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Rate Constants and the Limiting Diffusion Flux for Reactions on Microelectrodes

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We present a new theory for rates of diffusion-controlled reactions on small electrodes in binary electrolytes. The theory reproduces the results of conventional theory for macroelectrodes and for microelectrodes with small electrode–ion interaction (as would apply for macroelectrodes) as compared to ion–ion interactions while allowing extension beyond this traditional macroelectrode regime. It predicts a new dependence of the limiting current on the parameters of the electrode and of the environment when the electrode–ion interaction is large.

1. Introduction

During the last decade, microelectrodes have become a popular tool in studies of fast electrode kinetics. The continuous monitoring of chemical parameters, usually the concentration of chemical species, is gaining increasing attention in chemical production and environmental and medicinal science. Microelectrodes offer new possibilities in most applications where voltammetric and amperometric electrodes are employed. They also widen the area of applications into those demanding high sweep rates, low potential drops, low capacitance, and minimized influence from redox-active surface adsorbents.^{1–3} Microelectrodes can be used successfully in corrosion control and monitoring of different industrial processes such as processes in heat exchangers, engines, and cracking tubes.

For the interpretation of microsensor data, it is very important to determine “scaling down”⁴ laws which govern the dependence of the sensor response (electrical current) on the parameters of a chemical environment and on the sensor scale size. The size of microsensors, R , varies in wide limits from 10 \AA to 10^5 \AA , and the simple attempt to use the scaling laws, i.e., the dependence of the current on the physical size scale, R , defined for “macro”electrodes is not valid for several physical reasons. Among these are the following: (1) For small electrosensors, the width of the diffuse and compact layers is not small compared to R and fluctuation of electrical fields and ion concentrations become important.⁵ The results of the conventional theory of the screening of small nonreacting particles in electrolytes are not valid for microsensors because the screening effects are changed by the reaction on the microelectrode surface, since it reduces the feedback flux of A from the sensor as compared to the flux of the positive ions from the surface of the negative ion in the system without the reaction.

One of the most important results of the theory of diffusion-controlled reactions is the Smoluchowsky effective reaction rate constant for the diffusion-limited bimolecular reactions of the particles without long-range interaction

$$k_s = 4\pi RD \quad (1)$$

where R is the reaction radius. (R is equal to the sum of the radii of reacting particles. For microsensor reactions, it equals the sum of the reacting ion radius and the sensor radius). D is the sum of the diffusion coefficients for the reacting particles.⁶

This result, and a similar one for effectively two-dimensional systems, have been derived for microelectrode theory⁷ by Szabo. In ref 8, these results are extended and mutual sensor influence in arrays of microsensors is studied. For reactions of charged particles with macroelectrodes in binary electrolytes (solutions without inert buffer electrolyte), a similar result (which differs only by the numerical factor 2) can be obtained by standard methods.⁹ The additional multiplier arises since the anion–cation electrostatic attraction leads to effective local electroneutrality of the solution, and therefore, the diffusion of the nonreacting component of the electrolyte increases the relaxation of the concentration gradients of the active (reacting) component.

For reactions of charged particles in systems without screening effects (or for the reactions of particles with other long-distance interactions), Debye¹⁰ showed that the effective reaction rate constant is equal to the Debye effective reaction rate constant,

$$k_D = 4\pi R_D D \quad (2)$$

where R_D is an effective reaction radius,

$$R_D^{-1} = \int_R^\infty \frac{e^{U(r)/k_B T}}{r^2} dr \quad (3)$$

where $U(r)$ is the spherically symmetrical energy of the interaction for two reacting particles (or for the reacting particle with the electrode) and k_B is Boltzmann’s constant.

Comparison of eq 2 with the eq 1 leads to the conclusion that for $r < R_D$ the drift of an ion in the field of the sensor (or more generally the drift of a reacting particles in the field of the other one) is faster than the diffusion and one can treat the boundary $r = R_D$ as the effective reaction surface with zero reagent concentration and ignore the field for $r \gg R_D$.

In this paper we show that for small microelectrodes with high charge Q in dilute electrolytes the effective rate constant and, therefore, the limiting diffusion current, can be drastically different from either the microscopic Debye result for small particles in systems without screening or the results for large macroscopic electrodes and present new explicit asymptotical results.

This paper is organized as follows. In section 2 we describe a model microsensor in a binary electrolyte, present the results of the conventional theory for the scaling laws for the limiting flux, and announce the new scaling laws and their ranges of validity. In section 3 we present the basic equations for the density of ions and potential distributions for the microsensor

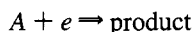
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model; in section 4 we present the solution of the system of steady state equation for concentrations and potential within the Debye–Huckel approximation for electrodes with small electrode–ion interaction and strong screening. In section 5 we consider microelectrodes with strong electrode–ion interaction, small screening, and small electrode size. Finally, in section 6, a brief summary is presented.

2. Model and Overview of Scaling Laws for the Limiting Current

Consider a spherical negative electrode of radius R in a binary electrolyte solution containing cations A , anions B , and a buffer electrolyte. For simplicity, we assume that the diffusion coefficients of A and B are equal. The origin is the center of the microelectrode, and we denote the local concentration of positive ions $c_+(\mathbf{r})$ and the local concentration of negative ions $c_-(\mathbf{r})$. Particles A react on the surface of the microelectrode



The inverse reaction takes place on a macroelectrode which is spaced far from the microelectrode. It supports the constant concentration C of A as the distance r from the microelectrode tends to infinity

$$c_+(r, t)_{r \rightarrow \infty} = C \quad (4)$$

Since the potential of electrode–ion interaction $\phi(r)$ tends to zero when r tends to infinity,

$$\phi(r, t)_{r \rightarrow \infty} = 0 \quad (5)$$

and the anions B are inert and do not react with the electrodes,

$$c_-(r, t)_{r \rightarrow \infty} = C \quad (6)$$

The solution can also contain other inert buffer ions.

A very important characteristic of sensor response is the limiting diffusion current, J . The concentration dependence of J can be represented in terms of an effective reaction rate constant k_{eff} :

$$J = k_{\text{eff}} C \quad (7)$$

Three length scales determine the sensor response: (1) the sensor radius R and (2) the electrical screening characteristic length (Debye length)

$$a^{-2} = 4\pi e^2 C / k_B T \quad (8)$$

where e is the ion charge. For electrolytes that contain a buffer, one should use the buffer concentration instead of C in eq 8. This length determines the rate of the decrease of the screened ion–ion interaction due to the accumulation of ions of the opposite sign near each other in the system *without reaction*. And the third is the Onsager length (We use the parameter γ for a nonscreened potential since, as we show below, the screening in the systems with reaction is very different, and we skip the dielectric permeability of the solvent.)

$$\gamma = 4\pi Q e / (k_B T) \quad (9)$$

When the ion–electrode distance, r , is equal to γ , the energy of ion–electrode interaction, $4\pi Q e / r$, is equal to the thermal energy, $k_B T$, where Q is the charge of microelectrode. Note that for the electrostatic interaction $U(R) = e\phi(r)$ and for the Coulomb potential $R_D = \gamma$. For an arbitrary interaction, when

$U(R) \gg k_B T$, γ can be determined as the solution of the equation

$$U(\gamma) = k_B T \quad (10)$$

and again, $R_D = \gamma$.¹¹

In binary electrolytes, a can vary from several angstroms for concentrated systems to 10^4 Å for small concentrations of ions. The value of γ can be smaller than a , approximately equal to it, or much larger. For microelectrodes, both a and γ can be much larger than R .

We can now qualitatively distinguish scale regimes and make precise the distinction between micro- and macroelectrodes:

For *macroelectrodes* with large size, when $R \gg \gamma$, a , one can show⁹ that

$$k_{\text{eff}} = 2k_s \quad (11)$$

For *microelectrodes* with the small ion–electrode interaction (small γ) and small screening effects (large a), when $\gamma \ll R \ll a$,

$$k_{\text{eff}} = k_s \quad (12)^7$$

When $a \gg \gamma \gg R$ (which implies that $\gamma a \gg R^2$), the screening of the electrode–ions and anion–cation attractions is small and the Debye result is valid

$$k_{\text{eff}} = k_d = 4\pi D \gamma \quad (13)$$

In section 4 we present the solution of the system of steady state equation for concentrations and potential within Debye–Huckel approximation for electrodes with small electrode–ion interaction and/or strong screening, i.e., for $\gamma a \ll R^2$. This solution leads to the following interpolation result for the transition from the macroelectrode with small electrode–ion interaction (eq 11) to the microelectrode with small electrode–ion interaction (eq 12),

$$k_{\text{eff}} = k_s \sqrt{2}(\sqrt{2}R + a)/(\sqrt{2}a + R) \quad (14)$$

In section 5 we consider a more interesting case, when $\gamma \gg a$ and

$$\gamma a \gg R^2 \quad (15)$$

which corresponds to the electrodes with strong electrode–ion interaction small screening, and/or small electrode size. The Debye–Huckel approximation fails in the limit, and new methods for the solution of the problem are required. For this scaling regime, we present an asymptotic analysis of the system of equations for concentrations and potential. This analysis leads to the new result

$$k_{\text{eff}} = 8\pi D g \quad (16)$$

where

$$g \propto \sqrt{\gamma a} \quad (17)$$

which can implicitly depend on R if Q is R dependent. Comparing this result with the eqs 2 and 1, we conclude that for $r < g$ the drift of the ions A is much faster than the diffusion and that the surface $r = g$ acts as the effective reaction surface. Our analyses shows that the concentration of A ions grows in the region $R < r < g$ from zero to C and forms the charge, which screens the microsensor. The total charge of A ions in this region is approximately equal to the sensor charge. The

concentration of B particles in this region is small and it grows to C in the small interval near the surface $r = g$.

3. Equations for Density and Potential Distributions

The time-dependent equations for the local concentrations read^{9,12}

$$\frac{dc_+(r,t)}{dt} = \nabla(\nabla + \beta\nabla\psi(r))c_+(r,t) \quad (18)$$

$$\frac{dc_-(r,t)}{dt} = \nabla(\nabla - \beta\nabla\psi(r))c_-(r,t) \quad (19)$$

where $\beta = e/k_B T = \gamma/4\pi Q$. The first terms in the right-hand sides of eqs 18 and 19, $\nabla^2 c_{\pm}(r,t)$, describe diffusion of A and B; the second terms, $\pm\beta\nabla\psi(r)c_{\pm}(r,t)$, describe their drift in the potential. The electrical potential, $\psi(r)$, is

$$\psi(r) = -\frac{4\pi Q}{r} + \varphi(r) \quad (20)$$

The first term on the right-hand side of eq 20 represents the nonscreened Coulomb potential of the microsensor; the second term represents the potential that is produced by the A and B ions, which shield the microsensor. The later potential obeys the Laplace equation

$$\nabla^2 \varphi(r) = -4\pi e(c_+(r,t) - c_-(r,t)) \quad (21)$$

or

$$r^{-2}\nabla r^2 E = 4\pi e(c_+(r,t) - c_-(r,t)) \quad (22)$$

where $E = -\nabla\psi$ is the intensity of the electric field and $\Phi = 4\pi r^2 E$ is the flux of E through the sphere of the radius r . Equations 18 describe the increase of the $c_+(r,t)$ and the decrease of the $c_-(r,t)$ in the layer near the electrode surface due to the electrostatic interaction with the electrode via the potential $\psi(r)$. Equation 21 describes the decrease of the potential (screening) due to the accumulation of A and repulsion of B, which provides a screening charge near the electrode.

The boundary condition for the positive ions is

$$4\pi R^2 D(\nabla + \beta\nabla\psi(R))c_+(R,t) = kc_+(R,t) \quad (23)$$

where k is chemical reaction rate constant, which depends on the boundary potential. For large potential and, therefore, for large k , eq 23 leads to

$$c_+(R,t) = 0 \quad (24)$$

Negative ions do not react at the surface of the sensor and the flux of B is equal to zero:

$$(\nabla - \beta\nabla\psi(r))c_-(r,t)|_{r=R} = 0 \quad (25)$$

For large k , eqs 23 and 24 require the rapid decrease of the concentration of A in the vicinity of the electrode surface due to the electrochemical reaction. This effect competes with the accumulation of A ions, which is caused by their electrostatic attraction to the electrode.

In the steady state for the spherically symmetric case, which is under consideration, eqs 18 and 19 reduce to

$$J = 4\pi r^2 D \left(\frac{dc_+}{dr} + \beta c_+ \frac{d\psi}{dr} \right) \quad (26)$$

and

$$\frac{dc_-}{dr} - \beta c_- \frac{d\psi}{dr} = 0 \quad (27)$$

where J is the steady flux of A through the electrode surface. It is equal to the limiting current divided by the ion charge, e . Equations 23, 26, and 27 with the boundary conditions eqs 4–6, 21, and 24 determine the steady distributions for the potential and A and B concentrations, and the steady flux J . The steady distributions for A and B concentrations read

$$c_+(r) = \exp(-\beta\psi(r)) \int_R^r \frac{J e^{\beta\psi(x)}}{4\pi D x^2} dx \quad (28)$$

$$c_-(r) = C \exp(-\beta\psi(r)) \quad (29)$$

However, as an explicit closed-form solution for $\psi(r)$ is not possible, we analyze the limiting asymptotic regimes in the following two sections.

4. Debye–Huckel Approximation

Consider the limit, where

$$\gamma a \ll R^2 \quad (30)$$

Within the Debye–Huckel approximation,

$$|\nabla\varphi(r)\nabla c_{\pm}(r,t)| \ll |C\nabla^2\varphi(r)| \quad (31)$$

the time-dependent equations for the local concentrations, eqs 18 and 19, together with the definition of the potential and with Laplace equation, eqs 20 and 21, lead to

$$\frac{dc_+(r,t)}{dt} = \nabla^2 c_+(r,t) - a^{-2}(c_+(r,t) - c_-(r,t)) - \frac{\gamma}{r^2} \nabla c_+(r,t) \quad (32)$$

$$\frac{dc_-(r,t)}{dt} = \nabla^2 c_-(r,t) + a^{-2}(c_+(r,t) - c_-(r,t)) - \frac{\gamma}{r^2} \nabla c_-(r,t) \quad (33)$$

The first terms in the right-hand sides of eqs 32 and 33, $\nabla^2 c_{\pm}(r,t)$, describe the diffusion and the second terms, $\pm a^{-2}(c_+(r,t) - c_-(r,t))$, describe the tendency to equalize local A and B concentrations, which arises due to their mutual attraction. These equations do not take into account the screening of the microelectrode potential by the local difference in the distributions of A and B charges near the electrode. However, the nonscreened ion–electrode interaction term $\pm\gamma/r^2 \nabla c_{\pm}(r,t)$ is negligible since $\nabla c_{\pm}(r,t)$ is of the order of $c_{\pm}(r,t)/a$, $R < r$, and $\gamma a \ll R^2$. This means that the mutual attraction of A by B is much stronger than the ion–electrode interaction for $\gamma a \ll R^2$, and therefore, the effective charge density is small, and the potential of the electrode does not affect the motion of the effectively neutral solution.

Thus, neglecting the $\pm\gamma/r^2 \nabla c_{\pm}(r,t)$ terms in eqs 32 and 33, we obtain

$$\frac{dc_+(r,t)}{dt} = \nabla^2 c_+(r,t) - a^{-2}(c_+(r,t) - c_-(r,t)) \quad (34)$$

$$\frac{dc_-(r,t)}{dt} = \nabla^2 c_-(r,t) + a^{-2}(c_+(r,t) - c_-(r,t)) \quad (35)$$

Remarkably it turns out that eqs 34 and 35 are formally identical

to those used to study gated diffusion-influenced reaction.¹³ The steady state solution of eqs 34 and 35 takes the form

$$c_+(r,t) = C + \frac{\sigma}{r} + \frac{\delta \exp\left(-\sqrt{2}\frac{r-R}{a}\right)}{r} \quad (36)$$

$$c_-(r,t) = C + \frac{\sigma}{r} - \frac{\delta \exp\left(-\sqrt{2}\frac{r-R}{a}\right)}{r} \quad (37)$$

where the arbitrary constants σ and δ are determined from the boundary conditions, eqs 24 and 25, with the zero potential:

$$\delta = \frac{\sigma a}{(a + \sqrt{2}R)} \quad (38)$$

$$\sigma = -\frac{CR}{1 + a/(a + \sqrt{2}R)} \quad (39)$$

Note that δ tends to zero proportionally to $a/2R$ when $a \ll R$. Therefore, in this limit

$$c_-(R,t) \approx 0 \quad (40)$$

The steady flux is equal to

$$J = 4\pi DR^2 \nabla c_+(r,t)|_{r=R} \quad (41)$$

Substitution of $c_{\pm}(r,t)$ from eqs 36 and 37 with constants from eqs 38 and 39 into eq 41 leads to

$$J = 4\pi DR^2 \nabla c_+(r,t)|_{r=R} = 4\sqrt{2}\pi DCR \frac{a + \sqrt{2}R}{a\sqrt{2} + R} \quad (42)$$

This result coincides with eq 14, as announced in section 2. One can prove that for the solution presented in this section the inequality

$$|\nabla \varphi(r) \nabla c_{\pm}(r,t)| < c_{\pm}(r,t) |\nabla^2 \varphi(r)| \quad (43)$$

is valid for $r \geq R$. The strong inequality (eq 31) is strictly valid only for $r \gg R$. This is the major problem with the Debye–Huckel approximation for almost all applications. In our case, it can lead to small corrections in the numerical factor in the results, eqs 42 and 14. However, these results present the correct behavior in the limiting cases, which coincide with eqs 11 and 12, and the correct scaling dependence on the parameters for intermediate regime.

5. Asymptotic Analysis

Now consider a system with strong electrode–ions interaction, i.e., with $\gamma \gg a$ and $\gamma a \gg R^2$. Let us introduce a certain length scale, g ,

$$\gamma \gg g \gg a \text{ and } R \quad (44)$$

and suppose that the energy of the screened electrical interaction is larger than the thermal energy for $r < g$ and that it is smaller than the thermal energy for $r > g$. Since $\gamma \gg g$ and for $r < \gamma$ the nonscreened sensor–ion interaction is larger than the thermal energy (see eqs 9 and 10), for $r < g$, the energy of the electrostatic repulsing of particles B by the microsensor is much larger than the thermal energy and $c_-(r) \approx 0$ for $r < g$. More precisely, we divide the interval $R < r < \infty$ into the following parts: (I) $R < r < R + \epsilon_1$, (II) $R + \epsilon_1 < r < g - \epsilon_2$, and (III) $g - \epsilon_2 < r$ (see Figure 1). For region I, the screening effects

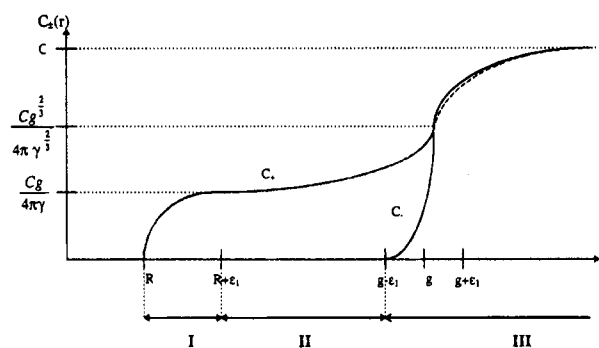


Figure 1. Schematic dependence of the c_{\pm} on the distance from the microelectrode. In region I, c_- is approximately equal to zero (see eq 47) and c_+ is determined by eq 46. It grows here from zero to the limiting value determined by eq 52. In region II, c_+ increases according to eq 71 and c_- is still negligibly small. In the small transient region $g - \epsilon_2 < r < g + \epsilon_2$, c_- rapidly grows from zero to approximately c_+ . For the rest of region III, c_+ and c_- obey eqs 36 and 37.

are small and the potential is equal to the nonscreened sensor potential,

$$\psi(R) = -\frac{4\pi Q}{r} \quad (45)$$

For region II, the diffusion term is much smaller than the interaction term in the equations for $c_+(r)$ and $c_-(r) \approx 0$. In this region, the A ions accumulate near the sensor and form the screening potential. Region III contains the transient interval from high to low potential regimes, $g - \epsilon_2 < r < g + \epsilon_2$, and the low potential region, $g + \epsilon_2 < r$, where the diffusion term is much larger than the sensor–ion interaction term and $c_-(r) \approx c_+(r)$.

Below we find the asymptotic solutions for regions I and II. For $r > g + \epsilon_2$, in region III the solution that is presented in the section 4 is valid. For the transient interval, $g - \epsilon_2 < r < g + \epsilon_2$, in region III all terms are of the same order, which complicates the explicit analysis. However, for region III, we present rigorous lower and upper bounds for the flux. We prove that these bounds coincide in the limiting case, when the strong inequality (eq 44) is valid and show that the lengths of the transient regions are small, i.e., ϵ_1 and $\epsilon_2 \ll g$, and that the asymptotic solutions are self-consistent; i.e., the ranges of validity of these solutions for the neighboring regimes overlap and the conditions of the validity of the asymptotic expansions, which provide the asymptotic solutions, are valid for these solutions.

(1) **Region I, $R < r < R + \epsilon_1$.** Since the screening factor is small for $r < R + \epsilon_1$, eqs 28 and 29 with the nonscreened potential of the microsensor, eq 45, may be combined to give $c_{\pm}(r)$. Thus

$$c_+(R + \Delta_1) = \frac{J \left(1 - \exp\left(-\frac{\gamma}{R} \left(1 - \frac{1}{1 + \Delta_1/R} \right) \right) \right)}{4\pi D\gamma} \quad (46)$$

$$c_-(r) = C \exp\left(-\frac{\gamma}{R + \Delta_1}\right) \quad (47)$$

where $\Delta_1 = r - R$. Expanding the ratio $1/(1 + \Delta_1/R) = 1 - \Delta_1/R + \dots$, we obtain

$$c_+(R + \Delta_1) = J/4\pi D\gamma \quad (48)$$

for $\Delta_1 \gg R(R/\gamma)$. Note that $R(R/\gamma)$ is much smaller than R since $R \ll \gamma$. It is also much smaller than a (and therefore

than g) since $\gamma a \gg R^2$. From eq 47 we conclude that, for the nonscreened potential of the microsensor, which is presented by eq 45, $c_+(r) \approx 0$ for $r \ll \gamma$.

(2) **Region II**, $R + \epsilon_1 r < g - \epsilon_2$. This is a region of high ratio of electrostatic energy to thermal energy. Let us perform an asymptotic expansion of the right-hand side of eq 46 by means of the steepest decent method. This leads to

$$4\pi D r^2 \beta \frac{d\psi(x)}{dx} \Big|_{x=r, c_+(r)} = J \quad (49)$$

Equation 49 coincides with eq 26 without the first (diffusion) term in the right-hand side. This term can be neglected if it is much smaller than the drift term,

$$\left| \frac{dc_+}{dr} \right| \ll \beta c_+ \left| \frac{d\psi}{dr} \right| \quad (50)$$

Substituting the gradient of the potential from the eq 49 into eq 50 we obtain

$$\left| \frac{dc_+}{dr} \right| \ll \frac{J r^{-2}}{4\pi D} \quad (51)$$

From eqs 46 and 48 we determine the boundary condition at $r = R + \epsilon_1$,

$$c_+(R + \epsilon_1) = J/4\pi D \gamma \quad (52)$$

Note that eq 48 and, therefore, eq 52 is valid if

$$\epsilon_1 \ll R^2/\gamma \quad (53)$$

Substituting

$$c_-(r) = 0 \quad (54)$$

into eq 21, we obtain

$$r^{-2} \frac{d}{dr} r^2 \frac{d\varphi(x)}{dx} = -4\pi e c_+(r) \quad (55)$$

Denote

$$r^2 \frac{d\psi(r)}{dr} = y \quad (56)$$

By definition (see eq 20),

$$r^2 \frac{d\varphi(r)}{dr} = y + 4\pi Q \quad (57)$$

Substituting eq 57 into eq 55, we obtain

$$\frac{1}{4\pi e} r^{-2} \frac{dy}{dr} = -c_+(r) \quad (58)$$

Substituting

$$c_+(r) = J/4\pi D \beta \gamma \quad (59)$$

from eq 59 into eq 58 we obtain

$$\frac{1}{e} y \frac{dy}{dr} = -\frac{J r^2}{D \beta} \quad (60)$$

which leads to

$$\left(y^2(x) = -\frac{2eJx^3}{3D\beta} \right) \Big|_{x=R+\epsilon_1}^{x=r} \quad (61)$$

Let us choose an arbitrary ϵ_1 from the interval

$$R \ll \epsilon_1 \ll R^2/\gamma \quad (62)$$

Since for $x = R + \epsilon_1$ the screening is small and $R \ll \epsilon_1$, the potential at the point $r = R + \epsilon_1$ is equal to the nonscreened sensor potential and

$$y^2(R + \epsilon_1) \approx y^2(R) = (4\pi Q)^2 \quad (63)$$

Taking advantage of the definition of y , eq 56, we obtain the solution for the gradient of the potential

$$x^2 \frac{d\psi(x)}{dx} = -4\pi Q \sqrt{1 - \frac{eJx^3}{6\pi D \gamma Q}} \quad (64)$$

where $x = r - R$.

The similar solution for the concentration of A

$$r^{-2} \frac{d}{dr} \left(\frac{J}{4\pi D \gamma c_+(r)} + Qe \right) = -4\pi e c_+(r) \quad (65)$$

$$\frac{d}{dr} \frac{1}{c_+(r)} = -\frac{r^2 4\pi D \gamma c_+(r) e}{JQ} \quad (66)$$

$$1/c_+(r) = f(r) \quad (67)$$

$$\frac{d}{dr} f^2 = -\frac{r^2 8\pi D \gamma e}{JQ} \quad (68)$$

leads to

$$f^2(r) - f^2(R + \epsilon_1) = (8\pi D \gamma e / JQ) (r^3 - (R + \epsilon_1)^3) \quad (69)$$

Since $R \gg \epsilon_1$, we obtain the result for the concentration

$$c_+^2(x) = \frac{c_+^2(x)_{x=\epsilon_1}}{1 - (8\pi D \gamma e c_+^2(x)_{x=\epsilon_1} / 3JQ) x^3} \quad (70)$$

where $x = r - R$. Substitution of $c_+(R + \epsilon_1)$ from eq 52 leads to

$$c_+(x) = \frac{J}{4\pi D \gamma} \frac{1}{\sqrt{1 - (eJ/6\pi D \gamma Q) x^3}} \quad (71)$$

Let us choose

$$g = \sqrt[3]{6\pi D \gamma Q / eJ} \quad (72)$$

At the point $r = g$, the total positive charge of the cloud of A ions around the sensor is equal to the charge of the sensor, and therefore, the intensity of the total electric field tends to zero (see eq 64). The concentration dependence, which is presented in eq 71, apparently tends to ∞ when $r \rightarrow g$. It signals that the approximation of the large drift, eqs 50 and 51, which is accepted for region II, is not valid in the vicinity of the point $r = g$. Substituting the results from eqs 71 and 64 into the criteria of the smallness of the diffusion term, eq 50, we obtain for $x = g - \epsilon_2$, $g \gg \epsilon_2$,

$$g - r \gg \epsilon_2 = g^{4/3} / \gamma^{1/3} \quad (73)$$

The flux of E through the spherical surface $r = g - \epsilon_2$ according to eq 64 equals to

$$x^2 \frac{d\psi(x)}{dx} \Big|_{g-\epsilon_2} = -4\sqrt{3}\pi Q(g/\gamma)^{1/3} \quad (74)$$

which means that the absolute value of the total negative charge inside the sphere $r < g - \epsilon_2$ is equal to

$$\tilde{Q} = \sqrt{3}Q(g/\gamma)^{1/3} \quad (75)$$

The concentration of A at the point $r = g - \epsilon_2$ according to eq 71 is equal to

$$c_-(g - \epsilon_2) = (J/4\sqrt{3}\pi D\gamma)(\gamma/g)^{1/3} \quad (76)$$

(3) Region III, $r > g - \epsilon_2$. The Lower Bound. The excess of negative charge inside the sphere $r < g - \epsilon_2$ attracts positive A ions from the outside region $r > g - \epsilon_2$ and, therefore, increases the reaction rate. In order to obtain the lower bound for the reaction rate, we consider the flux in the system with zero potential outside this sphere, i.e., in the region $r > g - \epsilon_2$, and with the boundary concentrations, which were calculated for the real system for the region $r < g - \epsilon_2$ (see eqs 54 and 76). For $a \ll g \ll \gamma$, these equations lead to the zero limiting boundary conditions for both A and B. Recalling the results of section 4, we obtain the following lower bound

$$J \geq J_{lb} = 8\pi D(g - \epsilon_2)C \quad (77)$$

Since $g \gg \epsilon_2$, it leads to

$$J_{lb} \rightarrow 8\pi DgC \quad (78)$$

The Upper Bound. The maximum flux that can be provided by the outside region is realized when the concentration of A particles at the boundary tends to zero. In order to obtain the upper bound, we consider the flux in the system with zero concentration of A particles at the boundary $r = g$, zero flux of B particles, nonscreened charge \tilde{Q} (see eq 75) with the spherical symmetry inside the sphere $r \leq g$ and ignore the screening of this charge by the local difference in A and B concentrations outside this sphere. This leads to the equations of the type of eqs 32 and 33 with the renormalized potential:

$$\frac{dc_+(r,t)}{dt} = \Delta^2 c_+(r,t) - a^{-2}(c_+(r,t) - c_-(r,t)) + \frac{\tilde{\gamma}}{r^2} \nabla_{c+}(r,t) \quad (79)$$

$$\frac{dc_-(r,t)}{dt} = \nabla^2 c_-(r,t) + a^{-2}(c_+(r,t) - c_-(r,t)) - \frac{\tilde{\gamma}}{r^2} \nabla_{c-}(r,t) \quad (80)$$

where $\tilde{\gamma} = \gamma\sqrt{3}(g/\gamma)^{1/3}$. The ion-electrode interaction terms $\pm(\tilde{\gamma}/r^2)\nabla_{c\pm}(r,t)$ are negligible since $\nabla_{c\pm}(r,t)$ is of the order of $c_{\pm}(r,t)/a$, $g < r$, and $\tilde{\gamma}a \ll g^2$. It means that the mutual A to B attraction is stronger than the ion-electrode interaction for $\tilde{\gamma}a \ll r^2$ and therefore

$$J \leq J_{up} = 8\pi DgC \quad (81)$$

Thus, the limiting values of the upper and lower bounds coincide and, therefore,

$$J = 8\pi DgC \quad (82)$$

(4) The Result and the Proof of Self-Consistency. Substituting J from eq 82 into eq 72 and using the definition of a ,

eq 8, we finally obtain

$$g = \sqrt[4]{3/4}\sqrt{\gamma}a \quad (83)$$

$$J = 4\sqrt[4]{12}\pi D\sqrt{\gamma}aC \quad (84)$$

and

$$k_{eff} = 4\sqrt[4]{12}\pi D\sqrt{\gamma}a \quad (85)$$

Substitution of these values into the eqs 44, 47, 48, 51, 73, and 76 proves the self-consistency of our assumptions. From solutions for region II, eqs 64 and 71, we conclude that the potential is nonscreened and the concentration is equal to the boundary value, which is determined by eq 59 for any $r \ll g$. On the other hand, the asymptotic solution for region I, eqs 48, which provides the same result as eq 59, is valid for any $r - R \gg R^2/\gamma$. Since $\gamma \gg R$, $g \gg a$, R , and $\gamma a \gg R^2$, the ranges of validity of these solutions overlap.

(5) Microsensor Potential. According to eq 64, the gradient of potential equals zero for $r > g$. Taking $r = \infty$ as a reference point, $\psi(\infty) = 0$, and integrating eq 64 from $r = R$ (the electrode surface) to $r = \infty$, we obtain

$$\psi(R) = \sqrt{\frac{6\pi Q}{D\gamma}} \frac{2\sqrt{6\pi D\gamma Q} - eJx^3}{3x} \Big|_R^g + \sqrt{\frac{6\pi Q}{D\gamma}} \int_R^g \frac{eJx}{\sqrt{6\pi D\gamma Q} - eJx^3} dx$$

The first term in eq 86 is the small R limit, $R \ll g$, equals the potential in the system without the reaction and without A and B ions (nonperturbed potential)

$$\psi_0(R) = (4\pi Q/R)$$

In order to obtain a first approximation for the second term, we change the lower integration limit R ($R \ll g$) to 0:

$$|\delta\psi(R)| \approx \sqrt[3]{9egR^3 c/2Q\gamma} |\psi_0| I$$

where

$$I = \int_0^1 \frac{z}{\sqrt{1-z^3}} dz \approx 0.86237...$$

Since R^3c , g/γ , $e/Q \ll 1$, we obtain

$$|\delta\psi(R)| \ll |\psi_0(R)|$$

and

$$\psi(R) \approx \psi_0(R)$$

Thus, since in the case under consideration the concentrations of A and B ions are small in the vicinity of the microsensor surface and the potential gradient drops rapidly to zero at the vicinity of the spherical surface $r = g$ (see Figure 1), the potential of microsensor is not perturbed by A and B ions.

(6) Simple Qualitative Estimate. In order to obtain a simple qualitative scaling estimate for J , let us assume that the A concentration in the region $R + \epsilon_1 < r < g$ is equal to the boundary value, $c_+(R + \epsilon_1) \approx J/D\gamma$ and that the concentration of B in this region is equal to zero. The total positive charge of A ions inside the sphere $r < g$ is proportional to the ion charge, the volume of the sphere, and the concentration; i.e. it is proportional to $(Je/D\gamma)g^3$. Since this charge screens the

TABLE 1: Scaling Laws for Effective Reaction Rate Constant

macro ($R \gg \gamma, a$)	micro ($R \ll \gamma$ and/or $R \ll a$)		
	$a \gg \gamma > R$	$\gamma a \ll R^2$	$\gamma a \ll R^2, \gamma \gg a$
$k_{\text{eff}} = k_S \propto DR$	$k_{\text{eff}} = k_D \propto D\gamma$	$k_{\text{eff}} = (2R + \sqrt{2a})k_S/(R + \sqrt{2a})$	$k_{\text{eff}} \propto D\sqrt{\gamma a}$

charge of the electrode, it is equal to Q ,

$$(Je/D\gamma)g^3 = Q \quad (87)$$

Substitution of the flux for the zero potential region, $r > g$, $J = 8\pi Dg$, into eq 87 leads to

$$g \propto \sqrt{a\gamma} \quad (88)$$

6. Summary

Thus our results presented in eqs 42, 83, 84, and 85 lead to the conclusion that physical phenomena, which are important on small length scales, can drastically change microsensor response as compared to macrosensor response been renormalized with the help of the usual macroelectrodes scaling laws. The results are summarized in Table 1.

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