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INVESTIGATING THE FORM OF EQUILIBRIUM AND STRUCTURE OF COMPLEXES
 IN THE SYSTEM ISOQUINOLINE-TRIFLUOROACETIC ACID BY ANALYSIS
 OF THE TRANSMISSION MATRIX IN THE ELECTRON SPECTRA

G. S. Denisov, V. A. Mikheev, A. B. Sokornov,
 T. V. Sokornova, B. S. Terushkin, and V. M. Shraiber

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Spectral investigations of systems containing strong proton donors AH and acceptors B are often complicated by the simultaneous presence of complexes of different type. Equimolar complexes AHB may have a molecular or ionic (with a transferred proton) structure; at the same time, the formation of more complex aggregates with two or more donor or acceptor molecules is possible [1-5]. The spectra of different complexes usually overlap to a greater or lesser degree. However, to study the form of equilibrium and identify all the forms and to obtain information on their structure and the potential function of the proton, it is very important to be able to distinguish the spectra of the individual components, primarily the spectra of the equimolar complexes. Of definite interest are data on the complex of composition 2:1, allowing nonadditive effects in the energetics of association to be traced, as well as changes in the character of the donor-acceptor interaction on introducing a third molecule. One promising approach to the solution of the problem of distinguishing spectra of different forms that are in equilibrium is that based on simultaneous analysis of a family of spectra taken at different equilibrium positions (on account of variation in concentration, temperature, pressure, etc.). Computer analysis allows the most probable number of absorbing forms to be determined and, after developing a model of equilibrium, their thermodynamic characteristics and the spectra of the individual forms may be determined [6-10].

In the present work, an attempt is made to investigate the electronic absorption spectra of the system isoquinoline-trifluoroacetic acid (IQ-TFAA) in different solvents, with the aim of determining the individual spectra and the structure of equimolar and more complicated complexes and the influence of interaction with the surroundings on the structure and elucidating the concentration and temperature ranges in which the various complexes exist. Investigations of the IR spectra in the region of the TFAA carboxyl-group bands [11] show that, with increasing interaction with the solvent, the structure of the complex changes from purely molecular to typically ionic, passing through an intermediate structure with a quasisymmetric bond of which the proton is not bound predominantly with the oxygen atom of the nitrogen atom. Study of this unusual system from the proton-acceptor bands is possible using the electron spectrum, in particular the IQ band 1L_b in the near-UV region. This also offers the possibility of using solvents that are more inert than in [11] — hydrocarbons — and expanding the concentration range by two or three orders of magnitude; the transparency of the solvents allows IQ solutions of 10^{-4} – 10^{-5} M and less to be investigated. This in-

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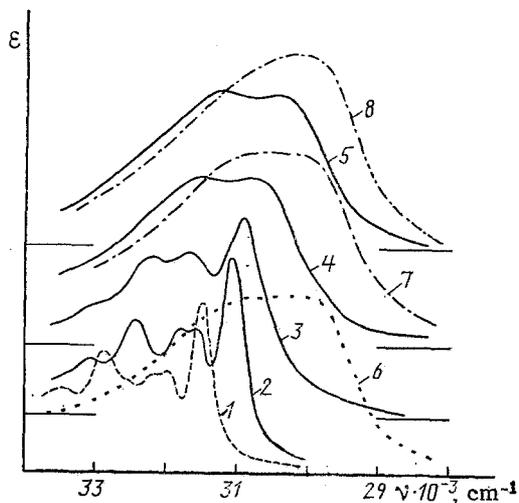


Fig. 1. Spectra of IQ in octane (1); the complex IQ + TFAA of composition 1:1 in octane (2), CCl_4 (3), toluene (4), acetonitrile (5), and water (6); and the complex IQ + TFAA of composition 1:2 in toluene (7) and acetonitrile (8).

increases the probability of realizing an equimolar concentration in some range of TFAA concentration and making a smooth transition to a complex of composition 2:1 or more complicated complexes.

On the SPECORD UV-VIS instrument, spectra of IQ and TFAA solutions in hexane, octane, isooctane, CCl_4 , toluene, butyl chloride, chloroform, and acetonitrile were obtained in the range $28,000\text{--}34,000\text{ cm}^{-1}$. Cuvettes of standard type with quartz windows were used. Solutions in toluene were also investigated at different temperatures in the range $25\text{--}94^\circ\text{C}$. The TFAA molecule does not have an absorption band in the given range.

In solutions in saturated hydrocarbons, as in CCl_4 , the IQ band has a well-resolved vibrational structure (Fig. 1, curve 1). Its center of gravity lies close to $32,500\text{ cm}^{-1}$, and the most intense vibronic component, evidently corresponding to purely electronic transition, has a maximum at $31,500\text{ cm}^{-1}$. For comparison, curve 6 in Fig. 1 shows the band of the IQ ion, which may be observed in aqueous IQ solution in the presence of a strong acid, HCl or TFAA. This band is shifted to a lower frequency than the IQ band (with a center of gravity around $30,300\text{ cm}^{-1}$), is practically structureless, and is of great width and intensity.

A more complex picture depending on the concentration ratio of the components is observed in the spectra of IQ and TFAA solutions in aprotic solvents (Fig. 2). Adding a small amount of TFAA to an IQ solution in octane (or in another similar hydrocarbon solvent) is associated not only with a certain decrease in intensity of the vibronic maxima of the IQ bands but also with the appearance of new maxima belonging, according to the available information, to a band redshifted by approximately 400 cm^{-1} with respect to the IQ band. This is most clearly evident in the appearance of a new maximum at $31,200\text{ cm}^{-1}$ (Fig. 2a). Such variation is often observed in the bands of $\pi \rightarrow \pi$ transitions in *asa*-aromatic molecules on the formation of a hydrogen bond $\text{AH}\dots\text{N}$; see [12, 13], for example. With increase in concentration of the acid, the maximum at $31,200\text{ cm}^{-1}$ intensifies, and absorption is observed in the region characteristic of a cation band. With a considerable excess of acid, this absorption is dominant in the spectrum, and at $2.5 \cdot 10^{-2}\text{ M}$ TFAA the spectrum becomes practically identical to that of the aqueous solution (Fig. 2a). Approximately the same picture is seen in CCl_4 , although in this case the new vibronic maximum is somewhat broadened, and shifted hardly any more in the direction of the band of the ionic form. Thus, it may be supposed that in these solvents the new band with shifted maxima of the vibronic structure belongs to a complex of IQ with TFAA of composition 1:1, in which the interaction of the partners does not proceed beyond the formation of a strong hydrogen bond. Proton transfer and the stabilization of the cation occurs in complexes of more complicated composition, the formation of which is responsible for the appearance of a structureless band. In butyl chloride and aromatic solvents — benzene, chlorobenzene, toluene — the new maxima appearing with excess IQ are strongly broadened, and the spectrum is intermediate in position and form between the molecular and ionic cases (Fig. 2b). In strongly polar acetonitrile, the structureless band grows at once; it is similar to that present in less active solvents only when there is an excess of acid* (Fig. 2c). The introduction of excess in this case leads only to a small change, as the band approaches more closely that of a cation in aqueous solution.

*It is characteristic that an analogous picture is also observed in chloroform, a solvent

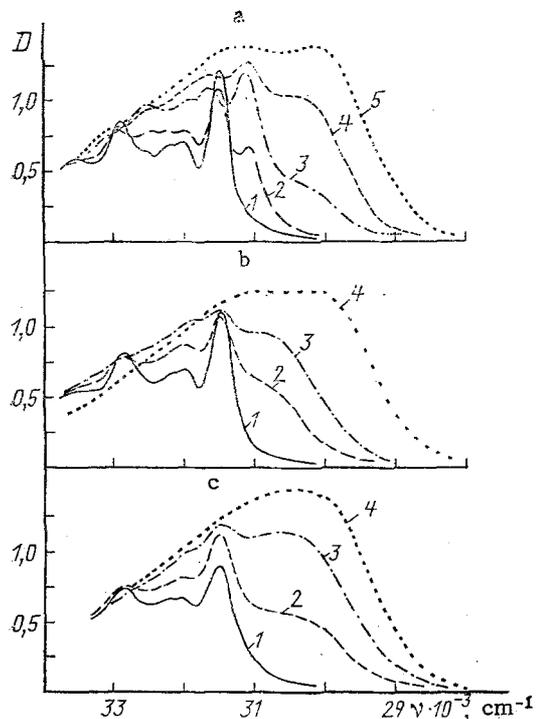


Fig. 2. Concentrational variation in the spectra of the system IQ-TFAA in solutions in octane (a) with 0 (1), $3.0 \cdot 10^{-4}$ (2), $1.0 \cdot 10^{-3}$ (3), $2.5 \cdot 10^{-3}$ (4), and $2.5 \cdot 10^{-2}$ M (5) TFAA; and in solutions in butyl chloride (b) with 0 (1), $3.0 \cdot 10^{-4}$ (2), $6.0 \cdot 10^{-4}$ (3), and $2.5 \cdot 10^{-2}$ M (4) TFAA; and in acetonitrile (c) with 0 (1), $2.2 \cdot 10^{-3}$ (2), $6.5 \cdot 10^{-3}$ (3), and $6.2 \cdot 10^{-2}$ M (4) TFAA; $d = 1$ (a, b), 0.05 cm (c); $4.0 \cdot 10^{-4}$ (a), $3.0 \cdot 10^{-4}$ (b), and $6.2 \cdot 10^{-3}$ M (c) IQ.

It follows from the general form of the UV spectra observed and also the IR spectra of similar system [11] that, in inert solvents, complexes with more than one acid molecule are formed, the IQ molecule being protonated in these complexes. To determine the number of components, their individual spectra, and the equilibrium constants, the approach described in [10, 15] is used. Its advantage is that it includes no a priori assumptions regarding the form of the spectra being analyzed. The results are analyzed on a BESM-6 computer by a program permitting the analysis of a set of 15 spectra, each of which is specified by 50 points at the same frequencies in all the spectra. The experimental spectrum is represented by a vector, each element of which (the transmission T or optical density D) is at a certain frequency. The set of such vectors forms a matrix (the vector becomes a row or column of the matrix). The number of absorbing forms here is equal to the dimensionality of the basis within which all the experimental vector spectra may be analyzed, within the limits of error [10]. The dimensionality of the basis is determined by the rank of the optical-density matrix of the given family of spectra. To determine the rank of matrix D, a square matrix of the same rank $P = DD^T$ (or $Q = D^T D$) of dimensionality $J \times J$ is formed; J is the number of frequencies at which measurements are made. The number of nonzero eigenvalues of matrix P (or Q) is equal to the desired rank of the matrix D, i.e., the number of absorbing forms. However, some of the eigenvalues may prove to be nonzero only because of experimental errors in determining the transmission [6]. Therefore, the eigenvalue set obtained is analyzed using significant-difference criteria [10], together with the method of estimating the dispersion of each eigenvalue and methods of superposition of the random noise and expansion taking account of weights [16, 17].

Analysis of families of nine spectra in isoctane with a fixed IQ concentration and TFAA concentrations varying from zero to a fivefold excess at 34°C (45 points in each) shows that the spectra of the given solutions consist of five strongly overlapping spectra belonging to free IQ molecules, their complexes with TFAA of equimolar composition, and those with two or more acid molecules. Successive elimination from the set of spectra of solutions taken with the greatest excess of acid (five-, four-, and threefold) does not change the result: for a family of six spectra of solutions with a maximum TFAA concentration twice that of IQ, the number of components is again five. Therefore, another series of seven spectra of IQ and TFAA solutions exists at 34°C in octane with a maximum TFAA concentration of $3 \cdot 10^{-4}$ M at an IQ concentration of $4 \cdot 10^{-4}$ M. Analysis of the number of components shows that the experimental spectra are superpositions of two individual spectra which obviously belong to free molecules and a 1:1 complex. As a control, sets of six and five spectra with successive elimination of

that is considerably less polar than acetonitrile but has proton-donor properties, which facilitates the stabilization of the ionic forms [14].

the spectra of solutions with a maximum TFAA concentration are analyzed, the number of components always remaining constant (two).

In toluene, a more active solvent, a series of 13 spectra, is obtained at 30°C, with an IQ concentration of $3.5 \cdot 10^{-4}$ M, and a TFAA concentration varying in the range $0-32.5 \cdot 10^{-4}$ M. Analysis of the number of molecules shows that, in these conditions, the picture observed is determined by the superposition of three strongly overlapping spectra, the relative intensity of which varies with the TFAA concentration. This means that in the solution, as well as free IQ molecules, there are complexes containing one and two TFAA molecules.

In acetonitrile, a series of 13 spectra with IQ concentrations of $4.1 \cdot 10^{-3}$ and $6.2 \cdot 10^{-3}$ M and a TFAA content of $0-1.95 \cdot 10^{-2}$ M at 34°C is recorded. Comparison of the eigenvalues of the optical-density matrix leads to the conclusion that, up to a 50-fold excess of TFAA, the spectrum consists of three overlapping individual spectra, so that the complexes here are again of composition 1:1 and 2:1.

To determine the spectra of the complexes and the equilibrium constants, a program is written allowing these quantities to be found (simultaneously with the equilibrium concentrations of all the forms for each solvent) for systems in which there exist the equilibria $AH + B \rightleftharpoons AH \cdot B$ with a constant K_1 and $AH \cdot B + AH \rightleftharpoons (AH)_2 \cdot B$ with a constant K_2 , i.e., the free molecules B are in equilibrium with complexes of composition 1:1 and 2:1. To solve the problem, it is necessary to find a minimum of the functional

$$\Phi = \sum_{i=1}^N \sum_{j=1}^J (D_{ij} - d_i \{E_{1j}[B]_i + E_{2j}[AB]_i + E_{3j}[A_2B]_i\})^2 w_{ij} \quad (1)$$

(D_{ij} is the experimental optical density at the j -th frequency in the i -th spectrum; E are the absorption coefficients of three forms at the j -th frequency; w_{ij} is the weight; d_i is the cuvette thickness in the i -th spectrum; N is the total number of the spectra; J is the number of frequencies) with superposed bounds: two equations of mass balance and two equations of the law of effective masses

$$\begin{cases} [A]_i + [AB]_i + 2[A_2B]_i = [A_0]_i, \\ [B]_i + [AB]_i + [A_2B]_i = [B_0]_i, \end{cases} \quad (2)$$

$$\frac{[AB]_i}{[A]_i [B]_i} = \lambda_1^2, \quad \frac{[A_2B]_i}{[AB]_i [A]_i} = \lambda_2^2, \quad (3)$$

where $\lambda_1^2 \equiv K_1$, $\lambda_2^2 \equiv K_2$.

The values of D_{ij} , d_i , the initial concentrations of the components $[A_0]_i$, $[B_0]_i$, and the weight w_{ij} are known from experiment; the absorption coefficients E_{1j} , E_{2j} , E_{3j} ($3J$ quantities) and the concentrations $[B]_i$, $[AB]_i$, $[A_2B]_i$ ($3N$ quantities) remain to be determined. Hence, the maximum number of unknown quantities in Eq. (1) is $3(N + J)$ and, in the present case, is 195. However, the concentrations $[B]_i$, $[AB]_i$, $[A_2B]_i$ — and also $[A]_i$, which do not appear in Eq. (1) — may be expressed in terms of the initial concentrations and equilibrium constants using Eqs. (2) and (3) by reducing the latter to the corresponding system of nonlinear equations. The problem of finding $3N$ unknown concentrations here reduces to determining only the two unknowns K_1 and K_2 . In addition, to reduce the bulk of the calculations, use is made of the method of principal components [16], based on the representation of the absorption spectra of the individual forms as an eigenvalue expansion of the matrix P (or Q). Then, instead of the $3J$ unknowns determining the spectra of the three individual forms, there are nine coefficients in the expansion of the spectra of the forms in terms of the known eigenvectors.

Thus, the functional in Eq. (1) is minimized by selecting 11 parameters altogether. A modified Newton's method is used for the minimization. It is obvious that, in the scheme outlined, no preliminary hypotheses regarding the form of the spectra $E(\nu)$ of the individual components are required; they may be arbitrary in form.

Spectra obtained in three solvents — octane, toluene, and acetonitrile — are analyzed by computer. The series of seven spectra in octane obtained with an excess of IQ (see above) are described by a model with one equilibrium $A + B \rightleftharpoons AB$. For solutions in toluene and acetonitrile, a model with two equilibria $A + B \rightleftharpoons AB$ and $A + B \rightleftharpoons A_2B$ is used. The spectra of

the complexes AB and A₂B obtained are shown in Fig. 1. It is evident from Fig. 1 that, in octane, the band of the 1:1 complex is actually similar to the band of free IQ and is only shifted by about 450 cm⁻¹ toward lower frequencies and intensified (curve 2). A somewhat larger shift and blurring of the vibrational structure is observed in the band of a 1:1 complex in CCl₄ (curve 3). This band is obtained experimentally in conditions of an excess of IQ by compensation of this excess in the comparison channel of the spectrophotometer. In acetonitrile (curve 5), the band of the 1:1 complex is strongly broadened, is free from vibronic structure, and is similar (but not identical) to the cationic band. This indicates ionic structure of the equimolar IQ-TFAA complex in acetonitrile, in agreement with the results of investigating IR spectra [1]. In toluene, the band of the 1:1 complex again resembles the cationic band in form, but its center of gravity is shifted to higher frequencies by about 800 cm⁻¹ and lies approximately halfway between the band centers of IQ and the cation. Together with the results of [11], this implies a structure of the complex intermediate between molecular and ionic. The spectra of the complex of IQ with two TFAA molecules in both toluene and acetonitrile are typically ionic in both position and form (curves 7 and 8): the addition of a second TFAA molecule to the equimolar complex initiates the complete transfer of the proton to the nitrogen atom of the IQ. The spectra of the more complicated complexes (3:1, 4:1, etc.) forming in hydrocarbon solvents are evidently of similar form.

At the same time, the values obtained in the calculation for the equilibrium constants are: K₁ for the reaction of equimolar-complex formation in octane, 3810 ± 20 liters/mole (34°C); in toluene, 17,930 ± 610 (30°C); in acetonitrile, 36,500 ± 2100 (34°C); K₂ for the formation of a 2:1 complex in toluene, 1530 ± 20 liters/mole; in acetonitrile, 400 ± 15.

Thus, the investigation of electronic spectra shows that, in the system IQ + TFAA, the structure of the 1:1 complex depends on the interaction with the solvent: in saturated hydrocarbons and in CCl₄, this is a complex with a hydrogen bond OH...N; in polar acetonitrile, it is an ionic pair with a transferred proton; in aromatic solvents and butyl chloride, the structure is intermediate. There is not one case in which the simultaneous existence of complexes 1:1 of molecular and ionic type has been observed; this would be indicated by the presence of two minima on the free-energy surface of the system complex + solvent. Complexes of more complicated composition (2:1, 3:1, etc.) are ionic. Their spectra are less sensitive to the nature of the solvent.

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