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The Metabolemeter: I A New Apparatus to Detect the Phase Transitions of Mesogens

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The Metabolemeter: I A New Apparatus to Detect the Phase Transitions of Mesogens

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For the most organized mesophases, no really efficient routine method to detect phase transitions exists for small quantity. In these cases, the first order phase transitions of a compound enclosed in a metallic cell are occurring with an important pressure increment. In the measure of the pressure versus the temperature, intensive data only occur and miniaturization is possible. A new apparatus (metabolemeter) using this principle is described. Its efficiency was tested on the crystal-mesophase transitions of the two first terms of the alkoxybenzylidene butyl aniline series and of the octylcyanobiphenyl. For these three compounds, the studies of the nematic-liquid transitions show this barometric method is sensitive.

I. INTRODUCTION

To detect the phase transitions of mesogens, the calorimetric (1 p. 354) and the dilatometric (1 p. 366) methods, the neutron (1 p. 242) and X-Rays Diffractions (1 p. 221), the Nuclear Magnetic (1 p. 427) and Electron Spin Resonances (1 p. 495), the dielectric constants (1 p. 174) or the Positron Annihilation (1 p. 246) measurements are used. In these

† Equipes de recherche associées au C.N.R.S. (E.R.A. n^{os} 465 et 542)

methods, the signals are proportional to the quantity of tested matter. The quick procedures for the elaboration and the purification of organic compounds give only small quantities (less than ten milligrams) and it is interesting to adapt physical methods to these amounts. In the microscopic method (1 p. 1), very little samples may be used (typically 1/20 mg).[2] But even for a trained microscopist, certain transitions between two organized phases such as crystal, smectic E, H and G, or columnar discophases are difficult and sometimes impossible to detect.

A new quantitative method, using only intensive data consists in measuring, versus temperature, the pressure of a mesogenic sample enclosed in a cell. The principle of this barometric method is presented here; then, the working up apparatus is described. After that, experimental tests performed on the melting of the octylcyanobiphenyl (8 CB) and both methoxy and ethoxy benzylidene butyl aniline (MBBA and EBBA) are presented. The studies of the clearing transitions of these three compounds show that this new barometric method is sensitive.

II. PRINCIPLE OF THE BAROMETRIC METHOD

At constant pressure (P), every first order phase transition is attended at a temperature T, with the changes ΔV for the molar volume and ΔH for the molar enthalpy. For a compound enclosed in a rigid but dilatable cell (Figure 1), the transition may be detected by the measure, versus the temperature, of the sample pressure, with suitable sensors. The simultaneous recording of both data gives thermobarograms. Pressure and temperature are intensive values: in principle, miniaturization is possible.

III. TYPICAL VALUES FOR THERMOBAROGRAMS

For two phases in equilibrium of a pure compound, the temperature pressure dependence is given by the Clapeyron's relation $(dP/dT)_e = \Delta H/T.\Delta V$.[3] At constant volume, out of the equilibrium, the thermal expansion α_M and isothermal compressibility χ_M of the phase occur: $(dP/dT)_v = \alpha_M/\chi_M$. Thermodynamic data relative to the phases and transitions of mesogens have been collected in the literature;[4] the following results can be deduced:

—for the few cases where α_M and χ_M are known, the ratio α_M/χ_M is very often smaller than 13 bars $°K^{-1}$ for solid, mesomorphic and liquid phases.

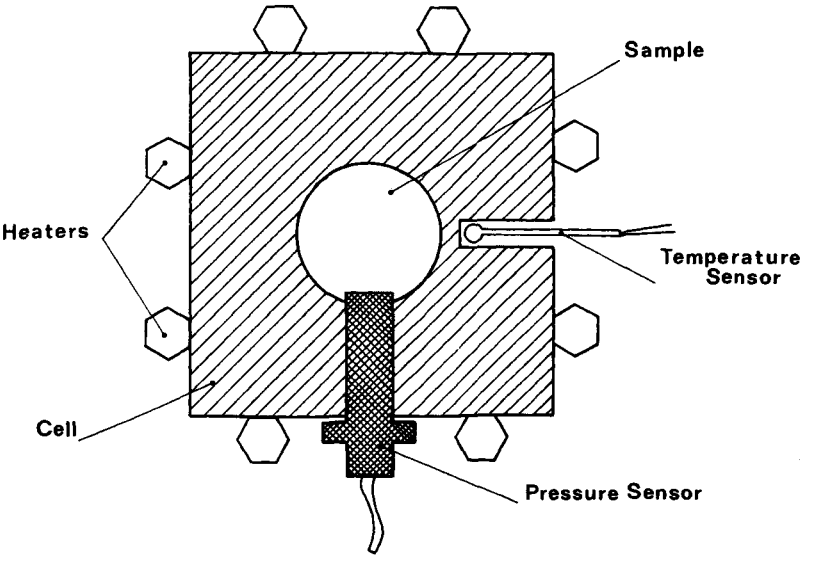

FIGURE 1 Schematic representation of the cell.

—in many cases, the Clapeyron's coefficient is higher than 26 bars $°K^{-1}$.

Then, generally, the slope is twice bigger at the phase changes than beyond the transitions.

At the phase transformation, the volume V_M of the mesogen is given by the relation

$$V_M = \frac{m}{\mu}[x v_{M_1} + (1 - x) v_{M_2}]$$

where x is the proportion of compound in the state stable at lower temperature; v_{M_1} and v_{M_2} the molar volumes of the two phases in equilibrium and stable respectively at lower and higher temperature; m the mass of the sample and μ the molecular mass of the compound.

For a temperature change dT, the x value change and pressure change are respectively dx and dP; so the mesogen volume variation is, on using the thermal expansions α_{M_1} and α_{M_2}, the isothermal compressibilities χ_{M_1} and χ_{M_2} of the two phases and with $v_{M_2} - v_{M_1} = \Delta v$.

$$dV_M = \frac{m}{\mu}\{-\Delta\nu dx + [x\alpha_{M_1}\nu_{M_1} + (1-x)\alpha_{M_2}\nu_{M_2}]\,dT - [x\chi_{M_1}\nu_{M_1} + (1-x)\chi_{M_2}\nu_{M_2}]\,dP\}.$$

If the cell is obtained by hollowing a small cavity in a steel block large enough, the compressibility of the cavity can be neglected.[5] More, the thermal expansion of steel ($0.4.10^{-4}$ °K^{-1} [6] is much smaller than the mesogens one ($3.10^{-4} < \alpha_M < 7.10^{-4}$ °K^{-1}).[4] As $\Delta\nu \ll \nu_{M_i}$ and, in first approximation, the thermal expansions and isothermal compressibilities are the same for two phases in equilibrium,[4]

$$-\Delta\nu dx + \alpha_M\nu_M dT - \chi_M\nu_M dP = 0$$

All the quantities that occur in this relation are temperature and pressure functions. For the pressure dependence of the relative volume change ($\Delta V/V$) and Clapeyron's slope $(dP/dT)_e$, experimental studies are known in few cases;[7,8] except for reentrant mesomorphism,[9] generally, under 1,5 k bars, $\Delta V/V$ decreases of less than 20% and $(dP/dT)_e$ increases of less than 25%. To calculate an order of magnitude of the transition pressure change, these effects are, in a first approximation, neglected. So the integration of the last expression gives:

$$(\Delta P)_T = \frac{\Delta\nu}{\alpha\cdot\nu\cdot\left(\frac{\chi_M}{\alpha_M} - T\frac{\Delta\nu}{\Delta H}\right)}$$

Typically, for a middle value for the slope beyond a transition, for Clapeyron's slope and for the thermal expansion (respectively 8 bars °K^{-1}, 30 bars °K^{-1}, 4.10^{-4} °K^{-1}) and with the following relative volume changes under constant pressure:[4] 6%, 0.6% and 0.06%, the corresponding calculated pressure variations are 1636 bars, 163 bars and 16 bars. If now for the (P,T) dependence of $\Delta V/V$ and $(dP/dT)_e$ respectively a 20% decreasing and 25% increasing are considered, the pressure change data are 1220 bars, 122 bars and 12 bars. A ten bars pressure increment is already a phenomenon easy to detect, and this method is very sensitive. In fact, it is to consider the maximum pressure that the sensor can accept without damage.

IV. CHOICE OF CHAMBER'S VOLUME

If the pressure is measured by the deformation of a metallic membrane, the respiration (membrane incurvation variation) increases the cavity

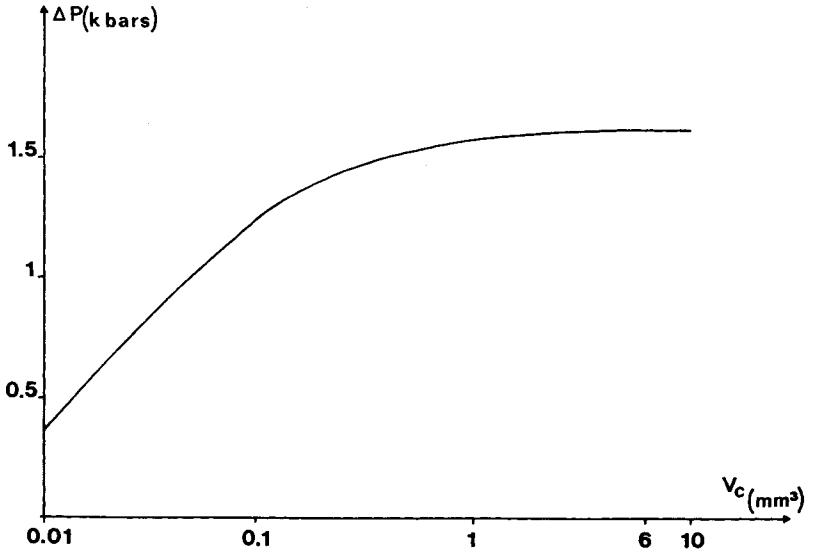

FIGURE 2 Maximum pressure change versus the volume of the chamber, calculated for a middle value for the slope beyond a transition (8 bars $°K^{-1}$), for the Clapeyron's slope (30 bars $°K^{-1}$), for the thermal expansion (4.10^{-4} $°K^{-1}$) and when the relative volume change is 6% at atmospheric pressure.

volume and can decrease the phenomenon fullness. For a given pressure sensor, it is always possible to determine the minimal volume of the cell for which the respiration is negligible. Amidst the industrial transducers, we have chosen the one (HEM 375-20000-Kulite International) that, between −55°C and +260°C (typically studied temperature range for mesogens) and under 1700 bars pressure, gives the minimal volume respiration $2.26\ 10^{-3}$ mm^3). That last one is proportional to the pressure increment (proportionality coefficient: $K = 1.33\ 10^{-6}$ mm^3 bar^{-1}). As the volume V_M of the mesogen is equal to the chamber one V_c and with the previous approximations:

$$(\Delta P)_T = \frac{\Delta v}{\alpha \cdot v \left(\frac{\chi_M}{\alpha_M} - T\frac{\Delta v}{\Delta H} + \frac{K}{\alpha_M V_c} \right)}$$

For a 6% relative volume change, a typical curve for the variation of the maximal pressure change ΔP versus chamber volume V_c and calculated with the previous datas, is plotted on Figure 2. In this case as in all the other studied, the asymptotic value of the pressure is always obtained when the volume overtakes 6 mm^3, which value is used for our

tests. For 0.4 mm^3 of mesogen, the pressure change is still higher than 90% of the optimal one; very small samples can be used.

V. GASES PRESENCE

If a meticulous degazing is not performed, gases are included in the cell. In first approximation (gases assumed perfect) the thermal expansions and solubilities are respectively T^{-1} and P functions.[10] By heating, the pressure increases in the cell and the gases dissolution in the mesogenic material occurs. If the heating begins at a sufficiently low temperature, all gases will be dissolved before the transition occurs; this is necessary to observe the faint volume change transformations, nematic-liquid transition (N-I) for instance, when the volume change is important, crystal-mesophase transitions (K-M) for instance, part of the transition pressure change can be used to dissolve gases; here the heating may begin near the transition temperature.

VI. APPARATUS

The apparatus (Figure 3) described here permits to record the pressure changes in the cell detected with a transducer, versus the temperature, taking up with a resistor thermometer. This arrangement is convenient to detect the first order phase transitions; so we suggest to name it a METABOLEMETER (of the greek $\mu\varepsilon\tau\alpha\beta o\lambda\eta$: transformation and $\mu\varepsilon\tau\rho o\nu$: measure). The choice of the pressure sensor has been already given. The transducer ① has a flushing sensible membrane ② with a diameter smaller than the captor head one. The cell is composed by a crucible ③ in which is machined a cavity ④ ($V = 5.97$ mm^3); the pressure sensor is used as a cover. The material of the cell is the same as this of the pressure sensor (17 − 4 PH stainless steel) to obtain homogeneous deformations of the chamber. The tightness is insured by a tin joint ⑤, located between the crowned insensible surface ⑥ of the pressure transducer and the plane surface ⑦ of the crucible. The transducer is fixed on a rigid support ⑧; two orthogonal horizontal translation movements ⑨ and ⑩ center the crucible under the transducer. The important factor which experimentally occurs to have a good tightness is the sensor-crucible faces parallelism. This is obtained by using a crucible with an hemispherical base placed on ball bearings: three steel balls ⑪ sandwiched between two aluminium plates ⑫ and ⑬ (soft

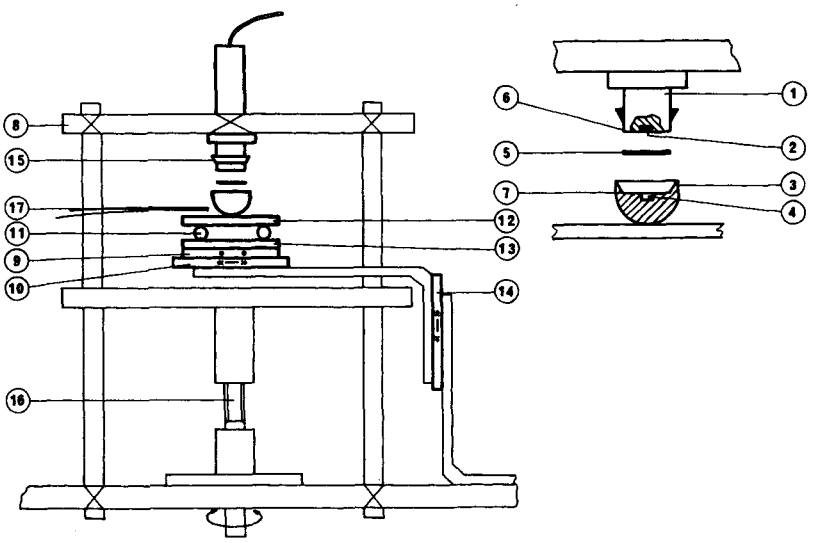

FIGURE 3 The metabolemeter: ① Pressure transducer (Kulite International, HEM 375 20000); ② Flushing sensible membrane; ③ Crucible (17-4-PH stainless steel); ④ Chamber (6 mm^3); ⑤ Tin joint; ⑥ Crowned insensible surface of the head transducer; ⑦ Plane surface of the crucible; ⑧ Pressure sensor support; ⑨ and ⑩ Horizontal translation movements; ⑪ Steel balls; ⑫ and ⑬ Aluminium plates; ⑭ Vertical translation movement; ⑮ Centring cone; ⑯ Screw; ⑰ Temperature sensor.

material); so when closing the apparatus (vertical translation movement ⑭), the crucible sets in parallel to the transducer by rolling on his support without sliding; a cone ⑮, gliding along the pressure sensor, assumes the permanent centring. With the screw ⑯ the cell is hermetically closed. The apparatus is placed in an oven (the speed of heating is regulated, and the temperature is detected with a platinum resistor thermometer ⑰. The signals of the pressure sensor and thermometer are respectively connected to the X and Y inputs of a recorder.

VII. EXPERIMENTAL RESULTS

The first experiments are made to verify the principle of this new method. We have observed transitions (meltings) involving important volume changes for pure compounds exhibiting Clapeyron's coefficients higher than the slope beyond the transition. To test the sensitivity transitions (clearings) with small volume changes and faint changes of slopes are studied. To simplify the preliminary experiments, transi-

TABLE I

Experimental and literature data of temperature, Clapeyron's slope and relative volume change for the studied transitions

TRANSITIONS	K-M^a					N-I				
	Temperature (°C)		Relative volume change (%)	Clapeyron's slope (bars °K^{-1})		Temperature (°C)		Relative volume change (%)	Clapeyron's slope (bars °K^{-1})	
COMPOUND	Lit.	Exp.	Lit.	Lit.	Exp.	Lit.	Exp.	Lit.	Lit.	Exp.
MBBA	21 [11]	20[b]	5.1[12]	40 [12] 39.1 [13] 32 [14] 37.5 [15] 39.26[16]	36[b]	48.5[11]	47[b]	0.2 [17] 0.11[18] 0.13[19] 0.16[12]	31.75[12] 25.6 [20] 27.8 [13] 25.3 [8a] 26.6 [14] 26.4 [21] 27.5 [22] 30.7 [15] 25.6 [18] 28.4 [17]	18[b]
EBBA	34.5[11]	33[b]		35.9 [14]	39[b]	79.7[11]	80[b]	0.27[23] 0.26[17] 0.21[7a]	25.5 [8b] 33.8 [14] 25.3 [8a]	24[b]
8 CB	21 [25]	22[b]		36.4 [9b] 40 [9a] 41.7 [25]		40 [25]	43[b]	0.17[26] 0.35[27]	25.6 [9b] 25.8 [9a] 26.9 [25] 28.73[24]	30[b]

[a] M = N for MBBA and EBBA and S_A for 8 CB
[b] Middle value for several thermobarograms

MBBA : $CH_3O-C_6H_4-CH=N-C_6H_4-C_4H_9n$

EBBA : $C_2H_5O-C_6H_4-CH=N-C_6H_4-C_4H_9n$

8 CB : $nC_8H_{17}-C_6H_4-C_6H_4-C\equiv N$

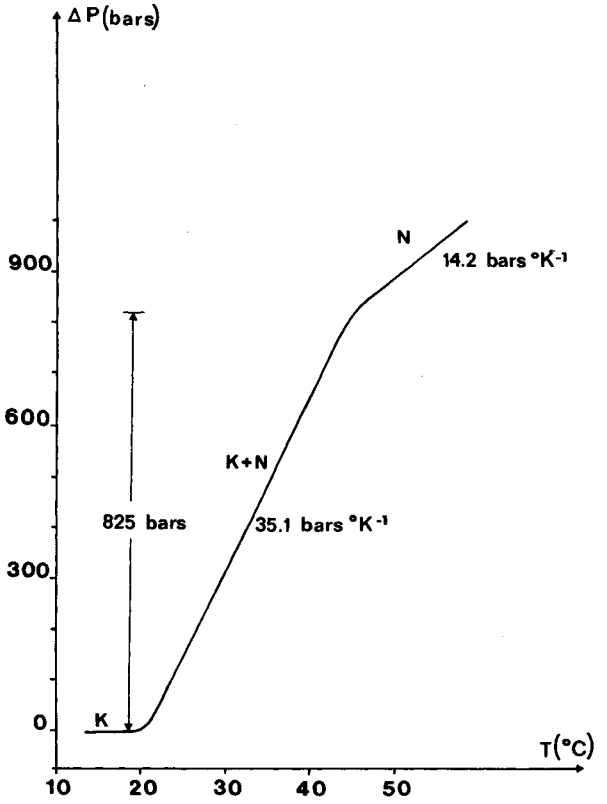

FIGURE 4 Experimental thermobarogram showing the melting transition of MBBA.

tions near the room temperature of commercial compounds are selected. So we have studied first the crystal-nematic transition (K-N) of MBBA and EBBA and the crystal-smectic A transition (K-S_A) of 8 CB and, second, the clearing transitions (N-I) of these three compounds (transitions datas in the Table I).

VIII. VERIFICATION OF THE METHOD

The compound in solid state is introduced in the cell in excess, then melted and last crystallized again. The excess of crystal is abroaded and the cell closed off.

An example of thermobarogram obtained by increasing the temperature of MBBA is given on Figure 4. As predicted, the melting is ac-

TABLE II

Experimental and calculated data for the slopes out of the transitions α/χ and for the pressure increments at the transformation $(\Delta P)_T$ of the melting and clearing thermobarograms of MBBA.

	α/χ (bars °K^{-1})				$(\Delta P)_T$ (bars)	
	Nematic phase		Isotropic phase			
TRANSITION	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
MELTING THERMOBAROGRAM	12.7	14[a]			1700	900[a]
CLEARING THERMOBAROGRAM	12.7	13[a]	14.4	13[a]	50	90[a]

[a] Middle value for several thermobarograms

companied by a big change of slope and an important increment of pressure. All gases have not been dissolved in the mesogen before the transition, so we don't observe the dilatation of the crystalline phase. If no leak appears, when the pressure increases during the transition, after all the compound is in nematic state, the nematic dilatation is observable. For numerical calculation of $(\Delta P)_T$ are used middle values for the transition datas and for α and χ of the crystalline phase (no numerical data are known) middle values for the solid phases of mesogens respectively 4.10^{-4} °K^{-1} and 4.10^{-10} m^{2}N^{-1}. The calculated pressure increment is then near 1700 bars, value always more elevated than the experimental one (825 bars on Figure 4) (Table II). That difference can be understood by the approximations in the calculation of $(\Delta P)_T$, by the incertitude on numerical datas and also by gases presence in the cell. The experimental slope after the transition agrees with the slope calculated with middle values for α and χ of the nematic phase (respectively 8.6 10^{-4} °K^{-1} and 6.79 10^{-10} m^{2}N^{-1})[4] (Table II). For the three studied compounds, the experimental data of the transition temperature and Clapeyron's slope of the melting are in good agreement with the literature data (Table I). The efficiency of the new barometric method and of the metabolemeter is proved.

IX. SENSITIVITY TESTS

For these studies, the compound is introduced in excess in the cavity in the nematic state; a convex meniscus appears. When closing off the

cell, the mesogen must not get out of the cavity and only little gas quantity must be included in. This conditions are satisfied if the top of the meniscus is a little lower than the upper surface of the joint. The convenient volume that must be introduced in the cell is determined on using a microsquirt (Drummond Scientic C°, Ziptrol), the meniscus height being observed with a microscope (Leitz, Ortholux).

A thermobarogram showing the clearing transition of MBBA is given (Figure 5). Here the cell was closed at a temperature much lower than the transition one. So all gases have been dissolved in the mesogen by the pressure increment due to the nematic dilatation. This last one is then observable and the transition appears later at a pressure superior to the atmospheric one. Extrapolations are necessary to obtain the transition temperature at atmosphere pressure. For MBBA, all the useful thermodynamic data are known. In the calculations are used middle value for the transition data (Table I). For the nematic phase, the middle value for α and χ are respectively 8.3 10^{-4} °K^{-1} and 5.75 10^{-10} m^2N^{-1}.[4] The experimental and calculated slopes out of the transitions are in good agreement (Table II); for $(\Delta P)_T$ (Table II), the difference between the experimental (98 bars on Figure 5) and calculated (50 bars) can be explained by the approximations in the calculations of $(\Delta P)_T$ and by the incertitude on the relative volume change and on the

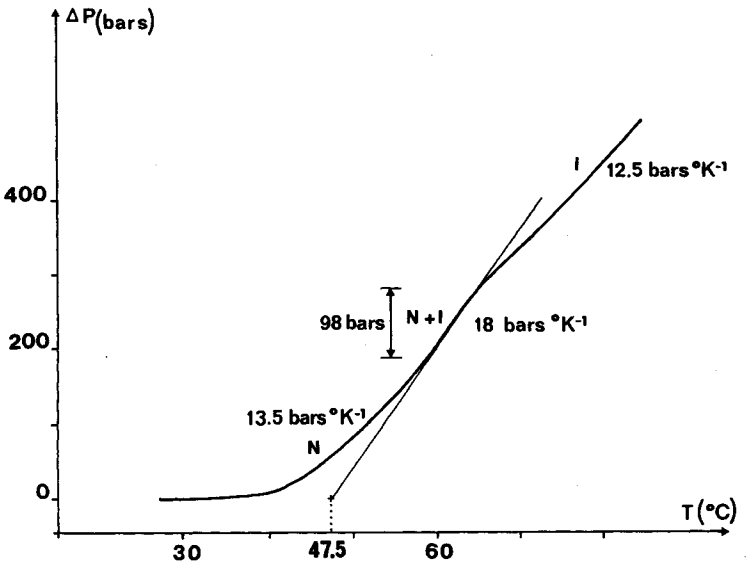

FIGURE 5 Experimental thermobarogram showing the clearing transition of MBBA.

Clapeyron's literature data of the transition temperature at atmospheric pressure and of the Clapeyron's slope are in good agreement (Table I); the new barometric method is then sensitive.

X. CONCLUSION

The quantities of mesogens elaborated by the chemists are generally very small, so many classical methods to detect the phase transitions are not the more convenient. The microscopical observations are sometimes difficult. Another way is to record the variation of an intensive value as a temperature function: the pressure of a sample enclosed in a metallic cell. To test this new barometric method, a metabolemeter was built. The validity of the principle was verified on the melting transitions of the methoxy and ethoxy benzylidene butyl anilines, and of the octylcyanobiphenyl. The obtained thermobarograms show an abrupt change of slope at the phase transformation. For MBBA, the calculated pressure increment is in order of 1.7 k bars and the experimental ones are in average near 900 bars. In these cases, miniaturization is possible. The sensitivity of this method was tested on the nematic-liquid transition of the three compounds. The transition is clearly observable; in average for MBBA, the pressure change at the transformation is near 90 bars for a 0.11% relative volume change. In all the studied cases, there is an agreement between the experimental and literature data of the transition temperature and of the Clapeyron's slope. More, the experimental slopes out of the clearing transition and after the melting transition agree with the one that could be calculated for MBBA.

Numerous uses of the new barometric method and the metabolemeter can be considered. They concern the studies of pure compounds and mixtures exhibiting strong vapor pressure and then of very organized mesophases. These studies are useful for the determination of the temperature existence range of the mesophases and for building the binary phase diagrams.

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