

## SPECTROPHOTOMETRIC STUDIES ON CHARGE TRANSFER COMPLEX OF IODINE WITH MORPHOLINE

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Spectrophotometric studies on the charge transfer complexes of I<sub>2</sub>-morpholine in different organic solvents are reported. The thermodynamic and the spectral properties of the 1:1 complex formed in solution are determined. The equilibrium constant decreases as the polarizability function of the solvent increases. The data obtained suggests strong donor-acceptor interaction indicating that morpholine forms strong molecular complex with iodine via its nitrogen site.

### INTRODUCTION

Charge transfer CT, complexes between n-donors and different types of acceptors have been reviewed [1-4]. It is of interest to study charge transfer complex of morpholine (tetrahydro-1,4-oxazine) with iodine since the former is an extremely powerful solvent and has considerable uses in organic and biological chemistry. Moreover, morpholine has the chemistry of a typical secondary amine [5].

### EXPERIMENTAL

Pure morpholine (BDH) b.p. 128 ° was used. Solvents were of optically pure grade (BDH). However, the solvents used are chosen on the basis of their supposed interest toward iodine to avoid the complications arising from iodine-solvent interaction (i.e. the formation of CT complexes between I<sub>2</sub> and solvents). Iodine was of analytical grade.

A Pye-Unicam SP 1800 spectrophotometer equipped with temperature regulated cell holder was employed for the measurements.

For all the equilibrium constant determinations, a series of six to eight solutions with iodine concentration ( $7.8 \times 10^{-4}$  M) and variable morpholine concentrations (from  $8.0 \times 10^{-4}$  M to  $9 \times 10^{-3}$  M) were used. These determinations were carried out at four temperatures, 25, 30, 37 and 43 ° ± 0.2 and in the four different solvents, Table 1.

Liptay method [6] was used for the computation of the equilibrium constant of the 1:1 complex of morpholine with iodine using absorbance data determined at four wavelengths; 390, 400, 410 and 420 nm. A correction for the absorption of iodine over this wavelength range was made.

The thermodynamic functions,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the studied CT complex as a function of solvent were evaluated from the plot of  $\ln K$  versus  $1/T$ .

### RESULTS AND DISCUSSION

Fig. 1 represents the variation of the visible absorption spectrum of iodine solution with different morpholine concentration in CCl<sub>4</sub> at 30°. When iodine is added to morpholine, two pronounced changes in the spectrum occur. A blue shift is detected in the iodine peak and a new band arises in the ultraviolet region which is due to charge transfer transition. The existence of a sharp isos-

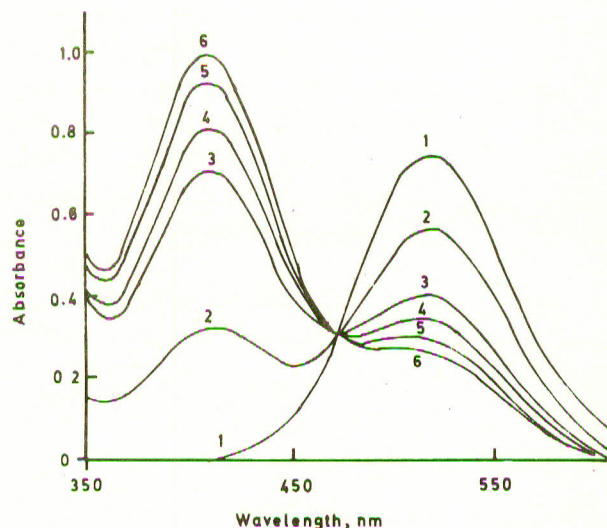


Fig. 1. The variation of visible absorption spectrum of (1) I<sub>2</sub> solution in CCl<sub>4</sub> ( $7.8 \times 10^{-4}$  M) and the same I<sub>2</sub> conc with variable morpholine conc (2)  $8 \times 10^{-4}$  M (3)  $1 \times 10^{-3}$  M, (4)  $4 \times 10^{-3}$  M, (5)  $7 \times 10^{-3}$  M and (6)  $9 \times 10^{-3}$  M.



bestic point indicates that there are only two absorbing species in the system; namely free iodine and shifted (complexed) iodine. Similar observations are obtained in the other solvents and at different temperatures.

Using Job's method [7], the stoichiometry of the formed complex is determined. A maximum absorbance value is obtained at 0.5 mole fraction ( $I_2$ -morpholine) indicating a 1:1 complex composition.

In addition to the traditional Job's method the method of Coleman, Varga and Mastin [8] is used to demonstrate that only one complex species is present in solution. For a series of solutions the absorbance at one wavelength is plotted versus the absorbance at each other wavelength under study (wavelength range 390-420 nm). A set of lines radiating from the origin is obtained indicating the existence of a single complex species.

The obtained spectral data are summarised in Table 1. Upon complexation, the iodine band is strongly blue shifted reflecting strong donor-acceptor interaction. This blue shift of the iodine band,  $\Delta \bar{\nu}_{I_2}$ , was found to decrease with increasing  $f(n)$  of the solvent, but is not correlated with  $E_T$  value [9] or dielectric constant functions of the solvents. Moreover, the calculated  $\epsilon_{max}$  generally decreases and  $\lambda_{CT}$  slightly increases as solvent polarisability function

Table 1. Spectroscopic data for the CT complex of  $I_2$ -morpholine system in different solvents.

Solvent	$f(n)^*$	$\lambda_{CT}$ nm	$\epsilon_{max}$ $\text{L.mol}^{-1}\text{cm}^{-1}$	$\Delta \bar{\nu}_{I_2}$ $\text{cm}^{-1}$
$\text{CH}_2\text{Cl}_2$	0.255	298	3090	6493
Cyclohexane	0.256	298	2280	4562
$\text{CHCl}_3$	0.265	304	2400	5200
$\text{CCl}_4$	0.274	304	2100	5100

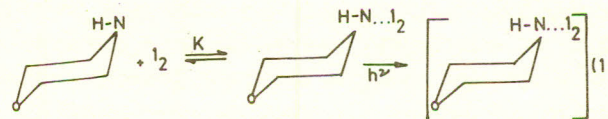
\* $f(n) = (n^2 - 1)/2n^2 + 2$ , where  $n$  = refractive index

Table 2. Thermodynamic data for  $I_2$ -morpholine complexes.

Solvent	$K, 30^\circ$ $\text{L.mol}^{-1}$	$E_T$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$ e.u.	$b^2/a^2$
		$\text{Kcal mol}^{-1}$				
$\text{CH}_2\text{Cl}_2$	1249	41.1	$11.0 \pm 0.6$	4.1	15.0	0.12
Cyclohexane	939	31.2	$12.3 \pm 0.5$	3.9	12.6	0.13
$\text{CHCl}_3$	539	39.1	$10.1 \pm 0.6$	3.6	13.0	0.11
$\text{CCl}_4$	264	32.5	$9.8 \pm 0.6$	3.2	9.2	0.10

increases. It has been shown that  $\lambda_{CT}$  in non polar solvents should suffer a red shift as the refractive index of the medium increases [3]. These shifts should be small owing to the small range of solvent refractive indices. That data of Table 1 confirms this prediction. However, there are several types of solute-solvent interactions which may be classified as general electrostatic solvent effects [3]. Moreover, where present, specific interactions such as hydrogen bonding or solvent-cage compression effects on the solute are likely to dominate solvent-solute interactions. On the basis of compression of the complex by the solvent, the results obtained can be qualitatively explained. It can be assumed that, as the polarizability function increases, solvent cavity tends to increase, therefore the complex will be less compressed by the solvent and the intermolecular distance between donor and acceptor will be increased. This results in smaller exchange repulsion and hence a decrease in  $\Delta \bar{\nu}_{I_2}$ . Also orbital overlap will decrease with consequent decrease in intensity [2].

Using the same argument, the apparent equilibrium constant according to equation (1), in different solvents, Table 2, could be reasonably explained.



Strong interaction between iodine and morpholine has been indicated by the high value of the ratio  $b^2/a^2$  10, calculated using equation (2)

$$b^2/a^2 \approx -\Delta H/h \lambda_{CT} \quad (2)$$

where (b) and (a) are the coefficients of the dative-bond function ( $\psi_1$  (donor<sup>+</sup>-acceptor<sup>-</sup>)) and of no-bond function  $\psi_0$  (donor-acceptor) which are linearly combined to give the eigen-function of the ground state of the complex  $\psi_N$ , equation (3).



$$\Psi_N = a \Psi_0(D-A) + b \Psi_1(D^+ - A) \quad (3)$$

On comparing the obtained K values with those of 1-4, dioxan-I<sub>2</sub> (K=1.01 mol<sup>-1</sup> at 25°)[4] and dimethylamine-I<sub>2</sub> (K=6800 I mol<sup>-1</sup> at 25°) [11], it was concluded that the bonding is predominantly through the nitrogen site of morpholine with lesser extent than secondary amine presumably due to steric hinderence of the morpholine ring.

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