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The First Step in the Swelling of Gelatin with Water. III

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The normal content of water in air dried gelatin is shown to be present as a solution of soluble gelatin. On this basis it is possible to give a detailed account of the progress of the watering of the gelatin.

In some earlier treatises [1] I have examined the speed of swelling of the Christensen-interference plate [2] with water. About five different plates were treated with water, each of them going through three successive treatments. It was thereby observed that after drying of the plates the edges of the extinction bands as a whole had shifted towards lower wavelengths.

In order to examine this peculiar phenomenon closer nine other plates were treated with water and dried, each one three separate times, in a single case four times, and the speeds of swelling and of the subsequent drying were examined. Thereby the said phenomenon was confirmed in all cases.

1. THEORY OF THE PHENOMENON

The wavelengths of the two edges of the extinction band (BB) are determined by the formula

$$\lambda_{\mathrm{I}} = 263 \left(n_{\mathrm{A}} \frac{v_{\mathrm{A}}}{100} + n_{\mathrm{G}}\right) \tag{1}$$

for the upper edge, and

$$\lambda_{\mathrm{II}} = 265 \left(n'_{\mathrm{A}} \frac{v'_{\mathrm{A}}}{100} + n'_{\mathrm{G}}\right) \tag{1a}$$

for the lower edge [3]. Here 263 and 265 are the thicknesses of the gelatin layer plus chromic oxide, n_{A} and n'_{A} the indices of refraction for silver bromide, n_{G} and n'_{G} the the same values for gelatin, and v_{A} and v'_{A} the percentage by volume of silver bromide.

Now, the falling off of the wavelength by subsequent treatment with water cannot be due to a loss of silver bromide as the solubility of this substance is extremely low. As the subsequent calculations show, the loss cannot be due to inorganic components (ashes) because then the found connections between the different amounts of water during the swelling process would be quite meaningless. Therefore the observed falling off must be due to a loss of gelatin.

2. EARLIER MEASUREMENTS

Pouradier[4] has found — using two homogeneous samples of gelatin — that up to 0.13 % of gelatin can be dissolved in cold water without any reduction of the molecular weight. It must be remarked that the examined samples of gelatin had been washed beforehand to remove impurities. Unlike Pouradier earlier investigators[5] had found that the high molecular gelatin had to be split up in smaller molecules in order to be soluble.

The loss of gelatin which I have found is of an entirely different nature. Each watering during two or three days caused a certain loss, and after drying renewed watering resulted in a further, but somewhat smaller, loss, tending against a maximal amount which cannot be exceeded. These maximal values lie between 2.8 and 5.7 % by volume of gelatin.

3. DIRECT MEASUREMENTS

About 1.5 g of Nelson I emulsion gelatin were dried to constant weight over calcium chloride and then for a total of ten days treated with cold water, which was renewed every second day. After removal of the water and spontaneous evaporation for some days the remainder was dried to constant weight over calcium chloride. Thereby were found losses of 16.4 and 16.8 % by volume, on an average 16.6 %.

As the values of G′, the percentage by volume of unhardened gelatin in the interference plates, lie between 31.4 and 22.2 for, respectively, the upper and the lower edge of the BB the values for the interference plates should lie between 3.7 and 5.2 if the densities are the same for the soluble and the insoluble parts of the gelatin.

It is commonly known that commercial gelatin must be regarded as a mixture of molecules of varying size, *e.g.* from 5 000 to 100 000. It may reasonably be taken for granted that only the smallest molecules are directly soluble, whereas the big molecules just swell with water, with the exception of the very small percentage of soluble gelatin which is found among the big molecules, as mentioned before.

4. THE WATER CONTENT OF THE GELATIN

It is commonly known[6] that commercial gelatin contains 10—20 % by weight of water, or 13.6—26.2 % by volume, if the density of completely dry gelatin is taken as 1.42 (see below).

In the course of the swelling experiments the amounts of water, V, which were absorbed during all series of watering were calculated for all values g of dissolved gelatin, from $g = 0$ to $g = g_{\infty}$. The differences V_0 to V_{∞} for the 9 examined plates (18 values) lie between 12.0 and 24.0 % by volume. This leads to the conclusion that the soluble gelatin in air dried gelatin is present as a solution. As the quotient $(V_{\infty}—V_0):g_{\infty}$ for the 18 cases varies irregularly between 3.8 and 4.5, average 4.1, the said solution must contain about 25 volumes of gelatin to 100 volumes of water.

The mean value of the 18 values measured here is 17.3. As the mean of 13.6 and 26.2 is a little higher (19.9) I have taken the value 18 as a general mean. The earlier [7] found value of d_G, the density of air dried gelatin, 1.32, consequently must apply to this water content. Therefore, the value of d_G for absolutely dry gelatin and for gelatin with other water contents can be calculated. The results are shown in Table 1.

Table 1.

Water	d_G
0	1.42
12	1.35
18	1.32
24	1.30

The same considerations apply to the values of n_G, the indices of refraction for gelatin, which I have measured on an earlier occasion [7]. Through use of the formula

$$\frac{n_G-1}{d_G} = \frac{(n_v-1)\frac{v}{100}}{1} + \frac{(n'_G-1)\frac{100-v}{100}}{1.42}$$

where n_v, n_G and n'_G are the indices of refraction for water, gelatin with 18 % by volume of water, and for pure gelatin, respectively, it is possible to calculate the indices of refraction for pure gelatin and afterwards for gelatin with different contents of water. Table 2 shows the results.

Table 2. n_G for different water contents.

λ	0	3	6	9	12	15	18	21	24
700	1.580	1.569	1.558	1.547	1.539	1.529	1.518	1.511	1.504
650	1.585	1.574	1.563	1.552	1.542	1.533	1.525	1.517	1.510
600	1.590	1.579	1.568	1.557	1.547	1.537	1.527	1.520	1.514
500	1.600	1.589	1.578	1.567	1.555	1.546	1.536	1.530	1.524

5. THE LOSS OF GELATIN BY WATERING OF THE INTERFERENCE PLATE

It is now possible to calculate the loss of gelatin. To this end the formula 1 must be altered in the following way:

$$\lambda_{\mathrm{I}} = \left(263—253\,\frac{\mathrm{g}}{100}\right)\left(n_{\mathrm{A}}\,\frac{v_{\mathrm{A}}}{100} + n_{\mathrm{G}}\,\frac{100—\mathrm{g}}{100}\right)$$

and formula 1a is altered in the same way. Here g is the percent loss of gelatin after each treatment with water for 2 or 3 days, and the number 253 is the thickness of the pure gelatin layer [8]. The values of g are found in Table 3 where the first column shows the number of the plate. Each plate of the size 9 × 12 cm was divided into small pieces, and the small index figure denotes the number of the examined piece of the particular plate. The figures I and II denote the upper and lower edges of the BB. The second column shows the number of days, D, during which the plate was treated with water, the third the successive values of the wavelengths, the fourth the values of v_{A}, the percentage by volume of silver bromide, the fifth the observed wavelengths after watering for 2 or 3 days. These wavelengths were found to be practically constant for each individual plate and edge. The values here quoted are the averages of the individual measured values. The sixth column shows the values of g.

6. THE MECHANISM OF THE ABSORPTION OF WATER

In the second paper in this series [9] I have found that the first absorption of water, v_0, takes place very rapidly. In the said paper I have also found that the speed of this first diffusion through the plate is 0.69 sec for each μ of thickness. The nine plates now examined have thicknesses from 9.6 to 12.0 μ, and the time for the first diffusion therefore varies from 6.6 to 8.3 sec, a quite negligible value compared with the much longer spaces of time for the following periods of watering.

As the new measurements show the subsequent absorption of water can be divided in two periods, both of which are first order. The first of these periods is ended in about 30 min, whereas the second takes 2 or 3 days.

Assuming, as said before, that the soluble gelatin is present as a series of solutions, situated between the higher molecular gelatin molecules, it is probable that some of these solutions are directly accessible, whereas others are protected by the big molecules. The first ones must therefore be diluted by the water and must hereby give the water the possibility to penetrate into the adjacent cavities between the big molecules. This process then takes about 30 min. Thereafter the dissolved gelatin has to diffuse out into the outer water, and the water in the layer has to force its way between gelatin and silver bromide, and then to fill all accessible cavities. These latter processes are very slow and take a total of about 2 or 3 days.

Furthermore, during the drying the whole network has the possibility of rearranging so that new regions of gelatin solution are made accessible to the next ingress of water. This is going on as long as there is any soluble gelatin available.

Table 3.

Plate No.	D	λ	v_A	λ_∞	g	v_0	v_1	V	Δ V	$\frac{\partial g}{\partial V}$	k_1	k_2	k_g
196$_7$I	0	628	38.5	552	0	81	—	136	20.0	—	—	—	0.074
	3	606			2.1	106	100	144.5		4.0	0.055	0.073	
	2	597			3.0	120	121	148		3.9	0.056	0.128	
	3	596			3.4	—	135	151		4.0	0.074	0.172	
	∞	—			5.0	—	—	156		4.0			
196$_7$II	0	566	26.0	541	0	90	—	147.6	12.4	—	—	—	0.068
	3	550			1.5	115.5	112	153		4.1	0.040	0.069	
	2	544			2.1	128.5	131	155		3.8	0.044	0.123	
	3	536			2.9	—	139	158		4.0	0.067	0.129	
	∞	—			4.0	—	—	162		4.0			
196$_{11}$I	0	565	26.2	556	0	97	—	158	12.0	—	—	—	0.149
	2	548			1.5	110	120	164		3.9	0.051	0.095	
	2	544			2.1	136	129	165.5		4.0	0.056	0.066	
	2	538			2.7	—	150	167		4.0	0.057	0.154	
	∞	—			3.0	—	—	170		4.0			
196$_{11}$II	0	527	19.4	542	0	102	—	159.5	14.5	—	—	—	0.153
	2	510			1.6	113	126	166		4.1	0.049	0.090	
	2	506			1.9	139	130	167		3.9	0.064	0.076	
	2	499			2.6	—	157.5	170		4.0	0.103	0.084	
	∞	—			3.1	—	—	174		4.0			
196$_8$I	0	546	24.2	546	0	82	—	156.5	20.0	—	—	—	0.062
	2	533			1.5	119	117	162.5		4.0	0.044	0.120	
	3	525			2.4	143	141.5	166.5		4.1	0.077	0.119	
	3	514			3.7	—	151	172		4.2			
	∞	—			4.9	—	—	176.5		4.1			
196$_8$II	0	511	18.0	534	0	85	—	158.5	20.0	—	—	—	0.122
	2	494			2.1	123	125	167		4.0	0.049	0.069	
	3	483			3.2	148	142	173		4.5	0.061	0.114	
	3	481			3.3	—	158	174		4.7			
	∞	—			4.5	—	—	178.5		4.4			
216$_9$I	0	632	39.1	516	0	69	—	113	20.5	—	—	—	0.067
	3	600			3.0	83	87	125		4.0	0.057	0.116	
	2	600			3.0	98	94	125		3.9	0.066	0.061	
	3	596			3.4	115	111	126.7		4.0	0.066	0.115	
	2	591			3.9	—	122.5	128.5		4.0	0.054	0.158	
	∞	—			5.1	—	—	133.5		4.0			
216$_9$II	0	571	30.0	501	0	81	—	121.5	22.2	—	—	—	0.059
	3	551			2.0	94.5	98	130		4.2	0.048	0.112	
	2	546			2.5	110	106	132		4.1	0.074	0.114	
	3	537			3.5	120	121	136		4.0	0.050	0.080	
	2	537			3.5	—	128.5	136		4.0	0.058	0.181	
	∞	—			5.4	—	—	143.7		4.1			
216$_{12}$I	0	575	28.6	503	0	74.5	—	122.5	14.6	—	—	—	0.139
	2	558			1.7	97.5	94	129.3		4.0	0.073	0.105	
	2	549			2.6	118.5	111	133.2		4.1	0.072	0.138	
	3	548			2.7	—	128.5	134		4.2	0.076	0.211	
	∞	—			3.6	—	—	137		4.1			
216$_{12}$II	0	547	22.6	486	0	75	—	120	12.0	—	—	—	0.122
	2	538			0.8	92	91	123		4.0	0.080	0.119	
	2	524			2.3	115	108	129		3.9	0.067	0.132	
	3	524			2.3	—	126	129		3.9	0.062	0.246	
	∞	—			2.8	—	—	132		3.9			

Table 3 (continued)

47_{3}I	0	605	33.8	492	0	62	—	107.5	14.5	—	—	—	0.074
	2	—			1.4	—	74.5	111.5		4.0	0.048	0.060	
	(3)	580			2.6	87	—	117.5		3.9	—	—	
	2	571			3.4	105	108	121		3.9	0.039	0.103	
	2	569			3.6	—	112	122		3.9	0.067	0.105	
		—			3.6	—	—	122		3.9			
47_{3}II	0	547	22.8	459	0	65.5	—	104	12.2	—	—	—	0.088
	2	—			1.1	—	80.5	107.8		3.8	0.050	0.057	
	(3)	524			2.3	88	—	112.7		3.8	—	—	
	2	516			3.2	102	101	115.5		3.8	0.053	0.155	
	2	516			3.2	—	110	115.5		3.8	0.064	0.166	
		—			3.5	—	—	116.2		3.8			
47_{10}I	0	555	24.6	454	0	58	—	99.5	12.4	—	—	—	0.121
	2	543			1.3	79.5	74	105		4.2	0.051	0.093	
	2	537			2.0	94.5	91	107		3.8	0.052	0.085	
	2	532			2.6	—	98.5	109		3.6	0.046	0.208	
		—			3.1	—	—	112		3.9			
47_{10}II	0	508	16.0	434	0	60	—	100.5	12.3	—	—	—	0.108
	2	494			1.1	79	74	105		4.1	0.068	0.115	
	2	487			1.8	94	88	107.4		3.8	0.081	0.122	
	2	483			2.3	—	100	109		3.7	0.050	0.151	
		—			2.9	—	—	110		3.9			
212_{10}I	0	615	36.7	568	0	101	—	149	24.0	—	—	—	0.072
	2	—			1.5	—	124	156		4.4	0.067	0.112	
	(3)	582			3.3	120	—	163		4.4	—	—	
	2	580			3.6	138	138	165		4.4	0.042	0.081	
	2	572			4.3	—	155.5	168		4.4	0.039	0.156	
		—			5.5	—	—	173		4.4			
212_{10}II	0	559	26.0	553	0	110	—	157	22.4	—	—	—	0.092
	2	—			1.5	—	135	163		4.0	0.050	0.145	
	(3)	530			3.7	128	—	171.4		3.9	—	—	
	2	526			4.2	146	145	174.6		4.2	0.057	0.097	
	2	522			4.6	—	163	176		4.2	0.046	0.156	
		—			5.3	—	—	179.4		4.1			
212_{11}I	0	638	40.3	583	0	—	—	152	20.3	—	—	—	0.158
	2	614			2.3	116	116	162		4.4	—	0.103	
	2	602			3.4	139	135	167.8		4.6	0.064	0.100	
	2	597			4.0	—	150	170		4.5	0.058	0.107	
		—			4.5	—	—	172		4.5			
212_{11}II	0	576	28.9	560	0	—	—	155	21.3	—	—	—	0.108
	2	555			1.9	122	127	163		4.2	—	0.082	
	2	545			3.1	142	142	168.5		4.4	0.069	0.132	
	2	537			3.8	—	155	171.5		4.4	0.062	0.172	
		—			4.9	—	—	176.3		4.3			

7. CALCULATION OF THE AMOUNT OF WATER

The results of the treatment with water were measured spectrographically after 1, 2, 4, 8, 15, 30, 60, 90 and 120 min, and then after 2 or 3 days. Prolonged watering had no further effect.

The wavelengths observed during the treatment with water are all of the second order. In order to convert these values into the corresponding wavelengths of the first order, I have calculated, with the aid of the indices of refraction for gelatin (with 18 % by volume of water), water and silver bromide, a series of curves which indicate the factor by which the observed wavelength has to be multiplied, for a series of different percentages by volume of water. In each case a probable value is found by a preliminary calculation, and if the finally calculated value for v_v differs too much from the supposed value the calculation is repeated until the supposed and the finally calculated values are practically the same.

The formula for the calculation for the upper edge of the BB is

$$\lambda_v = \left(263—253\frac{g}{100}\right)\left(n_A\frac{v_A}{100} + n_G\frac{100\text{-}g}{100} + n_v v_v\right)$$

and similarly for the lower edge.

For the first series of measurements of the individual plate the value of g is at first zero. During the further treatment with water the available amount of soluble gelatin, g, is dissolved and removed. The final value V therefore must be calculated with this value of g inserted in the formula. The same is the case for all the values in the third period — from 30 min to 2—3 days — when the solution of gelatin is diluted and removed.

I have, therefore, calculated two series of values of v_v, the first one for $g = 0$, the second for $g = g_1$. These two curves are practically parallel. Then I have drawn a curve from the beginning of the lower curve to the upper one in such a way that it coincides with the upper one after about 30 min and thereafter follows this curve to the end. For the next following treatments with water the two curves are calculated for $g = g_1$ and $g = g_2$, and so on.

The results are given in Table 3, where the 7th column contains the values of v_0, the momentary absorption of water, the 8th column the values of v_1, the second step, and the 9th column the values of V, the final amount of water. The 10th column shows the difference $V_\infty—V_0$, which indicates the amount of water in the air dried plate, the 11th column the quotient Δ V: Δ g and the 12th and 13th column the two reaction constants of the first order, where the time factors denote minutes and hours, respectively.

The table shows some irregularities. The plates 47_3 and 212_{10} were at first watered as usual. Then they were placed in water for 2 days without measuring the wavelength, only to find the speed of drying. After the drying they were measured again in the normal way during the following treatment with water. For No. 212_{11} it was impossible to measure the values up to 15 min on account of a technical hindrance. Therefore the values of v_0 could not be found in this case.

8. THE VALUES OF g_∞ AND V_∞

These values can be found in two different ways, either graphically, as points of intersection between the two curves which show the variation of

v_0 or v_1 with g, and of V with g, or by calculating the values of g as if varying after the first order, the time factor denoting days, and thereafter calculating the corresponding values of V_∞ as

$$\frac{V_\infty - V_0}{g_\infty - g_0} = 4.1$$

The values of k_g are to be found in Table 3, column 14.

9. THE VALUES OF v_0 AND v_1

If the theory here advanced is correct the values of v_0 must be a little higher than the immediately preceding values of v_1. The values of v_0 have been increased by the cavities, which were made free at the preceding treatment by removal of the soluble gelatin. Furthermore, this soluble gelatin itself has a certain volume, which has to be added to v_1 to give the next value of v_0.

The individual measurements are not accurate enough to allow a test of this kind. The only way is to examine the question in a statistical way. A total of 34 corresponding pairs of v_0 and v_1 have been measured. 22 of them give positive values of the difference $v_0 - v_1$, all of them together making 89.7. The other 12 give negative values, totalling 44.7. The total positive amount is 45.0, on the average 1.32.

The corresponding values of Δg for the 34 cases average 1.26. The two figures are identical.

10. THE SPONTANEOUS DRYING OF THE WET PLATE

In the last paper in this series [10] I have found that the spontaneous drying of the wet interference plate follows the equation

$$v_v = V_\infty \cdot 10^{-k_5 t/D}$$

where D is the thickness of the plate in μ. The thickness of the coating was measured as previously [11] by counting the number of interference lines. The piece of plate glass which was laid on to the edge of the coating was very small, and the distance from the scratched line to the edge of the plate was only 4.4 mm. It was illuminated with the yellow sodium line (589 mμ). Table 4

Table 4.

Plate No.	196_7	196_{11}	196_8	216_9	216_{12}	47_3	47_{10}	212_{10}	212_{11}	mean
D	11.5	11.7	11.0	9.6	12.0	10.3	9.6	10.6	10.6	
k_5 upper	2.33	2.59	2.60	2.51	2.88	2.57	2.27	2.24	2.45	2.48
k_5 lower	2.36	2.65	2.66	2.18	2.55	2.41	2.44	2.37	2.26	2.43

contains the results for the 9 examined plates. The first line of values for k_5 corresponds to the upper edge, the second one to the lower edge of the BB.

The total mean is then 2.46. In the earlier experiments the mean value 2.38 was found for 5 other plates. These two values must be regarded as identical.

11. CONCLUSIONS

1. It is found that by watering of the interference plates some per cent of gelatin is removed. After drying and renewed watering a further, but smaller, portion is removed, and so on, up to a certain limit.
2. The soluble gelatin is shown to be present in the air dried gelatin in the form of a solution of about 25 volumes of gelatin in 100 volumes of water.
3. By the aid of a simple model of the interference plate it is possible to divide the amount of swelling water into three parts which are absorbed with different speeds. It is possible to give a probable explanation of this phenomenon.

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