

THE EFFECT OF COMPLEX CONCENTRATION ON THE MICELLE-CATALYZED AQUATION REACTION RATES OF SOME IRON(II) PHENANTHROLINE COMPLEXES IN ACETONE

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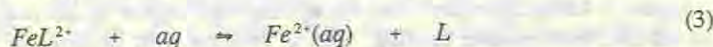
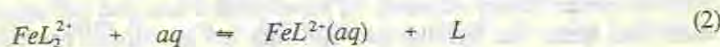
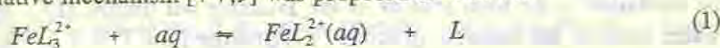
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ABSTRACT. The variation in the aquation rates of the complexes $\text{Fe}(\text{Ph}_2\text{Phen})_3^{2+}$, $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ and $\text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$ with their concentrations in acetone (as solvent) at a fixed surfactant (Triton X-100) concentration was studied. The k_q vs complex concentration profiles for the three complexes show similar patterns in which the aquation rates decrease exponentially with increasing complex concentrations, implying that the aquation reactions of the complexes are inhibited by increasing their concentrations. In each case, k_q drops sharply with increasing complex concentration at low complex concentration. Thereafter, aquation rates almost reached the minimum saturation levels, becoming virtually invariant. The relative aquation rates follow the order: $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+} > \text{Fe}(\text{Ph}_2\text{Phen})_3^{2+} > \text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$. This observation was rationalised on the basis of the differential distribution of the complex molecules between the micellar and the bulk solvent phase, the dissociation equilibria and the differential (relative) hydrophobic influence of the dissociated ligands and steric factor.

INTRODUCTION

The aquation reactions of iron(II) phenanthroline complexes, $\text{Fe}(\text{Phen})_3^{2+}$, and some of its ligand-substituted derivatives such as $\text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$ have been studied extensively in aqueous solutions, and to a much smaller extent in non-aqueous solvents and in aqueous-organic solvent mixtures [1-7]. The majority of these aquation reactions have been found either to be catalyzed or inhibited, quite significantly by surfactant micelles-through substrate solubilization in the micellar cores [3-9].

Generally, a dissociative mechanism [4-7,9] was proposed as follows:



giving an overall equilibrium constant K_d , thus:

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(L = ligand such as Ph₂Phen, etc.), where Equation 1 is the rate determining step. The rate constant K_d has been measured, in aqueous medium [5,8].

The aquation rates of these and other complexes are also influenced by factors such as nature of the solvent medium [9,10], the pH of the system [5-7,11], presence of additives [12-15], and the concentration of the complex itself.

We report here a comparative study of the influence of the complex concentration on the aquation reaction rates of the micelle-catalyzed aquation reactions of the complexes Fe(Ph₂Phen)₃²⁺, Fe(Me₂Phen)₃²⁺ and Fe(Me₄Phen)₃²⁺ in acetone as the bulk solvent. Most of the studies of this nature have been carried out in aqueous media [4-7,9]. The majority of these aquation reactions proceed to completion and follow first order rate law [4-6,9].

RESULTS AND DISCUSSION

Plot of k_q vs complex concentration at a fixed Triton X-100 concentration (2.0% v/v) are shown in Figure 1. This Figure shows that the aquation rates of these complexes decrease rather exponentially with increasing complex concentration. It further depicts the fact that at low complex concentration k_q decreases quite rapidly with increasing complex concentration after which the rate almost reached saturation.

Fe(Ph₂Phen)₃²⁺ manifests the most rapid decrease or inhibition of the aquation rate with a relative inhibition factor of 148 within the range of complex concentration covered. The corresponding relative inhibition factors for Fe(Me₂Phen)₃²⁺ and Fe(Me₄Phen)₃²⁺ are 50 and 56, respectively, within the concentration ranges covered for each of them (see Experimental section).

The observed exponential decrease in k_q with increasing complex concentration (Figure 1), for the complexes Fe(Ph₂Phen)₃²⁺, Fe(Me₂Phen)₃²⁺ and Fe(Me₄Phen)₃²⁺ can partly be rationalized on the basis of differential distribution of the complex molecules between the micellar phase and the solvent phase [16].



At a fixed concentration of Triton X-100 and H₂O and low complex concentration, the equilibrium in Equation 5 is predominantly shifted to the right and hence the complex is favourably distributed into the micellar phase where the aquation reaction is faster. This can be attributed to the high activity of the available but limited H₂O, most of which forms the water pools in the lamellar structure [17] proposed for Triton X-100 micelles. However, as complex concentration increases, its solubilization into and subsequent aquation in the fixed water pool within the micellar core becomes less favourable because more and more of the complex is being distributed into the hydrophobic region of the lamellar structure due to the favourable hydrophobic binding. This is coupled with increase in the concentration of the complex in the bulk solvent phase.

From the structural point of view, the three iron(II) complexes differ only in the arrangement of the methyl and phenyl groups on the phenanthroline molecule. The nature of the arrangement of the methyl/phenyl groups around the phenanthroline determines: (i) the hydrophobic or solvophobic character of the complex, and, (ii) the extent of complex solubilization or partitioning into the lamellar micellar water pools. Hence these two factors

directly or indirectly determine the extent of the binding and the dissociation (aquation), rates of these complexes in micelle-modified reaction systems.

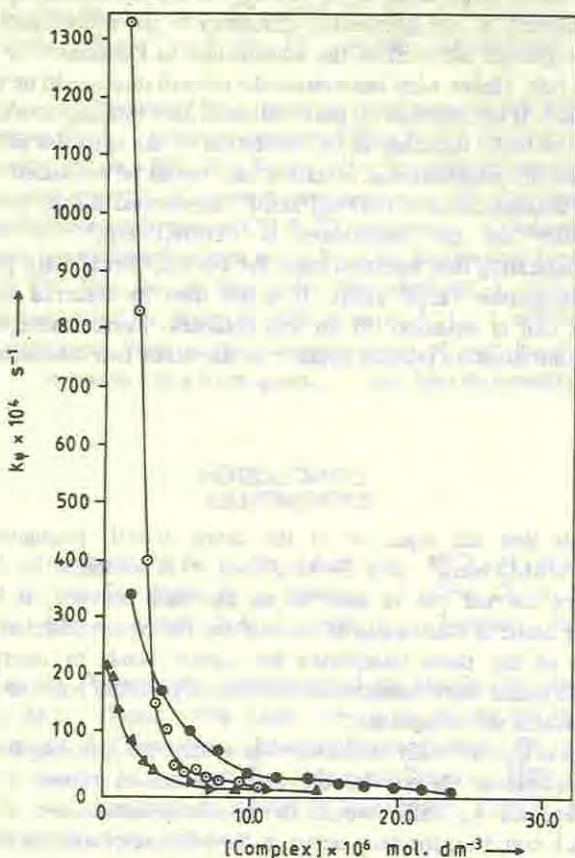
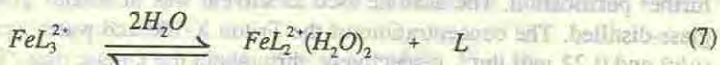


Figure 1. Dependence of the aquation rate constants k_q on the concentrations of the complexes at fixed [Triton X-100], ○ = $\text{Fe}(\text{Ph}_2\text{Phen})_3^{2+}$, ● = $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ and Δ = $\text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$.

Considering hydrophobic factor alone, it would be expected that $\text{Fe}(\text{Ph}_2\text{Phen})_3^{2+}$, being the most hydrophobic [18], should have the least k_q values at all the complex concentrations used, while $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ being the least hydrophobic [18], should have the highest k_q values except when the concentration of $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ is $1.98 \times 10^{-6} \text{ mol. dm}^{-3}$.

In addition to hydrophobic factor, the following equilibria can equally be considered:



In Equation 8, the micelle acts as a sink for the dissociated ligand, L, in Equation 7. This enhances the dissociation of the complex by shifting the equilibrium in Equation 7 to the right. The more hydrophobic L is, the greater the efficiency of the equilibrium in Equation 8 as a sink for L and the greater the shift of the equilibrium in Equation 7 to the right, i.e., the faster the aquation rate. Hence what determines the overall rate would be the balance between the Equations 6 and 8. If equilibrium (6) predominates, then binding between the substrate and the micelle would be high, resulting in the inhibition of the aquation process. On the other hand, if equilibrium (8) predominates, aquation rate would be enhanced.

Except for the concentration of $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ mentioned above, the generally observed aquation rate order for the complexes is $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+} > \text{Fe}(\text{Ph}_2\text{Phen})_3^{2+} > \text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$, indicating that aquation rates for $\text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$ are generally lower than predicated by hydrophobic factor alone. It could then be inferred that equilibrium (6) predominates over that in equation (8) for this complex. Furthermore, higher steric factor might reduce its solubilization process relative to the other two complexes, hence lowering the aquation rate.

CONCLUSION

This study reveals that the aquation of the three iron(II) phenanthroline complexes: $\text{Fe}(\text{Ph}_2\text{Phen})_3^{2+}$, $\text{Fe}(\text{Me}_2\text{Phen})_3^{2+}$ and $\text{Fe}(\text{Me}_4\text{Phen})_3^{2+}$ is inhibited by increasing complex concentration when carried out in acetone as the bulk solvent. It further shows that hydrophobic factor alone is inadequate to account for the observed relative inhibition of the aquation reaction of the three complexes but factors such as interplay of competing dissociation equilibria and steric hindrance also play significant roles in determining the net aquation rate of each of the complexes.

Additionally, this type of study could serve as a basis for planning further kinetic studies on each of the complexes. It enables the experimenter to choose a range of complex concentration where the k_a value would be relatively insensitive to slight changes in concentration which could erroneously occur in the process of mixing the complex solution for kinetic runs. This is particularly necessary for a system (such as the one being considered here), in which the aquation reaction is catalyzed (or inhibited), not only by the surfactant used but by the solvent medium employed.

EXPERIMENTAL

The complexes $[\text{Fe}(\text{Ph}_2\text{Phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Fe}(\text{Me}_2\text{Phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}(\text{Me}_4\text{Phen})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were synthesized and purified by following the methods described by Schilt [19] and Lolly [20]. The complexes were characterised by their visible spectra. Their respective molar extinction coefficients (ϵ_{max}) are 22300, 14000 and 13700 ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), at λ_{max} of 532, 510 and 500 nm, which are in agreement with the literature values [5,6,21,22]. Scintillation grade Triton X-100 (Aldrich Chemicals), was used without further purification. The acetone used as solvent was of Analar grade. The water used was glass-distilled. The concentrations of the Triton X-100 and water were kept constant at 2.0% (v/v) and 0.22 $\text{mol} \cdot \text{dm}^{-3}$, respectively, throughout the kinetic runs. The concentration ranges of the complexes employed are as follows:

$$\text{Fe}(\text{Ph}_2\text{Phen})_3^{2+} = 1.42 \times 10^{-6} - 10.65 \times 10^{-6} \text{ mol.dm}^{-3}$$

$$\text{Fe}(\text{Me}_2\text{Phen})_3^{2+} = 1.98 \times 10^{-6} - 23.76 \times 10^{-6} \text{ mol.dm}^{-3}$$

$$\text{Fe}(\text{Me}_4\text{Phen})_3^{2+} = 0.39 \times 10^{-6} - 14.66 \times 10^{-6} \text{ mol.dm}^{-3}$$

The aquation rate were measured by monitoring the change in absorbance of the complex with time at their respective λ_{max} values at constant Triton X-100 and H_2O concentrations. The absorbances were measured on a SP6, 400 Series 2 Pye Unicam spectrophotometer fitted with a thermostated cell compartment. A constant temperature of 25° was maintained throughout by employing a combination of Cryocool CC-60TT compressor, a Gallencamp thermostating unit and a fast Austen pump, which pumps water from the thermostated water bath around the cell compartment at 25° . The pseudo first order rate constants, k_p , for the aquation of the complexes were obtained from the slopes of plots of $\ln(A_t - A_\infty)$ vs t , which were always linear to more than two half-lives. Prior to the commencement of each kinetic run, the reaction components were mixed together in a 4 cm quartz cell and then thoroughly shaken to facilitate homogeneity.

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