

Neutral organic reagents in low ionic strength solutions:
how to assess the steady-state?

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With ultramicroelectrodes, it is possible to carry out voltammetry of uncharged organic substrates in solutions containing very low amount of supporting electrolyte. Studies of typical systems like ferrocene, TEMPO and fullerene carried out under these conditions reveal an unusual form of cyclic voltammetric waves (see Figure), where the forward and the reverse scan cross each other in two points. The key factor for the appearance of this type of hysteresis is the low support ratio (i.e., the ratio of concentrations of supporting electrolyte and reactant), usually below 0.1. For higher support ratios the hysteresis gradually disappears and the forward and backward scans merge to a single steady-state curve.

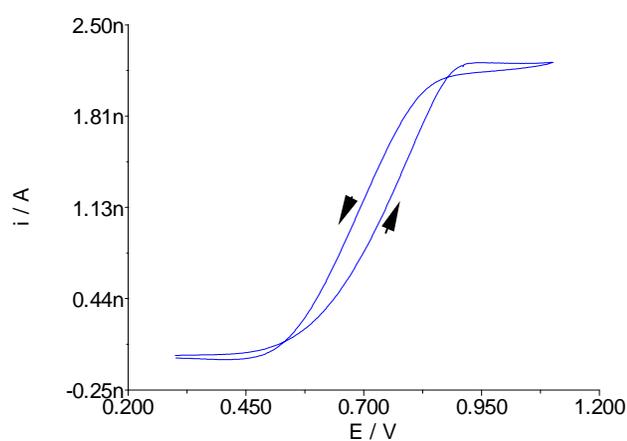


Figure: Cyclic voltammogram of ferrocene (10^{-3} M) in DMSO, no supporting electrolyte. Platinum electrode 22 μ m diameter, scan rate 20 mV/s.

The width of the hysteresis loop increases with lowering the support ratio, and with increasing the size of the electrode and scan rate. When the support ratio is kept constant, the hysteresis width practically doesn't change with the actual reactant concentration. If a number of scans is recorded, the hysteresis loop in the second and subsequent cycles is slightly narrower than in the first one, but does not disappear - instead, it reaches an almost constant width.

If the forward scan is stopped at the rising part of the wave and after that the current is recorded, its value increases. In the backward scan the current decreases after stopping the potential scan. In both cases the current eventually reaches a constant value, and the plot of these values versus the potential gives a line that lies between the forward and the reverse scan curves. The stopping of the scan at the wave plateau for prolonged periods doesn't influence the hysteresis loop width in the subsequent scans.

The described features allow us to conclude, that the observed hysteresis is caused by a difference in the iR -drop magnitudes in the forward and the reverse scans. Both waves are displaced by the ohmic drop, but the solution resistance in the backward scan is smaller than the corresponding resistance in the forward scan.

When a neutral reactant is oxidized or reduced at the electrode, the charge of the reaction product has to be compensated by the counterions attracted from the bulk of the solution. Because the reactant (and thus product) concentration significantly exceeds the concentration of ions in the bulk, a relatively large volume of the solution has to be depleted of counterions. As long as this process is not completed, the solution resistance changes and so does the iR -drop.

Therefore, to be able to speak about the steady-state in the discussed type of systems, one has to consider the situation in which all concentration profiles of ions in the solution and the concentration profile of the reactant do not change with time any more. This difference has quite important consequences, two of them will be presented below.

The driving forces for the transport of the reactant (diffusion) and the transport of the counterion (diffusion-migration) are different, and so are the time scales of these phenomena. The parameters that control the rate at which the steady-state profile of the neutral reactant is reached are the electrode radius and the diffusion coefficient of the reactant. The time necessary to accumulate the counterion and to establish its steady-state profile will also depend on the support ratio and the surface concentration of the electrode reaction product. This latter parameter depends, in turn, on the electrode potential.

If the steady-state is assessed by testing whether the height of the wave is independent of the scan rate, essentially only the reactant concentration profile is indirectly examined. The test whether the position of the wave along the potential axis is constant delivers the information about establishing a true steady-state with time-independent concentration profiles of all ions.

If a selected scan rate gives the voltammogram that has steady-state features in the presence of excess supporting electrolyte, the same scan rate for a significantly lower support ratio can give a non-steady-state voltammogram. Equivalently, a significant increase in the reactant concentration without change of the support electrolyte level can also lead to non-steady-state behaviour.

These differences become important when parameters believed to be measured under steady-state conditions are used in further analysis, e.g., in the determination of the formal potential of the redox couple.