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THERMODILATO-MICROSCOPY OF LIQUID CRYSTALS

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Liquid crystals exhibit successively several fluids and/or viscous phases and therefore microscopical methods play an important role for their characterization. No really efficient routine dilatometric method exist for rather small samples. By simple addition of a Michelson's interferometer objective and a photo-multiplier to the basic equipment for the investigation of liquid crystals – i.e. a polarizing microscope associated to a heating and cooling stage – dilatometric investigations as well as studies of phase transitions are getting accessible. In fact, when a droplet of liquid crystal, set up in a spherical stamp, is lightened through the interferometer with a quasi monochromatic source, equal thickness circular fringes are observable on the surface of the sample. A thermal expansion of the droplet leads to displacements of these fringes. The principle for the measurement of the volume changes consists by recording, versus the temperature, the variations of the light intensity of the central fringe. The volume of the sample, at given temperatures, is determined from photomicrographs of the whole interference feature. This volume is lower than 0.1 mm^3. Experiments on the pure compound octyl-cyanobiphenyl show that the method is convenient for the detection of the phase transition, even if the transformation is weakly first order as S_A-N. Tested with a commercial ternary mixture the expansivity of phases and the transitions volumes changes can be deduced from experiments.

Introduction

Five different methods have previously been used to study the thermodilatometric properties of liquid crystals for phases as well as for transitions (i.e. expansivity and volume changes) under atmospheric pressure [1–5]. Taking into account that for very new synthesized liquid crystals only 10 milligrams are generally disposable for physical tests, the capillary method [1] seems the most convenient one. However, the experiments are often delicate to perform and lead occasionally to errors for volume data and have previously induced serious mistakes of interpretation [6, 7].

We propose here an interferometric method of thermodilatometric analysis efficient on about 0.1 milligram of sample weight for fluid substan-

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ces. The method can be implemented using the basic equipment for liquid crystals. The first experimental results obtained on a pure compound and on a ternary mixture exhibiting several phases of liquid crystals are presented.

Method and experimental equipment

Basically, the thermodilato-microscopy consists in lighting, through a Michelson interferometer, a droplet of liquid crystal set on a crucible in order to obtain concentric rings on the sample surface of constant thickness.

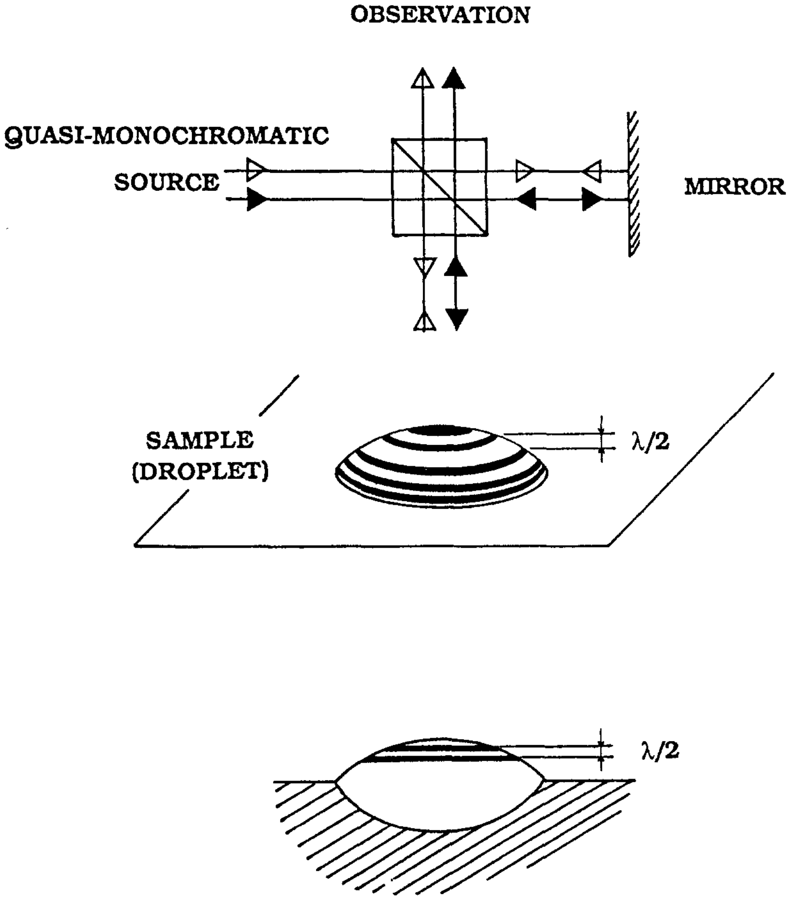

Fig. 1 Principle of the Michelson's interferometer objective: observing the upper face of a droplet. Sample: droplet set in a hemispherical cavity

The intensity changes of the central fringe induced by the volume changes of the whole sample are recorded *vs.* temperature of the droplet.

In fact, the crucible is constituted by a metallic (copper or molybdenum) polished disk in which is stamped, with a small calibrated steel ball, an hemispherical cavity. For diameters of the balls lower than 2 millimeters, very small volumes (<0.1 mm^3) can be obtained for such a cavity. A small droplet is laid down to the cavity using a capillary (for all the compounds which are fluids near room temperature). A little excess of liquid crystals leads to a convex surface of the droplet. After filling in, the crucible is set on the heating stage (0, +80° stage, Leitz) of an optical microscope (Panphot-Leitz) basically used for phase sequences observations versus the temperature. Instead of the classical microscope objectives a Michelson objective (Watson Barnet, England) is used, acting as a simple Michelson interferometer i. e. one of the mirrors is the upper sample surface (see enlargement in Fig. 1). The droplet is lit with quasi-monochromatic light (Na lamp 5890 Å or Hg lamp with 5461 Å interferential filter). A lens system enables to observe the whole interference feature occurring on the sample surface as usual through the microscope. A photomultiplier fixed on the right tube of the microscope, completes the optical set up. An entry diaphragm limits the light intensity measurements to the central fringes at the top of the droplet. A rotating semi-transparent slide enable to illuminate the photomultiplier and/or the camera.

The temperature is detected by a platinum resistor probe set in the crucible. For heating and cooling rates in the range of 1 deg/min, the temperature can be regarded as homogeneous for the whole sample. Up to date, experiments can be performed between +5 and +60°. Both signals issued from the photomultiplier and thermometer are connected to an X-Y recorder.

Results and discussion

Experiments have been performed in order to test i) the sensitivity of the method to detect phase-transitions ii) the efficiency to determine thermodilatometric data. We present here results obtained on one pure compound, Octyl-Cyanobiphenyl (CB 8) exhibiting the phase sequence [8]:

$$K\ 21\quad S_A\ 32.5\quad N\ 40\quad I$$

and one ternary commercial mixture (ZLI 1083, Merck):

$$K\ {-3}\ N\ 52\ I$$

with *K*: crystal, S_A: smectic phase *A*, *N*: nematic phase, *I*: isotropic liquid; the numerical data are the transition temperatures given in degrees Celsius.

Figure 2 shows an example for the complet interference feature obtained by using the camera for the ternary mixture in nematic phase set in little excess in a molybdenum crucible. The diameter of the droplet is .86 millimeter yielding a sample volume of 0.0801 mm^3. The volume of materials is less than 0.1 mm^3 for all the samples investigated. Anchoring effects of the droplet on the brink of the cavity are observable by comparing two photos at close temperatures.

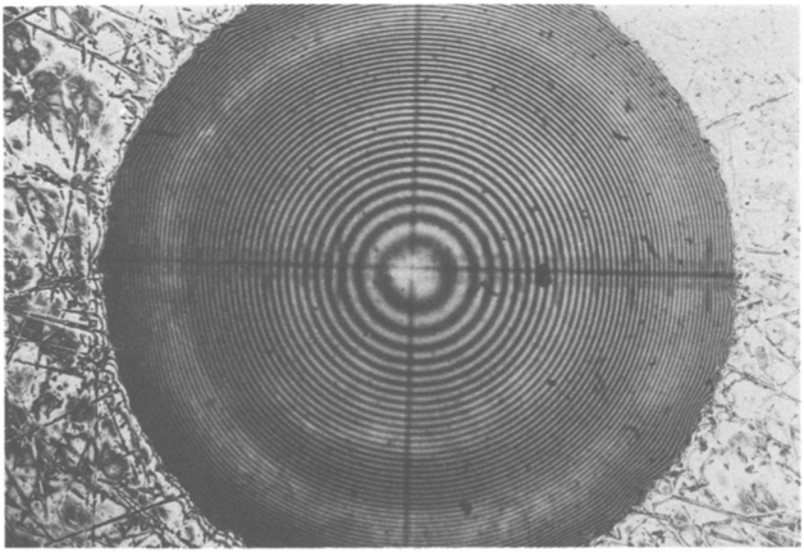

Fig. 2 A complete interference feature on a droplet of ZLI 1083 (Merck) in nematic phase (30°C). The diameter of the sample is 0.86 mm millimeter. The spherical cavity was obtained with a 1 mm diameter steel ball

The light intensity changes at the top of the droplet versus the temperature are given in Figs 3a and 4a for ZLI 1083 and CB 8 respectively. Each interfringe corresponds to a vertical displacement of $\lambda/2$ (λ: incident light wavelength) at the upper part of the droplet. In full phases (*N*, S_A and *I*), the interfringe is bounded to the expansivity. At the transitions, a rapid defiling of the fringes occurs bounded to the volume change for the transformation. For both studied compounds the transitions can be easily detectable directly on the recordings or by plotting the semi-interfringe width data versus the temperature, (Figs 3b and 4b respectively). Especially, regarding the S_A-*N* transition of 8 CB which is first order and of a rather small enthalpy change, namely 0.13 kJ/mole [8], it can be claimed that the method is rather sensitive (Fig. 4). The transition temperatures are in good agreement with observed data.

Dilatometric data i.e. expansivity and volume change, can be deduced from interfringes data and diameter measurements on the sample

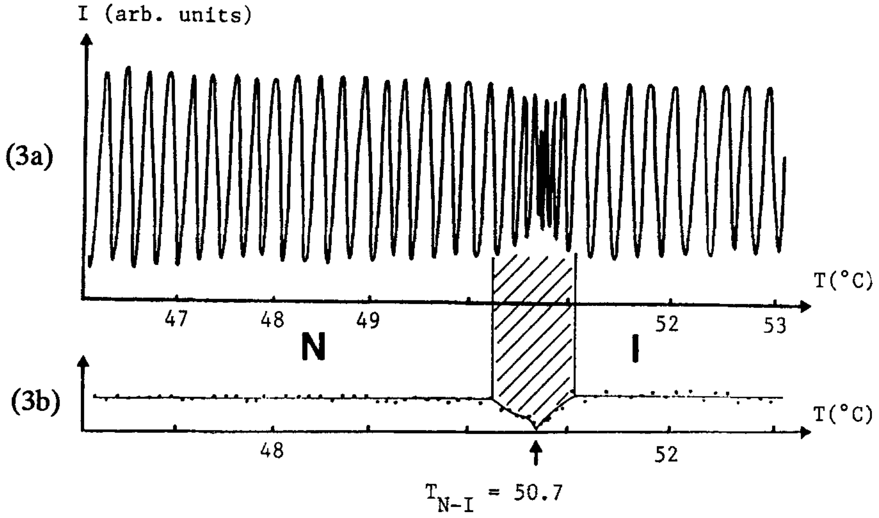

Fig. 3 Recording of the light intensity variations *vs.* the temperature (3a) at the top of the droplet of ZLI 1083 and plottings of the semi-interfrange width *vs.* the temperature (3b).

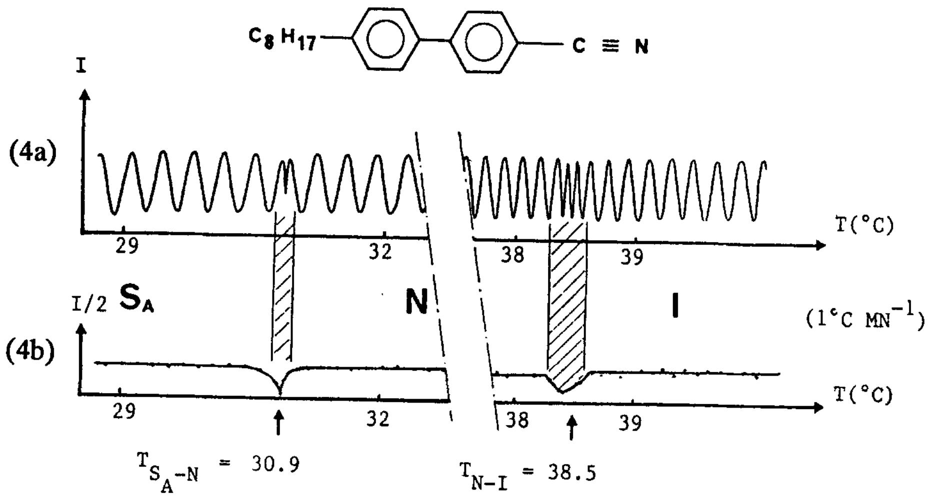

Fig. 4 Recording of the light intensity variations *vs.* the temperature (4a) at the top of the droplet of CB 8 and plottings of the semi-interfrange width *vs.* the temperature (4b)

photographs of both droplet and interferences rings [9]. However, anchoring effects must be taken into consideration to evaluate the real deformation of the upper face of the sample. Tests have been performed on liquid mercury and have allowed to confirm the validity of the calculation method of dilatometric data [9]. Examples of experimental data are given below:

for CB 8: $\Delta V_{SA\text{-}N} = 0.28\ \mathrm{cm}^3 \cdot \mathrm{mole}^{-1}$, $\Delta V_{N-I} = 0.6\ \mathrm{cm}^3 \cdot \mathrm{mole}^{-1}$.

The literature data for CB 8 are [10]

$$\Delta V_{SA-N} = 0.1\ \mathrm{cm}^3 \cdot \mathrm{mole}^{-1}, \Delta V_{N-I} = 0.5\ \mathrm{cm}^3 \cdot \mathrm{mole}^{-1};$$

for N 1083: $\alpha_N = 10.1\ 10^{-4}\ {}^\circ\mathrm{C}^{-1}$, $\alpha_I = 7.2\ 10^{-4}\ {}^\circ\mathrm{C}^{-1}$ and $(\Delta V/V)_{N-I} = 0.6\%$.

A certain agreement between the literature and our data is existing.

Conclusion

By using the basic equipment for the studies of liquid crystals, we have set up a thermodilatometric method of analysis which can be applied to very small quantities of fluid material. Examples of application of two liquid crystals have shown that the method is convenient for the detection of phase transitions, even when the transformation is associated with an extremely small enthalpy change. The expansivity of the phases and the volume chang-es at the transformations are deduced from experimental data. This method is especially suitable for the studies of opacous phases of fluid materials. However, it can only be used when the pressure vapour effect can be neglected and for non hydroscopic compounds.

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Zusammenfassung — Flüssige Kristalle besitzen mehrere flüssige und viskose Phasen, so dass zu ihrer Charakterisierung mikroskopische Methoden eine grosse Bedeutung besitzen. Zur Zeit besteht keine routinemässig einsetzbare dilatometrische Methode im Mikromassstab. Durch die Erweiterung eines Mikroskopes mit einem Interferometer nach Michelson und unter Einsatz eines Photoelektronenvervielfachers bei gleichzeitiger Verwendung eines Kühl- und Heiztisches werden sowohl dilatometrische Messungen als auch Untersuchungen von Phasenumwandlungen zugänglich.

Es werden in der vorliegenden Arbeit Messungen an Oktyl-cyano-biphenyl und an einer ternären Mischung dargestellt und diskutiert.