Version: Accepted manuscript version

Jadreško, D., and M. Zelić. 2015. "Square-Wave Voltammetry of Electroinactive Surfactants." *Electroanalysis* 27 (7): 1669–75. doi:10.1002/elan.201400692.

Square-wave voltammetry of electroinactive surfactants

Dijana Jadreško*, Marina Zelić

Division for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

*e-mail address: djadresko@irb.hr

Abstract

Under the influence of previously published and some new theoretical results, potential-dependent adsorption and desorption of model electroinactive surfactants Triton X-100 (T-X-100 or polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) and sodium dodecyl sulfate (SDS) on the static mercury drop electrode (SMDE) were studied by square-wave voltammetry (SWV). Although (according to the theory) the resulting current – potential curve should consist of two highly separated peaks, only desorption signal could be seen on each experimentally obtained voltammogram, most probably because of the limitations concerning the available potential range. Different properties of the recorded peak are in good agreement with the theory indicating that square-wave voltammetry could be treated as a potential tool for tensammetric studies of electroinactive surface active substances.

Keywords

Adsorption/desorption, electroinactive substances, square-wave voltammetry, tensammetry.

1. Introduction

Electroanalytical studies of adsorption processes at electrode surfaces have been in focus for many years. The current response depends on whether the electro- active or inactive substances adsorb on the working electrode [1-12]. Modern electrochemical instrumentation enables independent measurements of the faradaic and capacitive components of the current that flows across the electrode-electrolyte interface. Therefore, alternating current voltammetry is the most commonly used technique for the study of surface processes without electron transfer [1,12-16]. Electroanalysis of electroinactive surfactants is based on recording of their influence upon the electrode double layer structure. During adsorption of a redox inactive substance, the electrical double layer capacitance and thus the capacitive current decrease [13]. The measurement of *ac* capacitive current as a function of electrode potential is called tensammetry [17,18] but the same term is used when other voltammetric techniques are applied for the similar purpose. The potential region of low-capacity values is limited on both high-potential and low-potential sides by adsorption-desorption peaks, which reflect sharp changes in the surface charge within a narrow potential range [1,19].

On the other hand, square-wave voltammetry is generally considered as being insensitive to capacitive current [20], i.e. one of the main advantages of SWV is its ability to effectively discriminate against charging current [21]. More precisely, SW voltammetry is a powerful electrochemical technique for kinetic and mechanistic studies as well as analytical examinations of faradaic processes [20,22-25]. Although some attempts of its application in the analysis of electroinactive surfactants were described [26], systematic studies of such a "new" method are not known. In the previous article from our laboratory [27] a basic theory of square wave voltammetry of surface-active, electroinactive compounds was developed. It was shown that tensammetric/desorption peak originates from the difference in surface coverage during the forward and backward series of pulses of SWV signal.

In this article, experimentally obtained SW current - potential curves of model electroinactive surfactants Triton X-100 and sodium dodecyl sulfate will be presented and treated in the light of previously published [27] and some new theoretical results.

2. Experimental

All chemicals used in the experiments were of the best grade commercially available (Sigma-Aldrich) and were used without further purification. Model solutions of surface active substances (Triton X-100 and SDS) were prepared by diluting the same concentrated solution

(i.e. 5.62 g/L and $1x10^{-2}$ mol/L respectively). All solutions were prepared with water purified in a Milipore Mili-Q system.

All voltammograms were recorded using a static mercury drop electrode (SMDE 663 VA Stand from Metrohm). A platinum rod served as a counter electrode whereas all potentials were given with respect to Ag/AgCl (3 mol/L KCl) with 3 mol/L NaCl in the electrolyte bridge (to prevent formation of sparingly soluble $KClO_4$ in the frit).

The electrode system was attached trough the corresponding IME (Interface for Mercury Electrode) module to the „PGSTAT 101“ instrument (from Eco Chemie, Utrecht), controlled by the electrochemical software “NOVA 1.5”.

Before starting each new set of measurements, the solution in the electrolytic cell was deaerated with high purity (99.999%) nitrogen for 15 min. The room temperature was maintained at 25 ± 1 °C. All measurements were carried out on “small size” mercury drops (S = 0.265 mm^2) using 1 mol/L $NaClO_4$ as supporting electrolyte.

3. The model

A simple potential dependent electrode reaction was assumed:

$$A \leftrightarrow (A)ads \qquad (1)$$

According to the previous results [27] the normalized SWV response is defined by expression:

$$i\cdot(SC_{\theta=0}f)^{-1} = \Delta E\cdot(C_{\theta=1}/C_{\theta=0} - 1)\cdot 50\cdot(\theta_{m-1} - \theta_m) \qquad (2)$$

in which $\Delta E = E - E_{pzc}$ whereas other symbols have their usual meanings, given in Table 1. The constant 50 on the right side of equation 2 reflects the applied time increment ($\Delta t = (50\cdot f)^{-1}$). Other details of the simulation procedure are given in reference [27].

The model was developed to simulate the experiments with static mercury drop electrode, assuming that 1) adsorption of the studied surfactant can be described by Langmuir or Frumkin isotherm (with attractive interactions) and 2) potential of zero charge is not affected by addition of surface active substances to the electrolyte solution.

From the practical point of view it is important that the normalized SW current depends on four parameters which are related to the a) bulk concentration of the reactant ($y = c^* D^{1/2}/(\Gamma_{max}\cdot f^{1/2})$), b) maximum adsorption constant ($b_0 = \beta_0\cdot\Gamma_{max}\cdot f^{1/2} D^{-1/2}$), c)

capacity of a double layer on the free electrode surface ($k_c = C_{\theta=0}\cdot(1 - (C_{\theta=1}/C_{\theta=0}))/(2RT\Gamma_{max})$) and d) ratio of capacities of totally covered and free electrode surfaces ($C_{\theta=1}/C_{\theta=0}$). In addition, SWV response depends on the Frumkin coefficient and the relationship between the potential of zero charge and the surface coverage as well.

4. Results and discussion

4.1. Theory

According to the published theoretical results [27], a square-wave voltammogram of an electroinactive surfactant is generally characterized by a well defined desorption peak, assuming that scanning in the negative direction starts near the potential of zero charge whereas the whole process could be described by equation 1. When a (much) more positive starting potential is applied instead, the response of the type given in Fig. 1A is to be expected. It consists of two highly separated peaks with a zero current range between them. As pointed out elsewhere [27], tensammetric peaks in SWV reflect the difference in surface coverage during forward and backward series of pulses. From Fig. 1B, which gives surface coverage in dependence on the electrode potential, it follows that the more positive peak results from the gradual adsorption of the studied surfactant whereas the more negative peak (at $E << E_{pzc}$) is a consequence of desorption process. In the range between them, the maximum coverage of the electrode surface ($\theta = 1$) is achieved. Taking into account that simple, potential dependent adsorption is assumed, the values of the initial and final potential from Fig. 1A could be interchanged. Such a scanning in the positive direction should give the same pair of peaks as before but oriented in the opposite direction (Fig. 1C) as a result of the difference in surface coverage at negative and positive pulses (Fig. 1D). In such an experiment the more positive signal is expected to be higher than the more negative one whereas in Fig. 1A the opposite is true. At higher values of the concentration parameter, the difference between two peaks gradually disappears.

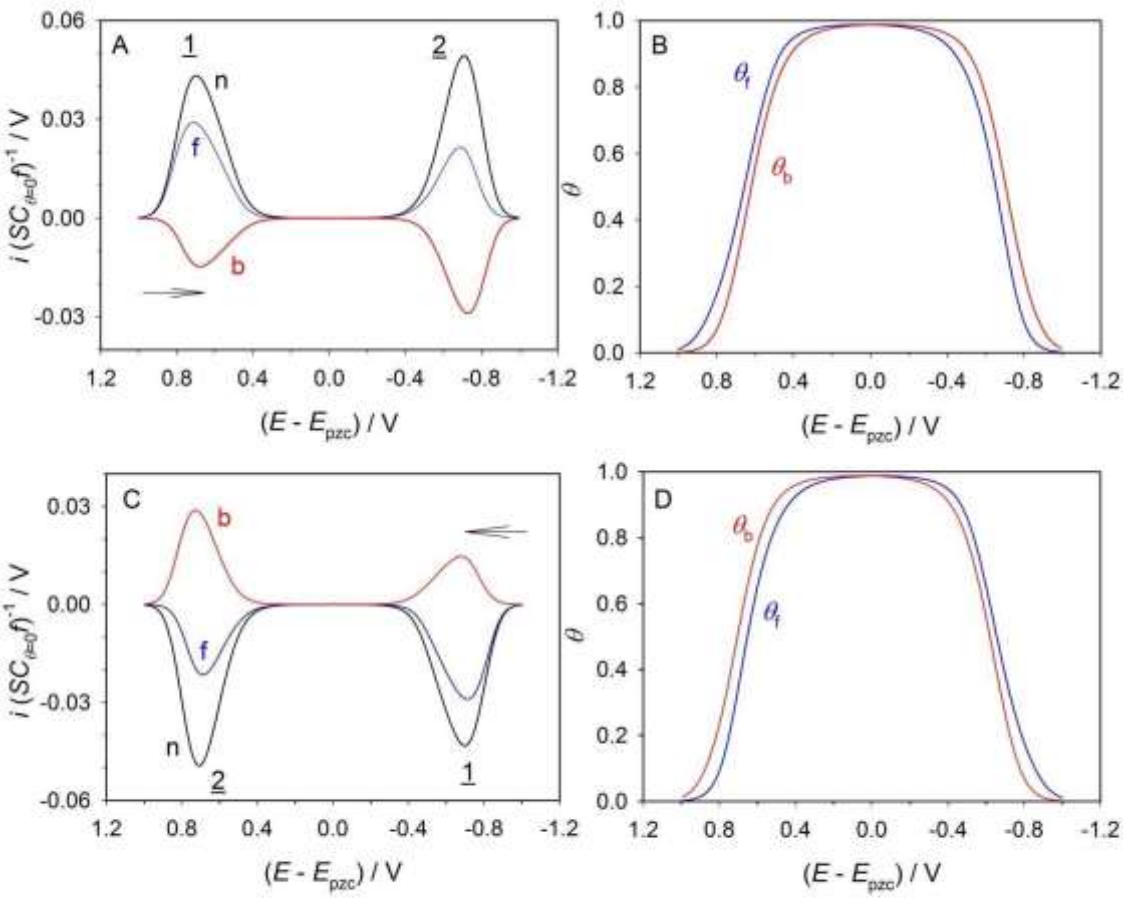

Figure 1

Fig. 1. **(**A) Normalized SW net voltammogram (n) along with its forward (f) and backward (b) components. (B) Dependence of the electrode surface coverage on the electrode potential. (C) and (D) The same as (A) and (B) but for the opposite scan direction (indicated by an arrow). Conditions: E_{st} = (-) 1 V vs. E_{pzc}, E_s = 5 mV, E_{sw} = 50 mV, y = 0.3, k_c = 10 V^{-2}, b_0 = 333, $C_{\theta=1}/C_{\theta=0}$ = 0.5, a = 0 and $E_{pzc,\theta=1} = E_{pzc,\theta=0}$.

4.2. Model experiments

- In order to test the theoretical results, experimental studies were performed with Triton X-100 and sodium dodecyl sulfate (SDS), as "representatives" of nonionic and negatively charged surface active substances. In Fig. 2, desorption peaks of Triton X-100 along with components of some net currents are given for the concentration range 0.50 - 9.80 mg/L. The concentrations are given in mg/L because molecular weight of Triton X-100 is not well defined [28] (as a result of the fact that in the formula $C_{14}H_{22}O(C_2H_4O)_n$, n = 9 -10). If the

approximate value of 625 is applied for calculations, it follows that the measurements were performed in the range 0.800 – 15.68 μmol/L.

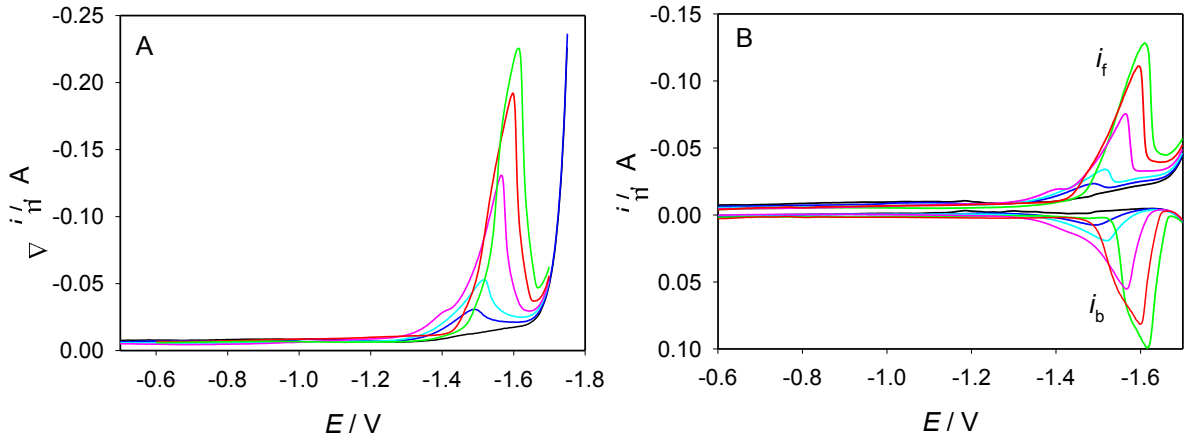

Figure 2

Fig. 2. (A) Square-wave net voltammograms of T-X-100. (B) Their forward (i_f) and backward (i_b) components. Surfactant concentrations: 0, 0.50, 1.00, 2.98, 5.93 and 9.80 mg/L in 1 mol/L $NaClO_4$. E_{st} = - 0.5 V, E_{sw} = 50 mV, E_s = 2 mV, f = 50 s^{-1}.

By inspection of Fig. 2, it could be noticed that adsorption peak does not appear, irrespective of the surfactant concentration, when scanning in the negative direction starts at -0.5 V. Shifting of the starting potential to the most positive values (accessible in experiments with SMDE), even after elimination of chloride ions from the electrolyte bridge (i.e. their substitution with nitrates) does not change the properties of the electrode response, i.e. adsorption peak stays "invisible". All desorption signals are of the similar shape, their backward components are well defined, whereas peak potential becomes more negative as the analyte concentration increases (dE_p/d log c = - 100 mV/d.u.).

When the similar set of voltamograms of SDS is recorded (Fig. 3), final conclusions are the same as for Triton X-100 as long as analyte concentration is kept within the range 5 μmol/L – 0.1 mmol/L. At (significantly) higher levels of the dissolved surfactant, the signal becomes extremely sharp and split in two close peaks. The formal origin of such splitting could be found in the fact that components of the net current are shifted, one with respect to the other (Fig. 3B).

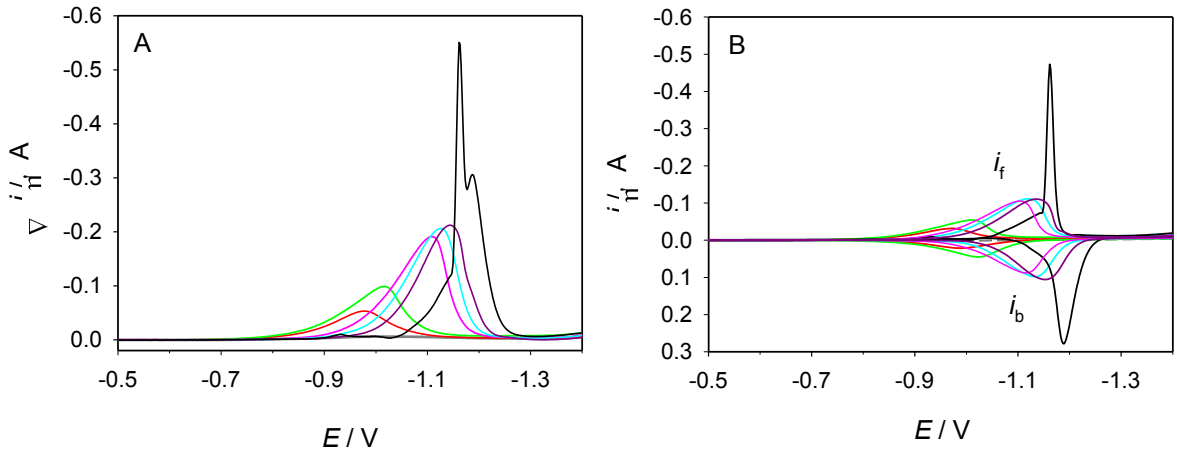

Figure 3

Fig. 3. (A) Square-wave net voltammograms of SDS. (B) Their forward (i_f) and backward (i_b) components. Surfactant concentrations: 0, 5.0, 10.0, 49.8, 69.5, 99.0 and 291.0 μmol/L in 1 mol/L $NaClO_4$. E_{st} = - 0.5 V, E_{sw} = 50 mV, E_s = 2 mV, f = 50 s^{-1}.

Similar effects, i.e. the dependence of *ac* experimental results on the reactant concentration were previously observed by other authors [29] and ascribed to different types of molecular associations. In order to avoid the mentioned "complications", all other measurements were performed at c(SDS) ≤ 2x10^{-5} mol/L. It is possible that the described and some other changes in the peak properties could be useful analytical tools for recognition of the systems, in which electrode reaction cannot be described as a simple, potential dependent adsorption of an electroinactive surfactant. For such an application of SWV, additional theoretical results and experimental measurements are needed.

Theoretical dependence of the normalized SWV peak current on the concentration parameter y is given in Fig. 4. It was calculated for k_c = 10 V^{-2}, $C_{\theta=1}/C_{\theta=0}$ = 0.5 [27] and b_0 = 236, corresponding to Γ_{max} = 10^{-9} mol/cm^2, D = 9 x 10^{-6} cm^2/s, β_0 = 10^8 cm^3/mol [27] and a value of SW frequency f = 50 Hz. Experimentally obtained current - concentration plot should be of the same type, when measurements (under otherwise identical conditions) are performed at increasing concentration of the studied surfactant. For Triton X-100, the agreement of experimental results with theory is good. The only (formal) difference could be found in the sign of current because its positive value was (arbitrarily) assumed during theoretical treatment of the whole problem, whereas measured value was always negative. The net peak current increases (linearly) with increasing surfactant concentration until the electrode surface saturation is achieved. Thus, the quasi-linear range for γ(Triton X-100) ≤ 3 mg/L (regression

line: - Δi_p / A = (0.0372·γ / mg L^{-1} – 0.0034) x 10^{-6}, R^2 = 0.994) could be suitable for determinations of T-X-100 with detection limit of 0.1 mg/L. The detection limit can be lowered by introduction of the accumulation step prior the potential scanning in SWV experiment. In addition, for practical purposes, such as measurement of an unknown concentration, it is useful to find conditions under which current-concentration plot could be described as a straight line with (virtually) zero intercept. This can be achieved by proper choice of square-wave amplitude.

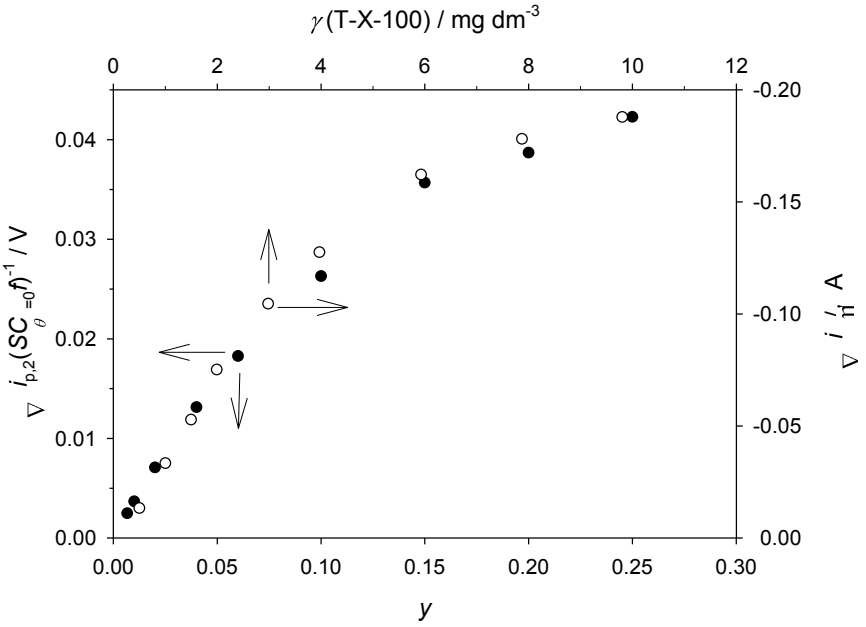

Figure 4

Fig. 4. (●) Theoretical influence of dimensionless concentration parameter y on the normalized desorption net peak current for E_{st} = - 0.2 V vs. E_{pzc}, E_{sw} = 50 mV, k_c = 10 V^{-2}, $C_{\theta=1}/C_{\theta=0}$ = 0.5, a = 0, $E_{pzc,\theta=1} = E_{pzc,\theta=0}$, b_0 = 236 and E_s = 2 mV. (○) Dependence of the real desorption net peak current on concentration of T-X-100 (in 1 mol/L $NaClO_4$) for conditions given in description of Fig. 2.

The absence of adsorption peaks on all experimentally obtained tensammetric SWV curves is not fully unexpected. According to model calculations, for conditions given in description of Fig. 1, separation of the two signals should be highly pronounced and additionally dependent on the value of Frumkin coefficient (Fig. 5). In other words, one peak could be shifted with respect to the other for 1.4 – 1.5 V (or even more) under real conditions. At the same time the half-peak width could be highly reduced in comparison with the value for a = 0.

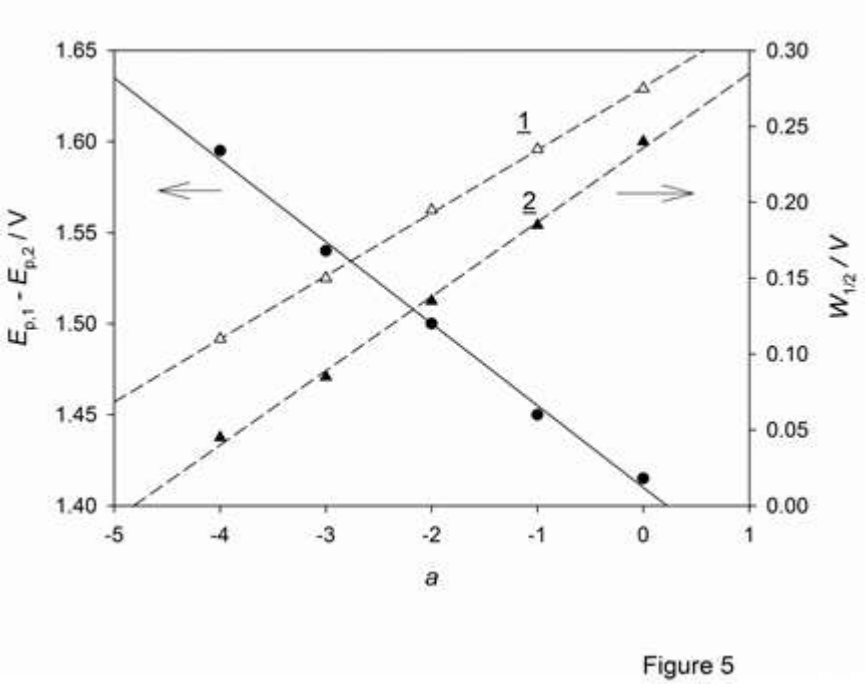

Figure 5

Fig. 5. (●) Theoretical dependence of potential difference between adsorption (1) and desorption (2) peaks of SWV signal and (Δ, ▲) their half-peak widths on Frumkin coefficient. Other parameters are given in description of Fig. 1.

Although tensammetric measurements are generally performed on mercury (because its clean surface can be obtained again and again without difficulties), the additional application of some other electrode material, on which scanning in a wider potential range (that includes more positive values than in the present case) is possible, seems promising for some purposes. The point is that only in such a way the electrode response from Fig. 1A could be obtained in real experiments. When only desorption peak appears, it could be a problem to make difference between it and the signal that reflects reduction from the adsorbed state, because current – frequency linearity (Fig. 6) and current – concentration plots of the same type (Fig. 4) arise from both electrode processes.

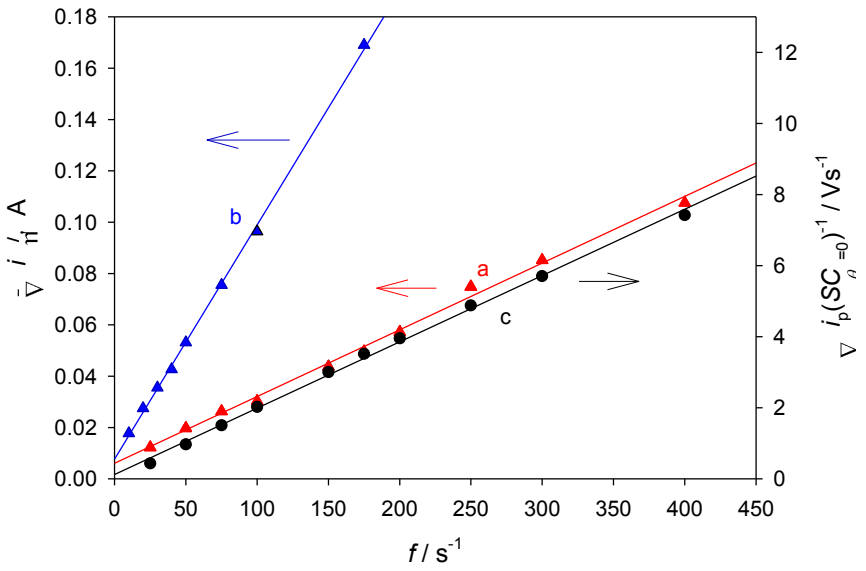

Figure 6

Fig. 6. Dependence of the experimentally obtained (a, b) and normalized theoretical (c) desorption SWV net peak currents on SW frequency. Conditions: a) 1 mg/L T-X-100 (E_{sw} = 20 mV) and b) 5x10^{-6} mol/L SDS (E_{sw} = 50 mV) in 1 mol/L $NaClO_4$; E_s = 2 mV. c) $D = 9 \times 10^{-6}$ cm^{2}s^{-1}, $c^* = 10^{-3}$ mol/L, $\Gamma_{max} = 10^{-9}$ mol/cm^2, $\beta_0 = 10^8$ cm^3/mol, $a = 0$, $E_{pzc,\theta=1} = E_{pzc,\theta=0}$, E_s = 2 mV and E_{sw} = 20 mV.

Therefore only the full tensammetric curve with two well defined and highly separated peaks becomes the best qualitative indicator of the electroinactive surfactant and its surface reactions. It is because in a Faradaic process, complicated by reactant adsorption, broadening of the signal or appearance of two, poorly separated peaks could usually be noticed at relatively high reactant concentrations [9] whereas only in the case of tensammetric signals, i.e. adsorption/desorption of surface active but electroinactive solutes, two well defined but highly separated signals are to be expected.

From Figs. 1A and 1C, it follows that cyclic square-wave voltammetry could also be applicable in experimental studies of electroinactive surfactants. The mentioned technique was recently developed and applied for characterization of kinetically controlled faradaic processes [30,31]. Its potential "strength" in tensammetry is not quite clear but it is worth further examination. An example of the resulting current – potential curves for different concentrations of anionic surfactant SDS is given in Fig.7.

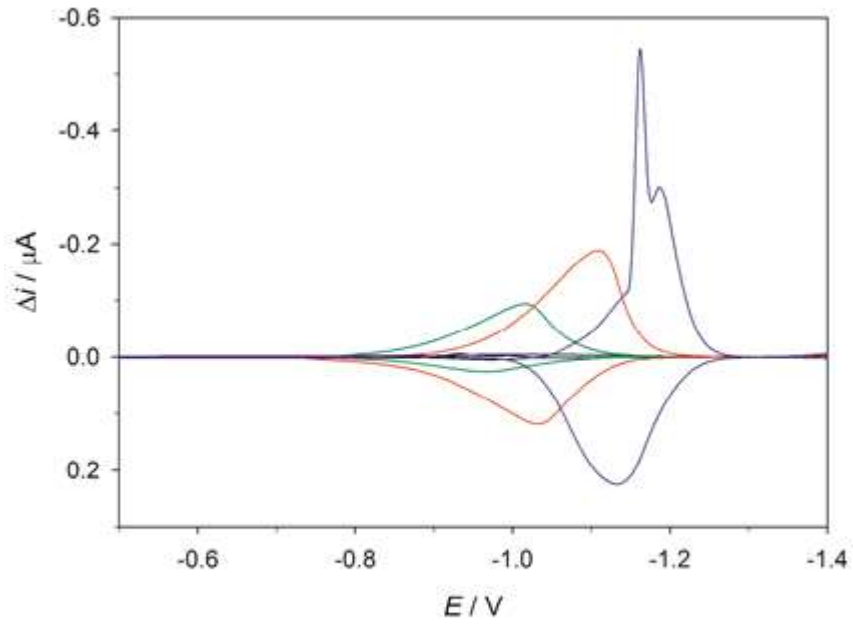

Figure 7

Fig. 7. Cyclic square-wave voltammograms of SDS for conditions given in description of Fig.2. Surfactant concentrations: 0 (black), 10.0 (green), 49.8 (red) and 291.0 (blue) μmol/L in 1 mol/L $NaClO_4$.

5. Conclusions

From the theoretical and experimental results, it follows that a pronounced electrode response is to be expected when square wave voltammogram of an electroinactive surfactant is recorded. This is important for at least three reasons because it indicates that: a) SWV signal obtained during analysis of an unknown sample does not always reflect a redox reaction b) SWV is not so insensitive to capacitive currents as usually stated and c) the technique is a potential tool for different studies of adsorption/desorption processes and trace analysis of surface active substances. The latter is possible because the signal could be highly increased if accumulation step is included.

Although the whole current – potential curve should consist of two highly separated peaks which reflect adsorption and desorption reactions, i.e. a pronounced change of surface coverage within a narrow potential range in each case, real measurements on SMDE give only a desorption signal. Most probably, the problem arises from the fact that really positive potentials are not available in experiments with a mercury electrode. For many practical

purposes, however, the presence of only one peak is sufficient especially because of the fact that its properties are in good agreement with the theory.

Taking into account that measurements of electroinactive surfactants is usually performed by *ac* voltammetry it is of prime importance to compare such results with those that arise from the application of square wave voltammetry, i.e. to find if SWV could be applied in addition to *ac* voltammetry or even instead of it.

Acknowledgements

The authors would like to thank to Dr. Sc. Milivoj Lovrić for helpful discussion and advices.

6. References

[1] A. N. Frumkin, B. B. Damaskin in *Modern aspects of electrochemistry no. 3* (Eds.: J. O. M. Bockris, B. E. Conway), Butterworths, London, **1964**, pp. 149-223.

[2] H. P. van Leeuwen, M. Sluyters-Rehbach, K. Holub, *J. Electroanal. Chem.* **1982**, *135*, 13-24.

[3] M. Lovrić, Š. Komorsky-Lovrić, *J. Electronal. Chem.* **1988**, *248*, 239-253.

[4] M. Seralathan, A. Ribes, J. O'Dea, J. Osteryoung, *J. Electroanal. Chem.* **1991**, *306*, 195-211.

[5] G. Wittstock, H. Emons, *Electrochim. Acta* **1992**, *37*, 2395-2401.

[6] H. P. van Leeuwen, J. Buffle, M. Lovrić, *Pure Appl. Chem*. **1992**, *64*, 1015-1028.

[7] Š. Komorsky-Lovrić, M. Lovrić, M. Branica, *Electroanalysis* **1995**, *7*, 652-655.

[8] Š. Komorsky-Lovrić, *Electroanalysis* **2000**, *12*, 599-604.

[9] M. Lovrić, *Electroanalysis* **2002**, *14*, 405-414.

[10] B. Gašparović, D. Risović, B. Ćosović, *Electrochim. Acta* **2004**, *49*, 3383-3396.

[11] M. Lovrić, M. Zelić, *J. Electroanal. Chem*. **2008**, *624*, 174-178.

[12] B. Ćosović, Z. Kozarac, S. Frka, V. Vojvodić, *Electroanalysis* **2010**, *22*, 1994-2000.

[13] B. B. Damaskin, *Electrochim. Acta* **1964**, *9*, 231-240.

[14] D. R. Canterford, *J. Electroanal. Chem*. **1981**, *118*, 395-403.

[15] Z. Lukaszewski, H. Batycka, W. Zembrzuski, *Anal. Chim. Acta* **1985**, *175*, 55-67.

[16] B. Ćosović in *Aquatic chemical kinetic* (Ed.: W. Stumm), Wiley, New York, **1990**, pp. 291-309.

[17] B. Breyer, H.H. Bauer, *Alternating current polarography and tensametry*, Wiley-Interscience, New York, **1963**.

[18] Z. Lukaszewski, *Electroanalysis* **1993**, *5*, 375-384.

[19] H. Jehring, *Elektrosorptionanalyse mit der Wechselstrom Polarographie*, Akademie Verlag, Berlin, **1974**.

[20] V. Mirčeski, Š. Komorsky-Lovrić, M. Lovrić, *Square-wave voltammetry*, Springer, Berlin, **2007**.

[21] J. G. Osteryoung, R. A. Osteryoung, *Anal. Chem*. **1985**, *57*, 101A-110A.

[22] J. Osteryoung, J. J. O'Dea in *Electroanalytical chemistry Vol. 14* (Ed.: A. J. Bard), Marcel Dekker, New York, **1986**, pp. 209-303.

[23] J. J. O'Dea, J. Osteryoung, R. A. Osteryoung, *Anal. Chem*. **1981**, *53*, 695-701.

[24] M. J. Nuwer, J. J. O'Dea, J. Osteryoung, *Anal. Chim. Acta* **1991**, *251*, 13-25.

[25] N. Fatouros, D. Krulic, *J. Electroanal. Chem*. **1998**, *443*, 262-265.
[26] A. Safavi, N. Maleki, H. R. Shahbaazi, *Anal. Chim. Acta* **2003**, *494*, 225-233.
[27] D. Jadreško, M. Lovrić, *Electrochim. Acta* **2008**, *53*, 8045-8050.
[28]https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma/Product_Information_Sheet/1/t8532pis.pdf
[29] B. Gašparović, D. Risović, B. Ćosović, A. Nelson, *Electrochim. Acta* **2007**, *52*, 2527- 2534, and references therein.
[30] D. Jadreško, M. Zelić, *J. Electroanal. Chem*. **2013**, *707*, 20-30.
[31] D. Jadreško, M. Zelić, J. Electroanal. Chem. **2014**, *714-715*, 30-37.

Table 1. List of symbols

a	Frumkin coefficient
b_0	dimensionless adsorption constant
c	concentration of the reactant
c^*	bulk concentration of the reactant
$C_{\theta=0}$	capacity of free electrode surface
$C_{\theta=1}$	capacity of totally covered electrode surface
D	diffusion coefficient
E	electrode potential
E_{pzc}	potential of zero charge
$E_{pzc,\theta=0}$	potential of zero charge of free electrode surface
$E_{pzc,\theta=1}$	potential of zero charge of totally covered electrode surface
E_s	SW potential step
E_{st}	starting potential
E_{sw}	SW amplitude
ΔE	difference between electrode potential and potential of zero charge
f	SW frequency
i	capacitive current
$i\ (S\ C_{\theta=0}\ f)^{-1}$	normalized SWV response
Δi	net current
i_f	forward component of net current in SWV
i_b	backward component of net current in SWV
Δi_p	net peak current
k_c	capacity parameter
R	gas constant
S	electrode surface area
T	temperature
$W_{1/2}$	half-peak width
y	dimensionless concentration parameter
β_0	adsorption constant at $E = E_{pzc}$
γ	mass concentration
Γ	surface concentration of the adsorbed reactant
Γ_{max}	maximum surface concentration of the adsorbed reactant
$\theta = \Gamma / \Gamma_{max}$	electrode surface coverage

1

Figures Caption

Fig. 1. (A) Normalized SW net voltammogram (n) along with its forward (f) and backward (b) components. (B) Dependence of the electrode surface coverage on the electrode potential. (C) and (D) The same as (A) and (B) but for the opposite scan direction (indicated by an arrow). Conditions: E_{st} = (-) 1 V vs. E_{pzc}, E_s = 5 mV, E_{sw} = 50 mV, y = 0.3, k_c = 10 V^{-2}, b_0 = 333, $C_{\theta=1}/C_{\theta=0}$ = 0.5, a = 0 and $E_{pzc,\theta=1} = E_{pzc,\theta=0}$.

Fig. 2. (A) Square-wave net voltammograms of T-X-100. (B) Their forward (i_f) and backward (i_b) components. Surfactant concentrations: 0, 0.50, 1.00, 2.98, 5.93 and 9.80 mg/L in 1 mol/L $NaClO_4$. E_{st} = - 0.5 V, E_{sw} = 50 mV, E_s = 2 mV, f = 50 s^{-1}.

Fig. 3. (A) Square-wave net voltammograms of SDS. (B) Their forward (i_f) and backward (i_b) components. Surfactant concentrations: 0, 5.0, 10.0, 49.8, 69.5, 99.0 and 291.0 μmol/ L in 1 mol/L $NaClO_4$. E_{st} = - 0.5 V, E_{sw} = 50 mV, E_s = 2 mV, f = 50 s^{-1}.

Fig. 4. (●) Theoretical influence of dimensionless concentration parameter y on the normalized desorption net peak current for E_{st} = - 0.2 V vs. E_{pzc}, E_{sw} = 50 mV, k_c = 10 V^{-2}, $C_{\theta=1}/C_{\theta=0}$ = 0.5, a = 0, $E_{pzc,\theta=1} = E_{pzc,\theta=0}$, b_0 = 236 and E_s = 2 mV. (○) Dependence of real desorption net peak current on concentration of T-X-100 (in 1 mol/L $NaClO_4$) for conditions given in description of Fig. 2.

Fig. 5. (●) Theoretical dependence of potential difference between adsorption (1) and desorption (2) peaks of SWV signal and (Δ, ▲) their half-peak widths on Frumkin coefficient. Other parameters are given in description of Fig. 1.

Fig. 6. Dependence of the experimentally obtained (a, b) and normalized theoretical (c) desorption SWV net peak currents on SW frequency. Conditions: a) 1 mg/L T-X-100 (E_{sw} = 20 mV) and b) 5x10^{-6} mol/L SDS (E_{sw} = 50 mV) in 1 mol/L $NaClO_4$; E_s = 2 mV. c) D = 9 × 10^{-6} cm^2s^{-1}, c^* = 10^{-3} mol/L, Γ_{max} = 10^{-9} mol/cm^2, β_0 = 10^8 cm^3/mol, a = 0, $E_{pzc,\theta=1} = E_{pzc,\theta=0}$, E_s = 2 mV and E_{sw} = 20 mV.

Fig. 7. Cyclic square-wave voltammograms of SDS for conditions given in description of Fig.2. Surfactant concentrations: 0 (black), 10.0 (green), 49.8 (red) and 291.0 (blue) μmol/L in 1 mol/L $NaClO_4$.

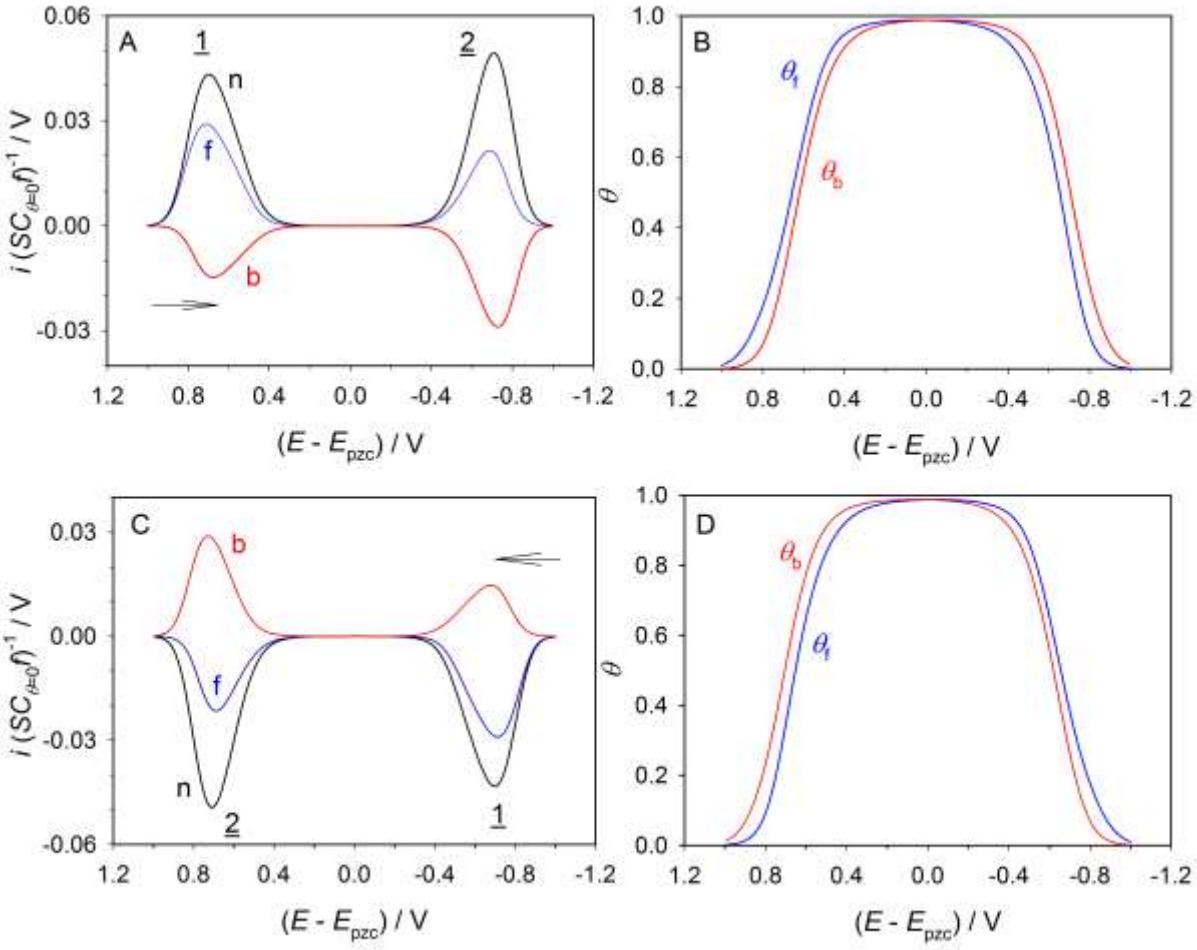

Figure 1

1

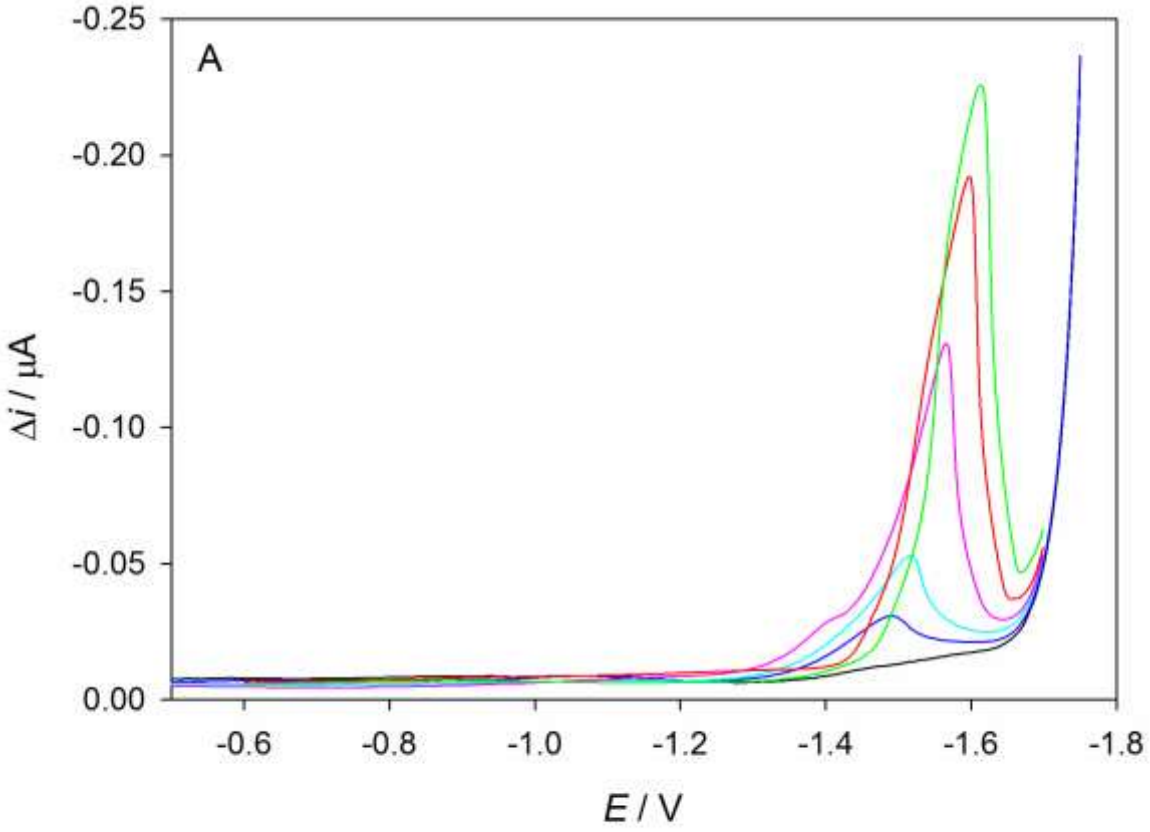

Figure 2A

1

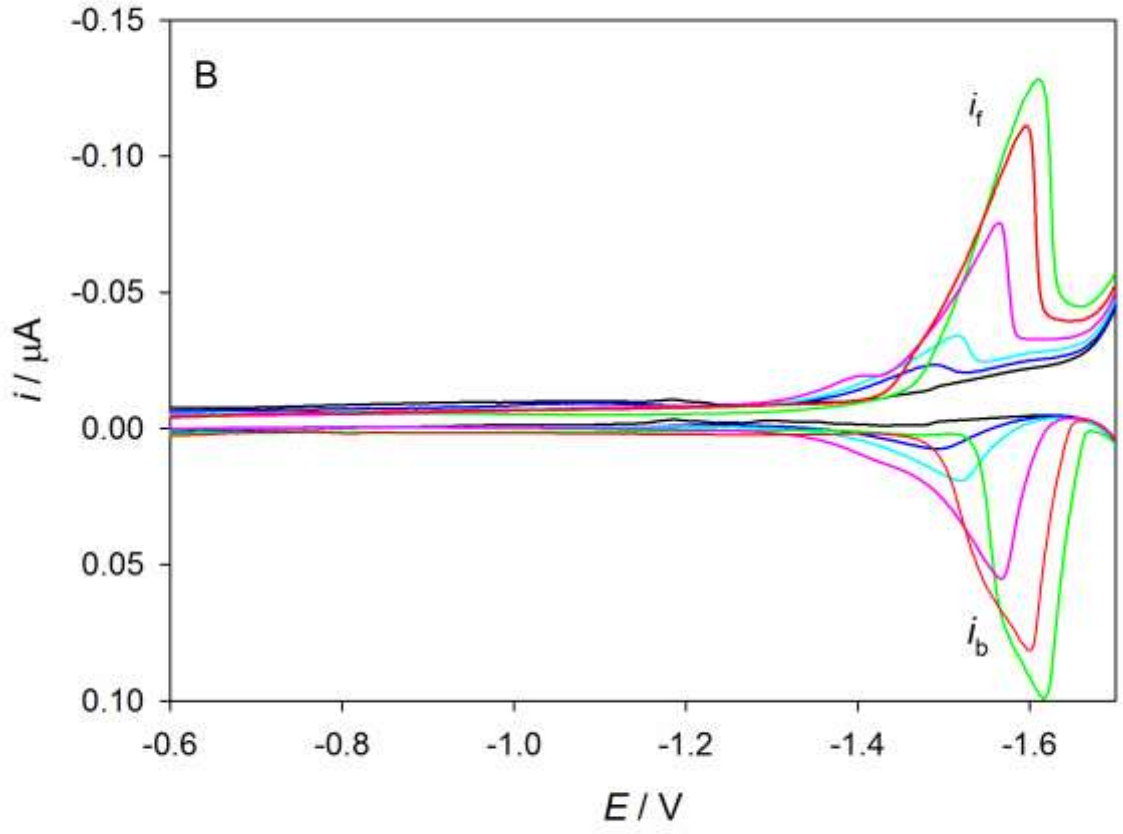

Figure 2B

1

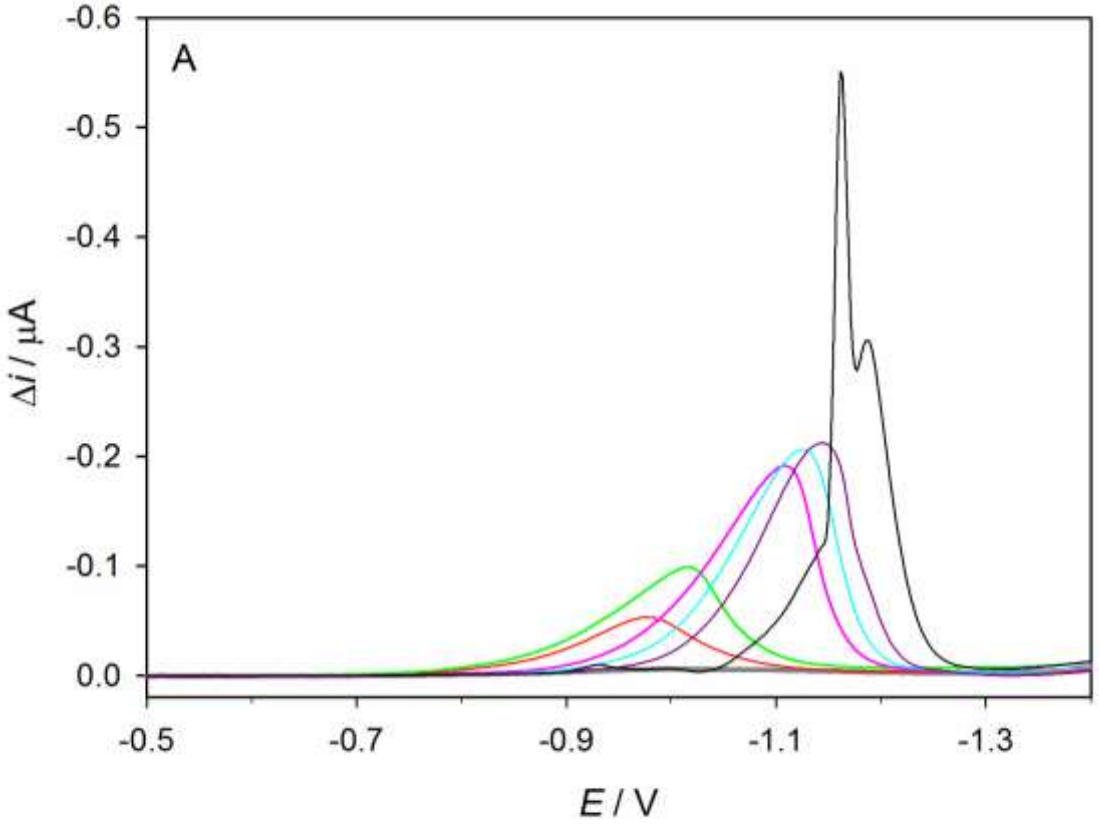

Figure 3A

1

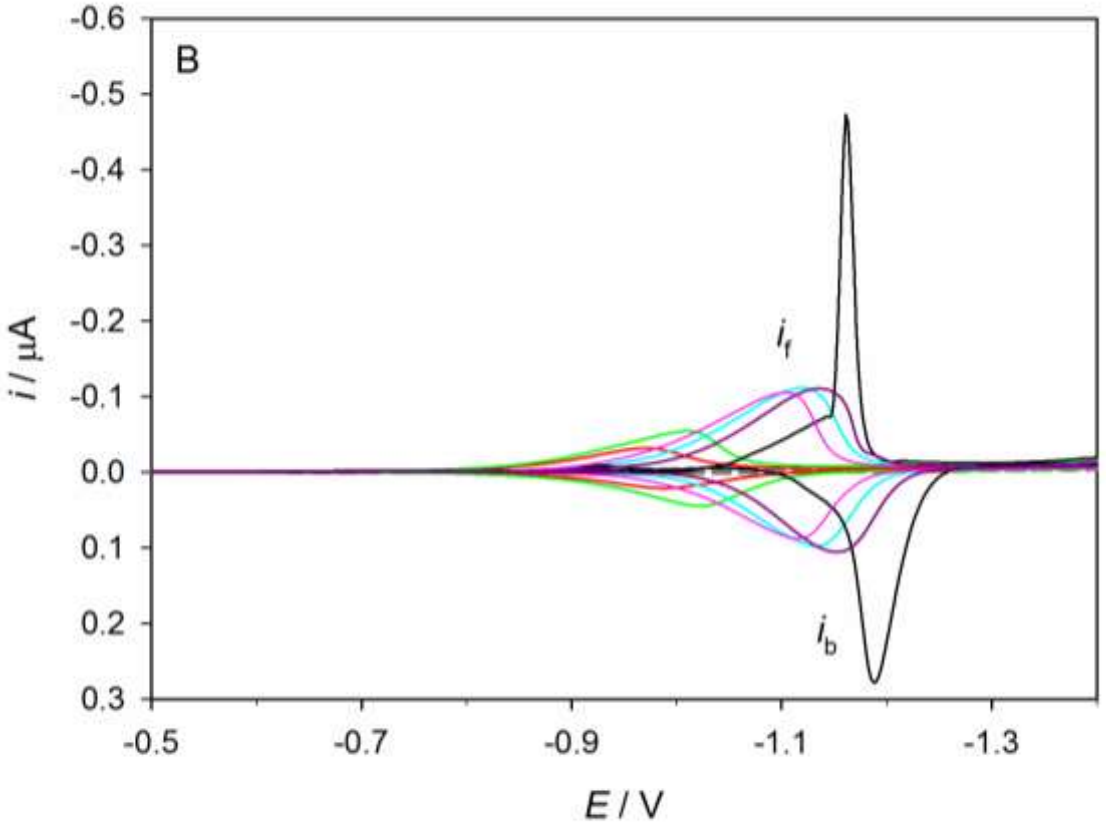

Figure 3B

1

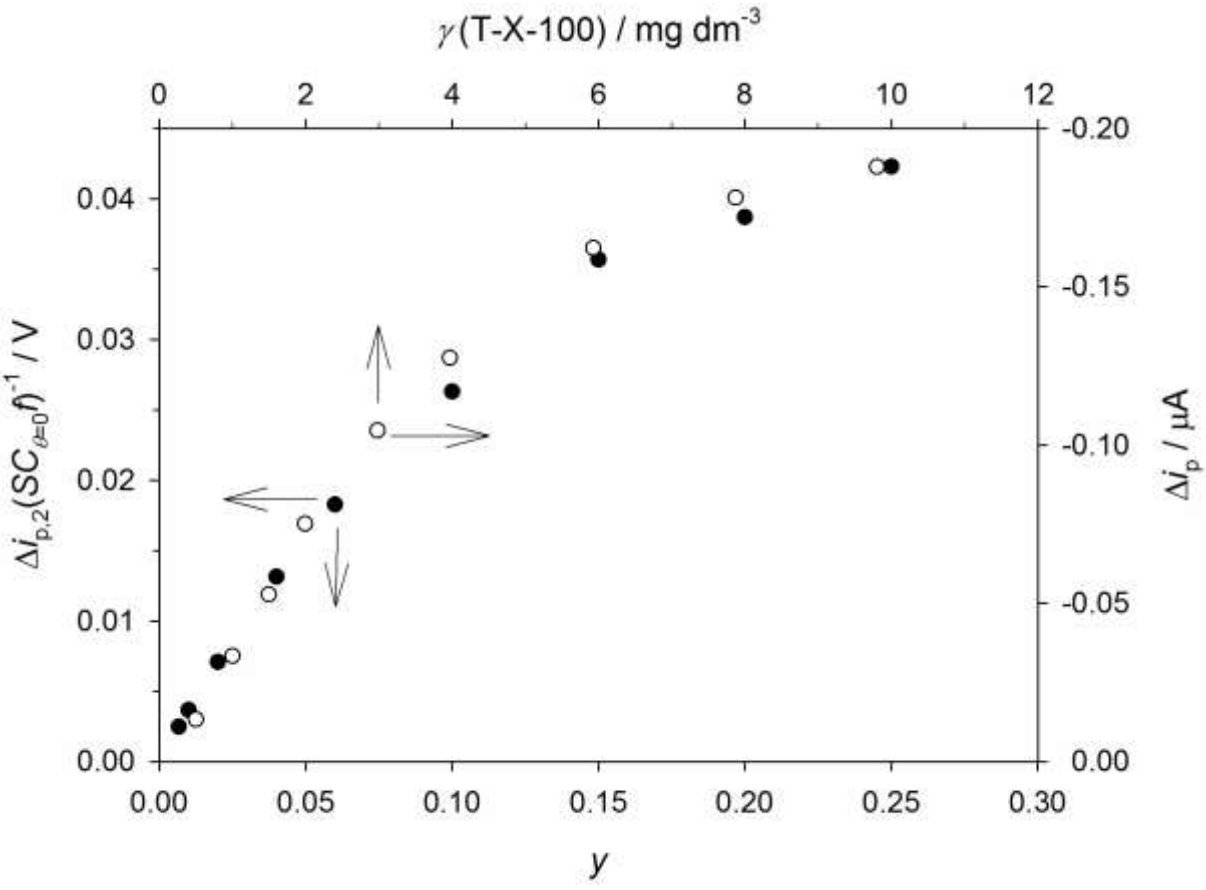
γ(T-X-100) / mg dm-3
0
2
4
6
8
10
12
0.04
0.03
0.02
0.01
0.00
-0.20
-0.15
-0.10
-0.05
0.00
0.00
0.05
0.10
0.15
0.20
0.25
0.30
y
Δip,2(SCi=0f)-1 / V
Δip / μA

Figure 4

1

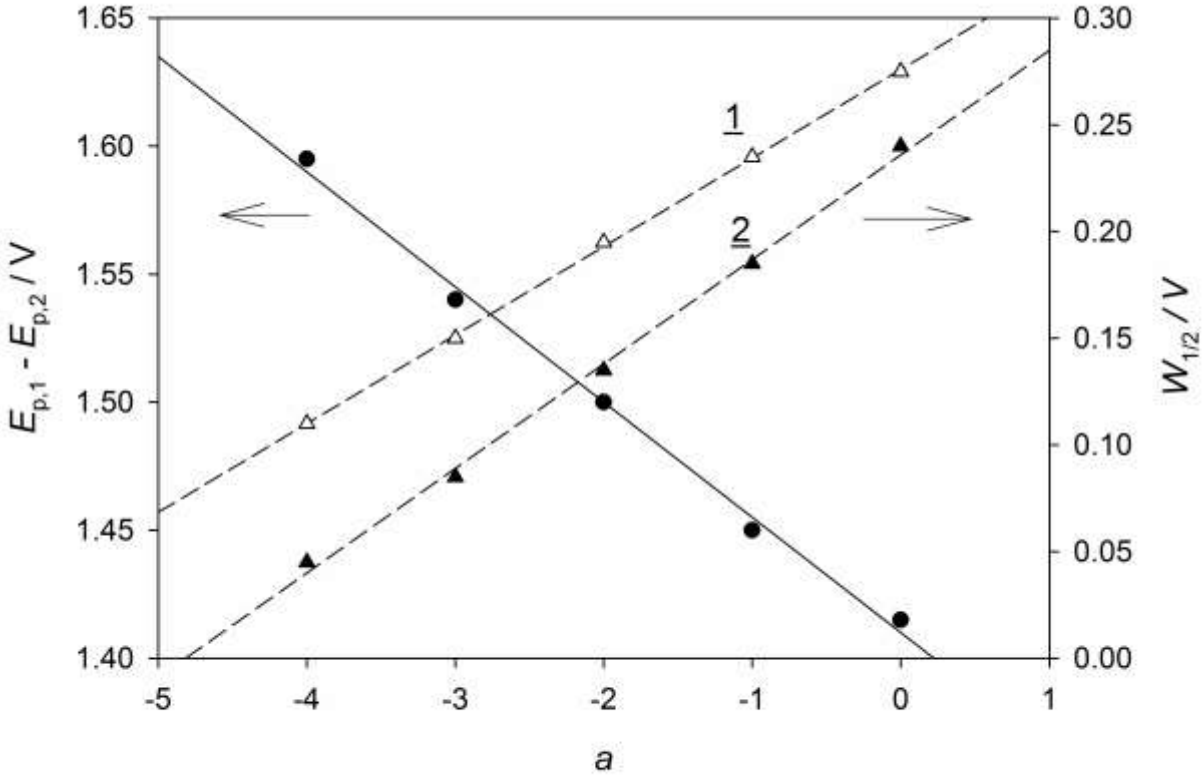
1.65
1.60
1.55
1.50
1.45
1.40
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-5
-4
-3
-2
-1
0
1
a
1
2
$E_{p,1} - E_{p,2}$ / V
$W_{1/2}$ / V

Figure 5

1

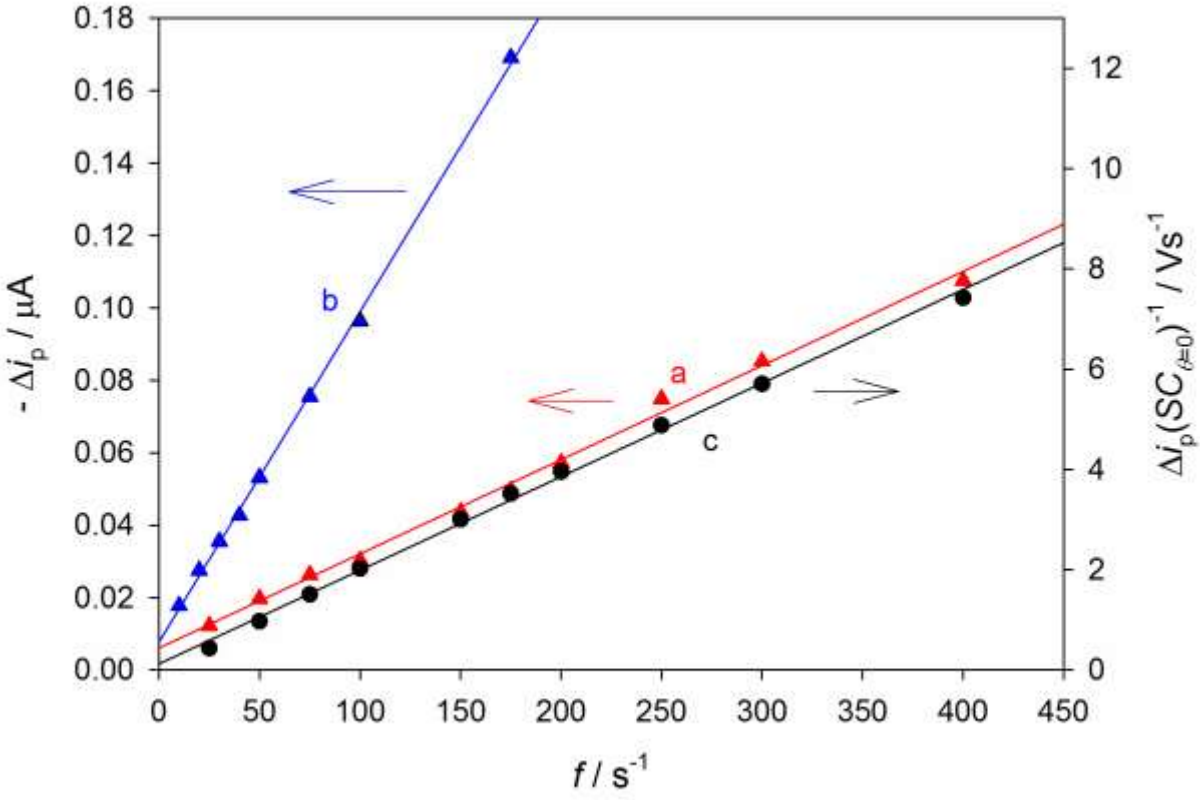
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
- Δi_p / μA
0
50
100
150
200
250
300
350
400
450
f / s^-1
12
10
8
6
4
2
0
Δi_p(SC_t=0)^-1 / Vs^-1
a
b
c

Figure 6

1

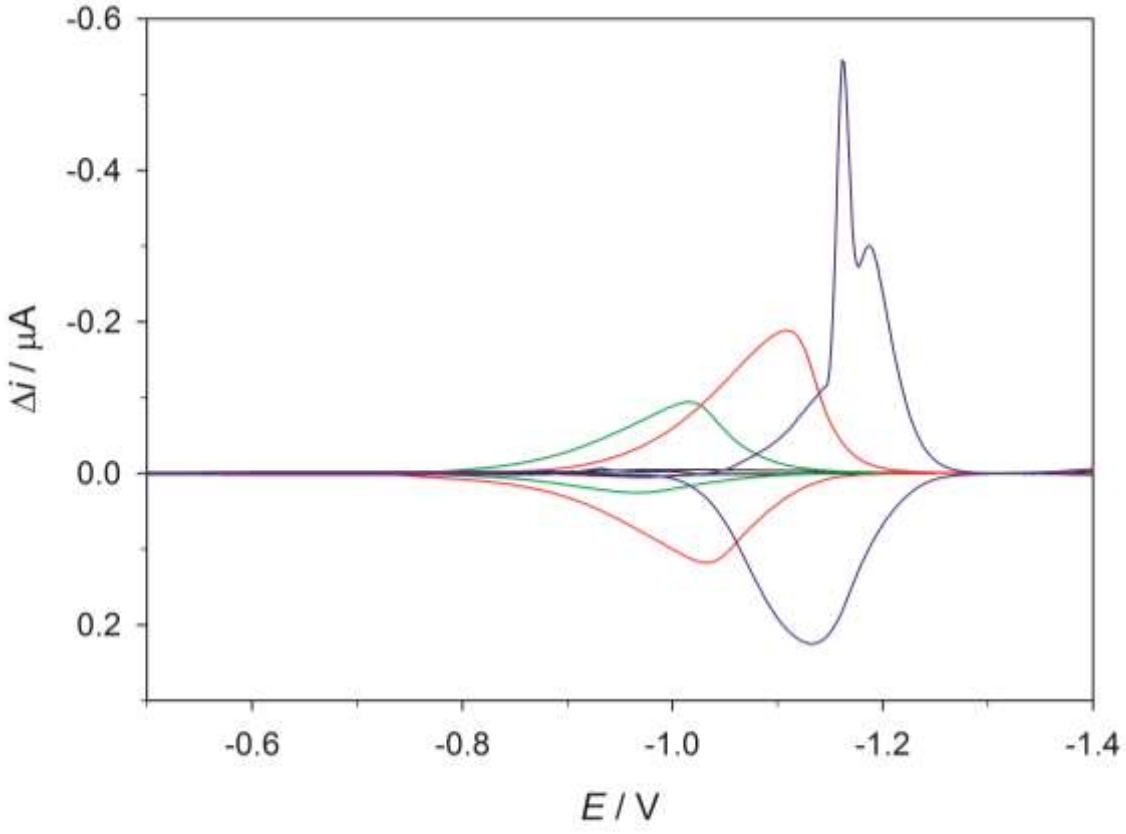

Figure 7

1