Modifying of the dielectric properties of adsorbed water in the force field of a solid surface

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Abstract. The results of thermodynamic and acoustoelectric studies of changes in the dielectric properties of adsorbed water under the influence of a solid surface force field are presented. It is noted that the dielectric properties of adsorbed water depend not only on the characteristic size of the system, but also on the interaction energy with the solid surface. Near the hydrophilic solid surface, the density of adsorbed water is increased and the mobility of molecules is reduced. The opposite effect occurs for hydrophobic surfaces. The frequency dependences of the dielectric properties of adsorbed water, as in the case of water in the solid and liquid phase, can be characterized using Debye relaxation theory. It is shown that a significant increase in the orientational dielectric relaxation time in adsorbed water can be explained by taking into account the energy of interfacial boundaries.

1. Introduction

The boundary layer of water adsorbed on the surface of a solid is under the influence of its force field. The molecules of the adsorption layer interact with all the molecules forming the solid phase. However, the direct and most intense interaction is between the molecules of the boundary layer and the molecules forming the surface of the solid. The adsorption boundary layer of a liquid changes the free energy of a solid surface, while the transition layers of a solid can change the charge distribution in the molecules of the boundary layer, causing their structural changes [1, 2].

The change in any structure-sensitive property of a fluid in the boundary state is due to the presence of an orientation induced by hydrogen bonding. As the distance from the solid surface (with increasing layer thickness) the modification of the boundary liquid properties decreases. The thickness of the boundary phase formed near the interface, with a special structure and properties different from those of the bulk liquid phase, varies widely. Both monolayer and multilayer orientations are possible. The structured boundary phase of polar liquids with a multilayer orientation reaches a thickness of the order of several tenths of a micron [3, 4].

The particular structure of the boundary layers of water on the solid surface can be explained by the epitaxial effect of the adsorbent. The active centers of the solid surface impose on adjacent layers of water a special structure (compared to a bulk liquid), which due to the directionality of hydrogen bonds in water extends to a distance of the order of several nanometers from the surface [4].

The adsorption boundary layer is formed on the hydrophilic surface of a solid as a result of polymolecular adsorption of water vapor. The structure of water in the boundary phase differs from its structure in the bulk liquid phase [3]. And as a consequence, the physical properties of adsorbed water (density, viscosity, compressibility, dielectric constant, etc.) differ from the physical properties of water in the bulk phase. A change in the physical properties of adsorbed water is indicated by the fact that the isotherm of polymolecular vapor adsorption \( h(p/p_s)_T \) crosses the saturation axis \( (p/p_s = 1) \) at a...
finite value of the boundary layer thickness, in contrast to the adsorption isotherms of non-polar liquids [4].

2. Influence of interface energy on the properties of the adsorbed liquid

In order to take into account the change in the interaction energy of the adsorbate molecules as a function of the vapor pressure, hence the distance to the adsorption centers, let us consider polymolecular adsorption under equilibrium conditions. To do this, place a solid with a smooth surface (adsorbent), whose temperature is $T_2$, in a closed volume (figure 1 a) above the surface of a liquid with a temperature of $T_1$. The vapors of this liquid are in thermodynamic equilibrium with the vapor of the liquid in the adsorption layer.

At sufficiently low temperatures, when the vapor above the liquid surface can be regarded as an ideal gas, the liquid – vapor coexistence curve equation is of the form [4]:

$$p_s = p_t \exp \left( \frac{Q_L}{RT_1} \right),$$

where $p_s$ is the saturating vapor pressure, $p_t$ is the thermal pressure of the liquid, $Q_L = N_A E_L$ the latent heat of evaporation (condensation) per mole of matter, $N_A$ is Avogadro's constant. The adsorbed liquid at equilibrium conditions at the same saturating vapor pressure $p_s' = p_s'$ has a higher temperature $T_2 > T_1$. This is possible when the latent heat of evaporation of the adsorbed liquid $Q(h)$ is also greater than $Q_L$, i.e., when $Q(h) = Q_L + \Delta Q$, therefore, we can write that

$$p_s' = p_t \exp \left( \frac{Q(h)}{RT_2} \right) \cdot \exp \left( \frac{\Delta Q}{RT_2} \right).$$

By equating the right-hand sides of expressions (1), (2) and making the necessary transformations, we obtain

$$\Delta Q = Q_L \frac{T_2 - T_1}{T_1} + RT_2 \ln \frac{p_s'}{p_t}.$$  

In determining the ratio $p_s'/p_t$, one can use an expression for the thermal pressure, which is obtained using free-volume theory with a rectangular approximation of the cell potential [4]:

$$p_t = \frac{3 k_B T}{V_a - V_d},$$

where $V_a$ and $V_d$ are the cell volume and the volume occupied by an sample particle.

Under the influence of the solid surface field the density of the adsorbed liquid is increased, we can assume that $V_a' < V_a$, therefore $V_a = V_a' + \Delta V$. Making a number of simplifications, the main of which is that the temperature changes of cell volumes of ordinary and adsorbed liquids are almost identical, we obtain the following expression for the particle adsorption energy $E(h)$ [4]:

$$E(h) = \frac{Q_L}{N_A \frac{T_2}{T_1}} + k_B T_2 \ln \left[ \frac{T_2}{T_1} \left( 1 - \alpha_i \Delta T \right) \right],$$

where $\alpha_i$ is the coefficient of thermal expansion of the liquid.

Equilibrium in energy flow in nanoscale adsorption layers, is established in finite time. The dielectric characteristics tend to equilibrium values during the relaxation process. After the establishment of local equilibrium, the relaxation stage follows, which is described using the hydrodynamic approach. It is assumed that the thermodynamic parameters of the system and the average mass transfer rate do not change significantly during the relaxation time. The adsorption layer, as a thermodynamic system, relaxes to an equilibrium state slowly [4].
Liquid molecules are in continuous thermal motion. Therefore, the dielectric properties of liquids must depend on the dynamic structure of the liquid. The dynamics of molecules is characterized by the relaxation time \( \tau \). The relaxation time depends on the intermolecular interaction potential and temperature. Therefore, the relaxation time depends on the dynamic properties of the dipole water molecule and the environmental parameters [4].

Dielectric relaxation in adsorbed water can be interpreted similarly to a phase transition, i.e., a transition from an ordered to an equilibrium state. The thermodynamic Gibbs potential must be complemented by the energy of the interphase boundary. From the condition of equality of the ordered and equilibrium state potentials we obtain

\[
\delta T = 1 - \frac{T}{T_0} = \frac{\Delta \sigma_s + \Delta \sigma_f}{\Delta F \cdot h} \tag{6}
\]

where \( T_0 \) and \( T \) are temperatures of the liquid in the bulk and boundary phases, corresponding to the same dielectric relaxation time (\( \tau_1 = \tau_2 \)); \( \Delta \sigma_s \) and \( \Delta \sigma_f \) are changes in the specific surface energy of the "solid-liquid" and "liquid-vapor" boundaries during relaxation; \( \Delta F \) is the relaxation process activation energy, \( h \) is the adsorption layer thickness.

The dielectric relaxation time is related to the change in the free activation energy of dipole relaxation \( \Delta F \) by the following relation [4]:

\[
\tau = \frac{2\pi h N_A}{RT} \exp \left( \frac{\Delta F}{RT} \right) \tag{7}
\]

where \( R \) – gas constant; \( \hbar \) – reduced Planck constant.

Substituting the activation energy of the relaxation process obtained from expression (7) into equation (6), we can write

\[
\frac{T}{T_0} = 1 - \frac{\Delta \sigma_s + \Delta \sigma_f}{h \cdot RT \cdot \ln \left( \frac{\tau RT}{2\pi h N_A} \right)} \tag{8}
\]

Thus, the energy of the liquid-solid interface \( \sigma_s \) in equation (8) characterizes the effect of the force field of the solid surface. In addition, the force field of the solid surface affects the formation of the adsorption layer. In equation (8), this influence is expressed through the thickness of the adsorption layer \( h \).

3. Results and Discussions

Experimental results of measurements of dielectric parameters of adsorbed water as a function of relative vapor pressure at fixed values of SAW frequencies are shown in Figure 1. Curves 1, 3 correspond to frequency \( f = 62 \text{ MHz} \), and curves 2, 4 – 440 MHz. The character of the dependence indicates the presence of a relaxation process with a relaxation time \( \tau \sim 10^{-8} \text{ s} \). The closest in time relaxation process (with a relaxation time of the order of \( 10^{-10} \text{ s} \)) in bulk water is the Debye dielectric relaxation [4]. Dielectric relaxation at fixed values of SAW frequencies can be explained by structural-kinetic changes in adsorbed water. As the thickness of the adsorption layer increases, the real part of the complex permittivity changes from the value corresponding to the high-frequency relaxation limit \( \varepsilon_\infty \) to the value of the static permittivity \( \varepsilon_s \) of bulk water.

As the frequency of SAW increases, the region of relaxation change in the dielectric permittivity of adsorbed water shifts to the region of higher values of vapor pressure. The character of the curve remains almost unchanged. Since the dependence of the adsorption layer thickness on the vapor pressure \( p/p_s \) is gradual, therefore, the same change in dielectric permittivity at higher frequency corresponds to a larger area of change in the thickness of the adsorption layer.
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Figure 1. Dependence of the real $\varepsilon'$ (solid line) and imaginary $\varepsilon''$ (dashed line) parts of the complex dielectric permittivity of adsorbed water on vapor pressure and thickness of the adsorption layer ($1$, $3 - 62$ MHz; $2$, $4 - 440$ MHz).

An experimental study of the dielectric permittivity dispersion of boundary water at fixed values of the adsorption layer thickness showed that the Debye relaxation frequency is significantly lower than that of bulk water (Figure 2, curve 4).

Figure 2. Dispersion of the real part of the dielectric permittivity of adsorbed water.

Figure 2 shows the dispersion of dielectric permittivity of adsorbed (at values of relative vapor pressure: $1 - (p/p_s = 0.6)$; $2 - (p/p_s = 0.7)$; $3 - (p/p_s = 0.8)$) and bulk water (4). Numerical estimation was performed in the frequency range $20 - 400$ MHz using the real part of the Debye equation. The markers indicate experimental data on the dielectric permittivity of adsorbed water calculated using the equation [4, 5]

$$
\varepsilon' = \frac{2(\varepsilon_i + 1)^2}{K^2 \varepsilon_p} \left( \frac{\Delta V}{h \omega} \frac{\rho_f}{2 \pi \rho_s} \sqrt{1 - \frac{V_f^2}{V_s^2}} \right).
$$

(9)
The frequency dependence of the imaginary part of the complex permittivity of adsorbed water is shown in Figure 3. Curves 1, 2, 3 of dispersion of dielectric permittivity of adsorbed water at values of relative vapor pressure, respectively, 0.6; 0.7 and 0.8 are constructed using the imaginary part of the Debye equation. Experimental values (points on curves 1 – 3, figure 3) were determined from the experimental isotherms of attenuation and relative change in the rate of SAW using the equation [4, 5].

\[
\varepsilon'' = \frac{(\varepsilon_p + 1)^2}{K^2 \varepsilon_p} \left( \frac{2\alpha V_f^2}{\hbar \omega^2} - \frac{\rho_f V_f \beta}{\pi \rho_s \omega \sqrt{1 - V_f^2/V_s^2}} \right). \tag{10}
\]

![Figure 3. Dispersion of the imaginary part of the complex permittivity of adsorbed water.](image)

It follows from the analysis of the figures that the dispersion of the dielectric permittivity of water in the adsorbed layer is well enough described by Debye's theory. Thus, it has been demonstrated that with variations in the relative vapor pressure or the thickness of the adsorption layer at fixed values of the frequency of surface acoustic waves, dielectric relaxation due to structural and kinetic changes in the adsorbed water is observed. It is shown that the real part of the complex permittivity, as the thickness of the adsorption layer increases, changes from the high-frequency to low-frequency values of the Debye relaxation.

4. Conclusions

The frequency dependences of the real and imaginary parts of the complex dielectric permittivity of water in adsorption layers of fixed thickness were investigated experimentally. It is shown that in the frequency range (20 – 400 MHz) the dielectric permittivity dispersion is detected. A significant increase in the dipole relaxation time can be caused by a change in the structure of water in the layer, under the influence of the crystal surface force field. From the analysis of the experimental data it follows that the dispersion of the dielectric permittivity of adsorbed water is described quite well by the Debye equation. The structuring effect of the adsorbing surface increases with decreasing thickness and temperature of the adsorption layer, which leads to an increase in the viscosity and dielectric relaxation time of the adsorbed water.

References

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