The Theory on the Constitution of a Thermoreversible Gel.

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Introduction.

Concerning the constitution of thermoreversible gel, the present author has discussed elsewhere⁽¹⁾ the constitution and the sol-gel transformation of gelatine solution which gives a typical thermoreversible gel. It has been found that the theory of micellar constitution of gel is most adequate to explain the experimental results of the studies on the physico-chemical properties of gel of gelatine and that the process of gelation may be explained on an assumption that the cause of gelation is in the fixation of the micelle particle in the system. By assuming that the micelle is of electric constitution and that the origin of rigidity of gel is in the mutually reacting electrostatical forces of these micelles, the experimental results of the measurement of rigidity have been examined, and an experimental equation has been found expressing the existence of a certain relation between the change of rigidity due to temperature and the change of dielectric constant of the intermicellar liquid of the gel due to the change of temperature. Taking into consideration the numerical values of modulus of rigidity and the concentration of the gel, and also the fact that the rigidity shows the maximum value at the isoelectric point of gelatine, it has been concluded that the mutually acting forces of the micelles may be considered to be of electric dipole nature.

In the present paper, the theoretical relation between the rigidity of gel and the dielectric constant of intermicellar liquid is investigated.

I. Consideration on the Constitution of Thermoreversible Gel. Among the theories on the constitution of gel, the theory that a gel is composed of micelles dispersed in a liquid, manifesting the elastic solid mass as a whole, seems to be most acceptable in the case of the gel of gelatine. The results of the studies made by the present author on the scattering of light by sol and gel of gelatine,⁽²⁾ on the electrolytic conductivity of sol

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(1) F. Hirata, *Rev. Phys. Chem.* (Japan), **11** (1937), 262; *Proc. Imp. Acad.* (Tokyo), **33** (1937), 266; *J. Chem. Soc. Japan*, **58** (1937), 1156 et seq.

(2) Duclaux and Hirata, *J. chim. phys.*, **30** (1933), 213.

and gel of gelatine,(3) on the ultrafiltration of sol of gelatine,(4) and on the refractive index of sol and gel of gelatine,(3) suggest that the process of gelation is nothing but the stoppage of the free translational and rotational motion, that is, of the Brownian motion of the micelles. It may be assumed that the direct forces of attraction and repulsion acting at a long distance are in action through the medium between the micelles in both sol and gel states. However, when the system is at high temperature, that is, in the sol state, the kinetic energy due to temperature of the micelles overcomes these forces in its action, and the micelles are free to move and consequently, the whole mass becomes a liquid. At lower temperature, that is, in the gel state, the intermicellar forces become superior in its action and these forces make the micelles take definite positions in the system. It may be said that the micelle is composed of an aggregate of particles of electric charges, and the rigidity of gel is the effect of the electrostatical forces of these micelles, which act through the intermicellar liquid. On the basis of the studies stated above, it may be assumed that the constitution of micelle is not affected by the change of temperature within the range of the present experiments. It follows, therefore, that the cause of the change of the rigidity of gel due to temperature exists not in the micelle itself but in the intermicellar liquid. Since the forces may be assumed to be of the electrostatical nature acting at a long distance through the intermicellar liquid, the change in the intermicellar forces may be ascribed to the change in the intermicellar liquid. If this assumption be correct, there must be a certain quantitative relation between the change of dielectric constant of the intermicellar liquid due to temperature and that of rigidity of the gel due to temperature.

II. **Method and Results of Measurement of Rigidity of Gel.** In order to investigate the constitution of thermoreversible gel, the study of the rigidity of gel, especially the study of the change of rigidity due to temperature must be one of the most important and the most direct process, for the difference between the gel and sol states in the case of thermoreversible gel seems to depend only on the difference of the mechanical rigidity of the colloidal system.

In the investigation of the constitution of gel from its rigidity, it is preferable to use a sample of as low concentration as possible for securing the simplicity of experimental conditions. In measuring the effect of temperature on the rigidity, it is necessary to use the method as ac-

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(3) These experiments have been made in the author's laboratory. Cf. *J. Chem. Soc. Japan*, **58** (1937), 1156, et seq.

(4) Duclaux and Hirata, *J. chim. phys.*, **30** (1933), 229.

curate as possible, since the gel loses its rigidity as the temperature rises and turns into liquid in the end. Moreover, the method must be such as will allow the temperature of the sample remain constant and keep it free from desiccation. From these points of view, the method of Michaud(5) seems to be the most satisfactory one.

The method of measurement used by the present author is a modified form of the method of Michaud used in an experimental study on cellulosic solutions by Duclaux and the author.(6)

In this method of measurement(7) the sample is held in a glass capillary tube and the whole is kept in a water thermostat. If a pressure is applied to the sample at one end of the capillary tube, every point of the sample gel will be displaced parallel with the axis of the tube. Let l and R be the length and the radius of the capillary tube, respectively, X_0 be the displacement of the sample at a point on the axis of the capillary tube and μ be the modulus of rigidity of the gel, and the following relation will be obtained theoretically:(7)

$$\mu = PR^2 / 4lX_0 \qquad (1),$$

where P is the pressure applied.

The results of measurement of P and X_0 for the gel of gelatine at the isoelectric point $p\mathrm{H} = 4.7$ are given in Table 1 to 6. The concentration of this gel was 25.97 g./l. Taking P and X_0 as ordinate and abscissa, respectively, the relations are shown in Fig. 1. In this figure it is

Table 1. $t = 5.80 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
2.000×10^4	4.104×10^{-4}	4.873×10^7
2.961×10^4	6.156×10^{-4}	4.810×10^7
3.882×10^4	9.234×10^{-4}	4.204×10^7
5.373×10^4	12.31×10^{-4}	4.364×10^7
6.294×10^4	14.36×10^{-4}	4.382×10^7
7.255×10^4	15.39×10^{-4}	4.714×10^7

Table 2. $t = 11.69 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
1.999×10^4	5.130×10^{-4}	3.897×10^7
2.999×10^4	9.234×10^{-4}	3.248×10^7
3.950×10^4	10.26×10^{-4}	3.859×10^7
5.429×10^4	12.31×10^{-4}	4.410×10^7
6.272×10^4	14.36×10^{-4}	4.367×10^7
7.213×10^4	18.47×10^{-4}	3.906×10^7
8.173×10^4	20.52×10^{-4}	3.983×10^7

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(5) Michaud, *Ann. phys.*, [9], **19** (1923), 63.

(6) Duclaux and Hirata, *J. chim. phys.*, **28** (1931), 538.

(7) Hirata, *Rev. Phys. Chem.* (Japan), **11** (1937), 262.

Table 3. $t = 15.00 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
1.940×10^4	5.130×10^{-4}	3.782×10^7
2.920×10^4	9.234×10^{-4}	3.162×10^7
3.900×10^4	9.234×10^{-4}	4.273×10^7
5.429×10^4	14.36×10^{-4}	3.779×10^7
6.330×10^4	16.42×10^{-4}	3.856×10^7
7.271×10^4	19.50×10^{-4}	3.730×10^7
8.192×10^4	20.52×10^{-4}	3.992×10^7

Table 4. $t = 18.00 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
2.017×10^4	8.208×10^{-4}	2.458×10^7
2.938×10^4	12.31×10^{-4}	2.386×10^7
3.918×10^4	19.49×10^{-4}	2.009×10^7
5.444×10^4	25.65×10^{-4}	2.123×10^7
6.404×10^4	25.65×10^{-4}	2.440×10^7
7.305×10^4	30.78×10^{-4}	2.373×10^7
8.245×10^4	33.86×10^{-4}	2.455×10^7

Table 5. $t = 20.50 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
4.895×10^3	5.130×10^{-4}	0.925×10^7
9.790×10^3	8.208×10^{-4}	1.193×10^7
1.469×10^4	14.36×10^{-4}	1.022×10^7
1.978×10^4	18.47×10^{-4}	1.068×10^7
2.428×10^4	20.52×10^{-4}	1.183×10^7
2.820×10^4	26.68×10^{-4}	1.057×10^7
3.290×10^4	31.81×10^{-4}	1.034×10^7
4.229×10^4	41.04×10^{-4}	1.030×10^7
5.189×10^4	48.22×10^{-4}	1.076×10^7
6.089×10^4	59.51×10^{-4}	1.021×10^7
6.931×10^4	68.74×10^{-4}	1.008×10^7
7.842×10^4	76.95×10^{-4}	1.019×10^7

Table 6. $t = 22.60 \pm 0.01$°C.

P (dyne/cm.^{2})	X_0 (cm.)	P/X_0
4.898×10^3	14.36×10^{-4}	3.411×10^6
9.992×10^3	30.76×10^{-4}	3.216×10^6
1.992×10^4	62.59×10^{-4}	3.176×10^6
2.978×10^4	92.34×10^{-4}	3.225×10^6
3.977×10^4	123.1×10^{-4}	3.232×10^6
5.937×10^4	179.6×10^{-4}	3.309×10^6
6.818×10^4	210.3×10^{-4}	3.247×10^6

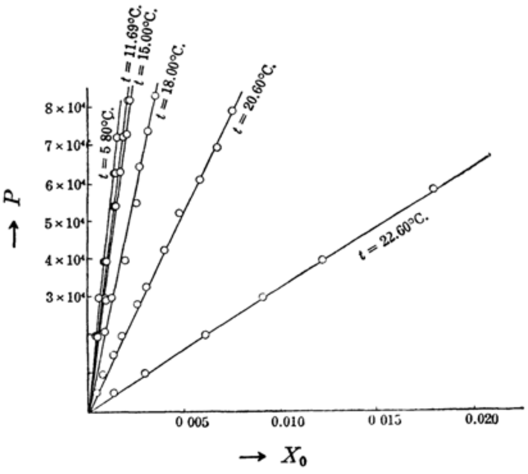

Fig. 1.

represented clearly that the relation between P and X_0 is perfectly linear, that is, the law of elasticity holds strictly within the range of the experimental temperatures and the pressures applied.

III. Theoretical Relation between X_0 and ε. As the magnitude of the modulus of rigidity has a direct connection with the displacement X_0, the change of rigidity due to temperature may be expressed in terms of the change of X_0 due to temperature. It is intended here to derive the theoretical relation which will hold between X_0

and ε, the dielectric constant of the intermicellar liquid of the gel for different temperatures.

In order to simplify the calculation, the micellar constitution of the gel of gelatine is assumed as shown in Fig. 2. Each micelle M which is supposed to be an electric dipole takes the position of each lattice point of a simple cubic lattice and the space between these micelles is supposed to be filled up by an intermicellar liquid.

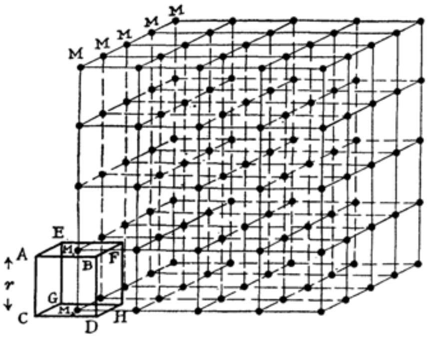

Fig. 2.

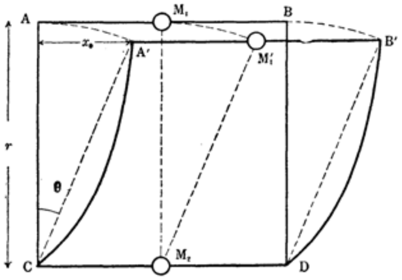

Fig. 3.

When such a gel is subjected to a holizontal shear, all the unit cube in the lattice will be deformed equally. Taking one of those unit cube, let us advance the consideration.

Let a unit cube be ABDC in Fig. 3, in which the cube is indicated by a cross section cut by a plane perpendicular to the side face ACGE of the cube ABCDEFGH in Fig. 2. M_1 and M_2 are the micelles which take the central position of each face shown as AB and CD in Fig. 3. If a pressure is applied at the side face AC, the base CD being fixed, the cube ABDC will be deformed and become the shape like A′B′DC. The micelle M_1 will be displaced to M_1' and the equilibrium of forces will be established. It is supposed that the mutual forces of M_1' and M_2 in the deformed state must produce the reactive elastic force. Let f_l be the direct active force between the micelles M_1' and M_2, and $f_l \sin\theta$ will be its horizontal component which appears in the horizontal direction. This component is nothing but the force which reacts as the rigidity of the cube. As already stated, the direct acting force is caused by the mutual action of the dipole micelles, the direct force between M_1' and M_2 is expressed in the following equation:

$$f_l = \frac{\gamma\sigma_0^2}{\varepsilon r^4} \qquad (2),$$

in which σ_0 represents the dipole moment of M_1' and M_2, γ the factor which is determined by the mutual orientation of the two dipole micelles in the deformed state, ε the dielectric constant of the medium which fills up the space between M_1' and M_2, and r the distance between the two micelles M_1' and M_2. The reactive horizontal force $-f_x$ will be given in the following form:

$$-f_x = -f_l \sin\theta$$

or

$$-f_x = -\frac{\gamma\sigma_0^2}{\varepsilon r^4}\sin\theta \qquad (3),$$

in which the negative sign of f_x indicates that the direction of the force is to the left.

When the temperature of gel changes, this horizontal force, $-f_x$ will be changed in its magnitude; for the rigidity of gel will change when the temperature of gel is changed. In equation (3), σ_0 and r may be assumed to be independent of temperature, but γ, ε and θ are supposed to change with temperature. In order to secure the simplicity of calculation, γ is assumed to be independent of the change of temperature.(8) Consequently, in this case only ε and θ are variable. If the measurement of rigidity, viz., the measurement of X_0 is executed for different temperatures but under a same constant pressure, the above force f_x may be taken as constant for the temperature of measurement. The following equation, therefore, is written for the reactive elastic force in the range of temperature of the measurements:

$$-f_x = k \qquad (4),$$

where k is a constant which is independent of temperature. From equations (4) and (3), we have

$$-\frac{\gamma\sigma_0^2}{\varepsilon r^4}\sin\theta = k \qquad (5).$$

If we summarize all of the constants in equation (5) which are independent of the change of temperature, by b, that is, $kr^4/\gamma\sigma_0^2 = b$, we get the following relation:

$$\sin\theta = -b\cdot\varepsilon \qquad (6).$$

Now we must find the relation between ε and $X_{0\cdot P}$. $X_{0\cdot P}$ means X_0 for a constant pressure P.

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(8) As for the value of γ which gives the orientation polarization caused by the stress, it will be treated in a later report.

Next suppose, on the other hand, a cube of homogeneous gel of side length r. This cube is, in the microscopic point of view, is equivalent to the cube which is given in Fig. 1 as ABCDEFGH, but in the present case it is supposed to be an entirely homogeneous, isotropic, elastic mass. Only the dimension of the cubes is assumed to be equal in both cases. This cube is shown as ABDC in Fig. 4 which is shown as the cross section analogous to Fig. 3.

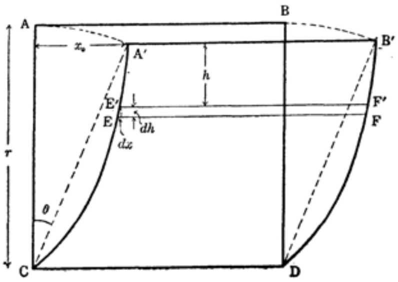


Fig. 4.

If pressure P is applied to the cube from the side face AC, the base CD being fixed, the cube ABDC will be deformed into A′B′DC when the equilibrium will be established. If we represent μ' as the modulus of rigidity of the gel under the deformed state, and consider the equilibrium condition of the acting and reacting forces which act horizontally to the plane E′F′, indicated in Fig. 3, of the infinitely thin gel block EFE′F′, we have the following equation:

$$Phr = -\mu' \frac{dx}{dh} r^2 \qquad (7).$$

The meaning of h, r, dh, dx in this equation is clearly shown in the figure. The left hand side of equation (7) represents the force that acts tangentially on the plane E′F′ in the right direction and the right hand side of the equation represents the reactive tangential force produced by the elastic property of the gel block EFF′E′. If we solve the equation (7), taking the limiting condition: $h = \sqrt{r^2 - x_0^2}$, when $x = 0$, we have

$$\frac{P}{2}(h^2 - r^2 + x_0^2) = -\mu' r x \qquad (8).$$

Putting $h = 0$ and $x = x_0$,

$$\frac{P}{2}(x_0^2 - r^2) = -\mu' r x_0 \qquad (9).$$

Rewriting, we have

$$\frac{P}{\mu'} = 2\frac{x_0}{r}\frac{r^2}{r^2 - x_0^2} \qquad (10).$$

We may write this equation in the following form, if we take the value of θ as the function of x_0, i.e., $\sin\theta = x_0/r$; $\cos\theta = \sqrt{r^2 - x_0^2}/r$,

$$\frac{P}{\mu'} = 2\sin\theta \,/\, \cos^2\theta \qquad (11).$$

If we express, on the other hand, the modulus of rigidity of the cube ABDC which is not deformed as μ, this modulus of rigidity μ must correspond to the value of μ measured directly by the method stated in paragraph II. In equation (1) of paragraph II, if we measure the value of X_0 under a constant pressure P, X_0 may be represented as $X_{0\cdot P}$. Rewriting equation (1), we have

$$\frac{P}{\mu} = \frac{4lX_{0\cdot P}}{R^2} \qquad (12).$$

To get the relation between μ and μ', it is necessary to determine the nature of the reactive elastic force. As already stated in the introduction of this paper, it may be concluded that the forces which cause the rigidity of gel is the electrostatic force between the dipole micelles of gelatine. Consequently, as the dipolar force are inversely proportional to the fourth power of the mutual distance of the micelles, the relation between μ and μ' may be represented in the following equation:

$$\frac{\mu'}{\mu} = \left(\frac{r}{r\cdot\cos\theta}\right)^4 = \frac{1}{\cos^4\theta} \qquad (13).$$

Combining equations (11) and (13), we have

$$\frac{P}{\mu} = 2\frac{\sin\theta}{\cos^2\theta}\frac{1}{\cos^4\theta} \qquad (14).$$

From equations (12) and (14), the following equation is given

$$\frac{4lX_{0\cdot P}}{R^2} = 2\frac{\sin\theta}{\cos^6\theta} \qquad (15).$$

Changing the form, we get

$$\frac{4lX_{0\cdot P}}{R^2} = 2\frac{\sin\theta}{(1-\sin^2\theta)^3} \qquad (16).$$

Neglecting the higher order of $\sin\theta$ in the denominator, we have

$$\frac{2lX_{0\cdot P}}{R^2} = \frac{\sin\theta}{1-3\sin^2\theta} \qquad (17).$$

Now, putting the value of sin θ expressed in equation (6), equation (17) will be written as

$$\frac{2lX_{0.P}}{R^2} = \frac{-b\cdot\varepsilon}{1-3b^2\varepsilon^2} \tag{18}$$

This equation represents the relation between the values $X_{0.P}$ and ε, and may be verified by using the results of the direct measurement of the modulus of rigidity.

If we change the form of equation (18), we have the following equation:

$$\frac{X_{0.P}}{\varepsilon} = 3b^2X_{0.P}\cdot\varepsilon - \frac{R^2}{2l}b \tag{19}$$

If we put

$$3b^2 = \alpha$$

and

$$-b\frac{R^2}{2l} = \beta \tag{20}$$

we have

$$\frac{X_{0.P}}{\varepsilon} = \alpha\cdot X_{0.P}\cdot\varepsilon + \beta \tag{21}$$

where α and β are constant which are independent of temperature. This equation tells that, independent of temperature, the linear relation between $X_{0.P}/\varepsilon$ and $X_{0.P}\cdot\varepsilon$ exists for thermoreversible gels. In this form of relation, the result of calculation of the values of $X_{0.P}$ and ε, and that of the observed values may conveniently be examined.

IV. **The Verification of the Relation Expressed by Equation (21).** The numerical data necessary to the verification of equation (21) are given in the following tables.

Table 7.

t	ε	$X_{0\cdot P}$	$X_{0\cdot P}/\varepsilon$	$X_{0\cdot P}\cdot\varepsilon$
5.80	85.73	$1.30_7\times10^{-3}$	$1.52_4\times10^{-5}$	0.112_1
11.69	83.51	$1.46_0\times10^{-3}$	$1.77_3\times10^{-5}$	0.123_6
15.00	82.19	$1.56_1\times10^{-3}$	$1.89_9\times10^{-5}$	0.128_5
18.00	81.07	$2.55_5\times10^{-3}$	$3.15_2\times10^{-5}$	0.206_7
20.50	80.15	$5.80_6\times10^{-3}$	$7.24_4\times10^{-5}$	0.465_3
22.60	79.38	$18.4_2\times10^{-3}$	$23.2_0\times10^{-5}$	1.46_2

Table 8.

t	$X_{0\cdot P}$ (calc.)	$X_{0\cdot P}$ (obs.)
5.80	$1.00_1\times10^{-3}$	$1.30_7\times10^{-3}$
11.69	$1.48_8\times10^{-3}$	$1.46_0\times10^{-3}$
15.00	$2.06_2\times10^{-3}$	$1.56_1\times15^{-3}$
18.00	$3.15_6\times10^{-3}$	$2.55_5\times10^{-3}$
20.50	$5.61_7\times10^{-3}$	$5.80_6\times10^{-3}$
22.60	$16.0_2\times10^{-3}$	$18.4_2\times10^{-3}$

All the values of $X_{0.P}$ in the table are the values determined under the pressure $P = 6 \times 10^4$ dyne/cm.^{2}. As for the values of ε, values of pure water have been adopted by reason that the gel is at its isoelectric point and that the measurement of electrolytic conductivity of the gel gives the values approximately equal to that of pure water. These values have been calculated by Drude's formula: $\varepsilon_t = 81.07[1 - 0.004583(t - 18) + 0.0000117(t - 18)^2]$. Taking the values of $X_{0.P}/\varepsilon$ and $X_{0.P}^{\mp}\cdot\varepsilon$ as the y-axis and the x-axis of co-ordinates respectively, their relation is shown in Fig. 5. It is clear from the figure that the relation represented by equation (21) holds in the region of the experimental temperatures. If we calculate the constants α and β by the method of least square, using the numerical values given in Table 7, the following values are obtained:

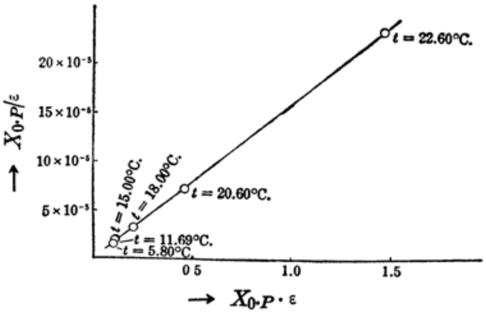
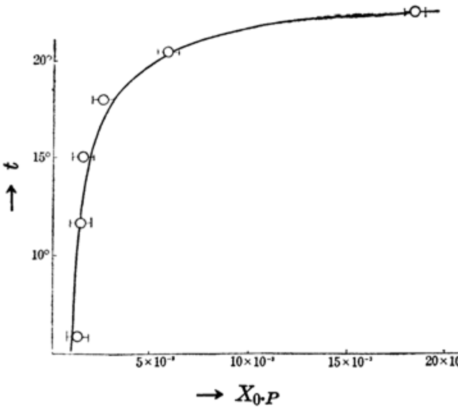


Fig. 5.



—— ... calculated values.
○ ... observed value.
|——| ... range of the allowable experimental error of $X_{0\cdot P}$.

Fig. 6.

$$\alpha = +1.602 \times 10^{-4},$$

$$\beta = -2.082 \times 10^{-6} \qquad (22).$$

Consequently, equation (21) may be written in the following form:

$$\frac{X_{0.P}}{\varepsilon} = 1.602 \times 10^{-4} X_{0.P}\cdot\varepsilon - 2.082 \times 10^{-6} \qquad (23).$$

By this equation and using the numerical values of ε, it is possible to calculate the values of $X_{0.P}$. The result of this calculation is given in Table 8, in which the calculated values are compared with the direct observed values. In Fig. 6 the calculated values and the observed values of $X_{0.P}$ are plotted as a function of the experimental temperature, t, instead of ε. From the above tables and figures, the validity of equation (21) may be accepted. Next, if we combine equations (6) and (20), the constants α and β of equation (21) may be expressed in the following form:

$$\alpha = \frac{3\sin^2\theta}{\varepsilon^2},$$

$$\beta = \frac{R^2}{2l}\frac{\sin\theta}{\varepsilon} \qquad (24).$$

Consequently, if the values of $\sin\theta$ and ε corresponding to the experimental temperature are known, the constancy of α and β may be examined by the experimental data as follows. If we solve equation (17), the value of $\sin\theta$ will be given by the following equation:

$$\sin\theta = \frac{1}{6}\left(-\frac{R^2}{2lX_{0.P}} + \sqrt{\frac{R^4}{4l^2X_{0.P}^2} + 12}\right) \qquad (25).$$

Taking values of R and l (in the present experiment, $R = 0.071$ cm. and $l = 10.01$ cm.)⁽⁹⁾ and also that of $X_{0.P}$, the values of $\sin\theta$ for every experimental temperature will be obtained. These values are shown in Table 9. Adopting these values of $\sin\theta$, the numerical values of the constants α and β are computed and are shown in Table 10. If we take into consideration the magnitude of allowable experimental error of the measurement of $X_{0.P}$, it may be said that the calculated values of α and β show a good agreement with the values given in equation (20) and also

Table 9.

t	$\sin\theta$
5.80	0.5460
11.69	0.5497
15.00	0.5511
18.00	0.5612
20.50	0.5702
22.60	0.5750

Table 10.

t	α	β
5.80	$1.21_7\times10^{-4}$	$-1.60_3\times10^{-6}$
11.69	$1.30_2\times10^{-4}$	$-1.66_1\times10^{-6}$
15.00	$1.34_9\times10^{-4}$	$-1.58_3\times10^{-6}$
18.00	$1.43_8\times10^{-4}$	$-1.74_3\times10^{-6}$
20.50	$1.51_9\times10^{-4}$	$-1.79_5\times10^{-6}$
22.60	$1.57_5\times10^{-4}$	$-1.82_4\times10^{-6}$

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(9) F. Hirata, *Rev. Phys. Chem.* (Japan), **11** (1937), 262.

that these values are approximately independent of the change of temperature.

V. Conclusion. Although it is certain that there is a difference between the true configuration of micelles in the gel and the configuration assumed in the present theoretical calculation, the results of the verification described above will allow us to conclude that the assumptions adopted in the course of the theoretical treatment are acceptable, that is to say, the assumptions that the cause of the change of rigidity of gel due to temperature can be ascribed to the change of dielectric constant of intermicellar liquid due to temperature and that the nature of the intermicellar forces which cause the rigidity of gel must be an electric dipolar one.

Summary.

A relation has been derived theoretically between the dielectric constant of the intermicellar liquid and the rigidity of thermoreversible gel and the relation has been examined using the results of measurements of rigidity of the gel of gelatine.

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