

The Excitation of Gelatinous Dyestuffs.

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Introduction.

In connection with the problem of excitation of gelatinous dyestuffs researches have been carried out by H. Mischung (1). The investigations of P. Fröhlich and Z. Gyulai led to the discovery of the effect of preexcitation (2), which was investigated in detail by the author (3). These researches suggested a method of measuring the time of saturation which seemed to give valuable data referring to the behaviour of the molecules of dye.

Since the number of excitable molecules is relatively small in some dyes and the duration of the excited state comparatively long (e. g. several seconds by Rhodulin Orange), there should exist a state in which practically all the excitable molecules are in an excited condition (4). This means that in the case of a constant exciting light the intensity of emission is increasing during the excitation and reaches a maximum. When this maximum is reached the phosphor is in time saturated and there is no increase in the intensity of emission by further excitation.

Experimental.

To measure the time of saturation I used the preexcitation effect (2, 3). If I excite the whole gelatine plate after the removing of the metal screen, by the intensive light used originally for preexcitation, there is also to be found a difference between the preexcited and not preexcited parts of the plate, but the difference soon disappears after the removing of screen. After a few seconds one cannot find any difference between the emission of the two parts. As I preexcited the plate for five minutes, the preexcited part of the plate was in time saturated, therefore the intensity of emission was not increasing during a further excitation. So the time of saturation is identical with that of the disappearance of intensity difference. I illuminated the plate by means of a 1000 watt tungsten-filament lamp so that a phosphorescing round spot was to be seen in the Becquerel phosphoroscope. One half of the spot was covered by a screen during the preexcitation. After the removing of the screen a sharp line parted the preexcited half of the spot from the other. I measured the time of disappearance of this line. This is the time of saturation.

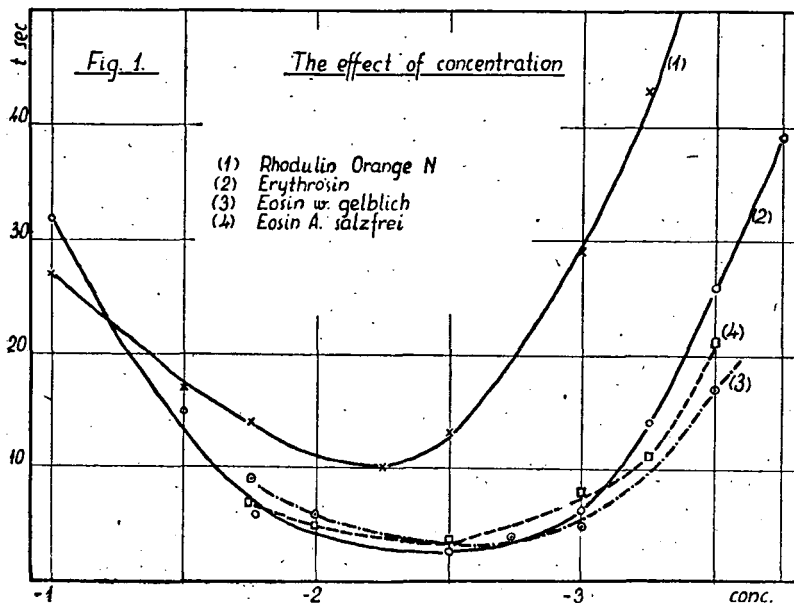
The experimental arrangement was the same as before (2). The disks of the phosphoroscope had four openings of $22,5^\circ$. The angle of the openings of the disk placed between the source of light and the gelatine plate could be varied from 0° to $22,5^\circ$. Therefore it could be used as a sector disk with variable openings, by means of which I was able to regulate the amount of energy falling upon the plate in the unit of time. As the angles of the openings of the other disk were not variable, the measurements did not happen in each case at the same moment of decay of phosphorescence emission. This slight change in the time of decay has no influence on the accuracy of the measurements.

I used gelatine plates of 0,1 mm thickness which were prepared according to P. Fröhlich (5). The concentrations are given in logarithmic ones.

Results.

1. Concentration dependence.

I investigated rigid gelatineous solutions of rhodulin orange N, erythrosin, eosin w. gelblich, and eosin A. salzfrei to know the influence of concentration on the time of saturation. I found that the time of saturation depends on concentration at a high rate. There is an optimal concentration, from which the time of saturation is increasing towards both the smaller and greater concentrations. Fig. 1. shows



that this optimal concentration is in the case of rhodulin orange N, erythrosin, eosin w. gelblich and eosin A. salzfrei at the concentrations of $-2,25$, $-2,40$, $-2,75$ and $-2,50$ respectively.

The time of saturation — according to the results referring to Lenard-phosphors — is longer when the decay is slow (6). The decay of gelatineous dyestuffs — especially in the case of eosin A. salzfrei — was investigated in detail by S. Benkő (7) at a wavelength of $558 \text{ m}\mu$. Benkő ascertained that the decay is slower when the concentration is increased. According to P. Fröhlich (8) the emission spectrum of eosin A. salzfrei has a selective maximum at the wavelength of $558 \text{ m}\mu$. As Benkő had to measure with wide slit his results may refer to the whole band. If the behaviour of this band is similar to that of the whole spectrum we may establish that the statement referring to Lenard-phosphors is also valid for gelatineous dyestuffs.

From the point of view of decay Benkő did not find any optimal concentration. As Benkő's measurement referred to concentrations from $-2,00$ to the smaller concentrations and the optimal concentration is near to the region of $-2,00$ we may suppose that he did not find an optimal concentration because he had not investigated the decay at greater concentrations than

—2,00. If this is the case then the statement above mentioned is generally valid. But if there is no optimal concentration from the point of view of decay, the statement is valid only for smaller concentrations.

2. *Connection between the time of saturation and the total amount of emitted energy.*

The dependence of the emission on concentration and temperature was investigated at rigid gelatinous solutions of rhodulin orange by P. Fröhlich and H. Mischung (9). The emitted energy referring to the whole spectrum

$$F = \int_0^{\infty} I_{\lambda} d\lambda$$

where I_{λ} is the intensity at the wavelength λ . The values of the emitted energy F were measured at different concentrations. The given numbers are relative values of energy. As my measurements were carried out at a temperature of 28° C I calculated the emitted energy belonging to the temperature of 28° C from the results of P. Fröhlich and H. Mischung by interpolation. So I gained the numbers shown in the second line of Table 1. These show that the total amount of emitted energy F has an optimal concentration of —2,25. The third line shows the values of time of saturation belonging to different concentrations taken from Fig. 1.

Table 1.

conc.	—1,00	1,25	—1,50	—1,75	—2,00	—2,25	—2,50	—2,75	—3,00	—3,25	—3,50
F	46	56	70	81	88	97	89	67	46	30	16
t	27	22	17	14	11	10,5	13	19	27	43	71
F.t	124	123	119	113	99	102	116	127	114	129	114

If we multiply the values of F and those of time of saturation (t) at each concentration we gain the same results within the greatest limit of error of 10,3%, taking the mean value of $F.t$ into account. Taking into consideration the circumstances which vitiated the results (errors involved in measurements of F and t and in the interpolation) and the irregular scattering of the values of $F.t$ we may establish that the products of emitted energy and the time of saturation are the same at each concentration.

3. *Connection between the time of saturation and the total amount of absorbed energy.*

The dependence of the absorption on concentration at rhodulin orange N was investigated by H. Mischung (1). She measured the absorption coefficients belonging to different concentrations. I calculated the total amount of absorbed energy from Mischung's absorption curves. The areas under the absorption curves (T) mean relative values of absorbed energy. These values are shown in the second line of Table 2. The third line shows the values of time of saturation belonging to different concentrations. The products of absorbed energy (T) and the time of saturation (t) are found in the fourth line.

Table 2.

conc.	—2,00	—2,25	—2,50	—2,75	—3,00	—3,25
T	148,0	78,5	42,1	29,5	17,0	11,9
t	11,0	10,5	13,0	18,5	30,0	46,0
T.t	1628,0	824,0	54,7	54,5	51,0	54,7

As is to be seen the values of the products are the same in the region of the concentrations of $-2,50$ — $-3,25$ within the greatest limit of error of 5,2%, but the deviation from the mean value is much greater at the greater concentrations. The concentration from which the product is not constant is identical with the optimal concentration found for the time of saturation ($-2,25$). According to Mischung the Beer's law is valid only for greater concentrations than $-2,25$. Therefore my researches show that the product of absorbed energy and time of saturation is not constant at concentrations for which the Beer's law is valid.

4. *The dependence of time of saturation on the intensity of exciting light.*

I varied the intensity of exciting light by means of the disk supplied with variable openings as I mentioned before, then I measured the time of saturation using exciting lights of different intensities. I ascertained that in the case of similar concentrations and similar temperatures the time of saturation is greater when the angle of the openings of disk are smaller. The results are shown in Table 3. If I consider the intensity of light falling on the gelatine plate through an angle of 1° as a unit then the data of opening of the sector mean relative intensities of exciting light in the first line of Table 3.

Table 3.

angle of opening in grad.	1	2	3	4	5	10
t	140	69	47	35	28	14
N	140	138	141	140	140	140

If I multiply these values with the correspondent times of saturations (t) I receive a constant number (N). These numbers are shown in the third line. This means that the dyestuff had to take up the same energy in each case. Therefore the existence of the state of saturation depends only on the energy used for saturation under the same conditions.

5. *The effect of frosting and heating on time of saturation.*

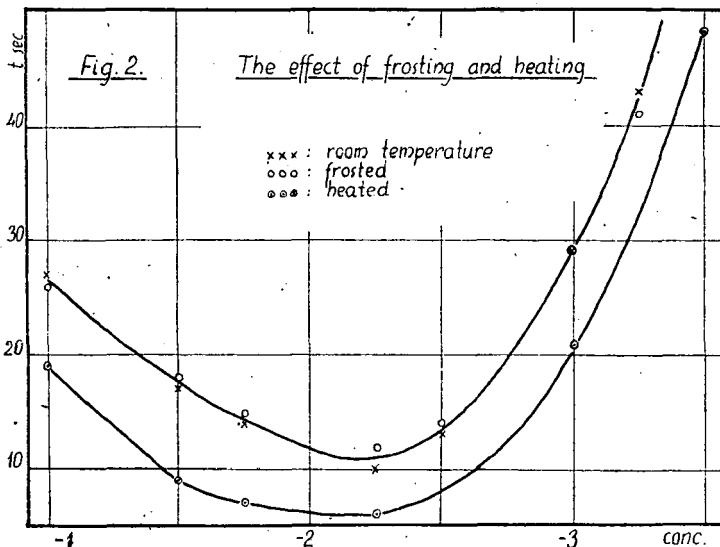
I cooled the gelatine plate by means of liquid air to a temperature of -190° C and after 10 minutes I heated it to room temperature. Then I measured the time of saturation. The heating was carried out by using an exsiccator to avoid the condensation of vapour. The frosted plates behave as if they had always been kept at room temperature. This is to be seen from Fig. 2. where the upper curve is belonging both to frosted and unfrosted plate.

The effect of heating manifests itself in a decreased time of saturation. I put the plate into a space having a temperature of 100° C for 10 minutes. After taking out of the space and cooling to room temperature I measured the time of saturation. The results are also shown in Fig. 2. The lower curve represents that the values of times of saturation are smaller after heating.

A similar behaviour of gelatineous dyestuffs was found on other point of view. We know from Gombay's researches (10) that both frosted and heated plates lose their conductivity and after frosting they regain their conductivity but after heating they do not. The same phenomenon was ascertained by H. Mischung (1)

from the point of view of absorption and by P. Fröhlich and L. Gombay (11) from the point of view of polarization.

Recent results confirm the fact that the behaviour of gelatinous dyestuffs is irreversible towards high temperatures and reversible towards low temperatures. This means that the heating has an essential influence on the structure of phosphorcentres.



Conclusions.

If I do not vary the angles of the openings of the sector disk the plate takes up the same energy during the same time. Therefore when I consider the energy falling on the plate in 1 sec as a unit, the times of saturation may be regarded as relative values of energy. According to these considerations the results referring to the connection between the time of saturation and the absorbed and emitted energy may be expressed in the following way. The connection between the time of saturation and the total amount of emitted energy show that more energy is necessary for saturation when the emissivity is smaller and less energy when it is greater. This is valid for each concentration. From the point of view of absorbed energy this statement is only valid for concentrations at which Beer's law is not valid, consequently for smaller concentrations.

These results may be explained in the following way. G. N. Lewis, D. Lipkin and T. T. Magel (12) discovered that the saturation in intensity may be explained by assuming the orientation of molecules. Later G. N. Lewis and D. Lipkin (13) pointed out a notable variation of the absorption with the direction of polarization studied with polarized light. Next year G. N. Lewis and J. Bigeleisen (14) carried out detailed investigations of the orientation effect. If I also suppose that the orientation effect is responsible for the time of saturation, the results may easily be explained. If the emissivity is small the orientation is hindered therefore the saturation needs more energy and when the emissivity is great the orientation is not hindered therefore the time of saturation — as well as the energy — is smaller. The absorptivity does not run

parallel with the emissivity excepting in the region of concentrations where Beer's law is not valid. Therefore the connection of time of saturation as well as the absorbed energy may also be explained, assuming the orientation of molecules. In the region of concentrations where Beer's law is valid the emissivity is hindered by concentration quenching.

The investigation of time of saturation in connection with the intensity of exciting light gave the result the saturation depends only on the energy falling on the plate under the same conditions. This ascertainment also supports the supposition of orientation of molecules.

The effect of frosting and heating show that the heated molecules are in a stabler state. (15)

Summary.

I investigated the time of saturation of gelatineous dyestuffs. The time of saturation depends on the concentration. There is an optimal concentration (e. g. —2,25 at rhodulin orange N). When the emissivity is smaller more energy is necessary for the saturation at each concentration. When the absorptivity is smaller more energy is necessary for the saturation at smaller concentrations where Beer's law is not valid. The behaviour of gelatineous dyestuffs is irreversible towards high temperatures and reversible towards low temperatures. The results are explained by assuming the orientation of molecules.

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