

Extension of classical relations used in electroanalysis to conditions of mixed diffusion - migration transport
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The knowledge of diffusion coefficients of ions and molecules are of great importance for any transport-related problem. Several methods are used to determine diffusion coefficients, however the electrochemical ones are particularly widely employed in the studies of transport phenomena, just because they are fast and relatively easy to implement.

We believe that it is apparently beneficial to evaluate diffusion coefficients in the low-supported (small ratio of concentrations of supporting electrolyte and substrate) media. Under such the conditions the determined values of diffusion coefficients are not affected by the ionic strength (if the concentration of electroactive species is in the order of 10 mM or less), and the obtained results are comparable to those obtained with non-electrochemical methods. It might be particularly useful to be able to study the transport properties of the redox species in the systems containing inert electrolytes at unknown concentrations. The systems where the introduction of excess supporting electrolyte is impossible or not recommended, e.g. low-polarity solvents, solid materials, environmental samples etc. are also interesting.

A new approach to the determination of diffusion coefficients of the substrate, D_S , and the product, D_P , of an electrode process is presented. This approach can be applied to reactions of the type $S^{z_S} = P^{z_P} + ne$ and to any ratio of the concentrations of supporting electrolyte and substrate (ξ). The diffusion coefficients can be evaluated sequentially from the two parts of the double potential step chronoamperogram, since the magnitude of the normalized chronoamperometric current of the first step depends on D_S , while that of the second step is controlled by both D_S and D_P . The corresponding, easy to use procedures have been derived on the basis of the numerical simulation (1,2). The examples of the calculated double potential step chronoamperograms for several classes of electrode processes are shown in Figure 1.

The proposed methods have been verified experimentally with charged and uncharged electroactive species under diffusional and mixed diffusion – migration conditions.

REFERENCES

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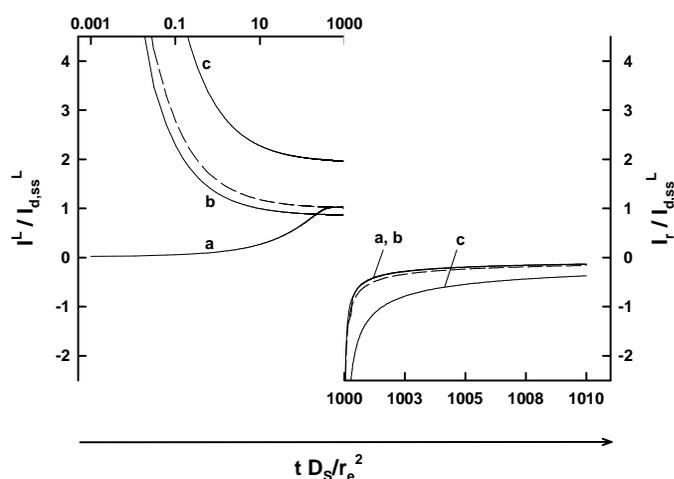


Figure 1. Calculated dimensionless chronoamperograms for several electrode processes carried out in unsupported- (solid lines) and fully supported systems (dashed lines). Chronoamperometric, generating and reverse, currents were made dimensionless with respect to the steady-state generating current for excess supporting electrolyte. The labels a, b, and c refer to: charge production process ($z_S = 0$, $z_P = +1$, $\xi = 0.001$), charge increase process ($z_S = +1$, $z_P = +2$, $\xi = 0$), and charge cancellation process ($z_S = -1$, $z_P = 0$, $\xi = 0$), respectively. $D_S = D_P$.