Synergistic inhibitive effect and related quantum chemical parameters of 2-ethoxy-4,6-dimethylnicotinonitrile and iodide ions on corrosion of mild steel in sulfuric acid

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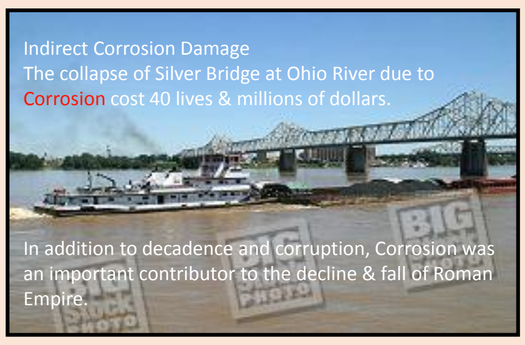
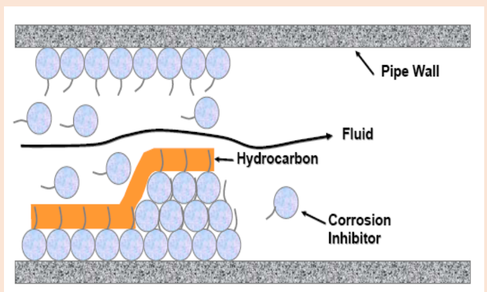
What is Corrosion ?

An irreversible, interfacial reaction of a material with its environment which results in a consumption of the material or in dissolution of a component of environment in to the material.



Corrosion Inhibitor

An Inhibitor is a substance which decreases the corrosion rate when present in the corrosive system in a suitable concentration without significantly changing the composition of corrosive agent.



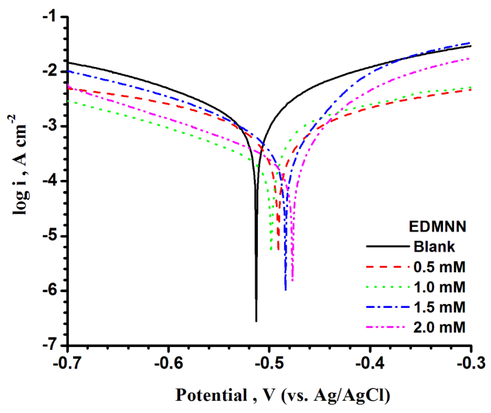
presentation of inhibitor action

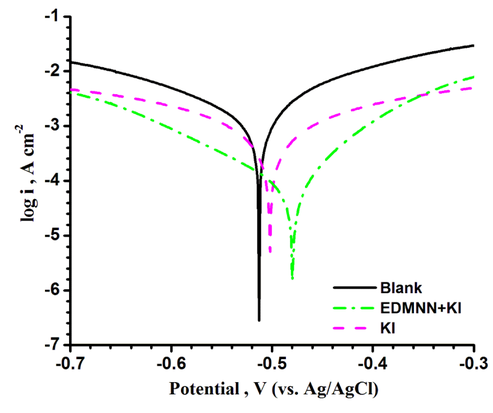
Inhibitors retard the corrosion process by :

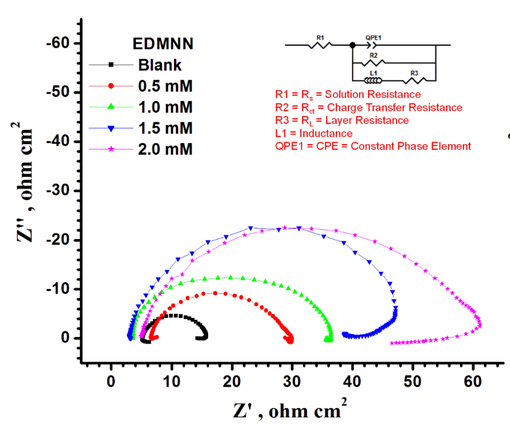
- ❑ **Increasing the anodic, cathodic or both polarization .**
- ❑ **Reducing the movement or diffusion of ions through the interface.**
- ❑ **Increasing the electrical resistance of metal environment interface.**

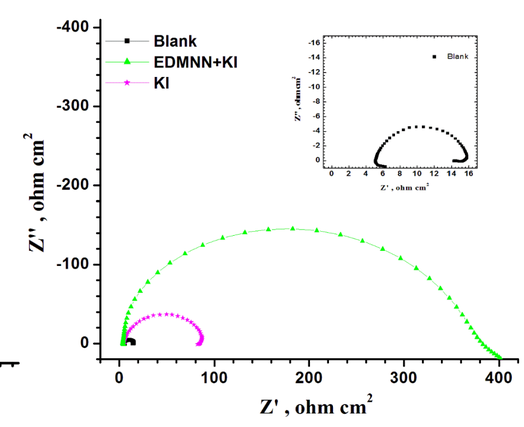
Results and discussion

Potentiodynamic polarization and Electrochemical impedance spectroscopic measurements

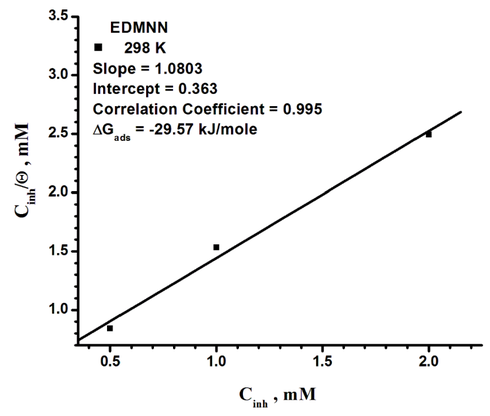








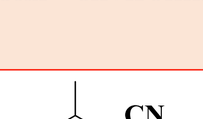
Langmuir adsorption isotherm



Tafel and Nyquist Plots in absence and presence of TODPCN and TODPCN with KI [synergistic parameter = 1.44 and 1.47]

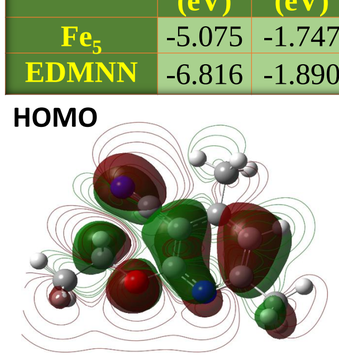
Theoretical study by DFT method [RB3LYP/6-311++G(D.P.)]

	E_H (eV)	E_L (eV)	$\Delta E_1 = E_{L(I)} - E_{H(Fe)}$	$\Delta E_2 = E_{L(Fe)} - E_{H(I)}$
Fe_5	-5.075	-1.747	----	---
EDMNN	-6.816	-1.890	3.185	5.069

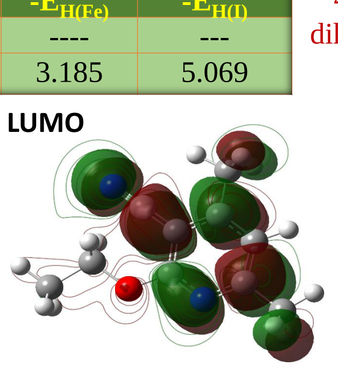


4,6-dimethyl-2-ethoxy-1,2-dihydro-pyridine-3-carbonitrile [EDMNN]

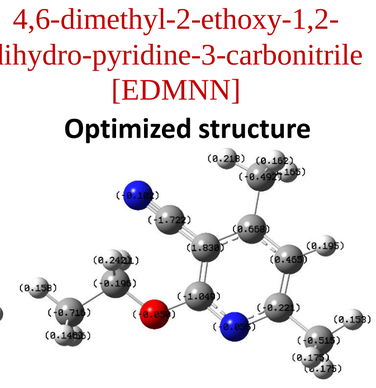
HOMO



LUMO



Optimized structure

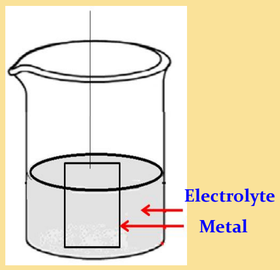


Gravimetric, potentiodynamic, linear polarization and EIS parameters as well as inhibition efficiency values in the absence and presence of different concentrations of EDMNN at 298 K.

Inhibitor	C_{inh}	C_R	η	E_{corr}	i_{corr}	η	R_p	η	R_{ct}	η
	mM	mg cm^{-2} h^{-1}	%	mV vs. Ag/AgCl	μA cm^{-2}	%	Ω cm^2	%	Ω cm^2	%
Blank	00	3.194	----	-513	2346	---	15.0	----	9.8	---
EDMNN	0.5	1.296	59.4	-491	1050	55.2	36.1	58.4	23.0	57.4
	1.0	1.115	65.1	-503	750	68.0	45.9	67.3	32.1	69.4
	1.5	0.885	72.3	-484	641	72.6	76.2	76.6	43.7	77.5
	2.0	0.632	80.2	-477	476	80.0	87.6	82.8	50.3	80.6
KI	2.0	1.492	53.3	-502	1054	55.1	34.6	56.6	22.6	56.6
EDMNN+KI	2.0+2.0	0.029	99.0	-480	113.0	95.2	192.4	92.2	374.0	97.4

Evaluation of Inhibition Efficiency

Gravimetric

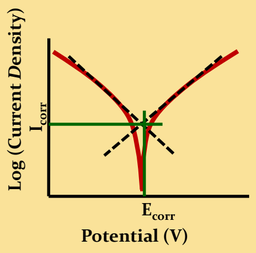


Finely polished metal sample were dipped in a known volume of solution with and without inhibitors for certain duration of time and weight change was measured.

$$\eta\% = \frac{W^0_{corr} - W_{corr}}{W^0_{corr}} \times 100$$

where, W_{corr} and W^o_{corr} are the weight loss of inhibited and uninhibited metal

Potentiodynamic Poarization

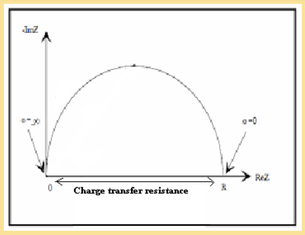


Corrosion current density (I_{corr}) values were determined by the extrapolation of linear Tafel segments of anodic and cathodic curves.

$$\eta\% = \frac{I^\circ_{corr} - I_{corr}}{I^\circ_{corr}} \times 100$$

I_{corr} and I^o_{corr} are the corrosion current densities with and without inhibitor

Electrochemical Impedance Spectroscopy

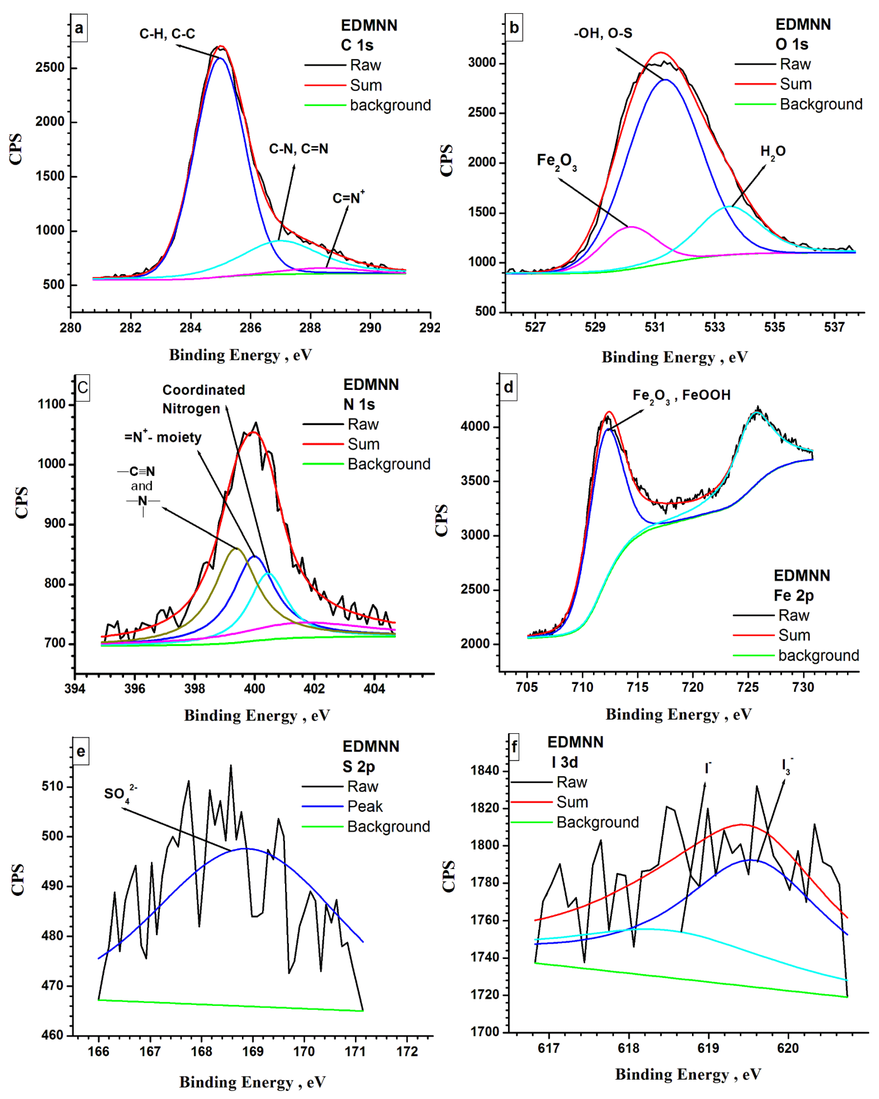


The charge transfer resistance (R_{ct}), values were calculated from the difference in the impedance at lower and higher frequencies.

$$\eta\% = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100$$

R_{ct} and R^o_{ct} are the charge transfer resistance in absence and presence of inhibitor

The XPS deconvoluted profiles of C 1s, O 1s, N 1s, Fe 2p, S 2p and I 3d for for mild steel in 0.5 M H_2SO_4 in presence of EDMNN + KI



Conclusion

- ➢ **EDMNN is a good inhibitor and η value is a function of concentration. On addition of KI, η value increases extensively.**
- ➢ **Polarization measurements show that EDMNN acts as mixed inhibitor.**
- ➢ **Inhibition of corrosion is due to the formation of adsorbed inhibitor film on mild steel.**
- ➢ **The adsorption of EDMNN obeys Langmuir adsorption isotherm.**
- ➢ **A cooperative mechanism between iodide anion and EDMNN cation is confirmed from XPS study.**
- ➢ **Theoretical study has been able to establish the link between the inhibitive effect and the electronic properties of EDMNN.**

SEM and AFM micrographs of surfaces

References

- ❑ P. Mourya, P. Singh, A. K. Tiwari, R. B. Rastogi, M. M. Singh, Corros. Sci. 95 (2015) 71.
- ❑ P. Mourya, S. Banerjee, R. B. Rastogi, M. M. Singh, Ind. Eng. Chem. Res. 52 (2013) 12733.
- ❑ A. A. Farag, M. A. Hegazy, Corros. Sci. 74 (2013) 168.