Effect of 1,1,2,2-tetrachloroethane on the ionizing ability of complexes of HCl with DMF

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The acidity function (H_0) of solutions of HCl (0—7.1 mol L^{-1}) in an equimolar mixture of DMF—1,1,2,2-tetrachloroethane (TCE) has been determined by the indicator method at 25 °C. Data on the relative ionizing activity of complexes of HCl with DMF with various compositions and structures have been obtained. In the ternary system HCl—DMF—TCE, the ionizing ability of the complexes of DMF with HCl of the compositions 2 : 1 and 1 : 1 with a quasiionic structure decreases compared to the HCl—DMF system, and that of the complex of the composition DMF·2HCl with a structure of an ion pair $Me_2NHCOH^+ \cdot (ClHCl)^-$ with a strong centrosymmetrical H-bond in the anion increases.

Key words: acidity, the indicator method; hydrogen chloride, *N,N*-dimethylformamide, complexes; 1,1,2,2-tetrachloroethane.

Solutions of HCl in aprotic solvents are efficient catalysts of many chemical reactions.[1] The quantitative approach to the analysis of kinetic data in aqueous and nonaqueous solutions of acids is based on use of the acidity functions.[2,3] The main factors that determine the catalytic activity of acids in solutions are the concentrations, compositions, and structures of the acid—base complexes, as well as the composition and nature of the solvent. For aprotic solvents such as DMF[4] and 1-methyl-2-pyrrolidone[5] (*N*-MP), a high solubility of HCl (up to 67 mol. %) is typical under ambient conditions. For the HCl—DMF system, the scheme of acid-base interaction HCl—solvent[4] (30 °C) has been established, and the scale of acidity[6] (25 °C) in the range of concentrations of HCl from 0 to 65.4 mol. % has been obtained. The HCl—*N*-MP system is homogeneous within narrow ranges of the concentrations of HCl (0—19 and 60—67 mol. %) at 25 °C. That is why the acid-base interactions of HCl with *N*-MP have been studied in the homogeneous HCl—*N*-MP—TCE system (TCE — 1,1,2,2-tetrachloroethane).[5] To predict the effect of composition of the solvent on the acidic properties of the solutions of HCl in aprotic solvents, in this work we measured the scale of the ionizing ability H_0 of the HCl—DMF—TCE system at 25 °C.

Experimental

Purification of solvents, HCl, and indicators and saturation of DMF with hydrogen chloride were carried out as described elsewhere.[4—6] The parent concentrated solution of HCl in DMF contained 60.48 mol. % (43.29 %) HCl. We used 3-nitroaniline (**1**), 4-nitroaniline (**2**), 2-nitroaniline (**3**), and 2-nitro-4-chloroaniline (**4**) as the indicators. Solutions of the needed composition were prepared by a weighting procedure. To calculate the concentrations in the molar scale, we determined the densities of solutions pycnometrically (Table 1).

The ratios of the concentrations of nonionized and ionized forms of indicators **1**—**4** (*I*) were determined spectrophotometrically in the visible range of the spectrum on a Specord UV-VIS spectrophotometer.

Table 1. Composition and densities of the HCl—DMF—TCE system

C_{HCl} (%)	ρ /g cm^{-3}	C^0_{HCl}*	C^0_{DMF}*	C^0_{TCE}*	C_{C-1}*	C_{C-2}*
0	1.329	0	5.44	5.55		
2.80	1.345	1.04	5.35	5.46		
5.26	1.359	1.96	5.27	5.38		
7.91	1.374	2.98	5.17	5.28		
10.52	1.386	4.00	5.07	5.18		
13.03	1.394	4.98	4.96	5.06		
14.92	1.394	5.71	4.85	4.95	3.99	0.86
16.71	1.393	6.38	4.74	4.85	3.10	1.64
18.57	1.392	7.09	4.63	4.73	2.17	2.46
0	0.947	0	12.96	0		
33.29	1.146	10.5	10.49	0	10.5±0.5	0.5±0.5
43.29	1.160	13.77	9.00	0	4.23	4.77

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

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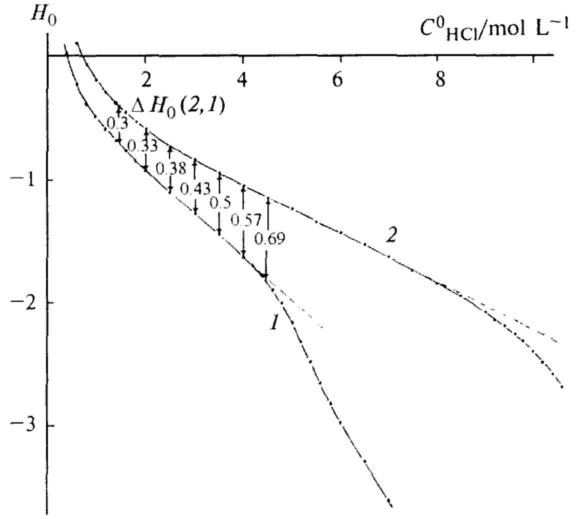

Fig. 1. Dependences of H_0 on analytical concentration of HCl in the HCl—DMF—TCE (*1*) and HCl—DMF (*2*) systems at 25 °C.

The values of the acidity function (H_0) of HCl—DMF—TCE system (I) were obtained in the range of the concentrations of HCl from $2.1 \cdot 10^{-3}$ to 7.1 mol L^{-1} at equimolar ratios of the analytical concentrations of DMF and TCE (which corresponded to 30.34 % DMF in the composition of the solvent) at 25 °C. To calculate H_0, we used the values of log*I* for compounds **1**—**4** in the range from 1.1 to −1.1 (Fig. 1, curve *1*).

Results and Discussion

Determination of the acidity function for the HCl—DMF—TCE system. To obtain the values of the ionizing ability H_0 of system I we used the indicator method.[7] The standard procedure for constructing the H_0 scale involves determination of log*I* values for a series of indicators with various basicities and their ionization constants (K_i). The measured value is the degree of transformation of the indicator to the ionized form. Therefore, the scale of acidity is a relative one. Upon standardization of H_0 and K_i, one obtains absolute H_0 values that depend on the standard state.

$$H_0 = \log I + pK_i \qquad (1)$$

An infinitely diluted solution of the acid either in water or in the solvent under study is usually used as a standard state. In the first case, to calculate H_0 by Eq. (1), the pK_i values known for the aqueous solutions of acids are used.[8,9] In the second case, one determines the ionization constant for the most basic indicator, and then finds the numerical values of pK_i by the overlapping method[7] by Eq. (2)

$$\Delta pK_{n,n-1} = \Delta \log I_{n,n-1}, \qquad (2)$$

where *n* is a number of the used indicators of different basicity.

For organic bases of various classes (B), different mechanisms of ionization are possible in the solutions of acids.[10—14] In aqueous solutions of acids, nitroanilines are protonated as a result of substitution of the molecule of water in the $H_5O_2{}^+$ ion by a molecule B with retention of the structure of an H-bond[10] (Scheme 1).

Scheme 1

$$B + H_5O_2^+ \xrightleftharpoons{K_{BH_3^+}} (H_2O\cdots H\cdots B)^+ + H_2O$$

The mechanism of protonation with the complete transfer of proton to the heteroatom of a molecule B is also possible.[11] Moreover, many examples of the addition of an acid HA to a base B in the equilibrium step of ionization (Scheme 2) are known.[12—14]

Scheme 2

$$B + HA \xrightleftharpoons{K_i} B\cdot HA \text{ or } BH^+A^-$$

In contrast to $K_{BH_3^+}$, the numerical values of K_i differ for the same indicator in the solutions of various acids.[13,14] The mechanism of ionization can change on going from aqueous to nonaqueous solutions of acids.[6,10] In this case, the use of the values of the ionization constants of indicators in aqueous solutions for H_0 calculation in nonaqueous solutions by Eq. (1) results in erroneous results.

The results obtained earlier[15,16] are an additional argument in favor of the standardization of the acidity scale to infinitely diluted solution of HA in the solvent under study. Mechanisms of ionization of indicators of different classes A and B (A are aliphatic alcohols[16] and B are nitroanilines[15]) in water-organic solutions correspond to Scheme 1. However, when C_{HA} = const the values of logI_A and logI_B vary with composition of the mixed solvent in different ways. In this case, the log*I* parameter reflects an influence of composition of a solvent on indicator properties, but not on the protonating ability of the medium.[15] Upon standardization of the acidity scale to the aqueous solution, any variation of log*I* is considered as a change in the ionizing ability of the medium (see Eq. (1)). Thus, the ionization constants of indicators obtained in aqueous solutions of acids would not always be appropriate for calculation of H_0 of other acid-base systems. This can result in wrong conclusions on the comparative activity of acids in various solvents.

The acidity scale for system I was obtained in the following way. The most basic indicator used is compound **1**, for which the constancy of the ionization constant is observed at $C_{HCl} = 2.1 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ mol L^{-1} (see Eq. (1)).

$$-(\log C_{HCl} + \log I) = 1.60 \pm 0.03,\ H_0 = -\log C_{HCl}$$

At $C_{HCl} = 1.5 \cdot 10^{-2}$ to 7.1 mol L^{-1}, the H_0 values are calculated by Eq. (1) (see Fig. 1, curve *1*). The pK_i values for indicators **2**, **3**, and **4** were obtained by the overlapping method (see Eq. (2)) and are equal to 0.1, −1.62, and −2.38, respectively. The dependences of log$I$ *vs.* C_{HCl} for indicators **1—4** are parallel in pairs. For example, for compounds **3** and **4** the overlapping range is found to be 3.9—5.8 mol L^{-1}, which corresponds to changes in log$I$ from 0.03 to −1.3 for **3** and from 0.8 to −0.53 for **4**; $\Delta \log I_{4,3} = 0.76 \pm 0.01$. In system I, the standard state for H_0 and K_i of indicators **1—4** is the infinitely diluted solution of HCl in a solvent of constant composition with DMF : TCE = 1 : 1 mole ratio (if the concentration of HCl is in mol L^{-1}). The values of H_0 and K_i in HCl—DMF system (II) were standardized similarly (see Fig. 1, curve *2*). In this case, we preferred to use the molar, rather than the molal[17] concentration scale.

We believe that indicators **1—4** in systems I and II are ionized by the same mechanism corresponding to Scheme 2, and HCl molecule is attached to a molecule of the indicator in an equilibrium step. For binary HA—DMF system, this conclusion was made based on the data on ionization of compound **1** in the solutions of HCl and H_2SO_4. For the mechanism of protonation under consideration[13] at the equal concentrations of various of acids, the degrees of ionization of the indicators are equal. They differ substantially for compound **1** in HCl—DMF and H_2SO_4—DMF* solutions.

Let us consider the effect of an addition of TCE on the pK_i value of indicator **1**. The pK_i value for compound **1** in systems I and II are 1.6 and 0.91, respectively, $\Delta pK = 0.69$. Indicator **1** is half ionized (log$I$ = 0) at the concentrations of HCl equal to 0.02 and 0.12 mol L^{-1} in systems I and II, respectively. The difference in the pK_i values is a result of the use of the molar scale upon standardization of H_0 and K_i in system I only partlially. Analytical concentrations of DMF in a pure solvent and in an equimolar mixture DMF—TCE at 25 °C are 12.96 and 5.52 mol L^{-1}, respectively. When the scale of concentrations for HCl connected with the mole ratios of HCl and DMF is used in system I, the difference between the pK_i values for indicator **1** in systems I and II persists, being 0.32. In water-organic solutions of acids, the influence of the composition of the solvent on pK_i reflects the change of the activity coefficient of the nonionized form of the indicator.[17] The different solvation of compound **1** in systems I and II could be one of the reasons for the change in its ionization constant.

Effect of the addition of TCE on the ionizing ability of complexes of HCl with DMF. In DMF solutions, hydrogen chloride is completely bound into complexes of various types that differ in composition and structure.[4] Using the HCl—*N*-MP—TCE system (III) as the example, it was established that addition of TCE practically does not affect the scheme of acid-base interaction and the structure of the complexes of HCl with a solvent (Solv = DMF, *N*-MP).[5] Depending on the ratio of the components HCl and Solv, complexes of the compositions Solv · HCl (C-1), Solv · 2HCl (C-2), and 2Solv · HCl (C-3) are formed. Conclusions on the compositions of the complexes in systems II and III are based on analysis of the concentration dependences of the absorption bands and background absorption in the IR spectra of the solutions.[4,5] For complexes C-1, C-2, and C-3, we obtained sets of bands in the IR spectra and lines in the Raman spectra, which differ one from another.[4,5,18] In a wide range of frequencies, the spectra of background absorption of each of the complexes in systems II and III coincide.[4,5] We suppose that in system I the same mechanism of acid-base interaction is realized. In systems II and III (except the narrow range of composition near an equimolar ratio of HCl and Solv), the equilibrium composition can be calculated from the stoichiometric one in the following way:

$$\text{at } C^0_{HCl}/C^0_{Solv} < 1 \qquad \begin{aligned} &C_{C\text{-}1} + C_{C\text{-}3} = C^0_{HCl}, \\ &C_{C\text{-}2} = 0, \\ &C^0_{Solv} = C_{C\text{-}1} + 2C_{C\text{-}3}; \end{aligned} \qquad (3a)$$

$$\text{at } C^0_{HCl}/C^0_{Solv} > 1 \qquad \begin{aligned} &C_{C\text{-}1} + C_{C\text{-}2} = C^0_{Solv}, \\ &C_{C\text{-}2} = C^0_{HCl} - C^0_{Solv}, \\ &C_{C\text{-}3} = 0, \end{aligned} \qquad (3b)$$

where C^0_{HCl} and C^0_{Solv} are the analytical concentrations. When $C^0_{HCl}/C^0_{Solv} = 1$, complexes C-1, C-2, and C-3 are present in the solutions at the same time. Relations (3a,b) were used for calculation of the concentrations of the complexes of HCl with DMF in system I (see Table 1).

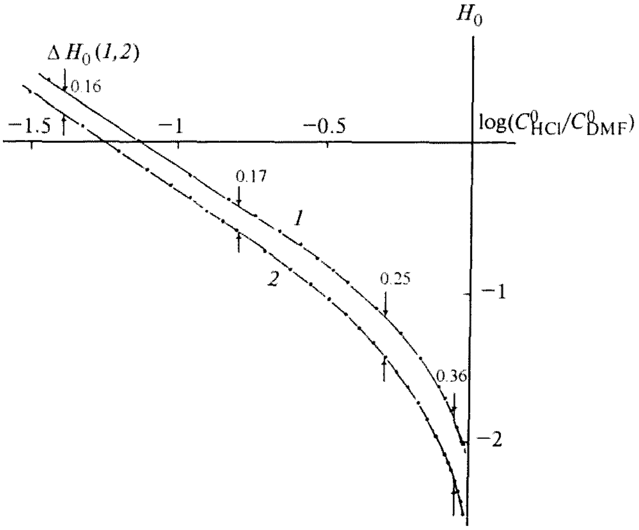

Fig. 2. Comparison of H_0 in the HCl—DMF—TCE (*1*) and HCl—DMF (*2*) systems with equal ratios of the analytical concentrations of HCl and DMF at 25 °C.

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* In aqueous solutions the acidity functions H_0 represents the protonating ability of the medium corresponding to Scheme 1. In this work the same symbol denotes another thermodinamic parameter of solution describing the addition of the molecule of the acid to the indicator by Scheme 2.

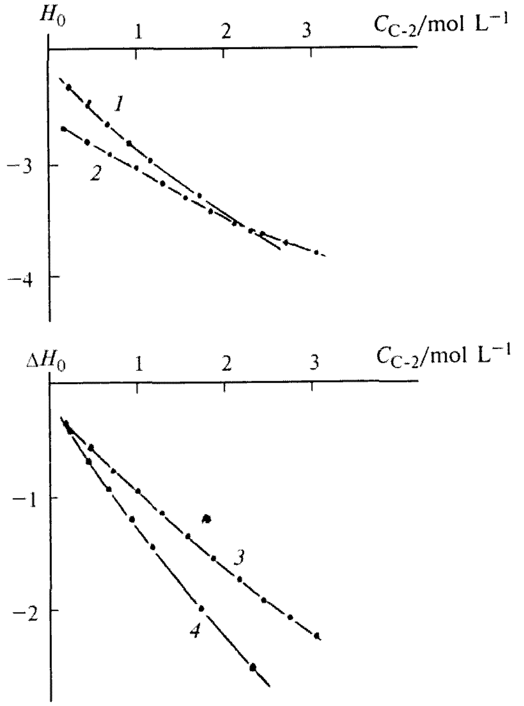

Fig. 3. Dependences of the experimental values of H_0 (*1, 2*) and contributions of complexes C-2 to acidity ΔH_0 (*3, 4*) on $C_{C\text{-}2}$ in the HCl—DMF—TCE (*1, 4*) and HCl—DMF (*2, 3*) systems at 25 °C.

The complexes of HCl with DMF of various composition differ one from another by the structure.[4,5] Complexes C-1 and C-3 are formed by a strong hydrogen bond with an intermediate position of proton between the O atom of the carbonyl group and the Cl atom. In complex C-3, two molecules of DMF are not equivalent. Addition of DMF to C-1 practically does not change the structure of H-bond, but addition of HCl is accompanied by its destruction and formation of the ion pair $Me_2N^+{=}C(H)OH \cdot (Cl\cdots H\cdots Cl)^-$.

Conclusions on the effect of the addition of TCE on the ionizing ability of complexes C-1, C-2, and C-3 and on their relative ionizing activity in systems I and II are based on the comparison of the values of H_0 and their equilibrium composition (Figs. 1—3). The scheme of the ionization of the indicator by the various complexes of HCl with DMF can be written as follows (Scheme 3).

Scheme 3

$$\mathrm{B} + \mathrm{Solv}\cdot\mathrm{HCl} \rightleftharpoons \mathrm{B}\cdot\mathrm{HCl} + \mathrm{Solv}$$

$$\mathrm{B} + \mathrm{Solv}\cdot 2\mathrm{HCl} \rightleftharpoons \mathrm{B}\cdot\mathrm{HCl} + \mathrm{Solv}\cdot\mathrm{HCl}$$

$$\mathrm{B} + (2\mathrm{Solv}\cdot\mathrm{HCl}) \rightleftharpoons \mathrm{B}\cdot\mathrm{HCl} + 2\,\mathrm{Solv}$$

When the concentrations are equal, the ionizing ability of the complexes is the same if the degrees of transformation of B into B · HCl according to Scheme 3 are equal. In systems I and II in a wide range of the compositions, several types of the complexes of HCl with DMF are presented in the solution at the same time. The change in the ratio of the concentrations of the complexes is accompanied with the change of its overall concentration. In some cases, this makes difficult to obtain the conclusions on their relative ionizing activity, although they are obvious for some complexes.

The dependences presented in Fig. 1 indicate the higher ionizing ability of complex C-2 as compared to C-1 in systems I and II. When $C^0_{HCl} > C^0_{DMF}$ and $C^0_{HCl} > 5.02$ mol L^{-1} in system I and $C^0_{HCl} > 10.5$ mol L^{-1} in system II, an increase in C^0_{HCl} resulted in a decrease of both the overall concentration of C-1 and C-2 and of the concentration of the complexes of C-1 type (see Eq. (3b) and Table 1), and the acidity of the medium (h_0) increases ($H_0 = -\log h_0$). The dependence of H_0 on C^0_{HCl} in system I at $C^0_{HCl} < C^0_{DMF}$ does not contradict to the conclusion[6] that complexes C-1 and C-3 are close in their ionizing ability. When $C^0_{HCl} > 1$ mol L^{-1} in system I, as in system II, HCl is bound in complexes C-1 and C-3 with the same structure of H-bond. The ratio of their concentrations varies in a wide range (see Eq. (3a)), and H_0 value changes almost linearly relative to C^0_{HCl} (see Fig. 1). As is shown below, this conclusion[6] is wrong. In Fig. 1, curves *1* and *2* are parallel up to $C^0_{HCl} = 2$ mol L^{-1}, and $\Delta H_0(2,1) = 0.3\pm0.03$. In the mentioned range of compositions, hydrogen chloride in systems I and II is bound only in complex C-3. In the more concentrated solutions, $\Delta H_0(2,1)$ increases up to 0.7 at $C^0_{HCl} = 4.5$ mol L^{-1}. The values of $\Delta H_0(2,1)$ at some concentrations of HCl are given in Fig. 1. The contribution of complexes C-2 in the ionizing ability of the medium at $C^0_{HCl} < 4.5$ mol L^{-1} can be neglected. The range of the concentration of HCl from 2 to 4.5 mol L^{-1} in system I corresponds to equilibrium composition with the comparable concentrations of C-1 and C-3, and in system II the acid is bound only in complex C-3, and $C^0_{DMF} = C^0_{HCl}$ at $C^0_{HCl} = 6$ mol L^{-1}. Therefore, the sharper change of H_0 in system I as compared to system II can be a result of both the effect of TCE on the ionizing ability of complexes C-1 and C-3 and the higher ionizing activity of C-1 than C-3.

In Fig. 2 the dependences of H_0 for systems I and II on the ratio of analytical concentrations of HCl and DMF are given. They can be used to estimate the effect of the addition of TCE on the ionizing ability of complexes C-1 and C-3, no matter what their relative ionizing activity is. Upon substantial excess of DMF, curves *1* and *2* in Fig. 2 are parallel up to the concentrations of HCl equal to 0.85 and 2 mol L^{-1} in systems I and II, respectively, and $\Delta H_0(1,2) = 0.16$. In more concentrated solutions, when C^0_{DMF}/C^0_{HCl}, is 2 ($C^0_{HCl} = C_{C\text{-}3}$) and 1.2 ($C^0_{HCl} = C_{C\text{-}1} + C_{C\text{-}3}$, $C_{C\text{-}1} > C_{C\text{-}3}$, $C_{C\text{-}2} = 0$), $\Delta H_0(1,2)$ increases up to 0.25 and 0.36, respectively. This indicates a small and almost the same decrease in the ionizing ability of complexes C-1 and C-3 in the solutions containing TCE. Hence, an influence of TCE should not be a reason for the increase in $\Delta H_0(2,1)$ shown in Fig. 1. Based on this, we can conclude that the ionizing ability of complex C-1 is higher than that of complex C-3.

When $C^0_{HCl} > C^0_{DMF}$, in systems I and II an acid is bound into complexes C-1 and C-2, which differ in structure and ionizing activity. In Fig. 3, H_0 and C_{C-2} for systems I and II are compared. In solutions containing TCE (see Fig. 3, curve *1*), H_0 changes more drastically. To estimate the effect of TCE on the ionizing ability of C-2, it is necessary to separate the contributions of complexes C-1 and C-2 to the value of H_0. The value of ΔH_0 corresponding to the contribution of complex C-2 to H_0 was determined in the following way. For some values of C^0_{HCl}, the equilibrium concentrations of C-1 and C-2 were calculated (see Eq. (3b)). For each pair C_{C-1} and C_{C-2}, the values of ΔH_0 in system I were obtained as differences between the numerical values of H_0 in curves *1* corresponding to the determined value of C_{C-2} (see Fig. 3) and to $C^0_{HCl} = C_{C-1}$ (see Fig. 1). For system II the values of ΔH_0 were calculated similarly using dependences *2* in Figs. 1 and 3. The ΔH_0 values obtained were compared with C_{C-2} (see Fig. 3, curves *4* and *3* for systems I and II, respectively). Comparison of dependences *3* and *4* in Fig. 3 indicates a significant increase in the ionizing ability of complex C-2 in solutions containing TCE. When we changed C_{C-2} from 0.4 to 2.3 mol L^{-1}, the values of $\Delta(\Delta H_0)$ in systems I and II were 1.85 and 1.35, respectively.

Thus, in the HCl—DMF—TCE system (I) in comparison with system II, the ionizing ability of all complexes of HCl with DMF changes. It decreases slightly for complexes C-1 and C-3 and increases drastically for C-2. The relative ionizing ability of the complexes in system I increases in the following sequence: C-3 < C-1 < C-2.

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