Further Investigations on the Saturation of Gelatineous Dyestuffs

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Introduction.

By using a constant exciting light the intensity of phosphorescence emission increases after initial excitation till it reaches a maximum. This phenomenon is termed saturation of phosphor. This saturation means that every molecule which can be excited by a given intensity of exciting light, is in an excited state and that the number of molecules entering this state during the unit of time, are identical to the number of emitting molecules.

Investigations concerning saturation have shown (1) that the phenomenon of saturation itself as well as the phenomena connected with it may be interpreted by assuming the orientation of molecules. Molecules are only excitable if their plane is normal to the beam of the exciting light. The molecules orientate under influence of irradiation, i. e. their planes take up the suitable position for excitation. Since the molecules deviate in a different manner from the oriented condition, the time required for single molecules to reach this oriented state is also different. The saturation is an orientation effect, and the time required for saturation is identical with the duration of the orientation.

On studying preexcitation, which necessitated further investigation of saturation, P. Fröhlich and L. Szalay (2) observed an interesting circumstance. They demonstrated that the positive preexcitation effect corresponds to normal orientation, and the negative preexcitation to that an of the abnormal one. (Concerning abnormal orientation see (3)). According to their results less energy is required for abnormal orientation, consequently the optimal concentration of the negative preexcitation effect is to be found at greater concentrations, than that of the positive preexcitation effect. It was further shown that the orientation increases with decreasing concentration. Regarding particulars of saturation and preexcitation see previous papers (1, 2, 4).

Since saturation is due to the orientation effect, it is important to investigate minutely the influence of temperature on saturation, partly to ascertain how far the above mentioned opinion concerning normal and abnormal orientation proves to be correct and partly because it is to be hoped that hereby further informations regarding the effect of orientation may be obtained.

Experimental method.

The experimental method was the same as adopted for previous investigations (1). The space between the discs of the Becquerel phosphoroscope could be electrically heated in order to obtain higher tempereatures. Low tempereatures were produced by solid CO_2. For details on the phosphoroscope which can be heated and cooled see previous papers (3). By using solid CO_2 a temperature of — 30° C could be obtained in the measuring space. Because of the deformation of gelatine plates, measurements above + 110° C were impossible.

For the measurements which were made by the method of F. Fröhlich (6). Gelatine plates of 0,1 mm thickness were used. The examined dyestuff was acridine orange N. The concentrations were logarithmic.

Results.

The duration of saturation of the dyestuff plates was established at the temperatures of + 110° C, + 55° C, + 28° C and — 30° C respectively. Table I. shows the results of these measurements.

Table I.

Temperature °C	concentration — c								
	1,00	1,50	1,75	2,00	2.25	2.50	3,00	3,25	3,50
	duration of saturation in seconds								
—30	31	19	—	13	—	12	18	29	38
+28	21	17	14	11	19	13	29	43	71
+55	14	11	9	10	13	—	40	61	—
+110	10	7	7	11	17	25	75	—	—

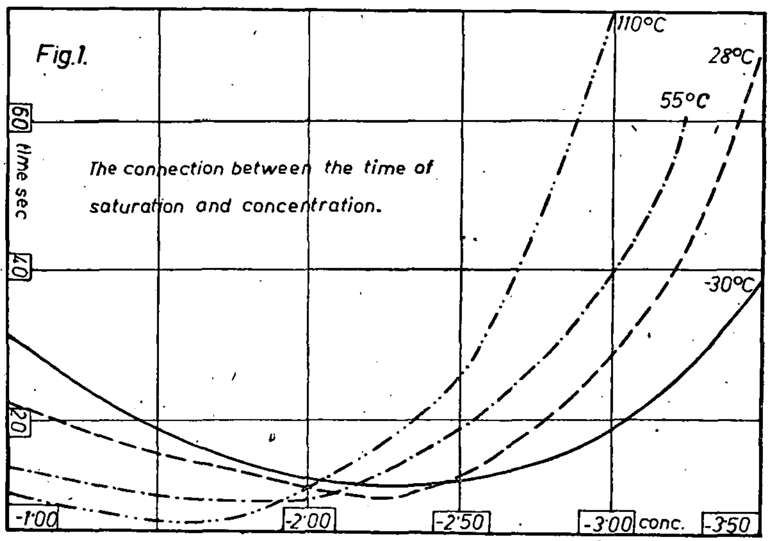


Fig. 1. was delineasted by using these data. Fig. 1. illustrates clearly the connection between duration of saturation, temperature and concentration. The logarithmic concentration was measured on the horizontal axis, and the time of saturation in seconds on the vertical one.

The object of these experiments was the further elucidation of the orientation effect of molecules; for this reason temperatures were selected proving from the point of view of orientation to be important for the acridine orange dyestuff. Preexcitation was without effect at a temperature of $+28°$ C, thus any permanent orientation at this temperature cannot be assumed, or even if it would occur the desorientating effect of the moderate measuring light would destroy it. The optimum of the negative preexcitation effect was found at $+55°$ C, consequently the optimum of abnormal orientation must also exist at the same temperature.

Fig. 1. shows that the duration of saturation has an optimal concentration at every temperature. The optical concentration shifts with increasing temperature to greater concentrations. The optimal concentration amounts to $-2{,}5$ at $-30°$ C, and to 1,50—1,75 at $+110°$ C. There exists a concentration — between $-2{,}00$ and $-2{,}25$ — where the duration of saturation is the same at every temperature. From this concentration towards greater concentrations the duration of saturation increases at decreasing temperature, while at smaller concentrations the duration of saturation diminishes with decreasing temperature.

It is to be noted that the method of measuring the duration of saturation revealed an interesting phenomenon. After removal of the screen the time which was necessary to eliminate the difference between the emission of the saturated and unexcited plate-parts was measured. This is termed the duration of saturation. It could, however, be observed, that the concealed plate-part, which had been kept in darkness, was not uniformly saturated after removal of the screen. First the sharp line, which was produced by the removal of the screen and which separated the dark and light surfaces faded; proceding from this line to the border of the plate the concealed plate-part became saturated. Since the surface of the plate was perfectly uniformly illuminated, the marked progress of the saturation from the centre of the plate towards its rim can only be explained by assuming the existence of self-excitation. The light of the emitting molecules arranged on one side of the separating line excite the unexcited molecules in their immediate vicinity.

In principle self-excitation is not impossible for the absorption and emission spectra mutually cross. However, its effect is so small, that it cannot be revealed by usual methods. An attempt to establish self-excitation in a direct manner is in progress.

Discussion.

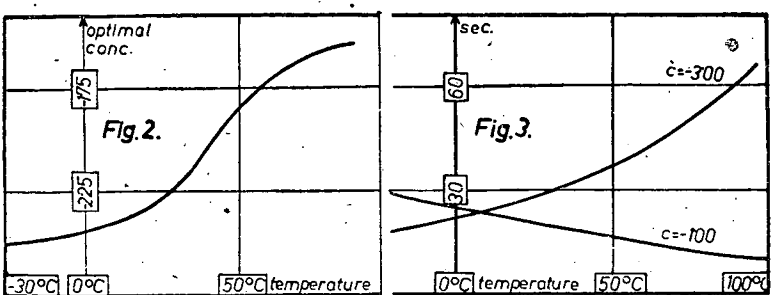
Considering the process of saturation as a process of orientation of molecules the results of saturation may be interpreted on the base of the hitherto achieved results as follows:

1. The optimal concentration.

As regards saturation an optimal concentration can be found at a certain temperature at which the saturation is completed in the shortest time. From this concentration on more time is needed for the saturation of preparations in the case of all other concentrations. As was mentioned above the process of saturation is the process of the orientation of the molecules. The capacity of the molecules to orientate increases with decreasing concentrations (2); similarly also the absorption increases and with it the emissivity. Thus the duration of saturation ought to diminish with decreasing concentration. The development of an optimal concentration cannot be satisfactorily explained for the present.

2. The shifting of optimal concentration.

The optimal concentration shifts towards greater concentrations with increasing temperature (2). According to the investigations about preexcitation (4), preexcitation has no effect at $+28°$ C. Thus permanent orientation is inconceivable. But even if permanent



orientation should exist, the desorientating effect of the moderate light used for measuring would eliminate it. At this temperature the optimal concentration concerning the saturation was — 2,25 which corresponded to the previous results relating to other phenomena (7). From $+28°$ C onwards the orientation effect was normal, and towards higher temperatures it was abnormal. Since less energy was required for negative preexcitation, thus also for abnormal orientation, the optimal concentration from the point of view of the duration of saturation shifted to greater concentrations. Similarly, the optimal concentration as regards the negative preexcitation effect, is greater than the optimal concentration of the positive preexcitation effect. This shifting of the optimal concentration is caused by the slighter disturbing effect of the neighbouring molecules in the case of abnormal orientation (2).

3. There exists a concentration at which the duration of saturation is the same at every temperature.

The curves representing the duration of saturation intersect in one point within the limit of error (Fig. 1.). This denotes that at a concentration of about —2,25 the duration of saturation is independent of the temperature. Thus the same energy is required to produce both normal and abnormal orientation at a concentration of —2,25. Comparing the correlation between the duration of saturation and the temperature at greater concentration (i. e. —1,00) we find that the duration of saturation increases with decreasing temperature (Fig. 3.). This means that at greater concentrations more energy is needed for normal, than for abnormal orientation. On investigating how far the duration of saturation depends on the temperature at smaller concentrations (i. e. —3,00) we find that the duration of saturation decreases with diminishing temperature (Fig. 3.). Since abnormal orientation changes with decreasing temperature into normal orientation, it is evident that at smaller concentrations more energy is required for abnormal orientation.

Considering that the optimal concentration of the positive preexcitation effect is smaller than that of the negative preexcitation effect, these results can be easily explained assuming that normal orientation corresponds to the positive, and abnormal to the negative preexcitation effect.

Thus it is also obvious that there exists a concentration at which the duration of saturation does not depend on temperature. At small concentrations abnormal, at greater concentrations normal orientation needs more energy. On approaching from the direction of small and great concentrations, the concentration at which the duration of saturation is independent of the temperature, a concentration can indeed be obtained at which the same energy is needed for normal as well as for abnormal orientation.

Thus recent investigations on the saturation of gelatineous dyestuffs, besides supporting the existence of the orientation effect, supply also important informations on the mechanism of the preexcitation effect.

Summary.

To what an extent the saturation of gelatineous dyestuffs depends on temperature was investigated. The main results were as follows:

1. The optimal concentration shifts with increasing temperature towards greater concentrations.

2. A concentration exists at which the duration of saturation is the same at every temperature.

3. At greater concentrations the normal, at small concentrations the abnormal orientation requires more energy.

Subsequently these investigations confirm the orientation of molecules, furnish also further informations on the mechanism of the preexcitation effect.

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