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The effect of salt on ion adsorption on a SiO_x alignment film and reduced conductivity of a liquid crystal host

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It is shown that the addition of salt to liquid crystal cells, using a SiO_x alignment layer, can actually reduce the ion concentration. This seeming contradiction may be explained by the ability of salt to complex with water and to aid the drying of the liquid crystal material. The results show a pathway to purifying liquid crystal devices to the extent needed for low-power low-refresh rate displays for e-book applications. © 2012 American Institute of Physics. [doi:10.1063/1.3676263]

I. INTRODUCTION

It has long been known that ions exist in liquid crystals (LC).^{1,2} Being charged, ions can drift under the influence of an external electric field, but also can create their own field. Therefore, in LC devices, the LC material can be shielded from the applied field in a time dependent and uncontrollable manner. The response of a LC to the apparent field (combination of ion-induced field and applied field) leads to unwanted light transmission modulation, resulting in degradation of image quality, e.g., image sticking and flicker, especially if any DC or low-frequency AC voltage is applied. To overcome the ion problems, a 60 Hz signal is typically used to drive the active matrix LCDs (AMLCDs) so that ions cannot accumulate at the interior surfaces of the substrates, and their problems are minimized.

However, when displaying a static image, this driving scheme also consumes extra power from the display electronics and the charging and discharging of the relatively large capacitance of the display panel. Hence, if the ion concentration in liquid crystals can be lowered to the extent that allows varying refresh rate according to the dynamic nature of displayed images, the power consumption of AMLCD can be decreased dramatically along with the new thin film transistor (TFT) design.^{3,4}

To address the ion problems in LC materials, people have studied the charge injection, generation and electrode interface polarization, which proves that ions in LCDs can easily come from the commonly used polyimide alignment layers.^{5,6} The dielectric spectroscopic technique was found to be a powerful tool to characterize the concentration and mobility in LC materials.^{7,8} Merck also built the model of ion solvation in LC, indicating that the ion solvation is determined by the interaction between ions and a polar group.⁹ The ions are also stabilized in the form of hydrated ions with water.¹⁰ Adding drying agent into LC can recover the water-contaminated LC.¹¹ The role of water in affecting ion concentration in LC was also confirmed by Kamoto.¹²

In our group, the observation was reported that the undesirable effects of ions are substantially reduced by the substi-

tution of a typical polyimide alignment layer used in LCD, with the inorganic alignment layer consisting of an obliquely evaporated layer of SiO_x.¹³ Also, a follow-up work revealed that it is the adsorption effect of 5° SiO_x alignment film that makes the cells equipped with 5° SiO_x film better in terms of ion property.¹⁴ Following our previous work, in this paper, we first consider the role of water in determining the ions concentration in LC. It is found the LC tends to have larger ion concentration with higher water concentration. Therefore, it is assumed that the 5° SiO_x film, which has strong adsorption ability,¹⁴ may actually adsorb water or ions associated with water. This postulation is confirmed by the dielectric measurement, since the calculated Stokes' radius of ions is corresponding to the colloids formed by water molecules.⁷ Based on this, we propose that adding salt into LC can help the adsorption of SiO_x film. It is shown that voltage holding ratios (VHRs) are improved more significantly with the addition of salt. Then, a further aging experiment with salt in LC confirms that the salt promotes the adsorption of water-associated ions on SiO_x alignment film.

II. MATERIALS AND METHODS

Water present in a liquid crystal material is known to increase its ion concentration.^{11,12} Therefore, to study the role of water in LC, we prepared two samples, called wet LC and dry LC respectively. The LC used in our study is ZLI4792 from Merck. Two samples were prepared at the same time. First, the same clean LC was put into two identical vials separately. For the wet LC, the vial was exposed to saturated water vapor at 26.7 °C for 72 h in a close environment. On the other hand, the dry LC sample was stored in a vacuum chamber for the same period of time. After the aging process, the water concentration of the LC samples was estimated by a Karl-Fisher coulometer, which shows that the water concentration of the wet LC is 204 ppm, while the water concentration in dry LC is 8 ppm.

For alignment layers, the SiO_x deposition equipment was from Kurt J. Lesker Company, and SiO_x materials were from CERAC, Inc. The amount of SiO_x evaporated during the deposition was monitored by an Inficon XTM/2 deposition monitor using a sensor-crystal (gold, 6 MHz, 0.550 in.

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diameter, Maxtek, Inc). The incident angle of the beam was set at 5° or 30° (with respect to the substrate). After getting the desired SiO_x film thickness (100 Å in our case), we assembled the substrates, and the ITO size is 1 cm^2 . The alignment film patterns can be obtained by using shadow mask during the deposition. For the sake of convenience, we will call the cells with 5° SiO_x alignment layers 5° cells, and the cells with 30° SiO_x alignment layers 30° cells.

To characterize the ion concentration in the test cells, the most intuitive method is a VHR measurement. In AMLCDs, the pixels are charged with a short voltage pulse, and then should hold that charge over a longer time period when the pixel is disconnected from the voltage source. However, owing to the existence of ions, the voltage experienced by the LC material changes with time, instead of being constant at the value of the applied voltage. Within the same period of time, the cell with larger voltage decay has larger ion concentration. In the VHR measurement system, a $50\text{-}\mu\text{s}$ switching pulse is generated by a complementary metal–oxide–semiconductor (CMOS) analog switch, MAX327CPE. This device is in a high-impedance state for the remainder of the measurement period. The voltage on the cell is detected using a model AD549 preamplifier. We checked the measurement system by measuring the VHR for an empty cell which showed a $\text{VHR} \sim 1$. VHR is defined as $\text{VHR} = V_{\text{end}}/V_{\text{peak}}$ where V_{peak} is the voltage at the beginning of half cycle, and V_{end} represents the voltage before the polarity is switched. In our measurement, we used 2 V applied voltage and 1 Hz driving frequency.

Though the VHR method can qualify the ion concentration, to study the insight of ion structure, the dielectric spectroscopy technique,^{7,8} is a more powerful tool. The dielectric analyzer is Solartron 1296. A sinusoidal wave with the amplitude of 0.03 V was applied on the test cells, and the frequency ranges from 0.0005 to 100 000 Hz. The equivalent circuit of a LC cell is shown in Fig. 1.

In the circuit, R_e is the resistance from the ITO and leads, which only has effect in the high frequency, and will not affect the low frequency region where ionic effect appears. R_D and C_D represent the resistance and capacitance components based on the contribution from the double layer formed at the electrode–bulk interface. In our case, the interface is formed by electrode–alignment layer, and bulk. R_B is a resistance independent of frequency. C_B is the capacitance of LC slab independent of frequency. $R_i(\omega)$ and $C_i(\omega)$ repre-

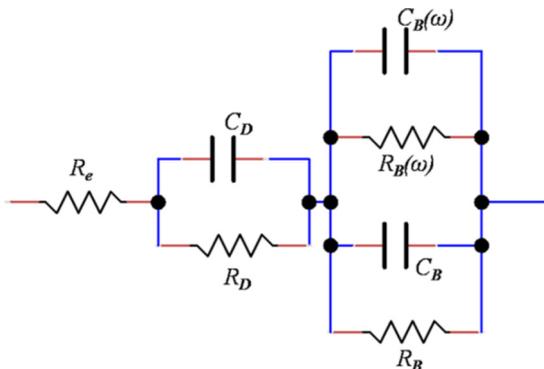


FIG. 1. (Color online) The equivalent circuit of a LC cell.

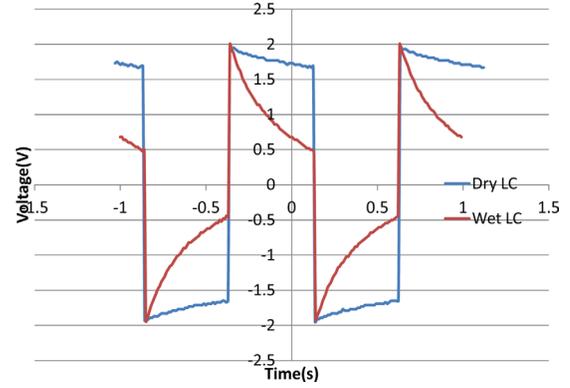


FIG. 2. (Color online) The VHR profiles of dry LC and wet LC.

sent the resistance and capacitance components contributed from the separation of ions. The dielectric contributions from ions are given by Eqs. (1) and (2):⁷

$$\varepsilon'_i(\omega) \left(\frac{nq^2D}{\omega\varepsilon_0kTA} \right) \times \left[\frac{1 + 2e^A \sin(A) - e^{2A}}{1 + 2e^A \cos(A) + e^{2A}} \right], \quad (1)$$

$$\varepsilon''_i(\omega) = \left(\frac{nq^2D}{\omega\varepsilon_0kT} \right) \times \left[1 + \frac{1 - 2e^A \sin(A) - e^{2A}}{A[1 - 2e^A \cos(A) + e^{2A}]} \right], \quad (2)$$

where n is the number density of ions, ε_o is the dielectric permittivity in vacuum, q is the unit charge, ω is the angular frequency, and D is the diffusion constant of the ionic impurities, and k is the Boltzmann constant, T is the temperature, and $A = d(\omega/2D)^{1/2}$, where d is the cell gap. If there are multiple kinds of ions, the total contribution from them can be express as the summation from different ions. $C_i(\omega)$ and $R_i(\omega)$ can be derived from $\varepsilon'_i(\omega)$ and $\varepsilon''_i(\omega)$, given $C_i(\omega) = \varepsilon'_i(\omega)\varepsilon_oS/d$ and $R_i(\omega) = d/\omega\varepsilon''_i(\omega)\varepsilon_oS$, S is the area of ITO. With the contribution from the polarization of ions, we can obtain the total impedance of circuit shown in Fig. 1, and thus the complex dielectric properties of the LC. By finding the complex dielectric properties from the experimental data, we can estimate the ion concentration, the diffusion constant of ions. In this way, we can have the insight of the ionic impurities in the LC.

In Ref. 7, the dielectric measurement was done in the cell without any alignment and barrier layer. Actually the model shown in Fig. 2 is also applicable to the cell with alignment film, which is discussed in detail in Ref. 15. In our case, to avoid any distortion from the potential electrochemical reaction between LC and electrode, we used the cells with 100 Å alignment layer, and applied 0.03 V rms sensing voltage in the measurement. In the fitting process, we found the dielectric constant at low frequency is still determined by R_D , C_D , and R_B similar to Ref. 7, which justifies our application of dielectric measurement⁷ to the test cells with alignment layer.

III. EXPERIMENT AND DISCUSSION

A. Water effect on the ion concentration in LC

Since we have two LC samples, the effect of water can be studied by comparing these two samples. Both samples were filled in 30° cells. The test cells were firstly characterized by

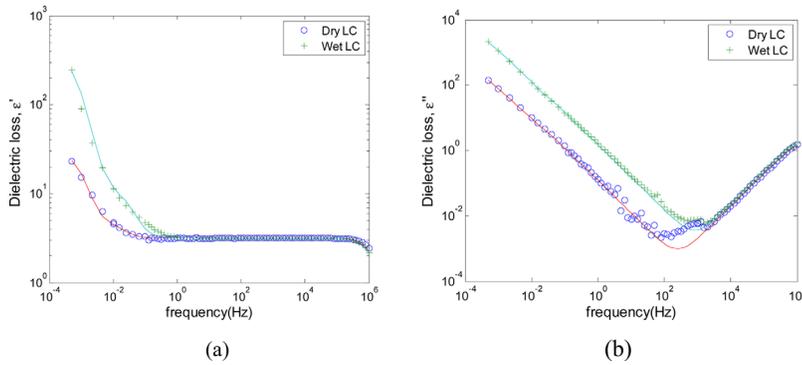


FIG. 3. (Color online) The dielectric spectra for (a) ϵ' , (b) ϵ'' . The solid lines are the fitting curves, and the circles and crosses are the experiment data.

the VHR measurement, in which the applied voltage is 2 V and the driving frequency is 1 Hz. The comparison between dry LC and wet LC is shown in Fig. 2.

From Fig. 2, it is indicated that the dry LC has a larger VHR than the wet LC. In the other words, the ion concentration in dry LC is smaller than the wet LC. To quantify the ion concentration more accurately, we implemented the dielectric spectroscopy technique. The two LC samples were filled into two 30° cells with 100 \AA alignment film. The cell gap of the cell with dry LC is 5.6 \mu m , while the cell thickness of the cell with wet LC is 5.1 \mu m . In the measurement, the ion concentrations of these two cells were calculated by fitting their dielectric spectra, which are shown in Fig. 3.

From Figs. 3(a) and 3(b), at high frequency, the dry LC looks similar to wet LC, and the dielectric constants ϵ' are about 3.1, which is the ϵ_{\perp} shown in the data sheet from Merck. The difference between two samples starts to emerge at the low frequency, where the contribution from ions to the dielectric constant becomes observable. To calculate the ion concentration in these two samples, we fit the data with the model shown in Fig. 1. R_D and C_D are obtained at the low frequency region of ϵ' . $R_D = 1 \times 10^8 \text{ \Omega}$ and $C_D = 2.5 \text{ \mu F}$ for the wet LC, while $R_D = 2.3 \times 10^9 \text{ \Omega}$ and $C_D = 0.1 \text{ \mu F}$ for the dry LC. C_B can be fit at high frequency, where R_e can be fit with ϵ'' which are 210 \Omega for the wet LC and 200 \Omega for the dry LC. R_B determines ϵ'' at low frequency. $R_B = 7.5 \times 10^8 \text{ \Omega}$ and $C_B = 0.545 \text{ nF}$ for wet LC, and the dry LC has $R_B = 1.1 \times 10^{10} \text{ \Omega}$ and $C_B = 0.505 \text{ nF}$, respectively. With the above parameters, the dielectric data can be fitted in the frequency region $<0.005 \text{ Hz}$ and $>1 \text{ Hz}$. To fit the data ranging from 0.005 to 1 Hz, we need introduce the contribution from ions. Here, to keep the model simple, we introduce one kind of ions to fit the data. The ion concentrations and diffusion constants, in which we are interested most, are shown in Table I.

According to Table I, we can see the ion concentrations have a direct relationship with the water content in the sample. The LC sample with larger water content has a larger

TABLE I. The water concentration, VHR, and ion concentration for wet and dry LC.

Parameters	Water (ppm)	VHR	n ($1/\text{m}^3$)	D (m^2/s)
Wet LC	204	0.25	5×10^{18}	6×10^{-13}
Dry LC	8	0.83	6×10^{17}	4.5×10^{-13}

ion concentration, consistent with the VHRs. Given the data obtained in the VHR and dielectric measurements, it can be concluded that the water concentration in LC has a big effect on the ion concentration in LC.

B. Ion adsorption on SiOx film

Now that water plays an important role in determining the ion concentration in LC, it was considered that water can promote the solvation of ions, so the existence of water in LC can increase the ion concentration.¹⁶ Previously, it is found that 5° SiOx alignment film has a strong ability to adsorb ionic impurities in LC.¹⁴ Considering the effect of water, we suspect that the 5° SiOx film may actually adsorb water or ions associated with water, so the ion concentration is lowered in the cells with 5° SiOx film.

To study the ion adsorption of 5° SiOx alignment, a double-patch cell, implemented in our previous study¹⁴ were used. Also a single 30° cell was made for comparison. The designs of test cells are illustrated in Fig. 4.

Figure 4(a) shows the single 30° cell for reference. Actually, for the sake of convenience, here we used the data of the 30° cell shown above, which was filled with wet LC. In the double patch cell, Fig. 4(b), there are two patches on one substrate which is achieved by using shadow mask in the deposition. Half of the substrate is covered by 5° film, while the rest is covered by 30° film, called patch 30 D. 5° film will adsorb the ions and purify the LC when the LC is filled from the 5° side. As a result, the ion concentration in LC will become lower after it reaches patch 30 D. By comparing the properties of the single cell and patch 30 D, we can observe the effect of adsorption on 5° SiOx film, and infer what kind

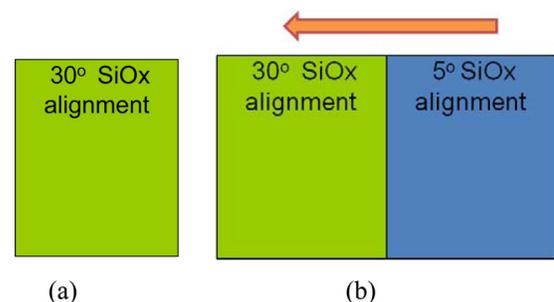


FIG. 4. (Color online) Top view of the test cells, (a) single cell, (b) double patch cell, the arrow means the filling direction of LC.

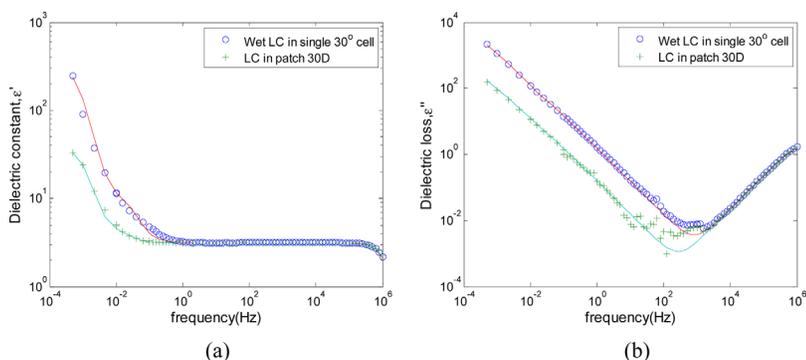


FIG. 5. (Color online) The frequency dependence of the complex dielectric constant, (a) ϵ' , (b) ϵ'' . The solid lines are the fitting curves, and the circles and crosses are the experiment data.

of ions is adsorbed by the 5° film. The cell gap of the double patch is $5.3 \mu\text{m}$.

In this experiment, since the wet LC has larger water concentration, it was used in order to observe more significant adsorption effect. The LC was filled from the side of 5° film in double patch cell. The complex dielectric constants were compared between the patch 30 D and the single cell with wet LC which was shown in last section. For patch 30 D in the double patch cell, $R_D = 2.4 \times 10^9 \Omega$, $C_D = 0.11 \mu\text{F}$, $R_B = 8.5 \times 10^9 \Omega$, and $C_B = 0.525 \text{ nF}$, $R_e = 210 \Omega$. The results are shown in Fig. 5.

From Fig. 5, we can see a big difference was found between patch NA and single ITO cell. The dielectric spectrum of patch 30 D looks similar to the single ITO cell at high frequency. When the frequency gets low, the dielectric constant for the wet LC in the single 30° cell, Fig. 5(a), shows a significant increase, due to the contribution of ionic impurities. On the other hand, such increase at low frequency is suppressed in Fig. 5(a) due to the adsorption of 5° SiOx film. The ion concentration n determines the contribution of ions to ϵ' at low frequency and the diffusion constant determines the frequency at which the separation of ions contributes to ϵ' . We followed the same fitting steps done in the last section to obtain the ion concentration and diffusion constant in patch 30 D, and compared them with those for wet LC in 30° cell in Table II.

We can see the ion concentration in patch 30 D after the adsorption of 5° SiOx film is substantially reduced. We can see the diffusion constant of ion after adsorption is in the same order as those of single 30° cells with wet and dry LC, so the ion species does not change after adsorption. The size of ions adsorbed on the SiOx film can be inferred by studying the diffusion constant, with which we can estimate the Stokes radius of the ions by Einstein relationship⁷

$$r = \frac{kT}{6\pi\eta D}, \quad (3)$$

TABLE II. The diffusion constants and ion concentrations of the ions at patch NA and single ITO cell.

Parameters	n ($1/\text{m}^3$)	D (m^2/s)
Single 30° cell with wet LC	5×10^{18}	6×10^{-13}
Patch 30 D	8×10^{17}	5×10^{-13}

where η is the dynamic viscosity of LC. Since our cells have planar alignment and the ions migrate in the vertical direction, the Miesowicz viscosity coefficient seen by ions is η_c , which is 0.65 P for ZLI4792 at room temperature.¹⁷ Using the diffusion constants in Tables I and II, we found that the size of ion is about 5.6–7.5 nm. The ion of this size range cannot be the free ions, e.g., Na^+ , or the solvated ions associated with LC, since their sizes are around 0.1 and 1 nm. Because of the large Stokes radius, the ion could be colloidal in nature.⁷ Water molecules are considered to play some role in colloid formation.⁷ Therefore, the ionic impurity adsorbed by 5° SiOx film is the ions associated with water. The reduction of water results in the decrease of ions in the LC. This result is consistent with our observation that the existence of water in LC can increase the ion concentration. Therefore, we consider the ions removed by 5° SiOx film are ions associated with water.

C. The effect of NaCl on the adsorption of 5° SiOx film

Based on the results shown in previous sections, we can see the ionic impurities adsorbed on 5° SiOx film are water or ions associated with water. It is known that ions prefer to bond with water molecules, and form larger clusters.¹⁵ Therefore, larger water or water-associated colloids can be formed by adding NaCl into LC. In this way, the diffusion constant of the ionic impurities formed by water becomes smaller, weakening the effect of kT in diffusion, which may help the ion adsorption of 5° SiOx. Following this idea, we added the crystals of dry NaCl into wet LC (called “wet and salted” LC), and stored the sample in a vacuum chamber for 24 h. NaCl was found to hardly dissolve into LC, so the sample was saturated solution. The ion concentrations were compared between wet LC and wet and salted LC by measuring their VHRs in the cells with 30° SiOx films which hardly adsorb ions. Therefore, studied was the effect of adding NaCl on the wet LC itself. The results are shown in Fig. 6.

We can see that for the 30° cell, the VHR of wet LC is 0.28. On the other hand, the addition of salt in wet LC seems to spoil the VHR, which decreases to about 0.1, meaning that more ions were solvated in LC. It is known that a 5° SiOx film has a strong ability to adsorb ionic impurities,¹⁴ owing to its highly porous surface structure. To study how the addition of NaCl affects the adsorption of 5° SiOx film,

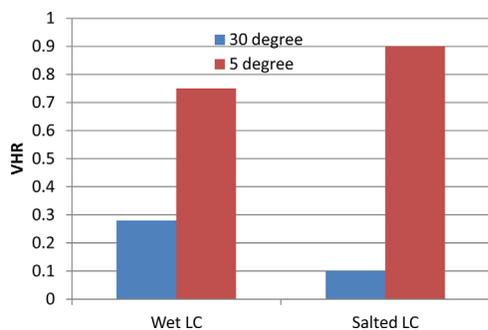


FIG. 6. (Color online) The VHRs for wet LC, "wet and salted" LC in 30° and 5° cells.

we filled wet LC and "wet and salted" LC into 5° cells. The VHRs were compared between the two samples in 5° cells, which are shown in Fig. 6. We can see, contrary to the result for 30° cells, the VHR of "wet and salted" LC becomes larger than that of wet LC. To explain this, we ascribed the better VHR of "wet and salted LC" to the addition of salt which promotes the adsorption of 5° SiOx film. It is considered that the ions from the salt cluster water molecules and form larger ionic colloids. As a result, the diffusion constant of water in LC is decreased, and thus the water can be adsorbed out by the 5° SiOx films more effectively, resulting in the improved VHR.

D. The aging process with NaCl in LC

At this point, water was found to promote the ion solvation in LC, and the impurities adsorbed on the 5° SiOx film are estimated to be water or water-associated ions. To further confirm the role of water in the ion solvation in LC and the ion adsorption on SiOx film, we conducted an experiment based on the double patch cell. The idea is illustrated in Fig. 7.

As shown in Fig. 7, the double cell is half covered by 5° and 30° SiOx films in two different areas. Dried salt was put inside the 30° patch, which was used for the aging process of LC. In the experiment, four different LC samples were compared, which are dry LC, wet LC, dry LC with salt, and wet LC with salt. The samples were filled into the double patch cells shown above, and their VHRs were measured at the 30° patches. Because of the adsorption effect of 5° film,¹⁴ the LCs have low ion concentrations in the bulk when they

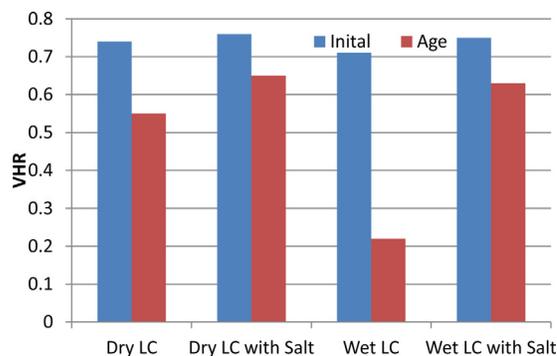


FIG. 8. (Color online) The VHRs for different LC samples, before and after aging.

reached the 30° patches. Therefore, comparably high VHRs are found for both dry and wet LCs in Fig. 8 before aging.

Since the samples have different initial water concentrations, and also the adsorption effect of 5° SiOx film would be different for individual sample, we expected the water concentration of these samples would be different when the samples reached 30° patches after the adsorption of 5° SiOx film. Therefore, based on our observation that water promotes the ion solvation in LC, if we age the LCs with salt for a long enough time, the VHRs in the 30° patch for different samples would vary due to their different initial water concentrations. The LC with larger water concentration would solvate more ions from salt after aging. To verify this, after filling, the double patch cells were broken into two parts to avoid the adsorption from 5° SiOx film. Then, the 30° patches with salt were put into vacuum chamber (avoid water from air), and aged for 5 d. After aging, the VHRs of the 30° patches were measured and compared with those before aging. The results are shown in Fig. 8.

From Fig. 8, we can see the VHRs for all samples decrease after aging, which can be attributed to the residual water content in LC. For the dry LC samples, no matter with or without salt, the VHRs did not change too much, since they initially have small water concentration. However, we can still see the change is less for the dry LC with salt which helps the adsorption. For wet LC with salt, the VHR almost kept unchanged, which means the water concentration is also small before aging. The low water concentration can be attributed to the addition of salt also promoting the adsorption of 5° SiOx film drying the LC. On the other hand, the

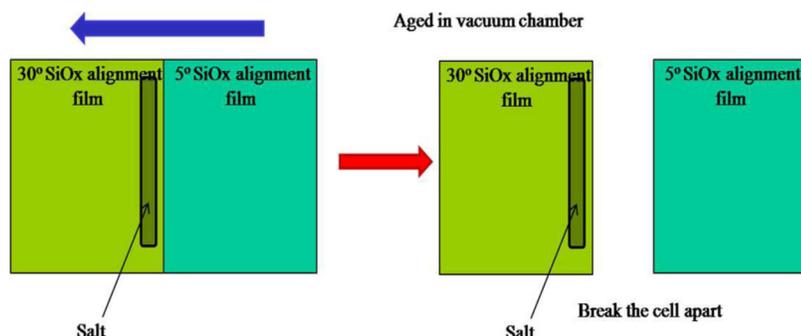


FIG. 7. (Color online) The top views of the double patch cell with salt and the experiment illustration.

VHR for the wet LC without salt degrades most after aging, which means the ion concentrations increase due to ion solvation. Thus, it can be inferred that the water concentration in wet LC without salt is highest among these LC samples before aging, and its adsorption effect is not as strong as that for the wet LC with salt. Hence, according to this experiment, it is confirmed that the addition of salt helps to promote the adsorption of 5° SiO_x film for water associated ions, due to a drying effect of the LC material.

IV. CONCLUSION

In this paper, it has been shown that the effect adding salt can decrease the conductivity of a liquid crystal material in contact with a SiO_x film. The postulation that 5° SiO_x films adsorb water or water-associated ions is confirmed by dielectric spectroscopy measurements since the Stokes' radius of the major ions, derived from the dielectric measurement, is corresponding to the colloid formed by water molecules. Also, an aging experiment with salt added to a LC host confirms that the addition of salt in LC promotes the adsorption of water-associated ions on the 5° SiO_x alignment film.

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