

## The Influence of Frequency on Fractal Dimension of Adsorbed Layers

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### Abstract

*Ac* voltammetry and electrochemical impedance spectroscopy are often the methods of choice for use in study of adsorption of organic molecules. The adsorption of organic molecules on interface may result in formation of fractal structures, whose fractal dimension can be estimated using the method of scaling the hanging mercury drop electrode (HMDE). The aim of present study was to check whether the estimated fractal dimension,  $D$  (or for that matter the fractal ordering of the adsorbed layer) shows any correlation (dependence) with change of applied frequency, and second, to check the possibility to extend the method to broad frequency spectrum compatible with impedance spectroscopy. The investigation included two surfactants nonionic Triton-X-100 (T-X-100) and anionic sodium dodecyl sulfate (SDS) and alcohol tert-butanol. All measurements were performed on HMDE at thermodynamic equilibrium employing broad frequency spectrum. The validity of the approach was checked by measurements on pure electrolyte and by comparison with previously obtained results for fractal layers. The results of the investigations show that: (1) the method of scaling the HMDE to obtain the fractal dimension of adsorbed layer is compatible with impedance spectroscopy and the combination of these methods can be used as a powerful tool to investigate fractal aspect of adsorption of organic molecules; (2) fractal ordering of adsorbed layer and the value of fractal dimension is not influenced by the frequency of applied sinusoidal voltage perturbations.

*Keywords:* frequency dependence; adsorption; fractal analysis; impedance spectroscopy; Triton-X-100; sodium dodecyl sulfate, tert-butanol

## 1. Introduction

The adsorbed layers may exhibit fractal properties that change during the adsorption depending on local conditions and involved molecular interactions. Once, when the fractal nature of the structure is established and its fractal dimension determined, such structures may be treated theoretically as stochastic/random fractals whose fractal dimension reflects the growth mechanism and whose changes can be correlated with the changes of interactions and structure of the considered system [1-3]. Thus estimation and monitoring of fractal dimension can provide additional valuable insight into the properties and dynamics of the studied system. Fractal ordering of adsorbed layers can be investigated by different methods comprehending electrochemical methods [4-7], atomic force microscopy [8], transmission electron microscopy [9], etc.

Previously we have devised a simple method for determination of fractal dimension,  $D$  of an adsorbed layer by the scaling of a hanging mercury drop electrode (HMDE) that is suitable for use in *ac* voltammetry [4]. The method was derived from basic principle that for a statistically scale-invariant structure, (physical realization of a mathematical fractal that appears the same on all length scales), the considered feature exhibits a power-law scaling. The “feature” used in the method is the capacitive current at a selected electrode potential and the “scale” is the electrode surface represented by the radius of the mercury drop:

$$I_c \sim r^D \quad (1)$$

In the *ac* voltammetric measurements the size of the mercury drop is varied stepwise over a broad size-range and  $D$  is obtained from the slope of the log-log plot of  $I_c$  vs.  $r$ . This method has been successfully used to determine and monitor the fractal dimension of adsorbed layers of organic substances and to relate it to structural changes, growth mechanisms and properties of the adlayer [4, 5, 10, 11]. However, such *ac* voltammetric measurements are usually conducted at a single frequency, typically from the low frequency range (few hundreds Hz or below). On the other hand, the impedance spectroscopy that is often used in the field of interfacial electrochemistry employs rather broad frequency spectrum comprehending frequencies in range from few Hz to many kHz.

In that context the aim of present work was twofold: first, to check whether the estimated fractal dimension  $D$  (or for that matter the fractal ordering of the adsorbed layer) shows any correlation (dependence) with change of applied frequency, and second, to check the

possibility to extend the method to a broader frequency spectrum compatible with impedance spectroscopy. Hence, here, we report and discuss the results of application of the HMDE-scaling method in impedance spectroscopy for estimation of adsorbed layer's fractal dimension in a broad frequency spectrum.

## 2. Experimental

In this study the impedance spectroscopy measurements in combination with scaling of the HMDE were used. For the electrochemical impedance spectroscopy an Autolab system, FRA 2 and  $\mu$ AUTOLAB Type III interface (Ecochemie, Utrecht, Netherlands), controlled with Autolab software were used. All instrumentation was enclosed in a grounded Faraday-cage. The impedance measurements were performed in a broad frequency spectrum ranging from 65 kHz – 0.1 Hz, with 0.005 V rms at selected electrode potentials of - 0.35 V and – 0.6 V in respect to Ag/AgCl/3 M KCl reference electrode and with a platinum wire as the auxiliary electrode. The working electrode was a hanging mercury drop electrode (HMDE) by Metrohm, Switzerland. The instrument provides the real and imaginary impedance components of the cell,  $Z'$  and  $Z''$ , respectively. Subsequently the measured impedance data were transformed to the complex capacitance plane, where the complex capacitance axes are expressed as  $\text{Re } Y\omega^{-1}$  and  $\text{Im } Y\omega^{-1}$ .

The same Autolab system was used in *ac* mode of operation ( $90^0$  out of phase) for the measurements of capacitance current *vs.* applied electrode potential. The frequency of the *ac* voltage was 170 Hz, the amplitude 0.010 V rms, potential step 0.005 V, while the modulation and interval times were 0.38 s and 1 s, respectively.

All measurements were conducted under the equilibrium -steady state conditions attained under the diffusion controlled adsorption. The attainment of steady state for the given experimental conditions (i.e. bulk concentration, electrode potential etc), is manifested as the lowest and constant capacitance current value in the recorded  $I_c$  *vs.*  $t$  curve. The change of capacitive current with time ( $I_c - t$  measurements) during the diffusion-controlled adsorption was measured by phase sensitive alternating current (*ac*) voltammetry ( $90^\circ$  out of phase) at a given electrode potential. The *ac* p-p voltage amplitude was 10 mV at frequency of 170 Hz.

The  $I_c$  vs.  $t$  measurements were performed by the EDT-ECP 110 Modular Research Polarograph (London, England) and digitized afterward.

Prior to each measurement the purity of the electrolyte was checked through  $I_c - t$  measurements (this plot should yield a constant capacitance value or exhibit a minimal decay rate for the whole investigated time range) and only then the investigated substance was added.

The experiments were carried out in electrolyte of 0.5 M NaCl and  $3 \times 10^{-2}$  M NaHCO<sub>3</sub> (pH 8.3) under nitrogen atmosphere. All solutions were prepared with deionised water obtained with the Milly-Q Water System (Millipore, Switzerland). Triton-X-100 (T-X-100), (CH<sub>3</sub>)<sub>3</sub>-CH<sub>2</sub>-C(CH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>-O-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>9-10</sub>H,  $M_w \approx 600$  g/mol (Sigma) was used without further purification. Sodium dodecyl sulfate (SDS), CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-O-SO<sub>3</sub>Na,  $M_w = 288.38$  g/mol (BDH Chemicals), was recrystallized from absolute ethanol and the purity was tested by surface tension measurements [12]. As SDS slowly hydrolyses in solution new stock solution of SDS was prepared each day. Tert-butanol, C(CH<sub>3</sub>)<sub>3</sub>OH,  $M_w = 74.12$  g/mol (Merck) was used without further purifications.

All impedance spectroscopy measurements were performed at the thermodynamic equilibrium conditions that are specific for the chosen organic molecule and its bulk concentration. The work under thermodynamic conditions is also desirable from the experimental point of view i.e. due to fact that the acquisition of the entire impedance spectrum usually takes several minutes.

For the sake of fractal analysis the electrode surface area was varied stepwise from  $8.8 \times 10^{-3}$  –  $3.8 \times 10^{-2}$  cm<sup>2</sup>. The fractal dimension,  $D$ , was determined from the slope of the log-log plot of capacitance vs. electrode size. The capacitances were calculated from the imaginary part of the measured impedance data for all frequencies from the investigated frequency spectrum. The measurements were performed each time with a freshly prepared new drop of a selected size that was not changed during the measurement and repeated at least two times.

The fractal dimension was also estimated from the zero frequency capacitance (ZFC). The ZFC was obtained by the extrapolation of the semicircle of the complex capacitance plane to the  $\text{Im}Y\omega^{-1}$  axis at low frequency [13].

### 3. Results and discussion

For this study of possible influence of frequency of sinusoidal voltage perturbations on the estimation of fractal dimension and/or on the fractal ordering of adsorbed layers on the HMDE, three different organic substances were chosen: nonionic surfactant Triton-X-100 (T-X-100), anionic surfactant sodium dodecyl sulphate (SDS) and alcohol, tert-butanol. All molecules are well known and their adsorption on mercury electrode has been previously widely studied [e.g. 5, 14, 15], thus, providing enough information relevant for the present study. For the nonionic surfactant T-X-100 it has been shown previously that under certain experimental conditions the adsorbed layer is fractal [5-7]. On the other hand SDS adsorption, including surface aggregation, formation of hemimicelles and condensation was extensively studied [e.g. 16, 17] but did not include any aspects of possible fractal ordering. Also, many aspects of tert-butanol adsorption were studied but not regarding possible fractal ordering [e.g. 18, 19].

To select the suitable potentials and bulk concentrations for our investigation we have first recorded the variation of differential capacitance vs. applied electrode potential for a broad potential range and different bulk concentrations of both substances. In Fig. 1 typical  $C$  vs.  $E$  curves are plotted for several bulk concentrations of T-X-100, SDS and tert-butanol together with a curve corresponding to a high bulk concentration at which the relative electrode surface coverage  $\theta = 1$ . The capacitances corresponding to this high surface coverage at selected potentials were subsequently used as the reference for calculation of surface coverages corresponding to selected bulk concentrations of T-X-100 and SDS. The curves were recorded at the steady state conditions, after diffusion controlled adsorption, by scanning from the selected potentials in the positive and negative direction.

From Fig. 1a it can be seen that T-X-100 is strongly adsorbed at  $E = -0.35$  V and up to a highly negative potential of  $E \approx -1.6$  V. In the bulk concentration range up to  $5 \text{ mg/dm}^3$  T-X-100 one desorption peak can be observed at  $E \approx -1.6$  V [18]. The height of this desorption peak is proportional to the logarithm of T-X-100 bulk concentration. Such behavior is usually associated with simple adsorption/desorption processes of monomers. SDS is strongly adsorbed over wide range of potentials extending to both sides from the potential of zero charge that, for the given experimental conditions on mercury electrode, occurs at  $E \approx -0.6$  V. Occurrence of a central capacitance pit surrounded with well defined plateaus observed at

bulk concentration of about  $10^{-4}$  M indicates formation of condensed film. The detailed discussion of SDS adsorption can be found in the literature [e.g. 16, 17]. Similarly to SDS tert-butanol is strongly adsorbed around  $E = -0.6$  V but at much higher bulk concentrations.

Based on these preliminary observations we have selected the electrode potentials and bulk concentrations for our further research. The selected electrode potentials for experiments were:  $E = -0.35$  V for T-X-100 and  $E = -0.6$  V for experiments with SDS and tert-butanol. The first selection was based on the fact that previous investigation has shown that at this potential T-X-100 indeed forms fractal structure and to facilitate the comparison of the results, while the second choice was made considering the strength of adsorption and distances from the desorption peaks and their changes with concentration. At these potentials the selected molecules are neither reduced nor undergo any chemical reactions. The bulk concentrations selected for the further investigations with T-X-100 were 0.5, 0.8 and 2 mg/dm<sup>3</sup> ( $\sim 8.4 \times 10^{-7}$  M,  $\sim 1.34 \times 10^{-6}$  M and  $\sim 3.4 \times 10^{-6}$  M, respectively), for SDS: 0.4, 0.7 and 1 mg/dm<sup>3</sup> ( $1.4 \times 10^{-6}$  M,  $2.4 \times 10^{-6}$  M and  $3.5 \times 10^{-6}$  M, respectively); and for tert-butanol: 2.60, 4.63 and 9.27 g/dm<sup>3</sup> (35.1, 62.5 and 125 mM, respectively). The calculated relative surface coverages for equilibrium adsorption corresponding to the selected T-X-100, SDS and tert-butanol bulk concentrations are  $\theta = 0.85, 0.87, \text{ and } 0.94$ ;  $\theta = 0.85, 0.91, 0.93$  and  $\theta = 0.15, 0.41$  and  $0.92$ , respectively. The fractional surface coverage ( $\theta$ ) was calculated from the measured capacitance currents from the following relation:

$$\theta = \frac{i_0 - i_c(\theta)}{i_0 - i_c(\theta = 1)} \quad (2)$$

Here,  $i_0$  represents the capacitive current corresponding to the interface capacitance without organic molecules,  $i_c(\theta)$  the capacitive current in the presence of adsorbed organic molecules and  $i_c(\theta = 1)$  the capacitive current obtained for the totally covered electrode.

The selection of potential and bulk concentrations for T-X-100 were based on previous investigations that had shown that at this potential the adsorbed layer is fractal for a broad

range of T-X-100 bulk concentrations [7]. In the case of SDS to avoid the possible complex adsorption [16] we have chosen the conditions of relatively low bulk concentration (well below the CMC that is  $4.3 \times 10^{-4}$  M in 0.5 M NaCl [16]) and the electrode potential of - 0.6 V at which we do expect a relatively simple monolayer adsorption. The simple monolayer adsorption is also expected for tert-butanol at  $E = - 0.6$  V [18, 19].

To investigate possible influence of the frequency of imposed sinusoidal voltage perturbation on determination of fractal dimension and/or fractal ordering of adsorbed layer we have implemented the HMDE scaling method in impedance spectroscopy measurements under equilibrium conditions.

The times needed to reach the equilibrium (steady state) at the selected potentials under diffusion controlled adsorption were estimated from the  $I_C$  vs.  $t$  measurements. These measurements were made for all substances at all investigated bulk concentrations. The results obtained for T-X-100 and SDS solutions together with those of pure electrolyte are depicted in Fig. 2. The purity of the electrolyte is indicated by absence of significant current decrease with time that would otherwise occur due to the adsorption of impurities (cf. Fig. 2, curves 1). The times needed to reach equilibrium at the selected tert-butanol bulk concentrations are almost instantaneous so that they are not included in the figure.

For a given substance the time needed to attain the equilibrium condition depends on the bulk concentration through an inverse power law. For the T-X-100 solutions with bulk concentrations of 0.5, 0.8 and 2 mg/dm<sup>3</sup> steady state is reached in about 1850 s, 750 s and 270 s, respectively at - 0.35 V. For the SDS solutions the corresponding times needed to reach steady state for the concentrations of 0.4, 0.7 and 1 mg/dm<sup>3</sup> are about 1700 s, 950 s and 500 s, respectively, at - 0.6 V.

All electrochemical impedance measurements at the selected electrode potentials and at different electrode sizes (scaling of HMDE for determination of  $D$ ) were accomplished at steady state conditions: first for pure electrolyte, and then for the solutions with different bulk concentrations of T-X-100, SDS and tert-butanol.

Typical Cole-Cole plots in the complex capacitance plane derived from the measured impedance data for pure electrolyte and the solution of 0.8 mg/dm<sup>3</sup> T-X-100 recorded at the electrode potential  $E = - 0.35$  V for nine HMDE sizes are shown in Fig 3a and b. The plots in complex capacitance plane are almost ideal semicircles indicating minimal or no capacitance dispersion at all. Similar results were obtained with SDS and tert-butanol.

In the whole investigated frequency spectrum the capacitance, calculated from the imaginary part of the impedance data obtained at particular electrode size, increases with increasing electrode surface area. The adsorption of organic substance, in the presented case of T-X-100, on the electrode surface, causes decrease of capacitance in respect to that of the electrolyte at the same electrode size.

Representative log-log plots of calculated capacitances,  $C$  vs. the electrode size,  $r$  for pure electrolyte and representative T-X-100 and SDS solutions are shown in Fig. 4. Such plots were used for estimation of the fractal dimension according to the Eq. 1. The fractal dimension was estimated for each frequency from the applied spectrum, and also for the zero-frequency capacitance (ZFC) [13].

The estimation of fractal dimension for pure electrolyte (i.e. bare electrode) should yield (within the experimental error) the value of Euclidean dimension  $D = d = 2.0$  reflecting the absence of the adsorbed molecular layer on a smooth non-fractal mercury electrode surface, regardless of experimental conditions such as frequency of applied sinusoidal voltage or applied potential. The results of determination of fractal dimension for pure electrolyte in a very broad frequency range 0.1 – 65000 Hz and at selected potentials are shown in Fig. 5a. As seen from the figure  $D \approx 2$  and is independent on frequency in a broad intermediate frequency range, while departures can be observed at the extreme frequencies. At these frequencies the estimated fractal dimension deviates approximately up to  $\pm 10\%$  from the true value ( $D = 2.0$ ). These deviations are the experimental artifacts occurring at very high or very low frequencies regardless of investigated material or bulk concentrations and are of no interest for the present work. Furthermore, to better determine the experimentally applicable frequency range for the proper estimation of  $D$ , the rate of change of  $D$  was also examined. Fig. 5b shows the derivation of  $D$  in respect to the  $\log f$  as the applied frequencies in the measurements increase logarithmically.

If we set that the acceptable frequency range is determined by condition that the absolute value of the deviation from the "true" value  $|\Delta D| \leq 2\%$  and simultaneously the rate of change

$\left| \frac{dD}{d(\log f)} \right| \leq 0.2$ , than we end up with acceptable frequency interval of 30 Hz - 21.8 kHz. The

average fractal dimensions determined for this frequency range from measurements of pure electrolyte at  $E = -0.35$  V and  $E = -0.60$  V are  $D = 1.995 \pm 0.014$ , and  $D = 1.984 \pm 0.014$ , respectively. These values are consistent, within the acceptable data errors, with the



theoretical value  $D = 2.0$  for a uniform, non-fractal electrode. Also, the excellent linear fit (regression coefficient  $R^2 \geq 0.9999$ ) of measured data in log-log plot of  $C$  vs.  $r$  for pure electrolyte (cf. Fig. 4) indicates that the mercury drop remains spherical even for the biggest electrode sizes used in the experiments. The linearity of the fit was preserved to a high degree in all measurements and remained uncorrelated with T-X-100, SDS or tert-butanol bulk concentration. This indicates that the change of Hg-electrode surface tension due to the adsorption does not affect its sphericity. Also, the repeatability of measurement results was very good: the standard deviation of capacitance determined from repeated measurements at particular electrode size ranged between 0.05% and 0.6 % with (overall) average value of 0.18 %.

Hence, we conclude that the acceptable frequency range for estimation of fractal dimension in impedance spectroscopy measurements is 30 Hz - 21.8 kHz. Consequently, in the next step, all further results obtained from measurements of selected substances are presented for this frequency range. First we will elaborate the results obtained with T-X-100.

Previously, using *ac* voltammetry, it has been established [4] that at the selected electrode potential,  $E = -0.35$  V, the adsorbed T-X-100 layers exhibit different fractal dimension depending on the relative electrode surface coverage. Hence, the impedance spectroscopy measurements were conducted at different electrode sizes at  $E = -0.35$  V for selected T-X-100 bulk concentrations/surface coverages at the steady-state conditions. The fractal dimension of the adsorbed layers in the relevant frequency range (30 Hz - 21.8 kHz) was calculated from the dependence of measured capacitances vs. size of the HMDE. The estimated  $D$  vs.  $f$  for adsorbed layers obtained at the T-X-100 bulk concentrations of 0.5, 0.8 and 2 mg/dm<sup>3</sup> are depicted in Fig. 6.

It can be seen that the different fractal dimensions corresponding to the different T-X-100 bulk concentrations (i.e. fractional electrode coverages) remain (within the acceptable data errors) practically constant in a wide frequency range. The measurement uncertainty at a particular frequency from the range is lower for higher frequencies (about  $\pm 0.4$  %) and is higher for frequencies below 100 Hz ( $\pm 1 - 2$  %) and represented by the corresponding error bars in the figures. The systematic minor oscillation of average  $D$  that can be observed at lower frequencies from the range, and that was also observed in measurements with SDS and electrolyte (cf. Figs 7 and 5), is still within the measurement uncertainty limits and hence can be treated as an experimental artifact associated with measuring system characteristic rather

than some subtle structural change of the adsorbed fractal layer. In the frequency range 30 Hz - 21.8 kHz the estimated average fractal dimensions of adsorbed layer of T-X-100 obtained at bulk concentrations of 0.5, 0.8 and 2.0 mg/dm<sup>3</sup> are  $2.28 \pm 0.02$ ,  $2.05 \pm 0.02$  and  $2.02 \pm 0.02$ , respectively. At relative electrode coverage of about  $\theta = 0.85$  (bulk concentration 0.5 mg/dm<sup>3</sup>) the layer exhibits relatively high fractal dimension  $D = 2.28$ . With increase of the bulk concentration the adsorbed layer gets more uniform and smoother as manifested by the decrease of fractal dimension. At high bulk concentration i.e. at high relative electrode coverage ( $\theta = 0.94$ ) the layer is compact and relatively "smooth" with  $D \cong 2$ . These results are in agreement with previously determined fractal dimensions for the corresponding relative electrode coverages [5].

The fractal dimensions were also calculated from the dependence of the zero frequency capacitances (ZFC) on electrode size. Fractal dimensions obtained from ZFC for solutions of 0.5, 0.8, and 2.0 mg/dm<sup>3</sup> T-X-100 are 2.29 ( $R^2 = 0.9987$ ), 2.06 ( $R^2 = 0.9989$ ), and 2.00 ( $R^2 = 0.9991$ ), respectively. These values are in excellent agreement with the corresponding frequency averaged values of  $D$  for the considered frequency range.

The same procedure was applied to different SDS bulk concentrations at the  $E = -0.6$  V. The impedance scans were performed after attainment of the steady-state conditions by diffusion as determined by  $I_c - t$  measurements. The results of fractal dimension estimates for 0.4, 0.7 and 1.0 mg/dm<sup>3</sup> bulk concentration of SDS are depicted in Fig. 7.

Here, trends similar to those in T-X-100 results can be observed: independence of estimated  $D$  on frequency of applied sinusoidal voltage for the whole investigated frequency spectrum, the decrease of fractal dimension with increase of the bulk concentration, i.e. relative electrode coverage, and increase of measurement uncertainty in the low frequency range ( $\pm 1 - 2$  % for  $f$  below 100 Hz versus about  $\pm 0.4$  % at higher frequencies). At the bulk concentration of 1 mg/dm<sup>3</sup> ( $\theta = 0.93$ ) the adsorbed layer is a compact and uniform monolayer with  $D \approx 2$ . The measured low differential capacitance of 3.2  $\mu\text{F}/\text{cm}^2$  supports this conclusion.

The estimated fractal dimension of adsorbed layer averaged over the frequency range 30 Hz - 21.8 kHz obtained at bulk concentrations of 0.4, 0.7 and 1.0 mg/dm<sup>3</sup> are  $2.10 \pm 0.02$ ,  $2.04 \pm 0.02$  and  $1.97 \pm 0.02$ , respectively. Corresponding fractal dimensions determined from ZFC for the same bulk concentrations are 2.08 ( $R^2 = 0.9953$ ), 2.04 ( $R^2 = 0.9978$ ), and 1.97 ( $R^2 = 0.9992$ ), respectively.

The representative results of fractal dimension estimates for 2.60, 4.63 and 9.27 g/dm<sup>3</sup> (35.1, 62.5 and 125.0 mM) bulk concentration of tert-butanol (corresponding to the relative electrode surface coverage  $\theta = 0.15, 0.41$  and  $0.92$ , respectively) are depicted in Fig. 8. It can be observed that contrary to the adsorbed T-X-100 and SDS layers the adsorbed layers of tert-butanol do not exhibit fractal structure at any fractional electrode coverage. The fractal dimension was also estimated for bulk concentrations between 7.8 and 125 mM, that covers electrode surface coverages  $\theta = 0.04$  to  $0.92$ , resulting in  $D = d \approx 2$  and therefore are not presented in the figure.

The estimated fractal dimension of adsorbed layer averaged over the frequency range 30 Hz – 21.8 kHz obtained at bulk concentrations of 2.60, 4.63 and 9.27 g/dm<sup>3</sup> are  $2.01 \pm 0.02$ ,  $2.00 \pm 0.01$  and  $1.997 \pm 0.020$ , respectively. Corresponding fractal dimensions determined from ZFC for the same bulk concentrations are 2.017 ( $R^2 = 0.9992$ ), 1.99 ( $R^2 = 0.9995$ ), and 1.999 ( $R^2 = 0.9997$ ), respectively.

For all investigated substances the fractal dimension determined from the ZFC is practically identical to the average  $D$  obtained for the investigated frequency range, thus providing further evidence that determination of  $D$  is not influenced by the frequency applied in the impedance spectroscopy or *ac* voltammetric measurements.

#### 4. Conclusions

We have investigated the possible influence of frequency of the sinusoidal excitation signal in the electrochemical measurements of adsorption phenomena on the estimation of fractal dimension and/or on the fractal ordering of adsorbed layers on the HMDE. Our results indicate that:

- The method of scaling the HMD to obtain the fractal dimension of adsorbed layer is compatible with impedance spectroscopy, hence, the combination of the methods can be used as a powerful tool to investigate fractal aspect of adsorption of organic molecules,

- The appropriate frequency range for the application of the scaling of HMDE for determination of fractal dimension in the impedance spectroscopy measurements is approximately 30 Hz - 21.8 kHz.
- In this frequency range the fractal ordering of adsorbed layer and the value of fractal dimension obtained by the method of HMDE scaling is not influenced by the frequency of applied sinusoidal voltage perturbations.

The values of fractal dimension, obtained by the scaling of HMDE in electrochemical impedance spectroscopy of T-X-100 solutions, are in agreement with the values obtained previously with *ac* voltammetry [3]. In all cases the fractal dimensions determined from the ZFC are practically identical to the average  $D$  obtained for the investigated frequency range, thus providing further evidence that determination of  $D$  is not influenced by the frequency applied in the impedance spectroscopy or *ac* voltammetric measurements. Thus, the value of fractal dimension of an adsorbed layer and its changes during the adsorption process reflect the structure and transformations of the layer. In that context the observed decrease of fractal dimension with bulk concentration reflects the fact that at high relative fractional coverages corresponding to high bulk concentrations the adsorbed layer tends to be more homogenous and/or transforms to a compact film that should have  $D \cong 2$ . Generally, differences in fractal structure or its absence, as in this case observed for tert-butanol, are related to specific molecular interactions and isotropy/no isotropy of molecular structure and shape.

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### Figure captions:

Fig. 1. Specific capacitance *vs.* applied potential: a) Pure electrolyte (curve 1), and T-X-100 at bulk concentrations of 0.5 mg/dm<sup>3</sup> (curve 2), 2.0 mg/dm<sup>3</sup> (curve 3) and 100 mg/dm<sup>3</sup> (curve 4). Dotted lines represent scans from -0.35 V to more positive potentials and full lines represent scans from -0.35 V to more negative potentials; b) Pure electrolyte (curve 1), and SDS at bulk concentrations of 0.4 mg/dm<sup>3</sup> (curve 2), 1.0 mg/dm<sup>3</sup> (curve 3) and 100 mg/dm<sup>3</sup> (curve 4). c) Pure electrolyte (curve 1), and tert-butanol at bulk concentrations of 2.60 g/dm<sup>3</sup> (curve 2), 4.63 g/dm<sup>3</sup> (curve 3) and 9.27 mg/dm<sup>3</sup> (curve 4). In b) and c) the dotted lines represent scans from -0.6 V to more positive potentials and full lines represent scans from -0.6 V to more negative potentials.

Fig. 2. Capacitive currents *vs.* *t* measured at selected potentials a) for pure electrolyte (curve 1) and T-X-100 at bulk concentrations of 0.5 mg/dm<sup>3</sup> (curve 2), 0.8 mg/dm<sup>3</sup> (curve 3) and 2 mg/dm<sup>3</sup> (curve 4) at - 0.35 V; b) for pure electrolyte (curve 2) and SDS at bulk concentrations of 0.4 mg/dm<sup>3</sup> (curve 2), 0.7 mg/dm<sup>3</sup> (curve 2) and 1 mg/dm<sup>3</sup> (curve 2) at - 0.6 V.

Fig. 3. Cole-Cole plots for nine electrode sizes for a) pure electrolyte and b) 0.8 mg/dm<sup>3</sup> T-X-100 solution obtained at  $E = - 0.35$  V.

Fig. 4. Typical log-log plots of measured capacitance *vs.* radius of HMDE used as a scale for determination of fractal dimension. Depicted are capacitances obtained at 821.9 Hz for pure electrolyte, 0.5 mg/dm<sup>3</sup> T-X-100, and 0.4 mg/dm<sup>3</sup> SDS solutions.

Fig. 5. a) Fractal dimension determined for pure electrolyte for a broad frequency spectrum at electrode potentials of - 0.35 V and - 0.60 V; b)  $dD/d(\log f)$  *vs.* *f* for pure electrolyte at  $E = - 0.35$  V and  $E = - 0.6$  V.

Fig. 6. Frequency dependence of the estimated fractal dimension obtained at equilibrium conditions for T-X-100 with different bulk concentrations. Symbols denote measured values and lines the corresponding B-spline fit.

Fig. 7. Frequency dependence of the estimated fractal dimension obtained at equilibrium conditions for SDS at different bulk concentrations. Symbols denote measured values and lines the corresponding B-spline fit.

Fig 8. Frequency dependence of the estimated fractal dimension obtained at equilibrium conditions for tert-butanol with different bulk concentrations. Symbols denote measured values and lines the corresponding B-spline fit.

Fig. 1.

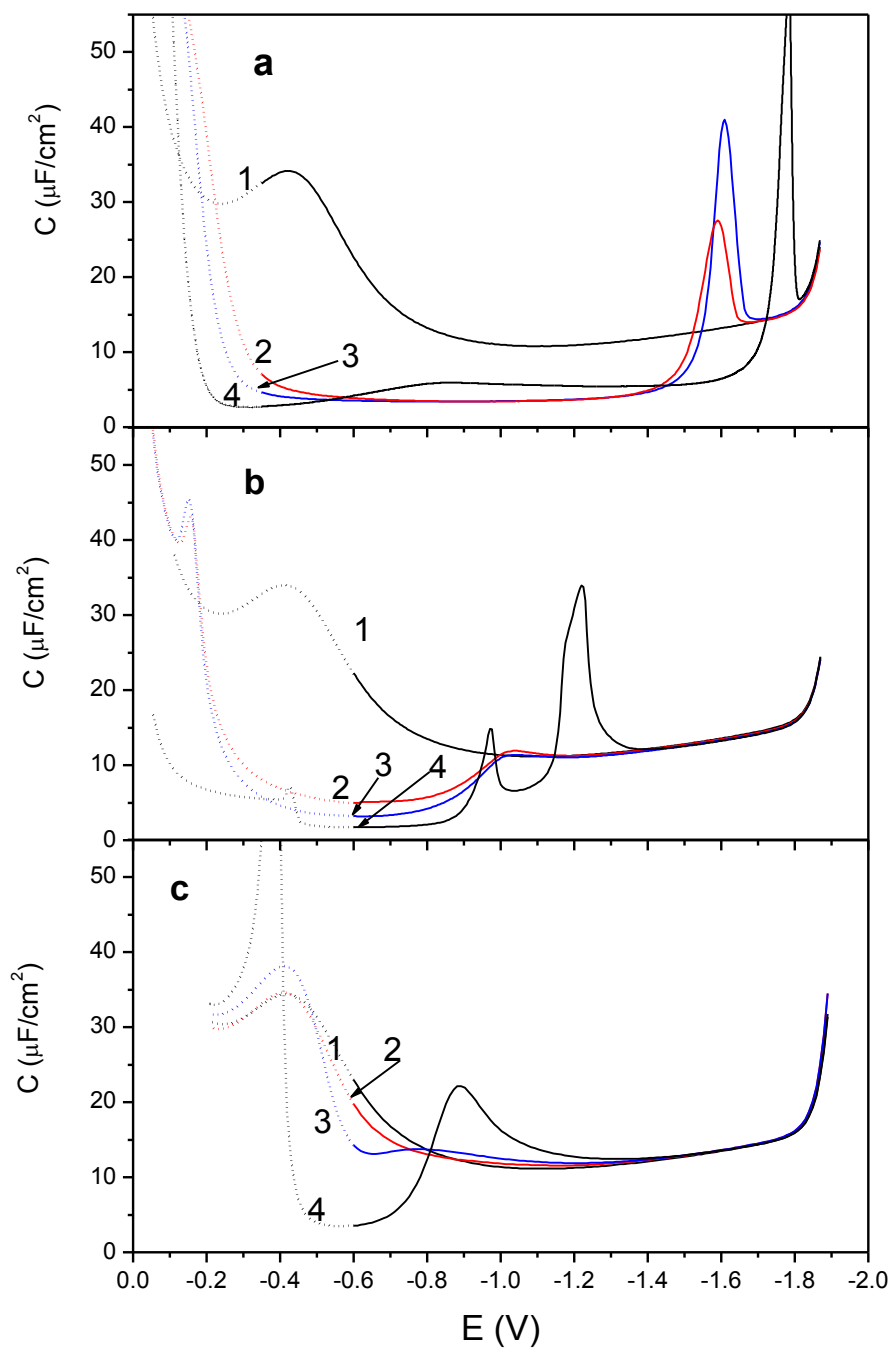




Fig. 2.

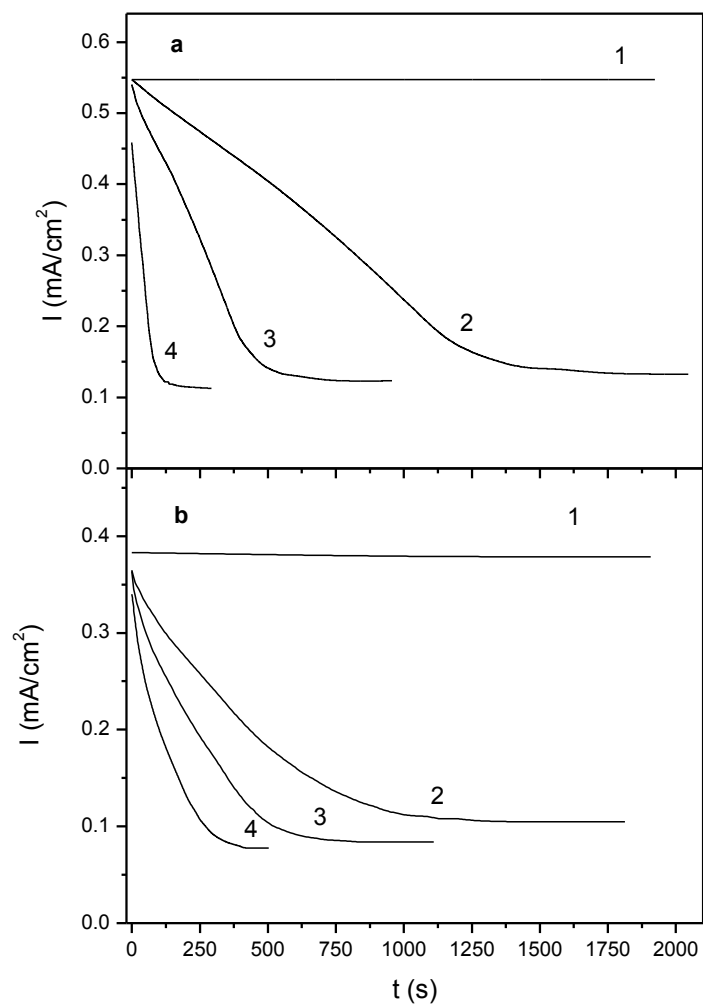


Fig. 3.

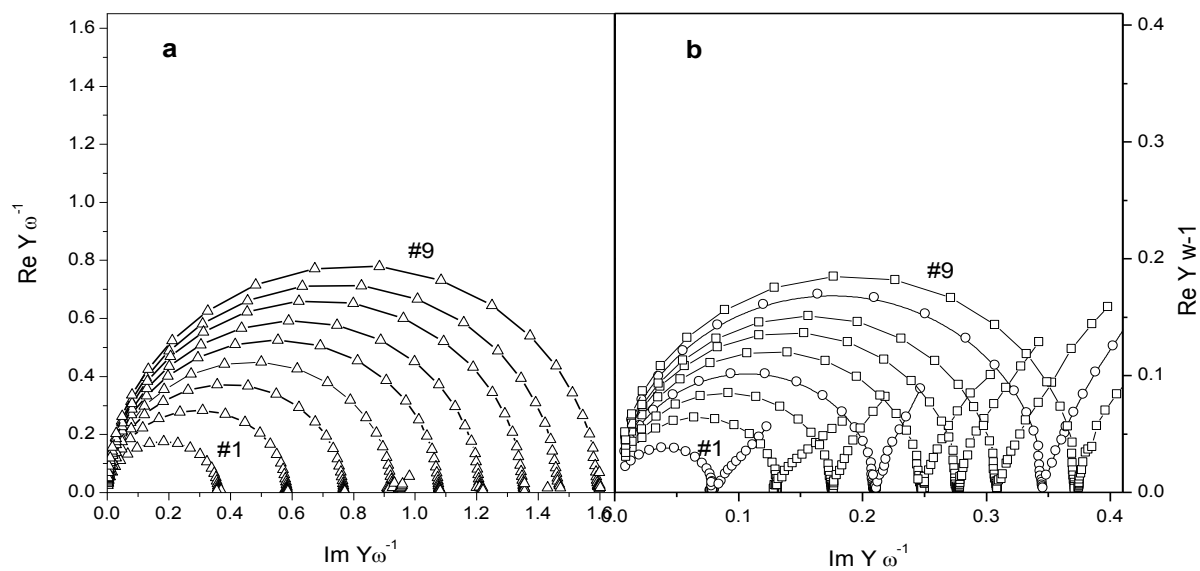


Fig. 4.

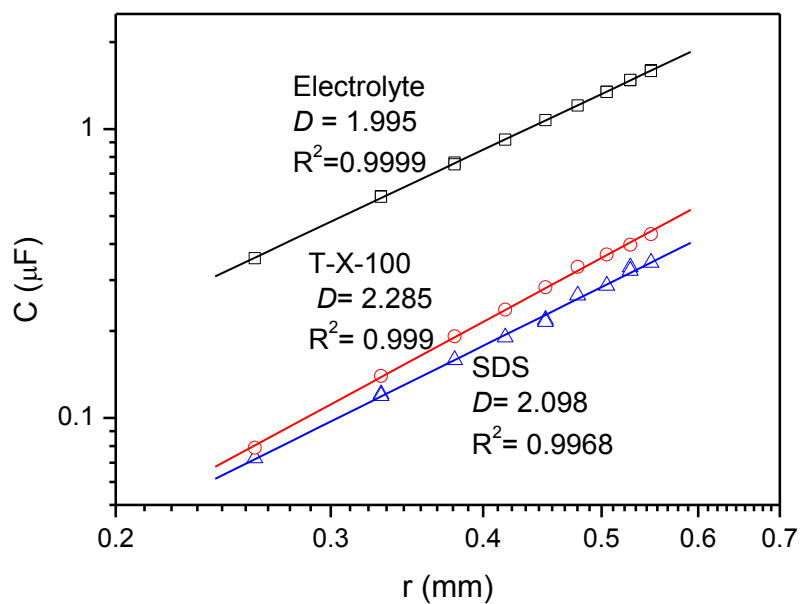


Fig. 5.

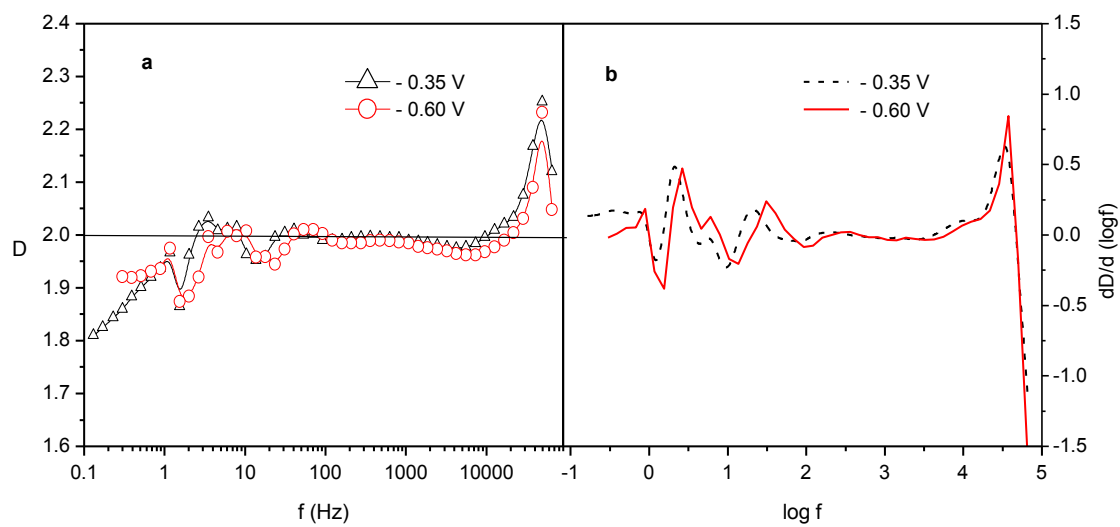


Fig. 6.

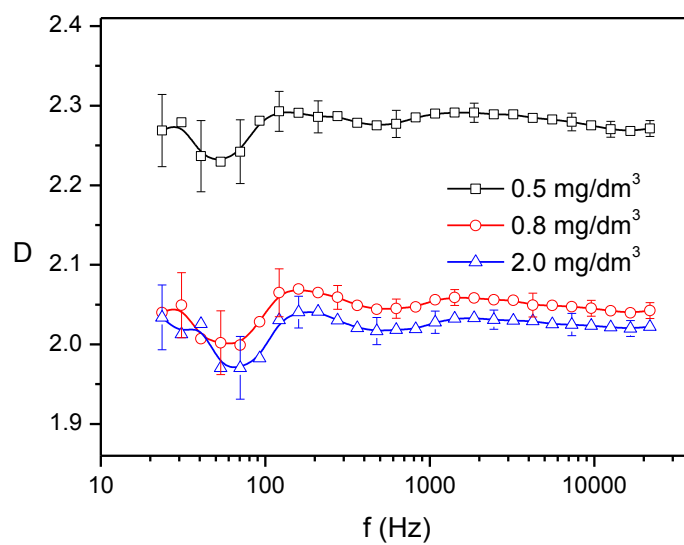


Fig. 7.

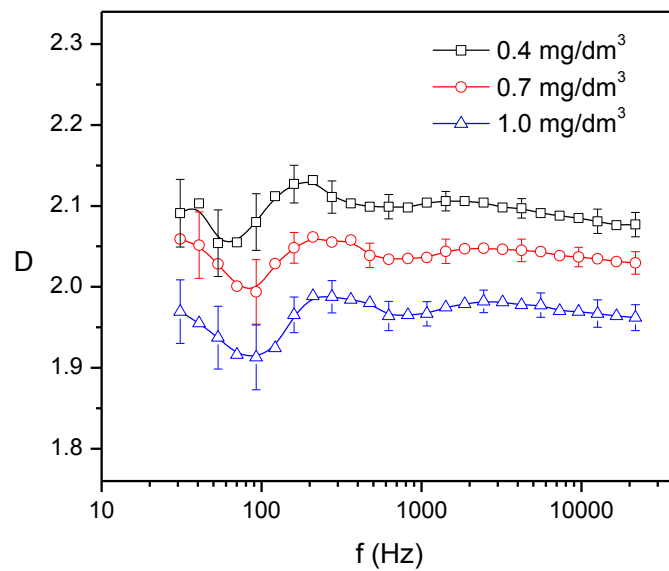


Fig 8.

