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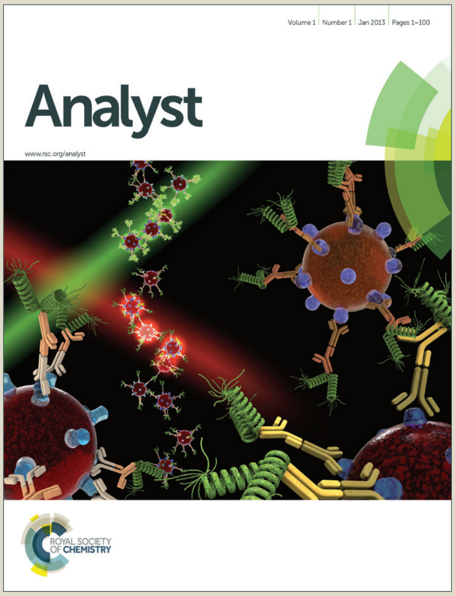

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Revisiting the analysis of impedance data for double layer capacitance*

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Abstract

A method was developed to extract double layer capacitance (C_{dl}) from data displaying time constant dispersion at frequency where phase angle reaches its maximum (f_1). This method was implemented in a set of synthetic data and the Kramers-Kronig (K-K) transformable experimental data for mild steel in acid solution. The double layer capacitance values were compared with ones extracted from constant phase element (*CPE*) parameters, Y_o and α, at frequency where imaginary part of the impedance reaches its maximum (f_2). Significant closeness of the results was reached for two different frequencies.

Key Words: Impedance Spectrocopy, Kramers-Kronig Transforms, Constant Phase Element, Capacitance

*Dedicated to Prof. Dr. Mehmet Erbil, one of the leading scientists in the field of electrochemistry, on the occasion of his retirement.

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1. Introduction

Graphical methods take the first stage to interpret impedance data. Many graphical methods that use a deterministic model for a given process are employed by several electrochemists in the literature [1-3]. A perusal of the literature shows clearly that either Nyquist plots or Bode plots are the plots in demand. Though no frequency dependency can be seen in Nyquist plots, they are among the most preferred ones due to the shape of the locus points which give in-depth insights into the possible mechanisms. On the other hand, Bode plots present the dependence on frequency despite their inadequacy for the electrochemical systems exhibiting an ohmic or electrolyte resistance [3].

Fitting a model is the following stage to evaluate the impedance data. Meanwhile, before proceeding to use such data, no question should be left in mind about the reliability of the data. Thus, before devising a model, the data need to be checked in terms of time-dependent phenomena with the Kramers-Kronig (K-K) transforms [4-6]. In this context, referring to K-K transforms is crucial for the analysis of the impedance data though they attract little interest due to the complex nature [7-12].

Several scientific software packages are in use to fit experimental impedance data to a simple equivalent circuit model. Though extraction of the circuit elements seems to be easy by such software packages, some initial guesses are required to start the process. Apart from this requirement, there are many works in which constant phase element (*CPE*) is used in the circuit model to increase the quality of the fit. However, in most of these studies, either the *CPE* parameter Y_o is given in s Ω^{-1} as a capacitance or as a capacitance converted with equations that give different results for the same Y_o and α [13,14]. The choice of proper equation for extraction of capacitance is essential since the source of the CPE is either surface time constant dispersion or normal time constant dispersion. While the former one requires the contribution of R_s on *CPE* behavior, the latter one doesn't [15].

The purpose of this paper is two-fold: first, to develop a method for extraction of double layer capacitance (C_{dl}) from data displaying time constant dispersion in the direction normal to the electrode surface at frequency where the phase angle reaches its maximum, and second, to test the suitability of method by using both model systems and experimental data associated with corrosion of mild steel in acid solution.

The layout of the paper is as follows; the experimental details are presented in Section 2, the discussion of the results is proposed in Section 3, and the conclusions are reported in final section.

2. Experimental Details

The working electrode was a mild steel rod with the following composition in wt %: C, 0.11; Mn, 0.45; S, 0.25; S, 0.050; P, 0.040; and the remainder, iron. It was stowed in a polyester resin to enable only a 0.5 cm^2 surface area to be exposed to the solution. 0.5 M hydrochloric acid solution was used as an electrolyte without and with various concentrations (0.5, 1.0, 5.0 and 10 mM) of Methionine (Met). Aqueous solution was prepared using hydrochloric acid of reagent grade and distilled water. The working electrode surface was pretreated with a series of grinding paper down to 1200 grade, degreased in acetone, rinsed with distilled water and dried with soft paper.

The measurements were done in a three electrode open cell containing 100 mL of stagnant solution at 25±1 °C after 0.5 h of exposure. The reference electrode was an Ag/AgCl (3 M KCl) and the counter electrode was a platinum sheet with 1 cm^2 surface area. The system response to ac signal, 5 mV peak to peak, was recorded in 100 kHz-10 mHz frequency range with CHI 604A AC electrochemical analyzer.

Generation of synthetic data, the K-K transforms and fitting experimental data to a suitable equivalent circuit were done with ZView software, Scribner Associates Inc.

A code, *Cdl*^{ezl}, was written in MATLAB by the present author to quickly automate the extraction of C_{dl} values through Eq. 5. It prompts the users only to click the command button immediately afterwards the opening of the data files of the measurements.

3. Results and Discussion

A model comprised a series of circuits in which charge storage capacity is decreasing away from the electrode surface can represent the time constant dispersion in the direction normal to the electrode surface. The situation is delineated in Fig. 1.

Fig. 1

The equivalent impedance ($Z_{\mathrm{eq}}(\omega)$) of above system is the sum of the individual circuits' impedances with series R_{s} (Eq. 1a).

$$Z_{\mathrm{eq}}(\omega) = R_{\mathrm{s}} + \sum_{\mathrm{i}=1}^{\mathrm{n}} Z_{\mathrm{i}} \tag{1a}$$

Considering the nonideal capacitive behavior, the summation symbol in Eq. 1a can be expanded as in Eq. 1b [1].

$$Z_{\mathrm{eq}}(\omega) = R_{\mathrm{s}} + \frac{R_{\mathrm{p}}}{1 + \left(\mathrm{i}\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha}} \tag{1b}$$

where α represents the degree of deviation from ideality.

In order to have the formulae of C_{dl} in Eq. 5, it is first necessary to separate Eq. 1b into its real part and imaginary part. Multiplying by the complex conjugate makes this separation possible, however, in this case the existence of the term α causes this process to be difficult. To compensate this difficulty, i^{α} can be written in polar form as exp(iπ/2α) which can be expanded by Euler's formula, exp(iφ)=cosφ+isinφ, as in Eq. 2:

$$Z_{\mathrm{eq}}(\omega) = R_{\mathrm{s}} + \frac{R_{\mathrm{p}}}{1 + \cos\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha} + \mathrm{i}\sin\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha}} \tag{2}$$

Now multiplying the denominator of Eq. 2 by its complex conjugate and rearranging with a useful trigonometric identity, $\sin^2\varphi+\cos^2\varphi=1$, leads into the real part and imaginary part as in Eq. 3.

$$Z_{\mathrm{eq}}(\omega) = R_{\mathrm{s}} + \underbrace{\frac{R_{\mathrm{p}}\left(1 + \cos\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha}\right)}{1 + 2\cos\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha} + \left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{2\alpha}}}_{Z_{\mathrm{Re}}(\omega)} - \mathrm{i}\underbrace{\frac{R_{\mathrm{p}}\sin\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha}}{1 + 2\cos\frac{\alpha\pi}{2}\left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{\alpha} + \left(\omega C_{\mathrm{dl}} R_{\mathrm{p}}\right)^{2\alpha}}}_{Z_{\mathrm{Im}}(\omega)} \tag{3}$$

Differentiating the ratio of $Z_{\mathrm{Im}}(\omega)/Z_{\mathrm{Re}}(\omega)$ with respect to ω and setting equal to zero, then certain algebra gives the formulae of C_{dl} for frequency at which the phase angle reaches its maximum (f_1):

$$\frac{\mathrm{d}}{\mathrm{d}\omega}\left(\frac{Z_{\mathrm{Im}}(\omega)}{Z_{\mathrm{Re}}(\omega)}\right) = \left(\frac{Z_{\mathrm{Re}}(\omega)\frac{\mathrm{d}}{\mathrm{d}\omega}\left(Z_{\mathrm{Im}}(\omega)\right) - Z_{\mathrm{Im}}(\omega)\frac{\mathrm{d}}{\mathrm{d}\omega}\left(Z_{\mathrm{Re}}(\omega)\right)}{\left(Z_{\mathrm{Re}}(\omega)\right)^2}\right) = 0 \tag{4}$$

$\therefore$

$$C_{\mathrm{dl}} = \left(\frac{1}{\omega R_{\mathrm{p}}}\right)\left(1 + \frac{R_{\mathrm{p}}}{R_{\mathrm{s}}}\right)^{\frac{1}{2\alpha}} \tag{5}$$

in which all the parameters have usual meanings.

Referring to Fig. 1, it is obvious that R_{s} has no direct effect on C_{dl}. The explanation for the appearance of R_{s} in Eq. 5 can be sought in the fact that this equation seeks a specific frequency for C_{dl} at which the phase angle reaches its maximum ($f_{\theta\mathrm{max}}$), and the magnitude of

$f_{\theta max}$ depends on the magnitude of R_s, i.e. the only contribution of R_s in Eq. 5 is to determine $f_{\theta max}$. Any increase/decrease in R_s results a decrease/increase in $f_{\theta max}$ (Fig. 2).

Fig. 2

Fig. 3 depicts two sets of synthetic data, for data set 1 α equals 1 (a) for data set 2 not (b), in the form of phase angle vs. log*f*.

Fig. 3

The C_{dl} values determined with Eq. 5 for synthetic data sets at f_1 are given in Table 1 with the one determined from CPE parameters, Y_o and α, at f_2. An excellent agreement between the initial C_{dl} value for the data set 1 and the one extracted from Eq. 5 for this data set was observed. A comparison of C_{dl} values for the data set 2 at f_1 and f_2 reveals that both approaches succeed in obtaining close values. Now it seems promising to implement Eq. 5 for real systems.

Table 1

As a representative example, a set of experimental data is presented for mild steel in 0.5 M hydrochloric acid solution containing 10 mM Met in the form of phase angle vs. log*f* (Fig. 4).

Fig. 4

The plot seems to behave ideal, however, after a close inspection of the plot, one may remark that the system indeed displays time constant dispersion which is also valid for all other experimental data sets. Before applying Eq. 5 to the above-mentioned system, the data were checked with the K-K transforms whether it was influenced or not by time dependent phenomena. As can be seen from Fig. 5 the results of transforms comply well with the experimental data particularly at high and intermediate frequencies, but there exists a difference at low frequencies. Very similar results were obtained with all other experimental data sets which are not surprising because electrode surface remains polarized for a longer time at low frequencies than intermediate and high frequencies which cause degradation of the quality of plots through data scatter.

Fig. 5

The C_{dl} values determined with Eq. 5 for experimental data sets at f_1 are given in Table 1 which also includes the values at f_2. As expected, a satisfactory closeness was found between the C_{dl} values for all the data sets.

4. Conclusions

1.A method was developed under the assumption of a dispersion in the direction normal to the electrode surface to extract C_{dl} values for the data displaying time constant dispersion and it was implemented for both synthetic and experimental data.

2.The applicability of method to real systems seems to be adequate considering the noteworthy closeness of C_{dl} values.

3.The K-K transforms were found in a reasonable agreement, except differences seen at low frequencies, with the experimental data at intermediate and high frequencies for validating experimental data.

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Figure Captions

Figure 1. Variation of properties in the direction normal to the electrode surface. OHP: outer Helmholtz plane R_{ct}: charge transfer resistance, R_d: diffuse layer resistance, R_p: polarization resistance, R_s: solution resistance.

Figure 2. Effect of R_s on the frequency at which the phase angle reaches its maximum ($f_{\theta max}$).

Figure 3. Phase angle vs. log*f* plots for synthetic data sets that correspond to the circuits;

(a)Parallel combination of a double layer capacitance (C_1:1.5 10^{-5}s Ω^{-1} cm^{-2}) and a resistor (R_2:150 Ω), both in series with the other resistor (R_1:25 Ω).

(b)Parallel combination of a constant phase element ($CPE_{1\text{-}T}$:1.5 $10^{-5}s^{\alpha}$ Ω^{-1} cm^{-2}, $CPE_{1\text{-}P}$:0,900) and a resistor (R_2:150 Ω), both in series with the other resistor (R_1:25 Ω).

f_1 equals 2.27 for data set 1 and 2.62 for data set 2, f_2 equals 2.13 for data set 2.

Figure 4. Phase angle vs. log*f* plots for mild steel in 0.5 M hydrochloric acid solution in the presence of 10 mM Met.

Figure 5. The absolute values of the differences between experimental and the K-K transformed data. ♦, real part ; ◊ imaginary part.

Table Captions

Table 1 The C_{dl} values with the unit of 10^6 s Ω^{-1} cm^{-2} for synthetic and experimental data sets at frequencies f_1 and f_2.

Table 1

The C_{dl} values with the unit of 10^6 s Ω^{-1} cm^{-2} for synthetic and experimental data sets at frequencies f_1 and f_2.

	Synthetic Data		Experimental Data[1]					
Frequency	Set 1, α=1	Set 2, $\alpha \neq 1$	C_{Met}(mM)	0.0	0.5	1.0	5.0	10.0
[2]f_1	15.1	7.50		30.9	22.4	21.6	15.8	16.3
[3]f_2		7.64		30.0	24.1	20.7	14.4	14.9

[1] α, determined from experimental data as described in Ref. 9.

[2] C_{dl}, extracted from Eq. 5.

[3] C_{dl}, extracted from CPE parameters, Y_o and α, as described in Ref. 14.

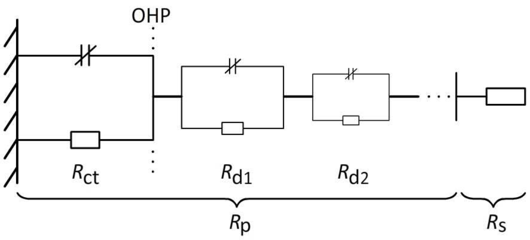

Figure 1.

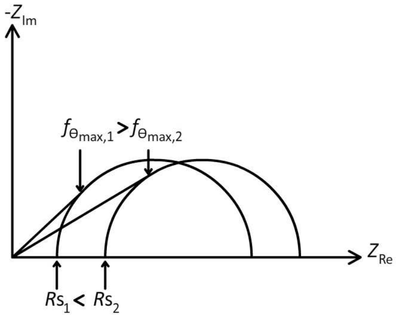
$-Z_{\mathrm{Im}}$
$f_{\theta\mathrm{max},1} > f_{\theta\mathrm{max},2}$
Z_{Re}
$Rs_1 < Rs_2$

Figure 2.

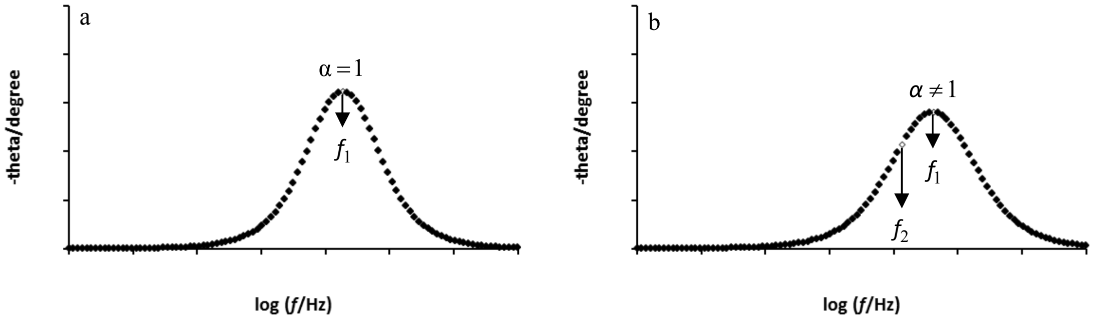
a
$\alpha = 1$
f_1
-theta/degree
log (f/Hz)
b
$\alpha \neq 1$
f_1
f_2
-theta/degree
log (f/Hz)

Figure 3.

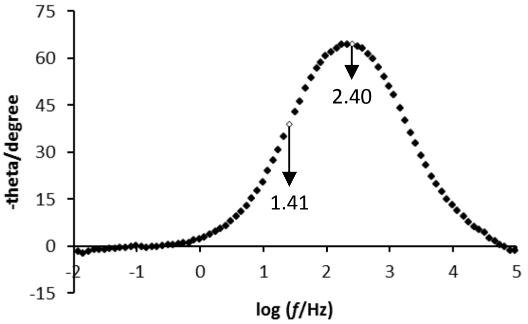

Figure 4.

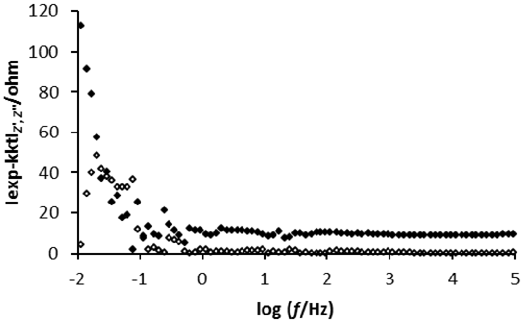

Figure 5.