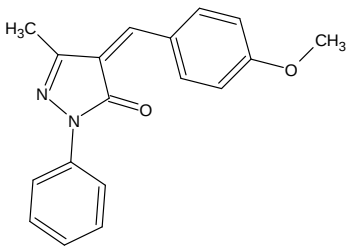
Another important method of corrosion inhibition of zinc is using of organic compound as inhibitor. Generally these compounds require in ppm and their effect on corrosion inhibition is very high. The earlier research work revealed the use of a large number of organic compounds of different nature as corrosion inhibitors for zinc [2-5]. Most of these organic compounds are adsorbed on the metal surface and provide a barrier between metal and environment, thereby reducing the rate of corrosion. The effectiveness of inhibition depends on the nature and surface charge of the metal, the nature of the medium, the nature and chemical structure of the inhibitor molecule such as functional groups, aromaticity, π orbital character of the donating electron, steric factor, electron density at the donor atoms and etc[6-7].

The literature on corrosion inhibitors revealed that majority of compounds control the corrosion through the formation of complex with metal. Taking this idea many research scientists wish to modify the surface of metal by dipping them directly into the solution of complexing agents before subjecting into accelerated corrosion study. Many reports in the literature are connected to modify the surface of metal by complexing it with organic compounds[8]. The complex forming ability of organic compounds with zinc was the main criteria for selecting them as surface modifiers [9]. In this modifying process the metal is immersed in the solutions of complexing agents. The immersion time varies from few seconds to several hours.

In the present work, new organic compounds were prepared and used for the zinc surface modification. The prepared molecule contains electroactive covalent (>N-N) and coordinating (>C=N- and >C=O) groups and aromatic ring. This facilitates delocalization of the π-electrons and enhances the complex formation ability with the surface metal atoms. The metal was treated by immersing in treatment solution of known concentrations for different time interval. The treated metal was subjected to corrosion study by accelerated techniques. The protective layers formed on the zinc surface after immersion in the treatment solutions were analyzed by SEM and IR studies.

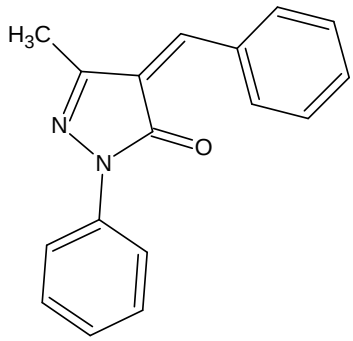
MATERIALS AND METHODS

The organic compounds used in this study were prepared by adopting the standard procedure[10]. BMP was prepared by dissolving the 0.01 M of substituted pyrazole in alcohol at 0-5^{0}c then 0.01 M aldehydes and 10% NaOH was added by dropping funnel then solution was stirred for getting the thick solution. Formation of the product was confirmed by TLC and FTIR spectra. MMDP was also prepared by using same procedure. Structure of the molecules is given in the fig 1. The treatment solution was prepared by dissolving the different concentrations (0.2 to 0.8%) of organic compound in alcohol and same was utilized for surface modification process.



(4*Z*)-4-(4-methoxybenzylidene)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one

(MMDP)



(4*Z*)-4-benzylidene-5-methyl-2-phenylpyrazolidin-3-one

(BMP)

Fig 1. Structure of compounds

The pure zinc plate (Cu=0.185%, Al=0.006%, Fe=0.004%, Mn=0.3%, Sn=0.003%, Pb=0.002%, Cd=0.002% and the rest zinc) was selected and coupons of desired shapes (5cm x 1cm x 4mm) were prepared. These samples were polished with SiC papers of different grit size (200 to 1200) and they were degreased with trichloroethylene vapours to remove oil and grease. The samples were rinsed with ethanol, followed by distilled water wash. The so prepared samples were immersed in the treatment solution for different time intervals.

Electrochemical measurement

Polarization studies

A conventional three-electrode system was used for electrochemical measurements. The modified and unmodified zinc specimen was used as working electrode. The surface area of specimen exposed for corrosion study was 1 sq. cm. The saturated calomel electrode (SCE) and platinum foil were used as reference and auxiliary electrodes. The SCE was connected very close to the electrode surface via Luggin capillary to minimize IR drop. All the potentials are referred with respect to SCE. The measurements were carried out in aerated, non-stirred solution.

The percentage inhibition efficiency (η) was calculated using the relationship;

$$\eta = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100$$

where I^{o}_{corr} and I_{corr} are the corrosion current densities before and after modification and were obtained from Tafel plots.

Linear polarization method

In order to determine the polarization resistance, R_p, the potential of the working electrode was ramped ±10mV in the vicinity of the corrosion potential at a scan rate of 0.1mVs^{-1}.Polarization resistances were determined from the slope of the potential versus current lines.

Where A is the surface area of the electrode.

$$R_P = A \frac{dE}{di}$$

FTIR spectroscopic studies

To examine the adsorption mechanism of organic compounds film on the metal surface the FTIR spectra of the compound scrapped from the metal surface and synthetically prepared compound were recorded using Shimadzu FT-IR 8400S instrument.

Surface analysis

The surface morphology of surface modified and unmodified zinc samples was investigated using SEM microscope (model: JEOL, JSM 6400). The SEM images of the metal surfaces of unmodified and modified zinc samples after anodic polarization were taken.

RESULTS AND DISCUSSION

Electrochemical Studies

Polarization curves of modified and unmodified zinc specimens in 0.1N HCl and 3.5% NaCl solutions were shown in Figs 2 –5. Various corrosion parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slope constants (b_a & b_c) and protection efficiencies from polarization measurements are given in Table-1.

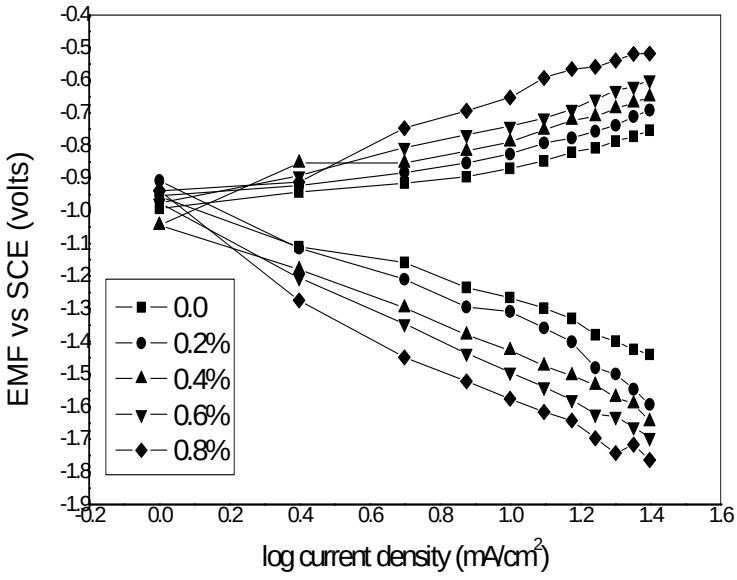


Fig 2. Polarization profile for BMP in HCl Medium

The effective surface modification was obtained from the treatment solution containing 0.8% of the organic compound. Above 0.8% gave almost same corrosion current, so it was fixed as optimum concentration.

The higher protection efficiency may be attributed to the presence of delocalized π electrons and presence of lone pair of electrons on oxygen and nitrogen atoms of >C=O- and >C=N- groups in BMP and MMDP molecule. Further the presence of activating methoxy group (-OCH_3) in MMDP increases the electron density on the nitrogen atom. This leads to the effective surface

modification of zinc. So in case of MMDP gives more corrosion resistance in both HCl and NaCl medium.

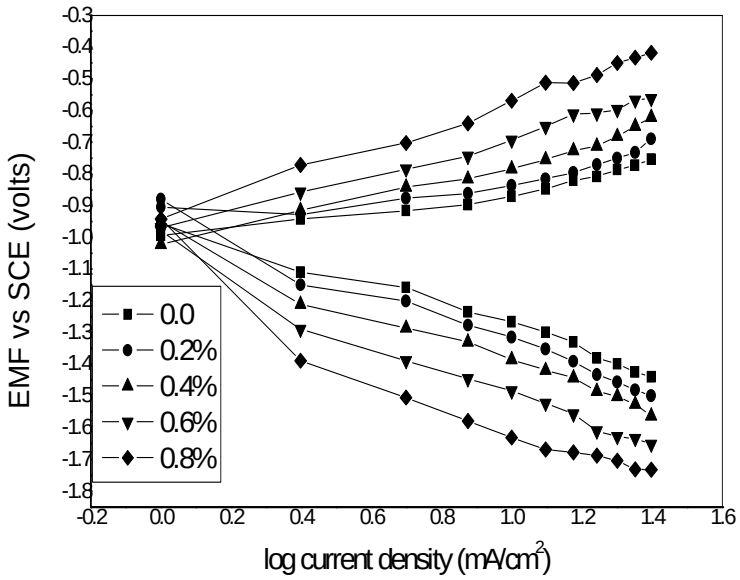


Fig 3. Polarization profile for MMDP in HCl medium

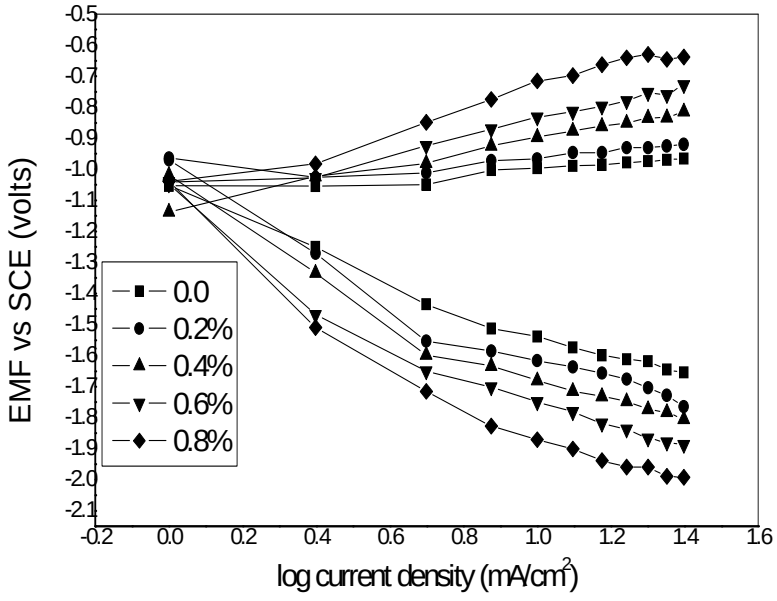


Fig 4. Polarization profile of BMP in NaCl medium

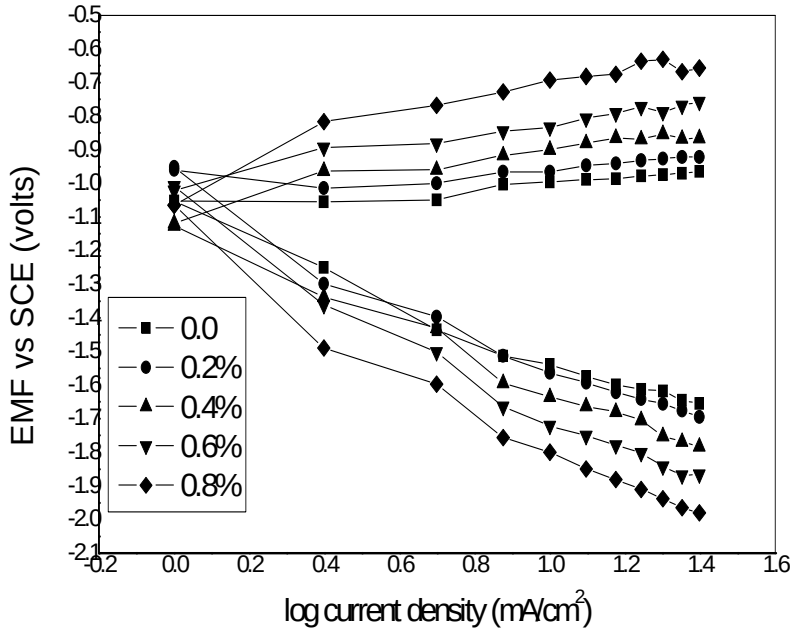


Fig 5. Polarization profile of MMDP in NaCl medium

To study the effect of treatment time, zinc specimens were treated in 0.8% solution at different immersion time varied from 2 to 8 hours. The good protection efficiency was observed for 2 hour modified sample, above 2 hour almost same protection efficiency was recorded. So 2 hours time was taken as optimum time for surface modification.

Polarization resistance values were determined from the slope of the polarization curves in the potential range ± 10mV with respect to the corrosion potential at a sweep rate of 0.1mVs^{-1}. The Rp values increased with increase in concentration for both compounds as seen from Table. 2. Same trend was observed in linear polarization method like polarization method.

SEM studies

Scanning electron microscopic technique was used to know the mode of attack of corrosive medium on modified and unmodified metal surface. Fig 6. a and c shows the SEM photo micrographs of unmodified sample after anodic polarization in NaCl and HCl respectively. Fig 6 b and d shows the modified sample after anodic polarization in NaCl and HCl respectively. In fig 6 a some cavities, pits and corrosion products were observed. In modified sample these pits and cavities were completely covered by organic compound. So pits were not appeared on the sample (6 b). In the same way HCl is highly corrosive in nature, so more number of cavities and pits with higher size was observed in unmodified sample (6c) but it was completely reduced after modification (6d). It indicates that the used compound is strongly adhered to the metal surface by making a strong complex with the metal surface and organic compound

Table 1: corrosion parameters obtained from polarization study for BMP and MMDP in NaCl and HCl medium

Concentration (%)	I_{corr} ($mAcm^{-2}$)	E_{corr} (mV)	β_a ($mVdec^{-1}$)	β_c ($mVdec^{-1}$)	%PE
For BMP in HCl					
0.0	5.01	-1.03	300	700	--
0.2	2.5	-1.03	.285	545	50
0.4	1.9	-1.07	327	545	62
0.6	1.4	-1.09	.275	535	72
0.8	1.1	-1.04	300	500	78
For MMDP in HCl					
0.0	5.01	-1.03	300	700	--
0.2	2.2	-1.0	350	400	56
0.4	1.5	-1.01	320	370	70
0.6	1.3	1.02	410	310	74
0.8	1.0	-1.05	500	330	80
For BMP in NaCl					
0.0	3.1	-1.16	220	285	--
0.2	1.62	-1.08	197	380	48
0.4	1.41	-1.08	187	400	54
0.6	1.2	-1.15	167	370	61
0.8	1	-1.18	166	350	68
For MMDP in NaCl					
0.0	3.1	-1.16	220	285	
0.2	1.5	-1.08	187	300	52
0.4	1.23	-1.08	176	375	60
0.6	1.1	-1.15	165	415	64
0.8	0.9	-1.18	153	500	71

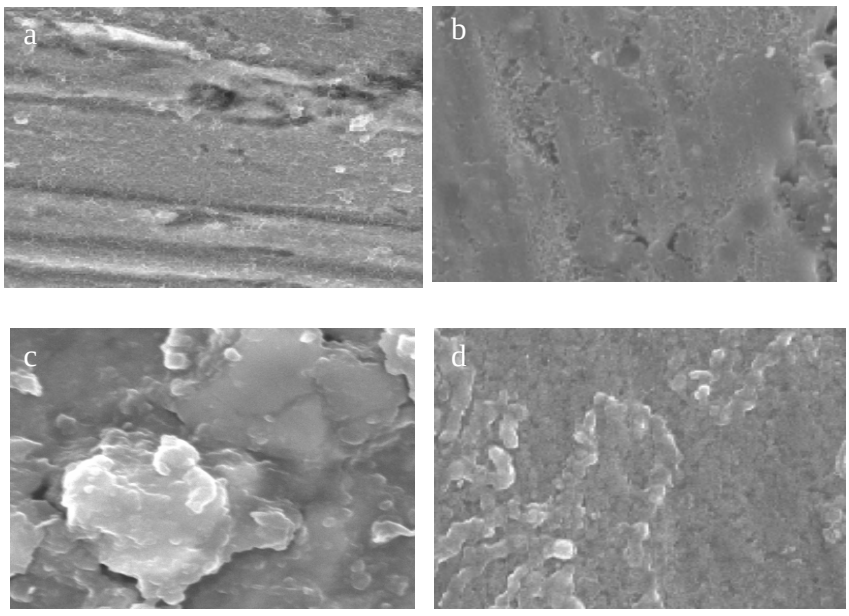


Fig 6. SEM Images of zinc surface after anodic polarization(a) without modification in NaCl (c) in HCl (b) with modification in NaCl (d) with modification in HCl

Table 2: corrosion parameters obtained from linear polarization study for BMP and MMDP in NaCl and HCl medium

Concentration	E_{corr}	Rp	%PE
For BMP in HCl			
0.0	-1.03	18.2	
0.2	-1.03	32.50	44
0.4	-1.07	46.70	61
0.6	-1.09	56.33	68
0.8	-1.04	74.04	75
For MMDP in HCl			
0.0	-1.03	18.2	
0.2	-1.0	36.84	50
0.4	-1.01	49.67	63
0.6	1.02	58.96	69
0.8	-1.05	86.32	79
For BMP in NaCl			
0.0	-1.16	17.39	
0.2	-1.08	34.77	50
0.4	-1.08	39.24	56
0.6	-1.15	41.63	58
0.8	-1.18	48.89	64
For MMDP in NaCl			
0.0	-1.16	17.39	
0.2	-1.08	33.34	48
0.4	-1.08	40.30	57
0.6	-1.15	46.60	63
0.8	-1.18	56.52	70

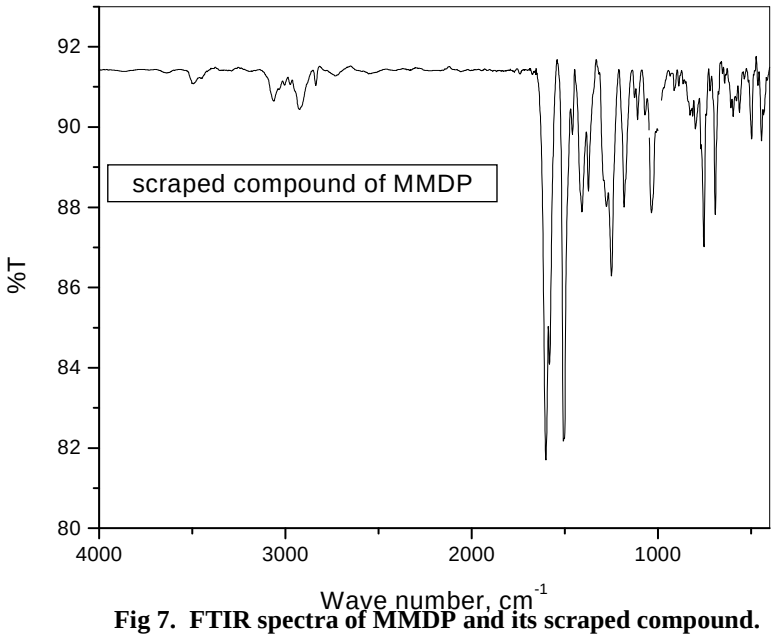


Fig 7. FTIR spectra of MMDP and its scraped compound.

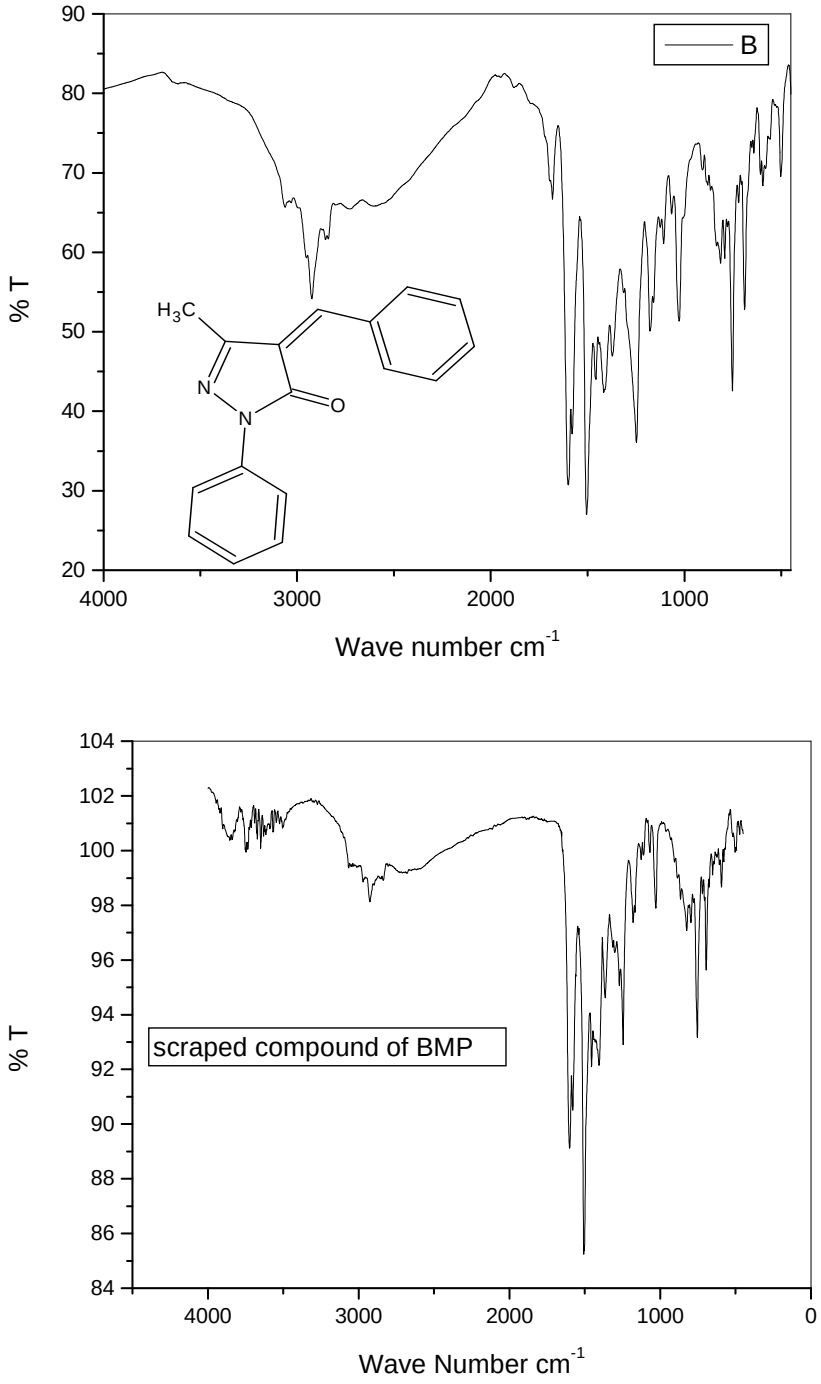
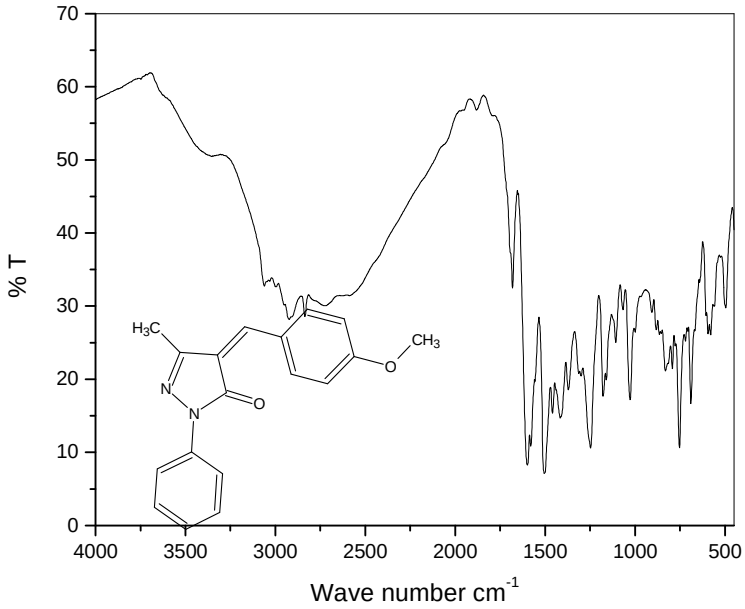


Fig 8. FTIR spectra of BMP and its scraped compound

FTIR studies

Figs 7 and 8 shows the FTIR spectra of prepared and scrapped compounds of MMDP and BMP. The prepared MMDP compound shows C-H stretching at 3040 to 3010cm^{-1} (Alkene) C=C stretching at 1670 cm^{-1}, carbonyl stretching frequency at 1725 to 1700 cm^{-1}, C=N bond at 1800 cm^{-1}. In the scrapped compound C=N bond was merged and the overall spectra was modified these data indicates the good interaction of MMDP with the zinc through C=N. The FTIR spectra of BMP compound was broden in 3000 cm^{-1} region and also overall spectra was brodened because of absence of methoxy group in the compound. In the scraped compound also same type of observations were noticed in the spectra. These spectral evidences indicated the formation of complex between metal and organic compound so it gives the good corrosion protection efficiency.



CONCLUSION

Electrochemical study showed that the surface modification of zinc metal with BMP and MMDP showed good protection against corrosion in acidic and neutral medium. MMDP shows slightly higher protection efficiency than BMP due to presence of methoxy group in the compound. The observed protection against corrosion was affected by the concentration of the compounds and treatment time. The treatment induced a basic modification of zinc surface and controls the corrosion by decreasing the electron transfer rate. The SEM images showed the formation of a passive film on the modified zinc. The FTIR data confirmed the formation of a stable organometallic film and it is strongly attached to the zinc surface through the establishment of chemical interaction through electroactive >C=N- group. Therefore, the prepared compound modifies the zinc metal surface and provides good protection to zinc against corrosion.

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