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Water complexes with organic solvents in liquid phase. An IR spectroscopic study

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ABSTRACT

An IR spectroscopic investigation indicates the formation of water complexes with organic solvents such as hexafluorobenzene, nitromethane, acetonitrile, and carbon tetrachloride. The IR bands in the 3000–2400 cm^{-1} region can be assigned to OH-stretching vibrations of an H_2O molecule in complexes with solvents in the liquid phase.

Water is a nucleophilic agent in many organic reactions and it is able to form donor–acceptor adducts with molecules having electrophilic fragments or atoms.[1] The hydrogen bonding in water is a typical example of a complex between nucleophilic and electrophilic centers.[2] Water adducts, $H_2O{\cdot}HX$ ($X = F, Cl$), were detected by IR spectroscopy at low temperature.[3,4] The formation in the liquid phase of water complexes with organic solvents, having electrophilic centers, might then be expected. Numerous data describe the influence of a solvent on water structure and properties in solution.[5–8] The intermolecular interaction in these systems is usually explained using Van der Waals and dispersion forces. We have examined IR spectra of hexafluorobenzene, nitromethane, acetonitrile, and carbon tetrachloride that have electrophilic centers.

The frequency of the water OH-stretching vibration is sensitive to structural changes in a molecule. A broad absorbance in the 4000–3500 cm^{-1} region is accompanied by two maxima at 3756 and 3657 cm^{-1} in the IR spectrum of water vapor.[5] For pure liquid water the OH-stretching vibration has a value of approximately 3490 cm^{-1} under normal conditions.[6] The location of this vibration for solvated water depends on the solvent: in CH_3NO_2 the bands are[9] at 3660 and 3590 cm^{-1}, in CH_3CN at[9] 3620 and 3540 cm^{-1}, and in CCl_4 at[6] 3420 and 3250 cm^{-1}. It is reasonable to expect that complex formation between water and a solvent may lead to a shift of the OH-stretching band to lower frequencies due to the increase of charge separation in the H_2O molecule[10] (see Schemes 1–3).

In hexafluorobenzene bands at 2685 and 2480 cm^{-1} were observed (Fig. 1a). Solvent distillation[11] did not lead to any significant changes of absorption in the range under discussion (see the experimental details below). These bands can be assigned to the OH-stretching vibration in H_2O complexed with C_6F_6 (Scheme 1). This conclusion is based on the knowledge that the 4000–2400 cm^{-1} spectral range corresponds to XH-stretching vibrations in numerous organic compounds (where X is an element of the second period).[10] In hexafluorobenzene there are no units which might have stretching frequencies in this spectral region. Thus we feel that it is reasonable to suppose that we have observed an H_2O-stretching band shifted to lower frequencies due to complex formation (Scheme 1).

For nitromethane, in the CH-stretching region, bands having isotopic (H/D) shifts (indicated in Fig. 2 as **A**) and bands (at 2926 and 2778 cm^{-1}) which do not shift in CD_3NO_2 (**B** in Fig. 2) were detected.

Therefore the indicated (**B**) bands can be assigned to the OH-stretching mode of the H_2O molecule complexed with nitromethane (Scheme 2). This IR absorption remains after distillation of the solvent.[11]

Similar IR bands were found for acetonitrile: the bands at 3165 and 3628 cm^{-1} have isotopic shifts, but the bands at 3091 and 2607 cm^{-1} are not sensitive to H/D substitution. The spectral picture remains unchanged after distillation of acetonitrile.[11]

The observed bands were assigned to OH-stretching vibrations of the H_2O molecule in a complex with acetonitrile (Scheme 2).

$$C_6F_6 \xleftrightarrow{H_2O} [C_6^{\delta+}F_6^{\delta-}]\cdots[H^{\delta+}(OH)^{\delta-}]$$

Scheme 1.

$$CH_3X \xleftrightarrow{H_2O} [(CH_2X)^{\delta-}H^{\delta+}]\cdots[(OH)^{\delta-}H^{\delta+}],\ \ X = NO_2, CN$$

Scheme 2.

$$CCl_4 \xleftrightarrow{H_2O} [Cl^{\delta+}(CCl_3)^{\delta-}]\cdots[H^{\delta+}(OH)^{\delta-}]$$

Scheme 3.

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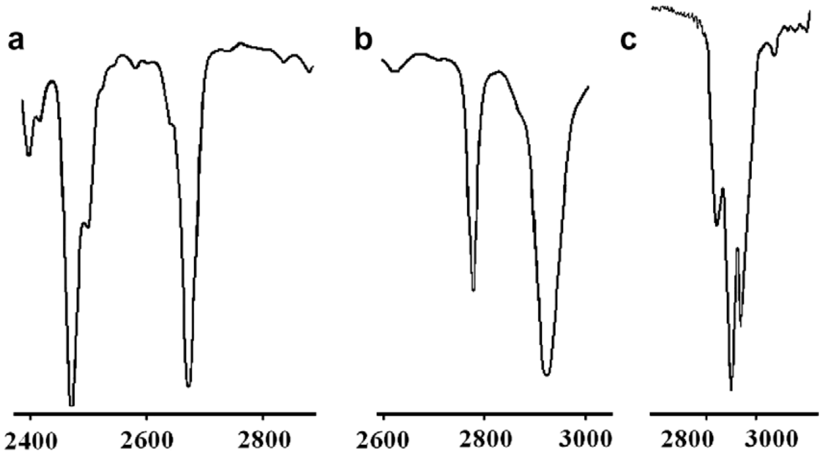

Figure 1. The IR bands in the 3000–2400 cm^{-1} spectral range for solvents: (a) hexafluorobenzene; (b) nitromethane-d_3; (c) carbon tetrachloride (the thickness of the NaCl cell was 0.2 mm). IR spectra (a) and (b) were recorded using a Fourier spectrometer, FSM 1202; (c) using a Perkin–Elmer model 180.

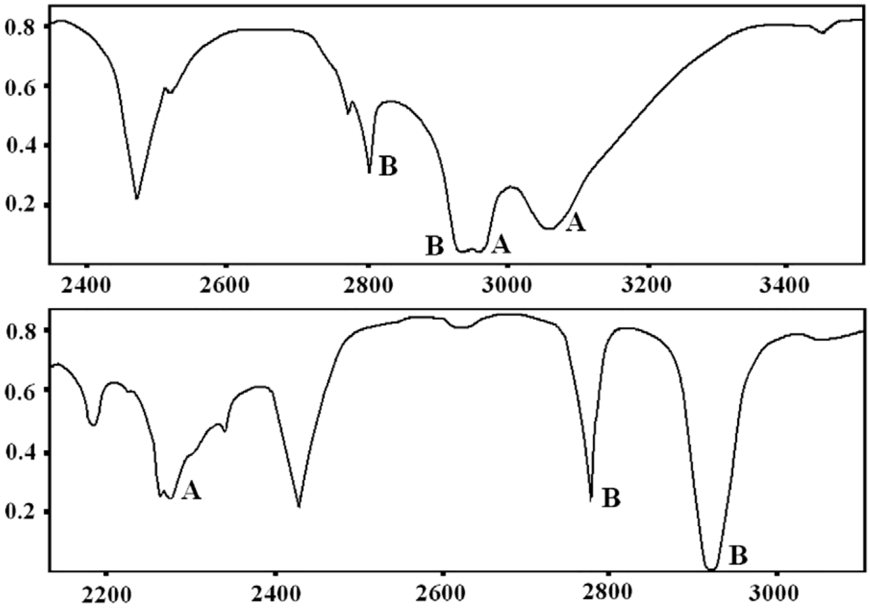

Figure 2. The IR bands in the 3400–2200 cm^{-1} spectral range for CH_3NO_2 (upper) and CD_3NO_2 (lower) (the thicknesses of the NaCl cells were 0.1 and 0.2 mm, respectively).

There are no bands in the IR spectrum of pure carbon tetrachloride in the 3000–2400 cm^{-1} region. However, absorption in this range appears after contacting the solvent with water by a special procedure (see experimental technique).

In the IR spectra of CCl_4, new overlapping bands appear at 2948, 2918, and 2846 cm^{-1} (Fig. 1c) for H_2O and weak bands at 2165 and 2105 cm^{-1} for D_2O. The calculated isotopic ratios (ν_H/ν_D) are 1.36 and 1.35, respectively. These results allow us to assign the bands in the 3000–2400 cm^{-1} range to stretching vibrations of the H_2O molecule complexed with carbon tetrachloride (Scheme 3).

The same procedure was used for the study of D_2O complexes with these solvents. For acetonitrile IR bands of D_2O stretching were not observed. Probably, in this case a much stronger CN-stretching absorption overlaps the D_2O-stretching band. For hexafluorobenzene two weak bands assigned to D_2O stretching were observed at 1948 and 1972 cm^{-1}. The calculated isotopic ratios (ν_H/ν_D) are 1.38 and 1.39, respectively. For nitromethane two similar weak bands appear at 2118 and 1992 cm^{-1} and the calculated isotopic ratios (ν_H/ν_D) are 1.38 and 1.39, respectively.

The IR spectra (Figs. 1–3) allow one to compare the intensities of the bands, assigned to OH stretching, in complexes (**B**) with the intensities of CH-, CD (**A**)-, or CN (**A**)-stretching vibrations in the solvent. This permits consideration of the relative intensities of IR bands of water complexes.

Thus the IR data lead to the conclusion that the bands in the 3000–2500 cm^{-1} region can be assigned to OH-stretching vibrations in H_2O complexes with solvent molecules shifted to lower frequencies.

Experimental technique. Commercial materials with 99.9% purity were used. Each solvent was dried by standard fractional distillation before recording the IR spectra.

The samples for the study of complex formation were prepared in the following way. Water (or D_2O) was added (1.0–1.5 ml) to 20–25 g of $CaCl_2$ or KOH (termed in the following text as 'solid phase'). The 'solid phase' was left at atmospheric pressure for 6–8 h at room temperature. One part ('first') of this phase with 25 ml of solvent was left to stand in a closed flask for 5–6 days. The other part ('second') of the 'solid phase' with 100 ml of solvent

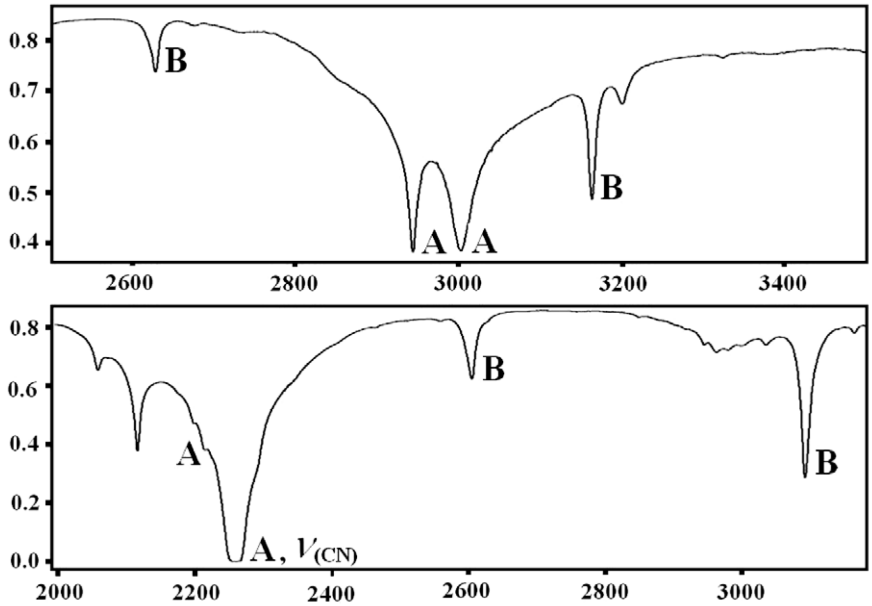

Figure 3. The IR bands in the 3400–2200 cm^{-1} spectral range for CH_3CN and CD_3CN (the thicknesses of the NaCl cells were 0.1 mm and 0.2 mm, respectively).

was heated at the boiling point. The heating apparatus consisted of a round-bottomed flask, fitted with the Liebig condenser to which a thermometer was attached. In both cases the solvent was separated from the 'solid phase' and distilled (see above). The IR spectral measurements were carried out after cooling of the solvents to room temperature. The comparison of IR spectra from the 'first' and 'second' parts of the 'solid phase' was similar.

The NaCl optical cell was washed before use with the solvent to be investigated. Then it was heated to 150 °C under vacuum (10^{-3} Torr). After cooling, the cell was filled with the liquid sample and placed in the IR instrument.

For the IR measurements, a Perkin–Elmer optical cell with variable thickness (NaCl windows) in 0.05–0.2 mm interval and optical cells (NaCl windows) with a constant thickness of 0.1 and 0.2 mm were used. IR spectra were recorded using a Perkin–Elmer model 180 spectrophotometer and on a Fourier-spectrophotometer FSM 1202 in the range of 4000–1000 cm^{-1}.

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