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.

Acknowledgements

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

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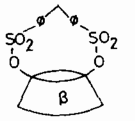
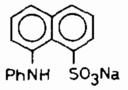
Cyclodextrin (α, β- or γ-) is known to accommodate appropriate guest molecule(s) in its cavity in aqueous solution, forming an inclusion complex. Major driving force to form this inclusion complex is as following by our thermodynamic consideration [1]; (*a*) destruction of water cluster originally developed along the surface of the guest molecule in water, (*b*) van der Waals interaction between the guest surface and the interior surface of guest molecule, (*c*) stabilization of water molecule(s) originally bound in the cavity. Capped cyclodextrin (I) thus shows the remarkably enhanced van der Waals stabilization, leading to very strong binding as shown by equilibrium constants.



I



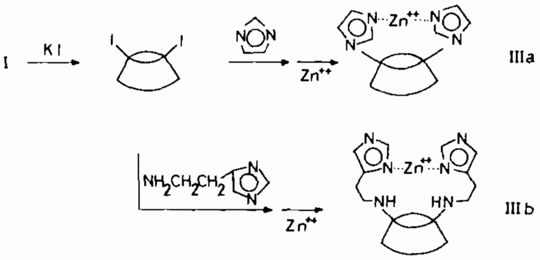
II

$$I + II \xrightleftharpoons{H_2O} I\cdot II; \qquad K = 1{,}300\,M^{-1}$$

$$\beta\text{-CD} + II \xrightleftharpoons{H_2O} \beta\text{-CD}\cdot II; \qquad K = 53\,M^{-1}$$

Therefore, strong hydrophobic nature of the capped cavity is evident [2, 3].

Carbonic anhydrase activity is said to require CO_2 and H_2O in hydrophobic environment around $(\text{imidazole})_3Zn^{++}$. This situation is reasonably modeled by IIIa or IIIb,

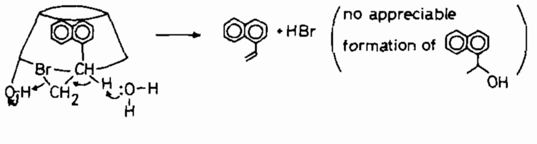


$$H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+$$

where H_2O solute seems to be strongly activated by Zn^{++} coordination and the hydrophobic environment as is seen from the catalytic constants.

	k_{cat} (M^{-1} sec^{-1})
imidazole	negligible
$(\text{imidazole})_2Zn^{++}$	2.0
IIIa	16.2
$(\text{histamine})_2Zn^{++}$	57.9
IIIb	166

When a water (solute) molecule appropriately approaches the 'rim' (edge) of the cavity, it is so activated as to promote efficient hydrolysis, as is seen in the example below.



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The Structure of Water in the Double Layer

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The origin of the concepts of water contributing a structure to the double layer is traced from the first equation involving a surface potential to Klein and Lange, through the first model suggestions of Bockris and Potter in 1952 to the more recent aspects of the situation as indicated by the optical spectroscopy of Bewich.

The models of water in the double layer are concerned with solvent–solvent and solvent–solute interactions, and are of relevance in interpreting major aspects of double layer phenomena.

The introduction of water into the double layer structure and basic equations which connect such structure with other properties of the double layer (Bockris, Devanathan and Mueller, 1963) contributed a fourth stage (after the classical ones of Helmholtz, Gouy and Stern) to ideas of double layer structure.

A presentation of current models and suggestions for future developments is given.

Copper(II) Chelate Complexes – Solute and/or Solvent Interactions

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Some problems of the specific interactions between copper(II) chelate complexes, and Lewis bases and/or acids added to the 'inert' solvents or