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## **ACCEPTED MANUSCRIPT**

## Heterogeneous versus Homogeneous electron transfer reactions at liquid-liquid interfaces: The wrong question?

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ABSTRACT: The exact mechanism of the electron transfer reactions at liquid-liquid interfaces still remains a source of interrogation. The purpose of this paper is to revisit this topic using a finite element simulation approach to analyze cyclic voltammograms for some previously published systems. Also, we compare the current obtained in the absence or presence of an adsorbed gold nanoparticle film. The current results indicate that the electron transfer between ferrocene in the organic phase and hexacyanoferrate(III) in the aqueous phase takes place by potential independent homogeneous reaction in the aqueous phase, while the observed potential dependence stems from that of the concomitant ion transfer reaction of ferrocenium. In the presence of the interfacial gold nanofilm the electron transfer takes place by a bipolar mechanism where the electrons are shuttled through the metallic nanofilm.

KEYWORDS: liquid-liquid interfaces, electron transfer, ion transfer, finite element simulations, redox catalysis

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