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ADVANCES IN THE INVESTIGATION OF THE NEMATIC-SMECTIC A TRANSITION: MAGNETIC STUDY OF MIXTURES OF MESOMORPHIC COMPOUNDS

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ABSTRACT.
Both dynamic and static magnetic measurements have been performed on mixtures which present a N-SA transition more and more weakly first order. An interpretation is attempted in terms of phenomenological as well as microscopic theories of that phase change.

1. Introduction.
A compound (the 4-4' dihexylazoxybenzene: \( C_6 \)) first quoted by de Jeu [1] was found to present a nematic-smectic A transition which would be quasi second order [2]: its transitional enthalpy approximates to zero. Moreover for such a substance it is easier to get over the problem of purity which is so crucial in the case of CBOOA as shown by P. E. Cladis [3]. Our aim in this work was to show a coherent evolution of the character of that phase change by the study of binary mixtures of the so called \( C_6 \) and its homologues the 4-4' diheptylazoxybenzene \( C_7 \) and the 4-4' dioctylazoxybenzene \( C_8 \) for which the nematic-smectic A transition is first order. To this end, we have performed measurements on three quantities:

- orientational order (magnetic anisotropy) and enthalpy,
- dynamic twist viscosity.

2. Enthalpic and static magnetic measurements.
In fact in this section, the idea is to connect the orientational order measurements to the ratio \( \frac{T_{NA}}{T_{NI}} \)\(^{(1)} \).

In the theories this ratio is a very important parameter in connection with the order of the transition [4]. By mixing the \( C_7 \) with the \( C_8 \) and then the \( C_6 \) and the \( C_7 \) one can obtain a quasi linear variation of this ratio as we can see in the figure 1.

2.1 Experimental results.
Thus we have studied six mixtures and three pure compounds as it is shown in the table I.

The magnetic anisotropy measurements give us the shape of the variation of the orientational order parameter.

\(^{(1)} \) \( T_{NA} \) and \( T_{NI} \) are respectively the temperatures for the nematic-smectic A transition and the nematic-isotropic transition.

We have performed our measurements by Faraday's method by using a strong electromagnet [5].

Our relative accuracy is \( 10^{-3} \) on the susceptibility. It is interesting to compare the possibilities of our apparatus with high resolution techniques. To this end,
we can consider the thermal variation of the anisotropy of the very studied CBOOA:

We can notice in the figure 2 a small discontinuity at the nematic-smectic A transition: only very accurate methods permit to detect this very weak first order character of this phase change [6].

Fig. 2. — CBOOA: thermal dependence of the magnetic anisotropy.

The shape of the curves for the different mixtures is almost the same as we can remark on the figure 3 and the following ones.

The step in the anisotropy, characteristic of a first order transition, decreases from the pure \( \{ C_8 \} \) to the mixtures \( \{ C_6 (50 \%), C_7 (50 \%) \} \) and then vanishes for the last samples.

Now to determine if it exists a link between the orientational order and a thermodynamical quantity we need enthalpic measurements.

These ones have been obtained by the way of a differential scanning calorimeter Perkin Elmer type II. The results are summarized in the table I.

Note that we have taken in account the whole enthalpic peak and not used the method presented by Johnson [7]: if we should use this one, for some mixtures the enthalpy would be zero when the step in the orientational order would be still unquestionnable.
2.2 DISCUSSION. — We can now compare the experimental values to the theoretical parameters.

We have plotted in the figure 7 the values of the transitional enthalpies versus the ratio $T_{NA}/T_{NI}$. If we extrapolate the curve to zero enthalpy the corresponding value for $T_{NA}/T_{NI}$ is about 0.9. This value is in good agreement with the predictions of the Kobayashi-McMillan's molecular theory [4] refined by Lee and Tan [8], it is an evidence if we compare the theoretical curves: straight line in the case of first theory, broken curve, for the Lee and Tan's refined model. Now if we plot the increase of the orientational order parameter at the nematic-smectic A transition versus $T_{NA}/T_{NI}$ (Fig. 8) we get a curve similar to the preceding one. If we extrapolate to zero change in orientational order, we obtain a value of $T_{NA}/T_{NI}$ about 0.89 which presents a good coherence with both the theory and enthalpic measurements.

Thus, a rod like molecule model seems to be suitable to describe a nematic-smectic A transition, at least for molecules geometrically analogous to these we have studied. This is confirmed by the values obtained for the CBOOA: triangles in both cases: enthalpic measurements (Fig. 7) and orientational order measurements (Fig. 8).

Indeed, the size of the rigid core of this chemically different compound is similar to these of the homologues of the serie: this agrees with the theory which considers that core as a preponderant parameter. Now,
we can plot $\Delta H_{\text{SA}}$ versus the step in orientational order (Fig. 9). We obtain a straight line the extrapolation of which includes the origin. This shows that according to the theories the variation of the orientational order parameter is proportional to the enthalpy of transition.

If we assume the meanfield approximation:

$$\delta\gamma_1(T) \sim (T - T_{\text{NA}})^{-0.33}$$

if we assume the analogy with superfluids.

This last result agrees with F. Brochard’s.

The very studied CBOOA provided many results trying to confirm either of those theories.

D. Salin et al. [13] using Light beating spectroscopy have found that both $\gamma_1$ and the Franck elastic constant diverge with the same critical exponent i. e. : 0.66 by comparison with previous measurement of the static coefficient [14].

On the other hand, the method of dynamic Freedericksz deformation [15] shows $\gamma_1$ to diverge with a critical exponent 0.37 ± 0.05.

Moreover, McMillan, using Rayleigh Light scattering [16], affirms that the critical behavior of the twist viscosity $\gamma_1$ is consistent with mean-field predictions. Finally D. Langevin proposes for the critical exponent of the viscosities the value 0.54 ± 0.08 [17].

We recall our result in the case of CBOOA [2]:

$$\nu = 1.07 \pm 0.05$$

The large diversity shown by these results (2) has led us to a systematic study on this serie of homologues.

3.2 EXPERIMENTAL RESULTS. — The temperature dependences of the twist viscosity coefficient have been determined for eight samples (see Table I) and are presented on the figure 10.

![Figure 9](image_url) Variations of the orientational order parameter at the N-SA transition versus the transitional enthalpies.

![Figure 10](image_url) Temperature dependences of the twist viscosity coefficient $\gamma_1$. (Note that the various samples do not come from the same origin.)
More enlarged the nematic domain is, more important both value and divergence of \( \gamma \), seem to be.

We point out here that the rotating field method employed permits no measurement closer than 0.1 °C to the N-S\(_A\) transition.

3.3 ANALYSIS OF THE RESULTS. — We are going to present this analysis through an example (i.e.: \( \{ C_6 \, (87 \%) \, C_7 \, (13 \%) \} \)).

The twist viscosity \( \gamma_1 \) should diverge as:

\[
\gamma_1 = \gamma_1^0 + \delta \gamma_1
\]

where \( \gamma_1^0 \) is the intrinsic twist viscosity non perturbed by a N-S\(_A\) transition.

That background term can be described according to two different ways:

\[
\gamma_1^0(T) = A \Delta \chi(T) e^{-B/T}
\]

or

\[
\gamma_1(T) = A' \Delta \chi^2(T) \exp \left[-\frac{B' \Delta \chi(T)}{T}\right]
\]

expression proposed by A. F. Martins [18].

Both have been applied to compounds presenting only a very large nematic phase (and consequently no smectic change): in such a case of an unperturbed evolution of \( \gamma_1 \), the best fitting seems to be the first [19].

In the continuation, we shall use this one.

\( \Delta \chi(T) \) represents the diamagnetic anisotropy. We determine the constants \( A \) and \( B \) by fitting the curves \( \gamma_1(T) \) in an interval located far from the N-S\(_A\) transition as well as from the N-I transition.

Thus we plot:

\[
\log \frac{\gamma_1}{\Delta \chi} \text{ versus } \frac{10^3}{T} \quad \text{(Fig. 11a)}.
\]

To this end, we need the thermal variation of \( \Delta \chi \) previously obtained by the classical Faraday’s method (Fig. 12).

We can now extrapolate the \( \gamma_1^0 \) values close to the N-S\(_A\) transition. So we deduce \( \delta \gamma_1 \) by difference between the experimental and theoretical values. At last we plot \( \delta \gamma_1 \) versus \( \Delta T \) (i.e.: \( T - T_{N\text{I}} \)) using a logarithmic scale (Fig. 11b) and so we get an experimental exponent.

The same treatment has been applied to the other mixtures. The results of the fitting are summarized in the figure 13 an in the table I.

![Fig. 11a. — \( \{ C_7 \, (13 \%) \, C_6 \, (87 \%) \} \) : fitting of the unperturbed part of the \( \gamma_1 \) evolution.](image)

![Fig. 11b. — \( \{ C_7 \, (13 \%) \, C_6 \, (87 \%) \} \) : fitting of the \( \gamma_1 \) divergence.](image)

![Fig. 12. — \( \{ C_7 \, (13 \%) \, C_6 \, (87 \%) \} \) : thermal dependence of the magnetic anisotropy.](image)

![Fig. 13. — Fittings of the \( \gamma_1 \) divergence for the various mixtures.](image)
3.4 DISCUSSION. — We can notice the monotonous evolution of the value of the exponent which decreases from the \( C_8 \).

Nevertheless it seems to reach an approximatively constant value rapidly enough.

It is to observe that the fitting is suitable in an interval the width of which is \( 1 \text{°C}-2 \text{°C} \) above the transition and the minimum \( \Delta T \) being \( 0.1 \text{°C} \).

Consequently, it is difficult to draw an unquestionable relationship between this exponent and the theoretical one. Indeed, the trend tends to show that the true divergence occurs for \( \Delta T \approx 0.1 \text{°C} \) (i. e. \( \Delta T \approx 10^{-3} \text{°C} \)). Anyway the extreme values for \( y \) could not permit us to decide in favour of either theory. However we can take advantage of the experimental fact:

If we admit that some divergence of \( y_1 \) can be yet pointed out at \( 1 \text{°C} - 2 \text{°C} \) above the N-SA transitions, that work shows the coherence of its evolution, together with the assumed change in the order of the transition. Moreover \( y \) does not seem to depend on the chemical constitution: we present the results obtained for the 404 (4-butoxybenzilidene 4'-butylaniline). The \( y \) value is in good agreement with the expected one in consideration of the thermodynamical characteristics of the material (\( T_{NI} \) and \( T_{N1} \)). In those conditions, even if our parameter is not the critical one provided for by the theory, the exponent that we deduce can help us to determine in what degree this or that N-S, transition approximates to a second order one.

As a conclusion, we can say that the first part of our work presents a very good autocoherence with regard to a rigid molecule model. And the divergence of the coefficient \( y \), shown in the second part, and reduced to an experimental exponent \( v \), would permit us to reach the same end with regard to F. Brochard's and McMillan's theories.

References

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