Publication of the Experimental Physical Institute of the University of Szeged
Director: Prof. PAUL FRÖHLICH

The Preexcitation of Gelatineous Dyestuffs.

by L. SZALAY (Szeged, Hungary).

I. Introduction.

A great amount of experimental work has already been done on the emission of the solid gelatineous solution of organic dyestuffs.[1] The interesting effect of preexcitation was covered by P. Fröhlich, working in collaboration with Z. Gyulai.[2] They illuminated a small part of the painted gelatine plate by an exciting light of great intensity and — when the phosphorescence emission ceased — they excited the whole plate by a light of much weaker intensity. They found that the preexcited small part of the plate phosphoresced much more intensively than its surroundings. The preexcitated state of the plate remained for a considerable time after the preexcitation, some of the different substances showing the effect two or three hours later. Fröhlich and Gyulai studied the solid gelatineous solution of Rhodulin Orange N.

Mischung's investigations referring to the absorption of gelatineous paintphosphors showed an increasing absorption during the excitation.[3] The influence of preexcitation manifests itself in an increased power of absorption and that of the influence of the preexcitation in the emission is the same. According to Mischung's opinion the intensive emission of the preexcitated surface is due to the increased power of the absorption, for the preexcitated surface takes up more energy than its surroundings,

It has been shown by Kautsky that the same effect can be found on Kautsky-phosphors.[4] A similar effect on Lenard-phosphors was not observed at all.

This paper is an attempt to examine the preexcitation effect.

Apparatus and experimental procedure.

To describe the influence of the preexcitation on the emission of the paint I had to compare two surfaces having phosphorescences of different intensity. I used for the comparison an absorbing wedge filter.[5] The gelatine wedge was put in a mounting. The mounting could be moved by a screw so that the transmission of the wedge could be varied in a familiar manner. By means of the wedge I made the intensive phosphorescence emission of the preexcitated surface as weak as the emission of the surroundings.

I calibrated the wedge by a thermo-junction and I found that the change of the absorption is proportional with the thickness of the wedge taking the needed part of the wedge into consideration. Therefore the degree of the moving of the wedge is suitable for describing the intensity of the preexcitated state. To give a description of the preexcitation I measured the moving of the wedge in mm-s.

The thickness of each plate was 0,1 mm. To give the concentration I used a logarithmic one.

The arrengement of the apparatus is shown in Fig. 1. The electric lamp A is enclosed in a box. (The lamp was Tungsram A78T41, 110 V, 1000 W), The phosphoroscope D was separated from the lamp by means of a black curtain. The curtain had a small slit in order to make the path of the beam of illuminating light to the phosphoroscope, free. Light from A passes through two lenses (L_1 and L_2). Between the source of light and the lense L_1 there was a water cooler to absorb the heat-rays. I used a Becquerel-phosphoroscope. A metal box was placed between the disks of the phosphoroscope which could be cooled and heated. The phosphoroscope was driven by an electromotor. The turning of the motor was 1150/min during the measurements. The absorbing wedge filter F was placed before the phosphoroscope. To weaken the preexcitating intensive light I used a glass plate covered with fine lampblack. This plate weakened the light at a rate of 2,6/1,0. This was measured by a thermo-junction.

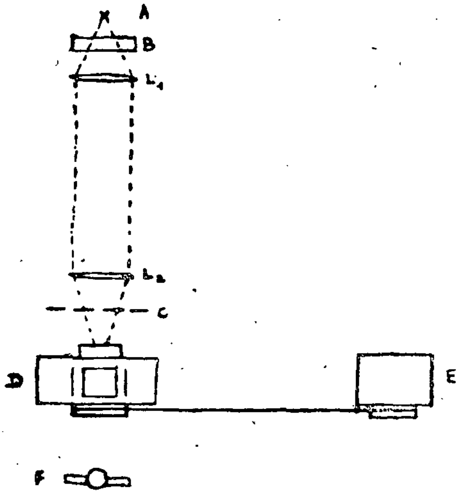

Fig. 1.

One half of the phosphorescing round spot was covered by a metal screen during the preexcitation so that a sharp line parted the preexcitated half of the spot from the other. The duration of the preexcitacion was ten minutes in every case. I began the excitation by a weak light 10 minutes after the ceasing of the preexcitation and I measured the intensity 10 minutes later.

Higher temperatures were made by electrical heating. I measured the temperature by placing a mercury thermometer into the measuring space through a thick felt-cork close to the plate to be investigated.

To make low temperatures I used solid CO_2 and liquid air. I measured the low temperatures by means of a penthanthermometer, The measuring space was closed by two glass plates being electrically heated to avoid the condensation of water vapour. By means of the solid CO_2 I reached a temperature of —20° C, The temperatures between —180° C and —20° C were obtained by a suitable supply of liquid air which caused a wavering of the temperature af about ± 5° C during the measurements. Taking into consideration that the change of the effect of preexcitation was not of high degree at these temperatures. the wavering of the temperature had no influence on the accuracy of the measurements.

II. Results.

a) *The extinction of the preexcitation.*
Extinction and temperature.

To investigate the duration of the preexcitated state I had to compare the phosphorescense emission of the preexcitated part of the plate with the other at different points of time after ceasing of the

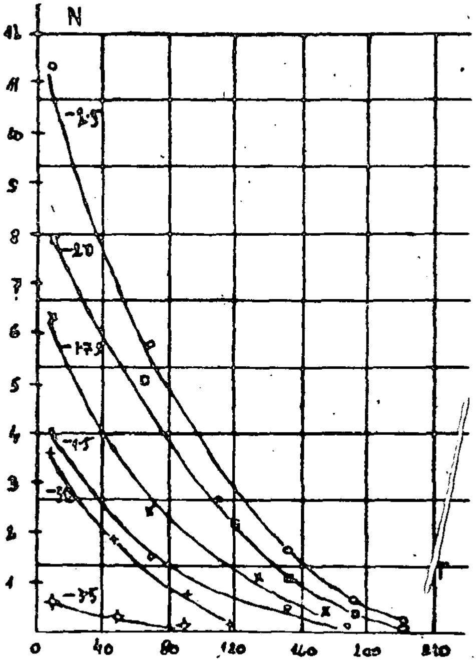

Fig. 2.

preexcitation. The extinction of the prexcitation in connection with the concentration is shown in Fig. 2. These measurements refer to Rhodulin Orange. N means the moving of the absorbing wedge filter in mm-s, T means the time of extinction in in minutes. The same appointments will be used later too. The extinction has a remarkable concentration dependence and the form of the curve can be characterised by an exponential function. Fig. 2. shows on the one hand that there is an optimal concentration considering the duration of the extinction and on the other hand that there is an optimal concentration from the point of view of the intensity of the influence of preexcitation in each moment of extinction. This can be seen from the fact that the extinction curve belonging to the concentration of —2, 5 goes everywhere above the curves belonging to the other concentrations. The duration of the influence of preexcitation is the longest at the concentration of —2, 5 and the shortest at the concentration of —3, 5.

Table 1.

c	after the preexcitation											
	T	N	T	N	T	N	T	N	T	N	T	N
— 1,50	10	4,1	70	1,5	153	0,6	190	0,2				
— 1,75	10	6,4	70	2,5	135	1,2	177	0,6	200	0,4		
— 2,00	10	7,9	70	5,3	120	2,3	152	1,2	192	0,5	222	0,3
— 2,50	10	11,3	70	5,8	110	2,7	153	1,6	193	0,7	223	0,4
— 3,00	10	3,6	45	1,9	92	0,8	118	0,2				
— 3,50	10	0,7	45	0,3	90	0,2						
— 3,75	10	0,5										

The results are shown in Table 1. where c means the logarithmic concentration. Further I have to mention that I have investigated several different dyes and found that they have a similar extinction but the time of extinction and the steepness of the curves are different. The extinction depends on the temperature too. In order to examine this dependence I investigated the influence on extinction of temperatures differing to a high degree. I used Rhodulin Orange wich had a concentration of —2, 5. The first experiment was made in the following way. I preexcited the painted plate at a temperature of 16° C and after the preexcitation I put into a space having a temperature of 130° C. I cooled the plates and I measured the intensity of the effect at different points of time. I found that the state of preexcitation ceased more rapidly in this case. On the other hand I put the preexcitated plate into a space having a temperature of —180° C. When heated to the original temperature of the preexcitation I measured the intensity at different points of time. These measurement indicated that the preexcitated state of the gelatine plate when cooled, remained for a much longer time than that of original temperature. The results obtained are in Table 2.

Table 2.

c	temperature	after the preexcitation											
		T	N	T	N	T	N	T	N	T	N	T	N
− 2,5	-180^0 C	95	7,9	165	3,9	235	2,1	335	1,4	415	0,9	475	0,5
	$+130^0$ C	34	4,7	70	3,1	95	2,3	120	1,3	180	0,2		

Further these investigations indicate that the painted plates being preexcitated at a temperature of 16^0 C keep their state after cooling and heating.

b) *Concentration dependence.*

The influence of preexcitation depends on the concentration of dye to a high degree. It can be seen in the second vertical column of Table 1. where the numbers, which characterise the intensities of preexcitation belonging to different concentrations, refer to an extinction time of 10 minutes. The dependence on concentration is shown very clearly in Fig. 3. This indicates the dependence of concentration in three ponts of time of extinction. The two extreme points of the middle

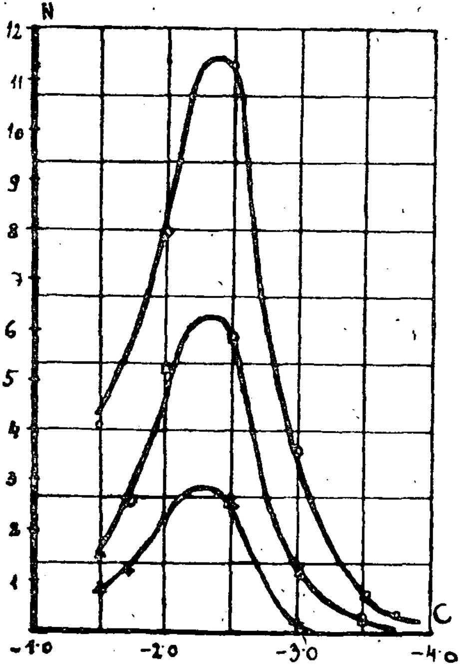

Fig. 3.

curve (concentrations of —3,0 and —3,5) belonging to an extinction time of 70 min was drawn by means of the suitable extinction curve on Fig. 2. by interpolation. The curve beloging to an extinction-time of 120 min was drawn in the same way. The logarithmic concentrations were measured on the vertical axis. As is to be seen, the intensity of the preexcitation increases when concentration is increased but a further increasing of concentration causes a decreasing of the intensity. The intensity curves have a selective maximum at a concentration of —2,3. This maximum does not depend on the extinction.

Moreover I investigated the concentration dependence of the intensity at Rhodamin S and Methyleosin. The results obtained are shown in Table 3. The behavior of these paints is similar to that of Rhodulin Orange in the former case. One can see that the intensity of preexcitation has a very remarkable concentration dependence in these dyes too.

Table 3.

c		— 1,75	— 2.0	— 2,25	— 2,5	— 3,0	— 3,5
Rhodamin S	N	weak	1,7	3,8	1,5	weak	—
Methyleosin		weak	0,5	—	0,7	1,4	0,2

The intensity curve of Rhodamin S has a maximum at a concentration of —2,25. The maximum of Methyleosin is at a concentration of —3,0.

I have to remark that I investigated gelatine plates without any dye and I found that there is a preexcitation effect of very small degree. But it was so weak that I could not measure it.

c) *Temperature dependence.*

I made a detailed investigation of the preexcitation effect on Rhodulin Orange preparations to know the influence of temperature on the effect. For that purpose I measured the intensity of preexcitation at different temperatures between —160° C and 110° C. I used painted plates of different concentrations. My first experience was that there is no effect at a temperature of —160° C and —110° C. At a temperature of —32° C I could measure the effect, though it was fairly weak. When the temperature was increased the intensity of preexcitation increased at each concentration too. But this increasing was not constant, az I reached a temperature of 4° C the rising of the curve ceased. The curve had here a selective maximum, the intensity decreased when temperature was increased.

There is a temperature at which one can find no effect. A very interesting fact is that this temperature at each concentration is the same, namely 28° C. This is to be seen on Fig. 4. where each intensity curve reaches the axis of temperature at the same point taking the error of measurement into account.

The temperature on which the gelatine plate was prepared was called by Fröhlich and Gombay[6] the ground temperature of the plate. Their investigations show that the percentage of partially polarized phosphorescence emission at the ground temperature is the highest. At is to be seen from my results the ground temperature is an important one from the point of view of preexcitation.

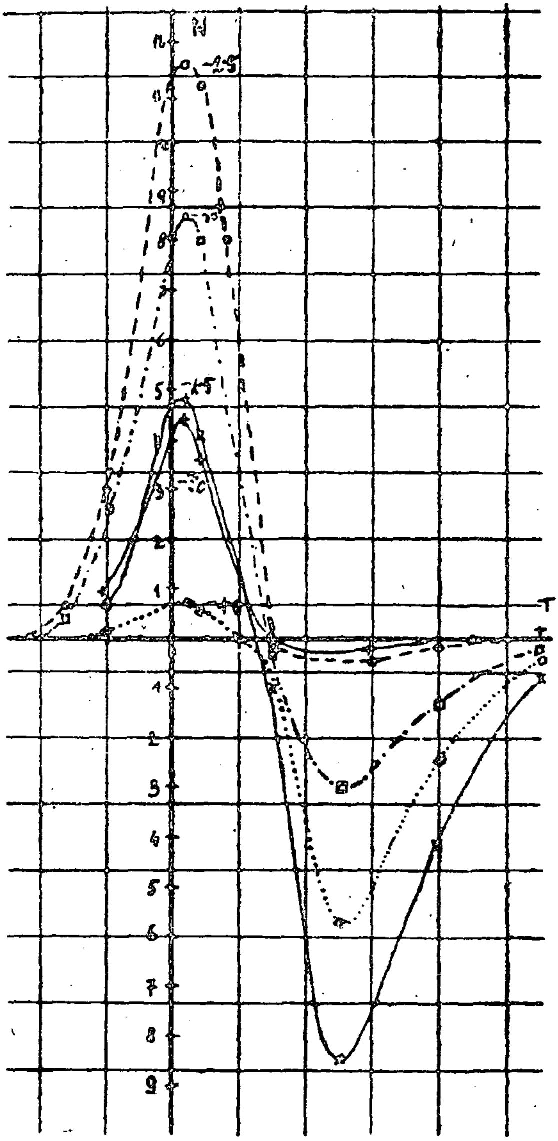

Fig. 4.

I notice that the intensity of preexcitation on plates having small concentrations will never be zero. I always observed an effect of very small degree by the concentrations of —3,5, —3,75, and —4,0 with a temperature of 4° C. This can be seen in the 7th horizontal line of Table 4. At higher temperatures than the critical 28° C, I found a very

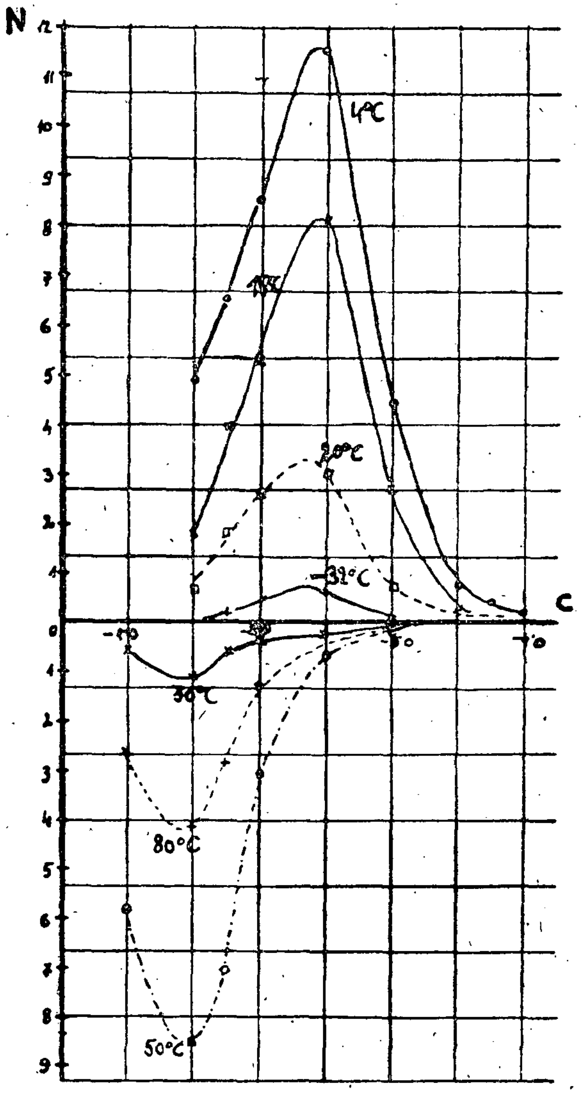

Fig. 5.

interesting and remarkable phenomenon which has never at all been observed till now. This interesting phenomenon manifests itself in the following way. The preexcitated little part of the plate has a weaker phosphorescence emission than its surroundings. I call this effect negative preëxcitation. The intensity of the negative preexcitation increases when temperature is increased as I observed at the positive preexcitation. There is a selective maximum here too at a temperature of 52° C. From this temperature the intensity of the negative preexcitation decreases,

Table 4.

c	N								
	−32° C	−20° C	+4° C	+8° C	−15° C	+30° C	+50° C	+80° C	+110° C
−1,00	—	0,2	0,8	0,6	0,2	−0,5	−5,8	−2,5	−0,4
−1,50	—	0,7	4,9	4,1	2,7	−1,2	−8,6	−4,2	−0,7
−1,75	0,3	0,8	6,4	6,2	3,9	−0,6	−7,1	−2,9	−0,3
−2,00	0,5	2,7	8,6	7,9	5,2	−0,4	−3,0	−1,3	−0,2
−2,50	0,7	3,0	11,6	11,3	8,1	−0,2	−0,6	−0,3	— weak
−3,00	—	0,9	4,5	3,6	2,7	—weak	−0,3	−0,2	— weak
−3,50	—	—	0,8	0,6	0,4	+weak	+ weak	+weak	+0,2
−3,75	—	—	0,2	0,5	—	+0,2	+0,2	+0,1	+0,3
−4,00	—	—	—	—	—	+0,2	+0,3	+0,2	+0,3
	only positive					positive and negative			

at last I found an intensity of a very small degree at a temperature of 110° C. I could not measure at higher temperatures on account of the alteration of the gelatine plates.

Consequently one cannot decide whether by a further increasing of the temperature a positive effect would be seen again. This question could be answered if we were to find a dye at which the negative effect could be detected at lower temperatures therefore the whole temperature-intensity curve would be moved towards lower temperatures. As a negative effect can be observed at other dyes it is not out of the question. To decide whether at a temperature higher than 110° C a positive effect would be seen again, I ought to have made a detailed investigation of more dyestuffs. As I already mentioned the plates of small concentrations have a peculiar behavior: I could not observe a negative effect on these.

As is to be seen the temperature has very interesting influence on preexcitation. From the ground temperature to the low temperatures there is a positive effect and to the high temperatures there is a negative one. There is an advantageous temperature from the point of view of both phenomena. From Fig. 4. can be seen that the advantageous temperature does not depend on the concentration.

I have to notice that the former statements are correct in the investigated period of the extinction of phosphorescence emission. As the measurements happened 0,005 min after the ceasing of excitation the results refer to this point of time of extinction. My observations show that this is an important circumstance for the investigation of preexcitation, because I observed that, though at a temperature of —70° C I could see no preexcitation — neither a positive effect nor a negative one — yet after the moving of the plate from the phosphoroscope, when the bright spot is fading on account of the extinction, I found a positive preexcitation. The observation is very easy on account of the low extinction time at this low temperature. One can suppose that the preexcitation depends on the extinction. To have a full description of this phenomenon I have to stretch the investigations.

The results referring to the temperature dependence of preexcitation are in Table 4. This shows that at low temperatures under of 15° C there is only positive preexcitation, from 30° C to 110° C at the high concentrations (from —1,0 to —3,0) there is only a negative one, but from a concentration of —3,5 at all temperatures there is a positive effect.

The concentration dependence of the positive and negative effect is shown in Fig. 5. At the investigation of the influence of concentration on preexcitation I found an optimal concentration of —2,3 from the point of view of preexcitation. The stretching of the investigations to different temperatures showed that the optimal concentration does not depend on the temperature. There is an optimal concentration from the point of view of the negative preexcitation and it is an interesting fact, that this optimal concentration is higher than that of the positive effect. Its value is —1,5 and it does not depend on the temperature.

As I already mentioned no influence of preexcitation can be observed at a temperature of —160° C. But if I cool the plate being preexcitated at the temperature of the laboratory to —160° C, and I investigate the cooled plate from the point of view of preexcitation, I find a positive preexcitation. This shows, that the preexcitated state can be frozen. Further I have to investigate whether the negative effect could be frozen. I need further investigations to compare the intensity of the preexcitation with that of the frozen one.

There are no detailed investigations referring to the different dyestuffs from the point of view of the influence of temperature. But I investigated some dyes at a temperature of 52° C. These observations show that Methyleosin, Rhodamin S and Rhodulingelb have a negative effect at this temperature. The behavior of Acridingelb G differs from that of the others, because I only observed a positive effect at the concentrations of —2,0, —2,5, and —3,0. But the dyes at which a negative effect could be observed show a positive one at small concentrations. The want of negative preexcitation at small concentrations, as these results show, can be found in a greater group of dyestuffs.

I beg to remark that I investigated the empty gelatine plate from the point of view of preexcitation at a temperature of 50° C. The phosphorescence emission was so weak at this temperature that I could not make any comparison. Therefore the existence of preexcitation does not influence my measurements.

III. Summary.

I investigated the preexcitation effect on gelatineous dyestuffs with a special regard to the influence of temperature. My most important results are the following:

From 28° C to a low temperature of —40° C I found a positive effect which had a selective maximum at a temperature of 4° C. From 28° C to 110° C I detected a new phenomenon — the negative preexcitation. This negative effect has a selective maximum at a temperature of 52° C.

The concentration at which the negative and positive effect has a maximum does not depend on the temperature, but the maximum of the negative effect is at smaller concentration than that of the positive one.

I found a positive effect at small concentrations at every temperature.

At each concentrations at which I found a negative effect the change from the positive effect to the negative one could be seen at the same temperature: all the intensitiy curves cut the axis of temperature at a temperature of 28° C.

* * *

An exact explanation of the phenomena of preexcitation is a difficult one at present. To have an exact explanation we ought to know the connection between it and other factors. Among others I have to investigate the temperature dependence of intensity in different points of the phosphorescence extinction perfectly.

There is no doubt that the preexcitation has an influence on the configuration of the phosphorcentren. This influence manifests itself as a positive effect at some temperatures and as a negative one at some other temperatures. This can be explained in the following way. There are temperatures at which the centres are in an advantageous configuration from the point of view of absorption and there are other temperatures at which they are not. It may be that in the latter case the absorption-electron is torn off the absorption resonator which causes a negative effect. A result of Gombay' s investigations referring to the electrical conductivity supports this supposition.[7] The maximum of the current being caused by negative or positive potential is at a temperature which is the most advantageous temperature from the point of view of negative preexcitation.

The concentration at which the negative effect turns to the positive one, is at every temperature the same (see Fig. 5.). This circumstance allows the supposition that the concentration plays an important part in the existence of preexcitation.

I hope that further investigations will give possibilities for an exact explanation of preexcitation.

* * *

This paper was prepared in Experimental Physical Institute of the University of Szeged. In conclusion I desire to record my sincere thanks to the director of the Institute, professor Dr. Paul Frőhlich for the introduction to the problem and for his constant encouragement and interest.

I wish to express my best thanks to Dr. Zoltán Zsebők councillor of the Hungarian Ministry of Education and Culture whose financial assistance made the publication of this paper possible.

References.

[1] *P. Frőhlich:* Mat. és Term. Tud. Ért. XLVII. 79, 1930.

P. Frőhlich and *H. Mischung;* Acta chem. min. et phys. VII. 93, 1939. Mat. és Term. Tud. Ért. LVIII. 927, 1939.

P. Frőhlich and *L. Gombay:* Mat. és Term. Tud. Ért. LIX. 846, 1940.

P. Frőhlich; Acta chem. min. et phys. IV. 1, 1934.

[2] *H. Mischung:* Acta chem. min. et phys. VI. 2—3, 1938. Mat. és Term. Tud. Ért. XLVII. 209, 1938.

[3] *P. Frőhlich* and *Z. Gyulai:* ZS. f. Phys. 104. 549, 1937.

[4] *Kautsky:* Ber. Dtsch. Chem. Ges. 65. 401, 1932.

[5] Apart from a few modifications I prepared the wedge according to Weigert: Optische Methoden der Chemie, Leipzig, 1927, p. 58. I used Gold DFG gelatine and Sólyom India ink.

[6] *P. Frőhlich* and *L. Gombay:* Kolloid ZS. 94. 147, 1941. Math. és Term. Tud. Ért. LIX. 3. 846, 1940.

[7] *L. Gombay:* Acta chem. min. et phys. 7. 102, 1939. Math. és Term. Tud. Ért. LVIII. 338, 1939.