gewählt. Die Summation in Gl. (35) wurde maximal bis $\nu_0 = 31$ durchgeführt. Die genügende Näherung dieser numerischen Rechnungen wurde durch Änderung der Stützpunktzahl und des ν_0-Wertes nachgewiesen.

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Concentration Quenching and Depolarisation of Photoluminescence in Solutions

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The emission anisotropy r/r_0 and quantum yield η/η_0 of the photoluminescence of glycerin-water solutions of Na-fluorescein has been measured at concentrations 10^{-6}–$3\cdot10^{-1}$ M. The drop of η/η_0 is connected with a repolarisation effect, which is interpreted by a completed theory of concentrational depolarisation of photoluminescence (CDPL), accounting the self-quenching by nonluminescent dimers and the remigration of excitation energy. The dimerisation constant and the critical concentrations have been determined.

1. Introduction

During the last 50 years, the CDPL has intensively been investigated. A survay of the existing CDPL theories is shown in the articles [1–4]. In this theories the influence of self-quenching on emission anisotropy is neglected; it is essential however at high concentrations [5]. Recently [6] we observed a repolarisation effect at high concentrations on glycerin-water solutions of rhodamin 6G connected with a strong concentration quenching by nonluminescent dimers [7]. We have compared these results with the CDPL theory regarding the self-quenching but neglecting the remigration of excitation energy [6]. A generalization [8] regarding the energy remigration from the next neighbours (see also Ref. [9]) gives the following expression for the emission anisotropy.

$$\frac{r}{r_0} = (1-\alpha f)\left[1+\frac{1}{2}\,\frac{(\alpha f)^2}{1-3(\alpha f)^2/4}\right], \qquad (1)$$

where

$$\alpha = \alpha_0 \frac{\gamma_D}{\gamma_D + \gamma_{D''}}, \qquad (2)$$

$$f \equiv f(\gamma) = \pi^{1/2}\gamma \exp\{\gamma^2\} \cdot \left[1 - 2\pi^{-1/2}\int_0^{\gamma} \exp\{-t^2\}\,dt\right], \qquad (3)$$

$$\gamma = \gamma_D + \gamma_{D''} = \frac{(\pi\eta_0)^{1/2}}{2}\left(\frac{C'}{C_0'} + \frac{C''}{C_0''}\right). \qquad (4)$$

α_0 is a dimensionless constant (not depending on concentration), C' and C'' are the concentrations of monomers D and dimers $D_{''}$, C_0', C_0'' the corresponding critical concentrations, η_0 is the quantum yield (at $C \to 0$).

According to [5] the relativ quantum yield is given by

$$\eta/\eta_0 = [1-f(\gamma)]/[1-\alpha f(\gamma)]. \qquad (5)$$

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2. Experimental

The emission anisotropy has been measured on glycerin-water solutions of Na-fluorescein ($C_{20}H_{10}O_5N_{a2}$, M.W. 376.29) at 303 °K. The Na-fluorescein (FOCh – Gliwice, Poland) was purified by recrystallization from ethanol-ethyl acetate mixtures. We prepared two series (I, II) of solutions with viscosities 3.3 and 0.43 poise, adding 1.2 or 2% NaOH respectively, thus obtaining pH values above 10 in both series. The glycerin (Strem-Poland) was used without further purification.

The emision anisotropy was measured by a photoelectric compensation method [10, 11]. The luminescence was excited by a DRSz – 250 lamp combined with a 436 nm filter.

In order to eliminate the influence of secondary fluorescence on emission anisotropy, we used microcuvettes [layer thickness 10 μm – 2 μm ($\pm 5\%$)]. At the highest concentrations, the measured values of emission anisotropy were corrected in regard of secondary fluorescence by the method given in Ref. [11]. Fluorescence spectra and the relativ quantum yields were determined as described in [12]. The spectral sensitivity of the photomultiplier and the reabsorption of fluorescence were corrected by the well-known method of Reference [13]. The quantum yield was measured in the spectral range 528 ± 13 nm, applying the method given by FÖRSTER [14] with certain corrections for secondary fluorescence [15] and emission anisotropy [16]. To measure the absorption we used a VSU2-P spectrometer.

3. Results and Discussion

Table 1 gives the data of emission anisotropy r/r_0 and quantum yield η/η_0 of both systems I, II corrected to all effects mentioned in Chapter 2. To compare these values with Eq. (1) and (5), the constants C_0', C_0'', α_0 and η_0 and also the concentrations of monomers C' and dimers C'' at each concentration C of active molecules should be known. C_0', C_0'' can be computed from the relation [7, 17] of the critical concentrations of excitation energy transfer

$$C_0 = 5.18 \cdot 10^{-10}\, n^2\, \bar{\nu}^2 \left[\eta_0 \int_0^\infty F(\nu)\, \varepsilon(\nu)\, \mathrm{d}\nu \right]^{-1/2} \mathrm{M/l}\,, \quad (6)$$

where n is the refractive index of the medium, $\bar{\nu}$ the mean value of the wave number of the overlapping

Table 1. Change in emission anisotropy, quantum yield and concentration of dimers with concentration for Na-fluorescein in glycerin-water solutions.

1	2	3	4	5	6	7	8	9	10
System I				System II					
C M/l	C'' M/l	r/r_0 exp.	η/η_0 exp.	C M/l	C'' M/l	r/r_0 exp.	r/r_0 theor.	η/η_0 exp.	η/η_0 theor.
6.00×10^{-6}	2.34×10^{-12}	1.000	—	1.00×10^{-5}	5.40×10^{-11}	1.000	1.000	—	1.000
9.40×10^{-6}	5.74×10^{-12}	—	1.000	1.50×10^{-5}	1.22×10^{-10}	1.004	0.996	—	1.000
1.94×10^{-5}	2.45×10^{-11}	0.991	—	2.00×10^{-5}	2.16×10^{-10}	—	0.994	1.000	1.000
7.39×10^{-5}	3.55×10^{-10}	0.975	—	3.00×10^{-5}	4.86×10^{-10}	0.997	0.993	—	1.000
1.00×10^{-4}	6.50×10^{-10}	0.955	0.998	4.00×10^{-5}	8.64×10^{-10}	0.980	0.992	—	1.000
2.00×10^{-4}	2.60×10^{-9}	0.955	—	6.00×10^{-5}	2.5×10^{-9}	0.977	0.988	—	1.000
3.99×10^{-4}	1.2×10^{-8}	0.869	—	1.00×10^{-4}	4.5×10^{-9}	0.962	0.980	—	1.000
7.99×10^{-4}	4.4×10^{-8}	0.819	—	1.50×10^{-4}	1.5×10^{-8}	0.970	0.970	—	0.999
1.01×10^{-3}	6.6×10^{-8}	0.767	0.998	2.00×10^{-4}	2.1×10^{-8}	1.002	0.958	0.983	0.999
3.00×10^{-3}	5.8×10^{-7}	0.568	0.971	3.00×10^{-4}	5.0×10^{-8}	0.980	0.938	—	0.999
4.00×10^{-3}	1.00×10^{-6}	0.502	0.998	6.00×10^{-4}	1.8×10^{-7}	0.918	0.884	—	0.997
6.00×10^{-3}	2.3×10^{-6}	0.407	0.922	8.00×10^{-4}	3.6×10^{-7}	—	0.852	0.990	0.996
				1.00×10^{-3}	5.5×10^{-7}	0.858	0.822	—	0.995
7.99×10^{-3}	4.2×10^{-6}	0.305	0.880	1.50×10^{-3}	1.2×10^{-6}	0.774	0.757	0.998	0.992
				2.00×10^{-3}	2.2×10^{-6}	0.756	0.702	0.971	0.989
10^{-2}	6.5×10^{-6}	0.219	0.900	3.00×10^{-3}	4.8×10^{-6}	0.694	0.612	1.00	0.981
				4.00×10^{-3}	8.6×10^{-6}	0.617	0.545	1.00	0.972
1.50×10^{-2}	1.5×10^{-5}	0.145	0.827	6.00×10^{-3}	1.9×10^{-5}	0.515	0.444	0.985	0.950
				8.00×10^{-3}	3.4×10^{-5}	0.416	0.382	0.942	0.925
2.00×10^{-2}	2.6×10^{-5}	0.104	0.781	1.00×10^{-2}	9.5×10^{-5}	0.366	0.324	0.890	0.888
				1.50×10^{-2}	1.2×10^{-4}	0.250	0.241	0.758	0.782
3.00×10^{-2}	5.8×10^{-5}	0.069	0.546	2.00×10^{-2}	2.1×10^{-4}	0.192	0.199	0.523	0.663
4.00×10^{-2}	1.0×10^{-4}	0.054	0.328	2.98×10^{-2}	4.5×10^{-4}	0.155	0.163	0.396	0.458
6.09×10^{-2}	2.4×10^{-4}	0.057	0.153	3.98×10^{-2}	8.0×10^{-4}	0.145	0.150	0.263	0.285
8.00×10^{-2}	4.1×10^{-4}	0.059	0.059	6.00×10^{-2}	1.7×10^{-3}	—	0.156	0.089	0.122
10^{-1}	6.3×10^{-4}	0.060	0.039	8.00×10^{-2}	3.0×10^{-3}	0.170	0.167	0.043	0.045
1.50×10^{-1}	1.4×10^{-3}	0.080	0.006	1.00×10^{-1}	9.0×10^{-3}	0.207	0.185	0.026	0.025
2.00×10^{-1}	2.5×10^{-3}	0.088	0.0015	1.50×10^{-1}	1.2×10^{-2}	0.219	0.222	0.008	0.011
3.00×10^{-1}	2.89×10^{-3}	0.096	0.0014	2.00×10^{-1}	1.6×10^{-2}	0.210	0.253	0.003	0.006

region of fluorescence quantum spectrum $F(\nu)$ and absorption spectrum $\varepsilon(\nu)$ of monomer or dimer molecules respectively. $F(\nu)$ is normalized to unity on a frequency scale. C_0' can be found without difficulties.

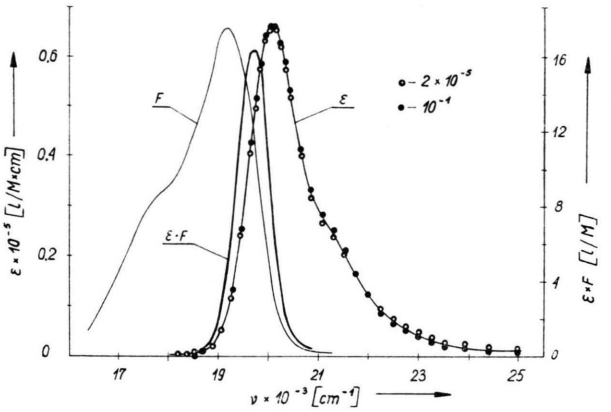

Fig. 1. Absorption spectrum (ε), fluorescence quantum spectrum (F) in arbitrary units, and the product of $\varepsilon \cdot F$ for Na-fluorescein in a glycerin-water solution.

Figure 1 shows the spectra of absorption (ε) and fluorescence (F) and the product $\varepsilon \cdot F$ of system I. Regarding the low associate concentration in our solutions the absorption spectrum of dimers $\varepsilon''(\nu)$ and the dimerisation constant K can not be determined from spectroscopic data as in Reference [18, 19]. So, C_0'' cannot be computed from (6), the dimerisation constant K, however, can be obtained by the concentrational dependance of r/r_0 and η/η_0 as in Reference [20]. Supposing, that in the solutions there are only monomers D and dimers $D_{,,}$, the mass action law implies

$$C'' = K C'^2 \tag{7}$$

using the definition (4) we can derive a dimerisation constant K_γ connected with K by

$$K_\gamma = \gamma_{D,,}/\gamma_D^2 = 2 K C_0'^2/(\pi \eta_0)^{1/2} C_0'' \tag{8}$$

consequently, the relations (1) and (5) may be written as functions of γ with K_γ and α_0 as parameters.

Computed curves of relation (1) and (5) using two different combinations of K_γ and α_0, are shown in Figure 2.

Considering the moderate dimerisation of Na-fluorescein in water and an even smaller one in glycerin-water solution [21] we may assume $C'' \ll C'$ at any concentration and so we get [Eq. (4)]

$$\gamma \cong (\pi \eta_0)^{1/2} C/2 C_0' \tag{9}$$

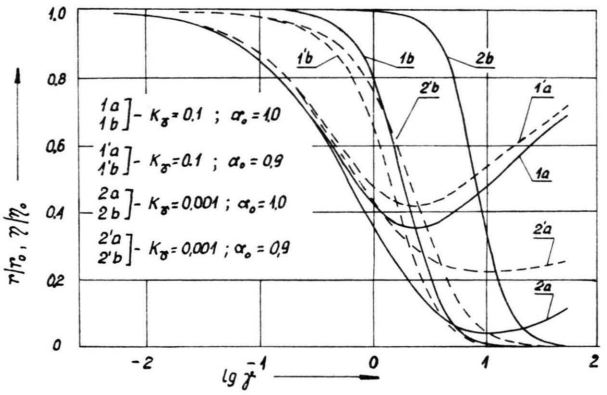

Fig. 2. Theoretical curves (1) and (5) for different values K_γ and α_0. Curves a refer to emisison anisotropy, curves b to quantum yield η/η_0.

according to relation (6) there follows

$$C_0' \sim \eta_0^{-1/2} \quad \text{or} \quad \gamma \sim \eta_0 [\overline{\varepsilon(\nu)}]^{1/2}. \tag{10}$$

$\overline{\varepsilon(\nu)}$ meaning the mean value of the absorption coefficient in the region of overlap. The value of η_0 has been determined using Equation (10).

Fitting the two theoretical curves $r/r_0(\gamma)$ and $\eta/\eta_0(\gamma)$ to the experimental values by simultaneous adjustment of the parameters K_γ and α_0 and a transformation according to (10) by suitable choice of η_0 we get the best values of K_γ, α_0 and η_0. The fitted curves are given in Figure 3. The value $\eta_0 = 0.89$, obtainend for system I, is in accordance to the value 0.95 given by SZALAY et al. [22].

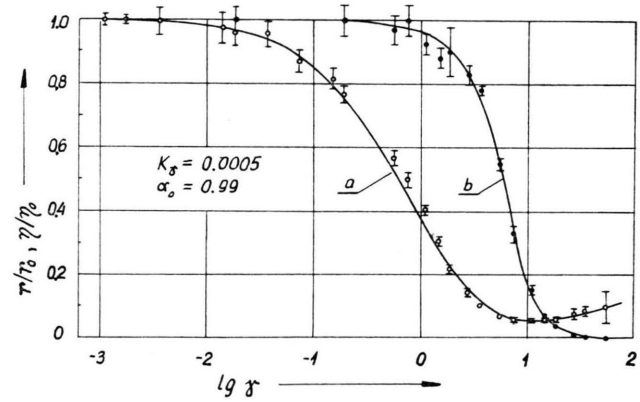

Fig. 3. Concentration dependence of emission anisotropy r/r_0 and quantum yield η/η_0 of photoluminescence of Na-fluorescein in a glycerin-water solution (system I); a and b — theoretical curves calculated from (1) and (5); o, • — experimental points for r/r_0 and η/η_0 respectively; I — experimental errors.

Table 2. Values of parameters characterizing the photoluminescence of glycerin-water solutions of Na-fluorescein.

	1	2	3	4	5	6	7	8	9	10	11	12
	η_{303} poise	n —	$\overline{\nu'}$ 10^3 cm^{-1}	$\overline{\varepsilon'(\nu)}$	$\overline{\varepsilon''(\nu)}$ 10^5 l/M.cm	C_0'	C_0'' 10^{-3} M/l	R_0' Å	$R_0''^{23}$	α_0 —	K_γ —	K l/M
system I	3.3	1.47	19.7	0.104	0.211	4.524	3.17	44.4	50	0.99	0.0005	0.065
system II	0.43	1.45	19.7	0.104	0.211	5.34	3.75	42	47.3	0.98	0.006	0.54

In order to determine the critical concentration C_0'', which cannot be computed from (6), we applied the spectral results concerning Na-fluorescein in water[21] delivering the ratio of absorption coefficients of dimers to monomers $\overline{\varepsilon''(\nu)}/\overline{\varepsilon'(\nu)} = 2.03$. With this value the ratio of critical concentrations $\varkappa = C_0'/C_0''$ results to be [corresponding relation (6) and setting $(\overline{\nu'}/\overline{\nu''})^2 \approx 1$]

$$\varkappa = C_0'/C_0'' \cong (2.03)^{1/2} = 1.425 .$$

If we assume that $\varkappa = C_0'/C_0''$ in glycerin-water solutions is identical to the value of water solutions, C_0'' can be obtained from the directly measured C_0' and from these $\varkappa$ value.

Knowing the parameter values K_γ, C_0', C_0'' and η_0, we can determine the dimerisation constant from relation (8) and values C' and C''. Data of C'', found in this way, are given in Table 1 and the values of the above mentionend parameters, characterizing system I, II, in Table 2. The values of the dimerisation constants are remarcably small, especially in the system I (with a smaller water content).

The limits of error given in Fig. 3 a correspond to the sum of three standard errors resulting from the fluctuation of the measured rotation angles of Arago compensator and from the error of determination of r_0. In Fig. 3 b the errors result from fluctuations of measured intensities and from uncertainties in the device of η_0. The errors of K_γ and α_0 can be estimated to be smaller than 25% or 2% respectively. In the light of the above given remarks we should accept the experiment to be satisfactory as more as it is obtained with the same value α_0 at both curves. In spite of a very deep depolarisation at high concentrations, repolarisation is noticeable, as the theory has predicted. At moderate concentrations the measured values r/r_0 are slightly higher than theoretical ones. It may be due to neglecting a certain contribution of molecules D_1 in the observed polarisation of photoluminescence in the CDPL theory. Similar regularities characterize the emission anisotropy of system II, given in columns 7 and 8 of Table 1. The higher content of water results in a higher value of dimerisation constant K (comp. Table 2) and the depolarisation is smaller as in system I. This also proves the new CDPL theory.

Concerning the concentration dependence of quantum yield, there is a remarcable full agreement with the theory at both systems I, II (comp. Fig. 3 and columns 9 and 10 of Table 1). It should be strongly emphasized, however, that this agreement is, among other things, a result of taking into account the multistep mechanism of transfer of excitation energy from D to D_n in the theory of concentration quenching[7, 24]. The CDPL phenomenon of glycerin-water solutions of Na-fluorescein has been investigated by several authors[25–28] but without an explanation of quenching mechanism.

The result of the present paper fully proves the hypothesis, brought forward by LEVSHIN[29] that the small degrees of association, undetectable spectroscopically, may correspond to sufficiently large absolute concentrations of dimers (comp. columns 2 and 6 in Table 1). The assumed mechanism of quenching of excitation energy durinig its transfer between the monomers ($\alpha_0 < 1$) has not been firmly proved. The found values $\alpha_0 = 0.99 \pm 0.02$ (system I) and $\alpha_0 = 0.98 \pm 0.02$ (system II) point only in the direction, that this quenching mechanism in the investigated systems is of secondary importance.

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Konzentrationsabhängigkeit der Thermodiffusion in D_2–H_2, HD–H_2 und D_2–HD bei 85 °C

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Dependence on Composition of Thermal Diffusion in D_2–H_2, HD–H_2, and D_2–HD at 85 °C

Measurements of the thermal diffusion factor (α) result in the relations

D_2–H_2: $\alpha = (0.182 - 0.057\ \gamma) \pm 0.003$,
HD–H_2: $\alpha = (0.116 - 0.036\ \gamma) \pm 0.003$,
D_2–HD: $\alpha = (0.064 - 0.017\ \gamma) \pm 0.002$

with γ the molar fraction of the heavy molecule. Earlier measurements on tritium systems are corrected and discussed in view of these results.

Die Untersuchung der Thermodiffusion bei rund 60 °C im isobaren System $D_2 - HT$ war von SCHIRDEWAHN, KLEMM und WALDMANN (1961) [1] mit einem Clusius-Dickelschen Trennrohr durchgeführt worden, um den möglicherweise kleinen Elementareffekt zu vervielfachen. Mit demselben Trennrohr wurden dann auch die Systeme $HT - H_2$ und $DT - D_2$ [1], sowie von REICHENBACHER und KLEMM (1964) [2] $T_2 - H_2$, $DT - H_2$ und $T_2 - D_2$ untersucht. Da das Trennrohr nur Relativmessungen gestattete, wurde es mit dem Gas $D_2 - H_2$ (2 Mol-% D_2) geeicht. Die ermittelten Thermodiffusionsfaktoren (α) der Arbeiten [1, 2] beziehen sich auf einen für dieses Eichgas auf Grund der vorhandenen Literatur angenommenen α-Wert 0,15.

Inzwischen hat nun SLIEKER (1965) [3] den α-Wert unseres Eichgases (2 Mol-% D_2) neu bestimmt. Er fand $0{,}179 \pm 0{,}007$ und korrigierte die α-Werte der Arbeit [1] entsprechend mit einem Faktor 1,193. Der Sliekersche Wert 0,179 wurde jedoch von GREW und HUMPHREYS (1966) [4] in Frage gestellt, die für $D_2 - H_2$ (50 Mol-% D_2) den Wert $0{,}155 \pm 0{,}005$ fanden und die für die Auflösung der Diskrepanz erforderliche starke Konzentrationsabhängigkeit von α für unwahrscheinlich hielten.

Um die Situation zu klären, wurde in der vorliegenden Arbeit die Konzentrationsabhängigkeit von α im System $D_2 - H_2$, und auch in den Systemen $HD - H_2$ und $D_2 - HD$ untersucht.

Messungen

Die Präparation der Ausgangsgase und die katarometrischen Gasanalysen erfolgten wie in der Arbeit [5]. H_2 und D_2 hatten eine Reinheit besser als 99,8%. HD war 99-prozentig. Seine Verunreinigungen waren etwa zu gleichen Teilen H_2 und D_2.

Die Thermodiffusionsversuche wurden mit einer gläsernen Zwei-Gefäße-Apparatur durchgeführt. Die übereinanderliegenden Gefäße (je 100 cm³) befanden sich in Temperaturbädern und waren durch ein enges Rohr (Länge 11 cm, Weite 0,5 cm) verbunden, das durch