



Voltammetric Investigation of Host–Guest Systems in the Absence of a Supporting Electrolyte

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Abstract. In the classic voltammetric approach to host–guest systems the investigations are carried out in excess of a supporting electrolyte, i.e., an inactive ionic salt. This approach ensures high electric conductivity of solution and ion migration is avoided. However, the presence of supporting electrolyte may introduce competitive equilibria and change activity coefficients, influencing the equilibrium constants using ultramicroelectrodes. Host–guest systems can be studied without addition of supporting electrolyte. Under such conditions, the interpretation of experimental results requires a theoretical description that accounts for migrational transport. Such a description is presented in this paper which also shows that migrational effects are so small that they can be neglected for some systems.

Key words: voltammetry of host–guest systems, supporting electrolyte, digital simulation, migration

1. Introduction

Voltammetry is a technique of choice for studies of redox properties of supramolecular complexes. It can also be used to study interactions and homogeneous equilibria between the host and guest molecules or ions, if at least one of them is electroactive. Electrochemical methods are particularly useful for studies of redox-switchable systems, where the binding strength significantly changes as the result of oxidation or reduction of the host molecule or ion. In a traditional approach, the voltammetric investigations have to be carried out in solution of a supporting electrolyte, i.e., in excess of ionic salt that does not participate in an electrode process. The supporting electrolyte ensures that electric conductivity of the solution is sufficiently high, so that diffusional transport predominates, while migration is negligible. The latter effect allows us to simplify the quantitative description of the electrode processes.

However, the presence of a supporting electrolyte may affect the investigated equilibria. That is, its presence may change activity coefficients of ions and, therefore, influence the equilibrium constants even though the concentrated electrolyte does not interact with the host and/or guest molecules. Moreover, comparison of

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the electrochemical results with other results (e.g., spectroscopic) may suffer from the fact that the properties of the compounds are measured under different solution conditions. There are cases for which the excess of supporting electrolyte cannot be even attained. One such case is related to the solubility problem. It is, for example, difficult to carry out measurements for solvents of low polarity, in which the solubility of ionic salts is low and their dissociation is impeded.

In the absence of a supporting electrolyte, two main effects may be encountered: high resistivity of the solution and the superposition of diffusional and migrational transport of ions. The first effect can be eliminated by using ultramicroelectrodes [1, 2] which are very well suited for measurements in resistive media and have been routinely applied for such systems.

The presence of the migrational transport component requires special treatment of the experimental data. In classic experiments, the current flowing through the electrode results from the diffusional transport of the reactant. So, the current density depends only on the concentration and diffusivity of the substrate, and the number of exchanged electrons, but it does not depend on the charge of the reactant. The situation is different in the absence of supporting electrolyte where both the substrate and product of the electrode reaction are exposed to the unscreened electric field. The transport of different ions toward the electrode surface is influenced in a different manner depending on the ion charge and the direction of the field. That is, transport of some ions is retarded while that of others is accelerated. In this way, the observed currents become dependent on the charge of the reactant. Thanks to this feature, an electrode process can be investigated in a very unique way in which, for example, the charge of the reaction products or intermediates can be identified, or rates of chemical reactions in solution can be measured. For that purpose, a theory describing mixed diffusional-migrational transport is needed. In recent years, this type of transport in other systems was described in a number of papers. So, the fundamentals of voltammetry without a supporting electrolyte are available [3–9].

In the present paper, we focus on voltammetric determination of the stability of supramolecular complexes. Our studies were carried out without a supporting electrolyte. We briefly present a theoretical basis of the experiments, followed by conclusions regarding the experimental work.

2. Theory

Due to their different behaviour under voltammetric conditions, two types of complexes are distinguished: labile (fast ligand exchange) and inert (very slow ligand exchange). In the first case, the main source of information on complex formation is the variation of the redox potential, in the second the change in the observed voltammetric currents. The labile and inert complex case will be discussed here separately because migrational phenomena influence the electrode potential and the currents in different manners.

2.1. LABILE COMPLEXES

In the complex formation, particularly in the case of formation of supramolecular complexes that exhibit redox activities, the complex stability constants at various oxidation levels are very important parameters. Values of these stability constants are essential in studies of, for instance, switchable receptors. The method often employed is a determination of the ratio of two complex stability constants from the shift of the voltammetric reduction or oxidation peak potential of the host system. Knowing one of these constants from other independent experiments (e.g., spectroscopic), one is able to calculate individual complex stability constants for oxidized and reduced forms of the complex. For this purpose, the equation

$$\Delta E_p = \frac{RT}{nF} \ln \left(\frac{1 + \sum_{i=1}^n K_{\text{ox},i} [L]^i}{1 + \sum_{i=1}^n K_{\text{red},i} [L]^i} \right) \quad (1)$$

is often used, provided that the electrode reaction is reversible and the complex is labile, i.e., the ligand exchange rate is large as compared to the time scale of the voltammetric experiment. If ox and red each form only one complex with a ligand, L , and that both $K_{\text{ox},1}[L] \geq 1$ and $K_{\text{red},1}[L] \geq 1$ then Equation (1) can be simplified to the form $\Delta E_p = (RT/nF) \ln(K_2/K_1)$.

In the absence of a supporting electrolyte, migration leads to changes in both the halfwave and peak potentials. The magnitude of this effect depends, in a rather complicated way, on the concentrations of all ionic substances present in the solution. However, with the increase of ion concentration the migrational effects gradually decrease. In the studies of complex formation, the presence of an ionic guest has the same effect as the presence of a supporting electrolyte of the corresponding concentration if, e.g., the host is electroactive. From a practical point of view, it is important to know, how large the migrational effects are and whether or not they can be neglected. Besides, it is also possible that the migrational effects could be used for identification of charges of the species involved in the electrode reaction. For such applications, it would be desirable that migrational effects are as large as possible in order to facilitate the interpretation of migrational experiments.

2.2. INERT COMPLEXES

If the studied complexes are inert, i.e., the ligand exchange rate is very slow as compared to the experiment time, all chemical equilibria are "frozen" and the rate of chemical reactions do not play any role during the experiment. For conventional voltammograms, i.e., in excess of supporting electrolyte, the variation of the peak height that is observed is directly proportional to the change of uncomplexed fraction of the electroactive species caused by the change of the host–guest molar ratio. If the concentration of the complexed fraction, combined with the total concentration balances of host and guest, is known, then the complex stability constant can be calculated.

However, in the absence of a supporting electrolyte direct proportionality between the current and the reactant concentration is not obeyed. Therefore, an adequate theory accounting for migrational effects is needed in order to determine the complex stability constant.

Calculation of the voltammetric signals at a deficiency of supporting electrolyte in order to determine the influence of migration on parameters determined at deficiency of supporting electrolyte, the equation describing migrational-diffusional transport, i.e., the Nernst–Planck equation has to be solved:

$$f = -D \left[\frac{\partial c}{\partial x} - zc \frac{F}{RT} \frac{\partial \phi}{\partial x} \right], \quad (2)$$

where f is the flux, D , diffusion coefficient, c , concentration, z , ion charge, ϕ , electric field, F , Faraday's constant, R , universal gas constant, and T , temperature. From our point of view, it is important that the system of Nernst–Planck equations written for a set of compounds involved in the chemical equilibrium is nonlinear and, therefore, more advanced mathematical techniques are required to solve it. In the papers where voltammetric systems are described by the Nernst–Planck equation, the explicit techniques of Feldberg's type (e.g., [6]) or variations of the Crank–Nicolson approach (e.g., [10]) are applied to solve the equation. Recently, a very promising Fast Implicit Finite Difference (FIFD) algorithm has been developed and shown to be applicable also to diffusion-migration systems [11, 12].

Important advantages of this technique consist of its extraordinary stability and the possibility of encapsulation of the computational procedures in such a form that the user can carry out the modelling of voltammetric responses without the need of an extensive knowledge of the underlying calculation algorithms. Therefore, we chose the FIFD algorithm for processing of voltammetric data for the host–guest systems.

For practical reasons, the calculations were carried out for hemispherical electrodes. However, the obtained parameters should be the same both for the hemispherical and disk electrode under the assumption that the observed system is electrochemically reversible. The values of current at hemispherical electrodes should be multiplied by a geometrical factor $2/\pi$ in order to get currents that would be observed at disk ultramicroelectrodes [13].

3. Results and Discussion

3.1. SIMULATED RESPONSES OF LABILE COMPLEXES

We have chosen a system in which the reactions can be presented with the following scheme



where

$$K_1 = [FM^+]/[F][M^+]$$

and

$$K_2 = [FM^{2+}]/[F^+][M^+] \tag{4}$$

are respective complex stability constants.

This system is often found for cation-binding molecules that have a redox-active ferrocene unit in it. The host molecule, F , is neutral, and, at the electrode, it is oxidized to a cation. The metal cation, M^+ , does not participate in the electrode process, nor do both complexes, FM^+ and FM^{2+} .

At ultramicroelectrodes, all measurements are usually performed under steady-state conditions that are established in a fraction of a second. A typical steady-state response is wave-shaped and the halfwave potential, $E_{1/2}$, and limiting current, I_{lim} are its characteristic parameters. The shift of the halfwave potential corresponds to the shift of the polarographic $E_{1/2}$ or the voltammetric peak potential at the conventional size electrodes. The differences between the potentials observed in the presence and in the absence of supporting electrolyte are shown in Figure 1. The following systems were considered: $\bar{K}_1 = \bar{K}_2 = 0$ (no complexation at all), $\bar{K}_1 = 10$, $\bar{K}_2 = 0$; $\bar{K}_1 = 10$, $\bar{K}_2 = 1$, $\bar{K}_1 = 100$, $\bar{K}_2 = 10$. The first system should be treated as a reference one. All data were simulated for a 1 : 1 mole mixture of host and guest. The complex stability constant \bar{K} is a dimensionless constant, defined as $\bar{K} = K \cdot c_{host}$. Therefore the results for $\bar{K} = 10$ apply equally well to the situation where $K = 10^4$ and $c_{host} = 10^{-3}$ M as well as $K = 10^3$ and $c_{host} = 10^{-2}$ M.

Noticeably, the differences between the $E_{1/2}$ potentials that would be observed with and without supporting electrolyte are fairly small and are quite often of the order of experimental errors. This small difference should not be surprising because the ionic guest and its counter ion also play a side-role as a supporting electrolyte for the electroactive host. Moreover, the host is a neutral molecule, so the migration influences only transport of the ionic oxidation product. Therefore, the ion concentration in the system is significant and migrational effects are weak although no supporting electrolyte is intentionally added. If one carries out a similar experiment, but with an, e.g., 5-fold excess of the guest instead of the 1 : 1 ratio, the migrational effects would be even more decreased and the difference between peak potentials determined at conventional electrodes and halfwave potentials determined at the ultramicroelectrode would be even smaller. Therefore, we can conclude that the removal of supporting electrolyte has no dramatic effect in the considered systems.

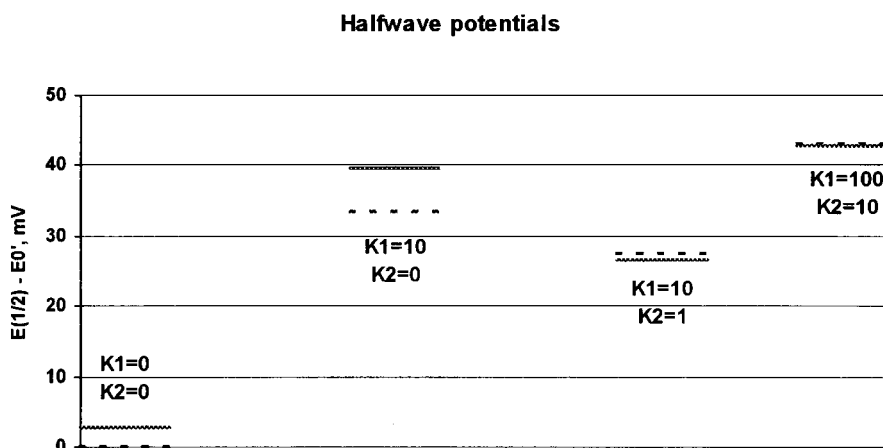


Figure 1. Simulated halfwave potentials for labile complex systems, of different \bar{K}_1 and \bar{K}_2 constants (note that all constants in the figure are dimensionless). (—) no supporting electrolyte added; (---) conventional voltammograms in excess of supporting electrolyte.

Although the systems obeying the reaction scheme (3) and (4) are probably the most frequently encountered systems in host–guest chemistry, other systems may behave differently. The complete analysis of the labile host–guest systems and its validation are under progress in our laboratory.

An important experimental detail worth mentioning here is how to measure the halfwave potential. In a cell with no supporting electrolyte added to the test solution, a typical reference electrode (e.g., silver/silver chloride or calomel) is inappropriate, because it is filled with concentrated electrolyte that may contaminate the solution. Therefore, either specially designed leak-proof electrodes should be used or a non-ionic redox system (e.g., ferrocene) should be added to the cell as an internal standard of potentials.

3.2. SIMULATED RESPONSES OF INERT COMPLEXES

In the case of inert complexes, the height of the voltammetric wave recorded at the ultramicroelectrode decreases with the increase of the concentration of the second component of the host-guest pair. The halfwave potential does not change. The reason for this behaviour is that only the uncomplexed fraction of the substrate is available for the electrode reaction; the chemical process is so slow that conversion of the complex to free components is negligibly small during the experiment.

Such systems have been already examined [14]. Figure 2 shows an example where the host was 1,4,8,11-tetraazacyclotetradecane (cyclam), and the Eu^{3+} cation served as a guest. The electrode process was the reduction of Eu^{3+} to Eu^{2+} and the height of the wave corresponds to the uncomplexed fraction of Eu^{3+} . The oxidation wave at positive potentials corresponds to the oxidation of ferrocene,

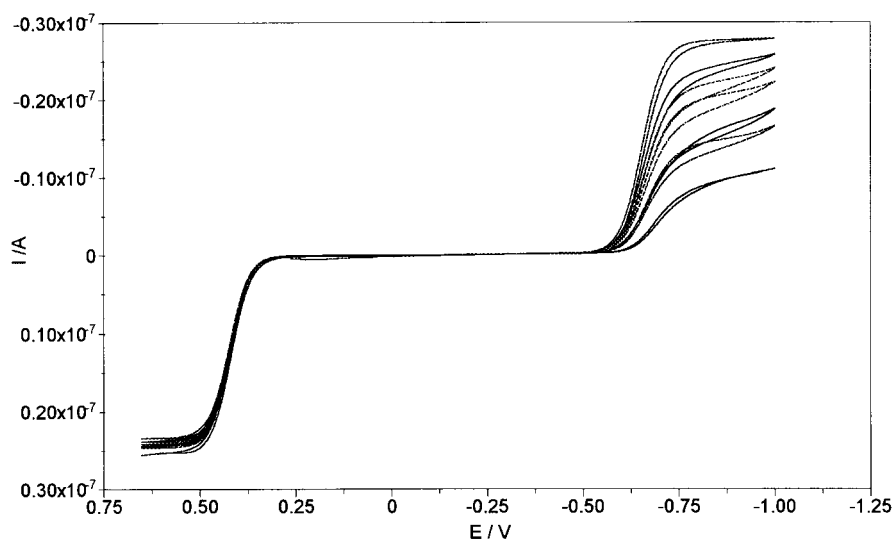


Figure 2. Cyclic voltammograms of an inert complex formed after addition of cyclam to the Eu^{3+} solution. Gold ultramicroelectrode ($38 \mu\text{m}$ diameter); no supporting electrolyte; 4 : 1 (v/v) mixture of methanol and DMSO; Eu^{III} $5.28 \times 10^{-3} \text{ M}$; scan rate 0.01 V/s . The waves at positive potentials correspond to the oxidation of ferrocene which is used as an internal standard of potentials.

that was utilized as the internal standard of potentials. It was shown [14], that the values determined in the presence and in the absence of supporting electrolyte agree very well with each other, the difference being approximately 0.1 of the $\log K$ unit. Importantly, it was possible to carry out fitting of the measured data to the on-line simulated voltammogram under diffusion-migration conditions by using a computer program that could be used as a “black box”.

4. Conclusions

The presented calculations for labile supramolecular complexes and the existing experimental results for inert complexes show that voltammetric determination of complex stability constants without supporting electrolyte is feasible. For the labile complexes considered the difference in potentials determined in excess of supporting electrolyte (diffusion control) and in its absence (diffusion-migration control) are very close to each other, indicating that migrational phenomena could be neglected. Still, the necessary calculation procedures can be included in a computer program that does not require significant computational skills if the results are to be processed with the migration taken into account.

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