# Poly(2-aminobiphenyl), Preparation, Characterization, Mechanism, and Kinetics of the Electropolymerization Process

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Received 23 August 2011; accepted 29 November 2011 DOI 10.1002/app.36621 Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Electropolymerization of 2-aminobiphenyl was carried out on glassy carbon, gold, and platinum electrodes, in aqueous–organic solvent mixtures, using a potentiodynamic technique. The choice of organic solvent strongly influences the film formation. In a mixture of 60% acetonitrile and 40% 1.0*M* HClO<sub>4</sub>, stable films were obtained. The poly(2-aminobiphenyl) films were characterized with cyclic voltammetry, where the electrochemical activity of the formed polymer films was investigated in acidic and neutral aqueous solutions containing perchlorates or in potassium ferrocyanide. The prepared films posses a remarkable stability in acidic aqueous solutions and are also stable in some organic solvents. The stability of the polymer films depends on the pH of the solution,

# INTRODUCTION

The study of electrodes modified with thin polymer films formed by electropolymerization of simple organic substances is a field of continuous interest in electrochemistry.<sup>1–3</sup> The electropolymerized conductive films have promising applications in lightweight (rechargeable) batteries,<sup>4,5</sup> electrochromic display devices,<sup>6–8</sup> biosensors,<sup>9,10</sup> and corrosion protection.<sup>11</sup> Some of these polymer films have shown good stability in aqueous media and normal atmospheric conditions.<sup>12</sup> Electrochemical polymerization of simple aromatic amines is usually done in acidic solutions to obtain a high degree of polymerization and to avoid N—N coupling.<sup>13,14</sup> Amino compounds can rather easily be polymerized in aqueous 1.0M HClO<sub>4</sub> solutions.<sup>15</sup> The polymerization in organic solvents is more difficult due to the high solubility of the reaction product and formation of very stable intermediates resulting in poor film formation.<sup>16,17</sup> Electropolymerization in aqueous-organic solvent mixtures overcomes the solubility problem of the

and the mechanism of the polymerization process involves deprotonation and head-to-tail coupling of oxidized monomers with its oligomeric radical cations. The kinetics of the electropolymerization process was investigated by determining the charge consumed during the electropolymerization as a function of time at different concentrations of the electrolyte components. The electropolymerization process follows first-order kinetics with respect to the monomer and negative order with respect to HClO<sub>4</sub>. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

**Key words:** conducting polymers; polymerization; cyclic voltammetry; poly(2-aminobiphenyl)

reaction product. There are only few reports on the polymerization of PANI and related compounds in aqueous–organic solvent mixtures.<sup>18–20</sup>

While the electropolymerization of unsubstituted aromatic amines has received a great deal of attention, the electropolymerization of the aryl-substituted aniline, especially o-substituted monomers, has got much less attention. Poly(4-aminobiphenyl) has been prepared successfully from solutions containing 0.02M 4-aminobiphenyl in a mixture of 2.0M HCl and acetonitrile (ACN; 68: 32 volume/volume).<sup>21</sup> The polymerization of 2-aminobiphenyl, in which a phenyl group is present in the *o*-position of the aniline moiety, seems to be an important subject for intensive investigation. The polymer film is expected to be stable in aqueous acidic solutions with an electroactive response in a wide potential range. It may possess electrochromic properties for some beneficial applications.

Many studies have been carried out to clarify the kinetics of the electropolymerization processes.<sup>22–29</sup> The study of the reaction order with respect to the monomer and the electrolyte in the electropolymerization process is an important issue. This study provides information about the nature of the reaction taking place at the electrode surface and the chemical structure of the polymer film beside the ways to improve its physical properties, e.g., its electrical conductivity.

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Journal of Applied Polymer Science, Vol. 000, 000–000 (2012) © 2012 Wiley Periodicals, Inc.

In this respect, we are aiming at the preparation of poly(2-aminobiphenyl) (PABP) films by the anodic oxidation of 2-aminobiphenyl (ABP). The optimization of the preparation conditions and the investigation of the electrochemical properties of the formed films in addition to the understanding of the mechanism of the electropolymerization, the kinetics of the process and the determination of the order of the reaction with respect to each component in the medium represent our main tasks.

## **EXPERIMENTAL DETAILS**

ABP, Merck, was used without further purification. HPLC grade ACN (Fischer) was used as received. The aqueous solutions were prepared using triply distilled water and analytical grade reagents. A standard all glass three-electrode electrochemical cell was used for all investigations. The electropolymerization process was slightly affected by the type of the substrate. It was found that the glassy carbon (GC), platinum (Pt), and gold (Au) discs are appropriate for the electrodeposition of the polymer film. Therefore, GC, Au, or Pt discs of 0.071 cm<sup>2</sup> geometric area were investigated as working electrodes. A silver/silver chloride (Ag/AgCl/3.0M KCl) was used as reference electrode and the counter electrode was a large area platinum spiral. Before each experiment the working electrode was polished mechanically with alumina powder (1.0-µm diameter), washed thoroughly with triply distilled water, and then rubbed against a smooth cloth. The electrochemical measurements were carried out using the electrochemical work station, IM6 Zhaner elektrik (Germany). All experiments were carried out at room temperature and the potentials were measured against and referred to the silver/silver chloride reference electrode ( $E^{\circ} = 0.222$  V vs. SHE).

The electropolymerization was carried out in solutions containing 10.0 mM ABP dissolved in a mixture of 1.0M HClO<sub>4</sub> acid and ACN (3 : 2, volume/volume ratio). The presence of ACN was essential for the solubility of the monomer in the mixed solvent. Details of all experimental procedures are described elsewhere.<sup>14,30</sup>

## **RESULTS AND DISCUSSION**

## Optimization of the electropolymerization process

It is worthwhile to mention that, attempts to electropolymerize 2-aminobiphenyl, under the same experimental conditions used for the preparation of poly(4-aminobiphenyl) have been failed.<sup>21</sup> Therefore, several aqueous and nonaqueous media were investigated for the electropolymerization of ABP at the platinum, gold, and GC electrodes. However, the



**Figure 1** (a) Typical cyclic voltammograms of the electropolymerization of ABP up to the 30th cycle from a solution of 10.0 mM ABP in 1.0M HClO<sub>4</sub>/ACN solvent mixture at a 3: 2 volume ratio. Scan rate is 100 mV/s in the potential range between 0.0 and +1.2 V. (b) Relation between the cycle number and the values of the anodic peak currents ( $I_{paIII}$ ) for the cycles between 3 and 30 during film formation as determined from (a).

majority of the tested media showed either low solubility of ABP or high solubility of oligomers at the initial stages of the electropolymerization process. The best medium for the electrochemical polymerization process was found to be  $1.0M \text{ HClO}_4/\text{ACN}$  mixed solvent of a 3 : 2 volume ratio. No film formation could be observed in either component of the mixed solvent when they were used separately. Besides the low price of GC compared with Pt and Au, polymer films formed on GC were found to be more stable because of better adherence to GC as amorphous material.<sup>14</sup> The whole experimental data presented in this work were carried out using GC rotating discs.

The cyclic voltammograms of the electropolymerization of 10.0 mM ABP dissolved in 1.0M HClO<sub>4</sub>/ ACN mixed solvent of a 3 : 2 volume ratio, respectively, are presented in Figure 1(a). The working electrode was a GC disc and the potential was swept continuously at a rate of 100 mV/s between 0.0 and +1.2 V. During the first positive potential scan, an irreversible current peak (I) was recorded at +0.97 V due to the oxidation of the amino group of the monomer molecule to a radical cation. On the reverse scan, this wave does not show a complementary peak, indicating the existence of very fast chemical followup reactions.<sup>31</sup> The reverse scan shows a small cathodic peak (II) at -0.62 V which disappears in subsequent cycles or rotating the disc electrode. This peak can be attributed to reduction of a soluble product, which was formed during the first cycle. On the other hand, the deposited products are detected as the peak system (III–IV) on the subsequent sweeps.



**Figure 2** (a) Effect of ABP concentration on PABP film formation 30th cycle between 0.1 and 100.0 mM ABP/ 1.0M HClO<sub>4</sub>/ACN (3 : 2, v/v), at scan rate 100 mV/s, in the potential range between 0.0 and +1.2 V. (b) Dependence of the anodic peak current value ( $I_{paIV}$ ) of the PABP film formation on the monomer concentration ranging between 0.1 and 100.0 mM.

The anodic peak potential (I) shifts to more positive values and a decrease of the peak current occurs with continuous cycling, which suggests that the resistance of the formed oxidized polymer film increases with time. By continuous cycling the peak current of the system (III–IV) increases, showing the characteristic behavior of electroactive film growth.<sup>31,32</sup> This is also confirmed when the modified electrode is cycled in free amine electrolyte solution.

The direct proportionality of the amount of polymer to the anodic peak current (IV) is fundamentally important for the studies of the electropolymerization process.<sup>33,34</sup> The anodic peak currents of the different cycles were measured and plotted as a function of the cycle number [Fig. 1(b)], which corresponds to the reaction time. The amount of polymer formation, which is directly proportional to the film thickness, increases linearly with the increase of the cycle number.<sup>4,32</sup>

The cyclic voltammograms of the 30th cycle at different monomer concentrations are presented in Figure 2(a). It is apparent that the amount of polymer formation depends significantly on the monomer concentration. This can be attributed to the increase in the number of nucleation sites on the electrode surface as the monomer concentration increases.<sup>33</sup> The anodic peak current, which is directly proportional to the amount of the formed polymer, is presented as a function of the monomer concentration in Figure 2(b). It is clear that the amount of the formed polymer increases linearly with the monomer concentration in the experimental range.

Figure 3(a) presents the cyclic voltammograms of the 30th cycle of the film formation as a function of the scan rate, v. The cyclic voltammograms qualitatively resemble those of solution-dissolved reactants diffusing to the electrode surface. The variation of the amount of polymer formed at the electrode surface, as presented by the anodic peak current,  $I_{paIV}$ , with v is shown in Figure 3(b). It is clear that the peak current increases as the scan rate increases. Plot of the anodic peak current versus the square root of the potential scan rate,  $v^{1/2}$ , was nearly linear from 20 to 1000 mV s<sup>-1</sup>, indicating that the charge transport through PABP film is apparently diffusion controlled.<sup>35</sup>

The prepared polymer films change their colors according to the polymerization time and the redox state of the polymer, for short electrochemical polymerization times (<2 min), a golden yellow film was formed. For longer polymerization times ( $\sim4$  min), a green colored film was obtained. Longer polymerization times ( $\sim10$  min) produce dark green to brown



**Figure 3** (a) Effect of scan rate on the 30th cycle of PABP film formation in the potential range between 0.0 and +1.2 V. (b) Relation between scan rate and the value of the anodic peak current ( $I_{paIV}$ ) of PABP polymer film formation in the scan range between 20 and 1000 mV/s. (c) Relation between  $v^{1/2}$  and the value of the anodic peak current ( $I_{paIV}$ ) of PABP polymer film formation in the scan range between 20 and 1000 mV/s.

Journal of Applied Polymer Science DOI 10.1002/app



**Figure 4** Cyclic voltammograms of PABP film electrochemical response in 1.0M HClO<sub>4</sub> solution at a scan rate of 100 mV/s, in the potential ranges between 0.0 and +1.0 V.

films. The produced films show multiple color changes according to the redox reactions occurring at different potentials. The color of the polymer film in 1.0M HClO<sub>4</sub> changes from golden yellow to green to dark green to dark blue and then to brown between 0.0 and +1.2 V versus silver/silver chloride electrode. The electrochromic properties are related to the formation of polarons, which are subsequently oxidized into diimine species followed by oxidation of the aromatic rings.

## Electroactive characteristics of the PABP film

Figure 4 shows the cyclic voltammograms of PABP in  $1.0M \text{ HClO}_4$  solution (pH = 0.01) at a scan rate of 100 mV/s between 0.0 and +1.0 V versus the Ag/AgCl reference electrode. The figure represents the redox system of the polymer backbone, which exhibits only a single redox couple at ~+0.48 V. The reversible redox wave corresponds to the oxidation of the amine nitrogen, i.e., polaron state formation like the polyaniline structure.<sup>36</sup> The figure shows that PABP-modified electrodes posses high stability.

The electrochemical response of PABP at different concentrations of HClO<sub>4</sub> is presented in Figure 5(a). Similar results have been obtained with other acids, e.g., HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, even with organic acids like oxalic acid. In general, the peak current increases with the increase of the acid concentration up to 2.0*M* and then no appreciable change could be recorded. The final (plateau) value of the peak current depends on the type of the acid and the order of its increase is HClO<sub>4</sub> > HNO<sub>3</sub> > HCl > H<sub>2</sub>SO<sub>4</sub> > oxalic acid [Fig. 5(b)]. This behavior can be explained as the bases of the anion effect on the peak currents and the mobility of these anions toward the interface. Anions are occluded in the film

Journal of Applied Polymer Science DOI 10.1002/app

structure either to neutralize protonic charges (acidbase equilibrium) or to compensate the excess plus charges produced by anodic oxidation of film structure (doping process).<sup>37</sup> Although the effect of anions and acid concentration is clear as presented in Figure 5(a,b), the peak current is much affected



**Figure 5** (a) Cyclic voltammograms of the PABP film electrochemical response 10th cycle in different HClO<sub>4</sub> concentrations from 0.1 to 5.0*M*, at a scan rate of 100 mV/s, in the potential range between 0.0 and  $\pm$ 1.0 V. (b) Relation between the acid concentration and the values of the anodic peak current of the 10th cycle of the PABP film electrochemical response in different concentrations between 0.1 and 5.0*M* HClO<sub>4</sub>, HNO<sub>3</sub>, and HCl, and 0.05–2.5*M* H<sub>2</sub>SO<sub>4</sub> and oxalic acid. (c) Effect of pH on the value of the anodic peak current of the PABP film electrochemical response.



**Figure 6** Cyclic voltammogram of the redox  $[Fe(CN)6]^{3-/4-}$  on bare GC and PABP-modified electrodes in 2.0 m*M* K<sub>3</sub>[Fe(CN)<sub>6</sub>]/0.5*M* KCl, at a scan rate of 100 mV/s.

by the solution pH. The relation between log  $I_{pa}$  and pH is linear [Fig. 5(c)] and can be formulated as:

# $Log I_{pa} = a - b pH$

The values of the constants a and b were calculated and found to be: a = 1.96, which is equivalent to 91.2  $\mu$ A for the peak current at pH = 0, and b = -0.256, which represents the rate of decrease of the peak current with the increase of the pH. The same holds for the cathodic peak currents, and for different acids without regard to the nature of the acid. The general trend is the decrease of the electroactive response as the pH of the electrolyte increases, which is related to the acid-base equilibrium of amino or imino nitrogen in the film with proton in the solution. With the increase of the solution pH, the equilibrium will shift toward the deprotonation of amino or imino nitrogen. The deprotonated film seems to lose its electrical conductivity.<sup>37</sup> In neutral solutions, the polymer film loses its electrochemical activity, which means that the presence of protons is essential for film stability and the redox reaction to occur. The stabilization and increase of the current after 10 cycles is considered to be an indication of relative film stability in acidic solutions. The stability of the polymer film was found to depend on the strength and concentration of the acid, the presence of a strong acid retards the decomposition of the fully oxidized polymer film by shifting the equilibrium of water protonation toward the hydroxonium ion  $(H_3O^+)$ .<sup>38</sup>

# Charge conduction through PABP film

The charge transfer reaction of the redox couple  $[Fe(CN)_6]^{3-/4-}$  on PABP-modified electrodes was

studied in a solution containing 2.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 0.5M KCl by cyclic voltammetry. Figure 6 shows CVs for the redox reaction on bare GC and PABPmodified electrodes. The redox processes of the couple are significantly inhibited in the presence of the polymer films and the degree of inhibition for the films formed by 30 cycles is higher than that formed by five cycles. The presence of the PABP polymer films decreases the peak currents and shifts the peak potentials to more positive value. The large potential shift,  $\Delta E_p$ , in the presence of the polymer film is attributed to an increased resistance overpotential, i.e., ohmic drop due to the low conductivity of the polymer film.

# IR spectroscopy of ABP and PABP

The IR absorption spectra of a KBr pellet of the PABP film and the monomer, ABP, were recorded and presented in Figure 7. The broadband between 3300 and 3600 cm<sup>-1</sup> is due to N—H stretching of the amine or imino groups of the PABP film, whereas two absorption peaks corresponding to the primary amino groups (free  $-NH_2$ ) stretching vibrations of the ABP, were recorded at ~3444 and ~3300 cm<sup>-1</sup>.<sup>39</sup> This fact suggests that the  $-NH_2$  groups are



**Figure 7** IR absorption spectra of the polymer film, PABP, and the monomer, ABP.

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Figure 8 Mechanism of the electropolymerization of 2-aminobiphenyl.

involved in the electropolymerization process. The peaks observed at ~1685 and 1697 cm<sup>-1</sup> for both the polymer and the monomer, respectively, are attributed to the bending vibration of the N—H bond. The C—N stretching bands, characteristic of aromatic amine, were observed between ~1216 and 1295 cm<sup>-1</sup>. The absorption peaks recorded at about ~1640 and 1392 cm<sup>-1</sup> for PAPB and ~1477 and 1431 cm<sup>-1</sup> for ABP are due to the C=C stretching vibrations.<sup>40</sup> The observed band in the region of ~1087 cm<sup>-1</sup> comes from the vibrational band of  $ClO_4^-$ . The absorption peaks corresponding to the stretching vibrations of the C=N bonds were recorded at ~1639 cm<sup>-1</sup>.

## MECHANISM OF THE ELECTROPOLYMERIZATION OF 2-AMINOBIPHENYL

It has been reported that, the electropolymerization mechanism of aniline proceeds via head to tail couplings of oxidized monomers with its radical cations.<sup>41</sup> A similar mechanism can be proposed for the electropolymerization of ABP since this monomer can be considered as an aniline derivative, bearing a phenyl substituent in the ortho position (o-phenylaniline). As shown in Figure 8, the oxidation of the monomer (I) produces the radical cation (II), which gives the structure (III) by mesomeric effect. The ABP radical cation can adopt a coplanar conformation, as reported for 4-aminobiphenyl radical cation that facilitates a strong electronic interaction between the two phenyl rings to stabilize the radical.<sup>42</sup> The radical cations (II) and (III) are quite reactive and undergo head-to-tail coupling to give the dimer (IV). The resulting dimmer (V) is subsequently oxidized and reacts with other monomer radical cations to produce a polymer with a structure similar to poly(aniline). An alternative dimerization pathway (not shown) would involve formation of a dimer cation radical by association of an amine cation radical with a parent molecule.43 The mechanism proposed in Figure 8 is consistent with the  $E(CE)_n$  reaction revealed from the results of the cyclic voltammetry and confirmed by the IR spectra. In general, cation radicals produced from aromatic amine derivatives couple rapidly to give dimers. These dimers are produced by C--C, C-N, and/or N-N coupling. The relative yields of these coupling depend on the experimental conditions, especially the type of the solvent. For example, in ACN C-C and C-N couplings were obtained<sup>44</sup> and in acidic solutions N-N coupling was inhibited.<sup>13</sup> Under the experimental conditions used in this study and from IR data, it is clear that the most probable coupling mechanism is the C-N coupling, and hence the dimer IV will represent the major component. The polymer film obtained is most likely, a linear chain structure similar to polyaniline.<sup>43,45</sup>

# KINETICS OF POLYMER FILM FORMATION

Assuming that the reaction takes place following the scheme:

Electrolyte (E) + Monomer (M)  $\rightarrow$  Doped polymer (P)

The kinetic equation will be:

$$R_p = \frac{d[W]}{dt} = k[E]^n [M]^m \tag{1}$$

where the polymerization rate  $R_p$  (mg cm<sup>-2</sup> s<sup>-1</sup>) is the generated polymer weight (*W*) per unit of polymerization time (*t*) and per square centimeter of electrode surface; *n* and *m* the reaction orders related



**Figure 9** (a) Polymerization charge versus time as a function of ABP monomer concentration at 0.97 V. (b) Logarithmic plot of polymerization rate versus ABP monomer concentration.

to the electrolyte and monomer, respectively; and *k* the rate constant.

We first calculated the reaction order with respect to the electrolyte concentration at a constant monomer concentration, so eq. (1) can be rewritten as

$$R_p = k'[E]^n \tag{2}$$

or logarithmically as

$$\log R_p = \log k' + n \log[E] \tag{3}$$

Similarly, by keeping the electrolyte concentration constant and varying the monomer concentrations, the kinetic equation could be expressed by the following exponential and logarithmic equations:

$$R_n = k'' [M]^m \tag{4}$$

$$\log R_p = \log k'' + m \log[M] \tag{5}$$

Electropolymerization data provide kinetic parameters on the assumption that only charge transfer takes place at the electrode. From the analysis of the *i*–*t* transients, the charge consumed during the polymerization (Q) can be evaluated by integration of the corresponding chronoamperograms when the electrolyte or the monomer was varied.<sup>25–27,29</sup>

If the generated polymer is the only species produced, the consumed electrical charge and the polymer weight produced will be proportional, that is,

$$W = k'''Q \tag{6}$$

where k''' is the charge productivity (polymer weight generated by a unit of electrical charge), and *W* is the polymer weight (mg) generated.

Taking into account eq. (1), then

$$\frac{dQ}{dt} = k_e \frac{d[W]}{dt} = k_e R_p = k_e [E]^n [M]^m \tag{7}$$

or expressed in a logarithmic form as

$$\log \frac{dQ}{dt} = \log k_e + n \log[E] + m \log[M]$$
(8)

Equation (8) is the equation used in the present work to evaluate the order of reaction with respect



**Figure 10** (a) Polymerization charge versus time as a function of  $HClO_4$  concentration at 0.97 V. (b) Logarithmic plot of polymerization rate versus  $HClO_4$  concentration.

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to the monomer and the electrolyte, m and n, respectively.

PABP was prepared potentiostatically from HClO<sub>4</sub>/ACN mixture at +0.97 V. Figure 9(a) shows the polymerization charge versus time plots associated with PABP electrogeneration from 1.0M HClO<sub>4</sub> concentration as a function of ABP monomer concentration in the range 6.0-10.0 mM and Figure 10(a) presents Q versus t plots associated with the PABP electrogeneration from a constant 10 mM ABP monomer concentration as a function of the electrolyte concentration in the range 0.3–1.5M. The polymerization time changes from 2 to 800 s. The graphs show good linearity between the polymerization charge and the electrogeneration time. The slopes of the lines resulting from the logarithmic plots, i.e.,  $\log dQ/dt$  versus log [ABP] and log dQ/dt versus log [HClO<sub>4</sub>], yield reaction order values with respect to the monomer and the electrolyte, respectively. The logarithmic plot in each case was constructed and presented in Figures 9(b) and 10(b). The values of the reaction order corresponding to ABP monomer, m, and HClO<sub>4</sub>, n, were calculated. The reaction order with respect to ABP was found to be 0.999, which means that the polymerization reaction is first order with respect to the monomer concentration. The calculated value for  $HClO_4$  was -0.27 which implies that perchloric acid has high solubility and inhibits the polymerization reaction.<sup>29,46–48</sup> The kinetic equation of the polymerization process is therefore

$$R_p = k[ABP]^{0.999} [HClO4]^{-0.27}$$

## CONCLUSIONS

- PABP film was prepared successfully by electrochemical oxidation of the monomer, ABP, in 1.0M HClO<sub>4</sub>/ACN mixed solvent of a 3 : 2 volume ratio. The use of this mixed solvent was essential for the electropolymerization process. Moreover, the ratio of the aqueous acidic solution to the organic solvent was quite important in improving the quality of the polymer film.
- The prepared modified electrodes are very stable in aqueous acidic solutions and have an electroactive response in the potential range between 0.0 and +1.0 V and also show electro-chromic properties.
- The polymerization process is obeying an  $E(CE)_n$  mechanism by C—N coupling to produce a polymer with a structure similar to poly(aniline).
- Chronoamperometry was used to determine the order of the electropolymerization reaction and the corresponding kinetic equations.

• The electropolymerization process follows firstorder kinetics with respect to ABP and follows negative order (-0.27) with respect to HClO<sub>4</sub>.

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