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 Λ (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.

References

1 A. Fratiello, J. P. Luongo, *J. Am. Chem. Soc., 85,* 3072 (1963).
2 Yu. N. Panchenko *et al., Optics and Spectry., 25,* 623 (1968).
3 J. R. Anacona, *Proc. IX Int. Conf. Organometallic Chem.,* P 24W (1979), Dijon, France

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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].