

Solid State Electronic Spectral Studies of Glycine-Halogen Charge Transfer Complexes

S.K. BARUAH

Department of Chemistry

Dibrugarh University, Dibrugarh-786 004, India

The electronic absorption studies have been made of the interaction between glycine and halogens (iodine, iodine-chloride and iodine-bromide) in solid states. It has been observed that glycine acts as a polar donor and probably ionizes the halogen molecule as $(\text{glycine})_n + 2\text{I}_2 \rightleftharpoons (\text{glycine}_n \text{I}^+) + \text{I}_3^-$ where $n = 1, 2, \dots$. The bands at *ca.* 294 and *ca.* 363 nm give the evidence of the formation of triiodide negative ion in case of glycine-iodine interaction. Similarly for iodine-chloride and iodine-bromide complexes, evidences for the formation of ICl_2^- and IBr_2^- have also been observed.

The formation constant (K) between glycine and iodine in methanol-water mixed solvent has been found to be 1.446 and 2.138. The K-values for *ca.* 292 and *ca.* 350 nm bands indicate the formation of 1 : 1 complexes. The free energy changes have been found to be -4.457 and -4.464 kcal/mol.

Key Words: Electronic spectral studies, Glycine, Halogens, Charge transfer complexes.

INTRODUCTION

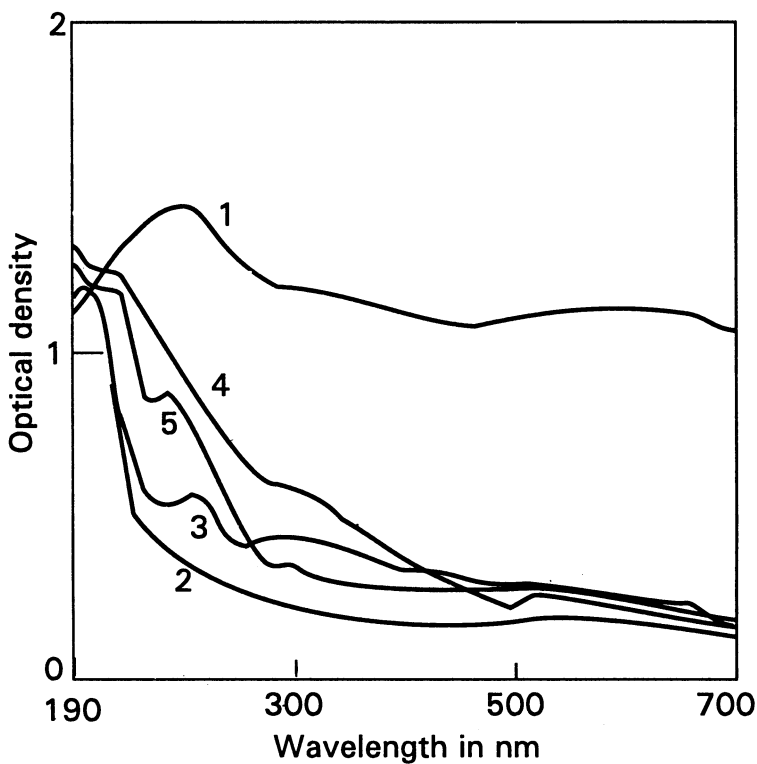
It was observed previously that amino acids and proteins are good electron donors^{1,2}. Slifkin² has suggested that the complexes of amino acids and proteins with iodine are in the form of [amino acids I⁺] or [proteins I⁺] in solution. The solution of iodine in water gives in two absorption bands at 353 and 287 nm, which are characteristic of the formation of triiodide negative ion³.

The interaction between glycine and iodine, iodine chloride and iodine-bromide have been discussed here in solid state. The individual components were mixed qualitatively and the UV and visible absorption spectra were recorded. From the spectra of glycine and iodine mixture, two distinct absorption peaks are observed, which may be characterized as triiodide negative ions. These two peaks are also observed in solution of glycine-iodine in methanol and water mixed solvent. Iodine bromide and iodine chloride also show that bands for ICl_2^- and IBr_2^- with glycine. The formation constant (K) has been evaluated using Bensi-Hildebrand method⁴. Further, the molar extinction coefficient and free energy change have also been calculated.

EXPERIMENTAL

Iodine, iodine chloride and iodine bromide have been purified as described⁵. Methanol was distilled under reduced pressure. Deionized water was obtained by distilling distilled water. Glycine was purified by recrystallization from warm distilled water.

The finely powdered glycine was mixed with iodine, iodine-chloride and iodine-bromide individually and kept over a desiccator. The UV and visible spectra were recorded of the above three mixtures on a computer controlled UV-visible spectrophotometer (Shimadzu UV 240) of wavelength range 190 nm–900 nm. The positions of the bands have been recorded (Fig. 1).



To study the glycine-iodine mixture in solution, a mixed solvent of methanol-water in 1 : 1 ratio has been prepared and two solutions of 10^{-2} (M) glycine and 10^{-3} (M) iodine were prepared in this solvent. A series of solutions were prepared by mixing the two solutions and the absorption spectra were recorded (Table 1 and 2).

TABLE-1
EVALUTION OF K AND ϵ_c FROM B-H EQUATION AT 292 nm

Path Length, $l = 1$ cm, Acceptor Concentration $[A] = 5 \times 10^{-4}$ mol/L, Temperature = 20°C

A_{obs} (optical density)	$[A]/A_{\text{obs}}$ (mol/L $\times 10^{-4}$)	D (mol/ L $\times 10^{-3}$)	$1/[D] \times 10^3$	K from the graph	ϵ_c from the graph	$G = -RT$ $\ln k$ (kcal/mol)
2.00	2.500	5	0.20			
1.93	2.590	4	0.25			
1.89	2.654	3	0.33			
1.78	2.806	2	0.50	1.446	4255	-4.457
1.63	3.070	1.5	0.67			
1.50	3.330	1	1			

TABLE-2
EVALUTION OF K AND ϵ_c FROM B-H EQUATION AT 350 nm

Path Length $l = 1$ cm; Acceptor Concentration $[a] = 5 \times 10^{-4}$ mol/L; Temperature = 20°C

A_{obs} (optical density)	$[A]/A_{\text{obs}}$ (mol/L $\times 10^{-4}$)	D (mol/ L $\times 10^{-3}$)	$1/[D] \times 10^3$	K from the graph	ϵ_c from the graph	$G = -RT$ $\ln k$ (kcal/mol)
1.29	3.875	5.0	0.20			
1.23	4.055	4.0	0.25			
1.21	4.130	3.0	0.33			
1.11	4.500	2.0	0.50	2.138	2702	-4.464
1.025	4.875	1.5	0.67			
0.95	5.260	1.0	1.00			

RESULTS AND DISCUSSION

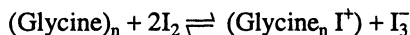
From the spectra (Fig. 1) it is observed that solid iodine has an intense peak at *ca.* 245 nm and a broad band at *ca.* 650 nm. The solid glycine has no characteristic absorption band in this region. But for glycine-iodine two distinct bands at *ca.* 294 and *ca.* 363 nm have been observed.

The absorption spectrum of chloranil in acetic acid is similar to the spectrum of chloranil in different inert solvents⁶. On the other hand, the absorption spectra of various chloranil-amino compound mixtures are similar to those of the amino acid-chloranil and proteins-chloranil mixtures. It is concluded that the amino groups in the amino acids and proteins form $n-\pi$ charge transfer complex is probably due to lone pair electrons from the nitrogen atom in the amino group being donated to the chloranil¹.

Lupinski⁷ suggested a scheme for the Beta carotene ($C_{40}H_{56}$) iodine interaction, where triiodide negative ion and a C-T complex ($C_{40}H_{56}I^+$) are formed with an excited state ($C_{40}H_{56}I^+$). The triiodide negative ion has characteristic absorption peak⁸ at 353 nm and 287 nm. From the interaction between iodine and water it was also suggested that I_3^- ion is responsible for the appearance of these bands³ at 351 nm and 287 nm.

The bands at *ca.* 294 nm and *ca.* 363 nm obtained for glycine-iodine mixture

thus may be assigned due to formation of triiodide negative ion. In this case glycine acts as a polar donor like other polar solvents and even in absence of any solvent glycine may ionise the iodine molecule to give triiodide negative ion as follows:



where

$$n \rightarrow 1, 2, \dots$$

The red shifted bands for I_3^- ions have been obtained, probably due to the less polar nature of glycine in solid state.

Similarly glycine-iodine chloride shows three weak bands at about 310 nm, 280 nm and 210 nm and for glycine-iodine-bromide shows three bands at about 450 nm and 370 nm and 205 nm. All these bands may be assigned due to the formation of triiodide ions⁹. Thus it may be concluded that glycine-halogen charge transfer interaction is possible in solid state also.

The absorption spectra were recorded for glycine-iodine mixture in methanol-water solvent. The spectral studies of the bands are done at 292 nm and 350 nm only. These two bands are due to I_3^- ion. The values of K at 292 nm and 350 nm are found to be 1.446 and 2.138 from B-H plot (Fig. 2) indicating that 1 : 1 charge transfer complex formation has taken place.

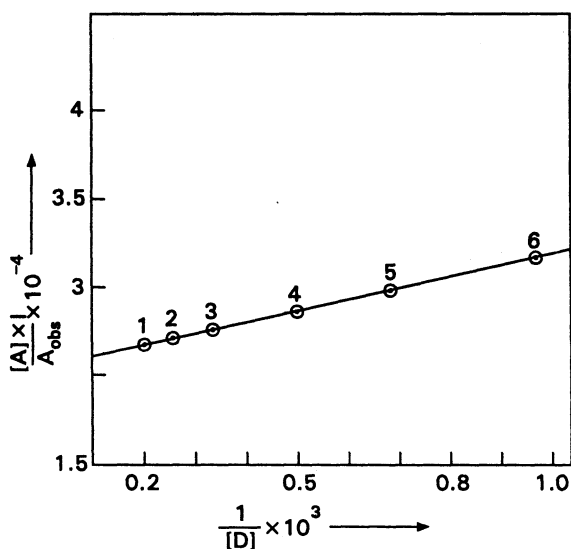


Fig. 2. B-H plot of $[A]/A_{\text{obs}}$ vs. $1/[D]$ at 292 nm

The higher value of K suggests the strong donor-acceptor interaction between glycine and halogens. The charge-transfer interactions of methanol-iodine and water- I_2 are considerably low because they also contribute to the formation of triiodide negative ions.

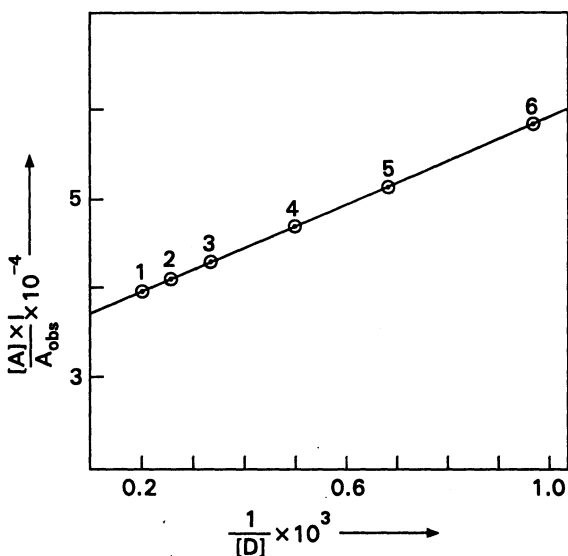


Fig. 3. B-H plot of $[A]/A_{\text{obs}}$ vs. $1/[D]$ at 350 nm

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