

# Using electrochemical impedance spectroscopy of salicylate anion selective electrode: simulation for behavior of electrode

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(Received September 12, 2012 ; Accepted March 15, 2013 )

## ABSTRACT

In this paper, the behavior of the salicylate anion-selective electrode was studied using the electrochemical impedance spectroscopy technique. Considering the diagram of the charge transfer resistance and -logarithm of the double layer capacitance versus -logarithm of the concentration, linear range concentration increased to  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M and  $1.0 \times 10^{-9}$ - $1.0 \times 10^{-1}$  M, respectively. Among the other characteristics of this study, it can be pointed out a wide pH range of 4.0-10.0. Then "one-impedance for one-concentration" method was used to measure the salicylate ion at the linear range of  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M. Finally, the impedance spectra of this electrode were simulated in which the obtained results of this simulation indicate proximity of experimental and simulation data.

**Keywords:** Salicylate, Anion-selective electrode, Electrochemical impedance spectroscopy, Simulation

## 1. INTRODUCTION

Salicylate and its derivatives, including acetylsalicylate (aspirin), are commonly used as effective analgesics and are available to the public in a wide variety of formulations. Aspirin, a prostaglandin biosynthesis inhibitor, is also an important antipyretic drug. Recently, a new therapeutic use has emerged based on unique antiplatelet

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aggregation property, so that aspirin is now being widely used to treat cardiovascular disorders [1]. Despite their utility as pain relievers and antipyretics, salicylates can be quite toxic if taken in large doses. Recommended therapeutic levels in plasma range from 0.15 to 2.1 mmol L<sup>-1</sup> (total salicylate); although a large fraction of this total salicylate may be bound proteins [2, 3]. The most widely used analytical method for determining total salicylate is based on the Triender reaction in which sample salicylate reacts with ferric ions to form a colored complex in acid solution [4].

In our previous paper using complex of 1,8-diamino-3,6-dioxaoctane nickel(II) perchlorate as ionophore for preparing salicylate-selective electrode was described. The optimum composition of the membrane was 29.0 wt.% PVC, 63.0 wt.% dioctylphthalate (DOP) as plasticizer, 6.0 wt.% ionophore, 2.0 wt.% methyltrioctylammonium chloride (MTOAC) as cationic additive. The characteristics of this electrode can be referred to a Nernstian response of  $-59.5 \pm 1.0$  mV decade<sup>-1</sup> over the concentration range of  $7.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$  M salicylate, the detection limit of  $5.0 \times 10^{-7}$  M and a wide pH range of 6.0-9.5. The prepared electrode was suitable for measuring the acetylsalicylic acid content in pharmaceutical samples without a significant interaction from concomitant anionic species. The results show that there was a coordination interaction between salicylate and the proposed carrier, which played an important role in the response characteristics and selectivity of the electrode [5].

Electrochemical Impedance spectroscopy (EIS) represents a powerful method for investigation of electrical properties of materials and interfaces of conducting electrodes. An electrochemical reaction at the electrode-electrolyte interface cannot be completely understood by traditional electrochemical measurements. Those methods provide only currents made of faradaic and non-faradaic components. On the other hand, non-steady-state measuring techniques are known to be extremely suitable for the investigation of the electrode kinetics of more complex electrochemical systems. A complete description requires impedance measurements made over a broad frequency range at various potentials and determination of all the electrical characteristics of the interface. Perturbation of the electrochemical system leads to a shift of the steady state. The rate at which it proceeds to a new steady state depends on characteristic parameters (reaction rate constants, diffusion coefficients, charge transfer resistance, double layer capacity). The small perturbation of the electrode state has the advantage that the used solutions of relevant mathematical equations are transformed in limiting forms that are normally linear [6, 7]. By using this technique, the calculation of parameters including  $R_{ct}$ ,  $C_{dl}$ , and the apparent rate constant ( $k_{app}$ ) is possible.

In our other research, EIS technique was used to investigate the performance of a sulfate-selective electrode and the impedance spectra of this electrode were simulated [8]. Also in this paper, behavior of the salicylate selective electrode was investigated by EIS

technique and its impedance spectra were simulated by Maple 13 software. In addition, full details of simulation steps are presented.

In order to simulation, the equations describing the system were defined and solved using the finite difference method. In this method, a numerical model of electrochemical systems was installed on a computer and was allowed to evolve by a set of algebraic laws derived the differential equations. Thus, a simulation of experiment is carried out in which the numerical representation of current functions, concentration profiles, potential transients and etc, can be extracted from it [9, 10]. There are many different approaches to solving the mathematical equations that describe electrochemical experiments [11]. The first numerical solution of the Nernst-Planck equation coupled with Poisson equation (NPP equations) was provided by Cohen and Cooley [12], who introduced a system of reduced units and space charge expressed by displacement current equation. The milestone in the field of the NPP numerical modeling is the paper written by Brumleve and Buck [13]. Their approach is free from approximate assumptions and directly relates the impedance spectra to the physical parameters (concentrations, heterogeneous rate constants and diffusivities). In recent years, several studies in simulation of EIS data have been performed that were only theoretical researches. Such researches mentioned by Gabrielly et al. in 2004 [14, 15] Kucza et al. in 2006 [16] and Grysakowski et al. in 2008 [17].

## **2. EXPERIMENTAL**

### **2.1. Materials and Reagents**

MTOAC was purchased from Sigma. PVC of high relative molecular weight, DOP and tetrahydrofuran (THF) were prepared from Merck (Darmstadt, Germany). The complex of 1,8-diamino-3,6-dioxaoctane nickel(II) perchlorate was synthesized in laboratory [5]. All solutions were prepared using double distilled water. Adjustments of pH were made with hydrochloric acid and sodium hydroxide solutions as required. A stock solution of salicylate  $1.0 \times 10^{-1}$  M was prepared by dissolving the appropriate amount of sodium salicylate in 100 mL of water and working solutions were made by successive dilutions in water.

### **2.2. Equipments**

A potentiostat/galvanostat instrument (Autolab PGSTAT 302, Eco Chemie B.V., Utrecht, The Netherlands) were employed to carry out EIS measurements. These measurements were carried out in a three-electrode mode, using the prepared electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a

platinum electrode as counter electrode. Impedance spectra were recorded over the frequency range from 10000 to 0.1 Hz, at zero DC potential, AC amplitude of 5 mV, room temperature and open circuit potential (OCP) conditions. A computer system with CPU Core i7 920 and 4 GB RAM was also applied for simulation.

### 2.3. Softwares

Impedance spectra were acquired and processed by using the Frequency Response Analyser (FRA) software. Analysis and interpret of the EIS data was performed by the ZView software (Scribner Associates Inc., Southern Pines). In this analysis, an equivalent circuit including a solution resistance ( $R_s$ ), a double layer capacitance ( $C_{dl}$ ) and a charge transfer resistance ( $R_{ct}$ ) was used to show how it connects its components as it is shown in Figure 1.

In order to simulate the impedance spectra, Maple 13 software (Maplesoft, Waterloo Maple Inc.) was used.

## 3. RESULTS AND DISCUSSION

### 3.1. Influence of the internal solution concentration

During this study that was carried out in concentrations of  $1.0 \times 10^{-1}$ ,  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-3}$  M sodium salicylate as internal solution (like its potentiometric method [5]) and in concentration range from  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-12}$  M of sodium salicylate as external solution and the effect of internal solution concentration on EIS spectra of salicylate ion-selective electrode was investigated. The complex plan plots of different concentrations of internal solution are showed in Figures 2-a, b and c. In these figures, points and lines indicate the experimental and fitting data, respectively. As can be seen with decreasing the concentration of internal solution, the complex plan plots are more regular. In order to further evaluation, values of the interfacial parameters ( $R_s$ ,  $R_{ct}$  and  $C_{dl}$ ) were estimated by approximation of the EIS experimental data and the diagrams of  $R_{ct}$  and  $-\log C_{dl}$  versus  $-\log$  of sodium salicylate concentration were plotted that are showed in Figure 3-a and 3-b, respectively. As can be observed using the EIS method and the internal solution concentration of  $1.0 \times 10^{-3}$  M sodium salicylate the linear range of the charge transfer resistance changes is achieved to  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M. Also by reduction of the internal concentration, the overall value of the charge transfer resistance decreases. Result of  $C_{dl}$  in Figure 3-b shows with application of  $1.0 \times 10^{-2}$  M sodium salicylate as internal solution, the linear range of the concentration is reached to  $1.0 \times 10^{-9}$ - $1.0 \times 10^{-1}$  M. It should be noted that the results of potentiometric studies showing the concentration of the internal solution does

not cause any significant difference in the potential response of the electrodes, except for an expected change in the intercept of the resulting Nernstian plots [5].

Finally, we can draw two calibration curves by using  $R_{ct}$  and  $C_{dl}$  obtained from the internal solution concentration of  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-2}$  M sodium salicylate, respectively that their characteristics are summarized in Table 1. These curves were used to determine the real sample concentration.

### 3.2. Influence of the pH

The effect of the pH of the test solution on EIS results was examined with concentration of  $1.0 \times 10^{-2}$  M sodium salicylate as external solution and compared with potentiometric results. In this study that dilute hydrochloric acid and sodium hydroxide were used for adjustment of the pH, the internal solution of electrode was  $1.0 \times 10^{-3}$  M sodium salicylate. The complex plan plots of these studies are given in Figure 4 that show pH changes do not influence on the impedance spectrum at a wide range of pH. In this figure, points and lines indicate the experimental and fitting data, respectively. According to the overlap of some spectra and more investigation, the diagrams of  $R_{ct}$  and  $-\log C_{dl}$  versus the pH changes of solution were plotted that are showed in parts (a) and (b) of inset at Figure 4, respectively. Applied pH range using the response curve obtained from  $R_{ct}$  is between 4.0 and 10.0. In this range,  $R_{ct}$  changes are negligible and also  $C_{dl}$  changes at the pH range between 5.0 to 10.0 are not great. Increasing  $R_{ct}$  and  $C_{dl}$  in low pH can be attributed to the salicylate ion protonation. In this case, the amount of free salicylate ions in solution is reduced that lead to low electrical conductivity. It must be noted that in potentiometric study, the potentials remain constant within a pH range of approximately 6.0-9.5.

### 3.3. Impedance measurement by "One-Impedance for One-Concentration" method

According to time-consuming of electrochemical impedance measurements in a wide range of frequency for several samples, data fitting, interpretation of equivalent circuits and its calculations, "one-impedance for one-concentration" method was introduced by Karimi et al. [18]. In this method for two first and last concentrations (here,  $1.0 \times 10^{-1}$  and  $1.0 \times 10^{-8}$  M sodium salicylate), measurements carried out in a range of frequencies (10000-0.1 Hz), while for middle concentrations (here  $1.0 \times 10^{-2}$ - $1.0 \times 10^{-7}$  M sodium salicylate) the two frequencies select as the start and end points of measurement. In this study that experiments were performed only at two frequencies of 520 and 120 Hz, the internal solution concentration was  $1.0 \times 10^{-3}$  M sodium salicylate. The complex plan plots of these

measurements are observed in Figure 5. To use these results for measurement of salicylate ion in real sample, the values of total impedance ( $|Z|$ ) was calculate by equation 1 and plotted versus the -logarithm of the concentration that is shown in inset of Figure 5. As can be observed, two calibration curves related to two frequencies were obtained in which their properties are given in table 1.

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (1)$$

### 3.5. Analytical application of electrode

In order to study the analytical application of this ion-selective electrode for measurement of salicylate ion using EIS method, this electrode was applied to determine the amount of salicylate in aspirin tablets. The results obtained from these measurements with three times irritation that are reported in Table 2, show this electrode can be used for determination of this ion in real samples using EIS and "one-impedance for one-concentration" methods. It should be mentioned; in previous work [5] the amount of salicylate ion in real sample was determined by potentiometric method and also by spectrophotometric method as a reference method [19].

## 4. SIMULATION OF IMPEDANCE SPECTRA

Simulation is a numerical approach that is valuable to develop an intuitive grasp of the important processes in an electrochemical system [20]. In this section, the impedance spectra of salicylate anion-selective electrode were simulated by finite difference method.

### 4.1. Design model

Complexity of this designed model depends on type of system and its conditions. In simple systems a distance division is only needed, while complex systems need the time division. In this work, our model included two divisions.

In distance division, we utilized Brumleve and Buck approach [13] that applied in series element with variable volumes. In this division,  $E_0$  and  $C_1$ , are defined as left interface, and  $E_N$  and  $C_N$  are defined as right interface. In other points, the electric fields (E) are placed at the boundaries of each element, while the concentrations (C) are defined in the middle of the elements, except at the interfaces, In addition the division of distance is contained many closely-spaced points near the interfaces (20 points) to characterize the double layer and a much wider spacing near the middle (31 points) to

economize on the total number of needed grid points, where there is effectively a half of a volume element.

In this model, time division begins at  $\Delta t = \tau_{\infty}/100$  and grows exponentially to  $\Delta t = \tau_d$ , where  $\tau_d$  and  $\tau_{\infty}$  are defined as follows:

$$\tau_{\infty} = K / \sum_i z_i^2 D_i C_i \quad (2)$$

$$\tau_d = d^2 / D_{\min} \quad (3)$$

In this relations, K is a constant equal to  $2C(L_D)^2$  that  $L_D$  is Debye lengths,  $z_i$ , the charge of species i,  $D_i$ , diffusion coefficient of species i,  $C_i$ , concentration of species i, d, the membrane thickness and  $D_{\min}$  is the smallest nonzero diffusion coefficient. In this simulation 400 points were used.

#### 4.2. Describing equations of the system

Four equations were used to describe our EIS system. Nernst-Planck equation is as follows:

$$f_i(x, t) = -D_i [\partial C_i(x, t) / \partial x - z_i C_i(x, t) (F / RT) E(x, t)] \quad (4)$$

In this equation,  $f_i(x, t)$  and  $C_i(x, t)$  are the flux and concentration of species i at distance x and time t, respectively and  $E(x, t)$  is the electric field of distance x at the time t. Also, F, R and T, are expressed the Faraday constant, the gas constant and the temperature, respectively.

Poisson equation is as follows:

$$\partial E(x, t) / \partial x = (4\pi / \varepsilon) \rho(x, t) \quad (5)$$

In this equation,  $\varepsilon$  is the dielectric permittivity coefficient and  $\rho(x, t)$  is defined as follows:

$$\rho(x, t) = \sum_i z_i C_i(x, t) \quad (6)$$

For purposes of the simulation, it is convenient to replace Poisson equation by the totally equivalent displacement current equation, as described by Cohen and Cooley [12]:

$$I = F \sum_i z_i f_i(x, t) + (\varepsilon / 4\pi) \partial E(x, t) / \partial t \quad (7)$$

The continuity equation is defined as follows:

$$\partial C_i(x, t) / \partial t = -\partial f_i(x, t) / \partial x \quad (8)$$

On the other hand, the total membrane potential at any time  $\phi(t)$  can be calculated by integrating the electric field across the cell of thickness d:

$$\phi(t) = \int_0^d E(x, t) dx \quad (9)$$

Then, the parameters of equations should be dimensionless. Solving differential equations in terms of dimensionless parameters that are normally created by dividing the variables of interest by one or more variables, describing some characteristic feature of the system and all the experimental situations are defined [10].

### 4.3. Putting the equations in the designed model

After making dimensionless parameters, equations 4, 7, 8 and 9 are converted to finite difference form compatible with designed model. Before proceeding to the solution of equations, the boundary conditions at each interface must be specified. In this simulation the approach of Brumleve and Buck [13] was used to determine the boundary conditions and a simple set of kinetic boundary conditions was selected to relate the interfacial fluxes to heterogeneous rate constants and concentrations.

### 4.5. Simulation of impedance spectra

In order to simulate, model and input parameters were defined in Maple 13 software. Then, the differential equations were written as codes in the model and solved by the Newton algorithm that is an iteration method for solution of equations by Jacobian matrix [21]. In this method, 100 iterations were used to achieve the convergent results and concentrations and potential were calculated at different times.

Impedance of system may be determined by using the Fourier transformation of the potential-time response to a small current perturbation that its relations are as follows:

$$Z^*(\omega) = -V^*(\omega) / I^*(\omega) \quad (10)$$

$$Z^*(\omega) = Z'(\omega) + jZ''(\omega) \quad (11)$$

$$V^*(\omega) = V'(\omega) + jV''(\omega) \quad (12)$$

$$I^*(\omega) = I'(\omega) + jI''(\omega) \quad (13)$$

In this relations,  $Z^*(\omega)$ ,  $V^*(\omega)$  and  $I^*(\omega)$  are impedance, transform of the potential time response and transform of the current perturbation, respectively. Also, "j" is the imaginary operator. Real and imaginary components of the potential-time response were obtained from following relations:



$$V'(\omega) = \int_0^{\infty} (V(t) - V_{\infty}) \cos \omega t \, dt \quad (14)$$

$$V''(\omega) = \int_0^{\infty} (V(t) - V_{\infty}) \sin \omega t \, dt + V_{\infty} / \omega \quad (15)$$

Components of the current perturbation transform were defined as follows:

$$I'(\omega) = 0 \quad (16)$$

$$I''(\omega) = -\Delta I / \omega \quad (17)$$

At last, these relations were written as codes in the software and impedance spectra of the salicylate anion-selective electrode were simulated. In order to compare the experimental and simulated data, this simulation carried out in the concentration range of  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  M as the external solution of electrode and  $1.0 \times 10^{-3}$  M sodium salicylate as the internal solution of electrode. Figure 6 shows the simulated complex plan plots of this electrode. In this figure, points and lines indicate the experimental and simulated data, respectively. As can be seen in all concentrations the simulated and experimental data are well adopted. Also simulated and experimental data of interfacial parameters and  $k_{app}$  are observed in Table 3.  $k_{app}$  is apparent rate constant that can be calculated by following equation:

$$k_{app} = \frac{RT}{n^2 F^2 R_{ct} C} \quad (18)$$

In this equation, R is gases constant, T is the temperature in Kelvin, n is the number of electrons, F is the Faraday constant,  $R_{ct}$  is the charge transfer resistance in ohms, and C is the concentration in  $\text{mol.m}^{-3}$ . By using this equation, the apparent rate constant is obtained in dimension of  $\text{cm.s}^{-1}$ .

Diagrams of the simulated and experimental  $R_{ct}$  and  $-\log C_{dl}$  was plotted versus the negative logarithm of salicylate concentration that are shown in parts (a) and (b) of inset at Figure 6, respectively. The results of this simulation expressing the parameters obtained from simulation are very close to the experimental data.

## 5. CONCLUSIONS

In this work the performance of a salicylate-selective electrode was investigated using EIS. In addition to the calculation of interfacial parameters such as solution resistance, charge transfer resistance and double layer capacitance, the detection limit using  $R_{ct}$  and  $C_{dl}$  were reduced to  $1.0 \times 10^{-8}$  and  $1.0 \times 10^{-9}$  M, respectively. Also the "one-impedance for one-concentration" method was applied for measuring the concentration of salicylateion with less time, increased rate and less calculations. Finally, the impedance

spectra of electrode were simulated using the software Maple13. The results of the simulations indicate the accuracy of experimental measurements.

**Acknowledgements.** The authors would like to thank Payame Noor University Research Council (center of Ardakan), Yazd University Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

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**Table 1.** Comparison of different techniques used to measure salicylate anion by salicylate-selective electrode

Technique		Slope	Linear range/M	pH range
Potentiometry [5]		$-59.5 \pm 0.1$ mV	$7.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$	6.0-9.5
Electrochemical impedance spectroscopy	By $R_{ct}$	1.001 Mohm	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	4.0-10.0
	By $C_{dl}$	0.058	$1.0 \times 10^{-9}$ - $1.0 \times 10^{-1}$	5.0-10.0
One-impedance for one-concentration	Freq.: 520 Hz	0.7029 Mohm	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	-
	Freq.: 120 Hz	0.9490 Mohm	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$	-

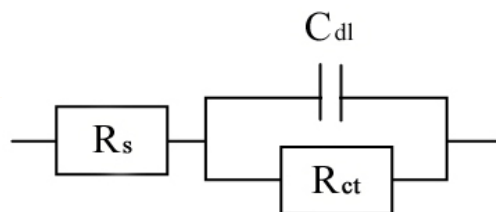
**Table 2.** Determination of salicylate in Aspirin tablets sample by using two methods; electrochemical impedance spectroscopy and one-impedance for one-concentration

Aspirin samples (100 mg)	Concentration of salicylate ion in sample (mg/tablet)			
	EIS	One-impedance for one-concentration	Potentiometry*	Spectrophotometry*
	$95.51 \pm 0.20$	$95.28 \pm 0.10$	$92.10 \pm 0.45$	$95.21 \pm 0.63$

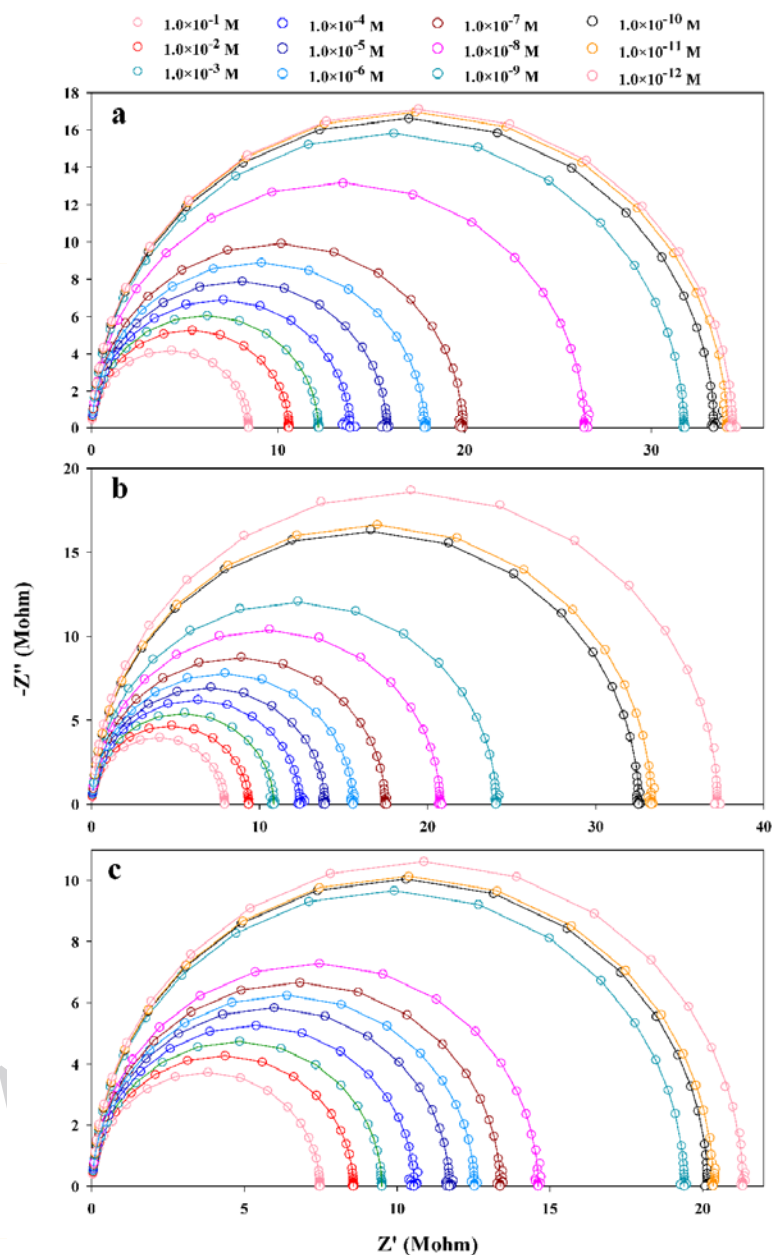
\*Potentiometric and spectrophotometric methods were carried out in previous paper [5]

**Table 3.** Values of the interfacial parameters estimated by approximation of the EIS simulated and experimental data obtained on salicylate-selective electrode with concentration of internal solution  $1.0 \times 10^{-3}$  M and different concentrations of external solution.

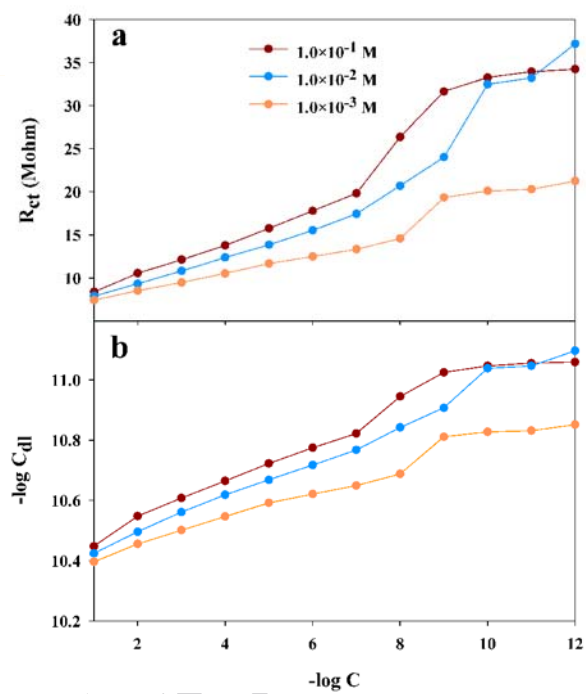
Concentration (M)	Experimental data			Simulated data		
	$C_{dl}$ (F.cm <sup>-2</sup> )	$R_{ct}$ (Mohm)	$k_{app}$ (cm.s <sup>-1</sup> )	$C_{dl}$ (F.cm <sup>-2</sup> )	$R_{ct}$ (Mohm)	$k_{app}$ (cm.s <sup>-1</sup> )
$1.0 \times 10^{-1}$	$4.02 \pm 0.1 \times 10^{-11}$	$7.45 \pm 0.1$	$8.94 \times 10^{-10}$	$4.041 \times 10^{-11}$	7.4305	$8.959 \times 10^{-10}$
$1.0 \times 10^{-2}$	$3.50 \pm 0.1 \times 10^{-11}$	$8.45 \pm 0.1$	$7.79 \times 10^{-9}$	$3.567 \times 10^{-11}$	8.4199	$7.906 \times 10^{-9}$
$1.0 \times 10^{-3}$	$3.16 \pm 0.1 \times 10^{-11}$	$9.47 \pm 0.1$	$7.03 \times 10^{-8}$	$3.191 \times 10^{-11}$	9.4105	$7.074 \times 10^{-8}$
$1.0 \times 10^{-4}$	$2.84 \pm 0.1 \times 10^{-11}$	$10.52 \pm 0.1$	$6.32 \times 10^{-8}$	$2.887 \times 10^{-11}$	10.4010	$6.400 \times 10^{-8}$
$1.0 \times 10^{-5}$	$2.56 \pm 0.1 \times 10^{-11}$	$11.68 \pm 0.1$	$5.70 \times 10^{-7}$	$2.636 \times 10^{-11}$	11.3920	$5.843 \times 10^{-7}$
$1.0 \times 10^{-6}$	$2.40 \pm 0.1 \times 10^{-11}$	$12.49 \pm 0.1$	$5.33 \times 10^{-6}$	$2.425 \times 10^{-11}$	12.3820	$5.376 \times 10^{-6}$
$1.0 \times 10^{-7}$	$2.25 \pm 0.1 \times 10^{-11}$	$13.34 \pm 0.1$	$4.99 \times 10^{-5}$	$2.246 \times 10^{-11}$	13.3730	$4.978 \times 10^{-5}$
$1.0 \times 10^{-8}$	$2.05 \pm 0.1 \times 10^{-11}$	$14.58 \pm 0.1$	$4.57 \times 10^{-4}$	$2.091 \times 10^{-11}$	14.3630	$4.635 \times 10^{-4}$



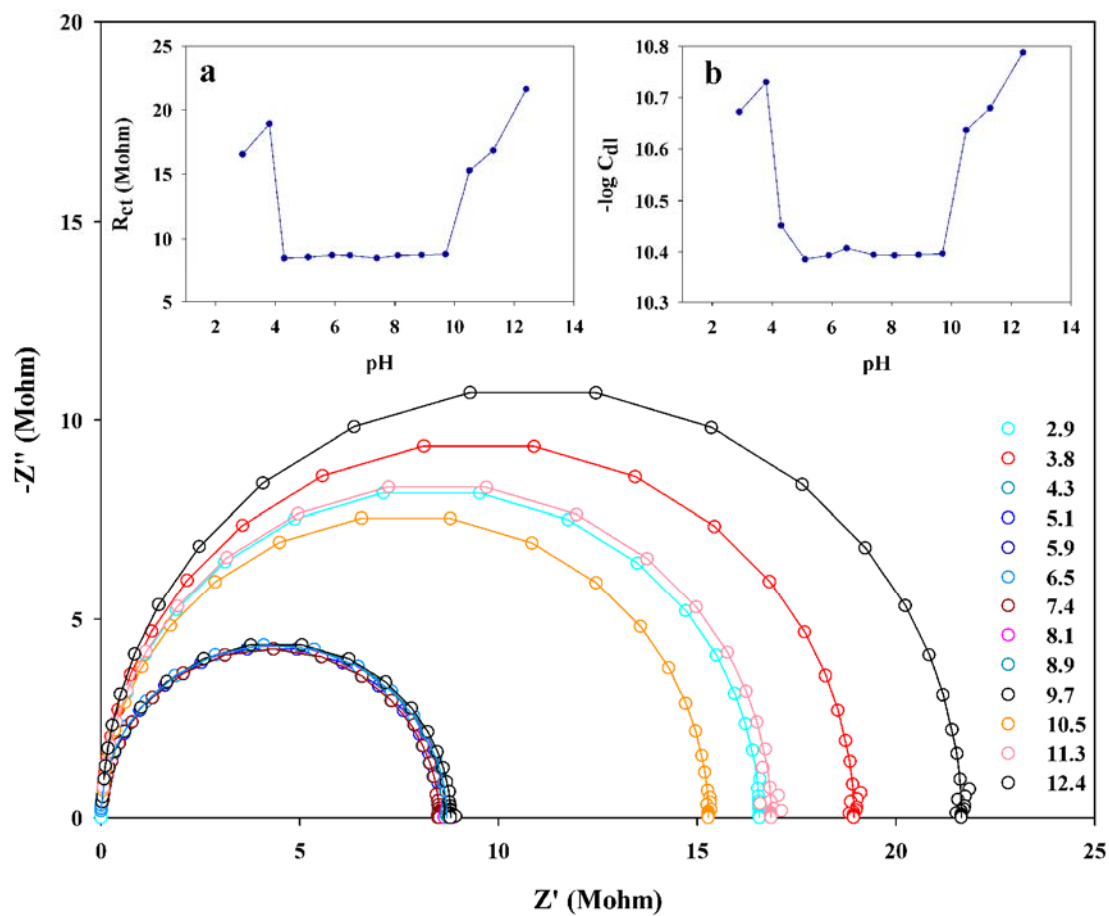
**Figure 1.** Equivalent circuit used to interpret the EIS results



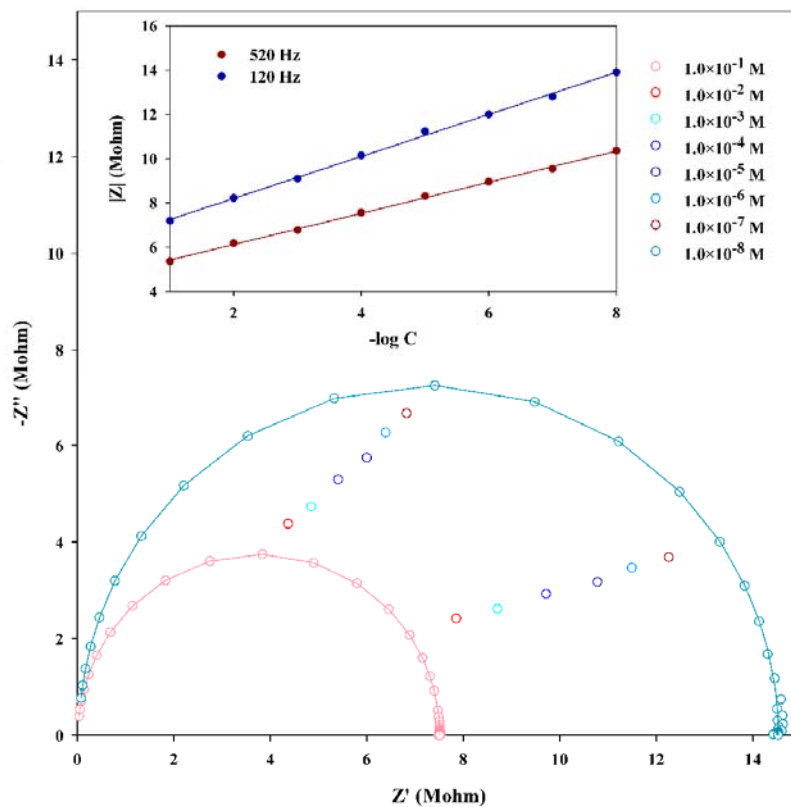
**Figure 2.** Complex plan plots of salicylate-selective electrode with internal solution concentration of a)  $1.0 \times 10^{-1}$  M, b)  $1.0 \times 10^{-2}$  M and c)  $1.0 \times 10^{-3}$  M (points and lines indicate the experimental and fitting data, respectively).



**Figure 3.** Influence of the internal solution concentration on a)  $R_{ct}$  and b)  $C_{dl}$ .

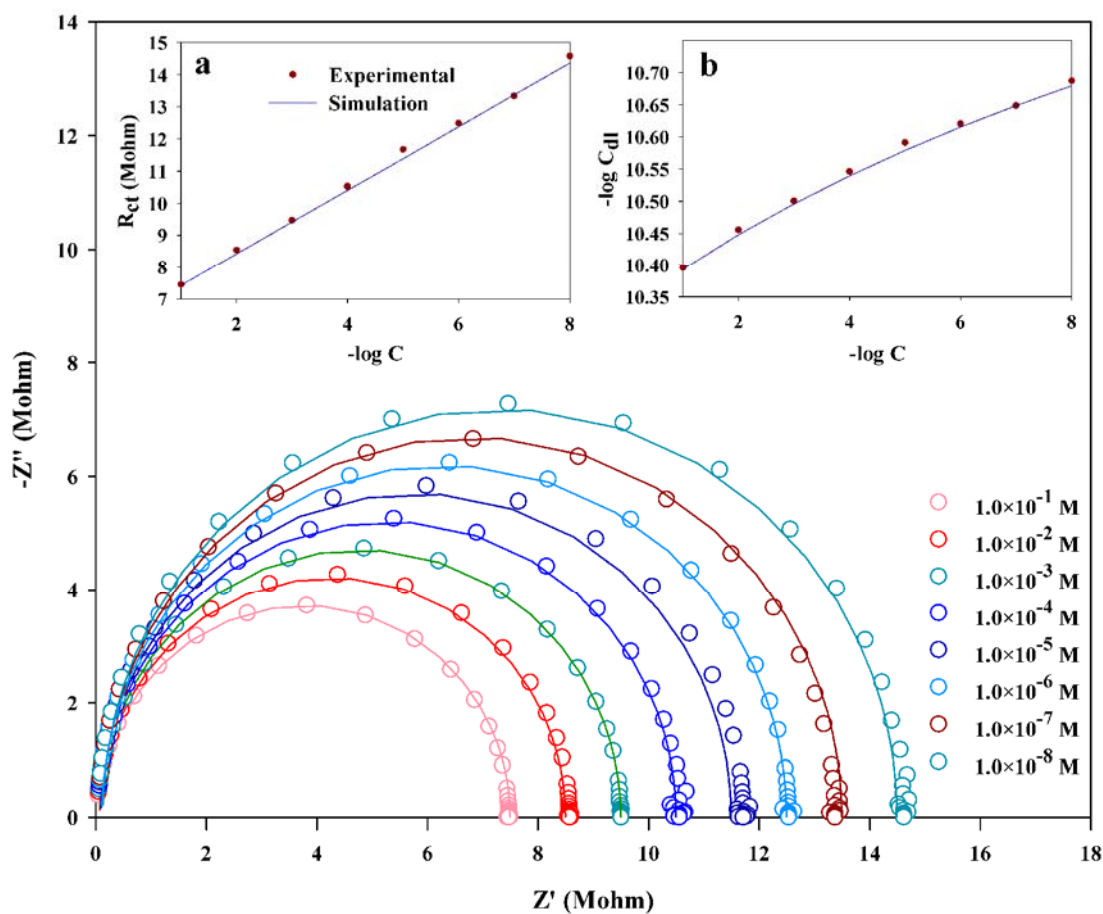


**Figure 4.** Complex plan plots of salicylate-selective electrode in different pH with external solution concentration of  $1.0 \times 10^{-2}$  M sodium salicylate (points and lines indicate the experimental and fitting data, respectively). The inset is the influence of pH changes on a)  $R_{ct}$  and b)  $C_{dl}$ .



**Figure 5.** Complex plan plots of the salicylate-selective electrode with internal solution concentration of  $1.0 \times 10^{-3}$  M sodium salicylate by "one-impedance for one-concentration" method in two frequencies of 520 and 120 Hz. The inset is two calibration curves obtained from this method in these frequencies.





**Figure 6.** Simulated complex plan plots of the salicylate-selective electrode with internal solution concentration of  $1.0 \times 10^{-3}$  M sodium salicylate (points and lines indicate the experimental and simulated data, respectively). The inset is simulated and experimental values of c)  $R_{ct}$  and b)  $C_{dl}$ .