



Time-resolved impact electrochemistry - A new method to determine diffusion coefficients of ions in solution

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ARTICLE INFO

Article history:

Received 16 February 2018
Received in revised form
2 June 2018
Accepted 2 June 2018

Keywords:

Nano impact electrochemistry
Diffusion coefficient
Temperature
Viscosity
Single entity

ABSTRACT

Diffusion is often the rate-limiting factor of reactions in condensed phase. Thus, knowing the diffusion coefficient is key in numerous aspects ranging from drug release to steering of reactions in both homogeneous liquid phase and electrochemical reactions. Cyclic voltammetry at macro electrodes and chronoamperometry at micro electrodes are well-established methods to determine the diffusion coefficients of redox-active species dissolved in a solution. However, if the formal potentials of the redox species are outside of the potential window of the solvent, then these methods cannot be readily applied. Here we demonstrate a new concept to determine the diffusion coefficient of ions to overcome this limitation. We use their reaction with a well-defined amount of a redox-active indicator substance, which is confined in a nanoparticle suspended in a solution containing the species of interest. Employing transformative nanoparticle impact analysis, the diffusion-limited reaction of an indicator nanoparticle with the species of interest is initiated and followed by chronoamperometry. Measuring the time it takes to fully convert the indicator particle enables the determination of the diffusion coefficient of interest. This concept is demonstrated for variety of (pseudo-)halides in aqueous solution using Ag nanoparticles as redox indicator. Using chloride as an example, it is further shown that this new methodology can be applied to study effects of temperature and viscosity on the diffusion coefficients. Given the multitude of nanoparticles that may serve as electrochemical redox indicator, this approach can be used to determine the diffusion coefficients for a large variety of species in different liquid environments.

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1. Introduction

For the majority of chemical reactions, diffusion of molecules or ions, together with the kinetic rate constant of the reactions, governs the reaction rate. The mass transfer aspect is particularly important for reaction in the liquid-phase or at solid/liquid interfaces, where diffusion is typically in the order of $10^{-9} \text{ m}^2 \text{ s}^{-1}$, and hence much slower than in the gas phase. Diffusion coefficients are not only crucially affecting chemical reactions, in terms of reaction speed and selectivity [1,2], they are also important in the pharmaceutical field for the determination of drug release rates [3,4], or the investigation of reaction kinetics involving diffusing redox shuttles [5], and the effect of molecular structures on diffusion coefficients of drugs [6,7]. Furthermore, it has been shown that diffusive mixing of the reactants strongly affects the reaction rates

within microfluidic devices [8,9]. Hence, for decades, researchers have been developing and improving techniques to determine liquid phase diffusion coefficients (D) based on very different principles. For optically active or fluorescent species, microfluidics device coupled with laser-induced fluorescence detection was developed to measure the diffusion coefficient [10]. Pulsed field gradient spin echo [11,12], first developed by Stejskal et al. enabled the possibility of determination of D using nuclear magnetic resonance.

Electrochemistry provides more affordable and more easily accessible methods to measure D in solutions, based on chronoamperometry at microdisk electrodes in aqueous solutions [13–17] or in ionic liquids [18,19] and cyclic voltammetry at rotating disk macro electrodes [2]. More recently, with the rapid advancements in the field of microfluidics [20], the determination of D by measuring the time of a redox species diffusing between interdigitated micro array electrodes [21] has been suggested for this purpose. This, innovative approach, however, involves more elaborate fabrication steps than the preparation of a micro or macro

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disk electrode.

The biggest limitation of these electrochemical methods is that a high-enough overpotential is needed for the redox species of interest to react under mass transfer control and this must fall within the electrochemical potential window of the solvent. Furthermore, the by-products of the redox reaction must not block the working electrode and migration and natural convection must be eliminated during the timescale of the experiment. Both boundary conditions are challenging. The addition of large amounts of supporting electrolytes to suppress migration may alter the activity coefficients of the species under investigation, for instance due to ion pairing. Hence, its thermodynamically accessible concentration is decreased, which complicates the determination of correct D values. At the same time local density [22,23] or temperature [24] changes caused by the electrochemical reaction itself may be inevitable at the usual experimental times of tens of seconds [22,25]. Practically it is also difficult to achieve a very smooth and well-defined electrode surface which is essential for the established electrochemical techniques and further limits their applicability [26]. Grooves and pits left by mechanical polishing, as well as microscopic disorders such as kinks and steps on electrode surface can all interfere with electrochemical measurements [27].

Our strategy for determination of diffusion coefficients, is to make the species of interest react with an *indicator* nanoparticle (NP) during electrochemical transformative impact analysis (TIA) [28–31]. Thus, the potential at which the ions under investigation react under diffusion control can be tune by selection of the NP material.

In this new approach, the chosen indicator NPs are suspended in a solution of species of interest, a micro electrode is then dipped into the suspended NPs and potentiostated to a certain potential. Due to the stochastic motion of the NPs, they sporadically impact the electrode and are polarized to this potential. This triggers the mass transport-limited reaction with the diffusing species of interest, which is dissolved in the surrounding electrolyte as shown schematically in Fig. 1. Recent studies have shown that TIA is a powerful tool to size various types of NPs by measuring the electric

charge that passes through the working electrode when the whole single NP reacts [32–34]. Works by Kanoufi et al. [35] and Unwin et al. [36], in which scanning electrochemical microscopy is employed, are two excellent examples for other indirect reaction-time based techniques to determine reaction kinetics or diffusion coefficients of species.

By using TIA, we are able to overcome those previously mentioned limitations in determination of diffusion coefficients of ions or molecules in solution. With this approach, the formal potential and reaction kinetics of the indicator reactions are not constricted by the diffusing species to be studied, but fixed via the choice of reacting indicator NP, which comes with great variety and provides more flexibility than the existing methods. If the applied overpotential is high enough, this NP-transformation is not limited by reaction kinetics, but only by the diffusion of the species of interest to the reacting NP. While in conventional NP ensemble studies, diffusion layers of the diffusing species merge, the reaction at a *single* NP guarantees well-defined mass transport. The mass transfer at such single nano entities can be described by analytical expressions and becomes stationary almost instantaneously [37–39]. As recently demonstrated [37], the time for a TIA event fully converting the impacting NP to a sparingly soluble compound, depends on the diffusion coefficient of the species diffusing to the NP. Here we advance from this observation and the work by Krause et al. [40], who used TIA to study the dependence of NP reaction time on the concentration of the diffusing ions. We demonstrate that by measuring the duration of the TIA event (i.e. the “spike duration”), the diffusion coefficient of ions in solution can be determined.

Notably, the double layer of the micro electrode and the total ion/molecule concentration in the vicinity of the electrode remains effectively unperturbed thanks to the ultra-small total number of the probed species reacting (typically in the order of attomoles) [41]. This allows us to omit electrostatic effects, and, hence, migration, even at low concentrations of supporting electrolyte of few tens of millimolar [41]. It also enables the study of multiple successive events to ensure excellent statistics of the data obtained. As the time scale for each transformative nano impact is shrunk to a few milliseconds or less, natural convection is effectively suppressed in this approach [31,42].

As a proof of concept, herein the diffusion coefficients of different anions in aqueous solutions are measured by diffusion-limited TIA. Five different electrolytes are used for that: KCl, NaCl, NaBr, NaI and NaSCN and 29 nm diameter silver nanoparticles were used as indicator substance. The size of the indicator particle was chosen to be large enough to produce an impact spike that can easily be distinguished from the noise, but small enough to ensure full conversion of the particle instead of partial oxidation. To further demonstrate the general applicability of this powerful method to also quantify temperature and viscosity effects on diffusion coefficients, the influence of these parameters on the diffusion of Cl^- was measured in addition. The obtained diffusion coefficients are compared to literature values to validate this newly developed analytical methodology.

2. Experimental

2.1. Nanoparticle preparation and characterization

The citrate-capped AgNPs employed in the measurements were synthesized according to a modified Lee-Meisel synthesis, optimized for size control by Gu et al. [43]. The detailed synthesis procedure is described in the supporting information (SI 1.1). Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) and UV–Vis spectroscopy were employed to confirm the size

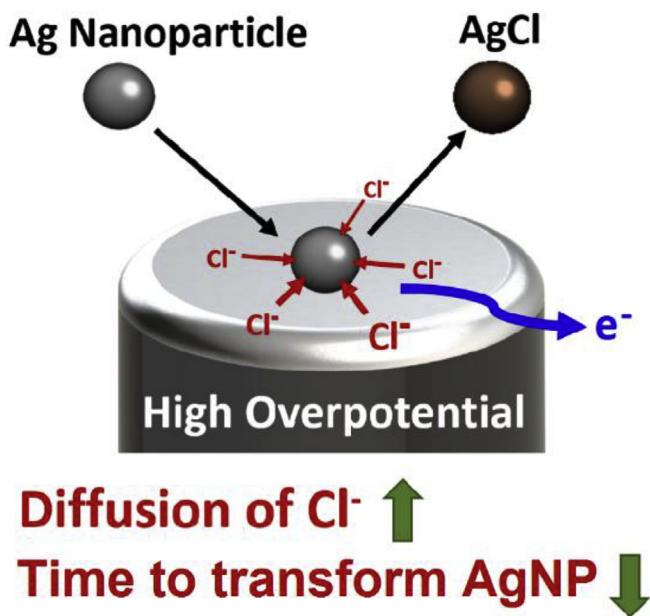


Fig. 1. Schematic of a silver NP impacting a potentiostated electrode and being oxidized to silver chloride. At high overpotential, the duration of the reaction is limited by mass transport of chloride to the reacting silver NP.

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