Effect of Free Ions on Time of Flight Mobility Measurements in a Discotic Liquid Crystal

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Abstract

Ionic impurities are a long-standing impediment to the accurate determination of the electronic transport properties of liquid crystalline organic semiconductors. We present measurements of hole transport in samples of the discotic mesogen HAT5 containing ionic impurities. By photogenerating the high mobility holes (high relative to ions) at variable times after the application of a potential across the cell, we are able to probe the effect of the spatial distribution of ions on the hole current. Comparison with simulations allows us to address two types of questions. Firstly, can one extract reliable values of charge carrier mobility from samples that are impure? Conversely, how can we use the holes as accurate probes of the distribution of ionic impurities as a function of time?
Discotic liquid crystalline semiconductors are a fascinating class of electronic materials:

Low Viscosity$^1$ → devices may “self-heal” defects and damage (i.e., spontaneously restore a damaged texture)

Liquid crystallinity → potentially simple fabrication methods for electronic devices

**However**

Low viscosity → mobile ionic impurities
→ Interferes with characterization (e.g. time-of-flight)
→ Mobile ionic space charge may effect device performance

To circumvent experimental obstacles, blocking electrodes may be used to prevent dc ionic flow and reduce electrochemical degradation of the semiconductor

 Ionic space charge may still modify internal field in a time-dependent fashion

The work presented here theoretically and experimentally analyzes the transport of charge carriers (holes) in the presence of an itinerant ionic background for a class of cell designs.

Results are quite general:

- Applicable to, e.g., free-standing films
- Apply to any substance with mobile space charge with mobility substantially less than that of the fundamental charge carriers (electrons/holes)
  - Glasses
  - Liquids
  - Liquid Crystals
HAT5 – a model discotic liquid crystal

Hexapentyloxytriphenylene (HAT5)[2,3] is a discotic mesogen exhibiting a columnar phase from 66 °C → 123 °C and has a high hole mobility $\mu \sim 2 \times 10^{-3}$ cm$^2$/Vs.

Comparison: amorphous Si[4,5] ~ 1 cm$^2$/Vs
ions in HAT5 ~ 10$^{-6}$ cm$^2$/Vs

HAT5 was synthesized and purified using modifications of literature techniques: purification left a low concentration of ionic impurities

**Theory**

For the experimental set up shown in figure 2, $V$ is the applied voltage and $L_1$ & $L_2$ and $\varepsilon_1$ & $\varepsilon_2$ are the thickness and the dielectric constants of the cover slip (glass) and the material respectively. In the absence of ions, the electric fields inside the glass and the material are respectively $E_{01}$ and $E_{02}$, the surface charge density on the top electrode is $\sigma_0$ and $t_0$ is the cationic time of flight.

![Diagram of the experimental cell](image)

**Equation:**

$$\sigma_0 = \frac{\varepsilon_0 \varepsilon_1 \varepsilon_2 V}{L_1 \varepsilon_2 + L_2 \varepsilon_1}$$
The surface charge density on the top ITO[6] electrode, in the presence of ions, is \( \sigma(t) \) and the volume charge density inside the material is \( \rho_i(x) = \rho_+(x) + \rho_-(x) \).

\[
E_1 = \frac{\sigma(t)}{\varepsilon_1\varepsilon_0}
\]

\[
E_2(x) = \frac{\sigma(t)}{\varepsilon_2\varepsilon_0} + \int_0^x \frac{\rho_i(x)dx}{\varepsilon_2\varepsilon_0}
\]

\[
V = E_1L_1 + \int_0^{L_2} E_2dx
\]

\[
V = \frac{\sigma(t)}{\varepsilon_1\varepsilon_0} L_1 + \frac{\sigma(t)}{\varepsilon_2\varepsilon_0} L_2 + \int_0^{L_2'} \int_0^{x'} \frac{\rho_i(x)dx'dx}{\varepsilon_2\varepsilon_0}
\]

\[
\sigma(t) = \sigma_0 - \frac{\varepsilon_1 L_2}{(L_1\varepsilon_2 + L_2\varepsilon_1)} \int_0^{L_2'} \int_0^{x'} \frac{\rho_i(x)dx'dx}{\varepsilon_2\varepsilon_0 L_2}
\]

\[
\tilde{\sigma}(t) = 1 - \beta \int_0^{\tilde{x}'} \int_0^\tilde{t} \tilde{\rho}_i(\tilde{x},\tilde{t})d\tilde{x}'d\tilde{t}
\]

where

\[
\beta = \frac{\varepsilon_1 L_2}{L_1\varepsilon_2 + L_2\varepsilon_1}
\]

\[
\tilde{x} = \frac{x}{L_2}, \tilde{t} = t / t_0
\]

\[
\tilde{\sigma}(t) = \frac{\sigma(t)}{\sigma_0} = \text{The normalized surface charge density}
\]

\[
\tilde{\rho}(\tilde{x}, \tilde{t}) = \frac{L_2 \rho_i(x,t)}{\sigma_0}
\]

Now the normalized electric field inside the sample is

\[
\tilde{E}_2(x) = \frac{E_2(x)}{E_02} = \tilde{\sigma}(\tilde{t}) + \int_0^{\tilde{x}} \tilde{\rho}(\tilde{x}, \tilde{t})d\tilde{x}
\]

Due to this field the change in the position of the cation and anion in time \( \delta\tilde{t} \) will be

\[
\delta\tilde{x}_+ = \tilde{E}_2 \delta\tilde{t}
\]

\[
\delta\tilde{x}_- = -R \tilde{E}_2 \delta\tilde{t}
\]

where, \( R \) is the ratio of the anionic to cationic mobility. The transient current that flows through the capacitor is given as

\[
\frac{\partial \tilde{\sigma}'}{\partial \tilde{t}} = -\frac{\partial \tilde{\sigma}}{\partial \tilde{t}} = \beta \int_0^{\tilde{x}'} \int_0^{\tilde{t}} \frac{\partial \tilde{\rho}(\tilde{x}, \tilde{t})}{\partial \tilde{t}} d\tilde{x}' d\tilde{t}
\]
\( \tilde{\sigma} \) is the areal charge at the bottom plate. Equation (6) assumes that only the charge carriers contribute to the time derivative because the charge carrier mobility is much larger than the ion mobility. For a charge carrier with mobility \( \mu \), the time of flight at a time \( t \) is

\[
\tau(t) = \int_0^{L_2} \frac{dx}{\mu E(x)}
\]

Then the normalized carrier time of flight at a time \( \tilde{\tau} \) is

\[
\tilde{\tau}(t) = \frac{\int_0^1 \frac{1}{E_2(\tilde{x}, \tilde{t})} d\tilde{x}}{\tau_0}
\]

where

\[
\tilde{\tau}(t) = \frac{\tau(t)}{\tau_0} \quad \text{and} \quad \tau_0 = \frac{L_2}{\beta V \mu}
\]

Technique – Synchronized charge generation and application of drift potential

Fig.3: Schematic of the experimental set up
Fig. 4: The timing diagram of the experiment. The timing of the photo generation pulse is indicated by the arrow.

Fig. 5: The experimental results in the discotic mesophase HAT5 at 80 °C. The x-axis is the delay time, t, between the cell potential switching between “–” and “+” polarity on the top plate and the photogeneration of holes, while the y-axis shows the hole time of flight $\tau$. The solid line is the theoretical fit and the dots are the experimental data. Note the overall shape concave downward with increasing $\tau$ with increasing t, possibly saturation as $t \to \infty$. Inset shows a typical time-of-flight trace ($t=17$ ms).
Fig. 6: Theoretical calculation which shows the normalized carrier tof as a function of normalized delay time for various total ionic charge densities and two choices of the ionic mobility asymmetry parameter $R$. The $\tilde{\rho}(\tilde{x},\tilde{t})$ values, in order from bottom to top for large $\tilde{t}$ are 0.05, 0.1, 0.25, 0.5 and 1.0. Note the similarity to the experimental results for small values of $\tilde{t}$ and the complex behavior at large $\tilde{t}$.

$$\sigma_0 = \frac{e_0 e_1 e_2 V}{(L_1 e_2 + L_2 e_1)} = 4.8 \times 10^{-5} \text{ C/m}^2$$

At $t=0$, $\rho_t(x) = \rho_0 \delta(x) - \rho_0 \delta(x-L_2)$ Fitting the data with the simulation by varying the parameters $\tilde{\rho}_+$, $R$, $t_0$ and $\tau_0$, the experimental result is similar to the theoretical result for small values of $\tilde{t}$ that gives the best fit value $\tilde{\rho}_+ = 0.39 \pm 0.014$

For $L_1=160 \, \mu\text{m}$, $L_2=21.2 \, \mu\text{m}$, $V=136 \, \text{V}$, $\varepsilon_1=9.3$ and $\varepsilon_2=2.8$

The anionic or cationic density $\rho = \sigma_0 \tilde{\rho} / L_2 \sim 0.89 \, \text{C/m}^3$

This corresponds to the charge density $\rho/e = 5 \times 10^{12} \, / \text{cm}^3$ (or a concentration of roughly 7 parts per $10^9$).
As seen in fig. 7, the experimental data resembles the theoretical results for large R. The best fit value is $R = 9.5 \pm 1$. The fit provides estimates of the impurity free ion tof, $t_0 = 20 \pm 1.3$ ms and the intrinsic carrier tof, $\tau = 71 \pm 0.1$ $\mu$s. By using the standard time of flight equation,

$$tof = \frac{L^2}{\beta V \mu}$$

We get the intrinsic charge carrier mobility $\mu = 0.0015$ cm$^2$/Vs, close to literature value and the ionic mobilities $\mu_+ = 5.3 \times 10^{-6}$ cm$^2$/Vs and $\mu_- = R \mu_+ = 5.3 \times 10^{-6}$ cm$^2$/Vs. Here $\beta = 0.304$. For $L_1 \sim 0$, $\beta \sim 1$ then one simply has to wait a time much longer than the ion drift time to recover the intrinsic carrier mobility.

Fig. 7: Hole time of flight as a function of the delay time for the fixed ion density $\tilde{\rho}$ and various ionic mobility asymmetries R. Note the qualitative change in overall shape as R increases.
Summary

The itinerant ionic space charges can drastically effect tof measurements when using blocking electrode. We have obtained data displaying such effects in a discotic liquid crystal. These data may be used to study the ionic mobility.

By measuring a sample with two or more ionic concentrations, one may also extract a carrier mobility value close to that of a ion free sample. The reason is that the sheets of oppositely charged ions present at \( t=0 \) eventually cross in the sample at a point determined by \( R \). At this moment, there are no net ionic charges in the sample and the hole conduction will be unaffected by the ions.

References

6. EHC, Incorporated, Japan.