Properties of Electrical Double Layer at Hg./Acetate-salt solution (aq.) Interface

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TO study the properties of the electrical double layer formed at the Hg / aqueous sodium acetate, potassium acetate and ammonium - acetate interface, impedance measurements have been done using a symmetrical Wien type a.c. bridge. The charge due to surface-excess of cations, the charge due to excess/deficiency of anions in the diffuse layer and the charge due to specific adsorption of acetate ion at the mercury surface have been computed and their dependence on the charge at the metal surface and electrolyte concentration has been discussed. The specific adsorption of acetate ion has been found to be less than that of chloride ions.

The geometry of the ion plays an important role in its specific adsorption at the metal surface. The present investigation was done to study the adsorption of acetate ion at the mercury surface and to compare the specific adsorption of acetate ions with that of the chloride ions which have simpler geometry. The results of these studies are presented in this paper.

EXPERIMENTAL

Essentially the same experimental set up as described previously [1,2] was used in present study.

Analar (B.D.H.) grade chemicals and conductivity water (Specific conductivity 0.1 - 0.2x10^{-6} mho cm^{-1}) were used for preparing test solutions. The solutions were pre-electrolysed and deaerated with purified high purity tank nitrogen.

The differential capacity measurements were done at eight electrolyte concentrations (viz. 0.05, 0.10, 0.25, 0.50, 0.75, 1.00, 1.50 and 2.00 m) in the potential range -0.10 to -1.40 volts. The potential of the dropping mercury electrode (DME) was measured against a normal calomel electrode. The potential of zero charge (PZC) was obtained by the drop-time technique. The surface area of the drop was determined from the rate of flow of mercury and the age of the drop.

Charge density at the metal surface (q^M) was obtained by integration of differential capacity per unit area (C) versus potential (E) curves. The integration constant was evaluated from the knowledge of PZC. The activity coefficients for sodium acetate and potassium acetate were taken from literature[3]. The activity coefficients for dilute ammonium acetate solutions were not available but were calculated using Debye-Huckel limiting law. Using the relations developed by Grahame[4] and Grahame and Soderberg[5], the charge due to surface excess of cations (q^+) and the components of charge due to surface excess of anions viz. the charge due to excess/deficiency of anions in the diffuse layer (q^d) and the charge due to specifically adsorbed acetate ions (q^i) were calculated for 0.10m ammonium acetate and 0.10, 0.25 and 0.50m potassium acetate and sodium acetate solutions.

RESULTS AND DISCUSSIONS

The differential capacity (C) versus potential (E) curves for various concentrations of CH_3COONa, CH_3COOK and CH_3COONH_4 are shown in Figs. 1, 2 and 3 respectively. Similar to the observations in many other aqueous electrolyte solutions, the main features of the capacity curves are (i) a minimum in capacity at $\approx$ 1.10 volt, (ii) a rise in capacity at extreme anodic potentials and (iii) a hump at intermediate potentials. The factors responsible for occurence of these features in the differential capacity curves are discussed elsewhere[1].

The hump observed in capacity curves for acetate salt solutions is less pronounced than for chloride ion[1,2]. According to Shvarts et al[6], the hump in the capacity curves is formed due to the arrest of specific adsorption of anions due to the decrease in the number of water dipoles absorbed with their negative end toward mercury surface at

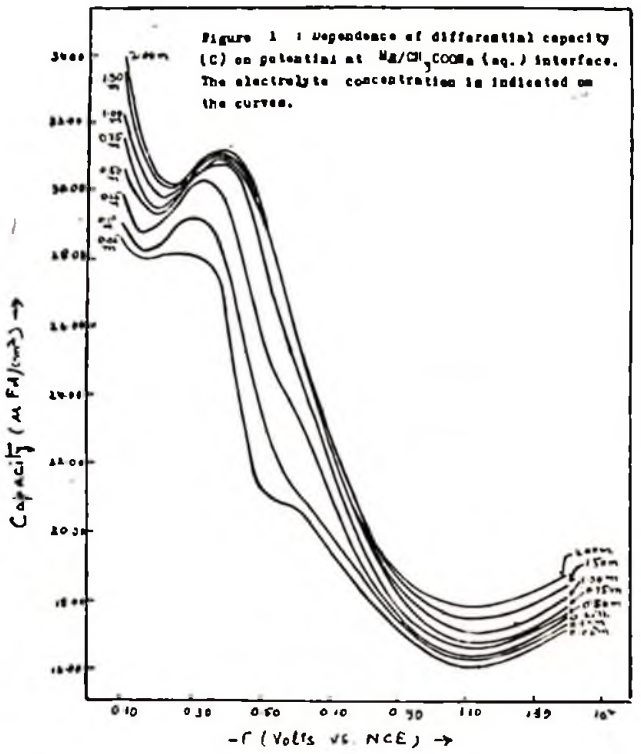


Fig. 1 Dependence of differential capacity (C) on potential at Hg/CH_3COONa (aq.) Interface. The electrolyte concentration is indicated on the curves.

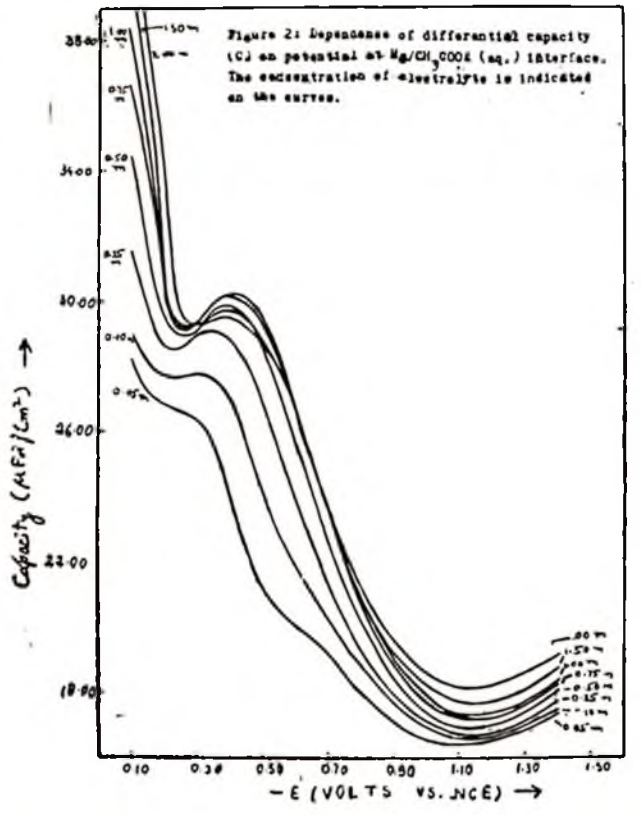


Fig. 2 Dependence of differential capacity (C) on potential at Hg/CH_3COOK (aq) interface. The electrolyte concentration is indicated on the curves.

PZC. The decrease in the number of water dipoles is caused by high polarizing power (capable of forming a hydration shell) of anions[6]. The observation of less pronounced hump for acetate ions compared to chloride ions is easily understandable. Although both the ions have a unit negative charge due to larger size and complicated geometry, the acetate ions will have lower polarising power compared to smaller and spherical chloride ions.

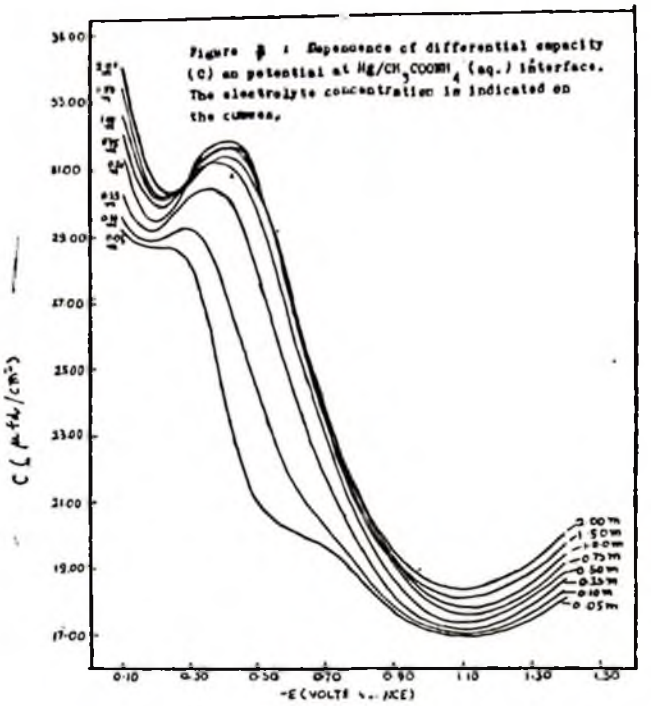


Fig. 3 Dependence of differential capacity (C) on potential at Hg/CH_3COONH_4 (aq.) interface. The electrolyte concentration is indicated on the curves.

The dependence of the charge due to the surface excess of cations (q^+), due to any excess or deficiency of anions in the diffuse layer (q^d_-) and due to specific adsorption of acetate ions (q^i) on q^M and electrolyte concentration is shown in Fig. 4 and 5.

Since the charge characteristics in the diffuse layer are controlled by the net charge and its sign on the electrode side of the outer Helmholtz plane (OHP), the observation of positive values of q^+ even at positive values of q^M (of Figs. 4 and 5) indicates the specific adsorption of acetate ions. The q^+ versus q^M curves pass through a minimum ($q^+_{min.}$) at an intermediate q^M value and this minimum shifts toward more cathodic charges with

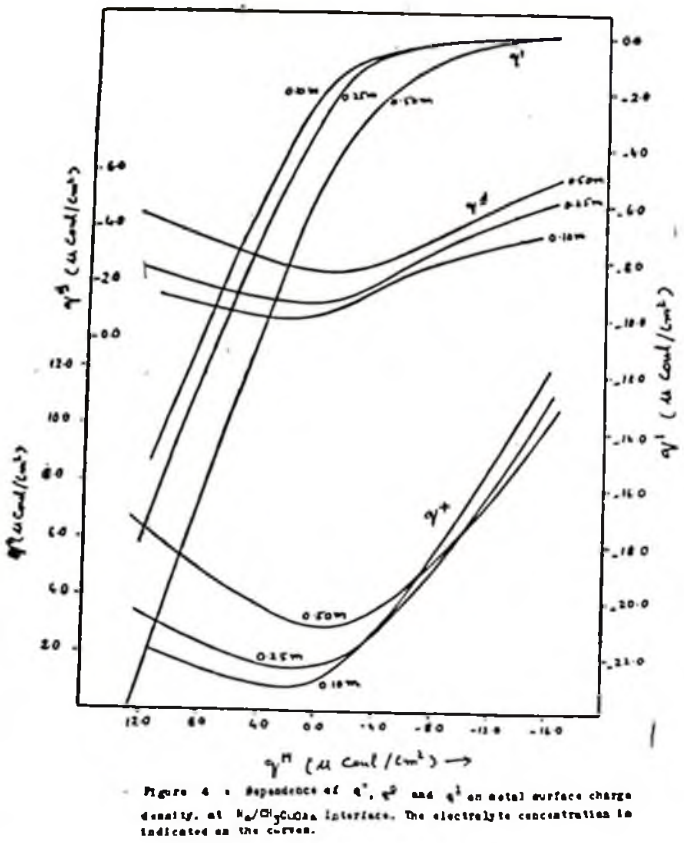


Fig. 4 Dependence of q^{+}, q^{d}_{-} and q^{1} on metal surface charge density at Hg/CH COONa (ag.) interface. The electrolyte concentration is indicated on the curves.

increase in salt concentration. The change in charge condition on the electrode side of the OHP, as the potential of the DME is changed, is governed by two competitive process; (i) the rate of charge of q^{M} with E (i.e. dq^{M}/dE) and (ii) the rate of specific adsorption of anions with potential ie. dq^{1}/dE. Hence the rise on either side of $q^{+}_{min.}$ is controlled by dq^{M}/dE and dq^{1}/dE; at q^{M} values anodic to $q^{+}_{min.}$, as the magnitude of the cathodic potential of the DME is decreased, the higher rate specific adsorption of anions than the rate of increase of positive (or decrease of negative) charge on the metal surface (ie. $|dq^{1}/dE| > |dq^{M}/dE|$) causes the presence of a net negative charge on the electrode side of the OHP. Similarly, at charges cathodic to $q^{+}_{min.}$ $|dq^{M}/dE| > |dq^{1}/dE|$ and hence as the magnitude of the cathodic potential of the DME is decreased, the net value of the negative charge on the electrode side of the OHP decreases. This causes a decrease in q^{+}. At $q^{+}_{min.}$ $|dq^{M}/dE| = |dq^{1}/dE|$. The shift of $q^{+}_{min.}$ to more cathodic charges with increase in electrolyte concentration is easily understandable in the increased rate of specific adsorption of acetate ions.

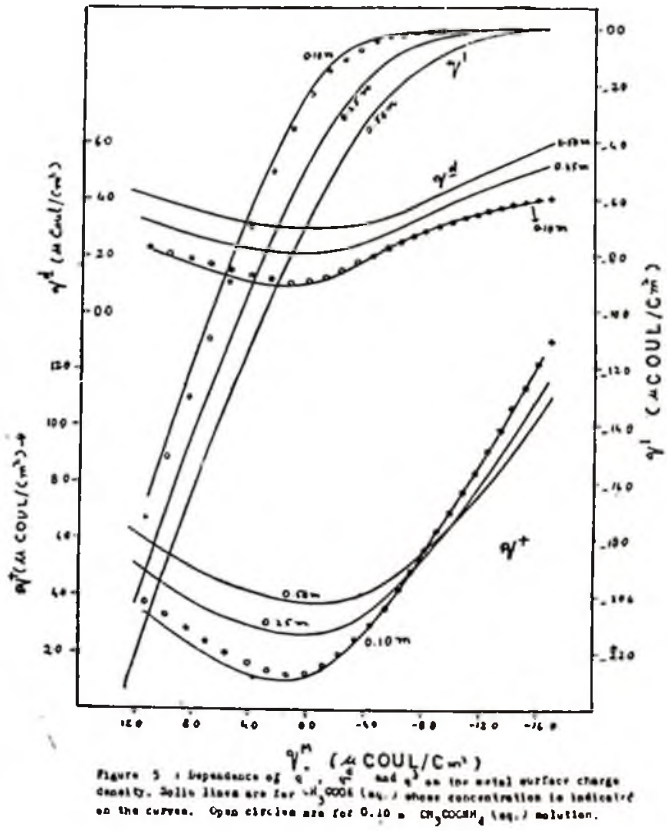


Fig. 5 Dependence of q^{+}, q^{d}_{-} and q^{1} on metal surface charge density. Solid lines are for CH COOK (aq.) whose concentration is indicated on the curves. Open circles are for 0.10 m CH_3COONH_4 (aq.) solution.

Similar to q^{+} (for cautions), q^{d}_{-} represents the the charge due to any excess or deficiency of anions in the diffuse layer and hence is dependent on the sign and magnitude of the charge on the electrode side of the OHP. q^{d}_{-} is positive (indicating the deficiency of anions in the diffuse layer) throughout the q^{M} range for all the concentrations of the three electrolytes studied (cf. Figs. 4 and 5). Similar to q^{+} curves, q^{d}_{-} curves also pass through a minimum ($q^{d}_{-min.}$) and for any fixed electrolyte concentration, the q^{M} values at which $q^{d}_{-min.}$ and $q^{+}_{min.}$ occur are identical. The $q^{d}_{-min.}$ and the rise on either side of $q^{d}_{-min.}$ are also explainable in terms of net rate of change or charge (and its sign)

on the electrode side of the OHP caused by the different magnitudes and opposite nature of dq^M/dE and dq^1/dE. The increase of q_2^d with increase of electrolyte concentration indicates that the deficiency of acetate ions in the diffuse layer increases.

The charge due to specific adsorption of acetate ions (q^1) is zero at extreme cathodic charges (indicating complete desorption of these ions from the inner layer at these charges) and as the magnitude of the negative values of q^M decreases, the magnitude of negative values of q^1 increases. At cathodic q^M, the dq^1/dE is small but at anodic values of q^M, a large dq^1/dE is observed (cf. Figs. 4 and 5). The potential of complete desorption of acetate ions from the inner layer shifts to more cathodic charges with increase in electrolyte concentration. At any fixed charge value, the specific adsorption of acetate ions increases with increase in electrolyte concentration. Compared to the specific adsorption of chloride ions[1,2], the specific adsorption of acetate ions is less for any fixed electrolyte concentration and q^M. This is possibly due to the fact that compared to chloride ions, accomodation of cumbursome acetate ions will require desorption of more water molecules from the metal surface. In addition to it the $-COO^-$ group, pointing toward OHP may hinder further entry of acetate ions in the inner layer, The possibility of higher lateral repulsion (Parallel to metal surface) compared to that in case of chloride ions can also not be ruled out.

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