371. *A Potentiometric Study of the Fluorescence of Mono- and Bis-(8-quinolinato-5-sulphonic acid)zincate*(II) *Anions in Aqueous Solution*

By R. E. Ballard

Ground-state equilibria are shown to control the fluorescence intensity of aqueous solutions containing zinc perchlorate and 8-hydroxyquinoline-5-sulphonic acid. The emission spectra of the mono- and bis-(8-quinolinato-5-sulphonic acid)zincate(II) anions are presented, the molar fluorescence intensity of the bis- being twice that of the mono-complex, indicating that their quantum yields are equal. The quenching of fluorescence by copper(II) ions is found to be an intramolecular process in aqueous solution.

It has been shown [1] that the fluorescence of 8-hydroxyquinoline-5-sulphonic acid is governed by excited-state equilibria in strongly acid solution, whereas the fluorescence of the *O*-methyl derivative in dilute acid solution is dependent upon the ground-state equilibria. These studies are now extended to the chelate complexes.

Because of their water solubility and intense fluorescence in aqueous solution, the chelate complexes formed by 8-hydroxyquinoline-5-sulphonic acid with non-transition metals are ideally suitable for both potentiometric and fluorimetric investigation. There have been several careful studies of the ground-state equilibria with a range of metals,[2] and one fluorimetric study of the mono-complexes of magnesium, calcium, and zinc.[3] In a less detailed treatment [4] of the pH-dependence of the fluorescence of solutions containing zinc and 8-hydroxyquinoline-5-sulphonic acid, it was suggested that a strongly fluorescent intermediate was present, and such species are reported among the (2-methyl-8-quinolinato)-zinc(II) chelates in absolute ethyl alcohol.[5]

The fluorescence intensity, f, of a solute, S, is given by eqn. (1), where Q is the quantum yield of fluorescence, I the intensity of the exciting light, a the molar absorbance in l.mole^{-1} cm.$^{-1}$, and l the path-length in cm.

$$f = QI\{1 - \exp(-al[S])\} \qquad (1)$$

If the absorbance at the wavelength of the exciting light is less than about 0·1, eqn. (1) reduces to eqn. (2):

$$f = QIal[S] \qquad (2)$$

In practice, Q and I are difficult to measure in absolute units, but with a given instrument, under given experimental conditions, we may write:

$$f = f_S[S], \qquad (3)$$

where f_S, the molar fluorescence intensity, is an arbitrary constant for S.

In a solution containing bivalent metal ions, M^{2+}, and 8-hydroxyquinoline-5-sulphonic acid, H_2L, the concentrations of the mono- and bis-(8-quinolinato-5-sulphonic acid)-zincate(II) anions, [ML] and $[ML_2^{2-}]$, respectively, are given by solving the simultaneous equations (4)—(9).

$$K_1 = [ML]/[M^{2+}][L^{2-}] \qquad (4)$$

$$K_2 = [ML_2^{2-}]/[ML][L^{2-}] \qquad (5)$$

$$K(H_2L) = [H^+][HL^-]/[H_2L] \qquad (6)$$

$$K(HL^-) = [H^+][L^{2-}]/[HL^-] \qquad (7)$$

$$\text{Total [metal ion]} = [M^{2+}] + [ML] + [ML_2^{2-}] \qquad (8)$$

$$\text{Total [8-hydroxyquinoline-5-sulphonic acid]} = [H_2L] + [HL^-] + [L^{2-}] + [ML] + 2[ML_2^{2-}] \qquad (9)$$

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[1] R. E. Ballard and J. W. Edwards, *J.*, 1964, 4868.

[2] J. Bjerrum, G. Schwarzenback, and L. G. Sillén, "Stability Constants," *Chem. Soc. Special Publ.*, No. 6, 1957.

[3] S. Watanabe, W. Frantz, and D. Trottier, *Analyt. Biochem.*, 1963, **5**, 345.

[4] O. Popovych and L. B. Rogers, *Spectrochim. Acta*, 1960, **16**, 49.

[5] D. A. Carter and W. E. Ohnesorge, *Analyt. Chem.*, 1964, **36**, 327.

The notation is that of ref. 2, $K(H_2L)$ and $K(HL^-)$ being the acid dissociation constants involving the nitrogen atoms and the hydroxyl group, respectively. The equations were solved, by means of a computer, for a range of pH values at intervals of 0·1 pH units, using the published values for the constants.

If the only fluorescent species are ML and ML_2^{2-}, and if excited-state equilibria are not attained within the lifetime of the fluorescent state, the fluorescence intensity is given by eqn. (10), where b is a constant due to light-scattering in the cuvette and instrumental noise.

$$f = f_1[ML] + f_2[ML_2^{2-}] + b \qquad (10)$$

In order to test eqn. (10), solutions were prepared containing various ratios of total [metal ion] to total [8-hydroxyquinoline-5-sulphonic acid] and the variation of f with pH determined.

Results and Discussion

In Figure 1a is shown a plot of [ZnL] against pH (full line) for a solution containing zinc perchorate (10^{-3}M) and 8-hydroxyquinoline-5-sulphonic acid (10^{-5}M) at 20°, calculated by means of eqns. (4)—(9), using the data of Albert.[6] This ratio of metal to ligand concentration ensures that the calculated concentration of the bis-chelate never exceeds 0·02% of that of the mono-chelate; the fluorescence intensity should therefore be proportional to [ZnL] if the ground-state equilibria hold. The experimental points are given, in arbitrary units, to the same scale as the theoretical line, and a good correlation exists. (A change in the value of log K_1 by ±0·1 units from its value of 8·4 appreciably shifts the

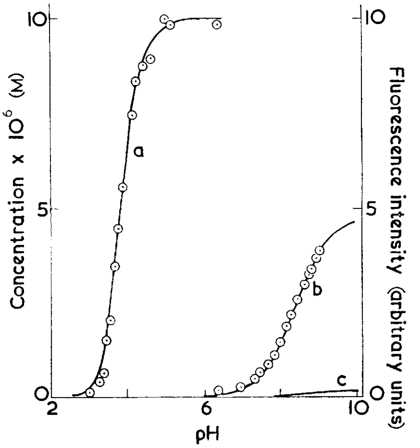

Figure 1

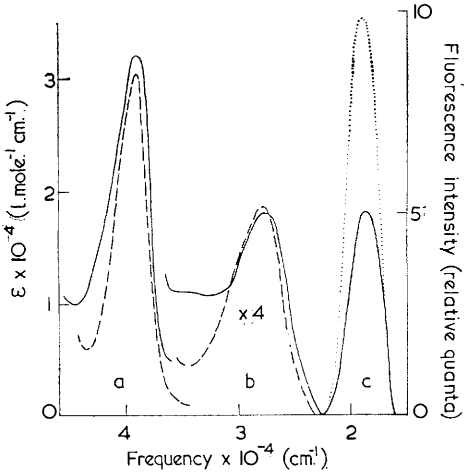

Figure 2

Figure 1. Experimental points (circles) show the variation of fluorescence intensity with pH. Lines show the concentration of complex calculated by means of eqns. (4)—(9). The experimental points are normalised to the same scale as the lines. Curve a, mono-(8-quinolinato-5-sulphonic acid)zincate(II) in an aqueous solution containing zinc perchlorate (10^{-3}M) and 8-hydroxyquinoline-5-sulphonic acid (10^{-5}M) at 20°; curves b and c, respectively, mono- and bis-(8-quinolinato-5-sulphonic acid)magnesium(II) in an aqueous solution containing magnesium perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2 × 10^{-5}M) at 25°.

Figure 2. The *absorption spectra* of the mono-(8-quinolinato-5-sulphonic acid)-zincate(II) anion in aqueous solution (full lines a and b) and the doubly charged anion of 8-hydroxyquinoline-5-sulphonic acid in 0·1M-aqueous sodium hydroxide (dashed lines a and b); and the *emission spectra* of the mono- and bis-(8-quinolinato-5-sulphonic acid)zincate(II) anions (full and dotted lines c, respectively).

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[6] A. Albert, *Biochem. J.*, 1953, **54**, 646.

theoretical line.) The absorption and emission spectra at pH 7, [ZnL] being 10^{-5}M, are given in Figure 2, together with the absorption spectrum of the doubly charged anion of 8-hydroxyquinoline-5-sulphonic acid, L^{2-}, in 0·1M-sodium hydroxide. There is an extra band in the spectrum of ZnL as compared with that of L^{2-}; this extra band is generally found among oxinates, the chelate spectra closely resembling those of the zwitterions.[7] The absorption and emission spectra of ZnL touch at 22,200 cm.$^{-1}$, this being the frequency of the 0–0 vibrational component of their common electronic transition, which, from specular mirror-image symmetry, is taken to be that of the lowest-energy absorption band. In the ligand, it can be seen (Figure 2) that the lowest-energy absorption band is displaced some 600 cm.$^{-1}$ to the blue with respect to ZnL, implying, by eqn. (11),[8] that log K_1 has diminished by about 1·3 units in the excited state.

$$\log K_1^* = \log K_1 + [E(\mathrm{ML}) - E(\mathrm{L}^{2-})]/2{\cdot}303\,\boldsymbol{R}T \qquad (11)$$

In eqn. (11), K^* is the excited-state stability constant, E(ML) the energy of the lowest-energy electronic transition of ML, $\boldsymbol{R}$ the gas constant, and T the absolute temperature.

The decrease in K_1 upon excitation is large enough to cause dissociation of the complex at pH 3·7 (the inflection point), and the experimental results are therefore consistent only with the ground-state equilibrium data.

Upon excitation of the ligand, there are very large increases in the acidity of the hydroxyl group and the basicity of the nitrogen atom, the logarithmic dissociation constants changing by about ten units in each case.[1] As far as the stability of the chelate is concerned, these effects work in opposite directions, so that the change in K_1 upon excitation is relatively small. In the excited state, the metal–oxygen σ bond must be much weaker than the metal–nitrogen σ bond.

The fluorescence intensity of an aqueous solution of magnesium perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2×10^{-5}M), as a function of pH at 25°, was found, in a similar manner, to follow the ground-state data of Nasanen and Uisitalo[9] (Figure 1b), the concentration of the bis-complex rising here to 5% of that of the mono-complex (Figure 1c). The constants reported by Irving and Rossotti,[10] for solutions in aqueous dioxan, also accounted well for the fluorescence of solutions of magnesium perchlorate and oxine in 50% dioxan at 20°, but the zinc oxinates did not fluoresce under these conditions.

In aqueous solution, with a ratio of concentrations of zinc perchlorate to 8-hydroxyquinoline-5-sulphonic acid of 1 : 2, the mono- and bis-complexes have comparable concentrations over a range of pH values, and, therefore, by measuring f at three pH values within the range, eqn. (10) can be solved to give f_1, f_2, and b. In Figure 3, can be seen the experimental points (circles) for a solution containing zinc perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2×10^{-5}M) at 25°, together with the theoretical curves (dashed lines) for the concentrations of the complex, calculated by using the data of Nasanen and Uisitalo.[9] Solution of eqn. (10), for pH values of 5, 6·5, and 8, gave values of f_2 and f_1 in the ratio 2·01 : 1; the theoretical line of pH against f, calculated by means of eqn. (10) by using the derived values of f_1, f_2, and b, is given in Figure 3, good agreement being obtained up to pH 8·5, beyond which the fluorescence intensity decreases because of hydroxide formation, instead of becoming constant. In the oxinate family, the molar absorbance of a chelate is proportional to the number of ligands attached;[11-13] hence, from eqn. 2 and the observed ratio f_2/f_1, the quantum yields of the mono- and bis-complexes are equal. No evidence supporting the existence of a strongly fluorescent intermediate was found, the results in aqueous solution therefore differing sharply from those in ethyl alcohol.[5]

[7] R. E. Ballard and J. W. Edwards, unpublished work.

[8] T. Förster, *Z. Electrochem.*, 1950, **54**, 42.

[9] R. Nasanan and E. Uisitalo, *Acta. Chem. Scand.*, 1954, **8**, 112.

[10] H. Irving and H. S. Rossotti, *J.*, 1954, 2910.

[11] T. Moeller and A. J. Cohen, *J. Amer. Chem. Soc.*, 1950, **72**, 3546.

[12] T. Moeller, F. L. Pundsack, and A. J. Cohen, *J. Amer. Chem. Soc.*, 1954, **76**, 2615.

[13] W. E. Ohnesorge and L. B. Rogers, *Spectrochim. Acta*, 1959, **15**, 27.

The emission spectrum of the bis-complex was obtained with a solution of zinc perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (10^{-4}M) at pH 8·0, [ZnL_2^{2-}] being 10^{-5}M under these conditions (Figure 2). The positions and shapes of the emission bands of the mono- and bis-complexes are seen to be the same, the intensity of the bis-complex appearing to be slightly less than twice that of the mono-complex, owing to the high absorbance of the 365-mμ exciting light, eqn. 2 being inaccurate for highly absorbing solutions.

The fluorescence of oxinates is quenched by transition-metal ions [14] and by iodide ions, neither the copper chelate [15] nor the methiodide [1] of 8-hydroxyquinoline-5-sulphonic acid being fluorescent in the solid state. The effect of successive additions of cupric ion upon the fluorescence intensity of a solution containing zinc perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2×10^{-5}M) at pH 8·5 is illustrated in Figure 4, where it can be seen that the replacement of half of the zinc complex by the copper complex reduces the intensity by one half, the intensity still being proportional to the concentration of the zinc complex. This result indicates that the quenching process is intramolecular. The addition of iodide ion up to a concentration of 10^{-3}M had no effect upon the fluorescence.

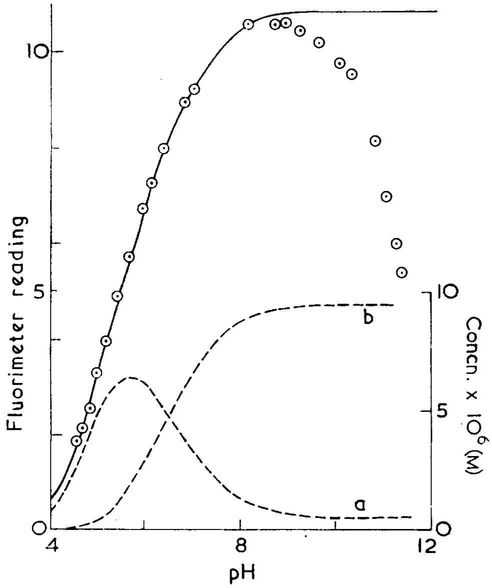

FIGURE 3

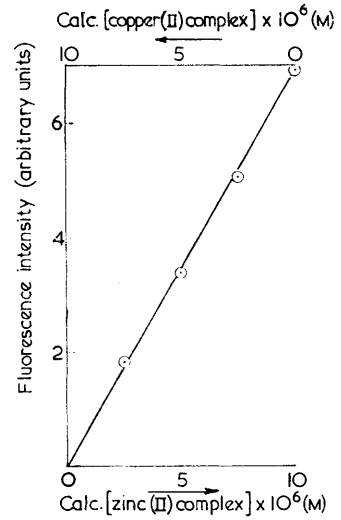

FIGURE 4

FIGURE 3. Experimental points (circles) show the variation of fluorimeter reading with pH. Dashed lines, a and b, show the concentrations of the mono- and bis-quinolinato-5-sulphonic acid)zincate(II) anions, respectively, calculated by means of eqns. (4)—(9), in an aqueous solution containing zinc perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2×10^{-5}M) at 25°. The full line is the theoretical plot of fluorimeter reading against pH, calculated from eqn. (10).

FIGURE 4. The fluorescence intensities of aqueous solutions containing fixed concentrations of zinc perchlorate (10^{-5}M) and 8-hydroxyquinoline-5-sulphonic acid (2×10^{-5}M) and various concentrations of cupric perchlorate (from zero to $7{\cdot}5 \times 10^{-6}$M) at pH 8·5.

EXPERIMENTAL

Materials.—8-Hydroxyquinoline-5-sulphonic acid was recrystallised three times from water, and dried at 105°. " Foodstuffs grade " perchloric acid (60%) was obtained from B.D.H. " Specpure " zinc, magnesium, and copper were obtained from Johnson Mathey & Co.

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[14] H. M. Stevens, *Analyt. Chim. Acta.*, 1959, **20**, 389.

[15] J. C. I. Liu and J. C. Bailar, *J. Amer. Chem. Soc.*, 1951, **73**, 5432.

Preparation of Solutions.—Solutions of the metallic ions were prepared by dissolving weighed quantities of the metal in the minimum volume of perchloric acid, and diluting to volume with water. In experiments in 50% dioxan as solvent, the procedure of Irving and Rossotti was followed.[10]

Measurement of Fluorescence Intensity.—Light from a 250-w, medium pressure, mercury-arc lamp was passed through a Chance OX filter, so as to obtain the 365-mμ line, and focused upon the solution contained in a rectangular silica cell of path-length 5 mm. The exciting light entered and left the cell through optically flat and polished faces, and the fluorescent light, passing through a third such face at right angles to the others, was focused upon the slits of a monochromator (Hilger " Uvispec "). A rotating chopper, between the cell and the monochromator, pulsed the fluorescent light at 800 c./sec. Two photomultipliers (6256 A; E.M.I.) were used, one to receive the fluorescent light from the monochromator and the other to monitor the exciting beam *via* a silica plate (set at 45° to the beam) and a rotating chopper. The signals from the photomultipliers were passed to two tuned amplifiers (Applied Electronics, type 800) and thence to a ratio recorder (Cambridge Electronics).

When intensities were being measured, the monochromator slits were opened fully; for the recording of spectra, they were set at 2 mm. The emission spectra were corrected, against a lamp of known colour temperature, for variation of instrumental sensitivity with wavelength.[16]

The silica cell was attached by a narrow neck to the bottom of a silica beaker (100 ml.) fitted with a rubber bung carrying glass and calomel electrodes, and with holes for the insertion of a microburette (Burroughs Wellcome " Agla ") and a capillary tube which could be raised or lowered into the cell. Nitrogen passing through the capillary effectively mixed the contents of cell and beaker, and excluded air. The effect of pH-variation upon fluorescence was studied by placing the solution (100 ml.) in the beaker, passing in nitrogen, and adjusting the pH with N-acid or -alkali from the microburette. The fluorescence intensity at any pH was found to be independent of whether the pH was attained from the acid or alkaline side.

Measurement of Absorption Spectra.—A recording instrument was used (Perkin-Elmer, 137 UV) with 4-cm. and 1-mm. cells.

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[16] J. H. Chapman, T. Förster, G. Kortüm, E. Lippert, W. H. Melhuish, G. Nebbia, and C. A. Parker, *Z. analyt. Chem.*, 1963, **197**, 431.