

3. Voir par ex. P. et R. Daudel: *J. Chem. Soc. London*. 1948.
4. J. M. Robertson et Collab.: Conf. du centre de chim. théor. de France. 1949, Paris.
5. L. Pauling: a été le premier à définir clairement cette notion. Voir: The nature of the chemical bond.
6. C. Vroelant et R. Daudel: *Bull. Soc. Chim. France*. 16. (1949) 36, 217.
7. C. Vroelant et R. Daudel: *Compt. Rend.* 228. (1949) 399.
8. J. M. Robertson et White:
9. R. Daudel et A. Pullman: *Compt. Rend.* 225 (1945) 888.
10. Par exemple: P. Daudel, R. Daudel, R. Jaques et M. Jean: *Revue Scient.* 84 (1949) 489. C. A. Coulson: *Trans Faraday Soc. Discussion on the labile molecule*
11. N. P. Bub-Hoi, P. et R. Daudel et C. Vroelant: *Bull. Soc. Chim. France* 16 (1949) 211.
12. Cook et Schoental: *J. Chem. Soc. London* 1948, 171.
13. Voir par exemple: R. Daudel: *Bull. du cancer*.
14. R. Daudel et O. Charlet: *J. de Chimie Physique* (sous presse).
15. J. Thile: *Liebigs Ann. Chem.* 311 (1900) 248.
16. M. Gomberg: *Ber. Deutsch. Chem. Ges.* 35 (1902) 3914. M. Gomberg et Sullivan: *J. Amer. Chem. Soc.* 44 (1922) 1833.

Experimental Physical Institute of the University of Szeged

On the Self-Absorption of Fluorescent Dyestuff Solutions

P. FRÖHLICH AND P. SZÖR

On comparing the absorption and emission bands of fluorescent dyestuff solutions it can be observed that they have a common area, (1) which means that the emitting solution itself partly absorbs the emitted energy, this phenomenon is called self absorption. In such a case the measured emission band is not identical with the real one. The existence of self absorption and its influence on the emission is reported by Lewis, Magel, Lipkin (2).

If we examine the fluorescence emission of a rigid boric acid solution of fluorescein observing it from the direction agreeing with that of the opposite side it is yellow. P Ször has also observed (3) that it is not possible to analyse the emission band at the wave lengths at which self-absorption occurs.

A method of calculation has been elaborated by means of which the emission band which does not contain the self absorption effect can under certain conditions be calculated on the base of the measured emission.

The Method of Calculation.

If on measuring the fluorescence emission the direction of the exciting light and that of the observation are perpendicular then the emission, taking the self absorption effect into account, can be calculated on the base of the following considerations.

The solution which is going to be investigated is placed into a parallel epipedon-shaped vessel, the width of which is t mm. The intensity of the exciting light is denoted I^e . The exciting light is adjusted in a manner enabling the light to illuminate the whole breadth of the vessel. In this case each layer of identical thickness absorbs the same amount of light consequently each layer emits light of similar intensity. Let us consider a layer of dt_x thickness the distance of which is t_x . The light emitted by layer dt_x must pass through the layer possessing t_x thickness. Let us select the λ wavelength from the emission spectrum the absorption coefficient of which is α and denote with I' the intensity of the light emitted by layer dt_x . The intensity of the light of the λ wavelength emitted from layer dt_x is taking the absorption into consideration:

$$J'e^{-\alpha t_x} \quad (1)$$

Let us divide the vessel of t_x width into n_x layers of similar thickness. Denoting the total emission with I the value of the emission emitted by layer dt_x is:

$$J' = \frac{J_e}{n} = \frac{J_e}{t} dt \quad (2)$$

Or more briefly

$$J' = J_e dt \quad (3)$$

where J_e denotes the intensity of the light emitted by a layer of a unit thickness.

Putting 3 into 1 we obtain

$$J'e^{-\alpha t_x} dt \quad (4)$$

the total intensity

$$J = \int_0^t J'e^{-\alpha t_x} dt = J'e \frac{1 - e^{-\alpha t}}{\alpha} \quad (5)$$

Let us examine the obtained equation in the following cases:

a) If the emitted light is not absorbed by the solution $\alpha = 0$, then: $J = J_e t = J_e$ (6)

In this case the measured intensity is equal to the total emission. Furthermore it can also be observed that the recorded emission is proportional to the thickness.

b) If $\alpha \rightarrow \infty$ $J \rightarrow 0$ (7)

we cannot perceive the emitted light i.e. the emission cannot be measured at this wave length as in such a case only the emission of the outermost layer can be measured, which is as compared with the total emission extremely slight.

c) If $t = 0$, then $J = 0$ (8)

d) If $t = \infty$, then $J = \frac{J_e}{\alpha}$ (9)

This equation expresses that if $\alpha > 0$, then on increasing the width of the vessel the measurable emission tends to the limit given in equation. 9. Expression 9 is also obtained if α is not high, but αt is so high that $e^{-\alpha t}$ will tend to 0, which means that at a definite α value from a certain vessel width on, the measured emission

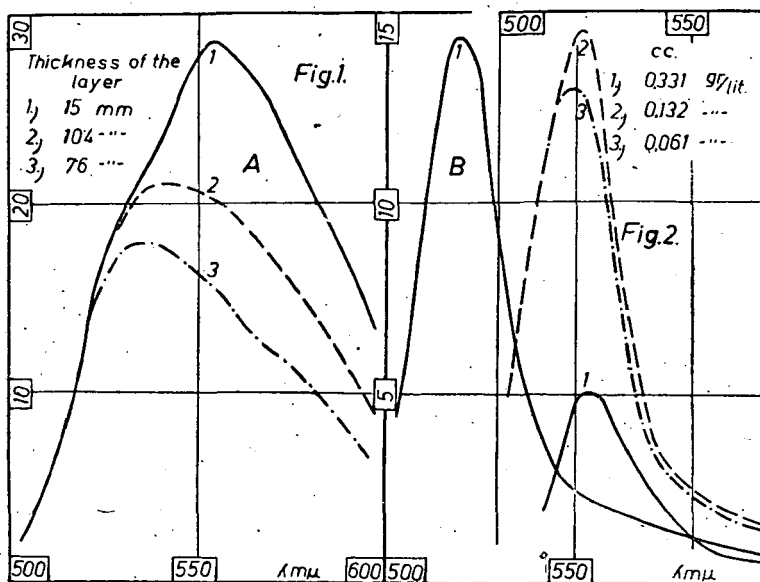
is given by 9 and thus does not change on further increase of the width.

Results.

Emissions of the same solutions were measured in vessels of different width. An alcoholic solution of acridine orange of 0.132 gr/l. concentration was used. The absorption spectrum was recorded by a photocell and the emission by the König—Martens-spectral-photometer. The results are shown on table I. and Fig. 1. (The values are given in arbitrary units).

Table I.

λ	a) absorption						b) emission		mean value
	$t = 15$ mm.		$t = 10.4$ mm.		$t = 7.6$ mm.		I_e		
	α mm ⁻¹	I_e	I_e	I_e	I_e	I_e			
612	—	9.5	0.63	6.3	0.61	4.5	0.59	0.61	
604	—	10.5	0.6					0.7	
596	—	13.5	0.7	9.5	0.9	6.7	0.88	0.97	
588	—	17.6	0.97					1.16	
581	—	20.2	1.15	14.0	1.35	10.4	1.37	1.33	
574	—	23.0	1.33	15.8	1.52	11.6	1.53	1.59	
567	—	26.0	1.71	17.7	1.70	12.5	1.65	1.61	
561	0.0075	27.2	1.91	19.1	1.91	14.2	1.92	1.90	
555	0.020	28.5	2.24	20.0	2.13	15.6	2.22	2.25	
549	0.048	27.2	2.53	21.0	2.51	16.4	2.57	2.56	
543	0.109	24.6	3.33	21.1	3.39	17.4	3.37	3.3	
537	0.23	22.0	5.30	21.0	5.32	18.1	5.04	5.2	
532	0.39	20.4	5.95	20.7	8.23	17.8	7.45	7.8	
527	0.63	17.8	11.2	17.2	10.8	17.0	10.7	10.9	
522	0.96	15.5	14.9	15.6	15.0	14.7	14.1	14.7	
517	1.33	10.0	13.3	10.7	14.2	10.5	14.0	13.8	
512	1.71	5.0	9.9	6.0	10.2	6.4	10.9	10.3	
507	2.04	2.7	7.5	3.7	7.5	3.7	7.5	7.5	



The curves denoted A demonstrate the emissions measured in vessels of different width. It can be seen that the intensity of the

emission ranging between $567 m\mu$ and $612 m\mu$ (where there is no absorption) changes proportionally to the width of the layer.

On the other hand, on the section where the absorption is very intense the measured intensities hardly diverge. This proves qualitatively that the emission is influenced by selfabsorption. On computing I_0 on the base of emission values measured using vessels of different width it can be seen that the computed values agree taking a certain limit of error into account well. (Table I.) This proves quantitatively the correctness of the equation. The computed emission curve is shown on Fig. 1 B. The shape of the computed curve differs from that of the measured one. The former one has a distinct maximum at $520 m\mu$, whereas the latter's maximum is not so distinct and its position depends upon the width of the vessel.

The measurements were also carried out at the following concentrations 0.351 gr/l., 0.0066 gr/l. and similar results were obtained. These have distinct maxima, however, their position shifts according to the concentration towards red.

Summary.

If on measuring the fluorescence emission the direction of the exciting light and that of the observation are perpendicular then the intensity of the emission, taking the selfabsorption effect into account, can be calculated according to:

$$I_0 = I \frac{\alpha}{1 - e^{-\alpha t}}$$

where I_0 denotes the intensity of the emission on subtraction of selfabsorption, I the measured intensity of the emission, α the absorption coefficient and t the width of the vessel.

The correctness of this equation was proved in the case of three solutions of different concentration.

The computed emission band shows that the maximum shifts according to the concentration towards red.

References.

1. P. Ször: Acta Chem. Phys. Univ. Szeged. P. Fröhlich, H. Mischung: Acta Chem. Min. Phys. 7 (1939) 93. P. Fröhlich, H. Mischung: Mat. Term. Tud. Ért. 58 (1939) 927. H. Mischung: Acta Chem. Min Phys. 6 (1938) 251, Mat. Term. Tud. Ért. 57 (1938) 209.
2. G. N. Lewis, T. T. Magel, D. Lipkin: J. Amer. Chem. Soc. 63 (1941) 3005.
3. P. Ször: Acta Chem. Phys. Univ. Szeged.