Chapter 6

Swelling and Release of Methylene Blue through PEG/P(NIPAM-co-AMPS) Hydrogels in Presence of Electric Field

6.1 Introduction

The electroresponsive hydrogels are usually prepared from polyelectrolytes, which are also respond to change in pH. These polyelectrolyte hydrogels are consisting of polymer network structure with ionizable groups that ionized at different pH of the medium. The resulting materials have capable of swelling and shrinking by exchanging solvent molecules under application of electric field. The electric field responsive hydrogels have an advantage over other stimuli responsive hydrogels, as it is easy to operate and regulate conveniently. Under electric stimulation, electro-responsive hydrogels exhibit change in volume or shape like gel swelling, shrinking, bending and transform electrical energy into mechanical energy. Thus, the electroresponsive hydrogels play an important role in area of energy exchange devices, controlled release of drug molecules, actuators, sensors and artificial muscles.

Poly (2-acrylamido-2-methylpropane sulphonic acid) hydrogels received attention in recent years due to presence of strongly ionizable sulfonate group that dissociate completely in the overall pH range and exhibit pH independent swelling behavior. Poly (N-isopropylacrylamide) is one of the most studied polymer for preparation of
thermoresponsive hydrogels. Poly (ethylene glycol), (PEG) is highly water-soluble, biocompatible and nontoxic polymer. The attractive properties of poly (ethylene glycol) help the researchers to design the copolymer hydrogels composed of these segments for many biotechnological applications.

The present purpose of the study is to investigate the effect of electric field on swelling kinetic, methylene blue (MB) loading and releasing characteristic of hydrogels based on N-isopropylacrylanide (NIPAM), acrylamido-2-methylpropane sulphonic acid (AMPS), poly(ethylene glycol) (PEG) in deionized water.

### 6.2 Results and Discussions

#### 6.2.1 Swelling Behavior of Hydrogels in Water

The swelling experiments were performed in deionized water at 20°C and measurements were done gravimetrically. The swelling phenomenon of ionic hydrogel is shown in Figure 6.1. The swelling ratio of hydrogels is affected by the hydrophilic or hydrophobic structure, ionic comonomer concentration, cross-linking density. In the present hydrogels, the cross-linking density remains constant so, hydrophilicity and ionic monomer concentration are the main factors affecting on equilibrium swelling ratio. In Figure 6.2, the data show that the swelling ratio value increases with increasing AMPS content in the feed composition at electric field intensity 429 V/m. The change in hydrogels volume in presence of an electric field is due to osmotic pressure difference caused by the concentration difference of mobile ions in and around the hydrogels in an aqueous solution. In the absence of an electric field, electro neutrality is maintained due
to the fixed positive charges in the ionic hydrogels matrix. When an electric field is applied, mobile ions inside and outside the hydrogels are rearranged and concentration gradient is established. The cationic concentration difference at anode side of the hydrogel is larger due to movement of cations toward cathode side. As a result, the osmotic stress due to cations and the corresponding swelling is larger at the anode side. The osmotic stress due to anion concentration gradients will be of lesser magnitude as shown in Figure 6.3.
Figure 6.1 (a) Schematic of an ionic polymeric hydrogels, (b) The swelling phenomena of ionic hydrogels.

Figure 6.2 Variation of swelling ratio versus time at 429V/m
The variation in swelling of the hydrogels under electric field intensity 429V/m and current 0.0375A were measured gravimetrically at definite time interval. Figure 6.4 show the normalized swelling ratio of hydrogels with different mole percent of AMPS in the feed composition in presence of an electric field intensity 429V/m at 20°C. The result shows that both normalized swelling ratio and rate of swelling increases with increasing AMPS content in the hydrogels. The hydrogels with higher content of AMPS absorbed high amount of water due to osmotic stress developed in presence of an electric field. It was also observed that the normalized swelling ratio of different hydrogels increases with increasing electric field intensity from 71V/m to 571V/m and further increase in an electric field leads to the rupture of hydrogels due to increasing osmotic pressure. Figure 6.5 shows that the normalized swelling ratio of hydrogels increases from 1.13 to 2.99 for
HG-102, 0.8 to 3.5 for HG-106 and 1.8 to 4.1 for HG-110 with increasing electric field intensity from 71V/m to 571V/m. The hydrogel sample without AMPS i.e HG-100 does not respond to an electric field.

**Figure 6.4** Variation of normalized swelling ratio versus time at 429V/m
6.2.2 Effect of pH on Swelling Behavior

The experiments were performed in 0.01 M NaOH and 0.01M H₂SO₄ solution at 20°C to study the swelling, shrinkage behavior of hydrogels. pH of the solutions affect the swelling ratio of the hydrogels. The swelling ratio of the hydrogels in 0.01M NaOH increases with increasing AMPS content in the feed composition in presence of electric field intensity (71-571 V/m). The obtained swelling ratio value is high as compared to value in deionized water with similar composition and electric field intensity. The change in hydrogels volume in the presence of electric field intensity is due to the osmotic pressure difference caused by the concentration difference of mobile ions inside and around hydrogels in an aqueous solution. The shrinkage of hydrogels takes place in 0.01M H₂SO₄ solution, which may be due prevention of ionization of polymer by the

![Normalized swelling ratio of hydrogel samples at different electric field intensity.](image)

**Figure 6.5** Normalized swelling ratio of hydrogel samples at different electric field intensity.
high acidity of swelling medium. In an acidic medium, the hydrogen ions do not
dissociate from sulphonate group of PAMPS unit due to the higher concentration of
hydrogen ions in the external solution. The current density also increases from 17.5 mA
to 50 mA in acidic medium with increasing electric field intensity from 71V/m to
571V/m. The electro active properties of hydrogels depend on the amount of AMPS
monomer present in feed composition as shown in Figure 6.6.
6.2.3 Diffusion in Hydrogels

Diffusion is the transport of water molecules into interstitial space between hydrogel chains through capillary action involves large segmental motion results, expands its network structure. Figure 6.7 show the mechanism of diffusion process. The nature of water molecules diffused into hydrogels was measured by using equation 1.3.2-1. The values of (n) and (k) were calculated from the slope and the intercept of the plot of lnF against ln(t) respectively. Diffusional exponents, (n) and diffusion constant, (k) are calculated and given in Table 6.1. The diffusion of water molecules into the superabsorbent hydrogels is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As solvent diffuses into the hydrogels, rearrangement of chains does
not occur immediately. The study of diffusion phenomena of water in hydrogels under electric field clarifies the polymer behavior. The diffusion coefficient (D) of hydrogel samples in deionized water was calculated by using equation 2.4.2-1. The obtained value of the diffusion coefficient of hydrogel samples varied from $1.41 \times 10^{-7}$ cm$^2$·s$^{-1}$ to $2.53 \times 10^{-7}$ cm$^2$·s$^{-1}$. The value of the diffusion coefficient of hydrogels increases with increasing AMPS content under electric field and without electric field. By incorporating AMPS as comonomer hydrophilicity of hydrogels increases thus, the diffusion coefficient of hydrogels increased.

**Table 6.1** The diffusion parameters of different hydrogels

<table>
<thead>
<tr>
<th>Samples</th>
<th>Diffusion exponent, (n)</th>
<th>Diffusion constant,(K)</th>
<th>Diffusion coefficient,(D) cm$^2$·s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG-100</td>
<td>0.82</td>
<td>-2.32</td>
<td>$1.41 \times 10^{-7}$</td>
</tr>
<tr>
<td>HG-102</td>
<td>0.87</td>
<td>-2.58</td>
<td>$2.48 \times 10^{-7}$</td>
</tr>
<tr>
<td>HG-106</td>
<td>0.89</td>
<td>-2.47</td>
<td>$2.37 \times 10^{-7}$</td>
</tr>
<tr>
<td>HG-110</td>
<td>0.91</td>
<td>-2.72</td>
<td>$2.5 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
6.2.4 Loading and Releasing of Methylene Blue

The loading and releasing experiments of cationic methylene blue (MB) (MW =319 g/mol) were performed for hydrogel samples i.e HG-100, HG-102 and HG-110. The methylene blue (MB) loading content %, entrapment efficiency % and cumulative amount released % were calculated by using equation 2.3.6-1, 2.3.6-2 and 2.3.6-3 respectively. In Figure 6.8 (a) & (b) shows the methylene blue release from hydrogels in presence of electric field intensity i.e. 286V/m and absence of electric field respectively. Rapid release of methylene blue (MB) through hydrogels under application of electric field intensity is due to exchange of ions between positively charged MB molecules and protons at the cathode. The higher amount of methylene blue released from pure hydrogel i.e. HG-100 as compared to hydrogels that content AMPS in the feed composition i.e.
HG-102 & HG-106. The release % of MB decreases with increasing amount AMPS content in the hydrogels due to increasing interaction between AMPS with cationic methylene blue (MB) molecules. The swelling of hydrogels at pH 7.0 in presence of an electric field also retards the release of methylene blue due to entrapment of methylene blue molecules within pores of the hydrogels. The similar releasing behavior was also observed for hydrogels without electric field but release % of methylene blue is very low. The entrapment efficiency for the hydrogels HG-100, HG-102 & HG-106 is 77.24%, 90.1% & 95.0%, respectively.

Table 6.2 The total methylene blue (MB) loaded and release data for hydrogels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total drug loaded (mg/g dry gel)</th>
<th>Entrapment Efficiency (%)</th>
<th>Drug release in Presence of electric field intensity (286V/m) For First 3hrs (%)</th>
<th>Drug release in Absence of electric field for First 3hrs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG-100</td>
<td>70.22</td>
<td>77.24</td>
<td>35.22</td>
<td>14.24</td>
</tr>
<tr>
<td>HG-102</td>
<td>577.6</td>
<td>90.1</td>
<td>11.1</td>
<td>4.5</td>
</tr>
<tr>
<td>HG-106</td>
<td>818.9</td>
<td>95.0</td>
<td>7.6</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Figure 6.8 Release of methylene blue from ionic hydrogels at 20°C
(a) Electric field (b) Absence of electric field
6.3 Conclusions

In this chapter, the swelling kinetics of hydrogel samples under the stimulation of the electric field was studied. The result shows that by application of electric field, the swelling ratio of hydrogels significantly increases and this behavior is more prominent for the hydrogels sample that content more amounts of AMPS in the feed composition. The swelling kinetics mechanism of the hydrogels was found to be Super Case-II diffusion, Non-Fickian diffusion with and without presence of an electric field respectively. In methylene blue (MB) loading and releasing experiments in presence of electric field intensity (286 V/m), the entrapment efficiency of MB on hydrogels increased from 77.24% to 95% with increasing AMPS content in the hydrogels. The amount of MB released through hydrogels is higher in presence of an electric field as compared to absence of an electric field. The amount of MB released decreases with increasing AMPS in the feed composition. According to the results presented here, the electro responsive hydrogels can be designed and fabricated by changing copolymer feed composition for biomedical applications such as sensors, artificial muscles, actuators, microelectromechanical system (MEMS) drug delivery device.