Influence of substituted benzothiazoles on corrosion in acid solution

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Compounds such as 2-aminobenzothiazole (ABT), 2-amino-6-chlorobenzothiazole (ACLBT), 2-amino-6-methyl benzothiazole (AMEBT) and 2-amino-6-methoxy benzothiazole (AMEOBT) have been synthesized and their inhibitive action on the corrosion of mild steel in 1 M HCl has been evaluated using weight loss, potentiodynamic polarization studies and hydrogen permeation measurements. Determination of inhibition efficiency in the presence of these compounds at different temperatures clearly indicates that ACLBT shows the best performance, even at a temperature as high as 60 °C. Potentiodynamic polarization studies reveal the fact that ABT and its derivatives act as cathodic inhibitors. All these compounds are found to reduce the permeation of hydrogen through mild steel in HCl solution. The adsorption of these compounds on mild steel from HCl solutions obeys Temkin's adsorption isotherm. The adsorption of 2-amino benzothiazole on the mild steel has been substantiated by Auger electron spectroscopy.

1. Introduction

Heterocyclic compounds are well known for their efficacy as corrosion inhibitors and those containing nitrogen have been frequently referred to in the literature [1–6]. However, heterocyclics containing both sulfur and nitrogen in the same ring have received minor attention. It has been reported by Patel *et al.* [7, 8] that 2-mercaptobenzothiazole inhibits the corrosion of copper and its alloys in different corrosive environments. Singh and co-workers [9, 10] have studied the effect of 2-mercapto-benzothiazole on the inhibition of corrosion of mild steel and hydrogen adsorption in acidic solutions. Recently some hydrazino-benzothiazoles have been synthesized and their usefulness as corrosion inhibitors for mild steel in acidic solutions has been evaluated by several authors [11, 12]. 2-amino-benzothiazole and its 6-substituted derivatives have not yet been investigated as inhibitors for the corrosion of mild steel in acidic solutions. In the present study the influence of 2-amino-benzothiazole and its derivatives on the inhibition of corrosion and permeation of hydrogen through mild steel has been investigated.

2. Experimental details

Mild steel strips of size 5 cm × 2 cm × 0.025 cm

having 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and the remainder Fe, were used for weight loss measurements and hydrogen permeation studies. For potentiodynamic polarization studies mild steel strips of the same composition with an exposed area of 1 cm^2 were used. Electrodes were polished successively with emery papers of 1/0, 2/0, 3/0 and 4/0 grade and then degreased with trichloroethylene. AR grade HCl (MERCK) was used for preparing all solutions. Double distilled water was used to prepare solutions of 1 M HCl for all experiments. 2-aminobenzothiazoles were synthesized following the general procedure reported elsewhere [13].

Weight loss measurements were carried out as described earlier [14]. Potentiodynamic polarization studies were carried out using an EG&G PARC potentiostat/galvanostat (model-173), a universal programmer (model 175) and an X–Y recorder (model RE 0089). Hydrogen permeation studies were carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell as described elsewhere [15, 16]. All the experiments were carried out at a room temperature of 35 ± 2 °C. A platinum foil of 3 cm × 3 cm and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The Auger electron spectrum was recorded for 2-aminobenzothiazole using a scanning Auger microprobe (SAM PHI model 590A, USA).

3. Results and discussions

3.1. *Weight loss studies*

Formulae of compounds under study are given in Table 1. Values of percentage inhibition efficiency for the corrosion of mild steel in 1 M HCl in the presence of different concentrations of amino-benzothiazole and its derivatives at different temperatures (35 to 60 °C) are given in Table 2. The inhibition efficiency increases with increase in the concentration of inhibitors from 100 to 500 ppm. Maximum inhibition efficiency is obtained at a concentration of 500 ppm and a further increase in the concentration does not cause any appreciable change in performance. Moreover, it is found that the inhibition efficiency of these compounds, except the chloro derivative, decreases with increase in temperature. This is probably due to the increased desorption of the inhibitor molecules at higher temperatures.

The inhibition efficiency values for amino-benzothiazole and its derivatives in 1 M HCl for a common concentration of 500 ppm at room temperature follows the order:

ABT > ACLBT > AMEOBT > AMEBT

However, at higher temperatures, 50–60 °C, the order of inhibition efficiency is

ACLBT > ABT > AMEOBT > AMEBT

The higher inhibition efficiency obtained for the chloro derivative is due to the fact that its dipole moment is greater than that of the parent amine (ABT). Smialowska *et al.* [17] have observed a similar behaviour for the chloro substituent in the case of thiophene derivatives. Gad-Allah *et al.* [18] have also reported that chloro substituted aminopyrazole gives higher inhibition efficiency than the parent compound during the acid corrosion of copper in the presence of aminopyrazoles.

The lower inhibition shown by methoxy and methyl derivatives as compared to the parent and its chloro derivative is attributed to the orientation of these groups in the ring in contact with the metal surface, which is responsible for influencing the extent of inhibition. These groups prevent a flat orientation of the molecules, resulting in lower coverage of the metal surface. A similar explanation has been given by Rengamani *et al.* [19] to explain the discrepancy in the order of inhibition efficiency for isomers of anisidines, while studying the influence of anions on the performance of anisidines as inhibitors of the corrosion of mild steel in acidic solutions. The superior performance of methoxy amine as compared to the methyl derivative can be explained on the basis of Pearson's HSAB principle [20, 21], according to which the methoxy derivative can be considered as a hard base. This forms a strong bond with ferrous and ferric ions, which leads to higher adsorption and greater inhibition. In the methyl derivative, the inductive effect of the methyl group makes the nitrogen centre a softer base. Thus ferrous and ferric ions form a weak bond with the soft base. This leads to less adsorption and thereby lower inhibition.
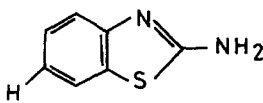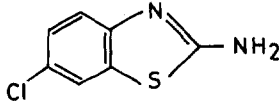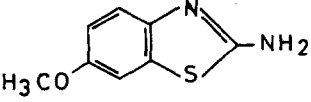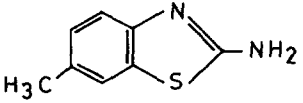
SI. No.	Name	Structure
1	2- amino benzothiazole (ABT)	
2	2-amino -6- chloro - benzothiazole (ACLBT)	
3	2- amino - 6- methoxy - benzothiazole (AMEOBT)	
4	2 - amino - 6 - methyl - benzothiazole (AMEBT)	

Table 1.

Table 2. Inhibition efficiencies for different concentrations of amino-benzothiazoles alone and in combination of KI for the corrosion of mild steel in 1 M HCl obtained from weight loss measurements at different temperatures

No.	Inhibitor and Conc. /ppm	Inhibition efficiency/%			
		35°C	40°C	50°C	60°C
1	ABT				
	100	89.0	84.0	39.0	22.0
	200	94.8	93.0	46.0	29.0
	300	97.5	96.6	55.0	42.0
	400	98.4	97.0	96.0	74.0
	500	99.2	98.6	98.0	78.0
	100 + 0.25% KI	94.0	90.0	50.0	32.0
2.	ACLBT				
	100	95.0	90.0	90.0	88.0
	200	93.5	92.0	92.0	91.0
	300	95.4	94.0	93.0	93.0
	400	96.4	95.0	96.0	94.0
	500	98.2	97.0	99.0	97.0
	100 + 0.25% KI	99.0	96.2	95.0	94.0
3	AMEOBT				
	100	35.0	30.0	21.0	5.0
	200	62.0	58.0	39.0	15.0
	300	84.0	77.0	49.0	23.0
	400	83.0	81.0	58.0	29.0
	500	87.0	84.0	76.0	42.0
	300 + 0.25% KI	90.0	84.0	57.0	36.0
4	AMEBT				
	100	35.0	32.0	29.2	7.2
	200	56.0	54.0	39.0	10.0
	300	70.0	67.0	46.0	18.0
	400	78.0	75.0	56.0	29.0
	500	82.0	79.0	69.0	41.0
	300 + 0.25% KI	85.0	76.0	54.0	29.0

The inhibition of corrosion of mild steel in acidic solution by ABT and its derivatives can be explained on the basis of adsorption on the metal surface.

(i) Benzothiazoles exist in acid solutions as neutral molecules or in the form of cations. They can adsorb on the metal surface in the form of a neutral molecule via the chemisorption mechanism [22] involving the sharing of electrons between the atoms of nitrogen and sulfur with iron. (ii) Adsorption of these compounds can occur through π-electron interactions between the benzene ring of the molecules and the metal surface and (iii) they can also occur in the form of a positively charged protonated species which can interact electrostatically with negatively charged metal surfaces [23]. As chloride ions are strongly adsorbed on the metal surface, the cationic form of these compounds can jointly adsorb on the metal surface without much difficulty.

Table 2 gives values of inhibition efficiency for specific concentrations of aminobenzothiazoles in combination with 0.25% KI at different temperatures. The addition of potassium iodide is found to enhance the inhibition efficiency for all the compounds. In the presence of iodide ions, maximum enhancement of inhibition efficiency is observed for compounds such as ABT, AMEOBT and AMEBT which show very low values of inhibition efficiency at higher temperatures. This observation brings out the fact that strongly adsorbed iodide ions are not easily desorbed even at very high temperatures, thereby enhancing the inhibition efficiency of these compounds. In the presence of strongly absorbed negative ions the surface charge is changed to negative by the specific adsorption of these ions, resulting in the joint adsorption of anions and amine cations [24]. Thus the synergistic effect of anion and cation on the inhibition of corrosion of mild steel in acids is dependent on their joint adsorption. Thiazolonium ion can adsorb on the negatively charged metal surface by the coulombic attraction using the positive charge of protonated species and thus brings down the self corrosion by the stabilization of the adsorbed ions and by the increase in surface coverage.
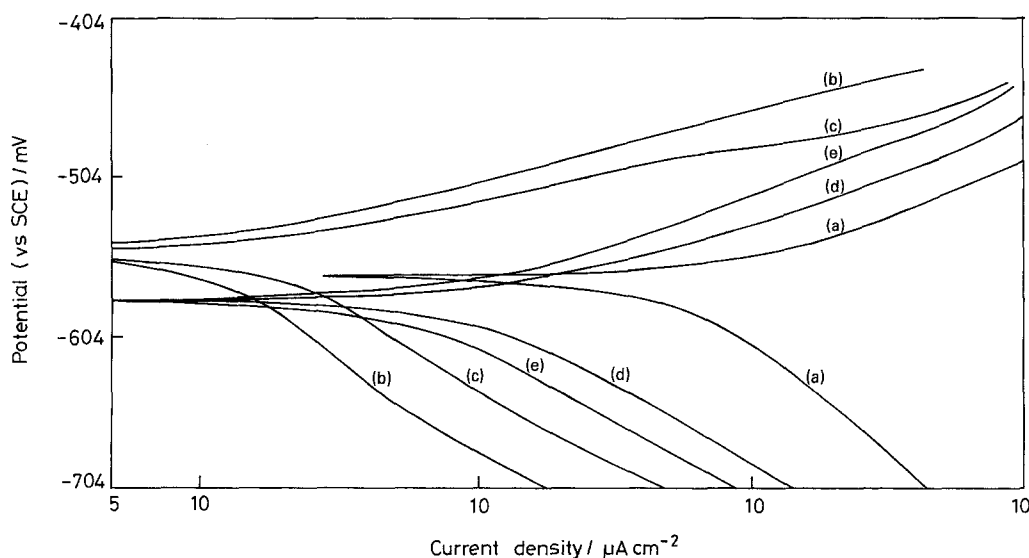

Fig. 1. Potentiodynamic polarization curves for mild steel in 1 M HCl in the absence and presence of substituted benzothiazoles (500 ppm). Curves: (a) blank, (b) ABT, (c) ACLBT, (d) AMEOBT and (e) AMEBT.

Table 3. *Corrosion kinetic parameters obtained from potentiodynamic polarization of mild steel in 1 M HCl in the presence of aminobenzothia-zoles alone and in combination with 0.25% KI. Temperature 35 °C*

Inhibitor and conc./ppm	E_{corr}/mv	I_{corr}/μA cm^{-2}	Tafel slopes		Inhibition efficiency/%
			b_c/mV dec^{-1}	b_a/mV dec^{-1}	
Blank	−576	350	110	50	—
1 *ABT*					
100	−560	100	100	50	71.4
300	−565	15	102	50	96.0
400	−570	13	105	52	96.0
500	−565	10	110	55	97.0
100 + 0.25% KI	−556	45	104	50	87.1
2 *ACLBT*					
100	−562	200	100	50	42.8
300	−565	50	100	52	86.0
400	−566	25	105	52	93.0
500	−566	15	105	52	96.0
100 + 0.25% KI	−558	55	105	50	84.2
3 *AMEOBT*					
300	−580	100	100	50	71.4
400	−590	80	100	50	77.0
500	−592	50	120	50	86.0
300 + 0.25% KI	−571	70	100	50	80.0
4 *AMEBT*					
300	−579	130	100	50	63.0
400	−592	110	115	52	68.0
500	−596	80	120	52	77.0
300 + 0.25% KI	−571	100	110	52	71.4

The degree of surface coverage (θ) for different concentrations of the benzothiazoles have been evaluated from weight loss measurements as described earlier [25]. Surface coverage (θ) values were fitted to a suitable adsorption isotherm. Plots of θ against log c yielded a straight line showing that the adsorption of benzothiazoles from HCl on mild steel surface obeys a Temkin adsorption isotherm.
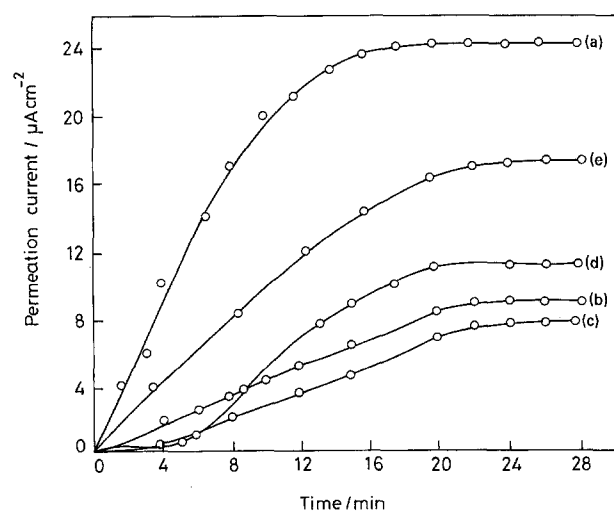

Fig. 2. Hydrogen permeation current against time curves for mild steel in 1 M HCl in the absence and presence of substituted ben-zothiazoles (500 ppm). Curves: (a) blank, (b) ABT, (c) ACLBT, (d) AMEOBT and (e) AMEBT.

3.2. Potentiodynamic polarization studies

Both cathodic and anodic polarization behaviour of mild steel in 1 M HCl, in the absence and presence of a specific concentration (500 ppm) of amino-benzothiazoles, is shown in Fig. 1. Electrochemical corrosion kinetic parameters are given in Table 3. The I_{corr} values decrease considerably in the presence of different concentrations of aminobenzothiazole and its derivatives. Inhibition efficiencies obtained from I_{corr} values follow the same trend as already observed in the case of weight loss measurements at room temperature. No definite trend is observed in the shift of E_{corr} values in the presence of different concentrations of these compounds. It is found that the value of cathodic Tafel slope (b_c) is found to change with change in inhibitor concentration, which clearly indicates the influence of these compounds on the kinetics of the hydrogen evolution reaction. However, the value of the anodic Tafel slope (b_a) is practically constant, as these compounds do not influence anodic dissolution. Thus, all these compounds act as cathodic inhibitors. The addition of KI is found to enhance the inhibition efficiency for all the compounds. This can be ascribed to the synergistic influence of iodide ions on inhibition efficiency. Similar observations have been recently reported by Azim *et al.* [26] for the corrosion of mild steel in 1 M HCl in the presence of dicyclo-hexylamine in KI.
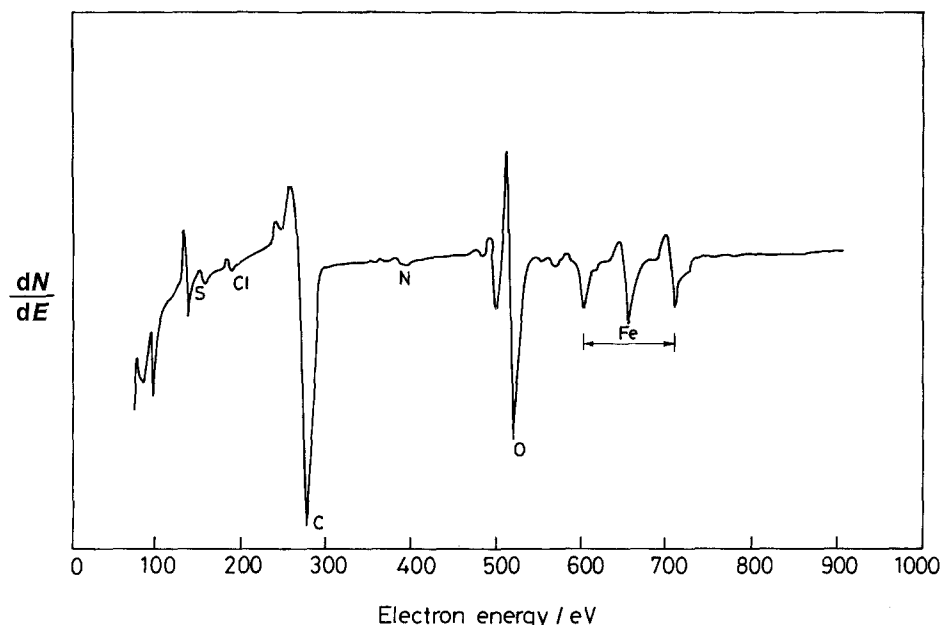
Fig. 3. Auger electron spectrum for mild steel surface exposed to 1 M HCl containing 2-aminobenzothiazole.

3.3. Hydrogen permeation measurements

The hydrogen permeation current against time curves for mild steel in 1 M HCl in the absence and presence of aminobenzothiazole and its derivatives (500 ppm) are shown in Fig. 2. All the compounds reduce the permeation current to the maximum possible extent. The extent of reduction in the permeation current in the presence of these compounds in 1 M HCl follows the order:

ACLBT > ABT > AMEOBT > AMEBT

The reduction in hydrogen uptake can be attributed to the formation of surface compounds by adsorption on the metal surface. These retard the discharge of hydrogen ions and decrease the coverage of the metal surface by hydrogen atoms, thereby resulting in less hydrogen permeation. The formation of hydrides by dissolving mild steel may also create a barrier for the transfer of hydrogen ions into the metal.

3.4. Auger electron spectroscopy

Figure 3 shows an Auger electron spectrum for a mild steel surface exposed to 1 M HCl containing 500 ppm of 2-aminobenzothiazole. The appearance of peaks at 156 and 387 eV, respectively indicates adsorption of this compound on the metal surface through the electron pair of the sulfur and nitrogen atoms in the ring.

4. Conclusions

(i) Aminobenzothiazole and its derivatives perform well as inhibitors of the corrosion of mild steel in acidic solutions, 2-amino-6-chloro-benzo-thiazoles shows the best performance, even at higher temperatures.

(ii) All these compounds behave as cathodic inhibitors by influencing the kinetics of hydrogen evolution.

(iii) They are found to reduce the permeation of hydrogen through mild steel in 1 M HCl.

(iv) Adsorption on mild steel obeys a Temkin adsorption isotherm.

(v) The addition of iodide ions to 1 M HCl enhances the inhibition efficiency of all the substances.

Acknowledgements

References

[1]   M. M. Osman, E. Khamis and A. Michael, Corr. Prev. and Control 41 (1994) 60.

[2]   E. Stupnisek-Lisac and M. Metikos-Hukovic, Brit. Corros. J. 28 (1993) 74.

[3]   S. L. Granese, B. M. Rosales, C. Oviedo and J. O. Zerbino, Corros. Sci. 33 (1992) 33.

[4]   F. Zucchi and G. Trabanelli, Proceedings of the 7th European Symposium on Corrosion Inhibitors, Ann. Univ., Ferrara, Italy, N. S. Sez, V. Suppl. 9. (1990) p. 339.

[5]   G. Subramaniam, K. Balasubramaniam and P. Shridhar, Corros. Sci. 30 (1990) 1019.

[6]   S. N. Banerjee and S. Mishra, Corrosion 45 (1989) 780.

[7]   N. K. Patel, M. M. Patel and K. C. Patel, Chem. Era 10 (1975) 24.

[8]   N. K. Patel, M. M. Patel and S. H. Mehta, ibid. 12 (1976) 460.

[9]   I. Singh and T. Banerjee, Corros. Sci. 12 (1972) 503.

[10] I. Singh, A. Lahiri and V. Altekar, Proceedings of the 5th International Congress on Metal Corrosion, Tokyo, Japan (1972) p. 570.

[11] M. A. Wajid Khan, M. Phil. Dissertation, Aligarh Muslim University, Aligarh, India (1992).

[12] M. Ajmal, A. S. Mideen and M. A. Quraishi, Corros. Sci. 36 (1994) 79.

[13] V. Mishra and D. K. Saxena, Synth. React. Inorg. Met. Org. Chem. 17 (1987) 987.

[14] P. B. Mathur and T. Vasudevan, Corrosion 38 (1982) 17.

[15] M. A. V. Devanathan and Z. Stachurski, *Proc. Roy. Soc., Lond. A* **270** (1962) 906.

[16] K. N. Srinivasan, M. Selvam and S. V. K. Iyer, *J. Appl. Electrochem.* **23** (1993) 358.

[17] Z. Szklarska-Smialowska and M. Kaminski, Proceedings of the 5th International Congress on Metal Corrosion, Tokyo, Japan (1972) 553.

[18] A. G. Gad-Allah, M. M. Abou-Romia and H. H. Rehan, *Ind. J. Tech.* **30** (1992) 252.

[19] S. Rengamnai, S. Muralidharan, M. Ganesan and S. V. K. Iyer, *Ind. J. Chemical Tech.* **1** (1994) 168.

[20] R. G. Pearson, *J. Am. Chem. Soc.* **85** (1963) 3533.

[21] R. G. Pearson, *J. Chem. Ed.* **45** (1968) 581.

[22] M. P. Soriaga, *Chem. Rev.* **90** (1990) 771.

[23] N. Hackerman, *Corrosion* **18** (1962) 332t.

[24] A. Frignani, F. Zucchi and C. Monticelli, *Brit. Corros. J.* **18** (1983) 19.

[25] S. Rengamani, S. Muralidharan, M. Anbukulanthainathan and S. V. K. Iyer, *J. Appl. Electrochem.* **24** (1994) 355.

[26] S. Syed Azim, S. Muralidharan and S. Venkatakrishna Iyer, *ibid.* **25** (1995) 495.