Soviet-era science, translated into English

Physics

1957

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195701.79941

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

Physics

P. I. Kudryashov and B. Ya. Sveshnikov

On the Theory of the Polarization of Fluorescence of Solutions

(Presented by Academician A. N. Terenin, 21 II 1957)

One of the fundamental propositions of the modern theory of fluorescence polarization is the dependence of this quantity on the viscosity and temperature of the solution, as well as on the volume of the molecule and the lifetime of its excited state. The quantitative relations among these quantities, according to V. L. Levshin ([1]) and F. Perrin ([2]), are determined by the formula

$$\frac{1}{p} - \frac{1}{p_0} = \left(\frac{1}{p_0} - \frac{1}{3}\right) \frac{kT}{v\eta} \tau, \tag{1}$$

where k is Boltzmann's constant; T is the absolute temperature; η is the viscosity of the solution; v is the molecular volume; τ is the lifetime of the excited state of the molecule; p is the polarization sought, and p_0 is the limiting polarization, i.e., the polarization at $\eta \to \infty$ and $\tau \to 0$.

This formula has been tested in the work of a number of authors ([1]-[3]), in some experiments the viscosity being varied by mixing two solvents in different proportions, in others the change in viscosity being accompanied by a simultaneous increase in the temperature of the solution, and in still others the lifetime of the excited state of the molecule being gradually varied by adding to the solution various amounts of a foreign quencher or by heating the solution.

Most experiments gave quite satisfactory results. However, we considered it necessary to carry out a new test of (1), specifically for the case of fluorescence quenching by foreign substances. The point is that, following, for example, F. Perrin ([2]), in all works in which the change in the degree of fluorescence polarization upon quenching by foreign substances is studied, τ in formula (1) is usually replaced by $\frac{B}{B_0}\tau_0$, where B and B_0 are the fluorescence yields, respectively, in the quenched and unquenched solutions; that is, it is assumed that the changes in lifetime and yield upon quenching are proportional to one another. Meanwhile, over the past 20–25 years many experimental data have accumulated showing that, when the fluorescence of solutions is quenched by foreign substances, the yield decreases considerably faster than the fluorescence lifetime. Most authors explained this phenomenon by the fact that, along with quenching that depends on the lifetime of the excited state of the molecule, there is also practically instantaneous quenching, independent of τ.

If this assertion were correct, it would be obvious that formula (1) should lead to good results if values of the fluorescence lifetime measured directly on a fluorometer were substituted into it, and to poor results if τ were replaced by $\frac{B}{B_0}\tau_0$. Meanwhile, according to the data of F. Perrin, S. I. Vavilov and I. M. Frank, and A. N. Sevchenko, replacing τ by $\frac{B}{B_0}\tau_0$ gives more or less satisfactory results, whereas substituting fluorometrically measured values of τ into (1), as we shall show below, leads to clearly poor results.

This contradiction between experiment and theory is explained by the fact that, applying (1) to quenched solutions, F. Perrin assumed that in this case as well the fluorescence decays according to an exponential law. Meanwhile, theoretical and experimental studies of the quenching of the fluorescence of solutions by foreign substances (^{4}) have shown that the decay law of quenched solutions is nonexponential, and that this circumstance is the cause of the different change in lifetime and yield upon quenching of the fluorescence of certain solutions. Under such conditions, in order to compare experimental data with calculated data it is necessary to replace formula (1) by another one, suitable for the nonexponential decay law that occurs in quenching by foreign substances. This is easy to do if, in the derivation of (1) proposed by F. Perrin, the fluorescence decay law is changed accordingly. For the case of excitation by polarized light, whose electric vector is parallel to the Z axis, we thus obtain:

$$I_x(t)\,dt = e^{-\alpha t-\omega\beta\sqrt{t}}\frac{dt}{3\tau}\left[(1+2e^{-6Rt})I_{x_0}+(1-e^{-6Rt})(I_{y_0}+I_{z_0})\right] \qquad (2)$$

and analogous expressions for $I_y(t)dt$ and $I_z(t)dt$.

In formula (2), $I_x(t)$, $I_y(t)$, $I_z(t)$ are the intensities of radiation of virtual linear oscillators along the axes OX, OY, and OZ in the presence of Brownian rotation of the molecules, and $I_{x_0}(t)$, $I_{y_0}(t)$, and $I_{z_0}(t)$ are the same in its absence; $R = \frac{1}{6}kT/v\eta$; the quenching constants α and β are determined by the known formulas (^{4})

$$\alpha = 4\pi\omega Drc + \tau_0^{-1}; \qquad \beta = 8\pi^{1/2}D^{1/2}r^2c, \qquad (3)$$

where ω is the probability of quenching in a single collision; c is the number of quencher molecules in 1 cm^3; r is equal to the sum of the kinetic radii of the colliding molecules; D is the diffusion coefficient.

Integrating (2) from 0 to ∞, we obtain expressions for the light sums L_x, L_y, L_z, emitted along each of the axes.

By definition of fluorescence polarization:

$$p = \frac{L_z - L_x}{L_z + L_x}, \tag{4a}$$

$$p_0 = \frac{L_{z0} - L_{x0}}{L_{z0} + L_{x0}}. \tag{4b}$$

Substituting into (4a) the values of L_z and L_x calculated from (2), after small transformations we have

$$\frac{1}{p} - \frac{1}{3} = \left(\frac{1}{p_0} - \frac{1}{3}\right)\left(\frac{kT}{v\eta}\frac{B}{B_0}\tau_0\delta_1 + 1\right)\frac{\delta_2}{\delta_1}, \tag{5}$$

where

$$\delta_1 = \left[1 - \sqrt{\pi}\,\gamma e^{\gamma^2}\left(1 - \int_0^\gamma e^{-z^2}\,dz\right)\right]^{-1}, \qquad \gamma = \frac{\omega\beta}{2\sqrt{\alpha}} \tag{6}$$

and δ_2 is obtained from δ_1 by replacing α by $\alpha + 6R$.

When $\beta = 0$, i.e., for an exponential law of fluorescence decay, $\delta_1 = \delta_2 = 1$, formula (5) becomes the usual Levshin–Perrin formula; on the other hand, for very strong quenching, when $\alpha \to \infty$, $p \to p_0$.

Verification of the validity of formula (5) was carried out by us for the quenching of the fluorescence of aqueous fluorescein solutions by potassium iodide. In the work of L. A. Kuznetsova, V. I. Shirokov, and one of us (^{4}) it was shown that, in this case, the absence of proportionality between the change in yield and the change in fluorescence duration with increasing concentration of the quencher is explained not by the presence of additional static quenching, but by the deviation of the fluorescence decay law of the quenched solutions from an exponential law. The verification of formula (5) consisted in the following: for each concentration of potassium iodide we calculated from (5) the values of p_0, substituting into the formula the experimental values B/B_0 and the values δ_1 and δ_2/δ_1 calculated from (6).

We wished to compare the values of p_0 thus obtained with the values of p_0 found by other authors from experiments in which the dependence of polarization on viscosity was studied. However, a survey of the literature data showed that the values of the limiting polarization of fluorescein fluorescence obtained from the indicated experiments by individual authors range from 0.36 to 0.44. This is apparently explained by a considerable arbitrariness in drawing the straight line when constructing the graph giving the dependence of $1/p$ on $1/\eta$.

Since we had at our disposal fluorometric values of the fluorescence duration in water ($4.8 \cdot 10^{-9}$ sec), in glycerin ($4.5 \cdot 10^{-9}$ sec), and in glycol ($4.7 \cdot 10^{-9}$ sec), and the values of the molecular volumes (according to Marinesco (^{5})), we decided to repeat the experiments on studying the dependence of p on η and to calculate the values of p_0 for each of the values of p measured by us.

All the fluorescein solutions used for the experiments had a dye concentration of $5 \cdot 10^{-6}$ g/cm^3 and an alkali concentration of $2 \cdot 10^{-2}$ g/cm^3. Excitation was carried out with polarized and carefully stabilized, according to the method of V. I. Shirokov (^{6}), filtered light from a mercury lamp (436 mμ). Observation was carried out through a filter crossed with the 436 mμ line, perpendicular to the exciting light, and the degree of polarization was determined by successive measurements of the fluorescence intensity at two positions of a Glan prism placed in front of the photomultiplier.*

In order to check the setup, we determined the degree of fluorescence polarization of an aqueous fluorescein solution under excitation by polarized and unpolarized light. In the latter case the measurements were carried out at two temperatures: 20 and 60°. The corresponding polarization values proved to be 1.8, 0.8, and 0.5%.

The experimental values of p obtained by us and the values of p_0 calculated from the experiments on the dependence of p on η are given in Table 1. The mean value of p_0 is equal to 40.8%.**

Table 1

Experimental values of the degree of polarization p and calculated values of the limiting polarization p_0 for mixtures of water with glycol, $\eta = 0.0144$—0.0994, and for mixtures of water with glycerin

η, poise	0.0144	0.0183	0.0259	0.0455	0.0994	0.872	0.91	1.56	4.55
p, %	3.3	3.7	5.00	8.00	12.8	30.0	31.5	33.8	37.7
p_0, %	44.6	44.0	43.7	42.9	40.0	36.5	38.4	38.0	39.4

In Table 2 are given, for various concentrations of potassium iodide, the values obtained by us of p, B/B_0***, τ/τ_0, the calculated values of δ_1 and δ_2/δ_1 and the values of the limiting polarization p_0, calculated: 1) by formula (1), in which τ is replaced by $\frac{B}{B_0}\tau_0$; 2) by the same formula with the fluorometric

---

* A detailed description of the setup will be given elsewhere.

** In doing this we assumed that all the values of p_0 obtained by us have equal weight. Of course, this assertion may raise certain objections. However, it is difficult to estimate the weights of the individual measurements.

*** In the tabulated yield data a small correction has been introduced, caused by allowance for the change in anisotropy of the radiation upon quenching (^{7}).

values of the fluorescence lifetime substituted instead of τ; and 3) by formula (5).

Comparison of the last three columns shows that the best results are obtained by calculation according to formula (5). In this case one obtains a comparatively small scatter of the calculated values of p_0, and the mean value of p_0

Table 2

Experimental values of the degree of polarization, yield, and fluorescence lifetime in fluorescein solutions quenched by potassium iodide, and values of the limiting polarization calculated according to (1) and (5)

C_{KJ} ml · l^{-1} · 10	B/B_0	$\frac{\tau}{\tau_0}$	$p, \%$	δ_1	δ_2/δ_1	$p_0\left(\frac{B}{B_0}\right)$	$p_0(\tau)$	p_0 according to (5)
1,5	0,34	0,336	4,54	1,31	0,8416	36,6	36,3	39,2
3	0,192	0,21	7,15	1,57	0,763	35,8	38,2	39,2
6	0,095	0,128	11,43	1,96	0,7370	34,2	40,4	40,0
9	0,0518	0,085	15,85	2,225	0,7675	33,2	43,3	41,5
12	0,0351	0,066	19,55	2,485	0,7821	34,0	45,8	41,5
15	0,0261	0,052	22,83	2,73	0,7828	35,4	46,7	44,5
18	0,0189	0,041	26,0	2,975	0,7850	36,2	47,1	42,9

is equal to 41.2%, i.e., it is very close to the mean value of p_0 calculated from experiments on the dependence of polarization on viscosity. The widely used method of calculation by formula (1), replacing τ by $\frac{B}{B_0}\tau_0$, gives underestimated values of the limiting polarization and, moreover, when there is a large discrepancy between the changes in B/B_0 and τ/τ_0, the use of this method has no theoretical justification. And, finally, calculation by formula (1), into which the fluorometric values of τ have been substituted for each concentration of potassium iodide, gives the worst result. In this case the values of the limiting polarization systematically and rather rapidly increase as the concentration of the quencher increases and, consequently, the dependence of $1/p$ on the fluorometric values of τ cannot be represented as a straight line, as required by formula (1).

Thus, it may be considered proven that, for the present case of fluorescence quenching, the discrepancy between the changes in the yield and in the fluorescence lifetime is explained by a nonexponential law of decay of fluorescence in the quenched solutions.

In conclusion, we consider it a pleasant duty to express our gratitude to F. S. Cheremisin, who took part in assembling the apparatus and in the calculations.

Received
8 II 1957

CITED LITERATURE

1. V. L. Levshin, *Zs. Phys.*, **26**, 274 (1924); **34**, 330 (1925).

2. F. Perrin, *Ann. d. Phys.*, **12**, 169 (1929); *Thèse*, Paris, 1929.

3. V. L. Levshin, *Photoluminescence of Liquid and Solid Substances*, 1951; S. I. Vavilov, I. M. Frank, *Zs. Phys.*, **69**, 100 (1931); A. N. Sevchenko, *Tr. GOI*, **14**, 65 (1941); F. Perrin, *Acta Phys. Polon.*, **5**, 335 (1936).

4. S. I. Vavilov, *Acta Phys. Polon.*, **5**, 417 (1936); B. Ya. Sveshnikov, *Acta Physicochim. URSS*, **3**, 257 (1935); *Tr. GOI*, issue 108 (1938) (dissertation); L. A. Kuznetsova, B. Ya. Sveshnikov, V. I. Shirokov, *Optika i spektr.*, **2**, 5, 578 (1957).

5. N. S. Marinesco, *Adsorption sur les molécules dissoutes*, Paris, 1927.

6. V. I. Shirokov, *Izv. AN SSSR, ser. fiz.*, **20**, 605 (1956).

7. B. Ya. Sveshnikov, *Acta Physicochim. URSS*, **4**, 354 (1936).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.