The Recombination Luminescence of Tryptophan in Aqueous Glasses, I
Quenching Effect of Electron Scavengers

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Recombination Luminescence, Tryptophan, Trapped Electron, Electron Scavenger

The quenching effect of $\text{SeO}_4^{2-}$ and $\text{NO}_3^-$ (scavenger for trapped electrons) on the delayed luminescence ('recombination luminescence') caused by the recombination of trapped electrons with mother tryptophan cations was investigated in aqueous 9 M NaOH and 9.5 M LiCl glasses at 77 K. The results show that the trapped electrons responsible for the recombination fluorescence were deep-trapped ones in 9 M NaOH glasses and shallow- and deep-trapped ones in 9.5 M LiCl glasses. However, trapped electrons participating in the recombination phosphorescence were almost shallow-trapped ones in the two glasses. The distribution of the trapped electrons is discussed.

Introduction

When tryptophan is irradiated with intense UV light in aqueous glasses, trapped electrons and tryptophan cations are generated by the photoionization of tryptophan through the two-photon process [1–3]. Trapped electrons recombine with mother cations to form excited singlet and/or triplet states of tryptophan, resulting in the occurrence of delayed luminescence called 'recombination luminescence' (RL). We classify RL as RF or RP by the shape of the spectrum.

It is known that the electrons ejected from tryptophan by the irradiation of UV light are trapped in shallow and/or deep traps, depending on the solvent nature. Recently, two types of electron scavengers ($\text{SeO}_4^{2-}$ for shallow-trapped electrons and $\text{NO}_3^-$ for shallow- and deep-trapped ones) were found by Buxton and Kemseley [4]. Accordingly, the quenching effect of these scavengers on the RL gives information about the trap-depth.

The present investigation was planned to obtain information about the trap-depth and distribution of trapped electrons responsible for the RL of tryptophan in aqueous glasses with high concentrations of NaOH or LiCl. For this purpose, the quenching effect of the electron scavengers $\text{SeO}_4^{2-}$- and NO$_3^-$ on the RL was studied in the two glasses at 77 K.

Abbreviations: RL, recombination luminescence; RF, recombination fluorescence; RP, recombination phosphorescence.

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Experimental

L-tryptophan from Katayama Co. was purified by recrystallization from distilled water. LiCl, NaOH, K$_2$SeO$_4$ and NaN$_3$ were of special grade and used without further purification.

A quartz vessel with a diameter of 10 mm and a depth of 2 mm was employed as a sample cell for the luminescence measurement. It was placed inside a copper block provided with two windows in rectangular directions for light excitation and detection. The copper block was placed in a dewar vessel filled with liquid nitrogen. The temperature of the sample was controlled by a heating element and measured with a copper-constantan thermocouple. The temperature was kept constant within ±0.1 K. The upper surface of the sample was irradiated, and the emission from the surface was measured.

Since the normal fluorescence decay of tryptophan was very fast (lifetime, about $10^{-6}$ sec), the RF was measured with a phosphorimeter which operated 0.5 msec after turning out the excitation. The lifetime of the normal phosphorescence was about 10 sec and its intensity was $10^4$ times larger than that of the RP. So, the RP intensity was obtained by integrating the photons emitted during the 1100 sec from 100 to 1200 sec after the excitation was stopped, to avoid mixing with the normal phosphorescence.

Details of the experimental methods are described in previous papers [5, 6].

Results and Discussion

The RL of tryptophan in aqueous 9 M NaOH and 9.5 M LiCl glasses at 77 K consisted of RF and RP. The former had a single peak at 320 nm and the latter three peaks at 405, 435 and 456 nm. These peaks coincided with those of the normal fluorescence and phosphorescence of tryptophan in aqueous glasses, respectively. The RF lasted for several
Fig. 1. Quenching of the RF by SeO₄²⁻ in aqueous 9 M NaOH (curve a) and 9.5 M LiCl (curve b) glasses at 77 K. I₀RF and I_RF: intensities of the RF in the absence and presence of SeO₄²⁻, respectively; concentration of tryptophan 10⁻³ M.

Fig. 2. Quenching of the RF by NO₃⁻ in aqueous 9 M NaOH (curve a) and 9.5 M LiCl (curve b) glasses at 77 K. I₀RF and I_RF: intensities of the RF in the absence and presence of NO₃⁻, respectively; concentration of tryptophan 10⁻³ M.

Fig. 3. Quenching of the RP by SeO₄²⁻ [A] and NO₃⁻ [B] in aqueous 9 M NaOH and 9.5 M LiCl glasses at 77 K. I₀RP and I_RP: intensities of the RP in the absence and presence of SeO₄²⁻ or NO₃⁻, respectively; concentration of tryptophan 10⁻³ M; Curves a and c: 9 M NaOH glasses; Curves b and d: 9.5 M LiCl glasses.

The quenching of the RF by NO₃⁻ is shown in Fig. 2. NO₃⁻ operated as quencher for the RF in 9 M NaOH and 9.5 M LiCl glasses.

Buxton and Kemseley [4] reported that SeO₄²⁻ scavenged shallow-trapped electrons but did not deep-trapped ones, and NO₃⁻ scavenged both deep- and shallow-trapped electrons. Therefore, the electrons responsible for the RF observed in 9 M NaOH glasses are considered to be deep-trapped ones from Curves a in Figs. 1 and 2, whereas those participating in the RF observed in 9.5 M LiCl glasses seem to be shallow- and a few deep-trapped ones from Curve b in Fig. 2 and the saturation of the quenching curve at high SeO₄²⁻ concentrations (Curve b in Fig. 1). The half-quenching concentrations were about 0.2 M of NO₃⁻ for deep-trapped electrons in 9 M NaOH glasses (Curve a in Fig. 2) and about 3 • 10⁻⁴ M of SeO₄²⁻ for shallow-trapped electrons in 9.5 M LiCl glasses (Curve b in Fig. 1).
rapid quenching appeared above $10^{-3}$ M of NO$_3^-$ in 9 M NaOH glasses (Curve c) and above $10^{-4}$ M of NO$_3^-$ in 9.5 M LiCl glasses (Curve d).

Miller [8, 9], Rice and others [10, 11] have proposed that trapped electrons generated in organic and aqueous glasses by the irradiation of high energy particles reacted with various electron scavengers by the electron tunneling mechanism. Ho, Moan and Kevan [12–14] suggested that the RL of indole derivatives and tetramethyl-p-phenylenediamine was caused by the electron tunneling from traps to mother cations in aqueous or organic glasses.

In our aqueous glasses containing electron scavenger (SeO$_4^{2-}$ or NO$_3^-$), two tunnelings of trapped electrons to tryptophan cations and electron scavengers may compete. Then, the quenching of the RL by electron scavengers is expressed as

$$I_0/I = 1 + k_s/k_r [S],$$  \hspace{1cm} (1)

where $I_0$ and $I$ are the RL intensities in the absence and presence of electron scavenger, respectively, and $k_r$ and $k_s$ the recombination rate of trapped electrons with tryptophan cation and the scavenging rate of trapped electrons, respectively. [S] is the mole concentration of scavenger.

The plots of $I_0/I$ against $[S]$ obtained from the quenching curves in Figs. 1, 2 and 3, gave straight lines. The quenching constants ($k = k_s/k_r$) obtained from the slope of these curves are given in Table I. The k values of NO$_3^-$ and SeO$_4^{2-}$ for the RF and RP in 9.5 M LiCl glasses were much larger than the corresponding k values in 9 M NaOH glasses. Moreover, the k values obtained from the quenching curves of the RP were much larger than those obtained from the quenching curves of the RF in two glasses.

Next, we evaluated roughly the distribution of trapped electrons participating in the RL in the two glasses. Using the equation proposed by Miller and others [8, 9, 14] for the tunneling rate of trapped electrons and assuming an electron to be trapped in a trap with the binding energy $B$ equal to the energy of acceptor level, one obtains

$$k_r = v \exp (- \beta r_{er}); \quad k_s = v \exp (- \beta r_{es}),$$  \hspace{1cm} (2)

where $\beta = 2(2mB)^{1/2}/\hbar$. $r_{er}$ and $r_{es}$ are distances (width of the potential barrier) between trapped electron, and tryptophan cation and scavenger, respectively. $v$ is the frequency factor and m the electron mass. Then, the quenching constant $k (= k_s/k_r)$ is given by

$$\ln k = \beta (r_{er} - r_{es}).$$  \hspace{1cm} (3)

Using the k values of NO$_3^-$ for deep-trapped electrons in 9 M NaOH glasses and SeO$_4^{2-}$ for shallow-trapped electrons in 9.5 M LiCl glasses for the RF in Table I, the following relation is obtained from (3):

$$(r_{er} - r_{es})_{Na}/(r_{er} - r_{es})_{Li} = 0.2(\beta_{Li}/\beta_{Na}).$$  \hspace{1cm} (4)

Further, since $\beta_{Li}$ for shallow-trapped electrons is much smaller than $\beta_{Na}$ for deep-trapped electrons, $\beta_{Li}/\beta_{Na} \ll 1$. Then,

$$(r_{er} - r_{es})_{Na}/(r_{er} - r_{es})_{Li} \ll 1.$$  \hspace{1cm} (5)

The subscripts Li and Na indicate "in 9.5 M LiCl and 9 M NaOH glasses", respectively. The half-quenching concentration of NO$_3^-$ in 9 M NaOH glasses was much higher (Curve a in Fig. 2) than that of SeO$_4^{2-}$ in 9.5 M LiCl glasses (Curve b in Fig. 1). This indicates $(r_{es})_{Na} \ll (r_{es})_{Li}$. Therefore, when tryptophan and scavenger are arranged homogeneously in the two glasses, $(r_{er})_{Na} \ll (r_{er})_{Li}$ from (5), i.e. deep-trapped electrons responsible for the RF in 9 M NaOH glasses are situated at much shorter distances from tryptophan cations than shallow-trapped ones in 9.5 M LiCl glasses. In the same way, the relation of $(r_{er})_{Na} \ll (r_{er})_{Li}$ was obtained for shallow-trapped electrons participating in the RP from the k values of SeO$_4^{2-}$ in Table I and Curves a and b in Fig. 3, assuming $(\beta_{Li} \sim (\beta)_{Na}$ for shallow-trapped electrons in the two glasses.

Fig. 4 shows the decays of the RP in 9 M NaOH and 9.5 M LiCl glasses at 77 K. The curves obey the Debye–Edwards law ($I(t) = m$), and the m value is $1.01 \pm 0.01$ in 9 M NaOH glasses and $1.06 \pm 0.01$ in

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<th>Table I. Quenching constant (k) (M$^{-1}$).</th>
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<td>Scavenger</td>
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