The Concentrational Changes of the Fluorescence Decay Time of Rhodamine B in Ethanol *

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Z. Naturforsch. **37a**, 74–77 (1982); received October 13, 1981

The photoluminescence decay time τ of neutral solutions of rhodamine B in ethanol was measured for concentrations c from 10^{-5} mol l^{-1} to 10^{-2} mol l^{-1} at 295 K. The $\tau(c)$ curve observed is atypical, showing two regions of decreasing τ. The drop over the range 4×10^{-4} to 10^{-3} mol l^{-1} was explained by the presence of two ionic forms of rhodamine B, and that at concentrations greater than 4×10^{-3} mol l^{-1} — by rhodamine B dimers.

1. Introduction

Rhodamine B is a xanthene dye whose solutions have been widely used as active media of dye lasers. In the last decade several papers devoted to the explanation of concentrational changes of the absorption spectra of rhodamine B in ethanol (RB/Et) at low concentrations have appeared [1–4]. It was shown in that the changes mentioned are not the result of dimerization [5] but occur due to changes of the acid-base equilibrium.

In the present paper we report on concentrational changes of the photoluminescence (PL) decay time of neutral RB/Et solutions.

2. Experimental

Rhodamine B ($C_{28}H_{31}ClN_2O_3$, m.w. 479.03) produced by GMBH & Co. (Schuchardt) has been purified by repeated crystallization from ethanol and vacuum evaporation. Analytically pure ethanol, manufactured by POCH-Gliwice, was used as the solvent without additional purification. The measurements of the mean PL decay time τ were done at 295 K with a phase fluorometer as described elsewhere [6]. To excite the fluorescence, frontal illumination with an HBO-200 lamp, providing, via an SPM-2 monochromator, light of (546 ± 8) nm wavelength was adopted. At the receiving end an OG-3 cutoff filter ($\lambda > 580$ nm) was employed. τ was measured using samples so thin that $2.3\,\varepsilon_{\max} c \iota < 0.1$, where $\varepsilon_{\max}$ is the maximum value of the extinction coefficient, c is the concentration and ι is the sample thickness. According to Ketskeméty et al. [7] the effect of reabsorption and secondary fluorescence on τ may be neglected under these conditions. The relative quantum yield was measured in the spectral range of (575 ± 8) nm using a method described by Förster [8]. The absorption spectra were measured with a VSU 2-P spectrophotometer, and the fluorescence spectra and the quantum yield — with a device described elsewhere [9].

3. Results and Discussion

Figure 1 shows electronic absorption and fluorescence spectra of RB/Et at various dye concentrations. Clearly, with increasing concentrations the absorption and fluorescence spectra are red shifted. The absorption curves for concentrations $6.3 \times 10^{-6} < c < 6.3 \times 10^{-3}$ mol l^{-1} go through isosbestic points, indicating two species in equilibrium within this range of concentrations. The pure spectrum for each of the species and also the equilibrium constant K were obtained numerically using the method described in [10], which is a modification of earlier methods developed by Förster and Levshin [11–13].

Figure 2 shows resolved spectra of both species, exhibiting maxima at 543 nm and 555 nm (curves 1 and 2). Shown are also the absorption spectra for RB/Et with NaOH trace and HCl trace (curves 1′ and 2′). They are almost identical with the resolved curves for the species 1 and 2. Hence the shift shown in Fig. 1 is caused by changes of the acid-base equilibrium. The slight difference in $\varepsilon_{\max}$ for curves 2 and 2′ may be caused by the fact that the

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* This work was carried out under the Research Project MR. I.9.

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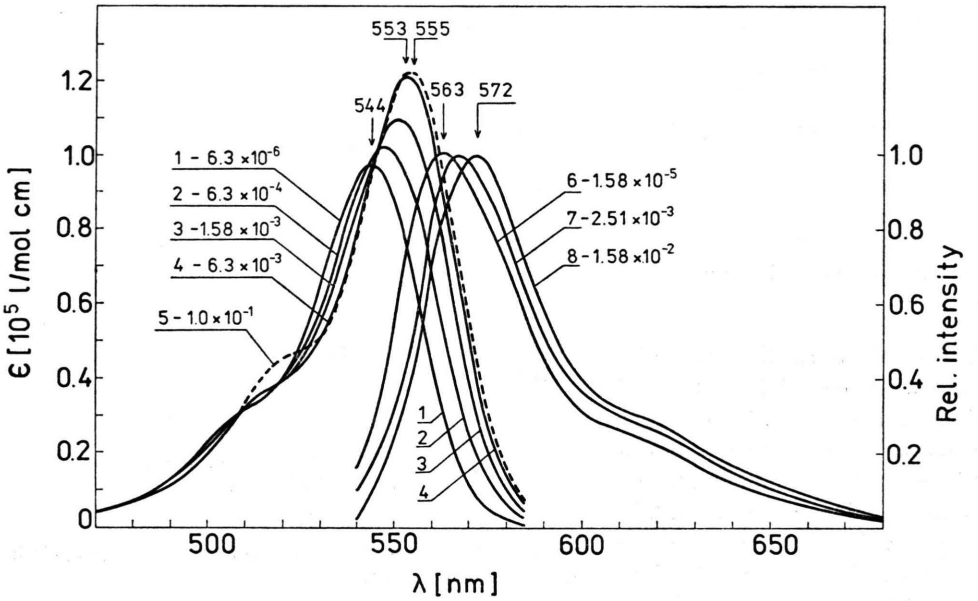

Fig. 1. Absorption (left) and fluorescence (right) spectra of rhodamine B in ethanol at different dye concentration at 295 K. Concentrations in mol l^{-1}.

calculations of the resolved spectra 1 and 2 were based on the absorption spectra for the concentration range $(3 \times 10^{-6} - 10^{-1})$ mol l^{-1}, where the assumption of two species only is not satisfied strictly.

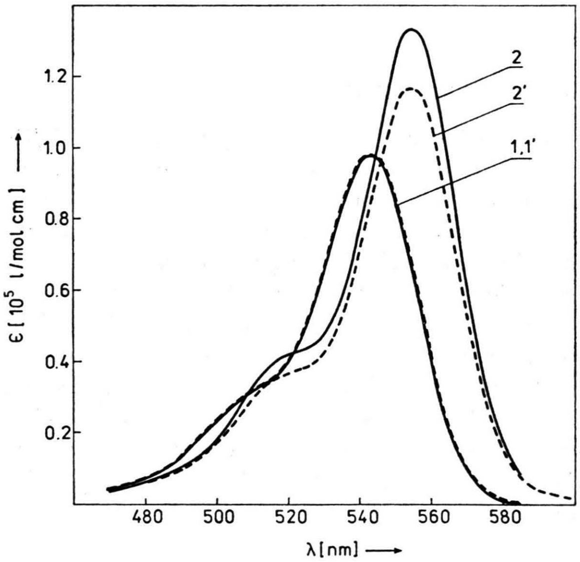

Fig. 2. Resolved distinct species absorption spectra for rhodamine B in ethanol (solid lines 1 and 2); absorption spectra for 1.58×10^{-5} mol l^{-1} RB/Et (dashed lines); 1′ — trace of NaOH added to solution, 2′ — trace of HCl added to solution.

Concentrational changes of RB/Et absorption spectra were investigated earlier [3, 5, 14, 15]. Selvyn and Steinfeld [5] measured the absorption spectra for RB/Et at much lower concentrations. They determined an equilibrium constant $K = 20400$ l mol^{-1} and also gave the absorption spectra of two different species, exhibiting maxima at 542 nm and 554 nm. They assigned these spectra to RB monomers and dimers, respectively. Ferguson and Mau [1, 2], and also Levshin et al. [3] showed that concentrational changes of RB/Et absorption spectra as observed in [5] reflect changes of the equilibrium between ionic forms of rhodamine B, namely between the base form (bipolar ion RB COO^{+-}) and the acid form (RB $COOH^{+}$ cation). In [3] it was also shown, based on measurements of the mean molecular weight of RB, that for concentrations up to 10^{-2} mol l^{-1} dimers are absent. However dimers are likely to exist in solutions of high concentrations. The slight bathochrome shift of the absorption band maximum accompanied by the appearence of a short-wave band at $\lambda = 520$ nm (cf. the dashed curve in Fig. 1) evidences this possibility.

Figure 3 shows the concentrational dependence of the PL decay time $\tau(c)$ of RB/Et neutral solutions (empty circles). Evidently two regions of τ decrease exist: $4 \times 10^{-4} < c < 10^{-3}$ mol l^{-1} and

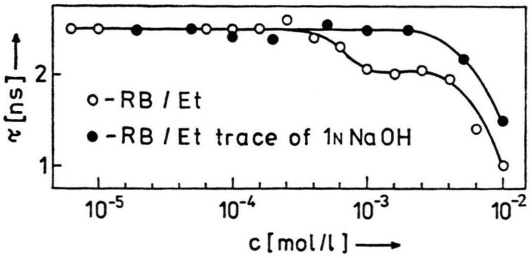

Fig. 3. Fluorescence decay time of rhodamine B in ethanol plotted against concentration.

$c > 6 \times 10^{-3}$ mol l^{-1}. The PL decay time was also measured for the same system containing a trace of 1 *n* NaOH (black circles). For the latter case the typical $\tau(c)$ dependence was observed; the shortening of τ for $c > 4 \times 10^{-3}$ mol l^{-1} may be explained by PL quenching by non-luminescent dimers. The explanation of the drop of τ for neutral solutions of RB/Et within the range of highest concentrations is similar. On the other hand the decrease of τ for moderate concentrations may be explained by changes of the acid-base equilibrium with rising concentration, tending to increase the contribution of the acid form exhibiting a lower absolute yield (η_0 equal to 0.71 and 0.49 for the base and acid form, respectively [2]). They exhibit also different values of the decay time τ_0. The measured values were 2.7 ns and 2.15 ns for the base and acid form, respectively, which are somewhat less than analogous values 3.1 ns and 2.5 ns as determined by Sadkowski and Fleming [4], or 3.5 ns and 2.8 ns as determined by Levshin et al. [3].

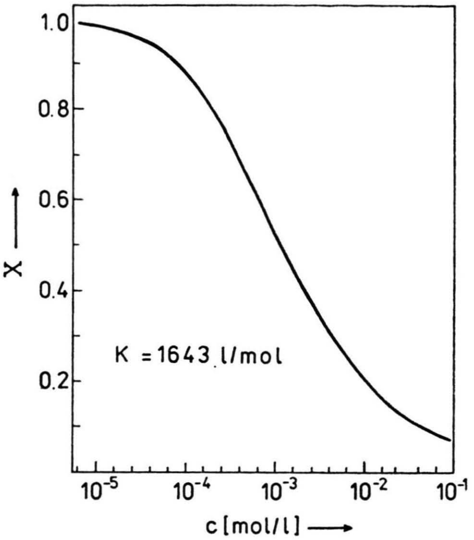

Fig. 4. Mole fraction X of the base form of rhodamine B in ethanol vs concentration.

Figure 4 shows the fraction X of the base form plotted against the dye concentration. For the calculations an equilibrium constant $K = c_{\mathrm{RH}^+}/c^2_{\mathrm{R}^{+-}} =$ 1643 l mol^{-1} was assumed, where c_{RH^+} and $c_{\mathrm{R}^{+-}}$ denote the concentrations of the acid and base forms, respectively. It is evident from Fig. 4 that significant changes of X occur within a relatively wide range of concentrations compared to the range in which the drop of τ has been observed. However, the shape of the PL decay time curve $\tau(c)$ is affected not only by values of τ_0 and η_0 for both forms, but also by nonradiative excitation energy transfer between molecules of these forms. Such a process may occur as the fluorescence spectrum for the base form and the absorption spectrum for the acid form of RB overlap considerably. For neutral solutions of RB/Et also the graph of the concentrational dependence of the relative quantum yield exhibits a similar atypical shape as the $\tau(c)$ curve. This was observed by Levshin et al. (see Fig. 1 in [3]) and also confirmed by our investigations.

4. Concluding Remarks

The $\tau(c)$ curve for neutral solutions of RB/Et provides a direct proof of the presence in the solution of two ionic forms of rhodamine B exhibiting different PL decay times. In order to quantitatively explain the experimental $\tau(c)$ curve, a nonradiative excitation energy transfer between molecules of two ionic forms should be taken into consideration. For high concentrations also the energy transfer to nonluminescent dimers must not be neglected. This problem seems to be difficult to solve, especially as the energy transfer may occur not only from the base to the acid form, but also in the opposite direction.

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