Solvent effect on catalytic properties of the HCl—DMF—1,1,2,2-tetrachloroethane system

I. S. Kislina,[a]* *S. G. Sysoeva,*[a] *and O. N. Temkin*[b]

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156
[b]*M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,*
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.
Fax: +7 (095) 430 7983

Ionization of 2- and 3-nitroanilines was studied in HCl—DMF—1,1,2,2-tetrachloroethane (TCE) solutions at 25 °C. The ionization capability of the medium and basicity constants pK_i of indicators change depending on the ratio of the components. The numerical values of pK_i are found to depend on the analytical composition of the DMF—TCE solvent. The solvent effect on pK_i is associated with a change in the solvation of the nonionized form of the indicators.

Key words: catalytic activity, basicity, solvation; hydrogen chloride, *N,N*-dimethylformamide, 1,1,2,2-tetrachloroethane, solutions.

Prediction of the solvent effect on the catalytic activity of acids in solutions is an important practical problem. For its solution, dependences of indicator ratios (I) of stable organic bases of different strengths with the known ionization mechanism on the composition of the acid-base system[1,2] can be used ($I = C_B/C_{BHA}$, C_B and C_{BHA} are the concentrations of the nonionized and ionized forms, respectively). The values of I are determined by the ionizing ability of the system and basicity of the indicator, which depend on the solvent. The acidity function most often serves as a quantitative measure of the ionizing ability.[3] The basicity of an organic compound depends on the solvation.[4]

The purpose of this work is to study the effect of the solvent composition on the catalytic properties of the HCl—DMF—TCE system. The mechanism of ionization of the indicators,[5] the composition and structure[6] of the complexes of HCl with DMF, and their comparative ionizing ability[7] are known for this system.

Experimental

Indicators, HCl, DMF, TCE, and DMF saturated with hydrogen chloride were purified as described previously.[5—7] The concentration of the initial solution of HCl in DMF (42.745 % HCl) was determined alkalimetrically. The weight method was used for the preparation of solutions. Densities (ρ) of solutions were measured pycnometrically for the calculation of concentrations. 3-Nitroaniline (**1**) and 2-nitroaniline (**2**) were used as indicators.

The values of I of compounds **1** and **2** were determined spectrophotometrically in the visible spectral region:

$$I = (\varepsilon_T - \varepsilon_{BHA})/(\varepsilon_B - \varepsilon_T),$$

where ε_B, ε_{BHA}, and ε_T are the molar extinction coefficients of the nonionized, completely and partially ionized forms of the indicator at the maximum of the absorption band of its nonionized form.

The I values for the HCl—DMF—TCE system at various concentrations of HCl at 25 °C were obtained for indicator **1** at the molar ratios DMF : TCE = 2 : 1 and 1 : 2 (Fig. 1) and for indicator **2** at the molar ratios HCl : DMF ~1 : 1 and 1 : 0.67 (Figs. 2 and 3).

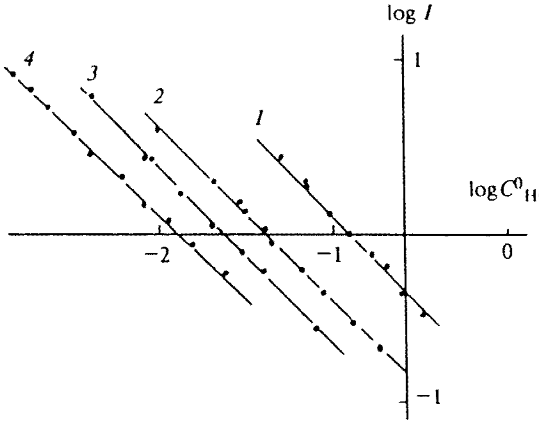


Fig. 1. Dependences of the values of log$I$ of 3-nitroaniline on logC^0_{HCl} in HCl—DMF—TCE solutions with various contents of TCE (mol. %): 0 (*1*), Ref. 5; 33.3 (*2*); 50 (*3*), Ref. 7; 66.7 (*4*) at 25 °C.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1446—1449, June, 1996.

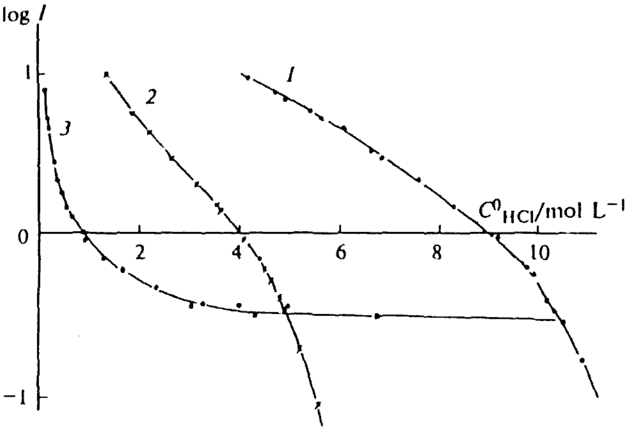


Fig. 2. Dependence of the values of log$I$ of 2-nitroaniline on the analytical concentration of HCl in DMF (*1*) by the literature data (Ref. 5), in the equimolar DMF—TCE mixture (*2*) (Ref. 7), and in the HCl—DMF—TCE system at HCl : DMF ≅ 1 : 1 (*3*) at 25 °C.

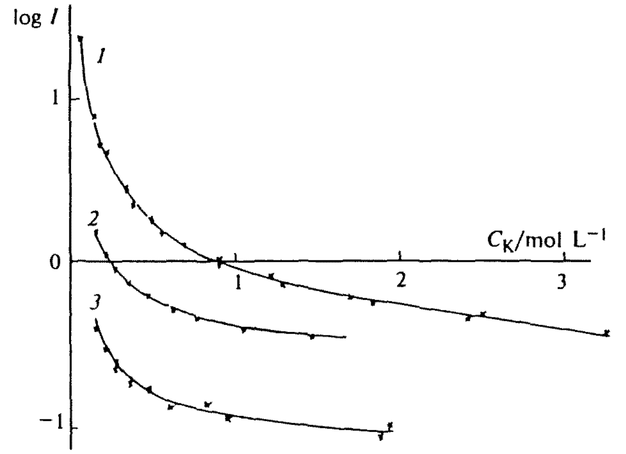


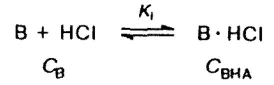
Fig. 3. Dependences of the values of log$I$ of 2-nitroaniline on the total concentration of complexes of HCl with DMF (C_K): *1*, $C_K = C_{K-1} + C_{K-3}$; *2*, $C_K \equiv C_{K-1}$; *3*, $C_K = C_{K-1} + C_{K-2}$, $C_{K-1} = C_{K-2}$ at 25 °C.

Results and Discussion

The catalytic effect of solutions of acids is determined in many cases by the equilibrium ionization of the reagent, a weak organic base, that forms the reactive form. It can be assumed that the catalytic activities of acid-base systems of various compositions are equal in the acid-catalyzed reaction, if the degrees of ionization of the same indicator are equal in these systems.

In the HCl—DMF—TCE system, hydrogen chloride is completely bound in complexes[6] with DMF: DMF · HCl (K-1), DMF · 2HCl (K-2), and 2DMF · HCl (K-3), whose ionizing ability increases in the series[7]: K-3, K-1, K-2. The ionization of indicators **1** and **2** corresponds to Scheme 1 with the equilibrium addition of an acid molecule[5]:

Scheme 1



$$\underset{C_B}{B} + HCl \overset{K_i}{\rightleftharpoons} \underset{C_{BHA}}{B \cdot HCl}$$

The position of the equilibrium in Scheme 1 and, hence, the values $I = C_B/C_{BHA}$ are determined by the values of the ionizing ability of the medium (H_0) and the thermodynamic ionization constant K_i:

$$\log I = H_0 - pK_i. \quad (1)$$

The obtained data on the ionization of indicator **1** in the HCl—DMF—TCE systems of various compositions demonstrate the solvent effect on its base properties. For compound **1**, the equilibrium (Scheme 1) is shifted to a noticeable extent to the right in strongly dilute solutions of HCl, for which $H_0 = -\log C_{HCl}$ (see Fig. 1). At C_{HCl} = const, variation in the content of TCE to 66.7 mol. % results in a substantial change in log$I$ of compound **1**. In the HCl—DMF—TCE system, the degree of ionization of **1** increases as the concentration of TCE increases. The concentration ionization constants for indicator **1** are unchanged for the range from 0 to 66.7 mol. % TCE in the binary solvent DMF—TCE

$$pK_i = -\log I - \log C_{HCl}.$$

The pK_i values obtained are presented in Table 1. Each of the K_i constants is standardized to a infinitely dilute solution of HCl in a solvent with the fixed ratio of DMF to TCE. In the solutions studied, HCl is completely bound in complexes K-3.

According to Eq. (1), an increase in the log$I$ value can be the result of the change in both the properties of the medium (H_0) and indicator (K_i). However, the ionizing ability of complexes K-3 decreases in the HCl—DMF—TCE system compared to the HCl—DMF system.[7] Therefore, the effect of TCE on the log$I$ value of indicator **1** is related to the change in its basicity. It is

Table 1. Values of pK_i of 3-nitroaniline and the position of a maximum of the absorption band of its nonionized form in the visible spectral region in HCl—DMF—TCE solutions of various compositions at 25 °C

Solvent DMF—TCE (mol. % TCE)	pK_i	λ/nm
0	0.91	393
33.3	1.41	390
50.0	1.60	385
66.7	1.90	381
100.0	—*	361

* pK_i was not determined due to the chemical instability of 3-nitroaniline.

established[4,8,9] for aqueous-organic solutions of acids that a decrease or increase in the log*I* value of indicators of the nitroaniline series upon variation of the solvent composition at C_{HA} = const is mainly caused by the change in the activity coefficient of the nonionized form of the indicator. The data in Table 1 testify to the different solvation of compound **1** in DMF—TCE solutions. An increase in the concentration of TCE is accompanied by the hypsochromic shift of the absorption band of the unionized form of compound **1**.

Thus, an increase in the catalytic activity of solutions of acids can be achieved by the targeted selection of the composition of the solvent of the acid-base system rather than by the change in the catalyst concentration.

The ionization curves of less basic catalyst **2** in solutions of HCl in DMF (curve *1*),[5] in the equimolar DMF—TCE mixture (curve *2*),[7] and in the HCl—DMF—TCE system at molar ratios DMF : HCl ≈ 1 : 1 (curve *3*) at 25 °C are presented in Fig. 2. As seen from Fig. 2, the higher the concentration of TCE, the lower are the concentrations of HCl needed to achieve equal degrees of ionization of compound **2**. Equation (1) is valid for any value of log*I* on curves *1—3* in Fig. 2. For each point, the numerical pK_i values are determined by the ratio of the concentrations of DMF and TCE in the HCl—DMF—TCE system, and H_0 is determined by the equilibrium composition of the complexes of HCl with DMF and their ionizing ability in the given solvent.[7] The variation of the ratio DMF : TCE at C_{HCl} = const results in a simultaneous change in both pK_i and H_0. It is noteworthy that an increase in C_{HCl} in the HCl —DMF—TCE system is accompanied by a substantial change in the equilibrium concentrations of DMF and TCE. The question arises, which composition of the solvent, stoichiometric or equilibrium, does determine the pK_i value of the indicators? The ionization of compound **1** ceases in the solutions of HCl in which stoichiometric and equilibrium concentrations of DMF and TCE almost coincide (see Fig. 1). For compound **2**, curves *1* and *2* (see Fig. 2) were obtained in solutions of HCl with a constant stoichiometric composition, but with a variable equilibrium composition of the solvent; by contrast, curve *3* was obtained with a variable stoichiometric composition of the solvent $C^0_{DMF} = C^0_{HCl}$, HCl and DMF are completely bound in complexes. It can be concluded that the reason for the virtual constancy of log*I* of indicator **2** at C^0_{HCl} from ~2 to 10.5 mol L^{-1} is a decrease in pK_i of this base. In fact, the degree of ionization of the indicator is unchanged as both the concentration and the ionizing ability[7] of complexes K-1 increase, which, according to Eq. (1), is impossible at constant pK_i. Therefore, the value of pK_i of a weak organic base is determined by the stoichiometric composition rather than by the equilibrium composition of the solvent of the acid-base system. Therefore, when the scale of the ionizing ability of the medium (of the H_0 type) of solutions of acids in binary or multicomponent solvents is measured by the indicator method, a necessary condition is the constant ratio of analytical concentrations of the components of the solvent at all C_{HA}. In this case, the dependence of the value of log*I* of any indicator on C_{HA} is caused only by the increase in the ionizing ability of the medium, and pK_i = const.

The previously drawn conclusions about the comparative ionizing ability of the complexes of HCl with DMF (K-1, K-2, and K-3) in the HCl—DMF—TCE system illustrates clearly and confirms Fig. 3:

for curve *1*

$$C_K = C_{K\text{-}1} + C_{K\text{-}3}, \qquad C_{K\text{-}3} \le 0.2\ \text{mol L}^{-1}$$

$$C^0_{DMF} = C^0_{HCl} + 0.2\ \text{mol L}^{-1};$$

for curve *2*

$$C_K = C_{K\text{-}1} + C_{K\text{-}2} + C_{K\text{-}3}, \qquad C_{K\text{-}2} = C_{K\text{-}3} \le 0.05C_K$$

$$C^0_{DMF} = C^0_{HCl};$$

for curve *3*

$$C_K = C_{K\text{-}1} + C_{K\text{-}2}, \qquad C_{K\text{-}1} = C_{K\text{-}2}$$

$$C^0_{DMF} = C_K;$$

here C_K is the total concentration of the complexes of HCl with DMF in TCE.

Dependence *2* presented in Fig. 3 was obtained in the solutions with equimolar ratios of stoichiometric concentrations of HCl and DMF. Complexes K-2 are formed according to Scheme 2.

Scheme 2

$$3\ \text{K-1} \rightleftharpoons \text{K-2} + \text{K-3}$$

The estimation of $C_{K\text{-}2}$ according to Scheme 2 is presented in the previously published work.[6] In the solutions in which dependence *1* was obtained (see Fig. 3), the equilibrium (Scheme 2) is almost completely shifted to the left due to some excess DMF compared to HCl.

For the same C_K, the change in the log*I* value of compound **2** (see Fig. 3) is associated only with the different ionizing abilities of the complexes of HCl, which increase in the following order: K-3, K-1, and K-2. In these solutions HCl and DMF are completely bound in complexes. The equilibrium composition of the solvent is constant (100 % TCE), and the stoichiometric composition changes as C_K increases. At C_K = const it is almost the same for three curves, and the log*I* value of indicator **2** is determined by the ratio of the concentrations of the complexes of HCl with DMF with different ionizing abilities.

Thus, the solvent effect on the catalytic properties of the HCl—DMF—TCE system is caused by the change in both the ionizing ability of the medium (H_0) and ionization constants (K_i) of the indicators used. The numerical values of K_i are determined by the stoichiometric composition of the solvent DMF—TCE.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-18356).

References

1. M. I. Vinnik, *Usp. Khim.*, 1966, **35**, 1922 [*Russ. Chem. Rev.*, 1966, **35** (Engl. Transl.)].
2. M. I. Vinnik, I. S. Kislina, and N. B. Librovich, *Dokl. Akad. Nauk SSSR*, 1980, **251**, 138 [*Dokl. Chem.*, 1980, **251** (Engl. Transl.)].
3. C. H. Rochester, *Acidity Functions*, Acad. Press, London—New York, 1970, Ch. 6.
4. S. G. Sysoeva, I. S. Kislina, and M. I. Vinnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 989 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 909 (Engl. Transl.)].
5. I. S. Kislina, S. G. Sysoeva, and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1025 [*Russ. Chem. Bull.*, 1994, **43**, 960 (Engl. Transl.)].
6. 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.)].
7. 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.)].
8. M. I. Vinnik, *Kinet. Katal.*, 1987, **28**, 100 [*Kinet. Catal.*, 1987, **28** (Engl. Transl.)].
9. S. Janardhanan and C. Kalidas, *Indian J. Chem.*, 1983, **22A**, 17.

Received January 12, 1996