Cosphere–Cosphere Overlap Effects on the Rates of Chemical Reactions in Aqueous Salt Solutions

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The dependence on salt of rate constants, $k_{obs.}$, for the hydrolysis of phenyl dichloroacetate in aqueous salt solutions at fixed ionic strength is accounted for in terms of cosphere–cosphere interactions between ions, the overall pattern being very similar to the corresponding dependence of $\ln\gamma_\pm$ where $\gamma_\pm$ is the mean ionic activity coefficient of the salt.

In general terms, the properties of aqueous salt solutions are determined by three factors; (i) the hydration characteristics of the individual ions, (ii) charge–charge interactions, and (iii) interactions between cospheres of solvent surrounding the ions.[1] Broadly, overlap in real solutions between cospheres having similar or dissimilar structures results in a stabilisation or a destabilisation respectively.[2] Rate constants for chemical reactions in salt solutions would be expected to reflect these same structural influences. In practice, most reports of salt effects on the kinetics of reactions concentrate on chemical reactions involving ions (for an exception see reference 3), the classic Bronsted–Bjerrum theory in conjunction with Debye–Huckel equations being used in the analysis of the dependence of rate constants on ionic strength. Deviations of observed from predicted dependences are discussed in terms of factor (ii), including ion pair formation. We report evidence for the importance of factor (iii).

The established mechanism[4] for the neutral hydrolysis of phenyl dichoroacetate involves rate determining water-catalysed attack by water at the carbonyl group. Rates of hydrolysis are characterised by first order rate constants $k_{obs.}$ which, for reaction in binary aqueous mixtures, depend on the composition of the mixture.[5] In the study reported here, we measured rate constants for this reaction in a range of 1 : 1 salt solutions (made acid with 10^{-2} mol dm^{-3} HCl to suppress catalysis by OH$^-$). All salt solutions had the same ionic strength, 0.9 mol dm^{-3}. At 298 K, a marked dependence of $k_{obs.}$ on salt was observed (Figure 1). The switch in order on going from fluoride to bromide salts is particularly interesting. Whereas the rate constant is significantly smaller for reaction in Bu$_4$NBr(aq.) than in water (rate constant k_0), the reverse applies for Bu$_4$NF(aq.).

The overall pattern is similar to that identified by Desnoyers[5,6] in connection with $\ln\gamma_\pm$, where $\gamma_\pm$ is the mean ionic activity coefficient for a salt in solution, Figure 1. In these terms, a key influence on the properties of Bu$_4$NBr(aq.) is the attraction between the cospheres around the hydrophobic ions. Repulsive interactions between the cospheres around
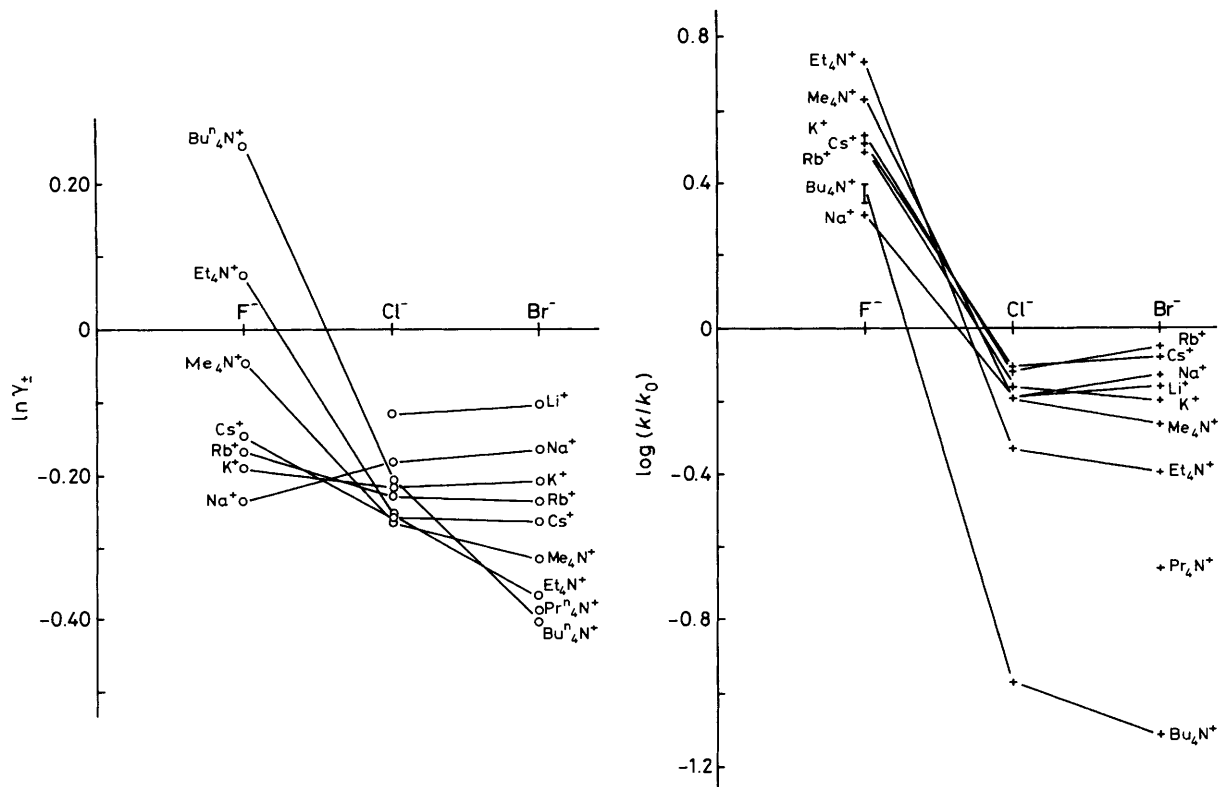
Figure 1. Comparison of the dependence on salt of $\ln \gamma_{\pm}$ for the salt itself and of $\log(k/k_0)$ for hydrolysis of phenyl dichloroacetate in the presence of that salt in acidified 1:1 aqueous salt solutions at 298 K where [salt] = 0.9 mol dm^{-3} and [HCl] = 0.01 mol dm^{-3}; each kinetic data point is the mean of four measurements; $k_0 = k_{obs.}$ where [salt] = 0.

Bu_4N^+ and F^- are the dominant influence on the properties of $Bu_4NF(aq.)$. Clearly $k_{obs.}$ for the above reaction is particularly sensitive to these cosphere effects because water is involved in the reaction, its activity being sensitive to the nature of the salt. The patterns (Figure 1) are a striking indication of the importance of cosphere effects in this class of reactions and, by extension, to systems where factors (i) and (ii) are also taken into account.

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