

The deviations must be of such a kind as if the plates of greater thickness would behave as if of greater concentration.

Therefore, finally, it is concluded that only gelatine plates of similar thickness can be compared. In this case the proportion of ground concentrations is the same as the proportion of final concentrations. Yet this circumstance has been taken into account up till now, because it was noticed that the results of measurements were not reproductive in other cases.

Further the properties of gelatine dyestuff plates may be influenced by the time and temperature of drying, as on one hand the associated condition can be changed till complete dryness is reached, on the other hand the temperature may have an influence. These researches are in progress.

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The Orientation of Molecules in Gelatinous Dyestuffs as the Cause of Preexcitation.

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Introduction.

P. Fröhlich and Z. Gyulai (1) discovered that the gelatinous dyestuffs have a more intensive phosphorescence emission when they are formerly illuminated by an exciting light of great intensity. They ascertained this phenomenon in the following way. They illuminated a small part of the preparation by an exciting light of great intensity until it was saturated. After stopping the excitation when the phosphorescence emission ceased they excited the whole plate by an exciting light of moderate intensity. The spot

illuminated formerly phosphoresced more intensively than its surroundings. This preexcited state of the preparation remained for a notable time.

Recently detailed researches were carried out referring to the effect of preexcitation by L. Szalay (2). Using a simple method Szalay measured the variation of preexcitation with the temperature. These researches led to the discovery of a new effect called negative preexcitation. He investigated the influence of higher temperatures on the preexcitation and found that from a temperature of 4° C the effect of preexcitation is decreasing with an increasing temperature in the case of rhodulin orange N. At a temperature of 28° C he could not notice any effect. By further increasing of temperature an interesting change could be ascertained in the state of gelatinous plate: the preexcited small spot had a weaker phosphorescence emission than its surroundings. This effect was called negative preexcitation. These results show that the excitation by an intensive light may cause two kinds of change in dyestuffs at different temperatures. On one hand the preexcitation may cause a greater emissivity and on the other hand it may cause a smaller emissivity.

This peculiar behaviour of the dyestuff was not explained in a satisfactory manner. The positive preexcitation is due to the greater absorptivity according to Mischung's investigations, who found an increasing absorptivity during the excitation (3). This explanation, however, does not interpret the mechanism of the phenomenon, because we ought to know what is the cause of the greater absorptivity. But even if we accept this explanation it is not suitable for the interpretation of negative preexcitation, because H. Mischung did not find a decreasing of absorptivity in one case. Therefore L. Szalay made an attempt to explain the negative preexcitation in another way supporting L. Gombay's investigations. (2)

Taking these considerations into account we conclude that neither the positive preexcitation nor the negative had been explained in a satisfactory and uniform manner. An observation in connection with our recent researches referring to the behaviour of dyestuffs in rotating magnetic field (4) which showed that molecules when they have come to an ordered state keep their condition for a considerable time, and the results of G. N. Lewis and his co-workers — which we shall discuss particularly later — suggested a possibility of an explanation of preexcitation. In this paper we shall give this explanation and its experimental support.

The orientation of molecules in dyestuffs.

G. N. Lewis and T. T. Magel (5) investigated the attainment of maximum phosphorescence of fluorescein in boric acid glass. The noticeable slow approach to saturation at high intensities of exciting light suggested to them that some molecules are harder to bring into the phosphorescent state than others. They supposed that the molecules differ only in their orientation with respect to a beam of light. Those molecules whose optical axes lie near the plane that is normal to the beam of light are readily excited while those molecules whose axes are parallel to the beam have very small probability of excitation. This is not important in the case

of molecules which are randomly oriented in all directions. If the molecules are called in the phosphorescent state P molecules then the slow approach to saturation may be explained in the following way. The molecules whose axes lie near the plane that is normal to the beam of light may readily be converted into P molecules even with moderate illumination. But those molecules whose axes lie parallel to the beam would only be excited at much higher intensities.

It was also shown that the molecules in a phosphorescent state have a main optical axis for absorption in the same direction as that of the molecules in the ground state. After illumination the orientation effect entirely disappeared. Later they found that the orientation effect persists in dark until the solvent is melted (6). This has been found in the case of crystal violet. The permanent orientation effect has been studied further by G. N. Lewis and J. Bigeleisen (7). They ascertained the optical axes of different dyestuffs and found two groups of molecules. There are cases in which the molecules illuminated by polarized light show a maximum of absorption with a light which has a polarization parallel to that of the exciting light. When this is the case they speak of a normal orientation effect. There are other cases in which the maximum absorption is found when the direction of polarization of exciting and measuring light are perpendicular. This is called an abnormal orientation effect. They have tried to point out the abnormal orientation effect with unpolarized light, and they found orientation effect by viewing at right angles to the exciting beam.

They also found that some dyestuffs although so similar in structure, show different orientation effects, being normal in one case and abnormal in another. Therefore slight changes in structure may cause a change in the orientation effect. This result is a very important one from the point of view of our investigations.

Experimental.

The apparatus used for investigating the preexcitation effect was constructed according to L. Szalay (2) excepting that the source of light was a 5000 watt tungsten-filament lamp. The intensity of phosphorescence emission of preexcited surface with that of the not preexcited one was compared by using an absorbing wedge filter. The preexcitation effect was characterized by the rate of moving of wedge in mm-s (given in N) when the phosphorescence emission of the preexcited surface seemed as weak as that of the surroundings on viewing it through the wedge.

In our experiments the exciting light was polarized by a nicol prism. The duration of preexcitation was also ten minutes in every case. For weakening the preexciting light we used a glass plate covered with fine lampblack.

The gelatine plates were prepared according to P. Fröhlich (8).

Results.

1. Positive preexcitation.

We carried out the following experiments with polarized light on rhodulin orange N. The thickness of the plate was 0,1 mm.

First we preexcited the gelatine plate with a vertically polarized light of great intensity. After 10 minutes the opening of the

phosphoroscope was covered and the intensity of exciting light was weakened. Then the cover was removed from the opening of the phosphoroscope and the excitation began with polarized light having the same plane of polarization as before. After 5 minutes we compared the intensities of the two halves of phosphorescing round spot by means of the wedge filter. The rate of moving of wedge (N_1) is shown in the first line of Table 1. This procedure was carried out at each concentration. The results are shown in Fig. 1. The 1. curve shows the concentration dependence of preexcitation. There is an optimal concentration agreeing with that found previously by us (1,2).

Table 1.

| conc. | -1,75 | -2,00 | -2,25 | -2,50 | -3,00 | -3,50 |
|-----------|-------|-------|-------|-------|-------|-------|
| N_1 | 11,50 | 15,70 | 21,30 | 12,40 | 7,10 | 3,20 |
| N_2 | 9,50 | 10,40 | 10,70 | 6,20 | 2,20 | 0,80 |
| N_1/N_2 | 1,2 | 1,4 | 2,0 | 2,0 | 3,2 | 4,0 |

Then we took another plate cut from the same preparation. This was also irradiated with a vertically polarized light of great intensity for 10 minutes. After preexcitation we excited the plate — removing the metal screen — with a horizontally polarized light of moderate intensity. So the plane of polarization of preexciting and exciting light were perpendicular. The effect of preexcitation was smaller in this case, as is to be seen from the second line of Table 1. where the numbers (N_2) mean the rate of moving of wedge belonging to different concentrations. The concentration dependence is shown very clearly on the 2. curve of Fig. 1. This curve also has a maximum at a concentration of -2,25, but this maximum is not so selective as in the former case. We shall discuss the difference between the two curves later.

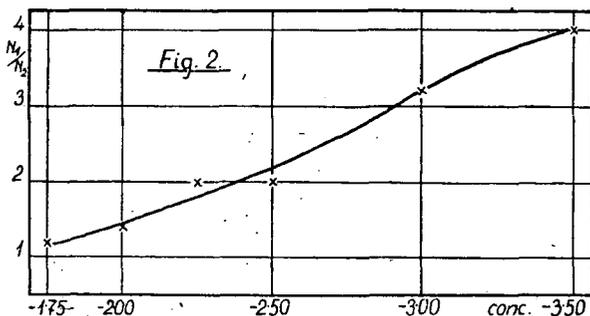
2. Negative preexcitation.

The intensity of the negative preexcitation effect increases when temperature is increased. At a temperature of about 50° C the intensity reaches its maximum (2), and from this temperature it decreases. Therefore we carried out our investigations at a temperature of 50° C. When we irradiated the gelatine plate with a polarized light of moderate intensity after the preexcitation with light polarized in the same plane, we found a negative preexcitation, just as it had been found previously (2). But if the planes of preexciting and exciting light were perpendicular the differences between the phosphorescence emission of the two halves of plate were smaller after the removing of the metal screen. The duration of preexcitation and that of the excitation with a light of moderate intensity were the same as in the case of positive preexcitation. As the results are also similar we do not give detailed results.

We have to notice an interesting fact referring to the negative preexcitation. Our first attempts at measuring the negative preexcitation showed that the negative preexcitation does not exist even at a temperature of 50° C in every case. The existence of the negative preexcitation depends on the rate of weakening of the

are parallel. Since the positive preexcitation effect is greater, according to our measurements, when the planes of polarization of preexciting and measuring light are parallel, there is no doubt that we have to consider the permanent orientation of molecules as the cause of preexcitation. Naturally, supposing an orientation of high degree, it would be also possible to ascertain a negative preexcitation instead of a positive one, when the planes of preexciting and measuring light are perpendicular. In this case the preexcited part of the plate would have a smaller emission than its surroundings. This phenomenon, however, has not been found. This may be explained by supposing an orientation of smaller degree, and by the deorientation effect of the measuring light itself.

The rate of orientation of molecules may be expressed as a quotient of N_1/N_2 , where N_1 means the rate of moving of wedge filter when the planes of polarization of preexciting and measuring light are parallel and N_2 the rate of moving of wedge when they are perpendicular. The number N_1/N_2 is not identical with the orientation ratio a/b used by G. N. Lewis and J. Bigeleisen. The rate of orientation depends on the concentration. We calculated the values of N_1/N_2 from the data shown in Table 1. The



results are found in the third line of Table 1. The connection between the rate of orientation and concentration is shown in Fig. 2. As we see, the rate of orientation is increasing when concentration is decreased. Apparently, this may be explained by the mutual effect of the neighbouring molecules. If the concentration is smaller, there is a greater distance between the neighbouring molecules, therefore they do not disturb each other.

As the rate of orientation is greater at smaller concentrations, it is a very surprising fact at first sight that we found an optimal concentration from the point of view of preexcitation. Since the rate of orientation is greater when concentration is smaller the effect of preexcitation would be also increasing when concentration is being decreased. But if the rate of orientation is increasing it means at the same time, that we need less energy for achievement of the state of orientation. As the intensity of measuring light was the same at each concentration, consequently it might have a greater deorientation effect at smaller concentrations. This deorientation effect also explains why L. Szalay did not find a negative preexcitation at small concentrations.

An explanation of the negative preexcitation supporting the measurements of absorption was not possible, because — as we mentioned above — H. Mischung did not find any decreasing of absorption during the excitation. G. N. Lewis and J. Bigeleisen, however, found that in some cases (investigations were carried out in the case of Wurster's blue) an abnormal orientation may be found. This abnormal orientation means that the absorption has a maximum when the planes of polarization of exciting and measuring light are perpendicular. There is no doubt according to our measurements that the abnormal orientation of molecules is responsible for the negative preexcitation. If the temperature is raised the orientation effect changes: at a temperature of e. g. 15° C the orientation is normal, and at a temperature of e. g. 50° C it is abnormal. In the latter case the preexcitation is negative. The discovery of the negative preexcitation is the first experience which has shown that both normal and abnormal orientation may occur in the same dyestuff under different circumstances. According to the investigations carried out up till now this ascertainment is not surprising. As we mentioned above G. N. Lewis and J. Bigeleisen (7) have pointed out that some dyestuffs which have a very similar structure, show different orientation effects; being normal in one case and abnormal in another. We assume that an isomer form of dyestuff is produced by the intensive illumination at such temperatures where the preexcitation is negative. This isomer form shows an abnormal orientation effect. G. N. Lewis, T. T. Magel and D. Lipkin (6) have found an evidence of an isomeric condition of crystal violet ion produced by illumination in rigid media. Possibly a similar phenomenon is responsible for the negative preexcitation, according to the statement above mentioned. Naturally we need further investigations to have a full description of this phenomenon.

Recent investigations of L. Szalay (2) showed that the negative preexcitation also has a maximum, but the maximum of the negative effect is at a greater concentration than that of the positive. The shifting of the concentration optimum towards the great concentrations may also be explained. We found that the existence of the negative preexcitation is influenced to a high degree by the rate of weakening of preexciting light. When $A < 2$ we could not notice the negative preexcitation. The existence of the positive preexcitation also depends on the rate of weakening of intensity of preexciting light, but the value of A may be smaller than in the case of negative preexcitation. If we do not find any preexcitation effect this means that a deorientation was caused by the moderate measuring light. Our investigations show that the deorientation needs more energy in the case of normal orientation than in the case of abnormal orientation. But if this statement is valid, it has also to be valid for the achievement of oriented condition. In the case of normal orientation we need more energy to orientate the molecules. Therefore the optimal concentration will be found at smaller concentrations. The energy which is necessary to orientate the molecules in the case of abnormal orientation is smaller. Therefore the optimal concentration will be found at greater concentration, because the disturbing effect of the neighbouring molecules is smaller in this case.

The rate of orientation (N_1/N_2) is increasing when concentration is diminishing. In spite of this fact smaller energy is necessary for orientation in the case of abnormal orientation where the optimal concentration is to be found at greater concentrations. This is clear when we suppose that in the case of the positive preexcitation the molecules of dyestuff are oriented in X direction, and in the case of the negative preexcitation in Y direction. (Fig. 1.)

Summary.

The preexcitation effect of gelatinous dystuffs has been studied theoretically and experimentally. The experiments were made with rigid gelatinous solution of rhodulin orange N. Both preexciting and measuring light were polarized. If the planes of polarization of preexciting and that of measuring light were perpendicular the effect was smaller. This was found for both positive and negative preexcitation. All the phenomena of positive and negative preexcitation have been explained by assuming the orientation of molecules. A new expression was used for describing the rate of orientation. It has been shown that the rate of orientation is increasing when concentration is diminished. It has been noticed that both normal and abnormal orientation may occur in the same dyestuff under different circumstances which has never been observed at all till now.

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