# Threshold field for switching the de Vries $S_A^*$ phase in a low molar mass organosiloxane material

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# Threshold field for switching the de Vries S$_A$* phase in a low molar mass organosiloxane material

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The existence of a threshold field for the onset of switching in the organosiloxane material, ETSiKN65, has been investigated. This material displays a de Vries smectic A* type phase, and the presence of the threshold confers an anti-ferroelectric-like response. However, it has been found that the value of the threshold depends on the thickness of the specimen, in fact it vanishes altogether if the specimen is more than 20 μm thick. It is concluded that the threshold is due to a complex anchoring mechanism at the interface with the cell walls.

**Keywords:** organosiloxane; de Vries phase

## 1. Introduction

Research on low molar mass organosiloxane liquid-crystalline materials was originally initiated [1–3] with the aim of developing liquid crystals that possessed the rugged mechanical properties of polymers while retaining the rapid response of conventional low molar mass materials. The molecules in low molar mass organosiloxane liquid-crystalline materials consist of one, two or four mesogenic moieties attached through an alkyl linkage to a short (1–5 repeat units) siloxane chain [1–7]. On cooling from the isotropic phase the siloxane moieties micro-separate from the mesogenic moieties and tend to agglomerate in layers, favouring the formation of a smectic phase with alternating siloxane- and mesogen-rich layers. The siloxane-rich layers can be regarded as an effective two-dimensional polymer backbone [4, 8] and the mesogenic moieties as side-chain pendants.

Low molar mass organosiloxane materials have proven to be interesting in many areas of liquid crystal research [9–13]. To give only one example, the micro-separation of the siloxane into an effective polymer back-bone makes it possible to introduce in the material, a high concentration of non-mesogenic components such as a dichroic dye, provided that the dye molecule is also attached to a siloxane moiety [14–16]. More recently it has been argued that in tilted smectic phases the siloxane-rich layer can cause a decoupling between the direction of tilt in adjacent mesogen-rich layers, resulting in a de Vries-type phase [17–19]. Such materials have great potential for grey-scale display applications. The material presented in the present paper is a mono-mesogen in which the siloxane moiety contains one silicon atom, and has been named

ETSiKN65. This is a homologue of the series of materials presented by Naciri *et al.* [17] and Selinger *et al.* [20] in which the siloxane moiety contains two or three silicon atoms, respectively. Prasad *et al.* have previously reported X-ray measurements on ETSiKN65 [21] suggesting that this material exhibits a transition from a smectic C* (S$_C$*) to a de Vries-type smectic A* phase. In the present paper, the interpretation proposed by Prasad *et al.* is discussed in the light of new experimental data.

## 2. The de Vries phase with chiral smectic character

In 1979 de Vries and co-workers [22] pointed out that since the order parameter is less than unity, the molecules in all smectic materials are tilted. However, in the smectic A phase the director, which is an averaged quantity, is normal to the smectic layers. In recent years there has been an increasing interest in the so called de Vries-type Smectic A phases, discussed in the review article by Lagerwall and Giesselmann [23]. A brief summary of the properties of the chiral de Vries-type smectic A phase relevant to the present study is presented below.

In a de Vries-type smectic A phase the mesogens are tilted with respect to the layer normal, but the directions of molecular tilt are randomly distributed on a cone with an apex angle equal to twice the molecular tilt, $\theta$. This lack of correlation with the direction of tilt confers to the material the symmetry of a smectic A phase. The optic axis of the material, determined by the average molecular orientation, is therefore normal to the smectic layers, as illustrated in Figure 1(a).

If the material is chiral, there is a local spontaneous polarisation in a volume whose dimensions are of the

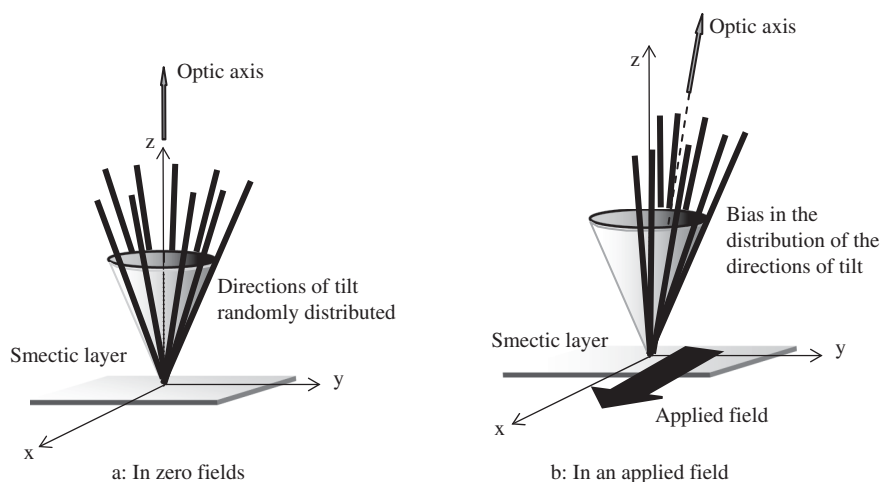*Corresponding author. Email: carlo@squ.edu.om

Figure 1. (a) In a de Vries phase the directions of tilt are randomly distributed on a cone of apex angle equal to twice the tilt angle of the mesogen; the resultant macroscopic optic axis is normal to the layers. (b) The application of an electric field biases the orientation of the local moments and therefore of the distribution of the direction of tilt; the optic axis is at a finite angle to the layer normal.

order of the correlation length between the directions of tilt. This local polarisation lies in the plane of the layers and is perpendicular to the local direction of tilt. Due to the lack of long-range order in the direction of tilt, the direction of the local spontaneous polarisations is randomly distributed, resulting in zero net macroscopic spontaneous polarisation. The application of an electric field in the plane of the layers biases the distribution of the local polarisations, and favours the orientation parallel to the direction of the field (Figure 1(b)). As a result there is a bias in the distribution of the directions of the molecular tilt, with the concomitant tilt of the average optic axis and change in the birefringence [18–20]. The bias is in the distribution of the directions of the local polarisation and therefore the tilt of the optic axis increases with the applied field and saturates when the direction of tilt is uniform throughout the material. At saturation, the tilt of the optic axis is equal to the molecular tilt.

### 3. The material, ETSiKN65

The material ETSiKN65 was synthesised following similar steps to those described by Naciri *et al*. [3,

17]. A schematic illustration of its molecular stucture is shown in Figure 2.

The transition temperatures and proposed phase sequence observed in ETSiKN65 by polarised light microscopy are summarised in Table 1, which for comparison also shows the corresponding transition temperatures reported for DSiKN65, TSiKN65 and TSiKN65F. DSiKN65 and TSiKN65 contain, respectively, two and three silicon atoms in the siloxane moiety, and TSiKN65F is a modification of TSiKN65 with a fluorine atom in the 3'-position on the benzoyl ring.

On cooling from the isotropic melt, all four of these materials display a direct transition to a de Vries-type $S_A^*$ phase. The three materials without the fluorine substituent display a $S_C^*$ phase at lower temperatures.

### 4. Experimental methods and results

Observations on ETSiKN65 were carried out using a polarised light microscope in conjunction with a heating/cooling stage and temperature controller (Linkam TMS 94). Specimens of different thicknesses (5 μm, 9 μm and 20 μm) contained in cells treated
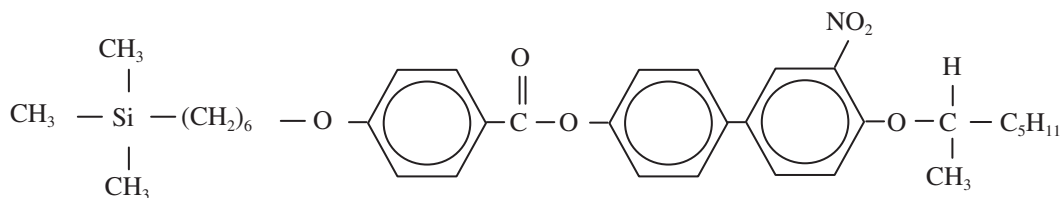


Figure 2. Structure of ETSiKN65.

Table 1. Transition temperatures of low molar mass organosiloxane materials in the SiKN65 series.

| Material | Reference | Phase sequence |
|---|---|---|
| ETSiKN65 | Present paper | $S_C^* \overset{40^\circ C}{\longleftrightarrow} S_A^* \overset{44^\circ C}{\longleftrightarrow} I$ |
| DSiKN65 | [20] | $S_C^* \overset{39^\circ C}{\longleftrightarrow} S_A^* \overset{55^\circ C}{\longleftrightarrow} I$ |
| TSiKN65 | [20] | $S_C^* \overset{24^\circ C}{\longleftrightarrow} S_A^* \overset{56^\circ C}{\longleftrightarrow} I$ |
| TSiKN65F | [17] | $S_A^* \overset{68^\circ C}{\longleftrightarrow} I$ |

for planar alignment were investigated; the cells were purchased from Instec (Colorado, USA), and the tolerance on the cell gap quoted by the manufacturer is $\pm 0.2\ \mu m$.

On cooling from the isotropic phase the material is seen to progress directly into the smectic phase. As is usually the case with low molar mass organosiloxanes, there is a temperature range of one or two degrees during which the isotropic and the smectic phase coexist. The smectic phase begins to appear at 44.5°C, and the specimen is completely smectic at 43.5°C. If the cooling is rapid the specimen displays a sanded texture. A texture with sufficiently large broken fans can be obtained by performing slow (0.1°C min$^{-1}$) temperature cycles between 44.0°C and 43.0°C in the presence of an applied square-wave electric field ($E_{pp} = 9\ V\ \mu m^{-1}, f = 1\ Hz$).

On further cooling, a texture change is observed at 40°C. At this temperature, pitch lines appear in the broken fans of the focal conic texture. The observed texture change suggests that there is a $S_A^*$–$S_C^*$ phase transition. However, both phases display a large in-plane switching of the optic axis when a bipolar square-wave of sufficiently large amplitude is applied. This observation would indicate that the $S_A^*$ phase is of the de Vries-type, in agreement with the X-ray measurements carried out by Prasad *et al.* [21], who found that at 39°C there was only a small (0.4 nm) change in the spacing of the layers.

The behaviour of the birefringence and of the tilt of the optic axis as a function of the amplitude of the applied field offers a means of identifying a de Vries-type phase [20]. The tilt of the optic axis, determined as half the angle between the two positions of optical extinction when the sample was switched between crossed polarisers, was measured as a function of the applied field. A very low frequency (50 mHz) bipolar square wave was applied to the specimen to switch the material between the two positions of extinction. Figure 3 shows the behaviour of the tilt of the optic axis at temperatures 38°C and 42°C, measured in a 5 μm thick specimen.
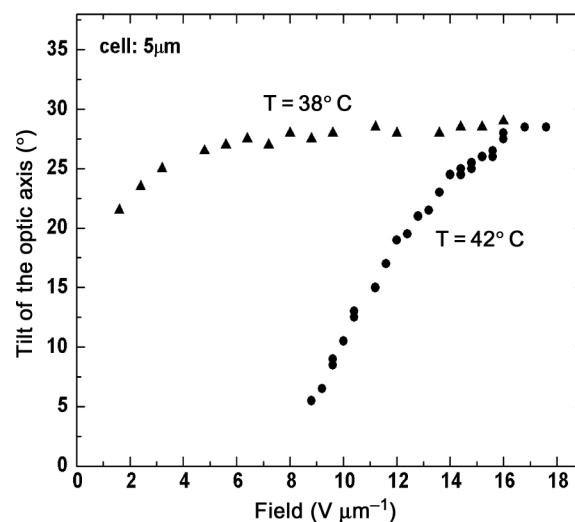


Figure 3. The tilt of the optic axis measured as a function of the amplitude of the applied field at temperatures above and below the $S_A^*$–$S_C^*$ transition.

At 38°C the tilt is $28^\circ \pm 1^\circ$, and is almost independent of the amplitude of the applied field. This is characteristic of a $S_C^*$ phase; the small drop in the measured tilt at low fields is almost certainly due to partial helix unwinding. At a temperature above the observed phase transition, the tilt of the optic axis increased with the amplitude of the applied field and reached saturation at $28^\circ \pm 1^\circ$ in a field of $16\ V\ \mu m^{-1}$. An increase in birefringence was also observed as a change of colour when the amplitude of the field increased. Such behaviour is characteristic of a de Vries smectic A* phase [20]. These observations, together with the very small layer change in spacing at the transition observed by Prasad *et al.* [21], confirm that the $S_A^*$ phase is a de Vries-type phase. However, it is observed in Figure 3 that in the de Vries $S_A^*$ phase there is a threshold value of the applied field below which no electro-optic switching could be observed. A similar behaviour was also observed in TSiKN65F [18].

The existence of a threshold field for switching a polar material, whatever its origin, results in a two-peak current response of the material when subjected to a triangular-wave electric field. Two current peaks were indeed observed in the material, as shown in Figure 4; a two-peak response has also been reported by Prasad *et al.* [21]. A threshold field and the associated two-peak response are usually associated with an anti-ferroelectric order in the material; however, the observation of the two peaks in the current response does not necessarily imply that there was an anti-ferroelectric order. A threshold for switching is sufficient.

Figure 5 shows the tilt of the optic axis as a function of the amplitude of the applied field, measured
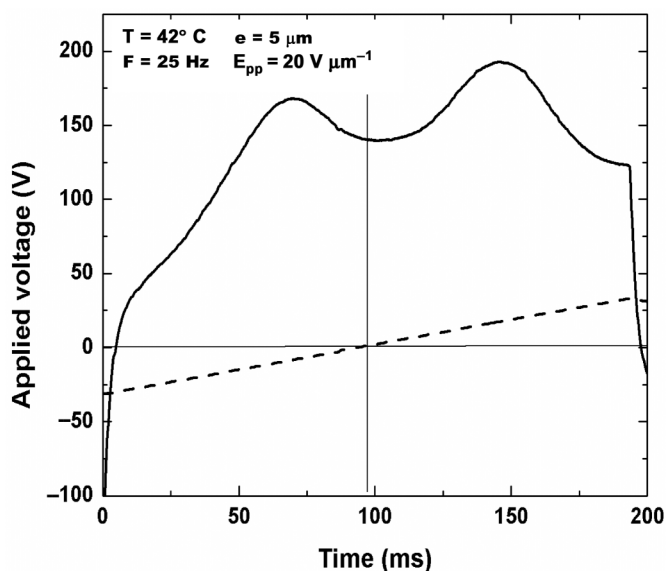
Figure 4. Two polarisation-reversal current peaks are observed in response to a triangular wave. The presence of the two peaks is due to the existence of a threshold in the switching field.
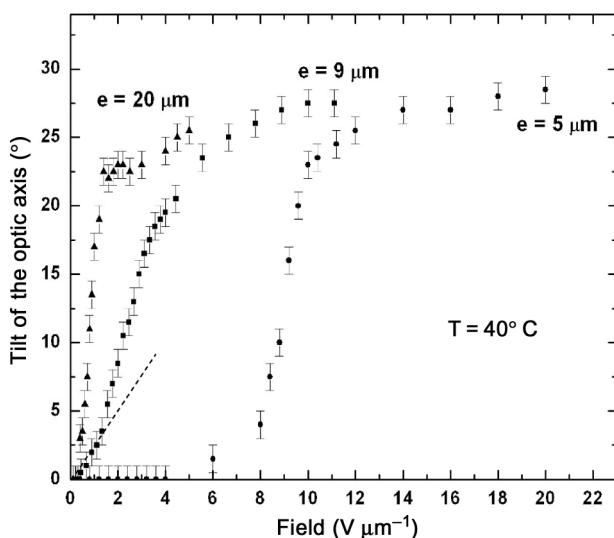


Figure 5. The tilt of the optic axis measured as a function of the amplitude of the applied field in cells of different thicknesses. The threshold is not observed in the 20 μm thick cell. In the 9 μm thick cell there is a small response below the threshold field, shown by the dashed line in the figure. The degree of uncertainty ($\pm$ 1°) was determined from the fluctuation observed in repeat measurements.

in cells of different thickness. The two-peak current response was observed in the 5 μm cell, whereas a single-peak response was observed in the 9 μm and the 20 μm cells.

It is clear from Figure 5 that the value, and indeed the existence, of the threshold depended on the cell thickness, in fact in the 20 μm specimen the threshold has almost disappeared. The gradual increase in the tilt of the optic axis as a function of the amplitude of the applied field above the threshold was observed in all the cells. The threshold field can be measured by extrapolation of the almost linear portion of the graph. In the 5 μm cell it is about 8 V μm$^{-1}$ and in the 9 μm it is cell only 1 V μm$^{-1}$. We note in passing that some switching, with a much lower gradient, occurs below the threshold.

## 5.   Discussion

From the data in Figure 5 one can conclude that the bulk of the material displays a de Vries smectic A* phase, and that near the surface there is a region responsible for the threshold. The existence of the threshold is therefore not an intrinsic property of the material, but it is due to the confinement. The existence of this threshold, which has also been observed in two homologous materials [18], is not yet clearly understood. In general a threshold field is observed in situations where the field causes a degree of frustration in the material, as is the case in the Freedericks transition, or in anti-ferroelectric switching. However, in the present case the frustration is not obvious. One might expect that a planar alignment at the surface would stabilise the ordering of the directions of tilt; if this were the case, the surface and the field would both favour the ordering of the directions of tilt – there is no frustration, and therefore no threshold. In the present case a simple Freedericks situation cannot be invoked to explain the existence of the threshold.

Our tentative interpretation of the experimental observations is to assume that there is, as suggested by Sandhya *et al*. [24] for a homologous organosiloxane material, a weak preference for an anticlinic arrangement of the molecules. The molecules may then be coupled in pairs with the azimuthal orientation of the pairs randomly distributed on the cone, as illustrated in Figure 6.

In the bulk of the material a weak field (less than 0.5 V μm$^{-1}$) is sufficient to break the anticlinic coupling and cause the molecules to adopt a synclinic alignment within a volume whose dimensions are of same order as the correlation length. However, the surface may stabilise the anticlinic alignment in a thin layer close to the surface, and a larger field (of the order of 7 V μm$^{-1}$ or more) is needed to overcome the forces that stabilise the anticlinic alignment. The threshold for switching thus varies across the thickness of the cell. The data in Figure 5 pertain to an optic axis, which is the result of an average over the thickness of the optically inhomogeneous specimen. In the 20 μm cell the specimen is mainly bulk and

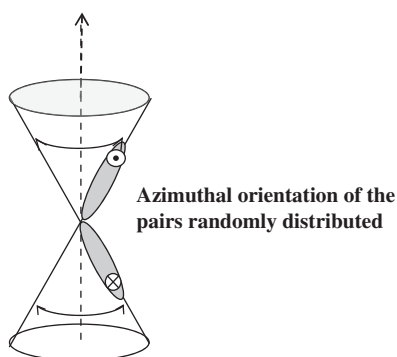**Azimuthal orientation of the pairs randomly distributed**

Figure 6. With a weak anti-ferroelectric coupling molecules can be locked in pairs. The azimuthal orientations of the pairs are randomly distributed on the cone.

therefore to a large extent optically homogeneous; the observed behaviour of the optic axis is that expected in a de Vries $S_A{}^*$ phase (without a threshold). In the 5 μm cell the surface-stabilised regions constitute a significant proportion of the specimen. At low fields only a small portion of the material in the middle of the cell is responding and the effect on the optic axis is negligible. Above 5 V μm$^{-1}$ the responding region starts to increase rapidly with the field. At the threshold value (8 V μm$^{-1}$) the entire specimen is switched out of the surface-stabilised anticlinic alignment, but this field is insufficient for the orientation of the optic axis to reach saturation. From Figures 3 and 5 the saturation field can be estimated to be about 16 V μm$^{-1}$. Hence the progressive reorientation of the optic axis that is observed above the threshold.

In conclusion, we wish to stress that the interpretation proposed is the only plausible one not in contradiction with the observations. Other plausible scenarios could be conceived. A detailed X-ray investigation of the specimen in the cells and in applied fields will be required to ascertain the origin of the threshold.

### Acknowledgements

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