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DETERMINATION OF FORMATION CONSTANT OF PARAQUAT(PQ) WITH ORGANIC DONORS CT COMPLEXES IN SDS MEDIUM

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ABSTRACT

Molecular complexes of Paraquat (PQ) with a few Organic donors *viz. p-hydroxy Phenyl hydrazone p-chloro Phenyl hydrazone and m-methyl Aniline* in Sodium Dodecyl Sulfate (SDS) micellar medium have been studied spectrophotometrically. The entire complexes exhibit one charge transfer band each in the region where neither of the components has any absorption. The formation constants of the complexes have been determined by using Fronasiero and Grieser method. The extinction coefficients (ε) and apparent formation constant of CT complexes have been determined by Rose-Drago method. The positions of the CT-Bands in surfactant (SDS) are close to those of the CT-Bands in methanol. The substituents in donor produced changes in the positions in the CT-Bands.

KEYWORDS: Paraquat, Sodium Dodecyl Sulfate (SDS), Micellar Medium, p-hydroxy Phenyl hydrazone, p-chloro Phenyl hydrazone and p-methyl Aniline.

1. INTRODUCTION

Paraquat (PQ) is an important biologically active molecule. It was proved to be an herbicide and a weedicide either independently or mixed with other activating compounds. It is a chief component in the commercial herbicides (Grammaxone and weedol). Paraquat is a di-cation and possesses a strong electron acceptor character with an electron affinity.[1] 1.24 eV. Although the biological activity of paraquat is known for a long time, its property of forming CT complexes, for the first time, was reported by Nakahara and Wang[2], using inorganic anions and anionic metal complexes as donors.[3-6] Later, the electron donor-acceptor interaction between some neutral organic donors and paraquat has been carried out by White.[1] Subsequently paraquat attracted the attention of many researchers in the field of molecular complexes and it has been shown to form CT complexes with a variety of electron donors.[7-14] The CT complexes of anilines, phenyl hydrazones, crown ethers, phenolates and purinates with PQ have already been reported.[15,16] For the study of CT interaction of substituted naphthylamine and praquat in SDS medium, Bertholoti *et.al*[17] found that paraquat strongly bind to SDS. The micelle bound PQ forms CT complexes with naphthylamine. Mortens and Verhoeven[18] studied the interaction of PQ with 3-methyl indole and pyrene in methanol and aqueous SDS media. Continuing our studies on organic donors in SDS micellar medium, PQ as an acceptor has been tested for the formation of CT complexes. The successful results of study are reported in the present paper.

2. EXPERIMENTAL PROCEDURE

Paraquat dichloride was prepared by the dimerisation of pyridine to 4,4’-bipyridyl, followed by quarternization with methyl chloride and isolation as the dehydrate.[1] Alternatively PQ dichloride was extracted from the commercial herbicide (Grammaxone) by repeated recrystallization from water, ethanol and ethanol-acetone mixture. The concentration of PQ was varied from 0.002M to 0.01 M, while those of organic donors were kept constant at 0.003M. The concentration of SDS micellar medium solutions was varied from 0.02M to 0.1M. The observed optical densities were in the range of 0.1 to 1.3 absorbance units. The absorption bands due to acceptor or donor individually have fallen to the base line much more before the wavelength of CT absorption.

The apparent formation constant (K_{App}) of the CT complexes were determined by varying the concentration of paraquat while the concentration of given donor was held constant in a fixed concentrated SDS micellar medium by using Rose-Drago[19] method, The absorbance data is used to determine the apparent formation constants (K_{App}).

$$K^{-1} = (d/\varepsilon) - ([Do] + [Ao]) + [Do]\,[Ao]\,\varepsilon/d$$

Where d is the absorption; ε, the molar extinction coefficient of the complex; [Ao] and [Do] are the initial concentrations of acceptor and donor respectively.

However micellar volume independent formation constants (K_{CT}) have also been calculated from the relation foot forwarded by Fornasiero and Grieser

$K_{CT}=K_{app} \times V_m/V_0$

$V_m= V_0[D_m]\,\overline{V}$

$K_{CT}= K_{app}.\overline{V}\,[D_m]$

Where K_{CT} is a micellar volume independent formation constant or stability constants in micellar pseudophase. K_{app} is apparent formation constant (stability constant) V_m is the micellar volume of the system, V_0 is the total volume of the system (Volume of the surfactant and water).$\overline{V}=0.14M^{-1}$ is a molar micellar volume.[20,21] and $[D_m]$ mecellized detergent concentration.

3. RESULTS AND DISCUSSION

Colorless solution of Paraquat(0.002M to 0.01M) in aqueous SDS solution produced characteristic color when a small volume(1ml) of solution of donor(0.003M) was introduced by syringe substituted donors are also produced colors when introduced in to SDS bound PQ solution the colors of the solutions are comparable to those of PQ donor in methanol. Colorization was not observed when donors are introduced in to simple SDS solution without PQ the color changes in the system are therefore attributed to the formation of CT complexes between PQ and donor in micellar pseudo phase. Each of the solution exhibited in an absorption band characteristic of CT complexes (Fig-1). The positions in the CT bands in the SDS pseudophase are close to those of CT bands in methanol. The substituents in the donors produce changes in the positions of the CT bands which are parallel to those observed in methanol. Hence the effect of substituents may be explained by mesomeric and inductive effects of substituents. The position of CT bands (λ_{CT}) of donors with PQ is found to be in the following order:

p-hydroxy Phenylhydrazone > *p*-chloro Phenylhydrazone > *m*-methyl Aniline.

3.1 Formation constants of CT complexes

The apparent formation constant (K_{App}) of the CT complexes were determined by varying the concentration of paraquat while the concentration of given donor was held constant in a fixed concentrated SDS micellar medium by using Rose-Drago[19] (Fig-2) method. The absorbance data is used to determine the apparent formation constants (K_{App}) Table-1. The same procedure is adapted to determine the stability constants of varies concentrations of SDS ranging from 0.02M to 0.1M The apparent stability constants observed in SDS are 100 to 1000 folds greater than those in methanol. The enormous increase in the stabilities of the complexes in the SDS may be attributed to increase in local concentrations of the components in micellar pseudophase (Table-2) As there is a not much change observed either in λ_{CT} or in the ε, we infer the remarkably high stabilities of the complexes to the changes in the local concentrations of the components of the micellar medium.

Table-1: Absorbance at varies acceptor concentrations and apparent formation constants of PQ-Organic donors *(p-hydroxy phenyl hydrazone)* CT complexes in SDS solution ($[D_0]$ = 0.003 mol.lit-1, λ_{max}CT= 518nm).

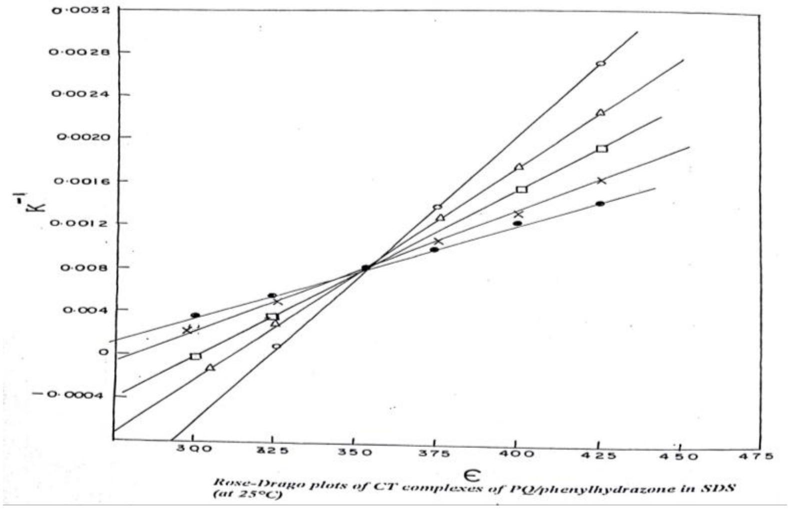
$[A_0]$ mol.lit^{-1} →	0.002	0.004	0.006	0.008	0.01	K_{app}	ε
Concentration of SDS ↓ (mol.lit^{-1})	Absorbance					(lit.mol^{-1})	(lit.mol^{-1}.cm^{-1})
0.02	0.46	0.72	0.85	0.91	0.95	1052	370
0.04	0.36	0.59	0.72	0.82	0.85	512	365
0.06	0.30	0.50	0.63	0.72	0.78	338	362
0.08	0.26	0.44	0.56	0.66	0.71	253	358
0.1	0.23	0.40	0.53	0.60	0.67	202	355

Table-2: CT Spectra and Stabilities of the PQ- Organic donors complexes in SDS.

Sl.no	Substituent	λ_{max} (nm)	ε_{max}	K_{CT}	K_{app}				
					Concentration of SDS (mol.lit^{-1})				
					0.02	0.04	0.06	0.08	0.1
1	*p-hydroxy Phenyl hydrazone*	522	360	2.80	526	256	169	126	101
2	*p-choloro Phenylhydrazone*	518	370	1.40	1052	512	338	253	202
3	*m-methyl Aniline*	435	435	2	751	366	242	180	144

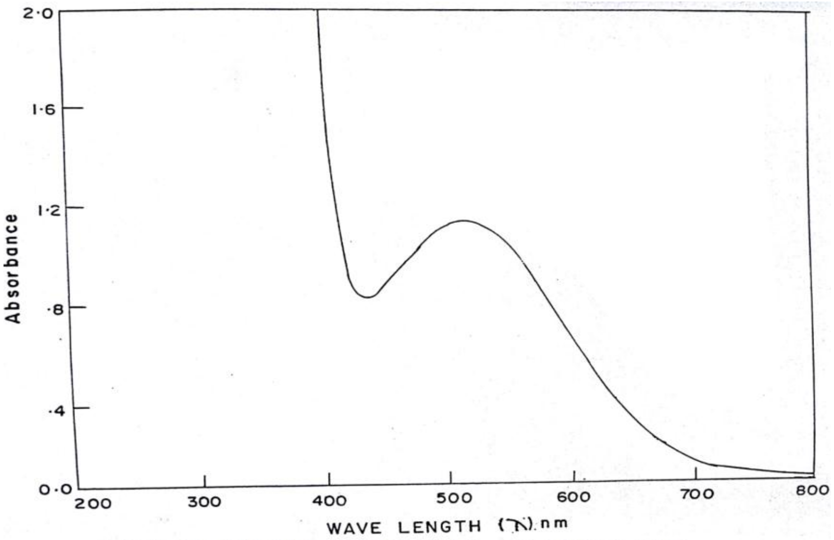
3.2 Effect of SDS concentration on the apparent formation constants

The apparent formation constants of the complexes decreased with the increase in concentration of SDS from 0.02 to 0.1M may be attributed to the increase in the effective volume of the residence (volume of the micelle in which components reside) of the donor and paraquat molecules, which results in decrease in the local concentration of the components and hence in apparent formation constants.



Rose-Drago plots of CT complexes of PQ/phenylhydrazone in SDS (at 25°C)

Fig: 1.



CT SPECTRA OF COMPLEXES OF PQ WITH p-HYDROXY PHENYLE HYDRAZONE IN SDS MICELLAR MEDIUM

Fig:2.

4. CONCLUSION

Stability constants are determined by the Ross-Drago method. Stability of a given complex in SDS is 100 to 1000 times greater than the stability in methanol. These constants are called apparent formation constants (K_{app}). The enhanced stabilities of complexes in SDS are attributed to the increasing in the local concentrations of the components. The stability constants K_{app} found to be decreased with increasing concentration of SDS this was attributed to increase in effective micellar volume. The micellar volume independent stability constants (K_{CT}) have been calculated using the relation:

$K_{CT}= K_{app}.\overline{V}\,[D_m]$.

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