

A Group Additivity Approach to Solvent Effects and Reaction Mechanisms for Aquation of an Iron(II) Complex in Aqueous Solutions

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Kinetic solvent effects for aquation of iron(II) complex ions, $[\text{Fe}(5\text{-NO}_2\text{-phen})_3]^{2+}$ (phen = 1,10-phenanthroline), in binary aqueous mixtures are accounted for in terms of a Group Additivity Scheme, highlighting a novel method for probing reaction mechanisms.

In aqueous solutions at 298.2 K, first-order rate constants k_1 for the aquation of $[\text{Fe}(5\text{-NO}_2\text{-phen})_3]^{2+}$ increase¹ when MeOH, EtOH, PrⁱOH, and Bu^tOH are added; Figure 1. The data refer to aquation reactions carried out in 0.1 mol dm⁻³ solutions. In all solvent mixtures studied here, aquation proceeded to completion and obeyed first-order kinetics for well over 2.5 half-lives. The ratio $\ln(k_1/k_1^0)$ is a linear function of the molality of added alcohol, m_2 ; k_1^0 is the first-order rate constant at $m_2 = 0$. The linear dependences can be understood in terms of the Savage-Wood Additivity Scheme² (or,³ SWAG). In the present context^{4,5} the effects of alkyl(R) and hydroxyl(OH) groups produced by added ROH on initial (IS) and transition(TS) states are described in terms of pairwise interaction parameters, $G(\text{R} \leftrightarrow \text{IS})$, $G(\text{OH} \leftrightarrow \text{IS})$, $G(\text{R} \leftrightarrow \text{TS})$, and $G(\text{OH} \leftrightarrow \text{TS})$; equation 1.

$$\ln(k_1/k_1^0) = [2/\text{R.T.}(m^0)^2] \cdot [G(\text{R} \leftrightarrow \text{IS}) + G(\text{OH} \leftrightarrow \text{IS}) - G(\text{R} \leftrightarrow \text{TS}) - G(\text{OH} \leftrightarrow \text{TS})] \cdot m_2 \quad (1)$$

The pattern in Figure 1 is consistent with TS being more hydrophobic than IS, the Fe-N bonds stretching on going from IS to TS. The slopes, $[d\{\ln(k_1/k_1^0)\}/dm_2]$ calculated using a linear least-squares procedure show constant increments with increase in the number of CH₂ groups in ROH as required if equation 1 is written in the form which re-expresses group R in terms of equivalent methylene groups; e.g., CH₃ = 1.5 × CH₂, C₂H₅ = 2.5 × CH₂ and C₃H₇ = 3.5 × CH₂. More significantly, perhaps, the increment is 21 J kg⁻¹, being close in magnitude to the pairwise methylene-methylene interaction parameter $G(\text{CH}_2 \leftrightarrow \text{CH}_2)$, -34 J kg⁻¹. This observation points to an increase in hydrophobic character of the

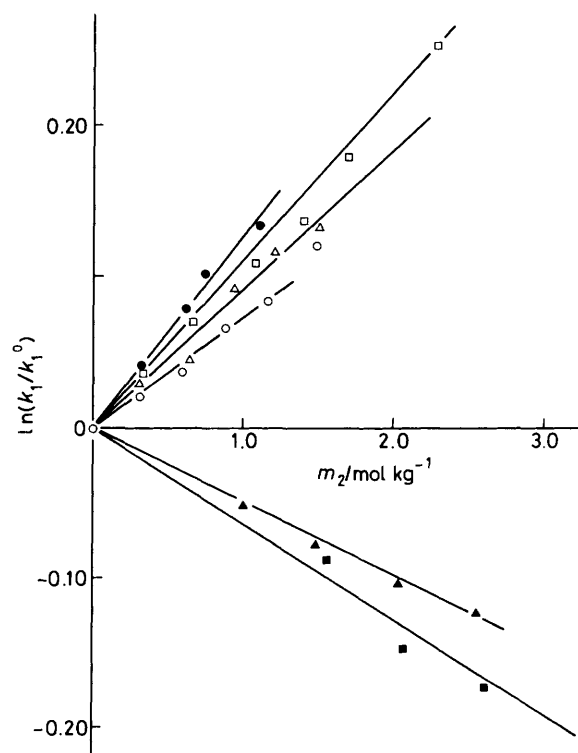


Figure 1. Dependence on molality of organic solute m_2 for $\ln(k_1/k_1^0)$ describing rate of aquation of iron (II) complex $[\text{Fe}(5\text{-NO}_2\text{-phen})_3]^{2+}$ in aqueous acidic solutions at 298.2 K. Solutes are MeOH (○), EtOH (△), PrⁱOH (□), Bu^tOH (●), ethanoic acid (▲), and methanoic acid (■).

iron(II) complex on going from IS to TS equivalent to approximately one methylene group. In other words, the comparison drawn in Figure 1 offers a basis for probing solvent effects and subtle details of reaction mechanisms.

Addition of the hydrophilic solute HCO_2H produces a decrease in rate constant. When MeCO_2H is added the same pattern emerges in that with increase in the number of CH_2 groups, the slope of the plot increases. Moreover the increment in slope is the same as that observed for monohydric alcohols although possible dimer formation between carboxylic acid molecules introduces a new complexity.

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