

RELATION OF THE DECAY TIME AND EFFECTIVE TEMPERATURE IN THE CASE OF LUMINESCENT SOLUTIONS

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The difference $\Delta T = T^* - T$ between real and „effective” temperatures as a function of decay time was investigated. In the case of quenched solutions a linear connection between $\ln \Delta T$ and τ was found. The values of τ calculated from NEPORENT's modified relation seemed to be in a good agreement with measured decay times.

1. Between absorption spectra $\varepsilon(\nu)$ and fluorescence spectra $f_q(\nu)$ of solutions, STEPANOV's relation holds in the neighbourhood of the frequency of pure electronic transition. This relation can be expressed in many cases in the form $f_q(\nu) = N\varepsilon(\nu)\nu^2 \exp(-h\nu/kT^*)$, where N is a normalization factor independent of frequency, h and k are Planck's and Boltzmann's constants, and T^* denotes an „effective temperature” differing but moderately from the real temperature T of the solution [1]. On the base of the absorption and emission spectra T^* can be calculated, and the difference $\Delta T = T^* - T$ is connected with the decay time τ of the solution by the relation

$$\Delta T = \Delta T_0 \exp(-\tau/\tau'), \quad (1)$$

according to considerations based on a simple model, given in [2]. In Eq. (1) ΔT_0 and τ' are constants characteristic for the solute and the solvent in the case of a given exciting frequency. [Eq. (1) is substantially NEWTON's law of cooling applied to a system consisted of excited molecules and it expresses that part of the energy transferred to the molecule during the excitation is transformed into heat which is — at least partly — transferred to the environment during the lifetime of the excited state of the molecule, thus raising the local temperature.] Eq. (1) has been supported by the fact that ΔT increased with increasing quencher concentration in quenched solutions. That can be namely interpreted by assuming that the heat exchange between the excited molecules and the solvent becomes more and more difficult with decreasing decay time. The values of τ' calculated on the base of Eq. (1) with the use of certain estimations were physically acceptable; this seemed to confirm Eq. (1) again. However, the immediate connection between decay time and ΔT has not been subjected to investigations up to the present. The aim of the present paper is to study STEPANOV's relation, partly on the base of Eq. (1), partly by checking NEPORENT's modified relation with the use of the measured decay times.

2. In order to study the dependence of ΔT on decay time, the absorption and emission spectra were determined with the experimental method given in [3] for the solutions of Table I and the temperature difference was calculated on the base of these spectra. The decay time of the solutions was measured with the phase fluorimeter of the Physics Department Nicholas Copernicus University, Toruń.

Table I

1 · 10 ⁻⁴ mole/l Fluorescein, 3% NaOH, 60 vol % glycerol + H ₂ O							
Quencher	c _{KI} (mole/l)	ΔT (°K)	$\tau \cdot 10^9$ (s)	Quencher	c _{KBr} (mole/l)	ΔT (°K)	$\tau \cdot 10^9$ (s)
KI	0	38	4,18	KBr	0	19	4,06
	1 · 10 ⁻¹	42	3,60		1 · 10 ⁻¹	23	3,89
	3 · 10 ⁻¹	49	3,10		6,3 · 10 ⁻¹	25	3,76
	6 · 10 ⁻¹	55	2,56		1	26	3,69
	1	64	1,71		1,585	29	3,55

A linear connection between $\ln \Delta T$ and τ was found, as it can be seen from the results plotted in Fig. 1, which was to be expected on the base of Eq. (1). From the slope of the straight the value for $\tau' = 4,7 \cdot 10^{-9}$ sec resulted and this was in good accordance with the values given in [2]. (It is to be noted that a similar diagram of solutions quenched with KBr is also linear, but the value $\tau' = 1,5 \cdot 10^{-9}$ sec was calculated from its slope. In order to interpret this divergence different quenching mechanism should be supposed for the quenchers KBr and KI.)

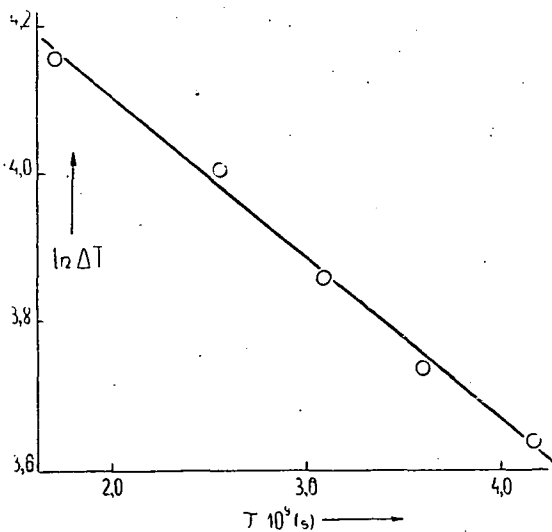


Fig. 1

If the decay time is decreased by the change of viscosity of the solvent rather than by the concentration of the quencher, the constancy of τ' in (1) cannot be expected according to [2]. Fig. 2 shows the diagram of $\ln \Delta T$ versus τ for the series of glycerol-water solutions listed in Table II. Obviously, this diagram is incompatible with Eq. (1) if τ' is taken for constant.

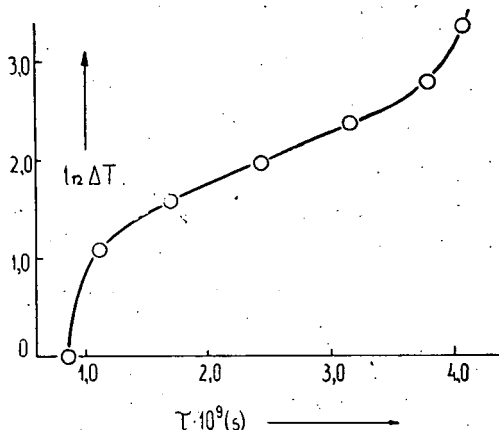


Fig. 2

3. It seemed of interest to check NEPONENT's modified relation resulting of STEPANOV's theory using the decay times, yield values and spectra determined with the methods mentioned above. This relation can be written in the form

$$\frac{\eta_m^2 f_q(\nu)/\tau}{\frac{8\pi n^2}{c^2} \nu^2 \eta(\nu) \frac{2,3026 \varepsilon(\nu)}{L \cdot 10^{-3}}} = \exp[-h(\nu - \nu_e)/kT], \quad (2)$$

where n is the refractive index, $\eta(\nu)$ and η_m denote the absolute yield of solution

Table II

1 · 10 ⁻⁴ mole/l Fluorescein, 3% NaOH, 3 · 10 ⁻¹ mole/l KI + H ₂ O								
c_{glyc} (%)	0	7,5	15	30	45	60	75	85
ΔT (°K)	-3	1	3	6	7	12	15	30
$\tau_m \cdot 10^9$ (s)	0,71	0,86	1,12	1,70	2,44	3,16	3,78	4,08
$\tau_c \cdot 10^9$ (s)	0,70	0,91	1,24	1,61	2,20	2,95	3,27	3,15
η_m	0,22	0,29	0,38	0,49	0,67	0,90	0,93	0,93
$\eta(\nu_e)$	0,92	0,92	0,92	0,91	0,91	0,90	0,90	0,89
$\nu_e \cdot 10^{-12}$ (s ⁻¹)	598	597	596	595	593	592	591	590

as a function of exciting frequency and its maximum respectively, L Loschmidt's constant, and ν_e the frequency of pure electronic transition. It may be expected that Eq. (2) which has been derived for the case $\Delta T=0$ should hold with a good approximation for the more general case $T^* \neq T$, as well, substituting ν_e for ν . Having calculated the decay time τ as a function of the glycerol concentration in

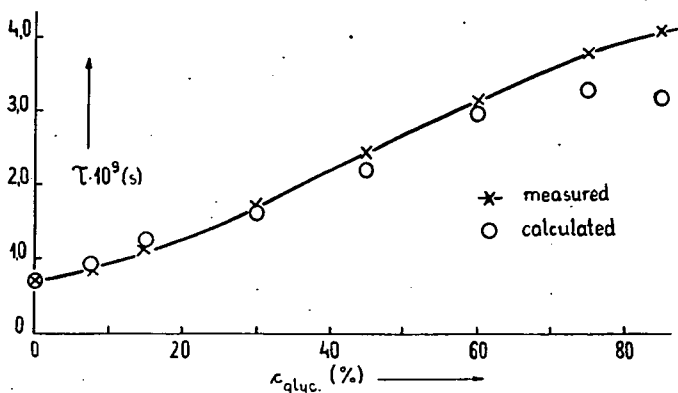


Fig. 3

this way for the solutions listed in Table II, the curve shown in Fig. 3 resulted; the little circles represent the measured decay times. The difference between the decay times measured and calculated does not seem considerable.

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СВЯЗЬ МЕЖДУ ВРЕМЕНЕМ ЗАТУХАНИЯ И ЭФФЕКТИВНОЙ ТЕМПЕРАТУРЕ ЛЮМИНЕСЦИРУЮЩИХ РАСТВОРОВ

Я. Хевеши, И. Кечкемети и Л. Козма

В случае растворов исследовалось изменение разницы опытной и эффективной температур ($\Delta T = T^* - T$) в зависимости от длительности затухания (τ). Показано, что у потушенных растворов $\ln \Delta T$ линейно зависит от τ . Значения τ , полученные из опыта и вычисленные из модифицированной формулы Непорента практически совпадают.