The simple electrochemical method for detection of 3d molecular reorientation in adsorbed layer of organic substances

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Abstract

Reorientation of initially flatly adsorbed molecules to slant or fully erected position on the electrode surface seems to be a common transition during adsorption of organic substances. However, the reorientation is not easily detected and its occurrence often questioned. In this paper we present a simple electrochemical method to detect 3d molecular reorientation at the electrode surface. The method is based on *ac* voltammetric measurement of a rate of change of capacitive current, dI_c/dt with time, during the adsorption process, that is qualitatively different for adsorption with reorientation in respect to that without it. The theoretical considerations of simple, diffusion-controlled adsorption without reorientation predicts monotonic decrease of dI_c/dt curve. This is experimentally demonstrated in the adsorption of nearly isotropic 1-aminoadamantanehydrochloride (ADA). Contrary to this theoretical prediction it is shown that in the cases when the orientational ordering and reorientation takes place the rate of change of capacitive current *vs.* time exhibits a plateau followed by steep decrease. Such behavior is demonstrated experimentally in adsorption of anisotropic, rod-like Triton-X-100 molecule. This has previously been shown that undergo reorientation during the adsorption process. Qualitatively the same behavior of dI_c/dt was observed for both molecules in a case of diffusion controlled adsorption as well as adsorption from stirred solution.

Keywords: adsorption, reorientation, capacitance, time, T-X-100, adamantane derivative.

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1. Introduction

The adsorption processes play an important role in the phenomena occurring on interfaces including natural and technologically induced phase boundaries. These processes are conveniently studied by electrochemical methods [1]. The large number of electrochemical studies dealing with adsorption of organic compounds is based on the measurements of the differential capacitance of the double layer, C_d, in relation to the bulk concentration and to the electrode potential. This due to the fact that the differential capacitance is much more sensitive to changes of the double layer structure than the interfacial tension [2]. Furthermore, the decrease in differential capacitance is directly proportional to the extent of adsorption of organic molecules. Since $I_c \propto C_d$, the measurement of the capacitive current (I_c) enables direct follow-up of the extent of adsorption of organic substances on the electrode surface. The relation [2]

$$\theta = \frac{I_{c0} - I_c}{I_{c0} - I_{cm}} \tag{1}$$

permits calculation of the fractional electrode surface coverage, θ, directly from the measured capacitive current, I_c. Here, I_{c0} represents the capacitive current corresponding to the interface capacitance without adsorbed organic molecules, I_c is the capacitive current in the presence of adsorbed organic molecules and I_{cm} is the capacitive current obtained for the totally covered electrode surface for given organic substance.

The theory of adsorption kinetics includes two limiting cases [2]: the rate of adsorption is determined either by the rate of adsorption itself - kinetic control, or by diffusion of the organic molecules to the electrode surface - diffusion controlled mass transport. In the later case the adsorption is not instantaneous, but the rate of adsorbed layer build up is controlled by diffusion process. In this case it is generally assumed that the adsorbate surface concentration is related to its volumetric concentration at electrode surface. Usually this situation is described by different adsorption isotherms that quantitatively describe the change of relative electrode surface coverage *vs.* adsorbate bulk concentration. These isotherms may include different parameters, such as adsorption equilibrium constant, coefficient of lateral molecular interactions, displacement number describing the number of solvent molecules displaced by one adsorbed organic molecule etc., that all depend on applied surface potential and temperature.

The measurement of capacitive current *vs*. time at constant potential and at the chosen organic substance's bulk concentration gives the possibility to follow the formation and evolution of organic films. The adsorption starts from the bare electrode surface and continues up to fully covered electrode surface and may include subsequent layer transformations including e.g. formation of compact film [3] or surface micelles [4]. The structure of the adsorbed layer changes during the film formation. These changes may include formation of ordered and/or fractal structures and comprise different transformational phases such as 2d nematization [5] and 3d reorientation as a second order phase transitions [5, 6]. However, its detection is not easy in electrochemical measurements. Recently, it has been shown that these processes can be detected by the corresponding changes of fractal dimension, D, of adsorbed layer [5, 6]. Moreover, the fractal dimension is also sensitive to the changes in hydrodynamic conditions and influences the basic material properties [7, 8]. To determine fractal dimension of adsorbed layer a new method was developed employing the scaling of hanging mercury drop electrode [6]. However, this method is limited to mercury drop electrode and even than can be time consuming. Here, we propose a new and simple method for detection and tracking of molecular 3d reorientation in adsorption of organic molecules at the electrode/electrolyte interface. The method is based on *ac* voltammetric detection of pronounced difference in the rate of change of capacitive current with time, dI_c/dt, in transition from uncovered to fully covered electrode surface for the case of adsorption with 3d reorientation (flat-to-perpendicular) in comparison to the adsorption that do not include reorientation.

2. Theory

Let us consider semi-infinite linear diffusion of a single molecular species to a stationary planar electrode. The use of the planar electrode model as an approximation to the spherical electrode, such as mercury drop electrode, is justified for sufficiently short measurement times. Namely, the effects of electrode sphericity can be neglected for $t \ll r^2/\pi D_0$, where r and D_0 are the electrode radius and the diffusion coefficient, respectively [1]. For example, introducing the values corresponding to T-X-100, $D = 5 \times 10^{-6}$ cm^2 s^{-1} [9] and $r = 0.5$ mm one obtains $t \ll 160$ s. As the relevant phenomenon observed in our experiment occurred at $t \leq 30$ s we consider that spherical corrections need not be included in our considerations.

Furthermore, at longer times the buildup of density gradients may cause a convective disruption of the diffusion layer, what usually results in capacitive currents that are lower than these predicted without convection. The onset of convective interference depends on different factors and is not easily predicted, but generally it is adopted that diffusion measurements at times longer than ~ 300 s are difficult and even measurements on scale longer than 20 sec may show small convective effects [1]. However, as pointed out before, in our measurements all relevant effects are observed at time scale < 30 sec, so we believe that the convective effect can also be neglected.

We assume that the adsorption obeys the characteristics of the Frumkin isotherm, which takes into account the possible specific interaction between molecules in the adsorbed layer [2]. We also suppose that the adsorbed substance is neither reduced nor undergoes any chemical reactions at the applied electrode potential. The concentration of adsorbate at the interface at a given time t is denoted by $\Gamma(t)$, and satisfies the corresponding isotherm that in general form can be written as:

$$BC(0,t) = f(\Gamma) \tag{2}$$

Here, $C(0, t)$ is the adsorbate concentration at the electrode surface in time t. Hence, by $C(x, t)$ we denote adsorbate concentration at certain distance x from the electrode surface at a given time t. Now, the rate of change of adsorbate concentration is given by the Fick's diffusion low:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{3}$$

Furthermore:

$$\frac{d\Gamma}{dt} = D\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{4}$$

Eq. (4) describes the situation in which the rate of change of net adsorption is determined by the diffusion flux at the interface.

The initial and boundary conditions are:

$$t=0 \qquad x\geq 0 \qquad C(x,t) = C^{*} \qquad \Gamma(t) = 0 \tag{5}$$

To describe Γ we have chosen Frumkin isotherm that is given by:

$$BC(0,t) = f(\Gamma) = \frac{\theta}{(1-\theta)}e^{-2a\theta} \tag{6}$$

where $\theta = \dfrac{\Gamma}{\Gamma_m}$, and Γ_m is surface excess concentration, B is adsorption coefficient and C^* is the concentration in the bulk of the solution. In Eq. (6) the implicit tacit assumption is that the bulk adsorbate activity is 1.

It was shown [10] that application of the Laplace transformation with respect to time to Eqs. (3) and (4) and taking into the account the initial and boundary conditions in Eqs. (5) and (6) results in an equivalent Volterra integral equation of the second kind:

$$\Gamma(t) = \frac{2C^* \sqrt{D}}{\sqrt{\pi}} \sqrt{t} - \frac{1}{B}\sqrt{\frac{D}{\pi}} \int_0^t \frac{f(\Gamma)}{\sqrt{t-\tau}} d\tau \tag{7}$$

Introduction of Eq. (6) (Frumkin isotherm) into Eq. (7) and defining nondimensional parameters:

$z = \Lambda t$ *and* $\eta = \Lambda \tau$, where $\Lambda = \dfrac{4C^{*2}D}{\Gamma_m^2 \pi}$, we obtain:

$$\theta(z) = \sqrt{z} - \frac{1}{2BC^*} \int_0^z \frac{\theta/(1-\theta)}{\sqrt{z-\eta}} e^{-2a\theta} d\eta \tag{8}$$

This is a Voltera's integral equation of second kind [11] for θ (z). It can be solved numerically by the method of finite sums [12] for different values of parameters BC^* and a. The solution provides time development of relative electrode coverage for given molecular species at bulk concentration C^*. Now, the Eq. (1) relating relative electrode coverage to the capacitive current provides means to calculate the time dependence of I_c corresponding to the calculated time change of θ:

$$I_c(t) = I_{c0} - (I_{c0} - I_{cm})\theta(t) \tag{9}$$

hence, the rate of change of capacitive current is then given by:

$$\frac{dI_c}{dt} = -(I_{c0} - I_{cm})\frac{d\theta}{dt} \tag{10}$$

Here, it is worthwhile to point out that the buildup of the adsorbed layer as described by Eq. (8) and consequently Eq. (10) does not imply any layer restructuring. The rate of change of relative electrode coverage depends only on the diffusion flux to the interface and hence is species and concentration but not structure dependant. Hence, this model is valid for the adsorption of isotropic molecules that form reorientation insensitive adsorbed layer for which the rate of change of capacitive current due to increase of relative coverage is described by Eq. (10).

The extension of this model to the more complex adsorption system that includes reorientation of adsorbate molecules considerably increases the mathematical complexity and is subject of the work in progress. However, the presented model provides means for discrimination of systems that due to reorientation do not comply with the prediction of this theory of simple adsorption. Hence, it may be expected that the reorientation during the adsorption process will be manifested in observable change in dI_c/dt *vs.* t in comparison to that predicted by the model of simple adsorption process.

To verify this hypothesis we have applied theoretical considerations to adsorption process of a geometrically nearly isotropic molecule, 1-aminoadamantanehydrochloride (ADA) (Fig. 1a), and to a highly anisotropic (rod-like) molecule, Triton-X-100 (T-X-100) for which it has been shown that during the adsorption process undergoes reorientation [5]. The experiments were conducted for diffusion controlled adsorption and in a case of adsorption from stirred solution.

3. Experimental

The change of capacitive current with time during the adsorption was measured by phase sensitive alternating current (*ac*) voltammetry (90° out of phase). The *ac* p-p voltage amplitude was 10 mV at frequency of 170 Hz. The time range involved in the measurement corresponded to attainment of maximal relative electrode coverage that, for the selected organic substance, is indicated by a constant and the lowest value of I_c. The I *vs.* t measurements were performed by the EDT-ECP 110 Modular Research Polarograph (London, England) and digitized afterward. The repeatability of capacitive current measurements was ≤ 3 %. All experiments were performed in a three-electrode system. Working electrode was hanging mercury drop (Metrohm, Switzerland), with Ag/AgCl/3 M KCl electrode as the reference and a platinum wire as the auxiliary electrode. All measurements were performed by diffusion and under the stirring of the solution (270 r.p.m.), and in 0.5 M NaCl electrolyte. The adsorption of ADA is performed at – 0.42 V, and T-X-100 at – 0.35 V.

1-aminoadamantanehydrochloride (ADA), M_w = 187 g/mol, (Fig. 1a) was chosen as the molecule with approximately spherical geometry that should result in nearly orientation independent adsorption. This is the hydrophilic derivative of adamantane having high antivirus activity that is explained by interactions with viruses' lipophilic areas [13]. Although adamantane is geometricaly isotropic (it is comprised of the smallest repeating unit of the diamond lattice, tricyclo (3.3.1.1(3.7)) decane [14]) it is highly insoluble in water, and hence unsuitable for our experiment, hence we used ADA.

The nonionic surfactant T-X-100, $M_w \approx 600$ g/mol, (Fig. 1b) was chosen as representative of rod-like molecules that at adsorption might have two limiting opposite orientations, namely, planar and perpendicular. These two orientations result in different surface area occupied by one molecule. T-X-100 is highly soluble in water, hydrophobic (calculated octanol/water partition constant, log $K_{OW} = 4.1$ [15]) and has a great tendency to adsorb onto surfaces.

T-X-100 (Rohm and Haas, Italy) and ADA (synthesized of high purity) were used without further purification. Mercury was purified by double distillation under reduced pressure. NaCl (Merck) was used without prior purification. All solutions were prepared with deionised water obtained with the Milly-Q Water System (Millipore, Switzerland).

4. Results and discussion

The results of the numerical solution of Eq. (8) corresponding to the model of simple Frumkian adsorption are represented in Fig. 2 together with the corresponding *dI/dt* derived from Eq. (10) for different combination of adsorbate bulk concentration, coefficient of adsorption, and coefficient of lateral interaction (*a*). To emphasize the influence of parameter Ψ, ($\Psi = BC^*$), the results of calculations for two different Ψ are shown in Fig. 2a and 2b, for Ψ = 1 and 10, curves 1 and 2, respectively. In Fig. 2a the increase of relative electrode coverage with time for diffusion-controlled adsorption is depicted. The rates of change of theoretical capacitive currents calculated from the Eq. (10), which corresponds to the fractional electrode coverage shown in Fig. 2a, is depicted in Fig. 2b. The results of calculations showing the influence of coefficient of lateral interactions are depicted in Fig. 2c and 2d. Here the relative surface coverage and corresponding dI_c/dt are presented for repulsive, attractive interaction and for the case of no interaction (a = 1, -1 and 0, respectively). It can be seen that the time needed to attain certain coverage is respectively shortened or prolonged for attractive or repulsive interaction in respect to the case without molecular interaction. For sufficiently short time the relative coverage is independent of the coefficient of lateral interaction and scales $\sim\sqrt{t}$. Furthermore, the shape of dI_c/dt curves for all types of interaction (attractive, repulsive or no interaction) remains similar and of monotonous increase without exhibiting any plateau or similar feature. Accordingly, irrespectively of the values of the involved Frumkinian parameters as the relative coverage increases the rate of change of capacitive current decreases monotonically in the entire coverage range, $0 \leq \theta \leq 1$.

This model of simple adsorption implies that the adsorbed molecules occupy the same electrode surface area irrespectively of their orientation hence, they are geometrically isotropic.

Now we will compare this theoretical prediction with experimental results obtained in diffusion controlled adsorption of two geometrically different molecules: nearly isotropic ADA and rod-like T-X-100.

Fig. 3a, curve 2 represents time dependence of the measured capacitance current during the formation of adsorbed layer at bulk concentration of 30 mg/dm^3 ADA. The curve 1 in Fig. 3a is obtained for the pure electrolyte indicating the purity of the system, and the corresponding derivative is shown in Fig. 3c, curve 1. The fractional electrode coverage for ADA, calculated from measured capacitance current, is represented in Fig. 3b, while the corresponding rate of change of I_c *vs.* t is shown in Fig. 3c, curve 2. It can be seen that the rate of change of dI_c/dt *vs.* t qualitatively follows the prediction of the theory as shown in Fig. 2c. Such behavior was expected considering the nearly isotropic shape of the ADA molecule supposedly granting that the adsorption is orientational insensitive

Recently it has been shown that during the adsorption of T-X-100 on the mercury electrode surface the molecules in the adsorbed layer are subject to orientational ordering in two and three dimensions including, at higher coverage, the reorientation from initial flat to the erected position. Such transformations are related to anisotropic, namely rod-like shape of molecule [5]. Hence, it may be expected that such molecules shall not follow simple adsorption behavior predicted by the presented theory. Consequently, during the T-X-100 film formation the rate of change of capacitive current *vs.* time should exhibit different behavior from the theoretically predicted. This is indeed confirmed by *ac* voltammetric measurements as shown in Fig. 4. In Fig. 4a, curve 2 shows the decrease of measured capacitance current with time for the T-X-100 bulk concentration of 4 mg/dm^3. The curve 1 is recorded for the pure electrolyte indicating the purity of the system. The corresponding changes in the fractional electrode coverage for the T-X-100 are represented in Fig. 4b. Fig. 4c shows corresponding rate of change of measured capacitive current for pure electrolyte (curve 1) and T-X-100 (curve 2). Here it can be seen that in the beginning of the T-X-100 adsorption, up to $\theta \approx 0.35$, the rate of change of measured capacitive current complies with theoretical prediction, apart from deviation at the very beginning generated by the inertia of electrochemical response. At higher coverage the rate of change does not decrease as predicted for simple adsorption, but rather a "plateau" in dI_c/dt, occurs, indicating that for certain period of time (approx. 12 – 25 s, corresponding to $0.35 < \theta < 0.7$) the change of adsorption rate is negligible. After the inflection point in dI_c/dt curve, corresponding to $\theta \approx 0.7$, the adsorption rate of T-X-100 starts to decelerate abruptly and afterwards follow the theoretically predicted behavior for the rate of change of capacitance current. The same qualitative behavior of dI_c/dt was also observed for measurements conducted at different T-X-100 bulk concentrations (namely, 0.1, 0.2, 0.3, 0.6 and 1 mg/dm^3) at E = - 0.35 V under conditions of diffusion controlled adsorption, but these results are not presented here.

The fundamental difference in experimentally observed change of dI_c/dt for T-X-100 in regard to the theoretical prediction is the occurrence of the "plateau" in the fractional electrode coverage range $0.35 < \theta < 0.7$ followed by abrupt decrease in the rate of change of capacitive current. The later is related to the possibility of adsorption of molecules in two positions, namely flat and perpendicular, and process of subsequent reorientation of initially flatly adsorbed molecules. Namely, the adsorption of T-X-100 starts with flatly adsorbed molecules. As the fractional electrode coverage increases the available space for adsorption is reduced. Further increase in coverage results in attainment of saturation coverage at which major layer transformations are induced [5]. Initially, isotropic to nematic ordering, representing two-dimensional arrangement manifested as the plateau in dI_c/dt curve, and subsequent reorientation of initially flatly adsorbed molecules manifested in steep decrease of dI_c/dt. As flatly lying molecules of T-X-100 occupy approximately 5 times more space than perpendicularly adsorbed, the adsorption in perpendicular or slant position at constant incoming molecular flux results in effectively slower increase in coverage. Furthermore, the erection of initially flat lying molecules in effect increases the available space for adsorption by partially uncovering, up to that time covered, electrode surface. The cumulative effect is that although the incoming flux of molecules to the electrode surface remains the same the apparent electrode surface coverage increases more slowly than theoretically predicted. These competitive processes continue up to the coverage at which practically all initially flatly adsorbed molecules are erected, and further adsorption proceeds with perpendicular adsorption. After that time the rate of change of relative coverage and consequently that of the capacitive current, is governed only by the diffusion flux, and complies with Eqs. (8) and (9). Hence, we suppose that the inflection point on dI_c/dt curve and subsequent steep decrease of rate of change corresponds to reorientation (erection) of initially flatly adsorbed molecules.

Qualitatively identical behavior of the dI_c/dt can be expected for all geometrically anisotropic molecules that can undergo 3d reorientation upon adsorption. The deviation from the theoretical prediction of simple adsorption is related to the degree of geometrical anisotropy.

As the method is sensitive to possible changes in the structure of adsorbed layer induced by the reorientation of adsorbed molecules the above considerations should be also valid in a case of adsorption from stirred solution. Hence, the behavior of dI_c/dt should be qualitatively identical. The only difference should be the contraction of time scale as a consequence of increased molecular flux to the electrode surface due to the stirring. Confirmation of this can be found in Fig. 5 where the results of experiments conducted with stirring of solution are presented. Fig. 5a and b show dI_c/dt *vs.* t derived from experimental data for adsorption of ADA and T-X-100, respectively. In the case of ADA the concentration is the same in both cases, and the compression of time scale is clearly visible. In the case of T-X-100 stirred solution the bulk concentration of 1 mg/dm^3 is 4 times lower in respect to that of non-stirred solution presented in Fig. 4. This difference in concentration is responsible for the similar time scales of observed changes. It can be seen that the general behavior of dI_c/dt in the case of stirring is qualitatively the same as in the case of diffusion controlled adsorption.

5. Conclusions

Here we have shown that the process of reorientation of initially flatly adsorbed geometrically anisotropic molecules to perpendicular orientation on the electrode surface results in significantly different behavior of dI_c/dt in comparison to that corresponding to the adsorption of molecules that are geometrically nearly isotropic, or are not subject to reorientation process during the adsorption. This is confirmed by comparing the theoretical prediction of dI_c/dt valid for simple adsorption of geometrically isotropic molecules and the experimental results obtained for the adsorption of nearly isotropic molecule ADA and anisotropic (rod-like) molecule T-X-100. The result compliant with the theory was obtained for nearly isotropic ADA molecule, that is reorientation insensitive due to nearly spherical structure of the molecule and whose adsorption consequently obeys the rules of simple adsorption. The molecular orientational ordering and subsequent reorientation from flat to perpendicular position in the case of T-X-100 is manifested in occurrence of the plateau followed by the steep decrease of dI_c/dt. This result completely differs from that predicted by the theory of simple adsorption of isotropic molecules for which dI_c/dt monotonically decreases. Qualitatively the same behavior was observed for both molecules in the case of diffusion-controlled adsorption as well as the adsorption from a solution under stirring. The observed behavior of dI_c/dt can be used to detect and track the reorientation of molecules adsorbed at the interface. This method is indicative and applicable in study of organic layer formation performed through capacitance/capacitive current measurements. The method is valid at not to short time scale (more than few seconds) that enables acceptable resolution of the rate of change of dI_c/dt in a whole coverage range $0 \leq \theta \leq 1$.

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Figure captions:

Fig. 1. The structures of ADA (a) and T-X-100 molecules (b).

Fig. 2. Theoretical predictions: (a) theoretical fractional electrode coverage *vs*. z ($z = t\frac{4C^{*2}D}{\Gamma_m^2\pi}$), calculated from Eq. (8) for Ψ = 1 and 10, curves 1 and 2, respectively, and a = -1 and (b) the rates of change of theoretical capacitive current, calculated from the Eq. (10) that correspond to fractional electrode coverage presented in Fig. 2a. (c) theoretical fractional electrode coverage *vs*. z, calculated for a = 1, 0 and -1, for Ψ = 1; (d) the rates of change of theoretical capacitive current, calculated from the Eq. (10) that correspond to fractional electrode coverage presented in Fig. 2c.

Fig. 3. Experimental results for the diffusion controlled adsorption of ADA: (a) measured capacitance current, I_c, vs. time, recorded at the electrode potential E = - 0.42 V and at the bulk concentration of 30 mg/dm^3 (curve 2), (b) the fractional electrode coverage *vs*. time calculated from the measured I_c, and (c) the corresponding rate of change of capacitive current for ADA (curve 2). The capacitance current of pure electrolyte and its derivative are presented as curves 1 in Fig. 3a and b.

Fig. 4. Experimental results for the diffusion controlled adsorption of T-X-100: (a) measured capacitance current, I_c, vs. time, recorded at the electrode potential E = - 0.35 V and at the bulk concentration of 4 mg/dm^3 (curve 2), (b) the fractional electrode coverage *vs*. time calculated from the measured I_c, and (c) the corresponding rate of change of capacitive current for T-X-100 (curve 2). The capacitance current of pure electrolyte and its derivative are presented as curves 1 in Fig. 4a and b.

Fig. 5. Experimental results obtained for adsorption from the stirred solution. The rate of changes of capacitive current obtained for (a) 30 mg/dm^3 ADA, recorded at the electrode

potential E = - 0.42 V, and (b) 1 mg/dm^3 T-X-100, recorded at the electrode potential E = - 0.35 V.

Fig. 1.

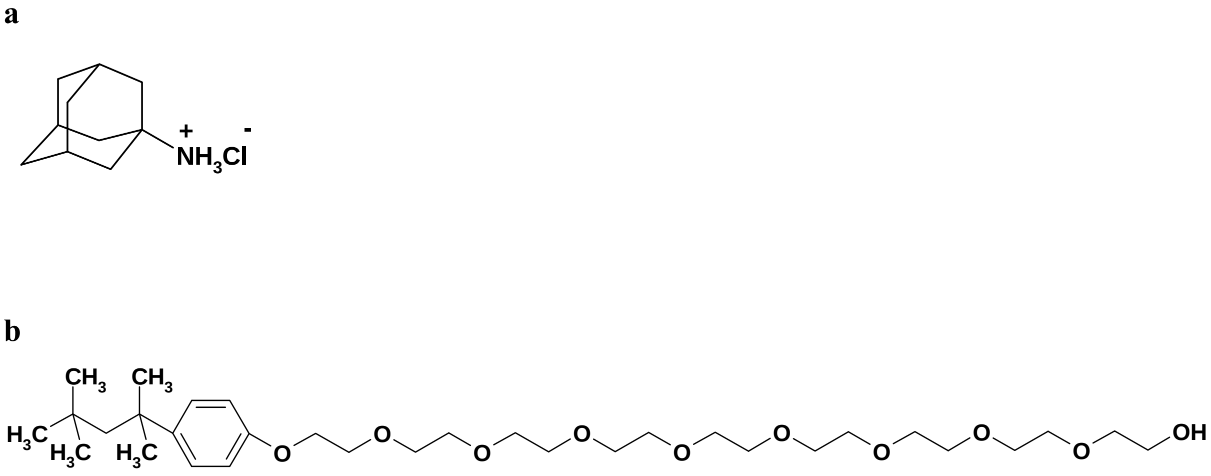
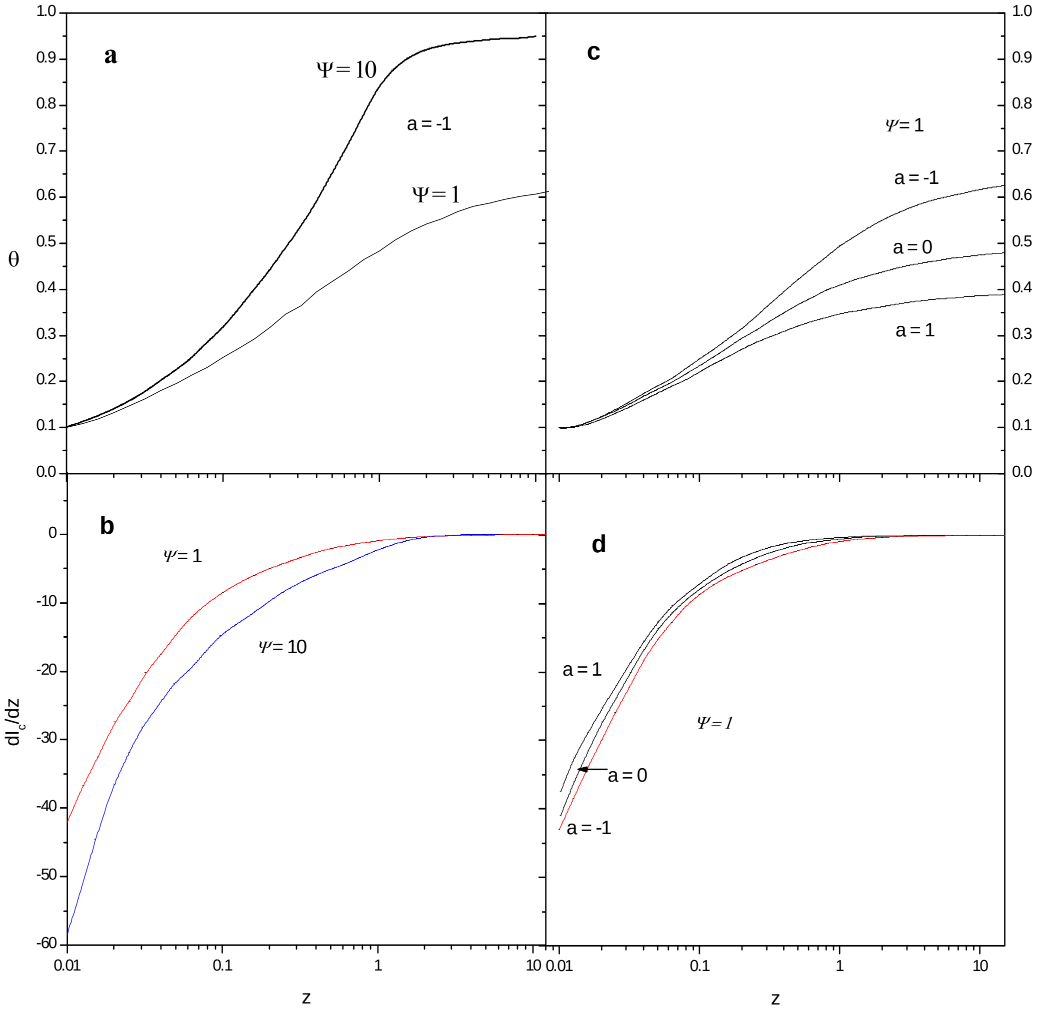


Fig. 2.


a
b
c
d
θ
dI_c/dz
z
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a = -1
Ψ = 1
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a = -1
a = 0
a = 1
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a = 0
a = -1
Ψ = 1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
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-20
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-40
-50
-60
0.01
0.1
1
10

Fig. 3.

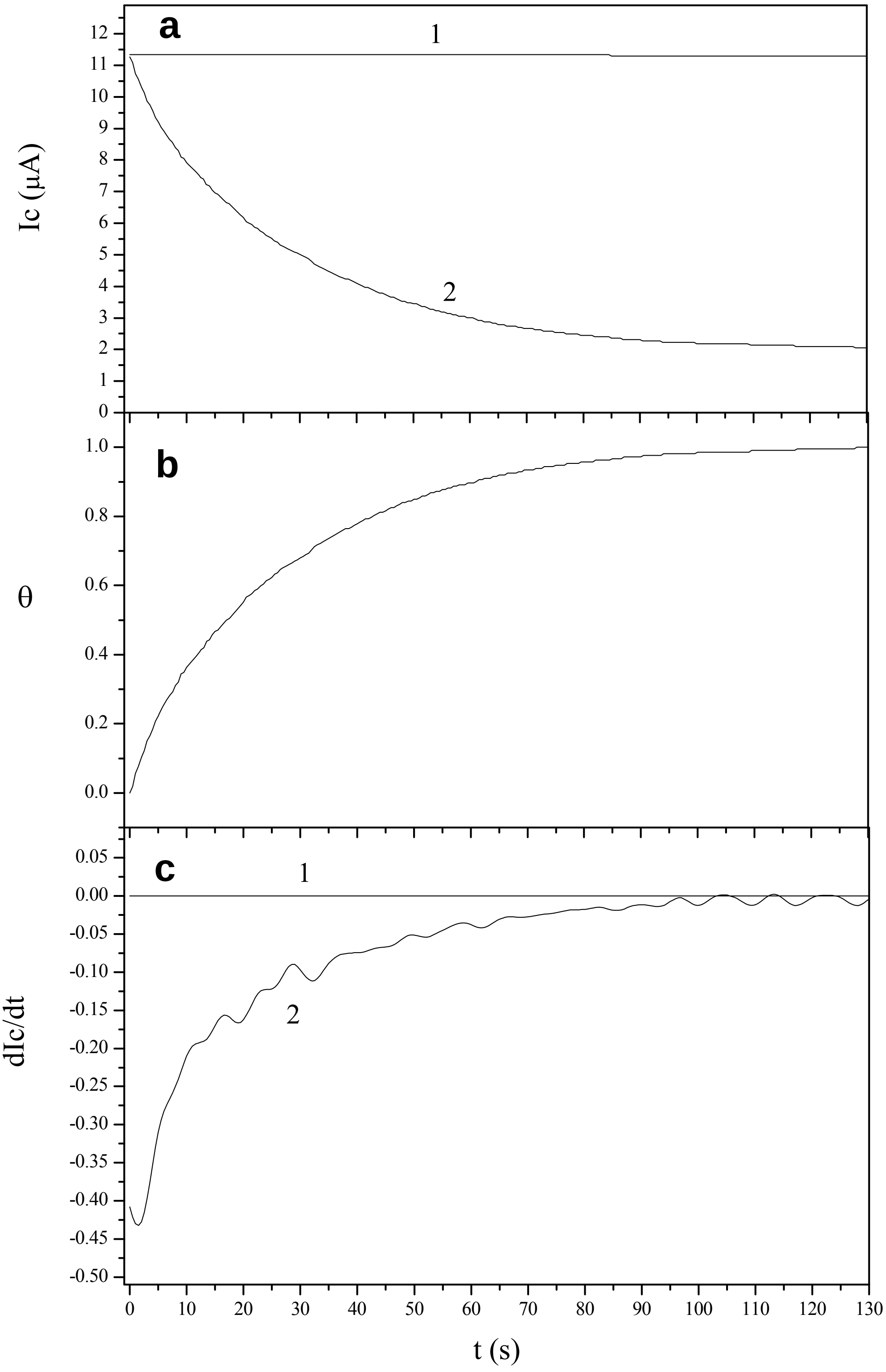
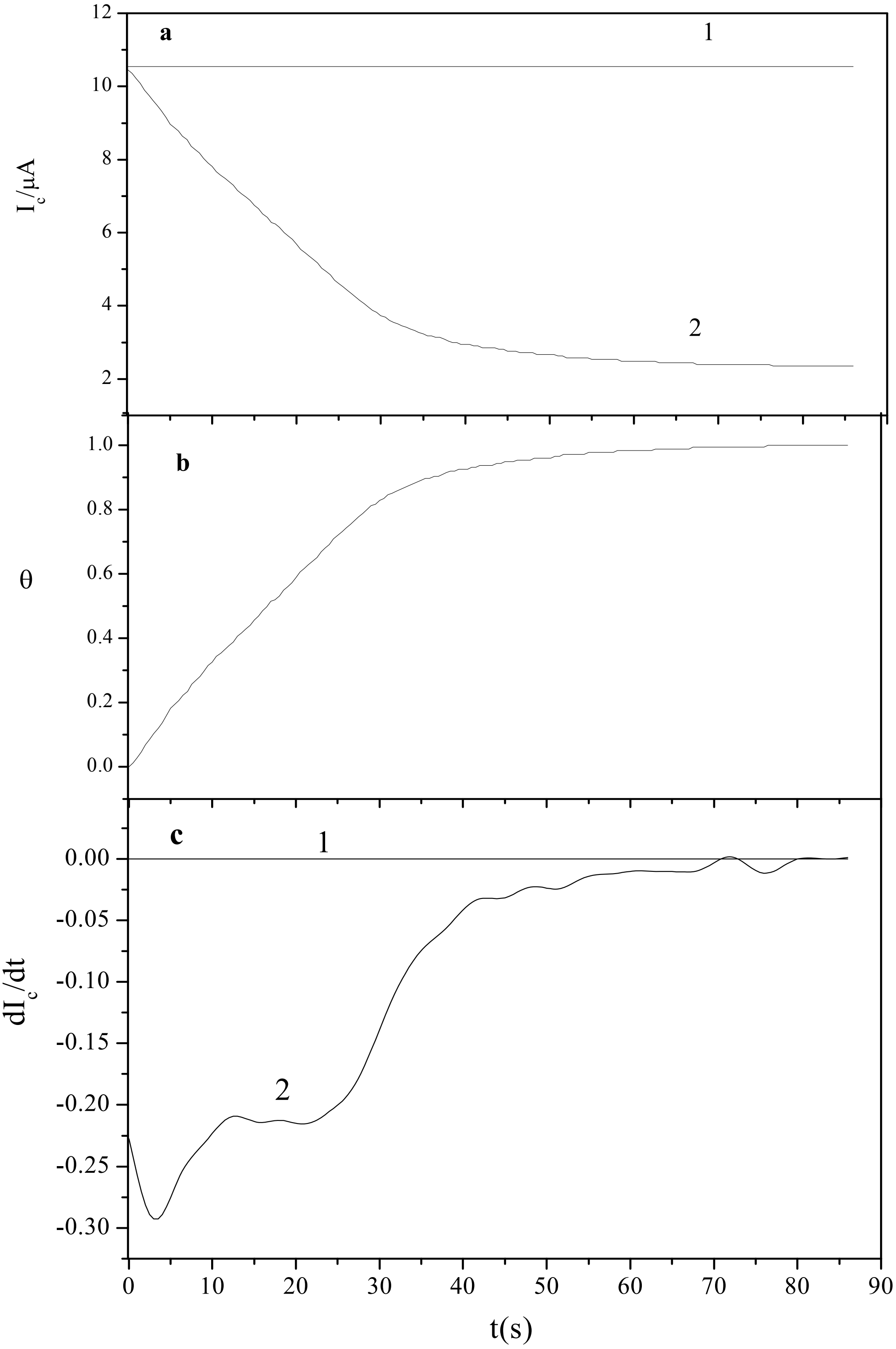

a
b
c
1
2
Ic (μA)
0
1
2
3
4
5
6
7
8
9
10
11
12
θ
0.0
0.2
0.4
0.6
0.8
1.0
dIc/dt
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
-0.45
-0.50
t (s)
0
10
20
30
40
50
60
70
80
90
100
110
120
130

Fig.4.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b
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I$_c$/μA
θ
dI$_c$/dt
t(s)
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4
2
1.0
0.8
0.6
0.4
0.2
0.0
0.00
-0.05
-0.10
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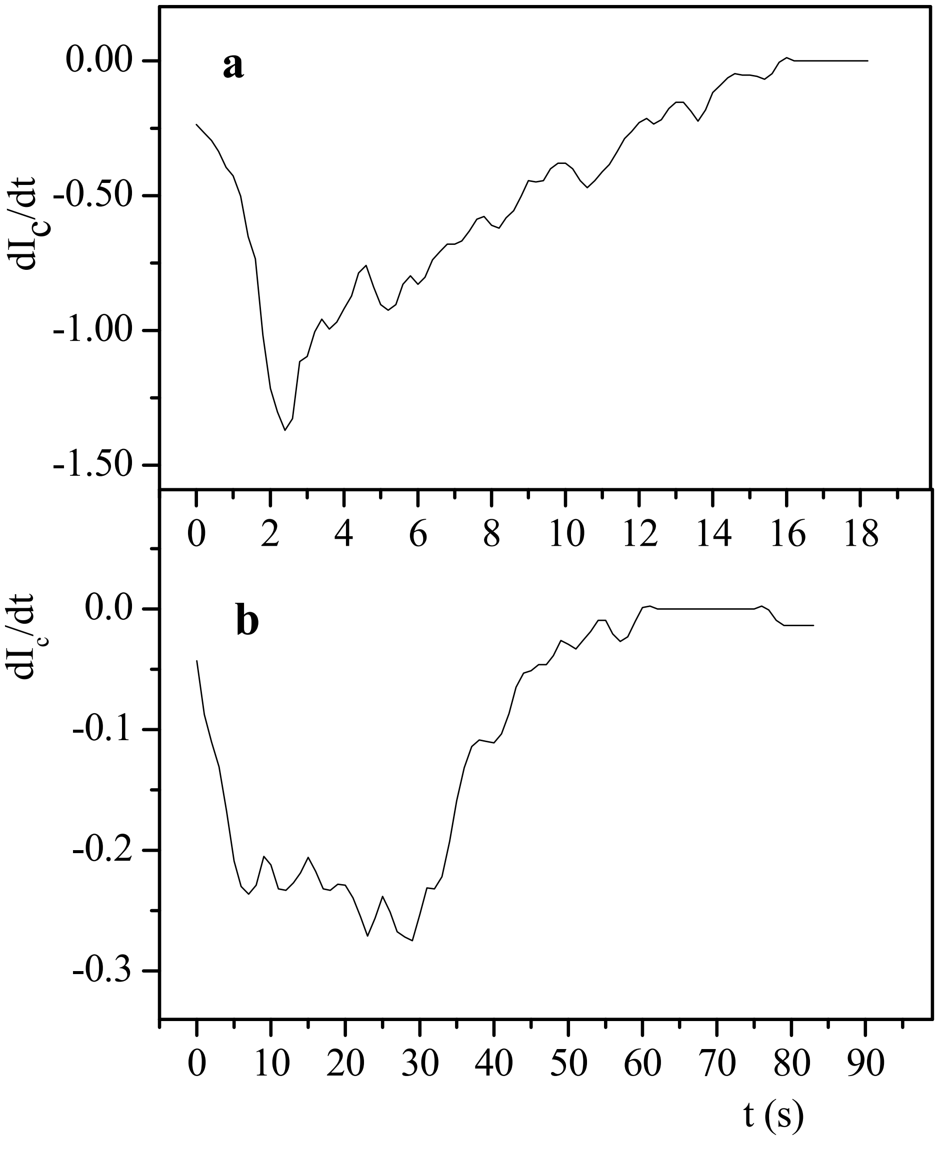
0
10
20
30
40
50
60
70
80
90

Fig. 5.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-1.00
-1.50
0
2
4
6
8
10
12
14
16
18
b
dI_c/dt
0.0
-0.1
-0.2
-0.3
0
10
20
30
40
50
60
70
80
90
t (s)