CHAPTER 4

FTIR STUDIES

4.1 INTRODUCTION

Results from FTIR spectroscopy will reveal interactions in the chitosan-NH_4I, (chitosan-PVA)-NH_4I, (chitosan-PEO)-NH_4I and chitosan-NH_4I-IL systems. These will be presented in this chapter. The interactions can be determined by observing changes in the peak position or wavenumbers of the functional groups in the spectrum of the polymer and in the vibrational mode of the salt. In chitosan, the nitrogen atom in the amine functional group and the oxygen atom in the carboxamide and hydroxyl groups each possess unused electrons. The presence of the carboxamide band is due to incomplete deacytelation of chitin in the process of producing chitosan. Lone pair electrons in PVA are located at the oxygen atom in the carbonyl and hydroxyl functional groups. The carbonyl band exists due to incomplete hydrolysis of poly(vinyl acetate) in the production of PVA. In PEO, the oxygen atom in the monomer possesses lone pair electrons. The cation of the doping salt will form a dative bond with the nitrogen and/or oxygen and thus a polymer-salt complex is formed. Hence, the carboxamide, amine and hydroxyl bands of chitosan are expected to shift. Likewise, the carbonyl and hydroxyl bands in the spectrum of PVA and C-O-C stretching mode in the spectrum of PEO are also expected to shift when the oxygen atom in the carbonyl, hydroxyl and C-O-C groups interact (weakly) with the cation of NH_4I. These few bands will be the focus of the present investigation.

4.2 INFRARED SPECTRA OF CHITOSAN FILM

Figure 4.1 depicts the infrared spectrum of (a) pure chitosan powder and (b) pure chitosan film in the region between 800 and 1800 cm^{-1}. In this thesis, pure chitosan film means film prepared from casting the solution of chitosan in 1% acetic acid without any additives such as salt or plasticizers.

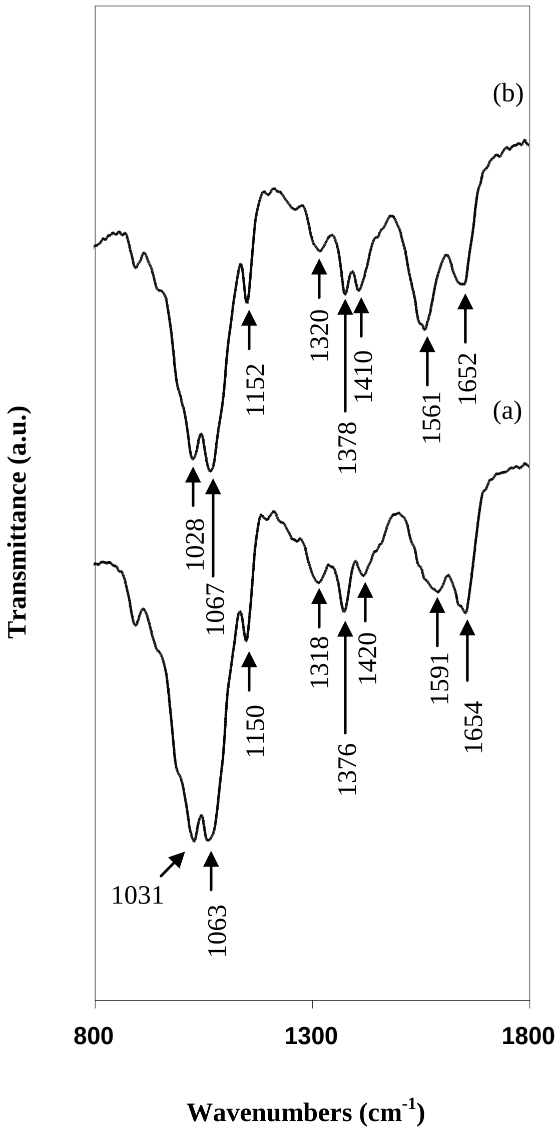

Figure 4.1: FTIR spectra of (a) pure chitosan powder and (b) pure chitosan film in the region between 800 to 1800 cm^{-1}. Focus is on the amine and carboxamide bands at 1561-1591 and 1652-1654 cm^{-1} respectively

The carboxamide (O=C-NHR) band for pure chitosan powder is observed at 1654 cm^{-1}, amine (NH_2) band at 1591 cm^{-1}, CH_3 symmetrical stretching at 1376 cm^{-1}, C–O-C asymmetric vibration at 1150 cm^{-1} and C-O stretching at 1063 cm^{-1} and 1031 cm^{-1}.

The amine band is observed at 1561 cm^{-1} in the spectrum of pure chitosan film. If in the spectrum of chitosan powder, this band is 1591 cm^{-1} then there must be some interactions between the acetic acid solution and the nitrogen donor of chitosan. Similar observation has been reported by Osman and Arof (2003). The carboxamide band is observed at 1652 cm^{-1} in the spectrum of pure chitosan film. As the resolution of the spectrometer used in this work is 2 cm^{-1}, the change in position of the carboxamide band in the spectrum of chitosan powder at 1654 cm^{-1} to 1652 cm^{-1} is not considered as a shift. Therefore, it is inferred that there is no interaction between chitosan and acetic acid at the carboxamide band. Likewise there is no interaction at the oxygen in the chitosan ring, but there is interaction between the acetic acid and the oxygen atom in the hydroxyl group since the shift observed for the C-O stretching from 1031 and 1063 cm^{-1} in the spectrum of chitosan powder to 1028 and 1067 cm^{-1} in the spectrum of chitosan film is more than 2 cm^{-1}.

Figure 4.2 shows the spectrum of pure chitosan powder and pure chitosan film in the region between 3000 and 4000 cm^{-1} that contains the hydroxyl band. The hydroxyl band of pure chitosan powder is observed at 3354 cm^{-1}. The band is shifted to lower wavenumber in the spectrum for pure chitosan film at 3346 cm^{-1}. This is proof that the interaction occurred between acetic acid and oxygen atom in the hydroxyl band of chitosan.

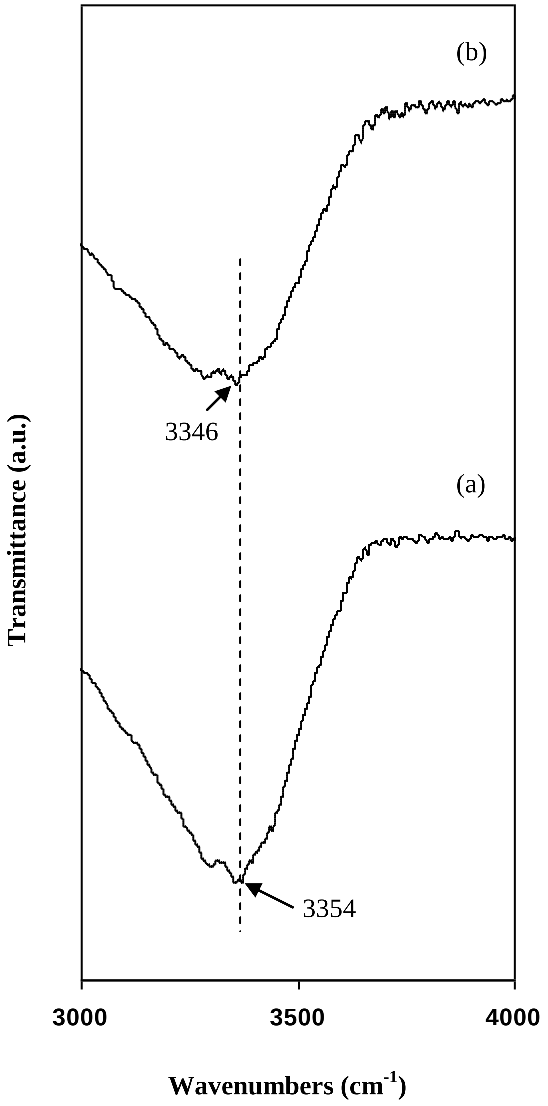

Figure 4.2: FTIR spectra of (a) pure chitosan powder and (b) pure chitosan film in the region between 3000 to 4000 cm^{-1}

Table 4.1 shows the comparison between pure chitosan powder and pure chitosan film. It can be seen that the interaction between chitosan and acetic acid only occurred for C-O stretching and amine (NH_2) bands.

Table 4.1: Vibrational mode of pure chitosan powder and pure chitosan film

Vibrational mode	Wavenumbers (cm^{-1})	
	Pure chitosan powder	Pure chitosan film
C-O stretching	1031 and 1063	1028 and 1067
C-O-C stretching	1150	1152
CH_2 wagging	1318	1320
CH_3 symmetrical deformation	1376	1378
CH_2 bending	1420	1410
NH_2	1591	1561
O=C-NHR	1654	1652
O-H	3354	3346

4.3 INFRARED SPECTRA OF CHITOSAN-NH_4I SYSTEMS

Figure 4.3 shows the spectra of chitosan-NH_4I electrolytes that contain the amine and carboxamide bands in the region between 1400 and 1800 cm^{-1}. It can be observed that carboxamide band in the spectrum of pure chitosan film has shifted. The shift can be as large as from 1652 cm^{-1} to 1619 cm^{-1} in the spectrum of 55 wt.% chitosan-45 wt.% NH_4I (Ch9) electrolyte. These shifts confirm that complexation has occurred between the cation of NH_4I and nitrogen in amine group and the oxygen atom of the carboxamide functional group of chitosan. The amine band also shifted from 1561 cm^{-1} to 1513 cm^{-1}. This confirms that complexation between the nitrogen atom in the amine group and the NH_4^+ ions.

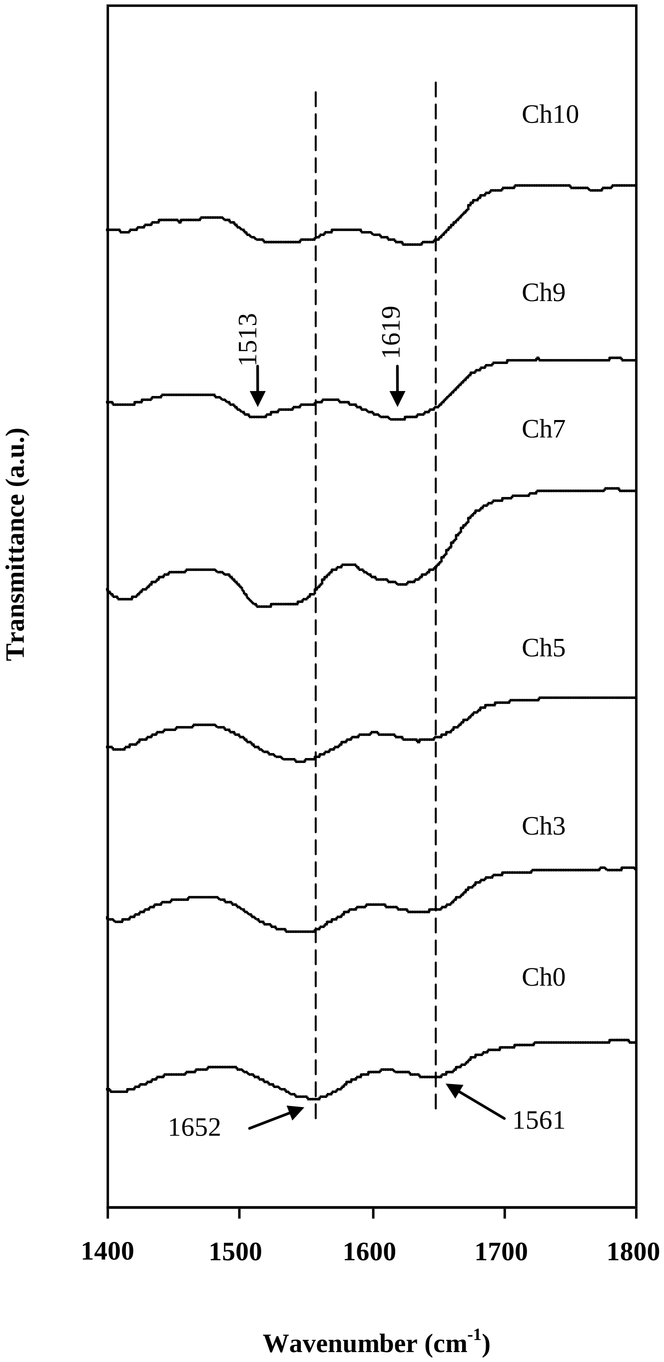

Figure 4.3: FTIR spectra of Chitosan-NH_4I electrolytes in the region of 1400 cm^{-1} to 1800 cm^{-1}

Figure 4.4 shows the spectra of chitosan-NH_4I electrolytes that represents the hydroxyl band in the region between 3100 and 3700 cm^{-1}. The hydroxyl band is observed to shift slightly from 3346 cm^{-1} to 3351 cm^{-1} in the spectrum of Ch9 electrolyte indicating that complexation also occurred at hydroxyl band between NH_4^+ and the oxygen atom in the hydroxyl band.

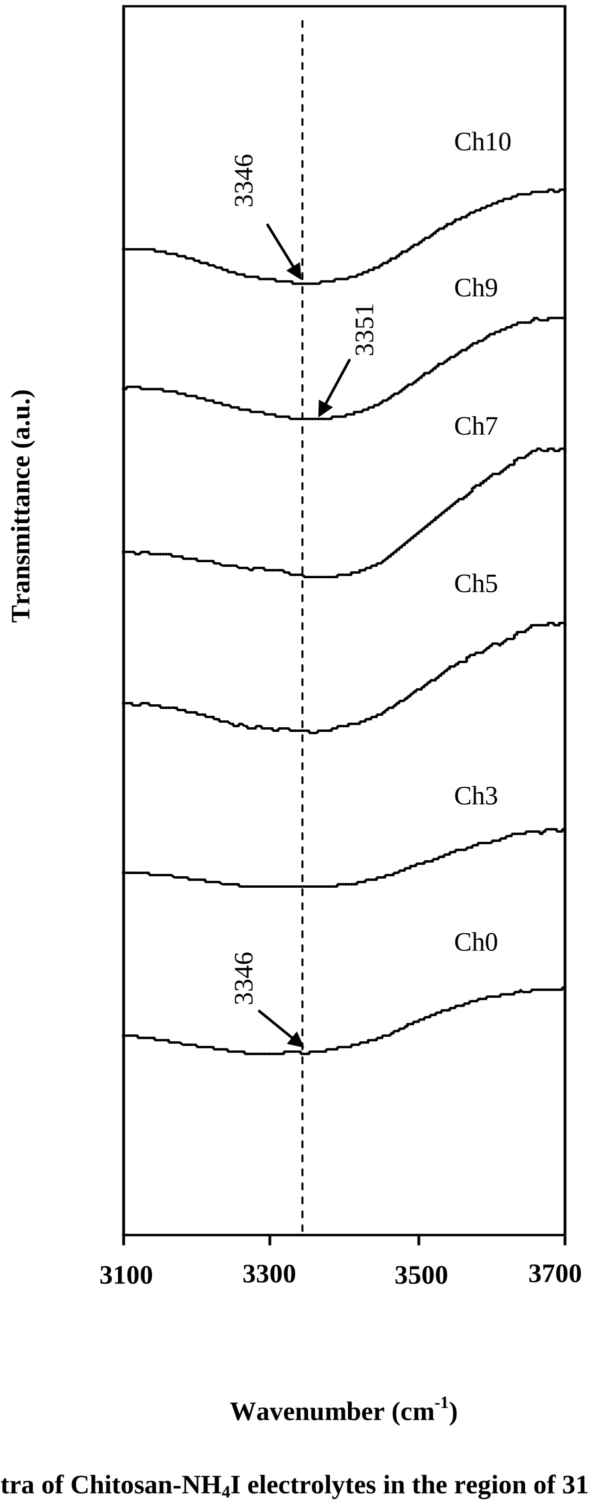

Fig. 4.4 FTIR spectra of Chitosan-NH_4I electrolytes in the region of 3100 cm^{-1} to 3700 cm^{-1}

Table 4.2 lists the carboxamide, amine and hydroxyl bands of electrolytes with different compositions of NH_4I.

Table 4.2: Carboxamide, amine and hydroxyl bands of chitosan electrolytes with different NH_4I concentrations

Electrolytes	Wavenumbers (cm^{-1})		
	O=C-NHR	NH_2	O-H
Ch0	1652	1561	3346
Ch1	1639	1552	3356
Ch2	1639	1544	3357
Ch3	1636	1544	3354
Ch4	1634	1541	3354
Ch5	1634	1540	3359
Ch6	1622	1518	3364
Ch7	1622	1518	3375
Ch8	1621	1511	3366
Ch9	1619	1513	3351
Ch10	1633	1539	3346

In summary, the interaction can be depicted as shown below:

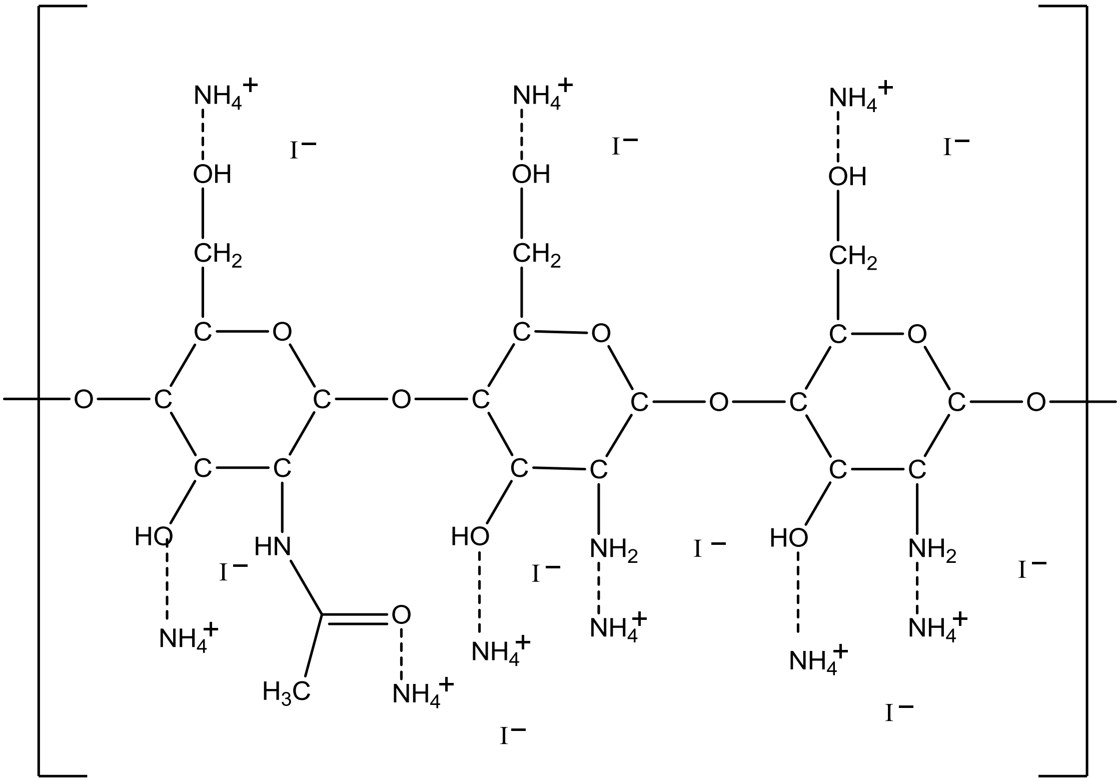

Figure 4.5: Schematic diagram of complexation for chitosan-NH_4I electrolyte

4.4 INFRARED SPECTRA OF (CHITOSAN-PVA) FILMS

Figure 4.6 depicts the spectra of pure (chitosan-PVA) films in the region between 1400 and 1800 cm^{-1}. The carboxamide and amine bands of the pure (chitosan-PVA) films are observed at around 1652 cm^{-1} and 1561 cm^{-1}, respectively. These positions are almost similar with the position of the carboxamide and amine bands of pure chitosan film within the resolution of the spectrometer and thus indicate that no interaction occurs between PVA and chitosan at these bands. An additional peak is observed at around 1734 cm^{-1} in the spectrum of pure (chitosan-PVA) film. This peak belongs to the carbonyl band of PVA. The addition of carbonyl band indicates that there is one extra complexation site in the pure (chitosan-PVA) film. Therefore, there is a possibility of more transit sites for the mobile ions enabling the ions to move easily with small activation energy in the blend host.

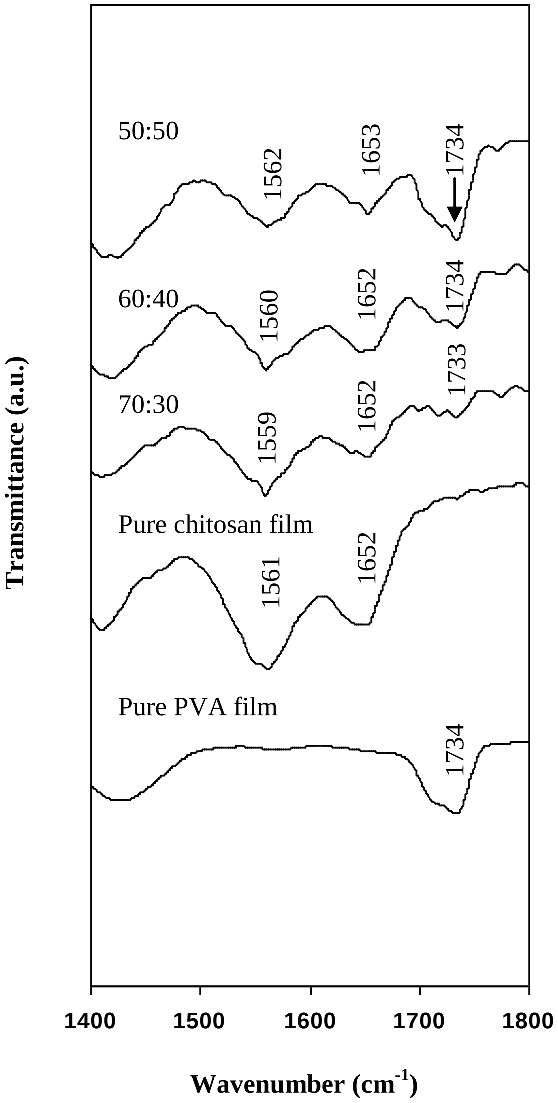

Figure 4.6: FTIR spectra of pure (chitosan-PVA) films in the region of 1400 cm^{-1} to 1800 cm^{-1} for several chitosan:PVA ratios.

Figure 4.7 shows the spectra of pure (chitosan-PVA) films that represents the hydroxyl bands in the region between 3000 and 3800 cm^{-1}. In the spectrum of pure PVA and pure chitosan films, the hydroxyl band is observed at 3313 cm^{-1} and 3346 cm^{-1} respectively. The hydroxyl band shifts to lower wavenumber in the spectrum of pure (chitosan-PVA) films. This indicates that some interactions have occurred between chitosan and PVA at the hydroxyl band. This maybe attributed to hydrogen bonding between the hydroxyl groups in the two polymers.

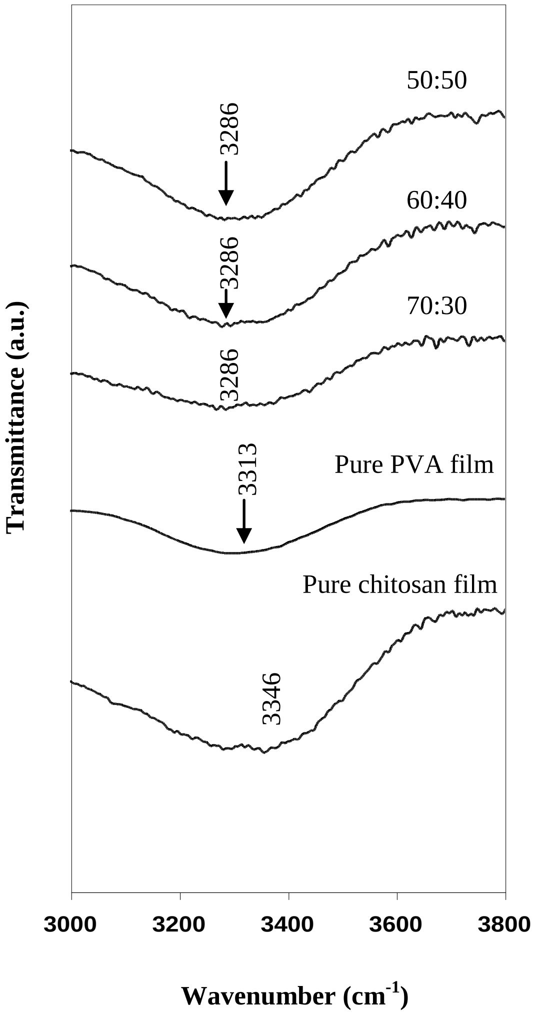

Figure 4.7: FTIR spectra of pure (chitosan-PVA) films in the region of 3000 cm^{-1} to 3800 cm^{-1} for several chitosan:PVA ratios.

Table 4.3 lists the carboxamide, carbonyl, amine and hydroxyl bands of electrolytes with different chitosan-PVA ratios.

Table 4.3: Carboxamide, carbonyl, amine and hydroxyl bands of pure (chitosan-PVA) films with different ratios of the polymer.

Electrolytes	Wavenumbers (cm^{-1})			
	O=C-NHR	C=O	NH_2	O-H
90 chitosan:10PVA	1649	1733	1562	3352
80 chitosan:20PVA	1649	1733	1562	3362
70 chitosan:30PVA	1652	1733	1559	3286
60 chitosan:40PVA	1652	1734	1560	3286
50 chitosan:50PVA	1653	1734	1562	3286
40 chitosan:60PVA	1654	1733	1568	3309
30 chitosan:70PVA	1654	1734	1562	3312
20 chitosan:80PVA	1653	1734	1559	3314

4.5 INFRARED SPECTRA OF (CHITOSAN-PVA)-NH_4I SYSTEMS

Figure 4.8 shows the spectra of several (chitosan-PVA)-NH_4I electrolytes in the region between 1400 and 1800 cm^{-1}. It is to be noted that the ratio of polymer blend to salt is 55:45 (in wt.%). The ratio of chitosan to PVA is as given in the figure. Thus, the actual composition of the spectrum labeled 50:50 is 55 wt.% (50 wt.% chitosan-50 wt.% PVA)-45 wt.% NH_4I or 27.5 wt.% chitosan-27.5 wt.% PVA-45 wt.% NH_4I. The O=C-NHR and amine bands of the pure (chitosan-PVA) films are located at 1653, 1652 and 1652 cm^{-1} and 1562, 1560 and 1559 cm^{-1}, respectively for the ratios of 50:50, 60:40 and 70:30. The bands shift to 1625 cm^{-1} in all these blended electrolytes and the amine band shifts to 1514 cm^{-1} for the electrolyte containing equal weight ratios of chitosan and PVA and to 1515 cm^{-1} for the blends with chitosan:PVA ratio of 60:40 and 70:30 when NH_4I was added to the blends. Also, the carbonyl band is observed to shift to lower wavenumber from around 1734 cm^{-1} to 1713 cm^{-1} upon the addition of NH_4I. This shows that NH_4I and the polymer blends have form complexes.

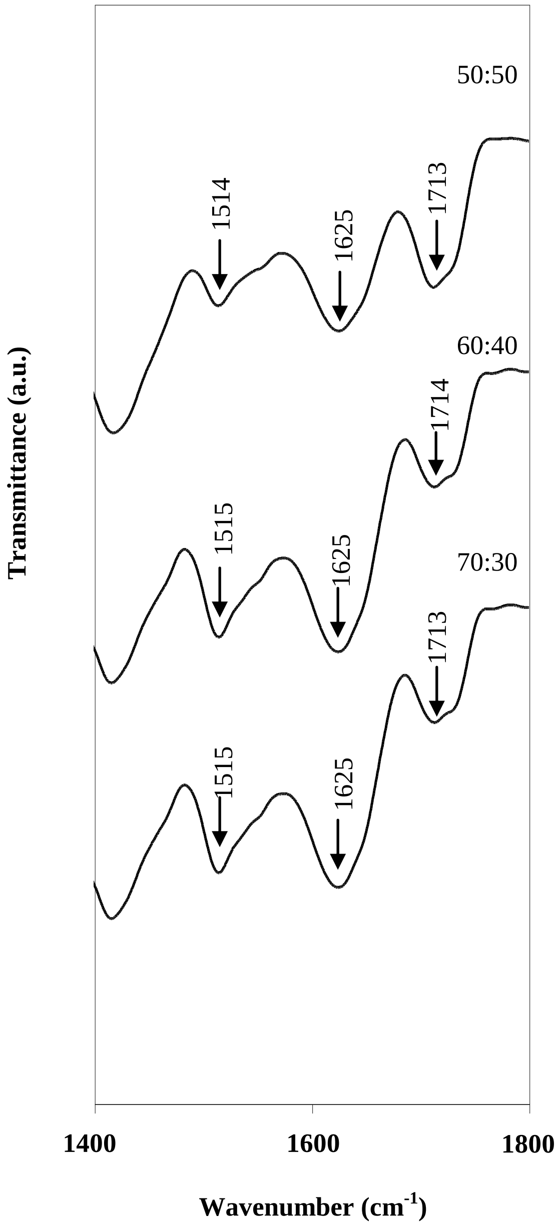

Figure 4.8: FTIR spectra of (chitosan-PVA)-NH_4I electrolyte in the region of 1400 cm^{-1} to 1800 cm^{-1} for several chitosan:PVA ratios.

Figure 4.9 shows the spectra of (chitosan-PVA)-NH_4I electrolytes that represent the hydroxyl band in the region between 3000 and 3800 cm^{-1}.

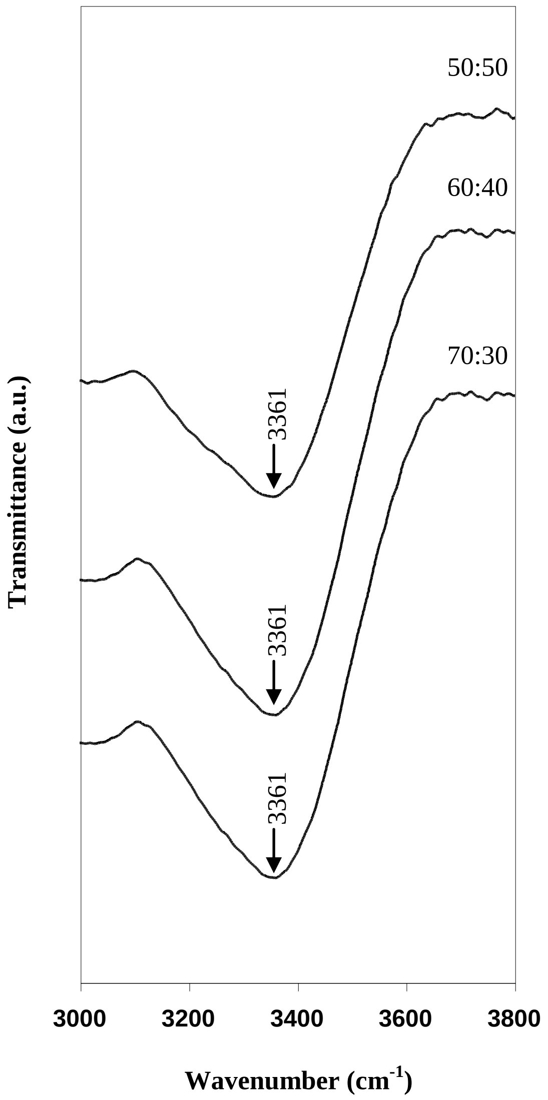

Figure 4.9: FTIR spectra of (chitosan-PVA)-NH_4I electrolyte in the region of 3000 cm^{-1} to 3800 cm^{-1} for several chitosan:PVA ratios.

Referring to Table 4.3, it may be inferred that the hydroxyl band in the pure blends located at 3286 cm^{-1} shifted to 3361 cm^{-1} indicating that complexation has also occurred at the oxygen atom of the hydroxyl group.

In summary, complexation can be depicted as follows:

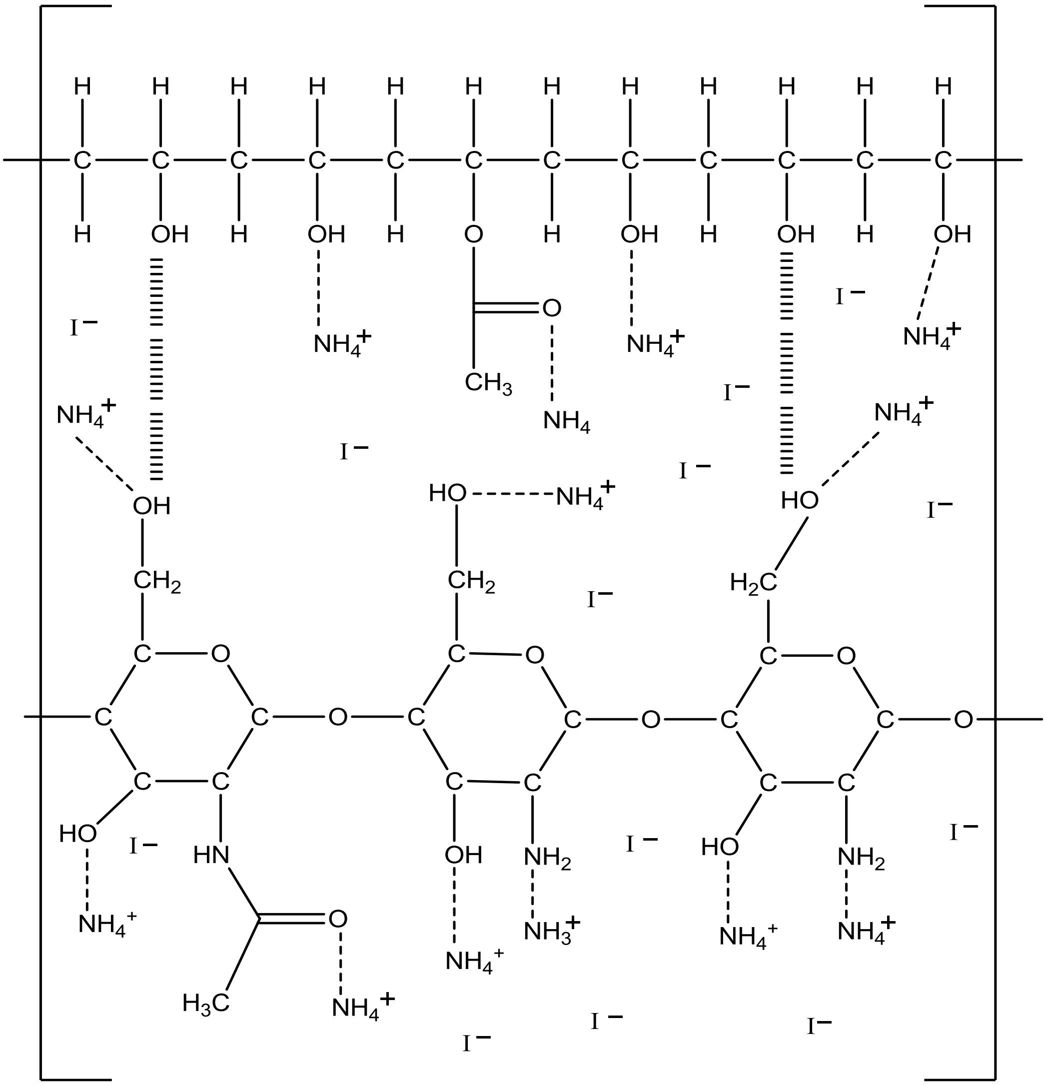

Figure 4.10: Schematic diagram of complexation for (chitosan-PVA)-NH_4I electrolyte

4.6 INFRARED SPECTRA OF (CHITOSAN- PEO) FILMS

Figure 4.11 shows the spectra of pure PEO and pure chitosan films in the region between 900 and 1300 cm^{-1}.

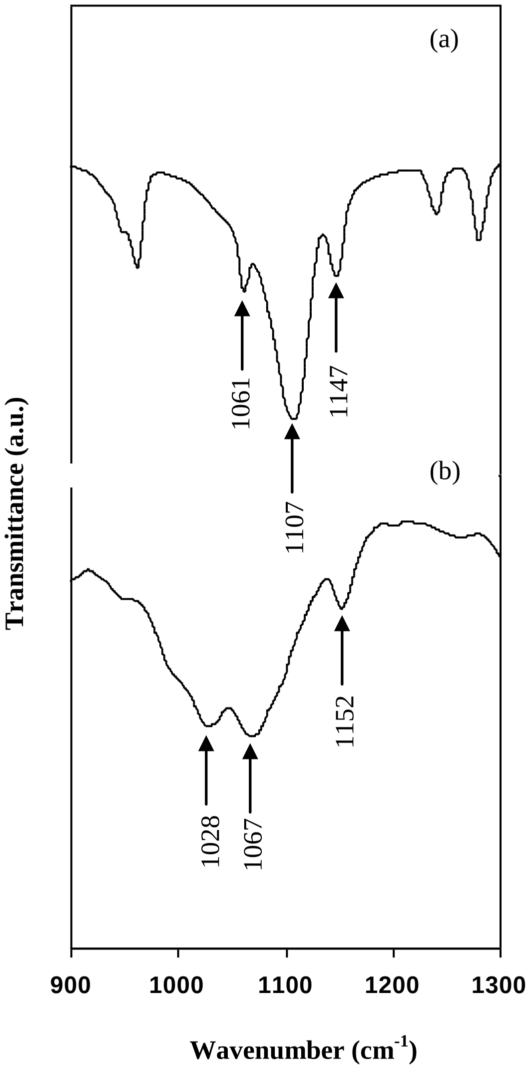

Figure 4.11: FTIR spectra of (a) pure PEO film (b) pure chitosan film in the region between 900 cm^{-1} and 1300 cm^{-1}

From Figure 4.11, the vibrational peak due to the symmetrical C-O-C stretching of pure PEO film is observed at 1061 cm^{-1}, 1107 cm^{-1} and 1147 cm^{-1}, respectively. The C-O-C stretching of pure chitosan is observed at 1152 cm^{-1}.

Figure 4.12 shows the spectra of pure (chitosan-PEO) films in the region between 900 and 1300 cm^{-1}. The C-O-C stretching at 1107 cm^{-1} is observed unchanged in the spectra of pure (chitosan-PEO) films and thus indicates that no interaction occurs between chitosan and PEO. The bands can be considered unshift within the resolution of the spectrometer which has been fixed to 2 cm^{-1}.

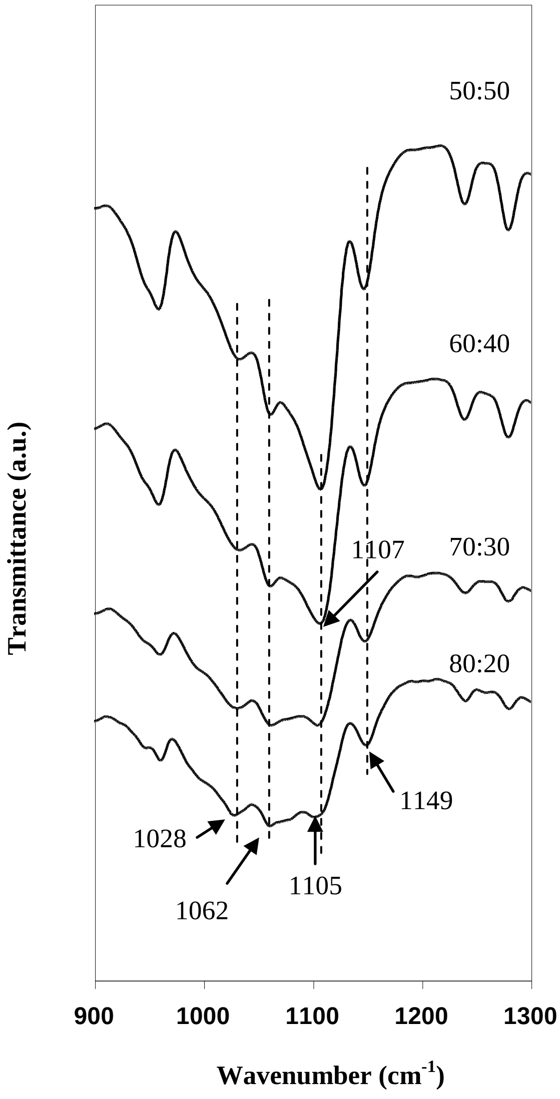

Figure 4.12: FTIR spectra of pure (chitosan-PEO) film in the region of 900 cm^{-1} to 1300 cm^{-1} for several chitosan:PEO ratios

Figure 4.13 shows the spectra of pure (chitosan-PEO) films in the region between 1500 and 1700 cm^{-1}.

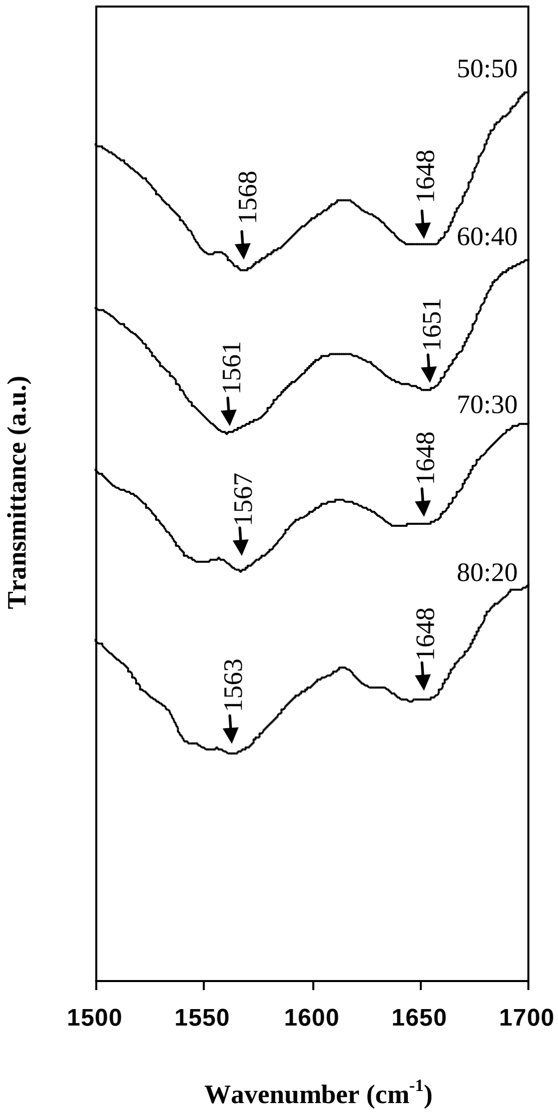

Figure 4.13: FTIR spectra of pure (chitosan-PEO) films in the region of 1500 cm^{-1} to 1700 cm^{-1} for several chitosan:PEO ratios

The carboxamide and amine bands of chitosan in the spectrum of pure (chitosan-PEO) blend electrolyte are shifted slightly to lower and higher wavenumbers as displayed in Figure 4.13. The carboxamide and amine bands of pure chitosan film is observed at 1652 cm^{-1} and 1561 cm^{-1} respectively (Figure 4.1 (b)). The carboxamide band is shifted to 1648 cm^{-1} in the spectrum of 80 wt.% chitosan-20 wt.% PEO film, 70 wt.% chitosan-30 wt.% PEO film and 50 wt.% chitosan-50 wt.% PEO film. The shifting of carboxamide band is attributed to the interaction between chitosan and acetic acid and also hydrogen bonding between CH group of PEO and carboxamide group of chitosan. The amine band is shifted to 1567 cm^{-1} in the spectrum of 70 wt.% chitosan-30 wt.% PEO film and to 1568 cm^{-1} in the spectrum of 50 wt.% chitosan-50 wt.% PEO film due to interaction between chitosan and acetic acid or hydrogen bonding between CH group of PEO and amine group of chitosan. In the spectrum of 60 wt.% chitosan-40 wt.% PEO film, the carboxamide and amine bands are observed at 1651 cm^{-1} and 1561 cm^{-1} respectively. The shifting cannot be observed at these bands for 60 wt.% chitosan-40 wt.% PEO film so no interaction occurred between chitosan and PEO at the carboxamide and amine bands for 60:40 ratio of chitosan-PEO blend.

Figure 4.14 shows the spectra of pure (chitosan-PEO) films that represent the hydroxyl band in the region between 3000 and 3800 cm^{-1}. In the spectrum of pure chitosan film, the hydroxyl band is observed at 3346 cm^{-1} (Figure 4.2 (b)) and it is observed to be shifted to 3360 cm^{-1}, 3356 cm^{-1}, 3357 cm^{-1} and 3365 cm^{-1} in the spectrum of 80 wt.% chitosan-20 wt.% PEO film, 70 wt.% chitosan-30 wt.% PEO film, 60 wt.% chitosan-40 wt.% PEO film and 50 wt.% chitosan-50 wt.% PEO film, respectively. This maybe attributed to hydrogen bonding between the CH group of PEO and hydroxyl group of chitosan.

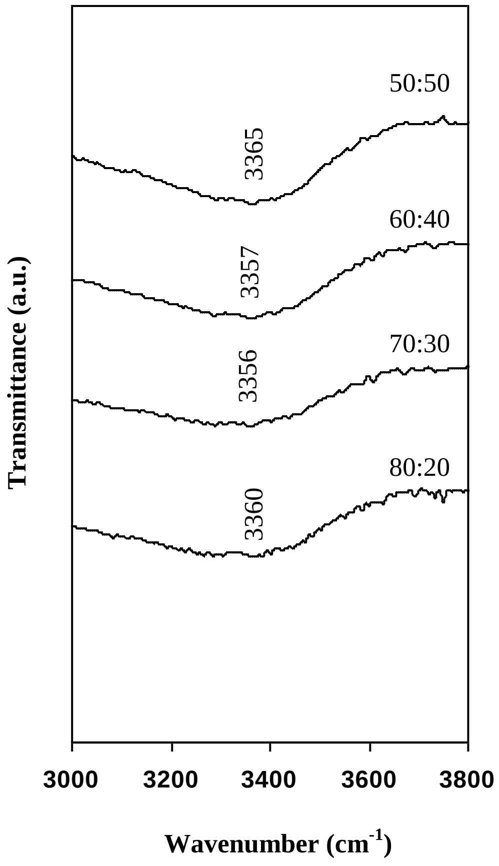

Figure 4.14: FTIR spectra of pure (chitosan-PEO) films in the region of 3000 cm^{-1} to 3800 cm^{-1} for several chitosan:PEO ratios

4.7 INFRARED SPECTRA OF (CHITOSAN-PEO)-NH_4I SYSTEMS

Figure 4.15 presents the spectra of (chitosan-PEO)-NH_4I electrolytes in the region between 900 and 1300 cm^{-1}. Upon the addition of NH_4I, the C-O-C band is clearly observed to broaden and shift to lower wavenumbers. The shift conforms to interaction between the ammonium salt and the lone pairs of the ether oxygen of PEO.

The two shoulders at 1061 cm^{-1} and 1147 cm^{-1} related to crystalline PEO in the spectrum of pure (chitosan-PEO) films are observed to reduce in intensity and almost disappear upon the addition of salt. The 1107 cm^{-1} band has shifted to 1089 cm^{-1} in the spectrum of the sample containing 50:50 chitosan to PEO ratio (27.5 wt.% chitosan-27.5 wt.% PEO-45 wt.% NH_4I). This band shifted to 1069 cm^{-1} in the spectrum of the sample containing chitosan:PEO ratio of 80:20.

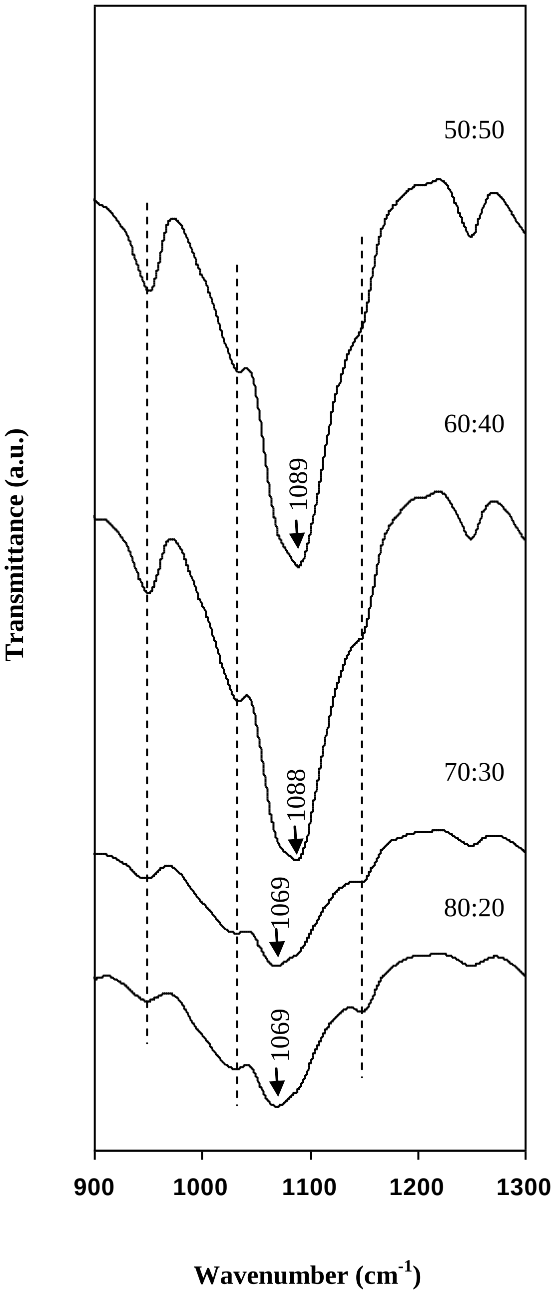

Figure 4.15: FTIR spectra of (chitosan-PEO)-NH_4I in the region of 900 cm^{-1} to 1300 cm^{-1} for several chitosan:PEO ratios

Figure 4.16 depicts the spectrum of (chitosan-PEO)-NH_4I electrolytes in the region between 1400 and 1700 cm^{-1}.

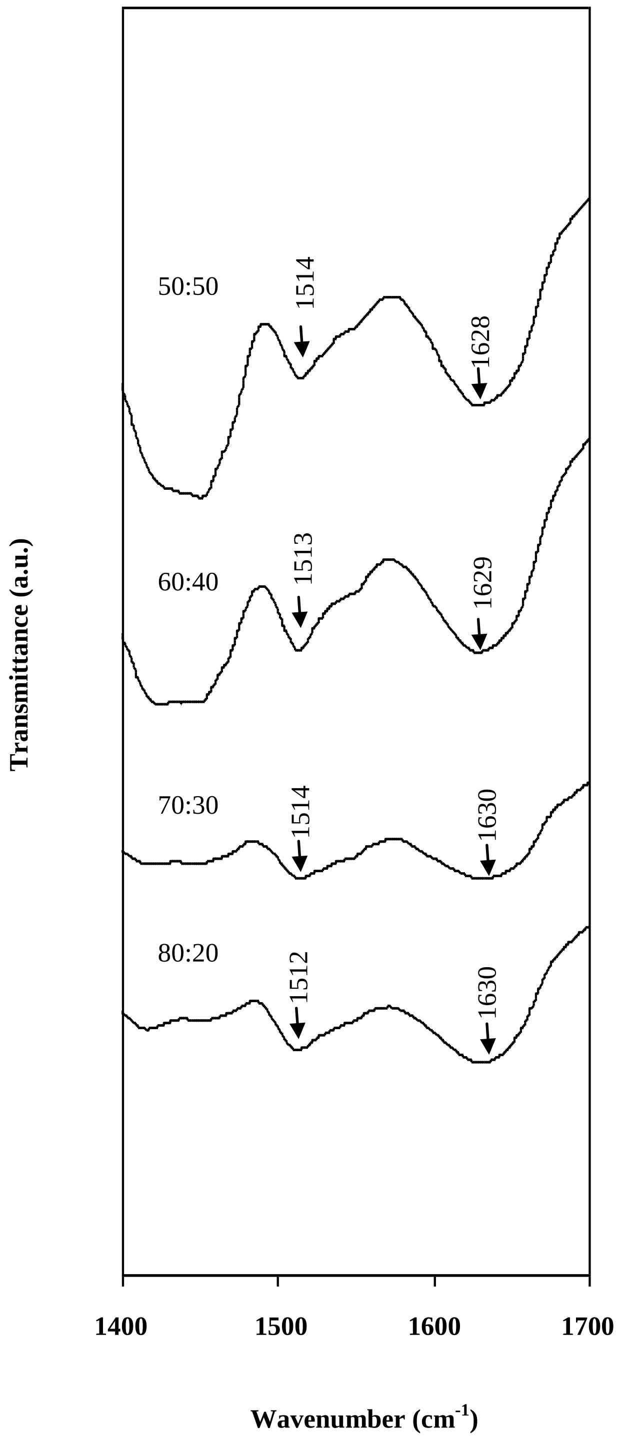

Figure 4.16: FTIR spectra of (chitosan-PEO)-NH_4I in the region of 1400 cm^{-1} to 1700 cm^{-1} for several chitosan:PEO ratios

In the spectrum of (chitosan-PEO)-NH_4I electrolyte, the amine band is observed at 1512 cm^{-1} for (44 wt.% chitosan-11 wt.% PEO)-45 wt.% NH_4I electrolyte, at 1514 cm^{-1} for (38.5 wt.% chitosan-16.5 wt.% PEO)-45 wt.% NH_4I electrolyte, at 1513 cm^{-1} for (33 wt.% chitosan- 22 wt.% PEO)-45 wt.% NH_4I electrolyte and at 1514 cm^{-1} for (27.5 wt.% chitosan-27.5 wt.% PEO)-45 wt.% NH_4I electrolyte. This is observed to be shifted to lower wavenumbers compared to the spectrum of pure chitosan-PEO film with chitosan:PEO ratio of 80:20 at 1563 cm^{-1}, 70:30 at 1567 cm^{-1}, 60:40 at 1561 cm^{-1} and 50:50 at 1568 cm^{-1} which confirms there is interaction between NH_4I and amine group in chitosan. The shift to lower wavenumber can also be observed for the carboxamide band in the spectrum of (chitosan-PEO)-NH_4I electrolyte. This indicates that the complexation also occurred at carboxamide band of chitosan.

Figure 4.17 shows the spectrum of pure PEO film, (30 wt.% chitosan-70 wt.% PEO) film and (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I electrolyte in the wavenumber region between 1300 and 1400 cm^{-1}. The CH_2 wagging of pure PEO film which is attributed to PEO crystalline phase are observed at 1342 cm^{-1} and 1360 cm^{-1} [Sim *et al.*, 2010]. It can be observed that the intensity of the band is reduced in the spectrum of (30 wt.% chitosan-70 wt.% PEO) film and thus making the blend more amorphous than pure PEO film. In the spectrum of (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I electrolyte, the band ascribed to CH_2 wagging is found to decrease in intensity and merge into one broad band at 1350 cm^{-1}. This shows that the crystallinity of the electrolyte is reduced with the addition of salt.

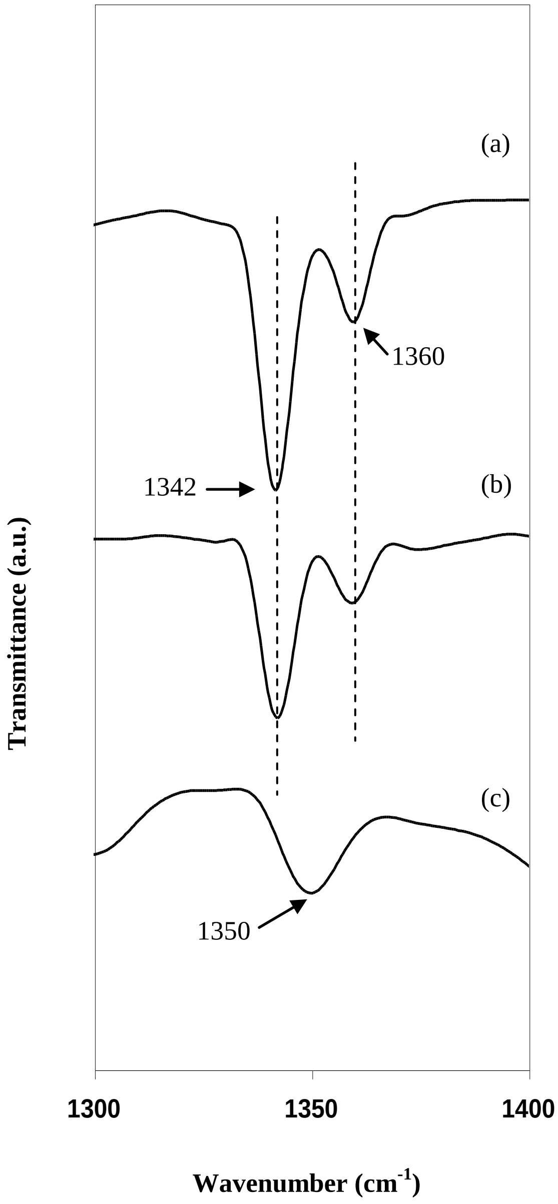

Figure 4.17: FTIR spectra of (a) pure PEO film (b) 30 wt.% chitosan-70 wt.% PEO film and (c) (16.5 wt.% Chitosan-38.5 wt.% PEO)-45 wt.% NH_4I electrolyte in the region of 1300 cm^{-1} to 1400 cm^{-1}

Figure 4.18 depicts the spectrum of (chitosan-PEO)-NH_4I electrolytes in the region between 3200 and 3600 cm^{-1}. The hydroxyl band is observed shifted from 3346 cm^{-1} in the spectrum of pure chitosan film (Figure 4.2 (b)) to 3397 cm^{-1}, 3394 cm^{-1}, 3388 cm^{-1} and 3398 cm^{-1} in the spectrum of 80 wt.% chitosan-20 wt.% PEO film, 70 wt.% chitosan-30 wt.% PEO film, 60 wt.% chitosan-40 wt.% PEO film and 50 wt.% chitosan-50 wt.% PEO film respectively. This maybe attributed to hydrogen bonding between the

CH group of PEO and hydroxyl group of chitosan and also between NH_4^+ and the oxygen atom in the hydroxyl band of chitosan.

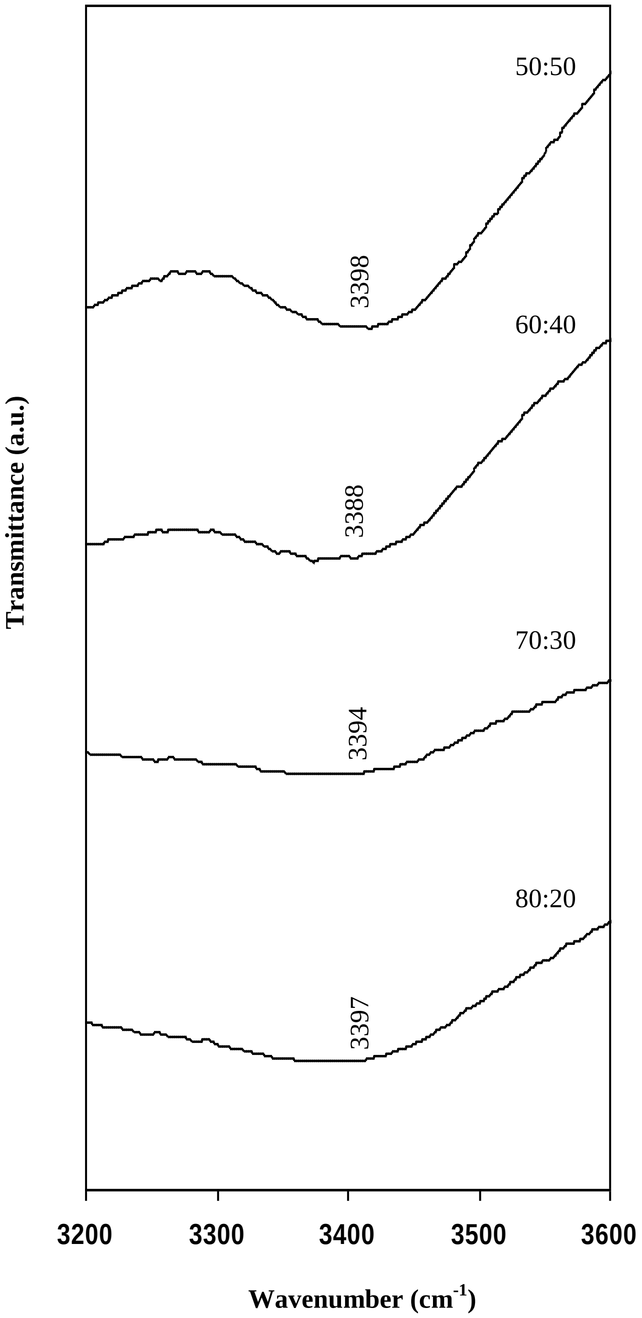

Figure 4.18: FTIR spectra of (chitosan-PEO)-NH_4I in the region of 3200 cm^{-1} to 3600 cm^{-1} for several chitosan:PEO ratios

In summary, the interaction can be depicted as shown below:

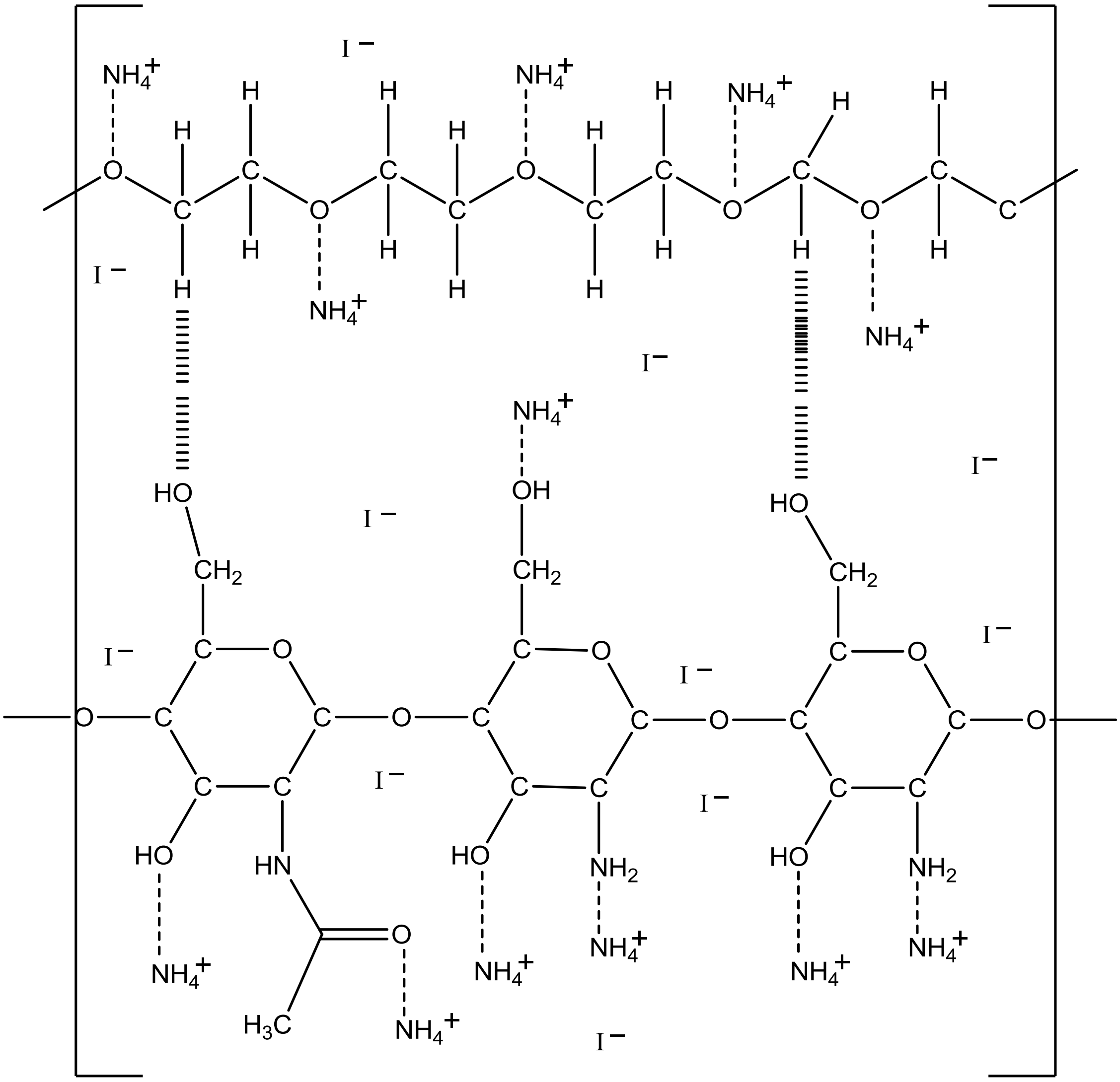

Figure 4.19: Schematic diagram of complexation for (chitosan-PEO)-NH_4I electrolyte

4.8 INFRARED SPECTRA OF CHITOSAN-NH$_4$I-IL SYSTEMS

Figure 4.20 shows the spectrum of chitosan-NH$_4$I-IL electrolytes in the region between 1480 and 1680 cm^{-1}.

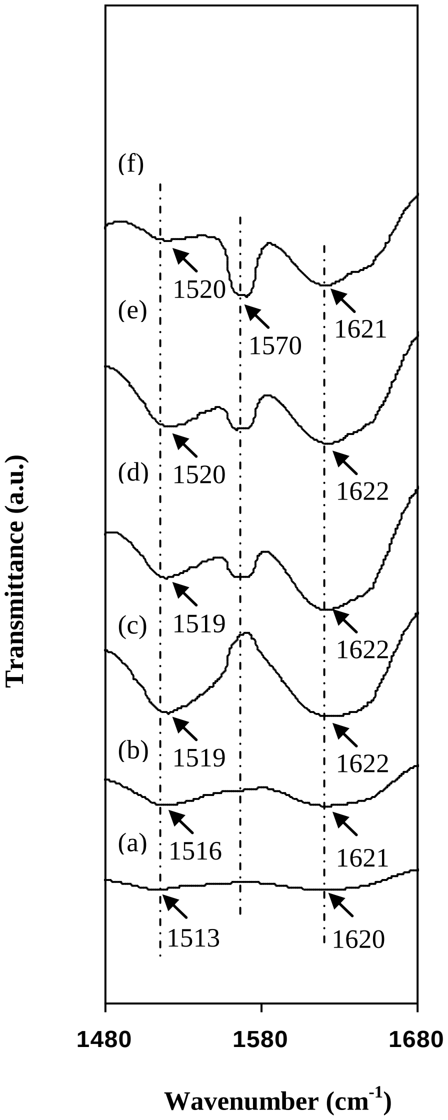

Figure 4.20: FTIR spectra of (a) Ch9 electrolyte (b) 90 wt.% Ch9-10 wt.% IL (c) 80 wt.% Ch9-20 wt.% IL (d) 70 wt.% Ch9-30 wt.% IL (e) 60 wt.% Ch9-40 wt.% IL and (f) 50 wt.% Ch9-50 wt.% IL in the region of 1480 cm^{-1} to 1680 cm^{-1}

In the spectrum of chitosan-NH$_4$I-IL electrolyte, the carboxamide is almost similar with or without IL which is at around 1621 cm^{-1}. No significant shift can be observed at the carboxamide band but the shifting can be observed at the amine band from 1513 cm^{-1} to 1520 cm^{-1}. One additional peak at 1570 cm^{-1} appeared in the spectra of 70 wt.% Ch9-30 wt.% IL, 60 wt.% Ch9-40 wt.% IL and 50 wt.% Ch9-50 wt.% IL . This peak is assigned to imidazole-ν (ring) [Ranga Rao *et al.*, 2009].

Figure 4.21 depicts the spectra of chitosan-NH_4I-IL electrolytes in the region between 3200 and 3600 cm^{-1}.

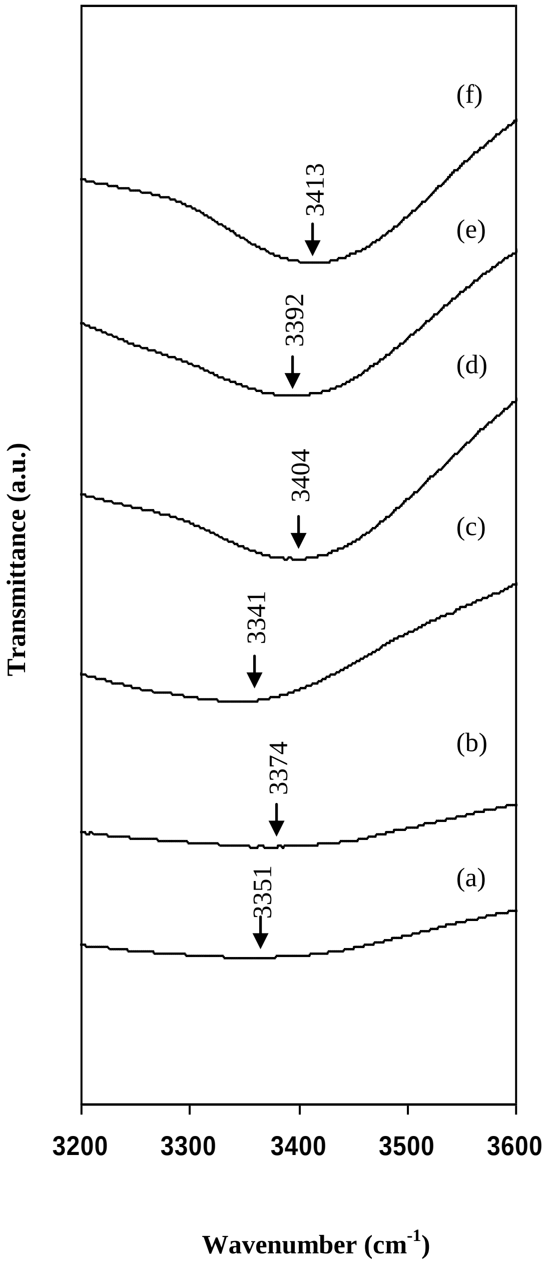

Figure 4.21: FTIR spectra of (a) Ch9 electrolyte (b) 90 wt.% Ch9-10 wt.% IL (c) 80 wt.% Ch9-20 wt.% IL (d) 70 wt.% Ch9-30 wt.% IL (e) 60 wt.% Ch9-40 wt.% IL and (f) 50 wt.% Ch9-50 wt.% IL in the region of 3200 cm^{-1} to 3600 cm^{-1}

The hydroxyl band is shifted slightly to higher wavenumber and observed at 3413 cm^{-1} for 50 wt.% Ch9-50 wt.% IL electrolyte. This is attributed to complexation between ionic liquid and hydroxyl group of chitosan. This complexation is illustrated as below:

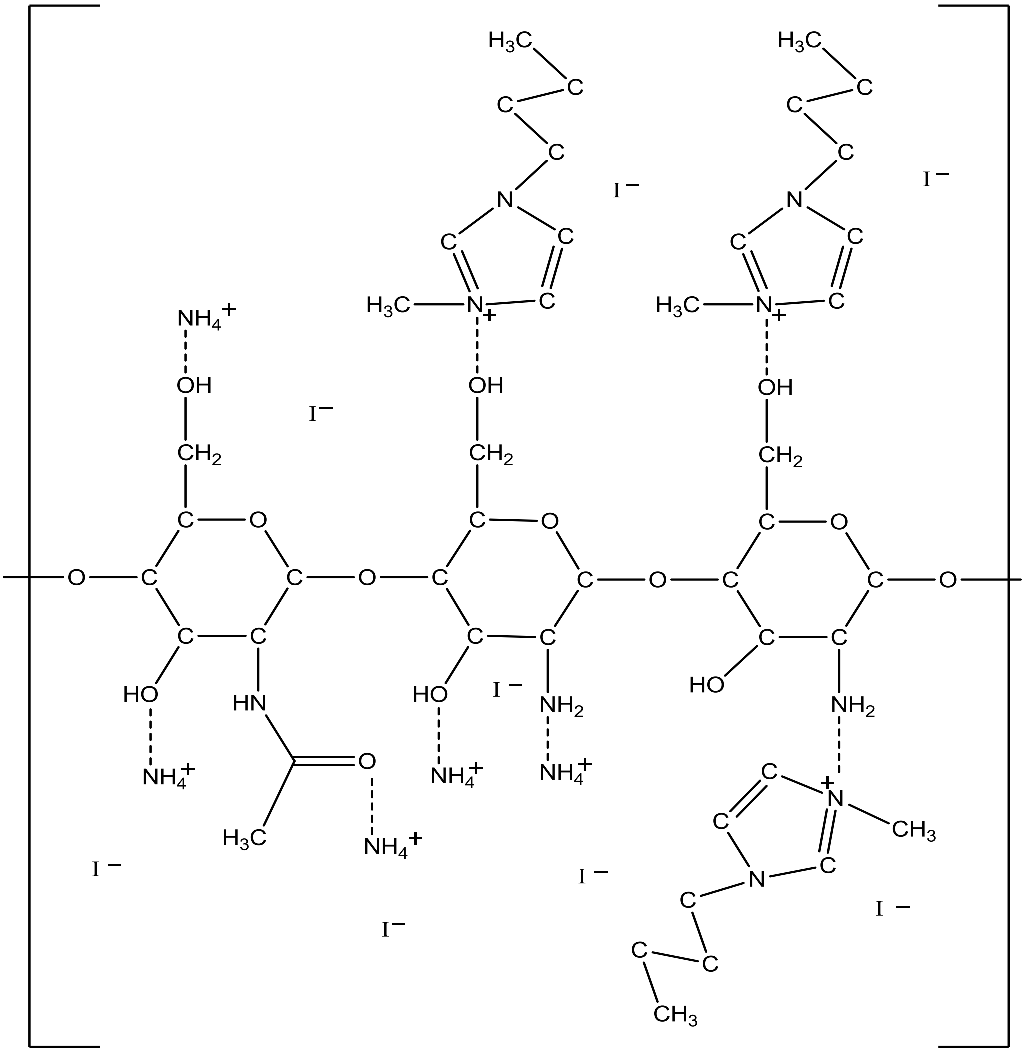

Figure 4.22: Schematic diagram of complexation for chitosan-NH$_4$I-IL electrolyte

4.9 SUMMARY

From FTIR studies, the carboxamide and amine bands of pure chitosan powder shift to lower wavenumbers in the spectrum of pure chitosan film indicating that some interactions have occurred between acetic acid and chitosan at the oxygen atom of carboxamide band and the amino group. This band further shifted to lower wavenumbers with the addition of NH_4I. This confirms that the complexation occurred between NH_4I and the nitrogen atom of the amine band in chitosan. For the chitosan-PVA electrolyte, one additional band due to carbonyl band of PVA is observed to provide more complexation sites for this electrolyte blend. The shift of the carbonyl, carboxamide, amine and hydroxyl bands of chitosan-PVA electrolytes are observed upon the incorporation of NH_4I. Apart from carboxamide and amine bands, shifting of C-O-C stretching is also observed with the addition of salt for (chitosan-PEO)-NH_4I electrolytes. With the incorporation of ionic liquid into the chitosan-NH_4I electrolyte, the interaction between ionic liquid and chitosan-NH_4I electrolyte was observed by the shifting at amine band and hydroxyl band of chitosan.