H$_2$O/Triton X-100 Solvent Effect in the Micellar Catalysis of the Aquation of Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II)

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The effect of triton X-100 micelles on the aquation of Fe(Me$_4$phen)$_3^{2+}$ has been investigated with triton X-100 as solvent. In liquid triton X-100, over a range of [H$_2$O]$_T$ (0.2–2.0 mol dm^{-3}), significant rate enhancement factors of 35–140 are observed. Acid inhibits the rate of aquation at fixed [H$_2$O]$_T$. A mechanism based on effective solvent participation in a chemical environment similar to that in reversed micelles is proposed in liquid triton X-100 with dispersed water pockets. This mechanism predicts direct H$_2$O substitutions into the coordination sphere of Fe(Me$_4$Phen)$_3^{2+}$ in the highly polar water pockets or cavities where the Fe^{II} complex molecules are solubilized. Changes in the tumbling rate, mobility, structure, nucleo-philicity and activity of water are suggested to account for the observed changes in the rate of aquation as a function of [H$_2$O]$_T$, in the peculiar chemical environment of the water pockets. All k_w–[H$_2$O]$_T$ profiles are structured and exhibit maxima with k_w(max) shifted to progressively higher [H$_2$O]$_T$ as the fixed concentration of [H$^+$]$_T$ is increased.

Recently, we reported[1,2] the effect of micelles on the aquation of phenanthroline complexes of iron(II). Our results reflect some of the kinetic and mechanistic features of micelle-catalysed systems and emphasise the significance of substrate partitioning between the micellar and bulk water phases.

Such substrate partitioning in pure surfactant medium must differ, as the bulk-water phase is now replaced by the bulk-surfactant phase with the H$_2$O molecules and Fe^{II} complex molecules dispersed in the latter. Few studies of chemical reactions in purely surfactant medium have been investigated in the literature. The effect of the pure surfactant medium on the overall kinetics and mechanism of the aquation reactions is therefore of interest. The present work is in this direction. We report the aquation of Fe(Me$_4$phen)$^{2+}$ in triton X-100, an important emulsifying agent which has 10 monomers in its aqueous micelle. Triton X-100 is a neutral surfactant for which hydrophobic interaction with the bulky and hydrophobic Fe(Me$_4$phen)$_3^{2+}$ will be significant.

With triton X-100 as the bulk solvent, addition of small amounts of water creates water pockets with a chemical environment which may be similar to that in reversed micellar systems.[3-13] The kinetics and mechanistic features of the dissociation of the Fe^{II} complex is therefore of comparative interest with respect to observed data in ordinary aqueous system.†

Experimental

Materials

Fe(Me$_4$phen)$_3$SO$_4$ (G. F. Smith Chemical Company) gave a molar extinction coefficient in good agreement with the literature[13] value at λ_{max} = 500 nm and was therefore used

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† We have studied the aquation of this complex in aqueous triton X-100. Inhibition was observed and inhibition factors of 2.4 to 2.7 were calculated.

without further purification. Scintillation-grade triton X-100 was also used without further purification. All other chemicals were of AnalaR grade (BDH). Because of the viscous nature of triton X-100, vigorous shaking was always necessary for thorough mixing in the reaction cells. The Fe^{II} complex concentration was fixed at 3.162×10^{-5} mol dm^{-3}, except where stated otherwise. H_2SO_4 was used preferentially because the iron(II) complex is precipitated in almost all the other mineral acids.

Kinetics

The aquation rate was followed by monitoring the disappearance of the iron(II) complex at $\lambda_{max} = 500$ nm, using an SP 500 series 2 Pye-Unicam spectrophotometer fitted with an automatic cell changer and theromostatted cell compartments. Constant temperature was maintained by immersion in a water bath fitted with a Gallenkamp thermoregulator and a cryocool CC-60T compressor coil. k_ψ, the aquation rate constant was obtained from the slopes of plots of $\ln(A_t - A_\infty)$ *vs. t*, which were always linear. Temperature was maintained at 25 °C.

Results

k_ψ *vs.* $[H_2O]_T$ profiles (fig. 1), at fixed $[H^+]_T$ (0.00–0.02 mol dm^{-3}), exhibit maxima with a shift in the position of the maximum to progressively higher $[H_2O]_T$ as fixed $[H^+]_T$ is increased. Comparison of the profiles indicates inhibition by acid. At the maxima, calculated catalysis factors (k_ψ/k_w†) are in the range 35–140. This is significant.

k_ψ decreases with increase in $[Fe(Me_4phen)]_T^{2+}$ at fixed $[H_2O]_T$ (0.6 mol dm^{-3}). Fig. 2 shows a 2.5-fold decrease in k_ψ for a threefold increase in complex concentration.

Mechanism and Discussion

In fig. 3, we propose that in trition X-100 solvent medium the surfactant molecules adopt an approximately reversed micellar arrangement‡ around the limited H_2O molecules ($< 4\%$ v/v H_2O) present,[4–12] with the polar OH headgroups pointing towards the centre of the polar cavities where the H_2O molecules are localised as in other reverse micellar systems.[4–12] The activity of water is highly enhanced in this environment owing to its reduced mobility/tumbling rate.[4, 6–12] Hydrogen bonding with the OH head group can only be such that the oxygen of H_2O points towards the centre of the cavity where, we propose, the bulky $Fe(Me_4phen)_3^{2+}$ is localised. Owing to the constraint of space in the cavity, the tumbling rate of the iron(II) complex is significantly reduced. This is enhanced by the inability of the substrate to escape into the bulk of the solvent because of the steric blockade of possible outlets by H_2O molecules hydrogen bonded to the OH headgroups. The iron(II) complex is therefore suitably oriented for direct attack by H_2O molecules.

Further support for the above proposed mechanism comes from lipid systems[15] (the liquids are just as viscous) where the tumbling rate of water, at low H_2O content (*ca.* 0.20% v/v), is negligible. Given this condition the mobility of the H_2O in the present system is influenced predominantly by the overall tumbling rate of the micelle and iron(II) complex. It is reasonable to expect that at higher water compositions additional water molecules are free with a mobility approaching that in bulk water, as has been observed for lipids and reversed micellar systems.[13, 15, 16]

The initial observed rate enhancement (fig. 1) and the observed maxima are well within the range of water concentration specified for the first type of H_2O molecules hydrogen bonded to the OH head groups. The rate enhancement is therefore a

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† k_w = aquation rate constant in micelle free medium (2.40×10^{-4} s^{-1} in 1.0 mol dm^{-3} H^+).

‡ In the absence of any calculations or experimental data on the size number of H_2O molecules in the water pools or cavities of pure triton X-100, the true number of substrates/monomers may be different from that illustrated in fig. 3.
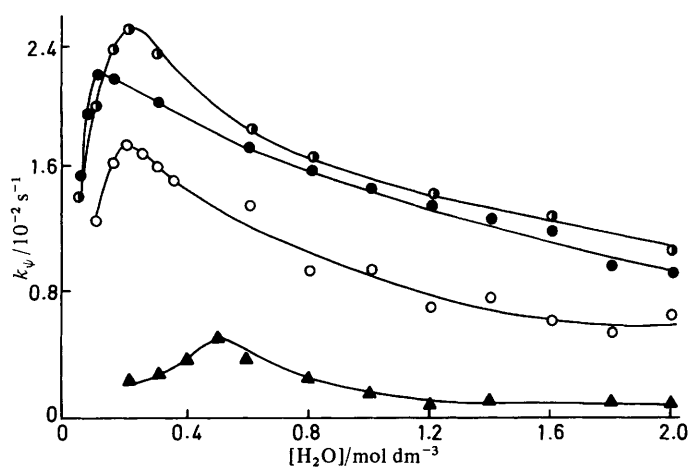
Fig. 1. Variation of aquation rate constant with $[H_2O]_T$ at H^+ concentrations (mol dm^{-3}) of 0.00 (◗), 0.002 (●), 0.010 (○) and 0.02 (▲). $T = 25\,°C$ (Triton X-100 solvent medium). $[Fe(Me_4phen)_3^{2+}]_T = 3.162 \times 10^{-5}$ mol dm^{-3}.
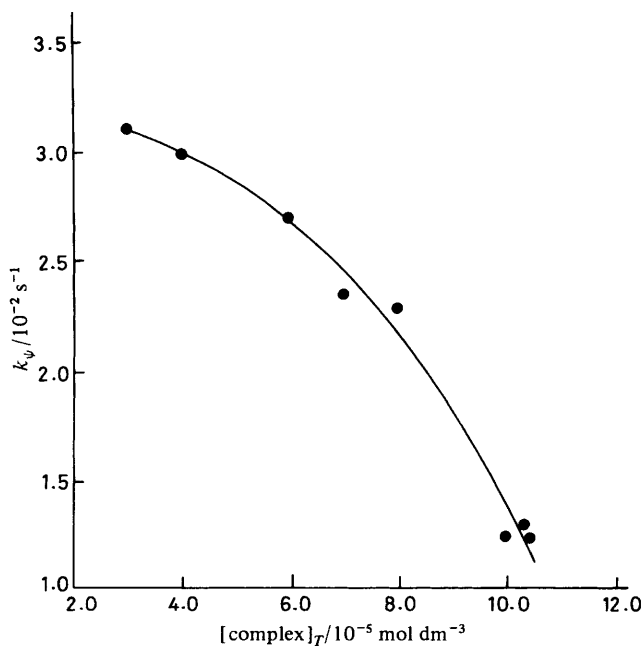
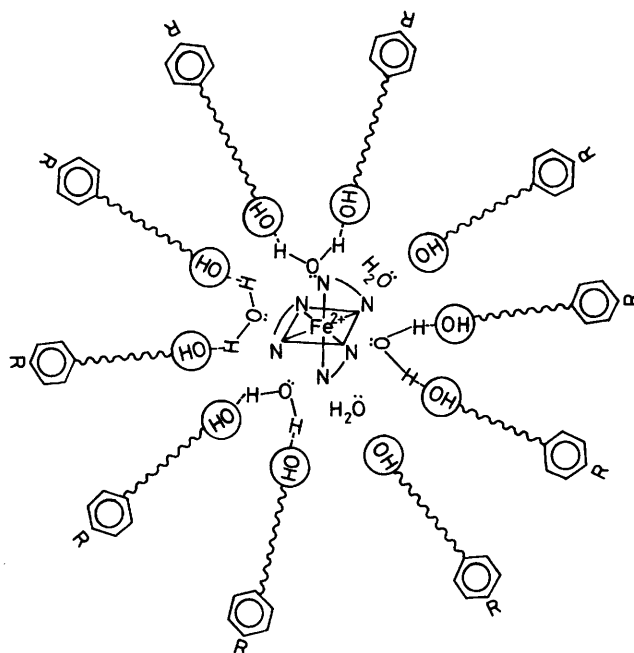**Fig. 2.** Variation of aquation rate constant with iron(II) complex concentration in triton X-100 solvent.

Fig. 3. Substrate–micelle interaction. $R = (CH_3)_3C—CH_2—C(CH_3)_2—$.

consequence of both the increased activity of water and the suitable orientation of the cornered iron(II) complex localised in the interior of the polar cavities and this enhances direct displacement of Me_4phen ligands from the coordination sphere of the iron(II) complex. The subsequent decrease in rate results in an increase in the tumbling rate of H_2O molecules and the iron(II) complex with an accompanying decrease in the activity of water, which gradually approaches that in bulk water at 2.0 mol dm^{-3} H_2O (3.7% v/v).

These observations are consistent with the following mechanism:

$$M + H_2O \rightleftharpoons M \cdot H_2O \qquad (1)$$

which expresses the bonding of H_2O, through hydrogen bonds, to the OH headgroups.

$$M \cdot H_2O + S^{2+} \rightleftharpoons M \cdot H_2O \cdot S^{2+} \qquad (2)$$
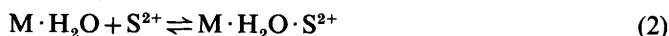
represents the solubilisation of S^{2+} in the polar cavities.

$$M \cdot H_2O \cdot S^{2+} \rightarrow \text{products} \qquad (3)$$

is the aquation path at low H_2O concentration, when the mobility of H_2O and other substrates in the polar cavities are significantly reduced, and

$$S^{2+} \rightarrow \text{products} \qquad (4)$$

is the aquation path at high H_2O concentration. It can be shown that eqn (1)–(4) yield

$$k_\psi = \frac{\text{rate}}{[S^{2+}]_T} = k_4 + \frac{K(k_3 - k_4)[H_2O]_T}{K[S^{2+}]_T + K[H_2O]_T + K_1 + 1} \qquad (5)$$

where $K = K_1 K_2$ and $[M]_T$ does not appear in the expression for k_ψ because the surfactant is the solvent, and hence to a good approximation $[M]_T$ is constant and is contained in K_1. Eqn (5) is reduced to

$$k_\psi = \frac{k_3 K[H_2O]_T}{K[H_2O]_T + K[S^{2+}]_T + K_1 + 1} \qquad (6)$$

at small $[H_2O]_T$ when reaction is predominantly through eqn (3) and predominantly through reaction path 4. k_ψ is then given by

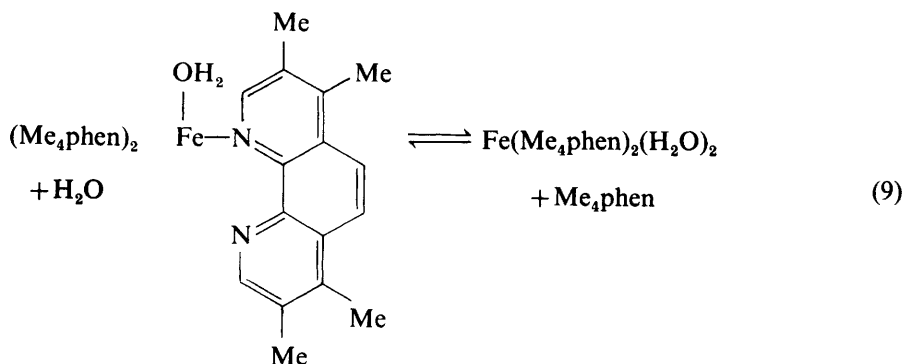$$k_\psi \approx k_4 - \frac{k_4 K[H_2O]_T}{K[H_2O_T + K[S^{2+}]_T + K_1 + 1} \qquad (7)$$

at higher $[H_2O]_T$ when conditions approach that in bulk water and reaction is predominantly through reaction path 4. Eqn (6) and (7) are in agreement with the observed variation of k_ψ at high and low $[H_2O]_T$.

Inhibition by acid (fig. 2) is due to the protonation of the OH headgroups, making the first type of favourably oriented H_2O molecules in the water pockets or polar cavities to form hydroxonium ions. This reduces considerably the nucleophilicity of the H_2O molecules for direct substitution into the coordination sphere of the positively charged iron(II) complex [*i.e.* there is Coulombic repulsion between H_3O^+ and $Fe(Me_4phen)_3^{2+}$]. Inhibition by acid contrasts with the observed† catalysis in micelle/micelle-free aqueous triton X-100 and strongly supports the postulate that aquation does not occur predominantly by dissociative mechanism.[1]
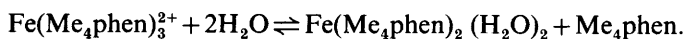
Direct substitution of H_2O into the coordination sphere of metal-ion complexes in reverse micellar medium has been proposed by Fendler and co-workers;[17] however, their system is quite different and hydrogen-bonding and proton transfer by H_2O molecules are central to their proposed mechanism for aquation. This is significantly complementary to the present study. Direct water substitution into the coordination sphere of $(Me_4phen)_3^{2+}$ in the polar cavities of triton X-100 is either by two consecutive steps,

$$Fe(Me_4phen)_3^{2+} + H_2O \rightleftharpoons (Me_4phen)_2 \quad \text{Fe—N} \qquad (8)$$
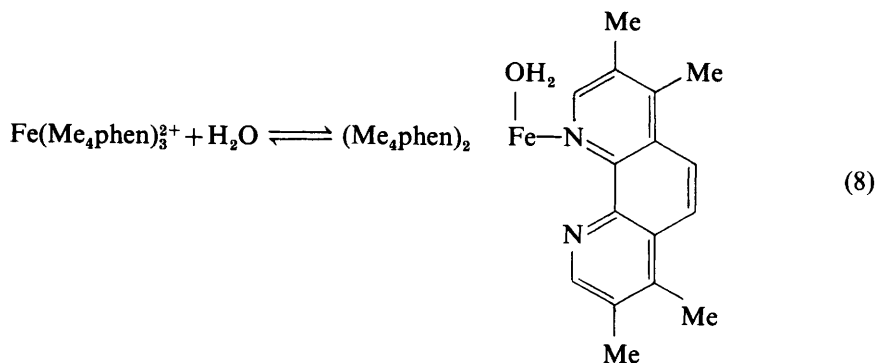
† The aquation rate constant (k_w), for the catalysis by acid in a micelle-free medium, fits the expression $k_w = k_0 + k[H^+]$ (k_0, k are constants). In aqueous triton X-100 medium, at fixed triton X-100 composition, a similar expression is obtained for the variation of the aquation rate constant (k_ψ) with $[H^+]$ at low surfactant compositions.

$$(Me_4phen)_2 \quad OH_2 \atop Fe-N \qquad \rightleftharpoons \quad Fe(Me_4phen)_2(H_2O)_2$$

$$+ H_2O \qquad\qquad\qquad + Me_4phen \qquad\qquad (9)$$

or by a single concerted attack by two water molecules

$$Fe(Me_4phen)_3^{2+} + 2H_2O \rightleftharpoons Fe(Me_4phen)_2(H_2O)_2 + Me_4phen.$$

The present kinetic data cannot distinguish between these two modes of water substitution.

Inclusion of eqn (10) [in addition to eqn (1)–(4)]

$$H^+ + H_2O \rightleftharpoons H_3O^+ \qquad\qquad (10)$$

in the derivation of the expression for k_ψ yields

$$k_\psi = k_4 + \frac{K(k_3 - k_4)[H_2O]_T}{K[H_2O]_T + K[S^{2+}]_T + K_8[H^+]_T + K_1 + 1} \qquad\qquad (11)$$

which predicts inhibition by acid.

The presence of SO_4^{2-} ions, the dissociation product of H_2SO_4, in addition, inhibits aquation by forming a negative field around the iron(II) complex. This effect is, however, only significant at high acid concentrations. The shifts in the position of the maxima progressively to higher $[H_2O]_T$ with increase in $[H^+]_T$ is a combination of both the decreasing activity of water and the changing number of surfactant headgroups surrounding the polar cavities.

The k_ψ vs. $[H_2O]_T$ profile in acid-free medium (uppermost curve in fig. 1) does not completely fit into the comparative trends in k_ψ at low fixed $[H_2O]_T$. While we cannot explain this deviation, we have observed a similar effect in k_ψ vs. $[SDS]_T$ profiles.[18]

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