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Aldimines – effective corrosion inhibitors for mild steel in hydrochloric acid solution

A. SUBRAMANIA[1*], N.T. KALYANA SUNDARAM[1], R. SATHIYA PRIYA[1], K. SAMINATHAN[2], V.S. MURALIDHARAN[3] and T. VASUDEVAN[2]
[1]*Department of Chemistry, Faculty of Engineering, PSG College of Technology, Coimbatore 641 004, India*
[2]*Department of Industrial chemistry, Alagappa University,Karaikudi 630 003, India*
[3]*Central Electrochemical Research Institute, Karaikudi 630 006, India*
*(*author for correspondence, e-mail: a_subramania@rediffmail.com)*

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Abstract

New and effective aldimine types of corrosion inhibitors namely, *N*-methylidene octylamine (MOA), *N*-ethylidene octylamine (EOA) and *N*-propylidene octylamine (POA) have been synthesized. Their inhibition efficiency was investigated for the corrosion of mild steel in 1 M HCl solution by various corrosion monitoring techniques. A preliminary screening of the inhibition efficiency of the inhibitors was carried out by weight loss and gasometric studies. They were found to behave as good inhibitors in 1 M HCl solution. Potentiodynamic polarization measurements show that aldimines are mixed type inhibitors. The extent of the decrease in the hydrogen permeation current through the mild steel surface was studied by the hydrogen permeation technique and it was found that the decrease was in the order POA > EOA > MOA. Double layer capacitance and charge transfer resistance values were derived from Nyquist plots obtained from AC impedance studies. The adsorption of these compounds on mild steel from 1 M HCl solution obeys the Temkin adsorption isotherm.

1. Introduction

Acid solutions are widely used in various industries for the pickling of ferrous alloys and steels. They are also used in oil and gas production to stimulate and increase the oil and gas flow and to descale encrustations in production wells. Among various acids, hydrochloric acid is widely used for this purpose. Because of the extremely aggressive nature of the acid medium the practice of inhibition is commonly used to reduce acid attack on the substrate metal.

A large number of aliphatic and aromatic organic compounds containing nitrogen, oxygen and sulphur atoms are found to cause a distinct decrease in corrosion rates of metals in acid media [1]. Among various compounds, several amines [2–4] and aldehydes [5, 6] alone have been tried as corrosion inhibitors for ferrous alloys and steel in hydrochloric acid. But condensation products of aldimine type have not been studied. Hence some imine type inhibitors, namely *N*-methylidene octylamine (MOA), *N*-ethylidene octylamine (EOA) and *N*-propylidene octylamine (POA) have been synthesized and their influence on the corrosion of mild steel in 1 M HCl has been studied using weight loss, gasometric studies and electrochemical techniques such as potentiodynamic polarization and AC impedance measurements.

2. Experimental details

Mild steel strips containing 0.07% C, 0.034% Mn, 0.08% P and the remainder iron and of size 5 cm × 2 cm × 0.025 cm were used for weight loss, gasometric and hydrogen permeation studies. The strips were mechanically polished and degreased with trichloroethylene before use. A cylindrical mild steel rod of the same composition embedded in a Teflon rod with an exposed area of 0.283 cm^2 was used for potentiodynamic polarization studies and AC impedance measurements. The electrode was polished using different grades of emery paper and then degreased. Analar grade HCl and double distilled water were used to prepare the solutions.

Aldimines were synthesized by condensation of octylamine with appropriate aldehydes [7] and the compounds were characterized through their spectral data and their purity was confirmed by TLC. The structural formulae of these compounds are shown in Table 1.

Weight loss and gasometric studies were carried out as described earlier [8, 9]. Inhibition efficiencies for different concentrations of aldimines were calculated both from weight loss values and volumes of gas collected in the absence and presence of the aldimines at 30 ± 2 °C.

Table 1. Structural formulae of aldimines

Sl. No.	Name	Structure
1	N-methylidene octyl amine (MOA)	$CH_3(CH_2)_6CH_2N{=}CH_2$
2	N-ethylidene octyl amine (EOA)	$CH_3(CH_2)_6CH_2N{=}CH{-}CH_3$
3	N-propylidene octyl amine (POA)	$CH_3(CH_2)_6CH_2N{=}CH{-}CH_2CH_3$

Potentiodynamic polarization studies were carried out using an EG&G PAR potentiostat/galvanostat (Model-173) , a universal programmer (Model-175) and a *X–Y* recorder (Model- RK0089) at a sweep rate of 1 mV s^{-1} . A platinum foil of surface area 2 cm^2 was used as the auxiliary electrode and a saturated calomel electrode as the reference.Both anodic and cathodic polarization curves were recorded in the absence and presence of different concentrations of aldimines.

The double layer capacitance (C_{dl}) and charge transfer resistance (R_t) values were obtained using AC impedance measurements as described earlier [9]. Experiments were carried out at the open circuit potential for the frequency range 10 kHz to 100 mHz using a PAR impedance electrochemical analyzer (M-6310) with M 38 software.

The hydrogen permeation study was carried out using an adaptation of the modified two compartment cell described earlier [10].

3. Results

The inhibition efficiencies obtained from weight loss and gasometric measurements for different concentrations of aldimines in 1 M HCl solutions are given in Table 2. All aldimines inhibit the corrosion of mild steel. Inhibition efficiency increases up to a concentration of 0.04% and a further increase in concentration reduces the efficiency. This may be due to the formation of soluble iron complex with the inhibitor that may enhance the metal dissolution. Moreover it is found that there is a good agreement between the values of inhibition efficiency obtained by weight loss and gasometric measurements.

Table 3 summarizes the values of kinetic parameters such as i_{corr},E_{corr}, anodic and cathodic Tafel slopes in the presence and absence of different concentrations of aldimines obtained from polarization curves. It can be seen from the table that the values of E_{corr} are not shifted significantly in the presence of inhibitors, suggesting that the aldimincs control both anodic and cathodic reactions to inhibit the corrosion of mild steel by blocking active sites on the steel surface [11]. Therefore aldimines exert mixed control. The corrosion current (i_{corr}) decreases with increase in inhibitor concentration and a maximum decrease in i_{corr} is observed at an optimum inhibitor concentration of 0.04%. It was found that POA produced a maximum decrease in i_{corr} followed by EOA and MOA. This order is similar to that observed from weight loss and gasometric measurements.

Impedance diagrams obtained for the frequency range 10 kHz to 100 mHz at the open circuit potential in the absence and presence of the optimum concentrations of aldimines (0.04%) are shown in Figure 1. The equivalent circuit models employed are as previously reported [12]. Impedance diagrams are not perfect semicircles and this has been attributed to high frequency dispersion [13, 14]. The charge transfer resistance values (R_t) were calculated from the low frequency impedance values

Table 2. Inhibition efficiency for different concentrations of aldimines for the corrosion of mild steel in 1 M HCl obtained by weight loss and gasometric measurements

Inhibitor conc. /% (v/v)	Inhibition efficiency /%	
	Weight loss	Gasometric
MOA		
0.02	91.0	90.7
0.03	92.2	91.5
0.04	96.5	95.7
0.05	94.2	93.5
EOA		
0.02	93.5	92.8
0.03	96.6	95.5
0.04	97.2	96.6
0.05	95.5	95.0
POA		
0.02	94.3	93.6
0.03	96.6	96.1
0.04	98.4	98.0
0.05	96.2	95.6

Table 3. Corrosion kinetic parameters obtained for the potentiodynamic polarization of mild steel in 1 M HCl in the presence of different concentrations of aldimines at 30 ± 2 °C

Inhibitor conc. /%(v/v)	E_{corr} /mv	i_{corr} /mA cm^{-2}	Tafel slopes /mV dec^{-1}		IE /%
			b_a	b_c	
Blank	−520	3.40	74	126	–
MOA					
0.02	−516	0.42	76	128	87.65
0.03	−514	0.35	79	131	89.70
0.04	−510	0.24	81	132	92.94
0.05	−508	0.32	83	134	90.59
EGA					
0.02	−516	0.39	70	129	88.53
0.03	−514	0.28	68	134	91.76
0.04	−513	0.18	72	135	94.70
0.05	−510	0.26	75	136	92.35
POA					
0.02	−518	0.32	78	130	90.59
0.03	−513	0.26	79	138	92.35
0.04	−515	0.12	85	139	96.47
0.05	−512	0.23	88	140	93.23

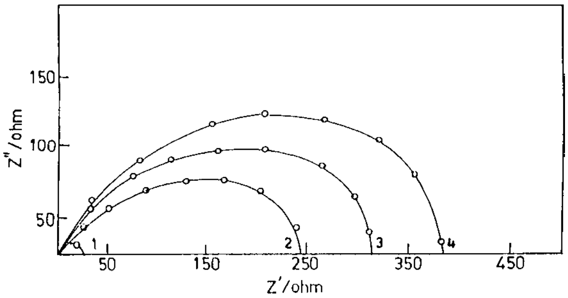

Fig. 1. Impedance diagrams for mild steel in 1 M HCl solution – effect of aldimines. (1) Blank (2) 0.04% (v/v) MOA (3) 0.04% (v/v) EOA (4) 0.04% (v/v) POA.

meeting the X-axis. The double layer capacitance (C_{dl}) was obtained from the value of imaginary component of the impedance obtained at the frequency maximum. $C_{dl}=1/2\pi R_t$ Where R_t is the charge transfer resistance.

$$\% \text{ IE} = \{(1/R_t^* - 1/R_t)/1/R_t^*\} \times 100$$

where R_t and R_t^* are the charge transfer resistances obtained in the absence and presence of inhibitors.

Table 4 summarizes the values of R_t and C_{dl} obtained for mild steel in the absence and presence of inhibitors. The inhibition efficiency follows the order POA > EOA > MOA. The inhibition efficiency values are almost equal to the values obtained from weight loss measurements. Double layer capacitance (C_{dl})is also reduced considerably in the presence of aldimines.

The hydrogen permeation studies in the absence and presence of 0.04% (v/v) aldimines in 1 M HCl solution arc shown in Figure 2. The decreases in the permeation current for different aldimines are given in Table 5.

Table 4. Impedance parameters for the corrosion mild steel in 1 M HCl containing different concentrations of aldimines

Inhibitor Conc. /%(v/v)	R_t /Ω cm^2	C_{dl} /μF cm^{-2}	IE /%
Blank	4.53	252	–
MOA			
0.02	38.12	118.4	88.12
0.03	45.84	116.4	90.12
0.04	70.18	109.3	93.54
0.05	52.00	111.0	91.29
EOA			
0.02	44.80	116.9	89.89
0.03	51.10	113.6	91.13
0.04	89.14	100.6	94.92
0.05	72.10	108.8	93.72
POA			
0.02	52.00	111.0	91.29
0.03	64.50	108.4	92.98
0.04	108.95	98.2	95.84
0.05	77.00	103.6	94.12

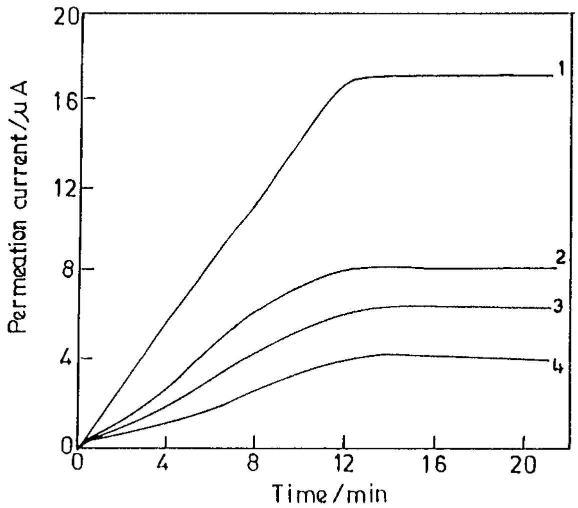

Fig. 2. Hydrogen permeation current vs time plots for mild steel in 1 M HCl solution – effect of aldimines. (1) Blank (2) 0.04% (v/v) MOA (3) 0.04% (v/v) EOA (4) 0.04% (v/v) POA.

Table 5. Values of hydrogen permeation current for the corrosion of mild steel in 1 M HCl alone and in the presence aldimines [0.04% (v/v)]

Inhibitor	Permeation current /μA	Decrease in permeation current /%
Blank	23.0	–
MOA	8.1	64.78
EOA	6.2	73.04
POA	4.3	81.30

4. Discussion

Organic compounds inhibit corrosion by adsorbing at the metal/solution interface. The principle types are electrostatic adsorption, chemisorption and adsorption resulting in π-bond interaction with the metal. Chemisorption of an organic molecule on a metal in a corrosive medium involves the displacement of water molecules from the metal surface and the eventual charge sharing or even actual charge transfer or charge sharing. The molecular structure mode of adsorption and chemical nature of the 'anchoring' inorganic group determines the efficiency of inhibition.

Aldimines adsorb on the metal surface and the following interactions may occur:

1. Interaction between the lone pair of electrons of the nitrogen atom in the aldimine molecule with the metal [15, 16].
2. Interaction between the aldimines cation formed in acidic solutions and the negatively charged metal surface.

The stability of the protonated form of aldimines increased with the electron density on the nitrogen atom. The presence of the electron releasing alkyl group in aldimines enhances the electron density on the nitrogen atom, which favours increased adsorption on the metal surface. The electron releasing capacity increases in the order: propyl > ethyl > methyl. Thus POA has greater

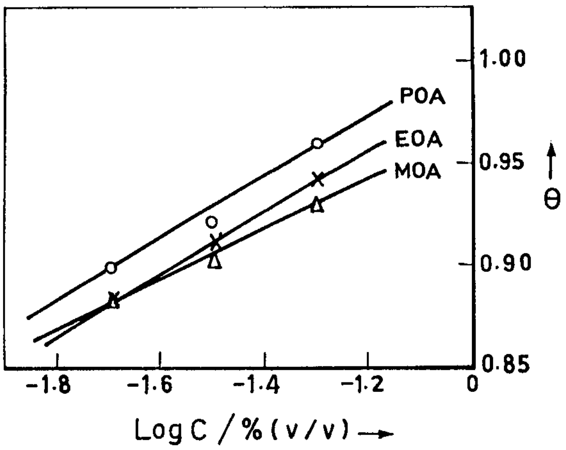

Fig. 3. Temkin adsorption isotherm plot for aldimines. (1)MOA (2) EOA (3) POA.

adsorption and hence more inhibition than EOA and MOA. The availability of lone pairs of electrons of the nitrogen atom and the presence of >C=N— group in the aldimine molecules favour greater adsorption on the metal surface. The decrease in the permeation current and the improved adsorption performance of POA over EOA and MOA can be attributed to the presence of an alkyl group with greater electron releasing tendency. The decrease in the permeation current follows the order POA > EOA > MOA which is the same as that for inhibition efficiency obtained from weight loss measurements (Table 5). A definite correlation exists between the extent of corrosion inhibition and the % decrease in permeation current. It is observed that all these compounds reduce both corrosion and the permeation current through the steel surface at a very low concentration of 0.04% (v/v).

The surface coverage (θ) values for different concentrations of aldimines have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A straight line was obtained when the surface coverage (θ) was plotted against log C for all the three aldimines. This shows that the adsorption obeys a Temkin adsorption isotherm (Figure 3).

5. Conclusion

1. MOA, EOA and POA perform well in 1 M HCl solution and inhibit the corrosion of mild steel in the order POA > EOA > MOA.
2. Aldimines control both anodic and cathodic reactions by blocking the active sites of steel surface and are thus inhibitors of mixed type.
3. Aldimines inhibit the corrosion of mild steel in 1 M HCl by strong adsorption on the metal surface.
4. The adsorption of aldimines on mild steel obeys Temkin adsorption isotherm.
5. Aldimines are able to decrease the hydrogen permeation current very effectively in HCl solution.

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