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Microwave synthesis, electrochemical studies and capacitance of benzalazine

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Abstract- Benzalazine was synthesized by the reaction of benzaldehyde and hydrazine dihydrochloride by microwave irradiation. Formation of benzalazine was confirmed by FT-IR and UV-Visible spectral studies. Percentage of crystallinity was found out by X-ray diffraction studies and it was found to be 43. Redox behavior was studied using cyclic voltammetry. Specific capacitance was calculated by electrochemical impedance spectroscopy. Specific capacitance was more for benzalazine at pH 7 with a value of 0.401μF/cm^2. Chronocoulometry was used to calculate the diffusion coefficient and it was found to be less in neutral medium.

Keywords- Benzalazine; specific capacitance; diffusion coefficient

1. INTRODUCTION

Class of compounds containing R^1R^2C=N-N=CR^3R^4 fragment are called as azines. The compounds which possess azomethine group (>C=N-) are normally called as a Schiff bases.[1] These azines have attracted the attention due to its applications in many fields. Some azines containing hydroxyl group which can acts as fluorescene chemosensor had been reported.[2] Azines can be used as nano optical sensors.[3] Literature revealed that symmetric azines which are having phenyl and thienyl groups were found to be efficient for organic field effect transistors.[4]

Azine can be synthesized by various methods. Normally by the condensation of aldehydes or ketones with hydrazine gives azine. Benzalazine is the azine obtained by the condensation of benzaldehyde and hydrazine. Apart from normal refluxing, several methods had been reported in literature for the synthesis of benzalazine. Synthesis of benzalazines by the reaction of benzaldehydes with thiosemicarbazide had been reported.[5] Green synthesis with self-condensation was reported by Ali Reza Molla Ebrahimlo et.al.[6] Solvent free reactions by grinding had also been reported.[7,8]. Here benzalazine was synthesized using microwave irradiation and its electrochemical behavior was studied.

2. MATERIALS

Benzadehyde and hydrazine dihydrochloride were bought from spectrum chemicals and used as such. Ethanol was bought from Jiangsu Huaxi, China. Indium tin oxide (ITO) coated glass plates which were used in cyclic voltammetry, electrochemical impedance spectroscopy and chronocoulometry studies were supplied by e-Merck.

Nicolet Si5 spectrometer (ATR) (model P-4600) was used to record FT-IR spectra. Jasco V-630 spectrophotometer was used to record UV-Visible spectra. These spectra were taken in the range of 200-800 nm. X'pert PRO power X-ray diffractometer was used to get X-ray diffraction patterns in the2θ position range 10 to 80 with copper as the anode material. Cyclic voltammograms, chronocoulograms and electrochemical impedance measurements were done using CH electrochemical work station Sinsil CH 650.

3. EXPERIMENTAL

3.1 *Preparation of benzalazine*

0.02M of benzaldehyde was dissolved in ethanol and 0.01M of hydrazine dihydrochloride was dissolved in distilled water. Both of the solutions were mixed and kept in the domestic microwave oven for 3 minutes. Then the solution was cooled and poured into water. Yellow solid was obtained and filtered, washed several times with ethanol and water to remove any unreacted benzaldehyde and hydrazine dihydrochloride respectively. The yellow colour precipitate was recrystallized from ethanol and used for further characterization.

4. Results and discussion

4.1 FT-IR studies

The peak for N-N stretch[9] was present at 956 cm^{-1}. The peak at 1623 cm^{-1} was owed to C=N stretch.[10] C=C stretching frequency of aromatic ring was present at 1573 $cm^{-1}$and 1490 cm^{-1}. C-H stretching frequency of aromatic ring was present[11,1] at 3027 cm^{-1}. The respective FT-IR spectrum is given in figure 1.

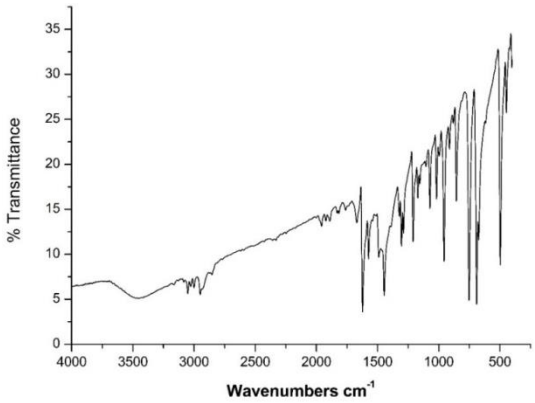

Fig. 1 FT-IR spectra of benzalazine

4.2 UV-Visible spectral studies

UV- Visible spectrum of benzalazine is given in fig.2. The band at 264 nm and 302 nm is due to π to π* transition of the aromatic ring.[9,12,13] n to π* transition of azomethine group was present at 376 nm.[1,9,14]

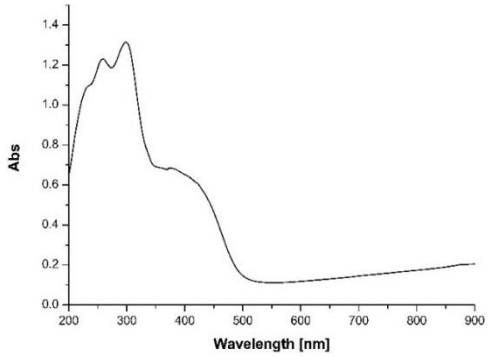

Fig. 2 UV-Visible spectra of benzalazine

4.3 X-ray diffraction Analysis

In the X-ray diffraction pattern, the peak with maximum intensity was obtained in the 2θ position 20.37. This peak corresponds to 100 plane. The other peaks were at 13.81, 20.56, 23.72, 28.91, 29.08, 42.42, etc. X-ray diffraction pattern of benzalazine was matched with the pattern from JCPDS No. 0371588 of benzalazine. The percentage of crystallinity was found to be 43%.

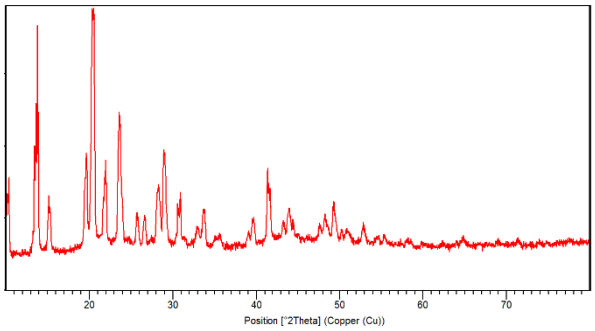

Fig. 3 X-ray diffraction pattern of benzalazine

4.4 Electrochemical studies

5.0 mg of benzalazine was dissolved in 3mL of ethanol and from that 0.05ml was loaded on the Indium tinoxide substrate of area 0.5cm^2. These coated ITO substrates were used as working electrode in electrochemical studies.

4.4.1. Cyclic voltammetric studies

Cyclic voltammograms were recorded in solutions of pH 1.0, 7.0 and 13.0 at different potentials. Cyclic voltammogram of benzalazine showed three oxidation peaks at -0.692 V, -0.622 V and 0.624 V. And two reduction peaks were obtained at 0.094 V and -0.689 V for pH 1.0. With increase in scan rate the peak potential remained same. The peak at -0.689 V was ascribed as the reduction of azomethine group present in the azine.

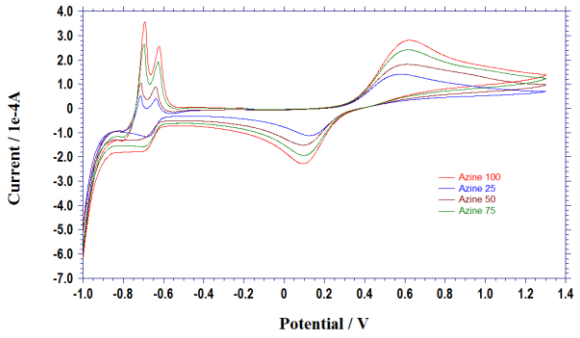

Fig.4 Cyclic voltammogram of benzalazine at pH 1.0

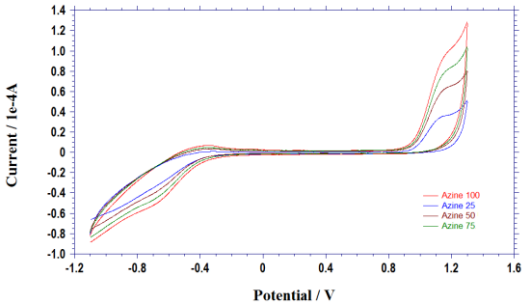

Fig.5 Cyclic voltammogram of benzalazine at pH 7.0

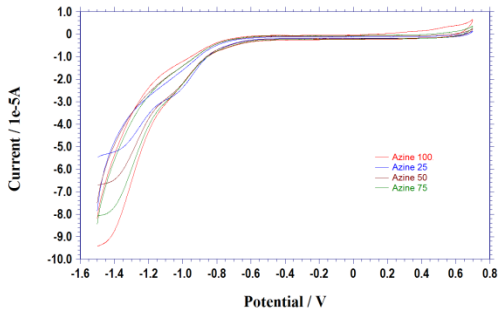

Fig.6 Cyclic voltammogram of benzalazine at pH 13.0

From the literature it was known that for benzalazine in acidic medium, reduction takes place with six electrons and is converted into benzylamine. In alkaline medium reduction takes place with four electrons and converted into benzaldehyde benzylhydrazone.[15,16] Three cathodic peaks and one anodic peak were reported for Schiff base ligand containing phosphorous.[17] Normally for the compounds containing azomethine groups, irreversible reduction was reported.[18] Only irreversible reduction without any oxidation was reported by Santiago Zolezzi et.al.[19] One step, two step reduction and ErCi oxidation mechanism for azines had been reported.[20]

Literature showed that with protons donors azines form radical anion.[18, 21] In pH 1.0 azine radical anions were formed, since more protons were available for its formation. And oxidation of that radical anion gave oxidation peaks. [21] Also the reduction of the oxidized products took place at 0.094 V. In pH 7.0 and 13.0 one reduction peak was observed at -0.664 V and -1.069 V respectively at the scan rate of 100 mV/s. No anodic peaks were obtained in pH 7.0 and 13.0. This proved that irreversible reduction of azomethine took place. At pH 13.0 the reduction of azomethine group took place at more negative potential than in pH 1.0 and 7.0.

4.4.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectra were recorded for solutions of pH 1.0,7.0 and13.0. The obtained data was fitted using Randles circuit. With increase in the pH, the capacitance of benzalazine decreases. There was an appreciable change in the capacitance of benzalazine when the pH was changed from pH 1.0 to pH 7.0.

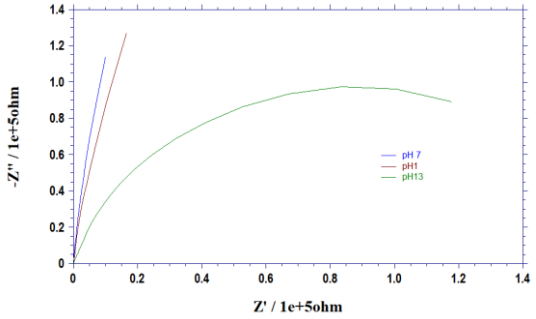

Fig. 7 Nyquist plots of benzalazine at different pH solutions

Table 1: Solution resistance, charge transfer resistance and specific capacitance of benzalazine at different pH solutions

pH	Solution resistance (ohm)	Charge transfer Resistance(ohm)	Specific capacitance ($\mu F/cm^2$)
1	87.89	4.233e6	0.169
7	35.15	9.099e5	0.401
13	54.05	1.631e5	0.150

Capacitance values can be seen from Y-axis magnitude of bode plot. From the magnitude of plot exhibits solution resistance, charge transfer resistance and double layer capacitance were noted. Normally for ideal capacitors the slope in the magnitude plot will be equal to -1 and the phase angle will be equal to -90.[22] For pH 1.0 the maximum phase shift was observed the value is -73° and with decrease in the frequency, the phase angle also decreased. In pH 7.0 the maximum phase shift was -87° and it remained unchanged for some frequencies and it decreased at low frequencies. For pH 13.0 the maximum phase shift was -77° and it remained same when the frequency is lowered. From this plots it was revealed that benzalazine possess maximum capacitance at pH 7.0. The slope values of benzalazine in pH 1.0, 7.0 and 13.0 were -0.75, -0.98 and -0.93 respectively. This also proved that at pH 7.0 benzalazine behaves like an ideal capacitor.

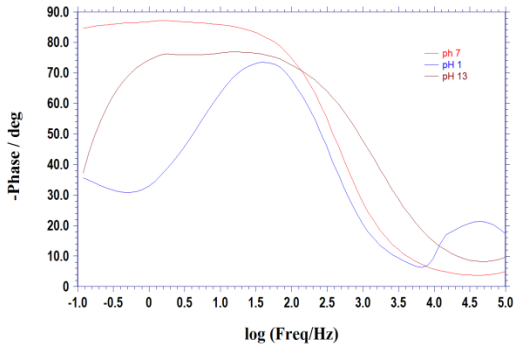

Fig.8 Bode phase angle plot of benzalazine at different pH solutions

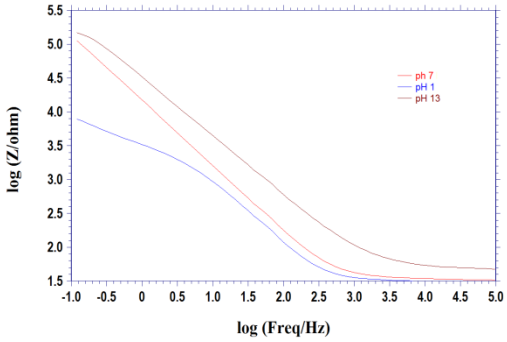

Fig.9 Bode magnitude plot of benzalazine at different pH solutions

4.4.3 Chronocoulometric studies

Normally in chronocoulometry, the charge is obtained from reduction in the forward step and a reduced species is formed. In the reverse step the reduced species undergoes oxidation thereby a decrease in charge is noted. In pH 1.0 the both reactions occurred at the same speed, so the curve for forward and reverse scan was almost similar. In pH 13.0 the reduction reaction was fast when compared to oxidation.

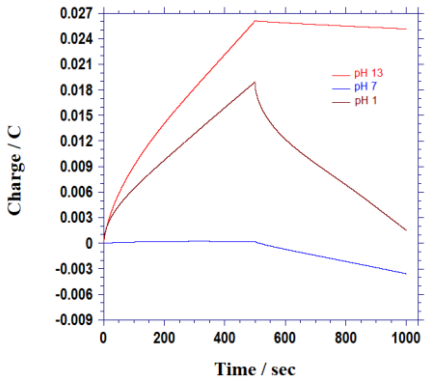

Fig.10 Chronocoulogram of benzalazine at different pH solutions

In Anson plot the curve did not meet the origin due to charge from the capacitance.[23] The reduction process in the forward scan requires some time to occur. At zero time the reduction process was not started. The charge at zero time corresponds to double layer. Therefore the intercept in the forward scan gives double layer capacitance. The linearity of the plot showed that this reaction was diffusion controlled. From the forward and reverse scan intercepts it was clear that the charge due to adsorption is negligible. Double layer charging for benzalazine at different pH's were -0.458e-4, 1.510e-4 and -0.527e-4 coulomb respectively. Charge obtained from benzalazine at pH 7.0 is more than other pH's.

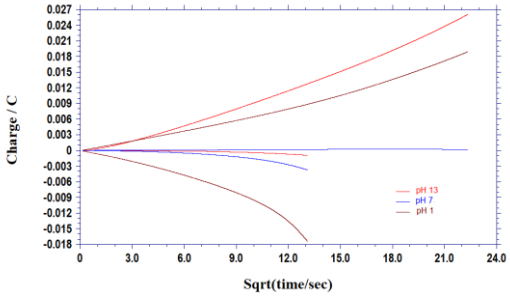

Fig.11 Anson plot of benzalazine at different pH solutions

The diffusion coefficient for the reduction of benzalazine in different pH solutions were calculated from integrated Cottrell's equation.(eq.1)

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2}$$

Slope $=2nFACD^{1/2}\pi^{-1/2}$
F= Faraday constant
A = Electrode area
C= concentration
D= diffusion coefficient
Diffusion coefficients were found to be $1.57*10^{-9}$, $6.96*10^{-12}$ and $3.15*10^{-9}$ /(cm^2/s) for pH 1, 7 and 13 respectively.

5. CONCLUSIONS

Benzalazine was prepared by the condensation of benzaldehyde and hydrazine dihydrochloride under microwave irradiation. Redox behaviour of azine was studied in three different pH solutions. At pH 1.0 intermediate formed during redox process. In neutral and basic pH no such intermediate was formed. Electrochemical impedance spectroscopy studies showed that benzalazine at neutral pH showed more capacitance than in acidic and basic pHs. The

diffusion coefficient of benzalazine is less in neutral medium.

6. ACKNOWLEDGEMENT

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