

# Effect of Water on Inorganic Acids Doped Polyaniline

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**ABSTRACT:** Based on gravimetric measurements, the effect of water on thin films of inorganic acids doped polyaniline (PANI) was developed. The starting point was the fact that PANI coating on the electrode of quartz crystal microbalances (QCM) showed significant frequency shifts under exposure to liquid water. The changes in the frequency as a function of treatment time in water were quantitatively measured. These changes suggested that the mass decreases under water exposure were due to dopant ions release. The data have been collected using doped PANI films with HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>. For PANI-HCl upon immersion in water showed rapid mass loss followed by slow kinetically dopant ions release with time. However, PANI-H<sub>3</sub>PO<sub>4</sub> and PANI-

H<sub>2</sub>SO<sub>4</sub> showed a slow kinetically release out of the film immediately upon immersion in water. The release process was well described by Fickian diffusion process. The diffusion coefficients (*D*) were determined and found to be dependent on the acid dopant utilized. They varied within the range of (1.68–14.7) × 10<sup>-14</sup> cm<sup>2</sup>/s. This work presented an attempt to find a simple method based on the QCM for investigating the diffusion of dopant ions out of thin PANI films upon immersion in water and determining *D*. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1384–1389, 2009

**Key words:** quartz crystal microbalance; polyaniline; thin films; dopant release; diffusion coefficient

## INTRODUCTION

Polyaniline (PANI) has attracted considerable attention because of its good environmental stability, good redox reversibility, and electrical conductivity. These properties indicate possible applications in battery electrodes,<sup>1,2</sup> electrochromic devices,<sup>3</sup> photoelectric cells,<sup>4</sup> light-emitting diodes,<sup>5</sup> and biosensors.<sup>6</sup>

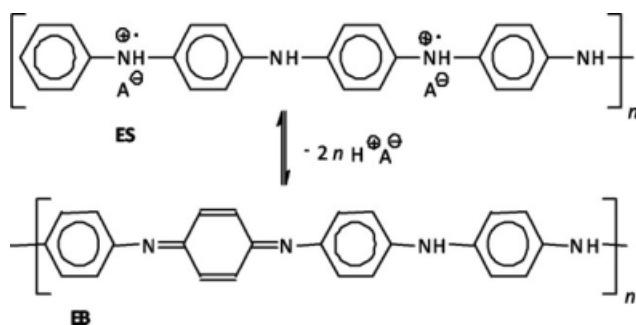
Aniline polymerization in an acidic aqueous medium yields the most conductive form of PANI salt, the emeraldine salt (ES).<sup>7,8</sup> ES may be converted to the corresponding emeraldine base (EB) by treatment with an alkali solution, or by rinsing with a large excess of water,<sup>7,9</sup> (Scheme 1). Imine sites of the EB form are easily protonated, with a distinctive insulator–conductor transition induced by the appearance of polarons in the lattice, while the number of  $\pi$ -electrons remains constant. As a consequence, new optical conducting and paramagnetic properties appear in doped PANI.<sup>10,11</sup> These properties are controlled by doping the polymer. Chiang and MacDiarmid<sup>12</sup> have suggested that highest degree of doping and the highest conductivity, respectively, were attained at pH 0–1.

Lubentsov et al.<sup>13</sup> have reported that the electrical properties of thin PANI films were increased when water vapor adsorption took place. They also mentioned that doped PANI was found to adsorb the greater amount of water as compared with undoped samples. Based on conductivity measurement, Passiniemi<sup>14</sup> has determined the diffusion coefficient (*D*) of water vapors in PANI-HCl pressed powder. *D* was measured to be  $\sim 5 \times 10^{-10}$  cm<sup>2</sup>/s at room temperature. However, Nechtschein et al.<sup>15,16</sup> have reported *D* which equals  $\sim 0.4 - 2 \times 10^{-9}$  cm<sup>2</sup>/s for the PANI powder and have suggested that the water molecules are adsorbed on the acidic sites of the polymer chains. Also, they have suggested a mechanism that involved a proton transfer from the PANI chains takes place in the presence of water molecules. Recently, Ostwal et al.<sup>17,18</sup> have studied the adsorption of water vapor by doped PANI powder and fibers. They have found that the adsorption of water is completely reversed when an electric current passes through the material.

Hobaica<sup>19</sup> has studied the effect of aqueous HCl (pH 1.18) on PANI-HCl powder. The results showed that the molecular weight and the chemical structure remained unchanged during immersion. However, a dopant ions diffusion was observed and *D* was measured and equals  $5.28 \times 10^{-12}$  cm<sup>2</sup>/s.

QCM has a wide range of applications in biochemistry, analytical science, and other fields. It can

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**Scheme 1** Doped PANI (ES) is dedoped by treatment with an alkali to PANI (EB).

be used concomitant with other techniques like electrochemistry (EQCM), FTIR and UV-visible spectroscopies, ellipsometry, atomic force microscopy, etc. In PANI studies, EQCM was used to study the redox reaction mechanism,<sup>20</sup> film formation,<sup>21</sup> ion-transport within the PANI films,<sup>22</sup> and PANI film degradation.<sup>23</sup> QCM technique was also used to monitor the chemical oxidation of aniline to form thin PANI films and as pH sensor by Ayad et al.<sup>24–26</sup> It also used to determine the dopant weight fraction ( $w$ ) associated with the PANI film doped in different inorganic acids (HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and CCl<sub>3</sub>COOH).<sup>27,28</sup>

Thin PANI films have more technological importance than powders for numerous applications,<sup>1–6</sup> therefore understanding the effects of the interface such as water on the dynamics of these films is essential for their application in technology. In addition, PANI may find applications in air dehydration and water recovery from atmospheric sources. As far as we know, there have been neither study of the effect of water immersion on PANI salt films doped with inorganic acids (e.g. HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) nor study to determine the  $D$  of dopant ions release in films. Thus, in the present article we have carried out the investigation for the effect of the PANI films prepared using the chemical method. The frequency changes of the QCM were measured against reaction time and  $D$  were determined. A simple method based on QCM for investigating the release of the dopant ions out of PANI films can be produced.

## EXPERIMENTAL

Aniline (ADWIC, Egypt) was distilled twice under atmospheric pressure using zinc dust. Ammonium peroxydisulphate (APS) (WINLAB, UK), HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and ammonium hydroxide (ADWIC, Egypt) were used as received without any further purification.

In a typical example for PANI film preparation, 0.03M solution of aniline was prepared in 50 mL of

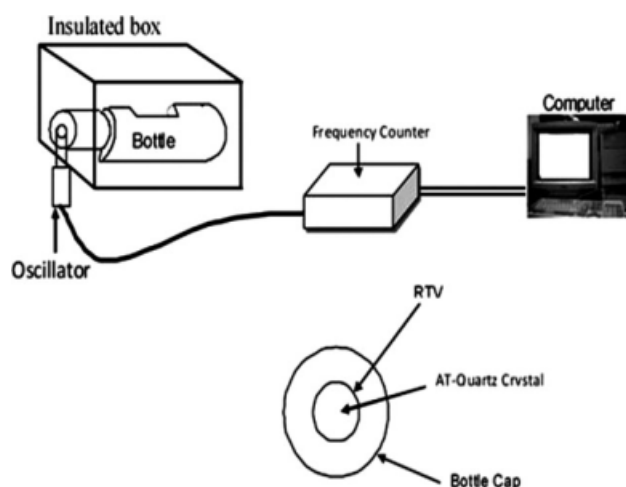
0.1M H<sub>2</sub>SO<sub>4</sub> and a solution of 0.015M APS was prepared in 50 mL of 0.1M H<sub>2</sub>SO<sub>4</sub>. The APS solution was added to the aniline solution. The APS/aniline molar ratio after mixing was 0.5. The experimental arrangement has been described elsewhere<sup>29</sup> and is sketched in Figure 1. The solutions of the reactants were added to the polypropylene bottle. The bottle served as the reaction vessel and the deposition film was monitored by mounting a 5 MHz-cut quartz crystal in the cap of the bottle. The resonance frequency of the crystal was determined by using the crystal as the frequency determining element of an electronic oscillator, the measurements being taken using a GW Frequency Counter, Model GFC-8055G. As the polymerization proceeds, the *in situ* PANI-H<sub>2</sub>SO<sub>4</sub> films were deposited onto the electrode of QCM. Similar PANI films were obtained in case of using HCl and H<sub>3</sub>PO<sub>4</sub> as media during the polymerization, respectively. The mass per unit area of the film,  $m'$  (g/cm<sup>2</sup>), was determined from the change in its resonance frequency. The time dependence of frequency was recorded at room temperature (23–24°C). The relation between the frequency change  $\Delta f$  and  $m'$  is well established from the work of Sauerbrey<sup>30</sup> and is given by:

$$\Delta f = -(2f_0^2 / \sqrt{\rho_Q \mu_Q}) m' \quad (1)$$

where  $f_0$  (in Hz) is the natural frequency of the quartz crystal,  $\rho_Q$  is the quartz density (2.649 g/cm<sup>3</sup>), and  $\mu_Q$  is the shear modulus ( $2.947 \times 10^{10}$  N/m<sup>2</sup>).

The thickness of the PANI film,  $L$  (cm), was determined from the relation:

$$m' = \rho L \quad (2)$$



**Figure 1** A sketch of the experimental arrangement, indicating the reaction vessel and the method of interfacing with the quartz resonator.

The density of the PANI is taken to be  $1.33 \text{ g/cm}^3$ , as determined in other studies.<sup>31</sup>

The ES film formed at the end of the polymerization was rinsed with the acid solution constituting the reaction medium. The film coating on the QCM electrode then immersed into 100 mL of bidistilled water for some time until the frequency changes attains a steady state variation with time. The latter film was exposed to 0.1M ammonia solution to give the EB film. The mass loss due to the dopant ions release was determined by calculating the increase in the frequency of the ES film coating on the quartz crystal.

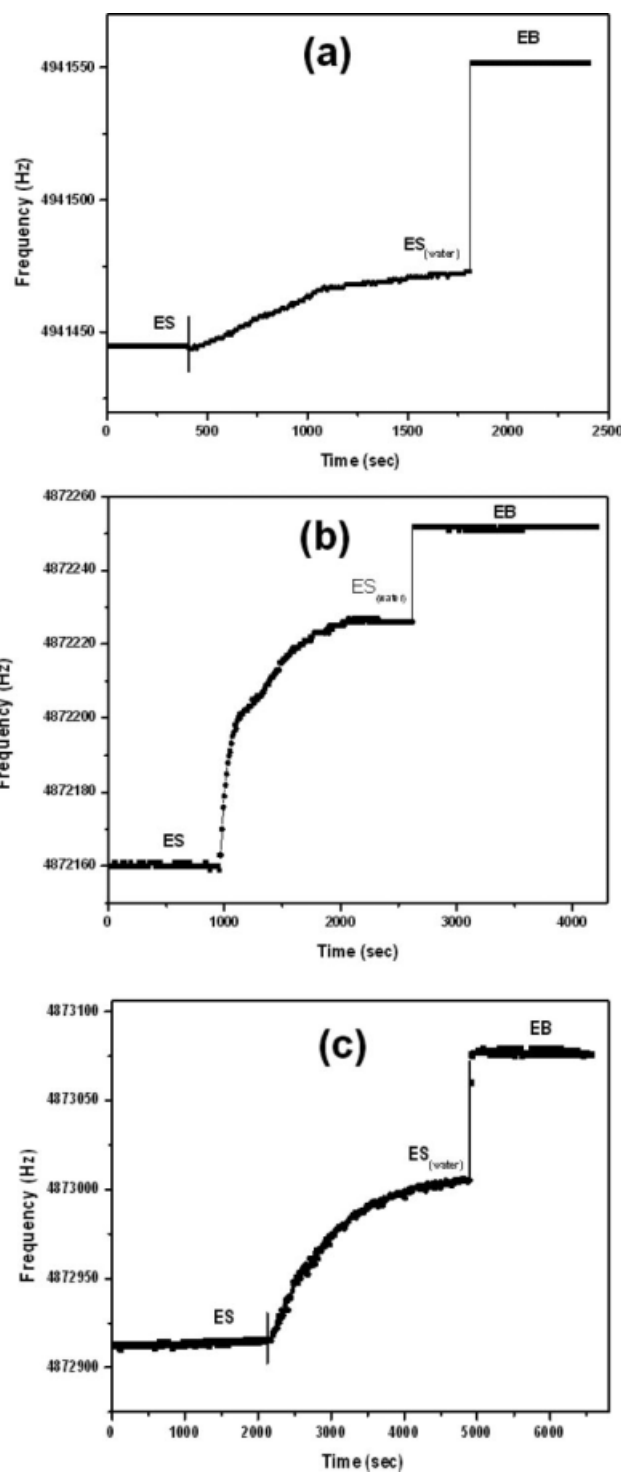
## RESULTS

The effect of water on PANI films doped in 0.1M  $\text{H}_2\text{SO}_4$  was investigated in detail as an example.

The polymerization in  $\text{H}_2\text{SO}_4$  medium ends with the formation of *in situ* doped PANI film, which is denoted as ES. *In situ* doping occurs due to the presence of  $\text{H}_2\text{SO}_4$ , constituting the reaction medium and also generated from the reduction of APS. The ES film was immersed in 100 mL water. It can be shown that the frequency of the ES film coating on the QCM increases slowly with time up to steady state condition to produce another film,  $\text{ES}_{(\text{water})}$ , i.e., there is a kinetic diffusion for the dopant ions ( $\text{H}_2\text{SO}_4$  ions) out of the film to the surrounding medium, Figure 2(a). The increases in the frequency can be attributed to mass loss in the film.

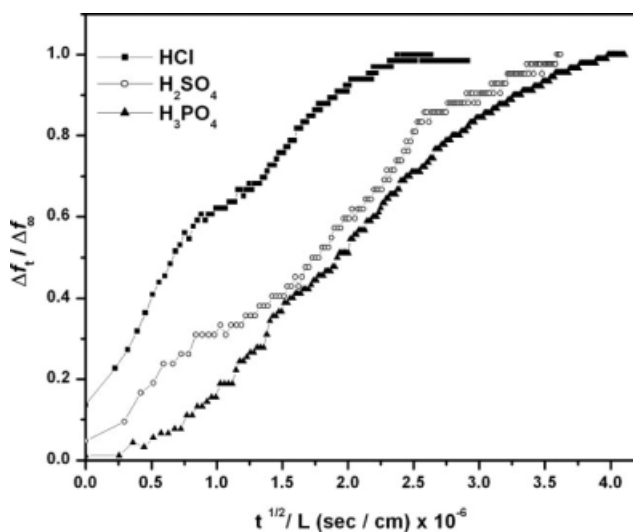
The ratio of the frequency change due to the mass loss in the ES film in comparison to the frequency change due to the ES film formation ( $\Delta f_{(1)}$ ) gives the dopant weight loss in protonated PANI.<sup>27,28</sup> Suppose  $f_o$  is the frequency at zero time of polymerization to obtain the ES film, and  $f_{\text{ES}}$  is the frequency of the ES film at the end of polymerization, then the frequency change  $\Delta f = f_o - f_{\text{ES}}$ , can be calculated, and it corresponds to the mass of the ES film (584 Hz). Also, if  $f_{\text{water}}$  is the frequency at the end of steady state due to the immersion of ES film in water, then the frequency change  $\Delta f_{\infty} = f_{\text{ES}} - f_{\text{water}}$ , corresponds to the mass loss in the ES film (41 Hz). Consequently, the value of the weight loss as a percentage due to immersion of the ES film in water is  $\Delta f_{\infty} / \Delta f \times 100 = 7.02 \text{ wt } \%$ .

Since, there is a slow release (diffusion) of the dopant ions out of the film to the surrounding environment, the kinetics of this release can be studied and  $D$  can be derived from the QCM measurements as a method of gravimetric determination. The mass decrease of a film of thickness  $L$  can be determined from the change in the resonance frequency using the Sauerbrey equation during the transient regime. This is based on the fact that the



**Figure 2** The effect of water and 0.1M ammonia on PANI films doped in 0.1M of various acids: (a)  $\text{H}_2\text{SO}_4$ , (b)  $\text{HCl}$ , and (c)  $\text{H}_3\text{PO}_4$ .

frequency shift  $\Delta f$  during the release process is related to the change in mass  $\Delta m$ . Suppose  $\Delta f_t$  is the frequency change due to  $\text{H}_2\text{SO}_4$  ions release at any time  $t$ , this parameter at time  $t$  can be given as follows:



**Figure 3**  $\Delta f_t / \Delta f_\infty$  as a function of  $t^{1/2}/L$  during the treatment of various ES films with water.

$$\Delta f_t = f_{ES} - f_t$$

where  $f_t$  is the frequency during the release process at time  $t$ . The frequency change ( $\Delta f_t / \Delta f_\infty$ ) corresponds to  $(\Delta m_t / \Delta m_\infty)$  at the same time  $t$ , where  $\Delta m_t$  is the weight of the dopant ions release at time  $t$  and  $\Delta m_\infty$  is the total dopant ions release at the steady state. Analysis of the obtained experimental data was based on solving Fick's second equation which has been reviewed by Crank.<sup>32</sup> The average value for  $D$  can be obtained from a plot of  $\Delta f_t / \Delta f_\infty$  as a function of  $t^{1/2}/L$  from the initial linear portion of the diffusion using

$$\frac{\Delta f_t}{\Delta f_\infty} = 4\sqrt{\frac{D}{\pi}} \frac{t^{1/2}}{L} \quad (3)$$

Figure 3 shows the relation between  $(\Delta f_t / \Delta f_\infty)$  and  $t^{1/2}/L$  and suggests that the diffusion process follows Fickian kinetics and that the dopant release undergoes the diffusion process.<sup>32</sup> The plots are linear for at least the first half of the curve, as shown in the figure. The value of  $D$  was calculated and equals  $1.68 \times 10^{-14} \text{ cm}^2/\text{s}$ .

Experiments were carried out to see the effect of water on PANI films doped in HCl and  $\text{H}_3\text{PO}_4$  instead of  $\text{H}_2\text{SO}_4$ . Similar behavior was obtained in case of  $\text{H}_3\text{PO}_4$  like that obtained in PANI- $\text{H}_2\text{SO}_4$  film, Figure 2(b). The value of the percentage of mass loss during the immersion in water was calculated and equals 13.7 wt %. Also, the  $D$  value was calculated and equals  $2 \times 10^{-14} \text{ cm}^2/\text{s}$ . In the case of PANI doped in HCl, different behavior can be seen in Figure 2(c). The process occurs in two stages: rapid mass losses followed by an exponentially loss with time until it reaches a steady state. The total value of the percentage of mass loss is 9.4 wt %.

$D$  was also calculated and equals  $14.7 \times 10^{-14} \text{ cm}^2/\text{s}$ . The values of the percentage of mass loss due to immersion in water and  $D$  for different systems are shown in Table I.

To see, if the ES films immersion in water causes a complete dedoping or not, the PANI- $\text{H}_2\text{SO}_4$  film at the end of its immersion in water was exposed to 0.1M ammonia solution, Figure 2(a). A frequency decrease occurred immediately upon immersion. This indicates a further dopant ions release and a complete dedoping process to obtain the EB film according to Scheme 1. Suppose  $f_{EB}$  is the frequency at the end of this process, then the frequency change  $\Delta f_{EB} = f_{ES} - f_{EB}$ , can be calculated, and it corresponds to the mass loss in the ES film to obtain the EB film. Consequently,  $w$  during the dedoping process is  $\Delta f_{EB} / \Delta f_{ES} \times 100 = 20.7 \text{ wt } \%$ . This experiment was repeated for PANI-HCl and PANI- $\text{H}_3\text{PO}_4$  films and showed similar behaviors. The percentages of the  $w$  were determined and are depicted in Table I.

## DISCUSSION

It has been mentioned that dedoping of ES powder can be carried out by treatment ES with an alkali solution, or by rinsing with a large excess of water.<sup>7,9</sup> However, there is neither investigation to see if the dedoping process and the dopant ions release occurred immediately or kinetically out of the polymer nor a justification of complete dedoping of the ES due to its immersion in water. The importance of these studies would be more, if we are dealing with thin PANI films, since thin films have large importance in comparison to the use of polymer powder in the technological applications.

In the present context, one should bear in mind that there is a vast difference in the morphologies between the polymer powder and film. It has been pointed by Chen et al.<sup>33</sup> that each particle of ES powder is an aggregate of many small granules, while the surface of the ES film is rather smooth and dense. Also, Porter et al.<sup>34</sup> have used scanning tunneling microscopic and atomic force microscopic to

**TABLE I**  
The Calculated Mass Loss Due to the ES Film Immersion in Water [mass loss<sub>(water)</sub>],  $D$  and  $w$  for Various PANI Films

PANI film	$L \times 10^6$ (cm)	Mass loss <sub>(water)</sub> %	$D \times 10^{14}$ ( $\text{cm}^2/\text{s}$ )	$w$ (%)
PANI-HCl	9.83	9.4	14.7	12.94
PANI- $\text{H}_2\text{SO}_4$	7.545	7.02	1.68	20.7
PANI- $\text{H}_3\text{PO}_4$	8.728	13.7	2.02	24.5

During the dedoping process  $L$  is the thickness of the film.

study of ES films and have revealed featureless and dense surface nanostructures.

In the present investigation, it is seen that the water has an effect on the ES film doped in different acids. There is mass decrease which attributed to a dopant ions release. However, there are differences of this release regime with time, depend on the type of the dopant ions. In case of PANI-H<sub>2</sub>SO<sub>4</sub> and PANI-H<sub>3</sub>PO<sub>4</sub> films, the dopant ions show a kinetic release out of the films immediately upon the films was immersed in water. In contrast, for PANI-HCl, a sharp mass decrease followed by dopant ions release exponentially with time up to a steady state. The achievements of the steady state condition are different and depend on the type of dopants. The times for attainment of the steady states are: ~ 3–4, 10 and 50 min for PANI-HCl, PANI-H<sub>2</sub>SO<sub>4</sub> and PANI-H<sub>3</sub>PO<sub>4</sub>, respectively. This is can be explained on the fact that chloride anions have higher hydrodynamic and lower van der Waals volumes than the other dopant anions. These characteristics enhance the diffusion of the HCl ions out of ES film. However, larger times were needed to release the H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> ions. The latter acid anions have lower hydrodynamic and higher van der Waals volumes than HCl. In addition, in case of PANI-H<sub>3</sub>PO<sub>4</sub>, the H<sub>3</sub>PO<sub>4</sub> molecule during its association with the polymer chains uses one proton to dope the polymer, and the other two OH groups to form hydrogen bonds with PANI chains. This is prohibited H<sub>3</sub>PO<sub>4</sub> ions diffusion out of the ES film. It worth noting that, Wan et al.<sup>35</sup> have studied the PANI films doped in HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> and have mentioned that the mechanical parameters of PANI films doped with H<sub>3</sub>PO<sub>4</sub> are relatively higher than that of PANI doped in other dopants. This was attributed to the same reason mentioned previously.

The values of  $D$  were in the range of  $(1.68\text{--}14.7) \times 10^{-14}$  cm<sup>2</sup>/s and are within a reasonable order similar to the rate of diffusion of molecules in a swollen polymer electrolyte.<sup>36</sup>  $D$  for HCl is higher than those of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, however the  $D$  for the latter two acids are approximately equals. The differences in the values of  $D$  can be explained on the basis of the differences in their molar masses and associations. The molecular weight of HCl is small than H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>; however the molecular weights of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> are equal. In addition, the latter acids are more involved in hydrogen bonding association than HCl. In general, we suspect that a combination of size, molar masses and association capability of the acid anion are important factors in the acid ions diffusion out of the PANI films.

The percentages of mass loss due to the immersion in water are in the order: PANI-HCl < PANI-H<sub>2</sub>SO<sub>4</sub> < PANI-H<sub>3</sub>PO<sub>4</sub>. These values are smaller than the ones obtained, when the ES film of various

acids under consideration were exposed to 0.1M ammonia. The latter solution was used for complete dedoping of the ES.<sup>7,9</sup> This indicates that, the ES films immersion in water did not attain a complete dedoping upon immersion in water and still some dopant ions were associated with the PANI chains.

In previous investigation the  $w$  values were calculated for the ES films doped in 0.1 M HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> media and equal 16.2, 20, and 25.3%, respectively. This indicated the presence of HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> counter ions, (A<sup>-</sup> in Scheme 1), as Cl<sup>-</sup>, ½SO<sub>4</sub><sup>2-</sup>, and ½ HPO<sub>4</sub><sup>2-</sup>, respectively.<sup>27,28</sup> These values are close to  $w$  values obtained in the present investigation for HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>, respectively.

Finally, it is important to realize that both the dopant ion release parameter will likely depend on the dopant loading up to the point where the polymer is "fully doped" and film thickness. It remains to be studied more fully in future work.

## CONCLUSIONS

PANI films doped in inorganic acids (e.g., HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) are treated with water. The dopant ions were released upon immersion and partial dedoping processes were obtained. However, a complete dedoping process was only obtained upon exposure to ammonia solution. The release of the dopant ions due to the film immersion in water seems well-fit by steady Fickian diffusion. The values of the diffusion coefficients ( $D$ ) were determined. They are within a reasonable order similar to the rate of diffusion of molecules in a swollen polymer electrolyte. Also, it has been shown that the size, molar masses and association capability of the acid anion are important factors in the acid ions diffusion properties out of doped PANI films.

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