

THE QUENCHING OF THE LUMINESCENCE OF SOLUTIONS BY FOREIGN SUBSTANCES

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THE study of the kinetics of luminescence occupies the most prominent place in S. I. Vavilov's scientific inheritance. In spite of the great breadth of his scientific interests, which extended far beyond the limits of luminescence research, Vavilov devoted as many as one-third of his original scientific articles to physical studies on luminescence kinetics, such as: diffusion-controlled quenching of the fluorescence of solutions by foreign substances, quenching of fluorescence by foreign substances which act by absorbing the luminescence, concentration quenching and depolarization of fluorescence, and the kinetics of the phosphorescence of organic compounds.

Vavilov's great interest in studying the kinetics of phenomena may be explained by the particular bent of his scientific creativity. S. I. always tried to establish quantitative regularities, and to construct theories giving a quantitative interpretation of the phenomena being studied. The study of luminescence kinetics naturally gave him wide latitude for his creativity.

From the thirties until his death, S. I. paid much attention to the creation of a staff and instrumentation for research on luminescence kinetics. He founded a small group studying luminescence kinetics of crystal phosphors directed by V. L. Levshin in the Physical Scientific Research Institute of Moscow State University in 1931. Owing to S. I.'s constant care and support, it grew over a period of twenty years by a factor of some tens, and matured greatly in the qualitative sense. He also founded a group in the Lebedev Institute of Physics of the Academy of Sciences to study the fluorescence kinetics of organic compounds, and directed it personally until 1951. As is well known, during S. I.'s lifetime, luminescence kinetics research on organic substances and crystal phosphors was one of the fundamental research lines among the activities of his Leningrad laboratory.

Instrumentation, usually rather complex, plays a large role in the development of experimental studies on luminescence kinetics. S. I. paid much attention to designing such instrumentation. Even in the thirties, L. A. Tumerman built under his direction the first Soviet taumeter in the Lebedev Institute of Physics. This apparatus played an important role in the well-known studies of M. D. Galanin on the kinetics of processes of migration of excitation energy. Even greater possibilities in the study of luminescence kinetics were created by the appearance of a new fluorometer developed by A. M. Bonch-Bruevich, V. A. Molchanov, and V. I. Shirokov, the taumeter (by N. A. Tolstoï and

P. P. Feofilov), and the ultrataumeter (by N. A. Tolstoï and A. M. and N. N. Tkachuk).

The present paper deals with only one of the branches of luminescence kinetics, the theory of diffusion-controlled quenching of the luminescence of solutions, the foundations of which were laid by Vavilov in the Twenties.

The first reports of the quenching of the fluorescence of solutions on adding foreign substances occur in Italian and Spanish medical books of the 16th century. The reason for the phenomenon was considered for a long time to be the destruction of the molecules of the fluorescent substance by addition of the quenching agent. Stokes questioned this hypothesis even in 1852 by pointing out that in a number of cases the luminescence of the quenched solutions may be considerably enhanced by dilution with pure solvent. Nevertheless, it has enjoyed some popularity even in the 20th century.

S. I. convincingly proved the existence of physical quenching of fluorescent solutions. His principal argument in favor of this idea was the fact that his theory on diffusion-controlled quenching of fluorescent solutions¹ gave the correct order of magnitude of that very important constant, the lifetime of the excited state of the molecule. I shall only present here the quenching formula which he derived, without giving the derivation:

$$\frac{B_0}{B} = 1 + \frac{2\tau_0 ckT (\sigma_1 + \sigma_2)^2}{3\eta\sigma_1\sigma_2}, \quad (1)$$

where B_0 and B are the fluorescence yields in the unquenched and quenched solutions, respectively, τ_0 is the lifetime of the excited state of the molecule in the unquenched solution, η is the viscosity, σ_1 and σ_2 are the radii of the colliding molecules, T is the temperature, k is the Boltzmann constant, and c is the number of molecules of the quenching agent per cm^3 .

It is greatly to Vavilov's credit that he pointed out the criteria by which we may distinguish quenching occurring during the lifetime of the excited state of the molecule from that due to interaction with unexcited molecules. This criterion is the proportionality of the change in the mean lifetime of the excited state to the change in the yield, and the absence of this proportionality in the latter case:²

$$\frac{\tau}{\tau_0} = \frac{B}{B_0}. \quad (2)$$

Here he showed that Eq. (2) is valid for any continuous time function describing the quenching of the excited

molecules, provided only that the decay law of the unquenched solution is exponential, and the probability of spontaneous emission is not changed by the quenching.

In the Twenties and Thirties, polarization measurements were used to test the validity of Eq. (2). According to the Levshin-Perrin formula:

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \frac{B}{B_0} \frac{kT}{v\eta} \tau_0, \quad (3)$$

where p is the polarization observed in the quenched solution, p_0 is the so-called limiting polarization, i.e., the polarization when $\eta \rightarrow \infty$ or $B/B_0 \rightarrow 0$, and v is the kinetic volume of the molecule.

Equations (1)–(3) have permitted a satisfactory explanation of the phenomenon, but have not given good quantitative agreement with experimental data. First, unlike Eq. (1), the experimental relation of B_0/B to c and η was non-linear. Further, the lifetime of the luminescence as measured with a fluorometer varied more slowly upon quenching than did the luminescence yield. Finally, Eq. (3) was not precisely verified.

My candidate's dissertation³ and a series of studies performed in our laboratory since 1956 have concerned the elucidation of the reasons for this discrepancy between theory and experiment.

I was able to arrive at a refinement of the quenching formula given in the cited paper of Vavilov by applying a more exact formula to calculate the number of initial collisions in the solution. This formula was derived by Smoluchowski from the solution which he had found for the diffusion equation for the case of spherical symmetry, and has the following form:

$$\nu = 4\pi DRc \left[1 + \frac{R}{\sqrt{\pi Dt}} \right] dt, \quad (4)$$

where ν is the number of collisions during the time from t to $t+dt$, D is the diffusion coefficient, R is the radius of the sphere in which diffusion takes place, and c is the number of molecules per cm^3 .

Ordinarily, in accordance with the example which Smoluchowski himself gave, the second term in the brackets may be neglected in comparison with the first term. I have shown⁵ that in calculating the diffusion over a time $\leq 1 \times 10^{-8}$ sec, the lifetime of the excited molecules, one can no longer do this, since the second term in the brackets is comparable with the first for these time intervals.

Smoluchowski's solution was derived under the assumption that a concentration gradient exists at the surface of the sphere R . However, A. N. Kolmogorov and M. A. Leontovich⁶ have shown that one may derive the same formula for the number of initial collisions on the basis of the Brownian movement of the colliding molecules. The advantage of this derivation consists in the fact that the physical meaning of the factor in brackets in Eq. (4) becomes clearer. At the beginning of the process, the moving point is surrounded by spheres,

none of which have yet been penetrated by it. Since we may count the penetration of a sphere by the point only once and disregard any repeated penetrations, the number of spheres penetrated by the moving point per unit time is greater at the beginning of the Brownian movement.

Since the probability of encounter of the excited molecule with a molecule of the quenching agent depends on the time which has elapsed from the moment of excitation, the decay law in quenched solutions must be non-exponential. This is so even when the decay law of the unquenched solutions is exponential, as is always assumed. In an article published in *Acta Physica Polonica*,⁷ Vavilov pointed out the importance of testing this relation. Unfortunately, it became possible to test the decay law of the fluorescence of quenched solutions only in 1956, when the phase fluorometer of A. M. Bonch-Bruевич, V. A. Molchanov, and V. I. Shirokov became available.⁸ Shirokov carried out this test. On varying the modulation frequency of the exciting light from 6 to 12 megacycles, he found that the mean lifetime of the luminescence of a glycerol solution of 3-aminophthalimide quenched by potassium iodide was decreased from 3.88×10^{-9} sec to 3.57×10^{-9} sec. These values were in complete agreement with the calculated values: 3.74×10^{-9} sec in the former case, and 3.44×10^{-9} sec in the latter. In an unquenched solution, the lifetime of the luminescence did not depend on the frequency of the modulation.

A direct consequence of the non-exponential decay law of the fluorescence of quenched solutions was the non-linear dependence of the ratio of the yield in the quenched solution to that in the unquenched solution on the concentration of the quenching agent and the viscosity of the solution.

The formula which I derived⁵ in 1935 for the quenching of the fluorescence of solutions differed from Eq. (1) in the factor δ :

$$\frac{B_0}{B} = \left[1 + \frac{2p\tau_0 ckTR^2}{3\eta\sigma_1\sigma_2} \right] \delta, \quad (5)$$

where

$$\delta = \left[1 - 2\gamma e^{\gamma^2} \left(\frac{\sqrt{\pi}}{2} - \int_0^\gamma e^{-z^2} dz \right) \right]^{-1},$$

$$\gamma = 2pR^{\frac{3}{2}} c^{1/2} \left(\frac{4\pi DRc\tau_0}{4\pi pDRc\tau_0 + 1} \right)^{\frac{1}{2}}$$

and R is the radius of the sphere.

Equation (5) has permitted a completely satisfactory explanation of the experimentally-observed relation of the variation in the fluorescence yield to the concentration of the quenching agent.

However, the reason for the difference in the changes in the yield and in the lifetime of the fluorescence upon quenching was still not clear at that time. The explanation for this appeared in the middle Fifties. The point was that, in deriving Eq. (2), Vavilov used the mean lifetime of the excited state of the molecule, as determined by the formula:

Table I

	$\frac{B_0}{B}$	$\frac{\tau_0}{\tau}$	$\frac{T}{\eta \cdot 10^2}$	χ	δ^{-1}	γ	$R \cdot 10^8$ cm	p
Quenching of fluorescein in water-glycerol solutions, 0.3 M in KI.	5.5	4.5	309	1.22	0.675	0.245	9.4	0.14
	4.1	3.5	238	1.17	0.755	0.185	7.02	0.20
	3.3	2.9	178	1.14	0.800	0.150	5.75	0.25
	1.8	1.6	84	1.12	0.824	0.130	8.6	0.12
Quenching of rhodamine in methyl, ethyl, or butyl alcohols, 0.2 M in aniline.	6.5	4.05	530	1.6	0.341	0.745	24	0.12
	5.9	3.63	278	1.64	0.320	0.745	22.5	0.16
	5.2	3.24	109	1.6	0.341	0.745	21.9	0.24

$$\tau = \frac{\int_0^{\infty} t \, dn}{\int_0^{\infty} dn}, \quad (6)$$

where dn is the number of excited molecules which lose their excitation energy during the time from t to $t+dt$. However, in measurements made with the fluorometer, just as in polarization measurements, we determine the mean lifetime of only those molecules whose existence in the excited state is terminated by emission. This quantity (τ'), which we have denoted as the mean lifetime for emission, is defined by the following expression:

$$\tau' = \frac{\int_0^{\infty} t \, dn_1}{\int_0^{\infty} dn_1}, \quad (7)$$

where dn_1 is the number of molecules undergoing emission during the time from t to $t+dt$.

When the decay law of the quenched solution is exponential, dn and dn_1 are proportional to each other. When the law is non-exponential, this is not so, and the mean lifetime for emission will be appreciably different from the mean lifetime of the excited state. The former quantity will vary more slowly upon quenching than the yield will.

L. A. Kuznetsova, V. I. Shirokov, and I have derived a formula⁹ relating the change in the luminescence yield to the change in the mean lifetime for emission:

$$\frac{\tau'}{\tau} = \frac{B}{B_0} \chi, \quad (8)$$

where $\chi = \left(1 + \gamma^2 - \frac{\delta - 1}{2}\right) \delta$.

Since in polarization measurements we also take into account only those molecules whose lifetime in the excited state is terminated by emission, it was necessary to derive a new formula to replace Eq. (3). This was done by P. I. Kudryashov and myself.¹⁰

From Eqs. (5) and (8), we can determine the values of both of the quantities characterizing the quenching of the fluorescence of solutions by foreign substances: p , the probability of quenching upon encounter of two molecules, and R , the radius of the sphere of action.

Table I gives values of p and R calculated by L. A. Kiyanskaya for several of the cases of quenching which she studied.

A comparison of the last two columns in the table shows that the values of R calculated in this way for fluorescein and rhodamine show quite satisfactory agreement with the sizes of the kinetic sphere calculated from Marinnesco's data.¹¹

Besides the cases given in Table I, I might add also the results of a study of the quenching by oxygen of the ultraviolet fluorescence of benzene, toluene, and *p*-xylene in hexane. According to the data of G. A. Mokeeva and G. V. Ivanova,¹² the radius of action for encounter of the activator molecule with oxygen is equal to or slightly greater than the kinetic value, and the probability of quenching is equal to unity.

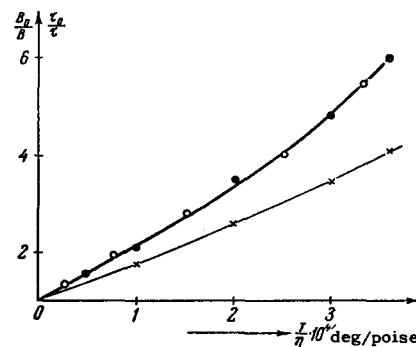


FIG. 1. The relation of the changes in the yield and the lifetime (circles) of fluorescence of water-glycerol solutions of fluorescein quenched with KI to the fluidity (crosses). O — changes in viscosity due to change in the percent glycerol; ● — changes in viscosity due to temperature change.

A most important proof of the diffusion theory of the quenching of fluorescent solutions by foreign substances would be an experimental check by this theory of the dependence of the quenching on the viscosity. Equations (5) and (8) specify an almost linear relation between the variations B_0/B and τ_0/τ and the fluidity, and the absence of quenching in solid solutions. In a number of cases, such a relation is actually observed (Fig. 1), but much more often, the dependence of the variations B_0/B and τ_0/τ on $1/\eta$ is more complex (Fig. 2).

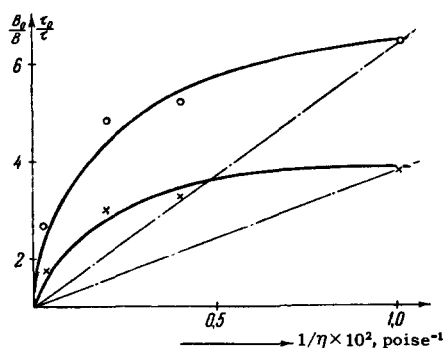


FIG. 2. The changes in the yield and lifetime of the fluorescence of rhodamine in various solvents with aniline as quenching agent. The symbols are the same as in Fig. 1.

If we search for an explanation of this complex relation in purely physical phenomena, we might point out two possible causes: first, the difference between the molar and the molecular viscosities, and second, the fact that we assume in deriving the quenching formulas that the sphere of action is sharply delimited (neglecting the dependence of p on the distance between the molecules and their time of interaction). The most general theory of quenching of luminescence in solutions would have to take into account both the law of intermolecular interaction and the Brownian movement of the molecules.

In this regard, we consider it very important to study the quenching of fluorescence by foreign non-absorbing substances in solid solutions. Such studies have been carried out by V. V. Zelinskii, V. P. Kolobkov, and their associates¹³ in order to prove the hypothesis that the quenching of fluorescence of solutions by halide ions involves an increase in the probability of transition of the fluorescent molecule into the phosphorescent state. Unfortunately, the cases which they studied are apparently not very suitable for the study of quenching kinetics. According to the data of L. A. Kiyanskaya, when iodides are added to a solution of one of the most strongly quenchable compounds, 4-acetylamino-N-methylphthalimide, a very strong new phosphorescence appears, with a mean lifetime approximately 100 times shorter than that of the ordinary phosphorescence of a solution of this phthalimide. We may assume that the appearance of this new phosphorescence is evidence that part of the molecules of the activator form some sort of com-

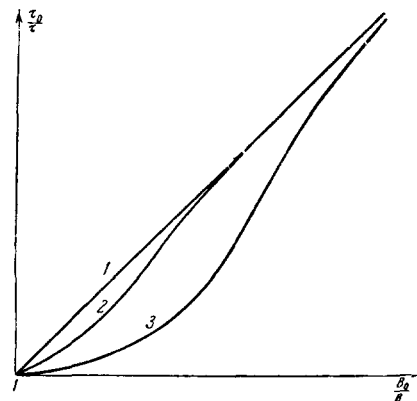


FIG. 3. Graph of the relation of τ/τ_0 to B_0/B for the case in which the probability of energy transfer between molecules (quenching) is $k_1 \exp(-r/r_0)$. 1 - $k_1 \ll 1$; 2 - intermediate values of k_1 ; 3 - $k_1 \gg 1$.

pound with iodides (complexes). Hence, studies of the quenching of fluorescence in solid solutions by foreign quenching agents will have to be performed on other objects.

At my request, V. I. Shirokov¹⁵ has calculated how great a discrepancy between the changes in lifetime and yield might be expected for quenching in solid media, assuming a statistical distribution of the molecules, with various laws of interaction between the molecules. He performed calculations for a case in which the interaction obeys a law $kr^{-n} dt$, where k is a constant coefficient, and made an estimate for the case in which the interaction obeys the law $k_1 [\exp(-r/r_0)] dt$. The data for the former case are given in Table II, and for the latter case, in Fig. 3.

As is known, the quenching of the fluorescence of solutions by foreign substances was applied in S. I. Vavilov's laboratory as a method for studying concentration depolarization and concentration quenching of fluorescence. In particular, F. M. Pekerman's studies¹⁶ showed that in solutions in which the fluorescence is quenched by foreign substances, the concentration quenching shows a slower increase than in the unquenched solutions. L. A. Kiyanskaya, P. I. Kudryashov, and I have shown¹⁷ that this phenomenon is observed only in mobile solvents (water, alcohol), such as Pekerman used in his experiments. The inverse phenomenon is observed in viscous solutions: the concentration quenching is enhanced by the addition of a

Table II

n	3-0	4	5	6	7	8	9	10	11	12
$\left[\frac{d\left(\frac{B}{B_0}\right)}{dc} : \frac{d\left(\frac{\tau}{\tau_0}\right)}{dc} \right]_{c \rightarrow 0}$	1.00	1.33	1.67	2.0	2.33	2.67	3.0	3.33	3.67	4.00
$\left[\frac{\tau}{\tau_0} : \frac{B}{B_0} \right]_{c \rightarrow \infty}$	1.00	1.42	2.04	3.0	4.5	6.56	10.0	15.4	22.7	35.0

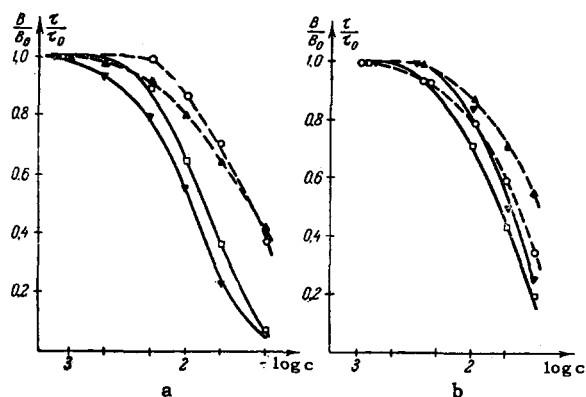


FIG. 4. Concentration quenching of the fluorescence of tryptophan in glycerol (a) and alcohol (b) solutions in the presence (▲) and absence (○) of aniline. The solid curves are for B/B_0 , the dotted curves for τ/τ_0 .

foreign quenching agent (Fig. 4). Here, the absorption and fluorescence spectra are not changed by the addition of the quenching agent. The reason for this phenomenon is obvious: in media of low viscosity, diffusion-controlled quenching by foreign substances and quenching by migration of energy are two competing processes; in viscous solutions, the diffusion-controlled quenching is small in extent, but at the same time, the migration of energy increases the probability of quenching by foreign substances, since the excitation energy can be transferred to a molecule in the vicinity of a molecule of the quenching agent.

I must also note the experiments on the quenching of phosphorescence of liquid solutions by foreign substances conducted in the Forties by P. P. Dikun and myself¹⁸ and recently by L. A. Kuznetsova.¹⁹ The remark has often been made in the literature that phosphorescence is much more sensitive to the presence of a quenching agent than fluorescence is. Of course, this statement is correct, but the high degree of quenching of phosphorescence is exclusively the result of the long lifetime of the molecules in the phosphorescent state. As for p , the probability of quenching upon encounter, it is considerably smaller in the phosphorescent state. Thus, for example, in the quenching of the luminescence of a glycerol-alcohol solution of acridine orange by aniline or hydroquinone, the probability of quenching of the phosphorescence is 100–500 times smaller than the probability of quenching of the fluorescence.

In conclusion, I would like to note that Vavilov's fundamental idea that the number of effective collisions between the reacting molecules in solutions must be calculated by diffusion methods has successfully endured the test of more than thirty years' time, and since 1936–38, it has gained recognition in the study of the kinetics of chemical reactions in solutions.

¹ S. I. Vavilov, *Z. Physik* **53**, 665 (1929).

² S. I. Vavilov, *Doklady Akad. Nauk SSSR* **3**, (12), 271 (1936).

³ B. Ya. Sveshnikov, *Trudy, State Optical Institute* **12**, No. 108 (1938).

⁴ M. V. Smoluchowski, *Z. phys. Chem.* **92**, 129 (1918).

⁵ B. Ya. Sveshnikov, *Acta Physicochim. USSR* **3**, 257 (1935).

⁶ A. N. Kolmogorov and M. A. Leontovich, *Phys. Z. Sowjetunion* **4**, 1 (1933).

⁷ S. I. Vavilov, *Acta Phys. Polonica* **5**, 417 (1936).

⁸ Bonch-Bruевич, Molchanov, and Shirokov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **20**, 596 (1956), *Columbia Tech. Transl.*, p. 541.

⁹ Kuznetsova, Sveshnikov, and Shirokov, *Оптика и спектроскопия (Optics and Spectroscopy)* **2**, 578 (1957).

¹⁰ P. I. Kudryashov and B. Ya. Sveshnikov, *Dokl. Akad. Nauk SSSR* **115**, 894 (1957).

¹¹ M. S. Marinesco, *Adsorption sur les molecules dissoutes*, Paris (1927).

¹² Ivanova, Mokeeva, and Sveshnikov, *op. cit.* ref. 9 (in press).

¹³ V. V. Zelinskii and V. P. Kolobkov, *Doklady Akad. Nauk SSSR* **101**, 241 (1955).

¹⁴ L. A. Kiyanskaya and B. Ya. Sveshnikov, *op. cit.* ref. 9 (in press).

¹⁵ V. I. Shirokov and B. Ya. Sveshnikov, *op. cit.* ref. 9 (in press).

¹⁶ F. M. Pekerman, *Dissertation (State Optical Institute, 1940)*.

¹⁷ Kiyanskaya, Kudryashov, and Sveshnikov, *Doklady Akad. Nauk SSSR* (in press).

¹⁸ P. P. Dikun and B. Ya. Sveshnikov, *Doklady Akad. Nauk SSSR* **60**, 791 (1948).

¹⁹ B. Ya. Sveshnikov and L. A. Kuznetsova, *Doklady Akad. Nauk SSSR* **121**, 1045 (1958).

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