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The Temperature Dependence of the Dielectric Properties of Unassociated Organic Solvents at Polarizable Interfaces

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As it was shown previously [1, 2], the three state model for solvent dipoles can be used successfully to describe the differential capacity at Hg/nonaqueous interface in the case of unassociated or weakly associated organic solvents.

The model may be tested further by examining the temperature dependence of the surface potential and the adsorption entropy as was done previously for Hg/aqueous interface [3, 4]. The temperature coefficient of the surface potential for a number of organic solvents with the exception for methanol is positive [5]. However the interpretation of this quantity in terms of solvent dipole orientation and the sign of the surface potential depends on the molecular model used to describe the dielectric properties of the solvent monolayer. Another quantity which is accessible experimentally is the solvent adsorption entropy. The only data available for nonaqueous solvents are those for Hg/propylene carbonate interface [6]. It is evident that the accepted interpretation based on a two state model is not valid in this case. The molar adsorption entropy has a maximum at a negative charge density which would suggest a preferred orientation at the uncharged mercury with the negative end of the propylene carbonate dipole pointing towards the metal and consequently, a negative surface potential. However the occurrence of the solvent capacity 'hump' at a high positive charge density would imply just the opposite.

The purpose of this paper is to discuss the temperature dependence of the dielectric properties of the Hg/solution interface in the case of N,N-dimethylformamide, methanol and acetone including also the literature data for propylene carbonate [5]. The adsorption entropy has been calculated on the basis of the temperature dependence of the double layer differential capacity following the thermodynamic arguments of Harrison *et al.* [7]. The results have been compared with the prediction of three state model.

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Solvent Effect on N-Methylthiourea. A ^{1}H-NMR Study

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The solvent influence on the spectroscopic properties of the solute can be used to obtain information about its configuration in solution. With this objective the influence of the temperature on the ^{1}H-nmr spectra of N-methylthiourea was studied in the following solvents 1,2-propanodiolcarbonate, trimethylphosphate, tributylphosphate and dimethylsulfoxide mixed with CCl_4 in a ratio 1:1 in volume. At low temperature the methyl group signals of thiourea split showing the signals corresponding to *cis* and *trans* positions of methyl protons. These results agree with the behaviour reported for other solvents.

However, the low field spectra corresponding to N–H and $N–H_2$ protons show a higher complexity as is shown in Fig. 1.

The splitting of the $N-H_2$ signal in two signals with different intensities, A and B, indicates the presence of two non equivalent configurations of

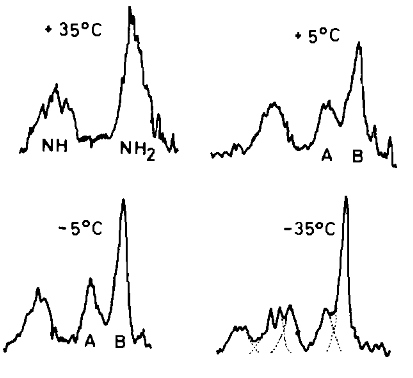

Fig. 1. The nmr spectra of N–H and N–H_2 protons of N-methylthiourea in 1,2-propanodiol–carbonate–CCl_4 mixture at different temperatures.

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.

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_2Pc 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_2Pc.

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.

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