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Journal of Advanced Research Design

Journal homepage:
https://akademiabaru.com/submit/index.php/ard
ISSN: 2289-7984

Structural Studies of Solid Biopolymer Electrolyte System Based on 2-Hydroxyethyl Cellulose Blend with Ammonium Chloride

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ARTICLE INFO

Article history:
Received 5 April 2024
Received in revised form 13 August 2024
Accepted 10 March 2025
Available online 28 March 2025

Keywords:
Biopolymer electrolytes; ionic conductivity; X-Ray Diffraction (XRD); Fourier Transform Infrared (FTIR)

ABSTRACT

The discovery of solid biopolymer electrolytes (SBE) made of biopolymer materials, 2-Hyroxyethyl Cellulose (2HEC) containing ammonium chloride (NH_4Cl), is presented in this article. The samples were measured using electrochemical impedance spectroscopy (EIS) to determine their ionic conductivities. The sample containing 16% NH_4Cl had the highest conductivity at room temperature, which was 1.74 x 10^{-3} Scm^{-1}. Based on the X-Ray Diffraction (XRD) results, all samples were mostly amorphous. In order to explore the production of biopolymer-based complexes, Fourier Transform Infrared (FTIR) spectroscopy was used to describe the interaction of biopolymer-based electrolyte films. These findings demonstrated the potential of the biopolymer-based electrolyte for use in electrochemical devices.

1. Introduction

A potential electrolyte for solid state electrochemical devices such as super capacitors, fuel cells, batteries, and solar cells is called solid biopolymer electrolyte (SBE) [1-4]. Due to zero electrolyte leakage or fire risk concerns, SBE application in these devices may increase user safety [5-8]. More notably, SBE demonstrates a stand-alone and flexible SBE membrane, which also lightweight, inexpensive, and easy to handle [9-11]. SBE is employed as a medium for ion transport, much as in any electrochemical device application, and also functions as a separator to avoid short circuits [12]. Because of this, SBE has to have an ideal conductivity (a minimum of 10^{-4} Scm^{-1}) before it can be used practically [13]. However, it may be difficult to generate SBE with high ionic conductivity, particularly when utilizing polymers with a natural basis. Various strategies should be taken into account.

Recently, biopolymer electrolytes have attracted a lot of interest because of their potential for biocompatible energy storage uses. Because they are non-toxic, biodegradable, and environmentally friendly, these materials present a possible substitute for traditional electrolytes. The use of

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https://doi.org/10.37934/ard.126.1.1525

biopolymers in energy storage devices is in line with the expanding market for environmentally friendly and sustainable technologies. Biopolymer electrolytes, such those made from pectin and calcium ion crosslinkers, have good mechanical stability and ionic conductivity, which makes them useful for a range of energy storage applications. Additionally, the biocompatibility of these materials guarantees safe use in wearable and medical devices, hence increasing the energy storage solutions' diversity and applicability [14].

With an annual production of around 5 metric tonnes, cellulose (a carbohydrate polymer) is the only naturally occurring polymer that is almost impossible to be deplete [15]. According to Hafiza and Isa [16], cellulose is a non-toxic and biodegradable polymer. One of the cellulose derivatives is 2-hydroxyethyl cellulose (2HEC). Due to its outstanding thickening and stabilizing properties, biocompatibility, strong chemical stability, inclination for adhesion products, and film formation, it has drawn a lot of interest from the industry and a group of researchers [17-19]. 2HEC is a highly water-soluble carbohydrate due to the presence of a hydroxyethyl group (CH_2CH_2OH). These benefits make it possible to create 2HEC as a solid polymer electrolyte. However, the ionic conductivity is rather low when natural polymer material is used in SPE. Thus, SPE's usage in electrochemical devices is constrained [20]. Blending [21,22], copolymerization, insertion of filler or doping material [23,24], and other techniques have all been used to increase the ionic conductivity of polymer electrolytes.

Recent studies have shown that the easiest and least expensive technique to potentially overcome the aforementioned constraint is the introduction of doping materials [3,25]. Since it supplies ions, namely proton (H^+) species, for the conduction process, ammonium salt, such as ammonium iodide (NH_4I), ammonium bromide (NH_4Br), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl), is currently among the high potential doping material in proton conducting electrolyte systems. According to Hema *et al.*, [27] ammonium salt is also regarded as an excellent proton donor that could support proton conduction through the polymer matrix and could promote ionic conductivity to a higher value. Few studies from previous researcher can be seen in Table 1 below.

Table 1
Designation and weight percentage of NH_4Cl salt for SBE samples

2 Hydroxyethyl Cellulose	Ammonium Formate	2.40×10^{-3}	Bokhari *et al.*, [28]
	Ammonium Thiocyanate	1.16×10^{-4}	Ramlli *et al.*, [29]
	Glycolic Acid	3.8×10^{-4}	Ramlli *et al.,* [18]
	Dodecyltrimethyl Ammonium Bromide	2.8×10^{-5}	Ahmad *et al.*, [17]
	Ammonium Nitrate	4.51×10^{-4}	Hafiza and Isa, [16]

Despite extensive studies on cellulose-based SPE, the 2-HEC NH_4Cl SBE system has not been the subject of any reports. Therefore, the current work uses an X-ray diffractometer (XRD) and Fourier transform infrared (FTIR) spectrum to investigate the impact of NH_4Cl on the structural characteristics of 2HEC SBE. To ascertain the SBE's amorphous nature, XRD analysis is performed. The correlation between the structural characteristics and ionic conductivity of 2HEC NH_4Cl was achieved using the study's findings.

2. Methodology
2.1 SBE Preparation

To prepare a thin film of solid biopolymer electrolyte via solution casting technique, 2.0 g of 2-Hydroxyethyl Cellulose, or 2HEC (Sigma-Aldrich Inc., 99.0% purity) was dissolved in distilled water. The 2HEC solution was then dissolved with various amounts of Ammonium Chloride or NH_4Cl (Sigma

Aldrich) ranging from 4 to 24% weight percentage (Table 2), which were then added and mixed until the mixture was homogenous. After full dissolution, the mixture was placed in a petri dish and heated in an oven at a constant temperature of 50°C for a few hours. The films were then placed in a desiccator (filled with silica gel) to continue drying.

2.2 Characterization

Using a Thermo Nicolet 380 FTIR spectrometer, the SBE films have been characterized. A germanium crystal-equipped Attenuated Total Reflection (ATR) accessory was used to measure the spectrometer with a spectra resolution of 4 cm^{-1}. The frequency range of 675 to 4000 cm^{-1} was used to measure the FTIR spectra of the SBE sample.

By using a Rigaku MiniFlexII, XRD patterns were captured at room temperature. SBE were positioned on a glass slide sample holder after being cut into the proper size (2cm × 2cm), thereafter emitting C_uK sources with a diffraction angle of 2θ = 5–60°.

The HIOKI 3532-50 LCR Hi-Tester was used to perform electrical impedance spectroscopy (EIS) in the frequency range of 50 Hz to 1 MHz at various temperatures between 303K and 353K. Between the blocking stainless steel electrodes of a sample container that was linked to a computer, a 2cm x 2cm SBE film was inserted. Eq. (1), where *t* is the thickness and *A* (cm^2) is the electrode-electrolyte contact area of PE films, was used to calculate the ionic conductivity.

$$\sigma = \frac{t}{R_b A} \tag{1}$$

The designation and weight percentage of NH_4Cl salt for each sample can be seen in Table 2. Meanwhile, in Figure 1, the amount of weight (g) for each NH_4Cl salt concentration is shown as in the figure.

Table 2
Designation and weight percentage of NH_4Cl salt for SBE samples

Sample	2HEC (g)	NH_4Cl wt%
2HEC-AC0	2	0
2HEC-AC4	2	4
2HEC-AC8	2	8
2HEC-AC12	2	12
2HEC-AC16	2	16
2HEC-AC20	2	20
2HEC-AC24	2	24

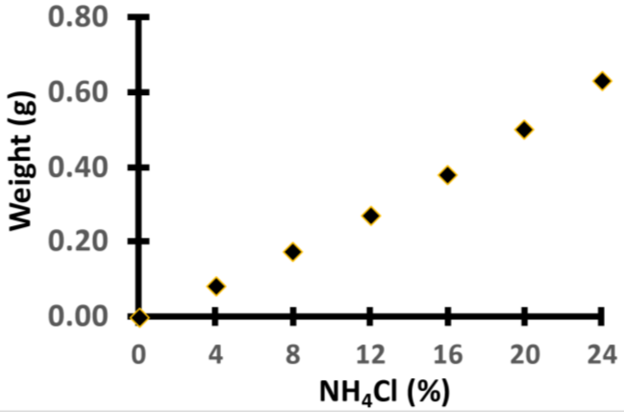

Fig. 1. Weight and NH_4Cl salt concentration for SBE samples

3. Results

3.1 Ionic Conductivity

Figure 2 depicts the physical characteristics of SBE. The SBE that was created showed clear, flexible, and free-standing thin films. Because of these outstanding characteristics, the SBE is ideal for a wide range of applications and is easy to use for characterization.

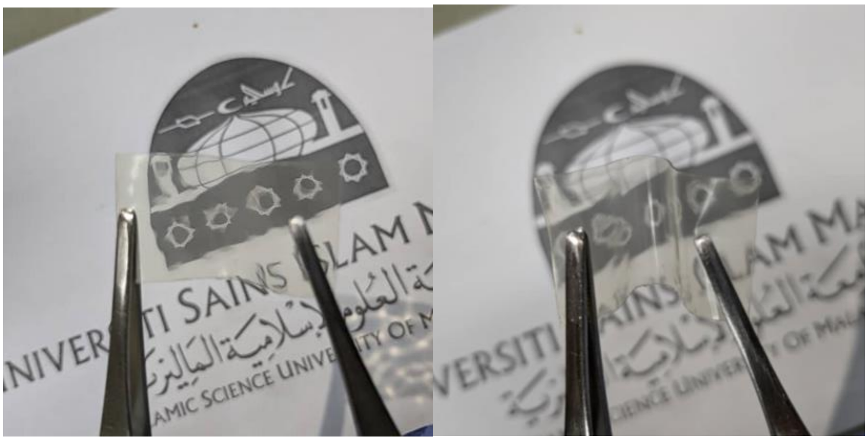

Fig. 2. A clear, free-standing, flexible 2-HEC based SBE

Figure 3 show the Cole-Cole plots for the chosen samples 2HEC-AC0 and 2HEC-AC16.The semicircle and spike region in the Cole-Cole plot for 2HEC-AC0 can be attributed to the SBE's partly resistive and capacitive characteristics. The absence of a semicircle in the Cole-Cole plot for 2HEC-AC16 may indicate increasing ionic mobility [7]. The semicircle and inclined spike can be intercepted using the Z_r-Axis to calculate the bulk resistance (R_b) value. Figure 4 shows the relationship between the ionic conductivity and NH_4Cl salt content of the SBE samples at room temperature. According to Figure 4, the ionic conductivity of the SBE rose when 4, 8, and 12% NH_4Cl concentrations were added and fell after NH_4Cl concentrations reached 16 wt%. The 2HEC-AC16 SBE sample had the greatest ionic conductivity, which was 1.74 x 10^{-3} Scm^{-1}.

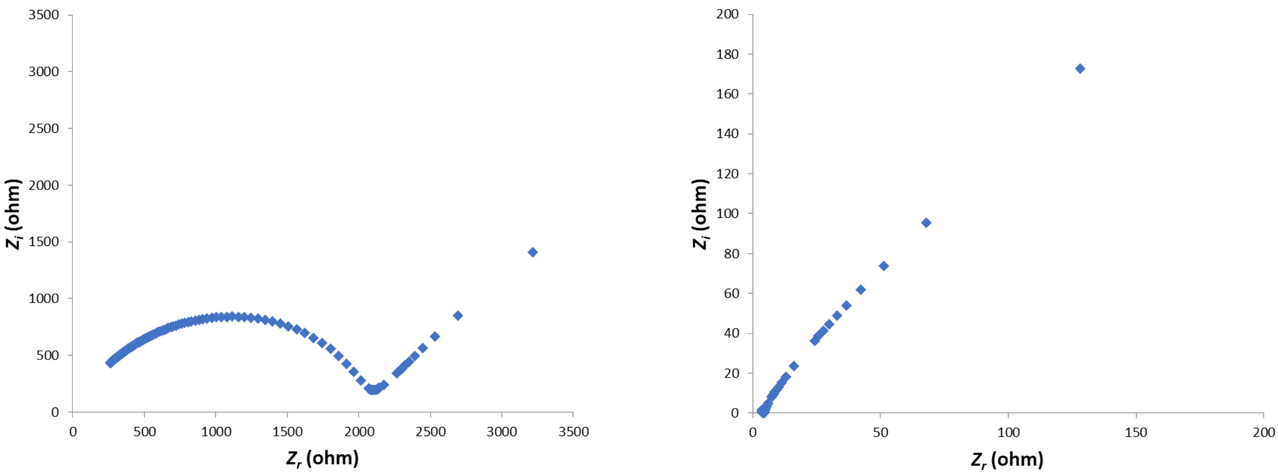

Fig. 3. Cole-Cole plot 2HEC-AC0 (left) and 2HEC-AC16 (right)

The interaction between 2HEC and NH_4Cl caused the dispersion of the proton, H^+ in the polymer salt systems, which led to the increase in ionic conductivity with the addition of NH_4Cl concentration. As a result of the dispersion, it boosts the SBE samples' ionic conductivity and quantity of mobile ions

[30]. However, it was shown that the ionic conductivity decreased when more than 16 wt% of NH_4Cl was added due to the free ions' dispersion. Ionic conductivity in the SBE system decreases as a result of these free ions forming clusters and impeding the flow of additional free ions [31].

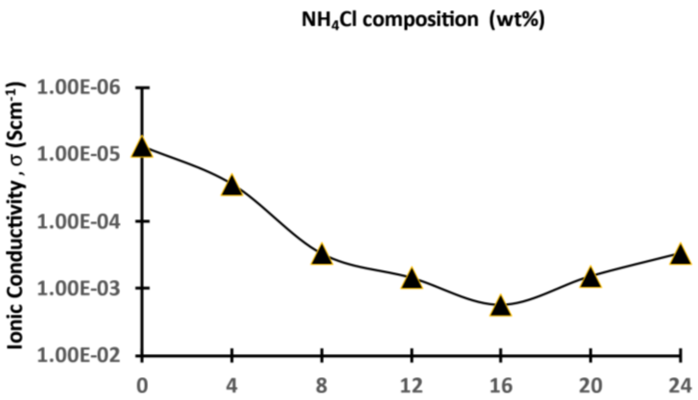

Fig. 4. Ionic conductivity of SBE at room temperature

3.2 XRD Analysis

The X-ray diffraction pattern of NH_4Cl salt at room temperature is shown in Figure 5. The XRD pattern for pure NH_4Cl salt revealed strong polycrystalline peaks at 23.25°, 32.95°, 47.50°, 53.05°, and 58.50°. For pure 2HEC (Figure 6), amorphous hump between 2 = 20° and 30° was seen in the 2HEC sample. For XRD patterns, amorphous hump (which refers to this wide peak) is an indication of amorphous materials [32].

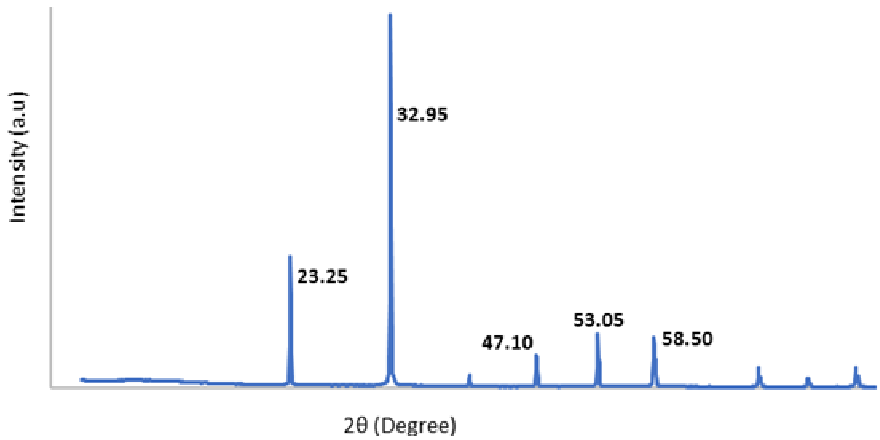

Fig. 5. XRD diffraction of NH_4Cl

The X-ray diffraction pattern of SBE samples with various NH_4Cl weight percentages is shown in Figure 6. When NH_4Cl salt was added to the SBE samples, the polymer's amorphous peak widened. The amorphous character of the SBE samples is shown by the enlarged amorphous hump [33]. However, there were few crystalline peaks that emerged from the NH_4Cl salt may be observed plainly. The presence of a clear, sharp peak at 8 wt% and 24 wt% of NH_4Cl, for example, at 2θ = 23.16°, 32.86°, 40.48°, and 58.44°, confirms the substance's crystalline form. These peaks suggest that the polymer was unable to solvate the salt, which would cause the crystallinity of SBEs to increase. As more crystalline peaks appeared, it would affect the performance of the conductivity of SBE. The addition of NH_4Cl to the SBE samples exhibited a semi-crystalline structure, according to the XRD data in Figure 6. The SBE samples' wide amorphous peaks and the presence of poly-crystalline peaks suggested that 2HEC-NH_4Cl had complexed with or interacted with the polymer-salt system. The 2HEC-NH_4Cl interaction in the SBE system has been further studied using FTIR analysis. 2HEC is a suitable matrix for SBEs due to its exceptional film-forming qualities and well-known flexibility. Its mechanical strength, meanwhile, might be a drawback in particular situations. Our goal is to increase the mechanical strength by forming NH_4Cl crystals by adding NH_4Cl to the 2HEC matrix.

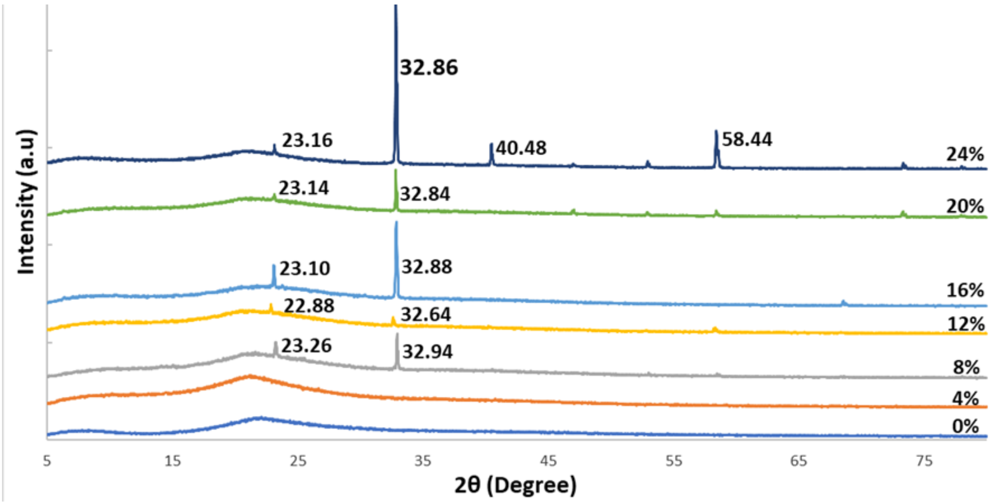

Fig. 6. XRD diffraction of SBE at various concentrations

The NH_4Cl crystallization in the 2HEC matrix can function as a reinforcing mechanism by giving the polymer structure more stiffness from the crystals. This reinforcing effect is comparable to fillers' function in composite materials, where the dispersed phase improves the matrix's mechanical characteristics. Comparable results have been documented in earlier research, wherein the addition of inorganic fillers to polymer matrices led to considerable increases in mechanical strength [34,35]. Our observation shows that the tensile strength and modulus of the 2HEC matrix are considerably enhanced by the addition of NH_4Cl crystals. This improvement is due to the NH_4Cl crystals' capacity to support loads, which more efficiently distributes stress throughout the composite. This observation is consistent with the findings of [36], who found that the mechanical characteristics of polymer matrices are improved by the presence of crystalline phases. According to Kim *et al.,* [37], these enhancements result in increased SBE stability and longevity, especially in battery applications where mechanical integrity is essential.

To prevent potential problems like brittleness, it is crucial to regulate the degree of NH_4Cl crystallization. The performance of the SBE in applications requiring flexibility and mechanical resilience may suffer from excessive crystallization, which can reduce flexibility [38].

Here, A_c = crystalline region, A_a = amorphous region, and χ_c = degree of crystallinity (%). As can be observed from Table 3, the addition of NH_4Cl content decreased the SBEs' degree of crystallinity. The percentage of crystallinity is inversely correlated with the amorphousness of the SBE, which means that a drop in χ_c corresponds to an increase in amorphousness of the SBEs, according to [39]. Due to the lowest value of χ_c, 2HEC-AC16 exhibits the highest degree of amorphousness in this work. This lends even more credence to the research that shows the SBEs' increased amorphous character as a result of the ammonium salt addition. The sample with 16 wt% NH_4Cl has the highest ionic conductivity. The reason behind this is the SBE's amorphous form, which facilitates ion diffusion and lowers the energy barrier for segmental motion of the polymer system, enabling free ions to flow more easily and increasing ionic conductivity.

Table 3
Degree of crystallinity of SBE samples

Sample	A_C	A_a	χ_c (%)
2HEC-AC4	10607	24265	43.71%
2HEC-AC8	6896	16775	41.11%
2HEC-AC12	6094	15203	40.09%
2HEC-AC16	5334	14421	36.99%
2HEC-AC20	4598	10469	43.92%
2HEC-AC24	5253	11102	47.32%

3.3 FTIR Analysis

The complexation of 2HEC and NH_4Cl was observed during FTIR measurement. Figure 7 depicts the FTIR spectra of a pure 2HEC and 2HEC-NH_4Cl systems. O-H stretching's broad absorption peak, which was originally at wavenumber 3383 cm^{-1}, has moved to wavenumber 3362 cm^{-1}. The peak becomes more intense as the concentration increases. When 12 wt% of NH_4Cl was added (2HEC-AC12), a new peak of primary amine (N-H) was seen at 3248 cm^{-1}, and when 24 weight percent of NH_4Cl was added (2HEC-AC24), it relocated to 3227 cm^{-1}. The appearance and movement of the N-H peak in the O-H region suggested that the oxygen atom's lone pair electron in 2HEC and the H^+ ion from NH_4Cl salt interacted [16]. According to Ahmad and Isa [40], 3041 cm^{-1} of the ammonium ions in NH_4Cl can be attributable to N-H stretching. As the concentration rises, the intensity starts to increase and can be detected at 3041 cm^{-1}, indicating that there has been interaction between the polymer host and salt. When ammonia (from NH_4Cl) is introduced, the water component intensities drop at peak 1638 cm^{-1}. However, the decline is constrained by the water molecules in the NH_3 solvated species [17]. C-H bending deformation (1459 cm^{-1}) was seen in Figure 7. It should be noted that the addition of NH_4Cl composition caused the intensity of C-H bending to dramatically rise from 18% and shift to a lower wavenumber of 1438 cm^{-1} as shown in Figure 7. The shifting of the C-H bending is less pronounced than the bending from the hydroxyl group. These bands appear to have developed as a result of interactions, which were likely coordinated by NH_4^+ ions and had an impact on other bands [41]. For 2HEC, a vibration frequency of 1459 cm^{-1} has been determined for C-H bending deformation. As for the FTIR spectra for 2HEC-NH_4Cl complexes, the relevant peaks have been moved to 1438 cm^{-1}. The vibration positions that were found were nearly identical to those that had been reported in earlier research by Monisha *et al.*, [3] and Hafiza and Isa [16]. This work unequivocally shows that the interaction between 2-HEC and NH_4Cl took place at the oxygen atom's lone pair electron at the end of the hydrocarbon chain (C-O bond) of 2HEC [16]. The peak at 1051cm^{-1} in Figure 7 represents the C-O stretching of CH_2OH. The peak now measures to be shifted to 1055 cm^{-1}. This has been further supported by Hafiza and Isa [16], who used gaussian analysis which predict the vibration frequency for 2HEC, where the C-O stretching for 2HEC was determined to be at 1055 cm^{-1}.

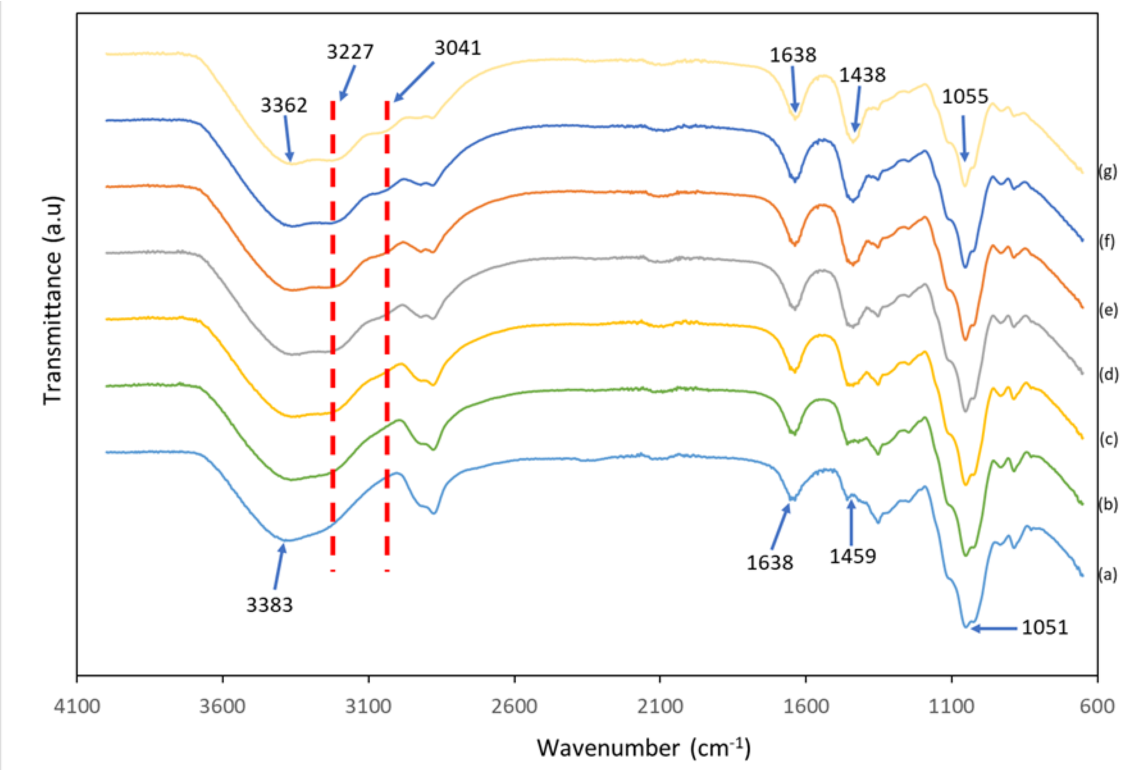

Fig. 7. FTIR spectra for 2-HEC SBE with (a) 0-NH_4Cl; (b) 4-NH_4Cl; (c) 8-NH_4Cl; (d) 12-NH_4Cl; (e) 16-NH_4Cl; (f) 20-NH_4Cl and (g) 24-NH_4Cl composition

4. Conclusions

By using the solution casting process, a novel class of solid biopolymer electrolytes based on 2HEC doped with NH_4Cl has been effectively applied. The impedance study revealed that adding 16% wt% NH_4Cl enhanced the ionic conductivity (2HEC-AC16). At room temperature, the highest conductive sample, 2HEC-AC16, with a conductivity of 1.74×10^{-3} Scm^{-1}, was obtained. The SBE samples are semi-crystalline in character, according to XRD examination. The FTIR analysis's revelation of shifting and appearing/disappearing bands demonstrated the presence of interactions in the polymer-salt system. Based on the findings, the 2HEC- NH_4Cl SBE system was recognized as a proton conductor.

Acknowledgement
This research was funded by grants USIM 19123.

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