SPECTRA AND MOLECULAR STRUCTURE OF NITRIC ACID IN SOLUTIONS

COMMUNICATION 3. COMPLEX FORMATION WITH CARBOXYLIC ACIDS

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Continuing our earlier investigations [1, 2] of the reaction of nitric acid with solvents, we turned to systems with carboxylic acids. The selection of such systems was dictated primarily by their widespread use in the practice of organic synthesis.

The best studied is the system nitric acid—acetic acid. Pictet [3] has asserted that if two moles of acetic acid is mixed with one mole of nitric acid, the compound \( \text{HNO}_3 \cdot 2\text{CH}_3\text{COOH} \) is formed. Miskidzh'yan and Trifonov [4], investigating the fusibility, viscosity, and density of this system, criticized Pictet's views and demonstrated that acetic acid forms a chemical compound with nitric acid, with the composition \( \text{HNO}_3 \cdot \text{CH}_3\text{COOH} \). The same viewpoint is maintained by the authors of [5]. In [6] the UV absorption spectra of mixtures of nitric acid with acetic acid were investigated all the way up to 50% acetic acid; however, no discussions of these spectra are cited. Later Mavel [7], studying the concentration dependence of the chemical shifts of the proton resonance of solutions of \( \text{HNO}_3 \) in \( \text{CH}_3\text{COOH} \), also arrived at the conclusion that there are complexes \( \text{HNO}_3 \cdot \text{CH}_3\text{COOH} \).

This work presents the results of spectral investigations of solutions of \( \text{HNO}_3 \) in acetic, propionic, butyric, and trifluoroacetic acids.

We used the Raman spectra and UV absorption spectra. An investigation of the molar integral intensities in the Raman spectra in many cases makes it possible to draw conclusions on the formation of complexes in solutions [2], while the UV absorption spectra contain interesting data on the intermolecular bond formed, if the latter affects the chromophore portion of the molecule [8]. The Raman spectra of solutions of nitric acid with the abovementioned solvents possess only lines pertaining to the components of the solution; therefore it is scarcely expedient to cite the spectra of all the solutions here. As an example, we shall present the spectra of solutions of \( \text{HNO}_3 \) in \( \text{CH}_3\text{COOH} \) in Fig. 1.

Just as before [1, 2], we measured the concentration dependence of the molar integral intensity of the Raman line at 1300 cm\(^{-1}\), belonging to the spectrum of nondissociated nitric acid. In this case, the concentration of the nondissociated molecules was selected equal to the analytical concentration of the acid, since the degree of ionization of \( \text{HNO}_3 \) according to the equation \( \text{HNO}_3 + \text{RCOOH} \rightleftharpoons \text{RCOOH}_2^+ + \text{NO}_3^- \) is so low that it lies beyond the limits of sensitivity of our experiments. The experimental data presented in Fig. 2 show that as \( \text{HNO}_3 \) is diluted with carboxylic acids, in all cases an S-shaped drop in the molar extinction of the line 1300 cm\(^{-1}\), characterizing the symmetrical vibration of the nitro-group in the \( \text{HONO}_2 \) molecule, is observed. At low nitric acid concentrations in mixtures with acetic and butyric acids (Fig. 2, a, b), the curve passes through a minimum, and a sharp increase in the intensity is observed. In the case of mixtures with propionic and trifluoroacetic acids, on the other hand (Fig. 2, c, d), only a slight increase is observed. In accord with the considerations expressed in our previous communication [2], the S-shaped drop in the intensity is evidently associated with the formation of complexes of the type \( \text{HNO}_3 \cdot \text{RCOOH} \) in solution, which leads to strong polarization of the \( \text{HONO}_2 \) molecules.

and consequently, to an increase in the ionic character of the N-O bond in the nitro group. The formation of complexes of this type is also indicated by the fusibility diagram of the nitric acid - acetic acid system, constructed according to the results of our experiments and [4]. In Fig. 3, the dystectic is not singular and corresponds to the stoichiometric composition 1:1, which agrees with the spectroscopic data.

Noteworthy is the increase in the intensity of the Raman line 1300 cm\(^{-1}\) in the region of low nitric acid concentrations. Within this concentration region, the structure of the solution is similar to the structure of the solvent, and consequently, the tendency of carboxylic acids to associate must be taken into consideration. In this case, evidently the relative proportion of HONO\(_2\) molecules not bonded to the solvent increases, and with it the molar intensity of the Raman effect. This effect should depend upon the energy of interaction among the solvent molecules. Actually, in mixtures with acetic acid it is the most substantial, in mixtures with trifluoroacetic acid it is almost absent, while with butyric acid it is greater than with propionic acid. Since carboxylic acids are constructed as flat zig-zag (trans) chains, in the case of an even number of carbon atoms a closer packing of the molecules is possible, and consequently, a greater energy of the intermolecular interaction than in the case of an odd number [9].

Then, if the hydrogen bonds formed during complex formation affect the nitro-group, this cannot help but have an effect upon the UV absorption of nitric acid. In particular, it is known [8] that in the formation of hydrogen bonds, the absorption bands corresponding to n-\(\pi^*\) transitions are shifted in the higher frequency direction (blue shifts), and their intensity decreases. In this case the value of the shift is determined by the difference of the heats of formation of the hydrogen bond in the ground and excited states, considering the Franck-Condon principle. We investigated the UV absorption spectrum of nitric acid in a solution with acetic acid within a broad range of concentrations. The data obtained are presented in Table 1 and in Fig. 4. When HNO\(_3\) is diluted with acetic acid, for the n-\(\pi^*\) transition (260 mp), a shift is observed in the direction of lower frequencies (red shift), along with an increase in the intensity. Since the widespread opinion of blue shifts for n-\(\pi^*\) transitions is based upon the general lack of contradiction of the