



Modeling the charge transfer at the electrode-ionic liquid interface in dielectric spectroscopy measurements



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ABSTRACT

The phenomena occurring at the interface between the electrodes and a liquid with ionic conductivity is manifested specifically in the spectrum of the dielectric permittivity. The theoretical model of the electrode polarization (charge space polarization) is met in the dielectric spectroscopy measurements in which electrodes are conductors (allow transfer of electric charge) and the adsorption-desorption of ions occurs on their surface. A pair of ions with equal and opposite charge is considered. The ions are produced by the association-dissociation of neutral molecules. We propose general boundary conditions (BCs) with charge transfer current which contains the adsorption-desorption parameters. The BCs and the basic equations of the Poisson-Nernst-Planck model, i.e. transport equations of charge carriers and Poisson equation, are re-formulated through new variables. The mathematical problem is solved analytically. The results allow finding a criterion for choosing a general and simple admittance expression, thus using a unified approach for different cases. We show that the small signal approximation is no longer needed, at least for modern dielectric spectroscopy equipment. The ions can be point-like or may have finite dimensions. For the last case a model of Stern compact layer with charge transfer is proposed, which allows to calculate the compact layer impedance. Finally we obtain the equivalent admittance of the physical system composed from metal electrodes and ionic liquid in the presence of the Stern layer and the space charge polarization. The limitations of the model are given by the hypothesis of “flat band” and the non-selective adsorption of ions.

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1. Introduction

This paper is a continuation of the author's work [1–3] on the study of the electrode polarization. Special attention is paid to the formulation of boundary conditions (BCs) for the ac electric circuit containing an ion conductive material placed between two metal electrodes. This is of interest for dielectric spectroscopy measurements of physical systems for which the mobile charge carriers are ions: ionic conductive solids, liquid crystals doped intentionally or accidentally, with one or multiple pairs of mobile ions, electrolytes.

The electrode polarization (space charge polarization) consists in the accumulation of mobile charge carriers (ions) under the effect of external electric field at the electrode-sample interface. The effect of electrode polarization is observed at low and very low frequencies and is manifested by the increase of both dielectric constant and dielectric loss in respect to their values in the bulk.

The accumulation of ions at the electrodes is inevitable as the mobile electric charge carriers with finite size cannot pass through the separating surface between sample and electrodes. If one takes into account the

existence of surface states and the adsorption/desorption rates, the electrodes can be classified as: blocking (the charge transfer on their surface) and conductor i.e. “permeable” or “semi-permeable” to the charge transfer. The charge transfer is done between ions and electrons from the external circuit.

An important issue is related to how the charge transfer at the interface, produced by the adsorption-desorption of ions at the electrode surfaces, can be designed and incorporated into the boundary conditions. The ions adsorption-desorption is described in Langmuir approximation by the kinetic equation that contains two phenomenological parameters: one associated with the adsorption, and other associated with desorption.

The equilibrium concentration of ions is nonuniform in the vicinity of each electrode due to adsorption, a contact electric field and a space charge region appear and the metal electrode is electrically charged. The electric charge of the electrode is situated in a very thin layer on the surface and consists of an excess or deficiency of electrons. So, an electric double layer (EDL) is formed in the fluid near the electrode. The EDL structure can be described using the Gouy-Chapman-Stern (GCS) model which considers the interface as composed by two layers of ions or molecules [4–8]: the compact Stern layer (SL) and the diffusion layer (DL) or Gouy-Chapman layer (GCL). SL is located in the

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immediate vicinity of the surface, and the ions are tightly bound to the surface due to adsorption and Coulomb interaction. SL is limited by two planes: the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). DL (GCL) is the region near the SL, in which ions can move freely under the effect of diffusion, thermal agitation or electric field.

The compact Stern layer structure is determined by different types of interactions between the ions and surface electrode. Near the surface, three types of ions can be considered [8]: a) the potential-determining ions are adsorbed directly on the surface; their equilibrium distribution produces the contact potential between surface and volume; the adsorbed ions up (forming) the electric surface charge; b) the specifically-adsorbed ions interacts strongly with the surface by any other interaction than pure Coulomb one; c) the indifferent ions are affected by the Coulomb force of charge on the electrode surface; thus, they are repelled by the surface charge of the same sign or are attracted to opposite charge. IHP is located in the center of specifically adsorbed ions and ions OHP is located in the center of indifferent ions [4]. As in [9], we assume that the specific absorption is absent and thus compact Stern layer is delimited only by the IHP surface.

The supply electrodes can be blocking or unblocking, i.e. they obstruct totally or partially the transfer of electric charge through their surface. For blocking electrodes the BCs can be formulated in a simple way, because the charge transfer is not possible. The electric current density can be zero for completely blocking electrodes or equal with the temporal variations of charge carrier concentrations adsorbed on the surface for adsorption-desorption blocking electrodes.

If the electrodes are non-blocking, the electric current density has a conduction component due to the charge transfer across the surface of the electrode. The charge transfer between the sample and the external circuit can be expressed in several ways [9,10]. According to the Chang-Jaffe model [11], the ionic current is proportional to the excess of ion concentrations in front of the electrode. Another, called ohmic electrodes model [9,10] assumed that ionic current density at electrodes is proportional to the surface electric field.

In an ionic liquid charge redistribution induced by the external electric field is described in the frame of Poisson-Nernst-Planck model (PNP) based on continuity equations for positive ions, negative ions and neutral molecules, and on Poisson equation for the electric field. These equations must be solved together with the BCs for the ion current densities on the surface of electrodes and with the relationship between electric field and applied voltage. The BCs take into account the properties of the electrodes.

A fairly general theoretical approach to the study of electrode polarization based on PNP model is presented in Macdonald papers [12,13]. To find the distribution of ions and electric field under the influence of external ac voltage, the system of differential equations is completely solved for a one-dimensional case. The generation-recombination of carriers is given by the association-dissociation of neutral molecules. The recombination rates of bi-particle interaction mechanism are considered. The Chang-Jaffe boundary conditions are used. The diffusion coefficients and the parameters that define the boundary conditions have arbitrary values.

Recently other papers analyzing the electrode polarization from individual points of view were published, analytical models can be ordered from simple to complex according to the level of difficulty and the limits of validity. The criteria that can be used are: the nature of the electrodes blocking [1–3,14–24] or conductor [9–13, 25–29], the values of diffusion coefficients or ion mobilities are equal [1,14–17,23,26,29] or different [2,18–20,24–25,28], for generation-recombination carriers the net recombination rate is negligible [1,2, 14–20,23,25,26,28,29] or not [3,12,13,21,22,24]; there is one mobile ion [9,10,22,27] or one pair of mobile ions [1–3,12–26,28,29]. These criteria allow finding what models have in common and what make them different.

Four hypotheses are common: the ions are point-like, the small signal approximation is valid (linearization theory); no external dc voltage is applied; in thermodynamic equilibrium state the system is neutral both globally and locally (“flat band approximation”) i.e. no contact electric field ($E_{eq} = 0$) and the ion concentrations are uniform and equal to each other ($p_{eq} = n_{eq} = const$). The thermodynamic equilibrium state is achieved when the adsorption-desorption of ions is absent (negligible) or selective; adsorption rates are equal $\Gamma_p = \Gamma_n$, and desorption times are equal $\gamma_p = \gamma_n$ [15,20,25,29]. In GC layer the equilibrium electric potential is zero.

In this paper we show that the small signal approximation is not required for dielectric modern spectroscopy equipment that can separate the fundamental and first harmonics. If the small signal assumption is removed, we must take into account the finite size of the ions. This is done usually by including Stern compact layer effect. In this case the mathematical formalism presented here is applied to the space between layers, and not to the space between the electrodes. In the presence of the charge transfer electric current the compact layer capacitance is replaced by compact layer impedance.

2. Theory

2.1. PNP model - basic relations

The ionic liquid characterized by dielectric constant $\varepsilon = \varepsilon_0 \varepsilon_r$ is placed between two planar parallel metal electrodes. The concentration of positive ions is $p(x,t)$ and of negative ions is $n(x,t)$. The electric charge of the ions are equal and opposite in sign ($q_p = -q_n = q$, q is the proton charge). The physical quantities used in transport description are the diffusion coefficients D_p , D_n and the mobilities μ_p , μ_n . The surface of the electrodes is S and the distance between them is L . X-axis is perpendicular to the electrodes and the origin is at the middle of the distance L .

The mobile carriers are generated either from dissociation of the liquid molecules or are derived from dissociation of certain impurities introduced intentionally or accidentally during the process of the sample or cell preparation. The generation-recombination rate of ions is $-r = -r_p = -r_n = r_N = Gn_N - Rpn$ [3,12,13,30], where n_N is the concentration of neutral molecules, G is the dissociation (carriers generation) rate and R is the association (recombination) rate. At thermodynamic equilibrium the net recombination rate is null: $Gn_{N,eq} - Rp_{eq}n_{eq} = 0$. Then

$$-r = G(n_N - n_{N,eq}) - R(pn - p_{eq}n_{eq}). \quad (1)$$

In what follows to simplify the presentation and the relationships, we use the following notation: the letters p and n , which designates both the ions concentration and their charge sign, will designate generic with η .

An alternative electric voltage $u_A(t) = U_A \exp(i\omega t)$ is applied to the system, where U_A is the amplitude and ω is the pulsation (angular frequency).

The electric current densities and the mobile ions flows are:

$$j_n = q_n J_n, J_n = \pm \mu_n \eta E - D_n \frac{\partial \eta}{\partial x}, \quad (2)$$

where $+$ is for cation ($\eta = p$) and $-$ for anion ($\eta = n$).

The transport charge density and the total electric current density must also be specified:

$$j(x) = j_p(x) + j_n(x) = q [J_p(x) - J_n(x)]. j_t(x) = j(x) + \varepsilon \frac{\partial E}{\partial t} \quad (3)$$

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