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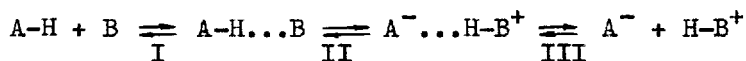
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SOLVENT EFFECTS ON THE INTERACTION OF ISOBUTYRIC
ACID WITH DIISOBUTYLAMINE

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In solutions containing active donors and acceptors of a proton the existence of not only hydrogen-bonded molecular complexes is possible but also of ionic pairs resulting from the proton transfer from a donor to an acceptor. In general, these two types of complexes are in equilibrium with each other, as well as with free molecules AH and B, and with ions A^- and BH^+ :



If molecules of a solvent act as donors or (and) acceptors of a proton, all these species participate in the hydrogen bond with the solvent. Equilibrium II was observed spectroscopically for solutions of carboxylic acids and amines¹⁻³. This paper is concerned with the effect of a solvent on the position of equilibria II and III for the isobutyric acid-diisobutylamine system.

In the spectrum of the acid in amine (Fig.I) the bands are present of the molecular form of the acid (doublet $\nu_{C=O}$ 1700, 1720 cm^{-1}) and of the carboxylate ion ($\nu_{\alpha} \text{CO}_2^-$ 1560 cm^{-1}) as well as the band $\delta_{\text{NH}_2^+}$ 1620 cm^{-1} of the dialkylammonium

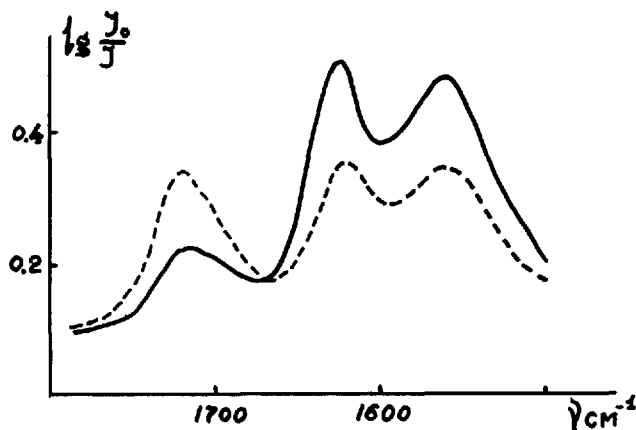
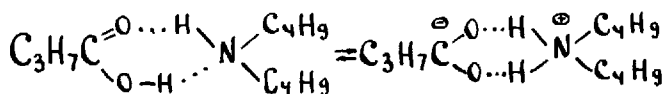


FIG. I

Infrared spectra of isobutyric acid solution in diisobutylamine, $C=0,6$ M, cell $45,7\mu$; ——— 20° , - - - $65^{\circ}C$

ion. In the excess of amine the probability of the existence of complexes containing two or more molecules of the acid is low, therefore the doublet at 1710 cm^{-1} may be attributed to the molecular isobutyric acid-diisobutylamine complex with the hydrogen bond $OH\dots N$ of composition 1:1. The frequencies of doublet components are the same as in the hydrogen-bonded complexes of isobutyric acid with piperidine³ and pyridine⁴. The bands of ionic form belong to the ionic pair $RCO_2^{\ominus}\cdot H_2N^{\oplus}RR$, since the dissociation into ions in solvents with the low dielectric constant does not practically occur. Simultaneous existence of molecular complex and ionic pair bands and the reversible variation of their intensity with temperature (Fig. I) are the evidence of the equilibrium



In comparison with the isobutyric acid-piperidine system⁵, where the constant of this equilibrium at $20^{\circ}C$ is equal to

100, in this case the shift of equilibrium II towards the ionic pair is not so important, the equilibrium constant estimated by the intensities of bands 1710 and 1560 cm^{-1} being about 4 at room temperature. Therefore, the isobutyric acid-diisobutylamine system appears to be convenient for the investigation of the effect of a solvent on equilibrium II.

In solvents with high dielectric constants, whose molecules are capable of forming a hydrogen bond as proton donors (D_2O , CH_3OH) the titration of an acid by amine is observed. In the methanolic solution, for instance, the intensity of $\nu_{\text{C=O}}$ band 1720 cm^{-1} , due to the molecules of an acid bonded with the molecules of an alcohol, decreases strictly proportionally to the amount of diisobutylamine added to the solution. At equimolar acid/amine ratio the band entirely disappears (Fig.2). Simultaneously, the bands $\nu_{\text{CO}_2^-}$ 1570 cm^{-1} of the acid anion and $\delta_{\text{NH}_2^+}$ of the dialkylammonium cation appear

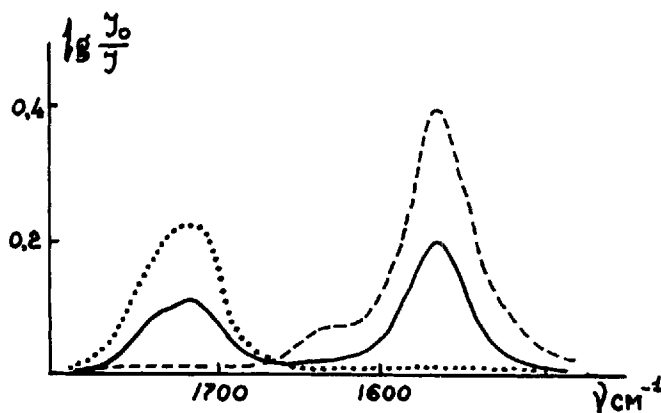


FIG.2

Infrared spectra of isobutyric acid and diisobutylamine solutions in CH_3OH , cell $45,7\mu$, $C_{\text{acid}} = 0,2 \text{ M}$,
 $C_{\text{amine}} = \dots\dots 0$; ——— 0,1; - - - - 0,2 M, 20°C .

in the spectrum. The same picture is observed in solutions in D_2O and CD_3OD ; however, the band δNH_2^+ is absent because of the hydrogen isotopic exchange with the solvent. In these solvents the band $\nu_a CO_2^-$ is shifted by 10 cm^{-1} to low frequencies. Under these conditions almost all of the ionic pairs are dissociated, i.e. equilibrium III is considerably shifted to the right, and the ions $C_3H_7CO_2^-$ and $(C_4H_9)_2NH_2^+$ are connected with the molecules of a solvent by hydrogen bonds. The absence of a band in the region $1680-1720\text{ cm}^{-1}$, typical for the hydrogen bonded molecular complex, justifies the conclusion that there are no such complexes in these solvents, and equilibrium II is completely shifted to the right.

A qualitatively different appearance have the spectra of isobutyric acid-diisobutylamine system in the solvents whose molecules can act only as proton acceptors in hydrogen bond (Fig.3). In dioxane ($\epsilon = 2$) and acetonitrile ($\epsilon = 36$), besides the ionic bands $\nu_a CO_2^-$ 1560 cm^{-1} and δNH_2^+ 1620 cm^{-1} ,

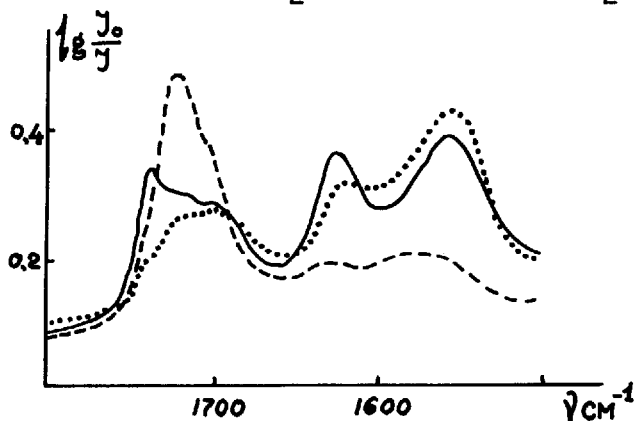


FIG. 3

Infrared spectra of isobutyric acid and diisobutylamine both 0,6 M in : ————— dioxane,acetonitrile, - - - - - dimethyl sulfoxide, 20°C , cell $45,7\mu$.

there is the doublet $\nu_{C=O}$ 1700, 1720 cm^{-1} of isobutyric acid molecules making up a molecular complex with amine, as well as the band 1736 cm^{-1} belonging to the C=O group of the acid sharing hydrogen bonds with the molecules of the solvent. In dimethyl sulfoxide ($\epsilon = 49$) the bands ν_{CO} of molecular complexes of an acid with amine and with a solvent are not observed separately (the frequency of the complex of an acid with dimethyl sulfoxide is lower than that of an acid bonded with dioxane and acetonitrile due to the higher electron donating power of the proton accepting group S=O) but the intensity of the ionic pair bands 1620 and 1560 cm^{-1} is lower than in the case of dioxane and acetonitrile solutions. With the increase of temperature the intensity of ν_{CO} bands in these solvents increases on account of the bands of ionic form. The presence of the ν_{CO} band of the acid-amine molecular complex in the spectrum of dioxane and acetonitrile solutions and, probably, also in that of a dimethyl sulfoxide solution means that a series of equilibria II, III in these solvents is conspicuously shifted to the left as compared to methanol and water solutions. The data obtained lead us to believe that stoichiometric proton transfer from isobutyric acid to diisobutylamine accompanied by the ionic pair dissociation, results from the proton donating ability of its molecules in hydrogen bond forming rather than from the high value of the dielectric constant of the solvent.

Most strikingly the influence of the hydrogen bond of the molecules of a solvent with the acid-amine complex on equilibrium II is illustrated by Fig.4, which shows the

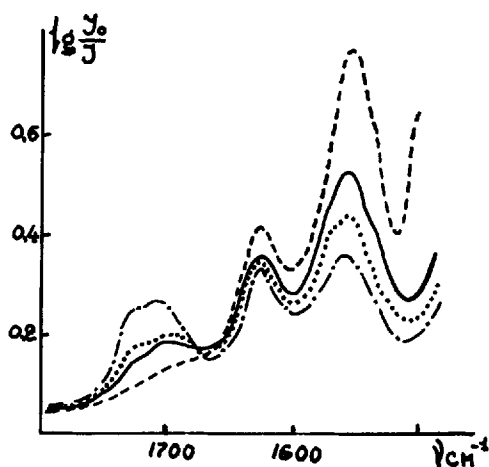
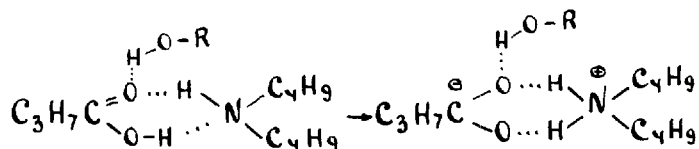


FIG. 4

Infrared spectra of isobutyric acid and diisobutylamine solutions both 0,5 M in CCl_4 containing 1,0 M alcohol: - - - - no alcohol; CH_3OH ; ———— β -chloroethanol; - - - - phenol.

spectra of isobutyric acid-diisobutylamine system in the presence of methanol, β -chloroethanol, and phenol. From these spectra one can see that with the increase of proton-donating power of the alcohol added, the intensity of ionic form bands $\nu_{\text{CO}_2^-}$ and $\delta_{\text{NH}_2^+}$ increases, whereas the intensity of the doublet $\nu_{\text{C=O}}$ 1700, 1720 cm^{-1} characteristic of the molecular complex acid-amine decreases. The influence of alcohol on the proton transfer can be explained by the fact of forming the hydrogen bond between its OH group and the CO group in the acid-amine molecular complex. This results in the shift of the electron cloud of the carboxylic group towards the OH group of alcohol, and the OH ... N bond in the acid-amine complex getting stronger, the proton more readily

transfers to the amine molecule. The additional gain in energy in the process



is provided by the hydrogen bond OH...O becoming stronger after the ionic pair formation owing to the increase in the electron density on the oxygen atom - acceptor of a proton.

Comparing the solutions of an acid in amine (Fig.I) and the solution of their equimolar mixture in CCl_4 (Fig.4) one can see that intensity of the doublet $\nu\text{C}=\text{O}$ increases. This is due to the appearance of some complexes of ionic type containing two acid molecules in which the terminal group $\text{C}=\text{O}$ of the second molecule possesses the band coinciding with the $\nu\text{C}=\text{O}$ band of the molecular acid-amine complex ^{1,3}. Although the possible existence of the complex 2:I can not be absolutely neglected in such solvents as dioxane, acetonitrile, dimethyl sulfoxide, still the similarity of the spectra of the equimolar mixture solutions in CCl_4 and, after excluding the νCO band of an acid bonded with the solvent, in dioxane and acetonitrile makes us believe that in these solvents the position of equilibrium II does not considerably differ.

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