in order to obtain linear dichroism spectra of 'guest molecules'.

Finally the problem of a possible influence of LC used as a solvent for chemical reactions will be discussed.

Reactions and Behaviour of Organic Anions in Two-Phase Systems

M. MAKOSZA

Institute of Organic Chemistry, Polish Academy of Sciences, Palace of Culture and Science, Warsaw, Poland

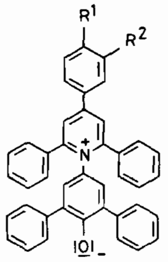
Two-phase systems are presently widely applied as convenient and versatile media for reactions of inorganic and organic anions with organic molecules. The main feature of this approach is that organic and inorganic reactants are located in two immiscible phases and that reactions proceed in the presence of catalysts – tetraalkyl ammonium or phosphonium salts or crown ethers. Consequently reacting anions are introduced into the organic phase and react with organic reactants in the form of salts with lipophilic cations supplied by the catalysts. Typical reactions and specific behaviour of organic anions generated in two-phase systems and role of the boundery between the two phases will be discussed.

Pyridinium-N-Phenoxide Betaine Dyes as Solvent Polarity Indicators. Some New Findings

C. REICHARDT*, E. HARBUSCH and R. MÜLLER

Department of Chemistry, University of Marburg, D-3550 Marburg, F.R.G.

The position of the long-wavelength, intramolecular charge-transfer UV/Vis. absorption band of pyridinium-N-phenoxide betaine dyes of the general formula 1 is very sensitive to changes in solvent polarity (negative solvatochromism) [1], temperature (thermo-solvatochromism) [2], external pressure (piezo-solvatochromism) [3], as well as to the introduction of substituents R^1 and R^2 in the 4-phenyl ring [4]. This extreme sensitivity of 1 ($R^1 = R^2 = H$) to small changes in the surrounding medium has been used to establish an empirical scale of solvent polarity, called the $E_T(30)$-scale [1, 5]. $E_T(30)$-values are simply defined as the transition energy of 1 ($R^1 = R^2 = H$), measured in kcal/mol (or kJ/mol). They are known for more than 150 organic solvents and numerous binary organic solvent/water mixtures, and they have found wide application [5, 6].



It will be shown that empirical parameters of solvent polarity such as the $E_T(30)$-values can be understood within the framework of Linear Free-Energy (LFE) Relationships [6].

Examples for the application of $E_T(30)$-values to correlate spectral, thermodynamic, and kinetic solvent-dependent data taken from different areas of chemistry will be given.

Finally, the improvement of the LFE-correlations of singular empirical parameters of solvent polarity such as the $E_T(30)$-values by means of multiparametric equations will be described.

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Solute–Solvent Interactions in Ring Formation

G. ILLUMINATI

Istituto di Chimica Organica, Università di Roma, P.le Aldo Moro 5, 00185 Rome, Italy

Physical organic investigations on ring forming reactions from bifunctional substrates over a broad range of ring sizes have led to some general as well as special effects concerning solute–solvent interactions of the open chain ground states and/or cyclic transition states.

Among the former, short bifunctional chains appear to suffer to varying extents from inhibition of solvation effects as it can be deduced from the entropies of activation. Furthermore, a systematic investigation of a ring forming reaction series provides a method to estimate the contribution of solvation to the entropy term for a given pair of polar end groups as functional groups of the intramolecular reaction.

Peculiar special effects can be revealed using effective molarity data as a diagnostic tool. An example is the formation of thiophenophan(1)ones by intramolecular acylation which is thought to suffer from a marked steric hindrance of solvation in the transition state due to the geometry requirements of the reaction mechanism and the perturbation effect of the bridging hydrocarbon chain over the heteroaromatic π-electron system.

NMR Studies of Calcium and Magnesium in Biological Systems

STURE FORSÉN, THOMAS ANDERSSON, TADEUSZ WIELOCH and EVA THULIN

Physical Chemistry 2, Chemical Centre, P.O.B. 740, Lund University, S-220 07 Lund, Sweden

Ions and ionic interactions play an important role in biochemical systems. For one thing, the physiological processes in our bodies take place in an electrolyte solution containing, as the major, simple ions: Na^+, K^+, Mg^{2+}, Ca^{2+} and Cl^-. These ions are by no means innocent bystanders to the cellular processes but play a very active biological role. It has, for example, become increasingly clear that Ca^{2+} ions in cells function as a kind of 'second messenger', often in parallel with cyclic AMP. The ions mentioned above have no suitable optical spectroscopic transitions that make them amenable to study. They have, however, all the magnetic nuclei that make NMR spectroscopic studies possible. Their spins, I, are greater than ½ and quadrupolar effects largely determine their NMR properties. Direct observation of NMR signals from the quadrupolar nuclei firmly bonded to a large slowly tumbling macromolecule is exceedingly difficult. It is, however, possible to obtain biochemically relevant information when there is a sufficiently fast chemical exchange between the macromolecular binding site(s) and the free solvated ion [1, 2].

Whereas NMR studies of $^{23}Na^+$ and $^{35}Cl^-$ are favoured by a reasonably high NMR sensitivity, studies of $^{25}Mg^{2+}$ and $^{43}Ca^{2+}$ in millimolar concentrations have only recently become feasible. The use of widebore high field superconducting magnets in combination with solenoid-type probes has been of particuar advantage. Some illustrative applications of ^{25}Mg and ^{43}Ca NMR to the study of calcium binding proteins, like troponin C, phospholipase A_2, hemocyanin and calmodulin, will be presented.

The properties of calcium in calcium binding proteins may also be studied indirectly by replacing Ca^{2+} with $^{113}Cd^{2+}$. The ionic radii of Ca^{2+} and Cd^{2+} are very similar and ^{113}Cd has spin $I = ½$ which allows direct observation of NMR signals from cadmium substituted calcium binding protein [3, 4]. ^{113}Cd NMR has proved to be a very sensitive probe of the nature and coordination geometry of the ligands. Recent results from ^{113}Cd NMR studies of the calcium binding proteins troponin C and calmodulin will be discussed.

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Direct NMR Studies of Ionic Solvation

PIERRE LASZLO*, ALFRED DELVILLE, CHRISTIAN DETELLIER, ANDRÉ GERSTMANS and ARMEL STOCKIS

Institut de Chimie Organique et de Biochimie (B6), Université de Liège, Sart-Tilman par 4000 Liège, Belgique

The nuclear magnetic resonance of quadrupolar ions provides a wealth of information about solvation thermodynamics and dynamics. The talk will deal with two main topics:

a) Use of cobalt(III) complexes.

Cobalt-59 (I = 7/2) has an enormous range of chemical shifts, due to low-lying excited states. The types of ion-solvent interactions to be monitored