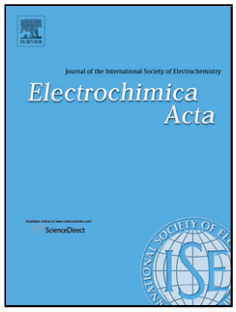

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Author: Mihai Buda

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On calculating reorganization energies for electrochemical reactions using density functional theory and continuum solvation models

Mihai Buda[1]

Abstract: An “all theoretical” method of calculating reorganization energies for electrode reactions using a procedure implemented in the commercial quantum calculation package Gaussian is proposed. The procedure relies in calculating both equilibrium and non-equilibrium Gibbs free energies in solution, eliminating the need to calculate separately inner and outer-sphere contributions to the total reorganization energy, while the molecule’s real shape is also considered. The procedure is intended as a tool for electrochemists to estimate reliably Marcus-type reorganization energies. The comparison is made for simple electrochemical reactions, for which the metal electrode is considered simply as an electron reservoir. The calculated values show good agreement with experimental ones, typically within 10%. The procedure, while not perfect, yields good estimates for reorganization energies of a large variety of electrode reactions and it is more suitable to be used by electrochemists than other methods.

1. Introduction

Following the renewed interest manifested of late in the Marcus theory of electrochemical reactions [1-4], this paper proposes an “all theoretical” method of calculating reorganization energies for electrode reactions using the procedure implemented in the commercial quantum calculation package Gaussian. The method relies on calculating both equilibrium and non-equilibrium Gibbs free energies in solution, with the non-equilibrium solvation (see e.g [5]) being calculated through the separation between fast and slow polarization as implemented in Gaussian 03 (see e.g. [6]). This method was successfully used for electronic transitions in various solvents with good results (see e.g. [7]) but, to the best of our knowledge, it was not applied to electrochemical reactions. The results presented further show that this method gives good estimates of reorganization energies for heterogeneous electron transfer as well. Of course, the shortcomings of the continuum model are, more or less, still the same as in the classical Marcus theory, yet further improvement of the PCM implementation in

[1] Dr. Mihai Buda
Department of Applied Physical Chemistry, Electrochemistry and Inorganic Chemistry
Faculty of Applied Chemistry and Materials Science, "POLITEHNICA" University of Bucharest
Calea Grivitei 132, 010737, Bucharest, ROMANIA
E-mail: mihai@catedra.chfiz.pub.ro