Nature of the room-temperature phosphorescence of cyclodextrin—aromatic compound complexes in water

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The lifetime of the room-temperature phosphorescence (RTP) of β-cyclodextrin—phenanthrene—chloroform complexes in water at 274 K increases from 1.7 to 2.3 s as the concentration of chloroform increases from $2.5 \cdot 10^{-3}$ to 0.125 mol L^{-1}. This dependence is explained by the formation of insoluble aggregates possessing RTP.

Key words: chloroform, β-cyclodextrin—phenanthrene complex, aggregate, lifetime, phosphorescence.

It is known that the room-temperature phosphorescence (RTP) of a cyclodextrin—aromatic compound complex is observed in an aqueous solution in the presence of a third component (most frequently with a heavy atom[1]) or when the aromatic compound itself contains a heavy atom.[2] Compounds with heavy atoms are used in almost all works[3,4] in which RTP has been studied, which may suggest that this is necessary for the appearance of RTP. However, aromatic compounds adsorbed on filter paper also manifest[5,6] RTP.

The heavy atom increases the rate of both the intersystem conversion and radiative transition (phosphorescence). It has been shown[7] that the RTP of the β-cyclodextrin—fluorene—acetone complex exists due to the triplet-triplet energy transfer from acetone upon the excitation of phosphorescence at λ = 315 nm, where fluorene does not absorb. Therefore, when the lowest triplet level of the aromatic molecule is populated, the phosphorescence is observed in the absence of the heavy atom as well. This fact allows one to draw the conclusion that the heavy atom is necessary to increase the singlet-triplet intersystem conversion and to populate the lowest triplet level.

The explanations presented above had to be refined after the appearance of publications in which the phosphorescence of a complex has been obtained without a heavy atom and a sensitizer, but with the participation of a third component.[8,9] In the present work, we attempted to refine the mechanism of the appearance of RTP and the role of the third component.

The lifetimes of the phosphorescence of the β-cyclodextrin—phenanthrene—chloroform complex in water at 273—313 K were measured at various concentrations of chloroform using the known procedures.[7] It could be expected that chloroform containing chlorine atoms would decrease the phosphorescence lifetime[10]; however, the phosphorescence lifetime increases as the concentration of chloroform increases (Table 1).

The literature data[1,9] and our observations[7,8] indicate that RTP in an aqueous medium exists, as a rule, only for "turbid" samples possessing light-scattering. This implies that the phosphorescence centers are localized in particles (aggregates), whose size is of an order of the light wavelength. Light-scattering and aggregates that cause it appear only after the addition of the third component to the solution. Light scattering (cloudiness) is considered[1] as an obstacle for measurements, but not as one of the conditions for the appearance of RTP.

The dependence presented in Table 1 can be explained by the fact that chloroform both decreases the phosphorescence lifetime due to the increase in the rate constant of the radiative process and favors the formation of a solid microparticle (aggregate), which restricts the phosphorescence quenching in the solution and,

Table 1. Dependence of the phosphorescence lifetime of the β-cyclodextrin—phenanthrene—chloroform complex in water on the concentration of chloroform at 274 K

Concentration of chloroform, $C \cdot 10^3$/mol L^{-1}	Phosphorescence life time/s	Mean square error /s
2.5	1.7	0.037
5.0	1.92	0.0025
7.5	2.02	0.017
12.5	2.3	0.024
25	2.3	0.044
125	2.3	0.022

Note. The concentrations of β-cyclodextrin, phenanthrene, and sodium sulfite are $2 \cdot 10^{-3}$, $5 \cdot 10^{-5}$, and 0.0025 mol L^{-1}, respectively.

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hence, increases the phosphorescence lifetime. When the second factor predominates over the first one, the increase in the concentration of chloroform can result in an increase in the lifetime.

The model suggested explains the whole totality of the phenomena altogether. A solution of the cyclodextrin—aromatic compound complex is transparent and does not exhibit phosphorescence. It is probable that under these conditions the rate constant for the nonradiative process is sufficiently high due to the interaction of the complex with its environment. The addition of the third component results in the formation of a suspension consisting of insoluble aggregates that possess RTP. The aggregate is a solid microparticle in which the aromatic compound is separated from water with a "coat" consisting of a great number of molecules of cyclodextrin and the third component, which initiated the formation of the aggregate. The heavy atom is not necessary for the appearance of RTP in solution. Aggregates with RTP are formed rather efficiently in the presence of compounds without a heavy atom: cyclohexane, benzene,[9] isooctane, and decalin.[8] However, halogen-containing compounds efficiently precipitate cyclodextrin from aqueous solutions[11] and, hence, they can favor the formation of cyclodextrin aggregates.

The aromatic compound in the aggregate is also partially protected from the quencher of triplet states (oxygen), which follows from the RTP experimentally observed in a nonevacuated solution (see Refs. 1, 2, and 9). Bromine-containing compounds (for example, dibromoethane) favor additionally the appearance of RTP due to a considerable increase in the rate constant for the radiative process, which can compete with nonradiative processes and quenching.

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