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New insights into the double layer structure from impedance measurements: Implications for biological systems

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Abstract

Impedance measurements using a static mercury drop electrode in aqueous 0.01 M KCl, KBr and KI suggest structural effects of water and solute–solvent interactions near the double layer. The ion–dipole orientation effects are more dominant for chloride and least for iodide. These effects are more easily manifested at potentials near the changeover of the double layer structure. The interaction with mercury ions increases from chloride to bromide to iodide. For 0.01 M solutions, the double layer changeover potential shifts from about 0.15 to 0.025 to −0.15 V. Mott–Schottky plots show both p-type and n-type semi conduction. Also when the potential is varied from −0.5 to +0.5 V, unique differences in the nature of admittance, Nyquist plots and Bode plots are observed for the different halides. The sensitivity of the phase angle near the double layer changeover potential becomes less with bromide and least with iodide. This is consistent with the water structure formation and the breaking characteristics of these anions. Water structure-breaking effects increase from chloride to bromide to iodide. Our data suggest that frequency and potential dependent orientation changes of water molecules around ions and biological molecules play an important role in their electronic properties in living systems.

Keywords: Double layer; Impedance; Biological implications; Mott–Schottky; Solute–solvent interaction

1. Introduction

Our interest in biological electronic circuits involving DNA (or RNA or proteins)-salt–water and other molecular interactions necessitated the need to understand the behavior of electrolytes. While the role of ions such as Na^+, K^+, $HCO_3{}^-$, $SO_4{}^{2-}$ and $H_2PO_4{}^-$ are somewhat known, the role of ions such as Cl^- in biological systems still eludes us. Also, to understand the unique impedance behavior of palladium lipoic acid (1:1) complex, an experimental chemotherapy agent developed in our laboratory, there is a need to study the behavior of background electrolytes such as NaCl [1]. Since almost all biological processes take place in the presence of electrolytes, it is important to understand their behavior. Impedance measurements of alkali chlorides with and without DNA using the mercury electrode [2,3] exhibited duplex semi conducting behavior, specific ion–DNA interactions and characteristic changes associated with the structure of water in the double layer as well as at the electrode surface. Differential capacity measurements and electrocapillary measurements of potassium halides [4–6] have revealed the nature of the specific adsorption and the double layer. However, these measurements have not been able to distinguish the subtle differences between the cations, such as lithium to cesium and the structural changes of water at and near the double layer. From double layer capacity measurements in aqueous KCl + KF mixtures at constant ionic strength, the adsorption of chloride ions on mercury has been measured [7]. These results demonstrated that the constant charge isotherms of chloride ion adsorption from KCl and from KCl + KF solutions cannot be superimposed irrespective of the choice of salt

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activity. On the other hand the specific adsorption of iodide from KI [6] was very similar to that from the mixed KI + KF solutions [8]. Our impedance, phase angle, admittance and Mott–Schottky measurements [1–3] indicate that frequency response analysis is a powerful tool to provide information on the nature of solute–solvent interactions at the double layer.

In our present studies we have explored the behavior of mercury in both the negative and positive range of potentials because in natural biochemical systems we have both positively and negatively charged surfaces at close distances where water molecules will be subjected to competing influences from the electric field of these charged centers as well as the charges from the electrolytes. We have used mercury as the working electrode because it allows us to get reproducible surface for our studies by using a fresh drop each time. Compared to using any other metal, fresh mercury drops allow repetitions and reproducibility better and easy. For example if we corrode a metal, it is not easy to clean and get the non-corroded surface again and again for each experiment.

2. Experimental

An EG & G PARC Model 303A SMDE tri electrode system (platinum counter electrode and Ag/AgCl (saturated KCl, reference electrode) along with Autolab eco chemie was used for cyclic voltammetric and electrochemical impedance measurements at 298 K. Analytical grade KCl, KBr and KI were used to prepare 0.01 M solutions. Distilled water was used for preparation of all solutions. Potassium iodide solution was prepared using water that was purged with nitrogen because traces of oxygen present in the water interact with the iodide. No other background electrolyte was used for the measurements. The solutions were purged with N_2 for about 10 min before the experiment. Impedance measurements were carried out using about 7 mL solutions in the frequency range 10,000 Hz to 40 mHz. The amplitude of the sinusoidal perturbation signal was 10 mV.

3. Results and discussion

3.1. Cyclic voltammetry

These measurements were made for 0.01 M potassium halides at a scan rate of 100 mV/s by scanning in three potential regions. The first region is in the range 0 to −1.0 V and back to 0 V. This falls within the conventional range of the mercury working electrode. The second range is 0.3 to −1.0 V and back to 0.3 V so that the mercury is slightly passivated and the halide begins to interact. The third range is 1.0 to −1.0 V and back to 1.0 V. This is the range where mercury seems completely passivated and all the halides interact strongly. Three scans were made for each potential region. The cathodic and anodic peak potentials for the third scan for the three halides are given in Table 1 and the results for the third range are shown in Fig. 1.

Table 1
Cyclic voltammetry of 0.01 M potassium halides

	Peak potential for scan 0 to −1.0 V and back to 0 V (V)	Peak potential for scan 0.3 to −1.0 V and back to 0.3 V (V)	Peak potential for scan 1.0 to −1.0 V and back to 1.0 V (V)
KCl			
Cathodic	No peak	0.053	−0.047
Anodic	No peak	0.261	0.268
KBr			
Cathodic	No peak	−0.059	−0.118
Anodic	No peak	0.178	0.194
KI			
Cathodic	−0.264	−0.398	−0.462
Anodic	No peak	0.112	0.104

The results indicate that the interaction of halide with mercury increases from Cl^- to Br^- to I^- and the cathodic peak is shifted to slightly more negative potentials. From the data in Table 1, it seems that for a particular halide the anodic peak stays nearly the same irrespective of the range of the potential scan. However a shift to slightly more negative cathodic potentials is observed when the initial potential of the scan is changed from 0.0 to +0.3 or +1.0 V. The shift is the highest when the starting potential is 1.0 V. Also we have observed that the cathodic current is higher (similar to higher cathodic current for iodide compared to bromide or chloride) when the starting potential is changed from 0 to 0.3 V and still higher when it is changed to 1.0 V. The observed potential shifts among halides, the increase in cathodic currents from chloride to iodide, and the observed increase in cathodic currents with increase in the starting potential of the scan are consistent with the ease with which halide complexes of mercury are formed and consequent higher interaction. The observations are in accordance with the characteristics of adsorption process. When there is strong adsorption, a post wave or post peak is often observed [9]. This contributes to higher cathodic currents. In the case of weak adsorption no post peak is observed, but only an increase in cathodic current. The data in Fig. 1 indicated strong adsorption of iodide with some post peak whereas it is weak for bromide and chloride. The higher cathodic currents with increase in the starting potential of the scan are indicative of adsorption by

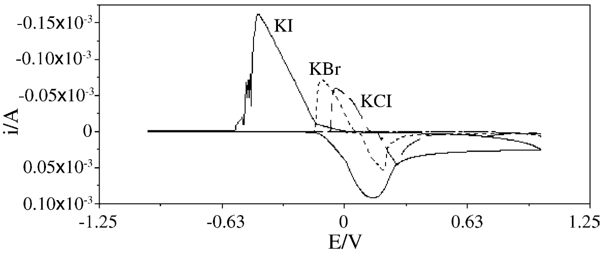

Fig. 1. Cyclic voltammetry curves of 0.01 M solutions of potassium halides.