# The structure of the ionized form of 3-nitroaniline in HCl—DMF solutions studied by IR spectroscopy

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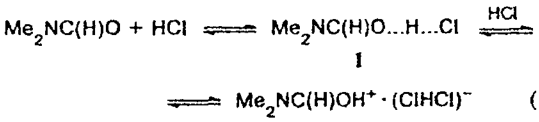
The composition and structure of the ionized form of 3-nitroaniline in the HCl—DMF system were found by Multiple Attenuated Total Reflectance IR spectroscopy. The stage of ionization is the replacement of a DMF molecule in the HCl · DMF complex by an indicator molecule. The ionized form contains the strong quasi-symmetrical N...H...Cl hydrogen bond.

**Key words:** IR spectra, solutions, acid-base interactions, ionization mechanism, hydrogen bond.

The $H_5O_2^+$ ion with the strong symmetrical H bond is the simplest stable proton hydrate in aqueous solutions of strong acids. The protonation of weak organic bases (reagents and indicators) in these solutions is the displacement of the water molecule from the $H_5O_2^+$ ion with retention of the central H bond.[1,2] In solutions of acids in aprotic solvents in a wide composition range, the acid-base interaction results only in the formation of quasi-ionic structures with incomplete proton transfer to the heteroatom of a solvent molecule.[3,4] In these systems, the mechanism of ionization of acid-base indicators is the addition of the acid molecule.[5]

The purpose of this work is to reveal the structure of the ionized form of the indicator 3-nitroaniline (Ind) in the HCl—DMF system.

At different ratios of components in the interaction of HCl with DMF, different complexes are formed according to the scheme[6]



$$\mathrm{Me_2NC(H)O + HCl} \rightleftharpoons \underset{\mathbf{I}}{\mathrm{Me_2NC(H)O...H...Cl}} \xrightleftharpoons{\mathrm{HCl}} \underset{\mathbf{II}}{\mathrm{Me_2NC(H)OH^+ \cdot (ClHCl)^-}} \qquad (1)$$

The composition and structure of complexes I and II were determined by IR [6] and Raman[7] spectroscopies and by XRD structural analysis[8] for I. The broad-band continuous absorption (CA) in the 900—3000 cm$^{-1}$ frequency range is the characteristic spectral property of the complexes indicated. The existence of CA indicates that the solution contains species formed by the strong quasi-symmetrical H bond. The shape and intensity of CA depend on the charge of these species and the composition of the complexes.[1,2,9]

For solving this problem, we obtained and analyzed the Multiple Attenuated Total Reflectance (MATR) IR spectra of the solutions with different concentrations of DMF, HCl, and Ind (Table 1). For samples 4—6, concentrations of HCl were chosen in such a way that the complete ionization of the indicator was achieved.[5] The procedures of purification of the substances and recording of the MATR IR spectra have been described previously.[5,6] For analysis of the spectra, optical densities of CA (relative to an empty cell) and bands of DMF and complex I (relative to basis lines) were measured.

Noticeable changes in the whole frequency range were observed in the spectrum of the Ind—HCl—DMF system as compared to those of binary HCl—DMF and Ind—DMF systems. The most intense bands of Ind at 1347 and 1525 cm$^{-1}$ are shifted to 1352 and 1534 cm$^{-1}$. Their intensities decrease. The absorption of stretching vibrations of N—H in the 3200—3500 cm$^{-1}$ range is absent. The CA spectrum changes strongly at $\nu > 1900$ cm$^{-1}$ (Fig. 1), as well as the intensities of the bands of complex I and DMF.

In the solutions studied (see Table 1), the acid exists entirely as complexes with the structure of a quasi-ionic pair I, and $C_I = C^\circ_{HCl}$. These are precisely the species which are the ionizing agents toward Ind. The ionization

**Table 1.** Stoichiometric composition and densities of solutions of 3-nitroaniline in HCl—DMF mixtures

| Sample | $C^\circ_{HCl}$ | $C^\circ_{DMF}$ | $C^\circ_{Ind}$ | $\rho$ | $C^\circ_{HCl} - C^\circ_{Ind}$ |
|---|---|---|---|---|---|
| | | mol L$^{-1}$ | | /g cm$^{-3}$ | /mol L$^{-1}$ |
| **1** | 4.54 | 12.02 | 0 | 1.044 | 4.54 |
| **2** | 5.84 | 11.71 | 0 | 1.069 | 5.84 |
| **3** | 0 | 11.20 | 1.32 | 1.001 | — |
| **4** | 5.90 | 9.88 | 1.32 | 1.118 | 4.58 |
| **5** | 5.56 | 9.10 | 1.86 | 1.138 | 3.70 |
| **6** | 5.20 | 10.63 | 0.93 | 1.094 | 4.27 |
| **7** | 0 | 12.96 | 0 | 0.948 | — |

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of Ind during the interaction with complex **I** can occur both with and without displacement of the DMF molecule from the complex. The data obtained previously[5] do not allow these two possibilities to be distinguished.

To solve this problem, we analyzed a change in the optical density of the bands of DMF at 1093 ($\gamma(CH_3)N$) and 1660 cm$^{-1}$ ($\nu(C=O)$) after the addition of Ind to a solution of HCl in DMF. The optical density at these frequencies is obtained by summation of the absorption of free DMF molecules and complexes **I**:

$$D_\nu = \varepsilon_1{}^\nu \cdot l_\nu \cdot C_I + \varepsilon_2{}^\nu \cdot l_\nu \cdot C_{DMF}, \qquad (1)$$

$$D_\nu/C_I = \varepsilon_1{}^\nu \cdot l_\nu + \varepsilon_2{}^\nu \cdot l_\nu \cdot C_{DMF}/C_I, \qquad (2)$$

where $C_I = C^\circ_{HCl}$ and $C_{DMF} = C^\circ_{DMF} - C^\circ_{HCl}$. The coefficients in Eq. (2) in the HCl—DMF system for frequencies of 1093 (1660) cm$^{-1}$ have the following values: $\varepsilon_1{}^\nu \cdot l_\nu$ = 0.011 (0.050) Lmol$^{-1}$ and $\varepsilon_2{}^\nu \cdot l_\nu$ = 0.052 (0.121) Lmol$^{-1}$ (Fig. 2). In solutions with Ind (see Fig. 2), the same values of the coefficients $\varepsilon_1{}^\nu \cdot l_\nu$ and $\varepsilon_2{}^\nu \cdot l_\nu$ correspond to the equilibrium composition:

$$C_I = C^\circ_{HCl} - C^\circ_{Ind}, \qquad (3)$$

$$C_{DMF} = C^\circ_{DMF} - (C^\circ_{HCl} - C^\circ_{Ind}).$$

This implies that the DMF molecule in complex **I** is replaced during ionization by the Ind molecule.

$$\text{Ind} + \text{I} \rightleftharpoons \text{Ind}\cdot\text{HCl} + \text{DMF}.$$

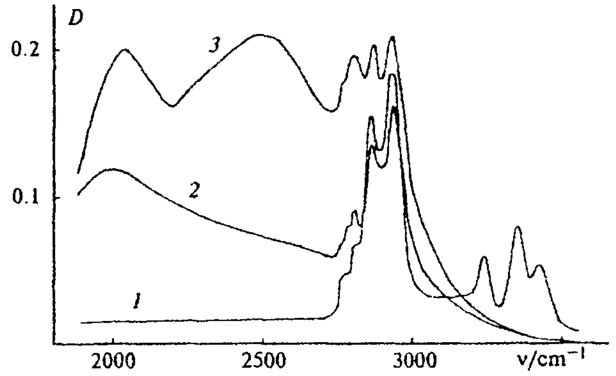

**Fig. 1.** MATR IR spectra at ν > 1900 cm$^{-1}$: *1*, Ind—DMF (sample 3); *2*, HCl—DMF (sample 1); and *3*, Ind—HCl—DMF (sample 5).

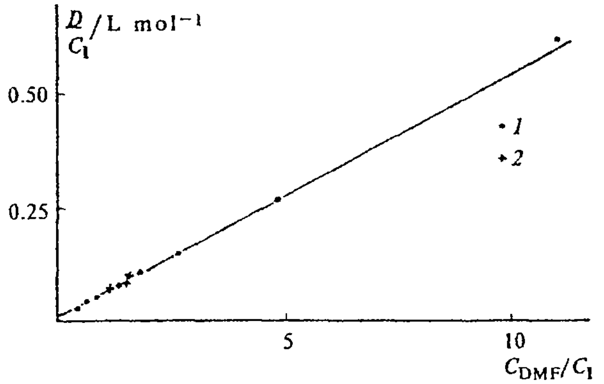

**Fig. 2.** Graphical solution of Eq. (2) for the band at 1093 cm$^{-1}$ in the HCl—DMF (*1*) and Ind—HCl—DMF (*2*) systems. The published data[6] and results of this work were used for the HCl—DMF system.

The ratio of components in samples **4—6** (see Table 1) should provide[5] the complete ionization of Ind. This is confirmed by the concentration dependences of the optical densities of the bands of complex **I** at 1122 and 1302 cm$^{-1}$. Their decrease during dissolution of Ind in the HCl—DMF system corresponds to the change in the concentrations of complex **I** according to Eq. (3). The complete ionization of the indicator is evidenced by the absence of absorption in the 3200—3500 cm$^{-1}$ region corresponding to the N—H stretching vibrations.

The spectrum of CA of the ionized form of Ind in the 980—2740 cm$^{-1}$ frequency range was isolated from the overall spectra of samples **4—6**. For each of the

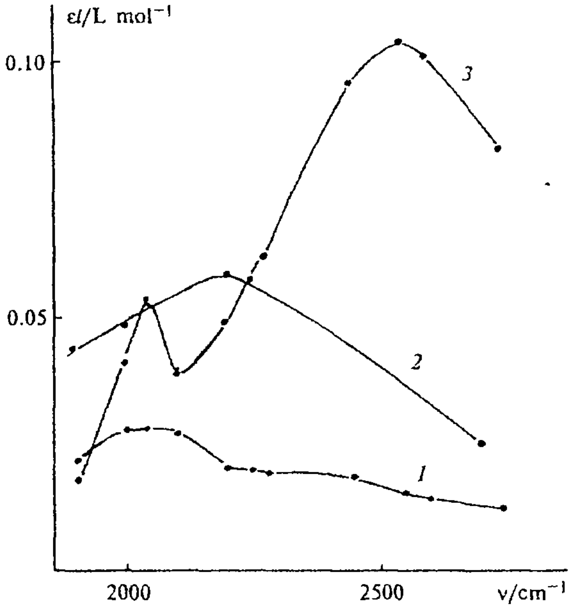

**Fig. 3.** Continuous absorption spectra in the 1900—2740 cm$^{-1}$ frequency range of complexes of HCl with DMF **I** (*1*), **II** (*2*), and of the ionized form of 3-nitroaniline (*3*).

frequencies, the absorption of complex I was subtracted from the total absorption of the solutions with different concentrations of Ind:

$$D^{\nu}_{\mathrm{Ind\cdot HCl}} = \varepsilon^{\nu}_{\mathrm{Ind\cdot HCl}} \cdot l_{\nu} \cdot C_{\mathrm{Ind\cdot HCl}} = D_{\nu} - \varepsilon^{\nu}_{\mathrm{I}} \cdot l_{\nu} \cdot C_{\mathrm{I}}. \quad (4)$$

The CA is absent in pure DMF. The $\varepsilon^{\nu}_{\mathrm{I}} \cdot l_{\nu}$ coefficients were measured in the HCl—DMF system. The concentrations of complex I in Eq. (4) were determined from Eq. (3). The coefficients of CA of the ionized form of the indicator were obtained from the linear dependences of $D^{\nu}_{\mathrm{Ind\cdot HCl}}$ on $C^{\circ}_{\mathrm{Ind}}$.

The spectra of the ionized form of Ind and the complexes of HCl with DMF (I and II) at $\nu > 1900$ cm$^{-1}$ differ substantially in the 1900—2740 cm$^{-1}$ frequency range (Fig. 3). At lower frequencies, CA in the IR spectrum of the Ind • HCl species is almost absent.

Thus, during the equilibrium ionization of the indicator in the HCl—DMF system, species are formed, whose IR spectrum contains intense CA at $\nu >$ 1900 cm$^{-1}$. The presence[1,9] of CA in the spectra of the Ind • HCl complexes indicates that a species with the strong quasi-symmetrical H bond (N...H...Cl) is formed during the substitution of the DMF molecule in the DMF • HCl complex by the Ind molecule.

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# Reactions of 2-polyfluoroalkylchromones with aliphatic diamines

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2-Polyfluoroalkylchromones react with aliphatic 1,2-diamines to give 2,3-dihydro-1*H*-1,4-diazepines. A similar reaction with 1,3-diaminopropane yields *N,N'*-trimethylenebis(2-hydroxyacetophenonimines) as a result of scission of the original chromones.

**Key words:** 2-polyfluoroalkylchromones, aliphatic diamines; 2,3-dihydro-1*H*-1,4-diazepines, *N,N'*-trimethylenebis(2-hydroxyacetophenonimines).

It is known[1—3] that chromones, when treated with ammonia or primary amines, undergo opening to give the corresponding enamino ketones. Reactions with ethylenediamine are ambiguous and, depending on the reaction conditions, yield either *N,N'*-ethylenebisenamino ketones or mixtures of 2,3-dihydro-1,4-diazepines with *N,N'*-ethyleneiminoenamino ketones and *N,N'*-ethylenebis(2-hydroxyacetophenonimines) resulting from chromone scission.[4]

We found that, unlike nonfluorinated analogs, 2-polyfluoroalkylchromones (**1a—l**), obtained by condensation of the corresponding 2-hydroxyacetophenones with alkyl polyfluorocarboxylates,[5] react with ethylenediamine in an ethanolic solution at room temperature to give only 5-aryl-7-polyfluoroalkyl-2,3-dihydro-1*H*-1,4-diazepines (**2a—l**) (Scheme 1). In the absence of a solvent, chromone **1l** gives a mixture of diazepine **2l** with *N,N'*-ethylenebis(2-hydroxy-5-chloroacetophe-

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