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Spectrophotometric Study of the Interaction of 4,6-Diamino-2-Methyl Mercaptopyrimidine with Iodine and Iodine-Monochloride

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The interactions of 4,6-diamino-2-methyl mercaptopyrimidine with iodine and iodine-monochloride have been studied with visible spectrophotometric method. Charge transfer complexes are formed between the components, as is evident from the appearance of a new band in the spectrum. The stability constants of the C.T. complexes in different solvents (single and mixed) have been determined by utilizing he Benesi-Hildebrand equation. The variations in the stability constants though cannot be properly interpreted, can be attributed to the dielectric constants of the medium.

Key Words : Spectrophotometric study, Charge transfer complex, Stability constants.

INTRODUCTION

The charge-transfer complexes are formed as a result of weak interactions of electron donors with electron acceptors. During the past couple of decades, lots of work on such complexes has been done and reported[1, 2]. The formation of C.T. complexes is indicated by an electronic absorption extra to the absorption of the donor or acceptor. Very often change of colour occurs due to the formation of CT complexes. Such complexes have been isolated and studied[3–5] qualitatively and quantitatively. In the present study the interactions of 4,6-diamino-2-methyl mercaptopyrimidine (DMMP) with iodine and iodine monochloride in single and mixed solvents have been studied spectrophotometrically. The study is confined to the determination of the formation constant (or the stability constant) of the CT complex and the influence of the solvent on the formation constant at varied temperature. It appears from the structural formula of the DMMP, the N-atoms of the amine groups and the sulphur atom may act as donors and also the aromatic ring itself may act as a π-donor.

EXPERIMENTAL

The DMMP (Sigma) was used as such without further purification. Iodine (E. Merck) was resublimed. Iodine monochloride (E. Merck) and iodine were stored over anhydrous $CaCl_2$ in a desiccator and were used without further purification.

Chloroform (BDH), Methyl chloride (E. Merck), 1,2-dichloroethane (BDH) were purified by the usual methods[6].

A stock solution of DMMP of concentration $\approx 4.5 \times 10^{-3}$ M was prepared with a solvent. Another solution of iodine/iodine monochloride, having the concentration $\approx 2 \times 10^{-3}$ M was prepared with the same solvent. Then a series of solutions

with a fixed concentration of iodine/iodine monochloride and varying concentration of DMMP were prepared in 10 mL volumetric flasks.

Absorption spectra were recorded on Shimadzu Model UV 240 spectrophotometer with temperature regulated cell holder. A match pair of stoppered quartz cells of 1 cm path length was used. All spectra were recorded with freshly prepared solution.

For IR study, the CT complex of DMMP and iodine monochloride was isolated from chloroform solutions of the components at nearly 0°C temperature. The yellow solid obtained was recrystallised from chloroform. The IR spectra were recorded with Perkin-Elmer 883 spectrophotometer.

The amount of iodine present in a definite amount of the DMMP-ICl charge-transfer complex has been estimated by standard method.

RESULTS AND DISCUSSION

The formation of CT complexes between DMMP and iodine and between

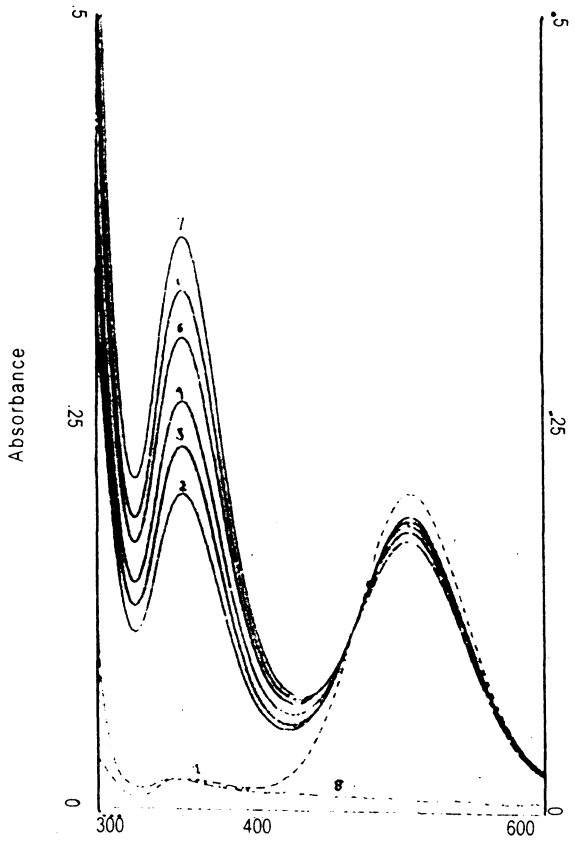

Fig. 1. The absorption spectra of iodine DMMP complex in chloroform at 20°C (1 cm cell). Concentration of iodine 2×10^{-4} M and concentration of DMMP (M) : (1) 0.0, (2) 13.5×10^{-4} (3) 18×10^{-4}, (4) 22.5×10^{-4}, (5) 27×10^{-4}, (6) 31.5×10^{-4}, (7) 36×10^{-4}. The curve (8) represents the spectra of DMMP of concentration 4.5×10^{-3} M

DMMP and iodine monochloride have been revealed by the appearance of new bands near 350 nm and 291 nm respectively. There is no absorption band in the spectrum of either DMMP or iodine or iodine monochloride in these regions. Iodine and ICl show broad absorption peaks around 496 nm and 344 nm respectively (Figs. 1 and 2).

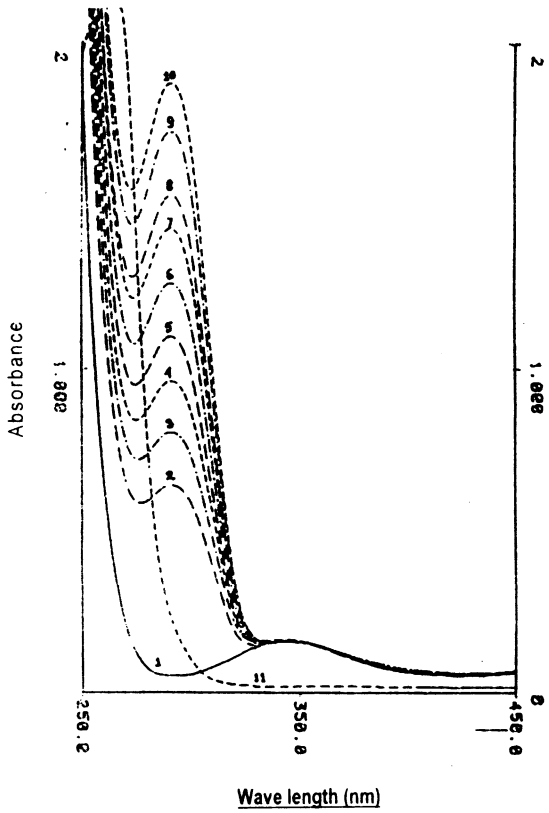

Fig. 2. The absorption spectra of iodine monochloride DMMP complex in chloroform at 25°C (1 cm cell). Concentration of iodine monochloride 2×10^{-4} M and concentration of DMMP M : (1) 0.0, (2) 2×10^{-4} (3) 2.5×10^{-4}, (4) 3×10^{-4}, (5) 3.5×10^{-4}, (6) 4×10^{-4}, (7) 4.5×10^{-4}, (8) 5×10^{-4}, (9) 5.5×10^{-4}, (10) 6×10^{-4}, The curve (11) represents the spectra of DMMP of concentration 4×10^{-4} M

The stability constants (K_{CT}) of the CT complexes has been calculated by using the Benesi-Hildebrand equation

$$\frac{[A]_0}{d} = \frac{1}{K_{CT}\varepsilon_{AD}} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_{AD}}$$

where $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and the donor, d is the absorbance of the complex, ε_{AD} is the molar extinction co-efficient of the complex AD. The values of K_{CT} obtained at different temperature and in different solvents are reported in Table-1.

TABLE-1
VALUES OF K_{CT} OF CT-COMPLEXES

Solvents	Dielectric constants	K_{CT} of DMMP + I_2 complex		K_{CT} of DMMP + ICl complex	
		25°C	35°C	25°C	35°C
1. Chloroform	4.7	210	163	520	470
2. Methylene chloride	8.9	458	418	402	390
3. 1,2-Dichloroethane	10.3	583	495	460	425
4. Chloroform and methylene chloride (1 : 1)	—	245	210	485	430
5. Chloroform and 1,2-dichloroethane (1 : 1)	—	252	230	523	495

(K_{CT} in $dm^3\ mol^{-1}$)

The results show that the complexes are less stable at high temperature. The variation of the stability constants in different solvents and mixed solvents has also been observed. It appears that the stability of the CT complexes increases with the increase in the dielectric constant of the solvent. However, there are some discrepancies.

The solid CT complex of DMMP and iodine monochloride has been isolated; but the attempts to isolate the solid CT complex of DMMP and iodine have failed. The IR spectrum of the purified sample of DMMP-ICl complex and pure DMMP have been recorded (Figs. 3 and 4). A comparison of the band positions of the IR spectra

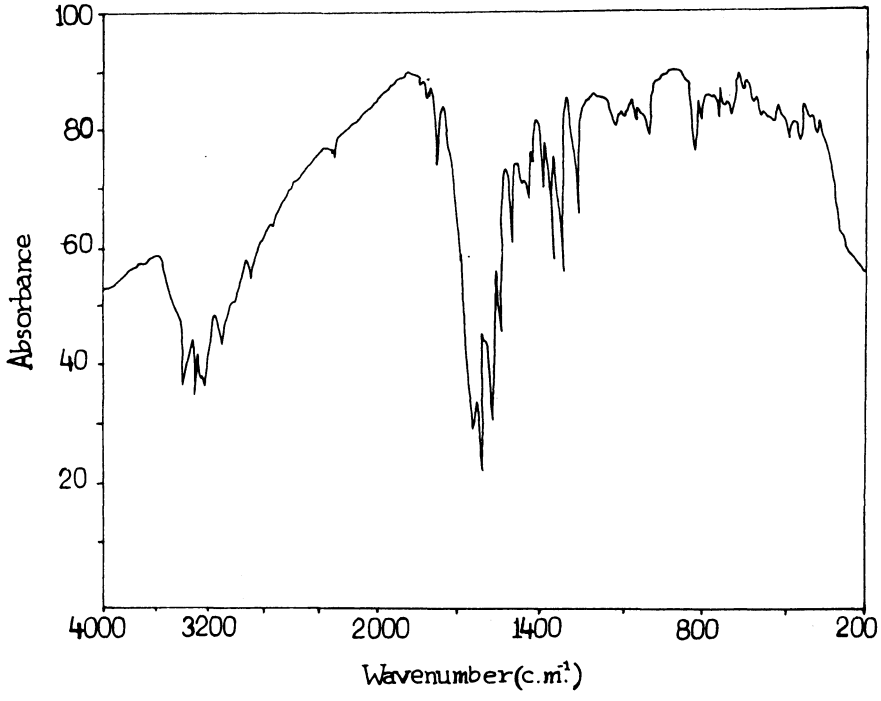

Fig. 3. IR spectra of DMMP-ICl complex

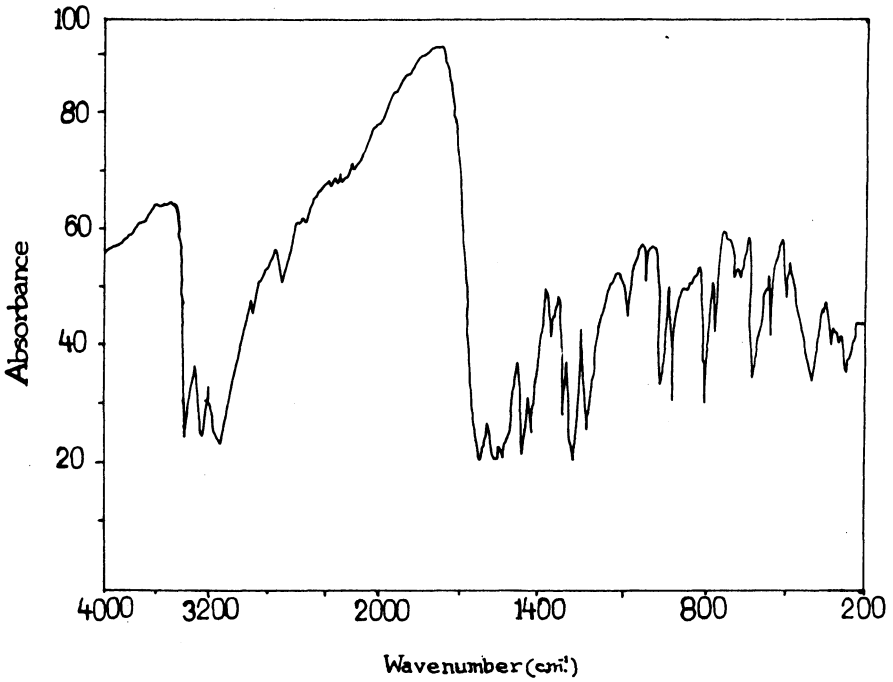

Fig. 4. IR spectra of pure DMMP

of DMMP and the C.T. complex has revealed that there are shifts in the positions of the bands due to N—H bending and N—H stretching vibrations. The positions of the bands at 1610 cm^{-1} due to N—H bending and at 3120 cm^{-1} due to N—H symmetric stretching and 3240 cm^{-1} due to N—H asymmetric stretching vibrations in the spectrum of DMMP have been shifted to 1640, 3240 and 3300 cm^{-1} respectively in the spectrum of the DMMP-ICl complex. These shifts indicate that the two NH_2 groups of the DMMP act as donor to form the C.T. complex with ICl.

A quantitative study of the DMMP-ICl complex has been carried out gravimetrically. A measured quantity of the complex has been dissolved in chloroform and then aqueous solution of $AgNO_3$ (A.R.) has been added until all the halides have been quantitatively precipitated. The precipitate of halides has been filtered through previously weighed sintered glass crucible and dried in a desiccator. From the results it appears that DMMP forms complex with ICl in the ratio 1 : 2.

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