Effect of temperature on the IR spectra of uncharged HCl—DMF complexes with a strong quasi-symmetrical H-bond

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The effect of temperature on the IR spectra of multiple attenuated internal reflection of uncharged HCl—DMF complexes formed by strong quasi-symmetrical H-bonds was studied. The optical density of individual bands of the complexes decreases as the temperature increases, and the background continuous absorption is almost independent of temperature in the whole frequency range (1200—2100 cm^{-1}). It was concluded that strong quasi-symmetrical H-bonds are only slightly sensitive to temperature changes.

Key words: IR spectra, hydrogen bond, temperature effect, HCl, DMF, solutions.

Acid—base complexes with different compositions[1] are formed in solutions of HCl in DMF depending on the ratio of the components: HCl · DMF (**1**), 2HCl · DMF (**2**), and HCl · 2DMF (**3**). Uncharged complexes **1** and **3** are formed by a strong quasi-symmetrical H-bond.[2] In complex **3**, the two DMF molecules are nonequivalent. The addition of the second DMF molecule to **1** almost does not change the structure of the strong H-bond between HCl and DMF. Complex **2** is an ion pair, $Me_2N^+{=}C(H)OH \cdot (ClHCl)^-$.

The IR spectra of complexes of HCl with DMF possess the same characteristic features as the spectra of ions formed by a strong symmetric H-bond.[3] According to the calculations, the IR spectra of these ions contain a great number of bands due to strong interaction of the vibrations of the central proton with all of the other vibrations of the complex.[4,5] Similar calculations for uncharged complexes with strong quasi-symmetric H-bonds are lacking. It can be assumed that their IR spectra are formed in the same way as those of ionic complexes. The purpose of this work is to study the effect of temperature on the IR spectra of uncharged complexes of HCl with DMF (**1**, **3**) formed by a strong quasi-symmetrical O...H...Cl bond. The high partial pressure of HCl vapor over concentrated solutions of **2** makes the quantitative comparison of their spectra at different temperatures very difficult.

Experimental

The initial concentrated solution (48.5% HCl in DMF) was obtained by the saturation[6] of purified and dried DMF with anhydrous HCl. The concentration of HCl in the initial solution was determined alkalimetrically. Solutions containing 28.90, 33.13, and 34.89% HCl were prepared by dilution of the initial solution.

IR spectra at different temperatures were recorded on a UR-20 spectrophotometer equipped with a thermostatted Multiple Attenuated Total Reflection (MATR)[7] attachment produced at the Institute of Chemical Physics of the Russian Academy of Sciences. A working Ge prism with an incident radiation angle of 45° and the number of reflections of 8 was used. One side of the prism contacted the thermostatted surface. The solution to be studied was placed in a Teflon cavity in contact with another side of the prism. The spectra were recorded in the 900—2200 cm^{-1} range. The effective thickness of the absorbing layer at a frequency of 2000 cm^{-1} was 1.75 μm. The temperature of the solution was monitored by a thermocouple. The measurements were carried out in the 30—70 °C range. The accuracy of measurement of the optical density was 5—7%.

Results and Discussion

The maximum concentration of complex **1** is achieved in an equimolar solution of HCl in DMF, C^0_{HCl} = 10.5 mol L^{-1}. According to the equilibrium

$$3\mathbf{1} \rightleftharpoons \mathbf{2} + \mathbf{3}, \qquad (1)$$

which is partially shifted to the right, complexes **2** and **3** are also present in this solution. According to the estimation,[1] $C_2 \approx 0.5$ mol L^{-1}, and all DMF is bound in complexes with HCl. A change in temperature can affect the position of equilibrium (1); therefore, the temperature measurements were carried out for three samples, whose compositions are presented in Table 1.

For samples *1* and *3*, the equilibrium composition at 30 °C can be calculated from the stoichiometric composition:[1]

at $C^0_{HCl} < C^0_{DMF}$ $\quad C^0_{HCl} = C_1 + C_3,$
$\quad C^0_{DMF} = C_1 + 2C_3;$

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Table 1. Stoichiometric and equilibrium composition of the studied solutions of HCl in DMF at 30 °C

Sample	Content of HCl (%)	C^0_{HCl}	C^0_{DMF}	C_1	C_2	C_3
		/mol L^{-1}				
1	28.90	8.9	10.9	6.9	0	2
2	33.13	10.4	10.5	9.9	~0.5	~0.5
3	34.89	11.0	10.3	9.5	0.8	0

$$\text{at } C^0_{HCl} > C^0_{DMF} \qquad C^0_{HCl} = C_1 + 2C_2,$$
$$C^0_{DMF} = C_1 + C_2.$$

A change in temperature can exert an effect on the position of equilibrium (1). However, even in this case the equilibrium concentrations of the complexes in samples *1* and *3* do not change.[1] For temperature measurements, we did not use more dilute solutions of HCl, in which complexes 3 are mainly present. The second DMF molecule in complex 3 spectrally differs only slightly[1] from DMF molecules not bound in complexes with HCl, which makes the analysis of experimental data difficult.

For all three samples, the spectra obtained correspond mainly to the spectrum of an uncharged complex with a quasi-ionic structure.[1] The IR spectra of these species[1,2] are a series of individual bands against a background of continuous absorption (CA) from 900 to 3000 cm^{-1}. The effect of temperature on the optical densities was analyzed for both CA (relative to an empty cell) at frequencies of 950, 1260, 1470, 1500, and 2100 cm^{-1} and for individual bands at 1315, 1600, 1670, and 1790 cm^{-1} (relative to the basic lines drawn as described previously[1]).

As the temperature increases, all measured optical densities (D) of both the background CA and the individual bands decrease. For all frequencies, the experimental data in D—T coordinates are described with satisfactory accuracy by linear dependences. The D_v values at 30 and 70 °C corresponding to these dependences are presented in Table 2. The observed decrease in the optical density can be caused by either the effect of temperature on the spectra of the complexes or a change in the refractive coefficient of Ge at the v frequency (n_v) as the temperature varies. The change in n_v results in a change in the effective thicknesses of the absorbing layer of the sample[7] and, hence, in the optical density in the spectra analyzed.

The calibrating spectra of 1,1,2,2-tetrachloroethane (TCE) in the 1000—1250 cm^{-1} frequency range and of H_2O at 1450—1750 cm^{-1} were used for taking into account the effect of temperature on n_v of germanium. According to the published data,[8] the optical density of the band of water bending vibrations is independent of temperature in the studied range. Therefore, the obtained temperature dependence of the optical density of the band of H_2O reflects the change in n_v of germanium. When the temperature increases from 30 to 70 °C, D_{1650} of water decreases by 7%. The same change is observed for the optical density of the band at 1206 cm^{-1} in the spectrum of TCE. For the band of TCE at 1024 cm^{-1}, the effect of temperature is substantially greater, and ΔD is ~20%. Based on this, we assumed that in the 1200—2100 cm^{-1} region, the change in n_v of germanium on going from 30 to 70 °C results in the same change (7%) in the optical densities of the solutions studied. In this case, the ratio of the effective thicknesses of the samples at 30 and 70 °C in the indicated frequency range is equal

Table 2. Effect of temperature on the optical densities (D) of individual bands and background absorption in solutions of HCl in DMF

Content of HCl (%)	D	Background absorption at v/cm^{-1}					Bands of complexes at v/cm^{-1}			
		950	1260	1470	1500	2100	1315	1600	1670	1790
28.90	D_{30}	0.085	0.550	0.386	0.419	0.184	0.281	0.286	0.600	0.065
	D_{70}	0.066	0.488	0.336	0.362	0.156	0.178	0.194	0.478	0.035
	D_{30}/D_{70}	1.29	1.13	1.15	1.16	1.18	1.58	1.47	1.26	1.86
	D^*_{70}	—	0.522	0.360	0.387	0.167	0.190	0.208	0.511	0.037
	D_{30}/D^*_{70}	—	1.05	1.07	1.08	1.10	1.48	1.37	1.18	1.74
33.13	D_{30}	0.082	0.580	0.402	0.417	0.214	0.344	0.322	0.510	0.089
	D_{70}	0.070	0.509	0.352	0.377	0.178	0.222	0.232	0.417	0.048
	D_{30}/D_{70}	1.17	1.14	1.14	1.11	1.20	1.55	1.39	1.22	1.85
	D^*_{70}	—	0.545	0.377	0.403	0.190	0.238	0.248	0.446	0.051
	D_{30}/D^*_{70}	—	1.06	1.06	1.03	1.13	1.45	1.30	1.14	1.73
34.89	D_{30}	0.095	0.527	0.359	0.373	0.195	0.407	0.320	0.568	0.091
	D_{70}	0.068	0.470	0.338	0.360	0.164	0.265	0.243	0.468	0.048
	D_{30}/D_{70}	1.40	1.12	1.06	1.04	1.19	1.54	1.32	1.21	1.90
	D^*_{70}	—	0.503	0.362	0.385	0.175	0.284	0.260	0.501	0.051
	D_{30}/D^*_{70}	—	1.05	0.99	0.97	1.11	1.44	1.23	1.13	1.78

Note. D_{30} and D_{70} are the optical densities at 30 and 70 °C corresponding to the linear dependences of the experimental data in the D_v—T coordinates. $D^*_{70} = 1.07D_{70}$, D_{30} and D^*_{70} correspond to equal effective thicknesses of the absorbing layer at each of the frequencies.

to 1.07. The values $D^*_{70} = 1.07D_{70}$ presented in Table 2 correspond to the effective thickness of the absorbing layer at 30 °C. The change in the optical densities from D_{30} to D^*_{70} reflects the effect of temperature on the spectra of the complexes that are present in the solution. The data obtained do not allow one to take into account a change in the effective thickness of the samples at $\nu < 1200$ cm^{-1}; therefore, the effect of temperature on the spectra of the complexes of HCl with DMF was analyzed only at $\nu > 1200$ cm^{-1}. The D_{30}/D^*_{70} ratios, which are convenient for comparing the effects of temperature at different frequencies with strongly different absorption intensities are also presented in Table 2.

As the temperature is varied, the changes in the optical density of CA at frequencies of 1260, 1470, and 1500 cm^{-1} are not greater than 5—8%, but they are somewhat greater (up to 11%) at 2100 cm^{-1}. The D_{30}/D^*_{70} ratios at 1260 and 2100 cm^{-1} are the same for all three samples studied. This suggests that the temperature affects similarly the absorption coefficients of complexes **1** and **2** at the frequencies indicated. An increase in the concentration of **2** in the sample (see Table 1) is accompanied by a decrease in the D_{30}/D^*_{70} value in the 1470—1500 cm^{-1} range (see Table 2). This can be related to different effects of temperature on the spectra of complexes **1** and **2**. The observed effect is small, and additional studies of solutions with high concentrations of complex **2** are necessary to draw conclusions that are better substantiated.

As the temperature is varied, the optical densities of all of the bands change considerably more than that of the CA (see Table 2). The greatest effect is observed for the bands at 1315 cm^{-1} (30%) and 1790 cm^{-1} (40%) and is almost the same for the three samples with different contents of HCl. Only complex **1** absorbs at 1790 cm^{-1}; therefore, it can be asserted that the absorption coefficient of precisely this complex decreases substantially as the temperature increases. The absorption coefficient of complex **2** at 1315 cm^{-1} is 1.5-fold higher than that of complex **1**.[1] Therefore, at this frequency, as the temperature increases, the absorption coefficient of complex **2** as well as complex **1** noticeably decrease. At 1600 cm^{-1}, the optical densities of solutions with concentrations of HCl of 28.9, 33.1, and 34.9% decrease by 27, 23, and 19%, respectively. This can be related to the different effects of temperature on the spectra of complexes **1** and **2**.

The smallest effect was observed for the band at 1670 cm^{-1} (see Table 2), which is characteristic of all types of complexes of HCl with DMF and of pure DMF. The effect of temperature on D at this frequency turned out to be almost the same for both complexes of HCl with DMF and for pure DMF. Almost no distinctions in the temperature dependences of D were observed at any frequencies studied for samples *1* and *2*, in which concentrations of **3** differ substantially. This can be explained by the similar effects of temperature on the spectra of complexes **1** and **3**, whose structural bases (O...H...Cl) are the same.

The analysis of the data obtained indicates that there is no noticeable change in the position of equilibrium (1) in the studied temperature range. In a 28.9% solution, HCl is bound to DMF only in complexes **1** and **3** at 30—70 °C. In sample *2*, all three types of complexes of HCl with DMF are simultaneously present, while sample *3* contains only complexes **1** and **2**. For both CA frequencies (1260, 2100 cm^{-1}) and individual bands (1315, 1790 cm^{-1}), the effects of temperature are almost the same for all three samples studied. This is possible only when temperature has no noticeable effect on the position of equilibrium (1), since the absorption coefficients of complexes **1**, **2**, and **3** at each of these frequencies differ at a fixed temperature.

Thus, temperature was observed to affect only individual bands of complex **1**. The continuous absorption is almost independent of temperature in the whole frequency range. Since CA is the characteristic manifestation of strong quasi-symmetrical H-bonds in IR spectra, it can be concluded that these bonds in uncharged complexes are weakly sensitive to changes in temperature.

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