

Light Output of Luminescent Plastics

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Efficiency of transfer of excitation energy from solvent to solute in a luminescent plastic solid solution is derived and compared to a previously published expression. Capture cross-section ratios and the nature of the quenching parameter are discussed.

LIGHT output, as a function of concentration of the fluorescent organic molecule in luminescent plastic solid solutions, involves energy transfer from the molecules of the base material to those of solute which is present, generally, in small concentrations. Swank and Buck¹ have shown that polystyrene, for instance, has a considerable probability of emission in the ultraviolet when excited by the passage of a charged particle, and that this radiation is quite completely absorbed by small concentrations of the solute molecule. They have shown also that nonradiative transfer is important.

Initially, a particle-induced excitation of a solvent molecule to a state from which transfer of the excitation energy can take place occurs; the efficiency of this initial excitation is low. Given such an excitation, the efficiency of energy transfer from solvent to solute in these materials, both by reabsorption of ultraviolet emission by the solvent and by some nonradiative process, is therefore given by

$$\eta_t = (p_{t(em)} + p_{t(nr)}) / (p_{t(em)} + p_{t(nr)} + p_q),$$

where the p 's are relative probabilities of (a) transfer by emission of the solvent, (b) nonradiative transfer, and (c) quenching in the solvent, respectively. Capture of a migrating quantum of excitation energy occurs with a relative probability $\sigma_0(1-c)$, where σ_0 is the cross section for capture by the solvent molecule and c is the concentration of solute. Probability of emission by the solvent, to which the probability for radiative transfer to the solute is equal in the presence of complete absorption by the solute, is then $q_0\sigma_0(1-c)$, where q_0 is the quantum efficiency of emission by the solvent. That is,

$$p_{t(em)} = p_{em} = q_0\sigma_0(1-c).$$

Nonradiative transfer probability (capture by the solute) is given by $p_{t(nr)} = \sigma c$, where σ is the capture cross section of the solute molecule. Therefore,

$$\eta_t = \frac{q_0\sigma_0(1-c) + \sigma c}{q_0\sigma_0(1-c) + \sigma c + (1-q_0)\sigma_0(1-c)} \quad (1)$$

The fraction of "nonadjacent" solute molecules capable of emission, assuming solute self-quenching takes place over a certain radius, is given by Johnson and Williams²

¹ R. K. Swank and W. L. Buck, Phys. Rev. **91**, 927 (1953).

² P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 323 (1950).

as $(1-c)^z$, where z is the number of neighboring quenching sites. The transfer efficiency to effective solute molecules is then $\eta_t(1-c)^z$. If the approximations $(1-c)^z \approx (1+zc)^{-1}$ and $(1-c) \approx 1$ are made, the effective transfer efficiency, to which the light output will be proportional, is given by

$$\eta_{t(eff)} \approx \frac{q_0 + (\sigma/\sigma_0)c}{1 + (\sigma/\sigma_0)c} \frac{1}{1+zc} \quad (2)$$

within ten percent if $zc \leq 0.5$.

Comparison of this relation to (9) of Swank and Buck¹ shows that their " σ " corresponds to the present ratio of capture cross sections, while their self-quenching parameter " m " is evidently related to the number of quenching sites z . Swank and Buck report good fit with a relation of the form of (2) above to data on light output vs concentration of a number of solutes. Their quenching parameter varies from zero to 100, corresponding to radii of strong quenching effects up to three molecular diameters. The mean separation of solute molecules at peak light output is roughly three times the range of strong quenching effects, as determined by z ; therefore this range is more like a radius at which quenching probability has fallen to 1/eth of its value at $r=0$ (see Johnson and Williams³). Swank and Buck¹ also show evidence that energy transfer is appreciable at solute concentrations no greater than 10^{-6} ; this corresponds to a mean distance of separation of solute molecules of near 50 diameters or, in the case of polystyrene as solvent, of roughly 300 Å. Ehrenberg and Franks⁴ suggest a "length of diffusion" of some undetermined energy-transporting agents as several microns for a luminescent plastic material.

Finally, although Johnson and Williams⁵ suggest that in the case of certain luminescent liquid solutions (where q_0 is approximately zero) the ratio σ/σ_0 is roughly a constant of the solvent, the data of Swank and Buck¹ on plastics show a range of σ/σ_0 from zero to 700 for a number of solid solutions with polystyrene the base material and indicate strong dependence upon the solute.

³ P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 1477 (1950).

⁴ W. Ehrenberg and J. Franks, Proc. Phys. Soc. (London) **B66**, 1057 (1953).

⁵ P. D. Johnson and F. E. Williams, Phys. Rev. **81**, 146 (1951).