

DEPENDENCE ON VISCOSITY OF THE DECAY TIME OF LUMINESCENCE IN VISCOUS DYE SOLUTIONS

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The fluorescence decay time τ is brought into connection with the volume (v) of the Frenkel holes characteristic for the solvent. According to our measurements $1/\tau$ is a linear function of v both for fluorescein of 10^{-4} M concentration in water-glycerol mixture and for rhodamine 6G of 10^{-4} M concentration in alcohol-glycerol mixture.

According to our earlier investigations [1—2], the decay time of luminescence resulted to be dependent on the viscosity of the solution both in the case of fluorescein of 10^{-4} M concentration in water-glycerol mixture containing 1 per cent NaOH and rhodamine 6G of 10^{-4} M concentration in ethanol-glycerol mixture with 10^{-2} M CH_3COOH . The true decay time of luminescence [3] was determined at 303 °K [1] with the phase fluorometer and the method described in [2] eliminating the tedious calculations for correction.

To obtain further information on the dependence of the decay time on viscosity, Frenkel's parameters [4] U (activation energy for the formation of the holes) and r (radius of the holes) were determined for sets of different glycerol content of both solvents mentioned above.

We measured the viscosity of the mixtures as a function of temperature and their surface tension at 303 °K. From the temperature dependence of the viscosity the activation energy U , then, knowing U and the surface tension, the radius r can be determined [5]. The measurements were made at normal atmospheric pressure. Our results are listed in Table I.

The common characteristic of the theories dealing with probability of spontaneous transition in luminescence

Table I

10 ⁻⁴ M fluorescein in water-glycerol			10 ⁻⁴ M rhodamine 6G in ethanol-glycerol		
μ	$1/\tau$ (1/nsec)	$r^3 \cdot 10^{24}$ (cm ³)	μ	$1/\tau$ (1/nsec)	$r^3 \cdot 10^{24}$ (cm ³)
0.00	0.286	5.8	0.0	0.172	36
0.04	0.287	7.0	0.1	0.183	39
0.12	0.282	11	0.2	0.185	42
0.21	0.316	14	0.3	0.188	44
0.22	0.316	15	0.4	0.176	46
0.34	0.307	21	0.5	0.177	46
0.49	0.320	27	0.6	0.187	47
0.66	0.330	36	0.7	0.179	48
0.96	0.342	48	0.8	0.182	48
			0.9	0.184	49
			1.0	0.187	49

μ = molar ratio of glycerol in the solvent

[6—10] is that all of them contain the so-called absorption integral and some function of the refractive index of the solution. Both the absorption integral and the refractive index being mostly dependent on viscosity, these theories give the possibility to clear up the dependence of the lifetime of luminescence on viscosity. This would lead to a phenomenologic description of the phenomenon. We tried, however, to approach the problem from another side, namely from the point of view of one of the models concerning the structure of liquids, the so called Frenkel's model.

Our conception concerning the explanation of this experimental dependence is exposed in the following. Let us examine which of Frenkel's parameters could be used to characterise the fluctuations of pressure (Δp) taking place in the envi-

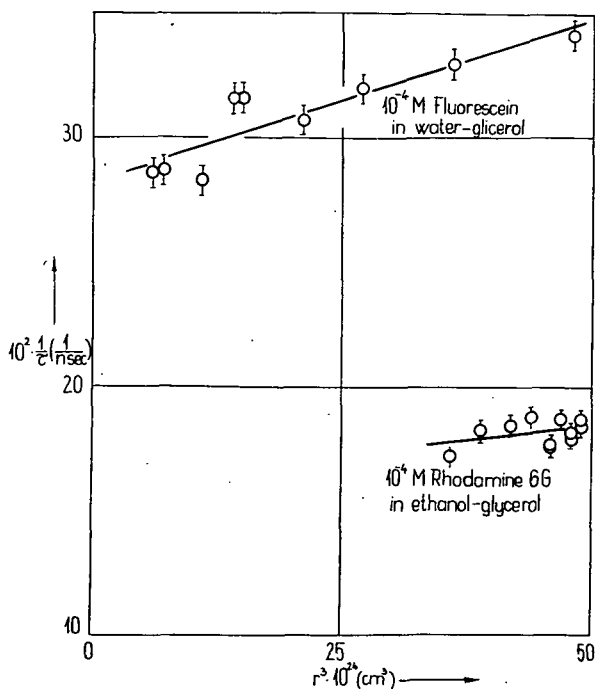


Fig. 1

ronment of the molecule capable of luminescence. The lifetime (τ^*) of the holes does not seem to be suitable, being the life-time of a settled and static state. Surely there exist identical fluctuations of pressure having different „lifetime”. The activation energy U is the measure of the fluctuation of energy. At constant temperature and external pressure the macroscopic volume of the liquid does not change, and so the hole of volume v formed in the liquid can only be produced on account of local increases in pressure. We suppose that the absolute value of the fluctuation of pressure is linearly proportional to the volume of the hole, i. e. $|\Delta p| \sim v$.

The probability of spontaneous transitions in luminescence is determined by fluctuation phenomena which partly occur inside of the molecule capable of luminescence and thus exist also in absence of external fields, and partly are brought about by the action of possibly present external fields. Let us suppose that the fluctuation inside the molecule originating from changes in the external field is linearly proportional to the fluctuation of pressure mentioned above. Then, approximately,

$$\frac{1}{\tau_e} = \frac{1}{\tau_0} + \text{const} \cdot r^3$$

where $1/\tau_0$ is the probability of spontaneous emission taking place also in absence of external field, r the radius of the hole considered as of spherical form, τ_e the so called natural decay time of luminescence, which in the case of our measurements differs only in a constant factor from the true decay time τ obtained by measurements.

Plotting $1/\tau$ as a function of r^3 in both solutions according to data of Table I, Fig. 1 is obtained.

It can be seen that the relation between $1/\tau$ and r^3 can be approximated by a straight line within the errors of measurements for both sets of solutions. This means that there exists a linear relation between the probability of spontaneous transition $1/\tau$ and the fluctuation of pressure in the solution.

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ЗАВИСИМОСТЬ ВРЕМЕНИ ЗАТУХАНИЯ ЛЮМИНЕСЦЕНЦИИ ВЯЗКИХ РАСТВОРОВ КРАСИТЕЛЕЙ ОТ ВЯЗКОСТИ

Л. Визе и Л. Гати

Устанавливается связь между временем затухания τ и объемом v дырки Френкеля, характерного для растворителя. По нашим экспериментальным данным значения $1/\tau$ в зависимости от v оказывается линейным для смеси флуоресцеина (10^{-4} моль/л) воды и глицерина, и родамина 6Ж (10^{-4} моль/л) спирта и глицерина.