

Acid Aquation of Octahedral Complexes in t-Butyl Alcohol-Water Mixtures

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RECENT spectroscopic and relaxation studies of t-butyl alcohol-water mixtures and solutions,¹ and earlier ultrasonic studies,² have all shown a marked discontinuity in physical property against solvent composition graphs at a t-butyl alcohol mole fraction of about 0.04. We have now studied spectrophotometrically, at 35.0°, rates of aquation of *cis*-[Co en₂ Cl₂]⁺ and [Fe(5NO₂-ophen)₃]²⁺ in various t-butyl alcohol-water mixtures, in the presence of sulphuric or hydrochloric acid. Ratios of first-order rate constants (k_x) to rate constants in pure water (k_0) are plotted against mole fraction t-butyl alcohol (x) in the Figure. Each graph has a break at $x = 0.04$; since this is independent of the ions present the phenomenon must be a function of solvent composition.

In aqueous mixtures t-butyl alcohol enhances the structure of the water at mole fractions below about 0.04; at higher mole fractions this enhancement is progressively disrupted. These effects may result in differences in solvation of ground or transition states. The simplest interpretation of the present kinetic results is that water-to-metal bond formation is important in formation of the transition state. On going from a t-butyl alcohol mole fraction of 0 to nearly 0.04 enhancement of water structure makes cation to incoming-water bonding progressively more difficult; as the proportion rises beyond 0.04 mole fraction, disruption of the water structure makes water molecules more

freely available and thus facilitates transition-state formation. This behaviour would lead initially to slower reaction, then increasingly rapid reaction as the mole fraction of t-butyl alcohol increases firstly to and then beyond 0.04. This is observed for the cobalt(III) complex. In this complex the solvation shell will be primarily water, modified by t-butyl alcohol in the bulk solvent; the slightly

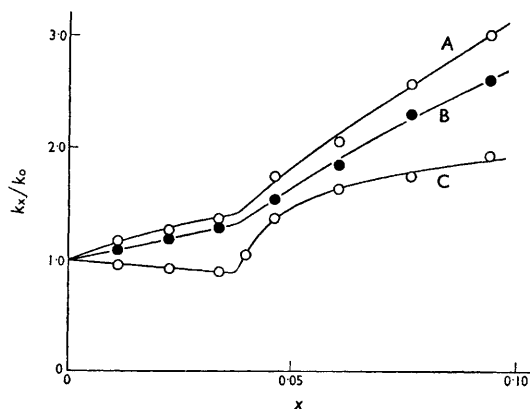


FIGURE. Ratio of first-order rate constants for acid aquation at various mole fractions t-butyl alcohol to rate constant in water (k_x/k_0) against mole fraction t-butyl alcohol (x). A: [Fe(5NO₂-ophen)₃]²⁺ in 0.055N-HCl; B: [Fe(5NO₂-ophen)₃]²⁺ in 0.11N-H₂SO₄; C: *cis*-[Co en₂ Cl₂]⁺ in 0.11N-H₂SO₄.

different behaviour of the iron(II) complex may result from solvation of the organic ligands by t-butyl alcohol as well as water. Differences in the curves for acid aquation of the iron(II) complex in sulphuric and hydrochloric acids of equal

(anion) molarity show that this simple picture must be modified, at least at t-butyl alcohol mole fractions above 0.04, to allow for the presence of anions in the cation solvation shell.³

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¹ M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wootten, *Chem. Comm.*, 1967, 273.

² M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *Chem. Comm.*, 1966, 342, and refs. therein.

³ Cf., M. L. Tobe, *Rec. Chem. Progr.*, 1966, **27**, 79.