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Charge neutralization process of mobile species developed during potentiodynamic conditions. Part 2: Simulation and fit of probe beam deflection experiments

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ABSTRACT

The theoretical model presented in Part 1 is employed to simulate and fit experimental probe beam deflection (PBD) data of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and Fe^{3+}/Fe^{2+} couples collected under voltammetric conditions. The dependence of beam deviation on the diffusion coefficients and on the charges of involved species is described. The fit of voltammetric curves was performed to get the values for the standard potential of each system as well as diffusion coefficients of electroactive species. The data were then employed to fit a set of experimental voltadeflectometric profiles collected at different beam-electrode distances. The least-squares Simplex algorithm was employed to fit proposed functions to experimental data. The data obtained from the fitted voltadeflectometric curves were consistent with values previously reported for chronodeflectometry profiles, supporting the hypothesis that the refraction index not only should be considered a function of the concentration of the neutral salts dissolved, but also depends on the concentration gradient of each soluble species. The effects of the scan rate and the beam-electrode distance are discussed in detail. In relation to this, simple relationships between these adjustable parameters and the angle of the deflected laser beam are also provided. Thus, it is now possible to perform a quantitative analysis on the response of techniques such as PBD when the heterogeneous charge transfer of electroactive species is studied with a cyclic linear potential scan.

1. Introduction

Electrochemical techniques involve a given sequence of potential (or current) perturbations at an electrode resulting in the spatial structuring of concentration profiles of substrates and products near the electrode. The current is directly related to the gradient of electroactive species at the electrode surface and reflects the rate of electrochemical processes occurring in the immediate vicinity of the electrode. As a result, it can be correlated to the kinetics of the chemical and electrochemical reactions [1]. Nevertheless, such purely electrical measurement lacks molecular specificity, since it only provides some information on the concentration gradients of species that exchange electrons with the electrode. Therefore, the data associated with the mass transport of non-electroactive species need to be assumed or estimated from theoretical works [2,3]. It should be noted that, although most electrochemical experiments require a relatively large amount of a non-electroactive salt to reduce the solution resistance and minimize the migration contribution of the electroactive species [1], it is still difficult to determine how, or rather why, some experimental profiles are affected by the presence of added salt [3–5]. The analysis of the mass transport of electroactive and non-electroactive species by specific and/or non-specific techniques is particularly useful for answering those questions which may account for the several attempts to monitor the species involved when the diffusion layer is developing near an active surface [6–12], into polymeric matrixes [13], above membranes [14,15] or at liquid/liquid interfaces [16,17]. Thus, considerable effort has been devoted to adapting microelectrodes [9,18] and spectroscopic techniques (UV–Vis, IR, EPR, Raman) to probe in situ electrochemical reactions [6,19–21].

There are several in situ techniques that can measure the concentration profile of one or more specific soluble species. In principle, those profiles could also be employed to calculate the concentration gradients produced during electrochemical experiments; however, they mostly lack the required precision or spatial resolution to achieve this. This explains why only interferometry [22] and probe beam deflection [8,23–25] (PBD) have been used to monitor concentration gradients through refractive index gradients. On the other hand, spatially resolved UV-visible spectroelectrochemistry [10,19], confocal enhanced Raman microscopy [6] and

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ultramicroelectrodes [9] were implemented for measuring concentration profiles of different species within the diffusion layer.

Regarding PBD, it is an in situ electrochemical technique applied to study the mass fluxes in front of the electrode/electrolyte interface from which fast and localized measurements of the dynamic behavior of anionic and/or cationic fluxes can be obtained [3,5,8,23–25]. It is based on measuring the deviation angle ($\Theta_{(t,x)}$) of a probe laser beam that crosses a transparent medium with a non-homogeneous index of refraction [8,23–27]. This probe beam is aligned parallel to the electrode surface at a given beam-electrode distance (x). Usually, the PBD technique is performed in aqueous solutions where the dependence of the refractive index (n) on thermal gradients is negligible compared to that on concentration gradients of dissolved species [27]. Thus, the dependence of $\Theta_{(t,x)}$ on the refractive index gradient can be approximated for small deflection angles as

$$\Theta_i^t = \frac{L}{n}\sum_{j=1}^{m}\left(\frac{\partial n}{\partial C_j}\right)\frac{\mathrm{d}C_{j,i}^t}{\mathrm{d}x} \tag{1}$$

where L is the interaction length between the beam and the zone of perturbed index, i and t refer to the finite difference parameters that specify a given space grid point and time level, m corresponds to the total number of soluble species, and n is the refractive index of solution. The parameter $(\partial n/\partial C_j)$ is a constant, usually called concentrative refractivity, that depends on the molecular (or ionic) volume and on the electronic structures of each jth solute [28]. In this sense, the deflection of the probe beam is caused by the contribution of every concentration gradient multiplied by the value of $(\partial n/\partial C_j)$ corresponding to each species in solution [8].

Normally, it is assumed that only those measurements performed in binary (one anion and one cation) electrolytes could be interpreted univocally [5]. However, the diffusion of neutral salts cannot neutralize the charge developed during the redox process [1,4,8]. In Part 1 it has been shown that the concentration gradient of each soluble species can be calculated as a charge neutralization process at a point near the electrode surface [29,30]. These equations are now used to evaluate the variation of the refractive index and the deviation angle of the probe beam at different distances from the electrode surface when the couples $\mathrm{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}}$ and the aqueous species $\mathrm{Fe^{3+}/Fe^{2+}}$ react on a gold electrode under voltammetric conditions.

Those couples are among the most widely used examples of outer sphere redox reactions; however, it is believed that the presence of supporting electrolyte would complicate the analysis of PBD signals. In this work it is shown that there is a relatively simple relationship between the fluxes of every ionic species and the changes of the refraction index of these solutions and that from these characteristics the role of the ions of a given supporting electrolytes can be evaluated [8].

2. Experimental

All solutions were prepared with ultra pure water (18 MΩ cm^{-1}) from a Millipore MilliQ system. Two systems were analyzed, one involving solutions of $\mathrm{K_3Fe(CN)_6}$ (Sigma) in 0.1 M KCl (Merck) at pH 7, and another with $\mathrm{Fe(NO_3)_3}$ (Sigma) and 0.1 M HCl (Merck) at pH 1. All chemical reagents were of analytical grade and used as received.

The electrochemical control of probe beam deflection experiments was performed using a potentiostat (AMEL 2049). The setup was controlled with a PC through an AT-MIO 16E AD/DA card running homemade software performed with LabView 5.1 (national instruments). The software developed was used to generate different kinds of potential scan programs, as well as to measure and save the deflection and electrochemical signals in the PC.

The probe beam deflection arrangement was similar to the one described before [7]. The basic components of the PBD system were a 5 mW He–Ne laser (Melles Griot, 05 LHP11) and a bicell position-sensitive detector (UDT PIN SPOT/2D). All parts of the system were mounted on an optical rail, resting on a stable optical breadboard (Melles Griot). The optical breadboard was resting on a padded table to dampen vibrations. The laser beam was focused by a 50 mm lens to a diameter of roughly 60 μm in front of the planar electrode.

The electrochemical cell, a 2 × 2 cm optical glass cuvette with 2 cm of path length, was mounted on a 3-axis tilt table (Newport). The working electrode was a slide of quartz covered with a sputtered film of gold. This electrode provides an optically flat surface of (0.897 × 3.5) cm and it was used without further treatment. The exposed area was measured with a relatively big error $A = (1.8 \pm 0.1)\ \mathrm{cm}^2$, but the interaction length between the beam and the zone of perturbed index was determined with good precision $L = (0.897 \pm 0.005)$ cm. A coiled Pt wire was the counter electrode and all potentials of experimental data are referred to a $\mathrm{Ag|AgCl|Cl^-}$ (3 M) reference electrode. The counter and the reference electrodes are situated facing the working electrode, outside the path of the beam.

A micrometric translation stage allowed controlling the positioning of the sample with respect to the laser beam in 10 μm steps. The position sensitive detector was placed 25 cm behind the electrochemical cell and had a sensitivity of 3 mV/μm, giving a deflection sensitivity of 1 mrad/V. The signal of the two photodiodes, which made the bicell detector, was subtracted and normalized to the overall signal in order to minimize the effect of laser intensity fluctuations.

The scans correspond to cyclic staircase voltammetry with potential steps of 1 mV. The frequency of these steps is given by the scan rate (v) of the experiment. A conditioning potential (E_{ini}) was applied during a given time (t_{ini}) to ensure stationary state before each potential scan. Usually, values of $t_{\mathrm{ini}} > 5$ min were required to avoid effects that could be associated with natural convection. In this regard, the potentiostat and PC were placed on a separate table to reduce their contribution to vibrations of the electrochemical cell. Moreover, most of the measurements were performed during the night to minimize the environmental noise.

The simulations and fits of curves were performed using a visual FORTRAN 6.0 software package.

2.1. Application of the model to fit probe beam deflection data

To evaluate the model presented in Part 1, theoretical curves were employed to fit experimental cyclic voltametric and voltadeflectometric profiles. It is well known that the concentration gradients of redox species at $x = 0$ are directly related to the current. Because of this, it is possible to obtain data on the diffusion and migration properties of redox species from the analysis of current. To achieve this, the so-called Simplex algorithm has been implemented to fit experimental voltammograms with theoretical curves developed from Eq. 25 of Part 1 [31,32]. These fits provided some parameters such as the diffusion coefficients of redox species and the standard potential of the electrochemical reaction, which are required further to fit PBD curves. For the implementation of the Simplex, it is considered that the N variables to fit define the N dimensions of a hypothetical figure of $N + 1$ vertices, and the program calculates how close the theoretical equation is to the ‘figure’ related to measured data. This is performed by the following equation of least squares:

$$\chi^2 = \sum_{i=1}^{\Omega}\left(\mathrm{Data_{exp}} - \mathrm{Data_{theo}}\right)^2 \tag{2}$$