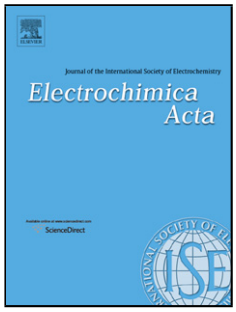

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Accounting for the concentration dependence of electrolyte diffusion coefficient in the Sand and the Peers equations

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Abstract. The equations for calculating the diffusion limiting current, i_{lim}, in steady-state voltammetry (known as the Peers equation in membrane science) and the transition time, τ, in chronopotentiometry (the Sand equation) are broadly used in electrode and membrane electrochemistry. The applicability of these equations is limited because they are deduced under the assumption of a constant diffusion coefficient. However, within the diffusion boundary layer, the diffusion coefficient, D, varies between the values corresponding to the bulk solution (D_b), and the infinitely dilute solution (D_0) near the electrode or membrane surface. In this paper, we explore two models, which account for the concentration dependence $D(c)$ in order to generalise the above fundamental equations. We show that the correct value of i_{lim} can be found via solution of a 2D model, while to find τ, a 1D non-stationary model is sufficient. Generally, the dependence of i_{lim} on the bulk concentration deviates from the proportionality. The similar situation occurs with the proportionality of τ to the squared concentration in the Sand equation. We show that the numerical