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Hydrogen bonds formed by methyl groups of acetonitrile: infrared and calorimetric study

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Abstract—Solutions of acetonitrile (I) in tetrachloromethane and deuterated solvents (S) (benzene, acetonitrile, acetone and dimethylsulphoxide) have been studied by IR absorption spectra. The observed solvent effect on the IR spectrum of I was explained in terms of the existence of complexes with hydrogen bonding of the type $\text{N}\equiv\text{C}-\text{CH}_3 \cdots \text{solvent (S)}$. The strength of the hydrogen bonding was characterized by enthalpies of specific interactions of I with solvents $\Delta H_{\text{int}}^{\text{I/S}}(\text{sp})$. The values $\Delta H_{\text{int}}^{\text{I/S}}(\text{sp})$ were determined both by IR spectroscopy and calorimetry and were found to be within the range 0.3–1.5 kcal mol⁻¹.

1. INTRODUCTION

ACETONITRILE (CH_3CN , I) is widely used as a solvent for chemical reactions and also for physico-chemical investigations. Thermodynamic and kinetic data of such investigations are partly determined by the interactions of I with the molecules studied. An important role in this may be played by the interaction of the type of hydrogen bonding. It is well known that the nitrile group of I exhibits proton acceptor properties [1]. On the other hand, its methyl group is probably a proton donor. As a rule, the latter fact is neglected and no proper answer can be found in the literature.

There is a view [2–5] that molecules of I form dimers in solutions and liquids. The dimers are attributed to dipole–dipole interactions between polar $\text{C}\equiv\text{N}$ groups, the hydrogen bonding not being involved. At the same time, on the basis of the frequency shifts of CH_3 stretching vibrations, it was concluded in Ref. [5] that the methyl group of I takes part in hydrogen bonding with anions. Furthermore, temperature and concentration dependencies of NMR chemical shifts of I dissolved in tetrachloromethane were interpreted in Ref. [6] as being a result of self-association of acetonitrile due to hydrogen bonding.

The present work is an attempt to make a more detailed analysis of the proton donor ability of I. For this purpose, both IR spectra and solvation enthalpies of I have been studied. Note that I was one of the model compounds in studying vibrational and orientational relaxation in condensed phases [2, 3, 7–13]. Since hydrogen bonding must affect the orientational diffusion of CH_3 groups, the latter process seems to be important.

2. EXPERIMENTAL

The IR spectra were registered with a Specord M80 spectrometer. The slit widths used were 1.5 and 2.5 cm⁻¹ which is much less than the widths of the bands studied (9–30 cm⁻¹), thus the apparatus distortions were not taken into account. To study CH_3 stretching vibrations, tetrachloromethane deuterated benzene, acetonitrile, acetone, dimethylsulphoxide were used as solvents. Acetonitrile and the solvents were dried and purified according to Refs [14] and [15].

For I dissolved in tetrachloromethane the concentrations of I were in the range $0.04 < C < 0.2 \text{ mol l}^{-1}$, where the absorption coefficients of CH_3 stretching bands do not depend on C, and therefore self-association may be excluded. For the rest of the solvents the concentration was within the limits 0.4–1.0 mol l⁻¹. The spectra were registered at room temperature.