




High ion conducting and thixotropic nature of water-soluble xanthan gum-based electrolytes

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Abstract. This research reports the preparation and characterization of xanthan gum (XG)-based gel electrolytes (GEs) comprising sodium hydroxide salt (NaOH) in deionized water (DW). The three-dimensional gel network has been formed without using any synthetic polymer or cross-linking agents. Ionic conductivity of GEs was evaluated with different parameters, such as salt concentration, gum concentration, temperature and with the passage of time. The maximum ionic conductivity of 74.8 mS cm^{-1} was observed at room temperature even after 55 days for XG-based GE containing 0.625 M NaOH . A small change in pH values for XG-based GEs have been observed with temperature in the range of $10\text{--}70^\circ\text{C}$ and at different time span. Thixotropic behaviour of GEs under the application of stress has also been analysed by rheological studies. There was no discernible change in ionic conductivity with temperature and with the passage of time, which make it desirable for their use in different device applications.

Keywords. Xanthan gum; gel electrolyte; ionic conductivity; pH; thixotropic behaviour.

1. Introduction

Gel electrolyte (GE) is a mixture of diverse components, i.e., salt, solvent and polymer, in which ions for conduction are provided by salt on dissolving in solvent, whereas polymer enhances the mechanical stability of GE by providing rigid backbone. Mostly GEs have been prepared and characterized by using different lithium salts (like LiBF_4 , LiPF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiClO_4 , etc.) due to their electrochemical stability and applicability in different solid-state ionic devices like solar cells, supercapacitors, sensors, fuel cells, etc. [1,2]. However due to limited availability, costlier, highly flammable, hygroscopic and toxic nature of lithium salt, various alternative efforts have been made time to time by different researchers. The proton conducting electrolytes have been studied due to their higher mobility than that of alkali/alkaline metal salt-doped gels [3]. A large number of GEs containing strong acids (like H_2SO_4 , H_3PO_4 , HNO_3 , HCl , etc.) have also been synthesized and studied, but these are not so promising towards device applications as it degrades the polymers. In order to overcome this difficulty, aromatic and aliphatic carboxylic acids have been used in GEs as these do not degrade polymer and also provides H^+ ions on dissociation [4,5].

In spite of these, hydrogels are also promising category of proton conducting GEs due to three-dimensional cross-linking network, which shows high elasticity, strength and memory to composition [6]. These hydrogels have been reported as super-absorbent materials with high ionic conductivity and can be classified as physically strong or weak on basis of their flow in steady state [7–9]. Thus, researcher's developed keen interest to synthesize environment friendly and non-toxic polysaccharide material-based electrolytes. These polysaccharide material-based natural gums (like gum tragacanth, karyya gum, rosin gum, gum acacia, xanthan gum (XG), etc.) are exuded from different gum trees and plants [10,11]. These materials have high molecular weight and adjacent *cis*-hydroxyl groups attached to one or more monosaccharide units that provide conductive gels along with sufficient mechanical strength in gel phase used in various fields like gelling agent, emulsifying agents and component of biomedical electrodes in diagnostic [12–14]. Natural gums or polysaccharide-based materials is a family of biopolymers, composed of multiple monosaccharide units joined with each other through glycosidic linkages have been studied and reported since 1934 with their unique features like low, medium and high molecular weights, linear and branched structures, biodegradable, water soluble or

insoluble properties, low toxicity/non-toxic in nature, environmentally safe, non-immunogenic, etc. [15,16]. Natural gums also provide three-dimensional crosslinking in GE that holds water with the ability to retain salt and tends to impart viscous and flexible gel matrix with improved mechanical strength, whereas the degree of crosslinking may be affected with reaction conditions such as temperature, pH, time of reaction, agitation, crosslinking agents, etc. [6,12]. Natural gum-based biopolymeric electrolytes with and without salts and their applications in various devices like proton batteries, dye-sensitized solar cells, fuel cells, etc. have been reported by various researchers [10,17–23]. A few literatures about XG-based hydrogels used as electrolyte with and without NaOH salt has been reported [10,17,22,24–27]. XG dissolved in water containing sodium hydroxide has been used as gels due to its special properties like biocompatible, biodegradable, high ionic conductivity, better thermal and mechanical stability. Keeping in view of these properties, XG-based GEs containing NaOH salt have been prepared and characterized through variation of ionic conductivity with salt concentrations, gum contents, temperature and time span in the present study. The effect of temperature on pH has also been discussed for these electrolytes. The gel rheology has also been examined to study the flow of these gels under applied stress.

2. Experimental

XG (in powder form) and NaOH pellets were obtained from Sigma-Aldrich and LOBA Chemie, India, respectively, and used as raw materials. Deionized water (DW) was used as a solvent with ionic conductivity of 7×10^{-3} mS cm⁻¹. XG-based GEs were prepared by using step process. In the first step, liquid electrolyte by dissolving an appropriate concentration of salt into DW with continuous stirring has been prepared. In the second step, GE was obtained by gradual addition of XG in liquid electrolyte with continual stirring at room temperature to maintain homogeneity. Digital weighing balance (Shimadzu, ATX 124) was used to measure the weight of XG and NaOH contents with an accuracy up to four decimal places. The conductivity measurements of the prepared samples have been performed in closed system by using WTW conductivity meter (Model: 3210), which is based upon four-probe method with $\pm 1\%$ accuracy in conductivity and $\pm 1^\circ\text{C}$ accuracy in temperature. pH metre (Model: S-210) from Mettler Toledo was used to measure pH values of liquid as well as GEs at different temperatures and time span. Thixotropic behaviour was studied by using Rheolab QC Rheometer (Anton paar, Germany) at room temperature to study variation of gel viscosity with time under the application of stress.

3. Results and discussion

3.1 Ionic conductivity

Room temperature variation of ionic conductivity for liquid electrolyte at different concentrations of NaOH in DW has been studied and the results obtained have been illustrated in figure 1. Figure 1 reveals that the ionic conductivity of liquid electrolytes is much higher (≥ 1 mS cm⁻¹) than that of pure solvent (DW; $\sigma \sim 7 \times 10^{-3}$ mS cm⁻¹). With an increase of salt (NaOH) concentration up to 2 molar, a linear increase in conductivity has been observed that may be due to the ionic dissociation of salt in liquid electrolyte, resulting in an increase in the number of free charge carriers as according to the relation:

$$\sigma = nq\mu,$$

where σ represents the ionic conductivity, μ be the ionic mobility, n be the number of free charge carriers and q is the charge on an ion. However, at higher salt concentrations (>2 M), deviation in linearly increasing conductivity value has been observed, which can be explained with ‘mass action considerations’ [28,29]. According to mass action model, linear behaviour suggests the availability of free ions and deviation from linearity indicates the aggregation of ions along with free ions. The maximum ionic conductivity of 416 mS cm⁻¹ has been obtained at 5 M NaOH concentration in DW. Above 5 M NaOH concentrations, a small decrease in conductivity was observed and is so probably due to aggregation of ions, presence of undissociated salt and increase in viscosity of liquid electrolyte.

Figure 2 shows the variation in ionic conductivity of GE with varying content of XG in DW at room temperature. From this figure, it has been observed that conductivity of XG-based GE shows a linear increase up to 1 wt% of gum content at room temperature. This may be due to the liberation, transportation and continuous interactions of free

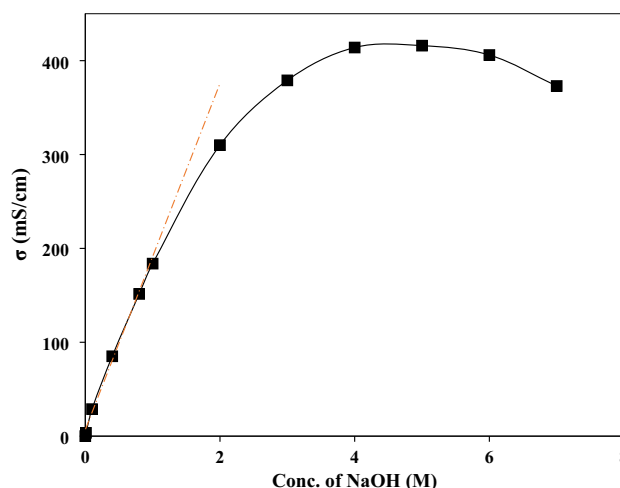


Figure 1. Room temperature variation of ionic conductivity for liquid electrolyte at different concentrations of NaOH salt.

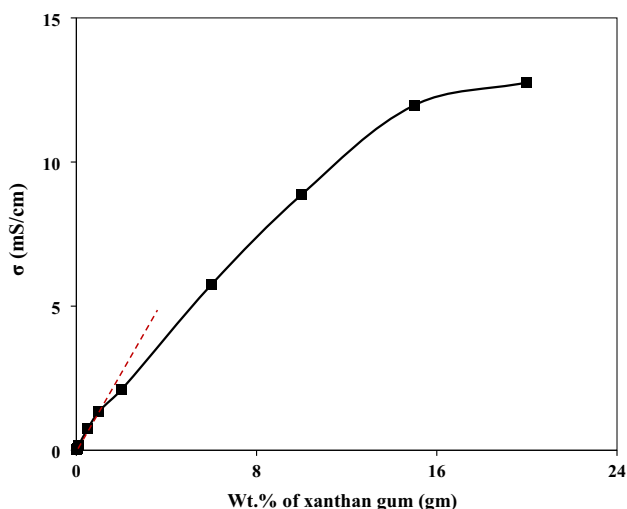


Figure 2. Conductivity variation of xanthan gum-based gel electrolyte without salt at different contents of xanthan gum at room temperature.

ions (H^+ , OH^- , H_3O^+ , etc.) in gel matrix due to swelling of gum in the water, as XG pertains abundant hydroxyl groups [24]. Further incorporation of XG contents (>1 wt% XG) enhances the viscosity of GE, resulting the deviation of conductivity from linear behaviour [9,30]. Also, ionic conductivity variation of XG-based GEs at different molarities of NaOH has also been studied as a function of XG concentration and the outcomes are manifested in figure 3. Figure 3 shows the higher ionic conductivity of GE containing high concentration of salt (5 M) as compared to low salt concentration (0.625 M), which is due to the dissociation of more number of ions at higher concentration of salt in gel matrix. Also, the conductivity decrement with the addition of different contents of XG at both concentrations of salt in GEs has been observed and has already been explained due to increase in viscosity of GEs with the incorporation of XG. The enhanced viscosity leads to lower

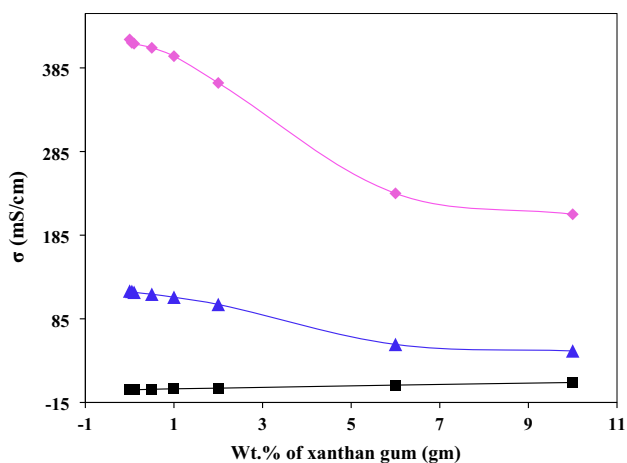


Figure 3. Room temperature conductivity comparisons of xanthan gum-based gel electrolytes with {0.625 M (\blacktriangle) and 5 M (\blacklozenge)} and without (\blacksquare) NaOH salt at different contents of xanthan gum.

values of mobility and thus conductivity as according to the relation: $\mu = q/6\pi\eta r$, where μ is the ionic mobility, q be the charge on an ion, η be the viscosity and r be the radius of ion [31]. Whereas, viscosity of gel matrix often depends upon temperature, hydration period, polysaccharide concentrations, pH, ionic strength of the electrolyte and the type of agitation employed [13].

Conductivity behaviour of XG-based GEs has been analysed with the rise in temperature. The variation of log conductivity with reciprocal temperature has been represented in figure 4. From figure 4, the decrease in ionic conductivity with an increase of temperature has been noticed that may be due to the evaporation of DW that tends to reduce the availability of medium for ionic movement, which is inconsistency with the Arrhenius concept, i.e., $\{\sigma = \sigma_o \exp(-E_a/k_B T)\}$ [32,33]. Figure 4 also represents the following conductivity pattern for XG-based GEs for different compositions:

$$\sigma(DW-0.625\text{ M NaOH-XG}) > \sigma(DW-0.015\text{ M NaOH-XG}) > \sigma(DW\text{-XG}),$$

which suggests that the incorporation of salt enhances the number of mobile ions and hence ionic conductivity. Time reaction plays an important role to define the electrochemical stability of gel. Therefore, room temperature variation of conductivity for XG-based GEs with and without NaOH has been measured at different time spans and the results are shown in figure 5. From figure 5, it has been noticed that ionic conductivity of GE without salt, increases with the passage of time and after certain time period (~ 39 days), the conductivity attains saturation. This may be because of continuous interactions of H^+ , H_3O^+ , OH^- , etc. ions in gel matrix and the existence of pressure fluctuations that has already been explained by ‘breathing polymer chain model’ by Chandra *et al* [4]. According to

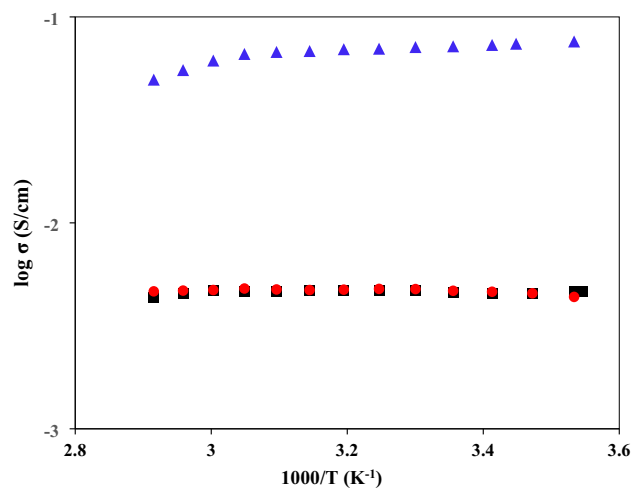


Figure 4. Temperature-dependent ionic conductivity of xanthan gum-based gel electrolytes comprising of DW-5 wt% XG (\blacksquare), DW-0.015 M NaOH-5 wt% XG (\bullet) and DW-0.625 M NaOH-5 wt% XG (\blacktriangle).

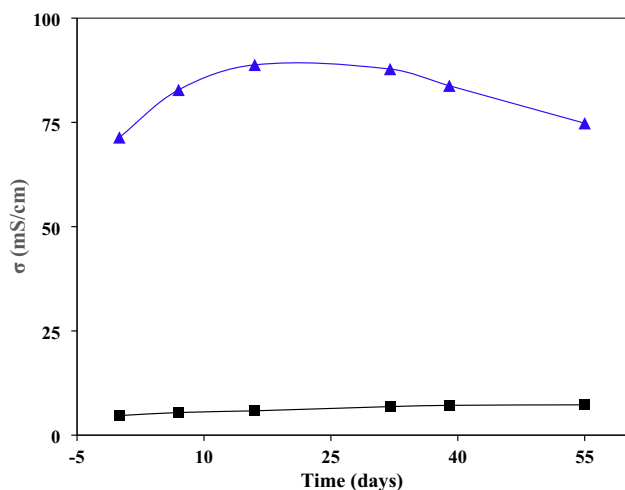


Figure 5. Ionic conductivity variation of xanthan gum-based gel electrolytes with (▲) and without (■) NaOH salt as a function of time at room temperature.

this model, the polymeric chains are supposed to breath in or out, as these get open or fold leading to change in volume occupied by polymeric chains. The change in volume further exert pressure on neighbouring ions and dissociate ion aggregates, which results an increase of charge carriers and ionic mobility. After certain period of time; these pressure fluctuations settle down, resulting in stable conducting region. Lawrence *et al* [6] synthesized gum-based GEs, which provide better strength and the ability to retain moisture, imparting spongy quality that do not degrade its structure [6] and making them suitable for various device applications [3,34,35].

GE comprising 0.625 M NaOH shows an increase in ionic conductivity followed by a small decrease with the passage of time at room temperature. However, the overall change in ionic conductivity value for this GEs is very less (change of 3 mS cm⁻¹) over a time period of 55 days that make it suitable for device applications like fuel cell, supercapacitor, solar cell, etc.

3.2 Thixotropic study

Viscosity measurements for XG-based GEs at different gel compositions: DW-5 wt% XG (Red), DW-0.015 M NaOH-5 wt% XG (Blue) and DW-0.625 M NaOH-5 wt% XG (Black) were performed with the passage of time at low as well as high shear rate and the results have been shown in figure 6. The process consists of three stages depending upon the implementation of shear rate. Initially in the first stage, a shear rate of 1 s⁻¹ was applied to a sample kept for 25 s then increased to 80 s⁻¹ held for 75 s during second stage. But in the third or final stage, the shear rate was again shifted to the initial value (i.e., 1 s⁻¹) and held for 250 s.

A sharp decrease in viscosity under the effect of high shear rate (80 s⁻¹) was observed, which may be attributed due

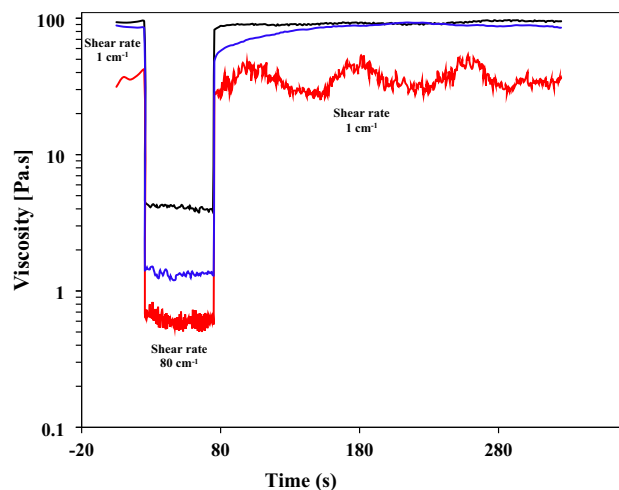


Figure 6. Viscosity measurements for DW-5 wt% XG (black), DW-0.015 M NaOH-5 wt% XG (red) and DW-0.625 M NaOH-5 wt% XG (blue) with the passage of time by varying shear rate.

to the segmental motion of polymer chains at high shear rate. This segmental motion may result in breaking of secondary bond interactions and thus gel to sol transition takes place. Whereas the shifting of shear rate from high to low value (i.e., 80–1 s⁻¹) resulted in time-dependent structure recovery ratio as shown in table 1. The structure recovery process was however slower at small time interval (after 10 s) as molecules in motion requires some time to restructure. Thus, sol again shifted to gel after removing the shear stress [36,37] and the viscosity values for GEs under the application of stress have been given in table 1. It was found that after 10 s, the structure recovery ratio become fast for the sample containing DW-5 wt% XG (92.29%). With the addition of salt at low concentration (0.015 M), the structure recovery ratio decreased to 73.32% and distorted curve was observed, which shows that the viscoelastic behaviour of the gel is reduced with the incorporation of salt at lower concentration in gel matrix. But the structure recovery ratio has been found to increase, i.e., 91.63% after 10 s for gel containing high salt concentration (i.e., 0.625 M), which may be due to increase in viscosity and implies improvement in viscoelastic behaviour of GE [38]. However, after 60 s the structure recovery ratio attained even higher value as compared to small time interval (10 s), which could be due to the fact that GE needs some time to regain initial structure/viscosity after lowering of shear rate or removal of shear stress as mentioned above. Thus, thixotropic study of these GEs depicts that high structure recovery ratio suggesting the viscoelastic behaviour of these gels that remains maintained even in the presence of NaOH salt.

3.3 pH measurements

pH variation of XG-based GEs as a function of temperature, salt concentration and time has been studied. pH values for

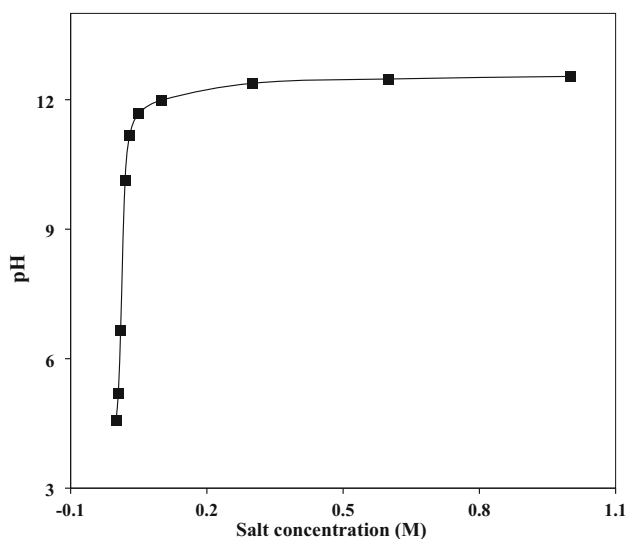
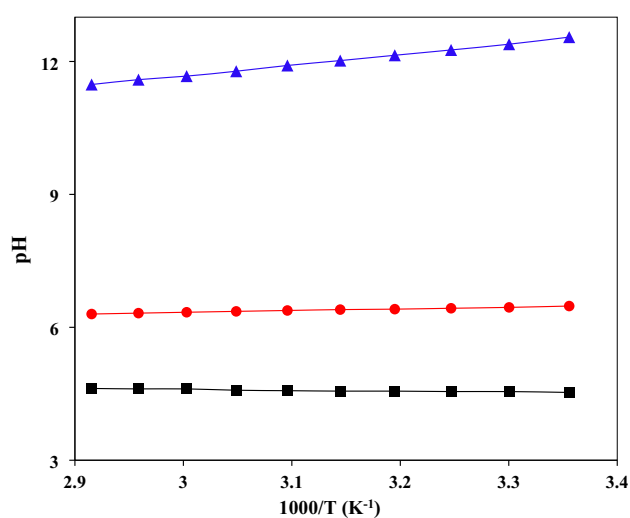
Table 1. Structure recovery ratio, viscosity, conductivity and pH values for xanthan gum-based gel electrolytes at room temperature.

Sample	Structure recovery ratio (after 10 s of removing stress)	Structure recovery ratio (after 60 s of removing stress)	Viscosity (Pa. s) under applied stress (shear rate 80 s^{-1})	Viscosity (Pa. s) after removing stress (shear rate 1 s^{-1})	Ionic conductivity (mS cm^{-1}) at 30°C	pH at 30°C
DW-5 wt% XG	92.29%	94.18%	4.61	81.9	4.69	4.55
DW-0.015 M NaOH-5 wt% XG	73.32%	90.37%	0.68	27	4.77	6.45
DW-0.625 M NaOH-5 wt% XG	91.63%	109.52%	1.42	47.9	71.4	12.39

XG-based GEs have been measured at different concentrations of NaOH and the results obtained have been recorded in figure 7. From figure 7, it has been noticed that, pH of DW shifts from near neutral region (6.31) to acidic (4.55) at room temperature with the addition of XG contents, probably is a result of the release of H^+ ions from carboxylic groups linked with gum chains. Whereas, pH of GE containing DW-XG again shifted to near neutral region (6.65) with the incorporation of low concentration (i.e., 0.01 M) of NaOH salt, as dissociation of salt provides OH^- ions that neutralize H^+ ions. Also, with the addition of high salt concentration, pH shifted towards basic region and GE containing 0.6 M of NaOH salt possessed the pH value of 12.48, which may be due to the liberation of higher number of OH^- ions. Further, the effect of temperature on pH for different GEs {gel compositions: DW-5 wt% XG (Black), DW-0.015 M NaOH-5 wt% XG (Red) and DW-0.625 M NaOH-5 wt% XG (Blue)} was analysed and the outcomes

are illustrated in figure 8. Figure 8 reveals that pH of GEs (i.e., DW-0.015 M NaOH-5 wt% XG and DW-0.625 M NaOH-5 wt% XG) decreases with an increase in temperature from 10 to 70°C . Increase of temperature may lead to the depletion of OH^- ions in gel matrix by getting neutralized with water as well as carboxylate ions connected to gum chains. Along with this, deprotonation of water takes place with increase of temperature that may be due to decrease in ionization constant. Both these factors play a vital role for enhancing free H^+ ions [12,39]. Whereas for the gel system without salt, comprising of DW-5 wt% XG, undergoes negligible increase in pH with an increase of temperature.

Figure 9 also illustrates the change in pH for GEs with the passage of time for 54 days. The study reveals that for GE without salt, pH shifts from acidic to neutral region after a certain period of time (31 days) followed by saturation over longer time period. Whereas, GE comprising 0.625 M NaOH

**Figure 7.** Room temperature variation of pH for xanthan gum-based gel electrolyte at different concentrations of NaOH salt.**Figure 8.** Temperature-dependent pH for gel electrolytes including DW-5 wt% XG (■), DW-0.015 M NaOH-5 wt% XG (●) and DW-0.625 M NaOH-5 wt% XG (▲).

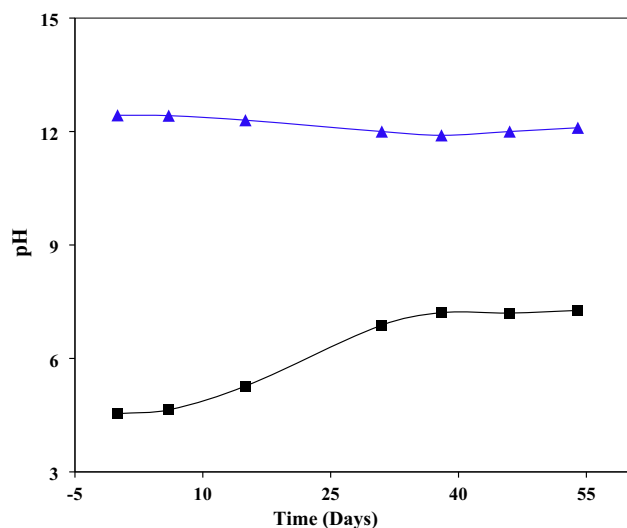


Figure 9. Room temperature variation of pH for gel electrolytes with (▲) and without (■) NaOH salt with the passage of time.

salt shows a little decrement in pH (from 12.5 to 12) after 31 days and then attains saturation. This saturation of pH for GEs over a longer period of time may be due to the relaxation of pressure fluctuations among the polymeric chains [4], which is desirable for their use in device applications.

4. Conclusion

Ionic conductivity of XG-based GEs containing different concentrations of NaOH decreases with the addition of XG contents. GEs having high salt concentration (5 M) shows higher ionic conductivity in comparison to that of containing low salt concentration (0.625 M NaOH) at all gum contents. A small change (factor-wise) in ionic conductivity as well as pH with the passage of time has been observed for GE containing 0.625 M salt concentration. Also, a small change in pH values of GEs has been recorded with an increase of temperature. On the other end, GEs reflect thixotropic nature under the effect of applied shear rate. Furthermore, the viscosity enhancement of GE with increase in salt concentration from 0.015 to 0.625 M has been observed, which reflects sol to gel transition. A small conductivity variation of GE incorporated with 0.625 M NaOH salt has been observed with temperature as well as time that make them applicable for their desirable use in many devices.

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