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Bromate Ion Specific Adsorption at Hg/KBrO$_3$(aq) Interface

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Synopsis. Adsorption analysis at polarized Hg/KBrO$_3$ (aq) interface through capacity measurements at 25 °C indicates bromate ion specific adsorption by the cathodic shift of zero charge potential with bulk electrolyte activity confirmed by means of q^1 (charge due to specifically adsorbed anions) *vs.* q^m(electrode charge) curves. At any concentration, $q^1 > q^m$ revealed bromate ion superequivalent adsorption. At fixed q^m, q^1 increases with electrolyte activity.

It was confirmed by Grahame and Soderberg$^{3)}$ that the specific adsorption of inorganic oxoanions, *e.g.* nitrate,$^{1)}$ perchlorate,$^{2)}$ at Hg/solution interface is more complex than that of simpler halide ions. This communication presents evidence (both qualitative and quantitative) of specific adsorption of BrO_3^- (an oxoanion) at Hg/KBrO$_3$ (aq) interface through capacity measurements.

Experimental

Differential capacity measurements were made on an a.c. bridge, described by Grahame$^{4,5)}$ using a dropping mercury electrode (DME) with a thin walled capillary and drop time *ca.* 8 s at zero charge potential (E_{pzc}) of mercury in 0.10 mol·kg^{-1} KCl-solution. The a.c. frequency used was 1000 Hz with an amplitude less than 5 mV across the cell. An electronic magnetic drop detacher helped to knock off the drop at about two-thirds of its natural life. The time between two successive knocks was determined with a stop watch, measuring time-interval up to 0.05 s. The bridge was balanced at the instant of drop detachment. The out of balance of the bridge amplified by a multistage transistor preamplifier (Marconi Type TM6591A) was displayed on a Dumont Oscillograph (Type 274). A large mercury pool electrode and 1 M KCl calomel electrode (NCE) were used as auxiliary and reference electrodes, respectively. Direct contact was made between the reference electrode and the test solution by a saturated-KCl salt bridge which minimized the liquid junction potential to be negligible. The potential applied, measured on a portable potentiometer (Pye-Cambridge), was accurate up to one millivolt. Differential capacities were measured in the potential range from -0.10 to -1.40 V *vs.* NCE. The zero charge potential was determined separately, using streaming mercury electrode.$^{6)}$ All the measurements were carried out in an air-thermostat controlled at 25±0.1 °C.

Mercury was purified by the procedure described by Trasatti.$^{7)}$ Twice crystallized KBrO$_3$ (BDH/AnalaR) was used. Solutions at required molalities were prepared in conductivity water and deoxygenated with purified and presaturated nitrogen gas before the experiments were carryied out.

Results and Discussion

The differential capacities of the double layer as a function of ploarization potential, for eight concentrations of KBrO$_3$ in the range 0.025—0.500 mol kg^{-1}, are shown in Fig. 1. The characteristic capacity-hump occurs at anodic polarization with respect to E_{pzc} which shifts towards more negative potential with bulk electrolyte activity. Activity values were derived from graphical interpolation of the reported data.$^{8)}$ A clear diffuse layer minimum appears for 0.025 mol kg^{-1} at more cathodic potential than E_{pzc}, due to the effect of superimposed steeply rising inner layer capacity. Complete disappearance of diffuselayer minimum in the capacity curves as the concentration approaches 0.10 mol kg^{-1} gives a clear indication of anionic specific adsorption.$^{9)}$

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 (*cf.* Fig. 2) can be taken as a semi-quantitative estimate of the extent of specific adsorption; $|\Delta E_{pzc}|$ is an approximate measure of the specific adsorption (Esin Markov effect$^{10)}$).

The charge on the electrode surface (q^m) was obtained by integration of capacity curves. Knowledge of E_{pzc} facilitated the evaluation of integration constant. The charge due to specifically adsorbed bromate ions (q^1) has been calculated from the equations developed by Grahame and Soderberg$^{3)}$ following diffuse layer theory. q^1 thus obtained, accurate up to ± 1 μC cm^{-2}, has been plotted against q^m at four concentrations in the range 0.05—0.40 mol kg^{-1} (*cf.* Fig. 3). At any concentration the magnitude of q^1 is greater than $q^m(>0)$, indicating superequivalent adsorption of bromate ions. At the highest concentration studied, there exists a finite value of q^1 even at $q^m = -6$ μC cm^{-2}, revealing a strong affinity of BrO_3^- to the metal. At any electrode charge, the magnitude of q^1 increases with increase in electrolyte activity.

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