

Electrochemical behaviour of 3-[benzothiazoly]azomethineindole

Rajeev Jain* and Akhilesh Bhadauria

School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

E-mail : gwlsosmica@sancharnet.in Fax : 91-751-2346209

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Electrochemical behaviour of 3-[benzothiazoly]azomethineindole was studied in the Britton-Robinson buffers in the pH range 2.5 to 12.0 at glassy carbon electrode. Cyclic voltammograms depicted a well defined irreversible peak ($2H/2e^-$) throughout the pH range studied. A shoulder before cathodic peak also appeared in the acidic medium but disappeared at higher pH, indicating the adsorption of solvent molecules at the electrode. Redox mechanism is established on the basis of cyclic voltammetry, controlled potential electrolysis, controlled potential coulometry and spectral studies.

The benzothiazole nucleus with its wide spread occurrence in natural systems is biologically active and has been the subject matter of much chemical investigations. Thiazoles, its alkyl and aryl derivatives are not electrochemically active. However, derivatives of thiazoles-2-carboxylic acid are reducible in alkaline solution and the reduction is assumed to take place in the nucleus.

Thiazoles can conveniently be prepared by the electrolytic reduction of 2-bromothiazole in acidic medium¹. Many thiazolium salts have been found polarographically reducible². 2-Aminothiazole has been investigated as inhibitor of corrosion of stainless steel in 10 M sulphuric acid solution³. Many heterocyclic derivatives of Schiff base complexes have been investigated due to their utility in various fields⁴⁻⁶.

Results and discussion

Linear sweep and cyclic voltammetry :

Cyclic voltammograms of 1.0 mM solution of 3-[benzothiazoly]azomethine indole was recorded at glassy

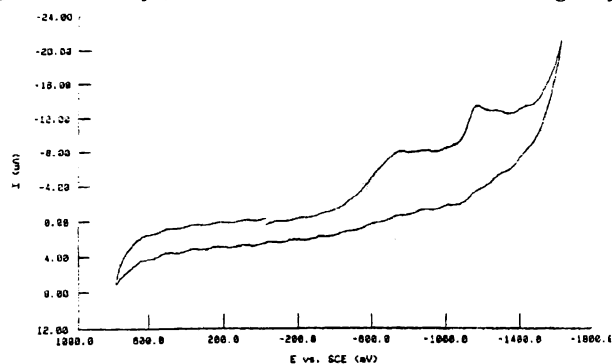


Fig. 1. Cyclic voltammogram of 1.0 mM solution of 3-[benzothiazoly]azomethineindole at glassy carbon electrode, pH = 8.8, $v = 50$ mV/s.

carbon electrode in the pH range 2.5 to 12.0. Cyclic voltammograms showed a well defined cathodic peak in the forward scan, however, no anodic peak was observed in the reverse scan. It suggests the irreversible nature of the electrode process. The typical cyclic voltammogram at pH 8.8 is presented in Fig. 1. The cathodic peak potential (E_p) is found to be pH dependent and shifted towards more negative potential with increase in pH. The dependence of E_p on pH clearly indicates involvement of proton in the reduction

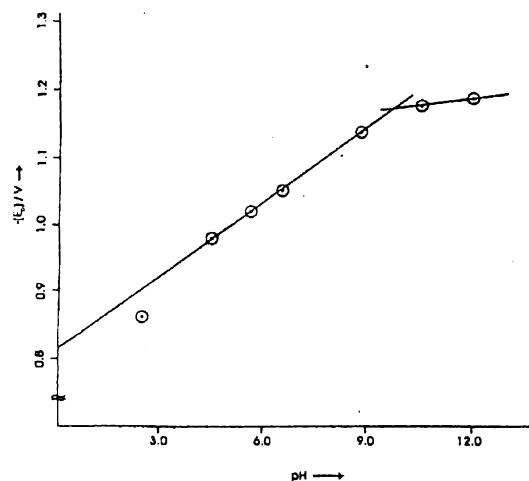


Fig. 2. Plot of E_p vs pH of 1.0 mM solution of 3-[benzothiazoly]azomethineindole at glassy carbon electrode. $v = 50$ mV/s.

process. The E_p vs pH plot (Fig. 2) exhibits a break at pH 9.0, indicating the pK_a value of the azomethine compound and corresponds to the association of proton at $-CH=N-$. The electrochemical characteristics have been compiled in Table 1. A shoulder before the first peak was also observed but disappeared at higher pH. This shoulder may be ascribed to the adsorption of solvent molecule at electrode in acidic medium.

Effect of concentration on peak potential as well peak current was studied in the range 0.6 mM to 1.8 mM. Peak current was found to be increasing with increase in concentration of the depolarizer, however, at higher concentration of the depolarizer the peak current became limiting. This behaviour of peak current suggests the involvement of adsorption complications in the electrode process⁸. The reversibility of electrode process was also confirmed by re-

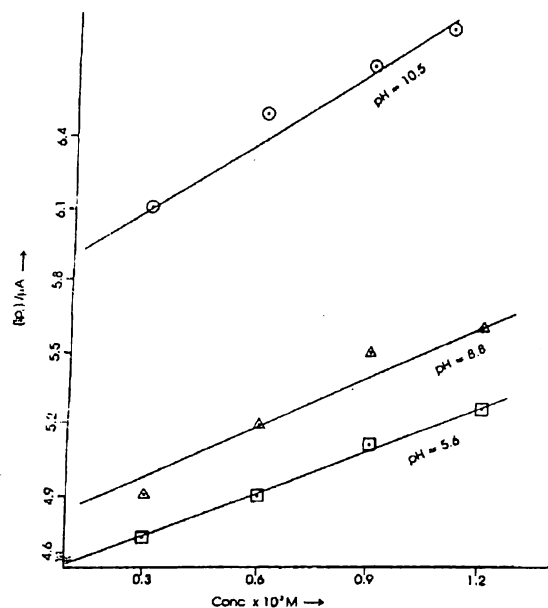


Fig. 3. Plot of i_p vs concentration of 3-[benzothiazolyl]azomethineindole at glassy carbon electrode, $v = 50$ mV/s.

ording cyclic voltammograms at different concentrations of the depolarizer. The peak current is found to be dependent on the concentration of the depolarizer. This behaviour

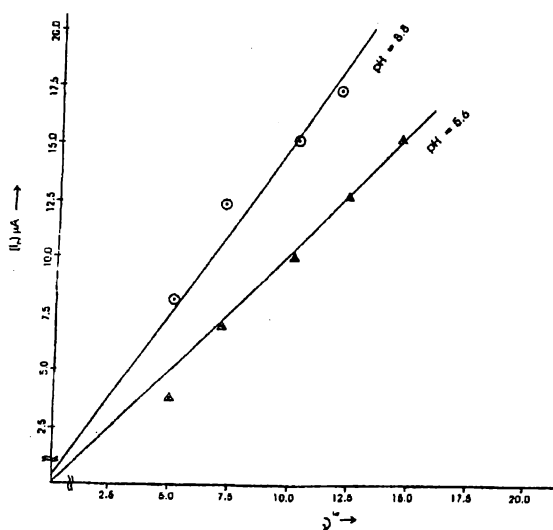


Fig. 4. Plot of i_p vs $v^{1/2}$ of 1.0 mM solution of 3-[benzothiazolyl]azomethineindole at glassy carbon electrode.

clearly indicates irreversible nature of the wave. A plot of i_p vs concentration is presented in Fig. 3, which is a straight line indicating the diffusion controlled nature of the electrode process.

To study the effect of sweep rate on reduction wave, sweep rate was varied from 25 mV/s to 200 mV/s. The cathodic peak potential was found to shift towards more negative potential with increasing scan rate. The plots of i_p vs $v^{1/2}$ (Fig. 4) are straight lines, passing through the origin indicating the diffusion controlled nature of the electrode process. The cyclic voltammograms showing the effect of scan rates on peak current are depicted in Fig. 5.

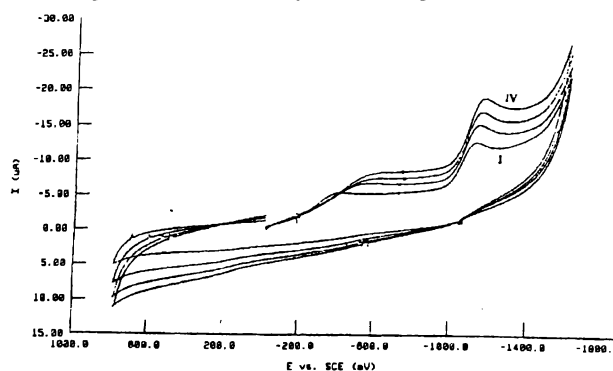


Fig. 5. Typical cyclic voltammograms of 1.0 mM solution of 3-[benzothiazolyl]azomethineindole at various scan rates : $v =$ (i) 50, (ii) 100, (iii) 150 and (iv) 200 mV/s.

Coulometry : Controlled potential coulometry of 3-[benzothiazolyl]azomethine indole was performed at different pH using potential slightly higher than the peak potential. During the course of electrolysis, the peak current was found to be decreasing with time and became constant after 90 min. The n value was calculated using $Q = nFC$ and found to be 2.0 ± 0.15 . The progress of electrolysis was monitored by recording cyclic voltammograms and UV-visible spectra at different time intervals. Decrease in peak current as well as in absorbance with time confirmed the reduction of $(-CH=N-)$ group.

Effect of cations and anions : For evaluating the effect of cations of the supporting electrolyte on the nature and shape of the voltammogram, the $i-E$ curve of the compound was recorded using LiCl, NaCl, KCl and tetraethylammonium bromide as supporting electrolytes. In all the cases one well defined peak was observed. The peak potential (E_p) shifted towards more negative potential with increase in the size of cation. This can be explained in terms of the structure of double layer⁹ at the electrode surface. This effect occurs due to the association (solvation, ion pairing, complex formation etc.) of cation with electroactive species or electrochemically generated intermediates¹⁰. The value

of $E_{1/2}$ was found to be independent of ionic strength, Ψ_1 for a particular supporting electrolyte and could vary from one electrolyte to another. However, Ψ_1 decreases as the size of the cation increases and reaction becomes more complicated with the result that E_p gets shifted towards more negative potential.

For evaluating the effect of anions on reduction characteristics of compound, voltammograms were recorded with different supporting electrolytes having common cation. Practically no change in E_p and i_p was observed, thus indicating that only cations predominates in the electrical double layer at that potential (Table 2).

Effect of different solvents and their composition :

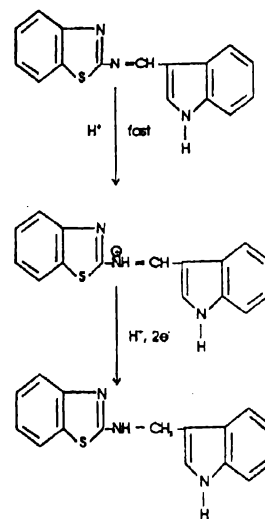
Effect of solvent composition on the cyclic voltammetric characteristics of the compounds was studied by recording cyclic voltammograms in *N,N'*-dimethylformamide at pH 8.8 by increasing its concentration gradually from 30 to 70%. It was found that E_p shifted towards more negative potential with the increasing concentration of the solvent in the solution mixture. On the contrary, the i_p values go on decreasing as percentage of solvent increases. At very high percentage of solvent the cathodic peak is found very ill defined (Table 3).

In electrode processes accompanied by preprotonation, the shift in E_p can be due to rise in pH of the solution¹¹ and increase in the dissociation constant of protonated species¹². Both these factors sharply lower the rate of preprotonation and consequently lead to the shift in E_p towards negative potential. Schwabe¹³ assumed this shift in E_p due to the inhibition of the electrode process by the solvent molecules absorbed on the electrodes. However, it appears that only these two factors are not responsible for the shift in half-wave potential. Because the shift observed is greater than what it would have been due to the change in pH and the dissociation constant. This additional shift in E_p may be ascribed to a decrease in adsorbability and hence surface concentration of the depolarizer with an increasing percentage of solvent in aqueous inorganic mixture¹⁴. Obviously decreased surface concentration would retard the electrode reaction resulting in decrease in i_p and shift in E_p towards more negative potential.

Redox mechanism :

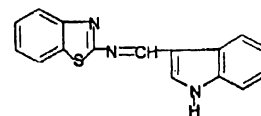
On the basis of cv, cpc, cpe and UV-visible spectrophotometric studies following mechanism has been postulated for the reduction of 3-[benzothiazolyl]azomethineindole at glassy carbon electrode.

In this mechanism first reductive site accept a H^+ ion to form a carbocation which in second step forms a secondary amine ($-CH_2-NH-$) by accepting $2e^-$ followed by proton.



Experimental

3-[Benzothiazolyl]azomethineindole (A) was prepared in the laboratory⁷ by condensation of 2-aminobenzothiazole with indole-3-carboxaldehyde in the ethanol.



(A)

Reagents and solutions : The stock solution (1.0×10^{-2} M) of 3-[benzothiazolyl]azomethineindole was prepared in dimethylformamide. 1.0 M KCl (A.R.) in doubly distilled water was used as supporting electrolyte. 1.0 M solutions of A.R. grade alkali metal salts and tetraethylammonium bromide were prepared to study the effect of cations and anions on the peak potential and peak current. To study the effect of pH on electrode process, Britton-Robinson buffers in the pH range 2.5 to 12.0 were prepared.

Table 1. Effect of pH on peak potential of 1.0 mM solution of 3-[benzothiazolyl]azomethineindole at GC electrode, scan rate 50 mV/s

Sl. no.	pH	$(-E_p)/V$	$(i_p)/\mu A$
1.	2.5	0.86	3.1
2.	4.5	0.98	2.3
3.	5.6	1.02	2.2
4.	6.5	1.05	2.4
5.	7.9	1.08	2.3
6.	8.8	1.11	2.5
7.	10.5	1.13	2.6
8.	12.0	1.14	2.3

Apparatus : Cyclic voltammetric studies were carried out on a potentiostat Verstastat EG & G II microprocessor based voltammograph. A three electrode cell was used for the purpose. The cell consists of a glass container with a cap having holes for introducing electrodes and tubing of nitrogen gas. Oxygen was removed from the solution by purging

nitrogen gas for about ten minutes and a blanket of nitrogen was maintained throughout the experiment. To obtain cyclic voltammograms, glassy carbon (GC) electrode was used as working, saturated calomel electrode as reference, and platinum wire was used as auxiliary electrode that was directly poured into the solution. The GC electrode was polished with fine grade emery paper followed by polishing alumina (0.5 μm), washed and activated by triangular voltage sweeps from +1.0 V to -1.0 V at the scan rate of 5 and 200 mV/s for five minutes. The activity of the electrode was tested from ferricyanide-ferrocyanide system in 0.1 M KCl.

Table 2. Effect of cations and anions on the electrode behaviour of 1.0 mM solution of 3-[benzothiazolyl]azomethineindole at pH 8.8, scan rate 50 mV/s

Sl. no.	Supporting electrolyte	(-E _p)/V	(i _p)/ μA
Anions			
1.	KCl	1.11	2.5
2.	KBr	1.11	2.5
3.	KI	1.11	2.4
Cations			
1.	LiCl	1.00	2.4
2.	NaCl	1.05	2.5
3.	KCl	1.11	2.4

Controlled potential electrolysis : Controlled potential electrolysis (cpe) and coulometric studies were carried out on BAS CV-27 voltammograph in connection with a digital omnigraph x-y/t recorder. A three electrode cell containing GC as working, Ag/AgCl as reference and platinum wire as auxiliary electrode was used. For the determination of number of electrons involved in the electrode process, 2.0 mL of depolarizer solution having buffer, solvent to prevent precipitation and supporting electrolyte was electrolysed by the application of a potential slightly more than the peak potential of the voltammogram to be studied. From the decrease in current or increase in coulombs with time, number of electrons transferred during electrode process was calculated. Progress of the electrolysis was monitored by recording cyclic voltammograms at different time intervals until the reduction wave was completely disappeared. ELICO 150 microprocessor based UV-visible spectrophotometer was used for following the rate of reaction of the electrode process. Absorbance at different time intervals was recorded during course of electrolysis.

Procedure : The cyclic voltammetric studies were carried out by mixing 1.0 mL solution of depolarizer, 2.0 mL of DMF (which was necessary to prevent precipitation), 1.0

mL of 1 M KCl and 6.0 mL of appropriate buffer solution. To maintain inert atmosphere the stream of nitrogen gas was passed through the solution for about ten minutes. Cyclic voltammograms were then recorded. Controlled potential electrolysis at a potential slightly higher than the peak potential was performed in a coulometer using three electrode system.

Table 3. Effect of solvent percentage on cyclic voltammograms of 1.0 mM solution of 3-[benzothiazolyl]azomethineindole, pH 8.8, scan rate 50 mV/s

Sl. no.	% Solvent (DMF)	(-E _p)/V	(i _p)/ μA
1.	30	1.11	2.5
2.	40	1.13	2.4
3.	50	1.15	2.2
4.	60	1.18	1.9
5.	70	1.21	1.7

The progress of electrolysis was monitored by recording cyclic voltammograms at different time intervals until the reduction peak disappeared completely. Thereafter, the electrolysis was stopped and the electrolysed solution was removed from the cell. This solution was then subjected to TLC and spectral analysis to characterise the end products.

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