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Acid–Base Interactions in the Dichloroacetic Acid–Ethyl Acetate System according to IR Spectroscopic Data

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Abstract—The method of multiple total internal reflection infrared spectroscopy (MTIRIRS) is used to study ion–molecular interactions in the system dichloroacetic acid–ethyl acetate in the range of concentrations from pure acid to pure base at 30°C. Depending on the ratio of components in the solution, molecular complexes with acid : base ratios of 1 : 1 or 2 : 1 are formed in the solutions. In the case of excess acid, base is not protonated and species with a strong symmetric hydrogen bond are not formed. It is shown that the absorption coefficient near 2000 cm^{-1} can be used to judge the type of the complex formed and the strength of a hydrogen bond in molecular complexes.

INTRODUCTION

The formation of ions and complexes with a strong symmetric hydrogen bond is a fundamental property of protons in solutions [1, 2]. The catalytic properties of acid solutions are primarily determined by the structure and concentrations of such species. The formation of uncharged 1 : 1 complexes with a strong symmetric hydrogen bond is characteristic of many nonaqueous systems [3–6]. Specifically, such complexes were registered in the solutions of methanesulfonic acid (MSA) in dimethyl sulfoxide and dimethylformamide (DMF) [3]. The interaction of weaker bases with an acid may restrict itself by the formation of molecular complexes, as in the MSA–propylene carbonate [7] and MSA–ethyl acetate (EA) systems [8]. In the solutions of MSA in EA, ionic complexes are formed only when the concentration of the acid is higher than 70 mol %. It is interesting to study conditions under which acid–base interaction in the liquid phase does not lead to the formation of complexes with strong symmetric hydrogen bonds, because proton position in an acid–base complex strongly affects the catalytic properties of an acid–solvent system. Molecular complexes possess high ionizing ability toward organic compounds in acid solutions. Therefore, it is important to have information on the conditions for the formation of molecular complexes.

This work is devoted to the study of complex formation in the dichloroacetic acid (DCAA)–EA system.

EXPERIMENTAL

We used DCAA (puriss grade) with a concentration of water lower than 0.05% and EA (puriss grade) with a concentration of water lower than 0.005% (Fluka). Solutions were prepared by the weight method. To calculate the molar concentrations of components, the densities of solutions were measured (Table 1).

IR spectra were obtained using a UR-20 spectrophotometer equipped with a multiple total internal reflec-

Table 1. Stoichiometric composition and densities of solutions of dichloroacetic acid in ethyl acetate at $T = 30 \pm 1$°C

$[\text{DCAA}]_0$, %	$[\text{DCAA}]_0$, mol/l	$[\text{EA}]_0$, mol/l	ρ, g/cm^3	$[\text{DCAA}]_0$, %	$[\text{DCAA}]_0$, mol/l	$[\text{EA}]_0$, mol/l	ρ, g/cm^3
0	0	10.21	0.900	71.24	7.21	4.26	1.305
11.60	0.85	9.47	0.944	74.10	7.64	3.90	1.329
27.18	2.15	8.43	1.020	79.67	8.48	3.17	1.372
41.92	3.59	7.27	1.104	85.37	9.40	2.36	1.420
50.20	4.51	6.55	1.158	91.10	10.44	1.49	1.477
58.98	5.56	5.66	1.215	96.33	11.43	0.64	1.530
63.10	6.09	5.21	1.244	100.00	12.15	0.00	1.567
66.79	6.58	4.79	1.27				

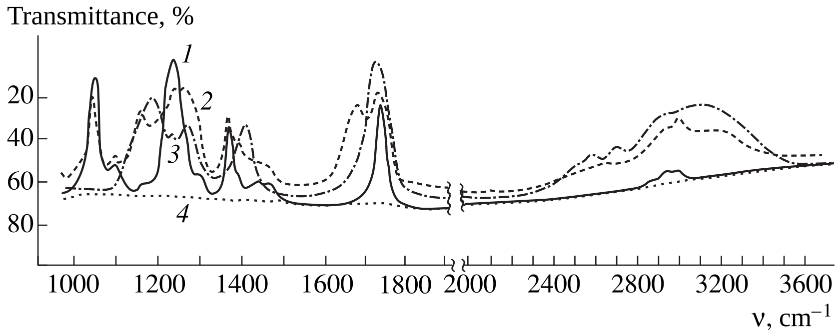


Fig. 1. Multiple total internal reflection infrared spectra of the solutions of DCAA in EA: (*1*) 100% EA; (*2*) 50 mol % DCAA; (*3*) 100% DCAA; (*4*) empty cell.

tion attachment [9]. A Ge prism with an incident angle of radiation of 30° was used. A sample solution was placed in Teflon cavities adjoining the prism faces. Depending on the filling of cavities, the number of reflections was 4 or 8, corresponding to the effective width of the absorbing layer at 2000 cm^{-1} equal to 1.93 and 3.89 μm.

The IR spectra of the DCAA–EA system in the range of acid concentrations 0–100% (Table 1) were registered in the range of frequencies 900–3800 cm^{-1} at 30°C. Absorbances were measured with reference to base bands or with reference to the absorbance of an empty cell. The accuracy in determining the absorbances was ±7%.

In the IR spectra of DCAA and EA (Fig. 1), there are several intense bands, ν, cm^{-1}:

DCAA [10]		EA [11]	
1195	δ(COH), ν_{as}(C–C–O)	1050	ν(C–O)
1275	δ(COH)	1240	ν(C–O)
1415	δ(C–H)	1373	δ(C–H)
1730	ν(C=O)	1740	ν(C=O)
2600, 3100	ν(O–H)		

DISCUSSION

As in the MSA–EA system [8], upon the addition of even a small portion (~1–2 mol/l) of DCAA to 100% EA, IR spectra contain all bands of DCAA molecules, including the bands of ν(OH) vibrations at 2600 and 3100 cm^{-1}, which are not available in the IR spectra of quasi-ionic pairs (e.g., $\text{MeO}_2\text{SO}^-\cdots\text{H}^+\cdots\text{O(H)CNMe}_2$) formed in the solutions of MSA in DMF [3]. Also, our spectra do not contain continuous absorption, which is characteristic of species with strong symmetric hydrogen bonds. The absorption coefficient at 2000 cm^{-1} is lower than 2.5 l mol^{-1} cm^{-1} over the whole range of compositions in the DCAA–EA system, although quasi-ionic pairs are characterized by values ranging from 50 to 60 l mol^{-1} cm^{-1}. These facts suggest that quasi-ionic pairs or ionic species with strong symmetric hydrogen bonds are not formed in the solutions of DCAA in EA.

On the other hand, the bands of ν(C=O) vibrations of EA and DCAA at 1730–1740 cm^{-1} change substantially. The absorption coefficients of acid bands at 1195 and 1415 cm^{-1} and EA bands at 1373 cm^{-1} in the case of the equimolar ratio of acid and base differ noticeably from the coefficients of pure components (Table 2).

Table 2. Absorption coefficients of EA–DCAA complexes at different frequencies at $T = 30 \pm 1$°C

ν, cm^{-1}	l_ν, μm	ε, l mol^{-1} cm^{-1}				
		B	B · HA	B · 2HA	B · HA + HA	HA
1240	3.11	480	325	330	390	66
1300	2.97	22	185	330	245	60
1373	2.80	110	220	–		45
1415	2.73	10	48	106	126	80
1685	2.29	10	315	–		54
1730	2.23	275	350	520	755	405
1740	2.22	350	365	620	710	345

Note: B is ethyl acetate, B · HA is the complex K1, B · 2HA is the complex K2, and HA is dichloroacetic acid. Absorbances at 1415, 1685, 1730, and 1740 cm^{-1} were measured with reference to base lines; the other absorbances were measured with reference to an empty cell.

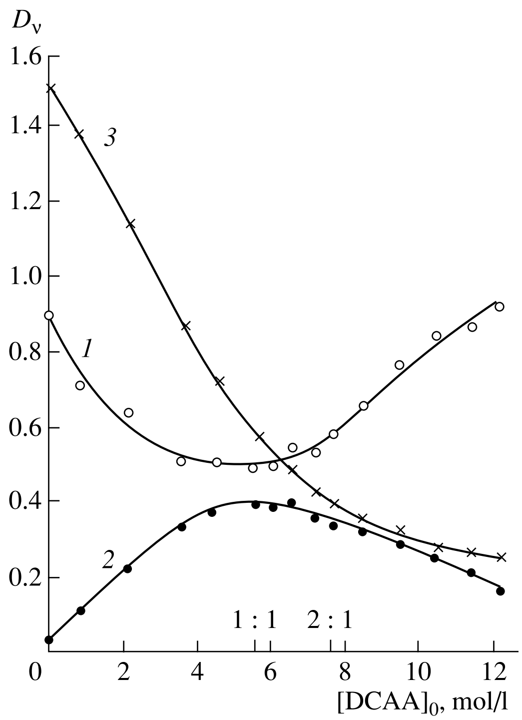


Fig. 2. Dependences of the absorbances of EA at (*1*) 1740 and (*3*) 1240 cm^{-1}, and (*2*) the band of the complex at 1685 cm^{-1} on the DCAA concentration.

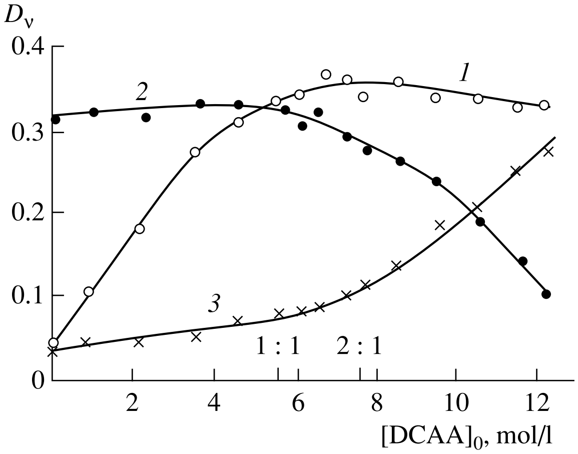


Fig. 3. Dependences of the absorbances at (*1*) 1165, (*2*) 1373, and (*3*) 1415 cm^{-1} on the DCAA concentration.

Furthermore, bands at 1165, 1300 (a shoulder in the contour of the band at 1275), and 1685 cm^{-1} appear (Figs. 2–4). These facts point to the strong interaction between DCAA and EA molecules. The band at 1685 cm^{-1} reaches its maximal intensity at the equimolar concentrations of components (Fig. 2). The absorbances of bands at 1195, 1415, 2600, and 3100 cm^{-1} are proportional to the concentration of DCAA up to a component ratio of 1 : 1 (Figs. 3, 4). This points to the almost complete binding of DCAA into 1 : 1 acid–base complexes (K1) in solutions with excess EA.

The absorption coefficients of bands at 1300, 1415, 1730, and 1740 cm^{-1} change in the range of acid : base ratios from 1 : 1 (5.6 mol/l DCAA) to 2 : 1 (7.64 mol/l DCAA; 3.90 mol/l EA) (Table 2). This means that, in addition to K1, complexes are formed with two acid molecules and one base molecule.

If only K1 complexes with the composition 1 : 1 were formed in the solutions under study, then a change in the absorbances would be determined by the absorbance of DCAA molecules and K1 complexes in excess acid:

$$D_\nu = \varepsilon^{\nu}_{\mathrm{DCAA}} l_\nu [\mathrm{DCAA}] + \varepsilon^{\nu}_{\mathrm{K1}} l_\nu [\mathrm{K1}]. \qquad (1)$$

Then,

$$[\mathrm{K1}] = [\mathrm{EA}]_0, \quad [\mathrm{DCAA}] = [\mathrm{DCAA}]_0 - [\mathrm{EA}]_0,$$

where $[\mathrm{DCAA}]_0$ and $[\mathrm{EA}]_0$ are the stoichiometric concentrations of DCAA and EA and l_ν is the effective width of the absorbing layer at the frequency ν.

Using Eq. (1), we arrive at

$$D_\nu/[\mathrm{EA}]_0 = \varepsilon^{\nu}_{\mathrm{DCAA}} l_\nu([\mathrm{DCAA}]_0 - [\mathrm{EA}]_0)/[\mathrm{EA}]_0 + \varepsilon^{\nu}_{\mathrm{K1}} l_\nu. \qquad (2)$$

If the 2 : 1 acid–base complexes (K2) are formed in the system, then the absorbance D_ν at $[\mathrm{DCAA}]_0/[\mathrm{EA}]_0 \geq$ 2 : 1 is the sum of absorbances of "free" DCAA molecules and K2 complexes:

$$D_\nu = \varepsilon^{\nu}_{\mathrm{DCAA}} l_\nu [\mathrm{DCAA}] + \varepsilon^{\nu}_{\mathrm{K2}} l_\nu [\mathrm{K2}]. \qquad (3)$$

Then,

$$[\mathrm{K2}] = [\mathrm{EA}]_0 \text{ and } [\mathrm{DCAA}] = [\mathrm{DCAA}]_0 - 2[\mathrm{EA}]_0 .$$

It follows from Eq. (3) that

$$D_\nu/[\mathrm{EA}]_0 = \varepsilon^{\nu}_{\mathrm{DCAA}} l_\nu([\mathrm{DCAA}]_0 - 2[\mathrm{EA}]_0)/[\mathrm{EA}]_0 + \varepsilon^{\nu}_{\mathrm{K2}} l_\nu. \qquad (4)$$

For absorbances at 1300, 1415, 1730, and 1740 cm^{-1} in the coordinates of Eq. (4), we obtained linear dependences. There are no such dependences for the frequencies 1300 and 1730 cm^{-1} in the coordinates of Eq. (2). This points to the formation of complexes containing two acid molecules and one base molecule in concentrated solutions of the acid (when the ratio is higher than 2 : 1).

Absorbances in the range of concentrations corresponding to the range of ratios from 1 : 1 to 2 : 1 are the sums of absorbances of complexes K1 and K2:

$$D_\nu = \varepsilon^{\nu}_{\mathrm{K1}} l_\nu [\mathrm{K1}] + \varepsilon^{\nu}_{\mathrm{K2}} l_\nu [\mathrm{K2}],$$

$$[\mathrm{EA}]_0 = [\mathrm{K1}] + [\mathrm{K2}]; \quad [\mathrm{DCAA}]_0 = [\mathrm{K1}] + 2[\mathrm{K2}],$$

$$D_\nu/([\mathrm{DCAA}]_0 - [\mathrm{EA}]_0) = \varepsilon^{\nu}_{\mathrm{K1}} l_\nu + \varepsilon^{\nu}_{\mathrm{K2}} l_\nu \qquad (5)$$

$$\times(2[\mathrm{EA}]_0 - [\mathrm{DCAA}]_0)/([\mathrm{DCAA}]_0 - [\mathrm{EA}]_0).$$

In the range from a pure base to the ratio 1 : 1, the absorbance is the sum of absorbances of EA and K1:

$$D_\nu = \varepsilon^{\nu}_{\mathrm{EA}} l_\nu [\mathrm{EA}] + \varepsilon^{\nu}_{\mathrm{K1}} l_\nu [\mathrm{K1}],$$

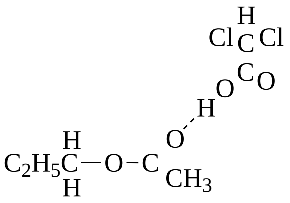
$$[\mathrm{K1}] = [\mathrm{DCAA}]_0; \quad [\mathrm{EA}] = [\mathrm{EA}]_0 - [\mathrm{DCAA}],$$

$$D_\nu/[\mathrm{DCAA}]_0 \tag{6}$$

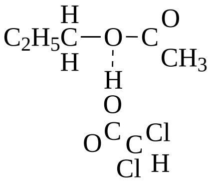
$$= \varepsilon^{\nu}_{\mathrm{EA}} l_\nu ([\mathrm{EA}]_0 - [\mathrm{DCAA}]_0)/[\mathrm{DCAA}]_0 + \varepsilon^{\nu}_{\mathrm{K1}} l_\nu.$$

Table 2 shows the values of absorption coefficients obtained from Eqs. (4)–(6) for various ranges of concentrations in the system. The coefficients of the same species obtained for different ranges of concentrations coincide within the accuracy of measurements. The data of Table 2 are also suggestive of the formation of K2 complexes. If there were no such complexes, the absorption coefficient at the ratio 2 : 1 would be equal to the sum of the coefficients of K1 and DCAA. For the frequencies 1300 and 1730 cm^{-1}, the sum $\varepsilon_{\mathrm{K1}} + \varepsilon_{\mathrm{DCAA}}$ noticeably differs from $\varepsilon_{\mathrm{K2}}$ (Table 2).

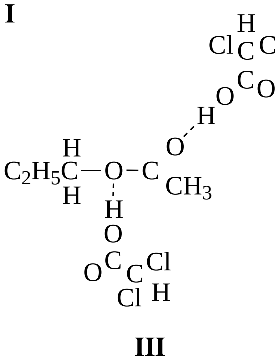
Ethyl acetate molecules have two base centers capable of forming hydrogen bonds with acid molecules: the carbonyl group C=O and an ether bridge C–O–C. In the MSA–butyl acetate system [12], acid molecules bond to these base centers with equal probabilities when the 1 : 1 complexes are formed. In the system under study, the absorption coefficient of the C–O–C band at 1240 cm^{-1} noticeably decreases when K1 complexes are formed (Fig. 2, Table 2). This points to the addition of the acid molecule to the ether bridge. Changes in the absorption coefficients of the C=O and C–O–C bands upon the formation of the K2 complex suggests that the K1 complex is a mixture of configurations **I** and **II**. In the 2 : 1 complex, acid molecules probably bind to both oxygen atoms (structure **III**):



I



II



III

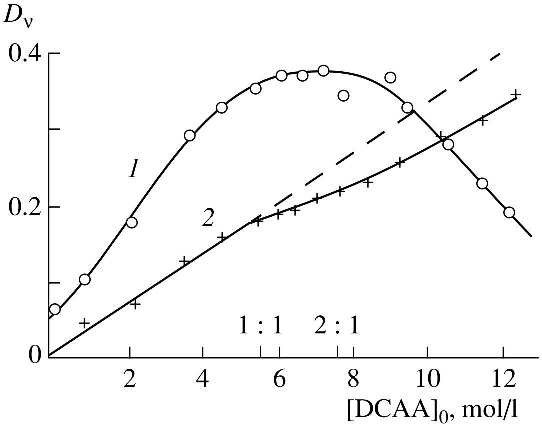


Fig. 4. Dependences of the absorbances at (*1*) 1300 and (*2*) 3100 cm^{-1} on the DCAA concentration.

In contrast to the MSA–butyl acetate system, where the base is protonated and the $(\mathrm{A}\cdot\cdot\mathrm{H}\cdot\cdot\mathrm{A})^-$ anions with a strong symmetric hydrogen bond are formed in a small excess of acid, the acid–base equilibrium in the DCAA–EA system restricts itself to the formation of molecular complexes. This is not surprising because dichloroaacetic acid is noticeably weaker than methanesulfonic acid.

Upon the formation of molecular complexes K1, the absorption coefficient of the band ν(OH) at 3100 cm^{-1} increases (Fig. 4). This is probably due to the strong self-association of DCAA [10].

The coefficient of continuous absorption at 2000 cm^{-1} in the system under study (2.5 l mol^{-1} cm^{-1}) is much lower than for the molecular complexes in some other acid–base systems (~25 l mol^{-1} cm^{-1}) [8, 12]. This is probably due to the difference in the strengths of the hydrogen bond in these complexes. Therefore, the value of the coefficient of continuous absorption at 2000 cm^{-1} can be used to judge both the formation of various complexes with a strong symmetric hydrogen bond [13] and the strength of molecular complexes.

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