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SOLVATION AND REACTIVITY OF INORGANIC COMPLEXES: F vs. H
AND CF₃ vs. CH₃

A. Al-Alousy and J. Burgess

Chemistry Department, University of Leicester, Leicester LE1 7RH (U.K.)

We are currently examining the effects of the replacement of H by F, and of CH₃ by CF₃, in the ligands of selected inorganic complexes on solvation and on reactivity. We are also comparing CF₃CH₂OH with CH₃CH₂OH, and CF₃CH(OH)CF₃ with CH₃CH(OH)CH₃ as solvents for inorganic complexes.

Solute-solvent interactions are being probed through transfer chemical potentials and through solvatochromism. We shall compare transfer chemical potential trends for complexes M(acac)₃, M(tfac)₃, and M(hfac)₃, and for some iron(II) complexes of diimine ligands and their fluoro-analogues, in binary aqueous solvent mixtures. The trends which are emerging show that replacement of H by F results in a significant increase in hydrophilicity, with the determined transfer chemical potentials giving a quantitative measure of differences. The solvatochromic properties of ternary iron(II)-diimine-cyanide give an alternative means of comparing solute-solvent interactions, both in relation to fluorine substitution in the diimine ligands and in respect of the solvating properties of the fluoroalcohols mentioned above.

Replacement of H by F, or of CH₃ by CF₃, in iron(II) complexes of Schiff bases derived from appropriate anilines results in much faster rate constants for base hydrolysis. It is hoped to present an initial state-transition state analysis of reactivity trends in methanol-water mixtures in order to establish precisely how solvation changes affect reactivities in this type of reaction.