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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 H_2O_2 – H_2SO_4. These zones differ in the nature of the limiting current: for H+ ions, Fe^{+2} ions, and hydrogen peroxide H_2O_2. The dependences of the limiting current on the concentrations of H_2SO_4 and H_2O_2 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 H_2SO_4 is significantly higher than that of H_2O_2. 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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