

SOLVATOCHROMIC BEHAVIOUR OF THE LOW ENERGY TRANSITIONS IN THE VISIBLE REGION OF HYDROXY STYRYL PYRIDINE AND QUINOLINE ETHIODIDE DERIVATIVES

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ABSTRACT

The electronic absorption spectra of hydroxy 2-styryl pyridine and quinoline ethiodides were recorded both in organic solvents of varying polarities and in ethanol-organic solvent mixtures. The longer wavelength visible band appearing in the spectra of the compounds under investigation is assigned to intermolecular C.T. interaction. This interaction involves the interpenetration of the electron cloud of the negatively charged iodide ion into the π -electron cloud of the positively charged ring. The spectra recorded in the C.T. complex region in mixed solvents proved the formation of molecular complexes between solute and ethanol, for which the stability constant and heat of formation were determined.

INTRODUCTION

THE synthesis and spectral behaviour of the styryl derivatives of N-aryl pyridinium and quinolinium quaternary salts were investigated by several workers¹⁻⁴. Assignment of the different ultraviolet and visible bands of some substituted styryl pyridine and quinoline ethiodides was previously described by us⁵. Tandon and Bhurta^{6,7} assigned the longer wavelength, visible band of some styryl pyridine and quinoline methiodides to $n-\pi^*$ transition. Due to the wide use of the styryl pyridine and quinoline alkyl iodides in photosensitizers⁸ and in other biological applications^{9,10}, the spectra of these compounds have been studied in detail. The present communication reports the results of a spectral study of some hydroxy styryl pyridine and quinoline ethiodides in organic solvents (EtOH, CCl₄, CHCl₃) and in solvent mixtures.

EXPERIMENTAL

The compounds used in the present investigation were prepared as described previously^{1,3,4}. The products obtained were crystallized from ethanol. The compounds prepared were 2-(2'-hydroxystyryl)pyridine ethiodide (I), 2-(4'-hydroxystyryl)pyridine ethiodide (II), 2-(2'-hydroxystyryl)quinoline ethiodide (III) and 2-(4'-hydroxystyryl)quinoline ethiodide (IV).

For studying the behaviour in mixed organic solvents, the measured volume of the stock solution (10⁻³ M) was placed in a calibrated measuring flask followed by the required volume of the low polarity solvent. The mixture was then made up to the mark with the high polarity solvent.

The solvents used were purified by standard procedures¹¹. The spectra were recorded on a UNICAM S.P. 8000 spectrophotometer within the 200-700 nm range using 1 cm matched quartz cell.

RESULTS AND DISCUSSION

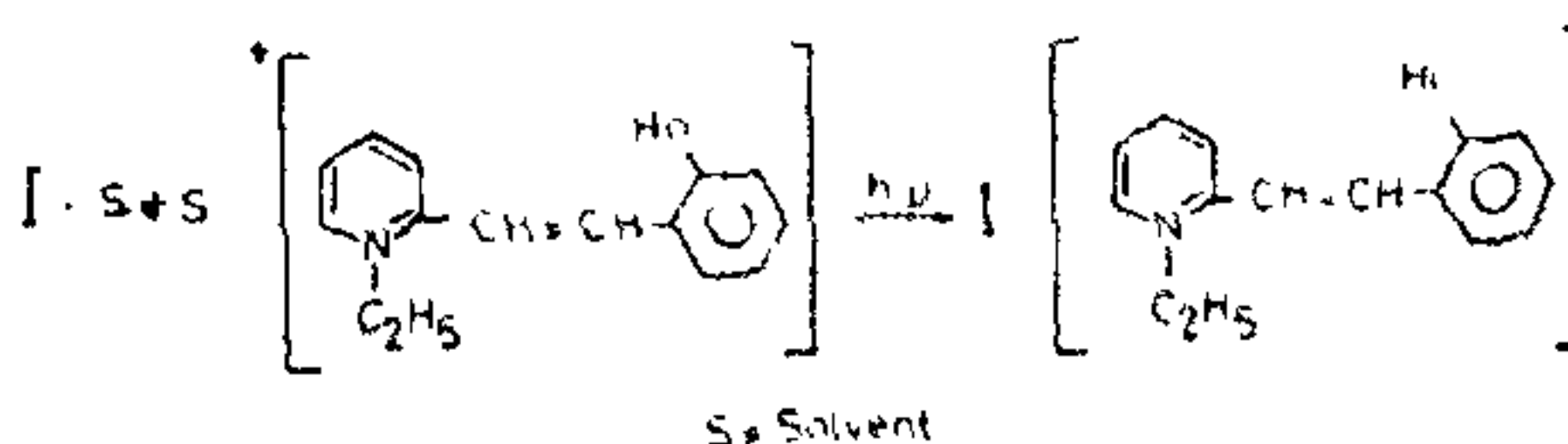
Spectra in Organic Solvents

The absorption spectra of compounds I-IV in ethanol, carbon tetrachloride and chloroform were recorded.

The ϵ_{\max} and λ_{\max} values of the visible bands observed in these organic solvents are listed in Table I.

The shorter wavelength visible band was assigned to an intramolecular charge transfer transition originating from the phenyl moiety⁵. The acceptor center is the delocalized molecular orbital on the pyridinium and quinolinium cations. In the light of the work of Kosower and co-workers¹², one can assign the longer wavelength visible band to an intermolecular charge transfer (C.T.) interaction and not to $n-\pi^*$ as previously described^{6,7}. This interaction involves the interpenetration of the electron cloud of the negatively charged iodide ion into the π -electron cloud of the positively charged hetero ring, leading to the formation of a charge transfer complex between these two ions.

Examination of the results of Table I reveals that these two bands display an apparent blue shift on changing the solvent from CHCl₃ \rightarrow CCl₄ \rightarrow ethanol (i.e., increasing Z-value). The blue shift observed for the intramolecular C.T. band can be interpreted as follows. Styryl pyridine and quinoline ethiodide derivatives exist in the ground state mainly in polar structure^{1,2}. Hence increasing the solvent polarity would result in a high stabilization of the ground state polar structure by polarization interaction forces and hence high excitation energy is required (blue shift). On the other hand, the blue shift observed in the C.T. complex band, when the solvent is changed from CHCl₃ \rightarrow CCl₄ \rightarrow ethanol, can be explained on the principle that the ground state of this transition is highly polar as shown below.



Thus increasing the solvent polarity will stabilize appreciably the ionic structure of the ground state

TABLE I

 λ_{\max} and ϵ_{\max} for the visible bands of compounds I-IV in different organic solvents

| Compound | Ethanol | | CCl ₄ | | CHCl ₃ | | Assignments |
|----------|--------------------------|-------------------------------|--------------------------|-------------------------------|--------------------------|-------------------------------|-------------|
| | λ_{\max} (nm) | $\epsilon \times 10^3$ max | λ_{\max} (nm) | $\epsilon \times 10^3$ max | λ_{\max} (nm) | $\epsilon \times 10^3$ max | |
| I | 373 | 14.7 | 380 | 15.6 | 386 | 13.8 | Intra. C.T. |
| | 500 | 2.4 | 520 | 1.5 | 525 | 1.6 | Inter. C.T. |
| II | 385 | 42.6 | 390 | 21.9 | 390 | 21.9 | Intra. C.T. |
| | 495 | 8.1 | 540 | 3.1 | 560 | 6.3 | Inter. C.T. |
| III | 393 | 25.0 | 413 | 19.4 | 413 | 25.4 | Intra. C.T. |
| | 563 | 27.2 | 615 | 10.4 | 620 | 22.8 | Inter. C.T. |
| IV | 433 | 32.8 | * | .. | 425 | 30.8 | Intra. C.T. |
| | 560 | 10.5 | .. | .. | 590 | 7.6 | Inter. C.T. |

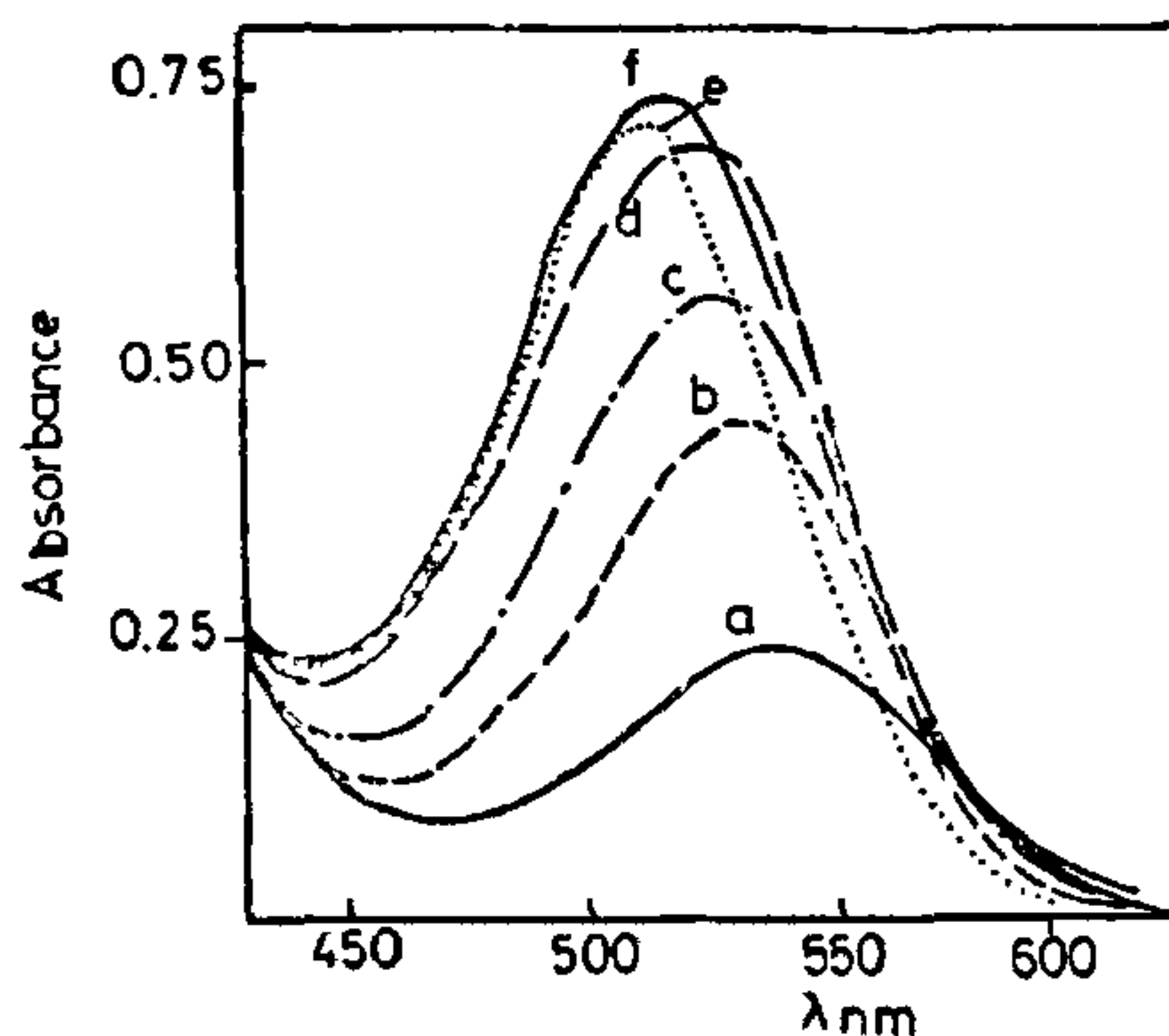
 ϵ_{\max} (mole⁻¹ cm²), * = insoluble.

FIG. 1. Spectra of 3.2×10^{-5} M of compound II in CCl₄-Ethanol mixtures. a—1.72M EtOH; b—3.43M EtOH; c—5.15M EtOH; d—6.87M EtOH; e—8.58M EtOH; f—10.3M EtOH.

through electrostatic interaction. This in turn will result in a high excitation energy and a blue shift in the λ_{\max} occurs as the Z-value of the solvent is increased. This behaviour can be considered as a strong evidence for the intermolecular C.T. transition of this band.

Spectra in Mixed Organic Solvents

The spectra in mixed solvents (Figs. 1 and 2) show a regular increase in the extinction coefficient of the longer wavelength visible band (intermolecular C.T. band) and its shift to blue takes place with the increasing proportion of the high polarity solvent.

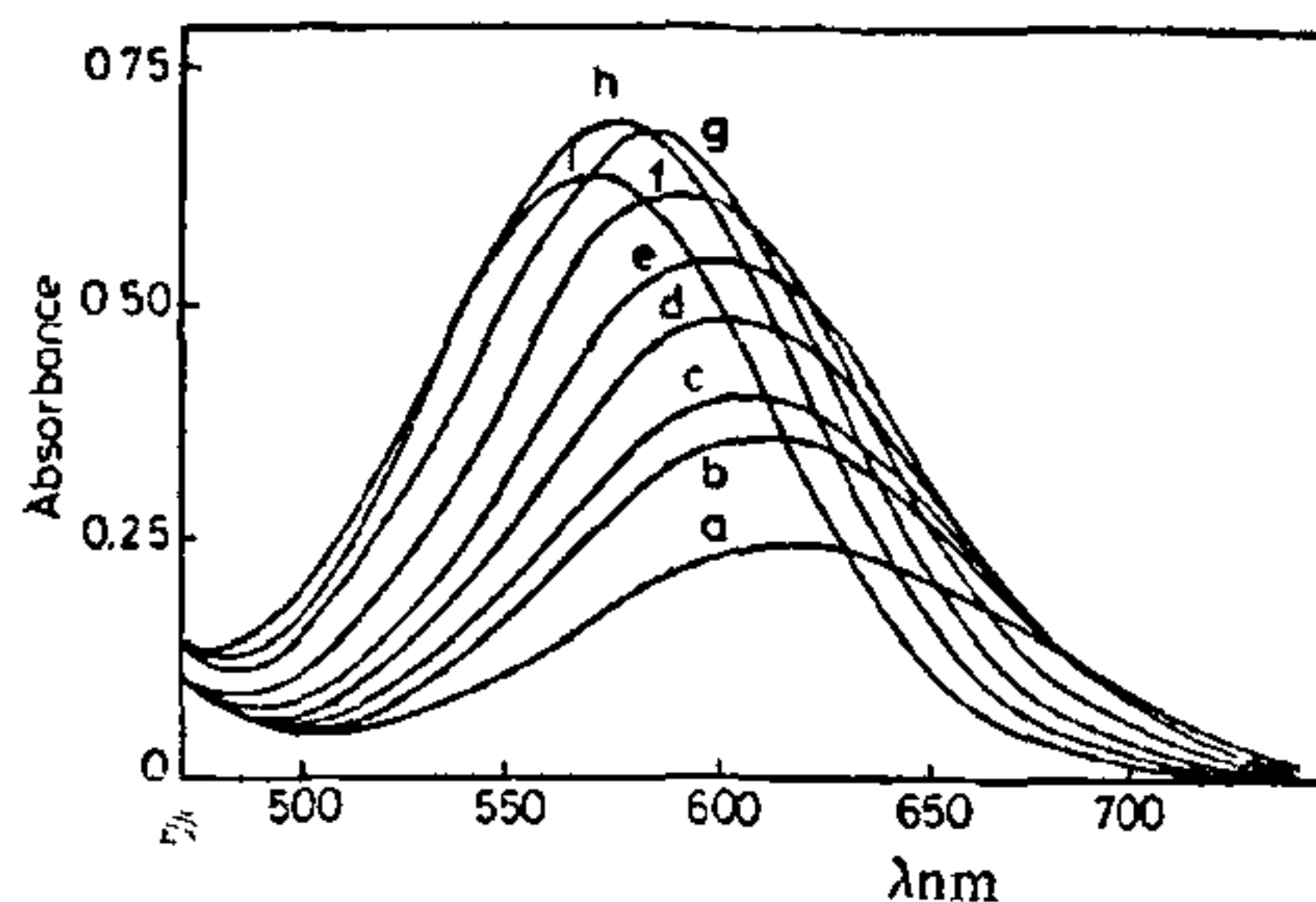


FIG. 2. Spectra of 2.46×10^{-5} M of compound III in CCl₄-Ethanol mixtures. a—0.34M EtOH; b—0.51M EtOH; c—0.69M EtOH; d—1.03M EtOH; e—1.37M EtOH; f—3.43M EtOH; g—6.87M EtOH; h—10.3M EtOH; i—13.74M EtOH.

To explain the effect of the dielectric constant (D) of the medium on band shift ($\Delta\bar{\nu}$), the relation of Gati and Szalay¹³ is used.

$$\Delta\bar{\nu} = (a - b) \left(\frac{n^2 - 1}{2n^2 + 1} \right) + b \left(\frac{D - 1}{D + 1} \right)$$

in which a and b are constants and n the refractive index of the medium.

The plot of $\Delta\bar{\nu}$ as a function of $\frac{D - 1}{D + 1}$ is a non-linear relation indicating that the band shift is governed by other factors besides the dielectric constant and the solvation energy of the medium. These factors include solute-solvent interaction through

H-bonding leading to the formation of some molecular complexes.

A support for the H-bond formation between solute molecules and ethanol can be had from the data on heat of formation (ΔG) of the molecular complex calculated by the relation :

$$\Delta G = -RT \ln K_f$$

The K_f value can be determined from a consideration of the behaviour in mixed solvents¹⁴. Thus the reaction leading to the molecular complex could be represented as follows :



for which

$$K_f = \frac{[x \dots (\text{EtOH})_n]}{[x][\text{EtOH}]^n}$$

For such an equilibrium, the following equation could be applied¹⁴:

$$\log C_{\text{EtOH}} = \frac{1}{n} \log K_f + \frac{1}{n} \log \left(\frac{A - A_0}{A_i - A} \right)$$

where A_0 = absorbance in the low polarity solvent.

A_i = limiting absorbance in the presence of excess ethanol.

A = Absorbance in the mixed solvent mixture.

The plot of $\log \frac{A - A_0}{A_i - A}$ vs. $\log C_{\text{EtOH}}$ yields a

linear relation with a slope = $\frac{1}{n}$ (n = number of

associated ethanol molecules). The value of K_f can be evaluated, since $\log K_f$ is equal to the value of $n \log C_{\text{EtOH}}$ when

$$\log \frac{A - A_0}{A_i - A} = 0.$$

The values of K_f , ΔG^* and n for some different cases are given in Table II. The results suggest that the molecular complex is formed through a weak intermolecular hydrogen bond and has the stoichiometric ratio varying from 1:1 to 1:3 depending upon both the substituent (x) and the nature of the low polarity solvent used.

TABLE II

Results obtained in mixed organic solvents

| Compound | System | n | $\log K_f$ | K_f | $-\Delta G$ K.cal/ mole |
|----------|------------------------|-----|------------|-------|-------------------------------|
| II | EtOH-CCl ₄ | 3 | 0.67 | 4.68 | 1.16 |
| III | EtOH-CCl ₄ | 1 | 0.04 | 0.11 | 0.07 |
| | EtOH-CHCl ₃ | 1 | 0.28 | 1.90 | 0.49 |
| IV | EtOH-CCl ₄ | 3 | 0.67 | 4.68 | 1.16 |
| | EtOH-CHCl ₃ | 2 | 0.57 | 3.71 | 0.99 |

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