Effect of 1,1,2,2-tetrachloroethane on IR spectra of HCl complexes with *N,N*-dimethylformamide and 1-methyl-2-pyrrolidone formed by a strong quasi-symmetric hydrogen bond

I. S. Kislina, V. D. Maiorov, and S. G. Sysoeva*

*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: 007 (095) 938 2156*

The effect of 1,1,2,2-tetrachloroethane (TCE) on the IR spectra of HCl complexes with *N,N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (*N*-MP) with strong quasi-symmetric hydrogen bonds was studied using Multiple Attenuated Total Reflection (MATR) IR spectroscopy. The addition of TCE does not change the background absorption spectra, but results in a change in the extinction coefficients of some bands of these complexes. The analysis of the spectra shows that the HCl—DMF complexes interact only with one molecule of TCE, and the HCl—*N*-MP complexes interact with two molecules of TCE. It is shown that the neutral component of the system (TCE) has no effect on the parameters of the strong quasi-symmetric H-bond in the complexes studied.

Key words: IR spectra; acid-base interactions, hydrogen bond; solutions, complexes; hydrogen chloride, *N,N*-dimethylformamide, 1-methyl-2-pyrrolidone, 1,1,2,2-tetrachloroethane, interaction.

Solutions of HCl in *N,N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (*N*-MP) are efficient catalytic systems.[1] The equilibrium ion-molecular composition and the structure of the acid-base complexes were previously established[2,3] for the HCl—DMF and HCl—*N*-MP—1,1,2,2-tetrachloroethane (TCE) systems. Complexes of three types were found at different ratios of the components: HCl · Solv (C-1), 2HCl · Solv (C-2), and HCl · 2Solv (C-3), where Solv is a molecule of DMF or *N*-MP. The complexes with different compositions differ from one another in the catalytic activity.[4]

The complex C-1 in the HCl—*N*-MP system is solid and has a high melting point (>80 °C). Therefore, the formation of a complex of HCl with *N*-MP in the liquid phase[3] was studied in the HCl—*N*-MP—TCE system. A change in the ionizing ability of the complexes of HCl with DMF of the types C-1, C-2, and C-3 in the presence of TCE was observed.[4]

In this work, we studied the solvent effect on the formation of complexes of HCl with DMF and *N*-MP using IR spectroscopy in a wide range of concentrations of the components, using TCE as an example.

Experimental

Solvents and HCl were purified, and DMF and *N*-MP were saturated with hydrogen chloride as described previously.[2,3] The concentration of HCl in the starting solutions was determined by alkalimetric titration. The concentrated solution of HCl in DMF contained 42.75% HCl, and that of *N*-MP contained 43.4% HCl. Solutions with the required composition were prepared by the weighed method. Densities of solutions were determined pycnometrically for the calculation of the molar concentrations of the components (Tables 1 and 2).

MATR IR spectra[5] were obtained in the region of 4000—900 cm^{-1} at 30 °C on a UR-20 spectrophotometer with a MATR-3 attachment (Ge as refractive element, incident angle 30°). The spectra were recorded with respect to air at the effective thicknesses of the absorbing layer equal to 1.7 and 3.3 mm at the frequency of 2000 cm^{-1}; the number of reflections was 4 and 8, respectively.

Series of solutions for recording IR spectra were obtained by the following methods (see Tables 1 and 2): (1) dilution of a solution of complex C-1 with the solvent (TCE); (2) dilution of a solution of complex C-2 (in the system with DMF, $C_{C\text{-}1} = C_{C\text{-}2}$) with the solvent (TCE); and (3) at different concentrations of HCl in the equimolar DMF—TCE mixture.

The ranges of concentrations of HCl for each series are presented in Tables 1 and 2.

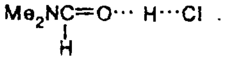
Results and Discussion

Effect of TCE on background absorption coefficients of HCl complexes with DMF and *N*-MP. We have previously shown[6] that C-1 complexes are quasi-ionic structures with strong quasi-symmetric H-bonds between the O atom of the carbonyl group and the Cl

---

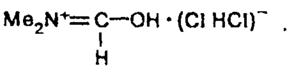
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 956—960, May, 1997.

atom. For example, the HCl complex with DMF of the C-1 type has the structure



$$\mathrm{Me_2N\underset{\displaystyle H}{\underset{|}{C}}{=}O\cdots H\cdots Cl}\ .$$

The addition of the second DMF (or *N*-MP) molecule to C-1 results in the formation of complex C-3 in which the quasi-ionic character of the bond with HCl is retained, and two DMF (or *N*-MP) molecules are nonequivalent. An excess of HCl destroys the quasi-ionic structure, and complex C-2 that formed has the structure of an ion pair, *e.g.*, for the complex with DMF



$$\mathrm{Me_2N^+{=}\underset{\displaystyle H}{\underset{|}{C}}{-}OH\cdot(Cl\,HCl)^-}\ .$$

Table 1. Stoichiometric composition and densities of the HCl—DMF—TCE system at 30 °C

[HCl] (%)	ρ /g cm^{-3}	C^0_{HCl}	C^0_{DMF}	C^0_{TCE}
			mol L^{-1}	
33.22	1.146	10.45	10.47	0
22.49	1.266	7.81	7.83	2.44
8.33	1.467	3.36	3.34	6.56
3.99	1.533	1.68	1.67	8.04
42.75	1.160	13.60	9.09	0
32.94	1.245	11.24	7.52	1.70
24.37	1.325	8.83	5.89	3.41
17.37	1.402	6.68	4.46	4.96
10.84	1.471	4.37	2.92	6.54
9.25	1.490	3.78	2.53	6.96
5.42	1.527	2.27	1.52	7.95
0	1.329	0	5.44	5.55
18.57	1.392	7.09	4.63	4.73
16.71	1.393	6.38	4.74	4.85
14.92	1.394	5.71	4.85	4.95
13.03	1.394	4.98	4.96	5.06
10.52	1.386	4.00	5.07	5.18
7.91	1.374	2.98	5.17	5.28
5.26	1.359	1.96	5.27	5.38
2.81	1.345	1.04	5.35	5.46

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

[HCl] (%)	ρ /g cm^{-3}	C^0_{HCl}	$C^0_{N\text{-}MP}$	C^0_{TCE}
			mol L^{-1}	
12.23	1.401	4.70	4.61	4.60
10.13	1.429	3.97	3.95	5.32
7.88	1.462	3.16	3.19	6.14
5.59	1.503	2.30	2.32	7.05
43.39	1.118	14.14	6.78	0
27.64	1.326	10.06	4.82	2.87
21.13	1.383	8.02	4.08	4.09
13.33	1.464	5.35	2.56	6.04
8.89	1.506	3.67	1.76	7.13

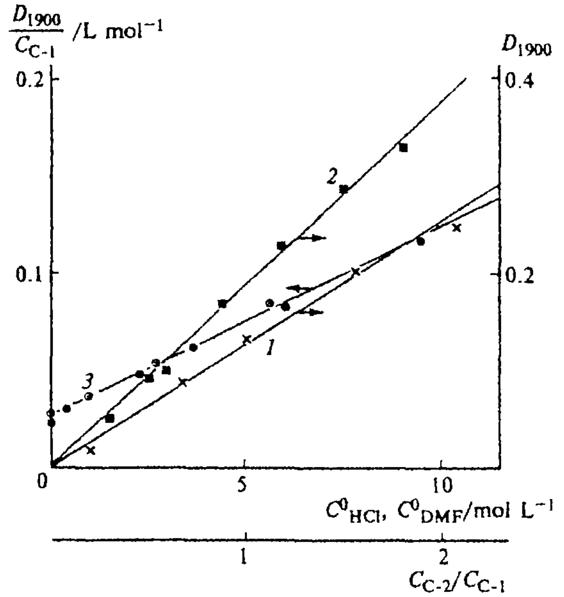


Fig. 1. Dependences of the optical densities of BA of complex C-1 on C^0_{HCl} (*1*) and of the equimolar mixture of complexes C-1 and C-2 on C^0_{DMF} (*2*) at the frequency of 1900 cm^{-1} in the HCl—DMF—TCE system. Graphic solution of Eq. (1) for the frequency of 1900 cm^{-1} (*3*).

The IR spectra of complexes C-1, C-2, and C-3 differ. The characteristic feature of these spectra is the very broad background absorption (BA) against which individual bands appear. The BA spectrum is formed due to the interaction of the vibrations of the central proton in the strong quasi-symmetric H-bond with other vibrations of the particles that form the complex.[7] Therefore, BA reflects first of all the properties of precisely these H-bonds. The intensity of individual blurred bands (see spectra described previously[2,3]), which are observed against BA, can give certain information on the vibrations of the particles that form the complex.

The optical densities of BA (D_v) were measured in the region of 900—2800 cm^{-1} relative to an empty cell at the frequencies where the absorption of individual bands is minimum (at the same frequencies as previously[2,3]). The absorption coefficients of the HCl complexes with DMF and *N*-MP of the C-1, C-2, and C-3 types in solutions in the absence and presence of the addition of the neutral solvent (TCE) in a wide concentration range (see Tables 1 and 2) were compared.

The optical densities of BA at the frequency of 1900 cm^{-1} and the composition of the HCl—DMF—TCE system are compared in Fig. 1. Dependence *1* in Fig. 1 was obtained due to the dilution of a solution of HCl in DMF (taken in equimolar amounts) with tetrachloroethane. In such solutions, HCl and DMF are almost completely bound in complexes C-1 ($C_{C\text{-}1} \approx C^0_{HCl}$). The proportional dependence of D_{1900} on C^0_{HCl} is evidence for the absence of the effect of TCE on absorption coefficient $\varepsilon_{C\text{-}1}$.

In the most concentrated solution of HCl in DMF (42.75% HCl), the components are completely bound in complexes C-1 and C-2:

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

$$C^0_{\mathrm{DMF}} = C_{\mathrm{C\text{-}1}} + C_{\mathrm{C\text{-}2}}.$$

The fact that the dependence of D_v on C^0_{DMF} (see Fig. 1, line *2*) obtained by the dilution of a 42.75% solution of HCl in DMF with tetrachloroethane is evidence that the absorption coefficient $\varepsilon_{\mathrm{C\text{-}2}}$ is constant at different concentrations of TCE.

Dependences similar to straight lines *1* and *2* in Fig. 1 are fulfilled for all ten frequencies at which the optical densities of BA are measured in case of the HCl—DMF—TCE system and for all 14 frequencies in the case of HCl—*N*-MP—TCE.

Unlike solutions in DMF, hydrogen chloride is soluble in the system with *N*-MP up to the ratio HCl : *N*-MP = 2 : 1. Dependences of type *2* were obtained by the dilution of the mixture containing only complexes C-2 with tetrachloroethane. For plotting the type *1* dependences, the greatest concentration of the HCl complexes with *N*-MP of the C-1 composition corresponds to a solution with the equimolar ratio of the components (HCl, *N*-MP, and TCE). At lower concentrations of TCE ($C_{\mathrm{TCE}} < C_{\mathrm{C\text{-}1}}$), the system becomes heterogeneous.[3]

At all frequencies of BA at $C^0_{\mathrm{HCl}} > C^0_{\mathrm{DMF}}$, both complexes (C-2 and C-1) make a contribution to the optical density D_v, and the following correlation is fulfilled:

$$D_\mathrm{v} = \varepsilon_{\mathrm{C\text{-}1}}C_{\mathrm{C\text{-}1}} + \varepsilon_{\mathrm{C\text{-}2}}C_{\mathrm{C\text{-}2}}$$

or

$$D_\mathrm{v}/C_{\mathrm{C\text{-}1}} = \varepsilon_{\mathrm{C\text{-}1}} + \varepsilon_{\mathrm{C\text{-}2}}(C_{\mathrm{C\text{-}2}}/C_{\mathrm{C\text{-}1}}). \qquad (1)$$

In the coordinates of Eq. (1) for all frequencies of BA, the data obtained for solutions of HCl in DMF and in the equimolar DMF—TCE mixture lie on the same linear dependence. This is possible only when the absorption coefficients $\varepsilon_{\mathrm{C\text{-}1}}$ and $\varepsilon_{\mathrm{C\text{-}2}}$ are constant at different ratios of the concentrations of TCE and complexes C-2 and C-1. For example, the dependence (line *3*) in the coordinates of Eq. (1) for ν = 1900 cm^{-1} is presented in Fig. 1. The values of the coefficients $\varepsilon_{\mathrm{C\text{-}1}}$ and $\varepsilon_{\mathrm{C\text{-}2}}$ obtained from dependences *1*, *2*, and *3* in Fig. 1 coincide for each frequency of BA.

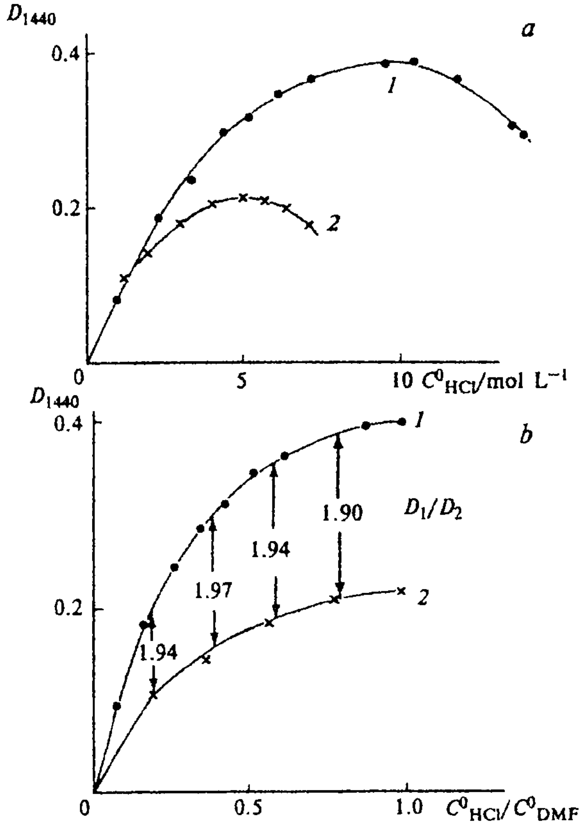


Fig. 2. Dependences of the optical densities of BA at the frequency of 1440 cm^{-1} for solutions of HCl in DMF (*1*) and in the equimolar DMF—TCE mixture (*2*) on the concentration of HCl (*a*) and on the ratio of concentrations $C^0_{\mathrm{HCl}}/C^0_{\mathrm{DMF}}$ (*b*).

The BA spectra of complexes C-3 and C-1 are identical at ν > 1900 cm^{-1} but differ significantly at lower frequencies. Figure 2 presents the concentration dependences of the optical densities of the solutions of HCl in DMF and in the DMF—TCE mixture of the composition of 1 : 1 (mol/mol) at the frequency of 1440 cm^{-1} for which the difference between the $\varepsilon_{\mathrm{C\text{-}3}}$ and $\varepsilon_{\mathrm{C\text{-}1}}$ values ($C^0_{\mathrm{HCl}} = C_{\mathrm{C\text{-}1}} + C_{\mathrm{C\text{-}3}}$) is maximum.[2] The initial regions of the dependences D_v—C^0_{HCl} (see Fig. 2, *a*) coincide for the solutions in which HCl is completely bound in complexes C-3, *i.e.*, TCE has no effect on $\varepsilon_{\mathrm{C\text{-}3}}$. It is noteworthy that in the HCl—DMF and HCl—DMF—TCE systems at the same content of C-3, the equilibrium concentrations of DMF are different (see Table 1). The divergence of the curves in Fig. 2, *a* in the region of the more concentrated solutions of HCl is explained by the fact that in the HCl—DMF—TCE system complexes C-1 appear at C^0_{HCl} > 2.5 mol L^{-1}, and in the HCl—DMF system they appear only at C^0_{HCl} > 6 mol L^{-1}. In Fig. 2, *b*, the D_{1440} values for the systems considered are compared at equal ratios of the concentrations of C-1 and C-3 (*i.e.*, at the same $C^0_{\mathrm{HCl}}/C^0_{\mathrm{DMF}}$ ratios). In the HCl—DMF and HCl—DMF—TCE systems, the same ratios of the concentrations of the complexes are achieved at substantially different C^0_{HCl}. Therefore, when TCE has no effect on $\varepsilon_{\mathrm{C\text{-}1}}$ and $\varepsilon_{\mathrm{C\text{-}3}}$, the corresponding curves cannot coincide, but should be entirely similar. Indeed, this can be seen in Fig. 2, *b*, where the ratios of the optical densities of two curves are presented for several $C^0_{\mathrm{HCl}}/C^0_{\mathrm{DMF}}$ values.

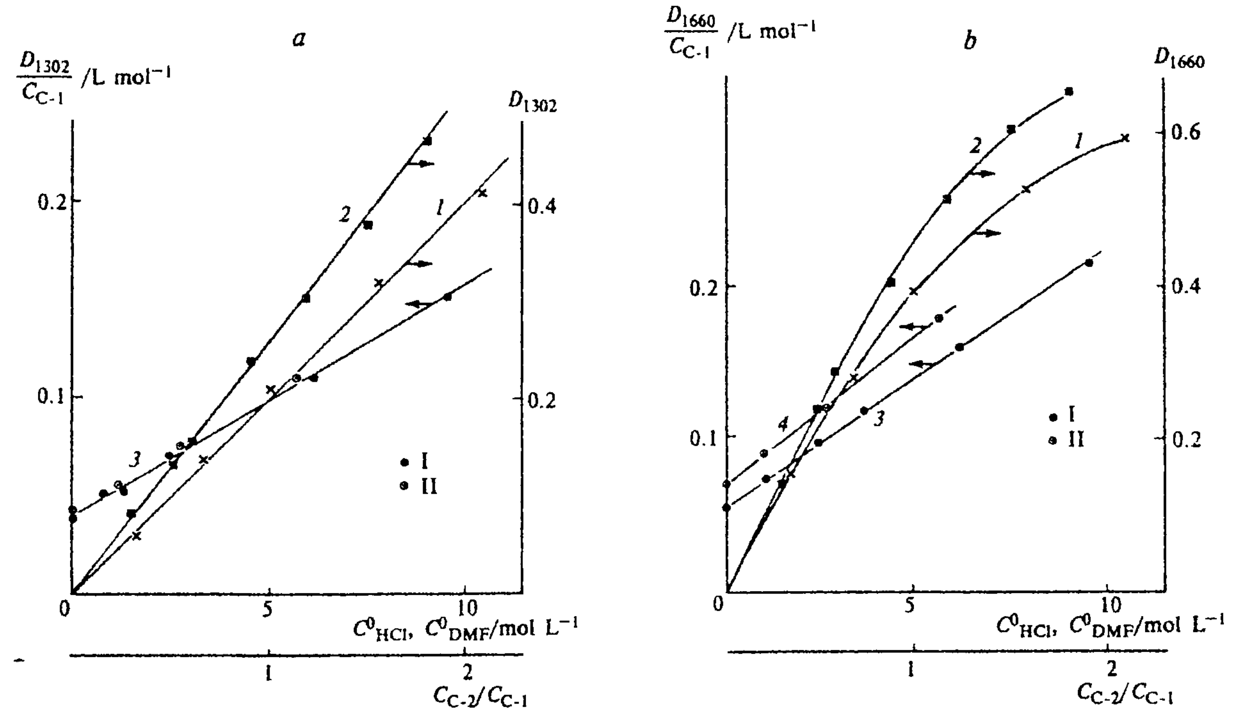


Fig. 3. Dependences of the optical densities of bands at 1302 (*a*) and 1660 cm^{-1} (*b*) on C^0_{HCl} (*1*) and C^0_{DMF} (*2*). Graphic solution of Eq. (1) for the frequencies of 1302 (*3*) and 1660 cm^{-1} (*3, 4*) for solutions of HCl in DMF (I) and in the equimolar DMF—TCE mixture (II).

Thus, for the complexes of HCl with DMF and *N*-MP, no effect of TCE on the background absorption coefficients of C-1, C-2, and C-3 was observed. This means that the neutral component of the system, TCE, has no effect on the parameters of the strong quasi-symmetric H-bond in complexes C-1, C-2, and C-3.

Effect of TCE on absorption coefficients of individual bands of HCl complexes with DMF and *N*-MP. The analysis of the experimental data has shown that TCE affects the absorption coefficients of some bands in the spectra of complexes C-1 and C-2. The observed effect is more pronounced for the HCl complexes with *N*-MP than for those with DMF. These conclusions are based on the comparison of the dependences similar to lines *1*, *2*, and *3* in Fig. 1 plotted for the optical densities of individual bands of the complexes in the solutions with different concentrations of TCE.

In the HCl—DMF—TCE systems with different compositions, no effect of TCE on the ε_{C-1} value at the frequencies of 1122, 1302, 1550, and 1600 cm^{-1} and on the ε_{C-2} value at 1122, 1302, 1418, and 1600 cm^{-1} was observed. For illustration, the dependences obtained for ν = 1302 cm^{-1} are presented in Fig. 3, *a*.

The greatest effect of TCE on the absorption of the HCl complexes with DMF of the C-1 and C-2 types manifests itself at the frequency of 1660 cm^{-1} (ν(C=O) in C-1 and C-2) (Fig. 3, *b*). For this frequency, the ε_{C-1} and ε_{C-2}-values increase significantly in the presence of TCE. Tetrachloroethane affects similarly the ν(C=O) band at 1673 cm^{-1} in the HCl—*N*-MP—TCE system. The addition of TCE to DMF and *N*-MP results in a change in the absorption coefficients of the bands of the vibrations of the C=O groups in the solutions in the absence of HCl as well. For example, when *N*-MP is diluted with tetrachloroethane to the ratio *N*-MP/TCE = 1 : 2 (mol/mol), an increase in the absorption coefficient at 1673 cm^{-1} is observed due to the interaction of TCE with the carbonyl group of *N*-MP. The coefficient ε_{1673} does not change as the concentration of TCE further increases. The interaction between TCE and the HCl complexes with *N*-MP is also indicated by the fact that the HCl—*N*-MP—TCE system becomes homogeneous when at least one TCE molecule falls per each molecule of the complex.

In the HCl—*N*-MP—TCE system, the strongest change in the absorption coefficients of complexes C-1 and C-2 at 1673 cm^{-1} occurs when the first TCE molecule is added. The interaction with the second TCE molecule is weaker because it results in considerably smaller changes in the absorption coefficients of the complexes. In the HCl—DMF—TCE system, the ε_{C-1} and ε_{C-2} values at the frequency of 1660 cm^{-1} change only when the content of TCE increases up to the ratio C_{HCl}/C_{TCE} = 1 : 1, *i.e.*, only one TCE molecule is bound to a molecule of the complex. The difference in solvation of the complexes formed by DMF and *N*-MP is probably caused by the differences in the sizes and geometry of these molecules.

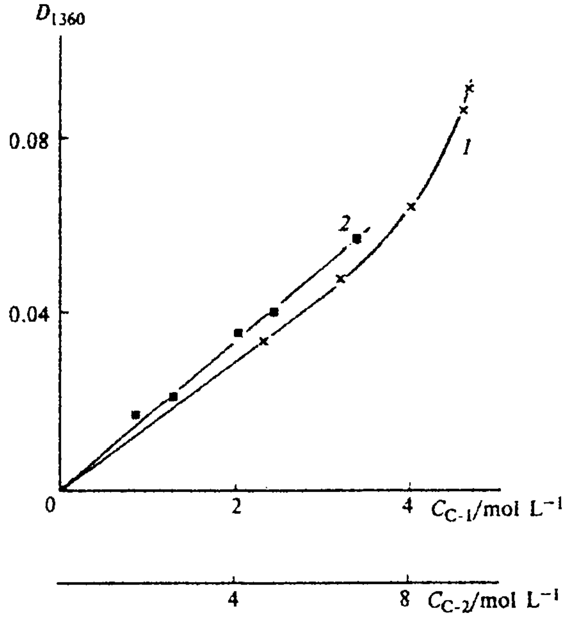


Fig. 4. Dependences of the optical densities of a band at the frequency of 1360 cm^{-1} on $C_{\text{C-1}}$ (*1*) and $C_{\text{C-2}}$ (*2*) in the HCl—*N*-MP—TCE system.

A weak band with a maximum in the region of 1780—1790 cm^{-1} is the second band sensitive to solvation. For both systems, the absorption coefficient of complex C-2 increases strongly at this frequency, while the absorption coefficient of complex C-1 somewhat decreases.

In the HCl—*N*-MP—TCE system, the effect of TCE on $\varepsilon_{\text{C-1}}$ at the frequency of 1360 cm^{-1} is observed (the coefficient decreases). At this frequency, the $\varepsilon_{\text{C-2}}$ value is independent of the concentration of TCE. It should be emphasized that the noticeable change in $\varepsilon_{\text{C-1}}$ is related to the region of the composition of the system with the ratio of the concentrations $C_{\text{TCE}}/C_{\text{C-1}}$ = 1—2 (Fig. 4). The addition of TCE affects the absorption of complex C-2 at 1410 cm^{-1}. When one TCE molecule per molecule of the base is introduced, $\varepsilon_{\text{C-2}}$ increases more strongly than when the second molecule is added. Complex C-1 does not absorb at this frequency. The coefficients $\varepsilon_{\text{C-1}}$ at 1480 cm^{-1} and $\varepsilon_{\text{C-2}}$ at 1235, 1480, and 1700 cm^{-1} are independent of the concentration of TCE.

Thus, differences were found in the effect of TCE on the BA spectrum and individual absorption bands of complexes C-1 and C-2 formed by HCl with DMF and *N*-MP. In the HCl—*N*-MP system, the addition of TCE results in a change in the absorption coefficients of a greater number of the bands than for the solutions of HCl in DMF.

In the HCl—DMF—TCE system, the interaction of complexes C-1 and C-2 with only one molecule of the solvent (TCE) was observed in the spectra, while in the HCl—*N*-MP—TCE system, interaction with two TCE molecules was observed. Since the interaction with molecules of the neutral solvent does not change the BA spectrum of the HCl complexes in the solutions studied, it can be concluded that this interaction has no effect on the parameters of the strong quasi-symmetric H-bond in these complexes. In our opinion, other neutral solvents most likely will not affect the structure of the H-bond as well.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34144).

References

1. L. F. De Buyck, *Jaussen Chim. Acta*, 1988, **6**, 29.
2. V. D. Maiorov, S. G. Sysoeva, O. T. Temkin, and I. S. Kislina, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1577 [*Russ. Chem. Bull.*, 1993, **42**, 1511 (Engl. Transl.)].
3. V. D. Maiorov, I. S. Kislina, S. G. Sysoeva, and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1757 [*Russ. Chem. Bull.*, 1995, **44**, 1688 (Engl. Transl.)].
4. I. S. Kislina, S. G. Sysoeva, and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 77 [*Russ. Chem. Bull.*, 1996, **45**, 69 (Engl. Transl.)].
5. N. J. Harrick, *Internal Reflection Spectroscopy*, Wiley Interscience, New York—London—Sydney, 1967.
6. V. D. Maiorov and I. S. Kislina, *Khim. Fiz.*, 1992, **11**, 660 [*Russ. J. Chem. Phys.*, 1993, **11**, 956 (Engl. Transl.)].
7. G. V. Yukhnevich, E. G. Tarakanova, V. D. Maiorov, and N. B. Librovich, *J. Mol. Struct.*, 1992, **265**, 237.

Received October 7, 1996