BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 45, 336—338 (1972)

The Effect of Pressure on the Sol-Gel Transformations of Macromolecules[1]

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(Received April 30, 1971)

The effect of pressure on the gelation of macromolecules, such as gelatin, polyvinyl alcohol, and methyl cellulose, was investigated in order to clarify which binding forces contribute to their gel formations. The values for ΔH and ΔV accompanying the gel formation were calculated from the Eldrige-Ferry's plot and the Clausius-Clapeyron equation respectively. The values for ΔH and ΔV in the gel fromations of gelatin and polyvinyl alcohol are both negative, while those in methyl cellulose are both positive. From the thermodynamical considerations, it has been found that the formation of hydrogen bonds results in negative values of ΔV and ΔH, while that of hydrophobic bonds results in positive values of ΔV and ΔH. Therefore, it may be assumed that the main binding forces in the gelations of gelatin and polyvinyl alcohol may be attributed to hydrogen bonds, and that those in methyl cellulose may be attributed to hydrophobic bonds, at least up to 6000 atm.

Gelations may be classified into three types according to the signs of enthalpy of gelation, ΔH; endothermic ($\Delta H>0$), exothermic ($\Delta H<0$), and athermal ($\Delta H=0$). In each case, there are reversible and irreversible sol-gel transformations. In the present experiment, the non-athermal reversible sol-gel systems are investigated. In reversible gelations, weak binding forces, such as the van der Waals type, hydrophobic bonds, hydrogen bonds, and ionic bonds, are considered to be mainly responsible for the gelation.

In investigating the pressure effect on gelation, it seems worthwhile to classify gelation from the point of view of the volume changes in gel formation, ΔV. The pressure effect can be predicted from the sign of ΔV. That is, the gelation in which ΔV is negative is prompted by hydrostatic compression, while in the gelation in which ΔV is positive, the pressure retards the gel formation.

From the thermodynamical data obtained in the appropriate model systems in which hydrogen bonds or hydrophobic bonds are involved, it has been found that the formation of hydrogen bonds results in negative values of ΔV and ΔH,[2,3] while that of hydrophobic bonds results in positive values of ΔV and ΔH.[4] Therefore, we can expect that the pressure will prompt the gel formation in which hydrogen bonds are concerned predominantly, while the pressure will retard the gel formation in which hydrophobic bonds are concerned predominantly.

In the present experiment, gelatin, polyvinyl alcohol, and methyl cellulose were used as samples; the binding forces which are concerned in gel formation will be discussed on the basis of the results of the pressure effect on gel formations.

Experimental

Samples. The gelatin was purchased from the Difco Lab. Co., the polyvinyl alcohol (M. W. 2700) was donated by the Kurashiki Rayon Co. and the methyl cellulose (M.W. 3400, 30.3% methoxyl) was obtained from the Japan Synthetic Chemicals Co., The water used was deionized through an ion-exchange column. These polymer solutions were not buffered.

Sol-Gel Transformation Measurement. The method for the determination of the sol-gel transformation was as follows. The solution was charged into a syringe-type cell, the inner diameter of which was about 10 mm. The cell was set in a high-pressure vessel, and the system was hydrostatically compressed for 10 or 20 min at the desired temperature. As soon as the pressure was released, the state of the system was checked to see if the ball (the diameter of which was 3 mm) inserted in the cell moved or not. In the cases of gelatin and polyvinyl alcohol, the compression was started at the sol state because the gels are formed by compression. The mean value of the lowest pressure at which

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[1] Presented at the 22nd International Congress of Pure and Applied Chemistry, Sydney, August, 1969, and the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2] I. M. Klotz, *Fed. Proc.*, **24**, S-24 (1965).

[3] E. Fishman and H. D. Drickamer, *J. Chem. Phys.*, **24**, 548 (1956).

[4] W. Kauzmann, *Adv. Protein Chem.*, **14**, 1 (1959).

the ball did not move and the highest pressure at which the ball did move was considered to be the sol-gel transition pressure. In the case of methyl cellulose, the gel formed at 1 atm was compressed, because the gel melts by compression. The difference between the highest and the lowest pressure was usually about ±50—100 atm.

Results

Figure 1 shows a sol-gel phase diagram of gelatin at various concentrations. The phase above each curve is a sol phase, while the phase below each curve is a gel phase. It can be seen in this figure that the gelation of gelatin is prompted by raising the pressure. The phase diagram of polyvinyl alcohol in Fig. 2, shows that the pressure favors the gel formation. The curves of the concentrations of 13.35 wt% and 15.24 wt% coincide with each other completely, and above a certain pressure the gel is always formed, whatever the temperature.

Figure 3 shows a sol-gel phase diagram of methyl cellulose at various concentrations. In this figure, the phase above the curve is a gel phase, and the phase below the curve is a sol phase. The methyl cellulose gel is melted by compression; *i.e.*, pressure retards the gel formation of methyl cellulose. This behavior is quite different from that of the two other gels discussed above.

Discussion

Figure 4 shows the relation between the logarithm of the gelatin concentration, *c*, and the reciprocal of the absolute temperature of sol-gel transformation at each pressure according to the plot of Eldrige and Ferry.5) The linear relationship is also applicable to polyvinyl alcohol and methyl cellulose except for the higher concentrations in polyvinyl alcohol. The heat of reaction, ΔH, for the formation of the cross-links in gel is calculated from the slope of Fig. 4 according to the following formula;5) $\log c = \Delta H/(2.303\,RT) + \text{constant}$. The calculated ΔH values are tabulated in Table 1, together with those of polyvinyl alcohol and methyl cellulose.

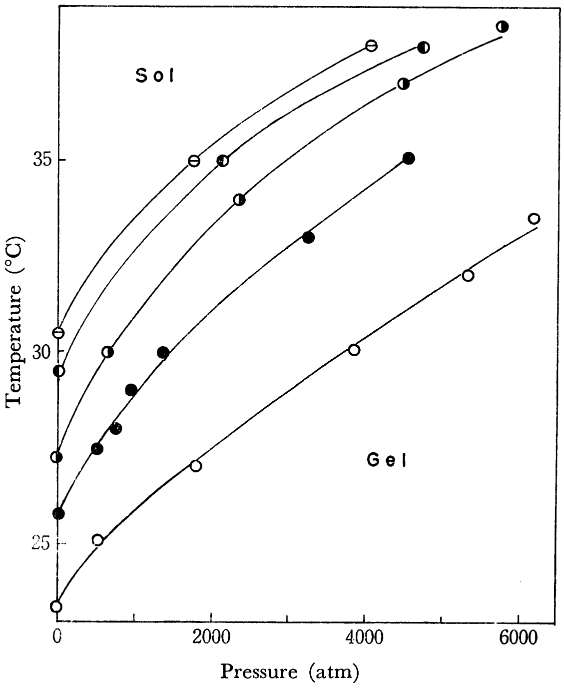

Fig. 1. Sol-gel phase diagram of gelatin-water system at various concentrations.
○: 5 wt%, ●: 10 wt%, ◑: 15 wt%, ◐: 20 wt%, ⊖: 25 wt%

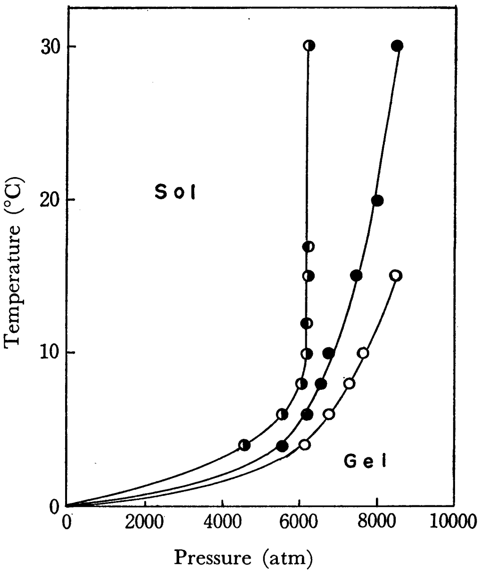

Fig. 2. Sol-gel phase diagram of polyvinyl alcohol-water system at various concentrations.
○: 9.83 wt%, ●: 11.19 wt%, ◑: 13.35 wt%, ◐: 15.24 wt%

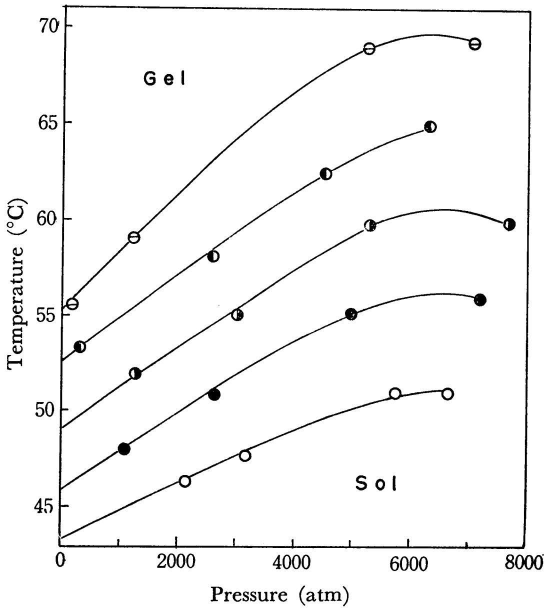

Fig. 3. Sol-gel phase diagram of methyl cellulose-water system at various concentrations.
○: 3.65 wt%, ●: 3.01 wt%, ◑: 2.51 wt%, ◐: 2.07 wt%, ⊖: 1.50 wt%

The volume changes in gel formation were calculated from the relation of Clausius-Clapeyron, $dP/dT = \Delta H/T\Delta V$, assuming that the sol-gel transfor-

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5) J. E. Eldrige and J. D. Ferry, *J. Phys. Chem.*, **58**, 992 (1954).

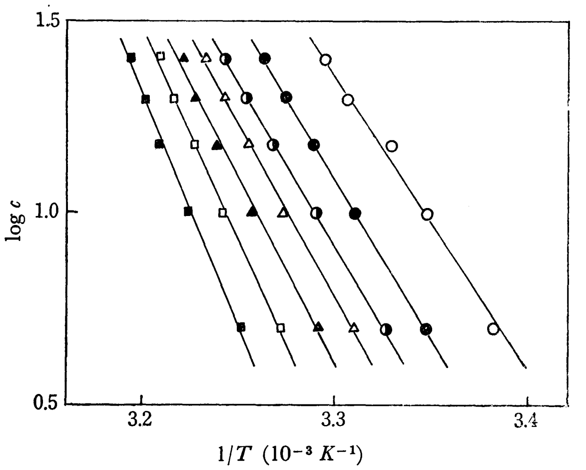

Fig. 4. Relation between the logarithm of the concentration of gelatin and the reciprocal of the absolute temperature of gelation at each pressure.
○: 1 atm, ●: 1000 atm, ◑: 2000 atm, △: 3000 atm, ▲: 4000 atm, □: 5000 atm, ■: 6000 atm

Table 1. Enthalpy changes, ΔH accompanying the formation of gel in gelatin-, polyvinyl alcohol-, and methyl cellulose-water systems

Pressure (atm)	ΔH (kcal/unit) Gelatin	Polyvinyl alcohol	Methyl cellulose
1	−39.4	—	15.0
1000	−42.0	—	13.8
2000	−42.0	—	12.8
3000	−47.6	−28.6	11.6
4000	−50.4	−22.8	10.9
5000	−58.6	−15.8	10.3

Table 2. Volume changes, ΔV accompanying the formation of gel in gelatin-, polyvinyl alcohol-, and methyl cellulose-water systems

Pressure (atm)	ΔV (cm^3/unit) Gelatin Temp. 30°C	Polyvinyl alcohol 5°C	Methyl cellulose 50°C
1	—	—	4.5
1000	—	—	4.2
2000	−8.2	—	3.9
3000	−9.3	−3.5	3.5
4000	−9.8	−3.4	3.3
5000	−11.4	−3.1	—

mation of these macromolecules can be treated as a phase transition. In Table 2, these values are listed. It can be found from Tables 1 and 2 that the gel formations in gelatin and polyvinyl alcohol are exothermic (*i.e.*, ΔH is negative) and are accompanied by a volume decrease and that the gelation in methyl cellulose is endothermic (*i.e.*, ΔH is positive) and is accompanied by a volume increase.[6]

As has already been explained in the introduction, when the values of ΔH and ΔV are both negative, hydrogen bonds contribute predominantly to the gel formation, while when the values of ΔH and ΔV are both positive, hydrophobic bonds contribute predominantly to the gel formation. Therefore, it may be assumed that the main binding forces in both gelatin and polyvinyl alcohol gels originate in hydrogen bonds, while in methyl cellulose hydrophobic bonds are mainly responsible for the gel formation.

The changes in ΔH and ΔV for gelatin at each pressure are different from those of polyvinyl alcohol. That is, the absolute values of ΔH and ΔV for gelatin increase with an increase in the pressure, while those of polyvinyl alcohol decrease. Therefore, we may assume that the mechanism for the gelation of gelatin is different in detail from that of polyvinyl alcohol. In methyl cellulose, (Fig. 3), the ΔV values tend to change in sign from positive to negative above 6000 atm. From these facts, it may be assumed that both hydrophobic and hydrogen bonds are concerned with the gel formation in the case of methyl cellulose, and that, with an increase in the pressure, the contribution of hydrogen bonds surpasses the contribution of hydrophobic bonds.

The finantial support given by the Ministry of Education is gratefully acknowledged.

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[6] The ΔV values accompanying the gel formation in gelatin (negative) and methyl cellulose (positive) have been obtained at 1 atm by Heymann from dilatometry.[7]

[7] E. Heymann, *Trans. Faraday Soc.*, **31**, 846 (1935).