

FURTHER INVESTIGATIONS ON DEGREE OF POLARIZATION IN VISCOUS QUENCHED FLUORESCENT SOLUTIONS

By J. HEVESI

Institute of Experimental Physics, Attila József University, Szeged

(Received December 15, 1965)

The earlier statement that PERRIN-LEVSHIN's linear relation is formally not fulfilled in the case of viscous quenched solutions is supported by further experimental results. It is shown that in viscous quenched systems the relation $1/p=f(T/\eta_v)$ is not linear. The validity of the expression obtained for the relation between these quantities is checked by experimental results.

1. Introduction

It has been shown in an *earlier* paper [1] that the linear relation

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \frac{k \cdot T}{v \cdot \eta_v} \cdot \tau \quad (1)$$

introduced by PERRIN and LEVSHIN [2] apparently loses its validity in the case of viscous solutions containing „dynamic quenchers”, inasmuch as the function $1/p=f(T/\eta_v)$ ceases to be linear. (In (1) p means the true degree of polarization, p_0 the fundamental polarization, k Boltzmann's constant, T absolute temperature, v volume of the fluorescent molecule, η_v viscosity of solution and τ lifetime of excited state.) This statement was supported by experimental data obtained for viscous solutions of fluorescein quenched by KI.

In that investigations the viscosity of solutions was varied by changing the temperature. The true degree of polarization p was determined from the degree of polarization p' obtained experimentally with the relation

$$p = \frac{p'}{1 - \kappa(1 - 0,6p')} \quad (2)$$

given by BUDÓ and KETSKEMÉTY [3]. (In (2) $\kappa = \kappa^{(1)} \cdot \eta$ is a correction factor for the effect of secondary fluorescence [4]; $\kappa^{(1)}$ and η can be determined by spectrophotometric measurements.) The experimental results obtained in this way actually showed the relation different from linear, which was to be expected (see Fig. 2 in [2]).

A quantitative relation was proposed [5] between p and T/η_v instead of the qualitative connection given in [1]. In the present paper the validity of this quantitative relation is supported by experimental results.

2. Theory

It is a known experimental fact that changes in the degree of quenching exert a considerable influence both on the yield and the degree of polarization of the luminescent system. Therefore VAVILOV [6] suggested as early as 1936 that the relative yield of luminescence η/η_0 and degree of polarization should be measured simultaneously. Namely, if the decay of luminescence obeys an exponential law, there will exist a proportionality between the relative yield and the lifetime τ of the excited state (see *p.* 133 in [2]), that is

$$\frac{\eta}{\eta_0} = \frac{\tau}{\tau_0}, \quad (3)$$

where η_0 and τ_0 are the yield and the decay time of the unquenched solution. Thus (1) can be written as follows

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \frac{k \cdot T}{v \cdot \eta_v} \cdot \frac{\eta}{\eta_0} \tau_0. \quad (4)$$

In the case of non-absorbing quenchers — when (3) is fulfilled — (4) gives a linear relation between η/η_0 and $1/p$. The value of τ_0 can be calculated from the slope of the straight line, if p_0 , v , T and η_v are known.

The validity of the linear relation mentioned above was verified by several authors [7]—[8] for different luminescent systems, among others in our paper [9]

Table I

N	Concentration of dyestuff (mole/l)	Additive agent	Quencher (mole/l)	Temperature (°K)
1.	Fluorescein ($1 \cdot 10^{-4}$)	3 vol. % NaOH	KI (0—1)	293—333
2.	Fluorescein ($1 \cdot 10^{-4}$)	3 vol. % NaOH	KBr (0—2)	303—333
3.	Rhodamine B ($1 \cdot 10^{-4}$)	3 vol. % NaOH	KI (0—1)	303—323
4.	Tripaflavine ($1,25 \cdot 10^{-4}$)	$1 \cdot 10^{-3}$ mole/l HCl	Rhodamine B ($0—2 \cdot 10^{-3}$)	303—323

dealing with the dependence of the degree of polarization on concentration of quencher and temperature in viscous solutions of fluorescein. The linearity of relation (4) supports our hypothesis that the decay of luminescence can be considered as obeying the exponential law — with a good approximation — in the case of the quenched systems which were investigated. In this case we can write in (4) instead of η/η_0

$$\frac{\eta}{\eta_0} = \frac{1}{1 + k' \cdot c} \quad (5)$$

which formula was derived by BAUR [10] for dynamic quenching. In (5) c means the concentration of quencher, $k' = 4\pi a N' D \tau_0$, where a is the radius of the active sphere of the excited molecules, D the constant of interdiffusion, and $N' = 6,02 \cdot 10^{23}$.

Substituting k' in (5), then (5) in (4) and reducing the constants in the equation obtained in the form

$$A = k \cdot \tau_0 \quad \text{and} \quad B = \frac{2}{3} a N' k \tau_0 \left(\frac{1}{r_l} + \frac{1}{r_k} \right) \quad (6a-b)$$

we have the relation

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3} \right) \cdot \frac{A}{v} \cdot \frac{T}{\eta_v} \cdot \frac{1}{1 + B \frac{T}{\eta_v} \cdot c} \quad (7)$$

In (6b) r_l is the kinetic radius of the luminescent particle and r_k that of the quencher.

It can be seen that relation (7) corresponds to PERRIN—LEVSHIN's classical formula for $c = 0$, that is in absence of dynamic quencher. In the case of quenched solutions, *i. e.* for $c \neq 0$, $1/p$ plotted as a function of T/η_v should give a curve concave from below.

Table II

C_{KBr} (mole/l)	$B \cdot 10^{-5}$ poise [(mole/l)·grad]	$1/p$ (meas.; calc.)	$T(^{\circ}K)$			
			303	313	323	333
0	0	meas.	5,43	6,35	8,11	11,30
		calc.	5,43	6,35	8,11	11,30
$1 \cdot 10^{-1}$	3,414	meas.	5,30	6,25	7,96	10,75
		calc.	4,87	6,25	7,94	10,98
$3 \cdot 10^{-1}$	3,397	meas.	5,16	6,06	7,57	10,25
		calc.	4,77	6,06	7,64	10,40
$6,31 \cdot 10^{-1}$	2,428	meas.	4,87	5,83	7,33	9,69
		calc.	4,62	5,83	7,31	9,79
1	2,813	meas.	4,59	5,48	6,86	8,92
		calc.	4,43	5,48	6,83	8,89
1,259	1,238	meas.	4,38	5,44	6,70	8,61
		calc.	4,35	5,44	6,83	8,97
1,585	0,409	meas.	4,24	5,20	6,34	8,12
		calc.	4,26	5,20	6,66	8,91
1,995	2,195	meas.	4,14	4,87	6,00	7,41
		calc.	4,04	4,87	5,99	7,63

3. Experimental methods and calculations

In order to check the validity of relation (7) function $1/p = f(T/\eta_v)$ was investigated for four series of solutions, the composition of which and the interval of temperature is given in Table I. The composition of solvent was 60 volume % glycerol and water in each case. The glycerol used was purified to spectroscopic purity by repeated vacuum distillation.

The degree of polarization p' was measured by a photoelectric polarimeter [11], with the method given in [1].

The values of lifetime τ_0 used for calculating A were measured with a phase-fluorometer [13]. The lifetimes τ_0 obtained with the different solutions (see in Table I) were $5 \cdot 10^{-9}$ s, $4,6 \cdot 10^{-9}$ s, $4,07 \cdot 10^{-9}$ s, and $3,27 \cdot 10^{-9}$ s, respectively.

The molecular volumes v were taken from a paper of SZALAY and co-workers [12], or were determined with the method given in that paper from the experimental data based on the case $c=0$ (unquenched solution). In these calculations the values of $1/p_0$ obtained by extrapolation to infinite viscosity were used.

Knowing A , $1/p_0$ and v the values of B were determined from (7) substituting the values of $1/p$ measured for different concentrations of quencher. The values of B were calculated with the same values of T for all series of solutions. Table II gives, as an example the values obtained for the series of solutions 2. It can be seen that these values are varying with the concentration of quencher. It was not possible to determine an unequivocal connection between the changes of these two quantities.

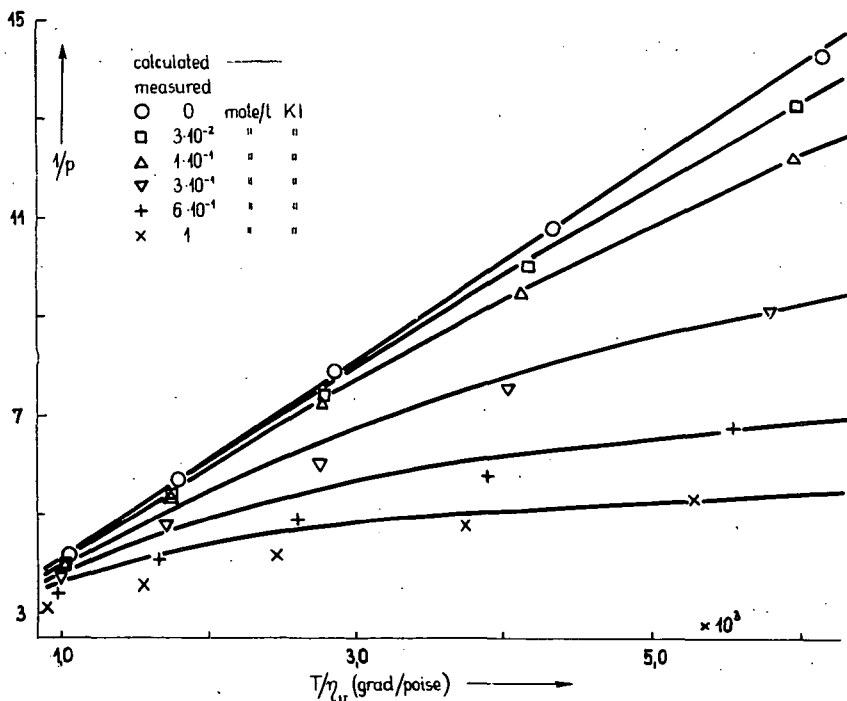


Fig. 1

4. Experimental results

The reciprocal values of true degrees of polarization p_m measured and the values of p_c calculated from (7) are plotted in Fig. 1 versus T/η_v for solutions of fluorescein quenched by KI (1st series). The figure shows clearly that the curves of $1/p=f(T/\eta_v)$ are concave from below for $c \neq 0$, whereas for $c=0$ the relation is linear. As it can be seen from the figure, the calculated values are in good agreement

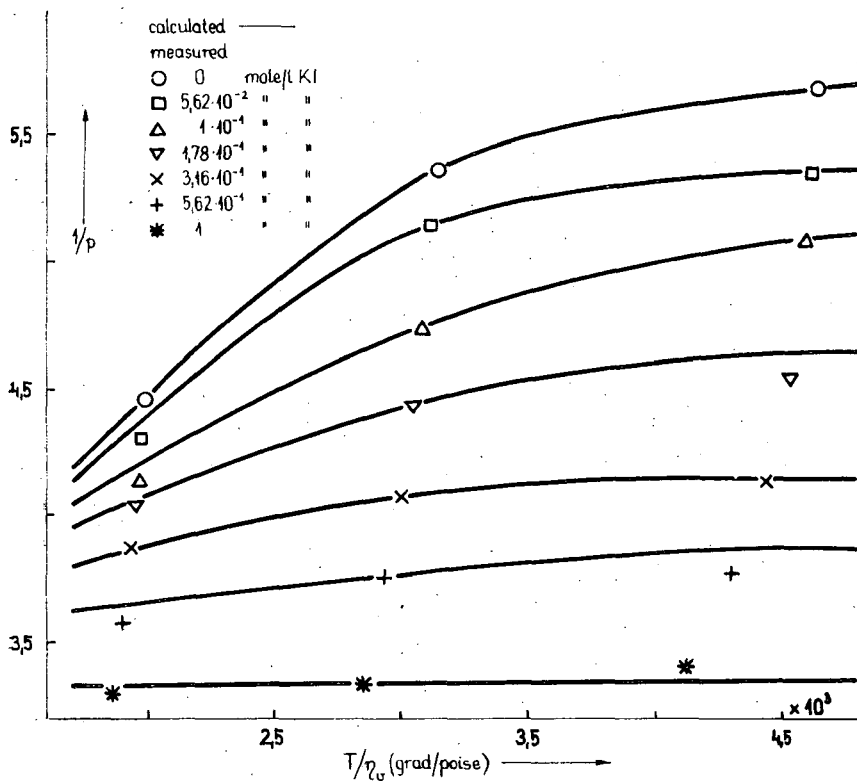


Fig. 2

with the measured ones, especially for lower concentrations of quencher. The divergence found for higher concentrations of quencher is probably connected with the fact that the optical properties of the system are altered by relatively high quantities of KI.

The values of $1/p_m$ and $1/p_c$ obtained with the 2nd series of solutions quenched by KBr are given in Table II. In this case the agreement between p_m and p_c is good again. A plot of these relations is not given because the degree of polarization shows only insignificant changes with concentration of quencher, because the quenching effect of KBr is very little. It can be seen from the table that the values of the degrees of polarization calculated and measured depend on both concentration of quencher and temperature.

Fig. 2 shows the values of $1/p_m$ and $1/p_c$ obtained with rhodamine B solutions quenched by KI (3rd series) as a function of T/η_v . It can be seen in the figure that in this case the agreement between p_m and p_c is also very good. As it is to be seen, the curves of $1/p=f(T/\eta_v)$ are concave from below again, but there exists no linear relation between $1/p$ and T/η_v even in the case of $c=0$ (unquenched solution). This can be attributed to the fact that concentration quenching takes place in the case of concentrations of dyestuff used in this series. Rhodamine B is known to associate at very low concentrations. These associates are generally not luminescent

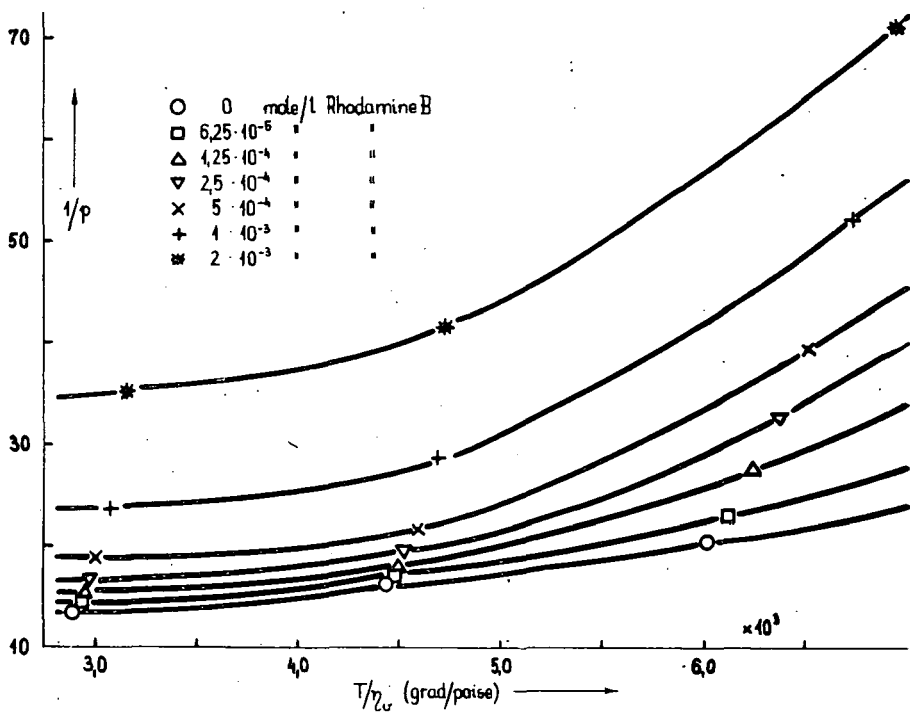


Fig. 3

(see e. g. LEVSHIN [14]; LEVSHIN and KROTOVA [15]), which, respectively the changing of τ_0 , may explain the divergence from linearity. In this case the system consists of more components (luminescent substances, solvent, non-luminescent associates) and changes in the energy state of the system are to be expected.

It can be seen from Fig. 3 that in the case of tryptaflavine quenched by rhodamine B (4th series, quenching by absorbing substance) the curves of the function $1/p=f(T/\eta_v)$ are quite different from those obtained with solutions quenched by non-absorbing substances. One of the causes of the relevant divergence can be found in the fact that the quenching mechanism in this system — energy transfer by resonance — is different from that taking place in systems quenched by non-absorbing substances. Another cause of the divergence can be found in the fact that the lifetime τ_0 of luminescence in the system tryptaflavine-rhodamine B depends

considerably on temperature, whereas in the case of fluorescein τ_0 is practically independent of temperature in the temperature interval under investigation (see e. g. STEPANOV [16] p. 210). Therefore relation (7), obtained for dynamic quenching, cannot be applied for this system.

The results mentioned above show that the function $1/p = f(T/\eta_v)$ is not linear in the case of viscous, quenched luminescent solutions. In the case of solutions quenched by non-absorbing substances the agreement between the measured true degrees of polarization p_m and the degrees of polarization p_c calculated with (7) is very good. For these systems (7) can be used for calculating the true degrees of polarization p by determining the quantities A , v , B from experimental data, whereas (7) cannot be applied for solutions quenched by absorbing substances because in this case the quenching mechanism is different.

* * *

The author is greatly indebted to Professor DR. Á. BUDÓ, director of the Institute for his interest in this work and for his valuable advices. Thanks are due to Professor DR. I. KETSKEMÉTY for the helpful discussions during the work.

References

- [1] Hevesi, J.: Acta Phys. et Chem. Szeged, **8**, 16 (1962).
- [2] Levshin, V. L.: Photoluminescence of Liquid and Solid Substances (Moscow-Leningrad, 1951).
- [3] Budó, Á.: Magyar Fizikai Folyóirat **9**, 269 (1961);
Budó, Á., I. Ketskemény: Acta Phys. Hung. **14**, 167 (1962).
- [4] Budó, Á., J. Dombi, L. Szöllösy: Acta Phys. et Chem. Szeged, **2**, 18 (1956).
- [5] Hevesi, J.: Dissertation, Szeged, 1965.
- [6] Vavilov, S. I.: Acta Phys. Polon. **5**, 417 (1936).
- [7] Vavilov, S. I., A. N. Sevchenko: DAN URSS **3**, 274 (1936).
- [8] Kudrjasov, P. I., B. Ja. Sveshnikov: DAN URSS **115**, 894 (1957).
- [9] Hevesi, J.: Doctoral thesis, Szeged, 1961.
- [10] Baur, E.: Z. Phys. Chem. **B16**, 465 (1932).
- [11] Ketskemény, I., L. Gargya, E. Salkovits: Acta Phys. et Chem. Szeged, **3**, 16 (1957).
- [12] Szalay, L., L. Gáti, B. Sárkány: Acta Phys. Hung. **14**, 217 (1962).
- [13] Bauer, R., M. Rozwadowski: Bull. Acad. Polon. Sci. **7**, 365 (1959).
- [14] Levshin, V. L.: Acta Phys. Polon. **26**, 455 (1964).
- [15] Levshin, V. L., L. V. Krotova: Opt. and Spectr. **13**, 809 (1962).
- [16] Stepanov, B. I.: Luminescence of Complex Molecules (Minsk, 1955).

ДАЛЬНЕЙШИЕ ИССЛЕДОВАНИЯ О СТЕПЕНИ ПОЛЯРИЗАЦИИ ВЯЗКИХ, ПОТУШЕННЫХ ЛЮМИНЕСЦЕНТНЫХ РАСТВОРОВ

Я. Хевеши

В настоящей работе с дальнейшими экспериментальными данными подтверждается то более раннее установление, что в случае вязких потушенных растворов линейное соотношение Перри́на — Лёвшина формально не выполняется. Показано, что для вязких, потушенных систем между обратным значением степени поляризации и абсолютной температурой, так же, как вязкостью растворов имеется нелинейное соотношение. Правильность соотношения, для вышеупомянутых величин подтверждается с экспериментальными данными.