ISSN: 2521-8107, June-2017

Temperature Dependency of the Swelling of Biopolymer gel

Israt Kabir[1]

Abstract-- Experimental investigations for the effect of temperature on swelling behavior in pure water of a biopolymer gel formed from Gellan were performed. The Gellan gel was prepared without any added salt. The swelling behavior of the gel was extensively studied by observing the swelling ratio as a function of time for various gel concentrations by changing the temperature of immersing water. The data were interpreted in terms of the equilibrium swelling ratio, Q_{eq}. Results suggest that with increasing concentration of Gellan gel, the swelling ability decreases which can be interpreted as being due to restricted mobility of the gellan polymer chains due to further associations of the chains induced by the metallic ions. On the other hand swelling ability of gellan gel decreases with the increase in temperature of water which can be attributed as being due to decrease in the solvent quality with the increase in temperature which may restrict water molecule to penetrate through the gel medium.

Keywords: Gellan gel, Effect of temperature, Equilibrium swelling ratio.

1. Introduction

Gellan gum is a water-soluble exocellular heteropolysaccharide gum produced by a pure culture fermentation of a carbohydrate by the micro Sphingomonas elodea [1], purified by recovery with isopropyl alcohol, dried and milled. The gellan is composed of tetrasaccharide repeating units. Its structure consists of four linked monosaccharides-one molecule of rhamnose, one molecule of glucoronic acid and two molecules of glucose.

Gel samples are usually prepared by dissolving a small amount of gelling agent in a liquid, usually by warming. This gelation involves the formation of double helical junction zones followed by a Gellan gumregation of the double helical segments to form a three-dimensional network by complexation with cations and hydrogen bonding with water [2]. The small, discrete cross-links are distributed through the covalently

1 Lecture, American International University-Bangladesh (AIUB), Banani israt@aiub.edu

cross-linked gel. This property leads to formation of gel with longer, flexible elastic chains and different swelling behavior. Designing slow-release devices for oral drugs in pharmaceutical industries and using in cosmetic ingredients, for producing storable foods in agricultural industry and in medical applications for developing artificial organs, the knowledge of the swelling kinetics of gel is important

Recently our group had investigated swelling behavior of gellan gel with different concentration immersed in aqueous solutions of monovalent (KCl), divalent ($CaCl_2$) and trivalent ($AlCl_3$) cations. Results suggest that the swelling ability of gellan gels drastically decreases in electrolyte solutions in comparison to that of pure water. Metallic ions showed significant effect on further association of gellan chains and thus restrict the gel to swell. This study also reveals that these gels were swelled in pure water and KCl solution but showed a shrinking tendency in $CaCl_2$ and $AlCl_3$ and the swelling ability of the gellan gels can be reduced by adding these salts in water where the gels are immersed. However this study was concluded at a fixed room temperature. It will be extremely necessary to see the swelling phenomenon for these gellan gels at several different temperatures as a function of time. The main objective of our present study is to see the effect of temperature on gel swelling as a function of time.

2. Experimental

I. Material

In this work, gellan gum was used as raw material which was donated by San Ei-Gen chemical industries, Osaka, Japan as the third common sample in the sodium form (NaGG-3) The metal content of dry gellan was analyzed as Na=0.42%, K=5.03%, Ca=0.37% and Mg=0.09% by a liberty inductively coupled plasma optical emission spectrometry (ICP-OES) system (Varian Inc. Palo Alto, CA, USA).

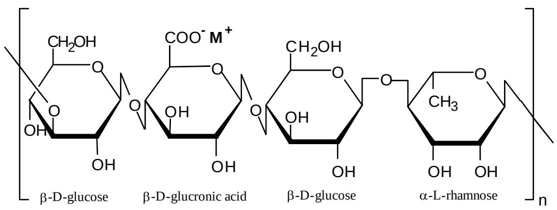


Figure: 1 Chemical structure of Gellan Gel.

II. Preparation of gellan gels

At first, powdered gellan gum was measured and mixed with necessary amount of distilled water in a conical flask for the required concentration of the gel. The powder was mixed properly with a magnetic stirrer in the conical flask. The cap of the conical flask was sealed by Teflon & adhesive tape and placed on the magnetic heater to be heated up for one hour at 90ºC. The heated solution was then poured instantaneously inside a cylindrical mould of length 15mm and diameter 10mm and kept at room temperature for half an hour. In the mean time, a sol-gel transition was occurred inside the cylinder mould and a cylindrical shape gel was taken out from the mould which was then ready for the investigation.

III. Method

At first, the initial weight of cylindrical shape gel was measured and was immersed in 50ml of distilled water to swell inside the water for 300 minutes at 25ºC. When the gel is immersed in water, the polymer chain becomes elongated due to flexibility of the chains so that the volume as a whole increases to some extent. Then the gel was removed from water and weighted again. The procedure was repeated until a constant weight was achieved. In the present study, the change in volume is so small that it is very difficult to measure the volume change precisely. Therefore we considered the weight swelling ratio which is equivalent to the volume swelling ratio.

The weight swelling ratio, Q of the gel was calculated by taking the ratio of the weight of the swollen gel, W_b to the weight of the gel before swelling, W_a and given by the following equation:

$$Q = \frac{W_b}{W_a}$$

The constant swelling ratio is known as the equilibrium degree of swelling, Q_{eq}.

The same procedure was repeated by increasing the temperature of water to 27ºC, 29ºC and 31ºC with three different concentrations of gel such as 3wt%, 4wt% and 5wt%.

3. Result and discussion

The swelling behavior of the gellan gels was studied as a function of time with different concentration of the gellan polymer and different temperature of immersing water.

Figure-2 shows the variation of swelling ratio of gellan gel for different concentrations of 2.5 wt%, 3 wt%, 4 wt% and 5 wt% as a function of time up to 300 minutes at temperature 25^{o}C.

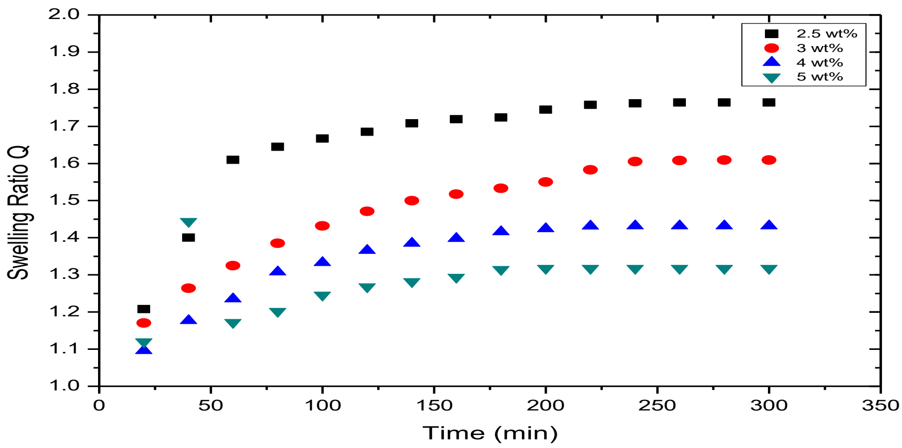
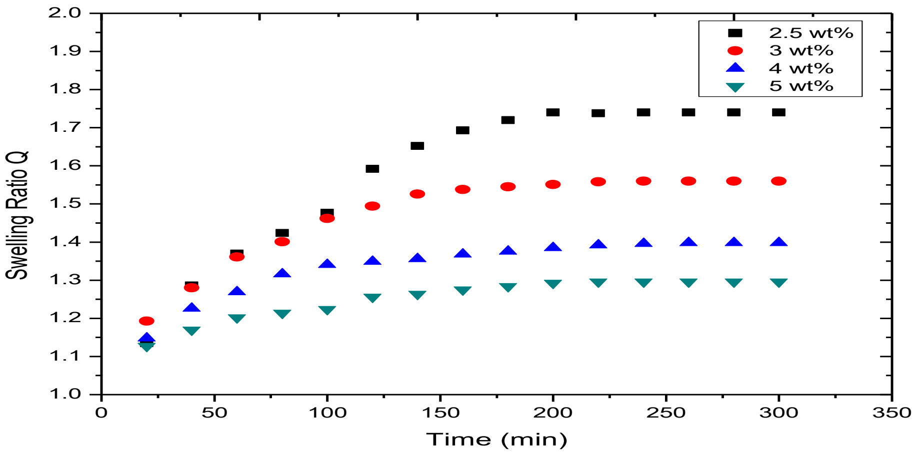


Figure-2: Plots of swelling ratio as a function of time for various gel



concentrations at temperature 25^{o}C.

Figure-3: Plots of swelling ratio as a function of time for various gel concentrations at temperature 27^{o}C.

For 2.5 wt% of concentration, the tendency of a sharp increase of swelling ratio with time upto 60 minutes was observed. After that the swelling ratio reached at an equilibrium state after 260 minutes. The reason for this equilibrium state is that the pressure and the solvent chemical potential of the gel converge to stable values that are equal to the bulk solvent pressure and chemical potential [4].

For 3 wt% of the gel concentration the swelling ratio approaches at equilibrium state after 280 minutes. As the concentrations were increasing, the equilibrium swelling ratio was observed earlier. The swelling ratios of the gels with concentrations 4 wt% and 5 wt% were increasing slowly compared to that of 2.5 wt% and 3 wt% of gellan gel. However, the swelling behaviors at different temperatures were quite similar for all concentration of the gellan gel as shown from figure-3 to 5. It is important to mention that in every case, the swelling ratios were greater than 1 which means that the gels were always swelling and no sign of shrinking was found.

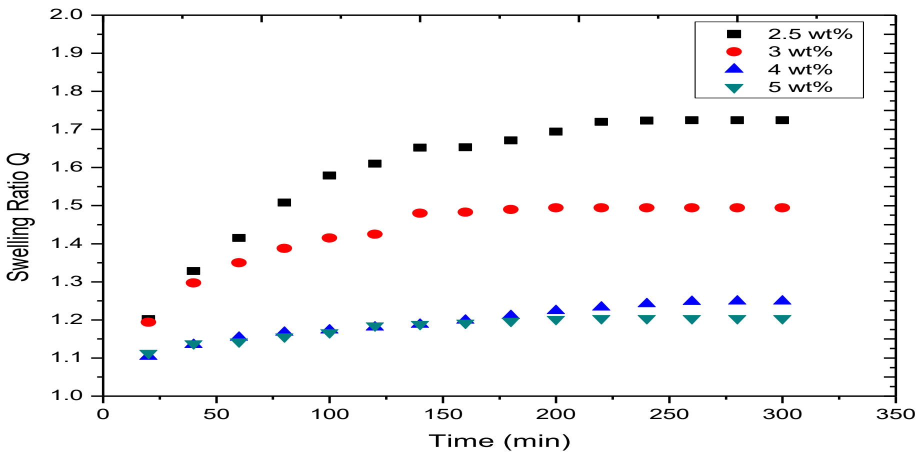


Figure-4: Plots of swelling ratio as a function of time for various gel concentrations at temperature 29^{o}C.

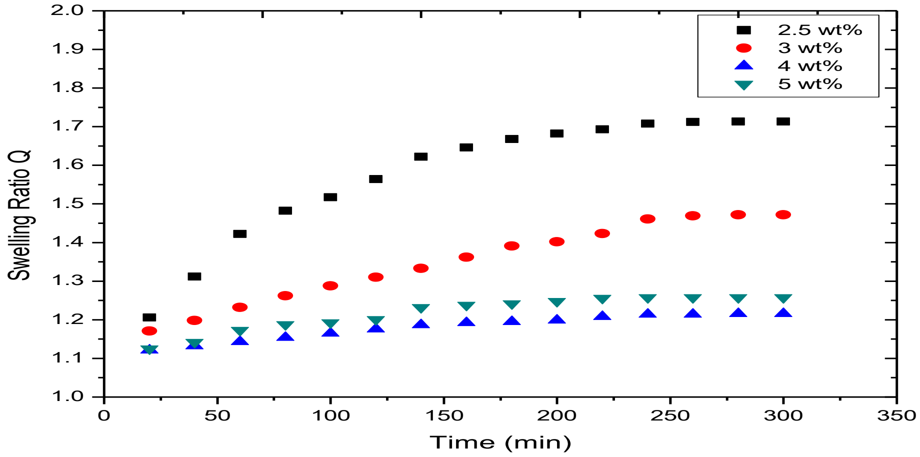


Figure-5: Plots of swelling ratio as a function of time for various gel concentrations at temperature 31^{o}C.

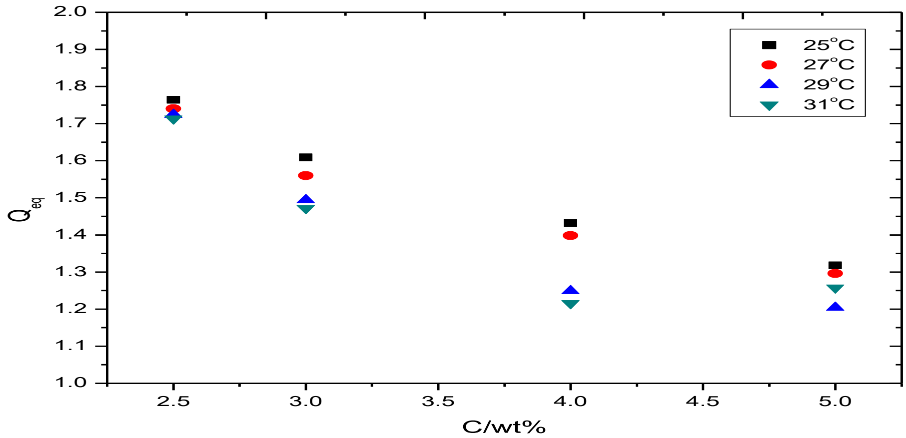


Figure-6 shows the value of the equilibrium swelling ratio as a function of gel concentration at different temperatures.

The equilibrium swelling ratio takes the maximum value at C_{gel}=2.5wt% and exponentially decreases with increasing gellan concentration and finally reached at a constant value. For low concentration of gel, since the inter chain spacing of network is high, the equilibrium swelling ratio has also large value and vice versa.

Figure-6: Plots of equilibrium swelling ratio as a function of gel concentration for different temperature.

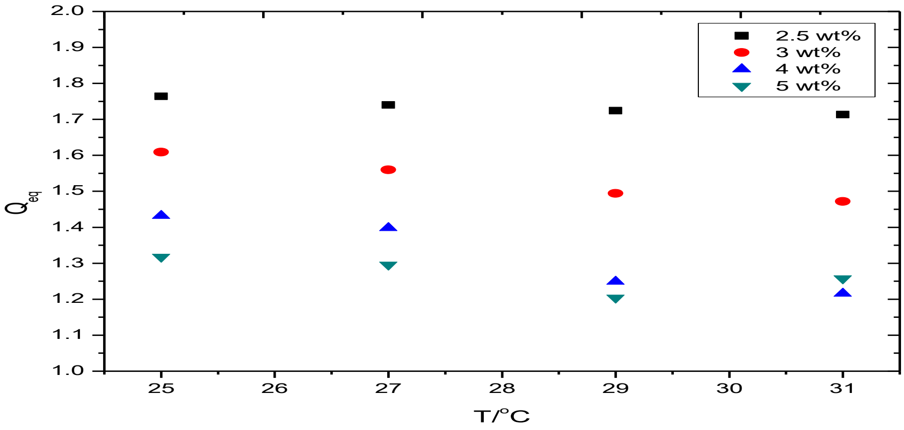


Figure-7: Plots of equilibrium swelling ratio as a function of temperature for different gel concentration.

Figure-7 demonstrates the behavior of equilibrium swelling ratio as functions of temperature for different gellan samples with concentrations from *C*=2.5wt% to 5.0wt%. For 2.5 wt% of gellan gel, when the temperature was raised from 25°C to 27°C, the equilibrium degree of swelling was decreased by 1.36%. As the temperatures were raised from 27°C to 29°C and from 29°C to 31°C, the equilibrium degrees of swelling were decreased by 0.91% and 0.63% respectively.

With the gellan gels of concentration 3 wt%, when the temperature was raised from 25°C to 27°C, from 27°C to 29°C and from 29°C to 31°C, the equilibrium degrees of swelling were decreased by 3.04%, 3.97% and 1.73% respectively. When the temperature was raised from 25°C to 27°C, from 27°C to 29°C and from 29°C to 31°C of a 4 wt% of gellan gel, the equilibrium degrees of swelling were decreased by 2.37%, 10.65% and 2.64% respectively.

Similarly, for 5 wt% of gellan gel, when the temperature was raised from 25^{o}C to 27^{o}C, from 27^{o}C to 29^{o}C and from 29^{o}C to 31^{o}C, the equilibrium degrees of swelling were decreased respectively by 1.67%, 2.39% and 0.55%.

As shown in figure-7, Q_{eq} decreases with increasing temperature. This is true for all samples with different concentration. However a gradual decrease of Q_{eq} is observed for 2.5wt% sample. On the other hand a relatively fast decrease in Q_{eq} is realized for higher concentration samples. Decrease in Q_{eq} is also observed when the gel concentration is increased and these behaviors are interpreted as restricted mobility of the gellan polymer chains due to further associations of the chains induced by the metallic ions [5].

It is widely believed that gellan takes random coil conformation at high temperature. On cooling, salt induced coil to double helix conformational change occurs which is followed by a cation mediated side by side helix-helix aggregation, leading to a three dimensional network. One of the important features of gellan gel is that it is thermoreversible gel. Therefore when the temperature of the gel is increased gradually, the dissolution of the network starts to occur gradually [6]. If we take it into consideration, the Q_{eq} should increase with increasing temperature simply because the thermal energy will help to break the aggregation of gellan chains which allow the gel to swell further.

But the situation is completely different as Q_{eq} decreases with temperature for all concentration samples as shown in the figure-7. The decrease in Q_{eq} with temperature can be interpreted as following: When temperature is increased solvent quality of the water outside the gel decreases i.e. the polymer-solvent interaction decreases [7]. Therefore there is less chance for water to diffuse into cylindrical gellan gel which may be ascribed as one of the reasons why Q_{eq} decreases with increasing concentration.

Our experiment is conducted by changing the room temperature to a desired value. Therefore it is highly probable that the temperature of the gel and the surrounding water is in thermal equilibrium. The temperature increase inside the gel may inhibit the water molecule to be bound with the gellan chains. Also the bound water may be converted into free water molecules. If this is really the case, there is a possibility of the free water to diffuse out of the gel leading to a decrease in gel swelling. Although deswelling behavior is observed for all the samples in our experiment, Q_{eq} always show values greater than 1.

There are some other possibilities which may be interlinked with the present swelling behavior. The osmotic pressure of the biopolymer gel determines the swelling ability of the gel. The rubber elasticity of the polymer network, the effect of counter ion of the ionic group on the polymer network, the interaction free energy between the polymer and the solvent and the mixing entropy contribute to the osmotic pressure of the gel. The equilibrium swelling ratio of the gel is determined by the balance of these four parameters.

Gellan gel is an aggregation of tetrasaccharide repeating unit that form a three dimensional network. This aggregation becomes condense as the temperature is increased. As a result, the swelling ability of the gel decreases.

Also as a surrounding medium, pure water was taken. The pH of pure water falls with increasing temperature. A number of studies have been reported regarding the effect of pH on swelling behavior which demonstrated that when the pH of surrounding medium falls, the swelling ability of gels decreases [13,14,17].

4. Conclusions

The dependency of temperature on the swelling behavior of biopolymer gel was investigated experimentally. When the gellan gel was allowed to swell or shrink inside pure water at specific temperatures and gel concentrations, the polymer chain of the gel became elongated due to the flexibility of the chains and hydrogen bonding between the polymer and water molecule. The weight swelling ratio was measured by measuring the weights before and after swelling. There was a tendency of sharp increase of swelling ratio for a time duration due to the osmotic pressure between the solvent outside and inside the gel. As swelling proceeds, the polymer concentration decreases and its contribution get less important and meanwhile, the elastic part increases progressively due to further stretching of the polymer chain. After a certain point, the degree of swelling attains the equilibrium state when the osmotic and elastic parts are equal. The equilibrium swelling ratio Q_{eq} tends to decrease with increasing temperature due to the decrease in solvent quality with increasing temperature which weakens the polymer-solvent interaction.

5. References

[1] De Rossi, D. Kajiwara, K.Osada, Y. & Yamauchi, A. Eds, 1991. “Polymeric Gels” , Plenum Press, NY.

[2] Clark, A.H. & Ross-Murphy, S.B. 1987.Adv.Poly.Sci.83,60.

[3] Flory,P.J. 1953.”Principles of polymer chemistry”, Cornell University Press, Ithaca, NY
[4] Doi, M. & Edwards, S.F.1986.”The Theory of Polymer Dynamics”, Oxford University Press, Oxford.
[5] Stauffer, D, Coniglio, A.& Adam, M.1982.adv.polym.Sci. 44,103.
[6] D Gennes, P.G. 1979.”Scaling Concept of Polymer Physics”, Cornell University Press, Ithaca, NY.
[7] Flory, P.J. 1974. Faraday Discuss.Chem.Soc.No. 57,7.
[8] Aharoni, S.M.Eds, 1992 “Synthesis, Characterization and Theory of Polymer Networks and Gels”, Plenum Press, NY.
[9] Levine, H. & Slade, L.1992.”Physical Chemistry of Food” (Eds, H.G Schwartzberg and R.W. Hartel), Marcel Dekker, NY.
[10] Ferry, J.D. 1980 ”Viscosity Properties of Polymers”, John Wiley, NY.
[11] Blanshard, J.M & Mitchell, J.R. Eds, 1988.”Food Structure- Its Creation and Evaluation”, Butteworth, London.
[12] Winter, H.H. 1989. “Encyclopaedia of Polymer Science and Engineering, Spplement Volume, 2nd edition, John Willey & Sons, NY.
[13] Haug, A., Larsen, B. & Smidsord, O. 1967. Acta Chem. Scand., 21,183.
[14] Hatta, H.Kitabatake, N.Doi, E. 1986. Agri. Biol.Chem., 50, 2083.
[15] Kitabatake, N. Hatta, H. & Doi, E. 1987, Agri Biol, Chem, 51, 771.
[16] Mori, T, Nakamura, T. & Utsumi, S. 1986. J.Agri food Chem., 34,33.
[17] Madeka, H.& Kokini, J.L. 1994. J. Food Eng.22,241.
[18] Koseki, T., Kitabatake, N.& Doi, E.1989.Food Hydrocoll.,3,123.
[19] P.J. Flory and Rehner, J.Chem.Phys.11, 512-1943.
[20] Ress, D. 1969, Adv. Carbohydr. Chem. Biochem.,24,267.
[21] Haris, P.1990.”Food Gels” , Elsevier, London.
[22] Araki, C & Araki,K, 1967,bull,Chem. Soc, Japan, 40, 1452.
[23] Hickson, T.G.L. & Polyson, A.1968. Biochem, Biophys, Acta, I, 165,43.
[24] Haug, A., Larsen, B. & Smidsord, O. 1967. Acta Chem. Scand., 20,669.
[25] Guenet, J.M. 1992 “Thermoreversible Gelation of Polymer & Biopolymer”, Academic Press, NY.
[26] Larsen, B. & Smidsord, O.Haug, A & Pinter, T.1969, Acta Chem.Scand., 23.2375.