Synthesis and corrosion inhibition phenomenon of benzophenothiazine derivatives with aluminium in acidic media

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ABSTRACT

2-Amino-6-substituted benzothiazoles (ASB) on diazotization afford 6-substituted benzothiazolyl-2-diazonium chlorides (SBDC). Reaction of SBDC with cold solution of β-naphthol in dilute NaOH furnishes α-(2-diazo-6-substituted benzothiazolyl)- β-sodionaphthoxides (DSBS) which on acidification with concentrated HCl gives α-(2-diazo-6-substituted benzothiazolyl)- β-naphthols (DSBN). Reaction of DSBN with p-substituted anilines gives α-(2-diazo-6-substituted benzothiazolyl)- β-(p-substituted aniline) naphthalenes (DSBSAN). Fusion of DSBSAN with sulphur in presence of iodine results in α-(2-diazo-6-substituted benzothiazolyl)-6-substituted [2,3-b] benzophenothiazines (DSBSB).
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INTRODUCTION

Aluminium, being an industrially important metal, is subjected to corrosion in service by various corrosive agents of which the aqueous acids are the most dangerous. Corrosion in an aqueous environment follows a complex pattern of reactions as a corroding metal as well as its environment play an important role in the corrosion process. Corrosion is electrochemical in nature. Thermodynamic considerations decide whether or not a corrosion reaction is possible, and it is the kinetics of the reaction involved that play a vital role in the ultimate or metal alloy by chemical or electrochemical reaction with its environment[1]. Corrosion of metal is also considered as extractive metallurgy in reverse[2]. The effect of amines[3], aldehydes[4] and heterocyclic compounds on the dissolution of metal in acid solution has been evaluated. Generally, the organic compounds containing hetero atoms such as N, O, S, and Se are found to be very effective corrosion inhibitors[5-10]. The efficiency of these compounds depends upon electron density of hetero atoms[11] occurrence of the corrosion process. Corrosion is a destructive attack on a metal. The present study deals with the preparation of benzophenothiazine derivatives.

Phenothiazine derivatives constitute an important class of compounds possessing wide range of therapeutic activities such as antibectirial[12-13], tranquilizers[14], antiviral[15], antiinflammatory[16], anticancer[17] and sedatives[18]. In addition some phenothiazine derivatives have been demonstrated to be associated with CNS activity[19-20]. These valid observations led the authors to undertake the synthesis of some new compounds of phenotiazine derivatives containing diazobenzothiazolyl

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moiety and to study their biological activities.

EXPERIMENTAL

Melting points are uncorrected. The purity of synthesized compounds has been checked by thin layer chromatography. IR spectra are recorded on FT-IR Perkin-Elmer (spectrumRX1) spectrophotometer(ν_{max} in cm^{-1}) using KBr disc. ^{1}H NMR spectra are recorded in $CDCl_3$ on a Bruker DRX-300(300MHz) using TMS as internal standard. The chemical shifts are reported as parts per million (ppm). UV spectra are recorded on Perkin Elmer Lambda 15 instrument.

Synthesis of substituted 2- aminobenzothiazoles (ASB)

These compounds were synthesized by methods reported earlier[21,22].

Synthesis of 6-substituted benzothiazolyl-2-diazonium chlorides (SBDC)

A solution of 1(.001mole) in 5N HCl (20ml) was cooled to 0^0C. To this solution was added a cold solution of sodium nitrite (1.0gm) drop wise with constant stirring. When the addition was complete, the resultant reaction mixture was left in ice- chest for 1hr. It was used as such for further reaction.

Synthesis of α-(2-diazo-6-substituted benzothiazolyl)- β-sodionaphthoxides (DSBS)

To the ice cold solution of 2,a cold solution of β-naphthol(0.05mole) in dilute NaOH was added drop wise with constant shaking. A dark red dye resulted which darkened on adding more alkaline solution of β-naphthol. When the addition was complete, the resultant reaction mixture was vigorously stirred and filtered off. It was dried and used for further reaction as such.

Synthesis of α-(2-diazo-6-substituted benzothiazolyl)- β-naphtholes (DSBN)

A saturated solution of 3(0.002mole) in water was neutralized with concentrate HCl. A solid separated out which was allowed to stand at room temperature for 30min. It was filtered off and washed with water. The compounds thus prepared, were recrystallised from redistilled ethanol.

Synthesis of α-(2-diazo-6-substituted benzothiazolyl)- β-(p-substituted anilino) naphthalenes (DSBSAN)

A mixture of 4 and p-substituted aniline (equimoler amount) containing anhydrous $ZnCl^-_2$ (1gm) in absolute ethanol (50ml) was heated under reflux for 5hr on a steam bath. The solvent was distilled off and the re-
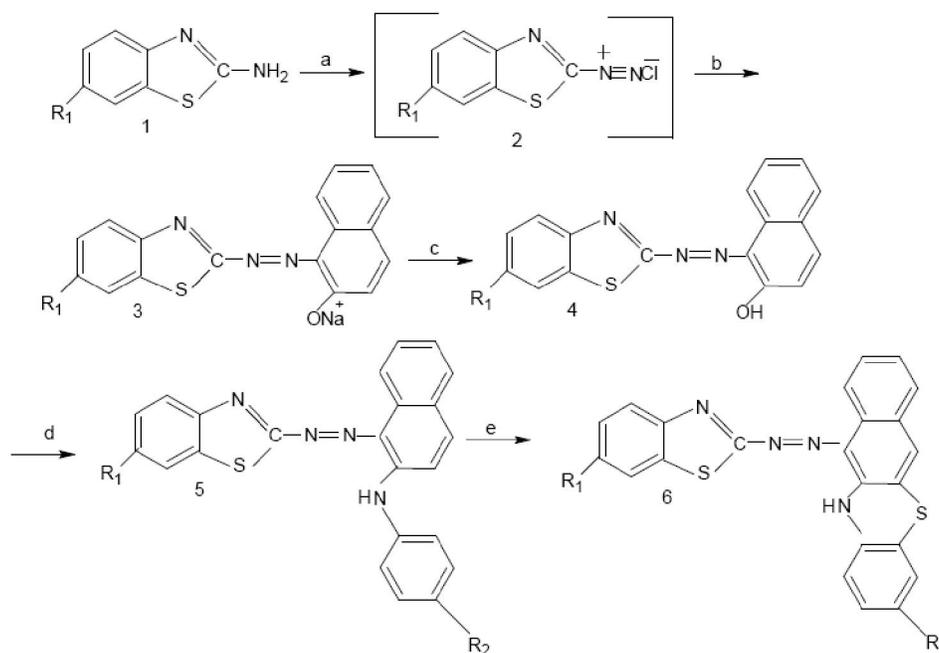
Scheme 1 : Reagents and condition: a) NaNO$_2$ / HCl, 0ºC, b) β- Naphthol / dil. NaOH, 0º – 5º C, c) Conc. HCl, d)p- substituted aniline / EtOH, anhyd. ZnCl$_2$ heating on steam- bath, reflux, 5hr., e) S, I$_2$ / heating on oil bath.

sidual solid was washed with water. It was dried in vacuo and recrystallised from methanol.

Synthesis of α-(2-diazo-6-substituted benzothiazolyl)-6- substituted [2,3-b] benzophenothiazines (DSBSB)

Heating a mixture of 5 (0.001mole), sulphur (0.002mole) and iodine(1% weight of reaction mixture) in an oil-bath for 2hr afforded a dark green solid which was cooled and washed repeatedly with water. It was dried and recrystallised from benzene as light green crystalline mass.

SPECIMEN PREPARATION

Aluminium specimens dimension 2.5cm * 1.5cm * 0.02cm containing a small hole of 2 mm diameter near the upper edge were employed for the determination of corrosion rate. aluminium specimens were cleaned with emery paper. The corrosion products were cleaned with Clark's solution[23]. The weight of the specimens before and after immersion was determined using a Schimadzu balance. Specimens were suspended by glass hook; the degree of surface coverage (θ) is calculated by following formula[24].

$$\theta = \frac{(\Delta Mu - \Delta Mi)}{\Delta Mu}$$

Where θ surface coverage and ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited acid respectively.

The corrosion rate mmpy (mili meter penetration per year) can be obtained by the following equation[25].

$$Corrosion\ rate\ (mmpy) = \frac{(Mass\ loss \times 87.6)}{(Area \times Time \times Metal\ density)}$$

Where mass loss is expressed in mg, area is expressed in cm² of metal surface exposed, time is expressed in hours of exposure, metal density is expressed in gm/cm³ and 87.6 is the conversion factor.

POLARIZATION TECHNIQUE

Experimental set up for the polarization measurements include a three electrode cells and potentiostat (Elico Model CL-95). Spontaneous reaction takes place on the metal surface due to potential difference between cathodes and anodes. When metal is immersed as an electrode in the aqueous environment and activation polarization of both reactions leads to decrease in corrosion rates. The potential and corresponding current densities are called as corrosion potential (Ecorr) and corrosion density (Icorr) respectively. Cathodic and anodic polarizations of the working electrode occur and the curves shift towards lower current densities with increasing concentration of additives[26].

$$I_{corr} = \frac{\{\beta a\beta c\}}{2.303(\beta a + \beta c)} \times \frac{1}{Rp} = \{\frac{\Delta i}{\Delta E}\}_{Ecorr}$$

Where βa and βc are Tafel constant and Rp is the polarization resistance then I_{corr} can be calculated using the above equation.

The perentage inhibition efficiency (η %) can be calculated as follows[27].

$$\eta\% = \frac{I - I_0}{I_0} \times 100$$

Where I and I_0 are the corrosion currents in uninhibited and inhibited solution respectively.

Corrosion rate can be calculated from I_{corr} values using the relation[28].

$$CR(mmpy) = \frac{0.1288 \times I_{corr} \times E}{D}$$

$$Current\ density = \frac{Current}{Area}$$

Where I_{corr} is the corrosion density in μA/cm², E is the equivalent mass of the metal in mg and D is the density in gm/cm³.

RESULTS AND DISCUSSION

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. The resultant functional group, $R^1HC=N-R^2$, is called an amine and is particularly for binding metal ions via the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocyclic. As the corrosion process is electrochemical in nature with four components which are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode. The adsorbed shiff base derivatives act to slow corrosion

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TABLE 1 : Effect of benzophenothiazine derivatives on mass loss data for corrosion of aluminium in 0.5N hydrochloric acid. Effective area of specimen: 3.875 cm². Temperature: 30 ± 0.5°C. Immersion Time: 24 hours.

Inhibitors Concentration (mM)	Mass Loss (mg)	Inhibition Efficiency (η %)	Corrosion rate (mmpy)	Surface Coverage (θ)	Log (θ /1-θ)
Blank	242.63		1416.30		
SBD					
1	55.67	77.04	325.02	0.7704	0.5260
2	46.93	80.65	274.00	0.8065	0.6201
5	40.34	83.36	235.57	0.8336	0.7003
10	33.95	86.01	198.26	0.8601	0.7884
15	28.76	88.13	168.01	0.8813	0.8716
20	24.35	89.94	142.28	0.8994	0.9528
DSBS					
1	47.45	80.43	277.07	0.8043	0.6141
2	40.73	83.21	237.85	0.8321	0.6950
5	34.79	85.64	203.17	0.8564	0.7763
10	29.17	87.98	170.41	0.8798	0.8644
15	24.96	89.70	145.85	0.8970	0.9406
20	21.15	91.27	123.44	0.9127	1.0208
DSBN					
1	44.54	81.63	260.04	0.8163	0.6482
2	35.23	85.48	205.62	0.8548	0.7706
5	27.96	88.47	163.27	0.8847	0.8850
10	22.36	90.76	130.63	0.9076	0.9934
15	18.07	92.55	105.58	0.9255	1.0946
20	13.75	94.31	80.47	0.9431	1.2209
DSBSAN					
1	35.70	85.28	208.45	0.8528	0.7631
2	29.96	87.64	174.94	0.8764	0.8513
5	24.98	89.69	145.87	0.8969	0.9404
10	20.83	91.41	121.66	0.9141	1.2076
15	17.82	92.64	104.10	0.9264	1.1008
20	14.74	93.90	86.08	0.9390	1.1899
DSBSB					
1	28.83	88.31	165.64	0.8831	0.8782
2	23.01	90.52	134.22	0.9052	0.9803
5	19.14	92.13	111.79	0.9213	1.0604
10	15.85	93.45	92.65	0.9345	1.1555
15	13.31	94.50	77.74	0.9450	1.2366
20	11.17	95.42	65.11	0.9542	1.3177

TABLE 2 : Effect of benzophenothiazine derivatives on mass loss data for corrosion of aluminium in 1N hydrochloric acid. Effective area of specimen: 3.875 cm². Temperature: 30 ± 0.5°C. Immersion Time: 24 hours.

Inhibitors Concentration (mM)	Mass loss (mg)	Inhibition Efficiency (η %)	Corrosion rate (mmpy)	Surface Coverage (θ)	Log (θ /1-θ)
Blank	288.54		1690.10		
SBD					
1	63.64	78.03	371.47	0.7803	0.5501
2	55.08	80.98	321.56	0.8098	0.6290
5	46.70	83.86	272.60	0.8386	0.7159
10	39.84	86.26	232.59	0.8626	0.7970
15	33.14	88.55	193.53	0.8855	0.8882
20	27.93	90.34	163.08	0.9034	0.9714
DSBS					
1	56.01	80.64	326.97	0.8064	0.6201
2	44.92	84.46	262.22	0.8446	0.7360
5	35.83	87.61	209.16	0.8761	0.8503
10	28.76	90.04	168.04	0.9004	0.9570
15	23.20	91.98	135.41	0.9198	1.0606
20	18.53	93.60	108.90	0.9360	1.1650
DSBN					
1	47.24	83.67	275.76	0.8367	0.7107
2	38.81	86.85	222.18	0.8685	0.8205
5	30.82	89.34	179.92	0.8934	0.9240
10	25.23	91.29	147.34	0.9129	1.0202
15	20.50	92.92	119.67	0.9292	1.1180
20	17.00	94.13	99.22	0.9413	1.2051
DSBSAN					
1	33.92	88.27	198.05	0.8827	0.8773
2	30.37	89.51	177.33	0.8951	0.9310
5	26.42	90.86	154.29	0.9086	0.9985
10	22.65	92.18	132.29	0.9218	1.0710
15	19.34	93.32	112.95	0.9332	1.1456
20	16.27	94.36	95.01	0.9436	1.2253
DSBSB					
1	29.82	89.71	174.06	0.8971	0.9404
2	25.23	91.28	147.33	0.9128	1.0200
5	21.72	92.50	126.78	0.9250	1.0902
10	18.25	93.67	106.57	0.9367	1.1720
15	15.41	94.68	89.98	0.9468	1.2505
20	12.44	95.72	72.75	0.9572	1.3403

process by either.

1 Increasing the anodic and/or cathodic polarization behaviour;

2 Reducing the movement or diffusion of ions to the metallic surface;

3 Increasing the electrical resistance of the metallic

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TABLE 3 : Potentiostatic polarization data for aluminium in 1.0N hydrochloric acid with benzophenothiazine derivatives. Effective area of specimen: 3.875 cm². Temperature: 30 ± 0.5°C.

Inhibitor Concentration (mM)	OCP (-mV)	Icorr mA/cm²	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)	βa mV/decade	βc -mV/decade	Rp (ohms)
Blank	499	3025.6		1382.52	88	159	0.0080
SBD							
1	491	868.83	71.25	396.81	90	157	0.0285
2	493	798.25	73.61	364.03	91	158	0.0313
5	486	717.76	76.29	325.28	93	161	0.0354
10	489	659.07	78.20	300.48	94	162	0.0390
DSBS							
1	484	797.94	73.61	362.89	91	158	0.0313
2	489	726.84	76.00	331.43	93	159	0.0350
5	487	657.25	78.29	298.65	95	161	0.0394
10	486	598.56	80.16	272.85	96	164	0.0442
DSBN							
1	484	716.55	76.38	324.73	94	161	0.0360
2	485	646.97	78.68	296.95	96	162	0.0404
5	480	596.44	80.36	271.88	96	164	0.0441
10	483	538.04	82.21	243.22	98	165	0.0496
DSBSAN							
1	486	666.93	77.98	303.07	93	163	0.0386
2	482	595.44	80.36	271.88	95	164	0.0437
5	481	503.55	83.39	227.47	97	166	0.0528
10	480	386.76	87.27	176.14	100	168	0.0705
DSBSB							
1	484	665.93	80.39	271.47	97	165	0.0445
2	488	496.69	83.66	223.88	98	166	0.0540
5	485	416.02	86.24	189.96	100	167	0.0652
10	486	324.13	89.33	148.55	104	169	0.0864

surface.

The inhibition efficiency (%) calculated from the mass loss measurement for hydrochloric acid solution and inhibitors are given in TABLES (1-10). It is observed that the inhibition efficiency increases with increase in the concentration of the inhibitor. The corrosion rate decreases with increases in concentration of inhibitors. Mass loss results are more important in gravimetric analysis and this method is preferred.

Schiff bases show the efficiency in the range from minimum 77.04% to maximum 95.42 % for aluminium in 0. 0.5N hydrochloric acid it shows 78.03% and maximum 95.72% for hydrochloric acid shows minimum 79.9% to maximum 98.4%. (TABLE-1&2) in

mass loss method. Potentiostatic polarization data have been shown with aluminium in 1N hydrochloric acid solution with aluminium (TABLE-3). Thermometric method (TABLE-4) shows minimum 20.57% and maximum 88.23% for 1N hydrochloric acid while 2N hydrochloric acid show minimum 38.66% and maximum 79.83% whereas 4N hydrochloric acid show minimum 39.56% and maximum 76.54% inhibition efficiency with aluminium. Inhibition efficiency increases with increase in inhibitor concentration. Potentiometric and thermometric results prove the previous statement (TABLE-3 and 4). The variation of the reaction number with inhibitor concentration indicates that the reaction number decreases with increasing inhibitor con-

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TABLE 4 : Thermometric data for aluminum in 1.0N, 2.0N and 4.0N HCl in presence of benzophenothiazine derivatives. Initial Temperature: 30 ± 0.1°C; Area of Specimen: 3.875cm².

Inhibitor Concentration (mM)	$\frac{1N}{RN}$	η %	$\frac{2N}{RN}$	η%	$\frac{4N}{RN}$	η %
Blank	0.1050		0.1849		0.3332	
SBD						
1	0.0820	20.57	0.1073	41.49	0.193	441.95
2	0.0660	34.76	0.0948	48.72	0.1708	48.73
5	0.0560	46.68	0.0865	53.21	0.1559	53.21
10	0.0420	60.13	0.0654	64.12	0.1178	64.64
15	0.0260	74.90	0.0558	69.82	0.1005	69.83
20	0.0241	76.86	0.0462	73.42	0.0920	72.38
DSBS						
1	0.0730	30.68	0.1134	38.66	0.2044	39.56
2	0.0610	41.47	0.1068	42.23	0.1925	42.53
5	0.0480	53.69	0.0913	50.62	0.1645	50.63
10	0.0300	71.30	0.0828	55.21	0.1492	55.22
15	0.0226	78.47	0.0621	66.41	0.1119	66.41
20	0.0210	83.56	0.0440	75.23	0.0870	73.88
DSBN						
1	0.0808	23.04	0.1032	44.07	0.1863	44.08
2	0.0642	38.85	0.0920	50.24	0.1658	50.24
5	0.0555	47.14	0.0841	54.51	0.1515	54.53
10	0.0423	59.71	0.0667	63.92	0.1202	63.92
15	0.0241	77.04	0.0534	71.11	0.0962	71.18
20	0.0203	86.43	0.0421	77.53	0.0845	74.90
DSBSAN						
1	0.0718	31.61	0.1021	45.26	0.1857	44.26
2	0.0604	42.47	0.0916	51.86	0.1643	50.69
5	0.0467	55.52	0.0832	54.23	0.1488	56.38
10	0.0342	67.42	0.0642	65.43	0.1167	64.97
15	0.0226	78.47	0.0564	68.47	0.0958	72.67
20	0.0200	87.21	0.0419	78.24	0.0839	75.69
DSBSB						
1	0.0741	29.42	0.1016	46.25	0.1849	45.39
2	0.0627	40.28	0.0913	52.64	0.1638	51.48
5	0.0474	54.85	0.0826	55.28	0.1469	57.84
10	0.0313	70.19	0.0636	66.57	0.1158	65.19
15	0.0220	79.04	0.0535	69.86	0.0955	73.58
20	0.0196	88.23	0.0413	79.83	0.0828	76.54

centration.

Temperature has a significant influence on metal corrosion rates. When the electrochemical corrosion reaction involves a cathodic process of hydrogen depolarization as mentioned in the present study, the corrosion rate increases exponentially with rise in temperature.

The following order of inhibition efficiency has been observed for five benzophenothiazine derivatives for aluminium in hydrochloric acid.

SBD< DSBS< DSBN< DSBSAN< DSBSB

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