Polyvinylferrocene (PVF) has long been used as a fundamental conductive polymer system for modeling the nature of the polymer-modified electrode/electrolyte interface. This choice is based upon the advantages of simple electrochemistry (a reversible one-electron process), high stability (allowing multiple measurements to be made over extended time scale), and the ease of deposition of thin films using a variety of methods. The application of PVF for biomedical purposes has occurred only in recent years. PVF-based amperometric sensors were developed for glucose and chlorine analysis by embedding glucose oxidase and chlorode oxidase in PVF.2-4 A PVF-modified electrode was also reported to mediate charge transfer of cytochrome c and ascorbate.5,6

The successful application of polymers in medicine depends on their physicochemical and special characteristics, for example, biological compatibility with tissues, stability, durability, and safety. The simplicity of PVF makes it an ideal model system to understand polymer interactions with biomolecules [e.g., amino acids, peptides, and diribonucleic acid (DNA)]. The redox activity of PVF is especially valuable as the ferrocene centers serve as built-in electrochemical probes at the polymer backbone. A natural starting point is to study the PVF interaction with amino acids. Amino acids are the building blocks of proteins. Many new possible roles have been recently proposed for amino acids in neurochemistry and neuropharmacology in addition to the classical ones, excitatory [glutamic acid (Glu) and aspartic acid (Asp)] or inhibitory [gamma-aminobutyric acid (GABA) and glycine (Gly)] neurotransmitters, metabolic intermediates (Glu, Asp, and Gln), or precursors [tryptophan (Trp), tyrosine (Tyr), and phenylalanine (Phe)]. Amino acid transmission modifications are thought to be present in many pathological conditions or neurological disorders such as ischemia, schizophrenia, and Alzheimer-type dementia. Moreover, amino acids are organic zwitterions and studying their interactions with PVF is of fundamental interest. No such studies have been reported in the literature. In this report, the transports of ions within the PVF film in an amino acid, in particular, glutamine (Gln) bathing solution, were investigated in detail during the PVF redox processes.

The transports of solvents and ions within the PVF films have great impact on the kinetics and thermodynamics of the redox behavior and on the film surface structure. Extensive studies of the transports of solvent and ions within the PVF films have been carried out in salt solutions such as NaClO₄, NaPF₆, sodium tosylate, etc. by Hillman and Bruckenstein. They visualized the redox switching process of PVF films in salt solutions as a sequence of several elementary steps: coupled electron/ion transfer, solvent transfer, and polymer reconfiguration. Each individual step could occur before or after coupled electron/ion transfer and on the same or different time scales.

In this paper, we investigated the polyvinylferrocene (PVF) redox behavior in contact with a bathing solution containing L-glutamine (Gln) by electrochemical quartz crystal microbalance (EQCM). Our study shows that the interaction of PVF with Gln is dramatically different from PVF redox behavior in salt solutions, e.g., NaClO₄. Rather than the doping of anion in anodic process and undoping of anion in cathodic process, Gln doping and undoping are observed in either anodic or cathodic process depending on the redox potential. This effect is rationalized by the strong preadsorption of Gln in the reduced PVF film and the local pH change that subsequently changes the Gln zwitterions charge states during the oxidation and reduction of PVF. OH⁻ ions also act as counterions and play critical roles in the redox switching of PVF processes in Gln bathing solution.

In this paper, we studied the PVF redox behavior in contact with a bathing solution containing Gln, a weak, uncharged amino acid by electrochemical quartz crystal microbalance (EQCM). Gln was selected for its electrochemical inertness in the PVF redox window (i.e., 0-0.8 V), its relatively better solubility and conductivity when compared with other amino acids, and its biological significance. Gln is the most abundant amino acid in the body, and plasma Gln levels are the highest of any amino acid. Recently, Gln has come to be regarded as one of the most important amino acids when the body is subjected to such metabolic stress situations such as trauma (including surgical trauma), cancer, sepsis, and burns. Under such conditions, Gln is critically needed and it is therefore very important to ensure adequate intake of the amino acid in order to meet the increased physiological demands created by these situations. Moreover, Gln is the structural analog of glutamic acid with its side chain carboxylic acid group amidated. Unique DNA codons exist for Gln separate from those for glutamic acid. The side chain of Gln cannot be protonated and is uncharged at physiological pH. We report here the study of the dynamic transport of Gln and its ions in the PVF film during the PVF redox cycling and compared with the characteristics of the ion and solvent transports in the same PVF film before and after the Gln in contact with 0.1 M NaClO₄. The ultimate goal is to understand physicochemical and special characteristics when conductive polymers interact with biomaterials. Our study shows that the interaction of PVF with Gln is dramatically different from PVF redox behavior in salt solutions. It depends not only on the nature of the amino acid but also on the oxidation state of PVF. This effect is probably caused by strong adsorption of Gln into the reduced PVF film and the local pH changes during the oxidation and reduction of PVF. To our knowledge, this is the first report of the electron/ion migration process of PVF in amino acid solutions and it can apply to account for the wide range of interactions with biological molecules that are obtained from electrodes coated with electroactive polymers.

Experimental

PVF was supplied by Polysciences, Inc., in polymerized form (molecular weight ca. 25,000). Methylene chloride (Fisher Scientific), tetrabutylammonium perchlorate (TBAP) (GIS), Gln (Acros), blocked (Bic)-Gln (ν-terbutylglutamine) (Fluka), and NaClO₄ (Aldrich) are all analytical reagents and used as received. Aqueous solutions were prepared from 18.3 MM deionized water. The PVF film was electrochemically deposited on a gold electrode evaporated on a quartz crystal from 2 mM PVF/CH₂Cl₂ solution containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) as described in our previous publications. Briefly, the electrode potential was stepped from 0 to 0.7 V vs SCE and then held at 0.7 V for 3 min. The

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potential step and hold process were repeated to achieve a uniform film. Freshly prepared film was left to dry in air for at least 45 min and then washed with deionized water and dried with pure N₂. 0.05 M Gln aqueous solution or 0.1 M NaClO₄ was used as electrolyte solution for EQCM experiments. The PVF film was always conditioned at 0 V for at least 15 min, then scanned between 0 and 0.8 V and stopped at 0 V. Before each experiment, the electrolyte solutions were purged by pure N₂ gas for 15 min.

The quartz crystals (International Crystal Manufacturing Co., Inc., Oklahoma City, OK) were AT-cut, 10 MHz, 5 μm finish plates with gold electrode (900 Å) evaporated on both sides. The piezoelectric and electrochemical active areas were 0.22 and 0.25 cm², respectively. The QCM, mounted to an electrochemical cell with PVF-deposited side faces in, was used as the working electrode. A platinum plate and a saturated calomel reference electrode (SCE) were used as counter electrode and reference electrode, respectively. EQCM experiments were done with a RQCM (Maxtek, Inc.) and a model AFRDE 5 bi-potentiostat (Pine Instruments Company) controlled with a PC.

Results and Discussion

Comparison of PVF film redox behavior in Gln and NaClO₄ solutions.—The redox behavior of PVF in 0.1 M NaClO₄ has been well studied and characterized.⁸,¹² We use PVF in 0.1 M NaClO₄ as a control system to characterize the freshly made PVF films before and after their study in the Gln solution. This experimental protocol reveals any changes in PVF film caused by the interaction with Gln.

Figure 1 shows the cyclic voltammograms (CVs), Δf vs E curves; (III) Q vs E curves; and (IV) Δf vs Q curves. The dashed arrows indicate the directions of the potential scan for all figures hereafter.

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Figure 1. PVF film redox behavior in 0.1 M NaClO₄ (a-solid), 0.05 M Gln (b-dashed), and 0.1 M NaClO₄ again (c-dotted) solutions at a scan rate of 5 mV/s: (I) CV curves; (II) Δf vs E curves; (III) Q vs E curves; and (IV) Δf vs Q curves. The dashed arrows indicate the directions of the potential scan for all figures hereafter.
gold or on PVF-covered gold over this potential range. It was also observed that the peak-to-peak separation increased from 0.12 V in NaClO₄ solution to 0.21 V in Gln solution, indicating a decrease of the electrochemical reversibility. Because the redox reaction of PVF film is electron/ion diffusion control, the low concentration of counterions in the Gln solution and the small value of Gln zwitterion mobility could lead to slow kinetics of the redox reactions.

Shown in Fig. 1 (II), the $\Delta f$ vs $E$ curve in Gln solution is quite different from that in NaClO₄ solution. In 0.1 M NaClO₄, during the oxidation and reduction processes, the mass increases and decreases between potential 0–0.4 V and remain constant from 0.4 to 0.8 V, corresponding to the counterion (ClO₄⁻) migration and H₂O diffusion in and out of the PVF film. In 0.05 M Gln solution, the frequency decreases (mass increases) from 0 to 0.52 V, indicating that counterions and H₂O moved into the PVF film, which resembles the processes found in NaClO₄ solution. However, after the $\Delta f$ value reached a maximum at ~0.52 V, the frequency starts increasing as the potential is swept from 0.52 to 0.80 V, suggesting ejection of species from the PVF film to the bulk solution. This is quite different from that found in NaClO₄ solution where the $\Delta f$ is no longer changed and remains almost constant between 0.4 and 0.8 V. During the cathodic scan, from 0.8 to 0.26 V, there was an increase in

Figure 2. The first three cycles of the $\Delta f$ vs $E$ curves of PVF in NaClO₄ after being redox scanned in Gln, 5 mV/s: (1st cycle) solid line, (2nd cycle) dashed line, and (3rd cycle) dotted line.

Figure 3. CV (I), $\Delta f$ vs $E$ (II), $Q$ vs $E$ (III), and $\Delta f$ vs $Q$ (IV) curves of PVF in 0.1 M NaClO₄ solution before the experiments in Blc-Gln (a-solid), 0.05 M Blc-Gln solution (b-dashed), and in 0.1 M NaClO₄ solution after the experiments in Blc-Gln (c-dotted). Scan rate 5 mV/s, shown here is the third cycle.
The PVF film properties were further investigated by studying the same film again in 0.1 M NaClO₄ after the Gln experiment. Shown in Fig. 1 (I), the oxidation and reduction peak potentials of the PVF film in 0.1 M NaClO₄ after it was cycled in Gln have a slightly positive shift, but the current peak heights were considerably smaller than before. The current peak heights are at similar amplitude to those in the Gln solution. These changes are much more apparent in Fig. 1 (III), the charge vs potential curves. In 0.1 M NaClO₄ solution, Fig. 1 (III) a, the charge begins to increase at 0.3 V and reaches a maximum value at 0.6 V. In Gln solution, the charge begins to increase at 0.4 V and continuously increase until 0.8 V. Fig. 1 (III) b. The total redox charge for PVF in 0.1 M NaClO₄ after Gln is almost the same as that in Gln, but much smaller than that in 0.1 M NaClO₄ before exposure to Gln. This implies that some electroactivity of the PVF film is lost after it was exposed to the Gln solution. Either the PVF film morphology changed significantly or those sites were occupied by other species and could not be reached by ClO₄⁻ anions. Even though the bathing solution is only 0.1 M NaClO₄, after PVF was exposed to Gln [Fig. 1 (II) curve c], the Δf vs E curve shows a behavior resembling the combination of PVF in 0.1 M NaClO₄ and 0.05 M Gln. During the anodic scan, the frequency decreases, indicating the doping of ClO₄⁻. At 0.35 V the frequency starts to increase, showing ejection of species from PVF film similar to the behavior in the Gln solution, but the potential for this process, 0.35 V, was less positive than that in Gln solution. This is probably due to the higher conductivity of the NaClO₄ solution and the faster redox process in such a solution. As the only possible source of species is the trapped Gln because the PVF film was scanned in the Gln solution first, we rationalize that the Gln trapped in the PVF film was ejected out. During the cathodic scan, the frequency increases indicate the ejection of Gln. There is a slight decrease in frequency between 0.16 and 0 V; because there was no bulk Gln in the solution, only a trace amount of Gln could readsorb into the PVF film.

As shown in Fig. 2, the Δf vs E curve of the first anodic scan is considerably different from that obtained in 0.1 M NaClO₄ before exposure to the Gln solution. There is −250 Hz frequency increase between 0.33 and 0.8 V, indicating the ejection of neutral and/or positive charged species. The amount of frequency changes at the anodic and cathodic scan becomes smaller in the second and subsequent scans, and the Δf vs E curve resembles that in pure Gln solution. These are strong evidences of trapping of Gln in the PVF film during its redox cycling in the Gln solution. During the first anodic scan, the majority of trapped Gln was ejected out; the subsequent scan involves the competitive doping/undoping of ClO₄⁻ and Gln⁺ anions. Note that the same PVF film showed greater current, Δf, and Q in NaClO₄ solution than in the Gln solution. This also supports high electroactivity or electrochemical reversibility of PVF in NaClO₄ solution.

**PVF redox behavior in 0.05 M Blc-Gln solution.**— We further investigated the mechanism of the interaction of Gln with PVF by using a structural analog of Blc-Gln, Scheme 1, in which one of the amine protons is replaced with a bulk tert-butyl group. Blc-Gln is bigger in size and is more hydrophobic than Gln.

Figure 3 shows the CV, Δf vs E, Q vs E, and Δf vs Q curves of PVF in 0.05 M Blc-Gln solution (b) and in 0.1 M NaClO₄ solution before (a) and after (c) the experiments in Blc-Gln solution. In the anodic scan, the amount of Blc-Gln doped between 0 and 0.54 V is

![Figure 4](image_url)  
**Figure 4.** The first three cycles of CV (a) and Δf vs E (b) curves in 0.05 M Blc-Gln, scan rate 5 mV/s.

![Scheme 1](image_url)  
**Scheme 1.**

![Scheme 2](image_url)  
**Scheme 2.**
much smaller and the amount of Blc-Gln ejected between 0.54 and 0.8 V is much larger than those in Gln solution. This can be rationalized by two characteristics of the Blc-Gln. First, the Blc-Gln is more hydrophobic; consequently, the amount of preadsorbed Blc-Gln to the PVF film to dope the positively charged ferricenium sites at 0–0.54 V is much bigger than that of Gln at 0 V. Second, the size of Blc-Gln is bigger than that of Gln. These two factors could result in fewer Blc-Gln− anions to move into the film in the potential range 0–0.54 V and more Blc-Gln to be pushed out of the film in the potential range 0.54–0.8 V. Accordingly, the amount of mass changes in the Δf vs Q curve between 0 and 0.54 V is much smaller, but it is much bigger (almost 10 times higher) between 0.54 and 0.8 V in Blc-Gln system. For example, the slopes of the Δf-Q curves between 0.54 and 0.8 V are −49 ± 0.4 g/mol in Gln and −502 ± 5 g/mol in Blc-Gln. The larger slope indicates that the processes between 0.54 and 0.8 V in Blc-Gln solution are predominant non-faradac processes. Because the amount of Blc-Gln doped to balance the FeIII center is small, it has little interaction and causes little disturbance to the PVF film. Shown in Fig. 3, the PVF film studied in 0.1 M NaClO4 solution after it was scanned in the Blc-Gln solution shows a redox behavior closely resembling the PVF film in 0.1 M NaClO4 before it was exposed to Blc-Gln.

Figure 4 shows the first three cycles of the CV and Δf vs E curves of PVF in 0.05 M Blc-Gln solution. The first scan has a larger anodic peak current than those subsequent ones, indicating a great increase in faradac doping in the first anodic scan. This is echoed in the Δf vs E curves, which show corresponding larger frequency decrease between 0 and 0.54 V in the first anodic scan. At 0.54 V, a larger frequency increase was observed indicating the ejection of species from the PVF film. However, little doping and undoping was seen at the subsequent scans between 0 and 0.54 V (anodic scan) and 0.8 and 0.54 V (cathodic scan), respectively. Similar to the processes observed in Gln solution, Blc-Gln anions moved into the PVF film to dope the positively charged ferricenium sites at 0–0.54 V and the ejection of cations and/or neutral species occurred at 0.54–0.8 V. These processes occurred at a much greater scale in the first scan than in subsequent scans, indicating the preadsorption and trapping of Blc-Gln in the reduced PVF film.

The proposed mechanism.— Summarizing the experimental data shown in Fig. 1–4, especially the Δf vs E curves, we can conclude that there are at least four processes occurring during a redox cycle of PVF in the Blc-Gln bathing solution (shown in Scheme 2): (i) during anodic scan, (a) process I (step AB and BC): decrease of frequency from 0 to 0.52 V; (b) process II (step CD and DE): increase of frequency from 0.52 to 0.8 V; (ii) during the cathodic scan, (c) process III (step EF and FG): increase of frequency from 0.8 to 0.26 V; and (d) process IV (step GH): decrease of frequency from 0.26 to 0.0 V. The mechanisms of the above processes can be rationalized by using Anson’s two-phase model. This model has been successfully applied to the interior of a swollen polycationic coating equilibrated with a supporting electrolyte solution containing both electroactive and electroinactive counterions.20 Anson et al. conceptually divided the coating into two regions. The first, termed the Donnan domains, represents the region where the counterions are confined by electrostatic forces to remain in the vicinity of the fixed-charge centers in the polyelectrolyte. The second, termed the non-Donnans domains, comprises the remaining volume of the coating that is assumed to be occupied by the supporting electrolyte solution. Each of the two phases has its own modes for charge transport, and the coupling between the transport processes in each phase may occur either parallel or in sequence.

Oxidized PVF could be considered as polycations. The reduced PVF film could be considered as an extreme state in which the charge is zero. Thus, the Donnan domain refers to the positively charged ferricenium and the polymer frame. The properties of the non-Donnan domain strongly depend on the redox state of the PVF. The frequency change reflects the total net mass change that occurred in both domains of the PVF film. At 0 V, the PVF is in a reduced state and is neutral; it is bathed with water (H2O, H+ and...
OH\(^{-}\)) and Gln (zwitterions, cations, and anions). At the initial oxidation of the ferrocene (Fc) to ferricenium (Fc\(^{+}\)), the anions pre-existed in the non-Donnan domain of PVF film bound to the PVF frame by electrostatic force and confined in the Donnan domain (Eq. I.2 and I.3, respectively, see Table I). The anions that participated in the doping of PVF, positively charged ferricenium, include both Gln\(^{-}\) and OH\(^{-}\) anions. Even though OH\(^{-}\) doping could be neglected in high salt concentrations, our early study showed OH\(^{-}\) in dilute salt solution (i.e., 0.01 M NaClO\(_4\)) transports to the PVF film at a significant level.\(^{21}\) In 0.05 M Gln solution, the concentration of Gln\(^{-}\) is about 1 \(\times\) 10\(^{-5}\)M calculated by using pK\(_a\) values (2.17, pK\(_{a1}\) and 9.13, pK\(_{a2}\)) of Gln. Therefore, the doping of OH\(^{-}\) will compete with that of Gln\(^{-}\). Further oxidation of the PVF requires that additional anions diffuse from the bulk and/or non-Donnan domain to bind with positively charged ferricenium in the Donnan domain shown in step BC (Eq. I.4 and I.5, respectively). The total mass change (\(\Delta m\)) of the film in step BC can be attributed to three factors

\[
\Delta m = \Delta m_{\text{Gln}} + \Delta m_{\text{OH}} + \Delta m_{\text{H2O}}
\]

where \(\Delta m_{\text{Gln}}\), \(\Delta m_{\text{OH}}\), and \(\Delta m_{\text{H2O}}\) are the net mass changes come from the diffusion/migration of Gln\(^{-}\), OH\(^{-}\), and H\(_2\)O in or out of the PVF film from the bulk, respectively. The overall process can be expressed as

\[
\text{Fc} \rightarrow \text{Fc}^{+} + n\text{Gln}^{-} + (1 - \alpha)\text{OH}^{-} + n\text{H2O}
\]

Thus, the equivalent molar mass \(M_{\text{equiv}}\) is

\[
M_{\text{equiv}} = 144\alpha + (1 - \alpha)17 + 18n
\]

Because \(\alpha\) (percentage of Gln\(^{-}\) doped) depends on the scan rate and Gln concentration, the \(n\) (number of water molecules transferred) depends only on the scan rate. Literature reports that \(n\) also varies with different systems and film conditions.\(^{22,23}\) The \(\alpha\) value could not be obtained using current experimental data. However, considering the molecular weight of Gln\(^{-}\) and OH\(^{-}\) are 144 and 17, respectively, and the measured equivalent mass \(M_{\text{equiv}}\) is 61 g/mol, this may indicate OH\(^{-}\) doping is predominant (i.e., \(\alpha\) is less than 50%) if we assume that the net water molecules transferred in the Gln solution was negligible due to preadsorbed Gln and solvent at 0 V.

The doping of the OH\(^{-}\) and Gln\(^{-}\) to the Donnan domain of the PVF film (step AB and BC) leads to the diffusion of OH\(^{-}\) and Gln\(^{-}\) from bulk to the non-Donnan domain of film (Eq. I.4 and I.5, respectively). It also drives the ionization equilibrium of Gln (Scheme 3) and H\(_2\)O in the film to produce additional anions (Eq. II.3), i.e., OH\(^{-}\). This process generates Gln\(^{+}\) ion as well. The positive charged Gln\(^{+}\) is ejected from the PVF film by electrostatic force (Eq. II.4). The oxidation of Fc occurs in parallel with the diffusion (Eq. I.4 and I.5) and hydrolysis process (Eq. II.3). Shown in the \(\Delta f\) vs E curve, process I, between 0 and 0.52 V, the diffusion process was dominant so that a mass increase was observed. As the potential swept more positively, the hydrolysis process becomes dominant. At a critical point, 0.52 V in this case, the electrostatic repulsion drove the Gln\(^{+}\) out of the PVF film and led to a mass decrease (step CD and DE). The total mass decrease is the summation of two parts

\[
-\Delta m = -(\Delta m_{\text{Gln}} + \Delta m_{\text{H2O}})
\]

The measured \(M_{\text{equiv}}\) is \(-49\) g/mol; therefore, the majority of the charge may be balanced by the OH\(^{-}\) rather than Gln\(^{-}\) from the bulk solution.

In the reverse scan, the bound OH\(^{-}\) and the Gln\(^{-}\) in the Donnan domain of PVF were ejected out because the Fc\(^{+}\) is reduced to Fc. This process leads to a further frequency increase (mass decrease, i.e., process III, step EF and FG). When most of the Fc\(^{+}\) was reduced, the electrostatic force vanished and the Gln in solution will diffuse into the non-Donnan domain of the film again. This process was the process IV (step GH), decrease of frequency [59.3 Hz in Fig. 1(b)] from 0.26 to 0 V. Process IV also led to the preadsorption of Gln in the PVF film. The slope (mass/time) in process II is larger (mass change faster) than the slope in process IV, indicating that the diffusion of Gln is a slower process than that of electrostatic repulsion of Gln\(^{+}\) in process II. This also led to a smaller total mass change in process IV than that of process II. The above proposed mechanisms can be used to explain the ion and solvent transports that occurred in the Blc-Gln solution. Due to the structure difference of Blc-Gln from Gln, the amount of preadsorbed Blc-Gln at 0 V is different from that of Gln. This leads to a quantitatively different ion and solvent transports at each step between Blc-Gln and Gln systems.

The redox processes of PVF film in the Gln bathing solution involves coupled electron and multi-ion transfer, solvent transfer,
Further evidence supports the proposed mechanism.—According to the proposed mechanism, processes I (step AB and BC) and III (EF and FG), the doping and undoping of counterions in the Donnan-domain of PVF film due to the Faraday process will have a smaller total mass change and a slower mass changing rate if the scan rate increased, because the rate-limiting processes of both I and III are the diffusion of Gln anions and OH\(^-\) into/out of the Fe\(^{3+}\) centers. At faster scan rates, the OH\(^-\) will share a greater portion of the doping of anions. However, the mass change of process II (step CD and DE) and IV (step GH), the ejection and readsorption of Gln in the non-Donnan domain of the PVF film, will depend on the amount of Gln previously present and the mass changing rate should have little dependence on the scan rate. Figure 5 shows the CVs and $\Delta f$ vs $E$ curves of PVF in 0.05 M Gln as a function of scan rate. The peak current of the CVs increases proportionally to the square root of the scan rate, which indicates a diffusion-controlled redox process. Consistent with above prediction, the rate of frequency change ($f$ vs $E$) is larger at slower scan rates. However, the slopes in processes CD and GH change very little with scan rate, as shown in Fig. 5.

Conclusion

Our data shows that the two-phase model which conceptually divides polycation systems to a Donnan domain and a non-Donnan domain, described by Anson et al., also applies to PVF films in contact with Gln solutions, although PVF is not a typical polycation substance. Either in oxidation or reduction processes Gln ingresses in and egresses out of the PVF film, depending on the redox potential, similar to a breathing effect. This effect is rationalized by the strong preadsorption of Gln in the reduced PVF film and a local pH change that subsequently changes the Gln zwitterions charge states during the oxidation and reduction of PVF. The preadsorbed Gln or BIC-Gln at 0 V significantly affects the level of doping/undoping of OH\(^-\), Gln\(^-\), and Gln\(^+\). OH\(^-\) ions are found to compete with Gln\(^-\) as counterions during the redox switching of PVF in Gln solutions. The contribution of OH\(^-\) ions becomes greater than Gln\(^-\) anions as scan rate increases. The experimental data adhered well to the predications derived on the basis of the two-phase model, which may prove generally applicable to a wide range of interactions of biological molecules with electrodes coated with electroactive polymers.

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