# Electrostatic control of ion adsorption in liquid crystal cells

**A. Gabovich, P. Korniychuk, S. B. Kwon, Yu. Reznikov\*,**
**O. Tereshchenko and A. Voitenko**
**Dept. of Physics, Institute of Physics of the National Academy of Sciences, 03028**
**Kiev, Ukraine**
Phone: +38(044)5255679, E-mail: yuri@iop.kiev.ua

## Abstract

*The ion adsorption on an aligning layer deposited onto a conductive electrode in a liquid crystal (LC) cell has been shown to depend strongly on the dielectric constants of the layer and its thickness d. Calculations made in the framework of the three-layer electrostatic theory showed that, depending on those and other intrinsic parameter of the problems, it is possible to observe either ion attraction or repulsion at the aligning surface. Tentative measurements of the ion adsorption dynamics on the aligning layers with various d qualitatively agree with the theory. The results obtained allow the memory effect in LCs and the sticking effect in LC displays (LCDs) to be controlled effectively.*

## 1. Objectives and Background

Sometimes, a residual image of the previous frame survives on an LCD, comprising the so-called sticking effect. This effect is especially strong for aligning surfaces with weak anchoring energy, may considerably impair the quality of LCDs, and needs diminishing. In particular, the sticking effect can originate from various physical memory phenomena. Since the LC phase always includes either intrinsic or extrinsic ions, their adsorption leads to the formation of a surface charged layer, which partially compensates the applied electric field in the LC bulk. The ion adsorption can be chemical or electrostatic. In the former case, it can be avoided using proper screen materials, while in the latter one, the problem can be solved by purely electrostatic means. This work deals with the analysis of how the dielectric properties of the LC, the aligning layer (AL), and the electrode affect ion adsorption on the aligning surface. The aim is to provide the effective control over the adsorption/desorption processes and to diminish the sticking effect.

## 2. Theoretical approach

A point charge near the interface between media with different dielectric permittivities polarizes them, changing its self-energy. In classical electrostatics, the emerging charge–interface interaction is called the image-force one [1]. The charge is attracted to (repulsed from) the interface if it is in the material, whose dielectric constant $\varepsilon_1$ is lower (larger) than that of the other medium, $\varepsilon_2$. From this viewpoint, ions in the LC would have not be adsorbed on the polymer ALs, since the typical dielectric constants of the latter are $\varepsilon_{pol} \approx 2$–3, and the LC dielectric constants are much larger. Experimental data do not confirm this hypothesis. The reason is that the metal electrode with effectively infinite dielectric permittivity attracts ions dissolved in the LC. To describe the electrostatic adsorption in the cell, we need to consider a three-medium system: (1) the electrolyte dissolved in the LC solvent (we restricted ourselves to symmetric electrolytes with ion charges equal to $\pm Ze$); (2) the buffer polymer interlayer; and (3) the metal electrode (usually, an ITO film). Earlier, we have obtained expressions for the image force energy $W(x)$ in the LC taking into account the spatial dispersion of the dielectric functions of all the media [2]. Here, $x$ denotes the coordinate normal to the sandwich plane and reckoned from the interface between media 2 and 3. On the basis of the

obtained $W(x)$, we calculated [3] the excess adsorption

$$\Gamma(n_0) = n_0 \int_0^\infty dx \left[ \exp\left( -\frac{W(x)}{k_B T} \right) - 1 \right] \qquad (1)$$

at the interlayer—electorlyte solution interface. Here, $k_B$ is the Boltzmann constant, $T$ the temperature, and $n$ the bulk concentration of each kind of ions. It was shown that the increase of the interlayer thickness $d$ leads to a rapid transition from positive to negative G's.

### 3. Theoretical results

While calculating the searched effects in the specific configuration of the three-layer system, we adopted the classical model of perfect screening for the metal electrode. It means that its dielectric constant was selected as $e_m \rightarrow 8$. Our previous estimations showed that such an approach is valid even at rather thin interlayers ($L = 5$ Å). At the same time, the spatial dispersion of the dielectric function was allowed for both the interlayer and the electrolyte solution. In particular, the dielectric permittivity of the electrolyte solution was considered as a combination

$$e_{sol}(\mathbf{k}) = e_I(\mathbf{k}) + e_{DH}(\mathbf{k}) \qquad (2)$$

of the solvent $e_I(\mathbf{k})$ and the solute $e_{DH}(\mathbf{k})$ dielectric function. The former is described by the Inkson model,

$$\varepsilon_I(\mathbf{k}) = \varepsilon_* + \frac{\varepsilon_0 - \varepsilon_*}{1 + \frac{\varepsilon_0}{\varepsilon_*}\Lambda^2 k^2}, \qquad (3)$$

where $e_0$ and $e_*$ are the long- (macroscopic) and short-wave dielectric constants, respectively, and ? is the intermolecular correlation length.. The dissolved ions give rise to the Debye-Hückel contribution

$$\varepsilon_{DH}(\mathbf{k}) = \varepsilon_0 \frac{\kappa^2}{k^2}, \qquad (4)$$

where ? is the inverse screening radius depending on the electrolyte concentration $n_0$,

$$\kappa^2 = \frac{8\pi n_0 e^2}{\varepsilon_0 k_B T}, \qquad (5)$$

The dielectric permittivity of the interlayer substance is also described by the dependence (3), but now the parameter ? means the correlation length of bound electrons.

It was rather interesting to learn the effect of the solution concentration on the image force energy. With this point in view, we made calculations for an interlayer and a solvent matrix without spatial dispersion. Some results are presented in Figure 1.
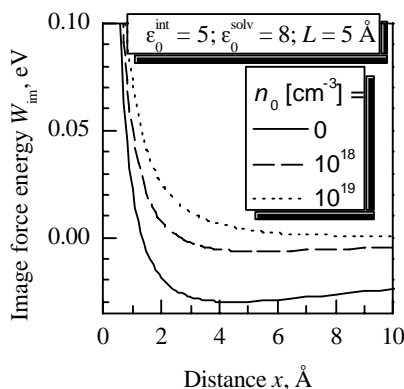


Figure 1. Image force energy profiles $W_{im}(x)$ for a unit charge in a 1:1 Debye-Hückel electrolyte solution. The dielectric functions of the interlayer and the solvent are dispersionless ( $\varepsilon_0^{int} = 5$ , $\varepsilon_0^{solv} = 8$ ), $L = 5$ Å.

In particular, one can easily see that at low concentrations of the solute and thin interlayers, the dissolved ions feel the attractive influence of the metal electrode exerted through the repulsive interlayer, so that the total adsorption is positive. But the screening effects bring about the effective repulsion of ions with one another and can change the whole picture drastically, so that the

total adsorption becomes negative even for thin interlayers. No doubt, that this effect will be only enhanced for thicker interlayers.

In the framework of the model proposed, the interlayer thickness turns out a very important parameter. It is evident that the thicker is the interlayer the lower is the influence of the metal electrode on dissolved ions. We illustrate this conclusion by Figures 2 and 3, which represent the so-called attractive ($\varepsilon_0^{int} > \varepsilon_0^{solv}$) and repulsive ($\varepsilon_0^{int} < \varepsilon_0^{solv}$) cases, respectively.
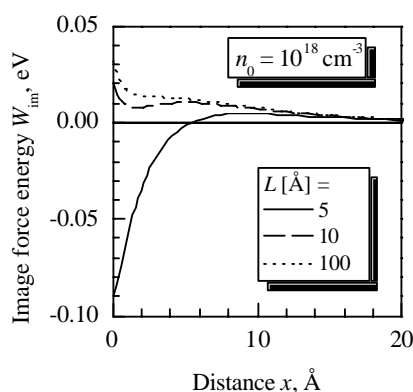


Figure 2. Image force energy profiles Wim(x) at $?^{int} = ?^{solv} = 5 \text{ Å}$, $\varepsilon_0^{int} = 10, \varepsilon_0^{solv} = 3$ ($\varepsilon_0^{int} > \varepsilon_0^{solv}$), and for various interlayer thicknesses $L$.



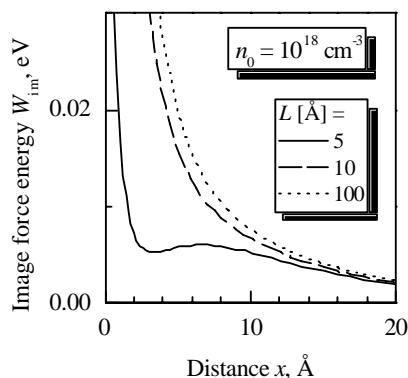Figure 3. The same as in Figure 2, but for $\varepsilon_0^{int} < \varepsilon_0^{solv}$ ($\varepsilon_0^{int} = 3, \varepsilon_0^{solv} = 10$).

We applied here a more realistic model, where the spatial dispersion of the dielectric function is taken into account for both the interlayer and the solution. In this case, by putting the parameter $\varepsilon_*$'s for those media equal to each other ($\varepsilon_* = 1$, in this case), we remove the unphysical divergence of the image force energy $W(x)$ at the layer-solution interface ($x \rightarrow 0$). One can see how effectively the interlayer screens the solution from the influence of the metal electrode: even at low solute concentrations and provided that $L > 10 \text{ Å}$, the profile of the image force energy becomes repulsive for the solution ions at an arbitrary distance from the interface. We may also assert that at $L > 100 \text{ Å}$ the effects induced by the metal electrode can be almost totally disregarded.

A lot of other theoretical results concerning the problem under investigation can be found elsewhere [3].

## 4. Experimental results

One of our main conclusions is that, due to the attraction by the electrode, it is difficult to avoid strong adsorption of ions for typical dielectric constants of LC materials and polymer ALs. The only remaining way is to screen the electrode by increasing the interlayer thickness $L$. As stems from our theory, at typical values of $\varepsilon_{pol}$ and $\varepsilon_{LC}$, the effect of the electrode would be negligible for $L > 100 \text{Å}$, which is a reasonable value for LCD technology. To verify the idea, we investigated the dynamics of ion adsorption in planar LC cells 6 μm in thickness, whose inner surfaces were covered with rubbed polyimide layers ($\varepsilon_{pol} \approx 2.3$). The pre-polyimide AL was deposited onto the quartz substrates from a solution by the standard spin-coating technique. Then, the layer has been imidized at $T = 180^o$ for 2 h. The thickness of the polyimide layers, $d_{pol}$, was controlled by changing the concentration of the pre-polyimide in the DMF solvent. We worked with cells, in which $L_{pol}$ was about 100 and 50 Å. The ion concentration in the LC, $C = 2 \times 10^{16} \text{ cm}^{-3}$, was measured by the capacitance technique. The cell was filled with a 5CB LC by applying the capillary effect at room temperature. After the LC had covered the electrode surface completely, we measured the electric conductivity, σ, of the cell at a frequency of 1kHz and a voltage $U = 0.2$ V

across the cell. The results are depicted in Figure 4. Qualitative distinctions in the temporal dependences of the conductivity $\sigma(t)$ are evident; the conductivity remained almost constant if thick (of about 100 Å) ALs had been deposited onto the electrodes, and strongly decreased in time, *t,* for thinner (of about 50 Å) ALs. These results were reproducible and could not be associated with any changes of the LC parameters, such as variations of ion mobility, changes of the charge density due to electrolytic processes or injection of carriers from the electrodes and aligning layer, etc. Therefore, we attribute the observed changes of $\sigma$ to the variations of the ion concentration due to the non-specific, electrostatic ion adsorption onto the aligning substrate. If specific chemical adsorption had taken place, $\sigma$ would have decreased for both thin and thick ALs. In accordance with the above theory, ion adsorption, which results in slow relaxation of the cell conductivity due to the formation of the layer of adsorbed ions on the aligning surface, is more essential in the thin AL case. The absence of such processes in the case of the thicker AL is due to the electrostatic screening of the polarization (image) interaction by the buffer interlayer.

## 4. Impact

Our theoretical arguments and tentative experiments show that the variation of the dielectric properties and the thickness of the AL allows the effective control of the ion adsorption onto the AL to be made. The metal electrode plays a crucial role in this process, because its effectively infinite dielectric constant stimulates ion adsorption onto the aligning surface. This undesirable effect can be suppressed by increasing the AL thickness. Estimations show that, at typical parameters of LC cells, the electrode effect can be effectively screened at $L_{pol} > 100$ Å, which is a reasonable value for the LC industry. Besides its experimental importance, our work is significant from a tutorial viewpoint, giving new simple analytical expressions for the image force energy, which are highly needed in the physics of heterostructures, solar cells, etc.

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[3]. A.M. Gabovich, Yu.A. Reznikov, and A.I. Voitenko, Phys. Rev. E **73**, 021606 (2006).
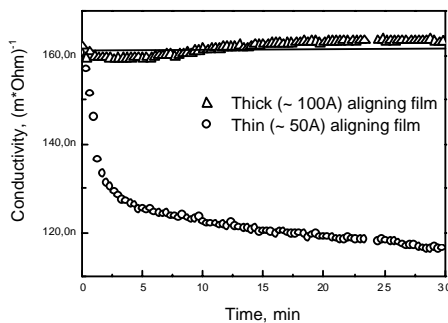
Figure 4. Time dependence $\sigma(t)$ of the conductivity after cell filling for various AL thicknesses $L_{pol} = 100$ (triangles) and 50 Å (circles).