The structure of complexes of HCl with *N,N*-dimethylformamide based on polarization measurements in the Raman spectra

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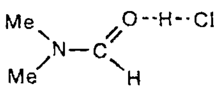
The Raman spectra of solutions of HCl in DMF were studied and the degree of depolarization of spectral lines was measured. Complexes of three types, 2DMF · HCl, DMF · HCl, and DMF · 2HCl, are formed depending on the ratio of the components. Examination of the structure of the contour of the ν(C=O) line showed that the acid-base interactions in the complexes occur through the O atom of the DMF molecule. On the basis of polarization measurements it was established that two DMF molecules in the 2DMF · HCl complex are nonequivalent.

Key words: dimethylformamide, hydrogen chloride, complexes; Raman spectra, degree of depolarization; solutions, acid-base interactions.

Solutions of HCl in DMF are used as catalytic systems for a number of chemical reactions.[1] The efficiency of catalytic systems of such a type is determined by composition and structure of the DMF complexes with HCl. Previously,[2] the binary systems DMF—acid have been considered as solutions in which weak donor-acceptor interactions play a significant role. Later, complexes 2DMF · HCl and DMF · HCl (**1**) with a strong quasi-symmetric H-bond as well as ionic pairs of composition DMF · 2HCl (**2**) have been found[3] in solutions of HCl in DMF using the Multiple Attenuated Total Reflection (MATR) IR spectroscopy.



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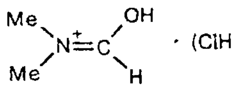

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Complex **1** is a quasi-ionic pair formed due to a strong quasi-symmetric H-bond between the O atom of the carbonyl group and the Cl atom. The formation of complex 2DMF · HCl (**3**) upon addition of one additional DMF molecule to complex **1** does not result in the cleavage of the strong quasi-symmetric H-bond between DMF and HCl. The two DMF molecules in **3** are nonequivalent. Previously,[4] the Raman spectra of complexes of such a type have been obtained for the first time and it was established that the formation of the complexes is accompanied by considerable changes in the frequencies and intensities of almost all lines of DMF molecules constituting them. In this work, Raman spectra of solutions of HCl in DMF were studied in a wider range of concentrations of the components and polarization measurements in the spectra were performed.

Experimental

The procedures for purifying the reagents and preparing the solutions have been described previously.[3]

The Raman spectra of solutions of HCl in DMF were recorded on a DFS-24 spectrophotometer equipped with a double monochromator and an improved registration system. The 488 nm line of an LG-106M argon ion laser was used as the source of excitation; the other lines of the laser were suppressed by an interference filter. The polarization plane of linearly polarized laser light was rotated by 90° with respect to the optical axis using a $\lambda/2$ plate. In all experiments, the optical widths of the slits were 3 to 10 cm^{-1}. To determine the relative degrees of depolarization of the lines (ρ) equal to the ratios of the line intensities obtained in the transversely and longitudinally polarized light, the spectrum of each solution was recorded 3 to 5 times in the correspondingly polarized light. The reproducibility of the intensity values was 10 to 15%.

The Raman spectra were obtained for neat DMF (C^0_{DMF} = 13 mol L^{-1}) and solutions with different content of HCl in DMF: C_{HCl} = 18.9% (sample *1* with the highest possible concentration of complex **3**: C_3 = 4.1 mol L^{-1}, C_1 = 1.4 mol L^{-1}, and $C_{DMF} \approx 2$ mol L^{-1}), C_{HCl} = 33.3% (sample *2* with the highest possible concentration of complex **1**: C_1 = 10±0.5 mol L^{-1} and $C_3 = C_2$ = 0.5±0.5 mol L^{-1}), and C_{HCl} = 43.3% (sample *3* with the highest possible concentration of complex **2**: C_2 = 4.8 mol L^{-1} and C_1 = 4.2 mol L^{-1}). In samples *2* and *3*, the whole DMF is bound to form the complexes. The equilibrium concentrations of the complexes in samples *1—3* were calculated using the published data.[3]

Results and Discussion

The frequencies and intensities of the lines in the Raman spectra and the data of polarization measurements are presented in Table 1. The assignment of the frequencies in the DMF spectrum is evident from ex-

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Table 1. Frequencies (ν), relative intensities (I), and data on depolarization of the lines in the Raman spectra of DMF and of solutions of HCl in DMF

ν/cm^{-1} (I), DMF	Type of vibration	ν/cm^{-1} (I)		
		18.9% HCl	33.3% HCl	43.3% HCl
—		—	—	275 (0.3) v.w, d
323 (1) w, d	τ(C—N)	320 (0.5) v.w, d	—	—
356 w	γ(Me—N—Me)	356 w	356 w	356 w
410 (4) m, d	δ(Me—N—Me)	410 (3.2) m, d	410 (5.6) m, d	412 (5.1) m, d
660 (10.4) s, p	δ(O=C—N)	640 (1.9) m, d	639 (5.7) m, d	638(7.4) m, d
		660 (4.8) m, p		
866 (12) v.s, s.p	ν_s(N—Me)	847 (1.9) m, p	848 (4.9) m, p	847 (5.3) m, p
		865 (6.5) s, p		
—		—	887 w, p	887 w, p
1011 v.w	γ(CH$_3$)N	1012 v.w	1017 v.w	—
1094 (3.9) m, w.p	δ(NCH)+ν(C=O)	1094 (1.8) m, w.p	—	—
		1127 (2.4) m, w.p	1128 (5.1) m, w.p	1130 (5.7) m, w.p
—		—	—	1157 v.w
—		—	1228 v.w	1228 v.w
—		1312 (0.2) v.w, p	1306 (0.7) w, s.p	1307 (1.3) w, s.p
1390 w	ν(C—N)	1386 w	1387 v.w	1385 v.w
1407 v.s, w.p	δ(C—H)	1409 s, w.p	1430 v.s,d	1430 v.s, d
1440 s, d	δ(NCH)+δ(CH$_3$)N+ν_s(N—Me)	1435 v.s, d	1430 v.s, d	1430 v.s, d
1510 w, d	δ(NCH)+ν(C—N) + ν_{as}(N—Me)	1482 w, d	1480 w, d	1482 w, d
1659 m, p	ν(C=O)	—	—	
1672 m, d	ν(C=O)	1670 m, w.p	1690 m, w.p	1690 m, d
—		—	1715 v.w	1720 m, s.p
1732 v.w	2 ν_s(N—Me)	—	—	—
2772 v.w		2777 v.w	—	—
2810 m, p		2818 m, s.p	2820 m, s.p	2820 m, s.p
2861 m, s.p	ν(C—H)	2865 w, s.p	—	—
2883 m, p		2886 w, p	—	—
2930 v.s, s.p	ν_s(CH$_3$)N	2946 v.s, s.p	2946 v.s, s.p	2948 v.s, s.p
2957 m, d		—	—	—
2995 m, d	ν_{as}(CH$_3$)N	2999 m, d	2992 m, d	3000 m, d
—		3020 w, d	3020 m, d	3020 m, d

Note. The following notations are used: v.w is very weak, w is weak, m is medium, s is strong, v.s is very strong, d is depolarized, w.p is weakly polarized, p is polarized, and s.p is strongly polarized line. The relative intensities were calculated per one DMF molecule in solutions; the intensity of the DMF line at 323 cm^{-1} was taken as unity.

amination of the IR and Raman spectra of DMF, DMF-d$_6$, DMF-d$_7$, ^{13}C-DMF, and ^{15}N-DMF in the liquid and gaseous state (see Ref. 5).

The changes observed in the Raman spectra of samples *1—3* as compared to the spectrum of pure DMF indicate a strong interaction between the HCl and DMF molecules. Thus, three intense singlet lines at 660, 866, and 1094 cm^{-1} are present in the spectrum of individual DMF. In the spectrum of sample *1*, the satellite lines at 640, 847, and 1127 cm^{-1} corresponding to the vibrations of generated complexes appear close to the above lines. In the spectrum of sample *2*, the DMF lines at 660, 866, and 1094 cm^{-1} disappear, while the intensities of the lines of complexes at 640, 847, and 1127 cm^{-1} increase substantially. The relative intensities of the lines common to samples *2* and *3* differ substantially. In addition, new lines (among which the line at 1720 cm^{-1} is the most intense) as well as the background scattering in the 1800 to 2600 cm^{-1} region appear in the spectrum of sample *3*. These facts indicate that samples *2* and *3* contain two different complexes (**1** and **2**).

Analysis of the degree of depolarization (ρ) of spectral lines confirms the conclusion drawn in Ref. 3 that the HCl molecule is bound to the O atom of the DMF molecule. Changes in the ρ values for the lines corresponding to the vibrations of the N atom and the C atoms of the methyl groups are insignificant. Thus, the DMF line at 866 cm^{-1} corresponding to the ν_s(N—Me) vibration remains polarized also in the spectra of solutions of HCl in DMF. Its shift to 847 cm^{-1} is due to weakening of the N—Me bonds upon complexation. For this line, the change in the ρ value does not exceed 0.1. The main contribution to the lines at 1094 and 1130 cm^{-1} comes from the δ(NCH) vibrations; for these lines, the ρ values are nearly the same (~0.7).[5] The strongly polarized lines at 2812, 2861, and 1930 cm^{-1} (ρ < 0.3) corresponding to the stretching vibrations of the CH and Me groups of the DMF molecule (see Table 1) behave analogously. Thus, complexation has little effect on the symmetry of the Me$_2$NH fragment of the DMF molecule.

The ρ values for the lines corresponding to vibrations of the O atom are changed more substantially. The line

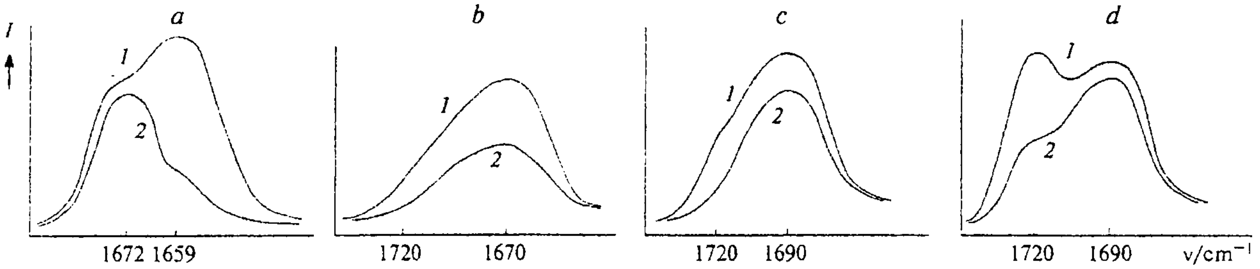

Fig. 1. Contours of the ν(C=O) lines in the Raman spectra of neat DMF (*a*) and in complexes of DMF with HCl: **3** (*b*), **1** (*c*), and **2** (*d*) obtained in longitudinally (*1*) and transversely (*2*) polarized light.

at 660 cm^{-1} corresponding to the in-plane deformation δ(NCO) vibrations of the O atom and polarized in the DMF spectrum ($\rho = 0.45$) is shifted up to 638 cm^{-1} and is completely depolarized in the spectra of samples *1*, *2*, and *3*.

Analysis of the data of polarization measurements of the ν(C=O) line provides important information on the formation of complexes between HCl and DMF. In pure DMF, this line is composed of two components with frequencies of 1659 and 1672 cm^{-1}. According to the published data,[6] we assigned the polarized line at 1659 cm^{-1} ($\rho < 0.3$) to vibrations of the chain dimers and to the synphase vibrations of cyclic dimers with close frequencies; the depolarized line at 1672 cm^{-1} was assigned to the antiphase vibrations of cyclic dimers (Fig. 1, *a*).

Only one broad weakly polarized line at 1670 cm^{-1} with an intense high-frequency diffuse wing (Fig. 1, *b*) is observed in the spectrum of sample *1*. The degree of depolarization of this line is the same across its whole width: $\rho_{1659} = \rho_{1672} = 0.55$ while that of the wing (ρ_{1690}) is equal to 0.50. The absence of polarized and depolarized components of the line at 1670 cm^{-1} indicates that the structure of DMF dimers is disrupted, while the absence of polarized component at the wing of this line near 1690 cm^{-1} shows that the solution contains no DMF monomers.[6] Hence, in sample *1* DMF is nearly completely bound to form complex **3**, in which for each HCl molecule there are two DMF molecules (according to the estimates obtained previously,[3] the content of free DMF in this sample is ~2 mol L^{-1}).

One broad line at 1690 cm^{-1} with $\rho = 0.75$ (Fig. 1, *c*) is present in the spectrum of sample *2*. The line at 1670 cm^{-1} completely disappears, which is in agreement with its assignment to complex **3**, and a weak intense wing of the 1690 cm^{-1} line appears in the region of 1715 cm^{-1}. A nearly completely depolarized line at 1690 cm^{-1} ($\rho = 0.9$) and a strongly polarized line at 1720 cm^{-1} ($\rho < 0.4$) (Fig. 1, *d*) with nearly equal intensities are observed in the spectrum of sample *3*.

The above data indicate that complexes of three types (**3**, **1**, and **2**) characterized by the lines at 1670, 1690 and 1720 cm^{-1}, respectively, are present in the HCl—DMF system. The concentrations of the complexes depend on the ratio of the components. Note that only the background absorption is different in the IR spectra of complexes **1** and **3**.[3]

The fact that the lines at 1690 and 638 cm^{-1} are depolarized and the small changes in the ρ values depending on the HCl concentration for the lines at 866 (847) and 1094 (1130) cm^{-1} make it possible to conclude that the interaction between the HCl and DMF molecules occurs through the O atom. This is also evidenced by the absence of DMF dimers in sample *1* and the fact that sample *2* is crystallized at room temperature (the melting point of a HCl—DMF solution of composition 1 : 1 is 37 °C [7]). If the interaction occurred through the N atom, complexes **1** (of which sample *2* consists) would have a dimeric structure similar to that of liquid DMF.

Let us consider the structure of the complexes formed in more detail. The fact that the frequency of the line at 1690 cm^{-1} is close to that of the ν(C=O) of the DMF monomers[6] (1687 cm^{-1}) determined from the spectra of diluted solutions of DMF in CCl_4 is accidental. Actually, the ν(C=O) line of DMF monomers is strongly polarized, whereas the line at 1690 cm^{-1} in the spectrum of sample *3* is depolarized and is very weakly polarized in the spectrum of sample *2*. It is likely that the line at 1690 cm^{-1} corresponds to the more complex multiparticle vibrations of complex **1** rather than to the ν(C=O). We failed to explain the presence of this line in the Raman spectrum of sample *2* in the framework of concepts of the complexes mostly formed due to electrostatic interaction with small contribution of the donor-acceptor component. For instance,[8] the ν(C=O) frequency in the spectra of the $LiClO_4$—DMF system is lower than the ν(C=O) frequency of the DMF monomers (1670 cm^{-1} *vs.* 1687 cm^{-1}, respectively).[6] The decrease in the ν(C=O) frequency is due to the electrostatic interaction between the Li^+ cation and the O atom of the DMF molecule resulting in the shift of the electron density of the C=O bond toward the O atom and weakening of the bond.

For complex **1**, the structure with a strong quasi-symmetric H-bond between the O and Cl atoms, $Me_2NC(H)O...H...Cl$, has been proposed,[3] which is confirmed by an intense continuous absorption in the IR spectra. The interaction in complexes with strong quasi-symmetric H-bonds has a donor-acceptor character[9] and is related to a covalent interaction. The vibrations of the central proton in these complexes strongly interact with normal vibrations of the molecules participating in the formation of the H-bond;[10] as a result, the structure of normal vibrations becomes considerably perturbed. This particularly affects the vibrations with participation of the O atom, since this atom is directly bound to the central proton of the strong H-bond. Thus, it can be assumed that complex **1** is formed due to the strong H-bond and the line at 1690 cm^{-1} can be assigned to a vibration involving other atoms of complex **1** in addition to the C and O atoms of the DMF molecule.

Unlike the lines of the DMF monomers,[6] the intense high-frequency wing in the spectrum of sample *1* is weakly polarized, broad, and, hence, it cannot be a line of the DMF monomers. The presence of this wing indicates that two DMF molecules in complex 3 (which can be considered as complex **1** solvated with one DMF molecule) are nonequivalent. In this case, the 1670 cm^{-1} frequency corresponds to the DMF molecules constituted **3** and different from those involved in the formation of the strong H-bond, while the wing in the region of 1690 cm^{-1} corresponds to the DMF molecule participating in this bond with HCl. It is likely that in the process of formation of complex **3** the DMF molecule is coordinated to complex **1** at the site of the central proton of the strong quasi-symmetric O...H...Cl hydrogen bond. This is in agreement with the decrease in the ν(C=O) frequency to 1670 cm^{-1} in the spectrum of sample *1* as compared to that of the DMF monomer (1687 cm^{-1}).

The drastic difference in the ρ values for the lines at 1690 and 1720 cm^{-1} indicates that they correspond to vibrations of different DMF atoms in complexes **1** and **2**, respectively. In the case of protonation of DMF and the formation of complex **2**, a considerable contribution to the 1720 cm^{-1} frequency should come from the ν(N$^+$=C) vibrations. For this line, this assignment corresponds to a ρ value lesser than 0.4 since the multiple bond vibrations are to a certain extent independent of those of the rest of the molecule and, hence, are rather symmetrical.

The absence of the line at 323 cm^{-1} in the Raman spectra of samples *2* and *3* makes it possible to assign it to the torsional τ(C—N) vibrations, which disappear as the order of the central C—N bond in the complexes increases. This line is depolarized, which corresponds to the out-of-plane character of such type vibrations.

The line at 3020 cm^{-1} in the Raman spectrum of sample *3* can be assigned to either the ν(C—H) or the ν(O—H). Since this line has a large intensity also in the spectrum of sample *2*, the first assignment is preferable. In this case, the formation of the complexes (see Table 1) causes the ν(C—H) frequency to increase by 159 cm^{-1}. The δ(C—H) frequency also increases (by 23 cm^{-1}, see Table 1). This points to the strengthening of the C—H bond in the HCl complexes with DMF. Direct observation of the ν(O—H) line in the spectrum of sample *3* failed because of the relatively low concentration of protonated DMF, superposition of the intense lines of methyl groups on this line, and its large width.

Thus, new data on complexation of HCl with DMF were obtained on the basis of polarization measurements in the Raman spectra. It was established that the acid-base interaction occurs through the O atom of the DMF molecule. Complexes **1**, **2**, and **3** are formed depending on the ratio of the components. The two DMF molecules in complex **3** have spectra differing in the frequencies and degrees of depolarization of the lines and, hence, are nonequivalent. The order of the central C—N bond increases upon the formation of complex **1**. In excess HCl, the DMF molecule is protonated with the formation of the N$^+$=C bond in complex **2**. These conclusions follow from examination of the contour of the ν(C=O) line of the DMF molecule as well as from the data of polarization measurements for other spectral lines.

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