

Short Communication

Unequal size of ions in modified Wicke-Eigen model of electric double layer

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Abstract. Numerous electric double layer models have been developed through the years to capture the complex electrode/electrolyte interface. In the present study, the Wicke-Eigen model of electric double layer is generalized to incorporate the asymmetric size of cations and anions. Analytical expressions for the spatial distribution of ions and water dipoles are derived. Asymmetric and symmetric Wicke-Eigen models are analysed. Arguments are given in favour of changing the recently adopted name of so-called Bikerman model/equation to Wicke-Eigen model/equation.

Key words: Electric double layer — Wicke-Eigen model — Bikerman model — Different ions size — Finite volumes

Electric double layer (EDL) created at the charged electrode/electrolyte interface has been initially modelled by Helmholtz (1853, 1879). The Helmholtz model assumes that the electrode surface attracts the neighbouring counterions in electrolyte solution, which form a single counterion layer to balance the electric charge of the electrode. Later, the spatial distribution of ions (considered as point-like particles/charges) near electrode surface have been captured using the Boltzmann spatial distribution function (Gouy 1910; Chapman 1913; Bergethon 1998). Finite size of ions has been firstly incorporated in EDL theory by Stern (1924) who took into account as a distance of closest approach and later further developed within mean-field theory (Bikerman 1942; Freise 1952; Wicke and Eigen 1952; Eigen and Wicke 1954). Their work was further upgraded in numerous theoretical studies (Kenkel 1984; Nielaba and Forstmann 1985; Caccamo et al. 1986; Kjellander and Marcelja 1986; Plischke and Henderson 1988; Mier-y-Teran et al. 1990; Bhuiyan et al. 1992; Strating and Wiegel 1993; Kralj-Iglič and Iglič 1996; Lamperski and Outhwaite 2002). Further modification of EDL theory included also orientational ordering of the water dipoles near the charged electrode surface (Outhwaite 1976, 1983; Butt et al. 2003; Abrashkin et al. 2007; Bazant et al.

2009; Iglič et al. 2010; Gongadze et al. 2011, 2013; Nagy et al. 2011; Misra et al. 2013) resulting in the predicted local decrease of the relative permittivity (Gongadze et al. 2014; Quiroga et al. 2014).

Recently, a mean-field model of EDL was developed (Gongadze and Iglič 2015) (referred as in this paper as modified GI model), which takes into account both, the orientational ordering of water dipoles, considered within modified Kirkwood approach (Fröhlich 1964) as the point-like dipoles at the centres of the spheres with permittivity equal to the square of optical refractive index of water, and also asymmetric finite size of anions and cations. Modified GI (MGI) model predicts the spatial dependence of relative permittivity due to orientational ordering of water dipoles in saturation regime and partial depletion of water near the charged surface (Gongadze and Iglič 2015). In this paper the limit case of the MGI model (Gongadze and Iglič 2015) i.e. the modified Wicke-Eigen model, is derived, where the finite and asymmetric size of ions are taken into account.

General model

The modified GI model (Gongadze and Iglič 2015), as a generalisation of the models of Bikerman (1942), Wicke and Eigen (Wicke and Eigen 1952; Eigen and Wicke 1954) and Freise (1952), simultaneously takes into account the asymmetry of the anion and cation finite sizes and the spatial

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dependence of the polarisation and relative permittivity. Unlike the Bikerman model, where the local polarisation does not depend on the spatial dependent average orientational ordering of water dipoles (Bikerman 1942), the MGI model allows to describe the reduction of the dielectric constant due to the saturation effect (Gongadze and Igljč 2015) influenced also by the volume excluded effect due to the competition between counterions and water molecules (Gongadze et al. 2014). Following the ideas of Bikerman (1942), Freise (1952) and Schlögl (1953), the modification of the GI model (Gongadze and Igljč 2012), considering the different size of positive and negative ions (Gongadze and Igljč 2015), was initially performed by Sin et al. (2015) within an approximate approach valid for small volume shares of ions everywhere in electrolyte solution only, where the number densities of ions and water molecules were obtained implicitly. Very recently the GI model was generalized also without taking into account the approximation of small volume shares of ions everywhere in electrolyte solution (Gongadze and Igljč 2015). In addition, the expressions for the spatial distribution of cations $n_+(x)$, anions $n_-(x)$ and water dipoles $n_w(x)$ in the electric double layer were derived analytically (Gongadze and Igljč 2015):

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)} \quad (1)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)} \quad (2)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta} \quad (3)$$

which then appear in the corresponding Poisson's equation:

$$\frac{d}{dx} \left[\varepsilon_0 \varepsilon_r(x) \frac{d\phi}{dx} \right] = 2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{D}(\phi, E)} \quad (4)$$

The spatial dependence of the relative permittivity $\varepsilon_r(x)$ is:

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \left(\frac{2 + n^2}{3} \right) \left(\frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E) E} \right) \quad (5)$$

and

$$\mathcal{D}(\phi, E) = 2n_0 \cosh(e_0 \phi \beta) + \frac{n_{0w}}{\gamma p_0 E \beta} \sinh(\gamma p_0 E \beta) \quad (6)$$

where $F(u) = L(u)(\sinh u/u)$ and $L(u)$ is the Langevine function. Here n_{0w} is the bulk number density of water molecules, n_0 is the bulk number density of anions and cations, n_s is the number density of lattice sites, $\beta = 1/kT$, k is the Boltzmann

constant, T is the absolute temperature, e_0 is the unit charge, Φ is the electric potential, p_0 is the magnitude of the external water dipole moment, E is the magnitude of electric field strength, ε_0 is the permittivity of free space, n is the optical refractive index of water and γ is given by (Gongadze and Igljč 2012, 2015):

$$\gamma = \frac{3}{2} \left(\frac{2 + n^2}{3} \right) \quad (7)$$

Further α_+ and α_- are the number of the lattice sites occupied by positive and negative ions, respectively, where $n_s = \alpha_- n_-(x) + \alpha_+ n_+(x) + n_w(x)$. In the bulk $n_s = \alpha_- n_0(x) + \alpha_+ n_0(x) + n_{0w}$

The water (solvent) molecule is assumed to occupy one lattice site.

The boundary condition at the charged plate, i.e. at $x = 0$ is:

$$\left. \frac{d\phi}{dx} \right|_{x=0} = - \left. \frac{\sigma}{\varepsilon_0 \varepsilon_r} \right|_{x=0} \quad (8)$$

where $\varepsilon_r(x)$ is defined by Eq. 5. In the limit of vanishing electric field strength ($E \rightarrow 0$) and zero potential ($\phi \rightarrow 0$), the above derived expression for the relative permittivity (Eq. 5) gives the Onsager expression for the permittivity (Onsager 1936):

$$\varepsilon_{r,b} \cong n^2 + \frac{n_{0w} p_0^2 \beta}{2\varepsilon_0} \left(\frac{2 + n^2}{3} \right)^2 \quad (9)$$

which results to a dipole moment of $p_0 = 3.1 D$ and bulk permittivity of $\varepsilon_{r,b} = 78.5$.

Limiting models without orientational ordering of water

Modified Wicke-Eigen model

We assume that the permittivity on the lhs of Eq. 4 is constant everywhere in the electrolyte solution and equal to its bulk value, i.e. $\varepsilon_r(x) = \varepsilon_{r,b} = 78.5$.

Further we neglect the energy of water dipoles in the electric field ($p_0 E \rightarrow 0$) so Eqs. 1–6 transform into:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{M(\phi)} \quad (10)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} \frac{n_s}{M(\phi)} \quad (11)$$

$$n_w(x) = \frac{n_{0w} n_s}{M(\phi)} \quad (12)$$

$$M(\phi) = \alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \quad (13)$$

$$\varepsilon_{r,b} \varepsilon_0 \frac{d^2 \phi}{dx^2} = 2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{M(\phi)} \quad (14)$$

where the corresponding macroscopic (net) volume charge density of co-ions and counterions $\rho_{free}(x)$ is:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{M(\phi)} \quad (15)$$

The boundary condition at the charged plate, i.e. at $x = 0$ is:

$$\left. \frac{d\phi}{dx} \right|_{x=0} = - \frac{\sigma}{\varepsilon_0 \varepsilon_{r,b}} \Big|_{x=0} \quad (16)$$

where $\varepsilon_{r,b} = 78.5$.

The limit equations of the MGI model for constant permittivity and neglected water dipole energy (i.e. modified Wicke-Eigen model) were recently derived also by Sin et al. (2015). However, within an approximate approach assuming the small volume shares of ions everywhere in the electrolyte solution, which is not justified in the region near the charged surface for high magnitudes of the surface charge density, σ , of the charged planar surface at $x = 0$. In addition, Sin et al. (2015) did not derive explicit formulas for the number densities of ions and water molecules (as are the above Eqs. 10–12, but the ions and water number densities were obtained only implicitly. The same limit Poisson differential equation for constant permittivity, neglected water dipole energy and small volume shares of ions everywhere in the solution as in Sin et al. (2015) were derived also in Popović and Šiber (2013) (again without explicit expression for ion and water number densities) following the approach/method of variation of the system free energy within lattice statistics described originally by Iglič and Kralj-Iglič (1994), Kralj-Iglič and Iglič (1996) and later in the same way also by Borukhov et al. (1997).

Wicke-Eigen Model

The above equations of the MGI model describe the case where negative and positively charged ions occupy more than one lattice site, while single water molecules still occupy just one lattice site. In the following, we assume that coions, counterions and water molecules occupy a single lattice site, i.e. $\alpha_+ = \alpha_-$ so Eqs. 10–15 become:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{W(\phi)} \quad (17)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} \frac{n_s}{W(\phi)} \quad (18)$$

$$n_w(x) = \frac{n_{0w} n_s}{W(\phi)} \quad (19)$$

$$\begin{aligned} W(\phi) &= n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \\ &= n_{0w} + 2n_0 \cosh(e_0 \phi \beta) \end{aligned} \quad (20)$$

$$\varepsilon_{r,b} \varepsilon_0 \frac{d^2 \phi}{dx^2} = 2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{W(\phi)} \quad (21)$$

where the corresponding macroscopic (net) volume charge density of co-ions and counterions $\rho_{free}(x)$ is:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{W(\phi)} \quad (22)$$

The boundary condition at the charged plate, i.e. at $x = 0$ is:

$$\left. \frac{d\phi}{dx} \right|_{x=0} = - \frac{\sigma}{\varepsilon_0 \varepsilon_{r,b}} \Big|_{x=0} \quad (23)$$

where $\varepsilon_{r,b} = 78.5$.

Eq. 21 has been sometimes named after Bikerman (see for example (Bazant et al. 2009; Gongadze et al. 2014) in honour of J. J. Bikerman who was first to study the influence of finite size of ions and water polarization on the properties of electric double layer within the mean-field approach (Bikerman 1942). However, ion distribution functions Eqs. 17–18 and the corresponding volume charge density Eq. 22 were first derived by Wicke and Eigen in 1952 (Wicke and Eigen 1952; cited also by Freise in his subsequently printed article (Freise 1952)), therefore in this article we name Eq. 21 Wicke-Eigen equation, Eqs. 17–19 Eigen-Wicke distribution functions and the corresponding model Wicke-Eigen model.

Results

The presented modified Poisson differential equations for spatial distribution of electric potential $\phi(x)$ (Eqs. 4, 14, 21) were solved numerically using COMSOL Multiphysics 5.0 where the boundary condition at $x = 0$ was taken into account. The parameters used in the simulations are bulk concentration of ions $n_0/N_A = 0.1$ mol/l, $\alpha_- = 11$, $\alpha_+ = 5$ (see also Marcus (1988)), dipole moment of water $p_0 = 3.1 D$, optical refractive index $n = 1.33$, bulk concentration of water $n_{0w}/N_A = 55$ mol/l, where N_A is the Avogadro number.

It was shown, that the calculated differential capacitance of the EDL within GI model monotonously increases as

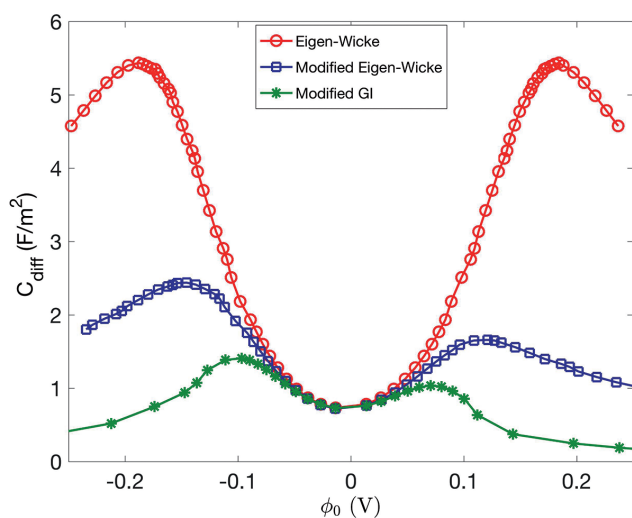


Figure 1. Differential capacitance C_{diff} as a function of the surface potential Φ_0 calculated within MGI, asymmetric Wicke-Eigen and symmetric Wicke-Eigen models.

a function of the increasing surface potential, while in Wicke-Eigen model starts to decrease after reaching a maximal value (Freise 1952; Bazant et al. 2009; Gongadze et al. 2014) as shown in Fig. 1.

For higher values of the surface potential, the calculated MGI differential capacitances (Gongadze and Igljč 2015) drop below the corresponding Wicke-Eigen values to very small values, in accordance with the experimental results (Lockett et al. 2008, 2010). Fig. 1 also shows that consideration of different sizes of positive and negative ions within modified Wicke-Eigen model may describe some characteristics of the experimentally observed asymmetric camel-like dependence of the differential capacitance on the surface potential/voltage (Grahame 1954; Lockett et al. 2008, 2010).

In this paper the modified Wicke-Eigen model, taking into account finite and asymmetric size of ions, was derived as a limit case of more general MGI model of EDL (Gongadze and Igljč 2015). The influence of size asymmetry of cations and anions in electrolyte solution was studied in the past also by Freise (1952). However, Freise have assumed equal volumes for the anions and cations and further that the ratio between the ion volume and medium solvent molecule is 2, 1 or $\frac{1}{2}$. Therefore, whilst we could study the influence of the ion asymmetry on the differential capacitance of EDL, Freise showed only the influence of equal ion size of ions. In contrast to a similar recent study (Sin et al. 2015), we abandoned the assumption of small volume shares of ions everywhere in electrolyte solution. Furthermore, we derived the analytical expressions for spatial dependence of anion and cation number densities.

In conclusion, J. J. Bikerman was the first who studied the influence of finite size of ions on the properties of electric double layer within the mean-field approach (Bikerman 1942). However, as mentioned above, Bikerman did not derive the ion distribution functions (Eqs. 17–18) and the corresponding Poisson differential equation for electric potential (Eq. 21), which were actually first derived by Wicke and Eigen in 1952 (Wicke and Eigen 1952). Consequently, in the present manuscript we correctly assign the Eq. 21 Wicke-Eigen equation and Eqs. 17–19 Eigen-Wicke distribution functions and the corresponding model Wicke-Eigen model and not Bikerman equations/model as it was done in some previous publications (see for example Bazant et al. (2009), Gongadze et al. (2014)). In this paper, the Wicke-Eigen model was modified by taking into account the asymmetric size of ions.

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