Theoretical Models – Ordered fluids

Molecular Force Field of Dioxane and Pyridine in Aqueous Mixtures

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Using published data on the vibrational spectra of dioxane, pyridine and water, a complete set of general quadratic valence force constants has been computed and their variations when each solvent forms aqueous mixtures has been analyzed.

Nuclear magnetic resonance studies on dioxane–water and pyridine–water mixtures revealed a marked concentration dependence of the proton chemical shift of all the species involved. This indicated hydrogen bonding. Previous spectroscopic studies [1] of these mixtures include infrared investigation of the water spectrum in dioxane and pyridine mixtures and extensive Raman investigation of the dioxane–water system.

The calculation was performed using the self-consistent method [2, 3] to solve the secular equation $F\ F\ L = L\ \Lambda$ (where the symbols have their usual meaning) simultaneously for each molecule and the deuterated analog. The calculation started with a diagonal matrix made with the approximate force constants and the final F square matrix belonging to the force constants is obtained from the average of the final F matrix belonging to each molecule and its deuterated analog. The results reproduce satisfactorily the experimental values. The molecular force field obtained for the pure solvents is then used to make the calculations when one considers the shifts that spectral bands show in solutions.

Dioxane: The portion of the pure dioxane infrared spectrum which was used consists of three groups of absorptions: four bands which arise from the C–H stretching modes appear at ~2900 cm^{-1}, four bands centered at ~1350 cm^{-1} result from C–H deformations, and three absorptions due to the C–O stretching in the 1100 cm^{-1} region.

Pyridine: The portion of the pure pyridine infrared spectrum which was used consists of three groups of absorptions due to: the C–H stretching modes (~3000 cm^{-1}), double bond (~1500 cm^{-1}) and hydrogen deformation or ring vibrations (~1100 cm^{-1}).

Water; The –OH vibration (3320 cm^{-1}) of water shifts to higher frequency when mixed with each of the two organic solvents, through the concentration range 100–0.8% water.

The vibrational force constants are calculated using the band position as a function of concentration for all the absorptions mentioned above for a series of solutions, ranging in concentration from 100 to 12% dioxane in water and pyridine in water.

The values for –OH stretching force constants in either solvent seems to indicate a reduction of the hydrogen bonding present in pure water. An attempt was made to correlate the infrared data with the published results of nuclear magnetic resonance studies of these systems.

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Solute–Solvent Interactions by NMR of Molecules Dissolved in Liquid Crystal Solvents

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Solute–solvent interactions have been shown to exist by means of NMR of dissolved solutes both in lyotropic and thermotropic liquid crystalline solutions [1, 2]. We mention, for example, the effects of solvent-induced molecular distortions on tetrahedral molecules [3, 4] and specific solute–solvent interactions in acetylene, methyl-fluoride and a variety of other small molecules [5].

As far as the last molecules are concerned, apparent geometrical distortions arise whenever the interacting nuclei are associated with small values of order parameters (S_{ij}) giving small values of direct dipolar couplings (D_{ij}). The observed dramatic geometrical effects have been explained by admitting a two-site (or multi-site) exchange mechanism within the ordered solvent, each site having its own geometry and orientation [2, 5].

We have recently found, however, that this kind of solute–solvent interactions is confined by no means to small molecules and the results concerning partially oriented spectra of two types of medium sized molecules will be discussed:

a) Substituted anilines: 3,5-dichloro and 3,5-dibromoaniline; 2,4,6-trichloroaniline;

b) Heterocyclic compounds: selenophene; tellurophene; isoxazole.

In the case of molecules *b*), in particular, it has been possible, by means of FT techniques, to obtain ^{13}C–^{1}H, ^{77}Se–^{1}H and ^{125}Te–^{1}H dipolar couplings which, after correction for the effect of molecular vibrations, allow a satisfactory determination of molecular geometry, so that a meaningful comparison with Microwave (M.W.) findings can be performed.

The geometrical incongruencies invariably found in the accurate treatments of overdetermined systems in liquid crystal mesophases suggest that solvent induced distortions and in particular multisite exchange are quite a common phenomenon in the NMR of thermotropic mesophases.

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Solute–Solvent Interactions in Ordered Phases: Asymmetric Induction in Cholesteric Liquid Crystals

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It is well known that diastereotopic solute–solvent interactions between a prochiral center and a chiral solvent can lead to some extent of asymmetric induction.

A cholesteric liquid crystal is indeed a chiral organized medium having a macrostructural helical shape. The question at the start of this work was to determine if the macrostructural handedness of the cholesteric liquid crystal used as a solvent of a chemical reaction can control the stereochemistry of the reaction.

Recently several papers pointed out a large controversy on such question. On the one hand, several research groups reported moderate extents of asymmetric induction during high temperature reactions conducted in cholesteric mesophases such as the Claisen rearrangement of O-allylarylethers [1], enantiomeric decarboxylation [2] or enantiomeric equilibration of sulfoxides [3]. On the other hand, Kagan and co-workers [4] did not succeed in reproducing these literature results and reported no detectable asymmetric induction during several photochemical processes. On the basis of these results these authors concluced by doubting that a cholesteric mesophase could afford appreciable asymmetric induction and that the effect of mesomorphic anisotropy ordering on asymmetric induction remains to be clearly established.

Our own results dealing with Hofman pyrolysis of quaternary salts in cholesteric medium and enantiomeric equilibraition of *trans*-cyclooctene offer evidence that the stereochemical outcome of the reaction conducted in liquid crystals is dependent on the *nature of the mesophase* and that the asymmetric induction is governed by the *'local' asymmetry of the mesophase and solute–solvent interactions* and not by the macrostructural handedness of the mesophase. The photochemical synthesis of chiral hexahelicene in a compensated nematic phase confirms strongly these conclusions. Some typical results: (*see overleaf*)

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