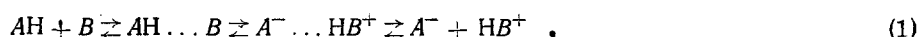


AN INFRARED SPECTROSCOPIC STUDY OF THE
MOLECULAR COMPLEX - ION PAIR EQUILIBRIUM
IN THE ISOBUTYRIC ACID - DIISOBUTYLAMINE
SYSTEM

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The role of hydrogen bonding in proton-transfer processes was established in work by N. D. Sokolov [1, 2], and the following scheme is now generally accepted for the equilibria established in a system containing molecules with sufficiently strong proton-donating and proton-accepting power [3]:



In the first stage, hydrogen bond formation takes place, after which the transfer of a proton from the donor to the acceptor leads to the formation of an ion pair, which under suitable conditions may dissociate to form ions. In solvents with a low dielectric constant, practically no dissociation takes place [4], and the last stage of the reaction is the formation of the ion pair. Proton transfer in complexes with hydrogen bonding is therefore best studied in solvents of this kind, since in these solvents we have the closest approach to true equilibrium between the molecular complex and the ion pair.

Despite the large number of papers devoted to the spectroscopic study of the reactions of acids with amines, almost no studies have been made of the equilibrium between a molecular complex and an ion pair. Some authors [2, 5] consider that proton transfer from a donor to an acceptor cannot take place at all in a medium with a low dielectric constant. On the other hand, the results of the first studies of the infrared spectra of carboxylic acid-amine systems in solutions in CCl_4 and $CHCl_3$ [6-8] were interpreted by the authors cited on the basis of the hypothesis that the products of the reaction are ionic, and the possibility that molecular complexes with hydrogen bonding exist was not considered. Extremely effective results were obtained in a study of a carboxylic acid-pyridine system in $CHCl_3$ [9]. On the basis of the bands in the range $1400-1800\text{ cm}^{-1}$, Barrow established for the first time the existence of an equilibrium between a molecular complex with hydrogen bonding and an ion pair. Subsequently, the concept of an equilibrium of this kind was introduced for the interpretation of experimental data on the dielectric polarization of phenol-amine [10, 11] and acid-amine [12, 13] systems. The last authors, however, in subsequent work [14], did not mention this equilibrium in the interpretation of the spectra of the adducts of acids with tripropylamine in solutions.

The simultaneous existence of acid-amine complexes of molecular and ionic types in equilibrium with one another was detected spectroscopically in [15, 16]. This means that the potential energy surface of the reaction in this system has two minima. The results obtained in [17] show that infrared spectroscopy makes it possible to measure the depth of each of these minima. In a continuation of this work [15-17], the present paper gives the results of a study of the isobutyric acid (IBA)-diisobutylamine (DIBA) system. In the study of the equilibria resulting from the transfer of a proton from the acid to the amine, the most informative range of the spectrum is the $900-1800\text{ cm}^{-1}$ range. Attempts to establish the existence of forms with proton transfer from the spectrum in the $\nu(XH)$ range led to contradictory results [18, 19]. In fact, the $\nu(OH)$ band of stable complexes of acids with proton acceptors is broad and has a complex structure, and it remains qualitatively unchanged when a proton is transferred from the acid to the amine [20].

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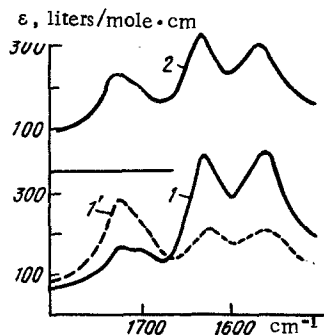


Fig. 1

Fig. 1. Spectra of solutions of IBA and DIBA. IBA concentration: 1, 1') 0.8; 2) 0.075 M. t: 1, 2) 20°C; 1') 90°C.

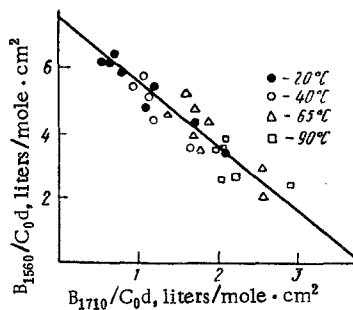


Fig. 2

Fig. 2. Determination of the integral absorption coefficients of the $\nu_a(\text{CO}_2^-)$ and $\nu(\text{C}=\text{O})$ bands.

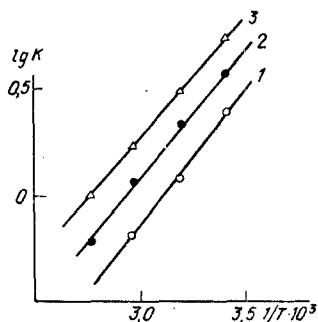
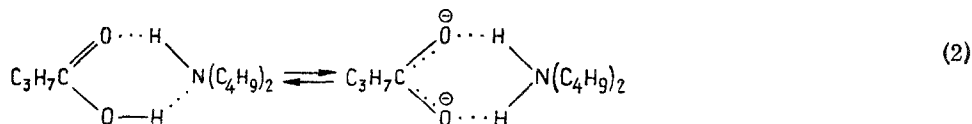


Fig. 3. Plots of $\log K$ against $1/T$ for solutions of IBA in DIBA. IBA concentration: 1) 0.075; 2) 0.2; 3) 0.8 M.

Comparison of the spectra of CCl_4 solutions of the acid, the amine, and their equimolar mixture shows that the spectrum of the mixture contains bands due to the carboxylate ion $\nu_a(\text{CO}_2^-)$ 1560 cm^{-1} , $\nu_s(\text{CO}_2^-)$ 1405 cm^{-1} , and the dialkylammonium ion $\delta(\text{NH}_2^+)$ 1620 cm^{-1} , $\nu(\text{CN}^+)$ 1029 cm^{-1} , which evidently belong to the ion pair $\text{C}_3\text{H}_7\text{COO}^- - \text{H}_2\text{N}^+(\text{C}_4\text{H}_9)_2$. At the same time the spectrum of the mixture shows bands due to an acid-amine molecular complex containing a hydrogen bond $\text{OH} - \text{N}$ - the doublet $\nu(\text{C}=\text{O})$ $1700, 1720 \text{ cm}^{-1}$, $\nu(\text{C}-\text{O})$ 1224 cm^{-1} , and $\nu(\text{CN})$ 1122 cm^{-1} . The bands of the IBA dimers, $\gamma(\text{OH})$ 938 cm^{-1} , $\delta(\text{OH})$ 1417 cm^{-1} , $\nu(\text{C}-\text{O})$ 1239 cm^{-1} , and the characteristic peaks of the $\nu(\text{OH})$ band at $2560, 2650, \text{ and } 2750 \text{ cm}^{-1}$ are not observed in the spectrum. With increase in the temperature of the solution of IBA and DIBA in CCl_4 , there is a reversible increase in the intensity of the bands due to the molecular complex and a decrease in the intensity of the bands due to the ion pair. This shows that the molecular

complex is energetically less favorable than the ion pair, that is, the second minimum on the potential energy surface is deeper than the first, as in the cases examined earlier [15, 17]. A typical feature of the spectra of solutions containing acid and amine is the presence of a continuous absorption background in the range $1000-1700 \text{ cm}^{-1}$. The existence of this background was noted in [21, 22] and was related to the tunnel effect of the proton [22].

In a solution of IBA in DIBA (Fig. 1) the displacement of the molecular complex-ion pair equilibrium to the right is not so marked as in case of piperidine [16]. Comparison of the spectra of solutions with different concentrations shows that the ratio of the intensities of the bands at 1560 cm^{-1} (or 1620 cm^{-1}) and the doublet at 1710 cm^{-1} decreases on dilution. The equilibrium



characterizes a monomolecular process, so that this ratio should not depend on the concentration. It may be assumed that the apparent change in the equilibrium constant of this process with change in concentration is due to the association of ion pairs by a dipole-dipole mechanism. The association of the ion pairs stabilizes the ionic complex, leading to a decrease in the proportion of molecular complexes. The dependence of the equilibrium constant of an analogous process on concentration was detected in [15] and was again attributed to the association of the ion pairs.

Analysis of the concentration and temperature dependence of the intensity of the $\nu(\text{C}=\text{O})$ and $\nu_a(\text{CO}_2^-)$ bands makes it possible to estimate the energy liberated on proton transfer in the acid-amine complex, and also the contribution of the dipole interaction to the energetics of the process. The equilibrium con-

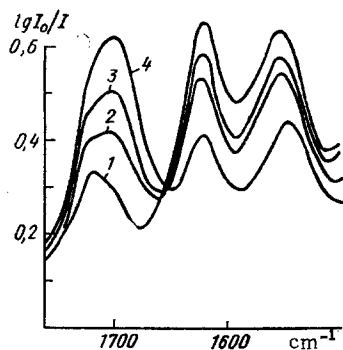


Fig. 4

Fig. 4. Spectra of solutions of IBA and DIBA in CCl_4 . IBA concentration 0.25 M and DIBA concentration: 1) 5.5; 2) 0.75; 3) 0.25; 4) 0.125 M.

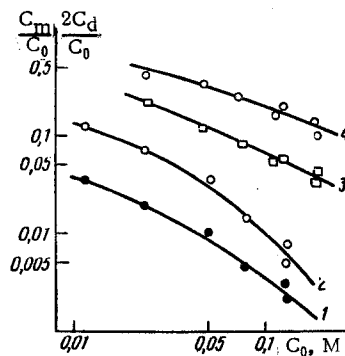


Fig. 5

Fig. 5. Dependence of the relative numbers of monomeric (C_m/C_0) and dimeric ($2C_d/C_0$) IBA molecules on the concentration of equimolar solutions of IBA and DIBA in CCl_4 : 1, 3) C_m/C_0 ; 2, 4) $2C_d/C_0$; 1, 2) 20°C; 3, 4) 73.5°C.

stant for the reaction of proton transfer through hydrogen bonding $K = C^{a^-b^+}/C^{ab}$ ($C^{a^-b^+}$ and C^{ab} are the concentrations of the ion pairs and molecular complexes) was determined from the integral intensity B of the bands at 1560 cm^{-1} and the doublet at 1710 cm^{-1} :

$$K = \frac{B_{1560}}{B_{1710}} \cdot \frac{A_{1710}}{A_{1560}}$$

The integral adsorption coefficients A were found from the relationship between B_{1560}/C_0d and B_{1710}/C_0d (C_0 is the total concentration of acid, and d is the thickness of the layer) as the intercepts cut off by the straight line on the coordinate axes (Fig. 2). The straight line was constructed using the values of B obtained at concentrations of the acid in the amine from 0.075 to 0.8 M and temperatures of 20, 40, 65, and 90°C. The error in the measurement of B is due to the inaccuracy of the graphical separation of the broad overlapping bands, and the appreciable background. The values found for A_{1560} and A_{1710} are $7.5 \cdot 10^4$ and $3.8 \cdot 10^4$ liters/mole $\cdot \text{cm}^2$, respectively. The first value almost coincides with the value $A = 7.7 \cdot 10^4$ liters/mole $\cdot \text{cm}^2$ for the $\nu_a(\text{CO}_2^-)$ band of a solution of IBA and DIBA in water, where it is determined with a high accuracy. The value of A_{1710} is close to the value of A for $\nu(\text{C}=\text{O})$ in IBA dimers [23] and IBA-pyridine complexes with hydrogen bonding [24]. In the concentration range indicated, the calculated value of K varies from 2 to 5, that is it is smaller by almost two orders of magnitude than in the case of a solution of IBA in piperidine [17].

Despite the marked dependence of the value of K on the concentration of IBA and DIBA, the plots of $\log K$ against $1/T$ for different concentrations are almost parallel straight lines (Fig. 3). This apparently means that the enthalpy of association of the ion pairs does not exceed the experimental error in the determination of the enthalpy ΔH of reaction (2). If on the other hand account is taken of the fact that the energy of the dipole-dipole interaction in solutions of trioctylammonium halides decreases with the size of the anion, and for the iodide is equal to 1.5 kcal/mole [25], it may be assumed that the energy of the van der Waals interaction between the molecules of alkylammonium salts of aliphatic carboxylic acids does not exceed 1-2 kcal/mole. The mean value of ΔH , calculated from the slope of the straight lines in Fig. 3, was found to be 5.3 kcal/mole, which is appreciably less than the corresponding value for the IBA-piperidine system [17]. We assume that the reliability of the value of $\Delta H = 5.3$ kcal/mole, with allowance for possible systematic errors [17], amounts to 1-2 kcal/mole.

For comparable concentrations of the acid and amine it is necessary to take account of the possibility that complexes containing two or more molecules of acid are formed. Study of the concentration and temperature dependence of the spectra of solutions of IBA and DIBA in CCl_4 made it possible to establish the presence of the 2:1 complex and to determine its spectral characteristics. Figure 4 gives the spectra of solutions in CCl_4 containing 0.25 M IBA and different quantities of amine. With decrease in the concentration of DIBA, the intensity of the 1700, 1720 cm^{-1} doublet increases, and that of the bands at 1560 and

1620 cm^{-1} decreases. The same changes in the spectrum take place with decrease in the concentration of solutions of an equimolar mixture of IBA and DIBA in CCl_4 . The $\nu(\text{C}=\text{O})$ band [with a contribution from $\delta(\text{OH})$] of the IBA dimers at 1239 cm^{-1} becomes weaker when DIBA is added to the solution, and a new band due to acid-amine molecular complexes appears at 1224 cm^{-1} . At a component ratio of 2:1, the 1239- cm^{-1} band can no longer be seen in the spectrum. In the presence of the amine there is also a decrease in the intensity of the $\gamma(\text{OH})$ band of the IBA dimers at 938 cm^{-1} , which disappears completely at a concentration ratio of 2:1. These results show that both a decrease in the proportion of DIBA and dilution of the solution lead to an increase in the quantity of the complexes consisting of two molecules of acid and one molecule of amine, which represent the product of the attachment of a molecule of the acid to the ion pair. This molecule of acid forms a hydrogen bond with the carboxylate ion, and its $\text{C}=\text{O}$ group makes a definite contribution to the intensity of the 1700, 1720 cm^{-1} doublet.

Comparison of the spectra of the complexes of IBA with different proton acceptors shows that with increase in the strength of the $\text{C}_3\text{H}_7\text{COOH}-\text{B}$ hydrogen bond, the $\nu(\text{C}=\text{O})$ band of the acid is displaced towards lower frequencies and acquires a doublet structure [24]. In the IBA-pyridine complex with energy 7.5 kcal/mole, the frequencies of the doublet are 1700 and 1720 cm^{-1} [the $\nu(\text{C}=\text{O})$ frequency of the IBA dimer is 1707 cm^{-1}], and on going to the more stable complexes with dimethyl sulfoxide and trimethylphosphine oxide, the frequencies of the doublet remain unchanged, although the energy of the last complex amounts to 12 kcal/mole. The integral absorption coefficient of the $\nu(\text{C}=\text{O})$ band also increases to a limiting value of $4 \cdot 10^4$ liters/mole $\cdot \text{cm}^2$ and subsequently remains unchanged in this series of complexes. It is therefore natural that the parameters of the $\nu(\text{C}=\text{O})$ band are the same for the 1:1 IBA-DIBA molecular complex and for the molecule of the acid forming a hydrogen bond with the carboxylate ion in the ion pair.

To determine the number of monomeric and dimeric molecules in the system, it is convenient to use the $\nu(\text{OH})$ range. Experiments of this kind were carried out for solutions of an equimolar mixture of IBA and DIBA in CCl_4 using the values of the monomer-dimer equilibrium constant for different temperatures and the integral absorption coefficient of the $\nu(\text{OH})$ band of the monomers from [23]. The results obtained are given in Fig. 5. It can be seen that the greatest fraction of dimers is realized in solutions with the minimum concentration at the maximum temperature. Under the conditions in which the spectrum in Fig. 4 was recorded, however, the proportions of the monomers and dimers are 0.1% and 0.2%, that is, the contribution of the dimers to the absorption at 1710 cm^{-1} is negligible.

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