Luminescence from $[Ru(bipy)_3]^{2+}$ Ions Adsorbed on Ion Exchange Surfaces. Dynamic Quenching Reactions between Adsorbed Cations

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Summary Luminescence lifetime measurements show that when both luminescent and quencher ions are adsorbed on cation exchange resin luminescence quenching takes place by dynamic bimolecular processes involving energy transfer or electron transfer at rates which are of the same order as those in homogeneous solution.

THE quenching of the luminescent excited state of $[Ru(bipy)_3]^{2+}$ by electron transfer reactions with ions such as Fe^{3+} and Cu^{2+} is well known.[1–4] It has recently been shown that the quenching efficiency of Cu^{2+} ions is increased in polyelectrolyte solutions but the measurements were of luminescent intensities only and did not establish whether the quenching was static or dynamic.[5] Enhanced quenching of the luminescence of UO_2^{2+} by Fe^{3+} in the presence of polyelectrolytes has also been reported.[6]

20 mg (dry weight) samples of cation exchange beads (Sephadex-SP, Pharmacia) were equilibrated with sufficient $[Ru(bipy)_3]^{2+}$ to occupy 5% of the exchange sites, washed, suspended in water, and allowed to settle. Luminescence lifetimes were measured for the settled beads.[7] The characteristic luminescence of $[Ru(bipy)_3]^{2+}$ (τ_0 600 ns, 24 °C; λ_{max} 610 nm) was observed from the beads. The aqueous phase contained no $[Ru(bipy)_3]^{2+}$ and no luminescence was observed from it. Adsorption of Fe^{3+} or Cu^{2+} ions on the beads containing the $[Ru(bipy)_3]^{2+}$ quenched the luminescence and the lifetime decreased as increasing amounts of quenching ions were adsorbed on a fixed quantity of resin (Figure). The lifetime approached a minimum as the coverage of exchange sites by the quenching ions approached 100%. No $[Ru(bipy)_3]^{2+}$ was lost to the aqueous phase at coverages less than the resin capacity. The quenching did not take place through the aqueous phase. Extra $[Ru(bipy)_3]^{2+}$ ions added to the aqueous phase had the same lifetime as in solution in the absence of quenching ions. Beads containing $[Ru(bipy)_3]^{2+}$ when mixed with an equal quantity of beads containing Fe^{3+} ions had a lifetime which was initially that for the beads containing $[Ru(bipy)_3]^{2+}$ alone but after long contact times (> 15 min) the lifetime fell as the $[Ru(bipy)_3]^{2+}$ and Fe^{3+} ions established equilibrium within the total resin sample.

The luminescence quenching by the adsorbed ions can be expressed by the Stern–Volmer relation (1) in which the homogeneous concentration of quencher in the normal

$$\tau_0/\tau = 1 + K_{S-V}N_q \quad (1)$$

Stern-Volmer equation is replaced by the number of moles of quencher ion adsorbed on a fixed quantity of resin, N_q (Figure). A similar plot, but of different slope, was obtained for the quenching by Cu^{2+} ions. The quenching by adsorbed ions is apparently similar to that in solution and the quenching effects are additive. The luminescence lifetime for samples of cation beads containing both Cu^{2+} (10% of total capacity) and Fe^{3+} (2·5% of capacity) was 248 ns. For the same adsorbed concentrations of Cu^{2+} and Fe^{3+} on separate resin samples the lifetimes were 330 and 345 ns. In solution, the lifetime τ_m in the presence of two independent quenching processes is given by equation (2)

$$1/\tau_m = 1/\tau_1 + 1/\tau_2 - 1/\tau_0 \quad (2)$$

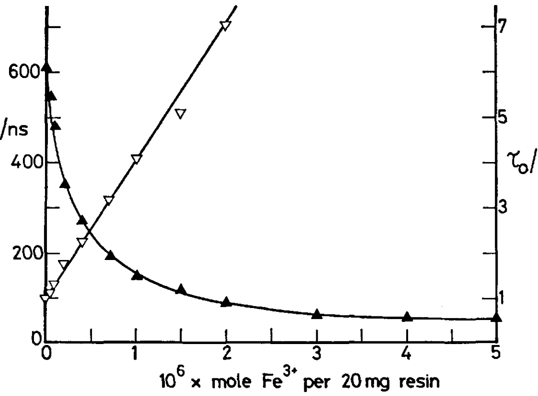

FIGURE. Dependence of the emission lifetime of excited $[Ru(bipy)_3]^{2+}$ adsorbed on Sephadex-SP cation exchange resin upon the quantity of Fe^{3+} adsorbed on the same sample of resin. ▲ lifetime, τ; ▽ Stern-Volmer plot of τ_0/τ.

(τ_1 and τ_2 are the lifetimes in the presence of the separate quenchers at the same concentrations as in the mixture, τ_0 is the unquenched lifetime). This relation also applies to Cu^{2+} and Fe^{3+} adsorbed on the resin. The lifetime predicted from the equation is 234 ns, in good agreement with the measured value, 248 ns.

The nature of the quenching reaction (energy transfer or electron transfer) on the resin has not yet been determined. No $[Ru(bipy)_3]^{3+}$ is produced on prolonged irradiation and attempts to detect transient changes following flash photolysis of quenched resin samples have not so far succeeded. The reductions in the emission lifetimes imply that the quenching processes are dynamic, not static, and take place by an essentially bimolecular process.[8] The linear relation (Figure) also indicates a bimolecular process. For quencher concentrations expressed as mol dm^{-3} of swollen resin beads, the slope of the straight line Stern–Volmer plots may be interpreted as pseudo-homogeneous quenching rate constants, with values of $6 \pm 2 \times 10^8$ dm^3 mol^{-1} s^{-1} for Fe^{3+} and $5 \pm 2 \times 10^7$ dm^3 mol^{-1} s^{-1} for Cu^{2+}, which are of the same order as those for quenching by the same ions in solution.[1,2,4] Either the ions bound to the resin are highly mobile on that phase or energy and electron transfer can take place by long-distance migration in the resin phase.

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