

IIT, Bombay and Dr D. K. Chattoraj, Jadavpur University, Calcutta for surface area and microelectrophoretic mobility measurements respectively.

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Adsorption of Thiophene at Dropping Mercury Electrode & Its Effect on the Kinetics of Electrode Process

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The effect of thiophene on the kinetics of electrode processes in which the adsorbed molecules themselves do not participate is examined. As a first step the properties of thiophene at dropping mercury electrode have been studied by electrocapillary and capacity measurements. The effect of thiophene adsorption on the apparent standard rate constant ( $K_s$ ) of the exchange Cd(II)/Cd(Hg) in 1N H<sub>2</sub>SO<sub>4</sub> has also been investigated.  $K_s$  values decrease with increasing concentration of thiophene. This has been interpreted in terms of increase in surface coverage by thiophene with increase in its concentration.

THE adsorption behaviour of some organic molecules on the dropping mercury electrode (d.m.e.) and on other solid microelectrodes have been previously studied<sup>1-3</sup>. Adsorption of thiophene was first

studied by Gaunitz and others by measuring the capacity and impedance on stationary mercury electrode in various solvents<sup>4</sup>. The changes in the charge during adsorption and partial charge transfer were found mostly small. In some cases, complicated adsorption phenomena was observed depending on the solvent. The effect of various substituents on thiophene on the inhibitor efficiency has also been studied<sup>5</sup>. Corrosion rate measurements in the various solutions indicate that the compounds were weak inhibitors. In this investigation adsorption of thiophene at d.m.e. and its effect on the kinetics of electrode process have been studied.

Stock solution of thiophene (Veb Laborchemie, pronanalysis) was prepared in absolute ethyl alcohol (99%). All measurements in thiophene solution were made in the presence of a constant concentration of alcohol, namely 2% by volume. Sulphuric acid used was of AR grade (BDH).

*Electrocapillary measurements* — A streaming capillary electrometer was used to set the isotension potential curves. A full description of the apparatus and method of calibration has been given previously<sup>6</sup>.

*Double layer capacity measurements* — Differential capacity measurements were made using an a.c. bridge of the Wien type<sup>7</sup>.

Electrocapillary curves and capacity measurements were all made in 1N H<sub>2</sub>SO<sub>4</sub> solution and in the presence of different concentrations of thiophene. Measurements were carried out in an air-bath adjusted at 25° ± 0.5° C. Saturated calomel electrode was used as the reference.

The parameters of the electrocapillary maximum of Hg,  $E_{max}$  and  $\sigma_{max}$  were determined in 1N H<sub>2</sub>SO<sub>4</sub> and at different concentrations of thiophene.  $E_{max}$  values at different thiophene concentrations were read from the  $\Delta p$  versus  $E(SCF)$  plots (Fig 1) and the values are recorded in Table 1 along with  $\sigma_{max}$  values. The mean deviations in the values of  $E_{max}$  and  $\sigma_{max}$  are ± 1mV and ± 0.5 dyne/cm.

The results show that  $\sigma_{max}$  decreases with increase in thiophene concentration. For  $E_{max}$ , however, the shift is irregular at low thiophene concentration (till  $0.5 \times 10^{-2} M$ ) while at higher concentration  $E_{max}$  exhibits a definite and measurable shift towards more negative potentials.

The results of differential capacitance measurements in the thiophene solutions of different concentrations are shown graphically in Fig. 2. The values quoted are those registered at the normal working frequency of 1000 Hz. With increasing

TABLE 1 — PARAMETERS  $E_{max}$   $\sigma_{max}$  OF MERCURY IN 1N H<sub>2</sub>SO<sub>4</sub> CONTAINING DIFFERENT CONCENTRATIONS OF THIOPHENE AT 25°C.

$10^{-2}$ [Thiophene] M	$E_{max}$ mV (vs SCE)	$\sigma_{max}$ (dyne cm <sup>-1</sup> )
Zero	435	420.7
0.5	437	420.4
1.0	440	419.9
2.0	450	418.9
3.0	455	413.8
4.0	460	408.1

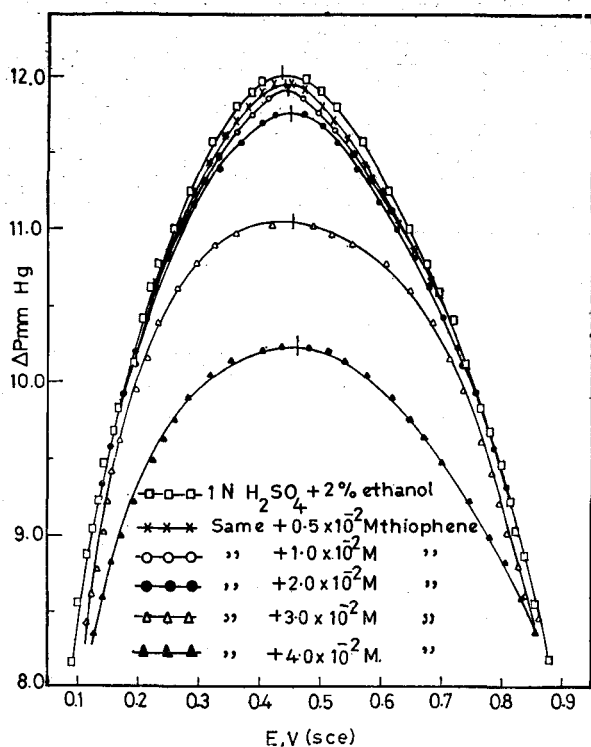


Fig. 1 — Isotension potentials.

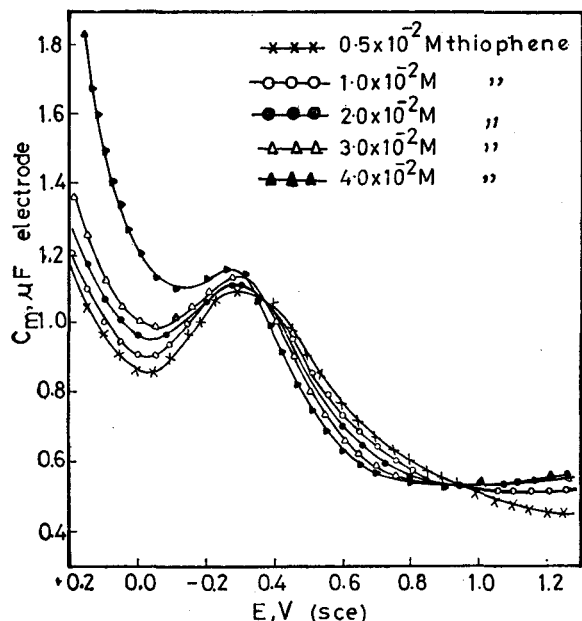


Fig. 2 — Differential capacitance curves in 1N H<sub>2</sub>SO<sub>4</sub> and varying concentrations of thiophene.

thiophene concentration, the capacity decreases monotonically in the region of  $E_{max}$ , showing that in the concentration range used the adsorption behaviour resembles that of simple organic molecules. Figure 3 shows representative capacitance-potential curves obtained during the reduction of Cd(II) at a concentration of  $7.5 \times 10^{-4}M$  in pure 1N H<sub>2</sub>SO<sub>4</sub> and in 1N H<sub>2</sub>SO<sub>4</sub> + 2% ethyl alcohol.

The appearance of a well-defined pseudo-capacitance in capacitance-potential curves clearly indicates that the reduction is quasi reversible. In the presence of alcohol, however, the pseudo-capacitance peak is relatively lower than in the pure acid which according to the theory of the faradaic impedance indicates a relatively lower exchange rate.

The results obtained during the reduction of Cd(II) in 1N H<sub>2</sub>SO<sub>4</sub> containing different thiophene concentrations are illustrated graphically in Fig. 4. It is found that increase in thiophene concentration leads to gradual decrease in pseudo-capacitance peak. Over the range of thiophene concentration employed, however, the reduction wave is a simple one and the limiting current is found practically constant.

The apparent standard rate constants  $K_s$  of the exchange Cd(II)/Cd(Hg) in the various solutions have been calculated using the simple Randles-Ershler model of the faradaic impedance<sup>8</sup>.

According to the theory  $K_s$  can be calculated from the relation(1).

$$R_r - \frac{1}{\omega C_r} = \frac{RT}{n^2 F^2 AC} \cdot \frac{1}{K_s} \quad \dots(1)$$

In Eq. (1)  $R_r$  is the resistive component of admittance,  $C_r$  the capacitive component,  $A$  the electrode area in cm<sup>2</sup>,  $C$  the depolarizer concentration in mol/cm<sup>3</sup>,  $n$  the number of electrons involved in the electrode reaction,  $\omega = 2\pi F$  where  $F$  is the applied frequency and  $R$  and  $T$  have their usual significance.  $R_r$  and  $C_r$  have been obtained by

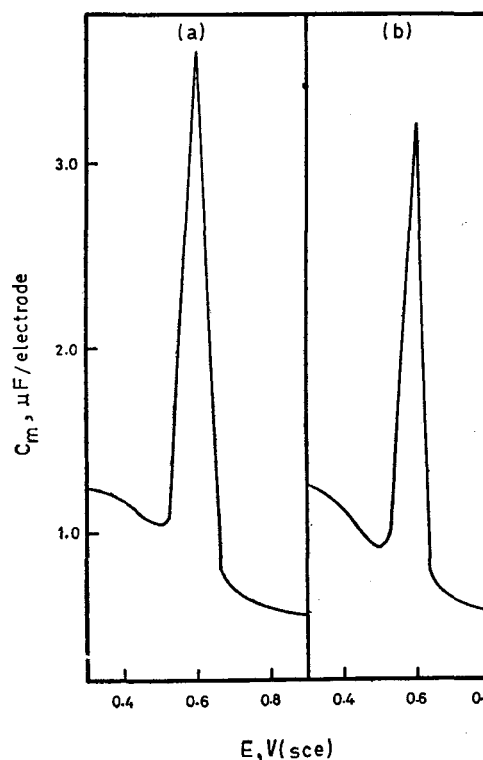


Fig. 3 — Differential capacitance curves for  $7.5 \times 10^{-4}M$  Cd(II) in (a) 1N H<sub>2</sub>SO<sub>4</sub> and (b) 1N H<sub>2</sub>SO<sub>4</sub> + 2% ethanol.

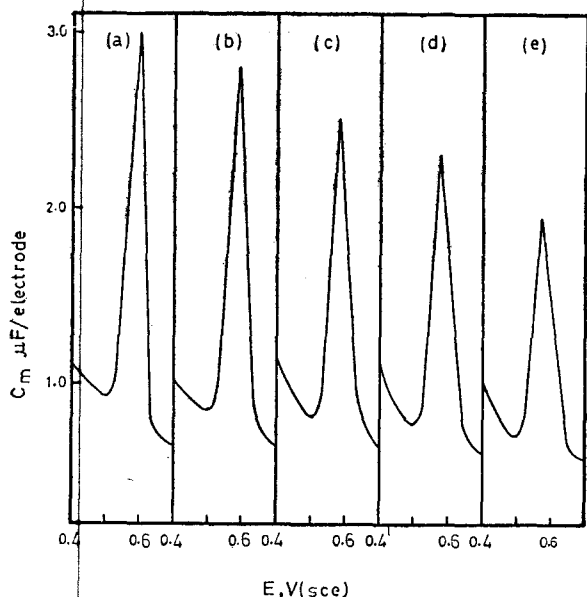


Fig. 4—Differential capacitance curves for  $7.5 \times 10^{-4} M$  Cd(II) in  $1N H_2SO_4$  and varying concentration of thiophene ([Thiophene] = (a)  $0.5 \times 10^{-2} M$ ; (b), 1.0 (c) 2.0 (d), 3.0 (e)  $4.0 \times 10^{-2} M$ )

TABLE 2—APPARENT STANDARD RATE CONSTANT ( $K_s$  AT  $25^\circ C$ , OF THE EXCHANGE Cd(II)/ Cd(Hg) IN  $1N H_2SO_4$  AT DIFFERENT THIOPHENE CONCENTRATIONS

[Cd(II) = $7.5 \times 10^{-4}$ g ion /litre]					
$10^4$ [Thiophene]	F	$C_m$	$R_m$	$\frac{R_r-1}{\omega_r}$	$K_s \times 10^3$
zero	1000	3.610	52	32	8.29
	3000	1.722	58	33	8.04
Zero + 2% ethanol	1000	3.203	68	40	6.69
	3000	1.130	58	42.5	6.31
0.5	1000	3.012	68	59	4.58
	3000	1.520	47	60.5	4.46
1.0	1000	2.804	95	61	4.35
	3000	1.503	70	64	4.15
2.0	1000	2.504	105	72	3.77
	3000	1.310	73	73.5	3.69
3.0	1000	2.300	110	80	3.42
	3000	1.090	77	82	3.34
4.0	1000	1.95	118	93	2.88
	3000	1.04	85	98	2.73

analysing vectorially the results of impedance measurements. This method is a simple one and has been used before to give reliable results<sup>9</sup>. The  $K_s$  values calculated for the exchange Cd(II)/Cd(Hg) in  $1N H_2SO_4$  and  $1N H_2SO_4 + 2\%$  alcohol and with different concentrations of thiophene are included in Table 2. In Table 2 are also given the various quantities involved in the calculation.

The results presented in Table 2 show that in  $1N H_2SO_4$ , the  $K_s$  values for the reduction of Cd(II) over the frequency range 1000-3000 Hz are highly satisfactory and the use of the simple model of faradaic impedance is quite justifiable under these conditions. The average  $K_s$  amounts to  $8.16 \times 10^{-2}$  cm/sec. This value agrees with those reported

earlier using different techniques in either neutral or acid sulphate media<sup>10-12</sup>.

In  $1N H_2SO_4 + 2\%$  alcohol as a base solution, the average  $K_s$  value amounts to  $6.5 \times 10^{-2}$  cm/sec. In the presence of thiophene,  $K_s$  values decrease with increasing thiophene concentration. This may be interpreted in terms of increase in the surface coverage by thiophene with increase in its concentration.

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#### Preparation & Characterization of a Few Coordination Compounds of Titanium(IV) with Schiff Bases

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Titanium(IV) complexes of dibasic tridentate schiff bases formed by the condensation of 2,4-pentanedione, 2-hydroxyacetophenone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde with 2-hydroxyethyl-, 2-hydroxy-1-propyl-, 3-hydroxy-1-propyl- and 1-hydroxy-2-butyl-amines have been prepared. The reactions between titanium isopropoxide, 4-(2-hydroxyethyl) amino-3-pentene-2-one ( $H_2acac$ ) and the schiff bases ( $SBH_2$ ) in 1:1:1 molar ratio result in the formation of several new derivatives of the type  $Ti(acac)(SB)$  in quantitative yields. The mixed complexes are monomeric in boiling chloroform. The coordination of oxygen (phenolic and alcoholic) and azomethine nitrogen of the schiff base to the metal atom is confirmed on the basis of infrared and proton magnetic resonance spectral studies.

REACTIONS of titanium alkoxides with nitrogen containing ligands have been studied<sup>1-5</sup>. However, the reactions of mixed ketamines and aldimines with titanium isopropoxide have not been investi-