Kinetics and mechanism of aquation of tris (3,4,7,8 - Tetramethyl - 1,10 - Phenanthroline) iron (II) Suphate in aqueous sodium lauryl sulpahate.

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Abstract:

In this thesis we report the kinetics and mechanism of the aquation of tris(3, 4, 7, 8-tetramethyl1,10 phenanthroline) Iron(II) sulphate in aqueous micellar solution of Sodium Lauryl sulphate(NaLS).

The aquation is inhibited by NaLS in the presence of H^+, OH^- , $SO4^{2-}$, $NH4^+$ and tetraethylammonium ion (Et4N*). The inhibition is attributed to the stable association or binding between the complex and the micelle and the decrease in the activity of water in the micellar phase. The partitioning of the substrate between the bulk water solution and the micellar phase is in favour of the latter. The kψ-[surfactant] profiles are structured due to micellar evolution.

A mechanism which fits kinetic data at low surfactant concentration is proposed. From the rate law obtained and kinetic data observed, the micelle-complex binding constant K1 and micelle-acid binding constant K_3 are calculated to be 2.81×10^5 and 13.80 $mol^{-1}dm3$ respectively in acid medium. Using Scat chard method, K_1 in neutral medium is 3.95×10^5 $mol^{-1}dm3$. The decrease in K_1 in acid medium is due to competition for the binding sites on the micelle by the acid proton H^+ and the complex ion.

The rate of reaction is a function of equilibrium distribution of all the substrates between the micellar phase and bulk water phase. The evolution of the micelle with respect to the c.m.c. is also a function of the nature of the substrate present in solution. Calculated activation parameters suggest strong steric stabilisation of the transition state with respect to enthropy. The magnitudes of activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ are functions of the surfactant concentration. $\Delta H^{\#}$ (KJ mol^{-1}) and $\Delta S^{\#}$ (JK^{-1} mol^{-1}) for the aquation in 0.00, 1.0×10^{-4} and 2.0×10^{-4} mol dm^{-3} NaLS are respectively: 100.40 ± 2.04, 22.58 ± 0.16; 111.48 ± 1.15, 48.94 ± 0.09; 119.19 ± 1.15, 67.16 ± 0.09 in 1.00M H_2SO_4.

Keywords: Kinetics/ mechanisms/ aqueous micellar solution/ tetraethylammonium ion/ micellar evolution/ surfactant concentration/ Scat chard method/ entropy

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