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# Effect of intermolecular hydrogen bonding and proton transfer on fluorescence of salicylic acid[1]

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## Abstract

Effects of intermolecular interactions, in particular the influence of intermolecular hydrogen bonds formed by salicylic acid (SA) as a proton donor with proton acceptors of different strength, on fluorescence spectra of SA in non-aqueous solutions have been investigated. Infrared spectra of studied systems have been analyzed in order to elucidate the ground state structure of the complexes formed. It has been found that at the room temperature in dilute solutions in non-polar or slightly polar aprotic solvents, where the SA molecule is not involved in intermolecular hydrogen bonding, the position of the main (blue) fluorescence component is determined by the excited state intramolecular proton transfer (ESIPT) in the lowest singlet excited state $S_1$. With increasing proton acceptor ability of the environment, when formation of weak or middle strength intermolecular H-bonds is possible, the emission band shifts gradually to lower frequency, the quantum yield falls and poorly resolved doublet structure becomes more pronounced, especially in the solvents containing heavy bromine atoms. As a possible reason for these effects, coupling between the $S_1$ and closely lying triplet term is considered. With the strongest proton acceptors like aliphatic amines, intermolecular proton transfer with ionic pair formation in the ground state and double (intra- and intermolecular) proton transfer in the excited state take place, resulting in a blue shift of the emission band. Similar emission is typical for the SA anion in aqueous solutions. The $pK_a$ value of SA in $S_1$ state has been found to be 3.1. Such a small value can be explained taking into account the ESIPT reaction following the excitation. The SA complex with pyridine exhibits emission spectrum containing both molecular-like and anion-like bands with relative intensities strongly dependent on the temperature and solvent properties. The most probable origin of this dual emission is the molecular-ionic tautomerism caused by the existence of two potential minima and reversible intermolecular proton transfer in the excited state. © 1997 Published by Elsevier Science B.V.

*Keywords:* Fluorescence spectroscopy; Infrared spectroscopy; Hydrogen bonding; Excited state intramolecular proton transfer; Salicylic acid

## 1. Introduction

The existence of a strong intramolecular hydrogen bond C=O···HO in salicylic acid and its derivatives provides the possibility of intramolecular proton transfer in the lowest excited state of these compounds and determines specific features of their fluorescence spectra [1–10]. In contrast to other molecules of this group, such as methylsalicylate or salicylaldehyde, the characteristics of the intramolecular H-bond in SA can be essentially influenced by intermolecular interactions, particularly by intermolecular H-bonds formed by the carboxylic group. The interdependence

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[1] Dedicated to Professor Henryk Ratajczak on the occasion of his 65th birthday.

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of intra- and intermolecular H-bonds in similar systems has been proved by NMR and IR studies described in Refs. [11,12]. Therefore it seems natural that ESIPT reaction in the case of SA, and, hence, the characteristics of SA fluorescence in solutions, should be very sensitive to concentration, the proton-donating or proton-accepting power of solvent molecules and to other properties of the surroundings.

Thus, it has been shown that self-dimerization of SA in non-polar aprotic solvents is responsible for its ''dual emission'', when two bands typical for fluorescence of two forms of excited SA, namely, with and without proton transfer, are observed simultaneously (in blue and UV regions, correspondingly) [3,13]. Recently, similar emission has been found also for heterodimers, formed by SA with other carboxylic acids, as well as for homo- and heterodimers of 2,6-dihydroxybenzoic acid [14]. In spite of some disagreement between conclusions made in Refs. [13,14] about the nature of the temperature and excitation wavelength dependencies of relative intensities of UV and blue components of the dimers fluorescence, the main reason for the intensity increase of the UV component in a dimer compared with the monomer seems to be clear: it is a weakening of the intramolecular hydrogen bond, caused by involving of the carbonyl group in the intermolecular H-bond with another acid.

On the other hand, it has been reported that addition of ethyl ether to SA solution in cyclohexane stabilizes the blue emission of the form with ESIPT [15], obviously due to breaking of the dimers and formation of complexes, where existence of intermolecular H-bond $COOH\cdots O(C_2H_5)_2$ strengthens the intramolecular one.

The goal of this work is to investigate the dependence of the fluorescence spectrum of SA on the character and strength of intermolecular hydrogen bonds formed by the carboxylic group, including weak H-bonds, which can affect only slightly the SA structure, and very strong H-bonds, when proton transfer is possible. For this purpose, a comparative study of fluorescence spectra of SA solutions in non-polar inert solvents (such as hexane, iso-octane, methylcyclohexane, carbon tetrachloride), in the same solvents containing additions of strong proton acceptors (dioxane, dimethylsulfoxide, pyridine, aliphatic amines), in polar aprotic solvents possessing weak proton-accepting power (butyl chloride, chloro- and bromoform, dibromoethane), as well as in aqueous solutions has been carried out. In order to obtain an independent evidence about the character of H-bonding in the ground state, IR spectra in the regions of $\nu$OH and $\nu$C=O bands for the most important systems were studied.

## 2. Experimental

Fluorescence and fluorescence excitation spectra were obtained with an SFL-2 fluorimeter with two double monochromators and the emission registration in the pulse counting regime. The temperature measurements within the range 90-300 K were performed using a modified JASCO CRY-1B optical cryostat. IR absorption spectra were recorded on a Hitachi 270-30 spectrometer using conventional cells and home-made cryostat with $CaF_2$ windows and 0.9 mm optical path length.

SA was purchased from Fluka and used without purification.

## 3. Results and discussion

1. IR absorption spectra of SA in $CCl_4$ solution reveal two bands in the $\nu$C=O region: 1697 and 1660 $cm^{-1}$ (Fig. 1(b)). Relative intensity of the band at 1697 $cm^{-1}$ increases, while that of 1660 $cm^{-1}$ decreases with decrease of concentration. These two bands belong to monomers and cyclic dimers correspondingly. Similar changes are observed in $\nu$OH region (Fig. 1(a)), where the narrow band 3540 $cm^{-1}$ corresponds to the carboxylic hydroxyl of monomer and the broader band near 3200 $cm^{-1}$ to phenolic hydroxyl involved in an intramolecular hydrogen bond. The latter band can be recorded correctly, when the concentration is low enough to eliminate the absorption of dimers.[2] At higher concentrations

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[2] The position and parameters of this band are rather close to those of $\nu$OH band of salcylaldehyde (see Ref. [16] for example). This confirms the dominative role of the structure with a $OH\cdots O{=}C$ intramolecular H-bond. An attempt to detect the rotamer with an $OH\cdots OH$ intramolecular H-bond by heating of SA solution in hexachlorobutadiene was unsuccessful because of decomposition of SA at temperatures higher than 100°C. Below this temperature no traces of such a rotamer were found.

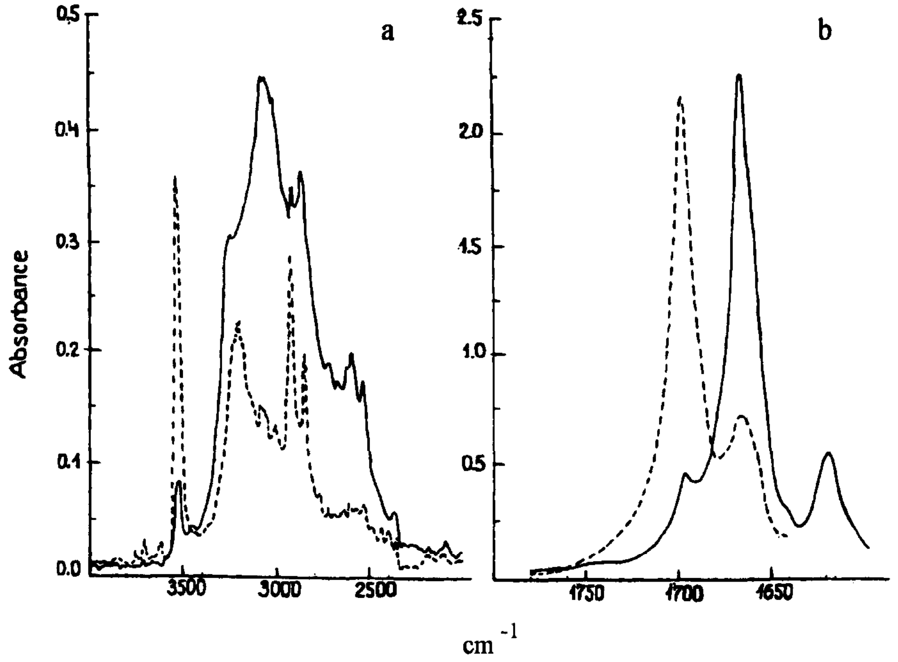
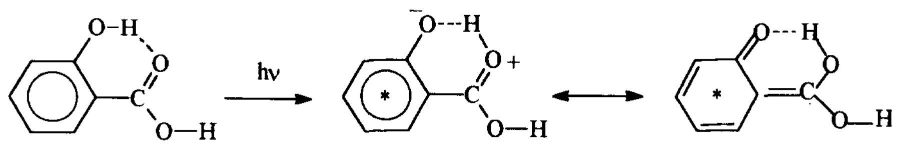


Fig. 1. IR spectra of SA solutions in $CCl_4$ ($10^{-2}$ mole $l^{-1}$ (———), $5 \times 10^{-5}$ mole $l^{-1}$ (- - -) in νOH (a) and νC=O (b) regions.

the band is overlapped by dimer absorption, including a similar νOH band of phenolic groups and a broader and lower frequency band of carboxylic OH groups involved in the intermolecular hydrogen bonding. The dimerization constant of SA in $CCl_4$, obtained by processing the series of spectra of solutions with different concentrations in the νC=O region is about $K_d$ = (0.9 ± 0.1) × $10^3$ mole$^{-1}$. In hydrocarbon solutions like hexane, $K_d$ value is higher, but exact measurements are hampered because of strong solvent absorption. In more polar solvents such as chloroform or methylene chloride, the $K_d$ value decreases (to ~0.2 × $10^{-3}$), the νC=O band of the monomer shifts about 4–5 cm$^{-1}$ towards lower frequencies.

2. When the total concentration of SA is less than ~$10^{-6}$ mole $l^{-1}$ in hexane or other hydrocarbons (and ~$10^{-5}$ mole $l^{-1}$ $CCl_4$), the amount of dimers at the room temperature is negligible. Under such conditions SA reveals a fluorescence band in the blue region with the maximum near 430 nm, independent of excitation wavelength (Fig. 2, curve 1), while the maximum of the long wave absorption band is close to 300 nm. An anomalously great Stokes shift of this fluorescence gives ground to interpret it, in accordance with Refs. [1–4,13–15], as emitted by a zwitterionic (or quinoic) structure formed due to ESIPT:



No pronounced maximum in the UV region is observed for hexane and other hydrocarbon solutions. Weak emission in this region, detected in $CCl_4$ solutions [14], can be explained by traces of dimers or complexes with HCl, which is present usually in $CCl_4$ as an impurity. However, a supersonic jet study performed in Ref. [17] has proved the existence of weak UV component in monomer emission. According to [17], both the rotamers of SA monomer are responsible for this component: emission of the

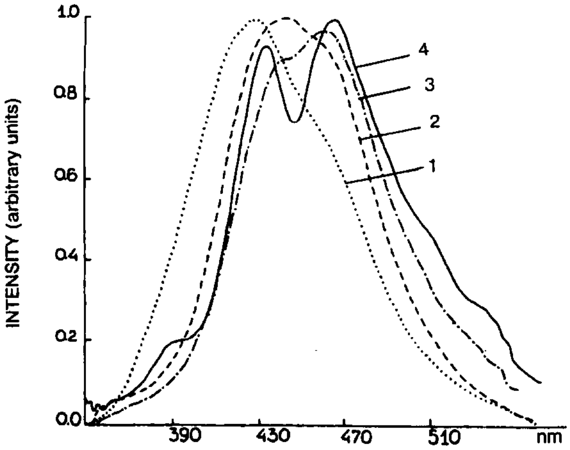


Fig. 2. Fluorescence band of SA in solutions: (1) iso-octane, $10^{-6}$ mole $l^{-1}$; (2) chloroform, (3) dichloroethane, (4) bromoform, $10^{-5}$ mole $l^{-1}$; $\lambda_{ex} = 290$ nm.

main rotamer with the intramolecular C=O···HO bond contains a weak UV component, while the OH···OH rotamer, which cannot undergo the ESIPT reaction, gives rise only to UV emission. In connection with this, a more careful IR study of the ground state rotameric equlibria in monomeric and dimeric forms of SA seems to be reasonable.

3. Another peculiarity of SA fluorescence in diluted solutions in aprotic solvents is that the profile and position of the main emission band of the monomer in the blue region turned out to be solvent dependent. Thus, in inert unpolar solvents, hydrocarbons and $CCl_4$, the band looks like an unresolved doublet with the center of gravity close to 440 nm. In more polar solvents (chloroform, dichloroethane) the center of gravity position shifts toward longer wavelengths with increasing polarity (Fig. 2) as if the long wave component of the doublet becomes stronger. The doublet structure is quite distinct when solvents containing bromine atoms, such as bromoform or dibromoethane, are used. In this case a pronounced hole between two maxima, distanced by about 40 nm, appears. One can mark also a significant decrease of the quantum yield with shifting the band center of gravity position in series of the solvents studied.

The changes of parameters of the doublet band observed upon variation of solvent properties are similar to the behaviour of resonance doublet in a vibrational spectrum rather than the changes caused by the shift of tautomeric or rotameric equilibrium. This suggests an idea that the splitting of the band is caused by interaction with some closely lying electronic state, the energy of which is nearly independent of solvent polarity. Existence of two or more close electronic terms in vicinity of $S_1$ has been suggested recently by Bisht et al. [17] (and earlier by Helmbrook et al. [18] for the case of methylsalicylate), basing on the fact of a sharp increase of non-radiative decay rate for excitation energies higher than 1100 $cm^{-1}$ from the origin. In Ref. [17], different possible channels of non-radiative decay process were analyzed, all of

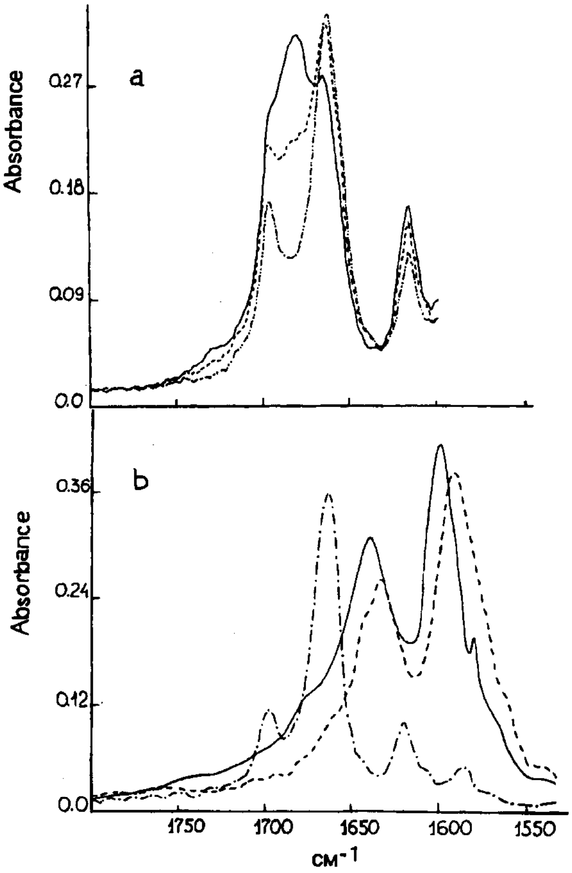
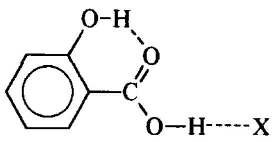


Fig. 3. IR spectra of SA solutions in $CCl_4$ in $\nu C{=}O$ region. (a) SA + dioxane; concentration of SA, $5 \times 10^{-5}$ mole $l^{-1}$; concentration of dioxane, $5 \times 10^{-3}$ (– · –), $2.5 \times 10^{-2}$ (- - -), $5 \times 10^{-2}$ mole $l^{-1}$ (———). (b) SA + tributylamine; concentration of SA, $10^{-2}$ mole $l^{-1}$; concentration of tributhylamine, 0 (– · –), $10^{-2}$ mole $l^{-1}$ (———); tetradecylammonium salicylate, $10^{-2}$ mole $l^{-1}$ (- - -).

them being connected with the neighbourhood of another singlet state, while in Ref. [18] a triplet state and possibility of the intersystem crossing are also mentioned. The data obtained in the present work, in particular, the increase of the band splitting in solvents containing heavy bromine atoms, seems to give an argument for presence of closely lying triplet state.

4. An addition of proton-accepting molecules, like dioxane or dimethylsulfoxide, to SA solutions in an inert solvent leads to a decrease of both monomers and dimers concentration due to formation of hydrogen bonded complexes



This is proved by decreasing the intensity of the $\nu$C=O bands at 1697 and 1660 cm$^{-1}$ and by the appearance of a new band near 1680 cm$^{-1}$ in the IR spectrum (Fig. 3(a)). The increase of the electron density on carbonyl group, caused by intermolecular hydrogen bonding of this type, leads to strengthening of the intramolecular H-bond and facilitates the excited state proton transfer. Correspondingly, under excess of proton-accepting additions or when using such substances as a solvent, the fluorescence spectrum reveals only the blue component. As an example, fluorescence band of SA in methylcyclohexane in presence of dimethylsulfoxide is shown in Fig. 4 (curve 2). Its position and shape is rather close to those observed in chloroform solution (compare with Fig. 2).

However, in the case of the strongest proton acceptors, aliphatic amines, a significant blue shift of the emission band (toward ~420–410 nm) was observed (Fig. 4, curve 3,4). To explain this effect, one can suggest that intermolecular ground state proton transfer takes place in SA–amine complex with formation of an ionic pair. Indeed, the IR spectrum of this system (Fig. 3(b)) reveals disappearance of the $\nu$C=O band and appearance of bands typical for salicylate anion. Nearly identical bands are present in the spectrum of tetradecylammonium salicylate solution. Hence, the fluorescence in the region 410–420 nm corresponds to emission of the anion.

It is remarkable, that a very similar band is observed in the fluorescence spectrum of water solution at pH = 6–7. The increase of pH by addition of KOH does not lead to essential spectral changes. It means that fluorescence detected in all these cases, including water solution at pH = 7, is emitted by the excited anion.

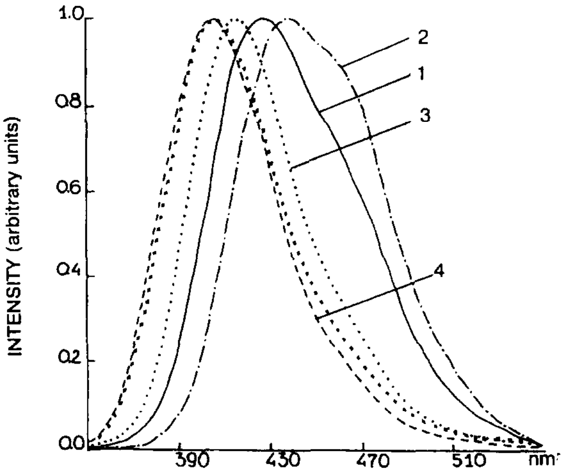


Fig. 4. Emission spectra of SA solutions ($10^{-6}$ mole $l^{-1}$) in methylcyclohexane, pure (1) and with additions of an excess of dimethylsulfoxide (2), tributylamine (3), octylamine (4); spectrum of water solution (pH ≈ 6) is shown by crosses; $\lambda_{ex}$ = 290 nm.

Such a conclusion seems unexpected since one could suppose an essential decrease of proton-donating power of SA upon excitation. Thus, the p$K_a$ value of benzoic and naphthoic acids increases from ~4 in the ground state to 10–12 in the first singlet excited state [4,19]. However, in the case of SA, intramolecular proton transfer following the excitation increases the acidity. Fluorometric titration measurements show the p$K_a$ of salicylic acid in $S_1$ excited state to be about 3.1 which is rather close to the p$K_a$ value of SA in the ground state.

5. In this connection, fluorescence spectra of SA solutions containing pyridine are of essential interest (Fig. 5). These spectra exhibit strong dependence on temperature and solvent polarity. Thus, at the room temperature, in the non-polar methylcyclohexane, the band in the region 450 nm typical for monomers or complexes with weaker acceptors is observed (Fig. 5(a), solid line). A similar band, shifted slightly to the blue direction, is observed in $CCl_4$ solution (broken line). If more polar and active chloroform or methylene chloride are used as a solvent, the band

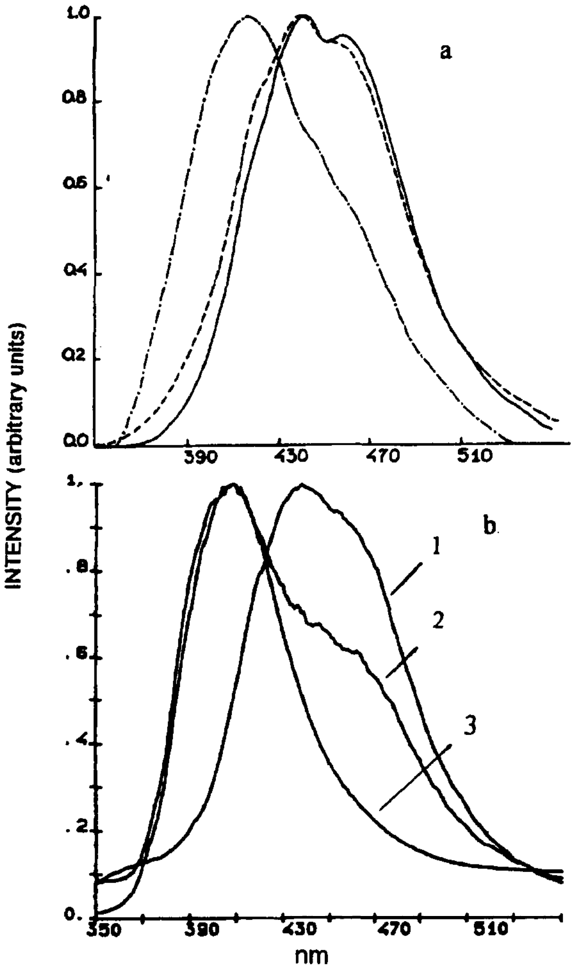


Fig. 5. Emission spectra of solutions containing SA and pyridine: (a) in methylcyclohexane (———), $CCl_4$ (- - -), chloroform (– · –), 300 K; (b) in butyl chloride at 300 K (1), 180 K (2), 80 K (3); SA/pyridine concentrations (mole $l^{-1}$): $10^{-6}/10^{-1}$ (a) and $10^{-4}/10^{-2}$ (b); $\lambda_{ex}$ = 290 nm.

reveals a significant blue shift and shape transformation which makes it rather similar to the anion-like band observed for the complexes with amines (dot-and-dash line). However, it seems that some traces of emission in 450 nm region are still present. One can suggest the existence of an equilibrium between two forms of SA–pyridine complex, with and without intermolecular proton transfer, emitting respectively in the regions close to 410 and 450 nm, the position of the equilibrium being shifted strongly to one side in methylene chloride and to the opposite side in $CCl_4$. This suggestion is confirmed by the temperature behavior of fluorescence spectrum in butyl chloride solution (Fig. 5(b)). At room temperature the usual fluorescence near 450 nm is observed. With the temperature decreasing, a doublet band appears with short wave component in the region close to the anion fluorescence. At 180 K the relative intensity of this component becomes greater. At 80 K only this emission can be observed practically.

The presence of two tautomeric forms of SA–pyridine complex with different fluorescence bands means that potential surface of the complex has two minima in at least one of two states, ground or excited, or in both of them.

According to the results of series of works [20–25], double-well proton potential and tautomeric equilibrium between molecular and ionic structures $A\text{–}H\cdots B \Leftrightarrow A^{-}\cdots H\text{–}B^{+}$ are typical for the ground state of the complexes formed by pyridine with some carboxylic acids in solutions. However, the noticeable presence of the ionic form in chloroform or methylene chloride solutions at room temperature was detected only for monohaloidoacetic and more strong acids. The systems with tautomeric equilibrium caused by fast reversible proton transfer reveal usually extremely intense and broad IR absorption corresponding to the proton stretching vibration. According to Zundel and Langner [25,26], the presence of such "continuum" absorption is a main manifestation of the double minima proton potential with low barrier. Fig. 6 shows that proton stretching band of SA–pyridine complex also is very broad and spread over the region of bending and skeletal vibrations. The intensity of absorption in the region below 1500 $cm^{-1}$ increases with increase of solvent polarity in the series, $CCl_4$, butyl chloride, methylene chloride, indicating that the intermolecular hydrogen bond becomes stronger. However, the relative intensity in this region is still weaker than in the typical systems with comparable amounts of ionic and molecular forms of the complex. No characteristic bands of salicylate anion in the $\nu C{=}O$ region are observed at the room temperature (Fig. 7(a)). Though some changes in this region take place with cooling of butyl chloride solution down to 153 K (Fig. 7(b)), the bands of anion do not appear. Thus, one can conclude that, if a molecular-ionic equilibrium in the ground state of the SA–pyridine complex really exists, it is shifted strongly in all these cases toward the

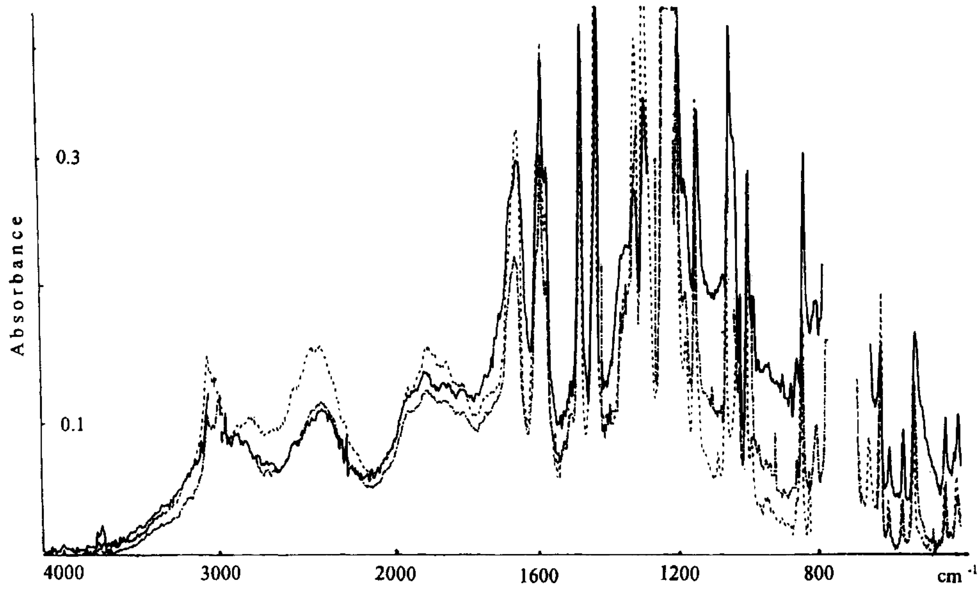


Fig. 6. IR spectra of SA (0.03 mole $l^{-1}$) + Py (0.06 mole $l^{-1}$) solutions in $CCl_4$ (- - -), $C_4H_9Cl$ (– · –) and $CH_2Cl_2$ (———).

molecular form. The potential minimum corresponding to this form seems to be much deeper. Therefore the appearance of a rather intensive anion-like component in fluorescence spectra of the same solutions can be treated as evidence of the existence of the double well potential in the excited state of the SA–pyridine complex with comparable depth of the wells corresponding to both tautomers.

## 4. Conclusions

Thus, the results of this work prove the fluorescence spectra of salicylic acid in solutions to be extremely sensitive to the character of intermolecular interaction of SA molecule with its surrounding. In diluted nonpolar or slightly polar aprotic solvents, where the SA molecule is not involved in strong intermolecular hydrogen bonding, the position and shape of the main (blue) fluorescence component are determined by the excited state intramolecular proton transfer reaction, and to some extent by the influence of another, most likely triplet, excited state lying close to $S_1$. The formation of intermolecular H-bonds with middle strength proton acceptors facilitates the ESIPT, but does not affect significantly the emission spectrum, though one can notice that such systems reveal the largest Stokes shift values. The interaction with the strongest proton acceptors, such as aliphatic amines, when the intermolecular proton transfer takes place in the ground state and the double proton transfer, intra- and intermolecular, in the excited state, results in the backward blue shift of the fluorescence band. Similar fluorescence is typical for aqueous (neutral and basic) solutions of SA. The $pK_a$ value of SA in the $S_1$ excited state turned out to be rather close to that in the ground state. The excitation of SA molecule and redistribution of the electron density connected with the excitation does not result in an increase of the $pK_a$ value due to ESIPT following the excitation. With pyridine and related N-heterocyclic molecules as acceptors, SA forms in the ground state complexes with very strong hydrogen bonds OH···N and proton position close to the intermediate, which is confirmed by presence of the broad absorption in the IR region. Such complexes exhibit emission spectrum containing simultaneously molecular-like and anion-like bands with relative intensities being strongly dependent on the temperature and solvent properties. The most probable reason for this dual emission is the molecular-ionic tautomerism caused by the existence of two minima on the excited state potential surface and the intermolecular proton migration between two positions.

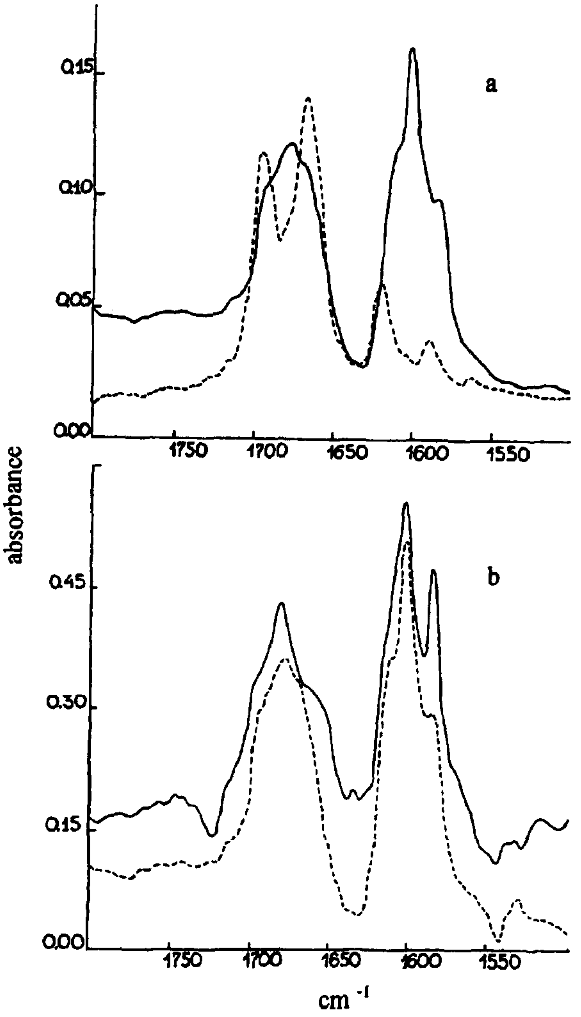


Fig. 7. IR spectra of solutions in $C_4H_9Cl$: (a) SA (0.03 mole $l^{-1}$) (- - -), SA (0.03 mole $l^{-1}$) + Py (0.06 mole $l^{-1}$) (———); (b) SA (0.03 mole $l^{-1}$) + Py (0.06 mole $l^{-1}$), 300 K (- - -), 153 K (———).

## Acknowledgements

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