

A New Method for the Determination of the Stability Constant of Metalloporphyrins: Use of the Catalytic Effect of Mercury(II) on Metalloporphyrin Formation

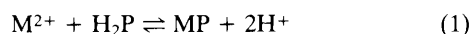
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The catalytic effect of the mercury(II) ion on metalloporphyrin formation provides the basis for determination of the stability constant of the zinc(II) porphyrin, the rate of formation of which is extremely slow in the absence of mercury(II).

The equilibrium between divalent metal ions (M) and free-base porphyrins (H₂P) forming metalloporphyrins (MP) may be represented by equation (1) (charges on porphyrins and metalloporphyrins are omitted throughout), with the equilibrium constant defined by equation (2). Because of the slow reaction of porphyrins with metal ions,¹⁻³ there have been few studies on equilibrium (1).^{4,5} The time required for the equilibration of zinc(II) with a porphyrin is reported to be about 50 h at 60 °C,⁶ while it is about 3 weeks for another porphyrin at 25.5 °C.⁷ Some porphyrins are gradually adsorbed on the surface of glassware during such a long period.



$$K = [MP][H^+]^2/[M^{2+}]^{-1}[H_2P]^{-1} \quad (2)$$

The incorporation into 5,10,15,20-tetrakis(4-sulphonatophenyl)porphine (H₄tspp) of medium-sized metal ions such as manganese(II), nickel(II), cobalt(II), copper(II), and zinc(II) was found to be accelerated in the presence of as low a concentration as 10⁻⁷ mol dm⁻³ of large metal ions such as cadmium(II), lead(II), and mercury(II).⁸⁻¹² Based on this finding, we have developed a new method for the determination of the stability constant of metalloporphyrins and determined the stability constant of Zn^{II}(tspp).

Because of the high stability of Zn^{II}(tspp), the stability constant was determined at pH 3.5, where H₂tspp is in the fully protonated form H₄tspp. A period of only 20 min is needed for the equilibration of zinc(II) (10⁻³ mol dm⁻³) with H₄tspp (10⁻⁶ mol dm⁻³) in the presence of 2.14 × 10⁻⁵ mol dm⁻³ of mercury(II) at pH 3.5 (chloroacetate buffer;

[ClCH₂CO₂⁻] + [ClCH₂CO₂H] = 2.0 × 10⁻³ mol dm⁻³), at 25 °C and with I = 0.1 mol dm⁻³ (NaNO₃).^{†‡} On the other hand, the time required for the equilibrium to be reached is >50 h in the absence of mercury(II) under the same conditions, and >20 days will be needed to attain equilibrium with 10⁻⁴ mol dm⁻³ of zinc(II).

$$\log \left\{ \frac{[Zn^{II}(tspp)]}{[H_4tspp]} \right\} + 4 \log [H^+] = \log K' + \log [Zn^{2+}] \quad (3) \ddagger$$

The equilibrium constant for the reaction of zinc(II) with H₄tspp, $K' = [Zn^{II}(tspp)][H^+]^4 \times [Zn^{2+}]^{-1}[H_4tspp]^{-1}$, leads to equation (3).[‡] At equilibrium absorption spectra of solutions containing various concentrations of zinc(II) (10⁻⁴–10⁻² mol dm⁻³) and H₂tspp (8.61 × 10⁻⁷ mol dm⁻³)

[†] Under the present experimental conditions, H₄tspp is in the monomeric form, and the formation of mercury(II) porphyrin is not appreciable as is evident from the stability constants [$\log K'' = -4.25 \pm 0.08$ for $K'' = [Hg_2(tspp)] \times [H^+]^4[Hg^{2+}]^{-2}[H_4tspp]^{-1}$ (M. Tabata and M. Tanaka, unpublished results) and $\log \beta_1 = 4.64$ for $\beta_1 = [Hg(ClCH_2CO_2)_2][Hg^{2+}]^{-1}[ClCH_2CO_2^-]^{-1}$ (A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum Press, New York, 1977, vol. 3, pp. 16–18)].

[‡] Units for [H⁺], [Zn²⁺], and K: mol dm⁻³; β₁, K₁, and K₂, mol⁻¹ dm³; K', mol³ dm⁻⁹; K'', mol² dm⁻⁶.

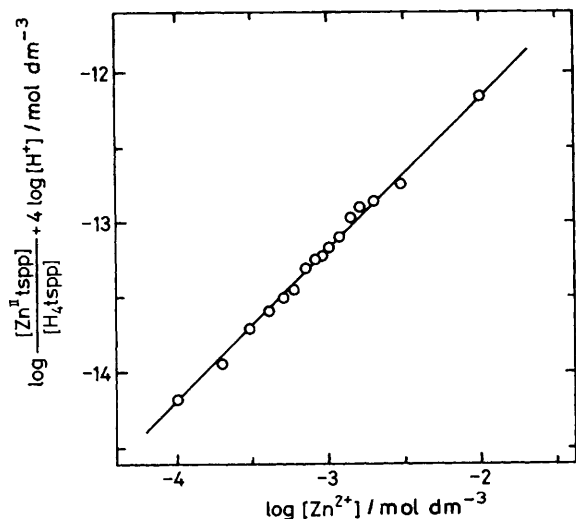


Figure 1. Plot of $\log \left(\frac{[\text{Zn}^{\text{II}}\text{tspp}]}{[\text{H}_4\text{tspp}]} + 4 \log [\text{H}^+] \right) / \text{mol dm}^{-3}$ vs. $\log [\text{Zn}^{2+}] / \text{mol dm}^{-3}$ for the reaction of H_4tspp with zinc(II) nitrate at 25°C and $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3).

exhibited a clear isosbestic point at 417 nm. A plot of the left-hand side of equation (3) vs. $\log [\text{Zn}^{2+}]$ (Figure 1) led to a value $\log K' = -10.19 \pm 0.03$. With protonation constants of H_2tspp determined in this work ($\log K_1 = 4.99 \pm 0.01$ for $K_1 = [\text{H}_3\text{tspp}][\text{H}_2\text{tspp}]^{-1}[\text{H}^+]^{-1}$; $\log K_2 = 4.76 \pm 0.02$ for $K_2 = [\text{H}_4\text{tspp}][\text{H}_3\text{tspp}]^{-1}[\text{H}^+]^{-1}$), $\log K$ defined by equation (2) for

the present system was found to be -0.43 ± 0.03 ($\log K = \log K' + \log K_1 + \log K_2$). This is $>10^9$ times as high as the corresponding values for cadmium(II) and lead(II) (-9.94 ± 0.04 and -9.97 ± 0.02 , respectively).¹³ Cadmium(II) and lead(II) are large and just 'sit' on the porphyrin nucleus, while medium-sized metal ions like zinc(II) fit well inside.¹²

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