Equilibrium and Kinetic Study of Imidazole Binding to Phthalocyaninatoiron(II) in Dimethyl Sulphoxide

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The reaction between imidazole (Him) and phthalocyaninatoiron(II) [Fe(pc)] in dimethyl sulphoxide (dmso) has been studied, at 20 °C, from both equilibrium and kinetic points of view. In the presence of excess of Him the adduct $[Fe(pc)(Him)_2]$ is formed *via* two consecutive pseudo-first-order processes. The observed rate constants have the general form: $k_{obs.} = k_{1f}[Him] + k_{1r}$ with $k_{1f}' = (9.8 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_{1f}'' = 5.4 \pm 0.15$ dm^3 mol^{-1} s^{-1}, for the binding of the first and second Him molecules, respectively. Equilibrium experiments yield $K_1' = (6.4 \pm 2.6) \times 10^5$ dm^3 mol^{-1} and $K_1'' = (7.4 \pm 0.5) \times 10^3$ dm^3 mol^{-1} for the stepwise formation of the [Fe(pc)(dmso)(Him)] and $[Fe(pc)(Him)_2]$ adducts, respectively. From the values of the second-order rate constants (k_{1f}' and k_{1f}'') and of the equilibrium constants (K_1' and K_1''), the dissociation rate constants have been estimated to be $k_{1r}' = 1.5 \times 10^{-2}$ s^{-1} and $k_{1r}'' = 7.3 \times 10^{-4}$ s^{-1}. The results are discussed in the light of related previous studies.

The axial reactivity of the phthalocyaninatoiron(II) molecule [Fe(pc)] with different ligands is being extensively studied not only because it may contribute to a better understanding of the reactivity of the structurally related porphyrins, but also because phthalocyaninatometal complexes are known to exhibit catalytic properties.[1]

Solution studies, which in view of the low solubility of the complex have been mainly restricted to dimethyl sulphoxide (dmso) as solvent, have shown that [Fe(pc)] binds axially molecules such as O_2,[2] CO,[3,4] NO,[5] pyridine (py),[6] and imidazole (Him).[7–10] Except with dioxygen, which leads irreversibly to the formation of a μ-oxo-bis[phthalocyaninato-iron(III)] derivative,[2,11] all other ligands (including dmso) bind reversibly,[3–10] so that both rate and equilibrium constants can be measured.

Although several literature reports are indeed available on both the equilibrium and kinetic aspects of the reactions (1) and (2) (free solvent omitted; throughout this paper equilibrium and kinetic constants will have the same symbols as used for the corresponding quantities in ref. 6), the results are somewhat conflicting with one another.[7–10] Contradictory conclusions reported for the analogous reaction with py were demonstrated by us to be due to a misinterpretation of spectroscopic data.[6]

$$[Fe(pc)(dmso)_2] + Him \underset{k_{1r}'}{\overset{k_{1f}'}{\rightleftharpoons}} [Fe(pc)(dmso)(Him)] \qquad (1)$$

$$[Fe(pc)(dmso)(Him)] + Him \underset{k_{1r}''}{\overset{k_{1f}''}{\rightleftharpoons}} [Fe(pc)(Him)_2] \qquad (2)$$

Following our current interest in this field, we have reinvestigated the reaction of $[Fe(pc)(dmso)_2]$ with Him, from both thermodynamic and kinetic points of view, providing evidence that some of the published data on this system[7–10] should be revised. The Him binding properties of $[Fe(pc)(dmso)_2]$ here reported have been analysed in parallel with those concerning py.[6]

Experimental

Materials.—Phthalocyaninatoiron(II) was an Eastman Kodak product and was purified as previously described.[3] Dimethyl sulphoxide (Merck AG, spectrograde) was distilled under reduced pressure over CaH_2 before use. Imidazole (Fluka AG) was recrystallised twice from toluene and dried under vacuum.

Equilibrium Measurements.—The Him binding was monitored spectrophotometrically at 426 and 662 nm where relatively large absorbance changes following the addition of the base to a dmso solution of [Fe(pc)] are observed (see below). A Varian Cary 219 instrument, equipped with a water-circulating thermostatting system, was used. A typical procedure was as follows: a spectrophotometric cell of suitable length (1 or 5 cm) was filled with a known volume (3 or 25 ml, respectively) of a dmso solution of [Fe(pc)] in the concentration range 2×10^{-7} — 1×10^{-5} mol dm^{-3} {an accurate value of the [Fe(pc)] concentration was obtained from the absorption at 653 nm ($\varepsilon = 7.49 \times 10^4$ dm^3 mol^{-1} cm^{-1})}.[12] As already reported,[2] there is no evidence of $[\{Fe(pc)\}_n]$ polymerisation in dmso, and therefore all the experiments reported here refer to the monomeric species [Fe(pc)]. A dmso solution of Him of known concentration was then added by means of a microsyringe. Added volumes were always negligible with respect to the starting volume and did not require any correction for dilution. At the [Fe(pc)] concentrations used in this work, the fraction of Him bound to the iron was always negligible compared to the total ligand concentration. After thermal equilibration (5 min) at 20.0 °C, the spectrum was recorded from 400 to 700 nm and the absorbance changes at 426 and 662 nm analysed as described below.

Further experimental details are reported in ref. 6.

Kinetic Measurements.—The kinetic processes which follow the addition of Him to $[Fe(pc)(dmso)_2]$ were studied spectro-

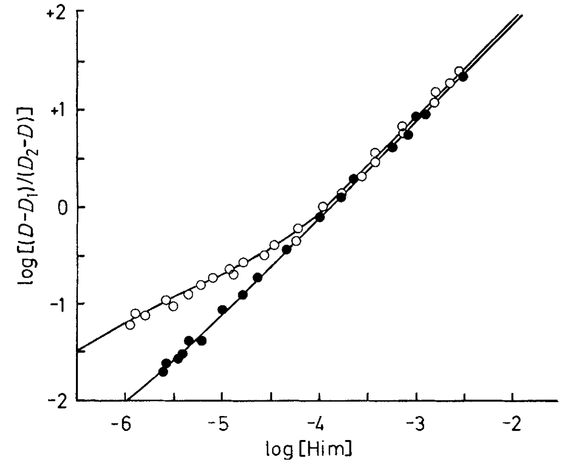

Figure 1. Plot of log$[(D - D_1)/(D_2 - D)]$ *versus* log[Him] at 662 (○) and 426 nm (●). Temperature 20 °C

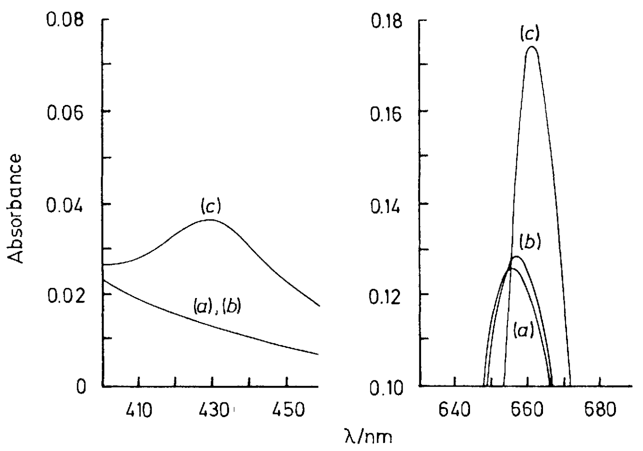

Figure 2. Spectra of a 1.6×10^{-6} mol dm^{-3} dmso solution of [Fe(pc)] in the absence (*a*) as well as in the presence of 3.0×10^{-6} (*b*) and 0.1 mol dm^{-3} (*c*) imidazole in the ranges 400—460 and 650—670 nm. Temperature 20 °C

photometrically by both stopped-flow and conventional techniques at 426 and 662 nm, and 20.0 °C.

Fast kinetics were studied on a Durrum-Gibson rapid-mixing stopped-flow apparatus, whilst conventional runs were monitored on a Varian Cary 219 instrument. The concentration of base was always in large excess ($\geqslant 50$ times) over the concentration of the iron complex. In all cases excellent first-order plots were obtained with excess of Him.

Further experimental details are given in ref. 6.

Results and Discussion

Equilibrium Measurements.—The optical changes measured on addition of Him to [Fe(pc)(dmso)$_2$] solutions are reported in Figure 1 as log$[(D - D_1)/(D_2 - D)]$ *versus* log[Him] (D_1 is the absorbance at the start, D that at a given concentration of free Him, and D_2 that after complete replacement of axial dmso).[6] At [Him] $> 1 \times 10^{-4}$ mol dm^{-3}, the observations at 426 and 662 nm lay on two parallel and very close straight lines of unit slope ($n = 1.00 \pm 0.02$). For lower Him concentrations the plot at 426 nm is still linear while that at 662 nm shows a marked deviation.

For a two-step equilibrium such as that shown in equations (1) and (2), equation (3) holds (see Appendix), where K_1' and

$$\frac{D - D_1}{D_2 - D} = \frac{K_1'[\mathrm{Him}](\varphi + K_1''[\mathrm{Him}])}{1 + K_1'[\mathrm{Him}](1 - \varphi)} \qquad (3)$$

K_1'' are the apparent equilibrium constants of reactions (1) and (2), and $\varphi = (\varepsilon_i - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1)$, ε_1, ε_i, and ε_2 are the molar absorbances of [Fe(pc)(dmso)$_2$], [Fe(pc)(dmso)(Him)], and [Fe(pc)(Him)$_2$], respectively.

The logarithmic plot of $(D - D_1)/(D_2 - D)$ as a function of log[Him] is expected to be an S-shaped curve with two linear asymptotes of slope 1 and $\log(K_1'\varphi)$ and $\log[K_1''/(1 - \varphi)]$ as intercepts for the limiting conditions [Him] $\longrightarrow 0$ and [Him] $\longrightarrow \infty$, respectively.

For a given value of the ratio K_1'/K_1'' the relative position of the linear asymptotes is, thus, determined by the product $\varphi(1 - \varphi)$, nevertheless the asymptote reached for [Him] $\longrightarrow 0$ will always refer to the first substitution equilibrium.

The shape of the plot shown in Figure 1 ($\lambda = 662$ nm) definitely indicates that $K_1'\varphi > K_1''/(1 - \varphi)$. A non-linear least-squares procedure applied to the logarithmic plot of Figure 1 gives $K_1' = (6.4 \pm 2.6) \times 10^5$ dm^3 mol^{-1}, $K_1'' = (7.4 \pm 0.5) \times 10^3$ dm^3 mol^{-1}, and $\varphi = 0.112 \pm 0.025$ (uncertainties are standard deviations). Any significant ($\pm 20\%$) change in one of the estimated parameters results in a considerable decrease of the accuracy of fitting.

The data measured at 426 nm are consistent with an absorption of the mixed complex [Fe(pc)(dmso)(Him)] very close to that of [Fe(pc)(dmso)$_2$] at this wavelength. If $\varphi \approx 0$, the first asymptote is reached at extremely low Him concentrations, well below the range explored. Indeed, good agreement between the experimental points and the calculated curve is obtained (see Figure 1) using the above reported values $K_1' = 6.4 \times 10^5$ dm^3 mol^{-1} and $K_1'' = 7.4 \times 10^3$ dm^3 mol^{-1} with a best-fit value $\varphi = 0.01$.

Spectra obtained under suitably selected conditions are shown in Figure 2, where the spectrum of a 1.6×10^{-6} mol dm^{-3} [Fe(pc)] solution is reported in the absence of Him [spectrum (*a*)], as well as in the presence of 3.0×10^{-6} [spectrum (*b*)] and 0.1 mol dm^{-3} [spectrum (*c*)] free imidazole. While spectra (*a*) and (*c*) correspond to [Fe(pc)(dmso)$_2$] and [Fe(pc)(Him)$_2$], respectively, 65% of the iron complex of spectrum (*b*) is calculated to be in the mixed form [Fe(pc)(dmso)Him)], according to the values of K_1' and K_1'', the remaining fraction being essentially [Fe(pc)(dmso)$_2$]. Since the increase in absorbance at 662 nm, caused by a 65% conversion into [Fe(pc)(dmso)(Him)], is 9% of the overall change for the substitution of both dmso molecules, φ may be calculated to be 0.13 in good agreement with the above best-fit value (0.112). On the contrary, no appreciable differences appear at 462 nm between the spectrum of the bis(dimethyl sulphoxide) adduct and that of the monoimidazole derivative. Thus, the increase in absorbance at 426 nm is related only to the substitution of both axial dmso by Him. This behaviour is not surprising since it has been observed in the closely related substitution of axial dmso in [Fe(pc)(dmso)$_2$] by py.[6]

Kinetic Measurements.—In complete agreement with the equilibrium observations discussed above, the time dependence of the absorbance of a dmso solution of [Fe(pc)] in the presence of Him at 662 nm shows two distinct decays of different amplitudes. The time-scales of the two processes are so different that they can be analysed without any interference. In the presence of excess of Him {typically, [Fe(pc)] $= 1.0 \times 10^{-5}$ mol dm^{-3}; $5.0 \times 10^{-2} >$ [Him] $> 4.0 \times 10^{-4}$ mol dm^{-3}}, both processes conform to a first-order rate law. The observed rate constants $k_{\mathrm{obs.}}'$ and $k_{\mathrm{obs.}}''$ are reported in Figure 3 as a function of [Him]. Again, at the highest *N*-base concentrations where the conversion into the bis-adduct is virtually complete, the

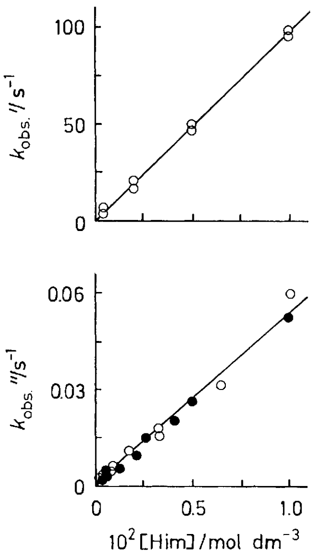

Figure 3. Observed rate constants for the reactions (1) and (2). The top panel shows the fast process observable at 662 nm, the bottom panel the slow process observable at 662 (○) and at 426 nm (●). Stopped-flow runs at [Him] = 5.0×10^{-2} mol dm^{-3}, not shown in the bottom panel for graphical reasons, agree very well with those at lower base concentrations. Temperature 20 °C

Table. Equilibrium and kinetic data (at 20 °C) for the reaction:

$$[Fe(pc)(dmso)L] + Y \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} [Fe(pc)L(Y)] + dmso$$

L	Y	$K_1{}^a$/ dm^3 mol^{-1}	$k_{1f}{}^b$/dm^3 mol^{-1} s^{-1}	$k_{1r}{}^b$/s^{-1}	Ref.
dmso	py	4.0×10^5	$\approx 1.5 \times 10^4$	$\approx 4 \times 10^{-2}$	4
dmso	Him	6.4×10^5	9.8×10^3	1.5×10^{-2}	This work
py	py	3.0×10^2	36	0.15	4
Him	Him	7.4×10^3	5.4	7.3×10^{-4}	This work

[a] $K_1 = K_1'$ or K_1'', as defined in this work. [b] $k_{1f} = k_{1f}'$ or k_{1f}'', and $k_{1r} = k_{1r}'$ or k_{1r}'', as defined in this work.

change in absorbance related to the first substitution is found to be 10 ± 3% of the overall change (*i.e.* including the second substitution step). Both $k_{obs.}'$ and $k_{obs.}''$ show a linear dependence on Him concentration, according to equations (4) and (5). The least-squares analysis of the data yields $k_{1f}' = (9.8 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_{1f}'' = 5.4 \pm 0.15$ dm^3 mol^{-1}

$$k_{obs.}' = k_{1f}'[\text{Him}] + k_{1r}' \quad (4)$$

$$k_{obs.}'' = k_{1f}''[\text{Him}] + k_{1r}'' \quad (5)$$

s^{-1}, whilst both intercepts k_{1r}' and k_{1r}'' are undertermined (statistical values: 1 ± 1 and $(1 \pm 1) \times 10^{-3}$ s^{-1}, respectively) (uncertainties are standard deviations).

Kinetic measurements have also been carried out at 426 nm and, consistent with the spectral results shown in Figure 2, only one exponential process could be detected at this wavelength, which has to be related to the entry of the second Him. Figure 3 shows that the observed rate constants measured at 426 nm under pseudo-first-order conditions nicely overlap with those measured at 662 nm for the slowest step, thus confirming the assignment of the process.

As both reactions (1) and (2) are reversible, the quantities k_{1f} and k_{1r} may be identified with the forward and the reverse constants, respectively, of the related processes. If the equilibrium constants are used together with k_{1f}' and k_{1f}'', the values $k_{1r}' = 1.5 \times 10^{-2}$ s^{-1} and $k_{1r}'' = 7.3 \times 10^{-4}$ s^{-1} are obtained; these values are too low to allow a direct determination from kinetic experiments, and are consistent with the least-squares intercepts calculated above.

Conclusions

Reactions (1) and (2) have been the subject of previous investigations by several authors from both equilibrium and kinetic points of view.[7–10] Jones and Twigg[7] reported that reaction (1) is rate limiting with a second-order rate constant of 2.3 dm^3 mol^{-1} s^{-1} at 20 °C. Essentially the same conclusion was reached by Bennetto *et al.*[8] on the basis of a study carried out over a much wider imidazole concentration range (up to 1.45 mol dm^{-3}). The apparent equilibrium constants $K_1' = 3.5 \times 10^3$ dm^3 mol^{-1} and $K_1'' = 6.3 \times 10^3$ dm^3 mol^{-1} were also quoted in ref. 7. In a subsequent paper Jones and Twigg[9] reported $K_1' = 1 \times 10^5$ dm^3 mol^{-1} and confirmed $K_1'' = 6.3 \times 10^3$ dm^3 mol^{-1}. Furthermore, a paper by Kadish *et al.*[10] describes the axial substitution of both dmso ligands by Him as occurring within a single observable step. This would obviously require that $K_1'' \gg K_1'$, contrary to previous reports.[7–9]

A comparison with present data shows that our K_1'' is reasonably close to the value quoted in refs. 7 and 9 while the present result for K_1' disagrees with previous reports, especially with the value given in ref. 7. Furthermore, our kinetic results indicate that the second-order process assigned in refs. 7 and 8 to reaction (1) instead refers to reaction (2).

The results presented in this paper and shown in the Table definitely demonstrate that the substitution of the axial dmso molecules of $[Fe(pc)(dmso)_2]$ is a stepwise process, correctly described by the overall equations (1) and (2), with the binding of the first imidazole occurring more rapidly and being thermodynamically favoured with respect to the binding of the second Him.

This antico-operative behaviour seems to represent a common feature for various stepwise substitution processes and, in particular, is closely similar to the behaviour of the $[Fe(pc)(dmso)_2]$–py system which has been the subject of a previous investigation.[6] As with pyridine,[6] the entry of the first imidazole into the co-ordination sphere of iron(II) causes only minor spectral changes, limited to the high-intensity charge-transfer band centred at 662 nm; these changes may well remain undetected unless a special effort is made to reveal them. The absence of any detectable effect of the first Him–dmso substitution in the blue region is also deceptive, since it might reinforce the idea that both reactions (1) and (2) occur in a single step. This is likely to be the explanation for most of the discrepancies in the literature, while the results described by Kadish *et al.*,[10] obtained with an experimental procedure very similar to ours, are still puzzling. Also unexplained is the difference of a factor of 2 between our result for k_{1f}'' and the rate constant quoted in ref. 7, for the same process [*i.e.* reaction (2)].

The Table reports the equilibrium and kinetic data for the substitution of an axial dmso in [Fe(pc)(dmso)L] by Y (L = inert, *trans* dmso or *N*-base, and Y = py or Him).

It has been proposed that axial substitutions of porphyrin and phthalocyanine derivatives are essentially dissociative with the formation of a highly reactive, five-co-ordinated intermediate,[13–17] so that the overall ligand substitution may be dissected into the steps (6) and (7).

$$[Fe(pc)(dmso)L] \underset{k_{+dmso}}{\overset{k_{-dmso}}{\rightleftharpoons}} [Fe(pc)L] + dmso \quad (6)$$

$$[Fe(pc)L] + Y \underset{k_{-Y}}{\overset{k_{+Y}}{\rightleftharpoons}} [Fe(pc)L(Y)] \quad (7)$$

It is readily demonstrated that if the observed pseudo-first-order rate constant has the form $k_{obs.} = k_{1f}[Y] + k_{1r}$ (such as in Figure 3), then $k_{1f} = k_{-dmso}k_{+Y}/k_{+dmso}[dmso]$ and $k_{1f} = k_{-Y}$. Furthermore since the labile intermediate is expected to be poorly selective ($k_{+dmso} \approx k_{+Y}$), then $k_{1f} \approx k_{-dmso}/[dmso]$. Some doubts have been put forward on a generalisation of the latter condition when Y = CO;[4] nevertheless, for the cases reported in the Table, the discrimination factor k_{+dmso}/k_{+Y} should not be very different from unity. Thus, the rate constants appearing in the Table suggest the following lability sequence:
(dmso)(dmso) ≫ (py)(dmso) ≈ (Him)(dmso) ≫ (py)(py) ≈
3×10^8 7×10^5 1×10^5 2×10^2
(dmso)(py) ≈ (dmso)(Him) > (Him)(Him); where only *trans*
60 20 1
(left hand) and leaving (right hand) ligands are shown and the numbers are rounded-off rate constants, k_{-dmso} or k_{-Y}, normalised to the slowest process.

Dimethyl sulphoxide is confirmed as the most labile ligand, very likely as a consequence of a comparatively weaker S–Fe σ bond.[6] It has been suggested[4] that the almost 500-times labilising effect of the (S-bonded) *trans*-dmso over *trans*-py on (S-bonded) leaving dmso is due to the mutual destabilisation of the axial ligands competing for the metal electrons through π-back bonding. If so, it is not surprising that dmso *trans* to imidazole is nearly as labile as dmso *trans* to pyridine, while the still lower lability of both py and Him *trans* to dmso may be explained by the greater strength of the Fe–N σ bond.

The relative positions of $[Fe(pc)(py)_2]$ and $[Fe(pc)(Him)_2]$, the first being 200 times more labile than the second, are not readily rationalised but it is worth noting that a similar situation has been found in acetone[17] where the release of *N*-base is 400 times faster for the first complex.

Indeed, a more complete study of the axial reactivity at the [Fe(pc)] moiety is required before any rationalisation of the structural effects can be made and to this purpose we are now extending this investigation to include an appropriate selection of ligands.

Appendix

The reactions (1) and (2) may be schematically represented as in (A1) and (A2) with A, B, and C standing for the bis-(dimethyl sulphoxide), monoimidazole, and bis(imidazole) derivatives, respectively. Hence expressions (A3) and (A4) are obtained.

$$A + Him \rightleftharpoons B \qquad (A1)$$

$$B + Him \rightleftharpoons C \qquad (A2)$$

$$K_1' = [B]/[A][Him] \qquad (A3)$$

$$K_1'' = [C]/[B][Him] \qquad (A4)$$

From equation (A5), involving the molar absorbances of A (ε_A), B (ε_B), and C (ε_C), the use of the mass-balance equation $[A]_0 = [A] + [B] + [C]$ leads to (A6) which can be rewritten as (A7) by using equations (A3) and (A4).

$$\frac{D - D_1}{D_2 - D} = \frac{\varepsilon_A[A] + \varepsilon_B[B] + \varepsilon_C[C] - \varepsilon_A[A]_0}{\varepsilon_C[A]_0 - \varepsilon_A[A] - \varepsilon_B[B] - \varepsilon_C[C]} \qquad (A5)$$

$$\frac{D - D_1}{D_2 - D} = \frac{[B](\varepsilon_B - \varepsilon_A) + [C](\varepsilon_C - \varepsilon_A)}{[A](\varepsilon_C - \varepsilon_A) + [B](\varepsilon_C - \varepsilon_B)} \qquad (A6)$$

$$\frac{D - D_1}{D_2 - D} = \frac{K_1'[Him] \cdot \dfrac{\varepsilon_B - \varepsilon_A}{\varepsilon_C - \varepsilon_A} + K_1'K_1''[Him]^2}{1 + K_1'[Him] \cdot \dfrac{\varepsilon_C - \varepsilon_B}{\varepsilon_C - \varepsilon_A}} \qquad (A7)$$

If $\varphi = (\varepsilon_B - \varepsilon_A)/(\varepsilon_C - \varepsilon_A)$, the ratio $(\varepsilon_C - \varepsilon_B)/(\varepsilon_C - \varepsilon_A)$ is equal to $1 - \varphi$, and equation (A7) becomes (A8), identical with equation (3) given in the text.

$$\frac{D - D_1}{D_2 - D} = \frac{K_1'[Him](\varphi + K_1''[Him])}{1 + K_1'[Him](1 - \varphi)} \qquad (A8)$$

Acknowledgements

The authors thank Professor Massimo Coletta for helpful discussions in the analysis of data.

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Received 28*th September* 1988; *Paper* 8/03859G