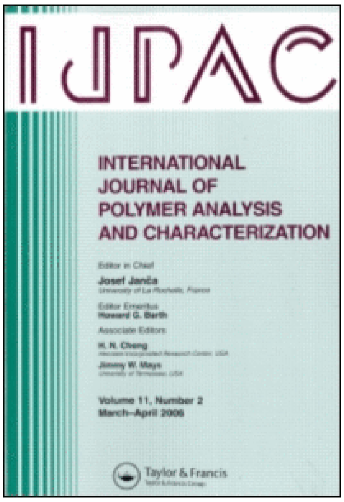

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Effect of the Chaotropic Nature of Supporting Electrolytes on the Electrochemical Properties of Conducting Polymers: A Study Using an *In-Situ/Real Time* Technique

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Effect of the Chaotropic Nature of Supporting Electrolytes on the Electrochemical Properties of Conducting Polymers: A Study Using an *In-Situ/Real Time* Technique

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The effect of the nature of the cation employed in the electrolyte during electrochemical switching of conducting polymers has been explored. It has been found that the nature of the cation, while not obvious in cyclic voltammetry, has a marked effect on the changes in resistance and mass that occur within the polymer upon reduction/oxidation. We suggest that the chaotropic nature of the salts employed be considered in interpreting results concerned with the "salt effect" on the properties of conducting polymers.

Keywords: Chaotropic properties, polypyrrole, conducting polymers

INTRODUCTION

An emerging area of materials science and technology involves the identification, study and utilization of dynamic polymer systems. Such systems, designed and assembled to respond to appropriate stimuli in a predeter-

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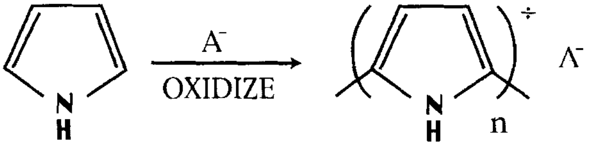
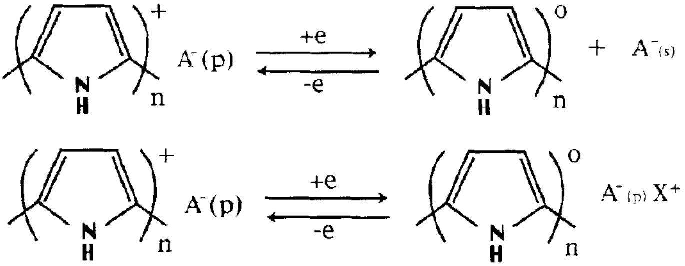
mined fashion can be used to produce structures capable of smart or intelligent behavior.[1–4] Contrary to conventional polymeric materials, these systems possess properties that are dynamic and that can be called upon when required. They are not inert.

One group of materials that appear particularly in this regard is conductive electroactive polymers such polypyrroles,[5] polythiophenes[6] and polyanilines.[7] The ability to change the properties of these polymer systems *in-situ* is due to the fact that they are readily oxidized/reduced. The polymerization and reduction/oxidation processes of polypyrrole (PPy) can be described according to reactions 1 and 2 respectively, depending on the mobility of the anion incorporated during synthesis (reaction 2a for a mobile anion and reaction 2b for an immobile anion).



(1)

(n = 2,4 for polypyrrole)



(2a)

(2b)

Where $A^-_{(p)}$ is a counterion incorporated during synthesis and $A^-_{(s)}$ is that anion which moves to the electrolyte solution; X^+ is the cation from the electrolyte solution. In this study $A^-_{(p)}$ is chloride (Cl^-) in reaction 2.a and dodecylbenzensulfonic acid (DBS^-) in the reaction 2.b.

Such dynamic polymeric materials have potential application in areas as diverse as new sensing technologies,[8] separations and controlled release,[9] and biomaterials.[10] However the ability to produce systems that perform satisfactorily in any of these proposed application areas depends on our understanding of how these electrodynamic systems operate at a molecular level. Polypyrrole is the most studied of the conducting polymer materials. However, even in this case a clear picture of what transitions accompany electrical stimulation and what parameters influence this behavior is required.

The above representations (reactions 2.a and 2.b) suggest that a single redox transition is initiated at a well-defined potential and this process is accompanied by anion movement in/out of the polymer. It is known that in most cases (if not all) these redox processes also involve movement of cations and solvent in addition to anions.[11–14] The extent of each depends on the relative mobility of the species involved, in solution, and throughout the polymer matrix. Consequently the switching process is known to depend on the anion incorporated during synthesis, the potential employed for growth, and the solvent electrolyte in which it is switched.[15]

We report here a study on the effect of the electrolyte on the switching process using a simultaneous *in-situ* analysis technique that allows current flow, mass changes and resistance changes to be monitored *in-situ* as the conducting polymer is oxidised/reduced. It is important to note that each of these changes have been well studied in separate studies. However, there is no report on the simultaneous monitoring of such changes in investigation of the chaotropic effect of the supporting salt electrolytes. The information provided in this paper enables us to collect important information such as the rate of changes in mass and resistance or the magnitude of the changes during solution experiments *in-situ* and *in real time*. In our investigation, we have paid particular attention to the effect of the nature of the salt employed (with and without chaotropic agents) on the switching process and on the physical properties of the resultant polymer.

EXPERIMENTAL

Reagents and Standard Solutions

All reagents were analytical grade purity unless otherwise stated. Pyrrole, sodium chloride, sodium dodecylbenzene sulfonate (DBS), potassium chloride, magnesium chloride, and lithium chloride were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin). Pyrrole was distilled before use.

Instrumentation

Voltametric data were obtained using a BAS CV27 voltamograph (Bio Analytical Systems, Lafayette, PA, USA). Data were collected using a Maclab (Analog Digital Instruments, Sydney, Australia) interface and a Macintosh computer. A resistometer (developed by CSIRO, Division of Mineral Products, Melbourne, Australia) was employed to collect the polymer's resistance. The Electrochemical Quartz Crystal Microbalance (EQCM) was used to collect data for the changes in the polymer's mass, based on the design previously published.[14,15]

Procedures

The polymer was galvanostaticaly (current density: 2 mA/cm^2 for 2 min) deposited into a gold crystal from a solution containing 0.1M pyrrole and 0.05M sodium DBS and sodium chloride. All experiments were carried out in a Faraday cage. An Ag/AgCl reference electrode and a platinum counter electrode were employed, electrochemical characterization was carried out using Simultaneous Multidimensional Analysis of Conductors (SMAC)[16] in NaCl, LiCl and $CaCl_2$ with the concentrations reported in the text. Nitrogen was used to deoxygenate solutions for 15 min prior to polymerization.

RESULTS AND DISCUSSIONS

Two polymer systems were studied in this work to achieve a better and clearer picture of the effect of varying the nature of the electrolyte cation on the switching processes of polypyrrole materials.

Polypyrrole/Cl

As shown in Figures 1 and 2, as this polymer is reduced in 1 M NaCl or 1 M LiCl, respectively, anion is expelled continuously from 0.60 to – 0.20 V. This is indicative of the model originally proposed by Tanguy[17] and subtantiated by other work.[18] This model suggests that the reduction/oxidation process is not discrete but that it occurs over a wide potential range.

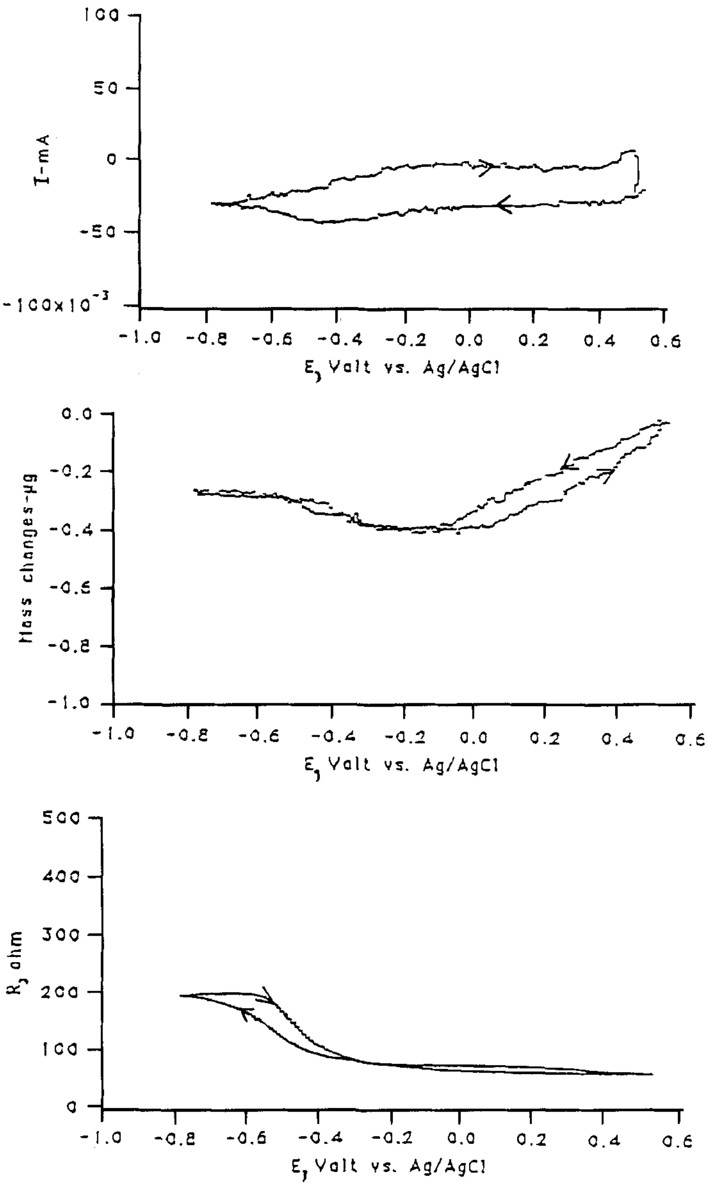


FIGURE 1 PPy/Cl in 1M NaCl; scan rate = 5 mV/s; monomer solution: 0.1M pyrrole + 0.05M NaCl; 15 min deoxygenation before polymerization; $C_d = 2$ mA/cm^2; $t = 2$ min; working electrode: gold crystal (0.25 cm^2); auxillary electrode: Pt plate; reference electrode: Ag/AgCl.

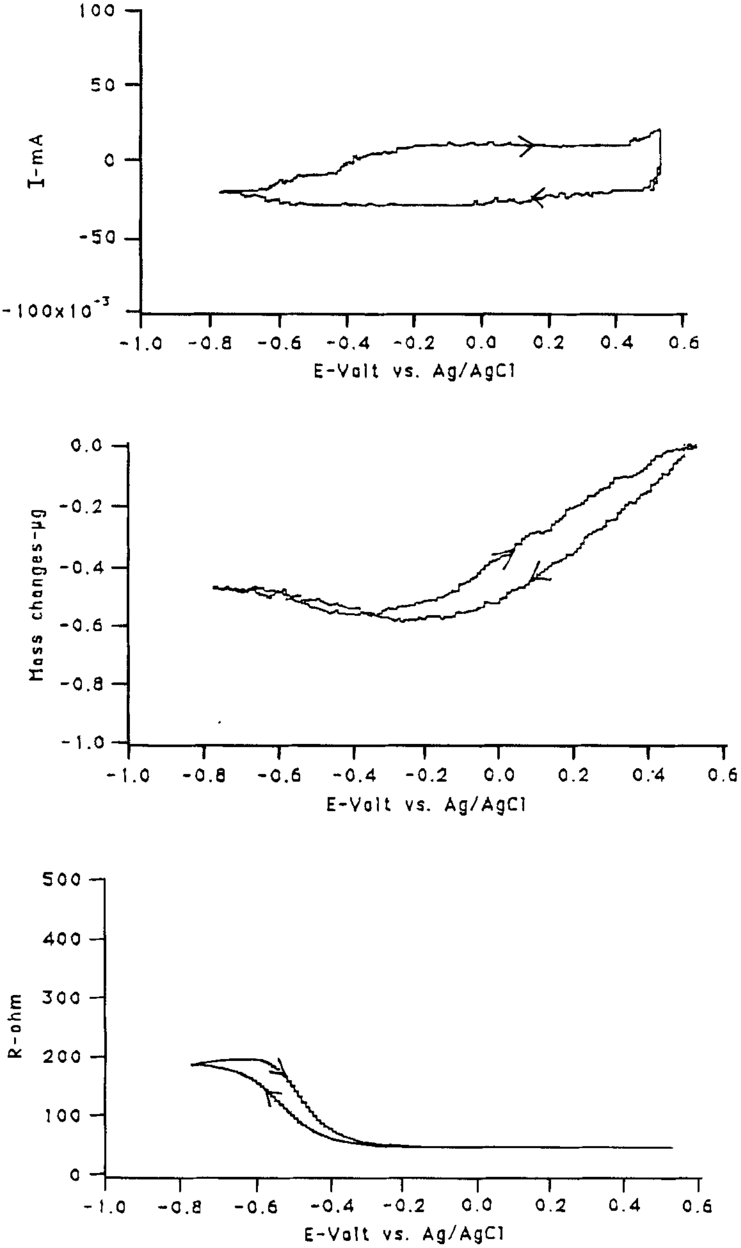
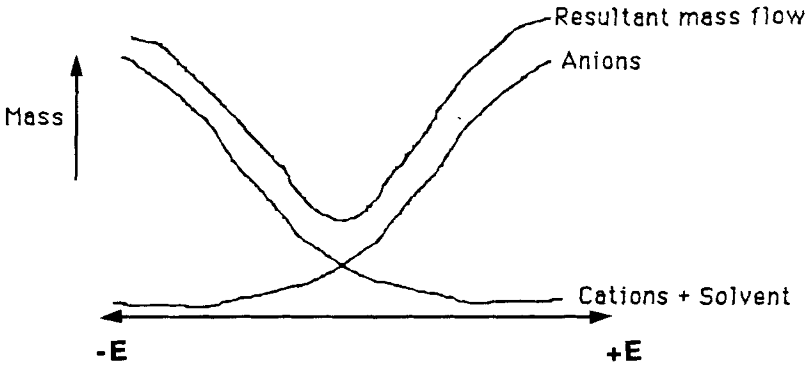


FIGURE 2 PPyCl in 1M LiCl, other conditions as in Figure 1.

The mass changes are essentially reversible with the ingress of ions lagging behind the expulsion due to the decreased diffusion coefficient of the ions in the polymer compared to diffusion in solution.[17,18] The resistance change, as expected, was encountered at a threshold level occurring at –0.40 V when the reduction of the polymer was essentially complete. Of course, since the reduction process results in increased electronic resistance, further reduction will be more difficult. The increased resistance observed has been associated with the removal of charge from the polymer backbone. This may also be accompanied by changed in will solvent content and/or polymer chain recomformations that will affect conductivity.

In the case of lithium containing electrolyte, it appears that the mass loss due to ion incorporation is less. However, as shown by others,[11–13] cation/solvent ingress can occur simultaneously with anion eggress and the resultant QCM plot is the total of all of mass changes recorded as shown in Schematic 1. The same amount of change flow was removed/inserted for both Li^+ and Na^+ containing electrolytes so the apparent difference in mass change was not due to electrochemical effects.

An interesting result is observed when the cation is changed to Ca^{2+} as shown in Figure 3. A 0.5 M $CaCl_2$ electrolyte was used to maintain a constant concentration for the chloride anion. In this case, the decrease in mass continues until –0.40 V and a mass increase that would reflect cation/solvent insertion is not obvious. The mass decrease was similar to that observed in NaCl solution. A marked difference is observed in that the



Scheme 1

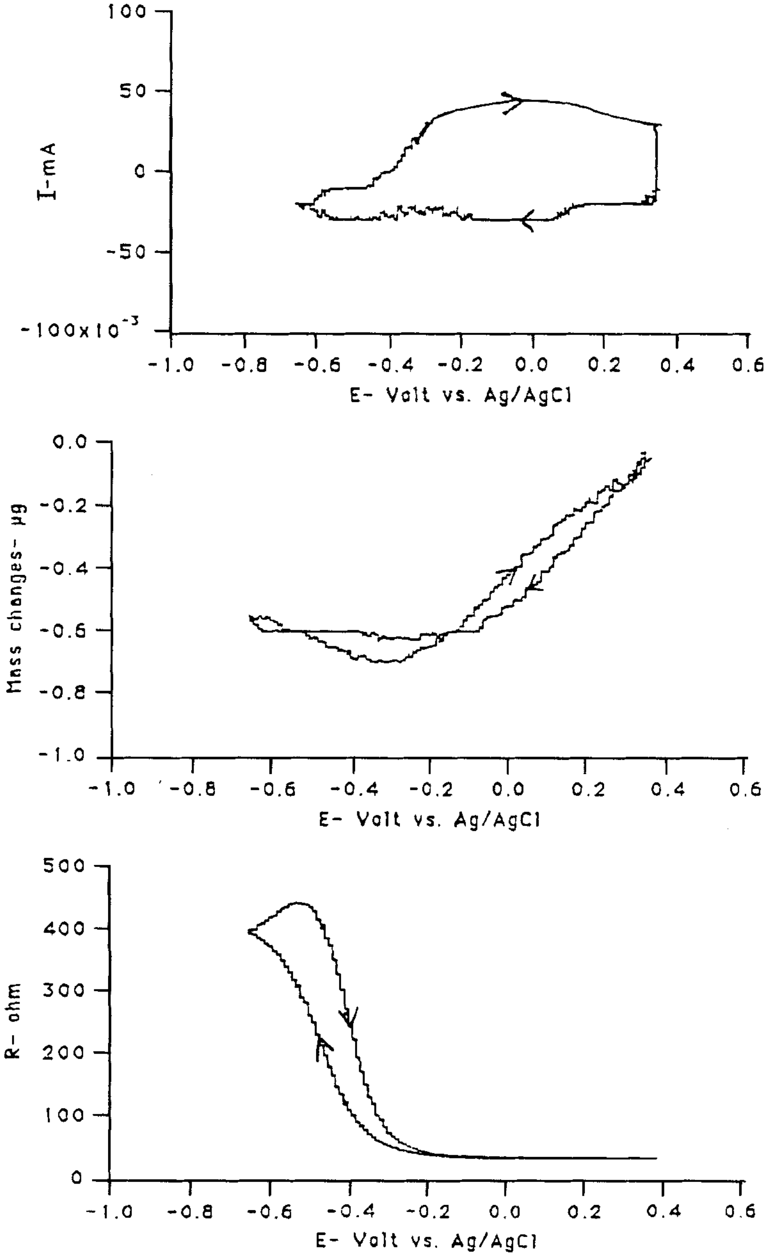


FIGURE 3 PPy/Cl in 0.5M $CaCl_2$, other conditions as in Figure 1.

change in resistance of the polymer is much larger. Similar results were obtained in $MgCl_2$ solutions.

This may be caused by a phenomenon well known to biopolymer researchers where the nature of the electrolyte can have a marked effect on water structure[19] and subsequently on the properties of the polymer. In biochemical studies it has been shown that certain salts can cause salting out-dehydrating biopolymers (proteins) and causing them to precipitate. Ions that do so are known to be chaotropic.[20] Strong chaotropic salts, for example, Mg^{2+}, Ca^{2+} disrupt the structure of water and thus increase hydrophobic interactions, while the more antichaotropic salts (Li^+, Na^+) do not strongly interfere with the hydrophobic interactions. The strong chaotropic agents, since they disrupt water structure, may also dehydrate the polymer chain causing changes in polymer chain conformation.

Such studies reveal that salts not only affect electrostatic interactions but also hydrophobic interactions with polyelectrolytes. Perhaps a similar way to "visualize" this is that ions with a high hydration number will compete with the polymer for waters of hydration. As water is removed from the polymer, salting out will occur. Thus this effect can be predicted by considering a lyotropic series of simple ions. Melander and coworkers[20] argued that this can be based quantitatively on the molal surface tension σ of the salt in solution. A selection of salts and their molal surface tension is shown below:

Salt	LiCl	NaCl	Na_2HPO_4	$NaSO_4$	$MgCl_2$
$\sigma \times 10^3$ (dyn-g/cm mol)	1.63	1.64	2.02	2.73	3.16

We therefore suggest that the nature of the electrochemical transition occurring in oxidation/reduction of conducting electroactive polymers is dependent not just on the anion exchange properties but also on the water ordering ability of the anions and cations employed. A reconsideration of the literature data on the "salt effects" on conducting polymers may be warranted with this in mind.

For example, as pointed out recently by Iseki and co-workers,[18] cations can deactivate the electrochemical properties of PPy-tosylate coatings. They suggest that both the size and hydrophobicity of the cation are important in this regard. We suggest that in addition, the chaotropic effect may play an important role. To provide more evidence for such claim we considered two other important experimental examinations by investigating the effect of ionic strength and by incorporating a less mobile counterion into polymer during synthesis.

Since we decided to use a solution with low ionic strength ($\mu = 0.1$), a higher scan rate needed to be used. The effect of scan rate on the resistance profile has been already discussed.[21] As can be seen from Figure 4, using the scan rate of 10 mV/s, the cyclic voltammetry result (I vs. E) does not show much difference in the physical and electrochemical properties of the polymer in the various solutions used. However, great changes were experienced in the resistance and mass profiles. The greatest changes in mass appears for NaCl with $\mu = 1$. This was expected and is in agreement with what was already discussed, since, for a lower ionic strength and involvement of a chaotropic agent, the combination of anion/cation expulsion/insertion dominates the total mass changes. Because of the same reason, almost the same trend of changes in resistance was experienced in the electrolytes with lower ionic strength and with chaotropic agent. In contrast, the change in resistance is less and has a different profile in the solution with higher ionic strength and no chaotropic agent. It is necessary to note that the background resistance is caused by the solution conductivity, and the changes in resistance is mainly due to changes in the conductivity of the polymer itself.[22]

Polypyrrole/DBS

Since the DBS ion has low mobility in the polypyrrole film and cannot be exchanged, cations will preferentially enter the polymer film during reduction of the polymer to compensate for the negative charge of the entrapped DBS anion. This is exactly what we observed using PPy/DBS in supporting electrolytes with antichaotropic and chaotropic agents (Figs. 5 and 6, respectively). As can be seen from Figure 5, the increase in mass occurs continuously as the polymer is reduced. However, when we considered the polymer in a solution with a chaotropic cation, the changes in mass again was dominated by the chaotropic nature of the inserted Ca^{2+}, which follows the movement of the water from the polymer, and to the polymer (polymer hydration/dehydration process). This happens when the polymer is in a more reduced form and there is a need for charge compensation by insertion of the cation from the solution into the polymer.

It is not unreasonable to assume that the alkaline earth DBS salts are insoluble,[23] and this may affect increasing the resistance of polymer film.

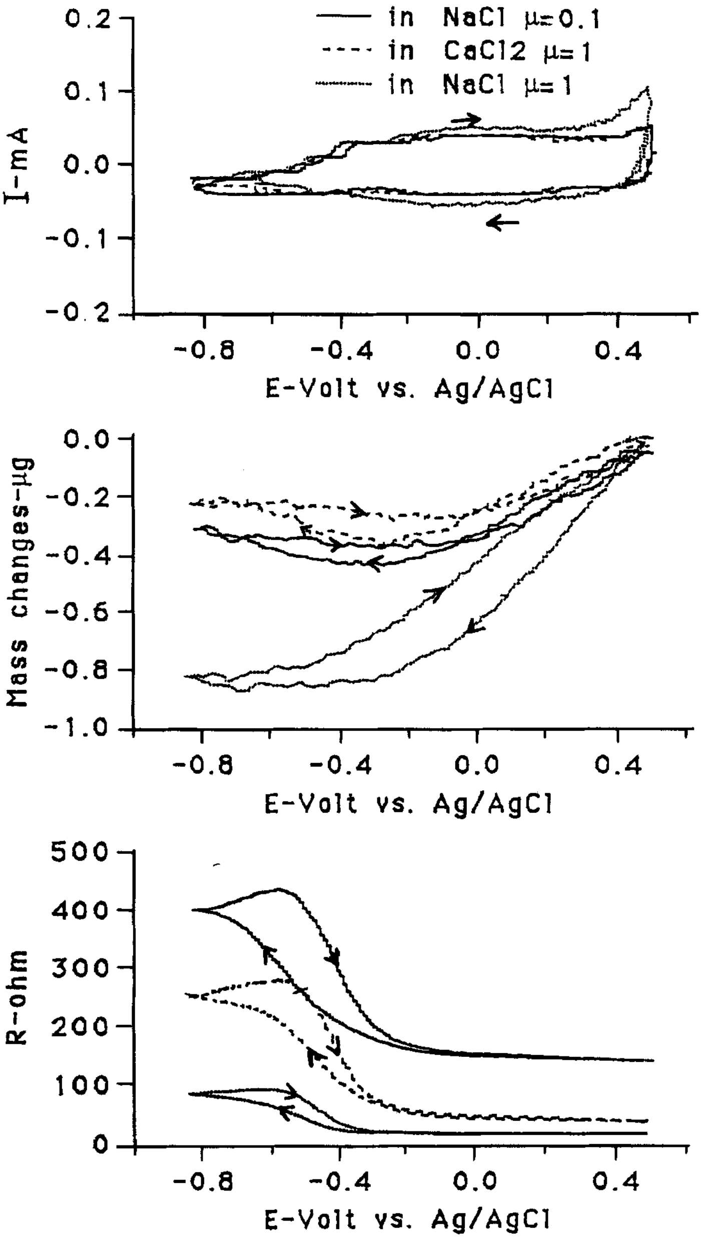


FIGURE 4 PPy/Cl in NaCl and $CaCl_2$ with scan rate = 10 mV/s, other conditions are the same as in Figure 1.

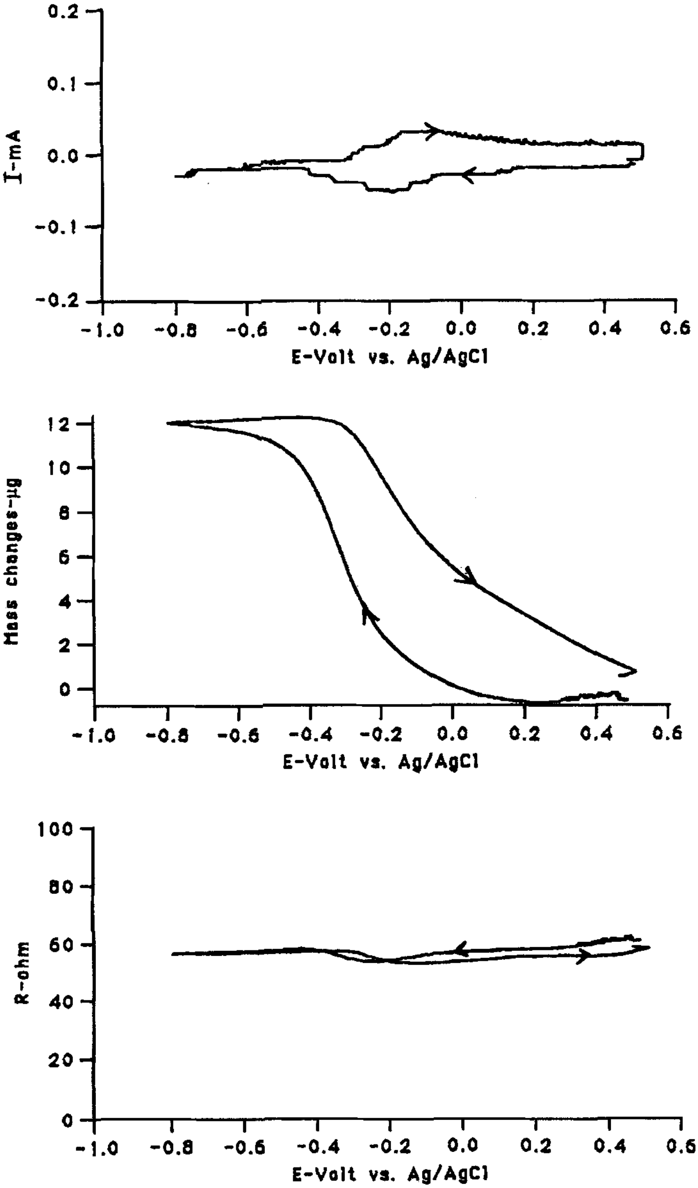


FIGURE 5 PPy/DBS in 1M LiCl; scan rate = 5 mV/s; monomer solution: 0.1M pyrrole + 0.05M DBSNa; 15 min deoxygenation before polymerization; C_d = 2 mA/cm^2; t = 2 min; working electrode: gold crystal (0.25 cm^2); auxillary electrode: Pt plate; reference electrode: Ag/AgCl.

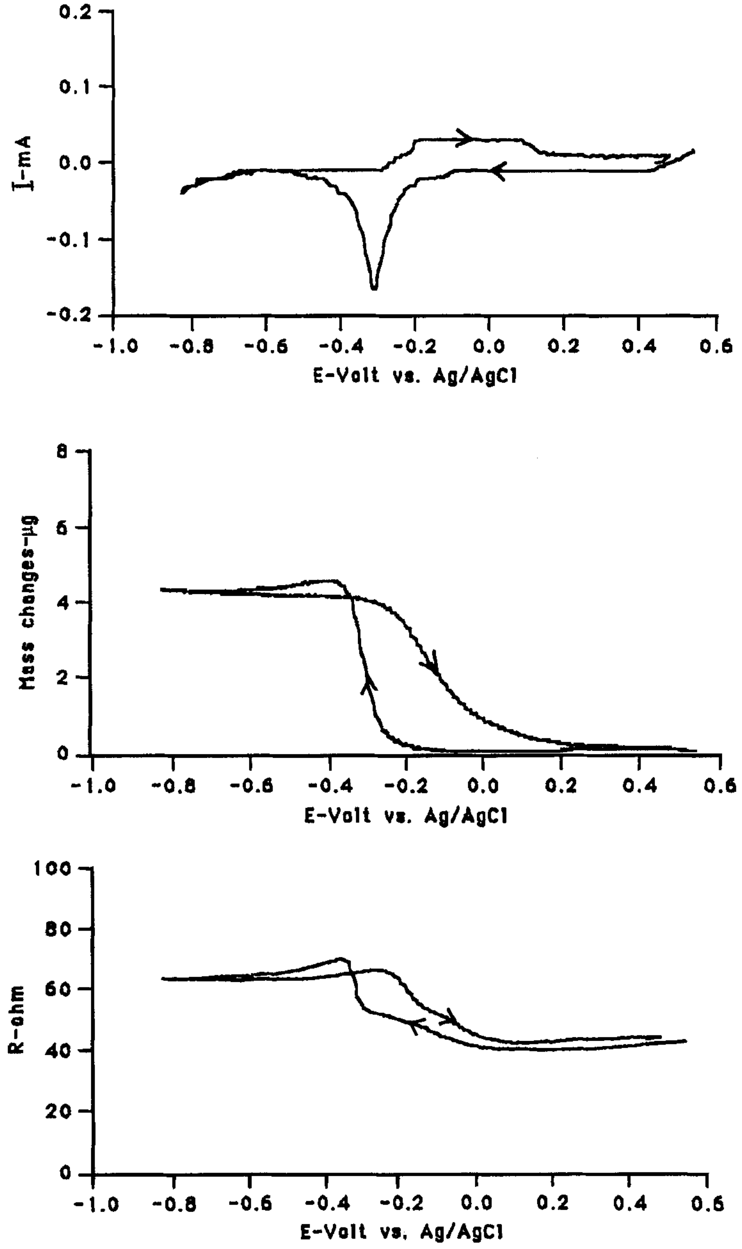


FIGURE 6 PPy/DBS in 0.5M $CaCl_2$, other conditions as in Figure 5.

However, we think that the dominant parameter is again the chaotropic nature of the cation in the supporting electrolyte. Resistance results in Figures 5 and 6 may provide more evidence to support our theory. The change in the resistance of the polymer in LiCl (Fig. 5) is small and is a combination of changes in the polymer and the supporting electrolyte. In comparison, the change in the resistance of the polymer in $CaCl_2$ is mainly due to the changes in the resistance of the polymer itself. An interesting observation is that the change in the resistance of the polymer follows almost the same trend as the change in the mass of the polymer (Fig. 6). This is because at the potentials where the polymer is in a more reduced form, the resistance and mass changes are affected by the chaotropic nature of the inserted cation, which is followed by the hydration/dehydration processes of the polymer chain.

CONCLUSION

With a new simultaneous analysis technique, the chaotropic effect was studied in an *in-situ real time* manner. Using this new technique, we were able to study the chaotropic nature of cations in the supporting electrolyte by examination of changes in current, mass, and resistance of two conductive electroactive polypyrroles. Two different polypyrrole materials, with and without a mobile counterion, were considered. Although we did not overlook the effect of ionic strength, we have found that a chaotropic agent, such as Ca^{2+}, creates different changes in the mass and resistance of the polymer in the reduced form, compared with using an antichaotropic agent such as Li^+. Such changes were more obvious when PPy/DBS was used because of charge compensation process by cation insertion at the reduced potentials.

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