Electrochemical Behaviour of Chloride Ion at Hanging Mercury Drop Electrode

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CYCLIC voltammetry of chloride ion at hanging mercury drop electrode has been investigated. Instead of one peak, as per the reaction $2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e$, a prepeak in addition to the main diffusion peak, was observed during anodic voltage sweep. The initial product of the electrode reaction is the formation of HgCl, a monolayer, which is adsorbed on the electrode surface giving rise to the prepeak. The surface area of the each adsorbed molecule was calculated to be 16 A^{02}, from the calculation of total change under the adsorption prepeak. This suggested that HgCl is adsorbed in the form of a monolayer. The chronopotentiometric and chronoamperometric studies of chloride ion confirms the appearence of prepeak due to the adsorption of HgCl in the form of a monolayer. The electrode mechanism is discussed.

INTRODUCTION

It is wellknown that chloride ion depolarizes the dropping mercury electrode with the formation of insoluble mercurous chloride. Kolthoff[1] has described the polarographic wave by simple equation which postulates that the wave should begin steeply and discontinuously, should be asymmetric about the halfstep potential and should shift to more negative potential with increasing chloride ion concentrations. Vlcek[2] investigated the behaviour of chloride ion at the dropping mercury electrode and found several departures from Kolthoff's postulates[1]. He found a small but distinct pre-step, the height of which did not vary with changing chloride concentration but increased in proportion to the mercury reservoir height. Vlcek also noted that (i) the total limiting current was not a linear function of bulk chloride concentration and (ii) at concentrations above 2mM the polarograms showed three or even four separate steps.

The a.c. polarography of chloride ion was first examined by Breyer & Hacobian[3], who found a sharp well defined a.c. wave corresponding to the anodic d.c. step. According to Biegler[4] the wave obtained in the a.c. polarography of chloride is attributed mainly to the adsorption of chloride ion which results in a differential capacity of the electrical double layer.

In the present work, the behaviour of chloride ion at hanging mercury drop electrode is studied using cyclic voltammetry, chronopotentiometry and chronoamperometry.

EXPERIMENTAL

Electroscan 30 (Beckman) was used in all the experiments. A tridentate cell constructed for this work, has three compartments. Two arms were isolated by G1 frit. A paste of agar-agar in saturated KNO_3 was poured in the arms. On the top of the paste saturated KNO_3 solution was poured. Saturated calomel electrode was connected via a Utube filled with KNO_3 agar bridge to avoid contamination of chloride ion concentration. The sample solution was added to the middle compartment and deaerated with purified nitrogen gas before each experiment. AnalaR grade chemicals were used in all the experiments.

RESULTS AND DISCUSSION

Cyclic voltammetry: Cyclic voltammetry of 0.4 mM of chloride concentration at various voltage scan rates were carried out in 0.1M KNO and 0.1M $HClO_4$ (Fig. 1 A, B). Instead of one peak according to the equation $2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e$, two peake were obtained during the anodic voltage sweep while in cathodic direction only one peak was observed. The first anodic peak (pre-peak) was obtained at + 0.245 V and the second at + 0.270 V vs SCE at scan rate of 10mV/sec.

The anodic current for the pre-peak increased very steeply as well as decreased very sharply before the second peak appeared (Fig 1 A). The second anodic peak was not well defined upto about 1mM of chloride concentration, while at higher concentrations at about 4mM it became well defined as shown in Fig. 1C. At 4×10^{-5} chloride concentrations or less, only one wave (not a peak) was observed.

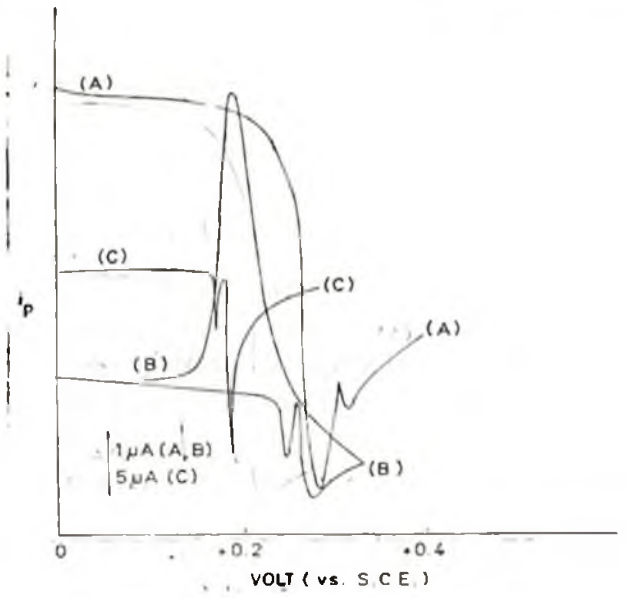


FIG 1 - VOLTAMMOGRAM OF 0.4mM CHLORIDE IN 0.1N $HClO_4$

(A) ν = 5mV / sec (B) ν = 100 mV / sec

(C) VOLTAMMOGRAM OF 4mM CHLORIDE IN 0.1 $HClO_4$, ν = 10mV / sec

Proportionality between concentrations and current was found to be satisfactory in the range of 0.4mM to 2mM at lower scanrates (10mV/sec & less). The current was measured from the base line of the first Peak and the maximum of the second peak.

According to Kolthoff[1] and Bieglar[4], the prewave should be discontinuous, however the first peak obtained here is quite steep and not discontinuous, which is in agreement with the Vloek's[5] observations. The current, (i p), of the prepeak is proportional to ν (scanrate), rather than $\nu^{\frac{1}{2}}$ (Fig. 2). The ratio of the prepeak current to second peak current increases with the increase of scanrate at lower concentrations of about 0.4mM. The area under the prepeak remained constant at 0.4 mM and above chloride concentrations.

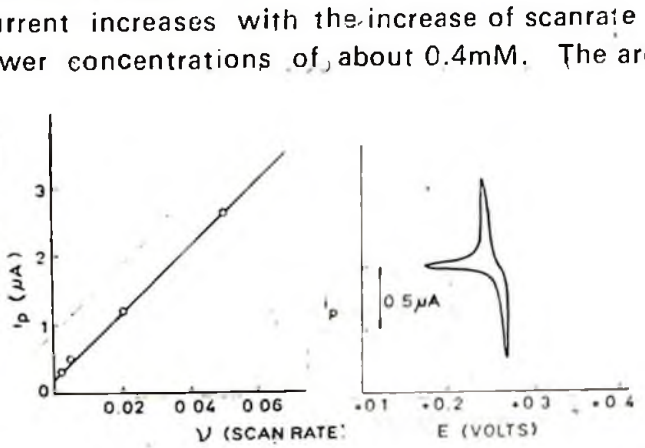


FIG. 2 PLOT OF PEAK CURRENT vs SCAN RATE
C = 0.4mM CHLORIDE A = 0.021 cm^2

FIG. 3 CYCLIC VOLTAMMOGRAM OF PREPEAK
0.4mM CHLORIDE IN 0.1M KNO_3
ν = 5mV / sec

The prepeak obtained by Blegler[4] in his a.c. polarographic work is attributed mainly to the adsorption of chloride ions which results in a high differential capacity of the electrical double layer. But in cyclic voltammetric studies by thiocyanate at HMDE, no prepeak was obtained as in the present work, although the SCN^- is strongly and specifically adsorbed at the electrode surface. Therefore, it seems that the prepeak is not due to the adsorption of chloride ion but is due to the initial electron transfer reaction with the formation of chloromercury, which is adsorbed on the electrode surface.

These observations show that the initial product of the charge transfer reaction which is HgCl, is adsorbed and is the primary process at low concentrations of chloride ion. As the concentration of chloride ion is increased, both processes *ie.*, adsorption as well as diffusion are observed. At higher concentrations, the diffusion procees is more predominent.

It is well known that when the reaction product is strongly adsorbed at the electrode surface, a prepeak is obtained. In this case also, a prepeak is obtained. Therefore, all the parameters as used by Wopschall and Shain[3], were evaluated. Using the value of Δ EW (*i.e.* the width of the adsorption peak at one half the maximum current), the value of σ_R and ψ_R (σ_R gives the potential dependence of the free energy of adsorption) and

$\psi_R = \frac{C^* \sqrt{\pi D_o}}{4 \sqrt{\tau_R{}^5 a}}$ could be known from the table II[5].

Thus the value of $\sqrt{\tau_R}$ saturation value at the maximum surface coverage obtained was, 3.7×10^{-8} mol/cm^2, using $D = 2.2 \times 10^{-5}$ cm^2/sec. And surface area of the each adsorbed molecule is found to be 21 A^2.

A second method involves the measurement of total charge under the adsorption prepeak. A value of the charge 100 $\mu c/cm^2$ is obtained from these results, the area of each adsorbed molecule is computed to be $16A^{02}$. The value calculated by Vlcek using the polarographic experiments was $18A^{02}$. The value reported by Huckel[6] for a Hg Cl

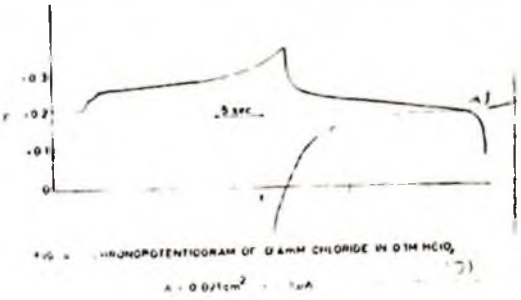
structure is 16A°[2]. It is thus clear that the supposition regarding the first peak, that it is due to HgCl adsorbed in the form of a monolayer is corroborated. This also shows that one chlorine atcm is attached to each mercury atom of the electrode surface.

It is of importance to know as to whether this adsorption prepeak follows the classical mechanism of Brdicka[7] or some other mechanism. *i. e.* a peak resulting from inhibition of the electrode reaction by the adsorption of the product of that reaction. In Brdicka' s model of adsorption two cathodic peaks are expected instead of one as obtained in the present work. Further more, on reversing the polarity just after the prepeak (adsorption peak) a desorption peak is observed and according to theory, potentials of these peaks should have been the same, but the difference here is about 30 mV (Fig. 3), which shows that the initial reaction is due to charge transfer only. Therefore, this fuither confirms that the prepeak observed is due to the formation of a monolayer of chloromercury at the electrode surface. This layer, which gives rise to a prepeak, acts as a barrier to the main charge transfer reaction for a diffusion process, which therefore proceeds with an appreciable over voltage in the presence of such a layer.

At potentials more positive than the prepeak the reaction proceeded by way of an intermediary Hg_2Cl^+ and the total current was proportional to the chloride concentrations with the formation of crystalline Hg_2Cl_2 at the electrode surface[2]. Thus ; the mechanism operating in this case is not similar to the class cal mechanism of Brdicks.

The difference in the peak potentials for the prepeaks as well as the main peak for the 0.4mM and 4mM chloride concentration, was found to be 70mMV instead of the theoretical 59mV. This deviation might be because of the appearance of the prepeak and the varying activity of the deposit during the electrolysis.

Chronopotentiometry : Anodic chronopotentiometry and current reversal chronopotentiometry of 0.4mM chloride in 0.1 M $HC10_4$ (Fig. 4), showed that first a small τ corresponding to a prepeak is observed and when the main chronopotentiogram is obtained, while only one chronopotentiogram is obtained on reversal.



This again proves as in cyclic voltammetric experiments that the initial product of charge transfer reaction forms a layer of calomel (chloromercury) at the electrode surface, which acts as a barrier to the charge transfer reactions which therefore, proceeds with overvoltage in the presence of of such a layer. Difference between the forward $E_{T/4(f)}$ and reverse $E_{T/4(r)}$ of the main chronopotentiogram, is about 35 mV, instead of being equal indicating the irreversibility of the electrode process. If the prepeak would have been absent, then $E_{T/4}$ for forward and reverse reactions, are same as can be seen from Fig. 5. A plot of log $(\tau^{\frac{1}{2}}-t^{\frac{1}{2}})^2$ vs E for the forward chronopotentiogram gave a slope of 35 mV.

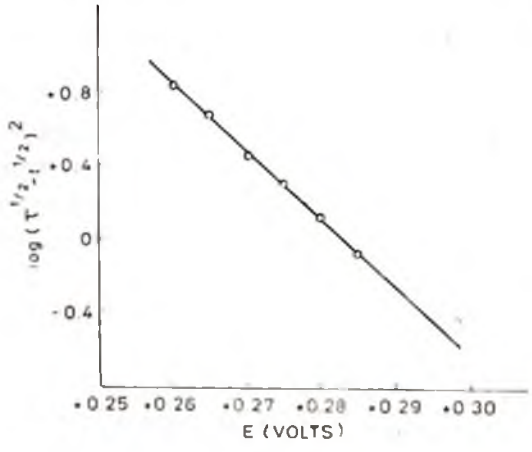


FIG 5 A PLOT OF log $(\tau^{1/2} - t^{1/2})^2$ vs. POTENTIAL
C = 0.4mM CHLORIDE IN 0.1M $HClO_4$
A = 0.021 cm^2

Chronoamperometry : Chronoamperogram of 0.4 mM Cl^- at different applied potentials + 0.27, + 0.28, + 0.29 and + 0.34V vs SCE were recorded as shown in Fig. 6. At + 0.27 V, probably an incomplete monolayer of HgCl is present, at the electrode surface while at + 0.28V, (corresponding to prepeak potential) current falls to minimum and then it remains practically constant with the increase of time. At this potential most probably a complete monolayer of HgCl is present on the

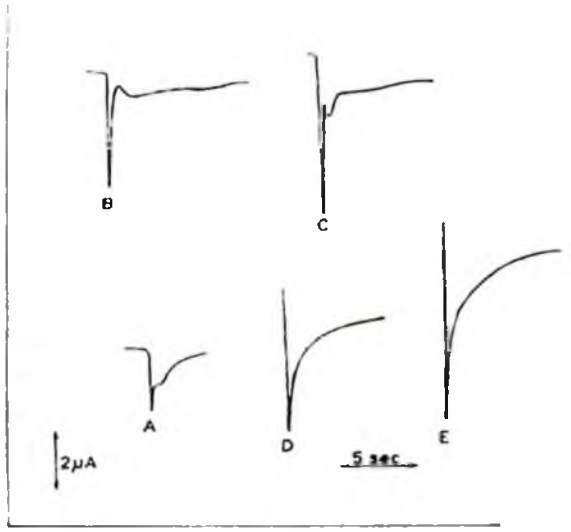


FIG. 6 CHRONOAMPEROGRAMS AT VARIOUS APPLIED POTENTIALS
A AT + 0.27V, B AT + 0.28V, C AT + 0.29V,
D AT + 0.30V, E AT + 0.34V
CONC = 0.4mM CHLORIDE A = 0.021 cm^2

electrode surface. On increasing applied potential + 0.29V and + 0.30V; the structure at the electrode solution interface changes and at higher potential of + 0.34 V a normal diffusion controlled chronoamperogram is observed. Diffusion coefficient of chloride ion was calculated by Cottrell's equation *viz.* 2.17×10^{-5} cm^2/sec.

Acknowledgement

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