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Theoretical method for simulation of potential swing and double layer capacitance in electrolytes containing different cations

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HIGHLIGHTS

- A new numerical method to describe the electrical double layer properties in different electrolytes.
- Both the electric potential swing and the electrode potential depend on the difference between cation and anion radii.
- The capacitance of Stern's layer controls the total capacitance of the electric double layer.

GRAPHICAL ABSTRACT
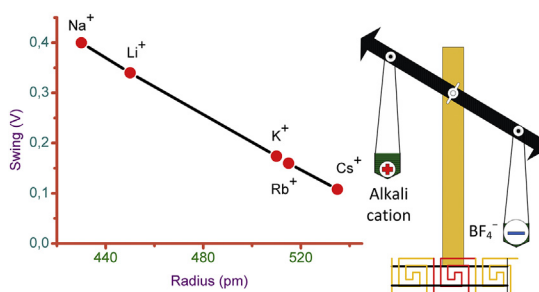
ABSTRACT

This paper aims to describe potential swings on electrodes in different electrolytes by simple but accurate theoretical method. The electric double layer capacitance was considered for spherical nano-electrodes operating in acetonitrile-based electrolytes. The model allows determining the potential swings via accounting for the finite ion size and the influence of the local electric field on the electrolyte dielectric permittivity. It is also possible to determine the thickness of Stern and diffuse layers. A series of acetonitrile solutions of the BF_4^- salts of Li, Na, K, Rb, Cs and $[(CH_3)_4N]^+BF_4^-$ were examined in a systematic study. In this study we investigate the potential swings dependence of the size of the solvation sphere around ions. It is shown that this solvation sphere significantly affects the total specific capacitance of the electrolytes under consideration. As simulating parameters of electric double layers under high concentrations we used the finite size of ions covered by solvation sphere, the chemical composition of electrolytes, and surface potential. Results of this study can be widely used to design electrochemical devices (e.g. electrodes and electrolytes for electrochemical sensors and electric energy storage devices) for novel technologies.

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1. Introduction

Investigation of the electric double layer (EDL) formed by electrolytes at the working electrode is of prime interest in electrochemistry. It is now very common to model the formation of EDL in terms of equivalent circuits for electrodes in a wide range of

inorganic, organic or biologically important systems. However, many of these reports give only qualitative description of electrode processes and even where quantitative data are provided, commonly simple variants of theory based on modified the Gouy−Chapman model (e.g. Refs. [1,2]) are used.

The development of energy harvesting technologies causes increasing interest to supercapacitors. It has been shown in a number of experimental, modelling and theoretical studies that ionic liquids undergo structural changes at a molecular level upon charging of the electrode/ionic liquid interface. This has direct effects on mass and charge transfer phenomena occurring at the interface as well as on both differential and total capacitance (C_{diff} and C_{tot}) dependence on the electrode potential $\varphi(0)$ [3–7] and temperature. The electrochemical properties of the charged electrolyte/electrode interface are critical for the EDL capacitance [1,3] and are under consideration in the present article. The developed theory allows one to investigate a wide series of electrolytes potentially applicable in supercapacitors, membranes and other devices, performance of which depends on the EDL properties.

2. Theoretical method

In the framework of the Gouy−Chapman−Stern model [1–3] the electric double layer includes the Stern layer (SL) and the diffuse layer (DL) (Fig. 1). The SL consists of immobile ions strongly adsorbed to the electrode surface; the DL is formed by mobile ions. It is assumed that the SL thickness is equal to the radius of solvated ions. To determine $\varphi(\mathbf{r})$ in both SL and DL, we use the Poisson equation

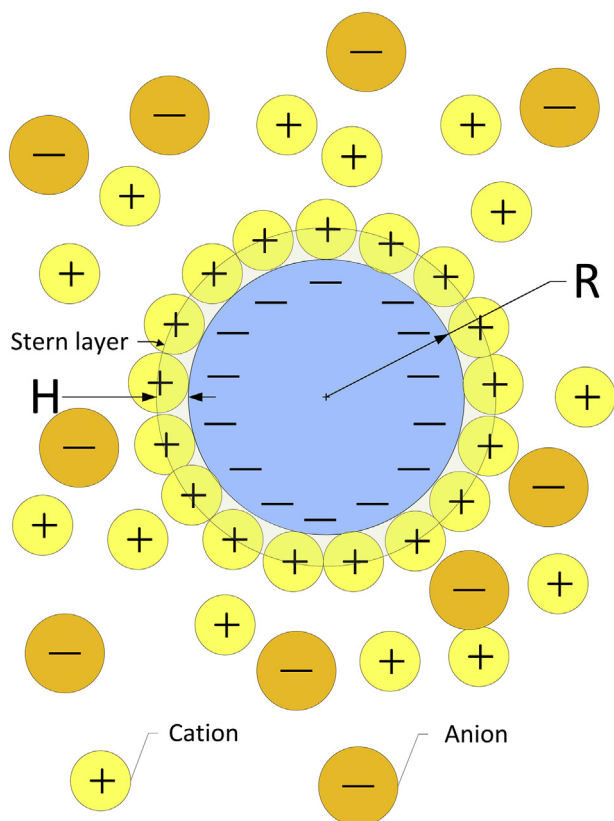$$\nabla \cdot (\varepsilon_0 \varepsilon(\mathbf{r}) \nabla \varphi(\mathbf{r})) = -\rho(\mathbf{r}). \tag{1}$$

Fig. 1. Schematic of the EDL structure showing the arrangement of solvated anions and cations in the SL and the DL.

Here ε_0, $\varepsilon(\mathbf{r})$ and $\varphi(\mathbf{r})$ are the free space permittivity, the relative permittivity of the electrolyte solution and the local electric potential respectively at location $\mathbf{r}$ in the electrolyte; $\rho(\mathbf{r})$ is the macroscopic (net) volume charge density of co-ions and counterions. In the SL, $\rho = 0$ by definition. It is assumed hereafter that φ equals zero far from charged electrodes.

The mean-field a discrete lattice-gas model of concentrated electrolytes is the most attractive method to simulate the potential distribution in EDL [1–4]. In this approach, the charge carriers are distributed over a three dimensional cubic lattice where the volume of a single cell is d^3, where d is the ion diameter. Thus, by dividing space into discrete cells (lattice sites) and limiting the occupation of each cell to a single ion, one introduces a short-range repulsion between the ions [8]. In the models discussed above, it is assumed that the cell volume is approximately equal to the ion volume to a numerical factor of order unity and the cell size of co-ions is the same as for counter-ions. However, from a physical point of view, it seems plausible that the presence of ions with large difference in size should lead to new physical properties of electrolytes. In order to take the difference between radii of counterions and co-ions into account, we introduce the different radii of ions in the following way. It is assumed that volumes of cells occupied by solvent molecules, anions and cations, are equal to their partial molar volumes v_s, v_- and v_+ respectively. The size effect can be described through the activity of ionic species [9] where the activity is defined in terms of the model developed by Cervera and co-researchers [9,10]. According to this model, the ionic-size effect can be explicitly incorporated into the master equation via the activity defined as

$$a_i = \frac{c_i}{1 - \sum_i v_i c_i}, \tag{2}$$

where a_i and c_i is the activity and concentration of the i-th ionic species, respectively; v_i is the relevant molar volume; for cations and anions the index i will be changed by "$+$" and "$-$" respectively. Note that, for simplicity, $v_- = v_+$ in Cervera's model. In our model, we assume that $v_- \neq v_+$, because this relation holds for most electrolytes (see, for instance, [11,12]). It gives the following form of Euler's equation:

$$v_s c_s + v_+ c_+ + v_- c_- = 1. \tag{3}$$

Here v_s and c_s are the molar volume and molar concentration of solvent molecules. Under the equilibrium conditions, we have

$$\ln a_i + z_i \tilde{\varphi} = \ln a_b, \tag{4}$$

where $\tilde{\varphi}(\mathbf{r}) = F\varphi(\mathbf{r})/RT$; z_i, a_b, T, F and R are the charge, bulk molar activity of ion species, the absolute temperature, the Faraday constant and the universal gas constant respectively. In the bulk $\tilde{\varphi} = 0$ and $a_i = a_b$. For the sake of simplicity, we shall consider the binary symmetric electrolytes. In binary symmetric electrolytes, $z_+ = |z_-| = z$ and $c_{b+} = c_{b-} = c_b$, where c_{bi} is the bulk molar concentration of ions. Substituting the activities a_i and a_b in Eq. (4) gives the system

$$\ln \frac{c_+}{1 - v_+ c_+ - v_- c_-} + z\tilde{\varphi} = \ln \frac{c_b}{1 - (v_+ + v_-)c_b}, \tag{5}$$

$$\ln \frac{c_-}{1 - v_+ c_+ - v_- c_-} - z\tilde{\varphi} = \ln \frac{c_b}{1 - (v_+ + v_-)c_b}. \tag{6}$$

Subtracting Eq. (5) from (6) yields, after exponentiation, the simple equation