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Contribution from the Experimental Physical Institute of the University of Szeged.

Director: Prof. Paul Fröhlich.

# The Dependence of the Emission of Gelatineous Dyestuffs on the Ground Concentration.

by P Szőr (Szeged, Hungary). (Received 4. XI. 1948.)

#### Introduction.

It is well known that the optical properties of gelatineous dyestuffs depend also on the method of preparation (1). Therefore P. Fröhlich and P. Szőr (2) carried out investigations in order to know the dependence of absorption on ground concentration. They discovered that this plays an important part from the point of view of absorption, because the absorption coefficient of rigid gelatineous dyestuff is independent of its thickness and concentration, but depends on ground concentration alone.

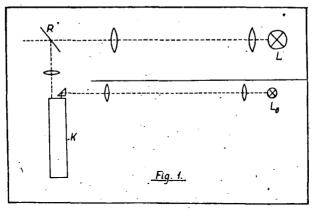
In this paper I have investigated the influence of ground concentration on the emission of rigid gelatineous dyestuffs. I carried out my researches chiefly on natrium fluorescein. The gelatine plates painted with natrium fluorescein have no measurable phosphorescence emission, therefore I could only examine fluorescence.

Experimental.

The measurements were carried out by means of the following arrangement. (Fig. 1.) The arrangement consisted of a light source (L) and a spectral photometer (König-Martens). The plate to be investigated was placed before the light so that the plane of plate and the beam of light formed an angle of 45°. The photometer (K) was placed perpendicularly in the direction of the beam of light. The fluorescence emission was focussed on to the photometer by means of a lense. The plate was put into a blackened metal holder to avoid the dissipation of light from the plate.

The intensity of emission was measured by comparing it-with the intensity of a tungsten-filament lamp (36 W, 12 V), (L), the spectral energy dis-

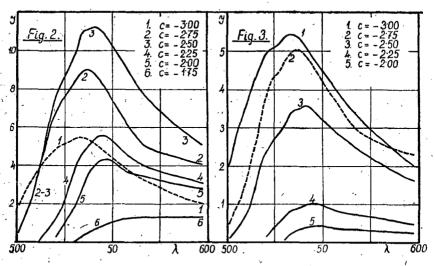
tribution of which was determined by a photoelectric cell. The intensity of fluorescence emission is given in an arbitrary unit because the measurements were relative.



### Results.

a) The dependence of emission on concentration.

In order to decide the influence of concentration on emission I prepared a nember of gelatine plates with natrium fluorescein each having the same thickness (0.15 mm) and different concentrations. The emission of gelatine plates of different concentrations are to be seen in Fig. 2.



The maxima of emission bands are shifting towards longer wavelenghts with an increasing concentration. The maximal value increases at first, but soon decreases. Consequently there is an optimal concentration. The same results have been found by P. Fröhlich and H. Mischung (3) with respect to the phosphorescence emission referring to unit concentration then the bands are to be found one under the other according to concentration. (Fig 3.)

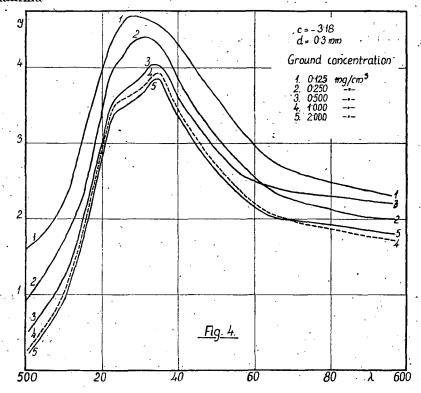
Consequently, on one hand the increase of concentration shifts

the maximum towards the longer wavelenghts and on the other hand lessens the maximal value of emission referring to unit concentration.

b) Ground concentration.

In order to decide the influence of ground concentration on the emission I prepared a number of gelatine plates of similar thickness (d=0.3 mm) and concentration (c=-3.18) but the ground concentration was altered.

The bands of emission (Fig. 4) are to be found one under the other according to the increase of concentration, while the maxima



shift themselves towards the long waves. The shifting of maxima towards the long waves and the diminishing of the bands show—as has already been seen—the increasing of concentration. Consequently the influence of the increase of ground concentration is just the same on the gelatineous dyestuff plate, as the increase of concentration. Similar results were found by P. Fröhlich and P. Szőr when measuring the absorption.

c) The case of similar ground concentrations and different final concentrations.

In order to clear up the role of ground concentration I prepared a number of plates, each of which had the same ground concentration. In this case the position of emission bands as well as that of the maxima did not change inside the limit of error.

d) The emission of other dyestuffs.

I have also investigated the connection between emission and ground concentration in other dyestuffs. In the case of acridingelb and eosin w. gelblich I discovered that ground concentration plays an important role. I also examined the phosphorescence band of eosin w. gelblich and found that the ground concentration had the same influence on it as on the fluorescence band.

Consequently these results confirm the important role of

ground concentration.

Summary.

1. The emission maxima of gelatine dyestuffs are shifting according to the increase of concentration towards the long waves.

2. There is an optimal concentration, but the emission bands calculated in unit concentration are to be found one under the other.

3. The ground concentration has an influence on emission as well as on absorption.

Explanation of results.

P. Fröhling and P. Szőr explained the important role of ground concentration by assuming that the associated ions or ion groups are unchanged in very diluted solutions when the watery solution becomes a rigid gelatine solution. The absorption is determined by the associated condition.

But we can suppose that the emission is determined by the absorption. Therefore the emission is also determined by the associated condition. In this case the ground concentration has also to influence the emission. This was proved by the result of measurements.

Consequently the experiments referring to ground concentration with respect to absorption and emission confirmed the important role of ground concentration. But this does not prove that the results up till now are not correct, because till now the ground concentration was neglected. These results, however, prove that care must be taken when preparing the gelatine dyestuff.

If we want to investigate the properties of gelatine dyestuff in different concentrations as being the function of concentration, then the ground concentrations (that is the ground concentration of the solution used for preparing gelatine plates) must be in

such a proportion as the final concentrations will be.

In addition, these researches show that plates of different thickness cannot be compared, because concentrations of solutions used for the preparation of gelatine plates, i. e. the ground concentration, on account of the method of preparation are not in such a proportion as the final concentrations. E. g. if a plate is prepared of a c=-2,50 and of a d=0,1 mm and one of a c=-3,00 and of a d=0,3 mm, as 20 cm³ solution will be needed for preparation of both plates, then the ground concentration will be 0,16 mg/cm³, because by the first plate the 20 cm³ solution must contain 3,0 mg dyestuff; while the ground concentration of the second plate must be 0,15 mg/cm³, because the 20 cm³ solution must contain 3,0 mg dyestuff. The proportion of final concentrations is  $10^{-2,5}:10^{-3,0}=3,16:1,00$ ; while the proportion of ground concentrations is 0,16:0,15.

One can also conclude when comparing plates of similar concentration and different thickness that deviation must be found. 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 Gelatineous Dyestuffs as the Cause of Preexcitation.

by P. Fröhlich and L. Szalay (Szeged, Hungary). (Received 5. XI. 1948.)

Introduction.

P. Frőhlich and Z. Gyulai (1) discovered that the gelatineous 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