Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Physical Organic Chemistry. *Reference Object Identifier* – ROI: jbc-01/17-52-11-53
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/17-52-11-53
Submitted on November 25, 2017.

Calculation of standard RedOx potentials by the semi-empirical methods AM1, PM7 and RM1 on wide set of organic compounds. Best scheme and accuracy.

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Keywords: PCM/AM1, PCM/PM7, PCM/RM1, standard RedOx potentials, accuracy, substituted anylines, phenols and quinones.

Abstract

The quantitative assessment by quantum chemistry methods of the standard RedOx potential changing of organic compounds at introduction on a surface of an electrode the various modifiers can be convenient criterion for selection of optimum modifiers. The range of the used modifiers is rather wide, up to use of high-molecular compounds. Therefore the choice of calculation method with optimal accuracy and efficiency is important task. We calculated the standard RedOx potentials for the big set of the substituted anylines (13), phenols (28) and quinones (12) by use of semiempirical NDDO method in the modern parametrizations AM1, PM7 and RM1. Solvation effects was considered by the continual model PCM. We submitted the results of the comparative analysis of accuracy of specified methods among themselves and with ab inito methods MP2/6-31G (d) and BPW91/cc-pVDZ. Also we carried out comparison of two RedOx potentials calculations schemes - scheme with using enthalpy of formation and scheme with using total energies.

It is shown that the most precise semiempirical method for calculating standard RedOx potentials is the parametrization RM1, whose results are comparable with accuracy of ab initio methods. It is also shown that the scheme of calculation of potentials using the total energies provides the best accuracy for all options of the parameterizations. It is established that accuracy of calculation of standard RedOx potential depends on structure of compounds. The accuracy of RM1 for the substituted anylines is MUE_{RM1} = 0/10 V, while accuracy for the substituted quinones is MUE_{RM1} = 1.24 V. General MUE_{RM1} does not exceed 0.6V. Calculated values can be corrected by the correlation equation $E^{0\ (RedOx)} = 0.1514 * E^{0\ (RedOx)}calc + 0.5282$; R^2 = 0.2195.

References

[1] A.V. Sidel'nikov, V.N. Maistrenko, R.A. Zil'berg, Yu.A. Yarkaeva, E.M. Khamitov. An enantioselective voltammetric sensor for the recognition of propranolol stereoisomers. *Journal of Analytical Chemistry*. **2017**. Vol.72. No.5. P.575-581.

[2] M. Trojanowicz. Enantioselective electrochemical sensors and biosensors: a mini-review. *Electrochem. Commun.* **2014**. Vol.38. P.47-52.

[3] R.A. Zil'berg, A.V. Sidel'nikov, V.N. Maistrenko, Yu.A. Yarkaeva, E.M. Khamitov, V.M. Kornilov and E.I. Maksyutova. A Voltammetric Sensory System for Recognition of Propranolol Enantiomers Based on Glassy Carbon Electrodes Modified by Polyarylenephthalide Composites of Melamine and Cyanuric Acid. *Electroanalysis*. **2017**. Vol.29. P.1-8.

[4] Y. Kong, W. Zhao, S. Yao, J. Xu, W. Wang, Z. Chen. Molecularly imprinted polypyrrole prepared by electrodeposition for the selective recognition of tryptophan enantiomers. *J. Appl. Polymer Sci*. **2010**. Vol.115. P.1952-1957.

[5] B.C. Iacob, E. Bodoki, A. Florea, A.E. Bodoki, R. Oprean. Simultaneous enantiospecific recognition of several β-blocker enantiomers using molecularly imprinted polymer-based electrochemical sensor. *J. Anal. Chem.* **2015**. Vol.87. No.5. P.2755.

[6] B.C. Iacob, E. Bodoki, C. Farcau, L. Barbu-Tudoran, R. Oprean. Study of the molecular recognition mechanism of an ultrathin MIP film-based chiral electrochemical sensor. *Electrochim. Acta*. **2016**. Vol.217. P.195.

[7] I. Pandey, S.S. Jha. Molecularly imprinted polyaniline-ferrocenesulfonic acid-carbon dots modified pencil graphite electrodes for chiral selective sensing of D-ascorbic acid and L-ascorbic acid: a clinical biomarker for preeclampsia. *Electrochim. Acta.* **2015**. Vol.182. P.917.

[8] Yu.A. Yarkayeva, L.R. Kabirova, Yu.R. Provorova, R.A. Zil’berg, N.G. Gileva. Enantioselective recognition of propranolol on the glass carbon electrode modified by cyclodextrins. *Reports of the Bashkir State University.* **2017**. Vol.2. No.3. P.375-379. (russian)

[9] I.G. Smirnova, G.N. Gildeeva, V.G. Kukes. Optical isomerism and biological activity of medicines. *Reports of the Bashkir State University.* **2012.** Vol.53. No.3. P.147. (russian)

[10] V.N. Maistrenko, A.V. Sidel’nikov, R.A. Zil’berg. Enantioselective voltammetric sensors: new decisions. *Anal. Chem*. **2018**. Vol.73. No1. P.3-13. (russian)

[11] V.M. Potapov. Stereochemistry. 2nd edition. *Moscow: Chemistry.* **1988.** 399p. (russian)

[12] C.A. Reynolds. Density Functional Calculation of Quinone Electrode Potentials. *Iternational jounal of quantum chemistry*. **1994**. Vol.56. No.6. P.677-686.

[13] T. Liu, M-M. Liu, X-W. Zheng, C-Y. Du, X-Y. Cui, L. Wang, L-L. Han, Z-Y. Yu. Substient effects on the redox potentials of dihydroxybenzenes: theoretical and experimental study. *Tetrahedron*. **2014**. Vol.70. P.9033-9040.

[14] P. Winget, E. Weber, Cr.J. Cramer. Computational electrochemistry: aqueous one-electron oxidation potentials for substituted anilines. *Phys.Chem*. **2000**. Vol.2. P.1231-1239.

[15] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart. *J.Am. Chem. Soc*. **1985**. Vol.107. P.3902.

[16] J.J.P. Stewart. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and reoptimization of parameters. *J. Mol. Modeling*. **2013**. Vol.19. P.1-32.

[17] G.B. Rocha, R.O. Freire, A.M. Simas, J.J.P. Stewart. RM1: A Reparameterization of AM1 for H, C, N, O, P, S, F, Cl, Br, and I. *Comp. Chem.* **2006**. Vol.27. No.10. P.1101-1111.

[18] J. Rezac, P. Hobza. Advanced Corrections of Hydrogen Bonding and Dispersion for Semiempirical Quantum Mechanical Methods. *Journal of Chemical Theory and Computation*. **2012.** Vol.**8**. No.1. P.141-151.

[19] L.E. Roy, E. Jakubikova, M.G. Guthrie, E.R. Batista. Calculation of one-electron redox potentials revisited. Is it possible to calculate accurate potentials with density functional methods. *J. Phys. Chem*. **2009**. Vol.113. No.24. P.6745-6750.

[20] J. Tomasi, B. Mennucci, R. Cammi. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**. Vol.105. No.8. P.2999-3094.