



Molecular interaction model for frequency-dependence of double layer capacitors



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ABSTRACT

Electric double layer capacitances at electrodes exhibit frequency-dependence, decreasing with the frequency in accordance with the power law even at frequency as low as 1 Hz. Since the capacitance is mainly caused by orientation of dipoles of solvent molecules in the Helmholtz layer, the frequency dependence may be associated with the rate of the orientation. The frequency of the orientation on molecular scale is of the order of GHz, whereas the observed frequency domain is less than 10 kHz. The difference implies that the frequency dependence should not be controlled by simple flips of the dipoles but be caused by a slow process induced by the orientation. This belongs to a cooperative phenomenon. We consider here as the inducing causes the solvent–solvent interaction, the image force of the dipoles to the electrode and the orientation by the external field. The energy balance indicates that most dipoles are confined regularly on the electrode surface as a 2D phase. The 2D–Monte Carlo simulation similar to that for the Ising model is performed in the light of the competition of the interaction and the orientation. The simulation demonstrates aggregation of the oriented dipoles which are hindered by the interaction. The aggregation and hence the capacitance grow gradually with the time of voltage application. The increasing rate obeys the experimentally observed power law.

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1. Introduction

Capacitances of electric double layers are known to vary with applied ac-frequency in the polarized potential domain [1–3]. The frequency dependence can be empirically diminished with a decrease in surface roughness [4–7] as well as with a use of single crystal surfaces [8–10]. It has been considered to be caused by fractal dimensions of electrodes [11,12], adsorption [13–16], lateral charge spreading in the double layer [17], harmonic components [18], and heterogeneities of electrodes on the atomic scale [19]. It is also associated with dielectric loss [1], cracks on electrodes and/or insulators [2] and cell geometry [20]. Quantitative work on the frequency dependence has not yet been reported, to our knowledge, and the subject is still under debate [21,22].

The frequency dependence has often been analyzed by use of equivalent circuits composed of ideal resistances and ideal capacitances. It is difficult not only to represent the frequency dependence as combinations of ideal electric elements but also to interpret the physical meaning of the equivalent circuits. A strategy

of the analysis without complicated equivalent circuits is to introduce an intrinsically non-ideal capacitance, which has a function of the capacitance as the frequency. When the capacitance, C , varies with the frequency or the time, t , the current caused by the capacitive charge, $q = CV$, is given by $I = dq/dt = CdV/dt + VdC/dt$ for a time-varying voltage V . The second term is nothing but the functional form to be determined. When the ac-voltage, $V = V_0 e^{i2\pi ft}$, is inserted into the above equation, the current can be rewritten as [23]

$$I = 2\pi fV[iC - f(dC/df)] \quad (1)$$

The first term in the bracket is an imaginary number, whereas the second one is a real one. The simple sum of an imaginary admittance and a real admittance suggests a parallel combination of an ideal capacitance and an ideal resistance in the equivalent circuit. We evaluated the frequency dependence of the parallel component of C (denoted by C_p) at Pt [23,24–26] and highly oriented pyrolytic graphite (HOPG) electrodes in KCl aqueous solutions in the polarized potential domain by use of Eq. (1) [27]. Fig. 1 shows an example of the plot of the $\log C_p$ against $\log f$ at the HOPG electrode [27]. The linearity indicates $C_p = (C_p)_{1\text{Hz}} f^{-\lambda}$, where λ is a positive constant close to 0.1. By inserting this empirical relation into Eq. (1), the term $f(dC/df)$ is reduced to $-\lambda C$.

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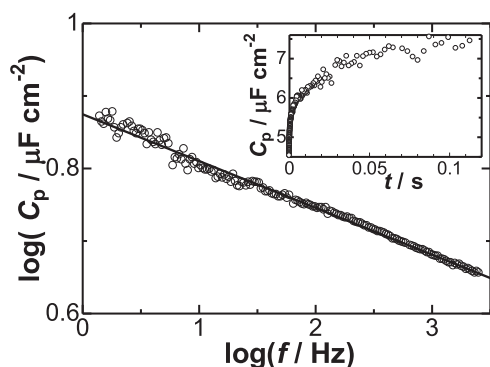


Fig. 1. Plots of $\log(C_p)$ at the HOPG electrode against the logarithm of the ac-frequency obtained in 0.5 M KCl solution [27]. The inset is the variation of C_p with the time which is equal to $1/2\pi f$.

Consequently Eq. (1) is rewritten as

$$l = 2\pi fVC_p(i + \lambda) \quad (2)$$

where C in Eq. (1) has been replaced by C_p . The sum $i + \lambda$ demonstrates clearly the validity of the parallel equivalent circuit for the double layer impedance. We have proved that the double layer resistance, $1/(2\pi fC_p\lambda)$, in Eq. (2) is almost inversely proportional to f [23,24,25,26]. The form of Eq. (2) agrees with the constant phase element (CPE) [11,28–30], which has the parameter α satisfied with $\tan(\alpha\pi/2) = 1/\lambda$ [27]. The power law of the frequency dependence has been seen in commercially available electrolytic capacitors, as found in technical notes supplied from each industry [31].

A question is why the frequency dependence appears as a result of surface roughness or morphology of electrodes. The capacitance is mainly controlled by localization of charge of solvent dipoles due to external field rather than ions, as has been demonstrated with the dependence of the capacitance on ionic concentrations [24,26] and kinds of solvents [25]. If the orientation of the dipoles were to depend only on the electric field, it should take a period of the nano-second order for the orientation. The actual relaxation time as long as 1 s in Fig. 1 cannot be realized by motion of a single molecule, but should be attributed to any macroscopic behavior including a huge number of collisions of dipoles. Development of a microscopic, molecular motion to a macroscopic behavior belongs to cooperative phenomena such as due to ferromagnetism by spin-spin interaction and phase formation of alloys and liquid crystals through molecular interactions [32]. It has been embodied with the Ising models and other extended models [33]. Analysis of these models indicates that next neighboring interaction among particles can generate macroscopic phase in large domains after a huge number of collisions [34–36]. It is predicted that the two-dimensional arrangement of dipoles activated by the electric field would exhibit the power law of the time as in Fig. 1 owing to the dipole-dipole and dipole-electrode interactions. This report deals with modelization of the capacitance in the Helmholtz layer, and then with carrying out computer simulation of the two-dimensional arrangement of dipoles in the context of the power law and the phase formation.

2. Molecular Model in Helmholtz Layer

We discuss semi-quantitatively the delay of the response of the capacitance in aqueous solution. Dipoles of water are not oriented on an electrode until they are free from the confinement by the dipole-dipole interaction and the dipole-electrode interaction. We describe here the energetic relation of the orientation with these interactions.

Water molecules may be adsorbed on the electrode owing to the electrostatic image force between the partial charge of water molecules and the electrode. This force is always attractive for any charge to an electric conductor. When a point charge, q , is located from an planar electrode by the distance, l , in vacuum, the force between the charge and the electrode is given by $-q^2/(16\pi\epsilon_0 l^2)$, according to the image force calculation [37], where ϵ_0 is the permittivity of vacuum. Since we deal with water molecules, q is the partial negative charge $-0.33e$ at the oxygen atom [38,39], where e is the elementary charge. It is assumed that the oxygen atom of the adsorbed water molecule is separated from the electrode surface by a half the averaged distance of closest neighboring water molecules, a , i.e., $l = a/2$. When a is regarded as the cubic-root of the molar volume of the water molecule, $[M/(N_A d)]^{1/3}$, (M : molar mass, N_A : Avogadro constant, d : density) the electrostatic energy of the adsorbed oxygen atom is given by $U_{O-ad} = -(-0.33e)^2/(16\pi\epsilon_0 l) = -4.0 \times 10^{-20}$ J. The hydrogen atom in water has 0.16_5e , and hence the adsorption energy of two H atoms is given by $U_{2H-ad} = -2(0.16_5e)^2/(16\pi\epsilon_0 l) = -2.0 \times 10^{-20}$ J. Then the total adsorption energy by the image force per water molecule is

$$U_{ad} = U_{O-ad} + U_{2H-ad} = -6.0 \times 10^{-20} \text{ J} \quad (3)$$

Since the absolute value of U_{ad} is ca. 15 times larger than the thermally fluctuation energy $k_B T$ ($= 0.41 \times 10^{-20}$ J) at 25°C , most molecules are adsorbed on the electrode, where k_B is the Boltzmann constant. Quantitatively, the ratio of the number of the adsorbed molecules to that of the free molecules in equilibrium is 2.3×10^6 ($= \exp(U_{ad}/k_B T)$): 1.

Ions of supporting electrolytes would be adsorbed more strongly than water because the ionic valence numbers are integers rather than fractional number of H-atom (0.16) and O-atom (0.33). However, we have to take into account the following three effects. (i) Since the hydration energy of ions is ca. 300 times larger than $k_B T$, the ions should necessarily be hydrated strongly enough against the solvent-solvent interaction and the force by the applied electric field. The hydration varies the electric permittivity around the ion by ϵ_r -times, where ϵ_r is the dielectric constant, which suppresses the contribution of the adsorption. (ii) If the ion is surrounded with one layer of water molecules, the adsorbed ion may be separated from the electrode by ca. $1.5a$. The longer separation decreases obviously the adsorption force. (iii) Ionic concentrations increase the entropic contribution of the adsorption free energy by $k_B T \ln(55.5/c)$, where c is the molar concentration of univalent salt. When these effects are combined, the predicted adsorption energy of ions for $c = 0.1 \text{ mol dm}^{-3}$ and $\epsilon_r = 78$ is given by $U_{\text{salt-ad}} = -e^2/(16\pi\epsilon_0\epsilon_r(1.5a)) + k_B T \ln(55.5/0.1) = 2.4 \times 10^{-20}$ J. The positive value means that ions are not adsorbed electrostatically on the electrode. As a result, ions do not participate directly in the capacitance in the Helmholtz layer.

Water molecules are attracted each other with hydrogen bonds to form the tetragonal structure like sp^3 . This structure is geometrically not consistent with the planar arrangement of the triangular plane of the adsorbed H-O-H parallel to the electrode. The hydrogen bonding energy of water, $20 \pm 2 \text{ kJ mol}^{-1}$ [40] or

$$U_{hb} = -(3.3 \pm 0.3) \times 10^{-20} \text{ J per molecule} \quad (4)$$

is of the same order in magnitude as U_{ad} . Therefore, the tetragonal structuration by the hydrogen bond coexists with the parallel arrangement like sp^2 by the adsorption, which generates a dangling hydrogen bond. Since the dangling bonds decrease the force of both the adsorption and the hydrogen bond, the actual energy may be higher than the values in Eqs. (4) and (3). Fig. 2 illustrates a possible structure composed mainly of the adsorbed water molecules with the sp^2 type mixed with the sp^3 type. Most of

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