QUENCHING OF PHOTOLUMINESCENCE OF LIQUID SOLUTIONS

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KATHEDER's theory of quenching and the possibility of application of STEPANOV's relation has been investigated for aqueous solutions quenched by foreign substances. The relative yields calculated with the quenching constant are in good accordance with experimental results. The local temperature of molecules in excited states is higher than the temperature of the solution and depends on the concentration of the quencher. The results suggested *that* the quenching mechanism is dynamic for quenching by KI, whereas it is of mixed character for other quenchers.

Introduction

As a characteristic parameter of luminescent solutions containing foreign quenchers, the so-called „quenched solutions", the relative yield η_r is widely used, which is the quotient of the absolute yields η and η_0 of the quenched and unquenched solutions respectively [1]. The dependence of η_r on concentration is characteristic of the quenching mechanism and can be relatively easily determined experimentally. The applicability of theories of quenching taking into account the mechanism of quenching can be verified by systematical experiments. Good accordance between the measurements and the values calculated with the formulas giving the dependence of luminescence characteristics on concentration of quencher will prove the applicability of the quenching mechanism supposed.

a) According to FÖRSTER [2] the quenching processes caused by foreign substances can be divided in two groups; static and dynamic quenching. In discussing the static quenching, FÖRSTER makes use of KATHEDER's investigations [3], who gave a formula for the dependence of η_r on the concentration of quencher based on reaction kinetical considerations. Starting from the supposition that molecules of the luminescent substance A colliding with those of the quenching substance B give loosely connected double molecules AB, which are not capable of luminescence, and taking into account the chemical reactions, he finds for the relative intensity the formula

$$\frac{I}{I_0} \equiv \frac{\eta}{\eta_0} = \frac{1}{1 + \frac{1}{K}C(B_0)}, \tag{1}$$

where $K = C(A) \cdot C(B)/C(AB)$ and $C(A)$, $C(B)$ and $C(AB)$ are the equilibrium concentrations of the luminescent substance, the quencher and the double mole-

cules AB, respectively, and $C(B_0)$ the measured concentration of the quencher added to the solution. The „quenching constant" K has a clear physical meaning: it must be equal to the half value concentration of the quencher. This means that Eq. (1) can be considered to be in good accordance with the measurements if the same values of K are found to belong to different concentrations $C(B_0)$ of the quencher. KATHEDER calculated the constant K for the quenching of an aequeous solution of $2 \cdot 10^{-5}$ mole/l eosin quenched with KI and phenol respectively, using Eq. (1) and KORTÜM's experimental results [4]. He found an acceptable accordance between the experiments and the calculated theoretical curves using $K = 2,6 \cdot 10^{-1}$ mole/l for the quenching with KI, and $K = 6 \cdot 10^{-2}$ mole/l for the quenching with phenol. A closer inspection of the results shows that divergences of nearly 100 per cent can be found in the region of higher concentrations of the quencher.

KATHEDER interpreted the internal mechanism of quenching as an electron transition process on the basis of the theory of WEISS and FISCHGOLD [5]. His investigations were restricted to the determination of the quenching curve and he did not deal with the dependence of further luminescence characteristics on the quenching substances or on the degree of quenching.

Therefore, as well as with respect to the significant divergences between the theoretical and experimental results, it seemed justified to study the applicability of this quenching theory, using more recent experimental data for other quenched solutions, as well.

b) In addition to the relative yield, the changes in the absorption and luminescence spectra and the life-time of excited state with the concentration of quencher have been investigated. We studied further, whether STEPANOV's relation [6, 7]

$$\frac{f_q(\lambda)}{k(\lambda)} = \mathrm{d}(T)\,\frac{1}{\lambda^4}\,e^{-\frac{hc}{kT\lambda}} \tag{2}$$

describing the connection between the absorption spectrum $k(\lambda)$ and the luminescence spectrum $f_q(\lambda)$ holds for the quenched solutions examined: $d(T)$ in the formula is a constant independent from the wavelength λ, h Planck's, k Boltzmann's constant, and c the velocity of light. For the experimental checking of the formula we proceeded in the usual way, by transforming Eq. (2) into logarithmical form [8].

Plotting this relation as a function of $1/\lambda = \bar{v}$, straight lines should be obtained. From the slope of these straights the connection between the temperature T^* and the temperature T of the solution can be determined and used to characterize the quenching process (see e. g. [9]).

Solutions and experimental methods

For the purpose outlined above the solutions were prepared in concentrations conform to those used by KORTÜM [4] and KATHEDER [3]. As a luminescent substance eosin was used, in aqueous solutions of low concentration, to assure the absence of concentration quenching. KI, phenol and pyrocatechine were used in suitable concentrations (Table I).

Distilled water repeatedly purified by vacuum distillation was used as solvent. Eosin was purified with repeated precipitation unto spectroscopical purity (constance of the absorption spectrum). Purification of KI was performed with similar care. Phenol was purified by vacuum distillation in nitrogen stream, pyrocatechine by sublimation.

The absorption spectra $k(\lambda)$ were determined with a grating single-beam autocollimating spectrophotometer *Optica* (Milano) Type CF-4 [10]. Luminescence spectra $f_q(\lambda)$ and relative yields η_r were determined with the same spectrophotometer with suitable fittings. Experimental data were evaluated with methods elaborated earlier [11, 12]. The effect of reabsorption on the measurement of luminescence spectra was taken into account with the method described in [2]. The effect of secondary luminescence in quenched solutions being less, it was possible to neglect this correction by a suitable choice of the experimental conditions [13, 14]. Our measurements were performed at room temperature, 25 $\pm$2 °C.

Table I

Luminescent substance	Concentration of quencher (mole/l)		
	KI	phenol	pyrocatechine
	0	0	0
	$3\cdot10^{-3}$	$3,16\cdot10^{-3}$	$3\cdot10^{-3}$
$2\cdot10^{-5}$ mole/l eosin+ $1\cdot10^{-3}$ mole/l NaOH+ H_2O	$1\cdot10^{-2}$	$1,05\cdot10^{-2}$	$1\cdot10^{-2}$
	$3\cdot10^{-2}$	$3,16\cdot10^{-2}$	$3\cdot10^{-2}$
	$1\cdot10^{-1}$	$1,05\cdot10^{-1}$	$1\cdot10^{-1}$
	$3\cdot10^{-1}$	$3,16\cdot10^{-1}$	$3\cdot10^{-1}$
	$6\cdot10^{-1}$	$6,32\cdot10^{-1}$	$6\cdot10^{-1}$

Experimental results and discussion

Our results show that in solutions quenched with KI an increase in the concentration of the quencher did not cause any essential change in the shape of the luminescence spectrum and in the wavelength corresponding to the maximum. The intensity of the luminescence spectra, however, decreased with the increase of quenching. These findings agree with earlier results of one of the authors [15]. In the case of quenching with phenol and pyrocatechine a shift of both absorption and luminescence spectra towards longer waves was found with increasing concentration of quencher. In Fig. 1 spectra of an unquenched ① and a moderately
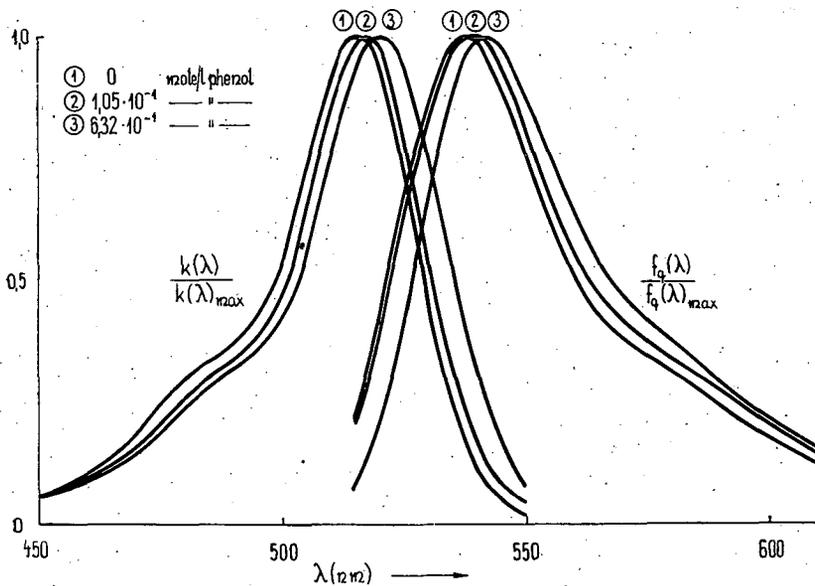

Fig. 1

quenched solution ② and those of the highest concentration of quencher ③ are shown for the quenching with phenol. The shift of the maxima between curves ① and ③ amounts to 5 nm for phenol and to 7 nm for pyrocatechine. The absorption coefficients $k(\lambda)_{max}$, corresponding to the maxima of the absorption spectra, showed no systematical changes, varying near a mean value, practically independently of the concentration of quencher. An increase in concentration of the quencher did not cause significant changes in the shape of the absorption spectra but showed a strong influence on the luminescence yield of the system. In Fig. 2 the
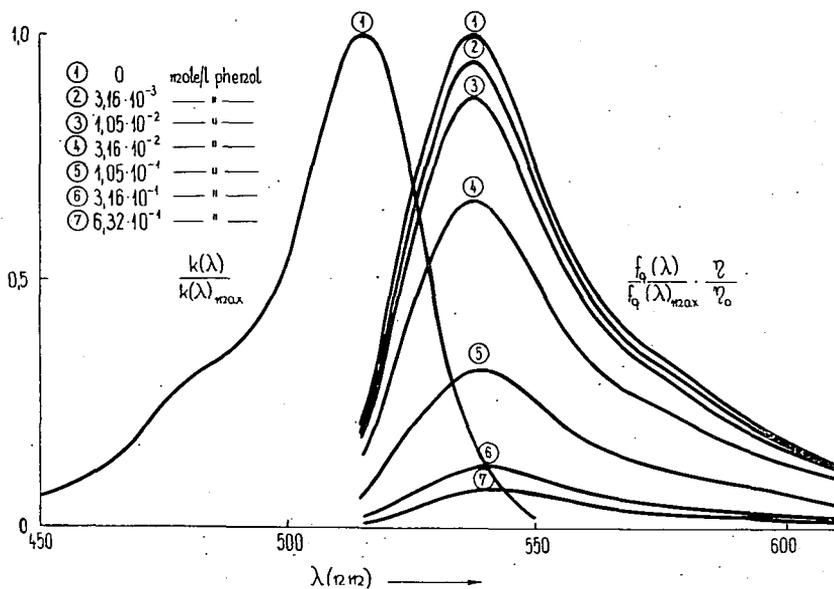

Fig. 2

functions $f_q(\lambda)/f_q(\lambda)_{max}$. η/η_0 for solutions quenched with phenol are plotted besides the absorption spectrum of the unquenched solution. It can be seen that along with the increase of the phenol concentration by two orders of magnitude, the relative values of the maxima of the luminescence spectra decreased from 1.0 to 0.08.

On the basis of our measurements of the relative yield η/η_0, the quenchers examined are to be arranged in the following order with respect to increasing quenching effect KI, phenol, pyrocatechine. This is in good agreement with earlier results [4, 16].

The quenching constant K calculated with Eq. (1) on the base of our results is given in Table II.

It can be seen from Table II that there is a very good agreement between the results obtained with different quencher concentrations for quenching with phenol. The results show also a good agreement in the case of quenching with phenol except the both last data. The divergence in the values obtained for most strongly quenched solutions can be explained with the fact that intensity of luminescence was very strongly decreased in consequence of the strong quenching (see

Table II

| $C(B_0)$ (mole/l) | KI | Pyrocatechine | $C(B_0)$ (mole/l) | Fenol |
	$K \cdot 10^{-2}$ (mole/l)			$K \cdot 10^{-2}$ (mole/l)
$3 \cdot 10^{-3}$	42,8	2,91	$3,16 \cdot 10^{-3}$	5,02
$1 \cdot 10^{-2}$	23,3	3,25	$1,05 \cdot 10^{-2}$	5,39
$3 \cdot 10^{-2}$	29,4	3,21	$3,16 \cdot 10^{-2}$	5,66
$1 \cdot 10^{-1}$	28,2	2,67	$1,05 \cdot 10^{-1}$	4,93
$3 \cdot 10^{-1}$	22,0	1,76	$3,16 \cdot 10^{-1}$	4,56
$6 \cdot 10^{-1}$	17,4	0,693	$6,32 \cdot 10^{-1}$	5,09

Fig. 2), and the measurement of low luminescence intensities always involves great experimental errors. The results for quenching with KI do not present such a good agreement, though they do not show as great divergences as those of KATHEDER [3].

The mean values of K for the three quenchers listed in Table II, as well as the half-value concentrations determined from the experimental data are presented in Table III. It can be seen that a very good agreement between the quenching constant K and the corresponding half-value concentration can be found for all the three quenchers. (It should be noted that in determining the mean value of K for solutions containing pyrocatechine the two most divergent data have not been taken into account.) The obtained values of K are in good agreement with those of KATHEDER for KI and phenol ($2,6 \cdot 10^{-1}$ and $6,0 \cdot 10^{-2}$ mole/1 respectively). This agreement and the substantially less deviations of K from the mean values are a proof of the reliability and accuracy of our experimental results.

With the use of the mean values of K given in Table III and Eq. (1), theoretical curves for the dependence on quencher concentration of the relative yield η/η_0 were calculated. The calculated curves are plotted with full lines, measured values with points in Fig. 3. It can be seen that Eq. (1) can be very well used for describing quenching with phenol and pyrocatechine, whereas for KI considerable deviations between calculated and measured data can be found. This divergence, which is most
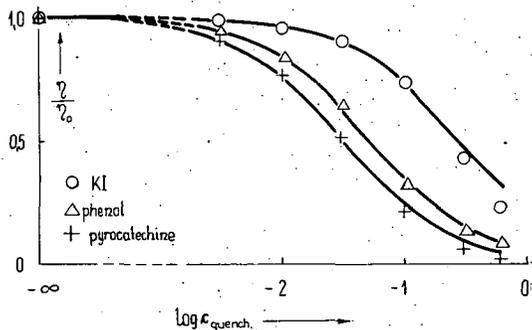
Table III

Quencher	$K \cdot 10^2$ (mole/l)	Half-value concentration $\cdot 10^2$ (mole/l)
KI	27,2	25,0
Phenol	5,11	5,3
Pirocatechine	3,01	3,2

○ KI
△ phenol
+ pyrocatechine

$\log c_{quench.} \longrightarrow$

Fig. 3

Table IV

| C(B_0) (mole/l) | Quencher | | | | C(B_0) (mole/l) | Quencher | |
| | KI | | Pirocatechine | | | Fenól | |
	T^* (°K)	η/η_0(%)	T^* (°K)	η/η_0(%)		T^* (°K)	η/η_0(%)
0	333	100	333	100	0	333	100
$3 \cdot 10^{-3}$	339	99,3	374	90,7	$3 \cdot 16 \cdot 10^{-3}$	351	94,1
$1 \cdot 10^{-2}$	344	95,9	396	76,5	$1 \cdot 05 \cdot 10^{-2}$	357	83,7
$3 \cdot 10^{-2}$	347	90,8	420	51,7	$3 \cdot 16 \cdot 10^{-2}$	363	64,2
$1 \cdot 10^{-1}$	351	73,8	—	—	$1 \cdot 05 \cdot 10^{-1}$	372	31,9
$3 \cdot 10^{-1}$	355	42,3	—	—	$3 \cdot 16 \cdot 10^{-1}$	379	12,6
$6 \cdot 10^{-1}$	361	22,5	—	—	$6 \cdot 32 \cdot 10^{-1}$	386	7,5

important at higher quencher concentrations, is probably due to the circumstance that the quenching mechanism involved in quenching with KI is different from that taking place with both other quenchers. This divergence between theory and experiment is not sufficient to draw unambiguous conclusions concerning the quenching mechanism, as for less concentrations of quencher the agreement is satisfactory even with solutions quenched by KI.

In addition, further calculations were made which the use of Eq. (2) giving the connection between absorption and emission spectra. A sequence of straight lines, like that partly shown in Fig. 4 for the quenching with phenol, was obtained KI and pyrocatechine, too.

The values of T^* calculated from the slope of the straights are given in Table IV.

The same table contains the experimental values of η_r shown in Fig. 3. It can be seen from the table, that the effective temperature T^* of the excited molecules is higher by $\Delta T = 37°$ than the temperature of the solution. This ΔT difference in the temperature increases with increased quenching. The values of T^* versus lg $c_{quencher}$ are plotted in Fig. 5 for the three quenchers examined. On comparison of Fig. 3 and Fig. 5 it can be seen that the values of T^* are much

$F(\hat{\nu}) + C$

① 0 mole/l phenol
② 1,05·10² ——·——
③ 1,05·10⁻¹ ——·——
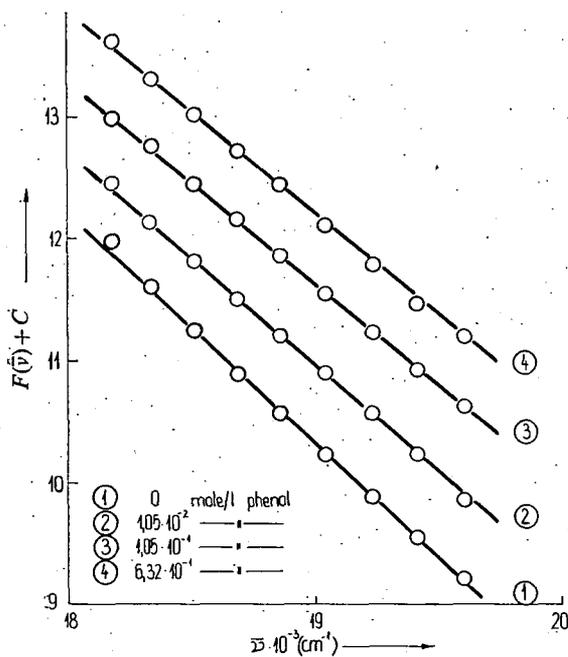④ 6,32·10⁻¹ ——·——

$\bar{\nu} \cdot 10^{-3}$ (cm⁻¹) ⟶

Fig. 4

higher in the case of pyrocatechine which has a stronger quenching effect, as e. g. for KI. The increase in the effective temperature T^* with increasing quencher concentration can be interpreted on the base of the circumstance [17] that, since the mean lifetime τ of the excited state of the molecules decreases with increasing quenching, they can only emit part of the absorbed energy. The remaining energy gives rise to the temperature T^* (see also [18]).

Fig. 5

In order to clear up more precisely the quenching mechanism, we determined also the mean life-time of the fluorescence of our solutions. The experimental equipment and the method of measurement have been published earlier [19]. The mean life-times τ determined for three concentrations of KI showed a remarkable decrease with the increase of the quenching. This is in good agreement with earlier literature data and indicates a dynamical quenching mechanism. With solutions quenched by phenol and pyrocatechine the decrease is markedly less than what could be expected on the basis of the increase in concentration of the quenchers. This indicates different quenching mechanism. The quotient of the relative changes in life-time, τ/τ_0, and in the relative yield values, η/η_0, is 0,86 for KI, 0,92 for phenol and 1.11 for pyrocatechnine.
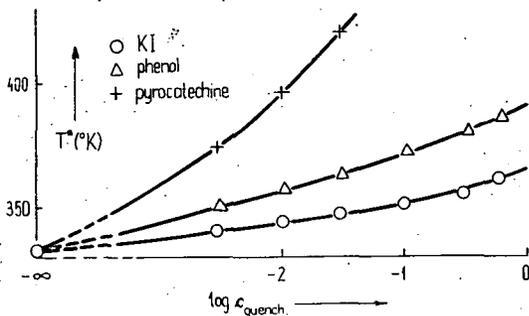
Conclusions

a) In solutions quenched by KI shape and position of the absorption and luminescence spectra were not changed by the quencher; some divergences between the measured data and those calculated with KATHEDER's formula were found; the life-time decreased proportionally to the relative yield, in agreement with numerous data in literature concerning the quenching effect of KI in other systems. From these it follows that the quenching in this system can be interpreted with a dynamic mechanism.

b) The quenching mechanism for the other systems studied is not so easily explained. The shift of the maxima of the spectra towards longer waves as well as the fact that KATHEDER's formula, based on the supposition of chemical interactions, can be well used to describe the dependence of the relative yield on concentration, prove that static effects are involved in the quenching process. The decrease of the life-time with increasing quencher concentration and the changes in the „local temperature" T^* of the micro-environment including the excited molecule and solvent molecules, obtained from STEPANOV's formula, indicate that the quenching can also be considered as a dynamic one. The simultaneous presence of both effects of different kind supports FÖRSTER's considerations [2] concerning the quenching of photoluminescence with organic substances. According to this opinion, purely static quenching cannot occur in such systems, but in some cases it can prevail over the dynamic quenching.

c) The good agreement between the quenching constant K and the corresponding half-value concentrations indicates that the static quenching mechanism predominates in the systems quenched with phenol and pyrocatechine.

d) STEPANOV's formula describing the connection between the absorption and luminescence spectra can be well used in the case of the systems examined. The calculated effective temperatures T^* seem to be correlated with the decrease in the mean life-time of the excited molecules with increasing concentration as well as with the quenching mechanism.

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The authors are indebted to sincere thanks to Prof. A. BUDÓ, Director of the Institute of Experimental Physics, and to Professors L. SZALAY and I. KETSKEMÉTY, for valuable help during the course the work.

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ТУШЕНИЕ ФОТОЛЮМИНЕСЦЕНЦИИ В ЖИДКИХ РАСТВОРАХ

Е. Балинт, Я. Хевеши

Исследовалось теория тушения по Катедере, а также рассмотрелось данное Степановым соотношение применения в случаях водных растворов, тушенных посторонними веществами. Вычисление значения относительного выход с использованием константа тушения показывает хорошие совпадения с экспериментальному данными. Эффективная температура возбужденных молекул более высокая, чем экспериментальная температура и она зависит от концентрации тушителя. По данным установлено что механизм тушения в случае применения KJ имеет полностью динамичный, а в случае же применения других тушителей смешанный характер.