can be tailored at will simply by changing the nature of the ligands coordinated to the central Co^{3+} cation and/or changing the counter ions.

For instance, the $Co(CN)_6^{3-}$ ion measures the polarity of dipolar solvents, and will rank protic solvents according to their hydrogen-bond donor ability. Conversely, an ion such as $Co(NH_3)_6^{3+}$ will interact with solvents depending upon their strength as hydrogen-bond acceptors. Changes in net ionic charge can also be exploited to reveal details of the interactions between these cobalt complexes and other solute and solvent molecules.

b) Investigation of sodium cation solvates.

Sodium-23 (I = 3/2) nmr has good enough sensitivity that it can be applied to rather dilute (c*M*/m*M*) solutions of sodium salts. The observed changes in *both* the ^{23}Na chemical shifts and linewidths, in binary solvent mixtures, are successfully interpreted on the basis of competition for tetracoordination of the sodium cation by organic solvents such as THF, glymes, pyridine and other unidentate or polydentate amines. We have applied, to account *jointly* for the chemical shift and the relaxation rate data, the Hill formalism: mathematically, preferential solvation of a tetracoordinated ion, and binding of a ligand to one of four equivalent sites in a biomolecule, constitute one and the same problem. The powerful Hill formalism allows the determination of the magnitude of the chelate effect present for certain bidentate and polydentate ligands. It also leads to fairly accurate measurement of microscopic equilibrium constants for the successive steps in the replacement, in the sodium coordination sphere, of a solvent A by another solvent B.

Metalloenzymes and Model Systems. Carbonic Anhydrase: Solvent and Buffer Participation, Isotope Effects and Activation Parameters

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It is a general dilemma in biophysical chemistry that although small perturbations are theoretically most desirable, they tend to produce small effects which in turn are difficult to interpret, especially when systems are as large and complex as those encountered in the study of enzyme catalysis. In this regard the replacement of H_2O by D_2O is slowly becoming a powerful tool, especially in hydration–dehydration studies, because it gives measurable results from a modest perturbation of those molecular properties which are sensitive to mass. The ubiquity of CO_2 has prompted us to investigate one of life's most fundamental reactions, the reversible hydration of CO_2. We find that many general bases, and especially metal ion–hydroxo complexes catalyze this reaction, but the most potent of these catalysts is the zinc metalloenzyme carbonic anhydrase (carbonate hydro-lyase EC 4.2.1.1) from red blood cells. The mammalian enzyme is especially versatile catalyzing not only the reversible hydration of CO_2 but also that of aliphatic aldehydes, pyridine carboxaldehydes, pyruvic acid and alkyl pyruvate esters. The enzyme is also an efficient esterase, catalyzing the hydrolysis of certain carboxylate, sulfonate, phosphate and imidate esters. Substitution of zinc(II) by cobalt(II) gives an active enzyme which is being studied by observing its response to perturbations induced by substrates, buffers and inhibitors. We have recently studied the effects of pH, buffer concentration, steric hindrance, solvent composition (H_2O *vs.* D_2O) and inhibitor binding on CO_2 hydration, HCO_3^- dehydration and ^{18}O exchange in the CO_2–HCO_3^- system at four temperatures ranging from 7° to 35 °C. Our findings allow us to eliminate a number of anomalous mechanisms pertaining to isotopic exchange and provide us with a suitable framework for transition state characterization. Furthermore, our work shows that the Haldane relation is obeyed at every pH (pD), buffer and inhibitor concentration studied. Compliance with this relation shows that the system meets all the criteria required for the attainment of a chemical equilibrium.

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New Insights into the Host-Guest-Solvent Interaction of Some Inclusion Complexes

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Cyclodextrin (α, β- or γ-) is known to accommodate appropriate guest molecule(s) in its cavity in aqueous solution, forming an inclusion complex. Major driving force to form this inclusion complex