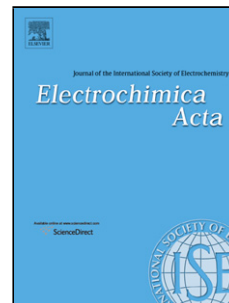


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## Accounting for the concentration dependence of electrolyte diffusion coefficient in the Sand and the Peers equations

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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,  $\tau$ , 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  $\tau$ , 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  $\tau$  to the squared concentration in the Sand equation. We show that the numerical

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