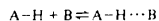


Chemical Society Reviews

Volume 22 Issue 2 Pages 73-141 April 1993

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Scales of Solute Hydrogen-bonding: Their Construction and Application to Physicochemical and Biochemical Processes

By Michael H. Abraham (pp. 73-83)

The construction of scales of hydrogen-bond acidity and hydrogen-bond basicity, using 1:1 hydrogen-bond complexation constants in tetrachloromethane, is set out. These 1:1 scales can be used to develop 'effective' or 'summation' scales of hydrogen-bond acidity and hydrogen-bond basicity that are appropriate for situations in which a solute is surrounded by an excess of solvent molecules. Together with other solute descriptors that have also been developed, the summation scales of solute hydrogen-bonding can be incorporated into LSERs and QSARs that can be applied to numerous physicochemical and biochemical processes, and can be used to assess quantitatively the role of hydrogen-bonding in these processes.

Polymer-Micelle Interactions: Physical Organic Aspects

By Josephine C. Brackman and Jan B. F. N. Engberts (pp. 85-92)

This review presents a summary of attempts to characterize the morphology of the complexes formed between ionic and non-ionic surfactants and water-soluble polymers. It is now generally accepted that complex formation involves the binding of micelles to the macromolecule. This binding process modifies the size and properties of the micelles and affects the Gibbs energy of the polymer. A complex combination of interaction forces provides the driving force for complexation. Criteria for polymer-micelle interaction are discussed. Particular emphasis is placed on the role of charge and structure of the surfactant headgroup and on the effect of polymers on the micellar structure and properties of cetyltrimethylammonium salts.

MELDOLA LECTURE. Reactions of Group 13 Alkyls with Dioxygen and Elemental Chalcogens: From Carelessness to Chemistry

By Andrew R. Barron (pp. 93-99)

This article details the path by which an accidental reaction of $\text{In}(\text{Bu}^t)_3$ with dioxygen led to the synthesis of stable Group 13 alkylperoxides, as well as the first examples of Group 13 alkyldisulfides and chalcogenide clusters. The synthesis of these new compounds is presented and the reaction chemistry of the alkylperoxide compounds with simple phosphorus substrates is also described. In the case of the chalcogenide compounds a unique topological rearrangement is presented. Finally, a schematic view of the reaction of a Group 13 alkyl with elemental chalcogens is discussed.

How Do Diesel-fuel Ignition Improvers Work?

By P. Q. E. Clothier, B. D. Aguda, A. Moise, and H. O. Pritchard (pp. 101-108)

A wide-ranging study of the effect of free-radical initiators, especially *i*-octyl nitrate and di-*t*-butyl peroxide, on the spontaneous ignition of diesel fuel is reported. The important kinetic processes induced by these additives occur in the gas phase, and not in the liquid droplets. Di-*t*-butyl and *i*-octyl nitrate peroxide work in different ways: the nitrate is involved in the ignition process itself, whereas the peroxide competes for sulfur-containing inhibitors in the fuel.

The Role of NMR in Boron Chemistry

By David Reed (pp. 109-116)

This article shows, with use of examples, how NMR spectroscopy can help in the study of boron hydride chemistry. The examples highlight some of the range of problems that can be analysed using combinations of one- and two-dimensional NMR techniques.

Motion of Sorbed Gases in Polymers

By Wen-Yang Wen (pp. 117-126)

The mobility of sorbed gases in polymers is an interesting scientific problem with important technological implications. Motional mechanisms for penetrant diffusion are considered to depend strongly on whether the polymer matrix is in the rubbery or glassy state. The dual-mode model, which has been employed by a large number of polymer chemists and engineers, is now under scrutiny by some investigators. Early results of a few NMR experiments and computer simulations are beginning to shed new light on the motional dynamics of both the penetrants and polymer chains.

Thermodynamic and Related Studies of Amphiphile + Water Systems

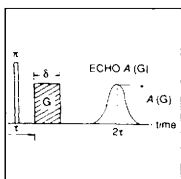
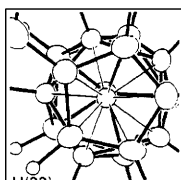
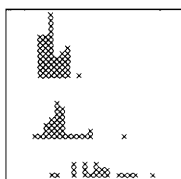
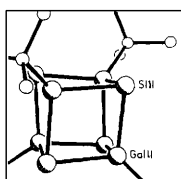
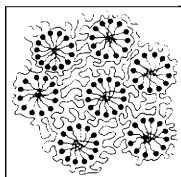
By Michael I. Davis (pp. 127-134)

Modest sized amphiphiles play an important role as aqueous co-solvents. Thermodynamic studies of their aqueous mixtures appear to indicate that they are capable of mimicking the important schemes of self-aggregation that are known to be characteristic of detergents and lipids. Attention is focused upon the alkyl poly(ethylene glycol) monoether + water systems. The composition dependence of their thermodynamic properties is discussed in terms of both graphical and numerical analyses and possible interpretations of the effects of molecular aggregation.

The Solubility of Gases in Water-Alcohol Mixtures

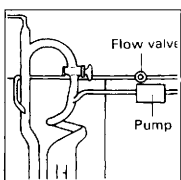
By Robert W. Cargill (pp. 135-141)

The solubility of gases in liquids can now be measured to a high level of precision and accuracy. Analysis of data from studies on several gases dissolved in aqueous alcohols has allowed ΔH^0 and ΔS^0 values to be calculated for the equilibrium. A two-structure model for water has been used to obtain a temperature coefficient for the mole fraction of 'clusters' present in water, and the gases have been classified according to their hydrophobic interactions. These hydrophobic interactions have been interpreted in terms of size and shape of the solute molecules.



B₂ formed under
pressure, is:
$$= x_A(G_{m,A}^* + RT \ln)$$

and $G_{m,B}^*$ are the res



Articles that will appear in forthcoming issues include

CENTENARY LECTURE. The Pursuit of Selectivity in Radical Reactions **A. L. J. Beckwith**

Discovery and Development of Anthracycline Antitumour Antibiotics **J. W. Lown**

Some Recent Synthetic Routes to Thioketones and Thioaldehydes **W. M. McGregor and D. C. Sherrington**

The Nature of the Ammonium and Methylammonium Halides in the Vapour Phase: Hydrogen Bonding *versus* Proton Transfer **A. C. Legon**

Electrolytes in Binary Solvents: Experimental Approach **S. Taniewska-Osińska**

Computer Simulations on Aqueous Solutions of Some Non-Electrolytes **K. Nakanishi**

Structural Systematics in Molecular Inorganic Chemistry **A. G. Orpen**

Biosynthetic Incorporation of Non-Natural Amino Acids into Proteins **J. Brunner**

The Physiological Role of Nitric Oxide **A. R. Butler and D. L. H. Williams**

Low Oxidation States of Indium **D. G. Tuck**

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