

Metallation of Porphyrins in Two-phase Systems using Carboxylic Acids, Thiols, and Phenols

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Metallation of meso-tetratolylporphyrin in a water-oil two-phase system is induced by cation-transfer surfactants such as carboxylic acids, thiols, and hydroxyaromatic compounds. The rate of metallation in a homologous series of surfactants depends on the ion-transfer capability of the surfactant as well as on the susceptibility of the transferred ion towards metallation. The studies reveal specificity and kinetic discrimination of the metals participating in the metallation of the porphyrin that depends on the type of surfactant being applied.

Metalloporphyrins are important essential ingredients in various biological systems.¹ Similarly, metalloporphyrins appear in sediments and crude oils (petroporphyrins).² Nevertheless, the nature of the metal associated with the porphyrin ligands suggests a preferential formation of metal-porphyrin complexes of metals normally present at relatively low abundance. For example, VO²⁺, and Ni²⁺-porphyrins appear in crude oils,³ Ga²⁺-porphyrin is found in coal,⁴ and Co-⁵ or VO²⁺-porphyrins⁶ are essential ingredients in natural systems. Thus, the metallation of porphyrins might be accompanied by some discrimination factors that favour the formation of metal-porphyrin complexes of metals of low abundance. Metalloporphyrins appear in nature in the hydrophobic-hydrophilic environments of membrane-aqueous interfaces. Also, petroleum is always associated with pore or formation water,⁷ and it has been suggested that aqueous salt solutions that wash the oil reservoirs induce the metallation of porphyrins.

The subject of phase-transfer catalysis has evoked substantial interest in recent years from theoretical aspects and practical applications.^{8,9} Various amphiphilic agents were applied in the study of anion transfer from aqueous systems to organic media as a synthetic means.¹⁰ Similarly, cation transport was induced with anionic surfactant compounds.¹¹ Petroleum is accompanied by various amounts of fatty acids,^{12,13} naphthenic acids,¹⁴ and phenols.¹³ Sulphur compounds are also major ingredients of crude oils.^{7,15} Although thiols are usually minor components of the sulphur-containing compounds in oils, various routes might lead to substantial amounts of thiols under geochemical conditions.¹⁶ Fatty acid, phenols, and thiols might act as surfactants for cations in water-oil two-phase systems. Thus, these compounds might assist metal ion transport from aqueous solutions to oil environments.

Here we report on the metallation of meso-tetratolylporphyrin (TTP) in organic-aqueous two-phase systems using carboxylic acids, phenols, and thiols as phase-transfer catalysts for metal ions. We find that different factors control the effectiveness of the metallation process which is not always related to the ion-transport capability of the surfactant. The studies also reveal selectivity towards specific metals using the different ion-transfer catalysts.

Experimental

The investigated systems were composed of an aqueous buffer solution (2 ml; pH 8.0) that included the corresponding metal (1×10^{-2} M), and a toluene phase (2 ml) that included TTP (1×10^{-4} M). The respective ion-transfer compounds were introduced into the two-phase system: carboxylic acids (5×10^{-1} M), thiols (2×10^{-1} M), and hydroxyaromatics (2×10^{-1} M). The systems were introduced into a thermostatically controlled bath

and stirred with a magnetic stirring bar. Aliquot portions (80 μ l) from the toluene phase were taken at time intervals of the reaction. These samples were diluted to 2 ml and the metallation process was followed spectroscopically with a Uvikon 860 spectrophotometer (Kontron) equipped with ψ -80 computer (Kontron) for spectra accumulation and manipulation.

Partition coefficients (K_p) of the metals between the two-phase systems were determined in the following way. The previously described systems, where TTP was excluded, were stirred with the corresponding surfactants under conditions similar to those of the respective metallation reactions. The systems were allowed to equilibrate overnight. Aliquot portions (100 μ l) of the aqueous phase were diluted 200-times and the metal concentration was determined by an atomic absorption spectrophotometer (Perkin-Elmer). Aliquot portions (1 ml) were also taken from the organic phase. The samples were evaporated and heated to 500 °C. The residues were digested by HNO₃ and diluted with triply distilled water (TDW). The ion concentrations were determined by atomic absorption. The ion concentrations in the two-phase experiments were then estimated by normalization according to the respective concentration factors.

Results and Discussion

Carboxylic Acids as Phase-transfer Catalysts.—The metallation of TTP dissolved in the oil environment of toluene was examined in the presence of an aqueous solution (pH 8) that included the metal ions Zn²⁺, Cu²⁺, and Mn²⁺. In this two-phase system the effect of added carboxylic acids (C_nH_{2n+1}CO₂H) on the metallation rate has been examined. For example, in the presence of C₈H₁₇CO₂H, TTP is metallated and forms Cu-TTP (Figure 1). It should be noted that in the absence of the carboxylic acid no metallation of TTP occurs, even after long periods of contact between the two phases under stirring conditions. Addition of carboxylic acids of different alkyl chain length (C_nH_{2n+1}) reveals that the metallation process proceeds at different rates, indicating that the metallation is affected by the length of the acid chain. The pseudo-first-order rate constants for the metallation of TTP by the different metal ions in the presence of the various carboxylic acids are summarized in Table 1. It can be seen that the metallation rate decreases as the chain of the acid is longer. For example metallation of TTP by Zn²⁺ is ca. 2 500-times slower with C₁₅H₃₁CO₂H in comparison with the system which includes C₅H₁₁CO₂H. Furthermore, it is evident that, in the presence of a specific carboxylic acid, the rate of metallation depends on the nature of the metal ion. For example, metallation of TTP in the presence of C₅H₁₁CO₂H by Zn²⁺ is 2 000-times faster than by

Table 1. Partition coefficients of the various ions and metallation rate constants of TTP in the presence of carboxylic acids

	$C_5H_{11}CO_2H$			$C_8H_{17}CO_2H$		
	Cu^{2+}	Zn^{2+}	Mn^{2+}	Cu^{2+}	Zn^{2+}	Mn^{2+}
K_p^a	7.6×10^{-3}	5.7×10^{-3}	13.2×10^{-3}	77×10^{-2}	7×10^{-2}	40×10^{-2}
k_{met}^b	6.6^b	74^b	3×10^{-2c}	3.2^b	4^b	3.6×10^{-1c}
k_{met}^d	5.2×10^{-2d}	71×10^{-2d}	$4.2 \times 10^{-4c,d}$	3.5×10^{-2d}	4.7×10^{-2d}	$2.5 \times 10^{-3c,d}$

	$C_{13}H_{27}CO_2H$			$C_{15}H_{31}CO_2H$		
	Cu^{2+}	Zn^{2+}	Mn^{2+}	Cu^{2+}	Zn^{2+}	Mn^{2+}
K_p^a	1.1	1.25	1.6	52	57.6	42.7
k_{met}^b	2.3^b	7.1×10^{-1b}	1.4×10^{-1c}	6×10^{-2c}	2.8×10^{-2c}	2.9×10^{-3c}
k_{met}^d	2.7×10^{-2d}	6.8×10^{-3d}	$1.7 \times 10^{-3c,d}$	5.5×10^{-4d}	3×10^{-4d}	$3.4 \times 10^{-5c,d}$

^a $K_p = [M^{n+}]_{org}/[M^{n+}]_{aq}$. ^b In toluene, 25 °C. ^c Metallation performed at 50 °C. ^d Two-phase system, 25 °C.

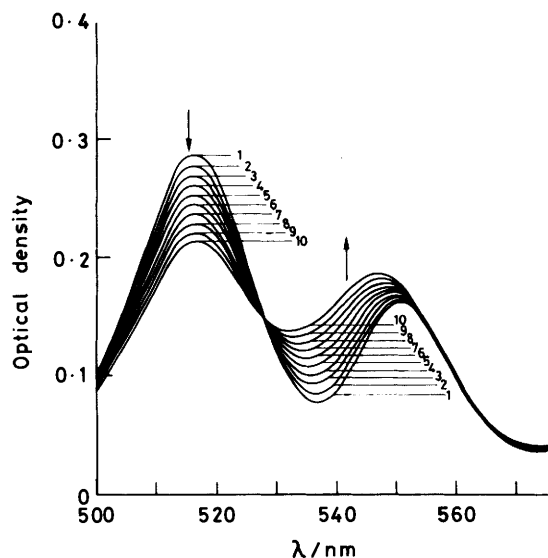
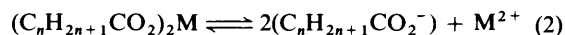
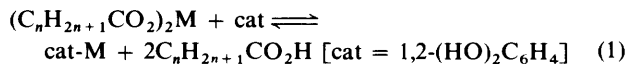


Figure 1. Metallation of TTP by Cu^{2+} in the presence of $C_8H_{17}CO_2H$. $[Cu^{2+}] 10^{-2}M$, pH 8, $[TTP] 10^{-4}M$, $[C_8H_{17}CO_2H] 5 \times 10^{-4}M$: 1—10 = time intervals (each 10 min) for sampling the organic phase

Mn^{2+} . The function of the carboxylic acids in the metallation process are attributed to phase transfer of the metal ions from the aqueous phase to organic phase *via* ion pairing to the carboxylate anions $(C_nH_{2n+1}CO_2^-)_2M^{2+}$. At the basic pH conditions of the aqueous solution, the acids are exclusively in their ionized forms. Consequently, the metal ions are transported by the hydrophobic acid anions from the aqueous to the oil medium where metallation of TTP occurs.

The metallation rates by the specific metal ions are expected to relate to the cation concentration transported by the carboxylic acid to the organic phase. The partition coefficients of the different metal ions in the presence of the various acids have been determined and are also summarized in Table 1. It can be seen that, for all investigated metal ions the ion-transfer capability relates to the hydrophobicity of the carboxylic acid and increases in the order $C_5H_{11}CO_2H < C_8H_{17}CO_2H < C_{13}H_{27}CO_2H < C_{15}H_{31}CO_2H$. Nevertheless, comparison of the metallation rates in the presence of the carboxylic acids reveals that the metallation process in the presence of $C_{13}H_{27}CO_2H$ and $C_{15}H_{31}CO_2H$ is inhibited as compared to the system that includes $C_8H_{17}CO_2H$. That is, although the ion-transfer capability of $C_{13}H_{27}CO_2H$ and $C_{15}H_{31}CO_2H$ are superior compared with that of $C_8H_{17}CO_2H$ the metallation rate is retarded in the presence of long-chain carboxylic acids.

Comparison of the metallation rates of TTP by the various ions in the presence of the short-chain carboxylic acids $C_5H_{11}CO_2H$ and $C_8H_{17}CO_2H$ shows some discrepancies. While the metallation of TTP by Zn^{2+} and Cu^{2+} is fastest with $C_5H_{11}CO_2H$, the less effective ion-phase transfer catalyst, metallation of TTP by Mn^{2+} is *ca.* 10-fold faster in the presence of $C_8H_{17}CO_2H$. These observations suggest an additional factor to the ion-transfer capability, namely, that the carboxylic acid is operative in controlling the metallation rates. To account for this behaviour, we have examined the metallation rates of TTP by the different metal carboxylates $(C_nH_{2n+1}CO_2^-)_2M^{2+}$, in a homogeneous toluene solution. The second-order metallation rate constants of TTP by the various metal carboxylates in a homogeneous toluene phase are also summarized in Table 1. It is evident that the metallation rate of TTP depends on the chain length of the carboxylic acid, and the longer the chain the more retarded is the metallation reaction, *e.g.*, for Cu^{2+} , the metallation of TTP by $(C_{13}H_{27}CO_2)_2Cu$ is *ca.* 1.5—3-fold slower than that with $(C_8H_{17}CO_2)_2Cu$ and $(C_5H_{11}CO_2)_2Cu$, respectively. In the case of Zn^{2+} these effects are even further emphasized and metallation of TTP by $(C_{13}H_{27}CO_2)_2Zn$ is 18.5—100-fold slower than the corresponding metallations by $(C_8H_{17}CO_2)_2Zn$ and $(C_5H_{11}CO_2)_2Zn$. The results clearly demonstrate that the ion-transfer capability of the carboxylate relates to its hydrophobicity and that the ion transfer from the aqueous phase to the organic phase is essential for the metallation. Using the long-chain carboxylates the process is retarded as compared with the short-chain carboxylates. To account for this behaviour we examined the dissociation constants [equation (1)] of the Cu-carboxylates, $(C_nH_{2n+1}CO_2)_2Cu$ in toluene. Determination of these dissociation constants was performed by equilibration of $(C_nH_{2n+1}CO_2)_2Cu$ with catechol forming Cu^{2+} -catecholate [equation (2)]. From the equilibrium



constants of this process, and knowing the association constant of Cu-catecholate, $K_{cat} 2.31 \times 10^3 \text{ l mol}^{-1}$, the dissociation constants for $(C_nH_{2n+1}CO_2)_2Cu$ were determined. The values for the different carboxylates are summarized in Table 2. It is evident that the dissociation constants are strongly affected by the carboxylate chain length, and as the chain length increases the dissociation constant decreases and thus the metal ion is less susceptible towards the metallation reaction. We thus conclude that the metallation of TTP is affected by two factors, the ion-transfer capability of the metal ion being essential to allow the

Table 2. Dissociation constants of $(C_nH_{2n+1}CO_2)_2Cu$ and $(C_nH_{2n+1}S)_2Zn$

K_d	$(C_nH_{2n+1}CO_2)_2Cu^a$			$(C_nH_{2n+1}S)_2Zn^b$		
	$C_5H_{11}CO_2^-$	$C_8H_{17}CO_2^-$	$C_{13}H_{27}CO_2^-$	$C_9H_{19}S^-$	$C_{12}H_{25}S^-$	$C_{16}H_{33}S^-$
	6.06×10^{-6}	5.5×10^{-6}	4×10^{-6}	5.9×10^{-5}	1.83×10^{-4}	6.6×10^{-4}

^a Determined by equilibration with catechol. ^b Determined by equilibration with dithizone.

Table 3. Partition coefficients of the various ions and metallation rate constants of TTP in the presence of thiols

	$C_7H_{15}SH$		$C_9H_{19}SH$		$C_{12}H_{25}SH$		$C_{16}H_{33}SH$	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
K_p^a	4	2	3	2	5.4×10^{-2}	1	3×10^{-2}	4×10^{-1}
k_{met}^b	N.d. ^c	1.4×10^{-5}	2.8×10^{-5}	4.1×10^{-5}	3.5×10^{-5}	6.1×10^{-5}	5×10^{-5}	7.3×10^{-5}
k_{met}^d		1.2×10^{-3}		1.8×10^{-3}		2.4×10^{-3}		2.9×10^{-3}

^a $K_p = [M^{n+}]_{org}/[M^{n+}]_{aq}$. ^b Two-phase system, 75 °C. ^c Not detectable in the reaction time. ^d In toluene, 75 °C.

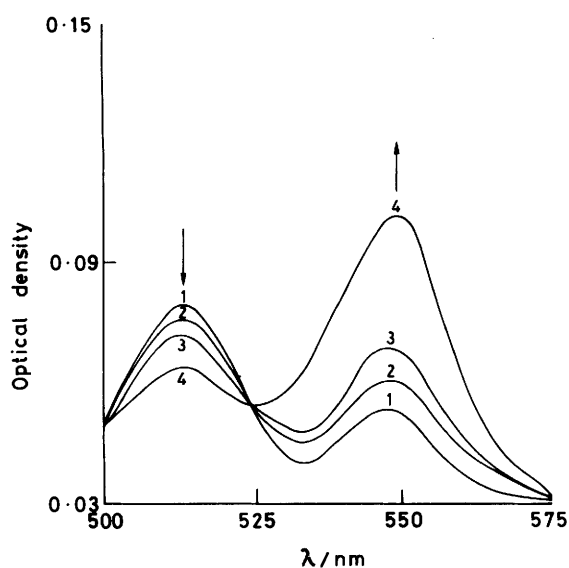


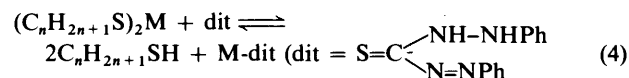
Figure 2. Metallation of TTP by Zn^{2+} in the presence of $C_{16}H_{33}SH$. $[Zn^{2+}] 10^{-4}M$, pH 8, $[TTP] 10^{-4}M$; $[C_{16}H_{33}SH] 2 \times 10^{-1}M$: (1), after 60 min; (2), after 120 min; (3), after 180 min; (4), after 420 min

metallation and the extent of dissociation of the transferred metal carboxylate in the organic phase. These two factors exhibit opposite behaviour as a function of the carboxylate chain length, and thus the metallation rates of TTP by Cu^{2+} and Zn^{2+} maximize with $C_5H_{11}CO_2H$ while for Mn^{2+} the highest metallation rate is observed with $C_8H_{17}CO_2H$.

Thiols as Ion-transfer Surfactants.—Other potential ion-transfer surfactants in water–oil two-phase systems are thiols. In conjunction with a basic aqueous phase (pH 8) the thiols will be present in the thiolate form, $(C_nH_{2n+1}S^-)_2M^{2+}$, which could have the capability to transfer metal ions into organic phases. Thus, we have substituted the carboxylates by thiols of different chain length as ion-transfer surfactants to induce the metallation of TTP in an organic phase by Zn^{2+} and Cu^{2+} . We find that thiols indeed function as phase-transfer surfactants for the cations and that metallation of TTP occurs in the oil phase. For example, Figure 2 shows absorption spectra changes of TTP upon metallation by Zn^{2+} in the presence of hexadecanethiol, $C_{16}H_{33}SH$. The metallation rate constants of TTP by Zn^{2+} and Cu^{2+} using the various thiols are summarized in Table 3. It is

evident that the metallation rate increases as the thiolate chain length increases. The partition coefficients of the metal ions in the two-phase systems in the presence of the different thiols were determined and are also summarized in Table 3. Surprisingly, in contrast to the carboxylates as ion-transfer surfactants the short-chain thiols are superior in their ion-transfer ability compared with the long-chain thiols, although the differences are small. To account for the enhanced metallation rates in the presence of the long-chain thiols we have prepared the series of zinc thiols, $(C_nH_{2n+1}S)_2Zn$, and have examined the metallation rates of TTP in a homogeneous toluene phase. The second-order rate constants are also summarized in Table 3. The results indicate that indeed the metallation by $(C_{16}H_{33}S)_2Zn$ is faster compared with that by $(C_7H_{15}S)_2Zn$.

Thus we can conclude that thiols function as ion-transfer surfactants that induce the metallation of the porphyrin in the oil phase. The rate of metallation does not coincide with the ion-transfer capability and depends on the chain length of the thiol. To account for this behaviour we have studied the extent of dissociation of the metal thiols in toluene as a function of the alkyl chain length [equation (3)]. The dissociation constants of the series $(C_nH_{2n+1}S)_2Zn$ was determined by equilibration with the ligand dithizone (dit) [equation (4)]. The progress of the formation of Zn-dithizone upon addition of the ligand to $(C_9H_{19}S)_2Zn$ and $(C_{12}H_{25}S)_2Zn$ is displayed in Figure 3. It is evident that with $(C_{12}H_{25}S)_2Zn$ the Zn-dithizone complex formation is facilitated over its formation from $(C_9H_{19}S)_2Zn$. These results imply that the association constant of $(C_9H_{19}S)_2Zn$ is higher than that for $(C_{12}H_{25}S)_2Zn$, namely, the dissociation constant of the latter is higher than that of $(C_9H_{19}S)_2Zn$. The values of the dissociation constants, K_d , for the series $(C_nH_{2n+1}S)_2Zn$ is also summarized in Table 2.



It is evident that the values of the dissociation constants increase as chain length increases implying that the metal is less susceptible towards metallation with the short-chain thiols. We thus conclude that the metallation rates of TTP by Cu^{2+} and Zn^{2+} are affected by the ion transfer capability in the form of the metal thiolate as well as by its dissociation in the organic phase. The phase-transfer ability decreases as the chain length $(C_nH_{2n+1}S^-)$ increases while the dissociation of $(C_nH_{2n+1}S)_2M$

Table 4. Partition coefficients of the various ions and metallation rate constants of TTP in the presence of hydroxyaromatic compounds

	Phenol		α -Naphthol		β -Naphthol		9-Hydroxyphenanthrene	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
K_p^a	3.1×10^{-3}	7.3×10^{-3}	1.5×10^{-1}	7.5×10^{-3}	3×10^{-3}	6.1×10^{-3}	5.5×10^{-1}	8.2×10^{-2}
$k_{met}^{b,c}$	2.8×10^{-3b}	5×10^{-3b}	77×10^{-3b}	11×10^{-3c}	15×10^{-3c}	4.3×10^{-3c}	2.7^b	2×10^{-2b}

^a $K_p = [M^{n+}]_{org}/[M^{n+}]_{aq}$. ^b Two-phase system, 25 °C. ^c Two-phase system; the reactions were performed at 50 °C.

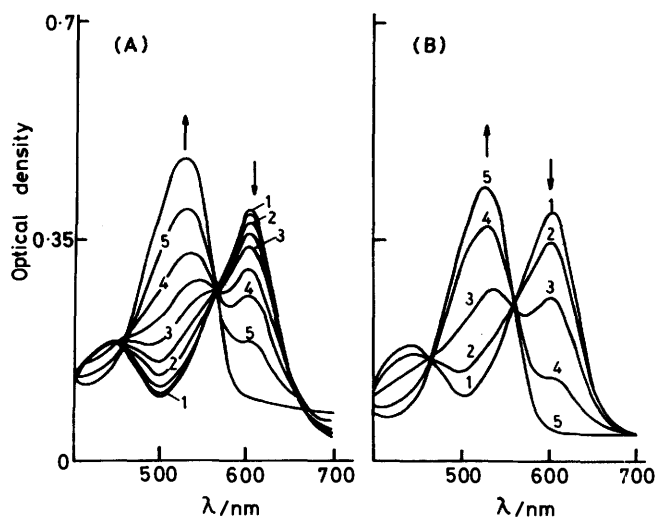


Figure 3. Spectral changes upon addition of (C₉H₁₉S)₂Zn to dithizone (A) and upon addition of (C₁₂H₂₅S)₂Zn to dithizone (B). In both experiments [dithizone] 1×10^{-5} M. For (A): [(C₉H₁₉S)₂Zn] added: (1), 0; (2) 1.24×10^{-4} M; (3) 1.22×10^{-4} M; (4), 1.21×10^{-4} M; (5), 1.20×10^{-4} M. For (B): [(C₁₂H₂₅S)₂Zn] added: (1), 0; (2), 6.23×10^{-5} M; (3), 6.21×10^{-5} M; (4), 6.20×10^{-5} M; (5), 6.18×10^{-5} M

increases as the chain length grows. A possible explanation of this behaviour might be the tendency of thiolates to aggregate and form clusters.^{17,18} With the long-chain thiolates this aggregate formation might be inhibited as a result of interchain steric repulsion, and consequently assist the dissociation of the metal.

Comparison of the metallation rates of TTP by the metal ions in the presence of carboxylates and thiolates reveals some important differences. The metallation rates in the presence of carboxylates are higher than with thiolates although the ion-transfer capability is improved with the latter surfactants. Also, while metallation by the carboxylates is enhanced in the presence of short-chain carriers, similar processes are favoured with the long-chain thiolates.

Phenols as Ion-transfer Agents.—A third class of compounds of potential capability to transfer cations into organic media are phenols. Since phenol derivatives appear in geochemical sediments, these compounds might give an insight into their possible functions in metallation of porphyrins in such environments (especially in coal). In conjunction with basic aqueous solution the phenolates could act as ion-transfer compounds. Thus, we have examined the metallation of TTP in a toluene-water (pH 8) two-phase system where hydroxyaromatic compounds act as the ion-transfer compounds. We examined phenol, α - and β -naphthol, and 9-hydroxyphenanthrene. We find that phenols are indeed excellent compounds that mediate the metallation of TTP. For example, the absorption spectra changes observed upon metallation of TTP by Cu²⁺ in the presence of β -naphthol are displayed in Figure 4. The pseudo-

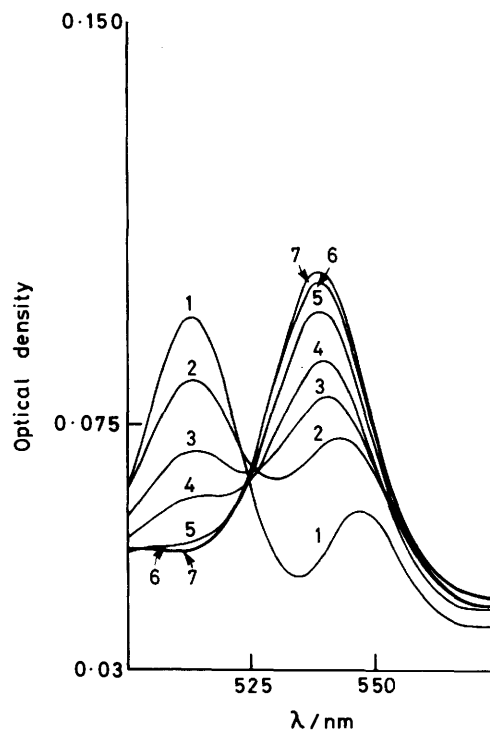


Figure 4. Metallation of TTP by Cu²⁺ in the presence of β -naphthol. [Cu²⁺] 10^{-2} M; pH 8; [TTP] 10^{-4} M; [β -naphthol] 2×10^{-2} M: 1—7 = time intervals (each 10 min) for sampling the organic phase

first-order rate constants for the metallation of TTP by Cu²⁺ and Zn²⁺ in the presence of the different hydroxyaromatic compounds as well as the partition coefficients of the metals between the phases are summarized in Table 4. It can be seen that the metallation rates of TTP by the two metals differ substantially and the metallation by Cu²⁺ using 9-hydroxyphenanthrene as ion-transfer catalyst is 200-fold faster than the reaction with Zn²⁺. It is also evident that the metallation rates follow the ion-transfer capability of the various hydroxyaromatics, and improved ion capability is reflected by enhanced metallation of TTP. Of particular interest is the observation that α -naphthol is more effective than β -naphthol in inducing the metallation process. For instance, the metallation rate of TTP by Cu²⁺ in the presence of α -naphthol at 25 °C is five-fold faster than the reaction with β -naphthol at 50 °C.

Comparison of the hydroxyaromatics as ion-transfer compounds with the previously discussed thiols and carboxylic acids reveals that the latter two compounds show improved cation-transfer properties into the oil phase. Nevertheless, the metallation rates by the three groups of surfactants indicate that the reaction in the presence of the hydroxyaromatic compounds is substantially faster than the process in the presence of thiols and of similar effectiveness to that observed with the carboxylic acids.

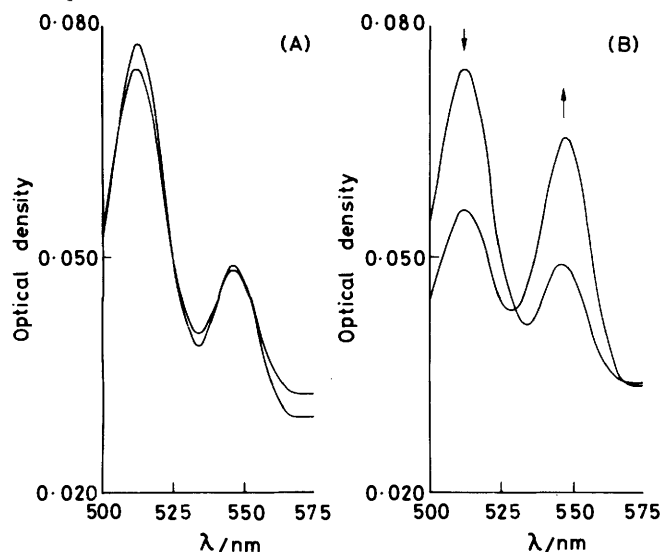


Figure 5. (A) Metallation of TTP by Ni²⁺ in the presence of C₁₆H₃₃SH. [Ni²⁺] 10⁻²M; pH 8; [TTP] 10⁻⁴M; [C₁₆H₃₃SH] 2 × 10⁻¹M. (1) Spectrum recorded after 8 h. (2) Spectrum recorded after 70 h. (B) Metallation of TTP by VO²⁺ in the presence of C₁₆H₃₃SH. [VO²⁺] 10⁻²M; pH 8; [TTP] 10⁻⁴M; [C₁₆H₃₃SH] 2 × 10⁻¹M. (1) Spectrum recorded after 4 h. (2) Spectrum recorded after 70 h

Metallation by Ni²⁺ and VO²⁺.—Metallation of TTP by VO²⁺ and Ni²⁺ has been examined in the two-phase systems where carboxylic acids, thiols, and hydroxyaromatics act as ion-transfer surfactants. With these metals the metallation process is substantially slower than that for Cu²⁺ or Zn²⁺. However, at 90 °C metallation of TTP by VO²⁺ and Ni²⁺ could be readily observed depending on the surfactant being applied. With carboxylic acids metallation of TTP by Ni²⁺ takes place, and the favoured surfactant is C₈H₁₇CO₂H. Under similar conditions, metallation by VO²⁺ is substantially slower and a clear kinetic discrimination for Ni²⁺ is observed. In turn, with thiols as surfactants, the situation is reversed. Namely, at 90 °C, metallation of TTP by VO²⁺ is almost completed, when the same process by Ni²⁺ is hardly detectable. For an example see Figure 5.

Conclusions.—The results imply that metallation of porphyrins in oil phases can be induced by cation transfer from aqueous environments with proper ion-transfer compounds. In our studies, carboxylic acids, thiols, and mono- and poly-cyclic hydroxyaromatic compounds have shown such ion-transfer properties. For the metallation process to occur, extraction of the cation from the aqueous phase is essential. The results indicate, however, that the rates of metallation are strongly affected by the nature of the anionic surfactants and that the effectiveness

of the process is not always controlled only by the ion-transfer capability of the surfactant. The dissociation of the surfactant-cation complex in the organic oil phase and consequently the susceptibility of the cation towards metallation of the porphyrin are important factors in controlling the process. Substantial differences in the metallation rates of TTP by the different metals and the various ion-transfer compounds are observed. This implies that selectivity in metallation of porphyrins can be induced by kinetic discrimination and specificity of the ion-transfer compounds. For instance, the metallation of TTP by Zn²⁺ is favoured over Cu²⁺ in the presence of carboxylic acids, while this trend is reversed in the presence of thiols or hydroxyaromatic compounds as surfactants. In view of the abundant occurrence of carboxylic acids, thiols, and hydroxyaromatic compounds in natural environments such as sediments and oil sources, we believe that such metallation reactions in aqueous-oil two-phase systems might lead to the formation of metalloporphyrins. The specificity observed for VO²⁺ and Ni²⁺ as a function of the nature of ion-transfer surfactant might reveal a relation between the nature of metalloporphyrins in oils and the depositional geochemical environment.

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