

Mechanism of surface charge creation due to image forces

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Abstract

The image force is considered to be one of the non-specific sources of surface charge and origin of the double charge layer in the interface between a non-polar liquid dielectric and a polar solid. It is assumed that there is no interaction between phases, neither chemical interaction nor preferential adsorption, due to their specific chemical nature. Two possible physical mechanisms have been investigated. The first takes into account the existence of a potential barrier to the charge movement as it leaves the surface. Therefore, the charges that are in liquid are attracted to the surface. The second is the reduction of dissociation energy of ion pairs close to the interface in comparison with bulk dissociation. Both mechanisms result in a decrease of recombination rate and a sharp increase of dissociation rate. It has been shown that both these mechanisms could lead to the creation and accumulation of an abnormal non-specific surface charge carrier.

1. Introduction

The problem of origin of near surface layers with high concentration of charge carriers (double electric layers) is important for several fields of physics and engineering. Non-polar liquids are jointly applied with polar solid dielectrics in electrical engineering (e.g. transformer oil + pressboard insulation) [1]. The charge creation and accumulation is a great problem for tube and tanker transport of fuel [2]. Double electric layers are also created near the electrodes in electrical devices and in many colloidal systems [3]. Usually the origin of double electric layers [4] is in the difference of electron levels in adjacent phases, chemical and electrochemical interactions and specific absorption of surface active ions. But the factor of near boundary dissociation increase with a polarizable sample has not yet been considered.

If charge e is situated near the boundary of two different phases with permittivities ε_1 and ε_2 , then because the dielectrics are polarized by its field, the charge experiences an image force F given by [5]

$$F = \frac{ee'}{4\pi\varepsilon_1\varepsilon_0(2h)^2} \quad (1)$$

where the image charge is

$$e' = \frac{e(\varepsilon_1 - \varepsilon_2)}{(\varepsilon_1 + \varepsilon_2)}. \quad (2)$$

Here h is the distance between the charge and the boundary. The ion behaviour in liquid with ε_1 near the sample with low ε_2 (e.g. bubble with $\varepsilon_2 = 1$) or near the surface of a dielectrics with $\varepsilon_2 > \varepsilon_1$ could be different. The same sign of the charge and its image in the case of bubble surface leads to the charge repulsion from the boundary. Near the surface of solids with high permittivity this force could attract charges from the bulk of liquid (see also figure 1). A similar effect seems to appear at a metal–liquid boundary. For a metal, ε_2 could be taken as $\varepsilon_2 = \infty$, so the force is negative too.

The attraction of charges from the liquid to the surface of the solid makes a layer with an increasing ion concentration. Ions are in a trap near the surface. This kind of near electrode ion behaviour was first proposed in [6, 7], where ions leaving an electrode are in a potential well, and for injection into bulk they have to overcome this additional barrier with the help of diffusion.

The image forces cause one more mechanism for the formation of electric double layer and surface conductivity.

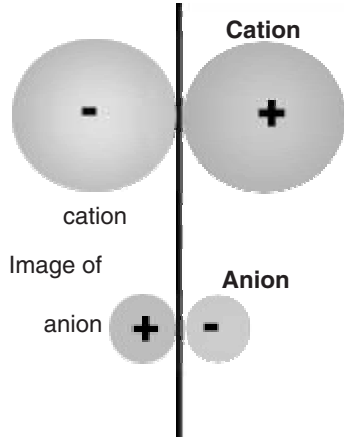


Figure 1. Ions and their images near the interface.

Dissociation in dielectric liquid is promoted with higher dielectric permittivity ε_1 because the dissociation energy is (ε_1 times) reduced. The presence of an adjacent phase with high dielectric permittivity facilitates the dissociation of molecules because the dissociation energy is decreasing near this surface [8].

The aim of this paper is to consider the creation of surface charge carriers at the interface between solid dielectrics with high permittivity and non-polar liquid dielectrics. It is assumed that there is no interaction between phases due to their specific chemical nature: neither chemical interaction nor preferential adsorption.

2. Energy considerations

Some doping is assumed to be dissolved in a non-polar liquid. Its molecules are in the form of ion pairs. One can get the energy of ion pair dissociation, W , by integration of Coulomb interaction force from some distance $R_1 + R_2$ till ∞ , where $R_1 + R_2$ is equal to the distance between ions in ion pair. The energy of dissociation in the bulk of liquid W_b will be

$$W_b = \frac{e^2}{4\pi\varepsilon_0\varepsilon_1(R_1 + R_2)}. \quad (3)$$

Let us suppose that dissociation occurs in a layer close to the surface (figure 1). During the separation of one charge from another in a direction along the surface one should take into account the Coulomb interaction between separable ions and between an ion and the ‘image’ of another ion. After integration of these forces the dissociation energy W_s will consist of two parts: $W_s = W_b + \Delta W$, the first one corresponding to bulk dissociation energy W_b . The sign of the other corresponds to the sign of e'/e . After mathematical treatment W_s could be represented as

$$W_s = W_b \left(1 + \frac{(R_1 + R_2)(e'/e)}{\sqrt{((R_1 + R_2)^2 + 4R_1R_2)}} \right). \quad (4)$$

If the dielectric permittivity of solid dielectrics is assumed to be much greater than this one of the liquid dielectrics, then $e' \approx -e$. Therefore, the energy of dissociation close to the surface will be less in comparison with the bulk dissociation energy. In the case of equal radii, $R_1=R_2$, the surface

dissociation energy W_s is approximately three times less than the bulk one, i.e. $W_s \sim 0.3W_b$. In the case of non-equal radii, e.g. if $R_1 = 2R_2$, $W_s \sim 0.27W_b$ and if $R_1 = 3R_2$, $W_s \sim 0.24W_b$. The decrease of energy is very important for the dissociation rate. Approximately, the number of ‘free’ ions, n_i , depends inversely exponentially on the dissociation energy. Therefore, the degree of ion pair dissociation is different in the bulk and close to the boundary. This effect could increase the surface conductivity due to the origin of charge carrier near the surface. A more precise estimation of the surface charge should include the consideration of dissociation and recombination processes close to the surface. From a mathematical point of view it is a difficult two-dimensional problem, but for physical estimation the problem could be separated into two different tasks:

- 1 Dissociation and recombination rates in the layer close to the surface are to be estimated approximately. The forces acting on charges are considered to depend on the distance between the charges. The eccentricity of forces is negligible.
- 2 The amount of charge close to the boundary is estimated by using the approach that the single ions attach and detach to the surface; that is why the ion–ion interaction is negligible.

3. Dissociation and recombination processes

According to the usual model of dissociation and recombination in liquids [9–11] the charge carrier density in liquid is supposed to be

$$n_i = \sqrt{\frac{n_0 k_D}{k_R}}, \quad (5)$$

where n_0 is the density of dissolved ion pairs, k_D is the constant of dissociation and k_R is the constant of recombination. Estimation of k_D according to Onsager theory gives the expression

$$k_D = \left[\frac{(D_1 + D_2)L_B^2}{R_{12}^4} \right] e^{-L_B/R_{12}}, \quad (6)$$

where D_1 and D_2 are the diffusion coefficients of ion 1 and ion 2, respectively, R_{12} is the sum of their radii, and L_B is the doubled so-called Bjerrum radius,

$$R_B = \frac{e^2}{8\pi\varepsilon_0\varepsilon_1 kT} \quad (7)$$

denoting the distance between ions where the thermal energy of ions, kT , is equal to the electrostatic energy of their interaction. In a non-polar liquid with $\varepsilon_1 = 2.3$ at room temperature, the Bjerrum radius is equal to 125 Å. More difficult is the estimation of ion radius. Usually organic compositions containing Br or Cl are used as dissociating additives to the bulk of the liquid. Inside the liquid they are transformed into small negative ions (radius of Br^- is equal to 1.02 Å), and bigger positive organic residuum ions with an approximate radius of 5 Å. This radius has been chosen for the estimation. For the ion recombination, we could take

$$k_R = 4\pi(D_1 + D_2)L_B, \quad (8)$$

from which the Langevin expression,

$$k_R = \frac{e(\mu_- + \mu_+)}{\varepsilon_0 \varepsilon}, \quad (9)$$

could be obtained, where μ_+ , μ_- are the mobilities of the positive and negative ions, respectively. According to (9), with $\mu_+ \sim \mu_- \sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $k_R \sim 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

The dissociation rate could be estimated using expression (6), that gives $k_D \sim 1.4 \times 10^{-7} \text{ s}^{-1}$. Substituting these values into (5) for usually practiced $n_0 \sim 10^{-4} \text{ mol l}^{-1}$, the charge density in liquid is to be approximately $n_i \sim 2 \times 10^{10} \text{ cm}^{-3}$. This quantity is very low, leading to an additional conductivity of no more than $3 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$.

The calculations proposed in [9, 11] could be applied for estimating the rate of charge disappearance and appearance near the boundary. Using these mathematical procedures the expressions similar to (6) and (8) could be obtained:

$$k_{DS} = (D_1 + D_2) \left\{ \int_{R_{12}}^{R_B} e^{-L_B/r - L_B/(r^2 + R_{12}^2)^{1/2}} r^2 dr \right. \\ \left. \times \left(\int_{R_{12}}^{R_B} \frac{e^{-L_B/r + L_B/(r^2 + R_{12}^2)^{1/2}}}{r^2} dr \right)^{-1} \right\}, \quad (10)$$

$$k_{RS} = 4\pi(D_1 + D_2)L_{BS}, \quad (11)$$

where $L_{BS} = (L_B R_{12}^2/2)^{1/3}$ is the analog of Bjerrum distance along the surface, and k_{DS} and k_{RS} are dissociation and recombination constants for processes close to boundary.

Computations of k_{DS} and k_{RS} according to (10) and (11) for the above mentioned parameters of ion pair and liquid ($\varepsilon_1=2.3$, $R_{12}=6 \text{ \AA}$, $D_1 \approx D_2 \approx 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) show that k_{RS} is approximately one order of magnitude less than the corresponding bulk coefficient and k_{DS} approximately seven orders of magnitude more than the corresponding bulk coefficient. The repetition of the computations for ion pairs situated far from the boundary gives values close to the estimations from (6) and (8).

As for the ion concentration near the boundary, expression (5) is valid despite the comparability of ion concentration with ion pair concentration. In this case the diffusion current of ion pairs from the bulk keeps its concentration close to the surface $n = n_0$, being independent of the amount of the ions.

4. Charge carrier attachment–detachment

The complex (ion + ion image, figure 1) could be treated as a pair of ions. The forces in this complex are very close to the forces between ions in a real ion pair. In this case the ion detachment from the surface is equivalent to the dissociation of an ion pair and the ion attachment to the surface is equivalent to the recombination of the ion pair.

Dissociation and recombination constants are to be different for positive and negative ions owing to their size differences:

$$k_{R_i} = 8\pi D_i L_B, \quad (12)$$

$$k_{D_i} = D_i R_B^2 / (2R_i^4) e^{-L_B/2R_i}. \quad (13)$$

Index i indicates correspondent characteristics of the positive and negative ions. As one can see from expressions (12)

and (13), there is a weak dependence of the recombination rate on the size of ions (through D_i), although there is a strong dependence of the dissociation constant on the ion radius.

The degree of dissociation of the complex ‘ion–ion image’ is to be roughly at the same low level as the degree of doping dissociation in the bulk of the liquid. So the interface attachment of ions permanently existing in liquids is a prevalent process. In their movement they are similar to free ions (with an additional friction due to image force) in surface directions, and trapped ions in the perpendicular direction. Their concentration n_s could be estimated as

$$\frac{dn_s}{dt} = k_{D_i} n_s - k_{R_i} n_i^2 \quad (14)$$

In equilibrium $dn_s/dt=0$, n_i is determined by bulk dissociation–recombination processes (5). After substitution n_i from (5), n_s is

$$n_s = n_0 \frac{k_D k_{R_i}}{k_{D_i} k_R}. \quad (15)$$

So, as $k_{R_i} \approx k_R$, and $k_{D_i} = k_D$ in the case of equal ion radii, the ion density near the surface is equal to the concentration of neutral doping in the bulk of liquid $n_s \approx n_0$.

In the case of non-equal radii of ions, the density of smaller ions is more than the density of the greater one. In the case of very large size difference the concentration difference is greatly increased. If the radius of the negative ion is 1 \AA and radius of the positive ion is 5 \AA , the concentration of negative ions close to the surface would exceed the concentration of the positive ions by more than 80 orders of magnitude. Therefore, at the surface (in absence of specific adsorption) a layer of positive ions could exist. Due to electrical neutrality the negative charge would be distributed in the bulk near the surface. This is similar to the picture of the well-known double electric layer. The smallest ions form the dense part of the layer and the biggest ones form the dilute part of double electric layer.

Both the dense part and the dilute part of the layer engage in the conductivity if the field is applied along the surface. The lower estimation of the surface resistance is $10^{13} \Omega$ in the case of equal ion radii (and ion pair concentration $10^{-4} \text{ mol l}^{-1}$) of doping, but at above-mentioned sizes of ions (1 and 5 \AA) it is much lower. If the field is perpendicular to the surface, injection of charges from the dilute part of the double electric layer into the bulk of liquid is expected only if the direction of the field promotes this movement. Otherwise, an additional conductivity is not expected to occur until the electric field is very high.

5. Influence of electric field

If the direction of the electric field is perpendicular to the surface, the dissociation rate k_{DE} increases due to electric field; k_{DE} is very close to the value obtaining by using the usual Onsager effect in weak electrolytes $k_{DE} = k_D F(p)$,

$$F(p) = \frac{I_1(4p)}{2p}, \quad p = \frac{e^2}{2kT} \left(\frac{E}{4\pi\varepsilon_0\varepsilon_1 e} \right)^{1/2}. \quad (16)$$

Here $I_1(p)$ is a modified Bessel function of first order. The typical field which causes strong increase of dissociation constant is $4p \sim 1$, approximately corresponding to 3 kV cm^{-1} .

If the electric field is parallel to the surface, the characteristic field could be estimated by lowering the potential barrier for the ion movement by the action of electric field. After a simple procedure, the characteristic field in this case could be estimated as

$$E^* \sim \frac{3kT}{2eL_{BS}} \quad (17)$$

approximately corresponding to 200 kV cm^{-1} . As for the field dependence, it is stronger than what is expected by using the usual Onsager law,

$$k_{DE} \sim k_D \exp\left(\frac{E}{E^*}\right)^{3/4}. \quad (18)$$

6. Conclusion

If non-polar liquid dielectrics containing some admixtures in the form of ion pairs are in contact with polar solid dielectrics or conductor, the interface obtains additional conductivity. In the case of unequal sizes of ions in the ion pair a double electric layer is formed. Smaller ions are situated close to the surface and bigger ions form in liquid another plate of double electric layer.

Two physical processes lead to these effects. The dissociation of ion pairs is promoted in the layer close to the surface as a result of the decrease of dissociation energy. Another way of surface conductivity increase is the attraction of ions from the bulk of the liquid to the surface.

As a result of these considerations, a new mechanism of surface charge and surface conductivity creation due to the

action of image forces near the surface of solid samples with high permittivity, including the conductor's surface, has been suggested.

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Page 4

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