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Effect of 1,1,2,2-Tetrachloroethane on the IR Spectra of Molecular and Ionic Complexes of Methanesulfonic Acid with Aprotic Bases

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Abstract— The method of multiple attenuated total internal reflection (MATIR) infrared spectroscopy is used to study the effect of 1,1,2,2-tetrachloroethane (TCE) on the spectra of the $\mathrm{BH^+ \cdot (AHA)^-}$ ionic pairs formed by methanesulfonic acid (MSA) with DMF or 2-pyrrolidone and the spectra of molecular complexes of MSA with ethyl acetate. In TCE solutions, the structure with a strong symmetric hydrogen bond in the $\mathrm{(AHA)^-}$ anions is preserved and the strength of the hydrogen bond practically does not change in molecular complexes. Changes in the absorption coefficients in the spectra are observed in the region of skeletal vibrations at frequencies below 1800 cm^{-1} up to a onefold excess of TCE for the ionic pairs $\mathrm{BH^+ \cdot (AHA)^-}$ and up to a fourfold excess of TCE for molecular complexes.

INTRODUCTION

It has been found in the study of acid–base interactions in the solutions of methanesulfonic acid (MSA) in various aprotic solvents that the type of acid–base interaction in the complexes formed is determined by the acid (HA) and base (B) strengths and weakly depends on the molecular environment [1–3]. In the MSA–ethyl acetate (EA) (0–50 mol % HA) system, only molecular complexes are formed [1] in which an acid proton is bound with the base molecule via a hydrogen bond $\mathrm{(AH\cdot\cdot B)}$. In MSA solutions in DMF and 2-pyrrolidone (Pyr) in an excess of base, neutral quasi-ionic pairs $\mathrm{(A\cdot\cdot H\cdot\cdot B)}$ are formed with a strong quasi-symmetric hydrogen bond. In excess acid, base molecules are protonated and the $\mathrm{(A\cdot\cdot H\cdot\cdot A)^-}$ anions with a strong symmetric hydrogen bond is formed [2, 3]. The IR spectra of both molecular complexes and complexes with strong symmetric hydrogen bonds, $\mathrm{(A\cdot\cdot H\cdot\cdot B)}$ and $\mathrm{(A\cdot\cdot H\cdot\cdot A)^-}$, have characteristic features allowing one to determine the extent of completeness of the acid–base interaction in a solution [1–4]. A specific feature of $\mathrm{(A\cdot\cdot H\cdot\cdot B)}$ and $\mathrm{(A\cdot\cdot H\cdot\cdot A)^-}$ species is the intense continuous absorption in the IR spectrum over a wide range of frequencies [4, 5]. Using the values of the coefficient of continuous absorption in the frequency range 2000–2200 cm^{-1}, we may judge the formation of species with a strong symmetric hydrogen bond in acid solutions and the charge of such species.

The degree of proton transfer in the complexes formed depends on the proton-donor and proton acceptor properties of acid and base molecules and on the molecular environment. Even the strongest donors and acceptors of proton (e.g., HCl and aliphatic amines [6]) only form molecular complexes in the gas phase. In the transfer of the complex from the gas phase into the solution, either a hydrogen bond becomes stronger with the conservation of molecular structure [7] or a proton transfers and the ionic pair is formed [8]. An increase in the solvent polarity also leads to the strengthening of the hydrogen bond in the molecular complex [7] and may stimulate the transfer of a proton to the acceptor molecule [9].

The general view has been accepted for a long time [10] that, both in the gas phase and low-polarity solvents, the acid–base interaction

$$\mathrm{AH + B \Leftrightarrow AH\cdot\cdot B \Leftrightarrow A^- + BH^+}$$

is limited by the formation of molecular complexes, whereas proton transfer becomes possible in a sufficiently polar medium due to solvation. More recently, it has been shown that proton transfer can occur in low-polarity solvents as well, whereas in the gas phase, no proton transfer is observed and only molecular complexes are formed [11]. Thus, in toluene solutions (ε = 2.38), when the ratio of the concentrations of acetic acid and dibutylamine is equimolar, the formation of both molecular complexes and ionic pairs with the 1 : 1 composition is observed. Shraiber [11] considered theoretical aspects of the effect of a low-polarity solvent on the step of proton transfer. It follows from his calculation that hydrogen bonds are stronger in an inert solvent and the proton position is shifted toward the heteroatom of the base molecule compared to the gas phase. This makes proton transfer possible.

The goal of this work is to study the effect of the neutral low-polarity solvent 1,1,2,2-tetrachloroethane (TCE) on the structure of ionic pairs $\mathrm{BH^+ \cdot (AHA)^-}$ formed by MSA with DMF and 2-pyrrolidone, as well

Stoichiometric composition and the densities (ρ) of the systems: MSA–EA–TCE; MSA–DMF–TCE; MSA–Pyr–TCE at 30°C

ρ, g/cm^3	[MSA]$_0$	[EA]$_0$	[TCE]$_0$	ρ, g/cm^3	[MSA]$_0$	[DMF]$_0$	[TCE]$_0$	ρ, g/cm^3	[MSA]$_0$	[Pyr]$_0$	[TCE]$_0$
	mol/l				mol/l				mol/l		
1.379	0	3.26	6.51	1.348	10.17	5.07	0	1.385	10.01	4.97	0
1.165	6.31	6.34	0	1.434	6.62	3.30	3.32	1.435	7.94	3.95	2.00
1.271	4.70	4.71	2.41	1.478	4.91	2.45	4.92	1.468	6.59	3.27	3.31
1.340	3.81	3.83	3.79	1.519	3.24	1.66	6.48	1.536	3.29	1.64	6.43
1.411	2.72	2.73	5.42	1.539	2.42	1.21	7.25	1.537	3.23	1.66	6.47
1.472	1.72	1.72	6.88	1.550	1.93	0.99	7.70	1.558	2.14	1.10	7.50
1.524	1.00	1.04	7.96	–	–	–	–	–	–	–	–

as molecular complexes of MSA with ethyl acetate, by IR spectroscopy.

It has been shown that the acidity function of the HCl–DMF–TCE system strongly depends on the concentration of the inert solvent [12]. The acidity function may change either because of the TCE effect on the degree of proton transfer in the H-complexes or because of a change in the molecular environment of complexes. The results of this work led us to determine which of these reasons results in the changes observed in the acidity function.

EXPERIMENTAL

To prepare the solutions, we used DMF, EA, MSA, and TCE (puriss) and Pyr (purum) from Fluka. The concentration of water was at most 0.05% in MSA and 0.01% in the solvents. The solutions were prepared by the weight method. To calculate the concentrations of components in a molar scale, the densities of solutions were measured with a picnometer (see table).

Multiple attenuated total internal reflection infrared spectra [13] were registered in the range 900–3800 cm^{-1} at 30°C using a UR-20 spectrophotometer equipped with an MTIR-3 attachment (refractive element, Ge; incident angle of radiation, 30°). The spectra were registered with respect to air. The effective widths (l) of the absorbing layer were 2.08 and 4.06 μm at a frequency of 2000 cm^{-1}, and the number of reflections were four and eight, respectively.

The series of samples for recording IR spectra were obtained by dissolving the solution of MSA in EA of a 1 : 1 composition and the solutions of MSA in DMF and Pyr of a 2 : 1 composition with a neutral solvent TCE. The concentrations of components for each series are shown in the table. Absorbances were measured with reference to the absorbance of the empty cell. The accuracy in determining the absorbances was ±7%.

We analyzed the dependences of absorbances on the concentration of acid–base complexes formed in the solutions at a number of frequencies ranging from 900 to 3100 cm^{-1}. These sets of frequencies involve all maximums and minimums of the spectra. The linearity of the dependences points to the absence of the TCE effect on the absorption coefficients. When the proportionality failed, linear portions were used to determine the absorption coefficients in excess TCE. Figure 1 shows the effect of TCE on the IR spectra of the molecular complex MSA · EA and the ionic pairs $BH^+ \cdot (AHA)^-$ in the solutions of MSA in DMF and Pyr. When obtaining the dependences *2*, *4*, and *6*, TCE absorbance was subtracted from experimental spectra.

DISCUSSION

Effect of TCE on IR Spectra of Molecular Complexes of MSA with EA

In the solutions of MSA and EA with concentrations ranging from 0 to 50 mol %, methanesulfonic acid is completely bound into molecular complexes $B\cdots HA$ with a 1 : 1 composition [1]. In these species, the proton is mostly bound with the fragment A. The formation of complexes is accompanied by a decrease in the absorption coefficient of the band ν(OH) of the MSA molecules by ~30%. Simultaneously, the absorption coefficient of the band ν(C=O) at 1738 cm^{-1} of the EA molecule almost halves, and a broad band at 1688 cm^{-1} appears (Fig. 2, curves *1* and *3*). The absorption coefficients of skeletal vibrations of complexes do not change upon complex formation.

When molecular complexes of MSA with EA are diluted with a low-polarity solvent TCE, the absorption coefficient noticeably increases in the range 900–1800 cm^{-1} (Figs. 1a and 2). For higher frequencies, the coefficients do not change; specifically, the absorption coefficient of the band ν(OH) in the complex is preserved. The positions of maximums in the spectra of

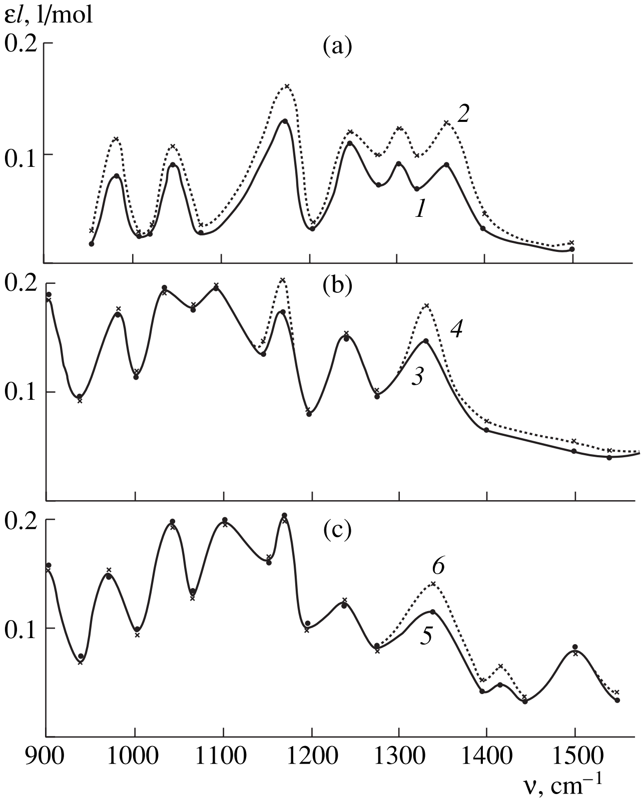

Fig. 1. Effect of TCE on IR spectra of (a) molecular complexes of (a) MSA with EA, (b) ionic pairs $BH^+ \cdot (AHA)^-$ in the solutions of MSA in DMF, and (c) in solutions of MSA in 2-pyrrolidone: (*1*, *3*, *5*) in solutions without TCE and (*2*, *4*, *6*) in solutions with a fourfold excess of TCE.

molecular complexes are independent of the TCE concentration. An exception is the band ν(C=O), whose maximum shifts from 1738 to 1723 cm^{-1}. The strongest change in the frequency occurs when one or two moles of TCE are added per one mole of the complexes: to 1730 and 1726 cm^{-1}, respectively. The same shift of the maximum is observed in the spectrum of the EA–TCE solution with a 1 : 2 composition compared to pure EA (Fig. 2, curves *1* and *2*).

Figure 1a demonstrates the maximal change in the absorption coefficient in the IR spectrum of molecular MSA–EA complexes in TCE solutions. This occurs up to a fourfold TCE excess over the concentration of the complex. In more dilute solutions, the coefficients are constant. The same effect of TCE is observed for the spectrum of EA (Fig. 2).

Thus, we found the same effect of TCE on the IR spectra of EA and molecular complexes of MSA with EA in the region of skeletal vibrations. Changes in the absorption coefficients for all bands with frequencies below 1800 cm^{-1} are associated with radical changes in the molecular environment of the complexes of MSA with EA, which cease when TCE is in fourfold excess but do not affect the strength of the hydrogen bond in the complex. In our opinion, this follows from the constant value of the absorption coefficient of the band ν(OH) of vibrations in MSA.

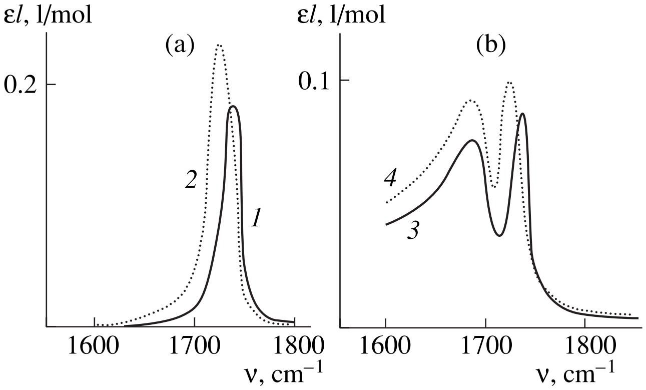

Fig. 2. Effect of TCE on IR spectra of (a) EA and (b) the molecular complex of MSA with EA: (*1*) EA without TCE; (*2*) EA–TCE (1 : 2); (*3*) MSA · EA without TCE; and (*4*) MSA · EA–TCE (1 : 2).

Effect of TCE on the IR Spectra of the Complexes of MSA with DMF and MSA with Pyr with a 2 : 1 Composition

It has been found [2, 3] that in the MSA–DMF and MSA–Pyr systems in the range of concentrations 50–100 mol % HA, base molecules are protonated and negatively charged double solvates of proton are formed $(A\cdot\cdot H\cdot\cdot A)^-$ with a strong symmetric hydrogen bond. In the double excess of acid with respect to the base, the components are completely bound into ions that are joined into the ionic pairs $BH^+ \cdot (AHA)^-$. In more concentrated solutions, the $(AHA)^-$ anions are solvated by several acid molecules and the ionic pairs possibly dissociate. The formation of $BH^+ \cdot (AHA)^-$ complexes is accompanied by considerable changes in the IR spectra compared to the spectra of components [2, 3].

At a frequencies higher than 1800 cm^{-1} as well as in the MSA–EA–TCE system, the neutral component does not affect the spectra of ionic pairs formed by MSA and DMF or Pyr. The constant value of the coefficients of absorption bands in the range 2000–2200 cm^{-1} [4] is preserved; that is, the structure of the strong symmetric hydrogen bond $O\cdot\cdot H\cdot\cdot O$ in the anions is preserved. In the solutions of TCE, the absorption coefficients of the band ν(NH) at 3000–3100 cm^{-1} of the protonated Pyr do not change either [3].

In the range of frequencies below 1800 cm^{-1}, when ionic pairs are diluted by TCE, changes in the coefficients are only seen near some frequencies (Fig. 1b and 1c). In DMF solutions, changes in the absorption coefficients noticeably change near maximums at 1168 and 1330 cm^{-1}. In Pyr solutions, the effect of TCE is seen for the bands with maximums near 1337 and 1415 cm^{-1}, as well as the bands at 1550 cm^{-1}. In the MSA–DMF (Pyr)–TCE systems with different compositions, no

TCE effect on the absorption coefficients of the ν(CO) bands of protonated base molecules near 1700 cm^{-1} was observed.

All apparent changes occur when one passes from the solutions of ionic pairs to the solutions with the equimolar ratio of the concentrations of $BH^+ \cdot (AHA)^-$ and TCE. In further dilution of the TCE solutions, the absorption coefficients do not change. In ternary systems, there are no shifts of the maximums in the spectra of complexes. An exception is the band ν(CO) of protonated DMF, for which the position of the maximum changes from ~1705 in solutions without TCE to ~1695 cm^{-1} in solutions with more than a fourfold molar excess of TCE.

Thus, in the solutions of TCE, insignificant changes in the spectra of ionic pairs $BH^+ \cdot (AHA)^-$ of the solutions of MSA in DMF and Pyr are seen, and the coefficients of continuous absorption at 2000 and 2200 cm^{-1} preserve their constant values. This fact suggests that the structure of the strong symmetric hydrogen bond in such complexes is preserved; that is, in the solutions studied, there are no changes in the degree of proton transfer. An analogous conclusion has been drawn in the study of the TCE effect on the IR spectra of the ionic pairs $BH^+ \cdot (ClHCl)^-$, where B is 1-methyl-2-pyrrolidone [14]. In our opinion, the results obtained suggest that a change in the molecular environment of ionic pairs in TCE solutions is the reason for the observed dependence of the acidity function on the concentration of the neutral component in the ternary HCl–DMF–TCE system [12]. The mechanism of interaction of the neutral solvent TCE with acid–base complexes of the ionic type is unclear, and additional studies on the effect of small amounts of a neutral solvent (up to the ratio 1 : 1) on the IR spectra of the ionic pairs $BH^+ \cdot (AHA)^-$ are needed. A further increase in the concentration of the solvent is not accompanied by changes in the spectra of such complexes. Different regularities are observed in the IR spectra of TCE solutions of molecular complexes. The absorption coefficients noticeably increase in the whole range of skeletal vibrations (900–1800 cm^{-1}). The effect of TCE on the IR spectrum of pure EA is the same.

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