Acoustoelectric method for determining dielectric characteristics the liquid in the boundary layer

I G Simakov, Ch Zh Gulgenov and S B Bazarova
Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences, 670047, Ulan-Ude, Russia
E-mail: baz_say@mail.ru

Abstract. The possibility of using surface acoustic waves has been demonstrated to determine the dielectric characteristics of a liquid in a layer adjacent to the surface of a piezocrystal. The developed acoustoelectric method allows to investigate the electrophysical properties of nanoscale coatings and films.

Currently there exist knowledge of the properties of gases and solids; however, there is no knowledge of the actual molecular structure of liquid.

Boundary layer with modified structure is formed in the liquid by the surface forces at contact of solid and liquid phase. Typical boundary layers are thin interlayers, wetting films and adsorption layers. The dielectric characteristics of the liquid in the boundary and bulk phases differ significantly, especially in layers of polar liquids. The study of the dielectric properties of a liquid in the boundary phase gives necessary information about its molecular structure, intermolecular interactions, dynamics and mechanisms of molecular processes. The application of experimental methods for studying the dielectric properties of liquids in the boundary phase is important because of the lack of theoretical methods for calculating. Determining the dielectric characteristics of the liquid in the boundary layer is encountering difficulties: the small size of the object of study, the dependence of the structure on surface forces and the dynamic nature of the equilibrium state. Surface acoustic waves (SAW) propagating in the “boundary layer of liquid - piezoelectric transducer” system is offered to use to study the dielectric properties of the liquid in the boundary layer. Dispersion of surface acoustic waves existing in this layered system is described by equations (1) and (2). Relative velocity variation $\Delta V/V$ and $\alpha$ attenuation of SAW they are proportional to thickness of liquid layer. The proportionality coefficients of these equations additively take into account mechanical and electrical perturbations of SAW propagation conditions [2]:

$$\frac{-\Delta V}{V} = \left(\frac{\rho_l V_l}{\rho_s V_s} \tan \theta + \pi K^2 \frac{e_p e'_l}{(e_p + 1)^2}\right) \frac{h}{\lambda},$$  \hspace{1cm} (1)

$$\alpha = \beta \frac{\rho_l}{\rho_s} \cot \theta + \frac{\pi \omega K^2 e'_p e'_l}{V_s (e_p + 1)^2} \frac{h}{\lambda},$$  \hspace{1cm} (2)

where $\rho_l$ and $\rho_s$ – liquid density and solid density, $e_p$, $e'_l$ – relative permittivity’s of piezoelectric $e_p = (e_{x2} e_{zz} - e_{yz}^2)^{1/2}$ and liquid, $\theta = \arccos (V_l/V_s)$ – the angle at which sound waves propagate in the
liquid layer, \( V_l \) – sound velocity in liquid, \( V_s \) – surface wave velocity, \( \omega = 2\pi f \) – angular frequency, \( K \) – electromechanical coupling coefficient. For Rayleigh-type waves \( K^2 = 2 \left( V_0 - V_m \right) / V_0 \) (\( V_m \) – SAW velocity for “metallized” surface, \( V_0 \) – SAW velocity for “open” surface), \( \beta \) – sound attenuation coefficient in the liquid, which takes into account the loss of viscous friction.

According to the dispersion equations (1) and (2), the attenuation and change in the velocity of SAW depend on the acoustic and dielectric characteristics of the layered system. Proceeding from the linear equations (1), (2), the real and imaginary parts of the complex dielectric constant of a liquid in a layer are related to the change in the acoustic parameters of the SAW by the following expressions.

\[
\varepsilon'_l = \frac{2(\varepsilon_p + 1)^2}{K^2 \varepsilon_p} \left( \frac{\Delta V}{h\omega} - \frac{\rho_f}{2\pi \rho_s} \sqrt{1 - V_s^2 / V_l^2} \right),
\]

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

Thus, the relative permittivity of a liquid in the boundary layer and the tangent of its dielectric loss angle (\( \tan \delta = \varepsilon'' / \varepsilon' \)) can be determined by registering the change in the attenuation and the SAW velocity, due to the influence of the boundary layer.

An experimental acoustoelectric method for studying the dielectric characteristics of boundary liquids was tested on adsorbed water (figure 1(a)). As is well known, in a vapour-gas medium a thin layer of adsorbed water is formed on the surface of a solid. The thickness of the adsorption layer depends on the vapor pressure in the adsorption zone and the adsorbing surface conditions. The necessary vapor pressure in the adsorption zone can be adjusted by varying the temperature difference between the vaporizing liquid (water) and the adsorbing surface.

![Diagram of the measuring cell](a)

![Dependence of the real part of the complex relative permittivity of the adsorbed water on the vapor pressure](b)

**Figure 1.** Diagram of the measuring cell (a): 1 – LiNbO\(_3\), 2 – bidistilled water, 3 – adsorbed water layer, 4 – vapor-gas medium. Dependence of the real part of the complex relative permittivity of the adsorbed water on the vapor pressure: 1 – 43.2 MHz, 2 – 388.8 MHz (b).

The dependence of the dielectric permittivity of adsorbed water on the relative vapor pressure (respectively, the thickness of the adsorption layer) is shown in figure 1(b). Curve 1 corresponds to the frequency \( f = 43.2 \) MHz, and curve 2 corresponds to 388.8 MHz. The type of the functional relationship indicates the presence of a relaxation process with a relaxation time of \( \tau \sim 10^8 \) s. The dielectric relaxation time of bulk water is about in \( 10^{-10} \) s. Dielectric relaxation process of bulk water is described by the theory of Debye [3]. With an increase in the SAW frequency, the region of
relaxation change in the dielectric constant of adsorbed water shifts to the region of higher vapor pressure values.

Distinction between the dielectric properties of adsorbed water and in bulk phase water is observed in the frequency range (20–400 MHz). The dispersion of water relative permittivity in three states (solid phase (ice), boundary state (adsorbed water) and bulk phase (liquid water)) is shown in figure 2.

**Figure 2.** The frequency dependence of the dielectric constant of water in the solid, liquid, and boundary phases (1 — ice (273 K), 2 — adsorbed water (293 K, $p/p_s = 0.7$), 3 — water (293 K)).

Dispersion curves of the relative permittivity (1 — ice, 2 — adsorbed water, 3 — liquid water) are constructed using the Debye equation. Values of relative permittivity of adsorbed water at different frequencies (markers in figure 2) were calculated from experimental data using the equation (3). The dielectric relaxation time has increased, presumably because of changes in the structure of the adsorbed water, under the influence of the force field of the adsorbing surface of the piezoelectric substrate.

Thus, surface acoustic waves, i.e. Rayleigh-type elastic waves propagating in the “boundary liquid layer – piezoelectric transducer” system can be successfully used to study the dielectric characteristics of the liquid in the boundary layer. Measuring the relative change in the velocity of surface acoustic waves, as well as registration the change in their attenuation at different frequencies, allows us to determine the dispersion of the dielectric characteristics ($\varepsilon'$, $\varepsilon''$, tan $\delta$) and the dielectric relaxation time $\tau$. The process of dielectric relaxation in adsorbed water, as in the case of bulk water phases, can be described by Debye theory.

**References**

[1] Churaev N V 2000 *Colloid Journal* **62**–5 581–9
[2] Simakov I G 2014 *Uchenyye zapiski fizicheskogo fakulteta Moskovskogo universiteta* **5** 145325
[3] Potapov A A 2000 *Orientational polarization: Search for optimal models*. Novosibirsk: Nauka 336
[4] Simakov I G, Gulgenov Ch Zh and Gomboev R I 2009 *Vestnik Buryatskogo gosudarstvennogo universiteta. Khimiya. Fizika* **2** 167–71