

DETERMINATION OF MEMBRANE HYDRATION NUMBER OF NH_4^+ IN CONDUCTING POLYMERS

M.J.M. Jafeen and U.L. Zainudeen

Department of Physical Sciences, South Eastern University of Sri Lanka,
Sammanthurai, Sri Lanka

Abstract

Polypyrrole polymer film doped with the large, immobile dodecylbenzene sulfonate anions operating in NH_4Cl aqueous solution has been used to determine the hydration numbers of NH_4^+ . Simultaneous Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM) technique was used to determine the amount of charge inserted and the total mass change during the reduction process in a polypyrrole film. From these values the number of water molecules accompanying NH_4^+ ion was evaluated. The number of water molecules entering the polymer during the initial part of the first reduction was found to be constant and independent of the concentration of the electrolyte below ~ 1 M. This well-defined value can be considered as the primary membrane hydration number of the cation involved in the reduction process. The primary (membrane) hydration number obtained for NH_4^+ in respective chloride aqueous electrolytes having low to moderate concentrations (0.02 M – 1 M) is 2.0-2.2 and the estimated value is very similar to that of K^+ estimated by the same method [9] and the sizes of the primary hydrated shells of NH_4^+ and K^+ in water are approximately the same.

Keywords: Polypyrrole, hydration number, cyclic voltammetry, EQCM

Introduction

The Nobel Prize for Chemistry in 2000 was awarded for the discovery and development of electronically conducting polymers by Shirakawa and co-workers and this discovery opened a new class of polymers with a wide range of applications [1]. This class of polymers is often referred as inherently conjugated polymers (ICPs) because the polymers are made up with alternate single and double carbon bonds (extended π bonds). The fascination of the ICPs is of their facile electroactivity-their ability to be electrochemically switched between different states at low voltage with very large changes in properties. The conductivity can change by 10 orders of magnitude; polymer colour changes; the polymer can switch from hydrophilic to hydrophobic; permeability to chemical species changes; the volume changes as does the mechanical properties [2].

From the discovery of electronically conducting polymers, continuous experimental and theoretical investigations of this group of polymer materials have explored a realm of new possibilities for both basic research and applications. In addition, this novel group of polymer materials may be used as a unique chemical environment to examine fundamental physical and chemical phenomena, which are not yet precisely uncovered due to experimental constraints: i.e. in a simple and direct method, the hydration number of ions may be systematically determined using electrochemical insertion of ions in a conducting polymer. This version of primary hydration number could be called membrane hydration number.

Recent research was demonstrated and reported that the primary hydration numbers of alkali metal cations can directly and accurately be determined using the unique physico-chemical environment of polypyrrole (PPy) doped with the large, immobile

dodecylbenzene sulfonate (DBS) anions operating in aqueous electrolytes [3]. The first electrochemical cathodic reduction of a freshly prepared PPy(DBS) film, which is in an oxidative form, operating in aqueous phase containing hydrated cations, has been used.

It is often regarded as NH_4^+ is similar to K^+ in chemical nature and was interested to study the hydration number of NH_4^+ and to compare it with K^+ . The present work aims to determine reliable value for membrane hydration number of NH_4^+ using the same method adopted in [3]. The membrane hydration numbers of NH_4^+ in respective chloride aqueous electrolytes having various concentrations ranging from 0.02 M to 1 M determined using PPy(DBS) conducting polymer are reported in this paper.

Methodology

The synthesis electrolyte consisted of 0.05 M sodium dodecyl benzene sulfonate (SDBS) and 0.05 M pyrrole monomer in pure water. PPy(DBS) films were galvanostatically electropolymerized on AT-cut quartz crystal electrodes with a current density of 1 mA/cm^2 as described elsewhere [4]. The electric current and time were chosen to form a film of 400 nm thickness, calculated from assuming that a charge passed during synthesis of 160 mC/cm^2 yields a 1 μm coating [5]. Simultaneous cyclic voltammetry (CV) and differential mass detection was performed on the deposited PPy(DBS) film.

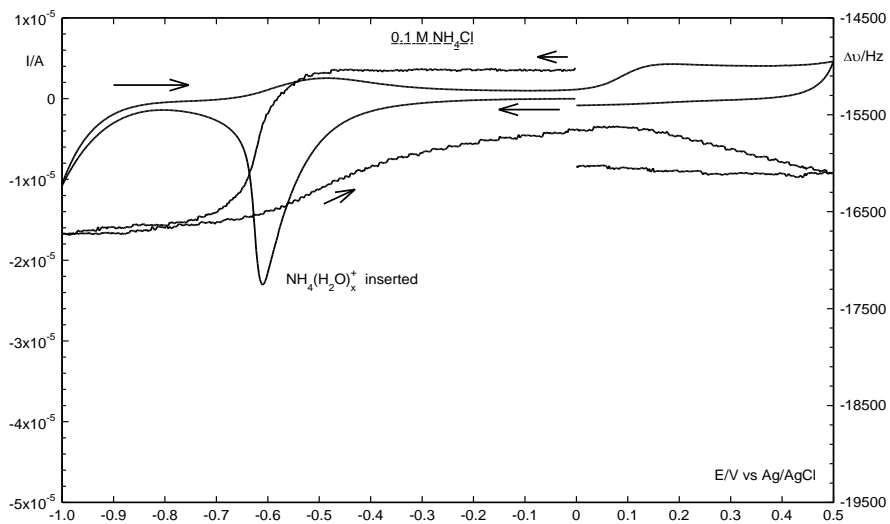
An electrochemical quartz crystal microbalance (EQCM) using an ICM 10 MHz crystal with a 0.20 cm^2 gold electrodes controlled by a Hewlett-Packard E4916A crystal analyzer in combination with a potentiostat (Autolab PGSTAT 30) were used to measure the change of mass during insertion of solvated ions. The cycling experiments with simultaneous CV and EQCM measurements were done in aqueous NH_4Cl electrolytes having various concentrations, ranging from 0.02 M to 1 M. For each experiment, a freshly prepared PPy(DBS) film of 400 nm thickness polymerized under the same experimental conditions was used. For all cycling, a constant scan rate of 2 mV/s was used as optimized in [3].

Results and Discussion

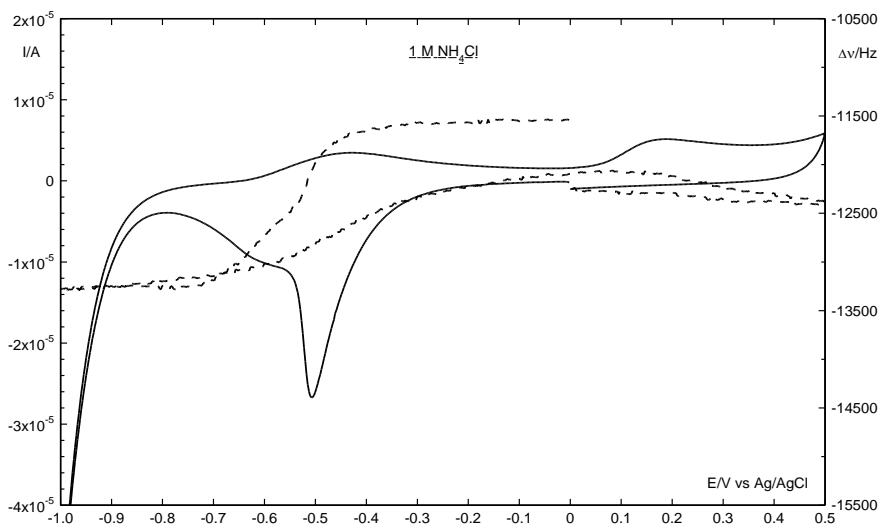
Figure 1 shows simultaneous cyclic voltammograms (solid lines) and the corresponding frequency changes (dashed lines) from EQCM measurements obtained for PPy/DBS films cycled in 0.1 M, 1 M and 0.02 M NH_4Cl electrolytes. For each experiment, the pristine film was first cathodically reduced from 0.0 V to -1.0 V (~) and subsequently oxidized up to +0.5 (~) to complete the first complete cycle. As can be seen in the figures, the main feature of the cyclic voltammogram in each experiment is a sharp reduction peak during cathodic reduction of the film, centered at -0.5 to -0.6 V versus Ag/AgCl in 3 M KCl. Since the PPy film is synthesized by oxidation, there are no cations inside the pristine film.

The only ions are the large, immobile DBS^- ions countering the positive charge on the polymer backbone. Moreover, these DBS^- anions permanently rests inside the film and are not involved in any subsequent redox mechanism because of the large size and strong entanglement between polymer chains. Hence, the first reduction therefore consists solely of the insertion of cation NH_4^+ (plus possible neutral water molecules) present in the cycling electrolyte into the polymer. More importantly, there are no complications arising from simultaneous anion expulsion possible in the first reduction of the film [6,7]. In this

context, the analysis of the first reduction process becomes simple and the amount of NH_4^+ ions inserted is determined by being directly proportional to the area of the reduction peak. The charge of the NH_4^+ moved in (the number of moles of NH_4^+) can be found from the area covered by the cathodic peak with reference to the zero current as the base line.



(a)



(b)

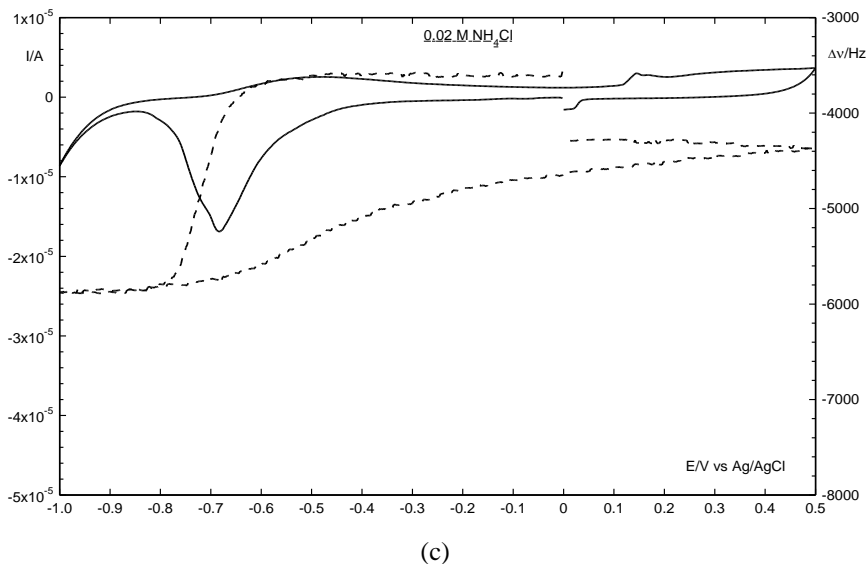


Figure 1. First cyclic voltammograms and simultaneous frequency differences of a 400 nm PPy/DBS film in (a) 0.1 M, (b) 1 M and (c) 0.02 M NH_4Cl electrolytes.

The frequency measurements during the cathodic reduction of the films give information about all moving species, both NH_4^+ and water molecules, into the film. On closer inspection of Fig. 1, the frequency curve during reduction can be clearly divided into three segments: No redox reaction – no frequency change; sharp reduction peak – a very steep frequency decrease; No significant redox reaction – but a large, continuous, but less steep frequency decrease. At end of the peak, there is a distinct shift in slope of the frequency curve. Furthermore, the steepest part of the curve corresponds closely to the maximum of the reduction peak.

The beginning and the end of the steep part also coincide closely with the beginning and end of the reduction peak. This leads to the identification of the mass change of the steep part with the insertion of the NH_4^+ ion together with tightly bound H_2O molecules – i.e. those of the inner hydration shell that are associated directly with the cation only. From the steep part of the frequency measurements in complement with cyclic voltammetry measurements, the number of moles of tightly bound H_2O with NH_4^+ can be estimated. Hence, the primary hydration number can now be determined as the number of moles of tightly bound H_2O , divided by the number of moles of NH_4^+ ions inserted, determined by the area of the reduction peak.

To minimize the errors and eliminate uncertainties, we have now further refined the method of finding the inserted amount of cations from the charge resulting in more precise values. Only the first part of the reduction is used – this prevents interference from the osmotic inserted water that dominates the mass increase at lower potentials. A second method involves graphical integration by visual inspection of the full first half of the reduction. The method yields only slightly different and robust results. The hydration numbers obtained are not simply a statistical average over the time of insertion, since earlier work has shown that the ratio between the mass and the charge inserted is constant

during the full first half of the reduction, and is therefore a well-defined characteristic of the insertion process [8].

It can also be seen from the figures that at very low voltages (close to -1 V), the negative current increases very rapidly. This current arises due to the reduction of H₂O molecules in the electrolyte. Since NH₄Cl has an acidic nature in aqueous electrolyte, It would induce more reduction of H₂O molecules.

Using the cyclic voltammograms and the simultaneous frequency differences in Figure. 1, the amount of NH₄⁺ ions and the amount of tightly bound H₂O inserted during the full cathodic peak were estimated and the values are given in Table 1.

Table 1. Amount of NH₄⁺ ions and the tightly bound water molecules inserted during the full cathodic peak in 0.1, 1 and 0.02 M electrolytes.

Concentration (M)	0.1	1	0.02
Frequency change during full peak(Hz)	854	1,094	974
Total frequency change(Hz)	1,696	1,732	2,285
Moles of cation moved in (×10 ⁻⁹)	13.765-14.106	17.287-17.153	15.841-15.858
Moles of solvated water moved in (×10 ⁻⁸)	2.925-2.959	3.761-3.775	3.302-3.304

The primary hydration numbers of NH₄⁺ in 0.1, 1 and 0.02 M electrolytes calculated are given in Table 2.

Table 2. Primary hydration number of NH₄⁺ in 0.1, 1 and 0.02 M electrolytes.

Concentrations (M)	0.1	1	0.02
Hydration Number	2.0-2.2	2.0-2.2	2.0-2.1

The above results reinforce the fact that the primary hydration number of NH₄⁺ also does not change in electrolytes of different concentrations up to 1 M, as for the alkali metal ions, alkali earth metal ions and transition metal ions. In order to compare the primary hydration number of NH₄⁺ with that of K⁺, the estimated value of NH₄⁺ is given in Table 3 with that of K⁺ [9] by the same method.

Table 3 Primary hydration number of NH₄⁺ and K⁺

Cation	NH ₄ ⁺	K ⁺
Hydration Number	2.0-2.2	2.3-2.5

It is clear that the primary hydration numbers for NH₄⁺ and K⁺ have approximately the same values; both ions have approximately the same size of the primary hydrated shell in water. It is reaffirmed a fact that the chemical behaviour of NH₄⁺ is similar to that of K⁺ even though the chemical structures of the two ions are so different.

Conclusion

The hydration number of NH_4^+ in aqueous electrolytes has been determined using the novel physico-chemical environment of polypyrrole. The primary (membrane) hydration number obtained for NH_4^+ in respective chloride aqueous electrolytes having low to moderate concentrations (0.02 M – 1 M) is 2.0-2.2. It is found that the estimated values of the primary hydration number of NH_4^+ is very similar to that of K^+ estimated by the same method [9] and the sizes of the primary hydrated shells of NH_4^+ and K^+ in water are approximately the same, even though the chemical structures of the two ions are so different.

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