EIS and differential capacitance measurements onto single crystal faces in different solutions
Part I: Ag(111) in 0.01 M NaCl
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Abstract
Differential capacitance versus frequency curves simulated for different equivalent circuits representing different cases of anion adsorption have been analyzed. The analysis showed that in all cases with an ideal, homogeneous electrode surface, the real value of the differential capacitance, representing the sum of the double layer and adsorption capacitances (independent of frequency) could be obtained only at frequencies lower than about 2 Hz. In the case of real surfaces, presented by introduction of a constant phase element instead of a double layer capacitance, differential capacitance versus frequency curves were found to be more complex, with no possibility to obtain values of the double layer capacitance at high and adsorption capacitance at low frequencies, since the differential capacitance was found to depend on frequency in the whole range of frequencies (10⁻⁴–10⁵ Hz). Chloride adsorption onto the Ag(111) face in 0.01 M NaCl solution was found to follow the approach initiated in this work by introducing a constant phase element instead of the double layer capacitance. It is shown that impedance diagrams deviate from the 'ideal double layer behavior' and that differential capacitance versus potential curves depend on frequency. It is confirmed by the analysis of differential capacitance versus frequency curves that this is the consequence of adsorption of chloride anions presented by adsorption resistance and capacitance connected in series, as well as of inhomogeneity of the real single crystal face.
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Keywords: Ag(111); Cl⁻ adsorption; Partial charge transfer; Differential capacitance; CPE

1. Introduction
Differential capacitance measurements (\(C_{\text{diff}}\) vs. \(E\) curves) were introduced in electrochemistry with the beginning of double layer structure investigations as a suitable technique for determining the double layer capacitance (\(C_{\text{dl}}\)) on both, liquid (mercury) and solid metal electrodes [1–3]. This technique was very convenient for determining the potential of zero charge, \(E_{\text{pc}}\) on solid electrodes as a minimum on \(C_{\text{diff}}\) versus \(E\) curves [1–4]. Since the minimum existed only in the presence of a diffuse part of the double layer [5,6], these experiments were performed in dilute solutions of the concentrations lower than 10⁻² M, usually of the order of 10⁻³ M [7–9]. In all these experiments ohmic resistance had to be compensated in order to obtain the real value of \(C_{\text{dl}}\). In such a case, the value of \(C_{\text{diff}}\) was equal to the value of \(C_{\text{dl}}\) and was independent of frequency. Accordingly, measurement at one frequency was sufficient to determine the value of the double layer capacitance.

With the introduction of single crystal surfaces, this technique in combination with cyclic voltammetry (CV), has frequently been used for determining \(E_{\text{pc}}\) as well as the adsorption behavior of different anions. Typical frequencies for these measurements varied between 10 and 20 Hz [10], while the sweep rate used was usually 5–10 mV s⁻¹. For interpretation of the results obtained concerning adsorption of anions, it was assumed that the ‘specific adsorption’ of anions does not involve the

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charge transfer between the electrode surface and adsorbed anions.

About 10 years ago, the equivalent circuit composed of $C_{dl}$ connected in parallel with a charge transfer resistance ($R_{ct}$) and adsorption capacitance ($C_{ad}$) was used for the first time for the analysis of adsorption of fluoride, sulfate, acetate and chloride anions onto silver single crystals [11–14]. The same equivalent circuit, with adsorption resistance ($R_{ad}$) instead of $R_{ct}$ was later used for the analysis of polyatomic species adsorption onto Au(111) from fluoride and sulfate containing solutions of different pH [15]. Recently, another component (Warburg impedance) has been added to the previously described equivalent circuit (in series with $R_{ad}$ and $C_{ad}$) in order to explain adsorption of halide anions of low concentrations (0.1–1 mM) onto gold single crystal surfaces [16,17]. This approach was not new since an identical equivalent circuit had been proposed by Sluyters-Rehbach and Sluyters [18] about 30 years ago. In recent papers [16,17], it was assumed that the single crystal surface behaves as an ideal, homogeneous electrode surface, having no ‘fractal character’. Moreover, in two recent papers [16,17] ideal double layer behavior for Au(111), Au(100) and Au(210) in dilute HClO$_4$ and KPF$_6$ solutions has been reported. Eberhardt et al. [16] presented $Z’$ versus $Z’’$ diagrams for Au(111) in 10 mM HClO$_4$ solution at the potentials of 0.05 V versus SCE, 0.25 V versus SCE and 0.45 V versus SCE (all potentials are more positive than the potential of zero charge, being in the region of the capacitance peak on $C_{diff}$ vs. $E$ curves) in the frequency range between 1 Hz and 10 kHz. The analysis of these diagrams showed linear dependence of $Z’’$ versus $Z’$ indicating ideal double layer behavior. Pajkossy et al. [17] also reported almost ideal double layer behavior for Au(111) and Au(100) in dilute HClO$_4$ solution in the frequency range between 0.1 Hz and 5 kHz. They found that the capacitance exhibits only minor frequency dependence at potentials more negative than 0.4 V versus SCE, with the ratio of the capacitance measured at 1 Hz and at 0.1 kHz differing from unity by a few percent only. They pointed out that the frequency dispersion could be a consequence of either phase transition at the interface, or specific adsorption of anions. In both papers [16,17], ‘frequency dispersion’ observed in the presence of specific adsorption has been explained by the adsorption of anions controlled by their diffusion.

Most recently, Kerner and Pajkossy [19] demonstrated that the frequency dependence of the capacitance on solid electrodes was due to the atomic scale inhomogeneities rather than due to the geometry aspect of roughness. They criticized old physical theories used for explaining capacitance dispersion as a function of surface roughness [20–23] and pointed out the physico-chemical approach of Pajkossy [24,25], claiming that the origin of the capacitance dispersion can be allocated in the double layer and that it can be attributed to the presence of atomic scale inhomogeneities—‘disorder’ of the electrode surface, together with the presence of some kinetic process, most probably with specific adsorption of anions [19].

Although the ordered structure ($\sqrt{3} \times \sqrt{3})R30^\circ$ of adsorbed chloride onto Ag(111) had been detected by ex situ LEED and Auger spectroscopy techniques [26,27], the introduction of in situ techniques (STM and surface X-ray scattering) in the investigation of the structure of adsorbed anions onto single crystal faces provided a significant contribution to the understanding of the process of anion adsorption [28–33]. It was shown that in the case of chloride and bromide ion adsorption onto Au single crystals, incommensurate, hexagonal-close-packed monolayers, compressing uniformly with increasing potential were formed [29–31]. The adatom spacing of these compressed structures was found to approach the van der Waals diameter, indicating at least partial discharge of anions [29–31]. Wandlowski et al. [32] showed by chronocoulometry (thermodynamic analysis) and surface X-ray scattering (SXS) that in the case of bromide adsorption onto Ag(100), an ordered $c(2 \times 2)$ structure was formed, with the charge number being $-0.85 \pm 0.05$ at constant chemical potential, indicating also the existence of partial charge transfer between adsorbed anions and the substrate. It is interesting to note that the differential capacitance versus potential curve, obtained at an ac-frequency of 18 Hz, 10 mV peak-to-peak amplitude and sweep rate of 10 mV s$^{-1}$, presented by these authors [32], was found to possess hysteresis (Fig. 1 of Ref. [32]) for bromide concentrations lower than 1 mM. The authors concluded that such data were not adequate for determination of any thermodynamic quantities [32] primarily due to mass-transfer limitations. Identical conclusions concerning differential capacitance measurements and the electrosorption valency were made by Shi and Lipkowski [34] in the study of chloride ion adsorption onto the Au(111) face. In situ X-ray absorption fine structure (XAFS) studies of bromide adsorption onto Ag(111) revealed the formation of a AgBr(111) monolayer with the Br–Ag bond distance of $2.72 \pm 0.05$ Å, indicating complete charge transfer between Br anions and the Ag(111) surface [33]. Hence, one can conclude that structural in situ X-ray analysis [29–31,33] and even thermodynamic analysis [32] of anion adsorption indicates the presence of partial charge transfer between anions and substrate during the process of anion adsorption.

In this paper, the dependence of differential capacitance as a function of frequency for different cases of simple and complex anion adsorption processes for ideal, homogeneous and ‘real surfaces’ (introducing a
resistance of the electrode impedance is presented by an ohmic electrode surfaces. Two cases of real surfaces are presented by CPE instead of C\text{v}

\[ C_{\text{dl}} \text{h a} \]

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capacitance represented by a constant phase element,ing an ideal, homogeneous surface); and (2) double layer adsorption

discussed.

Two cases are considered: (1) double layer capacitance for different cases of anion adsorption

Two cases are considered: (1) double layer capacitance represented by a parallel plate condenser (assuming an ideal, homogeneous surface); and (2) double layer capacitance represented by a constant phase element, CPE (assuming a ‘fractal character’ of the surface). \( C_{\text{diff}} \) versus \( f \) dependences were simulated in the frequency range from \( f = 10^{-4} \) to \( 10^5 \) Hz, since this is the widest range of frequencies offered by the producers of EIS measurement systems (Gamry Instruments Inc.).

2. Ideal, homogeneous surface

The equivalent circuit for ideal double layer behavior of the electrode impedance is presented by an ohmic resistance \( R_\Omega \) and double layer capacitance \( C_{\text{dl}} \) connected in series. The differential capacitance is by definition an imaginary component of electrode admittance over frequency and for such an equivalent circuit is given by the equation

\[
C_{\text{diff}} = \frac{Y''}{\omega} = \frac{C_{\text{dl}}}{1 + \omega^2 C_{\text{dl}} R_\Omega^2}
\]

In most cases, \( 1 \gg \omega^2 C_{\text{dl}} R_\Omega^2 \) and accordingly \( C_{\text{diff}} \approx C_{\text{dl}} \). On the other hand, in dilute solutions with a high value of \( R_\Omega \), the value of \( C_{\text{diff}} \) could be influenced by the ohmic resistance \( (R_\Omega) \), as shown in Eq. (1) [11–13]. Hence, the imaginary component of the electrode admittance should be corrected for ohmic resistance in order to obtain the real value of \( C_{\text{dl}} \). This could be done either by compensating \( R_\Omega \) during differential capacitance measurements (using the IR compensation technique on the potentiostat), or by subtracting it from the real component of the electrode impedance, \( Z_{\text{corr}} = Z' - R_\Omega \) and calculating \( Y_{\text{corr}}'' \) by the following equation (\( R_\Omega \)—determined from the high frequency intercept of impedance diagrams, or by some other technique)

\[
Y_{\text{corr}}'' = \frac{Z''}{(Z_{\text{corr}}')^2 + (Z'')^2}
\]

Hence, using \( Y_{\text{corr}}'' \) for determining \( C_{\text{diff}}(Y_{\text{corr}}''/\omega = C_{\text{diff}}) \) it is possible to obtain the real value of the differential capacitance.

In the presence of ‘specific adsorption’ presented by the adsorption resistance and adsorption capacitance connected in series, the differential capacitance (corrected for \( R_\Omega \)) should depend on frequency [11–13,15]. The simplest case of ‘specific adsorption’ is usually represented by the equivalent circuit shown in the inset of Fig. 1, case (a), with the adsorption impedance \( (Z_{\text{ad}}) \) being composed of the adsorption resistance \( R_{\text{ad}} \) and adsorption capacitance \( C_{\text{ad}} \) connected in series [11–13]. Simulated \( C_{\text{diff}} \) versus \( f \) dependences, obtained in the frequency range from \( f = 10^{-4} \) to \( 10^5 \) Hz for this equivalent circuit for different values of \( C_{\text{ad}} \) (20, 60, 120 and 200 \( \mu \)F, respectively) showed that the value of \( C_{\text{dl}} \) can be determined by using \( C_{\text{diff}} \) value recorded at frequencies higher than a certain critical frequency \( f_c(\text{dl}) \), which is very slightly dependent of the values of \( C_{\text{dl}} \) and \( C_{\text{ad}} \). In the low frequency range, \( C_{\text{diff}} \) is also independent of frequency and can be obtained at frequencies lower than a certain critical frequency \( f_c(\text{ad}) \), which is determined by the ratio between values of \( C_{\text{dl}} \) and \( C_{\text{ad}} \). With an increasing value of \( C_{\text{ad}} \) for one order of magnitude (from 20 to 200 \( \mu \)F), the critical frequency \( f_c(\text{ad}) \) decreases for almost two orders of magnitude (for a given value of \( R_{\text{ad}} = 100 \) \( \Omega \)). With an increasing value of \( R_{\text{ad}} \), the critical frequency for accurate determination of \( C_{\text{ad}} \) decreases and if the process of adsorption becomes very slow (high values of \( R_{\text{ad}} \), \( R_{\text{ad}} > 5000 \) \( \Omega \)), \( C_{\text{ad}} \) can be determined from the value of \( C_{\text{diff}} \) recorded at frequencies lower than about 0.003 Hz. The increase of \( R_{\text{ad}} \) for one order of magnitude causes the decrease of \( f_c(\text{ad}) \) for one order of magnitude too, so that with \( R_{\text{ad}} = 50 \) \( \Omega \), the critical frequency \( f_c(\text{ad}) \) becomes about 2 Hz. Hence, for faster
adsorption processes \( C_{\text{diff}} \) represents the sum of \( C_{\text{dl}} + C_{\text{ad}} \) at frequencies lower than about 2 Hz. The critical frequency for \( C_{\text{dl}} \) determination, \( f_c(\text{dl}) \), also increases with decreasing \( R_{\text{ad}} \), being 1 Hz for \( R_{\text{ad}} = 50 \, 000 \, \Omega \) and 1000 Hz for \( R_{\text{ad}} = 50 \, \Omega \). It is important to note that in the ‘intermediate frequency range’, between \( f_c(\text{ad}) \) and \( f_c(\text{dl}) \), measured values of the differential capacitance do not represent the real value of either \( C_{\text{dl}} \) or \( C_{\text{ad}} \) or their sum.

If the process of anion adsorption is controlled by the diffusion of anions to the electrode surface, the Warburg impedance must be added in series to \( R_{\text{ad}} \) and \( C_{\text{ad}} \) [16–18], as it is presented in the inset of Fig. 1, case (b). Assuming that the diffusion coefficient for anions amounts to \( 1 \times 10^{-5} \, \text{cm}^2 \, \text{s}^{-1} \) and using the equation for the Warburg constant \( \sigma \) [35], \( C_{\text{diff}} \) versus \( f \) curves are simulated for different concentrations of anions (0.01–10 mM). It was shown that with the increase of the Warburg constant \( \sigma \) (decrease of anion concentration), the frequency range where \( C_{\text{diff}} \) represents the sum \( C_{\text{dl}} + C_{\text{ad}} \) moves towards lower values and only at concentrations equal to or higher than 10 mM are mass-transport limitations negligible for a given value of \( R_{\text{ad}} \) (in this case \( R_{\text{ad}} = 50 \, \Omega \) should represent fast adsorption process). At concentrations lower than 1 mM, the low frequency plateau does not exist, indicating that in such a case even with the ideal, homogeneous electrode surface, real values of \( C_{\text{diff}} \), as well as \( C_{\text{dl}} \) and \( C_{\text{ad}} \) from \( C_{\text{diff}} \) versus \( f \) curves, cannot be determined. It should be emphasized here that most of the \( C_{\text{diff}} \) versus \( f \) curves [10] have been recorded for dilute solutions with a high possibility for the adsorption reaction to be diffusion controlled and consequently with a low possibility for \( C_{\text{diff}} \) to represent the sum \( C_{\text{dl}} + C_{\text{ad}} \). \( C_{\text{diff}} \) versus \( \omega \) dependence for this equivalent circuit (Fig. 1, case (b)) is given by the following equation

\[
C_{\text{diff}} = \frac{\omega^2}{\omega_0} = C_{\text{dl}} + \frac{\omega C_{\text{ad}}(1 + C_{\text{ad}}\sigma\omega^{1/2})}{(1 + C_{\text{ad}}\sigma\omega^{1/2}) + \omega^2C_{\text{ad}}^2(R_{\text{ct}} + \sigma\omega^{-1/2})^2} \tag{3}
\]

2.2. Real surface

Taking into account that even single crystal faces contain significant number of monoatomic terraces and cannot be considered as ideal, homogeneous surfaces (as shown by number of STM investigations [36]), the introduction of a constant phase element (CPE) defined as \( Z_{\text{CPE}} = \frac{1}{\omega^m} \) [35], in the interpretation of the double layer capacitance of atomically inhomogeneous, fractal surfaces, deserves special attention. Let us consider two simplest cases, ‘ideal double layer behavior’ (\( R_{\Omega} \) and CPE connected in series) and simple adsorption of anions presented by the equivalent circuit shown in the inset of Fig. 1 (case (b)), with \( C_{\text{dl}} \) being replaced by CPE.

In the case of \( R_{\Omega} \) and CPE connected in series (Fig. 1(c)), the value of \( C_{\text{diff}} \), independent of frequency for \( x = 1 \) and equal to the value of \( C_{\text{dl}} \), becomes dependent on frequency with the decrease of \( x \) in the whole frequency range between \( f = 10^{-4} \) and \( 10^3 \, \text{Hz} \). Hence, even if there is no ‘specific adsorption’ on real surfaces (pure double layer behavior), \( C_{\text{diff}} \) determined at one constant frequency cannot practically be used for determining \( C_{\text{dl}} \).

If for the case of simple anion adsorption, presented by the equivalent circuit shown in the inset of Fig. 1 (case (b)), \( C_{\text{dl}} \) becomes replaced by CPE (Fig. 1(d)), the differential capacitance for such an equivalent circuit is defined by the following equation

\[
C_{\text{diff}} = \frac{Y''}{\omega} = A_{\text{diff}}\alpha x^{-1}\sin \left( \frac{x\pi}{2} \right) + \frac{C_{\text{ad}}}{1 + \omega^2C_{\text{ad}}^2R_{\text{ct}}^2} \tag{4}
\]

According to Brug et al. [37], the value of \( C_{\text{dl}} \) is defined by Eq. (5).

\[
C_{\text{dl}} = [A_{\text{diff}}R_{\Omega}^{-x}]^{1/x} \tag{5}
\]

The influence of the value of \( x \) (fractal character of the surface) on \( C_{\text{diff}} \) versus \( f \) diagrams is presented in Fig. 2. As can be seen, the influence of the first part of Eq. (4) becomes significant already at \( x = 0.95 \) and, accordingly, determination of real values of \( C_{\text{ad}} \) and \( C_{\text{dl}} \) at low and high frequencies, as was the case for ideal surfaces, becomes impossible. Hence, to obtain real values for the parameters of such an equivalent circuit, \( C_{\text{diff}} \) versus \( f \) diagrams should be plotted for each potential and these dependences fit by Eq. (4), while the value of \( C_{\text{dl}} \) should be obtained from Eq. (5).

![Fig. 2. Simulated \( C_{\text{diff}} \) vs. \( f \) curves for the equivalent circuit (d) of Fig. 1: \( R_{\text{ads}} \) 50 \, \Omega; \( C_{\text{dl}} \) 60; \( C_{\text{ad}} \) 60 \, \mu\text{F}. Values of \( x \) are marked in the figure.](image-url)
3. Experimental

All experiments were carried out in a two-compartment electrochemical cell at 25 ± 1 °C in an atmosphere of purified (99.999%) nitrogen. The Ag(111) electrode (Monocrystals Company, d = 0.9 cm) was sealed in epoxy resin (resin EPON 828 + hardener TETA) in such a way that only the (111) disc surface was exposed to the solution. The surface area of the electrode exposed to electrolyte was 0.636 cm². The counter electrode (CE) was a Pt sheet and was placed parallel to the working electrode. The reference electrode (RE) was a saturated calomel electrode (SCE). The RE was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. Solutions of 0.01 M NaCl were made from supra pure (99.999%) NaCl (Aldrich) and EASY pure UV water (Barnstead). All potentials are given versus SCE.

Ag(111) was prepared by a mechanical polishing procedure followed by chemical polishing in the solution containing NaCN and H₂O₂ as explained in great detail in one of our previous papers [38]. Before each experiment, the electrolyte was purged with high purity nitrogen (99.999%) for 45 min, while, during the experiment, a nitrogen atmosphere was maintained over the solution to prevent contamination with oxygen.

Using a universal programmer PAR M-175, potentiostat PAR M-173 and an X–Y recorder (Houston Instrument 2000R), CV experiments were performed. FAS1 Femtostat and software EIS300 (Gamry Instruments) were used to perform EIS and differential capacitance measurements with an RMS amplitude of 5 mV. Differential capacitance versus potential curves were obtained by measurements of the real and imaginary components of the impedance at constant frequency and potential with the potential being stepped in a sequence of 10 mV from −1.0 V versus SCE to 0.05 V versus SCE at different constant frequencies ranging from 0.1 to 1000 Hz. Measured values for the real and imaginary components of the impedance were corrected for ohmic resistance (determined from the high frequency intercept on the Z’ axis of Z’–Z” diagrams) and converted into differential capacitances using Eq. (2).

4. Results

The cyclic voltammogram recorded at the Ag(111) face in 0.01 M NaCl solution at a sweep rate of 100 mV s⁻¹ is shown in Fig. 3. The voltammogram is in good agreement with our previous results [13,14], as well as with the results of other authors [27]. As can be seen, this voltammogram is characterized by almost reversible pairs of two broad peaks (shoulders) at potentials of about −0.75 V versus SCE and about −0.50 V versus SCE, respectively and by one pair of sharp peaks at the potential of about 0.00 V versus SCE.

EIS measurements were performed at several constant potentials. At the potential of −1.0 V versus SCE (negative with respect to the adsorption peaks), in the region of the two broad peaks (at the potential of the shoulder of about −0.75 V vs. SCE and at the potential of the broad peak at about −0.50 V vs. SCE) and in the region of the pair of sharp peaks (−0.05 V vs. SCE), Z’–Z” diagrams recorded at −0.55 V versus SCE and at −0.05 V versus SCE are shown in Fig. 4(a and b), respectively. As can be seen, both diagrams deviate slightly from the ‘ideal double layer behaviour’. In the insets of both figures are presented high frequency ends of the Z’–Z” diagrams. The ohmic resistance was determined by linear extrapolation to the Z’ axis giving the value \( R_Ω \approx 140.3 \Omega \) cm² for all potentials. It should be mentioned here that the shape of the Z’–Z” diagrams did not change with the potential, but the values of Z” were higher at more negative potentials.

Differential capacitance measurements (in steps of 10 mV, starting at −1.0 V vs. SCE and finishing at 0.05 V vs. SCE) were performed at the following frequencies: 1000, 700, 400, 200, 100, 70, 40, 20, 10, 7, 4, 2, 1, 0.7, 0.4, 0.2 and 0.1 Hz. Corrected values for the differential capacitance were obtained by using Eq. (2) and corresponding values of Z’ and Z” detected in these experiments. Some of the \( C_{diff} \) versus \( E \) curves obtained are shown in Fig. 5. It is interesting to note that almost identical diagrams were obtained at frequencies lower than 1 Hz, while \( C_{diff} \) was found to decrease with increasing frequency. At frequencies \( f \geq 700 \) Hz, the
dispersion of points on the $C_{\text{diff}}$ versus $E$ curves was significant and these results were not used for further analysis.

$C_{\text{diff}}$ versus $E$ curves recorded at the frequency of 1 Hz by changing the potential in both directions, from $-1.0$ V versus CSE to $0.05$ V versus SCE and back, are compared in Fig. 6. As can be seen identical curves were obtained, indicating high reversibility and stability of the system. The $C_{\text{diff}} (j/\omega)$ versus $E$ curve obtained from the anodic part of the voltammogram shown in Fig. 3 is also presented in this figure by the dotted line.

Using $C_{\text{diff}}$ values at constant potential (from $C_{\text{diff}}$ vs. $E$ curves) $C_{\text{diff}}$ versus $\omega$ curves were constructed. In the potential range between $-1.0$ V versus CSE and $-0.1$ V versus CSE, this has been done in steps of 50 mV, while in the region of the sharp peak on $C_{\text{diff}}$ versus $E$ curves this was done in the sequence of 10 or 20 mV. In order to obtain values for $A_{\text{dl}} (C_{\text{dl}})$, $C_{\text{ad}}$, $R_{\text{ad}}$ and $z$, fitting of $C_{\text{diff}}$ versus $\omega$ curves has been performed by using Eqs. (3) and (4). Good fits were obtained only with Eq. (4) and these results are further discussed. Most of the $C_{\text{diff}}$ versus $\omega$ curves are presented in Fig. 7. Experimental points are presented by squares, circles, triangles, etc., while the lines represent fitting curves. Potentials in V
versus SCE are marked in the figure for each curve. As can be seen, a good fit has been obtained. It should be mentioned here that identical results were obtained for the rest of Cdiff versus E curves not presented in Fig. 7.

Parameter α was found to change slightly with the potential and its dependence on potential is shown in Fig. 8 together with Cad versus E, Cdl versus E, (Cdl/Cad) versus E and α versus E curves obtained by fitting Cdiff versus ω curves for different potentials with Eq. (4), with Cad being obtained by Eq. (5).

5. Discussion

5.1. Simulated Cdiff versus f curves for different equivalent circuits

Considering the analysis of Cdiff versus f curves simulated for different equivalent circuits, representing different cases of anion adsorption cited in the literature [11–17], it is important to note that for an ideal, homogeneous surface two inflection points are present on these curves indicating the region of pure double layer behavior (f > f_c(dl)) and the region of adsorption (f < f_c(ad)). It is also important to note that in all cases with an ideal electrode surface, the real value of Cdiff...
concluded from this analysis that most of the results are representative of the electrode surface is not ideal and that the process of anion adsorption must be characterized by two inflection points at different frequencies, assuming that the adsorption capacitance is purely capacitive and that in such a case \( C_{\text{diff}} \) should be independent of frequency. Hence, if the former depends on frequency, then the process of anion adsorption must contain a resistive component in series with an adsorption capacitance and both of them in parallel with the double layer capacitance (as in the simplest case of anion adsorption presented in Fig. 1, case (a)). In the case that the electrode surface is not ideal and \( C_{\text{dl}} \) is replaced by CPE, \( C_{\text{diff}} \) versus \( f \) curves were found to be more complex, also depending on frequency (Fig. 2), with no possibility to obtain the values of \( C_{\text{dl}} \) at high frequency. In the case of the presence of \( C_{\text{ad}} \) and \( C_{\text{dl}} \) at low frequencies from the parts of \( C_{\text{diff}} \) versus \( f \) curves where \( C_{\text{ad}} \) (\( f < f_{\text{ad}} \)) and \( C_{\text{dl}} \) (\( f > f_{\text{ad}} \)) are independent of frequency. It should be emphasized here that in the presence of \( C_{\text{ad}} \) and \( R_{\text{ad}} \) (Fig. 2) these curves are also characterized by two inflection points at \( z \) values between 0.8 and 1.0. Hence, taking into account that all solid electrodes, including single crystal faces, possess to some extent ‘fractal character’ [36], it could be concluded from this analysis that most of the results obtained by measuring \( C_{\text{diff}} \) versus \( E \) curves, presented in the literature so far [10], most likely did not represent the real value of \( C_{\text{diff}} \). It should be emphasized that this statement is in agreement with the suggestions of Eberhardt et al. [16], Wandlovski et al. [32] and Shi and Lipokowski [34] that differential capacitance measurement at one frequency, or over a narrow frequency range, can give misleading results.

5.2. EIS and differential capacitance of Ag(111) in 0.01 M NaCl

As suggested most recently by Kerner and Pajkossy [39] if the concentration of adsorbing anions is in the range of 0.1–1 mM, the equivalent circuit presented in Fig. 1, case (b), could be applied in analysis of the EIS results. To avoid the eventual influence of anion diffusion [16,17,39], a higher concentration of NaCl of 0.01 M has been used for our experiments. Considering Fig. 9 (\( R_{\text{ad}} \) is seen to be higher than 50 \( \Omega \) \( \text{cm}^2 \) at all potentials) at the concentration used in this work (10 mM) mass-transport limitations are negligible and cannot influence the results obtained. Considering recent papers concerning in situ X-ray investigations of anion adsorption [29–33], it seems reasonable to assume that partial charge transfer occurs during this process and that the equivalent circuit presented in Fig. 1(d) should be used for the analysis of the results obtained, taking into account also that the single crystal surface is not ideal [36].

The \( Z''/Z'' \) diagrams shown in Fig. 4 for two potentials are typical for all potentials. The almost linear dependence of \( Z'' \) versus \( Z' \), deviating slightly from 90° indicates either the presence of anion adsorption, or the influence of surface imperfections (fractal character), or both. It is interesting to note that this deviation is more pronounced at the high frequency end shown in the insets of Fig. 4. The deviation at high frequencies deserves special attention. For most of the potentiostats used for EIS measurements, even with the best current distribution between the WE and CE, the high frequency range becomes a problem and in some cases an imaginary component becomes positive passing through the zero line on the \( Z' \) axis, while in some cases it reaches some value close to zero but still negative and then starts to increase to the negative direction with further increase of frequency. We believe that such behavior is a consequence of the influence of potentiostat circuitry rather than the real response of the system. This is very important for this work, as well as for some other results [16,17,39], since the ohmic resistance, determined by extrapolation of an imaginary component to zero, has been used for correcting the values of \( Z' \) and calculating \( C_{\text{diff}} \) using Eq. (2). As can be seen in Fig. 5, \( C_{\text{diff}} \) versus \( E \) curves recorded at high frequencies (700 and 1000 Hz) are characterized by dispersion of the points in a whole range of potentials. This is the consequence of the precision of ohmic resistance determination, since at high frequencies \( Z' \) approaches the value of \( R_{\text{eq}} \) and a small deviation of \( Z' \) values causes a high dispersion of \( C_{\text{diff}} \) values which are obtained by
using Eq. (2). To avoid this effect, $C_{\text{diff}}$ versus $E$ curves recorded at lower frequencies starting from 400 Hz were analyzed.

An attempt was made to fit $Z'$--$Z''$ diagrams with the equivalent circuit presented in Fig. 1(b) and (d). Unfortunately, it was not possible to obtain a good fit of the experimental results at any of the potentials investigated. This is due to the fact that employment of such a complicated combination of elements leads to rather high correlation factors between the fitted values and accordingly the individual elements can be determined only with a large uncertainty [16]. Taking into account that the commercial program for fitting impedance results by a certain equivalent circuit is based on a non-linear last-squares program that minimizes the sum of the $[(Z' - Z_{\text{calc}})^2 + (Z'' - Z_{\text{calc}})^2]/\text{Abs } Z^2$ and that only a small part of the semi-circle on the $Z'$--$Z''$ diagrams exists, a poor fit of the results obtained experimentally could be expected. At the same time, the analysis presented by Pajkossy et al. [17], using complex plane $C_{\text{re}}$ versus $C_{\text{im}}$ diagrams, failed, most probably because of the high concentration of chloride ions and the absence of diffusion limitations.

The dependence of the values of the differential capacitance, i.e. $C_{\text{diff}}$ versus $E$ curves, as a function of frequency, shown in Fig. 5, again indicates the presence of ‘specific adsorption’ or inhomogeneity of the surface, or both. According to the voltamogram presented in Fig. 3, it seems that Ag(111) in 0.01 M NaCl approaches an ideally polarized electrode very closely, although the potentials of the sharp peaks are not the same (the difference is only about 15 mV at a given sweep rate). It should be mentioned here that this difference decreases slightly, but still remains at lower sweep rates (down to 10 mV s$^{-1}$). The stability of the system is confirmed in Fig. 6, since there is no hysteresis on $C_{\text{diff}}$ versus $E$ curves recorded by changing the potential in both directions. It is interesting to note in Fig. 6 that $C_{\text{diff}}$ versus $E$ curves obtained by impedance measurements and obtained from the anodic part of the cyclic voltammogram (dotted line) are almost identical in the region of the broad peaks. The small difference in the shape of these curves is most likely the consequence of the fact that the cyclic voltammogram had been recorded at a relatively high sweep rate of 100 mV s$^{-1}$, while differential capacitance measurements were performed at constant potentials. A significant difference is observed in the region of the sharp peak. This indicates that in the region of the sharp peak, the process of chloride ion adsorption is not purely capacitive. Taking into account that the sharp peak on the cyclic voltammograms usually represents phase transformation from a randomly adsorbed to an ordered structure, this difference could be either caused by the presence of phase transformation, or by the presence of some other process, such as partial charge transfer between the electrode surface and anions.

The shape of $C_{\text{diff}}$ versus $\omega$ curves shown in Fig. 7 clearly indicates the presence of $R_{\text{ad}}$ and $C_{\text{ad}}$, as well as CPE, since the fitting procedure with Eq. (4) gave very good fitting curves.

If we compare our previous results [11–13] with the results presented in this paper, we can conclude that linear $1/Y'_{\text{ad}}$ versus $1/\omega^2$ dependences, obtained in the limited frequency range (10–100 Hz) in our previous papers, gave somewhat different results for $C_{\text{dl}}$ versus $E$, $R_{\text{ad}}$ versus $E$ and $C_{\text{ad}}$ versus $E$ curves than those obtained by the analysis used in this work (Figs. 8 and 9), which is most probably the consequence of the use of a limited frequency range in our previous work. By using the analysis presented in this work, $C_{\text{dl}}$ values were found to be higher than those of $C_{\text{ad}}$. Relatively high values of the double layer capacitance (about 50 $\mu$F cm$^{-2}$), dependent on potential, were detected in the work of Pajkossy et al. [17] in the case of bromide adsorption on gold single crystals, with the adsorption capacitance being much higher, but they used 0.1 M HClO$_4$ as a supporting electrolyte with only 0.15 mM of NaBr as the adsorbing substance. Considering the contribution of the double layer capacitance to the total capacitance of the system, one would expect an increase of the double layer capacitance with increasing concentration of electrolyte, since more anions should be incorporated in the inner layer and adsorbed at the surface at higher concentrations. It is interesting to note that the charge under the $C_{\text{dl}}$ versus $E$ curve amounts to 73 $\mu$C cm$^{-2}$, while the charge under the $C_{\text{ad}}$ versus $E$ curve amounts to 33 $\mu$C cm$^{-2}$, giving a total charge of 106 $\mu$C cm$^{-2}$. Taking into account the significant number of steps and terraces present on the single crystal surfaces [36], one can assume that a higher amount of charge than that needed for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbed structure of chloride ions (detected by different techniques for this system [26–28] and amounting to 74 $\mu$C cm$^{-2}$ for an ideal surface) should be obtained. Hence, one can conclude that because of adsorption of chloride ions at kinks and steps, this structure can be formed by complete charge transfer between chloride anions and the silver surface. Since the double layer capacitance by definition represents the purely capacitive component of the total electrode capacitance, it appears that only the charge under the $C_{\text{ad}}$ versus $E$ curve can be involved in the adsorption of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Taking into account that for this structure to be formed by complete charge transfer between chloride anions and a silver substrate, 74 $\mu$C cm$^{-2}$ for an ideal surface are needed and that the charge under the $C_{\text{ad}}$ versus $E$ curve amounts to 33 $\mu$C cm$^{-2}$, it is most likely that partial charge transfer is involved to some extent in the process of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.
formation. This is in contradiction with our previous results [13,14] that complete charge transfer occurs during the formation of this structure. This is obviously the consequence of the different approaches used in our previous and present work. It seems that considering the total charge under the voltammogram, or under the $C_{\text{diff}}$ versus $E$ curve, or under the $Q$ versus $E$ curve obtained by pulse experiments and subtracting the double layer charge assuming a linear increase of $Q_{\text{dl}}$ with potential (as we did in our previous paper [13]) is not the correct approach, since it is obvious that $Q_{\text{dl}}$ does not change linearly with potential, i.e. $C_{\text{dl}}$ is not constant over the whole potential range. Accordingly, the charge associated with adsorption should be determined under the $C_{\text{ad}}$ versus $E$ curves only. Hence, one can conclude that the approach presented in this work seems to be more reliable.

Some interesting features of our results deserve some further discussion. The first one is the fact that even in the potential range of ‘double layer behavior’ (between $-1.1$ V vs. SCE and $-0.9$ V vs. SCE on the voltammogram shown in Fig. 3) the $C_{\text{diff}}$ versus $\omega$ curve is characterized by the presence of one inflection point (an indication of a second inflection point at higher frequencies can be seen on these curves at higher sensitivities), indicating the presence of an adsorption capacitance and resistance ($C_{\text{ad}}$ and $R_{\text{ad}}$). It should be mentioned here that the second inflection point changes towards higher frequencies with decreasing values of $C_{\text{ad}}$ and $C_{\text{dl}}$ which is in accordance with our results. The limitation of frequency to 400 Hz for experimentally recorded diagrams is most probably the reason for this inflection point not to be well defined on $C_{\text{diff}}$ versus $\omega$ curves. Although one would assume that at this potential, $C_{\text{diff}}$ should be either independent of frequency (ideal electrode surface) or $C_{\text{diff}}$ should depend on frequency as a consequence of CPE (continuous dependence in the presence of adsorbing anions and its contribution in the total electrode capacitance, because of the assumption that adsorption resistance was not involved in the adsorption process.

Another interesting feature of this approach is the $\alpha$ versus $E$ dependence shown in Fig. 8. As can be seen in the region of (most probably) random adsorption of chloride anions (between $-0.8$ V vs. SCE and $-0.4$ V vs. SCE), $\alpha$ is seen to change slightly with potential having a minimum of about 0.95 at the potential of the maximum on the other three curves and indicating that the ‘fractal’ character of the surface is sensitive to the amount of adsorbed anions (and most probably to the position of their adsorption, at kinks or steps). At the potentials of the sharp adsorption peak, the values of $\alpha$ become very close or equal to 1, indicating that adsorption of chloride anions at these potentials makes the electrode surface almost ideal (covering all kinks and steps).

Finally, since this is practically the first attempt to analyze differential capacitance by the approach used in this work, more results on different surfaces, different substrates and with different anions, in the presence and in the absence of supporting electrolyte, are needed in order to clarify these findings.

6. Conclusion

Analysis of $C_{\text{diff}}$ versus $f$ curves simulated for different equivalent circuits, representing different cases of anion adsorption, has shown that in all cases with an ideal, homogeneous electrode surface, the real value of $C_{\text{diff}}$, representing the sum of $C_{\text{dl}}$ and $C_{\text{ad}}$ (independent of frequency) could be obtained only at very low frequencies, lower than the higher limit of $f = 10$ Hz. In the case of real surfaces, presented by CPE, $C_{\text{diff}}$ versus $f$ curves were found to be more complex, with no possibility to obtain the values of $C_{\text{dl}}$ at high and $C_{\text{ad}}$ at low frequencies, since $C_{\text{diff}}$ is dependent on frequency in the whole range of frequencies used ($10^{-4}$–$10^{5}$ Hz).
Chloride adsorption onto the Ag(111) face was found to follow the approach initiated in this work by introducing CPE instead of $C_{dl}$. It is shown that impedance diagrams deviate from the ‘ideal double layer behavior’ and that $C_{diff}$ versus $E$ curves depend on frequency. It is confirmed by the analysis of $C_{diff}$ versus $v$ curves that this is the consequence of adsorption involving adsorption capacitance and resistance, as well as of the inhomogeneity of the real single crystal face.

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