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Solute-Solvent Interactions from Impedance Measurements: 'π –way' Conduction and Water Structure-Enforced Ion Pair Formation in Aqueous Lidocaine Hydrochloride

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Admittance measurements of aqueous 0.01, 0.02, 0.05, 0.10, 0.40, and 0.80 M solutions of lidocaine hydrochloride and 0.10 M solution of lidocaine sulfate were investigated using a mercury working electrode. These measurements indicated an increase or decrease in admittance with decreasing frequency depending on the concentration of lidocaine hydrochloride. As the potential changes from negative to less negative, to zero and finally to positive, the admittance increased and passed through a maximum. There was also a slight anodic shift in the maximum with decreasing frequencies suggesting the role of solute-water interactions and orientation effects of water near the double layer changeover potential. To explain the admittance data, we have used the concept of "potential induced and water structure-enforced ion pair formation", at or near the double layer. The impedance data indicate negative differential resistance at negative potentials, suggesting the role of π electrons in the conduction process, similar to the 'π –way' in DNA. Sodium chloride affects the lidocaine hydrochloride double layer and impedes the 'π –way' conduction process, while lidocaine sulfate admittance data suggest a more complex self-assembly process near the double layer.

Keywords: admittance, potential induced and water structure-enforced ion pair, Gurney co-sphere, 'π –way'

1. INTRODUCTION

Lidocaine is one of the most widely used anesthetic drugs today, especially during surgery and dental procedures. Lidocaine was developed by the Swedish scientist Nils Löfgren in 1943 [1]. Additionally, lidocaine has been used as an antiarrhythmic agent. The drug works by inhibiting the stimulants needed to initiate neuronal impulses to the brain, resulting in the loss of pain. As a topical drug, lidocaine has a relatively short half-life of only 1.5-2 hours in an intravenous injection because it

is quickly metabolized by the liver (due to the presence of an amide group). Even though the time frame in which lidocaine works is extremely short, it is commonly used as the local anesthetic of choice among professionals due to its hypoallergenic quality.

There are two forms of lidocaine (2-diethylamino-N-(2,6-dimethylphenyl)acetamide): lidocaine hydrochloride (lidosalt), as shown in Figure 1, and lidocaine base (lidobase). Lidocaine hydrochloride is the anesthetically active form and is soluble in water, whereas lidobase is not soluble in water and anesthetically much less active.

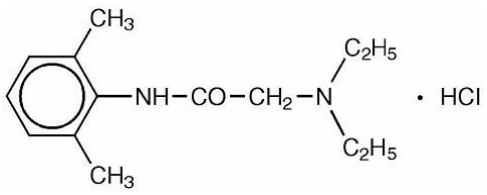

Figure 1. Lidocaine Hydrochloride

Lidocaine hydrochloride has a very interesting structure in water. The hydrate microcrystal theory of anesthesia, advanced by Linus Pauling [2] is closely related to the "iceberg" theory of ionic solutions and hydration of proteins. The ordered arrangement of water molecules around solute ions and protein side chains is considered as part of the clathrate structure. Later studies have shown that local anesthetics form a hydrogen bonded complex with a receptor in the membrane [3]. Lidocaine, a sodium ion channel blocker or nerve block, is a local anesthetic. A lidocaine cation can donate two protons and accept one. The crystal structure of lidocaine [4] indicates that adjacent chains are held together by chloride ions, each of which accepts an aqueous proton from one chain and an amino proton from the other. The double chains are held together by van der Waals forces. The structure is fully hydrogen bonded and '*endless chains'* of lidocaine cations are produced by water molecules.

Infrared spectra of lidocaine cation with different anions [5] indicate strong interactions between nitrogen and hydrogen and a small anion associated with an intense force field, such as a chloride ion. On the other hand, with a large polyatomic anion associated with a weaker peripheral force field, such as hexafluoroarsenate, the N^+-H stretching frequency is higher than that with a chloride ion. The neutral form of lidocaine is about five times *less* effective when compared with the cationic form [6]. With the physiologically active form of lidocaine being the cation [4, 7], the choice of an appropriate anion may also influence the rate of drug delivery as well as its mode of action.

Our interest in aqueous lidocaine hydrochloride was necessitated by our interest in developing medicated Pluronic gels for sustained drug delivery. The structure of lidocaine also offers some interesting possibilities for its double layer behavior because of the presence of polar groups, a phenyl group, and hydrophobic groups near the charge. We have chosen mercury as the working electrode because it is relatively easy to get a fresh drop of mercury each time and thus its ability to minimize surface inhomogeneities. It also offered opportunities to study the influence of surface area more easily because the size of the drop can be easily changed.

Our recent impedance measurements of sodium and potassium halides have revealed the structural effects of water and solute-solvent interactions near the double layer [8, 9]. Also our

impedance measurements of biological molecules, such as collagen [10] and prothrombin [11] along with our more recent admittance measurements of molybdates at different pH values [12], of the self-assembly of polyoxomolybdates [13, 14], hydrogen peroxide [15, 16] and cysteine [17, 18] have indicated the great potential of admittance measurements for obtaining information on solute-solvent interactions at or near the double layer.

Admittance (Y) and impedance are interrelated, $Y \equiv Z^{-1} \equiv Y' + jY''$. Since its introduction in 1969 by Bauerle for the determination of accurate conductivity of solid electrolytes [19], no serious attempts have since been made to utilize this concept. Our past measurements have pointed out its many potential uses. In this report we present one of the simplest drug molecules, lidocaine hydrochloride, and its interaction with water at or near the double layer.

2. EXPERIMENTAL PART

An EG & G PARC Model 303A SMDE tri electrode system (mercury working electrode, platinum counter electrode and Ag/AgCl (3.5M KCl, reference electrode) along with Autolab eco chemie was used for cyclic voltammetric and electrochemical impedance measurements at 298 K. Sigma lidocaine hydrochloride monohydrate, lidobase, 2N H_2SO_4, NaCl and distilled water were used for the preparation of all solutions. Lidocaine sulfate was prepared by neutralization of lidobase with sulfuric acid. The solutions were purged with N_2 for about 10 minutes before each experiment. Impedance measurements were carried out using about 7 mL solutions in the frequency range 1,000 Hz to 25 mHz. The amplitude of the sinusoidal perturbation signal was 10 mV. The absorption spectra were recorded on a Shimadzu UV1650PC.

3. RESULTS AND DISCUSSION

3.1 Absorption Spectra

The absorption spectra and the calibration curve for lidocaine hydrochloride solutions are shown in Figures 2a and 2b.

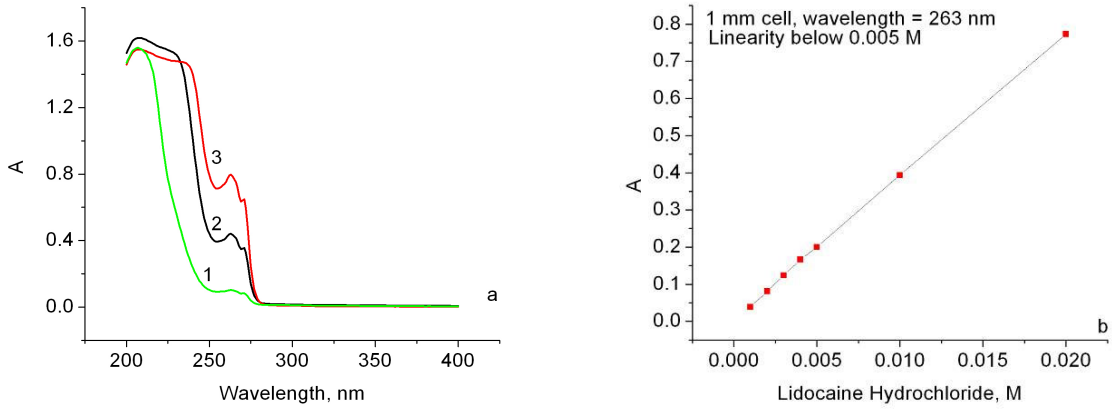

Figure 2 a. Spectra of 1) 0.02 M, 2) 0.10 M, and 3) 0.20 M Lidocaine hydrochloride, 1mm cell. **b.** Calibration curve.

Our spectrophotometric results at 263 nm indicated significant deviations from Beer's law above 0.005 M solutions of lidocaine hydrochloride, suggesting strong $\pi - \pi$ interactions at higher concentrations. It also suggests the possibility of 'endless chain' formation for lidocaine in solution as well as in the hydrated crystal formation [4].

3.2. Cyclic Voltammetry

We included a few studies of lidocaine hydrochloride in the presence of NaCl because it is the major electrolyte in biological systems. Cyclic voltammetric measurements were made for 0.02 M aqueous lidocaine hydrochloride and NaCl solutions, 0.10 M NaCl and 0.02 M lidocaine hydrochloride in the presence of 0.10 M NaCl at a scan rate of 100 mV/s in the potential range 0.3 to -1.0 V. There was no noticeable activity in the scan range 0 to -1.0 V. The results, as shown in Figure 3a, indicate slightly less cathodic and anodic currents for lidocaine hydrochloride, when compared with that of NaCl, indicating that the activity of the chloride is less in the presence of lidocaine probably due to strong ion pair interaction between the lidocaine cation and the chloride anion. Figure 3b shows that both cathodic and anodic currents are much less for 0.02 M lidocaine hydrochloride in the presence of 0.10 M NaCl when compared with that of 0.10 M NaCl, demonstrating a strong and competing or masking interaction of lidocaine cations for the chloride ion and consequent less passivation of mercury.

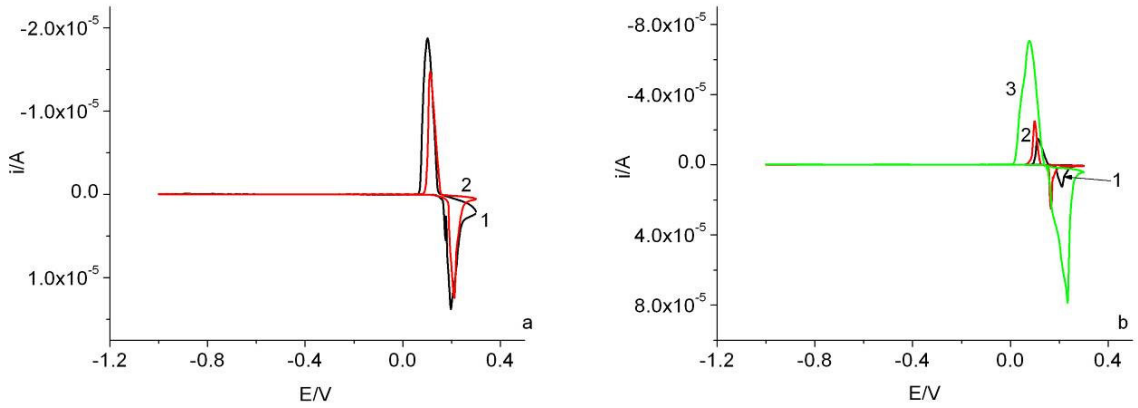

Figure 3 a. Cyclic voltammetry curves of 1) 0.02 M NaCl 2) 0.02 M lidocaine hydrochloride;
b. 1) 0.02 M Lidocaine hydrochloride; 2) 0.02 M Lidocaine hydrochloride containing 0.10 M NaCl; 3) 0.10 M NaCl. Scan from 0.3 to -1.0 V and back. The results of the third scan are shown in the figure.

3.3. Admittance

3.3.a. Lidocaine hydrochloride

The admittance data at 2000, 1000, 750, 500, 250, 100, 50 and 10 Hz for 0.01 M, 0.02 M, 0.05 M, 010 M, 0.40 M, and 0.80 M aqueous lidocaine hydrochloride, as shown in Figures 4-6, indicate

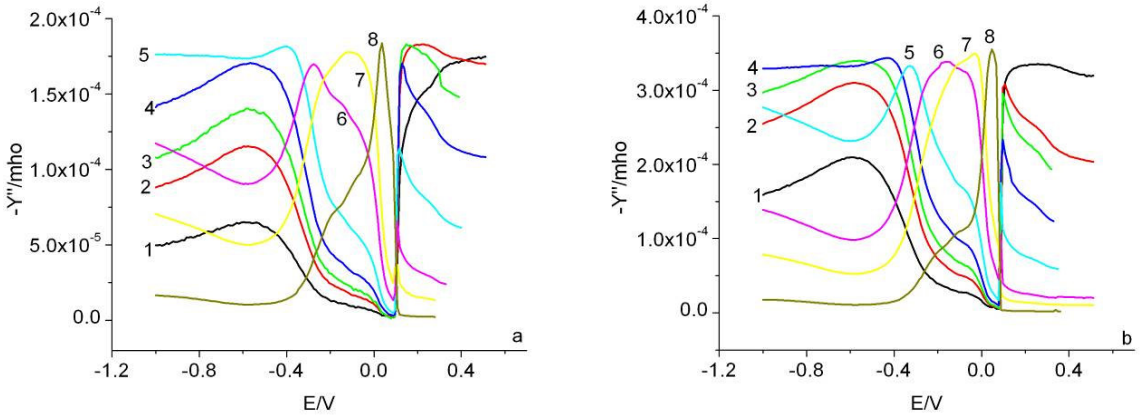

Figure 4. Admittance of **(a)** 0.01 M and **(b)** 0.02 M aqueous Lidocaine hydrochloride; 1, 2000 Hz; 2, 1000 Hz; 3, 750 Hz; 4, 500 Hz; 5, 250 Hz; 6, 100 Hz; 7, 50 Hz; 8, 10 Hz

several interesting features. 1. For 0.01 M lidocaine hydrochloride, the admittance increased from 2000 to 250 Hz in the cathodic range -1.0 to -0.4 V. With a further decrease in frequency, the admittance decreased in the most cathodic potentials. 2. Similarly, for 0.02 M lidocaine hydrochloride, the admittance increased from 2000 to 500 Hz and then decreased with further decrease in frequency. 3. For 0.05 M lidocaine hydrochloride the admittance increased from 2000 to 1000 Hz and then decreased with further decrease in frequency. 4. For 0.10 M, 0.40 M and 0.80 M lidocaine hydrochloride solutions, the admittance decreased monotonically with decreasing frequency. 5. In the potential range -0.4 to 0.0 V, the admittance increased first, reached a maximum and then decreased considerably. 6. The first admittance maximum near -0.4 V shifted more and more anodic with decreasing frequency. 7. When the first admittance maximum was shifting anodic, a second maximum or shoulder was growing near -0.1 V with decreasing frequency. When there was no more anodic shift in the first admittance maximum, the second one started shifting anodic with further decrease in frequency. 8. As the concentration of the lidocaine hydrochloride increased more and more, the value of the second admittance maximum started decreasing below 100 Hz.

The third sharp change in admittance was at positive potentials around 0.1 V for all solutions and corresponds to the chloride interaction with mercury or the passivation region.

Figure 7 shows a comparison of the admittance data at 1000 Hz for different concentrations of lidocaine hydrochloride. For the sake of clarity, the data for 0.10 M are again shown in Figure 7b. The salient features of the admittance data are that with increasing concentration, the admittance maximum near -0.4 V became sharper and sharper and the beginning of passivation near 0.1 V shifted slightly cathodic. The slight cathodic shift is more clearly demonstrated in Figure 7a than at the higher concentrations 0.1 to 0.8 M, as shown in Figure 7b. Also the lower the concentration, the more cathodic the potential at which the admittance started decreasing after the first maximum.

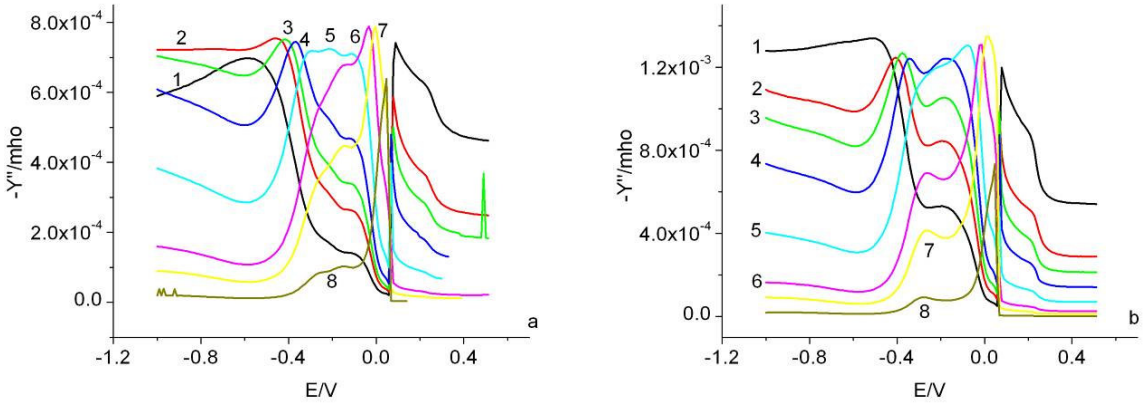

Figure 5 Admittance of **(a)** 0.05 M and **(b)** 0.10 M aqueous Lidocaine hydrochloride; 1, 2000 Hz; 2, 1000 Hz; 3, 750 Hz; 4, 500 Hz; 5, 250 Hz; 6, 100 Hz; 7, 50 Hz; 8, 10 Hz

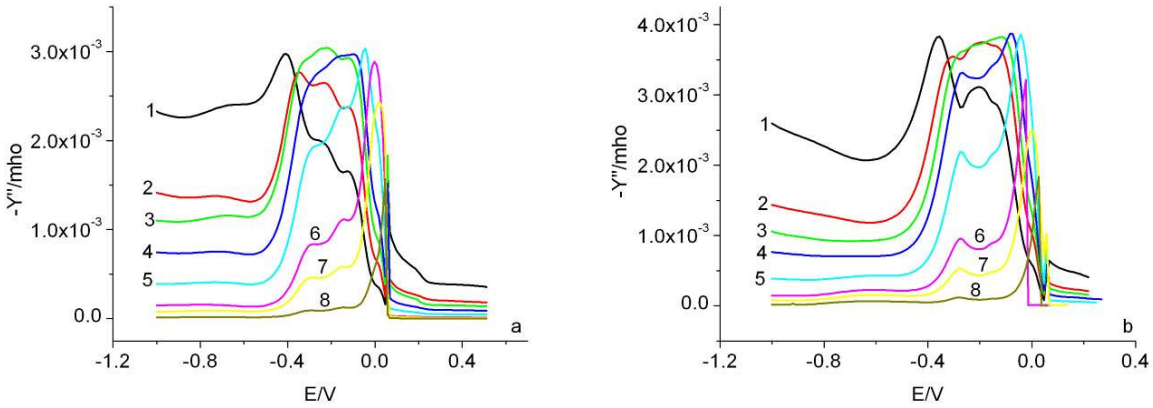

Figure 6 Admittance of **(a)** 0.40 M and **(b)** 0.80 M aqueous Lidocaine hydrochloride; 1, 2000 Hz; 2, 1000 Hz; 3, 750 Hz; 4, 500 Hz; 5, 250 Hz; 6, 100 Hz; 7, 50 Hz; 8, 10 Hz

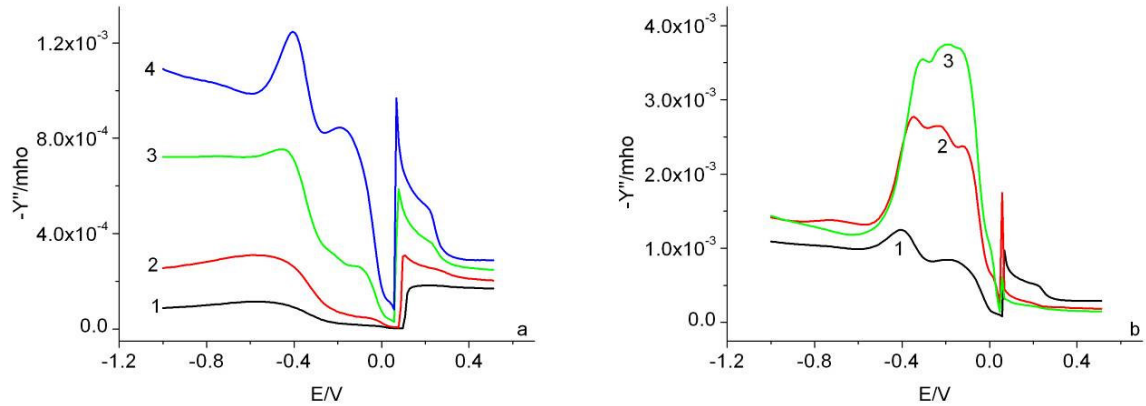

Figure 7 Admittance comparison at 1000 Hz **(a)** 1, 0.01 M; 2, 0.02 M; 3, 0.05 M; 4, 0.10 M; **(b)** 1, 0.10 M; 2, 0.40 M; 3) 0.80 M

3.3.b. Lidocaine sulfate

The admittance data for 0.10 M lidocaine sulfate are shown in Figure 8. As with 0.10 M lidocaine hydrochloride, the admittance decreased monotonically with decreasing frequencies.

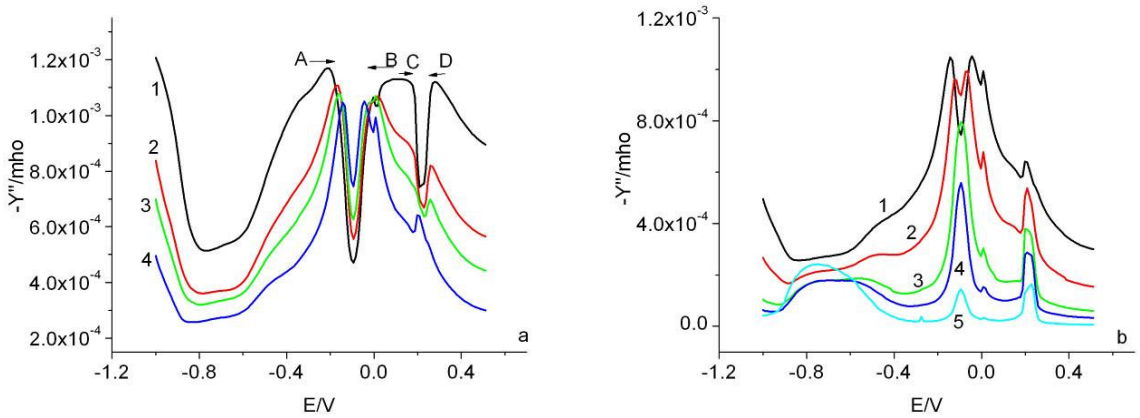

Figure 8 Admittance of 0.10 M aqueous lidocaine sulfate, pH 5.9; **(a)** 1, 2000 Hz; 2, 1000 Hz; 3, 750 Hz; 4, 500 Hz; **(b)** 1, 500 Hz; 2, 250 Hz; 3, 100 Hz; 4, 50 Hz; 5, 10 Hz

However, there are some major differences in the admittance behavior of lidocaine sulfate when compared with that of lidocaine hydrochloride. Of course, one has to recognize the fact that the lidocaine hydrochloride is a 1:1 electrolyte when compared with that of 1:2 electrolyte lidocaine sulfate. One has to suspect some contributions from lidocaine cation with HSO_4^- as the counter ion, when compared with that of SO_4^{2-} ion. In order to unravel that part of the problem, one has to investigate the admittance behavior as a function of pH by adjusting the concentration of H_2SO_4. The presence of a 1:2 electrolyte necessitates two lidocaine cations near the sulfate and the double layer behavior near the changeover potentials from negative to positive will be different from that of a 1: 1 electrolyte. To get a comparative view of the differences between chloride and sulfate, the admittance data at 1000 Hz are shown in Figure 9.

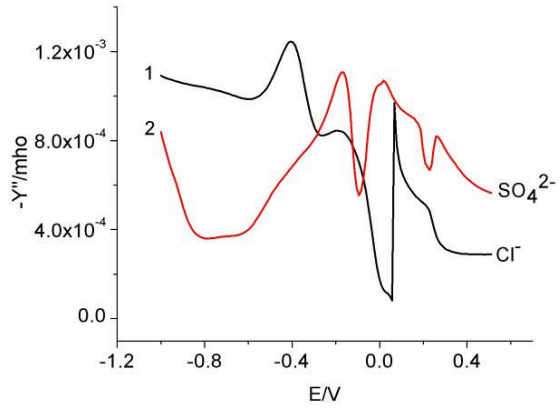

Figure 9 Admittance comparison of 0.10 M aqueous lidocaine hydrochloride and lidocaine sulfate at 1000 Hz.

The lidocaine sulfate admittance data show 4 maxima or shoulders, two in the cathodic region and two in the anodic region. The interesting feature is that the two maxima (A and B, Figure 8a) in the cathodic region shift in opposite directions when the frequency is decreased and merges into one. With further decrease in frequency, the admittance was decreased continuously. The same behavior is also exhibited by the other two maxima (C and D, Figure 8a) at anodic potentials. These are more clearly seen in Figure 8b.

3.3.c. Lidocaine hydrochloride in the presence and absence of NaCl

Since sodium chloride is the most common electrolyte in biological systems, we have briefly

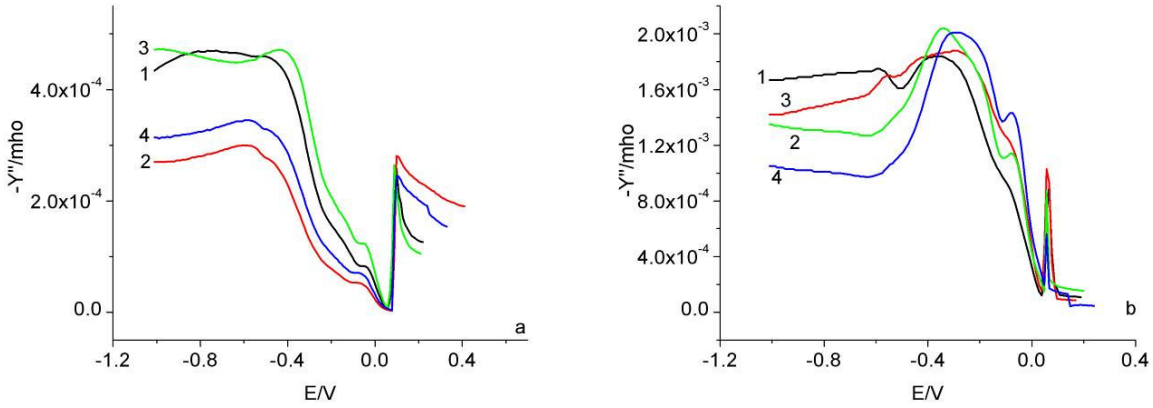

Figure 10 **(a)** Admittance comparison of 0.02 M NaCl, 1000 Hz (1) and 750 Hz (3), and 0.02 M lidocaine hydrochloride, 1000 Hz (2) and 750 Hz (4); **(b)** Admittance comparison of 0.10 M NaCl, 1000 Hz (1) and 750 Hz (3), and 0.02M lidocaine hydrochloride containing 0.10 M NaCl, 1000 Hz (2) and 750 Hz (4).

looked at the influence of 0.10 M NaCl on the admittance behavior of 0.02 M lidocaine hydrochloride. These results are shown in Figure 10. Figure 10 reveals that the admittance behavior is very similar for NaCl, lidocaine hydrochloride and lidocaine hydrochloride containing NaCl. However, the admittance was less for lidocaine hydrochloride compared to that of NaCl. The admittance for lidocaine hydrochloride containing NaCl was also less than that of NaCl. These results are consistent with that shown in the cyclic voltammetry data (Figure 3).

3.4. Double Layer Structure and Ion Pair Formation

Three types of ion pairs, Coulombic type ion pairs or Bjerrum type ion pairs, ion pair formation through the intermediary of a water molecule or localized hydrolysis, and water structure-enforced ion pair formation have been used to explain the conductance behavior as well as the trends in osmotic and activity coefficient data of electrolytes, such as NaCl, lithium acetate, and tetrabutyl ammonium iodide respectively [20-24]. We have recently used a simplistic view of those three kinds of ion pairs, as shown in Figure 11 to explain the admittance data of NaCl at different concentrations [8].

The water structure-enforced ion pair formation was introduced to explain the osmotic and activity coefficient data of large, unhydrated, and univalent ions, such as tetraalkylammonium iodides [24]. In order to maximize water-water hydrogen bond interactions and to minimize structure breaking, these ions, even in dilute solutions, are forced to form ion pairs by the hydrogen bonded water structure. On the other hand, oppositely charged small ions form traditional Coulombic ion pairs at higher concentrations. The ion exchange behavior of large ions on differently cross-linked strong acid ion exchangers and the anion exchange behavior of large anions [25, 26] have also been explained using the concept of water-structure enforced ion pairing.

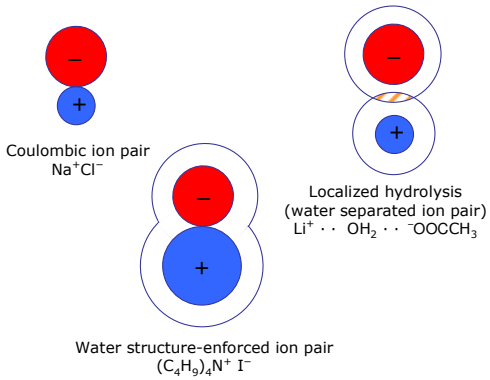

Figure 11 Ion pair formation in aqueous solutions [8].

The formation of Coulombic type cationic bridges has been suggested within the double layer but without any convincing evidence as to the nature of the alignment [27]. Similarly, the formation of "anionic bridges" between tetralkylammonium ions and iodide ions has been suggested to explain the electrocapillary data [28].

The 2-dimensional surface concentration at or near the double layer is about 10 times higher than the bulk 3-dimensional concentration [29]. Thus, the interionic effects as well as the co-sphere overlap effects at or near the double layer for a bulk 0.01 M solution of lidocaine hydrochloride is itself considerable. The deviations from Beer's law above 0.005 M are indicative of this effect even in the bulk solution.

Several double layer models have been investigated in great detail in the past [30-34]. In the simplest case, a monolayer of water may separate the charge on the metal from the charge on the solution. Double layer capacitance measurements and electro-capillary measurements of simple electrolytes have been used in the past to obtain information on the nature of the double layer.

Using statistical mechanical models, the activity coefficient data of 1:1 electrolytes and Setchenow coefficients [35-37] have been computed using the ion hydration co-sphere model, as shown in Figure 12. Conway has used this concept of co-sphere overlap, as shown in Figure 12, to explain ion-hydration co-sphere interactions in the double layer in the presence of tetrapropyl ammonium ions. Three kinds of ion hydration co-sphere overlap regions in the double layer, as suggested by him, are: "a) Lateral co-sphere overlap between hydration shells of specifically adsorbed

ions; b) Ion hydration co-sphere overlap with the co-plane of oriented solvent due to electrode surface charge, and c)Possible cosphere overlap with ions in the diffuse layer."

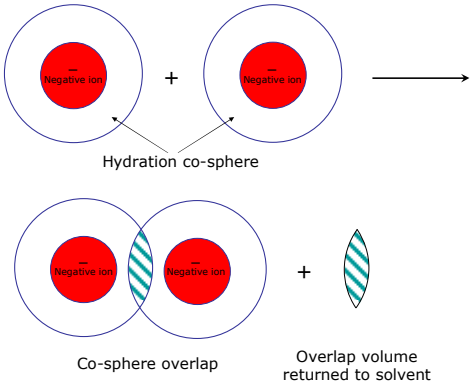

Figure 12 Gurney ion hydration co-sphere overlap [8]

The general nature of the admittance data, as shown in Figures 4-7 and Figure 10, are very similar to that exhibited by NaCl data at 0.01, 0.10 and 1.0 M [8]. We have postulated a new concept, "potential induced and water structure-enforced ion pair formation" to explain the admittance data of aqueous NaCl [8]. Since lidocaine hydrochloride is also a 1:1 electrolyte like NaCl, the same concept is used here to explain the admittance data. Instead of sodium ions we have the more exotic lidocaine cation which has polar groups, a phenyl group and a charge near two hydrophobic ethyl groups. Compared to the behavior of the spherically symmetrical Na^+, it is not easy to speculate the orientation of this charged cation near a mercury electrode, especially when the potential is gradually changed from negative to less and less negative, to zero, and finally to positive during admittance measurements. Similar to that of Na^+, the orientation of the positively charged lidocaine cation towards Hg has to slowly and gradually change to negatively charged chloride when the potential is changed gradually from negative to positive. During this process the accompanying water in the hydration layer as well as in the monolayer, if any, near mercury, has also to change orientation from hydrogen to oxygen. To minimize the disturbance of the water structure, it is preferable to have the lidocaine cation and the chloride ion form a water structure-enforced ion pair. The applied gradual potential change necessitates this type of ion pair formation so that when the potential becomes finally positive, the chloride ions are favored near mercury. The potential induced and water structure-enforced ion pair formation need not follow the criterion for the three types of ion pairs. The applied potential can induce the formation of all the three types of ion pairs during the changeover from negative to positive potentials.

The observed concentration effects on admittance with decreasing frequencies are similar to that of aqueous NaCl observed at 0.01, 0.10 and 1.0 M. In dilute solutions, the admittance increases with decreasing frequencies whereas the admittance decreases with decreasing frequencies at higher concentrations. One has to keep in mind that the co-sphere overlap effects increase with increasing concentration. Also the possibility of Coulombic type ion pair formation also increases with increasing

concentration. Since the concentration at the double layer is about 10 times that of the bulk concentration, this possibility is quite obvious.

The observation in Figure 7a showing the decrease in admittance after the first maximum occurred at more and more cathodic potentials with decreasing concentration of lidocaine hydrochloride is also very similar to that observed for NaCl [8]. One is forced to conclude that the influence of water structure-enforced ion pair formation is more obvious in these dilute solutions when the co-sphere overlaps are a minimum.

The admittance behavior of lidocaine sulfate, viz. the two pairs of admittance peaks collapsing into one each is somewhat similar to that observed for L-cysteine [17, 18]. For L-cysteine, at pH = 9.34, two pairs of admittance maxima moving in opposite directions with decreasing frequencies and merging into two peaks were observed. The first pair was assigned to the interactions between α-NH_3^+ and α-COO^- and the second pair to Na^+ and sulfhydryl S^-. The anodic shifts with decreasing frequencies were assigned to α-NH_3^+ and Na^+. The cathodic shifts with decreasing frequencies were assigned to α-COO^- and sulfhydryl S^-. The orientation of the water molecules around the oppositely charged ions must have opposite orientations and thus the opposite movement of peaks with decreasing frequencies is reasonable. We had attributed one pair of admittance peaks moving in opposite directions with decreasing frequencies, observed in polyoxomolybdates [13, 14], to the different orientation effects of inside and outside water in a large Keplerate structure at or near the double layer. Without additional data for lidocaine sulfate at different pH and different concentrations, it is not possible to speculate on any possibilities. The SO_4^{2-} makes the possibility of two adjacent lidocaine cations, whereas the presence of HSO_4^- adds more to the possibility of water structure-enforced ion pair formation. It is tempting, but premature, to assign the two pairs of admittance maxima to lidocaine cation and HSO_4^- and to lidocaine cation and SO_4^{2-}.

3.5. Impedance

The impedance data for different concentrations of lidocaine hydrochloride at -0.6 V are shown in Figure 13. While we admit the large scatter in data at frequencies below 1 Hz, we are indeed surprised to observe the negative differential resistance (NDR), a characteristic of tunnel diode behavior. Even though the admittance behavior for lidocaine hydrochloride and NaCl are very similar, NDR is not observed for NaCl. We did not observe any NDR at 0.80 M lidocaine hydrochloride. To illustrate the impedance behavior at the higher frequencies, the data for 0.40 M lidocaine hydrochloride are shown in Figure 14 in an expanded scale. The impedance data for 0.10 M lidocaine hydrochloride at different potentials are shown in Figure 15. We observe this weak NDR in the concentration range 0.01 M to 0.40 M and at potentials -0.6 to – 0.2 V.

We speculate that the source of this NDR is the π electrons in the lidocaine hydrochloride. The crystal structure of lidocaine [4] indicates that adjacent chains are held together by chloride ions, each of which accepts an aqueous proton from one chain and an amino proton from the other. The double chains are held together by van der Waals forces. The structure is fully hydrogen bonded and '*endless chains'* of lidocaine cations are produced by water molecules. Thus, it is possible to have strong $\pi - \pi$

interactions between adjacent molecules at or near the double layer and provide a conduit for charge transfer or a source for exhibiting NDR.

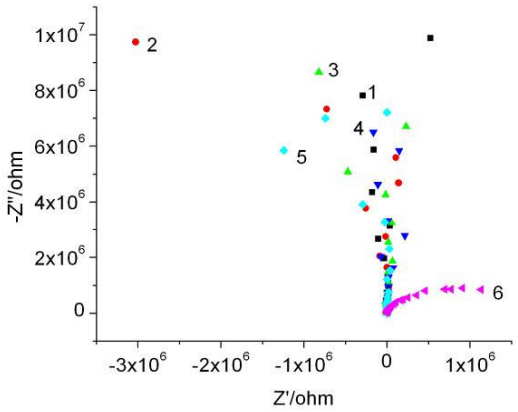

Figure 13 Nyquist plots at -0.6 V for 1) 0.01 M 2) 0.02 M 3) 0.05 M 4) 0.10 M 5) 0.40 M and 6) 0.80 M lidocaine hydrochloride, 1000 Hz to 100 mHz. NDR around 500 mHz for all except for 0.80 M

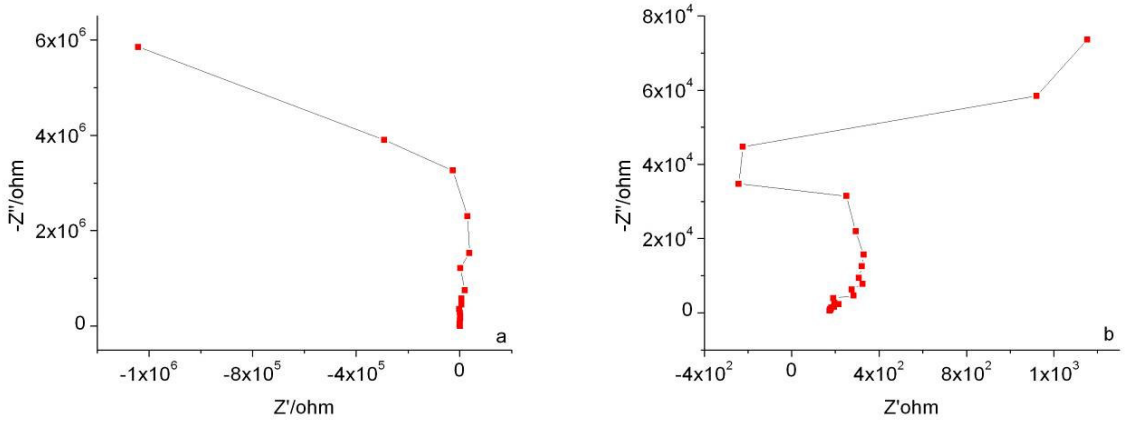

Figure 14 Nyquist plots at -0.6 V for 0.40 M lidocaine hydrochloride, (a) 1000 Hz to 176 mHz ; and (b) 1000 Hz to 8.2 Hz; Data from Figure 13 in expanded scale.

Numerous investigations have been carried out to understand the conductance behavior of DNA molecules, and depending on the nature of the experiment, differing answers such as a conductor, an insulator, or a semiconductor have been arrived at [38-43]. This is partly because of the sensitivity of the experiments that depend on the nature of the devices used to measure conductivity, the sequence and length of DNA, the dynamical motions of the base pairs that provide the π-stacks within the molecular stacks, sequence dependent inhomogeneities in energetics and base-base couplings, DNA bulges resulting from errors in recombination and replication, the type of contacts, the environment such as the nature of counter ions and amount of water or humidity. The conduit for extraordinarily fast, and distance independent electron transfer has been attributed to $\pi - \pi$ interaction between the stacked base pairs of double-stranded DNA. Charge transport in mesomorphic porphyrins

and phthalocyanins has similarly been attributed to the π- π interaction between the neighboring aromatic macrocycles [44-45].

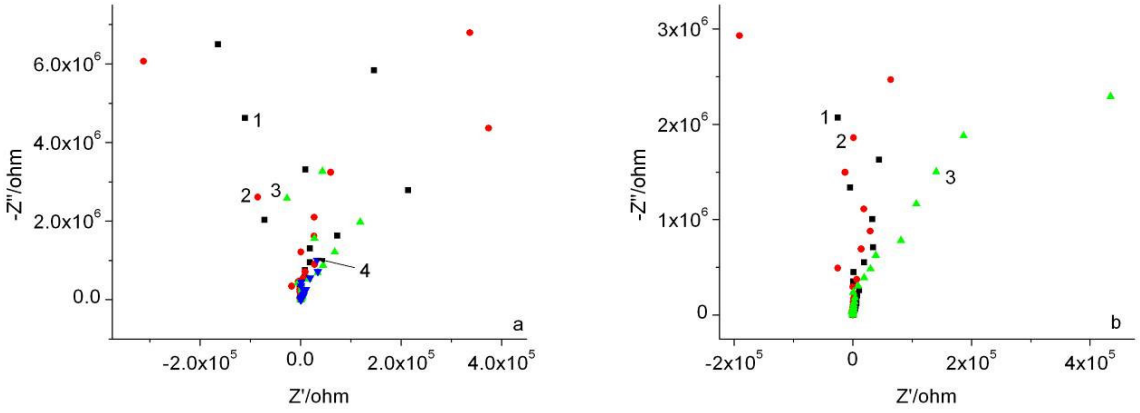

Figure 15 Nyquist plots at 0.10 M Lidocaine hydrochloride at **(a)** 1, -0.6 V; 2, -0.5; 3, -0.4 V; 4, -0.3 V; (b) 1, -0.3 V; 2, -0.2 V; 3, -01 V; 1000 Hz to 32 mHz.

We did not observe any NDR for 0.02 M lidocaine hydrochloride in the presence of 0.10 M NaCl. In the presence of 0.02 M NaCl, there was a tendency to exhibit NDR at very low frequencies. We suggest that the competition of NaCl with lidocaine hydrochloride at or near the double layer interferes with the stacking of the phenyl groups and consequent π- π interactions.

4. CONCLUSIONS

Our admittance data with different concentrations of lidocaine hydrochloride suggested the formation of potential induced and water structure-enforced ion pair formation between lidocaine cation and chloride anion at or near the double layer during the potential change from negative to positive. Whereas the classical Bjerrum type or Coulombic ion pairs are observed in concentrated solutions of bulk electrolytes, the potential induced and water structure-enforced ion pairs are formed even in very dilute solutions. The trends in admittance data with increasing concentration of lidocaine hydrochloride reflect the trends in increased co-sphere overlaps. The influence of water structure-enforced ion pair formation is more evident in dilute solutions when the co-sphere overlaps are a minimum. The impedance data with negative differential resistance at negative potentials indicated the influence of the 'π-way' in the conduction process. While numerous investigations have been carried out to show the 'π-way' in DNA, impedance technique seems to show a clear way of demonstrating this point. More work with other simple molecules with stacking properties or π- π interactions need to be done to confirm the usefulness of impedance technique to demonstrate the role of π electrons in the conduction process in aqueous systems at or near the double layer.

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