

Exercise Series 5

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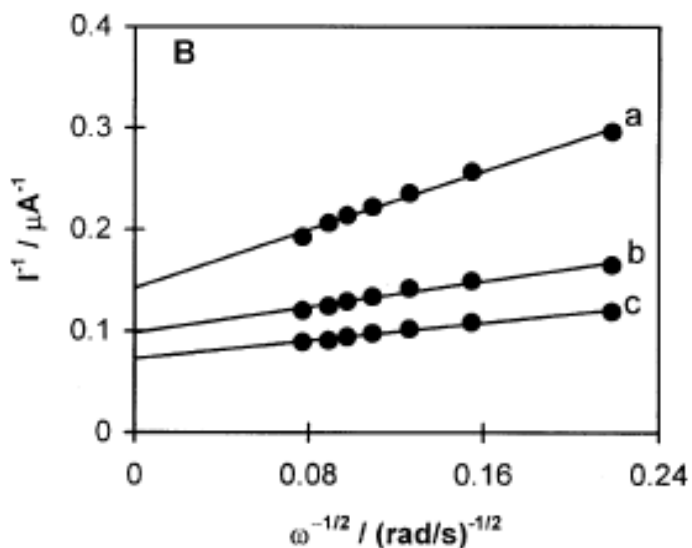
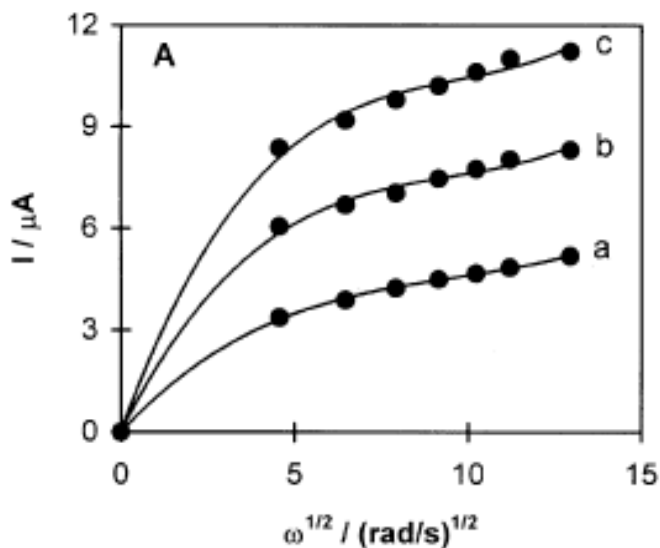
- In the lecture, examples of **voltammetric measurements** have been discussed.
 - Describe the basic principle of such a measurement. What is controlled? What is measured?
 - Describe the experimental set-up (draw a figure!) for a typical three electrode circuit (different electrodes and their functions, electrical devices). What are the current fluxes and potential differences between the different electrodes?
 - There are different techniques how to perform a voltammetric measurement. Show how the applied electrode potential varies as a function of time for three methods that you know.
- There is an **uncompensated solution resistance** R_u between reference electrode and working electrode that is due to the flux of charges between working electrode and counter electrode. This causes an unwanted potential drop in solution jR_u that the measured potential of the working electrode has to be corrected for.
 - Explain the occurrence of this potential drop, e.g. by drawing the potential profile in solution between working electrode and counter electrode.
 - Consider a galvanostatic experiment with fixed current density $j = 10 \text{ mA cm}^{-2}$, a solution with specific conductivity of $\sigma = 0.02 \text{ S cm}^{-1}$ and a planar electrode with disk-like shape and radius $r_0 = 0.05 \text{ cm}$. The separation between working electrode and reference electrode is $d = 0.1 \text{ cm}$. Calculate the value of jR_u .
 - Assume for the reaction at the working electrode that the exchange current density is $j^0 = 1 \text{ } \mu\text{A cm}^{-2}$ and $\alpha = 0.5$. Calculate the corresponding electrode overpotential η and compare it with jR_u . What will be the total value of potential between working electrode and reference electrode?
- Consider a **dropping mercury electrode** (DME). A typical drop has a radius of 0.1 cm. Depending on the time at which the drop detaches from the capillary, diffusion around the drop can be considered linear or spherical. Assume a typical diffusion constant of an electroactive species in aqueous solution.

What is the critical time of transition between the case of linear diffusion and spherical diffusion? For which times is the diffusion-limited current the same as for the linear case? For which times is it spherical?

[Hint: use your understanding of diffusion around spherical or hemi-spherical microelectrodes!]

4. Current measurements have been performed for the oxidation of hydrazine at a caffeic acid modified glassy carbon working electrode. Hydrazine, N_2H_4 , is a component of rocket fuel and a widely used chemical in industrial applications. [Ref.: S.M. Golabi and H.R. Zare, *Electroanalysis* 1999, 11, 1293.]. Its detection is of considerable analytical interest. The electrode reaction is $N_2H_4 \rightarrow N_2 + 4e^- + 4H^+$, i.e. overall $n=4$ electrons are transferred (this is the number of electrons that you have to insert into the diffusion equation or the Cottrell equation, since one mole of diffusing reactant molecules N_2H_4 confer 4 mole of elementary charges to the electrode).

- a) After a time of $t = 45 \text{ s}$ a total current of $I = 7.9 \mu\text{A}$ is measured in a solution with hydrazine concentration $c^b = 2 \text{ mM}$. The electrode surface area is $A = 0.031 \text{ cm}^2$. Under which assumption (prevailing limitation?) could you determine the diffusion coefficient of hydrazine in the solution? Which equation do you need? Calculate the value of D .
- b) Rotating disk electrode measurements have been performed at $\eta = 300 \text{ mV}$. Results are shown in two different representations in the figure below for concentrations (A) $c^b = 0.3 \text{ mM}$, (B) $c^b = 0.6 \text{ mM}$, and (C) $c^b = 1 \text{ mM}$ of hydrazine. Fig. A corresponds to a so-called Levich plot and Fig. B is a Levich-Koutecky plot. Use an equation provided in the lecture to explain, why the data plotted in the form of Fig. B exhibit a linear dependence. Determine the rate of oxidation, K_{ox} , for the three concentrations.
- c) Use the data, calculated or provided in (a) and (b) to estimate the kinematic viscosity of the electrolyte.



5. As you will see in this problem, it is rather difficult to determine kinetic parameters of rapid electrochemical reactions. Imagine, you want to determine Tafel slope, transfer coefficient α and exchange current density j^0 from a Tafel-plot. Assume that for a precise determination, the linear region should span at least 2 orders of magnitude for the current density. In other words, the relation between $\log_{10} [j / \text{A cm}^{-2}]$ and E (or η) should be linear for $j_{\min} < j < j_{\max}$ with $j_{\max} / j_{\min} = 10^2$. The problem is: for fast reactions it is very difficult to circumvent mass transport effects!

Assume that for (anodic) chlorine evolution $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ an approximate exchange current density of $j^0 = 0.5 \cdot 10^{-3} \text{ A cm}^{-2}$ (at Pt, 25°C) has been determined, using impedance spectroscopy. The diffusion constant for Cl^- in aqueous solution is $D = 1.8 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the kinematic viscosity of the electrolyte is $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$.

In order to obtain more information about the kinetics, you want to perform current vs. voltage measurements, i.e. record a voltammogram and then analyze it as a Tafel plot. Different experimental techniques will be compared to each other.

- First, you have to consider the **minimum current density**. Explain why data points with current densities below $j_{\min} \approx 3j^0$ are not useful?
- Now, focus on the **maximum current density**, j_{\max} . Calculate the required value of j_{\max} . Mass transport to the electrode has to be fast enough, such that $j_{\text{diff}} > 3j_{\max}$. Explain this condition.
- Now you can estimate how large j_{diff} should be. Calculate the corresponding **diffusion layer thickness**.
- Assume first, that the measurement had to be performed by **potential step experiments**. You can specify now the maximum allowed time up to which diffusion limitations would be negligible. What do you conclude from the fact that the measurement device has a minimum response time of 1 ms.
- Using a **rotating disc electrode** instead, what would be the angular velocity, required to maintain the diffusion limiting current j_{diff} calculated in c)? What do you conclude from your findings?
- As the last resort, consider a **microelectrode**. Which radius should it have in order to comply with the requirements?