Ion-molecular interactions and the equilibrium composition in the HCl—1-methyl-2-pyrrolidone—1,1,2,2-tetrachloroethane system according to IR spectroscopy data

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Multiple Attenuated Total Reflectance (MATR) IR spectra of solutions of HCl in 1-methyl-2-pyrrolidone (*N*-MP) (0—43.4 % HCl) were studied in the 900—4000 cm^{-1} range. Spectra were recorded for the *N*-MP—HCl—1,1,2,2-tetrachloroethane (TCE) ternary system at a TCE : *N*-MP ratio of 1 : 1. Depending on the ratio between the components, complexes of the composition *N*-MP·HCl (C-1), *N*-MP·2HCl (C-2), and 2*N*-MP·HCl (C-3) are formed in the system. Complex C-1 has a quasiionic structure, $(CH_2)_3N(Me)CO...H...Cl$, formed by a strong quasisymmetrical H-bond between the carbonyl O atom and the Cl atom. The addition of an *N*-MP molecule to complex C-1 yields complex C-3, in which the quasiionic character of the bond between *N*-MP and HCl is retained. When excess HCl is present, the quasiionic structure is destroyed, the *N*-MP molecule is protonated, and the Cl^- anion interacts with HCl to give an ion with a strong symmetrical H bond $(Cl...H...Cl)^-$. Complex C-2 is an ion pair.

Key words: IR spectra; acid-base interactions, hydrogen bond; hydrochloric acid, 1-methyl-2-pyrrolidone, solutions.

At present considerable attention is paid to the investigation of nonaqueous solutions of HCl. Catalytic activities of these systems are determined by the compositions and structures of complexes formed between the acid and the base (solvent). In particular, at an equimolar ratio between the components the effective rate constant (k_{eff}) of hydrochlorination of acetylene in the HCl—DMF system dramatically increases. When the concentration of HCl is further increased, the k_{eff} value continues to grow. This indicates that complexes of HCl with the solvent formed in concentrated solutions at $C_{HCl}/C_{DMF} > 1$ possess high catalytic activities.

The present work is devoted to an IR-spectroscopic study of ion-molecular interactions in solutions of HCl in 1-methyl-2-pyrrolidone (*N*-MP) carried out in a broad range of HCl concentrations, in order to determine the compositions and structures of the complexes formed. The experiments were carried out using the HCl—*N*-MP—1,1,2,2-tetrachloroethane (TCE) model system, which is homogeneous over the whole range of HCl concentrations.

Experimental

The starting concentrated solution of HCl in *N*-MP (43.39 % HCl) was prepared by saturating purified and dried *N*-MP with dry gaseous hydrogen chloride. The concentration of HCl in the starting solution was determined by alkalimetric titration. For this purpose, the starting solution was diluted with water until a centinormal concentration of HCl was attained, and freshly prepared solutions were titrated.

At 25 °C, solutions of HCl in *N*-MP are liquid only in narrow regions of composition of the system, *viz.*, 0—8.1 % HCl and 37.5—43.4 % HCl. Therefore, the studies of ion-molecular interactions between HCl and *N*-MP were carried out in HCl—*N*-MP—TCE ternary systems at a TCE concentration in the solvent of 62.86 %. This is the minimum content of TCE that ensures homogeneity of the ternary system over the whole range of concentrations of the components at 25 °C and corresponds to an equimolar composition of the solvent.

Process solutions were prepared by weighing. To calculate concentrations of the components (mol L^{-1}), densities (ρ) of the solutions were measured (Table 1).

The *N*-MP—HCl—TCE system was studied by Multiple Attenuated Total Reflectance (MATR) IR spectroscopy.[1] The MATR IR spectra of the solutions were recorded on a UR-20 spectrophotometer in the 940—3800 cm^{-1} range using an MNPVO-2 [MATR] unit produced at the Institute of Chemical Physics of the RAS. A Ge working prism with an angle of incidence of 30° was used. Solutions under study were placed in Teflon cavities adjacent to lateral faces of the prism. Measurements were carried out with both one and two cavities filled; the numbers of reflections were 4 and 8, respectively. The effective thickness of the absorbing layer was 1.73 or

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Table 1. Stoichiometric composition and density of the HCl—*N*-MP—TCE system (37.14 % *N*-MP in the solvent) at 30 °C; optical densities of some bands in the MATR IR spectra

C_{HCl} (%)	ρ /g cm^{-3}	C^0_{HCl}*	$C^0_{N\text{-}MP}$*	C^0_{TCE}*	D_{1264}	D_{1503}	D_{1540}	D_{1780}
0	1.339	0	5.018	5.015	0.065	0.129	0.009	0.024
2.141	1.349	0.79	4.946	4.944	0.052	0.086	0.061	0.031
3.250	1.354	1.207	4.908	4.906	0.051	0.076	0.084	0.042
4.822	1.364	1.804	4.861	4.861	0.039	0.060	0.096	0.055
6.397	1.371	2.406	4.807	4.807	0.026	0.050	0.119	0.068
8.296	1.381	3.143	4.743	4.744	0.017	0.042	0.132	0.086
9.800	1.386	3.726	4.681	4.683	0.014	0.038	0.145	0.101
11.047	1.394	4.220	4.643	4.646	0.009	0.032	0.150	0.108
12.218	1.399	4.690	4.597	4.600	—	0.029	0.154	0.126
12.229	1.401	4.700	4.609	4.602	0.005	0.024	0.154	0.141
13.300	1.399	5.105	4.541	4.544	0	0.026	0.146	0.141
14.007	1.400	5.380	4.511	4.508	0	0.040	0.143	0.135
16.016	1.396	6.133	4.388	4.393	0	0.053	0.131	0.116
18.621	1.394	7.122	4.256	4.247	0	0.059	0.118	0.100
19.480	1.391	7.431	4.190	4.196	0	0.061	0.122	0.088
21.130	1.383	8.016	4.081	4.088	0	—	0.108	0.079
22.134	1.380	8.308	4.030	4.020	0	—	0.101	0.067

* The concentrations are given in mol L^{-1}.

3.27 μm (depending on the extent of filling of the cell) at a frequency of 2000 cm^{-1}. The spectra were recorded at 30 °C.

The optical densities were measured for those lines, for which base lines can be correctly drawn, *viz.*, 1235, 1264, 1360, 1410, 1480, 1503, 1673, and 1780 cm^{-1}. The base lines were drawn for both individual bands and groups of bands in the spectrum (for example, from 1330 to 1520 cm^{-1}). In some cases, the correctness of the base line was checked by determining the optical density of a band relative to the minimum located near one of its wings (for example, D_{1780} was also measured with respect to the absorption in the minimum at 1870 cm^{-1}). The background absorption was measured with respect to the empty cell.

Results and Discussion

Equilibrium composition of the *N*-MP—HCl system. The IR spectrum of *N*-MP (Fig. 1, *a*) consists of a large number of overlapping bands. For quantitative measure-

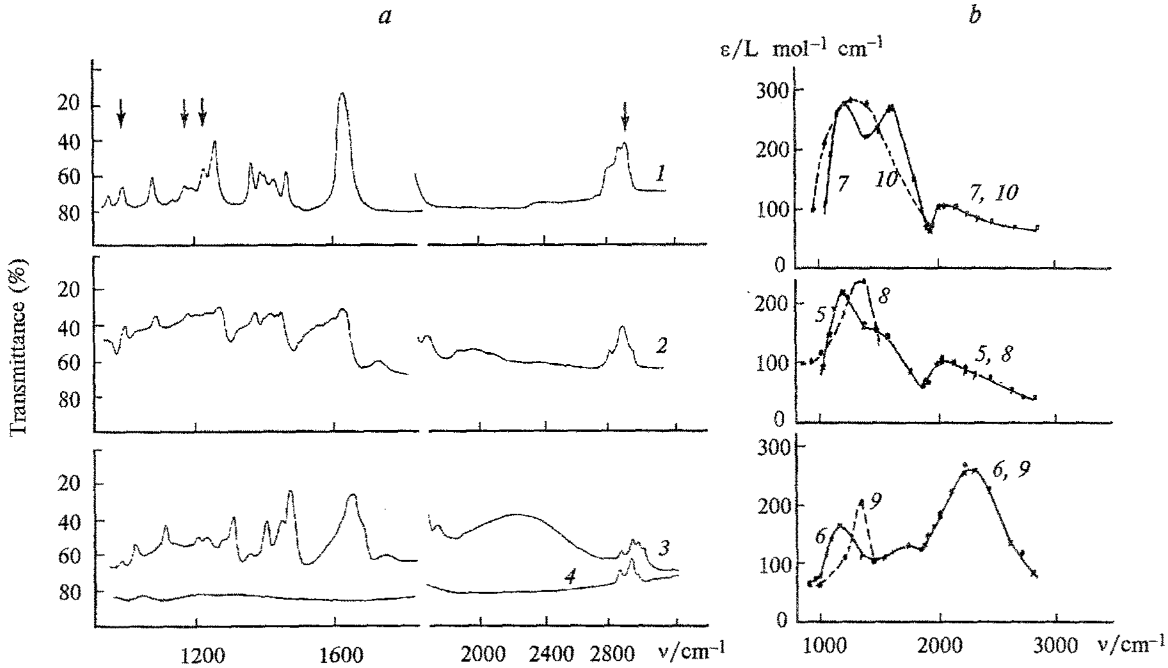

Fig. 1. MATR IR spectra of solutions of HCl in an *N*-MP—TCE equimolar mixture (*a*) at C^0_{HCl}/mol L^{-1} = 0 (*1*), 4.7 (*2*), 8.016 (*3*), for an empty cell (*4*), and also the spectra of background absorption coefficients (*b*) of complexes C-1 (*5*, *8*), C-2 (*6*, *9*), and C-3 (*7*, *10*) in HCl—*N*-MP—TCE (*5*—*7*) and HCl—DMF (*8*—*10*) systems.

ments of the optical densities we used the following bands of *N*-MP, ν/cm^{-1}: 1264 (N—Me), 1503 (C—N), and 1673 (C=O). The bands in the spectrum of *N*-MP were assigned in conformity with the published data.[2–4] The arrows in Fig. 1 point to the bands of TCE, *viz.*, 1020, 1200, 1278, and 2990 cm^{-1}. When HCl is added to *N*-MP up to a 1 : 1 ratio, a series of new bands appear, in particular, bands at 1360, 1480, and 1780 cm^{-1} and broad bands in the 1800—2400 cm^{-1} region; continuous absorption in the 1500—1660 cm^{-1} range near the low-frequency wing of the ν(C=O) band and intense background absorption in the 1000—1700 cm^{-1} range are also observed (see Fig. 1). When the concentration of HCl is greater than that of *N*-MP, bands at 1235 and 1410 cm^{-1} and also a very broad band with a maximum near 2200 cm^{-1} appear in the spectrum (see Fig. 1). The general character of the variations occurring in the IR spectra of solutions of HCl in *N*-MP depending on the ratio between the components is similar to that observed[4] in the spectra of the DMF—HCl system.

Previously[4] it has been shown that the DMF·HCl (C′-1) complex is a strong structural unit, which retains its individuality after one more DMF molecule adds to it to give the (DMF·HCl)·DMF (C′-3) complex, *i.e.*, the two DMF molecules incorporated in C′-3 are nonequivalent. In conformity with this, all of the bands corresponding to complex C′-1 were exhibited in the spectrum of C′-3 almost unchanged. The conclusion that complex C′-3 exists in the DMF—HCl system was mostly based on the analysis of concentration dependences of the background absorption. The formation of complex C-3 in the system under study may be judged from the concentration dependences of not only background absorption, but also the majority of bands in the spectra.

From the data on the optical density of the band at 1503 cm^{-1} (*N*-MP), which rapidly decreases as the content of hydrogen chloride increases (see Table 1), it follows that at concentrations of HCl, equal to 0.79 and 1.21 mol L^{-1}, each HCl molecule binds two *N*-MP molecules to yield complex C-3. Concentrations of C-3 at higher proportions of HCl were calculated from the concentration dependences of the optical densities of the band at 1480 cm^{-1} (Fig. 2) and the background absorption at 1540 cm^{-1} (see Table 1). For this purpose, absorption coefficients (εl)* of complexes C-3 and C-1 at frequency 1540 cm^{-1} were initially evaluated (see Table 1). The $(\varepsilon l)_{\text{C-3}}$ value was defined as a tangent of the slope of the straight line that passes through the first three points, since at these concentrations, the whole amount of HCl is bound into complex C-3. In order to evaluate $(\varepsilon l)_{\text{C-1}}$, we presumed that at an equimolar ratio between the acid and the base, only complexes C-1 are present in the system, *i.e.*, their concentration is equal to the stoichiometric concentration of HCl. We obtained $(\varepsilon l)_{\text{C-3}} = 0.0062$ L mol^{-1} and $(\varepsilon l)_{\text{C-1}} = 0.033$ L mol^{-1}.

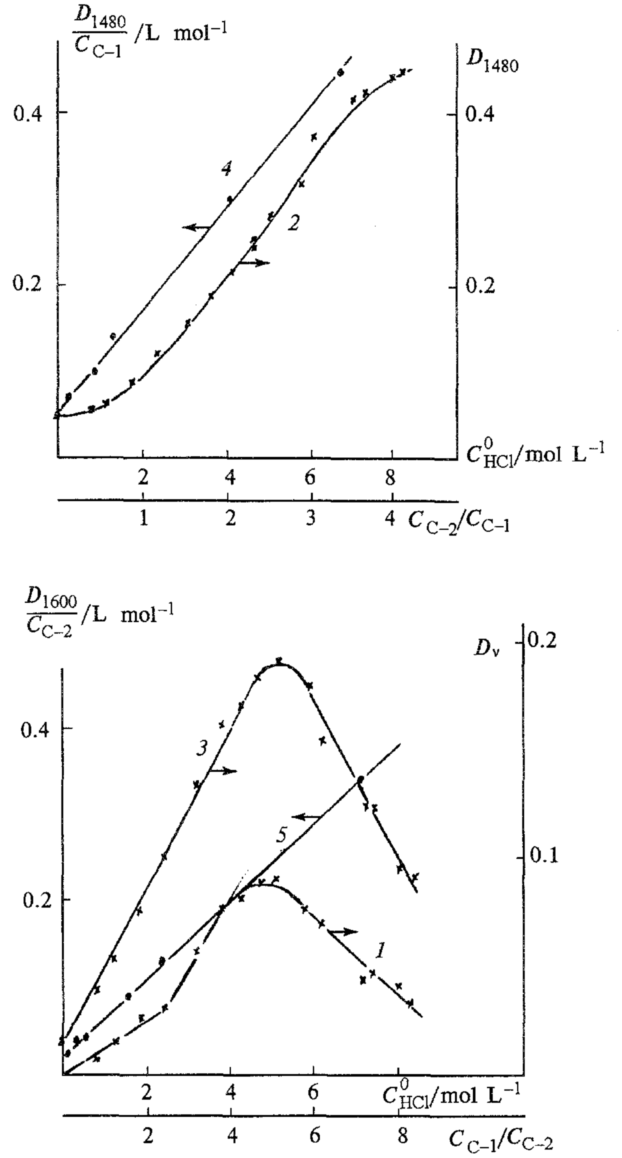

Fig. 2. Dependence of the optical densities of the bands at 1360 cm^{-1} (*1*), 1480 cm^{-1} (*2*), and the absorption at 1600 cm^{-1} (*3*) on the concentration of HCl. Graphical solutions of Eq. (4) for a frequency of 1480 cm^{-1} (*4*) and Eq. (5) for 1600 cm^{-1} (*5*).

The variation of the optical density at 1540 cm^{-1} can be described by the following relationships:

$$D_{1540} = (\varepsilon l)_{\text{C-3}} C_{\text{C-3}} + (\varepsilon l)_{\text{C-1}} C_{\text{C-1}}, \quad (1)$$

$$C^0_{\text{HCl}} = C_{\text{C-3}} + C_{\text{C-1}}. \quad (2)$$

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* To calculate concentrations of the components in a solution, we used the values of $(\varepsilon_\nu l_\nu)$, where ε_ν and l_ν are the extinction coefficient and the effective thickness of the absorbing layer at frequency ν (which is constant for the whole series of spectra), respectively.

From Eqs. (1) and (2) we obtained the concentrations of complexes C-3 and C-1 at $C^0{}_{HCl}/C^0{}_{N\text{-}MP} < 1$. To evaluate the concentrations of the complexes from the optical density of the band at 1480 cm^{-1} we used a relationship analogous to Eq. (1). It was assumed that vibrations of complex C-3 are not exhibited in this band, *i.e.*, $(\varepsilon l)_{C\text{-}3} = 0$. For the absorption coefficient of complex C-1 in the point corresponding to an equimolar ratio between the acid and the base, we found a value of 0.042 L mol^{-1}. As this was done, we assumed that the background absorption ($D = 0.051$, see Fig. 2) remains constant in the spectra at any concentration and subtracted its magnitude from D_{1480}. The values of the concentration of complex C-3 ($C_{C\text{-}3}$) determined from the optical densities at 1540 and 1480 cm^{-1} have been averaged and are presented in Table 2. The concentrations of complex C-1 calculated are also presented in this Table.

The maximum content of complex C-1 is attained near an equimolar ratio between HCl and *N*-MP, as follows from concentration dependences of the optical densities of the absorption bands corresponding to this complex, 1360, 1600, and 1780 cm^{-1} (see Table 1 and Fig. 2). As the proportion of HCl in the system is further increased, the concentration of C-1 rapidly decreases, which is explained by fact that C-1 adds the second HCl molecule to yield complex C-2. The latter is responsible for the absorption bands at 1235 and 1410 cm^{-1}, which appear in the spectrum (Fig. 3). The concentration dependences of the optical densities of the bands at 1360, 1480, 1600, and 1780 cm^{-1} can be described in the range of HCl concentrations exceeding the equimolar ratio between HCl and *N*-MP provided that the whole HCl is bound in complexes C-1 and C-2. In this case, optical densities (D_v) of bands can be represented as sums of the absorptions of complexes C-1 and C-2:

$$D_v = (\varepsilon l)_{C\text{-}1} C_{C\text{-}1} + (\varepsilon l)_{C\text{-}2} C_{C\text{-}2}. \qquad (3)$$

If one assumes that the HCl added to the system is being entirely bound into the complexes, the following relationships hold:

$$C_{C\text{-}1} + C_{C\text{-}2} = C^0{}_{N\text{-}MP},$$

$$C_{C\text{-}1} + 2C_{C\text{-}2} = C^0{}_{HCl},$$

hence, it follows that

$$C_{C\text{-}2} = C^0{}_{HCl} - C^0{}_{N\text{-}MP}.$$

By dividing both sides of Eq. (3) by $C_{C\text{-}1}$ or $C_{C\text{-}2}$ we obtained expressions (4) and (5), which were used for analyzing the concentration dependences of D_v in concentrated solutions of HCl in *N*-MP.

$$D_v/C_{C\text{-}1} = (\varepsilon l)_{C\text{-}1} + (\varepsilon l)_{C\text{-}2}(C_{C\text{-}2}/C_{C\text{-}1}), \qquad (4)$$

$$D_v/C_{C\text{-}2} = (\varepsilon l)_{C\text{-}2} + (\varepsilon l)_{C\text{-}1}(C_{C\text{-}1}/C_{C\text{-}2}). \qquad (5)$$

Table 2. Equilibrium composition of the HCl—*N*-MP—TCE system at 30 °C

$C^0{}_{HCl}$	$C^0{}_{N\text{-}MP}$	$C_{N\text{-}MP}$	$C_{C\text{-}3}$	$C_{C\text{-}1}$	$C_{C\text{-}2}$
0	5.018	5.018	0	0	0
0.79	4.946	3.36	0.79	0	0
1.207	4.908	2.6+0.1	1.1+0.1	0.1+0.1	0
1.804	4.861	2.0+0.2	1.1+0.2	0.7+0.2	0
2.406	4.807	1.4+0.3	1.0+0.3	1.4+0.3	0
3.143	4.743	0.6+0.2	0.8+0.2	2.3+0.2	0
3.726	4.681	0.4+0.15	0.6+0.15	3.1+0.15	0
4.220	4.643	0.1+0.1	0.35+0.1	3.9+0.1	0
4.700	4.609	0	0.3	4.1	0.3
5.105	4.541	0	0	3.98	0.56
5.880	4.511	0	0	3.14	1.37
6.133	4.388	0	0	2.64	1.74
7.122	4.256	0	0	1.39	2.87
7.431	4.190	0	0	0.95	3.24
8.016	4.081	0	0	0.15	3.94
8.308	4.030	0	0	0	4.03

Note. All of the concentrations are given in mol L^{-1}.

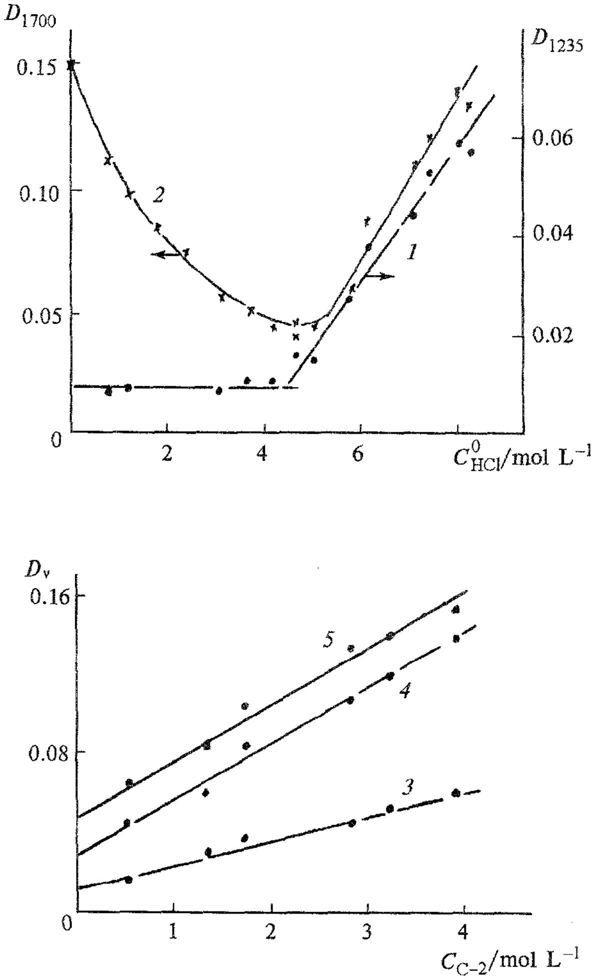


Fig. 3. Dependences of optical densities of the absorption at frequencies of 1235 cm^{-1} (*1, 3*), 1410 cm^{-1} (*4*), and 1700 cm^{-1} (*2, 5*) on the concentrations of HCl (*1, 2*) and complex C-2 (*3—5*).

For the bands at 1360, 1480, 1600, and 1780 cm^{-1}, which appear in the solutions of HCl, graphical dependences were plotted in the $C_{C\text{-}2}/C_{C\text{-}1}$—$D_v/C_{C\text{-}1}$ and $C_{C\text{-}1}/C_{C\text{-}2}$—$D_v/C_{C\text{-}2}$ coordinates; these dependences are straight lines (see Fig. 2). This proves the validity of the assumption that in concentrated solutions, HCl is bound in complexes of two types, C-1 and C-2.

The fact that HCl is almost entirely bound into complex C-2 is confirmed by the presence of linear dependences of the optical densities of the absorption bands at 1235 and 1410 cm^{-1} associated with C-2 (see Fig. 3 and Table 2). The absorption coefficient of C-2 for the band at 1480 cm^{-1} was determined from Eq. (4): $(\varepsilon l)_{C\text{-}2} = 0.116$ L mol^{-1}. We also evaluated the amount of HCl, not bound into complexes C-1 or C-2 in the most concentrated solutions. We found that at $C^0_{HCl}/C^0_{N\text{-}MP} \geq 2$, no more than 0.2 mol L^{-1} HCl, not bound into structures C-1 or C-2, is present in the system (see Tables 1 and 2), *i.e.*, in concentrated solutions, the equilibrium

$$\text{C-1} + \text{HCl} \rightleftharpoons \text{C-2}$$

is completely shifted to the right.

The equilibrium

$$3\,\text{C-1} \rightleftharpoons \text{C-2} + \text{C-3}$$

is not completely shifted to the left at a nearly equimolar ratio between HCl and *N*-MP. The concentrations of the complexes in a solution of the composition 1 : 1 were evaluated by the following way. The absorption of complexes C-1 and C-2 at 1264 cm^{-1} is equal to zero. From the concentration dependence of the optical density of this band (see Table 1) in the region of dilute solutions, where *N*-MP is bound only in complexes C-3, we determined the absorption coefficient of C-3: $(\varepsilon l)_{C\text{-}3} = 0.0106$ L mol^{-1}. Using this coefficient, we estimated concentrations of the complexes in a solution that corresponds to an equimolar ratio between HCl and *N*-MP ($C^0_{HCl} = 4.7$ mol L^{-1}) and contains no free *N*-MP: $C_{C\text{-}3} \approx 0.5$ mol L^{-1}; $C_{C\text{-}1} \approx 3.7$ mol L^{-1}; $C_{C\text{-}2} \approx 0.5$ mol L^{-1}. A similar evaluation was carried out using the optical density of the band at 1480 cm^{-1} (see Fig. 2). The absorption coefficient of complex C-1 at 1480 cm^{-1} was determined from Eq. (4): $(\varepsilon l)_{C\text{-}1} = 0.057$ L mol^{-1}. For a solution corresponding to an equimolar ratio between HCl and *N*-MP, we obtained: $C_{C\text{-}3} \approx 0.3$ mol L^{-1}; $C_{C\text{-}1} \approx 4.1$ mol L^{-1}; $C_{C\text{-}2} \approx 0.3$ mol L^{-1}. Table 2 presents the averaged values of the concentrations of the complexes.

The variations of the optical densities of the background absorption at $C^0_{HCl}/C^0_{N\text{-}MP} > 1$ at all of the frequencies correspond to the presence of complexes C-1 and C-2 in the system (see Eqs. (4) and (5) and Fig. 4). From expressions (4) and (5), background absorption coefficients of complexes C-1 and C-2 ($\varepsilon_{C\text{-}1}$ and $\varepsilon_{C\text{-}2}$) were determined. At frequencies below 1900 cm^{-1} the background absorption of complex C-3 differs from that of C-1 (see Fig. 1). The magnitudes of the coefficients of the background absorption of C-3 were obtained as tangents of the slopes of the initial sections of the concentration dependences of the optical densities of the background absorption, where all the HCl is bound into complex C-3 (see Fig. 4). At frequencies above 1900 cm^{-1} the background absorptions of C-3 and C-1 coincide. The resulting values of the background absorption coefficients of complexes C-3, C-1, and C-2 are presented in Fig. 1, *b*.

The structure of complexes *N*-MP with HCl. The general character of the variations in the IR spectra of the HCl—*N*-MP—TCE system and the regularities of the behavior of the optical densities of the bands of *N*-MP and the complexes are similar to the correspond-

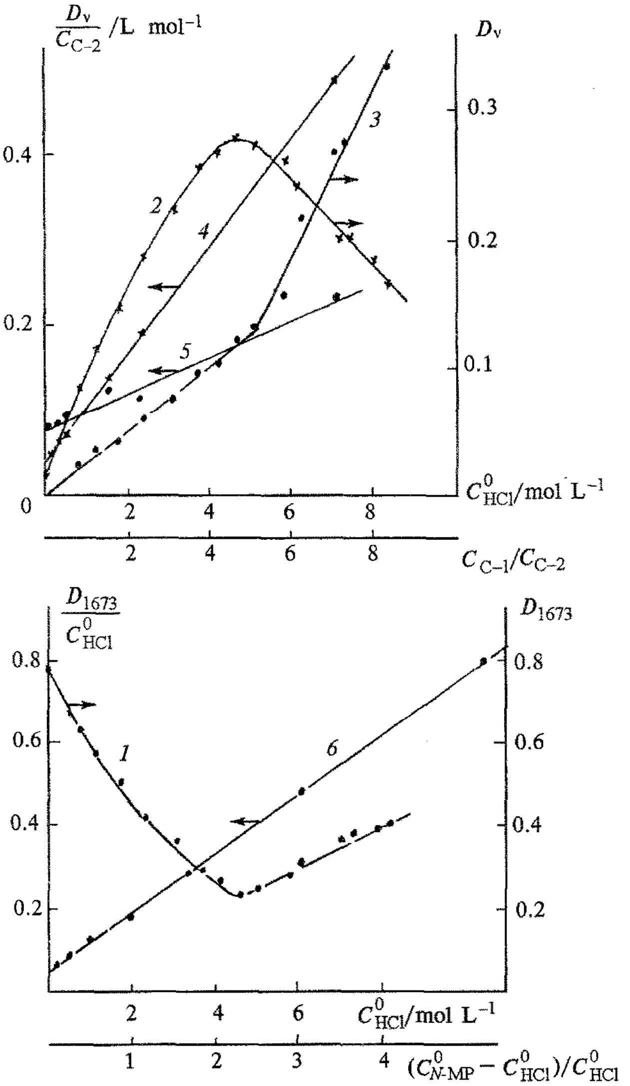


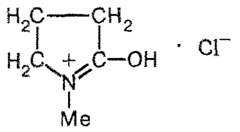
Fig. 4. Dependences of optical densities of the band at 1673 cm^{-1} (*1*) and background absorption at frequencies of 1080 cm^{-1} (*2*) and 2200 cm^{-1} (*3*) on the concentration of HCl. Graphical solutions of Eq. (5) for frequencies of 1080 cm^{-1} (*4*) and 2200 cm^{-1} (*5*) and Eq. (6) for a frequency of 1673 cm^{-1} (*6*).

ing variations in the IR spectra of the DMF—HCl system.[4] Not only does the form of the background absorption of complexes coincide in these systems, but also the absolute magnitudes of the background absorption coefficients at frequencies above 1900 cm^{-1} (see Fig. 1). This indicates that the acid-base interactions in these systems are identical.

The distinctions between the IR spectra of complexes C-1 and C-3 are small, and the bands associated with C-1 almost do not change as the second *N*-MP molecule adds to it. From this it follows that the addition of an *N*-MP molecule to the (*N*-MP · HCl) structural unit corresponding to a complex of the composition 1 : 1 to give complex C-3 virtually does not disturb its structure. Therefore, in the following discussion, the term C-1 will also mean the (*N*-MP · HCl) structural unit incorporated in complex C-3.

When HCl is dissolved in *N*-MP, no ions with strong symmetrical H-bonds of $(H_2O...H...OH_2)^+$ type are produced (see Refs. 5 and 6), since the two *N*-MP molecules incorporated in complex C-3 are nonequivalent. In addition, there is no continuous absorption typical of ions with strong symmetrical H-bonds.[7] The extinction coefficient at 2000 cm^{-1} is 100 L mol^{-1} cm^{-1}, which is substantially lower than its normal values for positively charged complexes with strong symmetrical H-bonds (160—180 L mol^{-1} cm^{-1}).[5]

The IR spectra observed at $C^0_{HCl}/C^0_{N\text{-}MP} < 1$, like those of the DMF—HCl system, do not correspond to the protonation of *N*-MP at the O atom of the carbonyl group with subsequent formation of the following ions[8,9]:



The spectrum exhibits no bands, characteristic of vibrations of an N=C bond. As complex C-1 is formed, the long-wave wing of the ν(C=O) band is appreciably blurred, and continuous absorption in the 1500—1660 cm^{-1} range appears. In addition, background absorption is observed (see Fig. 1), which reflects the formation of a strong H-bond in C-1.[10] The formation of a molecular complex of *N*-MP with HCl can be ruled out, since no bands corresponding to stretching vibrations of an H—Cl bond are observed in the spectra, and all of the vibrations of *N*-MP bound to HCl are essentially disturbed. The formation of a molecular complex also cannot account for the appearance of the continuous absorption in the 1500—1660 cm^{-1} range or noticeable background absorption.

The features of the spectra characteristic of complex C-1, like those of the DMF—HCl system,[4] can be interpreted by assuming that a quasiionic pair with an intermediate position of the proton is formed in C-1.[11,12]

$[(CH_2)_3N(Me)=CO...H...Cl]$

In this structure, vibrations of the C=O bond should be appreciably disturbed, owing to their interaction with the vibrations of the proton in the O...H...Cl bridge.[7] This leads to the continuous absorption in the 1500—1660 cm^{-1} range. Since the C—N bond is incorporated in the ring, it is not so much disturbed by the formation of C-1, as in the case of the DMF · HCl complex. Therefore, the continuous absorption in the 1500—1660 cm^{-1} range for the *N*-MP—HCl system is less intense than that for the DMF—HCl system. The O...H...Cl interaction is very strong and is accompanied by disturbance of the vibrations of all of the bonds, which is manifested by the spectral pattern of *N*-MP incorporated in the *N*-MP · HCl fragment completely changing (see Fig. 1). The presence of the strong quasisymmetrical H-bond in this structural unit accounts for the fact that the background absorption coefficients of complexes C-1 and C-3 in the *N*-MP—HCl and DMF—HCl systems coincide over a wide range of frequencies (see Fig. 1), since, as has been shown previously,[7] parameters of a strong quasisymmetrical H-bond depend only slightly on the environments of the atoms involved in its formation. In other words, parameters of the O...H...Cl bridges in $(CH_2)_3N(Me)C=O...H...Cl$ and $Me_2N—HC=O...H...Cl$ complexes are identical.

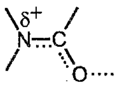
The spectrum of the second *N*-MP molecule incorporated in complex C-3 differs somewhat from the spectrum of free *N*-MP. The absorption coefficients of the bands at 1264 (ν(N—Me)) and 1503 (ν(C—N)) cm^{-1} corresponding to the vibrations of the N atom change significantly (see Table 1). At the same time, we found that the absorption coefficient at 1673 cm^{-1} (ν(C=O)) for the *N*-MP molecule bound to the (*N*-MP · HCl) structural unit in complex C-3 does not differ from the absorption coefficient of free *N*-MP. This can be demonstrated by representing D_{1673} as a sum of absorptions of two types of species, *viz.*, free *N*-MP and the *N*-MP incorporated in the (*N*-MP · HCl) structural unit:

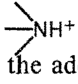
$$D_{1673} = (\varepsilon_{N\text{-}MP}l)C_{N\text{-}MP} + (\varepsilon_1 l)C_1,$$

$$C^0_{N\text{-}MP} = C_{N\text{-}MP} + C_1,$$

where $C_{N\text{-}MP}$ and C_1 are concentrations of free *N*-MP molecules and (*N*-MP · HCl) structural units, respectively, $C_1 = C^0_{HCl}$. By solving these equations, we obtain

$$D_{1673}/C^0_{HCl} = (\varepsilon_1 l) + (\varepsilon_{N\text{-}MP}l)[(C^0_{N\text{-}MP} - C^0_{HCl})/C^0_{HCl}]. \quad (6)$$

Figure 4 shows the graphical solution of Eq. (6). It yields a straight line in appropriate coordinates, which implies that the absorption coefficients of free *N*-MP and the *N*-MP bound to the (*N*-MP · HCl) structural units in complex C-3, coincide at this frequency. The vibration of the C=O double bond is not disturbed, when an *N*-MP molecule adds to (*N*-MP · HCl), while vibrations associated with the N atom are noticeably disturbed. This may occur in the case where the second molecule of the base in complex C-3 is coordinated through the N atom to the quasiionic pair. In our opinion, two structures are possible for complex C-3. First, the N atom of the second *N*-MP molecule can coordinate to the H atom of the O...H...Cl fragment without disturbing the vibrations of this strong quasisymmetrical H-bond, *i.e.*, the two *N*-MP molecules in complex C-3 are nonequivalent. One of these molecules is bound through the O atom by the strong quasisymmetrical H-bond, while the second molecule is bound through the N atom by a weaker bond. The possibility of coordination of the N atom of the *N*-MP molecule to the N atom of the  fragment of the quasiionic pair also cannot be ruled out.

When the second HCl molecule adds to complex C-1 (the formation of C-2), the quasiionic structure of C-1 is destroyed (see Fig. 1). The continuous absorption in the 1500—1660 cm^{-1} region disappears, and the background absorption substantially changes. It is also characteristic that the ν(C—N) band at 1503 cm^{-1} is absent from the spectrum of C-2 (see Table 2) (the absorption at this frequency in the region of concentrated solutions of HCl is due to superimposition of the neighboring band (see Fig. 1)), while a band at 1700 cm^{-1} appears in the spectrum (see Fig. 4). It is very unlikely that the second HCl molecule adds at the N atom. First, the spectrum contains no band associated with a substituted ammonium ion,  (2300—2850 cm^{-1}).[9] Second, it is unlikely that the addition of HCl at the N atom could disturb the quasiionic structure. Third, if the addition at the N atom had yielded a molecular complex, the spectrum would have exhibited vibrations of the H—Cl bond, which is not the case.

It seems more probable that the second molecule of HCl (as in the case of the DMF—HCl system) adds to the Cl atom of the quasiionic pair

$$(CH_2)_3N(Me)C{=}O...H...Cl + HCl \rightleftharpoons$$

$$\rightleftharpoons (CH_2)_3\overset{+}{N}(Me){=}C{-}OH + (Cl...H...Cl)^-$$

to give the protonated form of *N*-MP and the (Cl...H...Cl)$^-$ ion with a strong symmetrical H-bond. The spectrum of complex C-2 observed corresponds to the spectrum of the protonated form of *N*-MP (ν(C=N) ~1700 cm^{-1}), while the background absorption corresponds to the spectrum of the (Cl...H...Cl)$^-$ ion, superimposed on which is the absorption caused by vibrations of the O—H bond in the protonated *N*-MP. This is confirmed by the fact that the coefficients of the background absorption of complexes C-2 in systems *N*-MP—HCl and DMF—HCl in the 1500—3000 cm^{-1} range are identical. Thus, C-2 is an ion pair produced from the protonated *N*-MP and the (Cl...H...Cl)$^-$ ion with a strong symmetrical H-bond.

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References

1. N. J. Harrick, *Internal Reflection Spectroscopy*, New York, 1967.
2. A. E. Parsons, *J. Mol. Spectrosc.*, 1961, **6**, 201.
3. T. C. Jao, I. Scott, and D. Steel, *J. Mol. Spectrosc.*, 1982, **92**, 1.
4. V. D. Maiorov, S. G. Sysoeva, O. N. Temkin, and I. S. Kislina, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1577 [*Russ. Chem. Bull.*, 1993, **42**, 1511 (Engl. Transl.)].
5. V. D. Maiorov and N. B. Librovich, *Izv. Akad. Nauk, Ser. Khim.*, 1989, 967 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 872 (Engl. Transl.)].
6. V. D. Maiorov, G. I. Voloshenko, S. G. Sysoeva, and I. S. Kislina, *Izv. Akad. Nauk, Ser. Khim.*, 1991, 217 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 199 (Engl. Transl.)].
7. G. V. Yukhnevich, E. G. Tarakanova, V. D. Maiorov, and N. B. Librovich, *J. Mol. Struct.*, 1992, **265**, 237.
8. A. D. Roocker and P. De Radzitry, *Bull. Soc. Chim. Belg.* 1970, **79**, 531.
9. J. Brand and G. Elington, *Primenenie spektroskopii v organicheskoi khimii* [*The Use of Scpectroscopy in Organic Chemistry*], Mir, Moscow, 1967, 132 (Russ. Transl.).
10. V. D. Maiorov, I. S. Kislina, S. G. Sysoeva, V. M. Zakoshanskii, and M. I. Vinnik, *Izv. Akad. Nauk, Ser. Khim.*, 1991, 1001 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 887 (Engl. Transl.)].
11. A. A. Pankov, V. Yu. Borovkov, and V. B. Kazanskii, *Khim. Fizika*, 1985, **4**, 249 [*Chem. Phys.* (*USSR*), 1985, **4** (Engl. Transl.)].
12. V. D. Maiorov and I. S. Kislina, *Khim. Fizika*, 1992, **11**, 660 [*Chem. Phys.* (*USSR*), 1992, **11** (Engl. Transl.)].

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