

## THE ADSORPTION OF C.I. DIRECT RED 73 ON THE MERCURY ELECTRODE FROM DIFFERENT BASE ELECTROLYTES

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**The adsorption of C.I. direct red 73, a bisazo direct dye at the mercury/solution interface from 1 M solutions of NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> has been investigated using capillary electrometer. Thermodynamic parameters like charge on the metal surface ( $q^M$ ), the surface excess of organic molecule adsorbed ( $\Gamma_{org}$ ), surface coverage ( $\theta$ ) and free energy of adsorption ( $-\Delta G$ ) are evaluated and presented. The adsorption of C.I. direct red 73 obeys Langmuir's adsorption isotherm in all the three base electrolytes.**

**Keywords:** C.I. direct red 73, bisazo direct dye, capillary electrometer and Langmuir's adsorption.

### INTRODUCTION

Many of the dyes and dyestuff intermediates have been reported to be very good corrosion inhibitors for aluminium and its alloys in acidic and alkaline media [1-5]. Reports are also available on manganese and aluminium alloys [6-7]. Studies on the adsorption of organic compounds have important consequences, some of which have beneficial results. The role of brighteners, levelling agents and anti-pitting agents which help to produce bright, smooth and pit-free electrodeposits are explained in terms of the adsorption of these compounds at the metal/solution interface. The essential step in organic electrode reactions which generate electric power from chemical reactants is primarily the adsorption of organic molecules. Hence adsorption studies at metal/solution interfaces are of immense importance. The influence of anions on the adsorption of several organic molecules at the mercury/solution interface have been reported by several authors [8-15]. A thorough literature survey clearly reveals the fact that a study of adsorption behaviour of C.I. Direct Red 73 at the mercury/solution interface has not been reported earlier. So, it is of interest

to study the adsorption behaviour of this compound at the mercury/solution interface in the presence of different anions in the base electrolytes used.

### EXPERIMENTAL

The design of the capillary electrometer and the experimental cell used for the measurement of the interfacial tension are the same as described elsewhere [16-17]. All the chemicals used were of AR-BDH grade except C.I. Direct Red 73, which was obtained from Atul Products Ltd, Atul, Gujarat, India. The commercial name of the dye is Atul Corcein Scarlet MOO. The structure of this compound is given in Fig. 1. Purified hydrogen was used for the deaeration of the experimental solution. Mercury (Analar) was purified electrolytically and distilled in an all glass pyrex still under reduced pressure. All the measurements were carried out in an air thermostat at  $298 \pm 2$  K.

Depending upon the nature of the electrolyte, Hg/Hg<sub>2</sub>Cl<sub>2</sub>/1 M NaCl or Hg/Hg<sub>2</sub>SO<sub>4</sub>/1 M Na<sub>2</sub>SO<sub>4</sub> or Hg/HgNO<sub>3</sub>/1 M NaNO<sub>3</sub> was used as the reference electrode. Lead acid battery was used for applying the required potential (0-1.6 V) to the mercury in the

capillary electrometer using a precision potentiometer. All the potentials were measured using a digital multimeter (HIL 212).

## RESULTS AND DISCUSSION

### Electrocapillary curves

Electrocapillary curves for 1 M NaCl, 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M NaNO<sub>3</sub> in the presence of different concentrations of C.I. Direct Red 73 have been obtained. All the runs were duplicated and the results are reproducible to 0.2 dynes.cm<sup>-1</sup> at the electrocapillary maximum and ± 0.8 dynes.cm<sup>-1</sup> at the extremes of the curves. Fig. 2 shows electrocapillary curves for different concentrations of the compound in 1 M NaCl. The variation in the extent of adsorption of the compound around electrocapillary maximum (e.c.m) observed for different electrolytes is shown in Table I.

### Charge on the metal surface (q<sup>M</sup>)

The charge on the metal was evaluated by the graphical differentiation of the electrocapillary curves at 50 mV intervals. The plots of q<sup>M</sup> vs -E for 1 M NaCl in the presence of different concentrations of C.I. Direct Red 73 are presented in Fig. 3. The error limits for the charge density are 0.25 μC.cm<sup>-2</sup> around e.c.m. to ± 0.8 μC.cm<sup>-2</sup> at the extremes of the curve. Charge (q<sup>M</sup>) vs potential (-E) curves obtained for different concentrations of the dye in the presence of 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M NaNO<sub>3</sub> follow a similar pattern as in Fig. 3.

### Surface excess of organic molecules adsorbed (Γ<sub>org</sub>)

The surface excess of the organic molecules adsorbed was calculated by the graphical differentiation on the interfacial tension vs concentration curve (semi log coordinate) at constant potential values. Values of Γ<sub>org</sub>

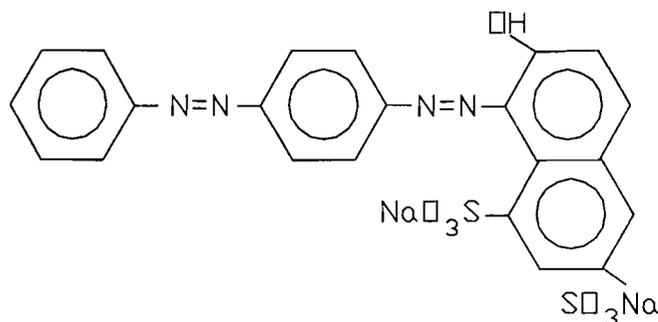


Fig. 1: Structural formula of C.I. Direct Red 73

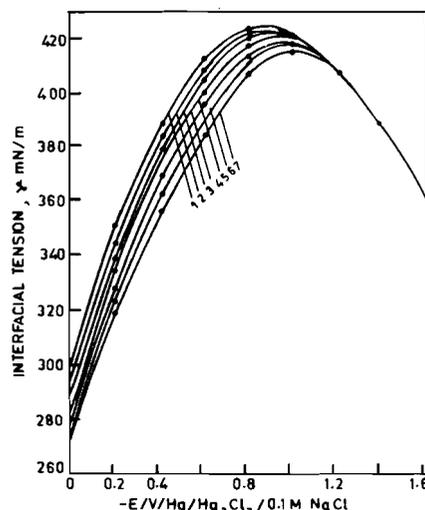


Fig. 2: Electrocapillary curves for 1 M NaCl in presence of different concentrations of C.I. Direct Red 73 (1) 1 M NaCl (2) 0.00005 M (3) 0.0001 M (4) 0.00025 M (5) 0.0005 M (6) 0.001 M (7) 0.002M

obtained for various concentrations of C.I. Direct Red 73 were plotted as a function of q<sup>M</sup> for 1 M NaCl and are shown in Fig. 4.

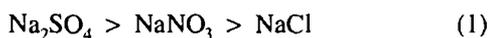
Electrocapillary curves obtained for different concentrations of C.I. Direct Red 73 from 1 M NaCl in the potential range 0 to 1.6 V are shown in Fig. 2. The results show that there is strong adsorption of this compound on the positive side of the electrocapillary curve in all the three cases. But the compound is found to desorb on the negatively charged mercury surface. The adsorption is found to be more near the electrocapillary maximum, where water molecules are loosely held on the

TABLE I: Adsorption of C.I. Direct Red 73 on mercury from different base electrolytes

Base electrolyte	Concn of C.I. Direct Red 73 10 <sup>-3</sup> M	Suppression in γ (Δγ) around e.c.m. (mN/m)
NaCl	2	30.0
NaNO <sub>3</sub>	2	34.5
Na <sub>2</sub> SO <sub>4</sub>	2	38.0

metal surface and therefore are easily displaced by organic molecules. The compound is found to adsorb strongly even at the extremes of the positive charge. This is because of the fact that on a positively charged mercury surface, water molecules are less polarised than organic molecules.

The adsorption on the positive side of the electrocapillary curve may be due to interaction of the delocalised  $\pi$ -electrons of the naphthalene and benzene rings of the compounds with the positively charged mercury surface [18]. The adsorption on the positively charged metal surface can also occur through the lone pair of electrons of nitrogen atoms of azo groups present in the molecules. The desorption of the compound on the negatively charged metal surface can be explained to be due to the strong attraction of water molecules on the metal surface, as compared to that of the adsorbate. It may also be due to the absence of interacting groups in the molecule which favours its desorption on the negatively charged surface. The extent of adsorption of C.I. Direct Red 73 from the three different base electrolytes as seen from Table I is found to follow the order given below.



Similar observations have been reported earlier [15].

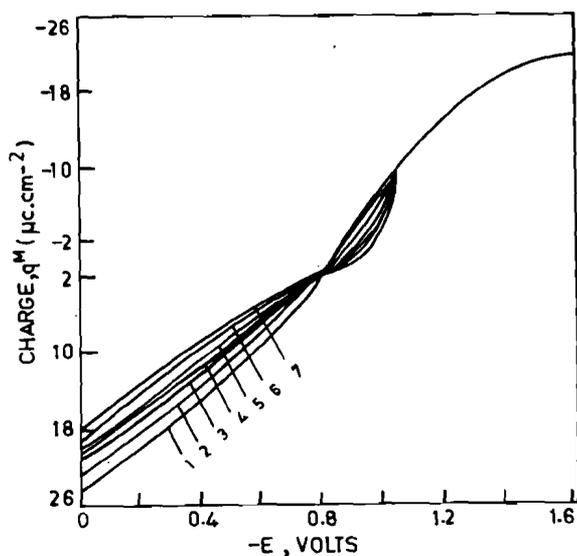


Fig. 3: Variation of charge ( $q^M \mu\text{C.cm}^{-2}$ ) with potential ( $-E$  volt) for 1 M NaCl in presence of different concentrations of C.I. Direct Red 73

(1) 1 M NaCl (2) 0.00005 M (3) 0.0001 M (4) 0.00025 M (5) 0.0005 M (6) 0.001 M (7) 0.002 M

The difference in the extent of adsorption can be explained as follows. Chloride ions are specifically and strongly adsorbed on the mercury surface. As there is strong adsorption by chloride ions, more space on the metal surface is occupied by them. So very few molecules of C.I. Direct Red 73 find sites on the mercury surface. But in the case of  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  the adsorption of nitrate and sulphate ions on the metal surface will be less. So more space is available on the metal surface for the adsorption of the organic molecule. Among the nitrate and sulphate ions, the adsorption is slightly less for nitrate ions. Hence maximum adsorption of C.I. Direct Red 73 takes place for sodium sulphate followed by sodium nitrate and sodium chloride in the decreasing order.

#### Charge ( $q^M$ ) vs potential ( $-E$ ) curve

It is seen from the Fig. 3 that all the curves intersect at a charge of around  $+2 \mu\text{C.cm}^{-2}$  as observed in the case of aromatic compounds. It is seen from these curves that there is no desorption of organic molecule even at extreme positively charged mercury surface and there is complete desorption on the negatively charged mercury surface. Similar observations have been made for the adsorption of the dye from the other two electrolytes also.

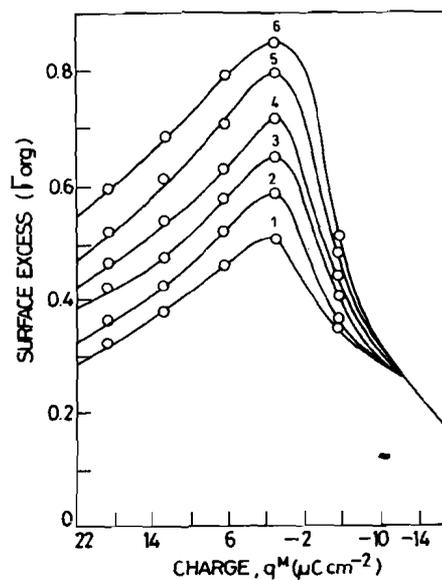


Fig. 4: Variation of surface excess ( $\Gamma^{\text{org}}$ ) with charge ( $q^M$ ) for the adsorption of different concentrations of C.I. Direct Red 73 in 1 M NaCl

(1) 0.00005 M (2) 0.0001 M (3) 0.00025 M (4) 0.0005 M (5) 0.001 M (6) 0.002 M

**Surface excess vs charge curve**

Values of surface excess for different concentrations of C.I. Direct Red 73 in 1 M NaCl as a function of ( $q^M$ ) are shown in Fig. 4. It can be observed from this figure that maximum adsorption occurs at a charge around  $+2 \mu\text{C}.\text{cm}^{-2}$ . Surface excess vs charge for the adsorption of C.I. Direct Red 73 from 1 M NaNO<sub>3</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub> follow a similar pattern. It is observed that the adsorption of the organic compound from the three electrolytes follows the order Na<sub>2</sub>SO<sub>4</sub> > NaNO<sub>3</sub> > NaCl as stated earlier. These curves clearly show that there is no desorption of the compound even at extreme positive charges but it desorbs completely on a negatively charged mercury surface.

**Application of adsorption isotherm**

The adsorption isotherms for explaining the adsorption characteristics of C.I. Direct Red 73 from 1 M NaCl, 1 M NaNO<sub>3</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub> requires the evaluation of surface coverage ( $\theta$ ). Surface coverage was evaluated using the relation  $\Gamma/\Gamma_m = \theta$ , where  $\Gamma_m$  is the surface excess maximum. Surface excess maximum ( $\Gamma_m$ ) was

evaluated by plotting  $C/\Gamma$  vs  $C$  for the charge at which maximum adsorption occurs ( $q^M = 0$ ) and by measuring the initial slope of the straight line obtained. Values of  $\Gamma_m$  were found to be  $6.15 \times 10^{-10}$  moles. $\text{cm}^{-2}$  for the adsorption from 1 M NaCl and  $6.4 \times 10^{-10}$  moles. $\text{cm}^{-2}$  for the adsorption from 1 M NaNO<sub>3</sub> and  $7.65 \times 10^{-10}$  moles. $\text{cm}^{-2}$  for the adsorption from 1 M Na<sub>2</sub>SO<sub>4</sub>. The choice of the suitable isotherm for the adsorption of C.I. Direct Red 73 from 1 M NaCl, 1 M NaNO<sub>3</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub> was tested by analysing the adsorption data graphically to choose a suitable isotherm.

It was found that in all cases a plot of  $C/\theta$  vs  $C$  for different values of  $q^M$  gave a family of parallel straight lines, all of them having a gradient equal to unity. Fig. 5 shows the adsorption isotherm curves for the dye for 1 M NaCl solution. This observation clearly proves the fact that the adsorption of C.I. Direct Red 73 from NaCl obeys Langmuir's adsorption isotherm. Values of intercepts were noted for each value of  $q^M$  which enabled the evaluation of free energy of adsorption. It was found that the adsorption of the dye from 1 M NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> also obeys Langmuir's adsorption isotherm.

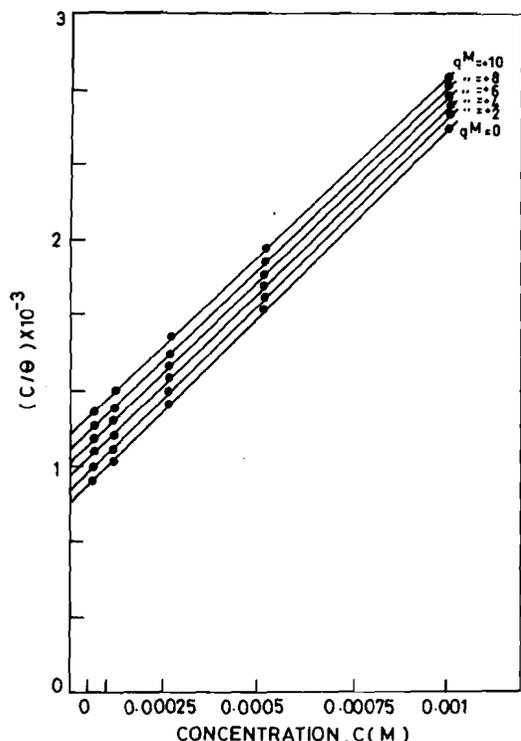


Fig. 5: Plots of  $C/\theta$  vs  $C$  for the adsorption of C.I. Direct Red 73 at different values of positive charge ( $q^M$ ) on the mercury surface from 1 M NaCl

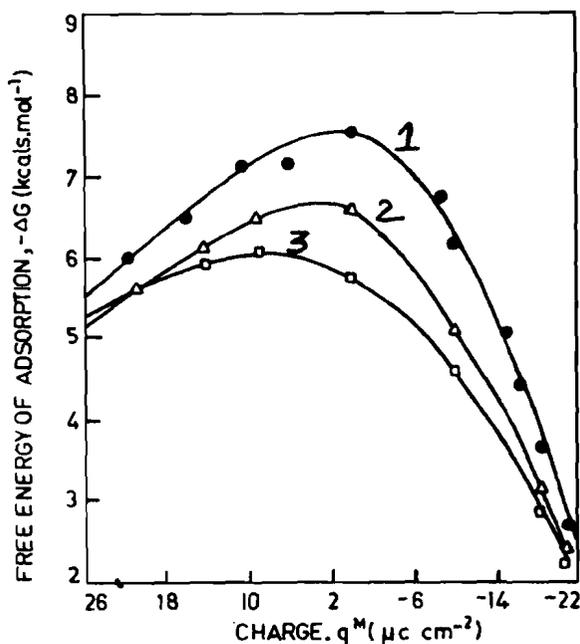


Fig. 6: Variation of free energy of adsorption with charge for the adsorption of C.I. Direct Red 73 from different base electrolytes (1) 1 M Na<sub>2</sub>SO<sub>4</sub> (2) 1 M NaNO<sub>3</sub> (3) 1 M NaCl

### Free energy of adsorption ( $-\Delta G$ ) as a function of charge ( $q^M$ )

The variation of free energy adsorption with charge for the adsorption of C.I. Direct Red 73 from 1 M solutions of NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> is shown in Fig. 6. All the three curves are almost similar, except the fact that the free energy of adsorption at a charge at which the maximum adsorption occurs (7.95 k.cal.mol<sup>-1</sup> from Na<sub>2</sub>SO<sub>4</sub>, 7.50 k.cal.mol<sup>-1</sup> from NaNO<sub>3</sub> and 7.05 k.cal.mol<sup>-1</sup> from NaCl medium) is different in different media. An almost constant value of  $-\Delta G$  on a positively charged metal surface indicates the fact that there is a constant interaction between  $\pi$ -electrons of the benzene and naphthalene rings and lone pair of electrons on the nitrogen atoms of azo groups present in the molecule with positively charged metal surface. Free energy of adsorption was found to be maximum around a charge of +2  $\mu$ C.cm<sup>-2</sup> as adsorbed in case of aromatic compounds. The decrease in free energy with increasing negative charge may be due to the lack of interaction between the negatively charged mercury surface and the organic compound.

So the above observation clearly proves the fact that the anions present in the base electrolyte influence the extent of adsorption only and there is practically no influence on other adsorption characteristics.

### CONCLUSION

C.I. Direct Red 73 is found to adsorb more on the positively charged mercury surface because of the interaction with  $\pi$ -electrons of different aromatic rings and also with lone pairs of electrons of nitrogen atoms present in the molecules. It is found to desorb on a negatively charged mercury surface due to the absence of interacting groups which can interact with the negatively charged mercury surface.

The adsorption is found to be more from 1 M Na<sub>2</sub>SO<sub>4</sub> followed by 1 M NaNO<sub>3</sub> and 1 M NaCl in the decreasing order. This can be attributed to the difference in the nature of anions present in different base electrolytes. Among the anions, the chloride ions which are strongly

adsorbed on mercury surface leaves relatively a few sites on the surface for adsorption by organic molecules. Hence, adsorption from NaCl base electrolyte is the least. Between nitrate and sulphate ions the former shows more adsorption than the latter. Hence, the amount of dye adsorbed will be less from nitrate containing base electrolyte than from solution containing sulphate.

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