The acidity scale of HCl solutions in N,N-dimethylformamide

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The scale of the thermodynamic acidity of HCl solutions in DMF has been measured at 25 and 39.5 °C up to 15 mol L^{-1} acid concentration by the indicator method. It is shown that in the HCl—DMF system the ionization of the nitroaniline-derived indicators occurs by the ion pair mechanism. Within the temperature range studied acidity is independent of temperature. Indicators of the nitroaniline series are used.

Key words: indicator method, ionization mechanism, acidity, hydrogen chloride, DMF.

Solutions of HCl in DMF are efficient acid-catalytic systems. In particular, they are considered to be promising systems for the hydrochlorination of acetylene derivatives.

In order to understand the nature of the catalytic effect of acids in non-aqueous solutions, one must know the ion-molecular composition and the structure of the proton solvates and the complexes of the acid with the solvent. The thermodynamic scale of the ionizing ability of a medium is a measure of the solution acidity. Moreover, acid-base ionization of organic bases may involve not only a protonation mechanism[1] but also the formation of ion-pair complexes of various compositions and structures.[2]

The study of ion-molecular interactions in the HCl—DMF[3] system made it possible to establish the formation of three types of complexes between DMF and HCl with the stoichiometric compositions 2:1 (K-0.5), 1:1 (K-1), and 1:2 (K-2) in which for all practical purposes the dissociation of the acid does not occur. The first two complexes have the structure of an uncharged quasi-ionic pair where the proton is positioned between the carbonyl oxygen atom and the chlorine atom. Protonation of the DMF molecule and the formation of the $(Cl...H...Cl)^-$ ion take place in the K-2 complex.

The purpose of this work is to obtain an acidity scale (ionizing ability) for solutions of HCl in DMF over a wide range of concentrations of HCl at 25 and 39.5 °C and to the elucidate the mechanism of the catalytic action of HCl in a non-aqueous system with the help of Hammett's basic indicators.

Experimental

An initial concentrated solution (48.55 % HCl in DMF) was prepared by the saturation of purified and dried DMF[4] with dry gaseous hydrogen chloride. The concentration of HCl in the initial solution was determined alkalimetrically, and the solutions of required composition were prepared by the gravimetric method. The previously determined densities of the solutions[3] were used to calculate the molar concentrations. 3-Nitroaniline (**1**), 4-nitroaniline (**2**), 2-nitroaniline (**3**), 4-chloro-2-nitroaniline (**4**), and 2,5-dichloro-4-nitroaniline (**5**) purified by recrystallization from aqueous ethanol were used as indicators.

Concentrations of the non-ionized forms of indicators **1—5** at various concentrations of HCl were determined spectrophotometrically on a Specord UV-VIS spectrophotometer at 25 and 39.5 °C using thermostatted quartz cuvettes. The measurements were performed at the maxima of the absorption bands of the non-ionized forms of **1—5** in the visible spectral range. The numerical values of the absorption coefficients ε_N and ε_D, which were necessary for the calculation of the ratios of the concentrations (I) of the non-ionized (N) and ionized (D) forms of **1—5**, were obtained in the following way. The values of ε_N for **1—5** were determined from the optical densities of their solutions without the acid, and those of ε_D for indicators **1**, **3**, and **4** were determined in solutions of HCl at concentrations that provided complete ionization of these indicators. The values of ε_D could not be determined for **2** due to the irreversible chemical transformation of this indicator at $C_{HCl}>3.3$ mol L^{-1}, and for **5** due to the insufficient ionizing ability of the initial concentrated HCl solution in DMF. Hence, in the calculations ε_D for **2** and **5** were assumed to be zero.

The concentration ranges of the acid at which the values of logI for **1—5** were obtained are given in Table 1.

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Table 1. Ionization constants of indicators (pK_p) and concentration ranges for the HCl solutions in DMF at 25 and 39.5 °C

Indicator	pK_p (*C/M*)	
	25 °C	39.5 °C
3-Nitroaniline(**1**)	0.91 (0.025—1.26)	—
3-Nitroaniline* (**1**)	0.59 (0.031—0.31)	
4-Nitroaniline(**2**)	−0.69 (0.52—3.12)	—
2-Nitroaniline(**3**)	−2.02 (3.36—11.37)	−2.07 (3.44—11.43)
4-Chloro-2-nitro (**4**) aniline	−2.67 (7.13—12.77)	−2.75 (6.97—12.68)
2,5-Dichloro-4- (**5**) nitroaniline	−3.64 (11.36—15.07)	−3.88 (11.1—15.02)

* For H_2SO_4—DMF.

Results and Discussion

The acidity of HCl solutions in DMF was determined using the method developed by Hammett.[5] The acidity scale obtained by the indicator method is a thermodynamic characteristic of solutions. Its standard state is an indefinitely dilute solution of the acid in the solvent studied. It should be mentioned that the indicator acidity scale may reflect both the protonating ability of the solution[1] and some other type of acid-base interaction between the acid and a weak organic base.[2] This depends on the ionization mechanism of the indicators used. The ionization of nitroaniline derivatives in aqueous solutions of strong acids results in a quickly established equilibrium of protonation:

$$B + H_5O_2^+ \xrightleftharpoons{pK_{BH_3O^+}} (B...H...OH_2)^+ + H_2O$$

This ionization mechanism of Hammett's indicators in aqueous solutions of strong acids is confirmed by the fact that the value of $pK_{BH_3O^+}$ does not depend on the acid anion and by the fact that the thermodynamic basicity constant $K_{BH_3O^+}$ is equal to the concentration constant $K_c = I \cdot C_{H_5O_2^+}$ in weakly dilute solutions of completely dissociated acids. For the nitroaniline derivatives, the protonation mechanism takes place not only in aqueous solutions of acids.[6,7]

The results of the previously published work[3] and those of the study of the ionization of indicator **1** in solutions of two acids, HCl and H_2SO_4, in DMF were also taken into account to support the ionization mechanism of indicators **1**—**5** in the solutions of HCl in DMF. The extent of ionization of indicator **1** at the same concentrations of HCl and H_2SO_4 in DMF is significantly different (Fig. 1). This attests to the participation of the acid anion in the ionization stage and makes it possible to conclude that the ionization of indicator **1** proceeds *via* an ion-pair mechanism. Although HCl does not dissociate in its dilute and moderately concentrated solutions in DMF,[3] it can form H-complexes with a strong centrosymmetric hydrogen bond with the structure of a quasi-ionic pair. We believe that the structure of the quasi-ionic pair is still retained in the ionized form of the indicator.

To plot the acidity scale by the indicator method one has to know the ionization constant (K_p) of the most basic of the indicators used. For the rest of the indicators the values of K_p are determined using the method of overlap. For indicator **1** in HCl and H_2SO_4 solutions, the values of K_p were equated to the concentration constants of ionization, which remain unaltered in the concentration range 0.094 to 0.313 mol L^{-1} for HCl and 0.104 to 0.311 mol L^{-1} for H_2SO_4 and equal 0.91 ± 0.03 and 0.59 ± 0.02, respectively (see Table 1). The steepness of the ionization curves of indicator **1** noticeably increases for $C_{HCl} < 0.1$ mol L^{-1} (Fig. 1). This dependence may be explained by the fact that partial ionization of the acid occurs in such dilute solutions of HCl but the ionization mechanism of **1** retains its ion-pair nature. The values of pK_p for **2**—**5** are also presented in Table 1. They are obtained from a comparison of the plots logI *vs.* $\log C_{HCl}$ (C_{HCl}) (Figs. 1, 2) over a fairly wide range of variation of logI. The determination of the pK_p value for **3** should be specially

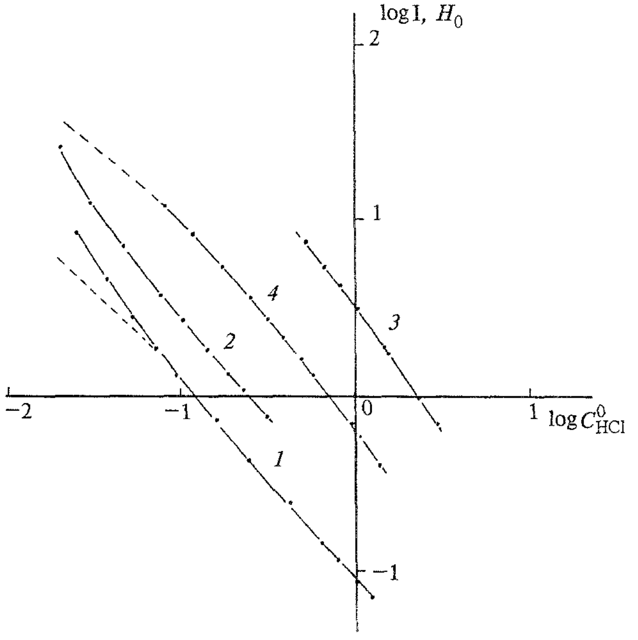

Fig. 1. Plots of logI (*1*, *2*, and *3*) and H_0 (*4*) *vs.* $\lg C^0_{HCl}$ for 3- (*1*, *2*) and 4-nitroaniline (*3*); *1* and *3* in HCl—DMF; *2* in H_2SO_4—DMF, H_0; *4* in HCl—H_2O, 25 °C.

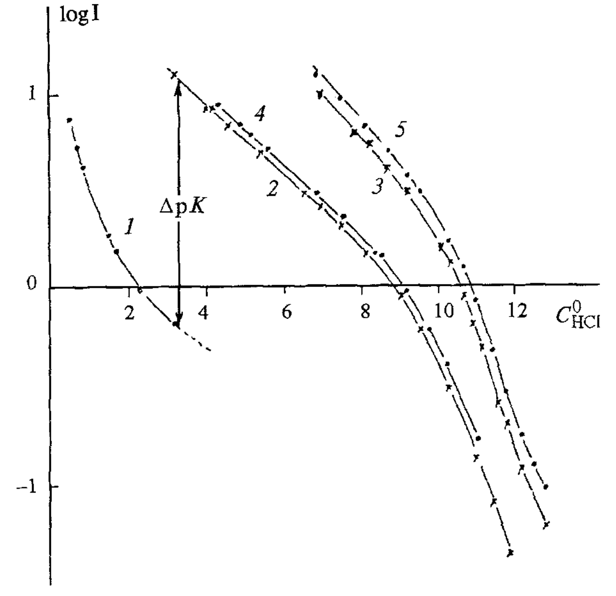

Fig. 2. Plots of logI *vs.* C^0_{HCl} for 4-nitroaniline (*1*), 2-nitroaniline (*2, 4*), and 4-chloro-2-nitroaniline (*3, 5*) at 25 °C (*1—3*) and 39.5 °C (*4, 5*) in HCl—DMF.

Table 2. Values of H_0 for various concentrations of HCl in DMF at 25 and 39.5 °C

HCl/*M*	$-H_0$	HCl/*M*	$-H_0$	HCl/*M*	$-H_0$
0.025	−1.78	4.0	1.05	10.6	2.69
0.04	−1.49	4.5	1.15	10.8	2.80
0.07	−1.16	5.0	1.24	11.0	2.91
0.1	−0.98	5.5	1.34	11.2	3.04
0.2	−0.64	6.0	1.43	11.4	3.17
0.3	−0.44	6.5	1.53	11.6	3.30
0.4	−0.32	7.0	1.63	11.8	3.44
0.6	−0.10	7.5	1.74	12.0	3.56
0.8	0.07	8.0	1.85	12.2	3.65
1.0	0.19	8.5	1.96	12.4	3.73
1.2	0.29	9.0	2.08	12.6	3.81
1.4	0.38	9.2	2.14	12.8	3.88
1.6	0.45	9.4	2.19	13.0	3.95
1.8	0.53	9.6	2.26	13.5	4.11
2.0	0.59	9.8	2.32	14.0	4.23
2.5	0.73	10.0	2.40	14.5	4.35
3.0	0.84	10.2	2.49	15.0	4.46
3.5	0.94	10.4	2.59		

mentioned. We have the values of logI for **2** with sufficient accuracy only from 0.9 to −0.17 due to the irreversible chemical transformation of indicator **2** at C_{HCl} > 3.3 mol L^{-1}. Therefore, the ranges of ionization for indicators **2** and **3** do not overlap but only approach one another. The value of $\Delta logI_{2-3}$ at the point of junction (see Fig. 2) was assumed to be equal to the difference between the logarithms of the ionization constants of **2** and **3**.

The acidity scale (denoted by the symbol H_0)* of HCl solutions in DMF at 25 °C was obtained using the values of pK_p (see Table 1) and logI of indicators **1—5**

$$H_0 = pK_p + logI$$

The averaged values of H_0 in the concentration range 0 to 15 mol L^{-1} for HCl are listed in Table 2. The accuracy of the determination of H_0 in the concentrated HCl solutions is ±0.05.

The ionization of indicators **3—5** was studied only at 39.5 °C; the measurements cover the range of HCl concentrations from 3.4 to 15 mol L^{-1}. For each of the indicators, the ionization curve at 39.5 °C is somewhat shifted to the range of more concentrated solutions (see Fig. 2) and the curves themselves are almost parallel. It is accepted for **3** that for equal concentrations of HCl the difference between the logI values at 25 and 39.5 °C reflects the change in pK_p of **3** with increasing temperature. Thus, the value pK_p = −2.07 was obtained for **3** at 39.5 °C. The values of pK_p for **4** and **5** at 39.5 °C were obtained by the method of overlap (see Table 1). Then the values of H_0 at 39.5 °C of HCl solutions in DMF were obtained by the usual method for the studied range of acid concentrations. The dependences of H_0 at 25 and 39.5 °C on the HCl concentration almost coincide. In our opinion, this result is very important, and the values of H_0 (see Table 2) may be used with sufficient reliability in the analysis of the kinetic data of HCl solutions in DMF over a wider temperature range.

The relationships presented in Fig. 3 make it possible to compare the values of H_0 in the HCl—DMF system

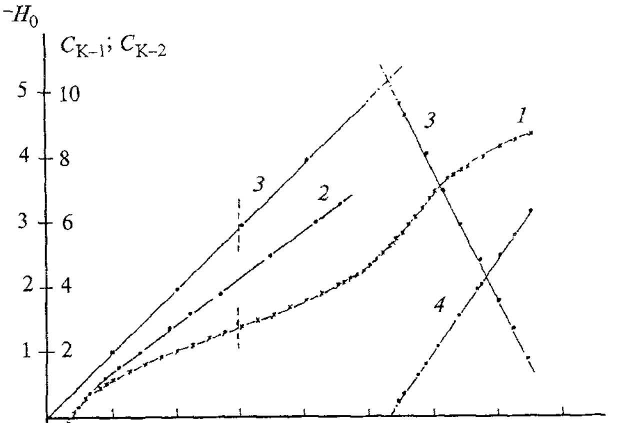

Fig. 3. Plots of C^0_{HCl}: $-H_0$ (*1*), C_{K-1} (*3*), and C_{K-2} (*4*) in HCl—DMF, $-H_0$ in HCl—H_2O (*2*) *vs.* C^0_{HCl}.

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* We do not introduce a new symbol for designating the acidity parameter in the HCl—DMF system obtained by the ionization of the indicators of the nitroaniline series. However, this function reflects the ionizing ability of the medium according to the ion-pair mechanism, unlike that of aqueous solutions in which H_0 is a measure of the protonating ability of the medium.

with its equilibrium composition and with the acidity function H_0 of aqueous solutions of HCl. The acidities in the two systems coincide quantitatively in a fairly wide range of HCl concentrations, from 0.1 to 1.6 mol L^{-1} (H_0 ranges from 0.98 to −0.45), while their ratio varies considerably in a wider range (H_0 of the aqueous system is significantly higher for concentrated HCl solutions). The value of H_0 changes much faster than the acid concentration does in the whole range of the compositions of the HCl—DMF system. H_0 changes more steeple in relatively dilute ($C_{HCl}<2$ mol L^{-1}) and concentrated solutions of HCl, which is related to the formation of K-2 complexes at $C_{HCl}>10.5$ mol L^{-1}. A uniform change of H_0 near the acid concentration of ~6 mol L^{-1} confirms the conclusion that the addition of a second molecule of DMF to the structural unit (DMF·HCl) in the formation of the K-0.5 complex does not distort the structure of the central hydrogen bond in the quasi-ionic pair.[3]

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