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Voltammetric studies of colloidal particle monolayer on a gold rotating disk electrode

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ABSTRACT

Adsorption of colloidal particles at a solid/liquid interface leads to a spontaneous formation of a porous structure, which may have a strong effect on the ion transport from the bulk solution to the adsorption surface. This effect can be investigated by employing the cyclic voltammetry and rotating disk electrode techniques. We used the cyclic voltammetry method to characterize monolayers of 1 μm sulfate polystyrene particles. We conducted measurements of the limiting diffusion current in a 1 mM solution of potassium hexacyanoferrate(III) at various rotational speeds of the disk. Before each experiment the gold rotating disk electrode was carefully prepared by mechanical polishing to obtain a smooth, clear, and reproducible gold surface. The state of the gold surface was then examined using optical microscopy, atomic force microscopy and cyclic voltammetry measurements. We used a diffusion cell for particle deposition under barrierless conditions. We demonstrated a good agreement between the experimental results and theoretically predicted limiting diffusion current at medium and high surface coverages of the rotating disk electrode. Our results suggest that the voltammetric method can be used for the characterization of monolayer thickness and porosity, as well as for the determination of surface concentration of deposited colloidal particles.

1. Introduction

Adsorption and deposition (irreversible adsorption) of colloids and bioparticles at solid/liquid interfaces are of great significance in many processes, such as water and wastewater filtration, membrane filtration, papermaking, flotation, protein and cell separation, enzyme immobilization, biofouling of membranes, and artificial organ implantation. To better control these phenomena, we need to understand the underlying mechanism of adsorption, especially under intense flows occurring in living and practical systems.

Numerous experimental techniques have been developed to study particle deposition. A convenient, well established method for determination of particle adsorption under well-defined flow conditions is the use of the rotating disk. Its major advantage is the constant diffusion boundary layer thickness. A disadvantage is that the disk moves during an experiment, which makes it very hard to directly observe the deposition process [1,2]. For that reason, Dąbroś and van de Ven developed the experimental technique using the stagnation point flow cell with radial symmetry [3]. However, a disadvantage of such cells is that the effective observation area is rather limited, usually much smaller than the cross-section of the capillary tube used for creating the flow [4,5]. To overcome this limitation, Adamczyk et al. developed the slot impinging jet cell [6]. By using such a cell, both the adsorption kinetics and particle distribution over the collector surface (pair-correlation function) can be measured directly for various flow conditions and other well-defined physicochemical parameters [6,7]. The parallel-plate flow cell is another widely used technique for particle adsorption experiments [8–10]. Under no-convection conditions, a number of researchers have used the diffusion cell in particle deposition experiments [11,12]. All these cells and methods have been used in studies of particle adsorption at homogeneous substrates [13].

In the last decade, many of experimental and theoretical studies on colloidal particle adsorption have also been carried out for surfaces modified by adsorption of polymers, surfactants, polyvalent ions, or chemical coupling agents (silanes), which change the natural surface charge of substrate surfaces [4,5,14–18]. In these systems adsorption occurs at heterogeneous surfaces bearing isolated adsorption sites. Recently, multilayer deposition of colloidal particles has also been studied both theoretically [19] and experimentally [20].

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The standard method for detection of adsorbed particle layers is optical microscopy. In the case of particles below 300 nm in diameter the deposited layer cannot be characterized by means of optical microscopy and we have to use other techniques, such as the quartz crystal microbalance, ellipsometry, reflectometry, fluorescence methods, or isotope labeling.

Adsorption of colloidal particles at a solid/liquid interface leads to a spontaneous formation of a porous layer, which may have a noticeable effect on the ion transport from the bulk solution to the adsorption surface. This phenomenon can be studied using the cyclic voltammetry (CV) method with the rotating disk electrode (RDE). CV has a solid theoretical basis and extensive applications. This experimental method can be useful in the analysis of solids as well as solutions, media with and without added supporting electrolyte, emulsions and suspensions, frozen solutions, polymers, membrane and liquid/liquid systems, and biological systems like enzymes or cultures of bacteria [21]. It is also used to determine the permeability of polymeric and polyelectrolyte films for electroactive molecules [22–24]. The ion transport in the RDE system was first described by Levich, and it has been well understood [25]. His theoretical analysis was further extended to membrane-covered RDEs. The first research on this subject was published by Gough and Leypoldt in 1979. They also developed a mathematical model of the system and compared the model-predicted and experimental results of the mass transport through a homogenous gel membrane covering the RDE [26]. The CV method with the RDE has several important advantages. The disk surface is equally accessible to the reactant and the diffusion boundary layer thickness is precisely determined. At low rotational speed of the disk the diffusion boundary layer is relatively thick and the major contribution to the total diffusion resistance is the transport through the solution. Under these conditions, even when the RDE is covered with a membrane, the limiting diffusion current is proportional to the square root of rotation rate. At high rotational speed, the thickness of the diffusion boundary layer is small, the resistance of the electrolyte solution is negligible, and the diffusion current is determined largely by the properties of the membrane which covers the disk. In this way, the CV with the RDE can be used to evaluate quantitatively the mass transport through a membrane or other thin films [26].

Because of a major practical significance of particle adsorption, this phenomenon has been extensively studied both theoretically and experimentally. However, to our knowledge, no results have been reported in the literature for the important case of the ion transport through layers of colloidal particles. Therefore, the objective of this work is to compare experimental and theoretical results of the limiting diffusion current for a bare gold rotating disk electrode and for the electrode with a monolayer of 1 μm latex particles at medium and high surface coverages. We report on the limiting diffusion current measured using cyclic voltammetry with the gold rotating disk electrode (Au RDE) in a solution of potassium hexacyanoferrate(III) at various rotational speeds of the electrode. In this paper we concentrate on the ion transport through monolayers of colloidal particles, while the transport through multilayers will be a subject of our future research.

2. Theoretical model

We can derive the equation for the limiting diffusion current at the RDE with a layer of particles from the model developed by Gough and Leypoldt [26]. They considered steady-state mass transfer of a solute that was consumed at the surface of the RDE covered by a homogenous gel membrane of the thickness δ_m. Using the method of Levich [25] and assuming no convective flow within the membrane they found that in the case of membrane-covered RDE, the diffusion current I can be described by the equation [26]

$$I = I_L\left(1 + \frac{DC\delta_m}{D_m C_m \delta_d}\right)^{-1}. \tag{1}$$

Here I_L is the current in the absence of the membrane, which was described by Levich [25]

$$I_L = 0.62nFSD^{2/3}\omega^{1/2}\nu^{-1/6}C_b, \tag{2}$$

where n is the number of electrons transferred during half-reaction, F is the Faraday constant, S is the surface area of the electrode, $\omega = \pi f/30$ is the angular frequency of the disk, where f is the number of rotations per minute, ν is the kinetic viscosity, and C_b is the bulk solute concentration; D and D_m are the ion diffusion coefficients in solution and in the membrane, respectively; C and C_m are the solute concentrations at the membrane-solution interface in solution and in the membrane, respectively; and $\delta_d = 1.61D^{1/3}\omega^{-1/2}\nu^{1/6}$ is the thickness of the diffusion boundary layer.

In our system the RDE has been covered by a porous layer of spherical particles instead of a homogeneous gel membrane. In this paper we approximate the layer by a homogeneous porous layer of the thickness $\delta_m = 2r$, where r is the particle radius, and of the constant porosity

$$\varepsilon = \frac{V_\nu}{V_m} = \frac{S\delta_m - N(4/3)\pi r^3}{S\delta_m} = 1 - \frac{2}{3}\theta. \tag{3}$$

Here $V_m = S\delta_m$ is the superficial volume of the porous layer, $V_\nu = V_m - V_p$ is the volume of the voids, where $V_p = (4/3)\pi N r^3$ is the volume of the particles, N is the number of adsorbed particles, $\theta = NS_p/S$ is the surface coverage, and $S_p = \pi r^2$ is the particle cross-section area.

Considering that flow penetrates the porous medium only when its solid volume fraction $\varphi = (V_s/V_m) = (2/3)\theta$ is less than 0.1 [27], we can neglect the convective flow within the particle layer if the surface coverage $\theta > 0.15$. If this assumption is fulfilled, we can calculate the limiting diffusion current using Eq. (1), with C_m representing the *superficial* solute concentration in the porous layer at the layer-solution interface, and D_m representing the effective diffusion coefficient in the porous layer.

The solute concentration is continuous everywhere in the *liquid phase* of our system, therefore at the layer-solution interface

$$C_m = C\frac{V_\nu}{V_m} = \varepsilon C. \tag{4}$$

The effective diffusion coefficient in porous media is equal [28]

$$D_m = \frac{D\varepsilon\delta}{\tau}, \tag{5}$$

where δ and τ are the constrictivity and tortuosity, respectively. In the case of colloidal porous materials and molecular solutes, when the average pore size is much larger than the size of solute molecules, this equation can be simplified by substituting $\delta = 1$. For the simple geometry of spherical particle layer, we can calculate the tortuosity using the method of Lanfrey et al. [29], as the average ratio of the actual path length and the straight line trajectory of the solute molecule. For a specific path of solute molecule, this ratio can be calculated from the formula

$$\tau_s = \begin{cases} \dfrac{r + \beta r + r - y}{2r} = \dfrac{1}{2}(2 - \sin\beta + \beta) & \text{at the particles} \\ 1 & \text{at the bare surface} \end{cases}$$

where the variables are defined in Fig. 1.