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Abstract

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CALCULATION OF LUMINESCENCE DEPOLARIZATION UPON CHANGES IN TEMPERATURE AND CONCENTRATION OF THE FLUORESCENT SUBSTANCE

S. I. Vavilov ([1]), proceeding from the concept of resonance migration of the excitation energy absorbed by fluorescent molecules, created a theory of concentration depolarization of fluorescence. The formulas obtained by Vavilov make it possible to calculate fluorescence depolarization when only the concentration of fluorescent molecules is varied, while the temperature and viscosity of the solution are kept constant. However, as numerous experiments show, fluorescence depolarization depends very strongly both on the temperature and on the viscosity of the solution. In the present work an attempt is made to introduce new variables—temperature and viscosity—into Vavilov's theory of concentration depolarization of fluorescence.

1. Let us calculate the probability of collision of fluorescent molecules in viscous solutions. Since these molecules are usually considerably larger than the solvent molecules, they may be regarded as Brownian particles. The validity of such an approach is confirmed by the Levshin–Perrin formula for rotational depolarization, which agrees well with experiment.

We shall consider the Brownian motion of fluorescent molecules, which is described by the theory of Einstein and Smoluchowski. According to this theory, the mean square displacement of a Brownian particle during time t is

$$\overline{\Delta r^2} = 6Dt. \tag{1}$$

For spherical particles

$$D = kT/6\pi\eta\sigma, \tag{2}$$

where σ is the radius of the Brownian particle. The probability that a Brownian particle undergoes collisions with other particles during time t is

$$W_{\text{coll}} = 1 - e^{-t/t_0}, \tag{3}$$

where t_0 is the coagulation time. For viscous liquids

$$t_0 = 1/8\pi D\sigma c. \tag{4}$$

Substituting (2) into (4) and the resulting expression into (3), we obtain

$$W_{\text{coll}} = 1 - \exp\left(-{}^4/_3 k\,\frac{\eta}{T}ct\right). \tag{5}$$

The probability of collision for nonspherical Brownian particles will differ from (5) by a coefficient multiplying $T/\eta ct$.

The migration of energy is influenced both by the concentration of fluorescent molecules c and by the velocity of their motion, which depends on T/η. A measure of this influence may be the number of collisions, which, according to (5), depends in the same way on both c and the ratio T/η.

2. Let us find the probability of transfer of excitation energy as a function of t, c, and T/η. Let us assume conditionally that in the fluorescent medium there are two

different kinds of molecules. The transfer of excitation energy to a molecule of the same kind is not accompanied by quenching. Let us denote the probability of the absence of such transfers by $q(c, T/\eta, t)$, where t is the time elapsed after excitation. The transfer of excitation energy to a molecule of the second kind may be accompanied by quenching. The probability of the absence of such transfers is $r(c, T/\eta, t)$. Molecules of one kind may differ from molecules of another kind, for example, in thermal state, orientation, i.e., they may transform into one another and back without chemical changes.

Let us carry out a static calculation of $q(c, T/\eta, t)$. Expanding $q(c, T/\eta, t)$ in a series, and also assuming that some molecules, being under certain conditions, can instantaneously give up their energy to other molecules, and carrying out the corresponding calculations (1), we obtain

$$q\left(c, \frac{T}{\eta}, t\right) = \exp\left[\ln q\left(c, \frac{T}{\eta}, t\right)\right] \exp\left[\frac{t}{\Delta t}\ln q\left(c, \frac{T}{\eta}, t\right)\right] \times$$
$$\times \left\{q'_t\left(c, \frac{T}{\eta}, t\right) \Big/ \exp\left[q\left(c, \frac{T}{\eta}, t\right)\right]\right\} t, \tag{6}$$

where $\Delta t = t/n$ is the mean value of the interval.

Let us determine the form of $q(c, T/\eta, 0)$ as a function of c and T/η, under the condition $q(c, T/\eta, 0) \neq 1$, and also the form of $q'_t(c, T/\eta, 0)$. We shall set the fluorescing volume equal to unity.

The probability of excitation-energy transfers, taking into account relation (5), can be written in the form

$$W_{\text{per}} = A\frac{T}{\eta}[1-\varphi(r,t)], \tag{7}$$

where A is a constant equalizing the dimensions; $\varphi(r,t)$ is Vavilov' s probability of the absence of transfers.

The probability of finding molecules in a spherical layer of radius r and thickness dr is equal to $c\cdot 4\pi r^2 dr$. The probability that the excitation energy during time t will not pass into the spherical layer $4\pi r^2 dr$ will have the form

$$W = \left\{1 - A\frac{T}{\eta}[1-\varphi(r,t)]\right\} c\cdot 4\pi r^2\, dr + 1(1 - c\cdot 4\pi r^2\, dr) =$$

$$= 1 - c\cdot 4\pi r^2\, dr\cdot A\frac{T}{\eta}[1-\varphi(r,t)]. \tag{8}$$

The total probability of the absence of transfers into any spherical layer surrounding the excited molecule is expressed by the product

$$q\left(c,\frac{T}{\eta},t\right) = \prod_{2\sigma}^{\infty}\left\{1 - c\cdot 4\pi r^2 A\frac{T}{\eta}[1-\varphi(r,t)]\,dr\right\} =$$

$$= \exp\left\{\sum_{2\sigma}^{\infty}\ln\left\{1 - c\cdot 4\pi r^2 A\frac{T}{\eta}[1-\varphi(r,t)]\,dr\right\}\right\}. \tag{9}$$

Replacing the summation by integration, we rewrite (9) in the form

$$q\left(c,\frac{T}{\eta},t\right) = \exp\left\{-c\frac{T}{\eta}A\int_{2\sigma}^{\infty}4\pi r^2[1-\varphi(r,t)]\,dr\right\} = \exp\left[-\lambda c\frac{T}{\eta}A\right]. \tag{10}$$

The constant λ does not depend on c and T/η and has the meaning of a "sphere of action," within which resonance transfer during time t is inevitable.

Expanding λ with respect to time and restricting ourselves to the first two terms, $\lambda = \lambda_0 + \lambda_0'\Delta t$, from (10) we find

$$q\left(c,\frac{T}{\eta},0\right) = \exp\left[-\lambda_0 c\frac{T}{\eta}A\right];$$

$$q_t'\left(c,\frac{T}{\eta},0\right) = -\lambda_0' c\frac{T}{\eta}A\exp\left[-\lambda_0 c\frac{T}{\eta}A\right].$$

Substituting these values into (6), we obtain:

$$q\left(c, \frac{T}{\eta}, t\right) = \exp\left[-\lambda_0 c \frac{T}{\eta} A\right] \exp\left[-\frac{t}{k_2} c \frac{T}{\eta} A\right], \tag{11}$$

where $1/k_2 = \lambda_0/\Delta t + \lambda_0'$ has the meaning of the rate of increase of the sphere of action under the condition $\lambda_0 \approx 0$.

Carrying out similar calculations for $r(c, T/\eta, t)$, we find:

$$r\left(c, \frac{T}{\eta}, t\right) = \exp\left[-\omega_0 c \frac{T}{\eta} A\right] \exp\left[-\frac{t}{k_1} c \frac{T}{\eta} A\right]. \tag{12}$$

The constant ω_0 has the physical meaning of a "sphere of action" for "instantaneous quenching."

In the particular case it is assumed that quenching should disappear as $c \to 0$. However, quenching is also observed at concentrations below the threshold, when migration may be neglected. Consequently, there exists internal quenching. Let us denote the probability of its absence by f_0 for direct absorption of light by a molecule and by f for subsequent transitions. Assuming that f does not depend on t and c, and neglecting the dependence of f on T and η, (12) may be written in the following general form:

$$r_1\left(c, \frac{T}{\eta}, t\right) = f \exp\left[-\omega_0 c \frac{T}{\eta} A\right] \exp\left[-\frac{t}{k_1} c \frac{T}{\eta} A\right]. \tag{13}$$

The total probability of the absence of any transitions of excitation energy in the medium is represented by the product of $q(c, T/\eta, t)$ and $r_1(c, T/\eta, t)$.

$$W\left(c, \frac{T}{\eta}, t\right) = f \exp\left[-(\omega_0 + \lambda_0) c \frac{T}{\eta} A\right] \exp\left[-t\left(\frac{1}{k_1} + \frac{1}{k_2}\right) c \frac{T}{\eta} A\right]. \tag{14}$$

On the basis of this formula, one can calculate the concentration depolarization of fluorescence if the type of the absorbing and emitting system is specified.

3. Vavilov' s formulas with the variables T, η introduced into them for concentration depolarization will now have the form:

a) In the case of not very large concentrations, when quenching may be neglected:

$$\frac{1}{p} = \frac{1}{p_0} + \frac{1}{p_0} \frac{3 - p_0}{3} \cdot \frac{\tau_0}{k_2} c \frac{T}{\eta} A. \tag{15}$$

b) For the decrease in the degree of polarization of fluorescence as it decays,

$$p(t) = \frac{p_0}{f \exp\left[-\Omega c \frac{T}{\eta} A\right] \frac{c}{k_2} \frac{T}{\eta} A} \exp\left\{ f \exp\left[-\Omega c \frac{T}{\eta} A\right] \frac{c}{k_2} \frac{T}{\eta} A t \right\}. \qquad (16)$$

Vavilov' s formulas for the concentration depolarization of fluorescence with the new variables T and η introduced into them, naturally, require careful experimental verification. It is possible that some discrepancy between theory and experiment will be observed, since these formulas were obtained under certain assumptions concerning the interaction of fluorescing molecules in viscous solutions.

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CITED LITERATURE

1. S. I. Vavilov, *Microstructure of Light*, Publishing House of the Academy of Sciences of the USSR, 1950.

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