

ADSORPTION OF C.I DIRECT BROWN 2: A BISAZO DYE FROM DIFFERENT BASE ELECTROLYTES

B MURALIDHARAN, S ALWARAPPAN, T VASUDEVAN AND S VENKATAKRISHNA IYER*

Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003. INDIA

* Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 28 January 1998 Accepted: 20 May 1998]

Electrocapillary curves for 1 M solutions of NaCl, NaNO₃ and Na₂SO₄ in the presence of different concentrations of C.I. Direct Brown 2 show that the organic compound adsorbs on the positively charged mercury surface. The extent of adsorption from these base electrolytes follows the order Na₂SO₄ > NaNO₃ > NaCl. Thermodynamic parameters like charge on the metal surface (q^M), the surface excess of organic molecule adsorbed (Γ_{org}), surface coverage (θ) and free energy of adsorption ($-\Delta G^0$) are evaluated. The adsorption of this compound is found to obey Langmuir's adsorption isotherm in all the cases, irrespective of the nature of the base electrolyte used.

Keywords: Adsorption isotherm, electrocapillary.

INTRODUCTION

The influence of anions on the adsorption of organic molecules at the mercury/solution interface has well studied [1-4]. The adsorption of aniline in the presence of anions [1] and from Na₂SO₄ and LiClO₄ [2], the isopentanol, pentanoic acid and benzyl alcohol from HClO₄, H₂SO₄, NaNO₃ and NaF and quinoline from KNO₃, KCl, Na₂SO₄ and HCl [4] have been described. The adsorption of o-aminobenzoic acid [5], o-methyl benzoic acid [6] and benzotriazole [7] from different base electrolytes have been discussed. Many dyes and dye intermediates have been reported to be good corrosion inhibitors for aluminium and its alloys in acidic and alkaline media [8-12]. Also reports are available with aluminium-manganese alloys [13-14]. Studies on organic adsorption have important consequences, many of which have beneficial results. The role of brighteners, leveling agents and antipitting agents which help to produce bright, smooth and pit-free electrodeposits are explained in terms of the adsorption of compounds at metal/solution interfaces. 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. In the present study the adsorption of C.I. Direct

Brown 2 on mercury from different base electrolytes have been investigated and the results are discussed.

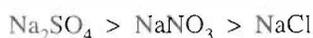
EXPERIMENTAL

The design of the capillary electrometer is the same as that used earlier [15-17] and the cell design used for the measurement is the same as that described elsewhere [16,18]. It consists of a main compartment, through which capillary electrometer can be inserted and two side connections - one leading to the reference electrode compartment, through the water seal top joint and the other to the hydrogen inlet. Purified hydrogen was used for deaeration. Mercury of Analar grade was further purified electrolytically and distilled in an all glass pyrex Hullet Still [19] under reduced pressures. The base electrolytes used viz. Na₂SO₄, NaNO₃ and NaCl were of Analar (B.D.H) grade. C.I. Direct Brown 2 chemically known as sodium [6-(4-hydroxybenzene-3-sodium carboxylate diazenyl)6'-biphenyl]diazonyl-7-amino-2-naphthyl-3-sulphonate was obtained from Atul Products Ltd., Atul Gujarat, India (Fig. 1). All experiments were carried out in an air thermostat controlled at a temperature of 298 ± 0.2 K. The mercury in the capillary electrometer was polarised to various values of potentials ranging from 0 to -1.6 volts applied using a precision potentiometer (ECIL Ltd., Hyderabad) in combination with 6 volts lead acid

battery. Reference electrodes used were $\text{Hg}/\text{HgCl}_2/1\text{ M NaCl}$ or $\text{Hg}/\text{HgNO}_3/1\text{ M NaNO}_3$ or $\text{Hg}/\text{Hg}_2\text{SO}_4/1\text{ M Na}_2\text{SO}_4$.

RESULTS AND DISCUSSION

Electrocapillary curves were obtained for 1 M NaCl , 1 M NaNO_3 and $1\text{ M Na}_2\text{SO}_4$ in the presence of different concentrations of C.I. Direct Brown 2 ranging from $0.05 \times 10^{-3}\text{ M}$ to $2 \times 10^{-3}\text{ M}$. All the runs are duplicated and the results are reproducible to 0.2 mN.m^{-1} at the e.c.m. and 0.8 mN.m^{-1} at the extremes of the curves. For the sake of comparison the electrocapillary curves obtained for different base electrolytes in the presence of C.I. Direct Brown 2 of concentration $2 \times 10^{-3}\text{ M}$ are shown in Fig. 2. It can be seen from this figure that the extent of adsorption of the dye from different electrolytes follows the order



Charge on the metal surface (q^M)

Fig. 2 shows that C.I. Direct Brown 2 has strong adsorption 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. Adsorption is found to be maximum near or around electrocapillary maximum. Adsorption of the compound may be due to the interaction between the π -electrons of benzene, biphenyl and naphthalene rings present in the compound with the positively charged mercury surface. The interaction of the lone pairs of electrons of nitrogen atoms of the azo group and the amino group with the positively charged metal surface may also play a significant role on the adsorption of the compound on the mercury surface [20-22]. The

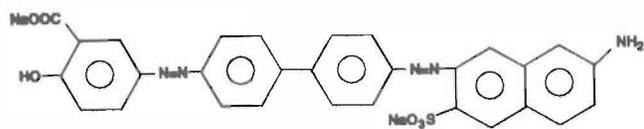


Fig. 1: Structure of C I direct brown 2 dye

desorption of the compound on a negatively charged mercury surface may be due to the fact that water molecules are more polarisable than organic molecules and therefore they easily displace organic molecules from the metal surface. Maximum adsorption of the compound at or near e.c.m. may be due to the fact that at $q^M=0$ water molecules are very loosely held to the metal surface and they can be easily displaced by organic molecules. Further it is seen that the adsorption of the organic molecule is more from $1\text{ M Na}_2\text{SO}_4$ than from 1 M NaNO_3 and 1 M NaCl . This difference in the extent of adsorption may be due to the fact that chloride ions get specifically adsorbed on the mercury surface leaving little space for the adsorption of organic molecules [1,4-6].

The difference in the extent of adsorption of the dye from Na_2SO_4 and NaNO_3 solutions can be attributed to the difference in the sizes of these anions and also due to the difference in the number of primary hydration sheaths surrounding them. Nitrate ions having lesser number of hydration sheaths around them can strongly adsorb on the metal surface leaving lesser space on the metal surface for the organic molecule to get adsorbed. On the other hand sulphate having larger number of primary hydration sheath can adsorb only to a lesser extent, leaving very large space on the metal surface.

Charge vs potential curves

It is found from the Fig. 3 that maximum adsorption for C.I. Direct Brown 2 occurs at a charge of $+2\text{ }\mu\text{C}/\text{cm}^2$. All the curves are found to merge on a negatively charged metal surface showing thereby that the compound gets desorbed

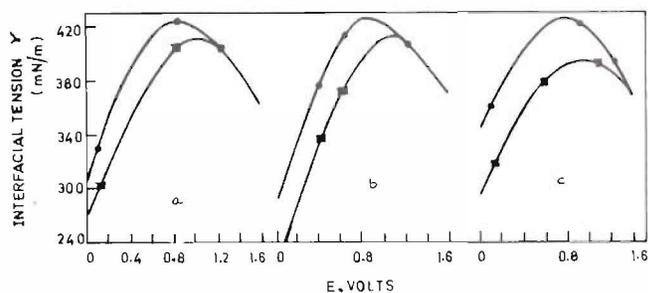


Fig. 2: Electrocapillary curves for (a) 1 M NaCl (b) 1 M NaNO_3 (c) $1\text{ M Na}_2\text{SO}_4$; (●) electrolyte only and (■) electrolyte + $2 \times 10^{-3}\text{ M}$ dye

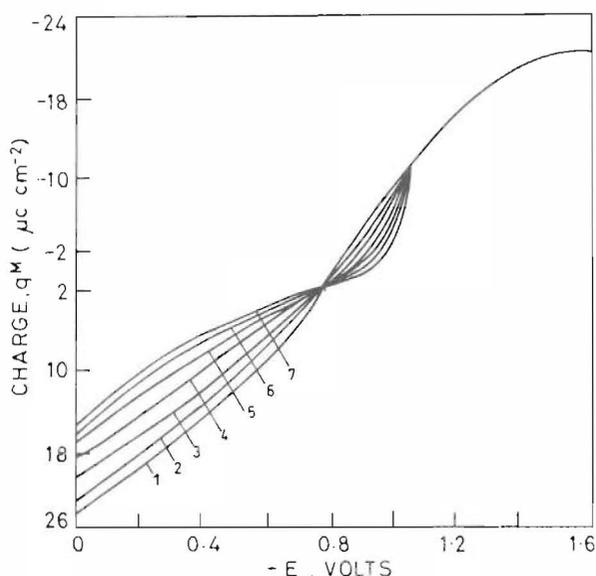


Fig. 3: Charge vs potential curves for 1 M NaCl in the presence of different concentrations of the dye
 (1) 1 M NaCl alone (2) $0.05 \times 10^{-3} M$ (3) $0.075 \times 10^{-3} M$
 (4) $1 \times 10^{-3} M$ (5) $1.25 \times 10^{-3} M$ (6) $1.5 \times 10^{-3} M$ (7) $2 \times 10^{-3} M$

on a negatively charged mercury surface. Similar features are observed for the adsorption of the dye from other electrolytes also.

It is seen from Fig. 4 that values of surfaces excess for different concentrations of the dye is found to be more on a positively charged metal surface and the extent of adsorption depends on the nature of the base electrolyte. This

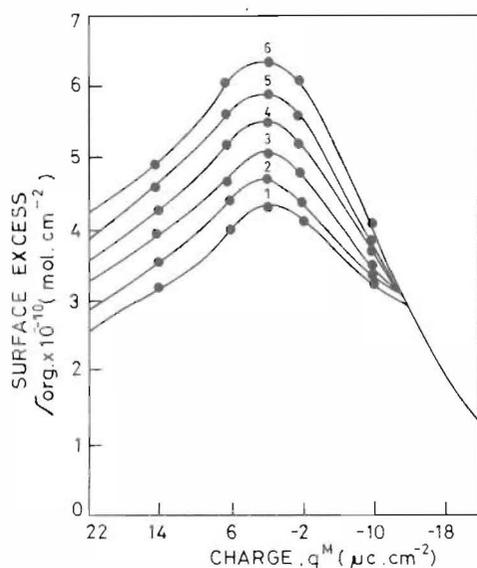


Fig. 4: Surface excess vs charge curves for 1 M NaCl in the presence of different concentrations of the dye
 (1) $0.05 \times 10^{-3} M$ (2) $0.075 \times 10^{-3} M$ (3) $1 \times 10^{-3} M$
 (4) $1.25 \times 10^{-3} M$ (5) $1.5 \times 10^{-3} M$ (6) $2 \times 10^{-3} M$

observation clearly proves the effect of anions in the base electrolyte on the extent of adsorption of C.I. Direct Brown 2 on the mercury surface. Moreover, it is found that the organic molecule is desorbed on the negatively charged mercury surface.

Coverage (θ) was evaluated using the relation $\Gamma/\Gamma_{max} = \theta$ where Γ_{max} is the maximum value of surface excess. Values of θ for the adsorption of C.I. Direct Brown 2 from different base electrolytes have been obtained using the above value of Γ_{max} .

Assignment of isotherms

The adsorption data obtained have been analysed graphically to choose a proper isotherm which can explain the adsorption characteristics of C.I. Direct Brown 2 on mercury for different base electrolytes. It was found that a plot of c/θ for various values of charges against concentration (c) gave a family of straight lines with a slope of unity. This shows that adsorption of C.I. Direct Brown 2 obeys Langmuir's adsorption isotherm. Similar graphs are obtained in other base electrolytes. Intercepts have been noted for each value of q^M , from which free energy of adsorption is evaluated.

Free energy of adsorption as a function of charge

The variation of the free energy of adsorption ($-\Delta G^0$) with charge for the adsorption of C.I. Direct Brown 2 from different base electrolytes (Fig. 5) are almost similar. These curves brings out the fact that $-\Delta G^0$ values for charge at maximum adsorption follows the order

$1 M Na_2SO_4 > 1 M NaNO_3 > 1 M NaCl$ (8.55 K.Cal/mol)
 (8.05 K.Cal/mol) (7.3 K.Cal/mol)

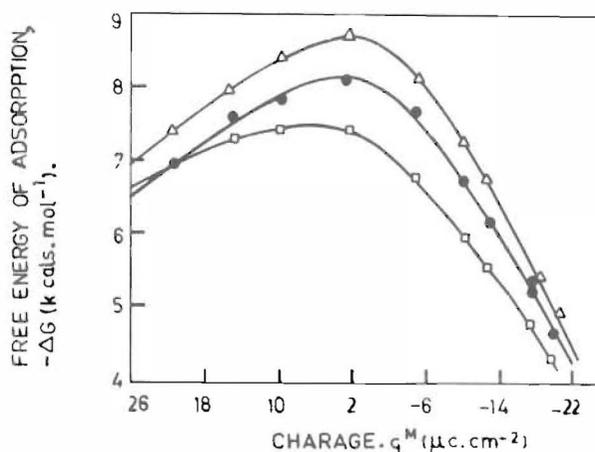


Fig. 5: Variation of free energy of adsorption with charge
 (Δ) 1 M Na_2SO_4 (\bullet) 1 M $NaNO_3$ (\square) 1 M $NaCl$

The decrease in the free energy with increasing negative charge may be due to the lack of interaction between the negatively charged mercury surface and the organic compound.

CONCLUSION

C.I. Direct Brown 2 is found to adsorb more on the positively charged mercury surface due to their interactions with π -electrons of different aromatic rings present in the compound with the positively charged mercury surface. The interaction between the lone pairs of electrons of nitrogen atoms of azo group and amino group and the positively charged mercury surface may also play a significant role on the adsorption of the compound. Anions present in the base electrolytes play a significant role in enhancing or decreasing the extent of adsorption on the metal surface. But they do not influence any other adsorption characteristic including the adsorption isotherm.

REFERENCES

1. K M Joshi, S I Mahajan and S Rajagopalan, *Indian J Chem*, **10** (1972) 279,619
2. L A Korshikov, V B Tatova, V D Bezuglyi and Adsorbtsiya Devoionic, *Elec Sloi Elektrokhim*, A N Frumkin (Ed) Nauka, Moskow, **71** (1972)
3. J J Buckfelder, *Report IST 888, Energy Research Abstr*, (1980)

4. M A Ghaly and A A Nazhar, *Surf Tech*, **16** (1982) 31
5. S Alwarappan, A Shiek Mideen, M Anbu Kulandainathan, P V Krishnamoorthy, P Manishankar, T Vasudevan and S Venkatakrishna Iyer, *J Electrochemical Soc India*, **39** (1990) 160
6. P V Krishnamoorthy, S Alwarappan, T Vasudevan, A Sheik Mideen and S Venkatakrishna Iyer, *J Surface Sci Technol*, **813** (1992) 319
7. V Balaramachandran and S Venkatakrishna Iyer, *Indian J Chem*, **34A** (1995) 224
8. J D Talati and J M Daraji, *J Indian Chem Soc*, **65** (1988) 94
9. J D Talati and D K Gandhi, *Werks Korros*, **33** (1982) 154
10. J D Talati and D K Gandhi, *Indian J Technol*, **23** (1985) 232
11. J D Talati and J M Daraji, *J Electrochem Soc India*, **35** (1986) 175
12. J D Talati and J M Daraji, *J Indian Chem Soc*, **68** (1991) 67
13. J D Talati and J M Daraji, *Programme 3rd Int Symp Advances Electrochem Sci Technol*, Madras, India, Dec 10-14 (1984)
14. F Tribonod and C Fiand, *Corros Sci*, **18** (1978) 139
15. M A V Devanathan, *Ph D Thesis*, University of London (1951)
16. P Peries, *M Sc Thesis*, University of Ceylon (1954)
17. M J Fernando, *M Sc Thesis*, University of Ceylon (1954)
18. S Venkatakrishna Iyer, *Ph D Thesis*, Univeristy of Kerala (1970)