Redox potentials of ubiquinone, menaquinone, phylloquinone, and plastoquinone in aqueous solution

Shinnosuke Kishi · Keisuke Saito · Yuki Kato · Hiroshi Ishikita

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Abstract Quinones serve as redox active cofactors in bacterial photosynthetic reaction centers: photosystem I, photosystem II, cytochrome bc1, and cytochrome b6f. In particular, ubiquinone is ubiquitous in animals and most bacteria and plays a key role in several cellular processes, e.g., mitochondrial electron transport. Their experimentally measured redox potential values for one-electron reduction $E_m(Q/Q^-)$ were already reported in dimethylformamide (DMF) versus saturated calomel electrode (SCE) by Prince et al. We calculated $E_m(Q/Q^-)$ of 1,4-quinones using a quantum chemical approach. The calculated energy differences of reduction of Q to $Q^-$ in DMF and water for 1,4-quinone derivatives correlated highly with the experimentally measured $E_m(Q/Q^-)$ in DMF and water, respectively. $E_m(Q/Q^-)$ were calculated to be $-163 \text{ mV}$ for ubiquinone, $-260 \text{ mV}$ for menaquinone and phylloquinone, and $-154 \text{ mV}$ for plastoquinone in water versus NHE.

Keywords Photosystem II · Bacterial photosynthetic reaction centers · Rhodobacter sphaeroides · Blastochloris viridis · Cytochrome $b_6f$ · Cytochrome $bc_1$

Introduction

Quinones can accept two electrons and two protons via the initial protonation of semiquinone ($Q^- \rightarrow QH^-$) and the second protonation of hydroquinone ($QH^- \rightarrow QH_2$). Ubiquinone serves as an electron acceptor at the $Q_A$ and $Q_B$ binding sites in reaction centers of purple bacteria (PbRC) from *Rhodobacter sphaeroides* and serves as an electron donor in cytochrome $bc_1$. Similarly, menaquinone (vitamin K2) is the acceptor at the $Q_A$ site in PbRC from *Blastochloris viridis*, whereas phylloquinone (vitamin K1) is the active center at the $A_{1A}$ and $A_{1B}$ sites in photosystem I (PSI). In reaction centers of green non-sulfur bacteria from *Chloroflexus aurantiacus*, menaquinones are also located at both $Q_A$ and $Q_B$ sites (Hale et al. 1983). It should be noted that phylloquinone and menaquinone have the same head-group structure (Fig. 2). Plastoquinone serves as an electron acceptor at the $Q_A$ and $Q_B$ sites in photosystem II (PSII) (Fig. 1) (Robinson and Crofts 1984; Rutherford et al. 1984; Okamura et al. 2000; Brettel and Leibl 2001; Wraight 2004) and serves as an electron donor in cytochrome $b_6f$. In PbRC and PSI, both $Q_A$ and $Q_B$ are located near the non-heme Fe$^{2+}$, and the Fe$^{2+}$ ligands (i.e., His-L190 and His-M217 (or M219) in PbRC and D1-His215 and D2-His214 in PSII) donate an H-bond to the carbonyl O atoms of quinones that are proximal to the Fe complex ($O_{prox}$) (Fig. 1a–c). The carbonyl O atoms of quinones at the distal position ($O_{dist}$) also form H-bonds with the proteins. On the other hand, the non-heme Fe$^{2+}$ is absent in PSI, but the Fe$_2$S$_4$ cluster $F_X$ is located near the two $A_1$ binding sites (Fig. 1d).

Redox potential values for one-electron reduction, $E_m(Q/Q^-)$, for 1,4-quinones, including ubiquinone, menaquinone (phylloquinone), and plastoquinone, were experimentally measured in dimethylformamide (DMF) versus saturated calomel electrode (SCE) by Prince et al.
(Prince et al. 1983). \( E_m(Q/Q^-) \) for 1,4-quinones were also experimentally measured in water versus normal hydrogen electrode (NHE) by Swallow (1982). Since \( E_m \) values for redox active sites in proteins are often reported as the values measured in water versus NHE, \( E_m(Q/Q^-) \) for ubiquinone, menaquinone (phyloquinone), and plastoquinone measured in water versus NHE are preferentially required when analyzing interaction between the quinone binding site and the protein environment in PbRC, PSI, PSII, cytochrome \( bc_1 \), and cytochrome \( b_6f \). However, as far as we are aware, experimentally measured \( E_m(Q/Q^-) \) for ubiquinone, menaquinone (phyloquinone), and plastoquinone in water versus NHE have not been reported (Fig. 2). Here, we report \( E_m(Q/Q^-) \) for ubiquinone, menaquinone (phyloquinone), and plastoquinone in water versus NHE, obtained using a quantum chemical approach.
Computational procedures

In reduction of the oxidized state (A) to reduced state (A\textsuperscript{−}) in aqueous solution, the redox potential \(E_m\) relative to the normal hydrogen electrode (NHE) is defined as

\[
E_m = -\frac{\Delta G_{aq}}{nF},
\]  

(1)

where \(\Delta G_{aq}\) is the free energy difference between A and A\textsuperscript{−} [i.e., \(\Delta G_{aq} = G_{aq}(A) - G_{aq}(A^\text{−})\)], \(n\) is the number of electron involved in the reaction (i.e., \(n = 1\) in the present case), and \(F\) is the Faraday constant. \(\Delta G_{aq}\) can also be approximated as

\[
\Delta G_{aq} = k\Delta E_{QM/PCM} + C,
\]  

(2)

where \(k\) is the scaling factor, \(\Delta E_{QM/PCM}\) is the energy difference between A and A\textsuperscript{−} in aqueous phase [i.e., \(\Delta E_{QM/PCM} = E_{QM/PCM}(A) - E_{QM/PCM}(A^\text{−})\)], which can be calculated using a quantum chemical approach with the polarizable continuum model (PCM) method, and \(C\) is a constant (Matsui et al. 2012; Hasegawa et al. 2017). The Eq. 1 can be written as Eq. 3 using Eq. 2.

\[
E_m = k'\Delta E_{QM/PCM} + C',
\]  

(3)

where \(k'\) is the scaling factor and \(C'\) is a constant (Matsui et al. 2012; Hasegawa et al. 2017). To determine \(k'\) and \(C'\), we calculated \(\Delta E_{QM/PCM(DMF)}\) (and \(\Delta E_{QM/PCM(water)}\)) for ten (nine) 1,4-quinones whose experimentally measured \(E_m(Q/Q^\text{−})\) are reported for DMF (Prince et al. 1983) [and water (Swallow 1982)].

We employed the unrestricted density functional theory (DFT) method with the B3LYP functional and 6-31g++\(*\) basis sets for Q\textsuperscript{−} (the total spin \(S = 1/2\)) and the restricted DFT method for Q (\(S = 0\)), using the Gaussian (Frisch et al. 2004) program code with the PCM method. Solvent molecules were considered implicitly, using the SCRF = water option and the SCRF = Dimethylformamide option with the values of 78.3553 for water and 37.219 for DMF for dielectric constant (i.e., default values), respectively. However, it should be noted that it is only one of many internal parameters used to define solvents in the PCM method (Frisch et al. 2004). Thus, simply changing the dielectric constant value will not define a new solvent properly.

Since the isoprene units do not comprised conjugated double bonds, the isoprene side-chain length \(n\) (Fig. 2) was set to 1 or 2 for the calculations of ubiquinone, menaquinone (phylloquinone), and plastoquinone similar to previous studies (Hasegawa et al. 2017). This could also reduce the number of possible conformations. In fact, the length of the ubiquinone does not practically affect its energetics, as demonstrated by the similar experimentally measured \(E_m(Q/Q^\text{−})\) values of ubiquinone-1 and -10 in DMF (−611 and −602 mV versus SCE, respectively) (Prince et al. 1983). It should also be noted that \(n = 0\), which corresponds to 2,3-dimethoxy-5-methyl-1,4-benzoquinone \([E_m(Q/Q^\text{−}) = −539 \text{ mV}\) in DMF versus SCE (Prince et al. 1983)], i.e., ubiquinone-0, as presented in Ref. (Cape et al. 2006), is a less relevant representation of \(E_m(Q/Q^\text{−})\) for quinones in PbRC, PSI, PSII, cytochrome \(b\), and cytochrome \(b_6f\). Ubiquinone-0 corresponds to 2,3-dimethoxy-5-methyl-1,4-benzoquinone rather than 2,3-dimethoxy-5,6-dimethyl-1,4-benzoquinone [in contrast to the statement in ref. (Prince et al. 1983)].

Results and discussion

Correlation of calculated energies with experimentally measured \(E_m(Q/Q^\text{−})\) for 1,4-quinones in DMF and water

The calculated \(\Delta E_{QM/PCM(DMF)}\) for reduction of deprotonated Q to \(Q^−\) for ten 1,4-quinones in DMF (\(\Delta E_{QM/PCM(DMF)}\)) and water (\(\Delta E_{QM/PCM(water)}\)) were highly associated with the experimentally measured \(E_m(Q/Q^\text{−})\) in DMF, ranging from −401 to −751 mV versus SCE (Prince et al. 1983), and the experimentally measured \(E_m(Q/Q^\text{−})\) in water, ranging from −240 to 99 mV versus NHE (Swallow 1982), which were best fitted to the following equations (Figs. 3a, b):

\[
E_m(Q/Q^\text{−}) \text{ in DMF versus SCE [mV]} = -32.1 (\Delta E_{QM/PCM(DMF)} + 108.54 \text{ [kcal/mol]})
\]  

(4)

\[
E_m(Q/Q^\text{−}) \text{ in water versus NHE [mV]} = -33.3 (\Delta E_{QM/PCM(water)} + 93.95 \text{ [kcal/mol]})
\]  

(5)

Using Eqs. 4 and 5, the calculated \(E_m(Q/Q^\text{−})\) in DMF versus SCE and \(E_m(Q/Q^\text{−})\) in water versus NHE for ten and nine 1,4-quinones, respectively, are listed in Table 1. Our results confirm that Eqs. 4 and 5 can reproduce the experimentally measured \(E_m(Q/Q^\text{−})\) in DMF versus SCE and \(E_m(Q/Q^\text{−})\) in water versus NHE, respectively. The overall root mean square deviation between the experimentally measured \(E_m(Q/Q^\text{−})\) in DMF versus SCE and the calculated \(E_m(Q/Q^\text{−})\) in DMF versus SCE based on Eq. 4 for the ten 1,4-quinones is ±21 mV. The overall root mean square deviation between the experimentally measured \(E_m(Q/Q^\text{−})\) in water versus NHE and the calculated \(E_m(Q/Q^\text{−})\) in water versus NHE based on Eq. 5 for the nine 1,4-quinones is ±16 mV. These deviations are sufficiently small with respect to those obtained in other theoretical studies [e.g., ±131 mV (Schmidt am Busch and Knapp 2005)].

Notably, to obtain Eq. 4, \(E_m(Q/Q^\text{−})\) for ubiquinone, menaquinone (phylloquinone), and plastoquinone in DMF versus SCE were not included [where \(k = -32.1 \text{ (mV mol/ kcal)}, C = -108.5\text{ (mV)}, \) excluding ubiquinone, menaquinone (phylloquinone), and plastoquinone]. Nevertheless,
the experimentally measured \( E_m(Q/Q^-) \) in DMF versus SCE (Prince et al. 1983) and the calculated \( \Delta E_{QMPCM(DMF)} \) for ubiquinone, menaquinone (phylloquinone), and plastoquinone can also be described by Eq. 4 [where \( k = -31.8 \) (mV mol/kcal), \( C = -108.8 \) (mV), including ubiquinone, menaquinone (phylloquinone), and plastoquinone] (Fig. 3a), which demonstrates that \( E_m(Q/Q^-) \) for ubiquinone, menaquinone (phylloquinone), and plastoquinone can be described accurately by Eqs. 4 and 5.

In contrast to other quantum chemical approaches, e.g., (Schmidt am Busch and Knapp 2005), the present approach neither need to calculate the zero-point vibrational energy and the excess vibrational free energy at 298 K for both \( Q \) and \( Q^- \) nor optimize the atomic radii of \( Q/Q^- \) for the solvation energy. Once \( k' \) and \( C' \) are uniquely determined, \( E_m(Q/Q^-) \) can be accurately calculated based on calculated \( \Delta E_{QMPCM} \), without considering further details of \( Q/Q^- \) and solvent. The strong correlation between experimentally measured \( E_m(Q/Q^-) \) in DMF versus SCE and the experimentally measured \( E_m(Q/Q^-) \) in water versus NHE (coefficient of determination \( R^2 = 0.97 \), Fig. 3c), in turn, suggests that \( k' \) and \( C' \) are similar for these 1,4-quinones.

In the present study, solvent molecules were considered implicitly. This treatment is more appropriate to describe H-bonds between quinones and bulk water/solvent molecules, in which the H-bond patterns are not unique, e.g., bulk solvent. Explicit water/solvent models may be able to describe H-bonds adequately when the H-bond pattern is unique [e.g., water molecules in the well-ordered cluster near the \( \text{Mn}_4\text{CaO}_4 \) cluster (Saito et al. 2011; Sakashita et al. 2017) or all possible (H-bond) conformations of water/solvent molecules can be evaluated, e.g., using molecular dynamics simulations; this is not the case for 1,4-quinones investigated in the present study.

We found that the experimentally measured \( E_m(Q/Q^-) \) for the nine 1,4-quinones in water versus NHE (Swallow 1982)
Equation 6 indicates that experimentally measured $E_m(Q/Q^-)$ in DMF versus SCE can be practically converted to $E_m(Q/Q^-)$ in water versus NHE by adding 480 mV. The $E_m$ difference of 480 mV may also contain a liquid junction potential between SCE in DMF and NHE in water. The liquid junction potential can be ignored when $E_m(Q/Q^-)$ are compared versus ferrocene (Fc/Fc$^+$); e.g., $E_m(Q/Q^-)$ for 1,4-benzoquinone is experimentally measured to be −401 mV in DMF versus SCE, where $E_m(Fc/Fc^+) = 524$ mV (Prince et al. 1983). Since $E_m(Fc/Fc^+) = 400$ mV in water versus NHE (Koepp et al. 1960), $E_m(Q/Q^-)$ for 1,4-benzoquinone is −925 mV in DMF versus Fc/Fc$^+$ and 301 mV in water versus Fc/Fc$^+$, which indicates that $E_m(Q/Q^-)$ for 1,4-benzoquinone in DMF and water originally differ by 624 mV in the absence of the liquid junction potential (Table 2). This holds true for all 1,4-quinones investigated. It seems likely that $E_m(Q/Q^-)$ for 1,4-benzoquinones already differ by 600 mV even in the absence of the liquid junction potential (Table 2). The presence of H-bond donor to $Q^-\cdot$ in water is partly responsible for the $E_m$ difference of 600 mV, since the presence of H-bond donor to $Q^-\cdot$ stabilizes $Q^-$ and increases $E_m(Q/Q^-)$. Nevertheless, the entire

### Table 1

| Compound                      | $E_m$ in DMF (vs. SCE) | $E_m$ in water$^a$ (vs. NHE) |
|-------------------------------|------------------------|-----------------------------|
| 1,4-Benzoquinone              | −401                   | 99                          |
| Methyl-1,4-benzoquinone       | −466                   | 23                          |
| 2,3-Dimethyl-1,4-benzoquinone | −543                   | −74                         |
| 2,5-Dimethyl-1,4-benzoquinone | −551                   | −66                         |
| 2,6-Dimethyl-1,4-benzoquinone | −547                   | −80                         |
| Trimethyl-1,4-benzoquinone    | −632                   | −165                        |
| Tetramethyl-1,4-benzoquinone  | −751                   | −240                        |
| 1,4-Naphthoquinone            | −581                   | n.d.                        |
| 2-Methyl-1,4-naphthoquinone   | −650                   | −203                        |
| 2,3-Dimethyl-1,4-naphthoquinone | −746               | −240                        |
| Ubiquinone-1                  | −611                   | n.d.                        |
| Menaquinone-1 (phylloquinone-1) | n.d.              | −738                        |
| Menaquinone-2                 | −709                   | n.d.                        |
| Plastoquinone-1               | −640                   | n.d.                        |

n.d. Not determined
$^a$ pH 7
$^b$ Ref. (Prince et al. 1983)
$^c$ Ref. (Swallow 1982)
$^d$ Duroquinone

### Table 2

| Compound                      | $E_m$ in DMF (vs. Fc/Fc$^+$) | $E_m$ in water$^a$ (vs. Fc/Fc$^+$) | $\Delta E_m$ (DMF–water) |
|-------------------------------|-----------------------------|-----------------------------------|--------------------------|
| 1,4-Benzoquinone              | −925                        | −301                              | −624                     |
| Methyl-1,4-benzoquinone       | −990                        | −377                              | −613                     |
| 2,3-Dimethyl-1,4-benzoquinone | −1067                       | −474                              | −593                     |
| 2,5-Dimethyl-1,4-benzoquinone | −1075                       | −466                              | −609                     |
| 2,6-Dimethyl-1,4-benzoquinone | −1071                       | −480                              | −591                     |
| Trimethyl-1,4-benzoquinone    | −1156                       | −565                              | −591                     |
| Tetramethyl-1,4-benzoquinone  | −1275                       | −640                              | −635                     |
| 1,4-Naphthoquinone            | −1105                       | n.d.                              | −613                     |
| 2-Methyl-1,4-naphthoquinone   | −1174                       | −603                              | −593                     |
| 2,3-Dimethyl-1,4-naphthoquinone | −1270          | −676                              | −606                     |
| Ubiquinone-1                  | −1135                       | n.d.                              | −593                     |
| Menaquinone-2 (phylloquinone-2) | −1233                      | n.d.                              | −600                     |
| Plastoquinone-1               | −1164                       | n.d.                              | −596                     |

n.d. Not determined
$^a$ pH 7
$^b$ Ref. (Prince et al. 1983)
$^c$ Ref. (Swallow 1982)
$^d$ Duroquinone
difference of 600 mV would not be explained solely by the first sphere water molecules that can directly form an H-bond with Q−. The surrounding water molecules (e.g., second and third sphere molecules) cannot directly form an H-bond with Q− but the Q− stabilization is pronounced by their dipole orientations (Takaoka et al. 2016). The corresponding effect may be ignored in DMF with respect to water.

As far as only $E_m$ differences among the redox active cofactors ($\Delta E_m$) are discussed in the same proteins, e.g., along the electron transfer chains, $E_m$ values of isolated cofactors measured in DMF, which are reported also for chlorophylls (Watanabe and Kobayashi 1991), might possibly be useful. On the other hand, when $E_m$ values in the protein environments are discussed, comparison with $E_m$ values of isolated cofactors measured in water is recommended, since $E_m$ values measured in DMF is originally 600 mV lower than those measured in water even in the absence of the liquid junction potential (Table 2).

$E_m(Q/Q−)$ for ubiquinone, menaquinone, phylloquinone, and plastoquinone in water versus NHE

To the best of our knowledge, experimentally measured $E_m(Q/Q−)$ for ubiquinone, menaquinone (phylloquinone), and plastoquinone in water versus NHE are not reported. By calculating $\Delta E_{QM/PCM(water)}$ and using Eq. 5, $E_m(Q/Q−)$ was calculated to be −163 mV for ubiquinone, −260 mV for menaquinone (phylloquinone), and −154 mV for plastoquinone in water versus NHE (Table 1).

In ubiquinone, one of the 2,3-methoxy groups lies outside the quinone ring. Hence, Zhu and Gunner proposed that $E_m(Q/Q−)$ for ubiquinone, a 2,3-dimethoxy-5-methyl-6-isoprenyl benzoquinone, is more similar to the $E_m(Q/Q−)$ for trimethyl-benzoquinone than to the $E_m(Q/Q−)$ for tetramethyl-benzoquinone (Zhu and Gunner 2005). Indeed, the calculated $E_m(Q/Q−) = −163$ mV for ubiquinone (Table 1) is close to the experimentally measured $E_m(Q/Q−) = −165$ mV for trimethyl-benzoquinone (Swallow 1982) in water versus NHE, which is consistent with their proposal. Although it was proposed that difference in the 2-methoxy orientation of ubiquinone was responsible for the $E_m$ difference of more than 160 mV between QA and QB in PbrRC (Taguchi et al. 2013), the similar $E_m(Q/Q−)$ values of trimethyl-benzoquinone and ubiquinone (ref. (Zhu and Gunner 2005) and Table 1) suggest that contributions of methoxy and methyl groups to $E_m(Q/Q−)$ are not significantly different. It should also be noted that estimation by Swallow resulted in a more negative value of $E_m(Q/Q−) = −230 ± 20$ mV for ubiquinone at pH 7 (Swallow 1982).

The present study shows that $E_m(Q/Q−)$ is −260 mV for menaquinone (phylloquinone) in water versus NHE (Table 1); the calculated $E_m(Q/Q−)$ can be confirmed by Eq. 6, which can be reproduced by adding 480 mV to $E_m(Q/Q−)$ in DMF versus SCE. Previously, Ptushenko et al. considered that $E_m(Q/Q−)$ was −800 mV for phylloquinone in DMF versus NHE by considering a liquid junction potential between SCE in DMF and NHE in water (Ptushenko et al. 2008). Using the low $E_m(Q/Q−)$ value of −800 mV for phylloquinone in DMF versus NHE, they obtained $E_m(A1A) = −671$ mV and $E_m(A1B) = −844$ mV (Ptushenko et al. 2008), and were able to reproduce the reported low $E_m(A1)$ in PSI [e.g., −810 mV (Vos and van Gorkom 1990), −754 mV (Iwaki and Itoh 1994), and lower than −700 mV (Brettel and Leibl 2001)]. This, in turn, suggests that the electrostatic interaction of the PSI protein environment at the A1 site is remarkably weak in their computational model. If this is the case, then $E_m(QA)$ of −150 mV for the same quinone species (menaquinone) would be regarded as being “unusually high” in PbrRC from Blastochloris viridis (Brettel and Leibl 2001), and the PbrRC protein environment must dramatically increase $E_m(Q/Q−)$ for menaquinone by more than 600 mV at the QA site in their computational model; obviously this is not the case for the PbrRC protein environment, as already demonstrated in theoretical studies (Rabenstein et al. 1998; Ishikita and Knapp 2004; Zhu and Gunner 2005). $E_m(Q/Q−) = −260$ mV for menaquinone (phylloquinone) in water versus NHE (Table 1) suggests that the PSI protein environment (e.g., the presence of negatively charged FX near A1 (Ishikita and Knapp 2003)) is responsible for low $E_m(A1)$ in PSI. When $E_m(Q/Q−) = −800$ mV for phylloquinone in DMF versus NHE is used, the resulting $E_m(A1)$ should contain the $E_m$ downshift of ca. 600 mV with respect to water versus NHE as an artifact (Table 2), since the PSI is not solvated in DMF but in water in the thylakoid membrane. One can directly focus on the influence of the PSI protein environment on $E_m(A1)$ when using $E_m(Q/Q−) = −260$ mV in water versus NHE. It seems plausible that using $E_m$ values measured in water is more recommended to analyze $E_m$ values for the redox active groups in proteins unless the proteins are solvated in DMF.

This fact would be more obvious when considering $E_m$ of heme proteins or flavin-binding proteins. $E_m$ of heme (Harbury and Loach 1960; Wilson 1983) and flavin (Draper and Ingraham 1968; Anderson 1983) were experimentally measured in water. These cofactors are often largely exposed to the protein bulk surface [e.g., heme (Kerfeld et al. 2003; Clarke et al. 2011) and flavin (Ludwig et al. 1997; Watt et al. 1991) proteins]. As these cofactors are released away from the binding site toward the bulk region, the $E_m$ values must be close to those experimentally measured in water; this is exactly the case for QB in PbrRC and PSII, which is located near the protein bulk surface. Using spectroelectrochemistry, Kato et al. directly determined $E_m(QB)$ to be +40 mV in PSII from Thermosynechococcus elongates versus NHE (Kato et al. 2016). $E_m(Q/Q−)$ is −154 mV for
plastoquinone in water versus NHE (Table 1) and would be −750 mV in DMF versus NHE (assuming $E_m$ downshift of ca. 600 mV, Table 2). If $E_m(Q/Q^-)$ measured in DMF were relevant, the PSII protein environment would need to increase $E_m(Q/Q^-)$ for plastoquinone by 840 mV at the QA site. In addition, $E_m(QA)$ was determined to be −145 mV in spinach PSII versus NHE, using spectroelectrochemistry (Brinkert et al. 2016); the PSII protein environment would also need to increase $E_m(Q/Q^-)$ for plastoquinone by 600 mV even at the QA site, which is less exposed to the protein bulk surface. It seems likely that $E_m$ values for quinones measured in water are more recommended when comparing with $E_m(Q/Q^-)$ in the protein environments. This would also hold true for the quinone binding sites in cytochrome $b_c$ and cytochrome $b_{0,f}$, at which quinones from PbRC and PSII can bind, respectively.

Conclusion

Experimentally measured $E_m(Q/Q^-)$ in DMF versus SCE (Prince et al. 1983) and $E_m(Q/Q^-)$ in water versus NHE (Swallow 1982) correlated highly with the quantum chemically calculated energy differences ($\Delta E_{QMP/PCM}$) between neutral and reduced states (Figs. 3a, b) and can be best fitted to Eqs. 4 and 5, respectively. It seems likely that $E_m(Q/Q^-)$ for 1,4-benzoquinones differ by 600 mV even in the absence of the liquid junction potential between DMF and NHE (versus Fe/Fe$^+$). $E_m(Q/Q^-)$ was calculated to be −163 mV for ubiquinone, −260 mV for menaquinone (phylloquinone), and −154 mV for plastoquinone in water versus NHE (Table 1). In particular, $E_m(Q/Q^-) = −260$ mV for phylloquinone in water versus NHE unambiguously demonstrates that remarkably low $E_m(A_1)$ in PSI does not originate from $E_m(Q/Q^-)$ for phylloquinone but from interaction with the PSI protein environment, as suggested previously (Ishikita and Knapp 2003). These $E_m(Q/Q^-)$ are prerequisite for analyzing the $E_m(Q/Q^-)$ shift caused by electrostatic interactions within the protein environment in photosynthetic reaction centers.

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