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ACCEPTED MANUSCRIPT Effect of Migration on Homogeneous Redox Electrocatalysis at Rotating Disk Electrode

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ABSTRACT

This work is devoted to the theoretical study of the effect of migration on homogeneous redox electrocatalysis of electrochemical reactions at the rotating disk electrode. The mathematical model involves the Nernst-Planck equations that take into account diffusion, migration, convection, homogeneous chemical reactions, and electroneutrality condition. For the convenience of solving and analyzing the results, the mathematical model was reduced to the dimensionless form. The numerical solution was performed by the finite volume method on the nonuniform grid. Based on the results of computational experiments, for the electrocatalytic reduction of hydrogen peroxide in the presence of ferric ions, three zones were observed in the plane of concentrations of H₂O₂ – H₂SO₄. These zones differ in the nature of the limiting current: for H+ ions, Fe⁺² ions, and hydrogen peroxide H₂O₂. The dependences of the limiting current on the concentrations of H₂SO₄ and H₂O₂ were determined with and without consideration of the ionic migration. It was found that the ionic migration may be ignored only in the cases that the concentration of H₂SO₄ is significantly higher than that of H₂O₂. It was shown that the strongest effect of ionic migration is reached on the boundaries between zones that differ in the nature of the limiting current.

Keywords: homogeneous redox electrocatalysis; Nernst-Planck equation; electroneutrality condition; numerical simulation; limiting current density

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