Complex Formation Constants between Mononuclear High-spin Iron(III) Phthalocyanine and Imidazole

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4,4′,4″,4‴-Tetradecyloxycarbonylphthalocyaninatoiron(III) (**1**) reacts with imidazole to form its mono- (**2**) and subsequently its di-imidazole (**3**) complexes with formation constants of $>10^8$ and 108 dm^3 mol^{-1} in dichloromethane at 20 °C, respectively.

Co-ordination of nitrogenous bases, in particular imidazole (Im), to iron porphyrins[1] and phthalocyanines[2] has been extensively examined by various methods, and is thought to proceed in two steps [equations (1) and (2)] (P = porphyrin or phthalocyanine, S = solvent or ligand), although, with a few

$$\mathrm{SFeP} + \mathrm{Im} \rightleftharpoons \mathrm{ImFeP} \quad K_1 = [\mathrm{ImFeP}]/[\mathrm{SFeP}][\mathrm{Im}] \qquad (1)$$

$$\mathrm{ImFeP} + \mathrm{Im} \rightleftharpoons \mathrm{Im_2FeP} \quad K_2 = [\mathrm{Im_2FeP}]/[\mathrm{ImFeP}][\mathrm{Im}] \qquad (2)$$

exceptions, only the overall reaction (3) is generally observed in thermodynamic studies. The failure to detect ImFeP has been taken as an indication that $K_1 \ll K_2$. We describe here the inverse behaviour ($K_1 \gg K_2$) observed in the reaction between the high-spin iron(III) phthalocyanine (**1**) and imidazole.†

$$\mathrm{SFeP} + 2\mathrm{Im} \rightleftharpoons \mathrm{Im_2FeP} \quad K_3 = [\mathrm{Im_2FeP}]/[\mathrm{SFeP}][\mathrm{Im}]^2 \qquad (3)$$

Figure 1 shows the spectral changes which take place when imidazole is added to (**1**). In the absence of imidazole, (**1**) exhibits peaks at 825 (ϵ 13 200), 652 (53 300), and 337 (50 000) nm. This spectrum changes dramatically on addition of *ca.* 1 equivalent of imidazole, with isosbestic points at 723, 670, 625, 485, and *ca.* 360 nm; for [Im]/[(**1**)] = 1.10, saturation occurs (see also the inset) to produce a spectrum with new peaks at 692 (ϵ 65 900) and 560 (15 100) nm. Further change in the intensity of these bands requires a >50-fold increase in [Im]. From these observations an approximate K_1 value can be estimated. Since neither Rose–Drago[4] nor Benesi–Hildebrand[5] methods can be used for the present conditions, Figure 2[6] was used. This figure indicates, for the general equilibrium (4), how the x/a ratio changes depending on $K\,[=x/(a-x)(b-x)]$ when a is fixed and b is varied. Accordingly, in the present case where A = (**1**) and B = imidazole, the curve shown as a broken line is obtained from the data in Figure 1, assuming that the spectrum at [Im]/[(**1**)] = 1.10 is that of the pure monoimidazole complex of (**1**). Using a = [(**1**)] = 2.97×10^{-5} mol dm^{-3}, it is concluded that K_1 in CH_2Cl_2 is $>10^8$ dm^3 mol^{-1} at 20 °C.

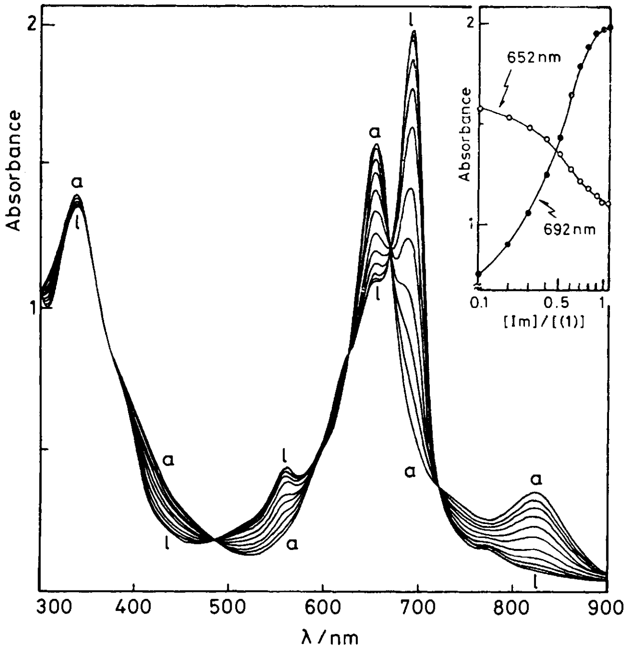

Figure 1. Spectral changes observed upon addition of imidazole to a 2.97×10^{-5} M solution of (**1**) in CH_2Cl_2. [Im]/[(**1**)] (mole/mole): a, 0.0; b, 0.1; c, 0.2; d, 0.3; e, 0.4; f, 0.5; g, 0.6; h, 0.7; i, 0.8; j, 0.9; k, 1.0; and l, 1.10. The inset shows a plot of the intensity at 652 and 692 nm *vs.* [Im].

$$\begin{array}{ccccc} m\mathrm{A} & + & n\mathrm{B} & \rightleftharpoons & \mathrm{A}_m\mathrm{B}_n\ (m = n = 1) \\ a - x & & b - x & & x \end{array} \qquad (4)$$

When a large excess of imidazole $\{50 \leqslant [\mathrm{Im}]/[(\mathbf{2})] < 20\,000\}$ is added to (**2**), the absorption peaks at 692 and 560 nm diminish and new peaks develop at 672 and 440 nm, indicating formation of the di-imidazole complex (**3**). The K_2 value evaluated from the Benesi–Hildebrand plot[5] in Figure 3 is 108 dm^3 mol^{-1} in CH_2Cl_2 at 20 °C.

In contrast to the di-ligation of imidazole to high-spin iron(III) porphyrins which is accompanied only by a high-spin to low-spin transition,[1] the mono- and di-ligation of imidazole to

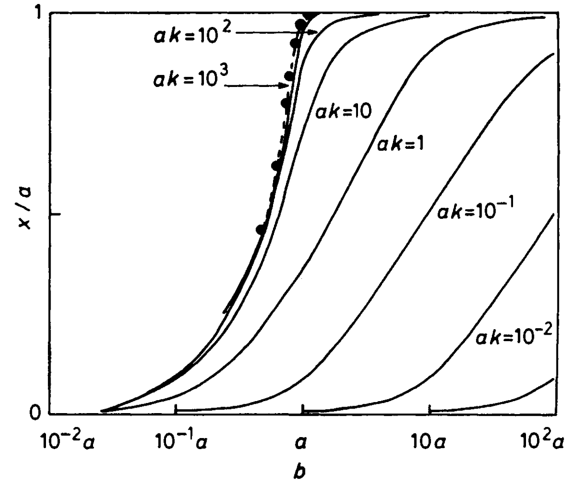

Figure 2. x/a Ratio in the general equilibrium (4) as a function of the equilibrium constant, *K*. *a*; constant, *b*; variable. Broken line is for the process (1) to (2), replotted from the data in Figure 1.

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† For structures (**1**)—(**3**), see preceding communication (ref. 3).

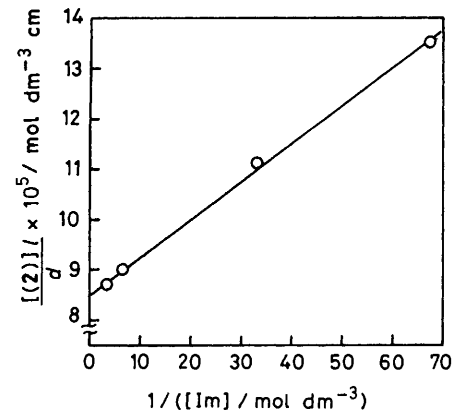

Figure 3. Benesi–Hildebrand plots for the (**2**)–imidazole system in CH_2Cl_2 at 20 °C. [(**2**)] = 2.97×10^{-5} M, [Im]/[(**2**)] = 5.0×10^2 to 1.0×10^4. Plotted from the intensity change at 440 nm. *l*: path length, *d*: absorbance at 440 nm − absorbance of (**2**) at 440 nm.

(**1**) are peculiar in that they cause a high-spin to low-spin transition and a reduction from iron(III) to iron(II), respectively.[3] Moreover, on the basis of the results of an n.m.r. study of high-spin iron(III) porphyrins, XFeP (X = Cl^-, Br^-, and I^-), which showed that the greater the extent of dissociation of X the larger the K_1/K_2 ratio becomes,[7] we conclude that the Fe–X bond in (**1**) is very weak, if present at all. The failure to detect halogen in the elemental analysis, and the high sensitivity to solvent of the effective magnetic moment of (**1**)[3] may be correlated with this phenomenon.

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