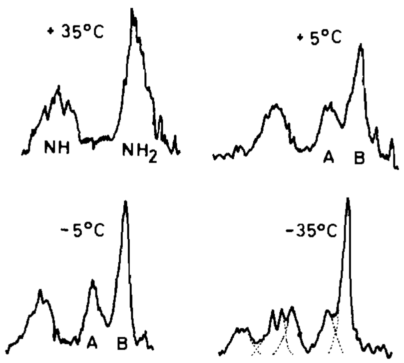

Fig. 1. The nmr spectra of N–H and N–H$_2$ protons of N-methylthiourea in 1,2-propanodiol–carbonate–CCl$_4$ mixture at different temperatures.

thiourea. The relative concentrations and the equilibrium constant between both configurations can be obtained from the areas under the signals.

Both, enthalpy and entropy changes – calculated from the temperature dependence of the equilibrium constant – show a clear dependence on solvent basicity (DN).

The influence of solvent basicity on the thermodynamics of the interconversion between forms A and B, added to the effect of the pure solvents and solvent mixtures on the chemical shifts at room temperature show that the two observed configurations differ on the planarity in the thiourea molecule. The planarity grade on the substrate would be mainly determined by the solute–solvent interaction through hydrogen bonds.

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## Interactions between Copper Phthalocyanine and Sulphuric Acid

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Electron spin resonance spectroscopy was used to study the nature of the solution of copper phthalocyanine (CuPc) in sulphuric acid. The electronic structure of the complex and its interaction with the protons respectively deuterons was especially investigated. In order to reduce the number of superhyperfine signals a nitrogen-15 labelled compound was prepared from nitrogen-15 urea as a starting material. Enriched copper-63 was used for the preparation of the complex in order to avoid line broadening from Cu-63/Cu-65 interaction. Also nitrogen-14 phthalocyanine with isotopically pure copper-63 was investigated in different matrices.

ESR measurements of CuPc/$H_2SO_4$, CuPc/$D_2SO_4$ and CuPcH$_2$Pc were carried out at a frequency of 9.27 GHz at various temperatures. The spectra obtained in the frozen solution differ in a significant way: the nitrogen-15 labelled compound dissolved in $D_2SO_4$ only shows a line broadening effect, whereas the nitrogen-14 compound exhibits an additional splitting of the ninefold nitrogen parallel superhyperfine lines and of the extra-absorption peaks at higher field strength.

In addition, we observed ESR spectra of all three systems over a wide temperature range. Between 213 K and 293 K there is a significant change at the high field part of the spectrum around g-perpendicular, which could not be found in CuPc diluted in H$_2$Pc.

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## NIR-Investigations on the H-Bond State in $H_2O$–Solvent Mixtures

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The formation of H-bonds of $H_2O$ with H-bond acceptors in dilute solutions has been shown by IR-spectroscopy in several systems [1, 2]. In comparison to these solutions the H-bonds in systems enriched in $H_2O$ seem to be poorly understood [3].

The $H_2O$ combination band ($\nu_3 + \nu_2$) is a useful tool for investigations of interactions of $H_2O$–organic molecules. With this method the strength and amount of H-bonds can be determined.

At mole fractions of $H_2O$ between 0.8 and 0.98 in acetone, tetrahydrofuran, *etc.* the spectra show the presence of H-bonds between $H_2O$ and the organic acceptors similar to those in dilute solutions; in addition the spectra indicate the presence of less free OH-groups and more H-bonds of intermediate strength in comparison to pure water.

The relation between these observations and the solubility of organic molecules in $H_2O$ as well as the two phase formation after addition of salts or sugars for example to these binary solvents is studied and will be discussed.

### *References*

1 W. A. P. Luck and D. Schiöberg, *Advan. Mol. Relaxation Processes, 14,* 277 (1979).
2 D. Schiöberg and W. A. P. Luck, *J. Chem. Soc., Faraday I, 75,* 762 (1979).
3 F. Franks, in: 'Water a Comprehensive Treatise', Vol. 4, p. 1, F. Franks ed., Plenum Press, New York (1975).