

DIMETHYL SULPHOXIDE AS AN INHIBITOR FOR THE CORROSION AND HYDROGEN PERMEATION THROUGH MILD STEEL IN ACIDIC SOLUTIONS

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The influence of dimethyl sulphoxide on hydrogen permeation and corrosion inhibition of mild steel in 1 N HCl and 1 N H₂SO₄ has been studied using weight loss measurements, gasometric studies, galvanostatic polarisation studies and hydrogen permeation measurements. The performance of this compound as an inhibitor of corrosion is not very much encouraging. It is found to perform as a mixed type corrosion inhibitor but predominantly as a cathodic inhibitor in both the acids. The adsorption of this compound on mercury from both the acids is studied using capillary electrometer. Dimethyl sulphoxide is found to bring down the extent of hydrogen permeation through mild steel in both the acids. The adsorption of the compound from the acids is found to obey Temkin's adsorption isotherm.

Keywords: Corrosion inhibition, dimethyl sulphoxide and Temkin's adsorption

INTRODUCTION

Organic compounds containing sulphur as the heteroatom, such as thiourea and its derivatives, thiazoles, mercapto triazoles and sulphoxide have been reported to function as efficient inhibitors for the corrosion of mild steel in acidic solutions [1-13]. But it is reported that thiourea and its derivatives are found to enhance the hydrogen entry into the metal [14], as they undergo partial decomposition to form hydrogen sulphide which accelerates the diffusion of hydrogen through steel. But a similar observation has not been made in the case of other sulphur containing organic compounds when used as corrosion inhibitors. The inhibitive action of a few aliphatic and aromatic sulphoxides was studied [13] and found that aromatic sulphoxides perform better than aliphatic sulphoxides. Influence of aliphatic sulphoxide, namely dimethyl sulphoxide on the corrosion of mild steel in H₂SO₄ and also its adsorption on mercury using capillary electrometer was studied [15]. But a thorough study on the mechanism of

inhibition of corrosion by dimethyl sulphoxide and its influence on hydrogen permeation through mild steel in acidic solutions containing different anions is still lacking. Hence, a systematic study has been carried out on the influence of anions on the inhibition of corrosion and hydrogen permeation through mild steel in acidic solutions in presence of dimethyl sulphoxide.

EXPERIMENTAL

Rectangular mild steel specimens of composition 0.07 wt% C, 0.08% P, 0.00% S and the remainder Fe and of size 5 x 2 x 0.025 cm were used for weight loss, gasometric and permeation studies. These strips were given mechanical polishing and then degreased with trichloroethylene before use. For polarisation studies a cylindrical mild steel rod of the same composition as above and embedded in Teflon with an exposed area of 0.283 cm² and provided with a screw type system for electrical contact was used. The electrode was polished using a sequence of emery papers an

then degreased. AR grade HCl and H₂SO₄ were used for preparing solutions. Dimethyl sulphoxide of extra pure grade used in the study was procured from SISCO Research Laboratories, Mumbai. Double distilled water was used to prepare all solutions. Triple distilled water and AR grade vacuum distilled mercury were used for capillary electrometer measurements.

Weight loss and gasometric measurements were carried out as described elsewhere [5]. Galvanostatic polarisation was carried out as reported earlier [5] at a temperature of 305 ± 1 K. A platinum foil of large surface area was used as the auxiliary electrode and Hg/Hg₂Cl₂/1 N HCl and Hg/Hg₂SO₄/1N H₂SO₄ were used as reference electrodes. The electro-capillary behaviour of dimethyl sulphoxide in both the acids was studied at 298 ± 1 K using a capillary electrometer as described in [16]. Hydrogen permeation studies were carried out using an adaptation of Devanathan and Stachurski's modified two compartment cell as described elsewhere [17].

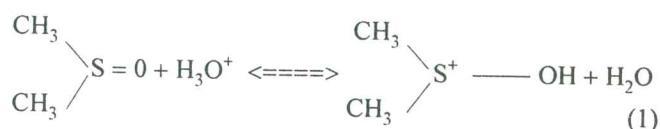
RESULTS AND DISCUSSION

Table I gives the values of inhibition efficiency for different concentrations of dimethyl sulphoxide in 1 N HCl and 1 N H₂SO₄ obtained from weight loss and gasometric measurements. It can be seen from the table that there is an acceleration of corrosion of mild steel in both the acids at the least concentration of 10⁻⁵ M. Similar observations have been made by earlier workers [13-15]. As concentration increases there is an inhibition of corrosion of mild steel in both the acids by dimethyl sulphoxide. But the performance is not very much encouraging as very low values of inhibition efficiency are obtained in both the acids even at a concentration as high as 10⁻¹ M. It can be seen that dimethyl sulphoxide perform better in 1 N H₂SO₄ as observed in the case of other sulphur containing organic compounds. The poor performance of dimethyl sulphoxide in acidic solutions can be explained as follows.

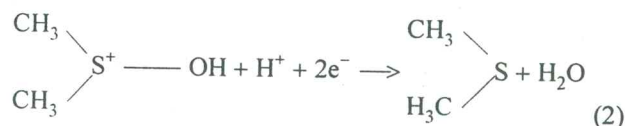
Dimethyl sulphoxide is freely miscible with water, owing to hydrogen bonding and also because of the tendency to form hydrate [18].

Usually the adsorption of neutral organic molecules at the metal/solution interface is caused by the "squeezing type of forces" which eject these molecules from the bulk of the solution to the metal surface [19-20]. But such type of forces can operate very effectively only when the solubility of the neutral organic molecule is low, as in the case of dibenzyl sulphoxide which gives comparatively higher values of inhibition efficiency than dimethyl sulphoxide [13]. It has already been proved by earlier studies that corrosion inhibition by sulphoxides is a case of secondary inhibition by sulphides formed, particularly for aromatic sulphoxides [22-24]. So the compound acts as a secondary inhibitor, i.e. its effect is due to the adsorption of dimethyl sulphide formed by reduction at the electrode.

Initially dimethyl sulphoxide is adsorbed on the mild steel surface from acidic solutions and the following equilibrium is established.



The reduction to sulphide takes place as follows



The sulphide with its two lone pairs of electrons is adsorbed much more easily than the parent sulphoxide and thus form a more stable chemisorption bond. The acceleration of corrosion in the presence of very low concentrations of the

TABLE I: Values of inhibition efficiency for different concentrations of dimethyl sulphoxide from weight loss and gasometric measurements

Inhibitor concn (M)	HCl	Inhibition efficiency (%)		H ₂ SO ₄
	Weight loss	Gasometric	Weight loss	Gasometric
10 ⁻⁵	-0.12	-0.08	-0.08	-0.06
10 ⁻⁴	2	2	5	4
10 ⁻³	10	10	13	14
10 ⁻²	22	24	26	26
5 × 10 ⁻²	31	33	36	37
10 ⁻¹	43	44	47	48

TABLE IIa: Corrosion kinetic parameters for mild steel in 1 N HCl in the presence of different concentrations of dimethyl sulphoxide

Inhibitor concn (M)	E_{corr} (mV)	Tafel slopes mV dec^{-1}		i_{corr} (mA.cm^{-2})	Inhibition efficiency (%)
		b_a	b_c		
Blank	-510	120	65	2.80	—
10^{-5}	-520	120	60	2.80	-2
10^{-4}	-525	120	60	2.65	5
10^{-3}	-508	125	68	2.45	13
10^{-2}	-503	128	70	2.15	23
5×10^{-2}	-500	130	73	1.90	32
10^{-1}	-495	135	75	1.45	48

compound may be due to the formation of soluble organometallic complexes by the reaction of the metal with the sulphide [25-26]. Considerably lower values of corrosion inhibition efficiency in the presence of different concentrations of dimethyl sulphoxide may also be ascribed to the formation of a sulphide which is volatile [13]. It is found that there is fairly good agreement between the values of inhibition efficiency obtained by weight loss and gasometric measurements.

Tables IIa and IIb give the corrosion kinetic parameters such as corrosion potential (E_{corr}), Tafel slopes (b_a and b_c), corrosion current (i_{corr}) and inhibition efficiency for the corrosion of mild steel in 1 N HCl and 1 N H_2SO_4 in the absence and presence of different concentrations of dimethyl sulphoxide. Kinetic parameters for mild

TABLE IIb: Corrosion kinetic parameters for mild steel in 1 N H_2SO_4 in the presence of different concentrations of dimethyl sulphoxide

Inhibitor concn (M)	E_{corr} (mV)	Tafel slopes mV dec^{-1}		i_{corr} (mA.cm^{-2})	Inhibition efficiency (%)
		b_a	b_c		
Blank	-915	130	70	2.20	—
10^{-5}	-922	130	64	2.24	-2
10^{-4}	-912	130	67	2.10	5
10^{-3}	-910	135	74	1.90	14
10^{-2}	-905	138	75	1.68	24
5×10^{-2}	-903	140	77	1.40	36
10^{-1}	-900	145	80	1.20	46

steel both the acids in the absence of dimethyl sulphoxide are found to be almost similar as reported earlier [5]. It can be seen from both the tables that E_{corr} value becomes more negative in the presence of lowest concentration (10^{-5} M) of dimethyl sulphoxide, because of the acceleration of corrosion of mild steel in both the acids. As the concentration increases E_{corr} values becomes less negative, because of the adsorption of the compound on the mild steel surface. Cathodic Tafel slope remains the same in the presence of the lowest concentration (10^{-5} M) of the compound, but anodic Tafel slope is found to be less. So the stimulation of corrosion in the presence of this concentration may be due to decrease in the energy barrier for anodic dissolution. As the concentration increases, there is an increase in the values of both the Tafel slopes in both the acids. But the increase is more for cathodic Tafel slope. So the inhibition of corrosion of mild steel in both the acids is under mixed control, but predominantly under cathodic control. Very negligible increase in the values of both the Tafel slopes in the presence of different concentrations of the compound is a reflection on the poor performance of the compound as an inhibitor. The value of i_{corr} is found to be a little more in the case of lowest concentrations of the compound in both the acids. This observation clearly brings out the acceleration of corrosion in the presence of 10^{-5} M dimethyl sulphoxide. As the concentration increases, there is a decrease in the values of i_{corr} . Values of inhibition efficiency obtained by weight loss method and galvanostatic polarisation studies show fairly good agreement. It is also found that the compound performs better in 1 N H_2SO_4 .

Figs. 1 and 2 shows electrocapillary curves for 1 N HCl and 1 N H_2SO_4 in the presence of different concentrations of dimethyl sulphoxide. It can be seen that there is no lowering of electrocapillary curve in the presence of 10^{-5} M and 10^{-4} M dimethyl sulphoxide. So there is practically no adsorption of the compound when concentrations are very low. This can be attributed to very high solubility of the compound which does not enable the squeezing type of forces to eject the molecules

of the compound from the bulk of the solution of the metal surface [19-21]. The compound is found to adsorb on mercury surface as the concentration increases. The adsorption of the compound is found to be considerably less even in the presence of the highest concentration of the compound ($10^{-1} M$). As the concentration of the compound in the bulk increases, the tendency to 'squeeze out' the neutral molecule from the solution increases and this leads to more adsorption. It is found that the adsorption is more on the positively charged mercury surface and the compound is completely desorbed on the negatively charged mercury surface. As there is no charge transfer in the case of mercury/solution interface, the adsorption cannot be attributed to the formation of sulphide formed by reduction of sulphoxide. Adsorption may be due to the interaction between the lone pairs of electrons of the sulphur atom the positively charged mercury surface. It can be also seen that the adsorption is more from H_2SO_4 ,

which is in support of the observation that the compound performs better in H_2SO_4 .

Hydrogen permeation current vs time curves for mild steel in 1 N HCl and 1 N H_2SO_4 in the presence of different concentrations of dimethyl sulphoxide are shown in Figs. 3 and 4. It is found that the permeation current is more for mild steel in 1 N HCl because of the more corrosive nature of chloride ions. It can also be seen that there is a small increase in permeation current in the presence of the lowest concentration of ($10^{-5} M$) of the compound in both the acids. This can be attributed to the acceleration of corrosion and more evolution of hydrogen which leads to more hydrogen entry into the metal. But as the concentration of compound increases, hydrogen entry into the metal is found to decrease to a very less extent. This observation is in keeping with very low values of inhibition efficiency obtained by this compound in both the acids.

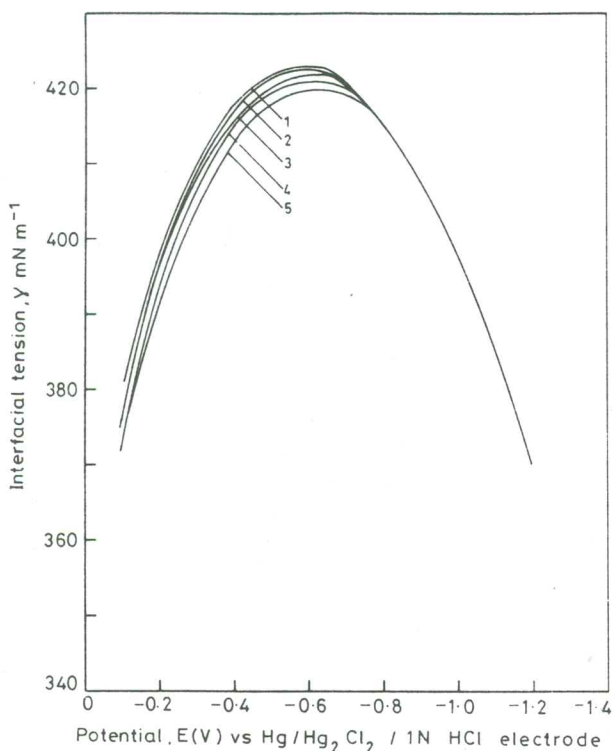


Fig. 1: Electrocapillary curves for 1 N HCl in the presence of different concentrations of dimethyl sulphoxide (1) 1 N HCl (2) $10^{-5} M$ (3) $10^{-3} M$ (4) $10^{-2} M$ (5) $10^{-1} M$

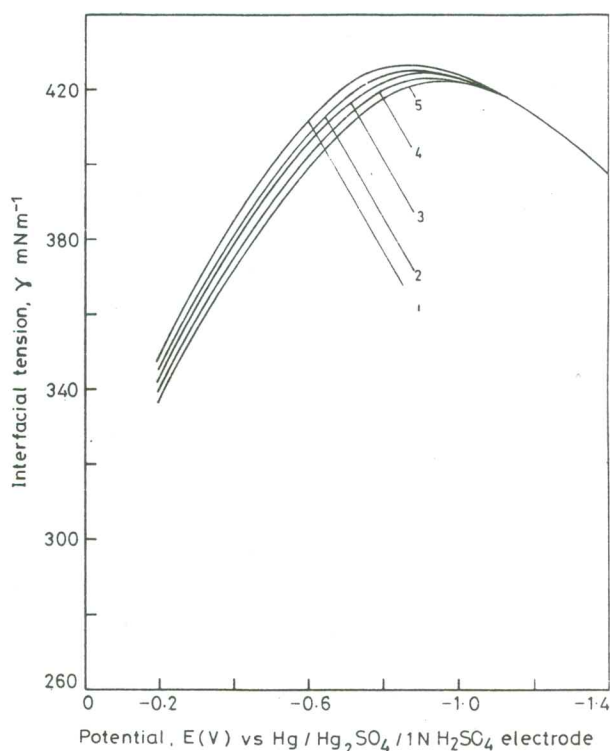


Fig. 2: Electrocapillary curves for 1 N H_2SO_4 in the presence of different concentrations of dimethyl sulphoxide (1) 1 N H_2SO_4 (2) $10^{-5} M$ (3) $10^{-3} M$ (4) $10^{-2} M$ (5) $10^{-1} M$

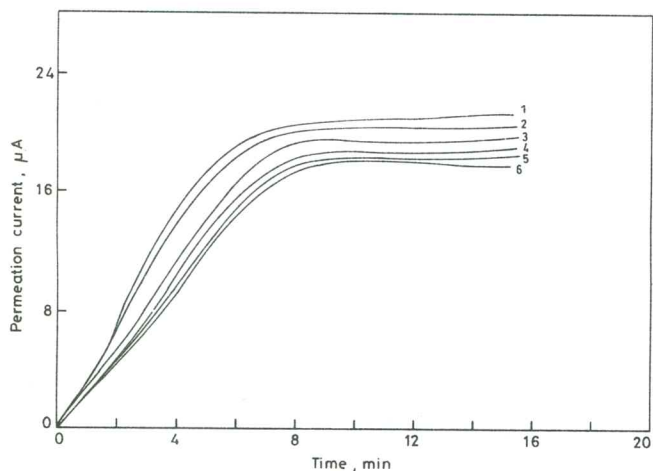


Fig. 3: Permeation current vs time curves for mild steel in 1 N HCl in the presence of different concentrations of dimethyl sulphoxide (1) 1 N HCl (2) 10^{-5} M (3) 10^{-4} M (4) 10^{-3} M (5) 10^{-2} M (6) 10^{-1} M

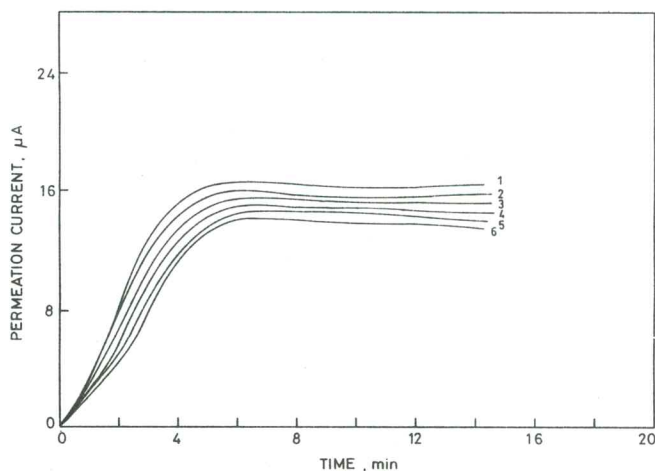


Fig. 4: Permeation current vs time for mild steel in 1 N H_2SO_4 in presence of different concentrations of dimethyl sulphoxide (1) 1 N H_2SO_4 (2) 10^{-5} M (3) 10^{-4} M (4) 10^{-3} M (5) 10^{-2} M (6) 10^{-1} M

Values of surface coverage (θ) for different concentration of dimethyl sulphoxide have been evaluated from the weight loss data using the following equation for both the acids.

$$\theta = 1 - \frac{W_{inh}}{W} \quad (3)$$

The data were tested graphically for fitting a suitable adsorption isotherm. It is found that a plot of θ vs $\log C$ gave a straight line in both the acids, thereby clearly proving that the adsorption of dimethyl sulphoxide on the mild steel surface from both the acids obeys Temkin's adsorption isotherm.

CONCLUSION

- Dimethyl sulphoxide inhibits the corrosion of mild steel in both the acids (1 N HCl and 1 N H_2SO_4) but more effectively in H_2SO_4 .
- The performance of this compound as an inhibitor in both the acids is not very much encouraging.

- The inhibition of corrosion of mild steel by dimethyl sulphoxide in both the acids is predominantly under cathodic control.
- The inhibition of the corrosion by dimethyl sulphoxide in both the acids is 'secondary type'.
- Dimethyl sulphoxide is found to bring down the entry of hydrogen into the metal in both the acids, except at very low concentrations.
- The adsorption of dimethyl sulphoxide on the mild steel surface from both the acids obeys Temkin's adsorption isotherm.

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