SPECIFIC ADSORPTION OF CHLORATE IONS AT Hg/$KClO_3$ (aq) INTERFACE

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Adsorption of chlorate ion at polarized mercury/$KClO_3$(aq.) interface was studied through differential capacity measurements at 25°C. The shift of potential of zero charge towards more cathodic polarization with bulk-electrolyte activity gave a qualitative indication for chlorate ion-specific adsorption, which could be confirmed quantitatively through the plots of charge due to specifically adsorbed anions (q^i) vs electrode charge (q^M). For any concentration the magnitude of q^i is greater than q^M (q^M, + ve) indicating superequivalent adsorption of chlorate ions; for a given electrode charge, the magnitude of q_i increases with the increase in electrolyte-activity.

Specific adsorption of the inorganic oxyanions like nitrate[1] and perchlorate[2] at the mercury-solution interface is more complex than that of the structurally simpler halide ions. Grahame and Soderberg[3] first recognized this aspect through their systematic study of specific adsorption phenomenon. Present work is an endeavour to investigate the specific adsorption of ClO_3^- (which is also an oxyanion) at Hg/$KClO_3$ (aq) interface through differential capacity measurements.

EXPERIMENTAL

Differential capacity measurements were made on an a.c bridge, similar to the one described by Grahame[4,5] using a dropping mercury electrode (DME) with a thin-walled capillary and giving 8 sec. droptime at the potential of zero charge (E_{pzc}) of mercury in 0.10 M KCl-solution. The frequency of the alternating current was 1 KHz with an amplitude of 5 mV across the cell. An electronically operated magnetic drop detacher was utilized to knock off the drop at about two-thirds of its natural life. The time between two successive knocks was determined by means of a stop-watch, measuring up to 0.05 second time interval, accurately. The bridge was balanced at the instant of drop detachment from the capillary-tip. The output signal of the bridge was amplified by a multistage-transistor-preamplifier (Marconi Type TM 6591A) and displayed on a Dumont Oscillograph (Type 274). A large mercury pool electrode and N KCl calomel electrode (NCE) were used as the auxiliary and reference electrodes, respectively. Direct contact was made between the reference electrode and the test solution by means of a saturated (KCl) salt-bridge which minimized the liquid-junction-potential to a negligible extent. The potential applied was measured on a portable potentiometer (Pye-Cambridge) measuring accurately up to one millivolt. Differential capacities were measured in the potential range −0.10 to −1 40 volt vs NCE. The point of zero charge was determined separately, using streaming mercury electrode[6]. All the measurements were carried out in an air-thermostat controlled at (25 ± 0.1)°C.

Following the procedure described by Trasatti[7], mercury was purified. Twice crystallized $KClO_3$ (BDH/AnalaR) was used. Solution at required molality was prepared in conductivity-water and deoxygenated with purified and presaturated nitrogen gas before carrying out the experiments.

RESULTS AND DISCUSSION

The differential capacity of the double-layer as a function of polarization-potential, for seven concentrations of $KClO_3$ in the range 0.025 to 0 50 M is presented in Fig. 1. The characteristic capacity-hump

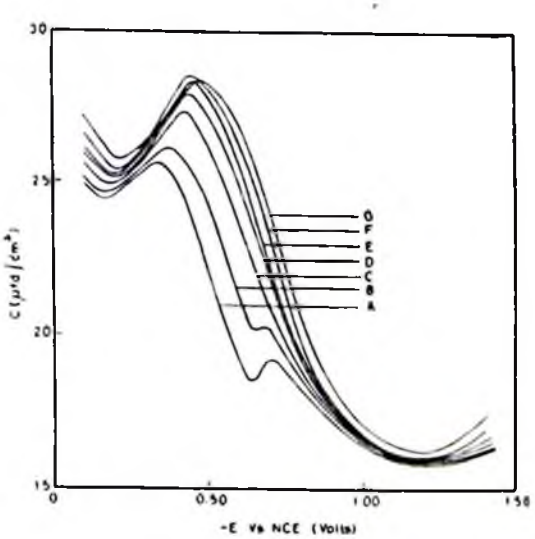


Fig. 1 Differential capacity-potential curves at Hg/$KClO_3$ (aq.) Interface at 25°C; (A) 0.025, (B) 0.05, (C) 0.10, (D) 0.15, (E) 0.20, (F) 0 30, (G) 0.50 M.

occurs at anodic polarization with respect to E_{pzc} which shifts towards more negative potential as the bulk-electrolyte concentration increases. A clear diffuse layer-minimum appears for 0.025 M solution at more cathodic potential than the E_{pzc}, due to the effect of the superimposed, steeply rising inner-layer-capacity. Complete disappearance of diffuse layer minimum in the capacity curves as the concentration increases to 0.10 M, gives the first clear indication for some specific adsorption of the anion[8].

The shift of E_{pzc} (from its value viz., −0.476 V vs NCE in systems with no specific adsorption e.g., fluoride solution) for the anion under investigation to more cathodic values with the increase in bulk-electrolyte activity (Fig. 2) can be taken as a semiquantitative

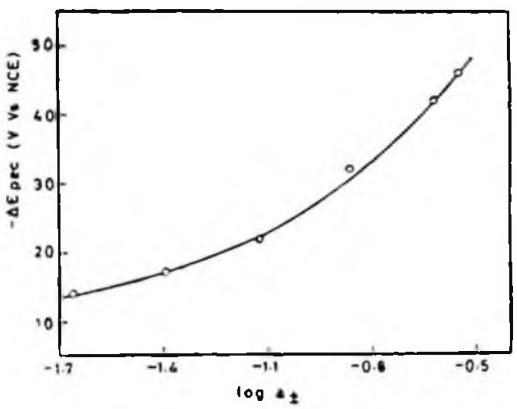


Fig. 2. Shift of Epzc as a function of logarithm of bulk-electrolyte-activity.

estimate of the extent of specific adsorption; ΔE_{pzc} being a direct measure of the specific adsorption.

Charge on the electrode surface (q^M) has been obtained by the numerical integration of capacity vs potential curves. Knowledge of E_{pzc} facilitated the evaluation of integration constant. Charge due to specifically adsorbed chlorate ions (q_i) has been calculated from the differential capacity data using the equations developed by Grahame and Soderberg[8] following diffuse layer theory. q_i thus obtained, accurate up to ± 1 $\mu c\ cm^{-2}$, has been plotted against q^M at four concentrations in the range, 0.05 to 0.40 M (Fig. 3). At any concentration, the magnitude of q^i is greater than q^M ($q.^M + ve$) indicating superequivalent adsorption of chlorate ions. At the highest concentration studied there exists a finite value of q^i even at $q^M = -6$ $\mu c\ cm^{-2}$, indicating a strong affinity of ClO_3 to the metal. At any electrode charge, the magnitude of q^i increases with electrolyte activity as expected.

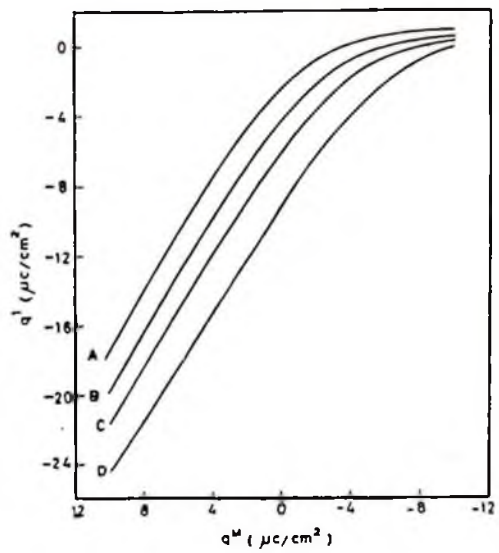


Fig. 3 Charge due to specifically adsorbed chlorate ions as a function of electrode charge; (A) 0.05, (B) 0.10, (C) 0.20, (D) 0.40 M.

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