Numerical study on the impact of a temperature step on the electrical double layer

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ABSTRACT

All electrohydrodynamics (EHD) applications find their roots from the properties of the electrical double layer existing at the interface formed by the contact of a liquid with a solid material. The more is known about the properties of this electrical double layer, the more useful and practical applications can be found. This paper aims at contributing in the study of the response of the double layer's charge in a dielectric liquid to a step of temperature applied to the interface. The analyses are made considering different conditions were intrinsic properties such as ionic mobility and dielectric permittivity are assumed directly dependent of temperature variations or not. The weight of each of these parameters in the numerical model is assessed through parametric studies when each of them is assumed separately. The results show two major competing effects of the temperature step: a strong chemical reaction activity and a charge redistribution in the liquid volume. The predominance of each seems to depend on the temperature state (transient or stable) as well as the numerical conditions considered.

1. Introduction

In recent years, a special attention has been brought to the electrical double layer (EDL) existing at liquid/solid interfaces, certainly due to the increasing number of EHD applications (industrial, research, technological …) exploiting its physical properties (characterization of electrostatic charge tendency, EHD pumps …). Even though the complexity of the physicochemical processes at the origin of the creation of this EDL are still not clearly understood, confidence in some of the key theoretical models has been strengthened along time due to a large number of experimental results. In addition, researchers have developed numerical tools based on these models for analyzing the static and/or dynamic development of the EDL as well as the influence of certain factors (external E-field, flow profile, temperature …) on its formation. For instance, since about a decade, a special physics module dedicated to the EDL has been developed at "Institut PPRIME" of University of Poitiers and implanted within the notorious numerical tool Code Saturne® for modeling the physicochemical processes based on the adsorption and corrosion theoretical models. With the help of the recent improvements of this special module, this paper provides a numerical analysis on the impact of a temperature step on a fully developed and statically balanced electrical double layer at a liquid/solid interface.

The approach consists, at a first stage, in modeling the full static development of the "electrical double layer" (EDL) at a fixed initial temperature and afterwards, at a second stage, a temperature step is applied to the liquid/solid interface and the impact of this step on the charge in the liquid is analyzed. Thus, a volume of liquid in contact with an ideal flat wall of a solid material is taken as the calculations geometry. The solid itself is not included in the calculations domain but its interactions with the liquid at the interface are taken into account. Therefore, the domain of study covers a liquid volume starting from its interface with the solid to its inner bulk. The goal is to analyze and compare the impact of the temperature step for several physical properties conditions where the thermal dependence of the permittivity and/or the ionic mobility of the liquid is either taken into consideration or not. Further parametric analyses help providing a deeper understanding on the weight of each of these properties on the whole impact of the temperature step over the charge in the EDL.

2. Theoretical model for the electrical double layer

Many theoretical models were developed with time since the 19th century to attempt providing a physical explanation of the mechanisms leading to the natural formation of the Electrical Double Layer (EDL) a liquid/solid interfaces. In particular, the "adsorption model" assumes that a dissociation of neutral impurities in the liquid leads to the generation of positive and negative ionic species, which can be chemically recombined later to re-form the neutral impurities. At the contact with a solid material, part of these ionic species are preferably adsorbed at specific "adsorption sites" allegedly existing on the surface of the solid wall to form chemical bonds with solid ionic species of those sites (see
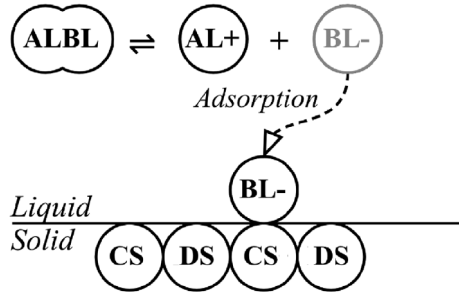

Fig. 1. Physicochemical model for the charge creation in the EDL according to the adsorption model.

Fig. 1). This eventually leads to an excess of charge of one sign in the liquid and of the opposite sign on the solid. For simplification purposes, one may assume that only one type of neutral impurities A_LB_L is present in the liquid. The reversible chemical reaction may then be expressed as:

$$A_LB_L \overset{k_d^L}{\underset{k_r^L}{\longleftrightarrow}} A_L^+ + B_L^- \tag{1}$$

where k_d^L $[s^{-1}]$ and k_r^L $[m^3.s^{-1}]$ are the dissociation and recombination kinetics constants, respectively while A_L^+ and B_L^- represent the positive and negative ionic species in the liquid, respectively. On the solid surface, the adsorption process may be chemically modeled with Equation (2) where k_{fn} $[m^3.s^{-1}]$ and k_{rn} $[s^{-1}]$ are the adsorption and desorption (as sites may also be freed) kinetics constants, respectively, assuming that the solid is composed of the molecules C_SD_L. Fig. 1 illustrates this process for the adsorption of the negative liquid ion B_L^-.

$$C_S + B_L^- \overset{k_{fn}}{\underset{k_{rn}}{\longleftrightarrow}} C_SB_L^- \tag{2}$$

In the liquid at rest, the motion of all the chemical species (neutral, negative and positive) is controlled by diffusion and migration. Therefore the global ionic transport flux Γ_i can be expressed as:

$$\Gamma_i = -D_i\nabla n_i \pm n_i\mu_i\nabla\psi \tag{3}$$

where D_i $[m^2.s^{-1}]$ is the ionic diffusion coefficient, n_i $[m^{-3}]$ the ions volume density (concentration), μ_i $[m^2.V^{-1}.s^{-1}]$ the ionic mobility and ψ $[V]$ the electric potential. In the special EDL module of Code Saturne®, the transport flux equation (3) can be coupled to Poisson's equation (4) and the Heat equation (5).

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_0\varepsilon_r} \tag{4}$$

$$\frac{\partial T}{\partial t} = \frac{k}{\rho_mC_p}\nabla^2T \tag{5}$$

In equation (4), ρ $[C.m^3]$ is the charge density while ε_0 $[F.m^{-1}]$ and ε_r are the vacuum's absolute and the liquid's relative permittivity, respectively. In equation (5), ρ_m $[kg.m^3]$ is the mass density of the liquid, C_p $[J.kg^{-1}.K^{-1}]$ the specific heat capacity, k $[W.m^{-1}.K^{-1}]$ the thermal conductivity and T $[K]$ the temperature. The ionic diffusion coefficient D_i is linked to the temperature according to the Nernst-Einstein relation (6) [1].

$$D_i = \mu_i\frac{kT}{e_0|z_i|} \tag{6}$$

Equations (7) and (8) provide the relations between the chemical kinetics constants k_d^L and k_r^L and the temperature. k_d^L is linked to temperature T through n_0 $[m^{-3}]$ as shown in equation (9).

$$k_r^L = \frac{e_0}{\varepsilon_0\varepsilon_L}(\mu_p + \mu_n) \tag{7}$$

Table 1
Input data for simulations.

Physical quantities	Symbol [Unit]	Value	Source
Electrical conductivity (293.15 °K)	σ [S.m^{-1}]	1.58×10^{-12}	Experimental Measurement
Permittivity (293.15 °K)	ε_r	2.01	Experimental Measurement
Thermal conductivity	λ [W.m^{-1}.K^{-1}]	0.2	Product data sheet
Mass thermal capacity	C$_p$ [J.kg^{-1}.K^{-1}]	1850	Product data sheet
Mass density	ρ_m [kg.m^{-3}]	856	Product data sheet
Ions mobility	μ	10^{-8}	Literature [4–9]
Mean ionic diffusion coefficient	D$_m$ [m^2.s^{-1}]	10^{-9}	Literature [6]
Debye length	δ_0 [m]	1.06×10^{-4}	Equation (11)
Ionic valence	z	1	Assumed
Elementary charge	q = z*e$_0$ [C]	1.6×10^{-19}	Universal constant
Ionized fraction	θ	0.1	Literature [2]
Reaction order	γ	1	Literature [2]
Initial concentrations A_L^+ and B_L^-	n$_0$	5.77×10^{-11}	Equation (9)
Initial concentrations of A_LB_L	n^{Lo}	5.19×10^{-12}	Equation (10)
Dissociation coeff A_LB_L	k$_d^L$	9.87×10^{-3}	Equation (8)
Recombination coeff A_L^+/B_L^-	k$_r^L$	1.8×10^{-16}	Equation (7)
Initial concentrations of Adsorption sites C$_s$	n$_{Cs}^0$ [sites.m^{-3}]	10^{25}	Literature [2]
Reference temperature	T$_0$ [°K]	293.15	Assumed

$$k_d^L = k_r^L\frac{n_0^2}{(n^{L0})^\gamma} \tag{8}$$

where γ [1] is the reaction order while n_0 $[m^{-3}]$ and n^{Lo} $[m^{-3}]$ are the initial concentration for the charged species (A_L^+, B_L^-) and neutral species (A_LB_L) in the liquid, respectively. The different chemical reactions can be calculated considering that the space charge density is assumed to be initially zero at the first contact with the solid wall. For this study, n_0 was estimated from the liquid's initial bulk electrical conductivity σ_0 $[S.m^{-1}]$ according to equation (9) while n^{Lo} is linked to n_0 according to relation (10) [2].

$$n_0 = \frac{\sigma_0kT}{e_0^2(D_p|z_p| + D_n|z_n|)} \tag{9}$$

$$n^{L0} = n_0\frac{(1 - \theta)}{\theta} \tag{10}$$

All these estimated values are summarized in Table 1 as key input data for the simulations.

3. Presentation of the calculation domain

The liquid chosen for the simulations was Cyclohexane, as this liquid was readily available for the experimental determination of certain physical properties (permittivity, for instance) and their dependence on temperature (see Fig. 16). Additional physical properties values for the simulations were calculated or borrowed from literature and data sheets; these are listed in Table 1. Stainless steel was chosen as the solid material in contact with the liquid cyclohexane as orders of magnitudes for key parameters such as the maximum charged density for a fully developed EDL ρ_{wd} $[C.m^{-3}]$ or the global physicochemical reaction kinetics coefficient K $[m.s^{-1}]$ are known from other experiments for this solid/liquid couple [6]. All the data which are not introduced in the Table 1 are calculated according the different equation [1–11] considering the different hypothesis introduced more latter.

The Debye length δ_0, expressed in Table 1, is a characteristic dimension of the charge distribution in the liquid which can be estimated with the expression of Equation (11) proposed by Touchard [3]. Indeed, δ_0 allows estimating the density of the charge near the interface as 87% of the charge is located between the interface and a distance equal to