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Modelling of electrification in steady state and transient regimes

D.A. Bograchev [a], S. Martemianov [b,*], T. Paillat [b]

[a] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, Moscow 119991, Russia
[b] Institut Prime UPR CNRS 3346, CNRS - Université de Poitiers – ENSMA, Departement FTC — Branche Fluide, 40, avenue du Recteur Pineau, 86022 Poitiers, France

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ABSTRACT

A microscopic model of electrification phenomena in steady state and transient regimes has been developed. The model has been applied for analysis of experimental data failing to be explained in the frame of classical macroscopic approach. Various boundary conditions have been studied regarding the possibility of experiential data fitting. The hybrid boundary condition has been suggested for explaining steady state and transient experiments. The proposed boundary condition can be related to the coexistence of two reactions on the active surface. The first reaction runs under the diffusion control (fast reaction) and the second one is limited by the kinetics (slow reaction).

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1. Introduction

The appearance of volume charges in dielectric liquid flows causes their electrification and probable ignitions or explosions in the petroleum and electrical industries [1–4]. The electrification of dielectric liquid flows has been studied in numerous works; it has been shown that this phenomenon concerns the diffuse part of electric double layer. Free charges (ions) can be removed from the surface by forced flow and cause the electrical current in liquid (streaming current). The streaming current depends on hydrodynamic conditions, liquid conductivity and surface properties which define the type of the liquid/surface interactions (interface reactions).

Various interface reactions and different mechanisms of the charge origin at the surface have been suggested in the literature [5–9]. However, usually the mechanism of the interface reactions is unknown and just postulated from some reasonable considerations. In addition, the nature of electrical conductivity, in other words the origin of free charges in weakly conducting liquids, is still a question.

A number of approaches for explanation of the electrification phenomena exist in the literature. In the frame of the macroscopic approach the space distribution of electrical charge $\rho(x,y)$ is assumed to be known:

$$\rho(x,y) = \rho_w(x)\frac{\cosh(y/\delta_0)}{\cosh(d/\delta_0)}, \quad (1)$$

where axis x is oriented along the flow, axis y is normal to the surface, ρ_w is the electrical charge on the surface, δ_0 is Debye length, d is the half thickness of the channel.

The main problem is related to the surface charge determining with respect to boundary conditions. In particular, the following relation between the wall current density and the charge density near the wall has been assumed in [10–13]:

$$i_w = K[\rho_{w\infty} - \rho_w], \quad (2)$$

where K — is an empirical coefficient for a given interface reaction, c_H is surface charge density in fully developed conditions. Fully developed conditions correspond either to the stagnant liquid or to the outlet of the very long channel. It is supposed also that the surface charge density in the inlet of the channel is equal to zero.

Eq. (1) is usually accepted in the frame of the macroscopic approach. It should be noted that the hyperbolic cosine profile, Eq. (1), is valid only if the electrical charge in the volume is much less than product of equilibrium concentration and the Faraday constant:

$$\frac{\rho}{Fc_0} << 1. \quad (3)$$

This is so called the small charge density assumption which allows linearization of the problem. Assumptions similar to inequality (3) have been used in some analytical studies in the frame of microscopic approach [14–17] for linearization of the

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* Corresponding author. Tel.: +33 5 49 45 39 04; fax: +33 5 49 45 44 44.
E-mail address: serguei.martemianov@univ-poitiers.fr (S. Martemianov).

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governing system of the equations. Nevertheless, there are some cases when condition (3) is not valid and the electrification problem should be treated without this traditional supposition.

The other type of the electrification theories are based on the microscopic approach. Microscopic models [7,8,14–33] are based on the diffusion equations for ions and Poisson's equation for the electric potential. The main result of these theories is the dependence of steady state streaming current on flow velocity. The streaming current is calculated as the integral of the free charge density and hydrodynamic velocity product. The free charge density is calculated using equations for the concentrations and the electrical potential fields.

For the microscopic model the boundary conditions concerning electrochemical surface process vary greatly. In many works [16,17,20] the constant boundary condition for concentration has been utilized. This boundary condition can be justified for the case of fast interfacial reaction when the electrification phenomena run under the diffusion control. In paper [23] the following relation has been used for describing electrochemical process at the surface:

$$J_i = K_{fP,N} c_i - K'_{fP,N}, \tag{4}$$

where J_i – molar flux on the surface ($J_i = -D_i \nabla c_i - (z_i F D_i / RT) c_i \nabla U$), $K_{fP,N}$ – adsorption rate, $K'_{fP,N}$ desorption rate. Eq. (4) is based on Langmuir adsorption isotherm, but in Ref. [23] the reduced form of this relation has been used (so-called 'radiation' boundary condition):

$$J_i = K_{fP,N} c_i \tag{5}$$

The similar conception of electrochemical processes at the surfaces has been developed in Ref. [7].

A free charge density dynamic approach has been developed in the works [14,29] on the basis of the diffusion equations and the equation for the electric potential. It is possible to reduce the problem to a single equation for the free electrical charge density by combining of these equations: The obtained single equation has been used for studying of various problems [14,30–32]. The validity of this approach is related to the small charge density assumption, Eq. (3).

Different types of forced flows have been studied in the literature on electrification. The most popular cases are the pipe Poiseuille flow [10,11,20,23] and the flat channel Poiseuille flow [13,19,27]. The flat channel flow in consideration of the inlet region has been studied in the works [30–32]. Turbulent pipe flows have been examined in papers [11,14,22]. The turbulent Couette flow between rotating cylinders has been studied in Ref. [7]. There are papers devoted also to electrification in rotating disc flow [17] and the forced flow along the plane plate [16]. The experimental studies of liquid flow electrification in the porous media are presented in Refs. [33,34].

The objective of this work is a microscopic model of electrification which can be used for explanation of electrification phenomena in steady state and transient regimes. The required experimental information for model verification is available in Ref. [13]. The macroscopic approach fails in explanation of the experimental data presented in this work. In the cited paper the conclusion has been done that the kinetic rate depends on the flow velocity and some scenarios have been reviewed when it could take place. This hypothesis is rather discussable.

Two types of experimental dependencies are presented in Ref. [13]. The first type is the dependence of stationary streaming current on hydrodynamic velocity of fluid at the channel. The streaming current varies in the range 30–120 pA for the mean flow rate 0.4–1.5 m/s. The second type of the dependences concerns a transient regime. To be exact, the liquid remains stagnant within a certain delay time t_d with the subsequent flow start up and the streaming current growth to a certain peak value and then it falls to a fixed stationary value, see Fig. 1. Additional information is related to the dependence of the peak streaming current on the delay time t_d. The limited value at the peak streaming current for infinitely large times is the necessary element of the macroscopic theory; this limited value is related to charge density distribution in fully developed conditions (infinitely long channel).

In present work we will try to explain experimental data from Ref. [13] by a microscopic model which takes into account the mass transfer of two types of ions and different boundary conditions for interfacial electrochemical processes. Despite of the model simplicity, this approach is very attractive as it is based on the exact transfer equations and the number of fitting parameters is reduced to a possible minimum. Thus, verification of some traditional assumptions used for interpretation of the electrification phenomena can be provided.

2. Governing equations of model and boundary conditions

Let us consider the liquid with two ions in a small concentration c_0, which flows through a rectangular channel, see Fig. 2. In the channel inlet the flow is electroneutral. A certain interface process generates a flux of the positive ions on the channel walls. Thus, a streaming electrical current arises in the channel outlet due to a charge disbalance.

The equations which describe the electrification phenomenon for the system with two kinds of ions can be presented as:

$$\frac{\partial c_+}{\partial t} + v \nabla c_+ = D_+ \Delta c_+ + \frac{z_+ F D_+}{RT} \operatorname{div}(c_+ \nabla U) \tag{6}$$

$$\frac{\partial c_-}{\partial t} + v \nabla c_- = D_- \Delta c_- - \frac{z_- F D_-}{RT} \operatorname{div}(c_- \nabla U) \tag{7}$$

$$F(z_+ c_+ - z_- c_-) = -\varepsilon_0 \varepsilon_L \Delta U \tag{8}$$

The Eqs. (6) and (7) correspond to the transfer of negative and positive ions by diffusion, convection and migration. Eq. (8) is Poisson equation for the electric potential U. It is assumed that the Einstein relation is valid. Here $c_\pm$ – ion concentrations, $z_\pm$ – ion charges, $D_\pm$ – diffusion coefficients, F – Faraday number, ε_0 – permittivity of free space, ε – relative permittivity of liquid, R – gas constant, T – temperature.

It is accepted that velocity in the channel is related to flat Poiseuille flow:

$$v_m = \frac{3}{2} \overline{V} \left(1 - \frac{y^2}{d^2} \right), \tag{9}$$

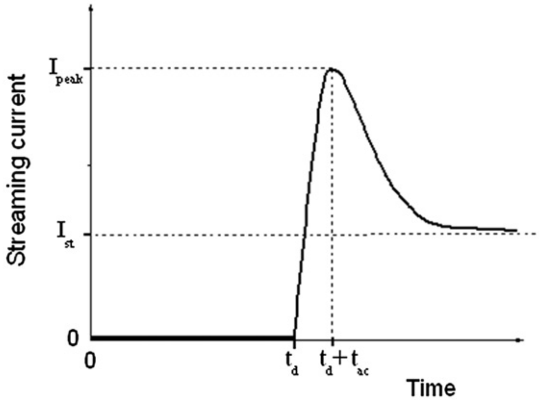

Fig. 1. Scheme of typical experimental curve.

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