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Kinetics of Porphyrin Metalation Reactions in Micellar Media. Singlet Emission Studies

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The kinetics of Cu^{2+}, Zn^{2+}, and Cd^{2+} incorporation reactions into *meso*-tetraphenylporphyrin (H_2TPP) have been studied in neutral and anionic surfactant media. Fluorescence spectroscopy employed in these investigations revealed many advantages in deriving the kinetic data. A general kinetic scheme is proposed that takes into account implicitly the influence of surfactant concentration and interphase effects on the rates of metal incorporation reactions. The enhancement of rates of porphyrin metalation reactions in micellar media relative to those found in homogeneous media is interpreted in terms of distribution of metal ions in the stern region of the micellar media. The relative rates of metal incorporation reactions in SDS micelles for different metal ions are found to follow the order $Cu^{2+} > Zn^{2+} > Cd^{2+}$. On the basis of the magnitude of protonation constant (pK_3) of H_2TPP in SDS micelles, a mechanism similar to that proposed in homogeneous media is advanced for the metal incorporation reaction in the micellar media.

Introduction

Studies on porphyrin metalation reactions are of considerable importance owing to the widespread occurrence of metalloporphyrins in biological systems. The kinetics of metal incorporation into the free-base porphyrins has been the subject of numerous investigations.[1] Most of the studies have been carried out in diverse homogeneous media, and a few studies have been reported in micellar media. Optical absorption spectroscopy has been used to follow the rate of the porphyrin metalation reaction in these studies. Employment of membrane mimetic agents, viz. micelles, vesicles, and monolayers, as the media for the study of these reactions provides appropriate biomimetic models since biological reactions are often mediated by membrane systems. Moreover, chemical reactions studied in surfactant media exhibit enhanced rates as well as inhibition of reactions.[2] Here, we report studies on kinetics of metalation reactions of porphyrins in micellar media and delineate the influence of the local microenvironment in enhancing the rates of metalation reactions of porphyrins.

The kinetics of metal incorporation into the free-base 5,10,15,20-tetraphenylporphyrin (H_2TPP) in homogeneous media has been interpreted on the basis of an associative mechanism.[1b] The rate law of Cd^{2+} insertion into the porphyrin is depicted as

$$H_2TPP + M^{2+} \overset{K}{\rightleftharpoons} M^{2+}\text{--}H_2TPP \xrightarrow{k_1} M(TPP) + 2H^+$$

$$\text{rate} = k_1 K[M^{2+}][H_2TPP] \qquad (1)$$

indicating first-order dependence with respect to the free-base and metal ion concentrations, while for the Cu^{2+} and Zn^{2+} incorporation in DMF an additional step

$$M^{2+}\text{--}H_2TPP + M^{2+} \xrightarrow{k_2} M(TPP) + 2H^+ + M^{2+}$$

is involved. The rate law is formulated as

$$\text{rate} = \frac{K[M^{2+}](k_1 + k_2[M^{2+}])}{1 + K[M^{2+}]}[H_2TPP] \qquad (2)$$

showing that the order with respect to the free-base concentration is 1. The dependence of rate on metal ion concentration is reported to be complex. The rate law (eq 2) is particularly useful since it covers a wide range of concentrations of metal ions. It can be seen that, over a limited concentration range, this rate expression is reduced to simpler forms resembling those proposed by other workers.[3] Introduction of micellar media in these reactions compel us to consider additional features, viz. (i) micellization of the free-base porphyrin, (ii) distribution of metal ions on the surface of the micelles, and (iii) the rate of metal ion permeability into the micellar space. We have developed a consistent kinetic scheme to explain the observed rates of incorporation of metal ions into the porphyrins.

The advantageous use of fluorescence spectroscopy for monitoring the rates of metal incorporation into H_2TPP has been exploited in the present study. Fluorescence spectroscopy has earlier been used by Lavallee et al.[4] for the estimation of low concentrations of porphyrins, and Das[1k] employed this technique for studying the metalation reactions of porphyrins in homogeneous media. The usage of this low-concentration technique permits one to keep the $[H_2TPP]/[\text{micelle}]$ ratio at very low values so as avoid possible dimerization or oligomerization of porphyrins. Moreover, the fluorescence spectral method offers a distinct feature that the singlet emission bands of H_2TPP on metalation either decreases in the intensity of the emission bands and/or shifts the fluorescence emissions. In the present study we investigated the rates of Cu^{2+}, Zn^{2+}, and Cd^{2+} incorporation into H_2TPP. Two types of surfactants, viz. an anionic (sodium dodecyl sulfate, SDS) and a neutral (Triton X-100) surfactant, are employed to demonstrate the effect of the nature of the surfactants on the kinetics of metal incorporation reactions. The employment of fluorescence spectroscopy as a tool to monitor the rates of metalation reactions has provided a valuable method for the study of kinetic features of these reactions.

Experimental Section

Materials. H_2TPP has been prepared according to the method of Rothemund et al.[5] and purified by using the procedure described by Barnett et al.[6] Metallotetraphenylporphyrins(MTPP) were prepared and purified by using the methods described in the literature.[7] SDS, procured from BDH, has been purified by washing it with ether and recrystallizing from ethanol.[2a] Triton X-100, from Aldrich Chemicals, was used as received. The metal carriers $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $CdSO_4 \cdot 8H_2O$, $Cd(OAc)_2 \cdot 2H_2O$, and (2,4-pentanedionato)zinc(II) (Zn(acac)) employed in the study are analytically pure. The aqueous me-

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(3) References 1d, 1e and 1j. These studies are limited to a narrow concentration range of metal ions. The order in the porphyrin metalation reactions in such systems is either unity or fractional with respect to metal ion. These studies provide evidence for the formation of a complex between metal ion and porphyrin from the Michaeli–Menten plots.

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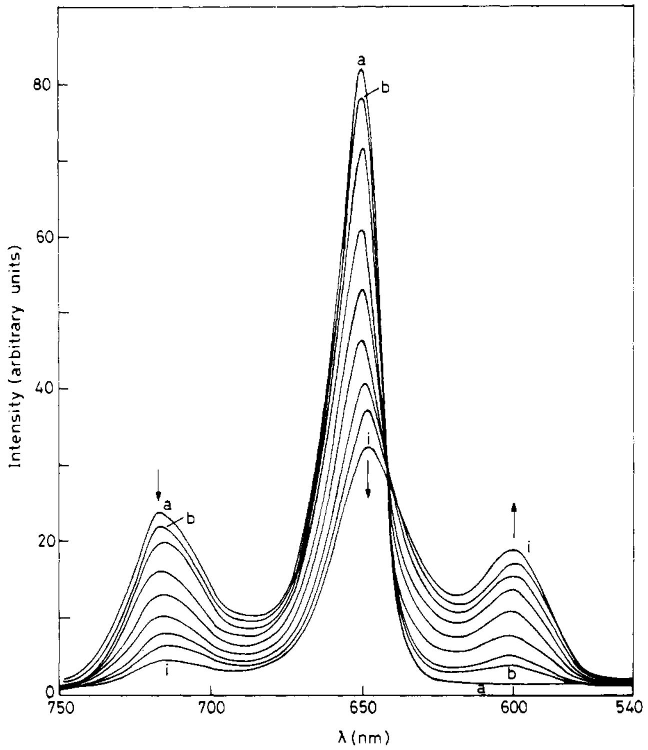

Figure 1. Singlet emission spectra of H_2TPP in presence of Zn^{2+} at various time intervals at 25 °C in SDS medium ($[H_2TPP] = 4.2 \times 10^{-8}$ M; $[Zn^{2+}] = 4.0 \times 10^{-2}$ M; [SDS] = 0.03 M): a = 0; b–i = 5–100 min.

dium employed in the study is made up of doubly distilled water.

A Hitachi (650–60) fluorescence spectrophotometer has been used to monitor the fluorescence emission of the porphyrins. A Beckman Model 25 UV–vis spectrophotometer has been used for the absorption spectral studies.

Method. H_2TPP was micellized by using the following procedure. A 1-mg sample of H_2TPP was dissolved in 250 mL of acetone to obtain a 6.0 μM stock solution. The concentration of H_2TPP in homogeneous medium is determined from the optical absorbance values of the visible-absorption bands. This solution was diluted further to get 0.5 μM H_2TPP in acetone. A 10-mL aliquot of this solution was solubilized in 2.6% aqueous SDS, and the acetone was allowed to evaporate on a water bath. A concentration ratio of $[H_2TPP]/[\text{micelle}]$ is maintained at ~ 10^{-4} to ensure complete micellization. The aqueous solutions of metal salt and H_2TPP in the micellar medium were equilibrated separately at 42.5 °C. The rate measurements were carried out by monitoring the intensity changes of the emission bands of H_2TPP in solutions containing 1 mL of the aqueous metal salt solution and 4 mL of H_2TPP in SDS at various time intervals. The emission intensity of the H_2TPP in SDS were measured independently and these serve as blank data. The effect of ionic strength on the rates of the porphyrin metalation reactions was investigated by using various concentrations of aqueous sodium perchlorate solution. The dependence of hydrogen ion concentration on the rates of these reactions was determined by using different concentrations of perchloric acid. It may be noted that employment of buffers to maintain hydrogen ion concentration leads to either formation of precipitates or complete inhibition of reaction. Thus, phosphate buffers result in the precipitation of metal ions while in citrate and tris buffers, no porphyrin metalation reactions proceed in SDS micellar medium. The protonation constant of H_2TPP in SDS micellar solutions was determined from the changes in the emission intensity at 680 nm upon titration with hydrochloric acid.

Results and Discussion

The fluorescence spectra of H_2TPP, ZnTPP, and CdTPP in SDS reveal that the free-base porphyrin (H_2TPP) exhibits two emission bands at 650 and 716 nm while in ZnTPP and CdTPP the positions of these bands are blue shifted respectively to 600 and 650 nm. CuTPP in SDS does not exhibit any fluorescence bands because of spin–orbit coupling of Cu(II), which promotes fast isc. It is found that the intensities of the 650- and 716-nm emissions of H_2TPP increase linearly with the increase in concentration of H_2TPP (range 0–0.1 μM), thereby permitting the evaluation of H_2TPP concentration as a function of fluorescence intensity. A typical fluorescence spectra of H_2TPP in the presence of Zn^{2+} ions in SDS at different time intervals is shown in Figure 1. The kinetic data for Zn(II) and Cd(II) incorporation into H_2TPP in SDS have been obtained by following the changes in intensity of the 716-nm emission of H_2TPP as a function of time, while the decrease in intensity of the 650-nm emission of H_2TPP was chosen for studying the rates of Cu(II) incorporation. The assertion that the decrease in intensity of the fluorescence bands of H_2TPP on metalation is caused only by the formation of M(TPP) is justified as follows: (i) The presence of a heavy metal ion quenching mechanism (of H_2TPP emission) can be ruled out since the half-lives of these reactions[8] are much shorter (μs) than those of metal incorporation reactions (min). (ii) With the advent of ZnTPP and CdTPP formation during metalation, the intensity of the 600-nm emission of ZnTPP and CdTPP increases while the emission intensity of H_2TPP at 716 nm decreases in a proportionate fashion. (iii) The optical absorption spectra of the SDS solutions at the termination of metal incorporation reactions correspond to the spectra of the M(TPP)'s in SDS micelles.

Table I. Pseudo-First-Order Rate Constants for the Incorporation of Metal Ions into the Free-Base Tetraphenylporphyrin in Micellar Media ($[H_2TPP] = 4.2 \times 10^{-8}$ M; $T = 42.5$ °C)

surfactant	metal carrier	concn of metal carrier, $\times 10^3$ M	pseudo-first-order rate const, k', $\times 10^5$[a] s^{-1}
SDS[b]	$CuSO_4{\cdot}5H_2O$	0.10	86
		0.25	225
		0.50	430
		1.00	862
		1.50	1320
		2.00	1700
	$ZnSO_4{\cdot}7H_2O$	10.0	7.0
		20.0	13.0
		40.0	26.3
		60.0	38.3
		80.0	53.7
	Zn(acac)[d]	40.0	1920
	$CdSO_4{\cdot}8H_2O$	8.8	0.260
		17.5	0.485
		35.0	1.037
		52.5	1.608
		70.0	2.087
	$Cd(OAc)_2{\cdot}2H_2O$	8.8	15.0
		17.5	28.9
		35.0	56.6
		52.5	87.0
		70.0	112.0
Triton X-100[c]	$CuSO_4{\cdot}5H_2O$	1.00	0.189
	$ZnSO_4{\cdot}7H_2O$	40.0	0.050
	$Cd(OAc)_2{\cdot}2H_2O$	35.0	0.031

[a] The errors associated with the rate constants determined are within ±10%. [b] [SDS] = 0.03 M. [c] [Triton X-100] = 2.0% (w/w). [d] In 30% (v/v) dioxane water mixture.

The linearity of the plot of log $[H_2TPP]$ vs. time for different metal(II) incorporation reactions (Figure 2) indicates the pseudo-first-order nature of the reactions. The pseudo-first-order rate constants (k') of these reactions were calculated at different metal ion concentrations (Table I) by using linear least-squares analysis. A plot of k' vs. the metal ion concentrations (Figure 3) is found to be a straight line passing through the origin, suggesting that the order of the reaction with respect to metal ion concentration is 1. The pseudo-first order rate constants obtained at different ionic strengths and at different hydrogen ion concentrations are

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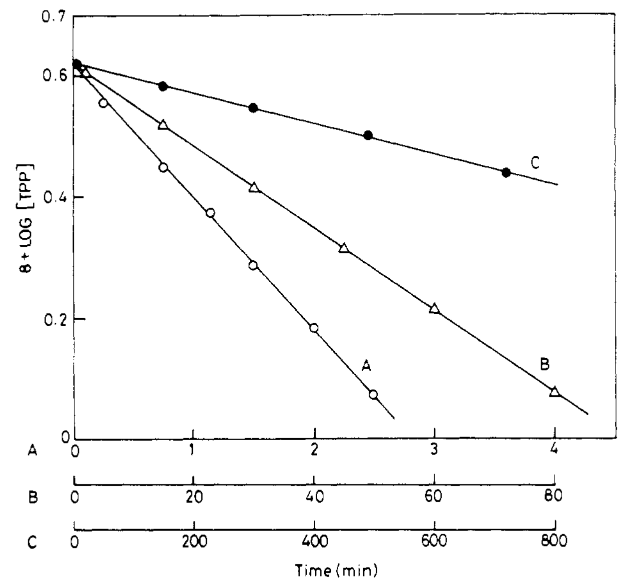

Figure 2. Pseudo-first-order plots of metal incorporation into H_2TPP in SDS micelles ([SDS] = 3.0×10^{-2} M): (A) [Cu^{2+}] = 1.0×10^{-3} M; (B) [Zn^{2+}] = 4.0×10^{-2} M; (C) [Cd^{2+}] = 3.5×10^{-2} M. The metal carriers employed are sulfates of the respective metal ions.

Table II. Effect of Ionic Strength (μ) and pH on the Zn^{2+} Insertion Reaction Rates ([H_2TPP] = 4.2×10^{-8} M; [SDS] = 0.03 M; T = 42.5 °C; [Zn^{2+}] = 0.04 M[a])

ionic strength (μ), M ($NaClO_4$)	pH	pseudo-first-order rate const, k', $\times 10^5$[b] s^{-1}
0.00	6.5	24.9
0.05	6.5	25.6
0.10	6.5	26.2
0.20	6.5	25.8
0.25	6.5	26.3
	5.6	23.3
	5.0	20.6
	4.6	17.1
	3.6	4.1
	3.0	2.4

[a] $ZnSO_4 \cdot 7H_2O$ is used. [b] The errors associated with the rate constants determined are within ±10%.

presented in Table II. The protonation of H_2TPP can be represented as

$$H_2TPP \underset{K_3}{\overset{H^+}{\rightleftharpoons}} H_3TPP^+ \underset{K_4}{\overset{H^+}{\rightleftharpoons}} H_4TPP^{2+} \quad (3)$$

The reciprocal of the fluorescence intensity of H_2TPP at 680 nm is found to depend linearly on the reciprocal of [H^+] (Figure 4). This indicates the monoprotonation of H_2TPP in SDS medium with a pK_3 value of 2.52. It may be noted that the protonation constant (p$K_{3,4}$) of H_2TPP in neutral Triton X-100 micellar medium is half of that observed in the anionic SDS medium.

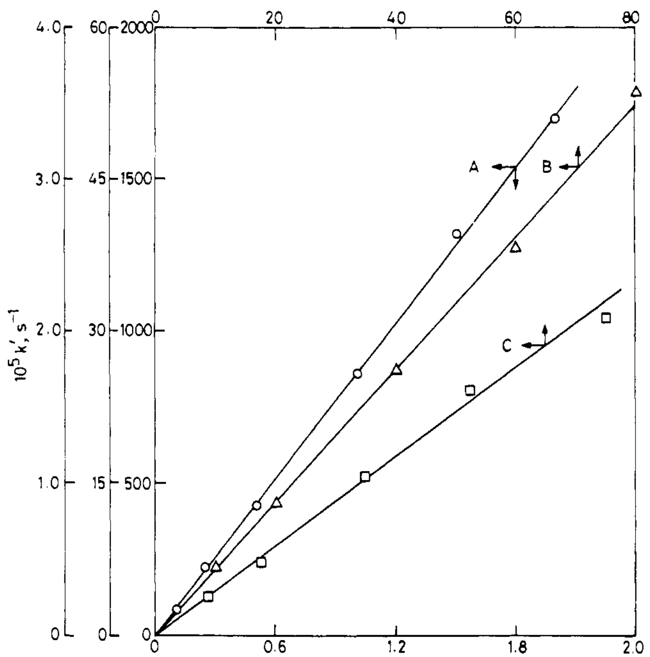

Figure 3. Effect of metal ion concentration on the pseudo-first-order rate constant, k' ([SDS] = 3.0×10^{-2} M; [H_2TPP] = 4.2×10^{-8} M): (A) Cu^{2+}; (B) Zn^{2+}; (C) Cd^{2+}.

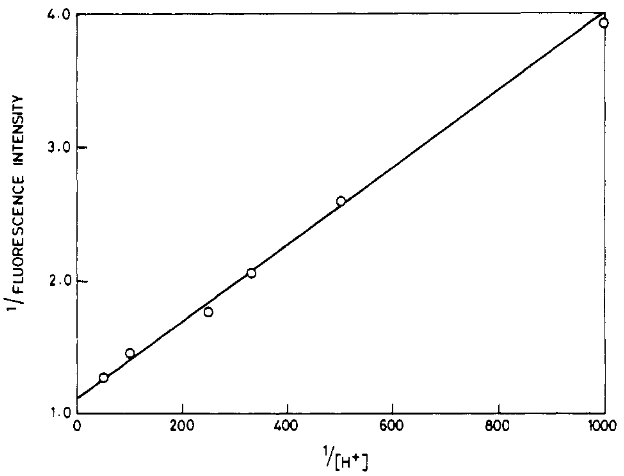

Figure 4. Effect of acid concentration on the fluorescence emission intensity of H_2TPP ([SDS] = 3.0×10^{-2} M; [H_2TPP] = 4.2×10^{-8} M).

An examination of the magnitudes of the rate constants obtained in the present study reveals that the metal incorporation rates in SDS micelles are much faster than that obtained in homogeneous media,[9] indicating the influence of the micellar phase in the enhancement of the reaction rates. This can be visualized as follows: The micellar phase preferentially partitions the neutral H_2TPP molecules into the hydrophobic interior. The metal ions under the present experimental conditions of neutral pH exist as bipositive metal ions[10] and are disposed at the exterior surface of the micelles through Coulombic interactions with the negative end of the anionic micelles. Such a situation would warrant that the reaction extensively takes place at the surface of the micelle, i.e. in the stern region. This derives support from the observation that the metal incorporation reactions in anionic SDS micellar solutions are much faster than those observed in neutral Triton X-100 (Table I). The manner by which the SDS micelles alter the metal incorporation rates into H_2TPP can then be considered. Before the proposition of a mechanism it is instructive to enquire about the nature of the reactive species and the role of pH on the magnitudes of k'. A perusal of Table II reveals that ionic strength has no effect on k', indicating the reactive species taking part in the metalation reaction is the neutral H_2TPP.[11] It is noted that

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(9) A comparison of the values of rate constants of metal incorporation reactions obtained in homogeneous media as reported in the literature is not possible because the method is different and also the experimental conditions employed are not commensurate. However, it is found that the rate constants for Cu^{2+} and Zn^{2+} incorporation into H_2TPP in dioxane–water medium (30% v/v) determined by fluorescence spectroscopy are negligibly small (<10^{-8} s^{-1}).

(10) In neutral aqueous solutions, these metal ions will exist as Cu^{2+}, Cd^{2+}, and Zn^{2+}. The pK_1 values of the hydrolysis are 8.0 (Cu), 9.9 (Cd), and 9.0 (Zn): Perrin, D. D. Boyd Dempsey "Buffers for pH and Metal Ion Control"; Chapman and Hall: London, 1974.

(11) Generally, addition of large quantities of electrolytes (to maintain constant ionic activity) to the micelles influence (i) cmc, (ii) aggregation number, (iii) pK_3 values, and (iv) counterion effects. However, in view of the constancy of rate constants at different ionic strengths, we assume that these effects are not appreciable.

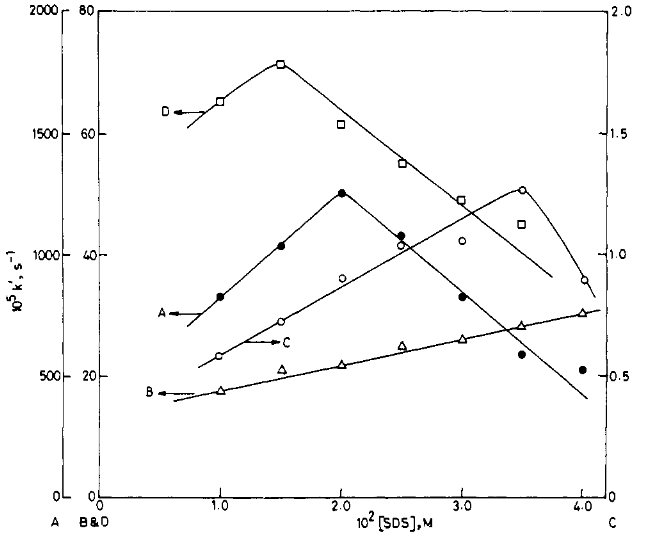

Figure 5. Effect of surfactant concentration on the pseudo-first-order rate constant, k' ([H_2TPP] = 4.2×10^{-8} M): (A) [Cu^{2+}] = 1.0×10^{-3} M; (B) [Zn^{2+}] = 4.0×10^{-2} M; (C) [Cd^{2+}] = 3.5×10^{-2} M; (D) [$Cd(OAc)_2$] = 3.5×10^{-2} M. The metal carriers are sulfates except that of curve D.

an increase in [H^+] decreases the rate of metal incorporation. This observation is similar to that of Cu(II) incorporation into pyridyltriphenylporphyrins.[1e] This is attributed to the progressive formation of the protonated porphyrin species H_3TPP^+. The following mechanism is proposed. It is pertinent to mention here that in the final rate equation, the concentration of the detergent is used instead of micelle concentration.

$$H_2TPP + nD \underset{K_D}{\rightleftharpoons} D_nH_2TPP \tag{4}$$

$$M^{2+} + nD \overset{K_1}{\rightleftharpoons} M^{2+}D_n \tag{5}$$

$$M^{2+}D_n + n'D \overset{K_2}{\rightleftharpoons} D_{n'}M^{2+}D_n \tag{6}$$

$$H_2TPP + M^{2+} \xrightarrow{k_0} \text{products} \tag{7}$$

$$D_nH_2TPP + M^{2+} \xrightarrow{k_1} \text{products} \tag{8}$$

$$D_nH_2TPP + M^{2+}D_n \xrightarrow{k_2} \text{products} \tag{9}$$

where D represents the detergent molecule, leading to the rate law

$$\text{rate} = \frac{[M^{2+}][H_2TPP](k_0K_D + k_1[D]^n + k_2K_1[D]^{2n})}{(1 + K_1[D]^n + K_1K_2[D]^n[D]^{n'})(K_D + [D]^n)} \tag{10}$$

This rate equation explains the first-order dependence of rate on the metal ion and H_2TPP concentrations. In principle, it should be possible to obtain from the kinetic data an estimation of binding constants (K_D, K_1, and K_2) and rate constants (k_0, k_1, and k_2). However, we are unable to arrive at these values owing to the complex dependence of the overall rate on these constants.

It is known that an increase in surfactant concentration alters the rate of a reaction in a complex fashion analogous to that of an enzyme-catalyzed reaction.[12] The effect of surfactant concentration on the rates of metal insertion into H_2TPP was studied, and the results are shown in Figure 5. It is found that in the case of Cu^{2+} and Cd^{2+} incorporation the rate increases rapidly with increase in surfactant concentration, reaches a maximum, and decreases at high detergent concentrations, while in the same range of concentrations the incorporation rate of Zn^{2+} increases steadily. While the increase in the rate is expected due to the surface effects, the decrease in rate at high surfactant concentrations can be ascribed to the progressive formation of an inactive $D_nM^{2+}D_{n'}$ species.[12]

At low concentrations of the surfactant $K_1[D]^n + K_1K_2[D]^n[D]^{n'} < 1$ and $k_2K_1[D]^{2n} < k_0K_D + k_1[D]^n$; thereby eq 10 reduces to

$$\text{rate} = \frac{[M^{2+}][H_2TPP](k_0K_D + k_1[D]^n)}{K_D + [D]^n} \tag{11}$$

and explains the increase in rate with increase in surfactactant centrations. But, at high concentrations of the surfactant $[D]^n > K_D$, $K_1[D]^n + K_1K_2[D]^n[D]^{n'} > 1$ and $k_2K_1[D]^{2n} > k_0K_D + k_1[D]^n$; thereby the rate equation reduces to

$$\text{rate} = \frac{k_2[M^{2+}][H_2TPP]}{1 + K_2[D]^{n'}} \tag{12}$$

Equation 12 explains the decrease in rate at high detergent concentrations. The facility of the formation of such an inactive species depends not only on the ratio of the metal ion concentration to the detergent concentration but also on the nature of the metal carrier. The free metal ion concentration in the hydrophilic phase is dictated primarily by the dissociation constant of the metal carrier, and thus it can be expected that the weakly dissociative metal carrier, $Cd(OAc)_2$, should not only exhibit higher rates of incorporation (relative to that of strongly dissociating $CdSO_4$) but also shift the maxima to the left in the rate vs. [SDS] profiles (Figure 5). The monotonic increase of rate in the case of Zn^{2+} incorporation may be traced to the limited range of the SDS concentration employed in the present study.

We examined the effect of the nature of the metal carrier on the reaction rate. It is found that an employment of a neutral carrier such as Zn(acac) enhanced the rate of metal incorporation into H_2TPP by 2 orders of magnitude relative to that of $ZnSO_4$. This enhancement in rate is anticipated since a neutral metal carrier would penetrate the micellar phase with ease relative to that of a doubly charged positive zinc ion and thereby enhances the rate.

The k' values found for different metal ion incorporation rates follow the order $Cu^{2+} > Zn^{2+} > Cd^{2+}$. This is essentially the same as that observed in the homogeneous medium, though the introduction of a micellar medium enhanced the rates of metal incorporation relative to that of the homogeneous medium. In order to ascertain whether the mechanism of metal incorporation into H_2TPP as proposed in the homogeneous media holds good also for the micellar systems, we considered the pK_3 value of H_2TPP protonation in the micelles. The widely accepted mechanism of metal incorporation into H_2TPP involves the primary step of distortion of H_2TPP owing to the protonation from the medium followed by the metal insertion. It is established that the rates of metal incorporation reactions into different porphyrins follow a more or less a linear relation with pK values of imino hydrogens of the various porphyrins. The experimentally determined pK_3 value of H_2TPP (2.52) is close to that observed for H_2TPP in homogeneous medium. Thus it is surmised that the basic mechanism involved in SDS micelles is the same as that proposed for the homogeneous medium.

The present studies, besides pointing out the use of fluorescence spectroscopy for the kinetic studies of metalation reactions of porphyrins, reveal the interphase effects induced by the micellar system in enhancing the metal incorporation rates. The general kinetic expression employed in the study is easily adaptable for other porphyrin metalation reactions as well.

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Registry No. SDS, 151-21-3; Triton X-100, 9002-93-1.

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