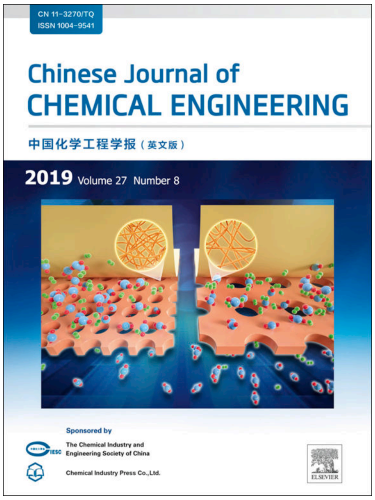


Review

Theoretical Insights on the Hydration of Quinones as Catholytes in Aqueous Redox Flow Batteries

Jipeng Li, Huan Xu, Jingqi Wang, Yujun Wang, Diannan Lu, Jichang Liu, Jianzhong Wu

PII: S1004-9541(21)00330-X
DOI: https://doi.org/10.1016/j.cjche.2021.06.016
Reference: CJCHE 2327

To appear in: *Chinese Journal of Chemical Engineering*

Received Date: 20 February 2021
Revised Date: 10 June 2021
Accepted Date: 21 June 2021

Please cite this article as: J. Li, H. Xu, J. Wang, Y. Wang, D. Lu, J. Liu, J. Wu, Theoretical Insights on the Hydration of Quinones as Catholytes in Aqueous Redox Flow Batteries, *Chinese Journal of Chemical Engineering* (2021), doi: https://doi.org/10.1016/j.cjche.2021.06.016

Article

Theoretical Insights on the Hydration of Quinones as Catholytes in Aqueous Redox Flow Batteries

Jipeng Li[1], Huan Xu[1], Jingqi Wang[1], Yujun Wang[1], Diannan Lu[1,*], Jichang Liu[2,*], and Jianzhong Wu[3,*]

[1] Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[2] State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

[3] Department of Chemical and Environmental Engineering and Department of Mathematics, University of California, Riverside, CA 92521, USA

*Corresponding author: ludiannan@tsinghua.edu.cn, liujc@ecust.edu.cn, and jwu@engr.ucr.edu

Abstract

Quinones have been widely studied as a potential catholyte in water-based redox flow batteries (RFBs) due to their ability to carry both electrons and protons in aqueous solutions. The wide variety of quinones and derivatives offers exciting opportunities to optimize the device performance while poses theoretical challenges to quantify their electrochemical behavior as required for molecular design. Computational screening of target quinones with high performance is far from satisfactory. While solvation of quinones affects their potential application in RFBs in terms of both electrochemical windows, stability, and charge transport, experimental data for the solvation structure and solvation free energies are rarely available if not incomplete. Besides, conventional thermodynamic models are mostly unreliable to estimate the properties of direct interest for electrochemical applications. Here, we analyze the hydration free energies of more than 1,400 quinones by combining the first-principles calculations and the classical density functional theory. In order to attain chemical insights and possible trends, special attention is placed on the effects of "backbones" and functional groups on the solvation behavior. The theoretical results provide a thermodynamic basis for the design, synthesis, and screening of high-performance catholytes for electrical energy storage.

Key words: Quinones; classical density functional theory (cDFT); quantum mechanics (QM); water-based redox flow batteries (RFBs); Solubility; solvation free energy

1. Introduction

Quinones are a large group of chemical species with more than one aromatic ring in each molecule. These chemicals can carry both electrons and protons and are commonly utilized in the metabolism of living organisms [1, 2]. In recent years, quinones have been considered good candidates as the electrolyte on the cathode side (a.k.a., catholyte) of water-based redox flow batteries (RFBs) owing to their attractive features such as material sustainability, low cost, and customizable electrochemical properties [3-5]. Successful examples include applications of 2,6-dihydroxyanthraquinone (2,6-DHAQ) and 4,40-((9,10-anthraquinone-2,6-diyl)-dioxy)-dibutyrate (2,6-DBEAQ) for long-lasting and high-density electrical energy storage [6-8]. At the same time, numerous theoretical studies have been reported to examine the effects of quinone chemistry on electron affinity and solvation [9, 10], interfacial electron transfer [11, 12], and Li-ion binding [13, 14]. However, the large number of different quinones makes it difficult to select the best molecules only by combinatory experimental trials.

Computational methods provide a valuable alternative to assessing the stability, electrochemical windows, and solvation properties of vast quinones potentially useful as the catholyte for water-based RFBs. With ever-increasing computer power, one can, in principle, predict the electronic properties of these chemical species and their intermolecular interactions in water through quantum-mechanical (QM) calculations and, subsequently, the solution behavior by using molecular dynamics (MD) or Monte Carlo (MC) simulations. Whereas reliable thermodynamic data can be obtained for ideal-gas systems from first-principles predictions, the conventional multiscale procedure is computationally too expensive to predict the properties of quinones in liquid systems. For practical purposes, particularly for high-throughput predictions, the application of simplified methods is inevitable to eschew the computational burden. Toward that end, we often rely on lower-level QM methods or semi-empirical force fields to describe intermolecular interactions and use liquid-state theories instead of MD/MC simulation to predict properties affiliated with a large number of thermodynamic systems.

In previous work [15, 16], we demonstrated that a combination of QM and classical density functional theory (cDFT) could be used to predict the hydration free energies for an extensive library of organic compounds. The theoretical performance of the multiscale procedure depends on approximations in the cDFT calculations as well as in QM methods that are employed to predict the molecular structure and the force-field parameters. It was shown that the optimal computational procedure reflects not only the accuracy of theoretical predictions at individual scales but often, more importantly, a reliable linkage between different theoretical methods for electronic structure and atomic representations to attain the best overall performance. Here, we study the hydration behavior of quinones with the same multiscale cDFT procedure. Based on molecular parameters attained from a previous study of polycyclic aromatic hydrocarbons (PAHs) [17], we investigate the hydration free energies of more than 1400 quinones at the ambient condition. Further, we analyze the effects of "backbones" and functional groups on hydration free energy and discuss its implication for catholyte molecular design in water-based redox flow batteries.

The energy density of quinone-based RFBs is dependent on the following three factors: (1) the selection of quinones as catholytes and their corresponding redox potentials, (2) the amount of quinones dissolved in water, and (3) the number of electrons participating in the redox reaction per quinone molecule. In this work, we focus on the hydration of quinones, which is intrinsically related to the solubility of quinones in water. Whereas energy density is of fundamental importance for the practical applications of RFBs, the solubility and the solvation behavior of all pertinent materials are fundamental for understanding their performance under a wide variety of solution conditions. An ideal catholyte should have a high energy storage capacity, which requires molecules to have excellent redox ability and good solubility in an electrolyte.

2. Theoretical methods

The theoretical methods to calculate hydration free energy have been discussed in our previous work [18, 19]. In brief, we define hydration free energy as the change of the grand potential of the solvent after inserting a solute molecule at a specific temperature and pressure. In this work, each quinone is treated as a rigid molecule due to a lack of flexibility. For a rigid solute with a fixed conformation, the grand potential can be assessed from cDFT calculations by minimization of the grand potential with respect to the density profile of the solvent molecules.

Our cDFT calculation requires as the inputs a semi-empirical force field for both solvent-solvent and solute-solvent interactions. Combining the QM optimization of the solute structure and force-field parameters, the multiscale procedure yields an accurate prediction of the hydration free energies, especially for hydrophobic chemical species [20]. For each solute, the molecular structure is obtained by energy minimization in a vacuum using the Hartree-Fock (HF) method [21]. The water molecules are represented by the SPC/E [22]. We use the GAFF [23] force-field parameters to describe the van der Waals (VDW) interactions between solute and solvent molecules, and AM1-BCC [24] charge distributions to assign the atomic charges. All QM calculations are based on the ORCA *ab initio* quantum chemistry package [25], and cDFT calculations are based on the home-developed programs. The effective hard-sphere (HS) diameter is set to 2.915 Angstrom in the hard-sphere bridge functional as that used in a previous study [17]. The same value is used without further optimization for all theoretical predictions discussed in this work.

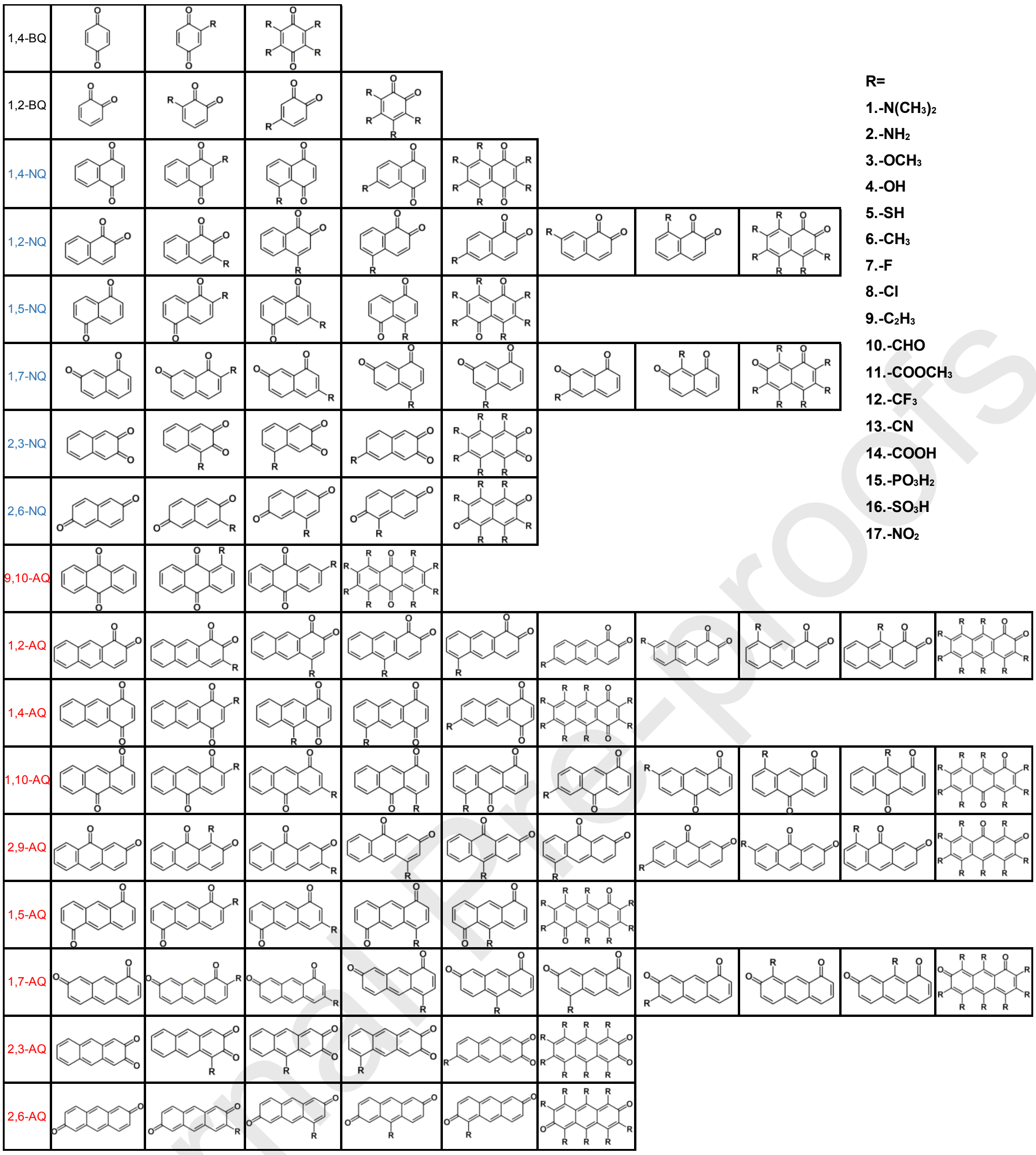
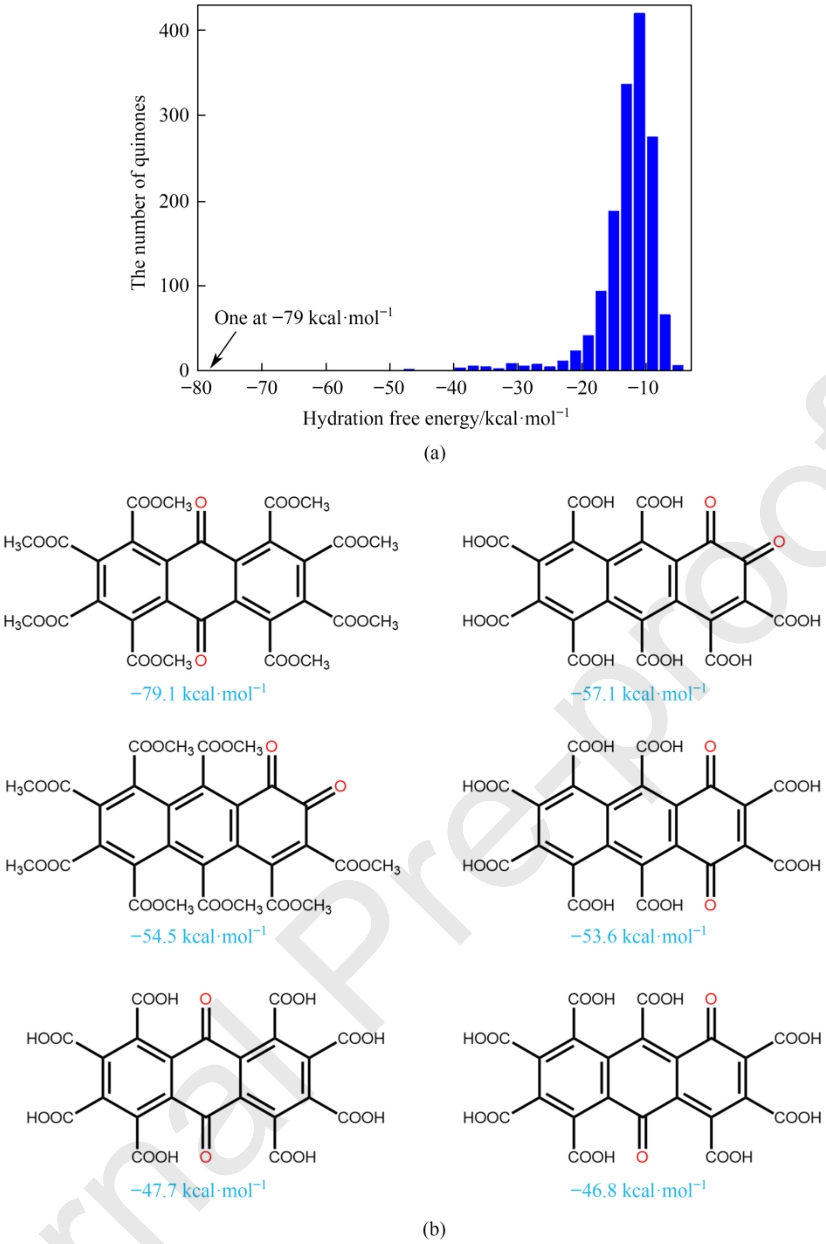


Figure 1. Molecular structures of some representative quinones studied in this work.

3. Results and Discussion

Figure 1 gives the typical molecular structures of quinones considered in this work. Based on the number of benzene rings, we divide quinones into several subgroups. BQs, NQs, and AQs are referred to quinone molecules containing one, two, and three benzene rings, respectively. These quinones can be further classified into 17 entries according to the relative positions of the carbonyl groups. We have analyzed the effect of the R-group on the solvation of all these seventeen functional groups.

Figure 2(a) presents the distribution of hydration free energies for all quinones studied in this work. Depending on the molecular size and identification of side chains, the hydration free energy varies from −80 to −4 kcal·mol^{-1}. Most quinone molecules have a hydration free energy in the range from −20 to −4 kcal·mol^{-1}. Eighty-two molecules are in the range from −40 to −20 kcal·mol^{-1}. Fig. 2(b) shows the molecular structures of six quinones with the most negative hydration free energies, ranging from −80 to −40 kcal·mol^{-1}. As expected, the addition of hydrophilic functional groups, namely —COOH and —$COOCH_3$, makes the hydration free energy more negative, which results in higher solubilities of these molecules in water. From a thermodynamic perspective, these six molecules are good catholytes for water-based redox flow batteries.



(a)

(b)

Figure 2. (a)The distribution of hydration free energies of 1,486 quinone molecules. (b)The structures of six molecules with considerably negative hydration free energy.1kcal=4.186 kJ

Figure 3 shows a comparison of the theoretical predictions with the experimental data for the hydration free energies of three quinone molecules: CAS 524-42-5, CAS 130-15-4, and CAS 84-65-1 [26]. The predicted hydration free energy for 1,2-naphthalenedione (CAS 524-42-5) is −7.66 kcal/mol, which is slightly higher than that from experiments (−9.22 kcal·mol^{-1}). The predicted hydration free energy for 1,4-naphthaquinone (CAS 130-15-4) is −7.49 kcal·mol^{-1} (−9.68 kcal·mol^{-1}

from the experiment), and –8.38 kcal·mol^{-1} for 9,10-anthracenequinone (CAS 84-65-1) (−9.57 kcal·mol^{-1} from the experiment). The deviations of theoretical predictions of the hydration free energies from experiments are 17%, 23%, and 12% for 1,2-naphthalenedione, 1,4-naphthaquinone, and 9,10-anthracenequinone, respectively. While these numbers are far from perfect, the comparison with limited experimental results indicates that our predictions are reliable to capture the trend.

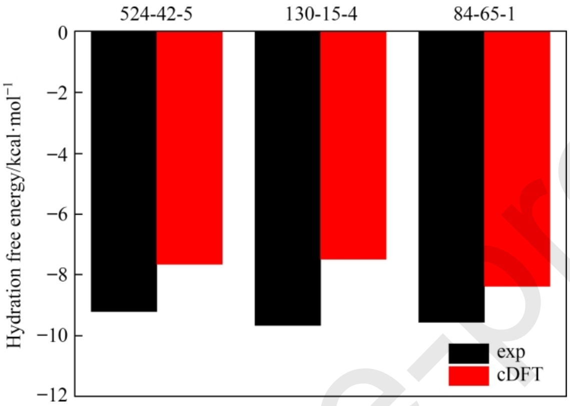


Figure 3. Experimental and predicted hydration free energy of three quinone molecules

The quinone molecules consist of benzene rings as the backbones and hydrophilic groups on the sidechains. The backbones of quinone molecules are often different in the arrangement of the benzene rings, which affects the hydration free energy. Fig. 4 shows the distributions of hydration free energies for different quinone groups, BQs, NQs, and AQs. The distribution of the hydration free energies of BQs is similar to that of NQs. Both of them have a relatively narrow distribution with a peak in the range from −10 to −6 kcal·mol^{-1}. The hydration free energies of AQs show a wider distribution compared to those for BQs and NQs, and its peak is between −14 to −12 kcal·mol^{-1}. Most molecules with large solubility belong to AQs. The large molecular volume for quinones in this group may be responsible for the low hydration free energy.

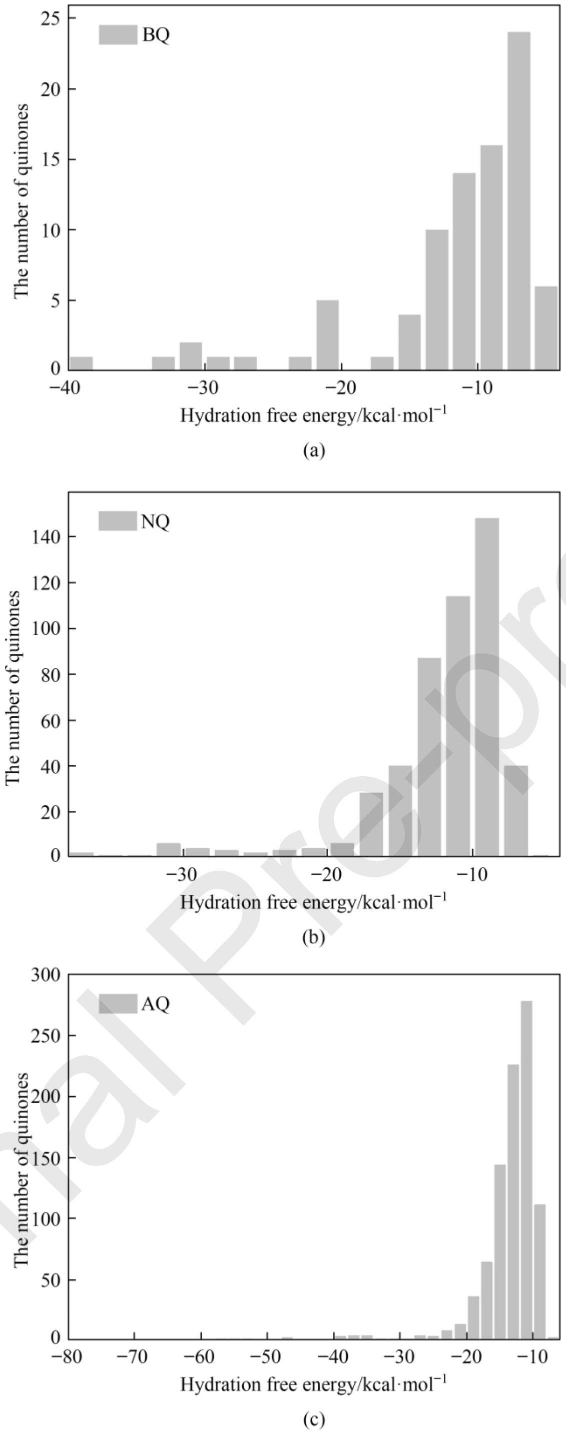


Figure 4. (a)The distribution of hydration free energies of BQ quinones. (b) The distribution of hydration free energies of NQ quinones. (c) The distribution of hydration free energies of AQ quinones.

As shown in Fig. 5, most quinone molecules have a hydration free energy in the range between −5 to −40 kcal·mol^{-1}. Only a few quinone molecules have a higher hydration free energy, ranging from −45 to −60 kcal·mol^{-1}, even as high as −80 kcal·mol^{-1}. Fig. 2(b) gives the molecular configurations of these specific molecules. Common features of these molecules are to have three rings, a large molecular volume, and many carboxyl groups on the side chain. Because of their strong interactions with water and excellent solubility, these molecules are highly stable in water, rendering them as good candidates of the catholyte for aqueous redox flow batteries with high energy density.

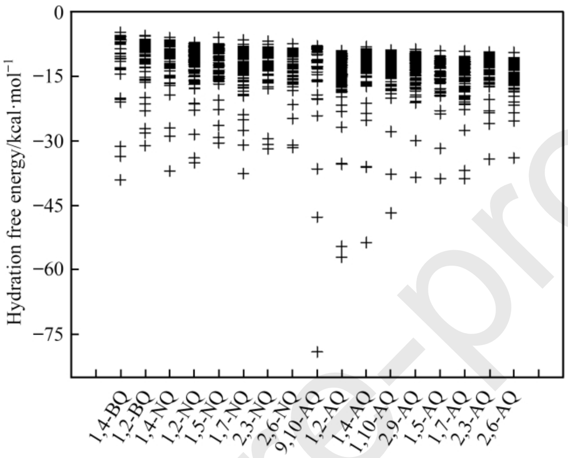


Figure 5. The distribution of hydration free energies of quinones with different "backbones".

The hydration free energies of quinones exhibit an interesting correlation with the functionality of the R-groups, as shown in Fig. 6. Several functional groups, such as —CH_3, —F, —Cl, —C_2H_3, —CF_3, are affiliated with quinones with a narrow distribution of the hydration free energies. Some other functional groups, like —CHO, —$COOCH_3$, —CN, —COOH, are responsible for a more scattered distribution of the solvation free energies, and these groups promote solvation in water. Such a solvation behavior may provide a useful rule of thumb for screening target molecules towards the water-based battery with higher energy and power density.

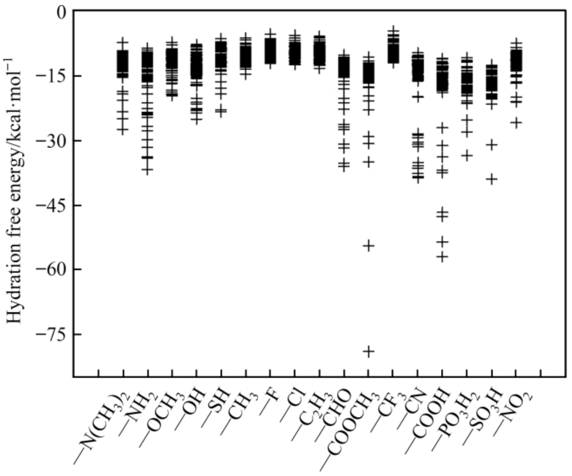
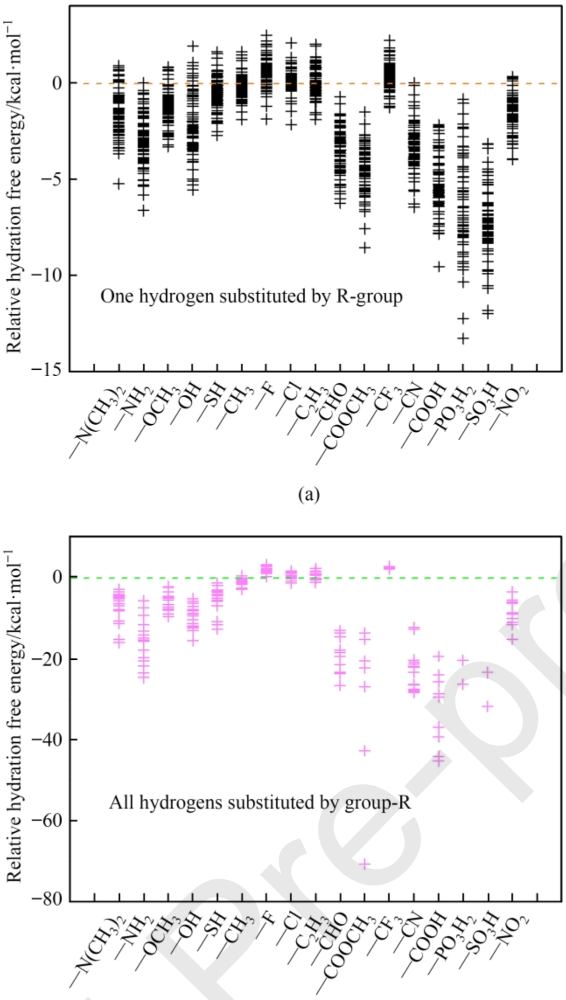


Figure 6. The distribution of solvation of quinones based on different functional groups

To further investigate the effect of the functional group and its relative position on solvation, we define the relative free energy as the extra free energy induced by substitution from hydrogen to the functional group. As shown in Fig. 7, the substitution of more hydrogens by the R-group leads to a more negative hydration free energy. If only one hydrogen is substituted by R-group, such as —CHO, —$COOCH_3$, —COOH, —PO_3H_2, and —SO_3H, it makes a positive effect for dissolving more quinone molecules in water. For all hydrogens substituted by R-group, the above substitutions still enhance solvation.



(a)

(b)

Figure 7. (a)The distribution of the relative hydration free energies of quinones with one hydrogen substituted by R-group. (b)The distribution of the relative hydration free energies of quinones with all hydrogens substituted by R-group.

The relative positions of the functional groups play a vital role in the properties of quinones in aqueous solutions. Here, the relative hydration free energy is analyzed based on two relative positions of carbonyl groups, namely *para*-quinones and *ortho*-quinones. As shown in Fig. 8, both *para*-quinones and *ortho*-quinones show a similar distribution. The introduction of —CHO, —$COOCH_3$, —COOH, —PO_3H_2, and —SO_3H also makes the quinone molecules more hydrophilic.

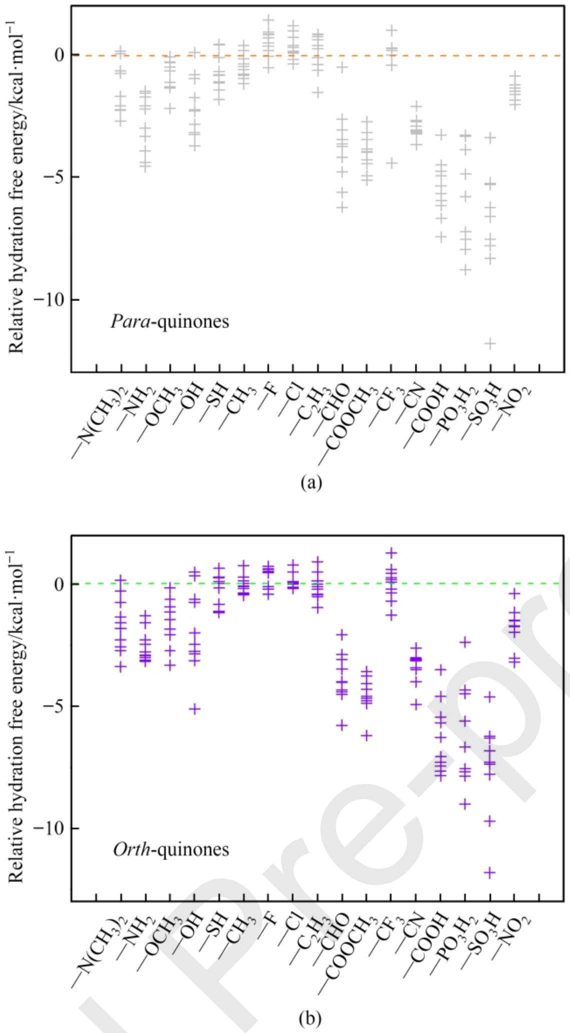


Figure 8. (a)The distribution of the relative hydration free energies of *para*-quinones based on different functional groups. (b)The distributions of relative hydration free energies of *ortho*-quinones based on different functional groups

4. Conclusions

In this work, we employed a multiscale procedure to predict the hydration free energies of a large library of quinones. The multiscale approach includes a quantum-mechanical method (HF) for structure optimization, classical density functional theory (cDFT) combining with GAFF force-field parameters for thermodynamic calculations, AM1-BCC charge sets, and SPC/E water model. We calculated more than 1400 hydration free energies and discussed the effect of "backbones" and functional groups. Introduction of —CHO, —$COOCH_3$, —COOH, —PO_3H_2, and —SO_3H cause higher hydration free energy. We hope that the thermodynamic model reported in this work would provide the first step toward molecular screening and design of catholytes for battery applications.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (U1862204) and the U. S. National Science Foundation (NSF-1940118). The numerical calculations were performed at the "Tianhe-2" platform supported by Guangzhou Supercomputer Centre.

References

[1] Takahashi, E. and CA Wraight, *Proton and Electron-Transfer in the Acceptor Quinone Complex of Rhodobacter-Sphaeroides Reaction Centers - Characterization of Site-Directed Mutants of the 2 Ionizable Residues, Glul212 and Aspl213, in the Qb Binding-Site.* Biochemistry, 1992. **31**(3): p. 855-866.

[2] Maroti, P. and CA Wraight, *Flash-Induced H+ Binding by Bacterial Photosynthetic Reaction Centers - Influences of the Redox States of the Acceptor Quinones and Primary Donor.* Biochimica Et Biophysica Acta, 1988. **934**(3): p. 329-347.

[3] Alt, H., et al., *Quinones as Rechargeable and Regenerable Battery Cathode Materials.* Journal of the Electrochemical Society, 1971. **118**(12): p. 1950-+.

[4] Miroshnikov, M., et al., *Power from nature: designing green battery materials from electroactive quinone derivatives and organic polymers.* Journal of Materials Chemistry A, 2016. **4**(32): p. 12370-12386.

[5] Han, C.P., et al., *Organic quinones towards advanced electrochemical energy storage: recent advances and challenges.* Journal of Materials Chemistry A, 2019. **7**(41): p. 23378-23415.

[6] Kwabi, D.G., et al., *Alkaline Quinone Flow Battery with Long Lifetime at pH 12 (vol 2, pg 1894, 2018).* Joule, 2018. **2**(9): p. 1907-1908.

[7] Lin, K., et al., *Alkaline quinone flow battery.* Science, 2015. **349**(6255): p. 1529-32.

[8] Huskinson, B., et al., *A metal-free organic-inorganic aqueous flow battery.* Nature, 2014. **505**(7482): p. 195-8.

[9] Kim, K.C., et al., *Unveiled correlations between electron affinity and solvation in the redox potential of quinone-based sodium-ion batteries.* Energy Storage Materials, 2019. **19**: p. 242-250.

[10] Er, S., et al., *Computational design of molecules for an all-quinone redox flow battery.* Chemical Science, 2015. **6**(2): p. 885-893.

[11] Sedenho, G.C., et al., *Effect of Molecular Structure of Quinones and Carbon Electrode Surfaces on the Interfacial Electron Transfer Process.* ACS Applied Energy Materials, 2020. **3**(2): p. 1933-1943.

[12] Newman, D.K. and R. Kolter, *A role for excreted quinones in extracellular electron transfer.* Nature, 2000. **405**(6782): p. 94-97.

[13] Kim, K.C., et al., *First-Principles Density Functional Theory Modeling of Li Binding: Thermodynamics and Redox Properties of Quinone Derivatives for Lithium-Ion Batteries.* Journal of the American Chemical Society, 2016. **138**(7): p. 2374-2382.

[14] Kim, K.C., *Design Strategies for Promising Organic Positive Electrodes in Lithium-Ion Batteries: Quinones and Carbon Materials.* Industrial & Engineering Chemistry Research, 2017. **56**(42): p. 12009-12023.

[15] Fu, J. and J. Wu, *Predicting thermodynamic data from first principles: hydration free energies for common organic molecules.* Fluid Phase Equilib, 2016. **407**: p. 304-13.

[16] Sheng, S., M. Miller, and J. Wu, *Molecular Theory of Hydration at Different Temperatures.* The Journal of Physical Chemistry B, 2017. **121**(28): p. 6898-6908.

[17] Li, JP, et al., *A Multiscale Procedure for Predicting the Hydration Free Energies of Polycyclic Aromatic Hydrocarbons.* Journal of Chemical and Engineering Data, 2020. **65**(4): p. 2206-2211.

[18] Liu, Y., S. Zhao, and J. Wu, *A Site Density Functional Theory for Water: Application to Solvation of Amino Acid Side Chains.* Journal of Chemical Theory and Computation, 2013. **9**(4): p. 1896-1908.

[19] Liu, Y., J. Fu, and J. Wu, *High-Throughput Prediction of the Hydration Free Energies of Small Molecules from a Classical Density Functional Theory.* The Journal of Physical Chemistry Letters, 2013. **4**(21): p. 3687-3691.

[20] Li, J., et al., *Predicting hydration free energies of amphetamine-type stimulants with a customized molecular model.* J Phys Condens Matter, 2016. **28**(34): p. 344001.

[21] Slater, J.C., *A simplification of the Hartree-Fock method.* Physical Review, 1951. **81**(3): p. 385.

[22] Berendsen, H., J. Grigera, and T. Straatsma, *The missing term in effective pair potentials.* Journal of Physical Chemistry, 1987. **91**(24): p. 6269-6271.

[23] Wang, J., et al., *Development and testing of a general amber force field.* Journal of computational chemistry, 2004. **25**(9): p. 1157-1174.

[24] Jakalian, A., D.B. Jack, and C.I. Bayly, *Fast, efficient generation of high-quality atomic charges. AM1-BCC model: II. Parameterization and validation.* Journal of computational chemistry, 2002. **23**(16): p. 1623-1641.

[25] Neese, F., *The ORCA program system.* Wiley Interdisciplinary Reviews: Computational Molecular Science, 2012. **2**(1): p. 73-78.

[26] Sander, R., *Compilation of Henry's law constants (version 4.0) for water as a solvent.* Atmospheric Chemistry and Physics, 2015. **15**(8): p. 4399-4981.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: