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ON THE RIGIDITY AND THE CONSTITUTION OF A THERMOREVERSIBLE GEL.

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It may be said that the constitution of a thermoreversible gel has not fully been investigated yet. The profound investigation of McBain and his collaborators on soap solutions is a principal one in this field. On gelatine, the typical substance which gives a thermoreversible gels, a number of investigations have been made, yet the problem concerning the constitution of gelatine gel has not been solved. This may be attributed to the reason that, as the substances which give thermoreversible gels have on the whole organic composition and give gels at relatively low concentration, more effectual methods of investigation, such as X-ray analysis or ultramicroscopic study, are inapplicable. Moreover, simple chemical treatments can not be utilized as in the case of soaps.

Gelatine seems to be better as a sample than any other thermoreversible gels, such as starch and soap, since it gives a gel at relatively low concentration while others are chemically less stable. In the present work gelatine was used as the sample on the ground that the condition of its gelation was very simple and that it had hitherto been studied by many investigators.

To study the rigidity of a thermorevesible gel, especially the change of elasticity due to that of temperature must be one of the most important and the most direct processes of investigating the constitution of the gel, for the difference between the gel and sol states in the case of a thermoreversible gel seems to depend only on the difference of the mechanical rigidity of the colloidal system. In the present paper, the results of the investigation made from this point of view are given.

There are a number of investigations on the rigidity of gelatine gel. Those carried out by Mauer,⁽¹⁾ v. Bjerken,⁽²⁾ and Fraas,⁽³⁾ are not to be consulted, for their experimental conditions, such as the quality of the sample, the temperature of measurement, and the concentrations of the sample solutions, are not reported. Leick has measured microscopically the elongation of a block of 45% gel and

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1) Mauer, *Wied. Ann.*, **28**, 628 (1886).
2) v. Bjerken, *Wied. Ann.*, **43**, 817 (1891).
3) Fraas, *Wied. Ann.*, **57**, 1074 (1894).
4) Leick, *Ann. Physik*, (4) **14**, 139 (1904).

found that Young's modulus changed as the square of the concentration of the gel. He studied also the effect of foreign substances. Sheppard and Sweet[5] measuring torsion of a cylindrical gel, have determined the modulus of its rigidity, and confirmed the above-mentioned relation of Leick. Studying the influence of pH, they have found one maximum value of the rigidity in both acid and alkaline sides. Furthermore, taking care of purifying the sample, Sheppard, Sweet and Benedict[6] have measured the modulus of rigidity of 4—10% solutions containing no inorganic impurities and no products of hydrolysis in the pH range from 1.3 to 12.3. Sheppard and Sweet[7] have measured the extensibility of a block of gel. Sauer and Kinkel[8], employing three different methods of measuring, have also measured the modulus of rigidity of 10%—45% gels. Scarth,[9] measuring the extensibility of 11% gel of cylindrical form, has found three maximum points in the modulus of rigidity at pH=4.7, 3, and 11, respectively. Instead of extending the gel, Hatschek[10] using a method of compressing the sample, has measured the diminution of length of the sample and determined Young's modulus with 8—15% concentrations. It may not be said that all those methods of measuring rigidity except that of Sauer and Kinkel are novel. In those methods it is necessary to use rather a highly elastic sample, and so the concentrations of the samples used are generally very high. In the investigation on the constitution of a gel, it is preferable to use a sample of as low concentration as possible for the simplicity of experimental conditions. The method of Freundlich and Seifritz[11] is satisfactory in its sensitivity. In this method the modulus of rigidity was determined by the displacement of one of the nickel particles dispersed preliminarily in the sample, the displacement of the objective particle being effected by an iron pin which could be magnetised by means of an electromagnet. The concentrations of the sample used were 0.7—2%. The methods of measuring used by Michaud,[12] and by Sauer and Kinkel[13] are also very sensitive. In these methods the sample being filled in a glass capillary tube and a pressure being applied at one end of the tube, deformation of a gel caused

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5) Sheppard and Sweet, *J. Am. Chem. Soc.*, **43**, 539 (1922).

6) Sheppard, Sweet, and Benedict, *J. Am. Chem. Soc.*, **44**, 1857 (1922).

7) Sheppard and Sweet, *Ind. Eng. Chem.*, **16**, 593 (1924).

8) Sauer and Kinkel, *Z. Angew. Chem.*, **38**, 413 (1924).

9) Scarth, *J. phys. chem.*, **29**, 1009 (1925).

10) Hatschek, *J. phys. chem.*, **36**, 2994 (1932).

11) Freundlich and Sefriz, *Z. physik. chem.*, **104**, 233 (1923).

12) Michaud, *Ann. de physique*, (9) **19**, 63 (1923).

13) Sauer and Kinkel, *Z. Angew. Chem.*, **38**, 413 (1925).

by the pressure was measured by the displacement of a point on the axis of the tube. In the method of Michaud, fine solid particles were dispersed preliminarily in the sample and a particle was chosen among those which lay on the axis of the capillary tube for the objective. With this objective particle the displacement on the axis of the tube was measured. In the method of Sauer and Kinkel the meniscus of the interface between a gel and the air was taken as the objective. Besides these methods of measuring there is a method used by Rohloff and Shinjo.[14] In this method a spherical body was suspended concentrically in a spherical vessel and the sample solution was filled in the space between these two. Applying a torsion of a certain angle to the outer vessel, the equilibrium position was determined by the action and elasticity measured. Analogous is the method used by Schwedoff.[15] In this method the sample solution was filled between two coaxial cylindrical vessels instead of a spherical one in the method of Rohloff and Shinjo. In the measurement of Schwedoff 0.5 (C.G.S. unit) of rigidity for 0.5% solution was obtained. Hatschek and Jane[16] have also adopted this method. All these methods may be satisfactory with respect to their sensitivities. Among all these measurements that of Leick was the only one in which the effect of temperature was studied. In the measurement, however, the sample was of high concentration. In measuring the effect of temperature on the rigidity of a thermoreversible gel, it is necessary to use the method as sensitive as possible, since the sample decreases its rigidity as the temperature rises and turns into liquid in the end. Also the method must be such one that makes the temperature of the sample remain constant and keeps it free from desiccation. From these points of view, the method of Michaud may be said to be the most satisfactory one.

Experimental.

The method of measuring used in the present experiments is the first of the methods used in an experimental study on cellulose solutions by Duclaux and the author.[17] In this method the sample solutions was held in a capillary tube and the whole of the tube was put in a water thermostat to make observation from the outside of the tube, and so the method may be the most satisfactory one as far as precision of measuring temperature and sensitivity of measurement

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[14] Rohloff and Shinjo, *Physik. Z.* 8, 442 (1907).

[15] Schwedoff, *J. de Physique*, 8, 341 (1889).

[16] Hatschek and Jane, *Kolloid-Z.*, 39, 300 (1926).

[17] Duclaux and Hirata, *J. chim. phys.*, 28, 538 (1931).

are concerned. The principle of the method is as follows. If a pressure P is applied at one end of a capillary tube of length l and radius R to the sample filled in the tube, a shearing force parallel to the axis of the tube will occur, provided that there is no sliding at the inner wall of the tube. Every point of the sample will displace parallel with axis, the magnitude of the displacement corresponding to the position of the point. Putting X_0 as the displacement at a point on the central axis of the tube and μ as the modulus of rigidity of the sample, the relation between these two values will be derived from the following consideration.

Suppose a hollow cylinder in the gels which is coaxial to the capillary tube, and let dr represent the thickness of this cylinder, and dx the displacement of the inner wall of the cylinder for the outer wall. This is shown in Fig. 1, where

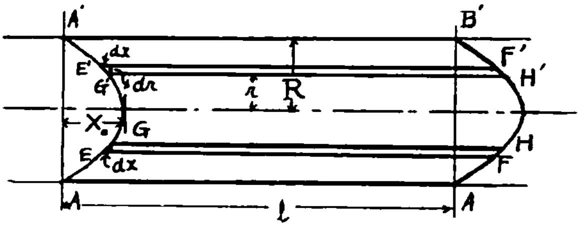

Fig. 1.

the longitudinal section of the capillary tube is indicated as E F G H E' F' G' H'. The force f_1, which acts tangentially to the inner wall and causes its displacement dx for the outer wall is brought forth by the pressure acting at the surface G G' of the cylinder G G' H H', so that the magnitude of this force will be given by the following equation:

$$f_1 = -\pi r^2 P, \qquad (1)$$

where the direction of the force is indicated thus: the left hand direction by the positive and the right hand direction by the negative. The reactionary force f_2 which counteracts the above-mentioned force in equilibrium condition is expressed by the following equation:

$$f_2 = 2\pi rl \cdot \mu \frac{dx}{dr} \qquad (2)$$

where $2\pi rl$ indicates the side area of the cylinder G G' H H', and $\mu = \frac{dx}{dr}$ the elastic strain per unit area which is to conform to the law of elasticity. It is supposed that an equilibrium is kept between these forces, so that

$$-\pi r^2 P = 2\pi rl \cdot \mu \frac{dx}{dr}. \qquad (3)$$

Changing the form,

$$dx=-\frac{Pr}{2l}\,\frac{dr}{\mu}\,. \tag{4}$$

Hence,

$$x=\frac{-Pr^2}{4l\mu}+i, \tag{5}$$

where i is an integration constant which will be determined by the condition that $r=R$ if $x=0$. And we have the following equation:

$$x=\frac{P}{4l\mu}(R^2-r^2). \tag{6}$$

Equation (6) indicates the relation between the displacement x of a point and the distance r of that point from the axis of the capillary tube. Putting $r=0$, we have X_0 the displacement of a point which lies on the axis, thus,

$$X_0=\frac{PR^2}{4l\mu}\,. \tag{7}$$

Hence, the modulus of rigidity will be given as follows:

$$\mu=\frac{PR^2}{4lX_0}\,. \tag{8}$$

Consequently, if R and l be known, the modulus of rigidity of the sample will be determined by measuring the displacement X_0 and the pressure P.

Apparatus.

The principal part of the apparatus used is a H-shaped glass tube, and its horizontal part is a thick walled capillary tube 10.01 cm. in length and radius 0.071 cm. At each end of this tube a vertical tube ca. 1.8 cm. in diameter and ca. 6 cm. in height, whose bottom is closed, is connected. One of these vertical tubes communicates to the atmosphere with a tube devised to prevent the sample from desiccating. The other vertical tube, being a similar tube for preventing desiccation, is connected with a manometer and an apparatus used for the application of the pressure P. Now, the sample, in which fine solid particles were preliminarily dispersed in the liquid state, was filled in the horizontal part of the tube and up to half of the two vertical tubes. Then the whole of this H-shaped glass tube and the tubes for preventing desiccation were set in a thermostat. After connecting the pressure apparatus with it, the H-shaped tube was left to stand to cool down to the temperature of the thermostat. Then a microscope was lowered vertically to the middle part of the horizontal part of the tube. As the objective lens of the microscope dipped in water, a small glass cap which had a flat bottom was put on it. To make the image of the objective particles in the microscope sharp, small pieces of flat glass were attached by means of balsam on and under the horizontal capillary tube just under the microscope. This device prevented light coming from the light source from converging at the curved surface of the outer wall of the tube. An incandescent lamp for photo-micrography of Leitz was used as the light source and a green colour filter was used so that the particles might contrast with background. The displacement of the particle lying on the axis of the capillary tube was measured by means of an ocular micrometer which had been set in the microscope. To select an objective particle in the field of microscope, it is necessary to set a focus at the axis of the capillary tube. For this purpose the scale of the ocular micrometer was set, at first, at right angles to the axis of the capillary tube, and by the image of the inner wall of the capillary tube, the microscope was adjusted so that the centre of the field in the microscope might coincide with the axis of the capillary tube. Revolving the ocular at right angles, the scale of the ocular micrometer is fixed so as to coincide with the axis of the capillary tube in the field of the microscope. Then focussing the microscope on the upper and lower limits of the inner wall of the capillary tube and using the readings of the two positions on the microadjustment of the microscope, the tube of the microscope was fixed exactly at the middle point of these two positions. Accordingly, the sharp image of the objective particle on the scale of the ocular micrometer could be identified as that of the particle which lay on the central axis of capillary tube. Applying a pressure at one end of the capillary tube the displacement of the image of the objective particle was measured with that of the image on the scale of the ocular micrometer and by means of a stop watch.

To apply the pressure, a water column regulated by a microadjusting device was used. The temperature of the thermostat used was accurate within 0.01°C. Every measurement was performed just an hour after setting the sample tube in the thermostat. By preliminary test it was confirmed that the elapse of time of this order was sufficient.

Sample.

Gelatine was prepared as follows. The purest of commercial gelatines, "Extra Gold Label, P.G.VI.," was washed with cold distilled water and was left to stand in a certain quantity of distilled water for 24 hours. Then the mixture was heated on water bath, much care being taken lest the temperature should rise over 60°C. The solution was filtered and its acidity was brought to the isoelectric point (pH=4.7) with pure hydrochloric acid solution. A small quantity of thymol was added to the solution as a preservative. The determination of the concentration of the solution was done as follows. A definite amount of the solution was evaporated to dryness on a water bath and then dried by heating to 105°C. in an electric air oven until its weight became constant. The concentration of the solution determined thus was 25.97*g*/*l*. The solid particles suspended in the sample for the determination of the displacement were those of carborundum. The method of preparing the particles was as follows. Commercial carborundum powder for grinding use was suspended in water to be left to stand for several hours. The middle part of the suspension was taken, and by means of a centrifuge was separated from water. The powder was then treated with concentrated hydrochloric acid and again separated from the acid by means of a centrifuge. It was washed several times with distilled water and made weakly alkaline with ammonia solution, and washed again. After such treatment it was dried up in an electric air oven. The mean diameter of the particles thus obtained was 5.3μ. The quantity of the particles added to the sample solution was in the order of 0.01g per 100 c.c.

Experimental Results.

The experimental results are given in Tables 1—6, in which P is the pressure applied; X_0, the displacement of the particle which lies on the axis of the capillary tube; and L, the reading on the scale of the ocular micrometer. In the last column of each table the ratio of P and X_0 is given, which appears to be constant. This shows that under those conditions of measurement the law of elasticity holds strictly and therefore the relation of equation (8) is applicable. The curves plotted from the data given in Tables 1—6 are shown in Fig. 2 in which X_0 and P are taken as the abscissa and the ordinate respectively. All the curves, as seen, are linear. The modulus of rigidity of the sample at different temperatures is shown in Table 7.

Table 1.

$t = 5.80 \pm 0.01\,^\circ\text{C}$

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	2.000×10^4	0.4	4.104×10^{-4}	4.873×10^7
2	2.961×10^4	0.6	6.156×10^{-4}	4.810×10^7
3	3.882×10^4	0.9	9.234×10^{-4}	4.204×10^7
4	5.373×10^4	1.2	12.31×10^{-4}	4.364×10^7
5	6.294×10^4	1.4	14.36×10^{-4}	4.382×10^7
6	7.255×10^4	1.5	15.39×10^{-4}	4.714×10^7

Table 2.

$t = 11.69 \pm 0.01\,^\circ\text{C}$

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	1.999×10^4	0.5	5.130×10^{-4}	3.897×10^7
2	2.999×10^4	0.9	9.234×10^{-4}	3.248×10^7
3	3.959×10^4	1.0	10.26×10^{-4}	3.859×10^7
4	5.429×10^4	1.2	12.31×10^{-4}	4.410×10^7
5	6.272×10^4	1.4	14.36×10^{-4}	4.367×10^7
6	7.213×10^4	1.8	18.47×10^{-4}	3.906×10^7
7	8.173×10^4	2.0	20.52×10^{-4}	3.983×10^7

Table 3.

$t=15.00\pm0.01$°C

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	1.940×10^4	0.5	5.130×10^{-4}	3.782×10^7
2	2.920×10^4	0.9	9.234×10^{-4}	3.162×10^7
3	3.900×10^4	0.9	9.234×10^{-4}	4.273×10^7
4	5.429×10^4	1.4	14.36×10^{-4}	3.779×10^7
5	6.330×10^4	1.6	16.42×10^{-4}	3.856×10^7
7	7.271×10^4	1.9	19.50×10^{-4}	3.730×10^7
6	8.192×10^4	2.0	20.52×10^{-4}	3.992×10^7

Table 4.

$t=18.00\pm0.01$°C

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	2.017×10^4	0.8	8.208×10^{-4}	2.458×10^7
2	2.938×10^4	1.2	12.31×10^{-4}	2.386×10^7
3	3.918×10^4	1.9	19.49×10^{-4}	2.009×10^7
4	5.444×10^4	2.5	25.65×10^{-4}	2.123×10^7
5	6.404×10^4	2.5	25.65×10^{-4}	2.440×10^7
6	7.305×10^4	3.0	30.78×10^{-4}	2.373×10^7
7	8.245×10^4	3.0	33.86×10^{-4}	2.455×10^7

Table 5.

$t=20.50\pm0.01$°C

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	4.895×10^3	0.5	5.130×10^{-4}	0.925×10^7
2	9.790×10^3	0.8	8.208×10^{-4}	1.193×10^7
3	1.469×10^4	1.4	14.36×10^{-4}	1.022×10^7
4	1.978×10^4	1.8	18.47×10^{-4}	1.068×10^7
5	2.428×10^4	2.0	20.52×10^{-4}	1.183×10^7
6	2.820×10^4	2.6	26.68×10^{-4}	1.057×10^7
7	3.290×10^4	3.1	31.81×10^{-4}	1.034×10^7
8	4.229×10^4	4.0	41.04×10^{-4}	1.030×10^7
9	5.189×10^4	4.7	48.22×10^{-4}	1.076×10^7
10	6.089×10^4	5.8	59.51×10^{-4}	1.021×10^7
11	6.931×10^4	6.7	68.74×10^{-4}	1.008×10^7
12	7.842×10^4	7.5	76.95×10^{-4}	1.019×10^7

Table 6.

$t=22.60\pm0.01$°C

No.	P(dyne/cm^2)	L	X_0(cm)	P/X_0
1	4.898×10^3	1.4	14.36×10^{-4}	3.411×10^7
2	9.992×10^3	3.0	30.76×10^{-4}	3.216×10^7
3	1.998×10^4	6.1	62.59×10^{-4}	3.172×10^7
4	2.978×10^4	9.0	92.34×10^{-4}	3.225×10^7
5	3.977×10^4	12.0	123.1×10^{-4}	3.232×10^7
6	5.937×10^4	17.5	179.6×10^{-4}	3.309×10^7
7	6.818×10^4	20.5	210.3×10^{-4}	3.247×10^7

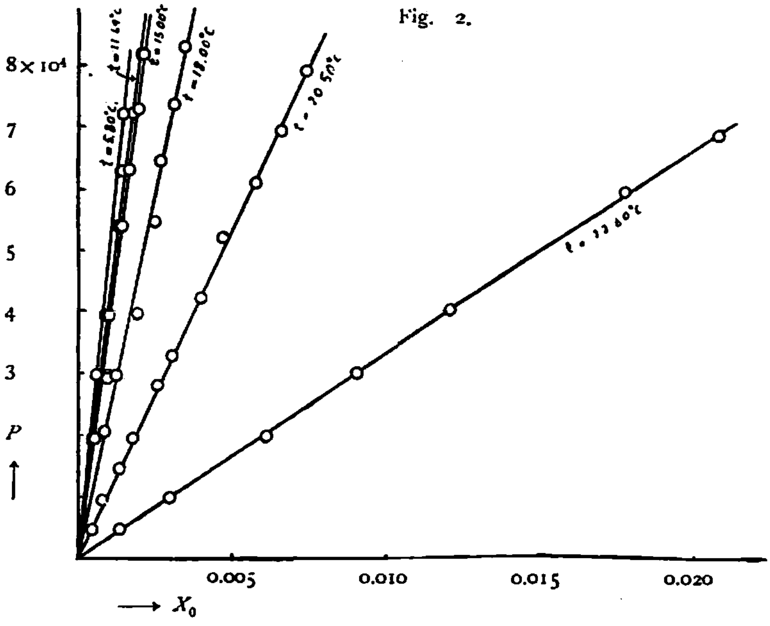

Fig. 2.

Table 7.

No.	t(°C)	μ (CGS unit)
1	5.80	5.78×10^3
2	11.69	5.10×10^3
3	15.00	4.80×10^3
4	18.00	2.96×10^3
5	20.50	1.30×10^3
6	22.60	0.410×10^3

Considerations on the constitution of a thermoreversible gel.

Among discussions on the constitution of a thermoreversible gel the theory that a gel is composed of micelles dispersed in an intermicellar liquid and forms a solid as a whole, seems to be most acceptable. From this point of view Mc-Bain has explained his experimental results on soap gels. It seems that the theory is also appropriate to gelatine gel in several respects. For example, the results of a study on the scattering of light by gelatine sol and gel,[18] of a study on the ultrafiltration of gelatine sol and gel,[19] of a study on the electrolytic conductivity of gelatine sol and gel,[20] and of a study on the index of their refraction,[21] suggest that the process of gelation is simply the fixing of the motion

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[18] Duclaux and Hirata, *J. chim. phys.*, **30**, 213 (1933).

[19] Duclaux and Hirata, *J. chim. phys.*, **30**, 229 (1933).

[20], [21] Studies made in the author's laboratory, which have not published yet.

of the micelles and not the result of enlargement of particles (the micelles). This micellar theory of gel constitution is applicable not only to gelatine gel but also those of other thermoreversible gels.

Why do the micelles which have been in kinetic motion become fixed as the temperature lowers? What is the origin of the rigidity of the gel brought forth by this gelation? It may be assumed that direct long distance forces both attractive and repulsive are in action between the micelles in either sol or gel state. At high temperature, that is in the sol state, the kinetic motion of particles (the micelles) due to the thermal energy exceeds these forces in its action so that the particles are able to move freely and the whole system becomes liquid. If the system is cooled, the kinetic motion of the particles due to thermal action slows down, so that the interaction of particles becomes intense and the forces make the particles take definite positions in the system. Then what sort of forces are they? It may be imagined that the process of gelation is comparable to that of crystallisation of a pure liquid. Accordingly, as for gelatine, the process of gelation may be compared to that of solidification of a fused sodium chloride. From the calculation of lattice energy,[22] the forces which make sodium chloride rigid crystals are an electrostatic attractive force which follows Coulomb's law and a repulsive force which is reciprocally proportional to the 8th power of the distance of the constitutional units, Na and Cl ions. It may be supposed, therefore, that the rigidity of the crystal of sodium chloride due to these forces, that is, the crystallisation of a fused sodium chloride takes place only when the fixation of ions does. The gelation of gelatine sol is a phenomenon quite analogous to this crystallisation. The difference between these two phenomena is that in crystallisation the constitutional units are ions, the space between these ions being nothing but a vacuum, while in the case of gelation of gelatine, the constitutional units are the micelles of gelatine, the space between these micelles being filled with the intermicellar liquid. The distance between the constitutional units in the crystal of sodium chloride is very small, thus, 2.8×10^{-8} cm., whereas in gelatine the distance between the micelles which is variable with concentration, is generally very great. In the present experiments this distance was computed to be 8.5×10^{-7} cm., assuming that the molecular weight of gelatine micelle was 10000. Although the constitution of the micelle of gelatine is quite unknown, yet it may be imagined that the micelle is composed of an aggregate of particles possessing electric charges. It follows analogically that the rigidity of gelatine

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22) A. Eucken, "*Lehrbuch der Chemischen Physik*," Leipzig (1932), p. 976.

is due to the electrostatical forces of the micelles which act through the intermicellar liquid. If the constitution of a micelle is not affected by the change of temperature of a gel, it may be assumed that the cause of the change of rigidity of the gel due to that of temperature lies not in the micelle itself, but in the intermicellar liquid. The change of the intermicellar forces in a gel may be attributed to that of dielectric constant of the intermicellar liquid since the forces may be assumed to be of the electrostatical origin acting for a long distance through the medium, or the intermicellar liquid. If this assumption is correct, there must be a certain quantitative relation between the change of dielectric constant due to temperature and that of the modulus of rigidity of gelatine. In fact, the present experimental results on the modulus of rigidity of gelatine gel verify this assumption.

As the magnitude of the modulus of rigidity of gelatine has a direct connection with the displacement X_0 on the axis of the capillary tube, the change of rigidity can be shown as that of X_0. It follows, therefore, that the change of rigidity due to temperature may be expressed in tne term of that of X_0 due to temperature. Consequently, a certain quantitative relation may exist between the change of the dielectric constant ε of the intermiceller liquid due to temperature and that of the modulus of rigidity of gelatine gel, or the displacement X_0. In the present experiments pure water was used as the intermicellar liquid, since gelatine gel was at its isoelectric point and the electrolytic conductivity of the gel was very small, being approximate to that of pure water. Between those two quantities the author found such an experimental relation as

$$X_{o\cdot p}=\frac{\beta\varepsilon}{1-\alpha\varepsilon^2}\,, \tag{9}$$

where, α and β are the constants which are independent of temperature, and they are calculated as $\alpha=1.602\times10^{-4}$, and $\beta=-2.083\times10^{-6}$ from the experimental data of $X_{o\cdot p}$ at the constant pressure $P=6\times10$ dyne/cm^2 and ε. Changing the form of equation (9), we have

$$\frac{X_{o\cdot p}}{\varepsilon}=\alpha X_{o\cdot p}\cdot\varepsilon+\beta. \tag{10}$$

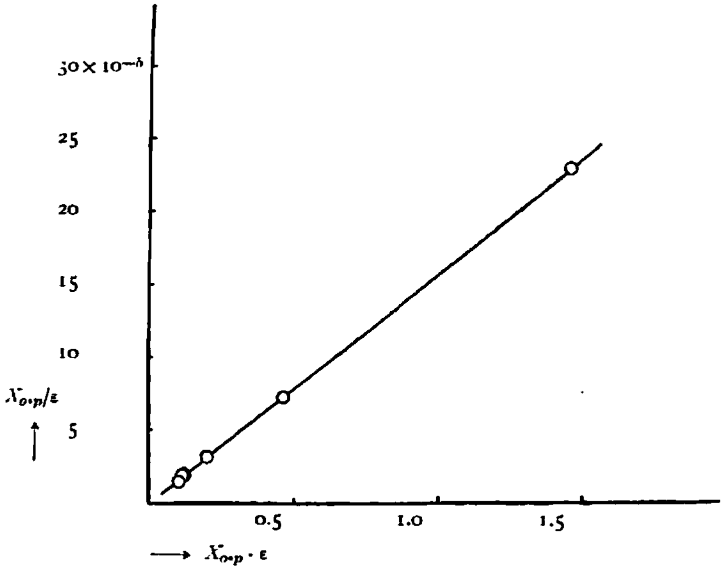
In this form, the relation between $X_{o\cdot p}/\varepsilon$ and $X_{o\cdot p}\cdot\varepsilon$ should be linear, and it is distinctly shown in Fig. 3 and the numerical values of $X_{o\cdot p}/\varepsilon$ and $X_{o\cdot p}\cdot\varepsilon$ are given in Table 8. In Fig. 3 it is clearly shown that all the points lie on a straight line. Fig. 3 indicates that equation (10) holds exactly at every temperature. Taking the accuracy of measurement in the present experiment into con-

Table 8.

No.	t	ε*	$X_{o\cdot p}$	$X_{o\cdot p}/\varepsilon$	$X_{o\cdot p}\cdot\varepsilon$
1	5.80	85.73	$1.30_7\times10^{-3}$	$1.52_4\times10^{-5}$	0.112_1
2	11.69	83.51	$1.46_0\times10^{-3}$	$1.77_3\times10^{-5}$	0.123_5
3	15.00	82.19	$1.56_1\times10^{-3}$	$1.89_9\times10^{-5}$	0.128_5
4	18.00	81.07	$2.55_5\times10^{-3}$	$3.15_2\times10^{-5}$	0.206_7
5	20.50	80.15	$5.80_6\times10^{-3}$	$7.24_4\times10^{-5}$	0.465_3
6	22.60	79.38	18.42×10^{-3}	23.20×10^{-5}	1.46_2

* Values calculated by Drude's formula: $\varepsilon=81.07\,[1-0.004583(t-18)+0.0000117(t-18)^2]$.

Fig. 3.



sideration, it may be admitted that the change of the rigidity of a gel due to temperature has its origin in that of dielectric constant of the intermicellar liquid due to the temperature change. From the measurement of electrolytic conductivity of gelatine gel, it may be said that the micelle does not consist of ion, and from the values of the distance between the micelles in the gel it must be of dipole nature.[23]

What has been discussed on gelatine gel here is probably applicable to all the thermoreversible gels.

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[23] In connection with this, the work of Marinesco (*Compt. rend.*, **189**, 1274 (1929)) may be noticed. He determined the numerical value of the dipole moment of the gelatine micelle assuming the micelle to be a dipole, that is, (dipole moment) 24×10^{-18} e.s.u..

Résumé.

The change of the rigidity of gelatine gel due to temperature has been measured.

A relation has been found between the dielectric constant of intermicellar liquid and the rigidity of gelatine gel, and an experimental equation which represents this relation has been obtained.

From the experimental results obtained, the constitution of a thermoreversible gel and the mechanism of its gelation have been discussed.

In closing, the author wishes to express his sincere thanks to Prof. S. Horiba for his kind guidance throughout this investigation.

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