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Electrochemical behaviour of acrylamide polymers functionalized with some schiff bases

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ABSTRACT

CV, SWV and CA have been used to investigate the electrochemical behaviour of 2-hydroxy-5-bromobenzaldehyde polyacrylamide (*PABSB*), 2-hydroxy-5-chlorobenzaldehyde polyacrylamide (*PACSB*) and 2-hydroxy-5-methylbenzaldehyde polyacrylamide (*PAMSB*) at the mercury electrode in aqueous media. The bromo- and chloro- derivatives were electroative while the halide-free compound, the methyl- derivative, was not. The analysis of the experimental data supports the formation of anion radicals as a result of C-X bond cleavage. Following the electron transfer step, a protonation reaction was thought to be occuring through the $E_{irr}C$ mechanism. The large polymeric molecules are adsorbed at the mercury electrode as expected contributing the adsorption current component to the diffusion one.

Keywords: Polymeric schiff base, electrochemistry of polyacrylamide, cyclic voltammetry, chronoamperometry.

1. INTRODUCTION

Schiff bases are a large class of organic compounds containing the azomethine group. They can be conveniently and easily synthesized from relatively cheap precursor materials [1-2]. They are derived from a large number of carbonyl compounds and amines resulting a vast number of schiff base derivatives. Furthermore, schiff bases have been amongst the most widely studied coordination compounds and are becoming increasingly important as biochemical, analytical, antimicrobial and pharmaceutical reagents [3-5]. Several researchers proposed that the redox potentials of schiff-bases are directly related to the biologically relevant chemical characteristics of the entire complex, e.g. dioxygen binding ability and nucleophilicity, increasing the importance of the determination of electrochemical properties of schiff bases [6-7].

However, the main disadvantage of schiff bases is their easy hydrolization in aqueous media. This characteristic restricts water's usage as solvent in practical studies especially in electrochemical experiments dealing with schiff bases and their metal complexes. Hence leaving organic solvents as the sole alternative, narrowing the usage of schiff bases and causing difficulty in analysis [8-9].

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Throughout the past decade, there has been much interest in the coordination chemistry of schiff base polymers due to their high thermal stability, chelate formation, and semiconducting or conducting properties. In addition, such substances have been shown to exhibit novel optical, electrical and catalytic properties not observed in classical metal complexes [10-13]. Thus, there has been an increasing tendency for synthesis of polymeric schiff bases within the last few years. This synthesis could be achieved through two different ways. First, it is possible to polymerize synthesized "schiff base monomers", thus enhancing its properties.   Second, through usage of polymer based reactives, one could obtain improved polymeric schiff bases in a single step [14-18].

At least known to us, there have not been many studies on the electrochemical behaviour of polymeric schiff bases. In this study, the electrochemical behaviour of polymeric schiff bases was examined at the Hg electrode in aqueous medium using various electrochemical techniques. To achieve this task, a group of polymeric schiff bases were synthesized through condensation reaction of polyacrylamide (PAA) with different substituents of benzaldehydes, as described elsewhere [19]. As these schiff bases carry polymer characteristics, they are water soluble and do not hydrolize in aqueous medium, as compared with the monomers.

2. EXPERIMENTAL

2.1. Preparation of Polymeric Schiff Bases

The polymeric schiff bases were prepared by adding dropwise polyacrylamide (1 mmol in hot water) to the solution of aldehydes (4 mmol in hot methanol) with stirring until the solution was dense, *ca.* 4 days. The mixture was evaporated to about 1/3 of the original volume and cooled to the room temperature. A crystalline yellow precipitate obtained was filtered and washed with a water-methanol mixture (1:1 v/v) and dried in a desiccator

over anhydrous $CaCl_2$. The structure of the resulting compounds was characterized using IR, ^{13}C-NMR, ^{1}H-NMR, elemental analysis [20].

### 2.2. Reagents and Apparatus

All experiments were performed with analytical-reagent grade chemicals and used without further purification. Ultra pure water was obtained from Human I$^+$ water purification system and output resistance was 18.3 MΩ.cm. The supporting electrolyte was Britton-Robinson (BR) buffer prepared in the usual way by adding appropriate amounts of 0.2 M sodium hydroxide to the mixture of boric acid, orthophosphoric acid and acetic acid (0.04 M each). The concentrations of polymeric schiff bases used in the electrochemical experiments were 1 mM.

The polarographic and voltammetric experiments were carried out using an electrochemical analyser (CHI 660B, USA) equipped with CGME cell stand (BAS, USA) and with three electrode system. Working electrode, reference electrode and counter electrode were Hg, Ag/AgCl/KCl$_{sat}$ and Pt wire, respectively. All solutions used for the voltammetric system were deaerated by passing argon through the solutions for at least 5 min prior to the voltammetric experiments. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behaviour of Schiff Base Polymers

The molecular structures of the polymeric schiff bases studied are given below (Scheme 1). The main differences are the bromo-, chloro- and methyl- substituents in the phenyl ring at the para- position with respect to the hydroxyl group.
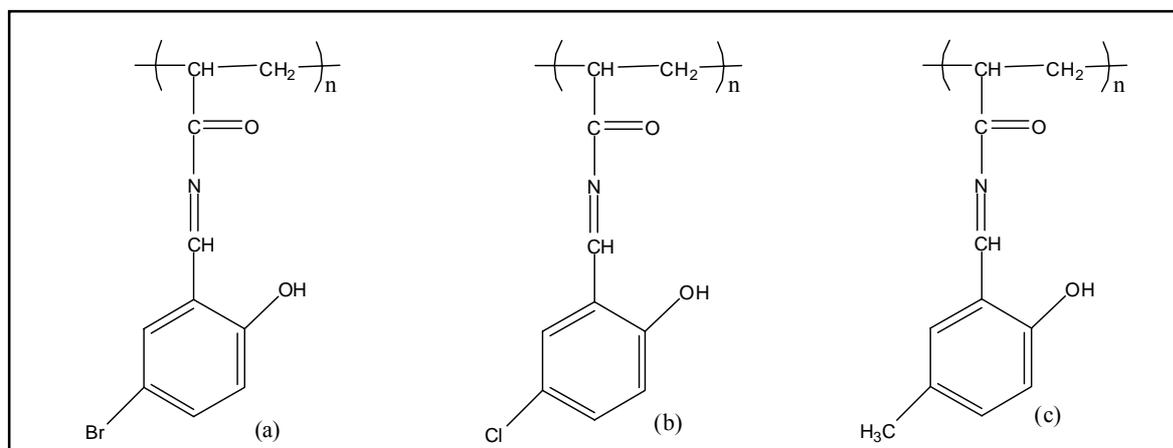
Scheme 1. Structure of polymeric schiff bases of: (a) 2-Hydroxy-5-bromobenzaldehyde polyacrylamide (*PABSB*), (b) 2-hydroxy-5-chlorobenzaldehyde polyacrylamide (*PACSB*), (c) 2-hydroxy-5-methylbenzaldehyde polyacrylamide (*PAMSB*).

Fig. 1 shows the square wave voltammograms (swv) of the schiff base polymers in BR buffer of pH 3. Only one cathodic peak is observed between pH 2.0 and 10.0 at the Hg electrode, for the bromo and chloro derivatives. Methyl derivative is electroinactive in this potential range at the mercury electrode as can be seen from Fig.1. SWV peak for the bromo- derivative was observed at -0.80 V while chloro- derivative was at -0.86 V in BR buffer of pH 3. This behaviour can be explained that the reduction is related to the halojen substituents in the aromatic ring and the mechanism of the reduction will be explained in the further steps. The peak that belongs to chloro-derivative is observed at the more negative potential with a lower peak current as compared to that of the bromo-derivative.
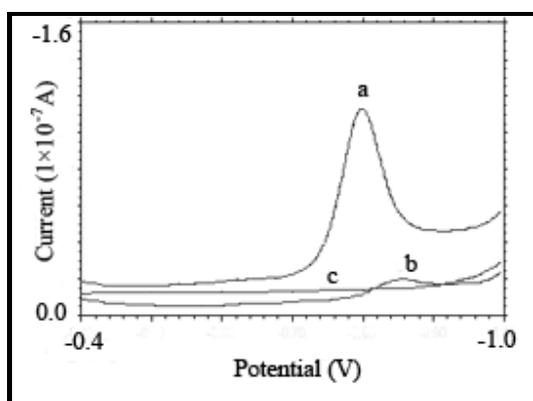
Square wave voltammograms of the bromo derivative *(PABSB)* in BR buffer solutions with different pHs are shown in Fig. 2. Reduction peak potentials of both *PABSB* and *PACSB* derivatives are observed to depend on pH. E_p is shifted to the negative potentials when pH is increased, indicating that hydrogen ions are consumed in the electrode reaction. A plot of E_p versus pH is observed to be linear with a slope of *75 mV for PABSB and 73 mV for PACSB* [21]. The graphs of E_p vs. pH for *PABSB* and *PACSB* are given Fig. 3.
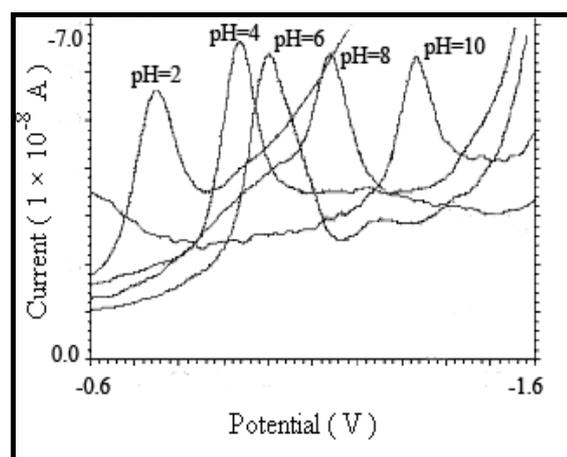

Fig. 1. Square wave voltammograms of polymeric Schiff bases for a) PABSB, b) PACSB, c) PAMSB in BR buffer of pH 3 vs. Ag/AgCl/KCl$_{sat}$. Puls amplitude is 25 mV, frequency 15 Hz.

Fig. 2. Square wave voltammograms of bromo- derivative of polymeric schiff base (PABSB) in different pHs of BR buffers vs. Ag/AgCl/KCl$_{sat}$. Puls amplitude was 25 mV and frequency was 15 Hz.
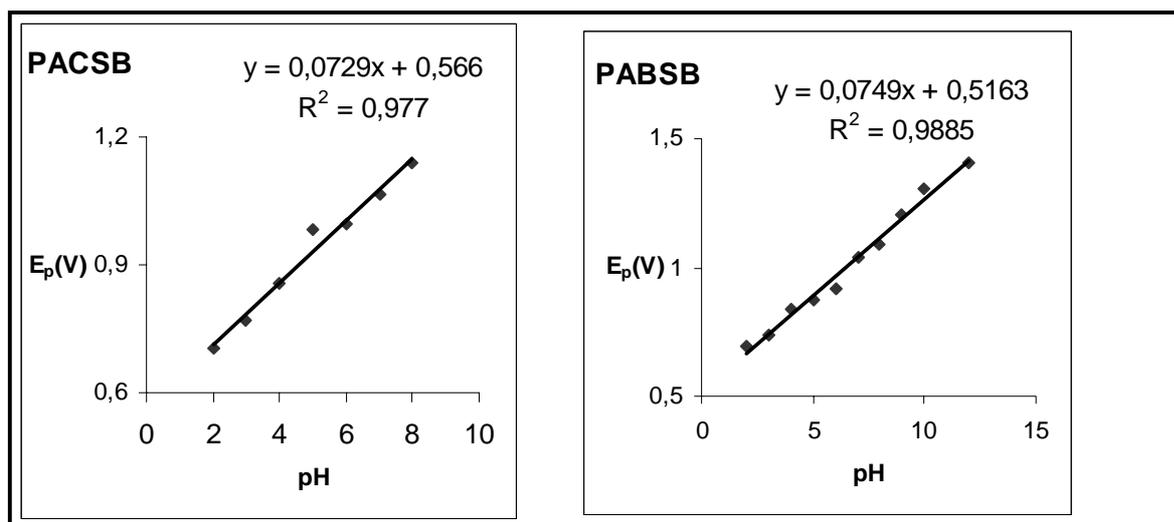

Fig. 3. The graph of square wave E_p vs. pH for PABSB and PACSB in BR buffers. Peak potentials were measured vs. Ag/AgCl/KCl$_{sat}$. Puls amplitude was 25 mV, frequency 15 Hz.

The number of protons involving in the rate-determining step (rds) of the reduction process is found to be equal to one, assuming one electron transfer in the rds and symmetry transfer coefficient (α) value is 0.8[22].

The peak current (i_p) of the polymeric schiff bases (PABSB and PACSB) is pH dependent in solutions between pH 2-12. The common characteristics of the peak current change for both derivatives is the observation of a maximum value of peak current at nearly pH 7 for PABSB and 6 for PACSB as shown in Fig. 4. This behaviour can be attributed to the protonation of the schiff base polymers which occurs at the electrode surface where the electron transfer is facilitated by the rate of protonation [22]. This pH value is nearly equal to the pKa of halogen derivative polymeric schiff bases [23].
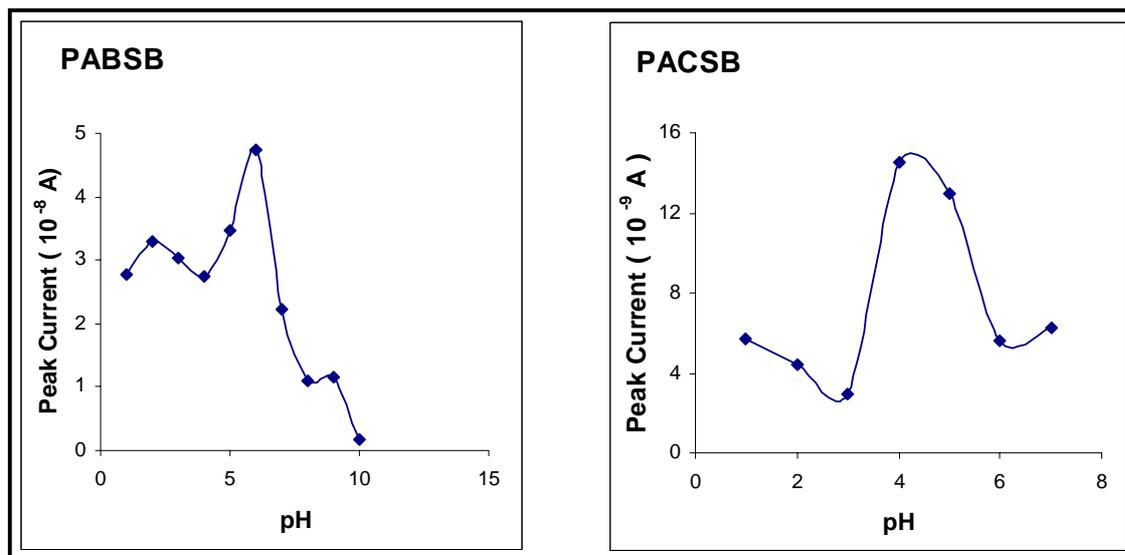

Fig. 4. The graph of i_p vs. pH for PABSB and PACSB in BR buffers at various pHs. Reference electrode is Ag/AgCl/KCl$_{sat}$. Puls amplitude is 25 mV, frequency 15 Hz.

3.2. Cyclic Voltammetric Measurements

Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the elucidation of electrode reaction mechanism of electroactive species. CV experiments were carried out in BR buffer at various pH values for 5.0×10^{-5} M polymeric schiff base derivatives. As shown in Fig. 5, only one cathodic peak was observed in both acidic and alkaline media for bromo- and chloro-derivatives and no peak was obverved on the reverse scan, indicating either the irreversible nature of the electrode reaction or the presence of a follow-up heterogeneous chemical reaction (EC mechanism). Neither cathodic nor anodic CV peak current was produced for methyl derivative, *PAMSB,* suggesting the electroinactive nature of this compound in the scanned potential range.
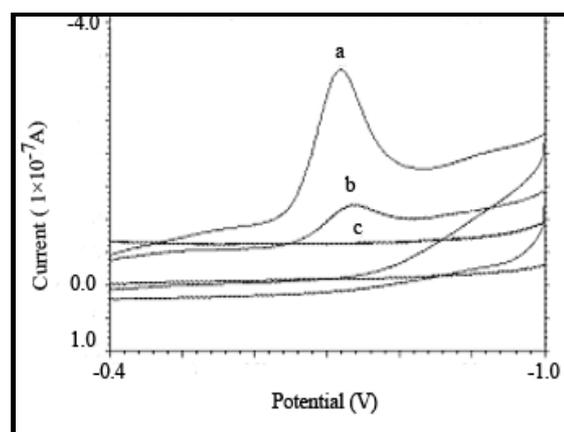

Fig. 5. Cyclic voltammograms (vs. Ag/AgCl/KCl$_{sat}$) of polymeric schiff bases at the Hg electrode for   a) PABSB, b) PACSB, c) PAMSB in BR buffer of pH 3. Scan rate was 100 mV/s.

It is well known that for the diffusion controlled current for CV, i_p-$\upsilon^{1/2}$ graph is linear according to Randles-Sevcik equation ($i_p = k\upsilon^{1/2}$). If the electrode reaction is affected by adsorption phenomena, the graph will deviate from linear behavior. In this case the peak current changes linearly with scan rate (υ) according to equation $I_p = A\upsilon^x$. The x values of 1.0 and 0.5 are expected for pure adsorption and pure diffusion controlled currents, respectively. For 5.0×10⁻⁵ M *PABSB* and *PACSB*, the regression of log (i_p) versus log (υ) gave a slope value of 0.89 and 0.85 respectively, as shown in Fig. 6, indicating reduction current was composed of diffusion and adsorption components [24]. This result is expected because polymers are generally adsorbed at the electrode surfaces due to their large molecular structure.
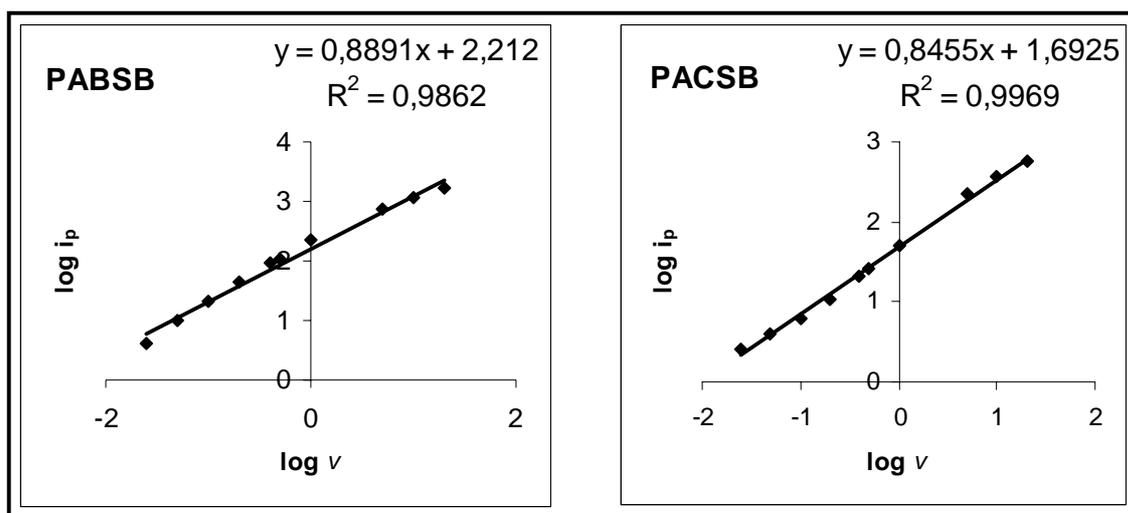

Fig. 6 The graph of log (i_p) vs. log (v) for *PABSB and PACSB* at different scan rate vs *Ag/AgCl/KCl$_{sat}$.* in cyclic voltammetric experiment.

Since the anodic peak was not observed in CV experiments for polymeric schiff bases and the peak potential was shifted towards more negative potential with the scan rate, the reduction process was thought to be either an irreversible electron transfer process or an electron transfer fallowed by a chemical reaction, as stated above. For an irreversible reduction process, peak potential (E_p) is a function of scan rate, shifting in a negative direction by an amount *of 30/α* mV (at 25°C) for each tenfold increase in *v*. [25]. Experimental values for the potential shift for bromo- and chloro- derivatives are 44 mV and 35 mV respectively for each tenfold increase in the scan rate. Therefore the electron transfer for the reduction of two halogen derivatives has irreversible character. It is sometimes useful to extend the scan rates to high values to see if the products of the reduction reaction are electroactive. Since no anodic current is observed even at very high scan rates, the electroactive product is changed to an electroinactive form by a following heterogeneous chemical reaction. Therefore the electrode mechanism of $E_{irr}C$ is probably operative for the reduction of the polyacrylamide polymers functionalized with some schiff bases.

3.3. Chronoamperometric Studies

Diffusion coefficients for polymeric schiff bases are calculated using the Cottrell equation [26]. Chronoamperometric measurements and CV experiments were carried out at a HMDE for 1 mM polymeric schiff base and 1 mM ferrocene solutions. Polymeric schiff base solutions were prepared in BR buffer at pH 3 and ferrocene solution is prepared in acetonitrile containing 0.05 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. Diffusion coefficients are calculated according to the well known Cottrell equation, $i_d = nFAD^{1/2}C/(\pi t)^{1/2}$, where i_d is the diffusion current (A), C is the analytical concentration of electroactive species (mole/cm³), A is the surface area of electrode (cm²), F is the Faraday constant, n is the number of electrons transferred. Diffusion coefficients were calculated using slope of the i_d versus $t^{1/2}$ graph. Firstly Cottrell slope was determined for ferrocene as a standard system and this value was used to determine to real surface area of the electrode as 0.3120 cm² ± 0.0004 cm². Then i_d versus $t^{1/2}$ graphs were plotted and diffusion coefficients were calculated for PABSB and PACSB as 3.129×10⁻⁸ cm²/s ± 0.024×10⁻⁸ cm²/s and 3.465×10⁻⁷ cm²/s ± 0.067×10⁻⁷ cm²/s, respectively. Standard deviation values are for four experimental results. The lower values of the diffusion coefficients for PABSB and PACSB suggest that the

reduction at the electrode surface is adsorption controlled as revealed from the log i_p – log v plots from the CV experiments.

3.4. Electrode Reaction Mechanism

Cyclic voltametric studies show that the reduction of the bromo- and chloro- derivatives of the polymeric schiff bases is related to the halogen substituents attached to the aromatic ring. As mentioned above, CV studies show the existence of an $E_{irr}C$ mechanism, where E_{irr} is the irreversible electron transfer and C is the follow-up chemical step. As can be seen from Fig. 5, in the reverse scan reoxidation waves are not observed, indicating that no further reduction process resulted due to a high speed

follow-up chemical reaction, that is probably the protonation of the radical anion. Even at very high scan rates, anodic voltammetric response is not observed, indicating the reoxidation of a short-lived radical anion is not possible due to a high protonation reaction rate. Furthermore, measurements of the peak current of the reduction wave showed that its current function ($i_p/v^{1/2}$) decreases with increasing scan rates. All these details are clear evidence of a following homogeneous reaction after the formation of the radical anion. The decreasing current function and the peak potential shift with the increase of scan rates reveal that the reduction wave results from one electron transfer step forming an unstable anion radical. The mechanism of the electrode reaction can be depicted as Scheme 2.
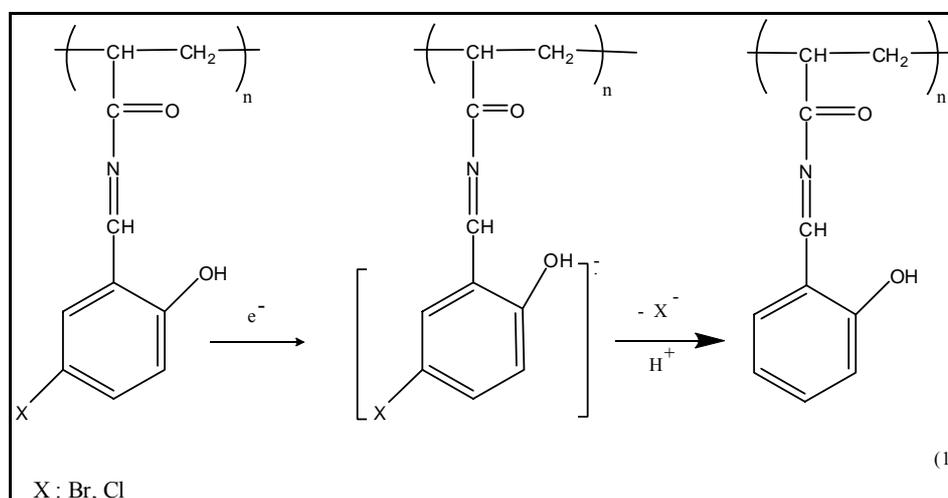
Scheme 2. Electrochemical reduction mechanism for polymeric schiff bases.

Electrochemical reduction mechanism has been investigated for halogen substituted aromatic compounds in the literature [27-28]. If a halogen substituent exist on the aromatic ring, electrochemical reduction leads to the formation of the unsubstituted products. In a similar mechanism, the electrochemical reduction of halogen substituted schiff base polymer produces unsubstituted product due to the fact that after the radical anion formation halogen is eliminated in a rather fast first-order reaction accompanying a fast protonation reaction [29].

4. CONCLUSIONS

The electrochemical reduction of polymeric schiff bases of 2-hydroxy-5-bromobenzaldehyde polyacrylamide (*PABSB*), 2-hydroxy-5-chlorobenzaldehyde polyacrylamide (*PACSB*) and 2-hydroxy-5-methylbenzaldehyde polyacrylamide (*PAMSB*) were studied at the mercury electrode in aqueous media. The bromo- and chloro- derivatives were electroactive while the halide-free compound, the methyl- derivative, was not. The reaction described in this paper is the first example of

a halide containing polymeric schiff bases where electrogenerated anion radicals are protonoted. The large polymeric molecules are adsorbed at the mercury electrode as expected contributing the adsorption current component to the diffusion one.

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