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# Molecular Crystals and Liquid Crystals

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## Resistivity Measurements on Aligned Amphiphilic Liquid Crystalline States

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## Resistivity Measurements on Aligned Amphiphilic Liquid Crystalline States

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We measured the resistivity of a ternary liquid mixture consisting of decylammoniumchloride, ammoniumchloride and water (45:5:50 wt%). The mixture forms a nematic phase between 41°C and 61°C; below 41°C a neat soap, and above 61°C an isotropic micellar solution. The resistivity decreases with increasing temperature. In the nematic and in the neat soap phases the resistivity is anisotropic, and it is higher for currents parallel to the director. The anisotropy increases strongly with decreasing temperature, due to a much stronger temperature dependence of the resistivity parallel to the director. The changes accompanying the phase transitions are small. The surprisingly small change of the resistivity parallel to the director at the nematic to neat soap transition indicates that the lamellae in the neat soap contain a large number of defects.

#### I INTRODUCTION

Measurements of the bulk resistivity have been presented by several authors and for a number of amphiphilic mesophases. Such measurements are reviewed in Ref. 1. The experimental objective of the present work is to determine the resistivity of amphiphilic mesophases to currents parallel to the director, and to currents perpendicular to the director, and to investigate the changes accompanying the nematic to neat soap phase transition. In the system studied here the volume fraction occupied by the surfactant is high (about 50%). Correspondingly the micellar interactions are strong enough to hinder their mobility. We believe, therefore, that the conductivity is mainly due to the counter-ions. If the mobility of the counter-ions is restricted by the lamellar structure of the neat phase, one should expect a substantial increase

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in resistivity along the director when passing from the nematic to the neat soap phase.

#### II EXPERIMENTAL PROCEDURE

For our experimental study we selected a ternary mixture consisting of 0.10 g ammoniumchloride, 1.0 g decylammoniumchloride and 1.1 g of water. The decylammoniumchloride was prepared by Radley, as described in Ref. 2. This system exhibits a nematic range of 20°C, separating the neat soap from the isotropic micellar solution. The neat soap to nematic phase transition occurs at 41°C. This transition appears to be second order. The nematic phase consists of disc-like micelles.<sup>2</sup> There is also a narrow two-phase region between the nematic and isotropic phases.

The ac voltage used in the experiments ranged between 0.4 and 0.6 volts, while the frequencies ranged between 1 kHz and 10 kHz. We used two kinds of cells in our measurements. To study the resistivity along the director we placed the mixture in an NMR glass tube (0.41 cm inside diameter). The stainless steel electrodes were spaced 2 cm apart. The sample was spun in the magnetic field (23 kG) of a Varian XL-100 NMR spectrometer. The spinning axis was normal to the field. Because of the negative diamagnetic anisotropy of the sample, the director assumed the orientation parallel to the axis of spinning. The spectrometer also enabled control of the sample temperature. After allowing sufficient time for thermal equilibrium at a given temperature, we interrupted the spinning, applied an ac voltage across the sample and determined the resistance. Knowing the geometry of the cell we were able to determine the resistivity along the director.

A second type of cell was constructed in order to study the resistivity perpendicular to the director. This cell consisted of two microscope slides separated by two parallel chromium wires (0.25 mm thick). The wires served both as spacers and electrodes. The cell was sealed laterally, and the mixture was introduced through small filling holes which were subsequently sealed. Special care was taken to keep the region between the two electrodes free of air bubbles. The sample alignment in this cell was induced by the boundaries. The cell was placed in a heating stage, which allowed simultaneous microscopic observation. Using a suitable controller† the resistance of the cell was measured every 0.2°C. As the geometry of the cell is not well defined, the resistivity cannot be obtained directly.

It should be mentioned that water evaporation from the mixture during the filling process resulted in changes in the transition temperatures and, possibly, concentration gradients in the sample.

<sup>†</sup> Hewlett-Packard Model 9825S.

#### III EXPERIMENTAL RESULTS AND DISCUSSION

The resistivity to currents along the director versus the temperature is plotted in Figure 1. Apart from the almost piecewise-linear variation, we

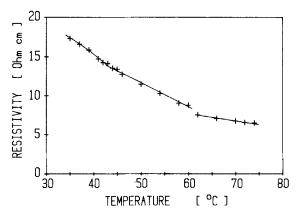


FIGURE 1 Resistivity versus temperature for currents along the director.

note two changes in slope at about 41°C and 61°C. The latter is accompanied by a jump. These two temperatures were identified by optical methods as the neat soap to nematic and nematic to isotropic transition temperatures for this system. The resistance to current normal to the director versus the temperature is plotted in Figure 2. At about 60°C we note a pronounced change. This change was identified as the nematic to isotropic phase transition for the system. The substantial width of the transition region reflects the

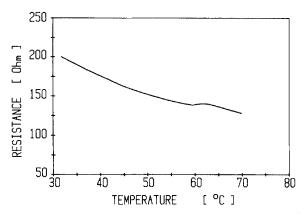


FIGURE 2 Resistance versus temperature for currents normal to the director.

two-phase region mentioned earlier. The nematic to neat soap transition is not clearly recognizable.

The major part of the temperature dependence of the resistivity is due to the temperature dependence of the viscosity of water. We plotted, therefore, in Figure 3 both principal resistivities divided by the viscosity of water at the

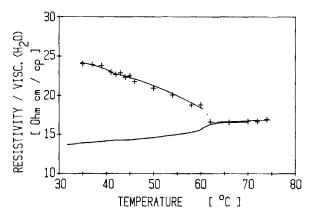


FIGURE 3 Ratio of resistivity over viscosity of water versus the temperature: + indicates component parallel to the director, and lower line indicates component normal to the director.

corresponding temperature. The resistivity normal to the director was evaluated by adapting the isotropic range of Figures 1 and 2. We note that compared to the resistivity normal to the director, the resistivity along the director is higher and more sensitive to temperature changes. We also note that the anisotropy of the resistivity increases strongly in the nematic phase. This can be understood in terms of the shape and orientation of the micelles. In the nematic phase, the director is preferentially normal to the disc-like micelles. Hence their effective cross-section is larger for currents along the director, and smaller for currents normal to the director. The difference between the effective cross-sections corresponding to the two principal directions increases with increasing micelle-size and degree of order. As the micelles are not readily penetrable by the counter-ions, the anisotropy increases with decreasing temperature. The small change in the resistivity along the director accompanying the neat soap to nematic transition, and the fact that the temperature dependence is similar for both phases, indicate that the basic conduction mechanism remains the same in both phases. Thus, the structure of the lamellae in the neat phase is very incomplete. Finally, we should mention that the resistivity did not seem to depend on the magnitude of the applied voltage, at least in the range of 0 to 1 volts. This is true of all three phases. However we detected a frequency dependence. More specifically the resistivity decreased with increasing frequency. It exhibits stronger variation at low frequencies (it decreases by 10% as the frequency increases from 1 kHz to 10 kHz) and levels off at higher frequencies.

### Acknowledgement

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