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THERMODILATOMETRIC MEASUREMENTS ON SMALL SAMPLES OF LIQUID CRYSTALS

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For liquid crystals exhibiting several fluid or viscous phases, no thermodilatometric method exists for small samples. By simply adding to the basic equipment for the investigation of liquid crystals a Michelson interferometer objective and a photomultiplier, dilatometric studies can be performed from photometric measurements on little droplets of fluid materials. The volume of the samples is about 0.1 cubic millimeter. Introducing the notion of useful radius, data for the isobaric thermal expansion coefficient and volume changes at the phase transitions are deduced from experiments. Efficiency and sensitivity tests are performed on two well known fluid compounds: mercury and silicone oil. The method is then applied to the determination of the thermodilatometric data of two pure liquid crystal compounds – pentyl et octyl cyano biphenyles – and of a commercial nematic liquid crystal mixture.

Introduction

For liquid crystals (L.C.), five methods are generally used to study the volume - or density - changes, *vs.* temperature, for the phases and the transitions under atmospheric pressure; they are known as the capillar method (10 mg) [1], diapason method (100 mg) [2], Bekkedhal method (1000 mg) [3], Archimed method (2000 mg) [4] and the indirect method of refractive index measurements (1000 mg) [5], where figures between brackets indicate the average required quantity of matter. The quick procedures for the elaboration of liquid crystals often give less than ten milligrams for physical tests. The capillar method seems to be convenient; however, it is delicate to perform and, as previously demonstrated [6], sometimes leads to experimental errors of density data that have resulted in important mistakes of inter-

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pretation. We propose here a thermodilatometric method of analysis (nomenclature in agreement with the IUPAC recommendations [7]) based on photometric measurements, which are efficient on little droplets of fluid materials and easily implemented with the basic equipment used in the laboratories for the L.C. characterization.

Experimental

Thermodilatometric method

The principle of the method is based on interferential measurements; by lighting a droplet of fluid sample, through a Michelson's interferometric set up, with one of the mirrors constituted of the droplet surface, equal thickness fringes appear on the sample surface. When a slight excess of the sample is placed in a metallic crucible with a circular section, the fringes are concentric rings (Fig. 1a). If λ is the wavelength of the incident light, the thickness between two successive rings is equal to $\frac{\lambda}{2}$. All volume changes of the sample induce modifications of the interference features with the appearance – or disappearance – of successively dark and bright rings at the top of the droplet. For two successive rings, the vertical displacement of the top of the droplet is equal to $\frac{\lambda}{2}$. Hence thermodilatometric measurements can be performed by recording, as a function of temperature, the intensity changes of the central interference fringe. Moreover, for a well defined crucible, the ring number measurements of the whole interference feature lead to the determination of the sample column in excess, and consequently, to the whole sample volume.

Experimental equipment

The experimental set-up (Fig. 1b) uses the basic equipment for liquid crystals investigation (phase identification and phase transition detection [8]), i.e. an optical microscope (Panphot – Leitz) equipped with a heating stage (FP 80 – Leitz, temperature range: 0 to 80°C) coupled to a PID electronic programmer. The microscope objective is changed into a Michelson one (Watson Barnet). Such a system enables observations as usual through the microscope. Crucibles, constituted by metallic (copper or molybdenum) polished disks having small spherical cavities, are used as support for the samples under study. The cavities are obtained by stamping the

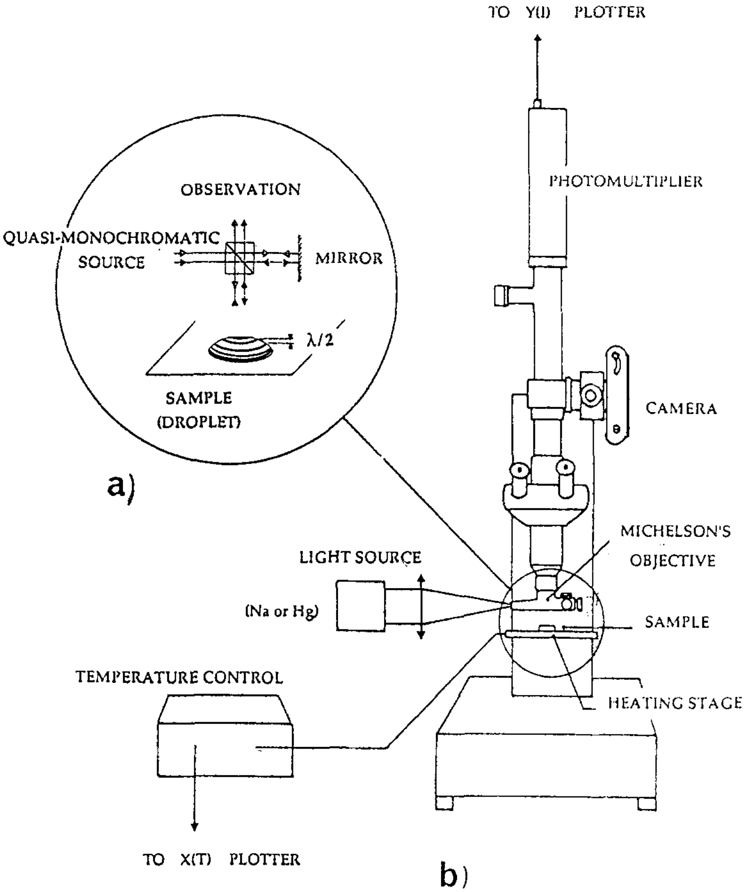

Fig. 1 Experimental equipment for the thermodilatometric analysis a) Michelson's interferometric set up b) Optical microscope equipped for thermophotometric measurements

disk with a small calibrated steel ball; with ball diameters lower than 2 mm, very small volumes for the cavities (< 0.1 mm^3) are easily obtained. The crucibles are placed on the heating stage of the microscope. The temperature is picked up with a platinum resistor probe mounted in the crucible. To date, experiments can be performed between +5 and +60°C. For heating and cooling rates close to 1 deg/min, the temperature can be regarded as homogeneous over the whole sample. The samples are lit with quasimonochromatic light (Na lamp 5890 Å or Hg lamp with 5461 Å interferential filter). Moreover, a photomultiplier fixed at the top of the barrel 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 enables the photomultiplier and/or a camera to be illuminated. The signals from the photomultiplier and the thermometer are connected to an X-Y recorder. The duration of an experiment is about 20 minutes.

Materials

Efficiency and sensitivity tests of the proposed method were performed on two well known fluid products: monodistillated liquid mercury (purity: 99.99, Hexalab) and a commercial silicone oil (Rhodorsil 308 V, Rhone-Poulenc).

The method is then applied to the determination of the thermodilatometric data of two pure liquid crystal compounds of the alkylcyanobiphenyl series (pentyl: 5CB and octyl: 8CB terms, BDH Chemical Ltd) whose general chemical formula is

C_nH_{2n+1}-Φ-Φ-CN

and a commercial ternary nematic mixture (ZLI 1083, E. Merck), exhibiting respectively the following phase sequences:

5CB K 22.5 N 35.0 I

8CB K 21.0 S_A 32.5 N 40.0 I

1083 K −3 N 52 I

with K: crystal, S_A: smectic A phase, N: nematic phase, I: isotropic liquid; the numerical data are the transition temperatures given in degrees Celsius [9–10] (Table 1). The volume changes occurring at the transitions between fluid phases are known for 5CB and 8CB [11] (Table 1). The S_A-N transition of 8CB is a first order one but with a very small (·129 J/mole) enthalpy change [12].

Experimental procedures

The samples are deposited in the crucible cavity using a capillar tube held by a micromanipulator; a little excess of compound leads to a convex surface at room temperature. For the experiments on silicone oil and liquid crystals, crucibles of molybdenum whose isobaric thermal expansion coefficient is low ($1.5\ 10^{-5}\ \cdot °C^{-1}$) compared with that of fluid phases of organic compounds ($10^{-3}\ \cdot °C^{-1}$) [14–15], are used. For the tests with mercury, copper crucibles have been used; the polished copper disks are initially dipped into nitric acid in the presence of mercury, in order to obtain a thin layer of Cu-Hg amalgam on the disk surface; the cavity is then stamped; such

Table 1 Experimental and literature data under atmospheric pressure: for mercury (Hg), silicone oil (308 V), pentyl-cyanobiphenyl (5CB), octyl-cyanobiphenyl (8CB) and the commercial ternary nematic mixture (ZLI 1083); with S_A: smectic A phase, N : nematic phase, I : isotropic liquid, T : Transition temperature (°C), α: Thermal expansion coefficient ($10^4\cdot{}^{\circ}C^{-1}$), ΔV : Volume change at the transition ($cm^3\cdot mol^{-1}$). $\left(\frac{\Delta V}{V}\right)$: Relative volume change at the trasition (%)

	Hg	308 V		ZLI 1083			5CB				8CB			Ref.
			N		I	N		I	S_A		N		I	
T /°C						–	35.0	–	–	32.5	–	40.0	–	[9]
			–	52	–									[10]
			–	52.2	–	–	34.8	–	–	32.4	–	40.0	–	
$\alpha /(10^{-4}\cdot{}^{\circ}C^{-1})$	1.806±0.006[a]													[13]
		9.5[b]												[14]
	1.78±0.09[a]	9.61±0.19[c]	10.1		7.2	14.8		12.9	7.0		15.6		13.9	
ΔV / $cm^3\cdot mol^{-1}$						–	0.49	–	–	0.1	–	0.5	–	[11]
						–	0.39	–	–	0.12	–	0.42	–	
										±0.02		±0.06		
$\frac{\Delta V}{V}$ / %			–	0.13	–	–	0.13	–	–	0.07	–	0.14	–	

a for 31 < T < 39°C
b for 25 < T < 125°C
c for 33 < T < 35°C

preparation enables easily the crucible to be filled with mercury using anchoring effects.

Results

Useful radius

For a droplet of fluid phase deposited, in little excess, in a spherical crucible, the upper surface of the droplet is not spherical due to anchoring effects on the brinks of the cavity [16]. At a given temperature, a photo of the interference feature makes it possible to know the exact shape of the surface of the sample by plotting the curvature radius *vs.* the diameter of the droplet. For both central and peripheral regions this radius can be assumed to be constant, but is higher in the former region than in the latter. The juxtaposition of two half-photos of the same mercury droplet, taken at two close temperatures (Fig. 2a), shows that the sample expansion primarily induces deformations of the central region of the surface; in the peripheral region no significant modification appears. These regions are separated by a circular one whose average radius is called 'useful radius' a_u. Experiments show that for small temperature changes (lower than ten degrees), anchoring effects of the droplet on the brink of the crucible are so that no sample deformation can be detected for radii higher than the useful radius.

Calculations and application to test products

As shown in Fig. 2b, the whole volume of the sample can be decomposed into three parts: the volume of the hemispherical cavity stamped in the crucible (V_{cav}), the volume of the central region of radius a_u (V_1) and the volume of the peripheral region of radii a and a_u (V_2). Assuming the V_1 and V_2 volumes to be portions of spheres, the three volumes are respectively given by the relations

$$V_{cav} = \left(\frac{\pi}{6}\right) \cdot H \cdot (H^2 + 3 \cdot a^2),$$

where

$2a$ is the diameter of the cavity measured on photos

H is the depth of the cavity easily calculated from $2a$ and the radius (r = 1 mm) of the stamping ball,

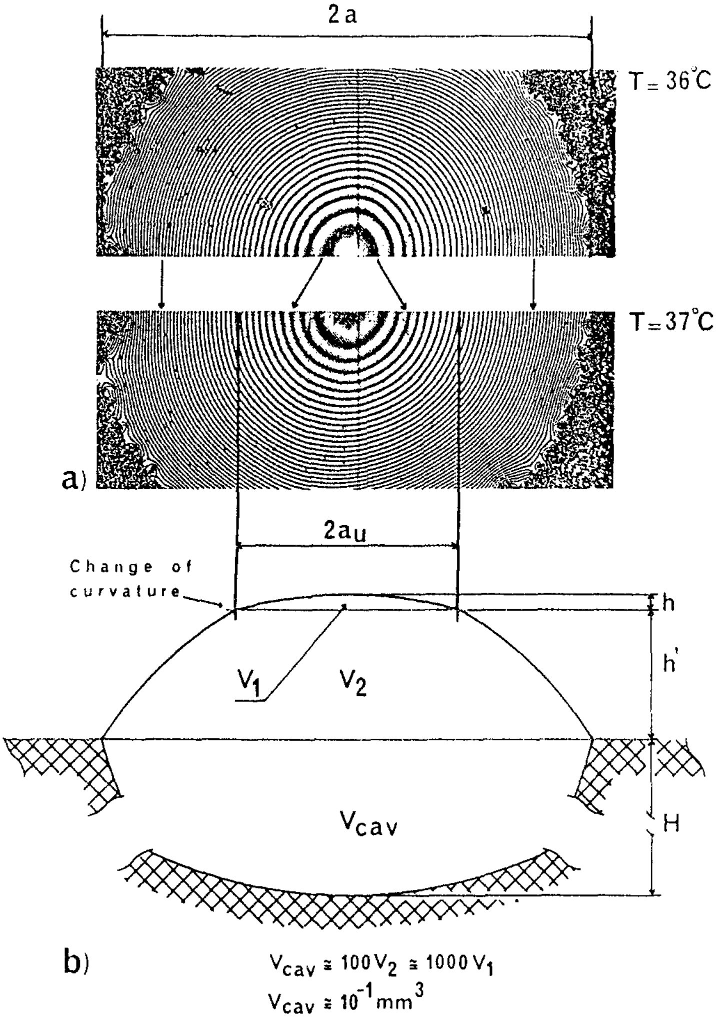

Fig. 2 Droplet of fluid compound deposited in a little hemispherical cavity: a) juxtaposition of two half photomicrographs taken at 36°C and 37°C for the same droplet of mercury. b) schematic sectional drawing (arbitrary dimension)

$$V_1 = \left(\frac{\pi}{6}\right) \cdot h \cdot (h^2 + 3 \cdot a_u^2),$$

where

h is the height of the portion of sphere that is known when counting the number of fringes in the central region,

$$V_2 = \left(\frac{\pi}{6}\right) \cdot h' \cdot (h'^2 + 3 \cdot a^2 + 3 \cdot a_u^2),$$

where

h' is the height of the trunk of sphere that is known when counting the number of fringes in the peripheral region.

However, h and h' are small ($<10^{-2}$ mm) compared to the radii a and a_u (0.4 and 0.3 mm respectively) and the following approximate formulas can be used for calculations:

$$V_1 = \left(\frac{\pi}{2}\right) \cdot h \cdot a_u^2,$$

$$V_2 = \left(\frac{\pi}{2}\right) \cdot h' \cdot (a^2 + a_u^2).$$

From the recording of the regular light intensity changes at the top of the droplet, *vs.* temperature, the number of fringes that defile per degree $\frac{dn}{dT}$, for a given droplet, can be calculated. This number includes thermal expansion of both sample and apparatus (crucible and heating stage). The linear dilatation of the apparatus represents 0.42 fringe per degree. So the effective displacement of the top of the droplet due to thermal expansion of the sample is

$$dh = \left[\left(\frac{dn}{dT}\right) - 0.42\right] \frac{\lambda}{2}.$$

The usual experimental expression for the isobaric thermal expansion coefficient

$$\alpha = \left(\frac{1}{V}\right)_i \left(\frac{dV}{dT}\right)_P$$

where 'i' means *initial* value

can be reformulated for the proposed thermodilatometric method, as follows:

$$\alpha = \frac{1}{(V_{cav} + V_1 + V_2)_i} \left(\frac{dV_1}{dT}\right),$$

owing to the fact that volume change is only observed in the central region of the droplet; using the measurable quantity $\left(\frac{\mathrm{d}n}{\mathrm{d}T}\right)$, α becomes

$$\alpha = \frac{\left(\frac{\pi}{4}\right)\cdot\lambda\cdot a_u^2\left(\frac{\mathrm{d}n}{\mathrm{d}T}\right)}{\left(V_{\mathrm{cav}} + V_1 + V_2\right)_i}\,.$$

In all the cases studied, the volumes are such that

$$V_1 + V_2 \equiv 10^{-3}\ \mathrm{mm}^3 \text{ and } V_{\mathrm{cav}} \equiv 10^{-1}\ \mathrm{mm}^3.$$

It follows that the volume of the whole sample can simply be approximated by the volume of the cavity. For the two test products (mercury and silicone oil) the isobaric thermal expansion coefficients have been measured near room temperature (25°C< T <40°C). The average values of these coefficients and the experimental accuracies are reported in Table 1; they coincide with literature data.

Application to liquid crystals

Figure 3 shows an example for the complete interference feature obtained with the camera for the ternary mixture (1083) in nematic phase. The diameter of the droplet is .86 millimeter corresponding to a .080 mm^3

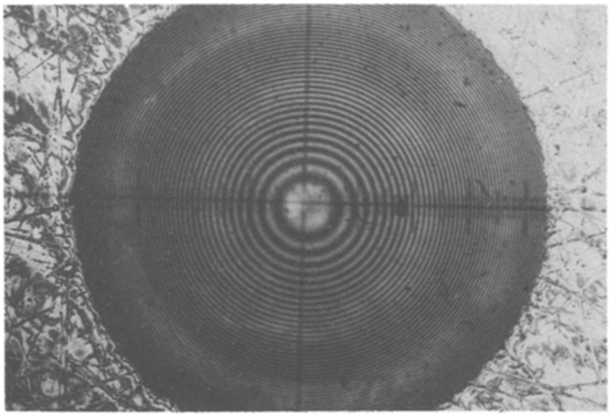

Fig. 3 A complete interference feature on a droplet of ZLI 1083 in nematic phase (31°C); sample diameter: .86 millimeter; sample volume: .08 cubic millimeter

sample. For all the cases studied the volumes of samples are always lower than .1 mm^3.

Examples of light intensity changes at the top of the droplet *vs.* temperature are given in Figs 4a and 4a' for 1083 and 8CB, respectively. The thermal expansion of the N, S$_A$ and I phases leads to a regular defiling of dark and bright rings. At the transitions, the fringes defile rapidly; their number is related to the volume change at the transformation. For all the compounds studied the transitions are clearly detectable on the recordings or by plotting the semiinterfringe width data *vs.* temperature as shown for 1083 and 8CB on Figs 4b and 4b' respectively. Especially, regarding the S$_A$-N transition of 8CB (Figs 4a' and 4b') which is a weak enthalpy transition [12], it can be claimed that the method is sensitive. The experimental and literature transition temperatures are reported in Table 1; there are good agreements with literature data.

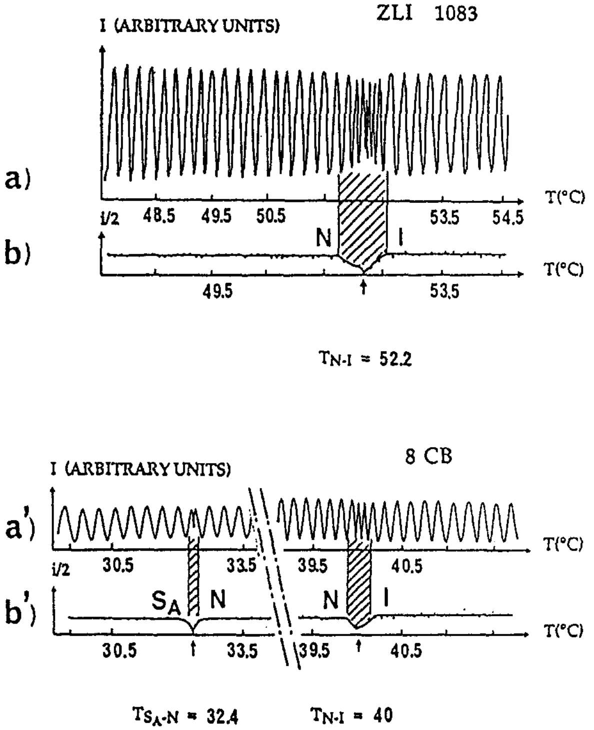

Fig. 4 Recording, *vs.* the temperature, of a) and a') the light intensity variations of the central interference ring (1 deg/min^{-1} heating rate) b) and b') the semi-interfringe at the top of a droplet of ZLI 1083 and 8 CB, respectively

Calculations have been done in the same way as those for test products to determine the thermal expansion coefficients for the phases of the liquid crystal compounds. In each phase the useful radius is measured by examining photos at close temperatures. Results for the expansion coefficients are also reported in the table; data are in the usual range (9 to 18.10^{-4} $\deg^{-1}$) previously obtained for liquid crystal phases [15].

At the transitions the volume change can be calculated as the volume modification dV_1 of the central region of the droplet. The transformations occurring in very small temperature ranges, the stage deformation does not need to be taken into account. Then, the molar volume changes can be expressed as

$$\Delta V = \left(\frac{M}{m}\right) \cdot dV_1,$$

where M is the molar mass and m is the sample mass; m is known by weighing but can be well approached by supposing a mean volumic mass equal to 1 mg/mm^3 [15]. For 1083, only the relative volume change $\frac{\Delta V}{V}$ can be determined because the molar mass is unknown. For the volume changes between the fluid phases of 5CB and 8CB, a good agreement exists between our data and those previously determined by D.A. Dunmur and W.H. Miller using a commercial dilatometer on .7 cm^3 samples [11] (Table 1).

For liquid crystals, the accuracy of our data depends mainly on the determination of the useful radius a_u and the number of fringes that defile per degree in single phases or that defile during the transitions. Although in single phases and for the ranges of temperatures under study, we have not observed anchoring changes *vs.* temperature, this effect does exist and can affect both the shape of the droplet and the useful radius. Moreover, in the calculation of the volume change at a transformation, some difficulties may appear due to the different values taken by the useful radius – resulting from the anchoring change – on both sides of a transition. Therefore, for the liquid crystals studied, it seems that only an accuracy of 10% on the isobaric thermal expansion coefficients of phases and volume changes at the transitions can be claimed, which corresponds to the results usually obtained by other authors for liquid crystals [15]. However, if the accuracy is worse than that given by very accurate methods [17], it must be said that the proposed method can be considered as a rapid routine one, and an efficient one on samples 10^2 to 10^4 times smaller.

Conclusion

Using the basic equipment for liquid crystals investigations, i.e. an optical microscope equipped with a heating stage, changing the microscope objective into a Michelson one and adding a photomultiplier, thermodilatometric analyses have been performed from interferometric measurements. Basically, this method consists in recording, as a function of temperature, the intensity changes of the interference central fringe at the top of a droplet lit by a quasimonochromatic light. It is efficient on very small quantities (< 0.1 mg) of fluid matter. Calculations based on the notion of useful radius make it possible to obtain, from experiments, thermodynamic data related to the thermal expansion. Efficiency and sensitivity tests have been performed on mercury and a silicone oil; the accuracy for the thermal expansion coefficient of these products is respectively 5% and 2%. Examples of application to the determination of thermodilatometric data for phases and transitions are given for two pure liquid crystals compounds – pentyl and octyl cyano biphenyles – and for a commercial nematic liquid crystal mixture; the results obtained for the Smectic A - Nematic transition of 8CB show the method is convenient, even when the enthalpy change at the transformation is very small. However it can only be used when the pressure vapour effects can be neglected and for non hygroscopic compounds. We will take advantage of this method for the dilatometric studies of opaque phases of fluid materials and for the determination of thermodynamic properties related to the thermal expansion of the central core and paraffinic chains of calamitic and pyramidic liquid crystals.

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Zusammenfassung — Für Flüssigkeitskristalle mit verschiedenen Flüssigkeits- und viskosen Phasen existiert keine thermodilatometrische Methode für kleine Proben. Fügt man einem Basisgerät zur Untersuchung von Flüssigkeitskristallen ein Michelson-Interferometer und einen Photovervielfacher hinzu, können anhand von photometrischen Messungen dilatometrische Untersuchungen an kleinen Tröpfchen von Flüssigkeitskristallen durchgeführt werden. Das Probenvolumen beträgt etwa 0.1 Kubikmillimeter. Durch Einführung des nutzvollen Radius können aus den Experimenten Angaben über den isobaren thermischen Ausdehnungskoeffizient und über Volumenänderungen an den Phasen-übergängen abgeleitet werden. Wirksamkeits- und Empfindlichkeitstests wurden an zwei wohlbekannten flüssigen Verbindungen durchgeführt: Quecksilber und Silikonöl. Das Verfahren wurde dann zur Bestimmung der thermodilatometrischen Angaben von zwei reinen Flüssigkeitskristallkomponenten (Pentyl- und Octylcyanobiphenylen) und von kommerziellen nematischen Flüssigkeitskristallgemischen angewendet.