

IMPROVED METHOD FOR DETERMINING THE TEMPERATURE DEPENDENCE OF INTERFACIAL TENSION AT LIQUID CRYSTAL-ISOTROPIC LIQUID INTERFACE

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We report improvements in the static drop shape method used to determine the temperature dependence of interfacial tension at the liquid crystal-isotropic liquid interface. The drop was formed above a capillary tip in glycerol, the density of which was higher than that of the liquid crystal. Images of the steady drop were recorded with a digital capture system that allowed reading up to 2000 points on the drop contour. The data were processed by an improved interpolation technique to trace the drop profile and a specially written program based on the Runge-Kutta integration technique of specific differential equations. As an example, we investigated an alkylcyanobiphenyl in the nematic and isotropic phases at the interface with glycerol. Upon increasing temperature, an upward jump was observed at the nematic-isotropic transition; anomalous temperature dependences were found on both sides of this transition. The results were compared with those in the literature.

Key Words: interfacial tension, liquid crystals, measurements

1. INTRODUCTION

The interfacial tension of liquid crystals in contact with air, liquids, and solids is an important quantity that helps characterize surface phenomena in liquid crystals. The accurate determination of liquid crystal surface tensions has been the topic of many studies [1-6]. However, scarce and rather conflicting experimental data have become available on interfacial tension up to now [7-13].

The aim of our paper is to present improvements of the drop shape method (sessile or pendant) to determine the temperature dependence of the interfacial tension at liquid crystal-isotropic liquid interface, by using computer techniques and automated data processing. This method to determine interfacial tension has some advantages over other methods. Being a static method based on an exact theory and requiring small amounts of liquid, it is particularly well suited for liquid crystals

In the following, the theory underlying the method is outlined using the notations in Figure 1.

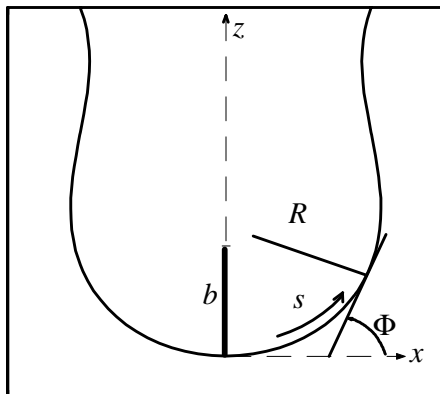


Fig. 1 The profile of a pendant drop

R – radius of curvature at the point (x, z)

Φ - the angle between ox and the tangent to the drop

s – the contour length as measured from the apex

b – the radius of curvature at the drop apex

The Laplace equilibrium condition for a curved surface that separates two media is [14]:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta \rho g z, \quad (1)$$

where γ is the interfacial tension of the two media in contact; R_1 and R_2 are the principal curvature radii of the surface at a point of z coordinate; g is the gravitational constant; and $\Delta \rho = \rho_1 - \rho_2$, with ρ_1 and ρ_2 the densities of the two media.

From the equilibrium condition (1), the profile of a pendant drop can be expressed in a parametric form as:

$$\frac{d\Phi}{ds} = 2 + \beta z - \frac{\sin \Phi}{x} \quad (1)$$

with

$$\beta = - \frac{g \Delta \rho b^2}{\gamma} \quad (2)$$

$$\frac{dx}{ds} = \cos \Phi \quad (3)$$

$$\frac{dz}{ds} = \sin \Phi \quad (4)$$

The system of equations (2-4) links the surface tension to the geometrical dimensions of the drop and is used to calculate the dimensionless parameter β .

The sessile and pendant drop methods were successively improved by increasing point numbers used in calculations and the technique of drop profile determination [15, 16]. The method initially involved the values of two particular diameters of the drop, then yet more diameters were added, but its accuracy was still not good enough because of errors in the first diameter location. Using computer techniques, a large number of readings could be used for describing the drop profile, and the accuracy of the method was thus improved to a value comparable to those of standard methods for surface tension measurement. To automate the method, we used a video camera connected to a computer that digitalized the image of the drop [17–19].

To calculate the theoretical profile of the drop, we integrated equations (2–4) by the Runge-Kutta technique. The interfacial tension was obtained by optimizing the fitting of up to 2000 points of the drop on the theoretical profile. As an example, the interfacial tension between pentylcyanobiphenyl (5CB) in the nematic and isotropic phases and glycerol was investigated and the results were compared with those provided in the literature.

2. EXPERIMENTAL

The measuring method consists in taking images of a steady drop using a digital capture system. The experimental setup for measuring the interfacial tension was schematically represented in Fig. 2. It was made up of two blocks: One was used to capture the image of the drop formed at the end of a steel capillary in communication with the liquid crystal reservoir, and the data processing system. The other contained the temperature measuring and control system.

The liquid drop placed in the thermostatted cell TLC was illuminated by an incandescence lamp LS. The picture of the drop was taken by a digital camera Kodak Model ES 1.0 (KDC) and captured on a computer PC1 that ran a program written at the National Institute of Materials Physics (INFM), Bucharest. The program reads the drop contour co-ordinates and stocks them in a computer file the name of which is the temperature value communicated by computer PC2. Another PC1 computing program, also developed at

INFM, takes over the file and compares the data produced by the first program with the theoretical profile. By fitting, the value $\gamma / \Delta\rho$ is obtained. This value together with the temperature and other parameters of the drop are written in a mixed file. Then, the interfacial tension is obtained by using the temperature dependence of the two liquids, $\Delta\rho(T)$. After completing this operation, computer PC1 opens communication (by COM) with computer PC2 and requests yet another acquisition. The system takes less than 30 seconds to capture and process an image.

The temperature of the cell that includes the liquid crystal drop is measured by the thermocouple TC1, which is linked to the digital thermometer DTM1 (Keithley 2000). Computer PC2 also records the time variation of the temperature.

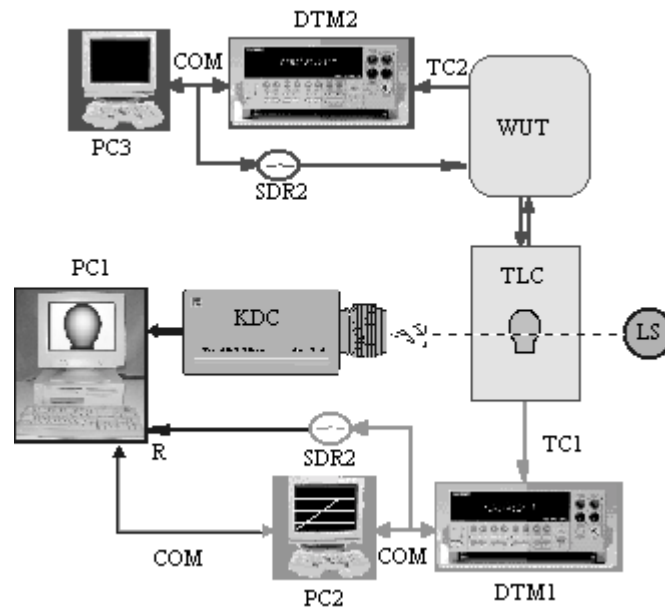


Fig. 2. Setup for interfacial tension measurement. LS-Light Source, TLC-Thermostatted Liquid Cell, WUT-Water Ultra Thermostat, TC1, 2-Thermo Couple, DTM1, 2-Digital Thermometer (Keithley2000), COM-Serial Port, SDR1, 2-Serial Driven Relay, R-re-trigger; PC1, 2, 3-Personal Computers, KDC-Kodak Digital Camera.

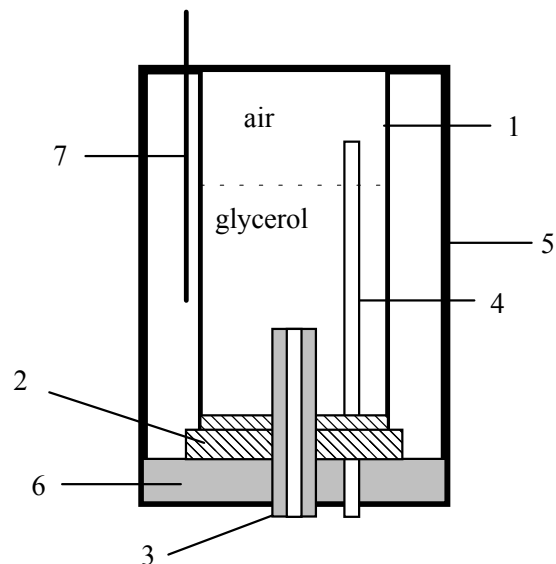


Fig. 3. Interfacial tension measuring cell: 1 – quartz cuvette; 2 – PTFE shutter; 3 – steel capillary tube; 4 – pressure equalizing tube; 5 – sealing device; 6 – PTFE cork; 7 – thermocouple.

The temperature control system includes a water circulating thermostat WUT, a thermocouple TC2, and a digital thermometer DTM2 (Keithley 2000). The latter, besides its temperature measuring role, also commands, via computer PC3, the SDR2 driven relay, which in turn commands the electrical supply of thermostat WUT heater. Linear variations of $0.05^{\circ}\text{C}/\text{min}$ in the transition temperature range and $0.1^{\circ}\text{C}/\text{min}$ out of this range were used. This corresponds to a separation of the experimental points by about 0.02°C and 0.05°C , respectively. The small temperature variations ensure a thermal quasi-equilibrium.

Details on the measuring cell (part of TLC in Fig. 2) are shown in Fig. 3. This component is placed inside a thermostated chamber.

The cell is designed for measuring interfacial tension at the liquid crystal-glycerol interface. A steel capillary, at the end of which the studied drop is formed, is put inside the quartz cuvette (1), well closed by the shutter (2). Since the glycerol density is higher than that of the investigated liquid crystals, the droplets, the profiles of which are determined, are stable only when they are formed over the tip. A pressure equalizing tube (4) is also introduced in the existing air above the glycerol inside the quartz cuvette (1). The quartz cuvette is protected by a sealing device (5) and tightly closed by (6). The temperature is measured by the thermocouple (7).

3. RESULTS AND DISCUSSIONS

As an example, Figure 4 illustrates the interfacial tension for a well-known thermotropic liquid crystal, pentycyanobiphenyl, 5CB, of the homologous series of alkylcyanobiphenyls, in the nematic and isotropic phases at the interface with glycerol. The liquid crystal 5CB (Aldrich, 98% purity) and glycerol (Aldrich, 99.5% purity) were used without additional purification.

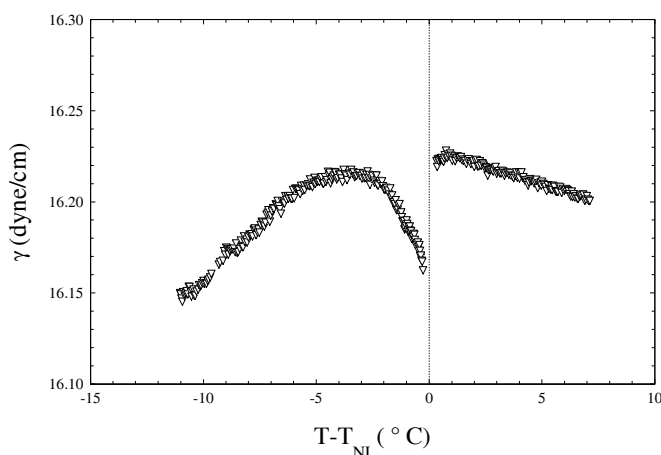


Fig. 4. Temperature dependence of interfacial tension γ , for 5CB/glycerol interface. T_{NI} - nematic to isotropic transition temperature.

Table 1. Temperature dependence of the liquid crystal and glycerol densities (g/cm^3)
T - temperature, T_{NI} - nematic to isotropic transition temperature in degrees Celsius.

Liquid crystal 5CB [2]	Nematic phase	$1.0239 - 1.243 \cdot 10^{-3}(T - T_{NI})$
	Isotropic phase	$1.0214 - 0.886 \cdot 10^{-3}(T - T_{NI})$
Glycerol		$1.2743 - 0.62523 \cdot 10^{-3}T$

As can be seen in equation (1), to calculate the temperature dependence of the interfacial tension, one has to know the temperature dependence of density for both the liquid crystal and glycerol. Table 1 shows the liquid crystal densities in the nematic and isotropic phases, as determined in a previous paper [2], and the glycerol density measured with a dilatometer that is provided with a capillary.

As is well known, the temperature dependence of the liquid crystals differs from that of isotropic liquids. In the latter case, the surface tension decreases with increasing the temperature, while for liquid

crystals, this dependence is much more complex with a possible positive or negative jump at the nematic to isotropic transition temperature. The obtained results for 5CB illustrate such an anomalous behavior. In Fig.4 we notice that at 5CB-glycerol interface, the temperature dependence curve has: a maximum in the nematic phase, an up-jump at nematic to isotropic transition, and a negative slope, except for a small temperature range after the phase transition, in the isotropic phase.

The interfacial tension value ($\gamma = 16.22 \text{ dyne/cm}$) we obtained for 5CB in isotropic phase at the N-I transition is close to that obtained by Tarakhan and Lavrentovici [10] ($\gamma = 16.4 \text{ dyne/cm}$), although they used a photographic method and only 4 points of the drop contour to calculate the interfacial tension. The method presented here was also verified in its pendant drop variant for the liquid-gas interface. For a water-gas interface at 30°C, we obtained $\gamma = 71.21 \text{ dyne/cm}$, which is in good agreement with results in the literature, $\gamma = 71.18 \text{ dyne/cm}$ [20].

4. CONCLUSIONS

The paper gives a detailed account of how we improved the method used for determining the temperature dependence of the interfacial tension of a liquid crystal in contact with an isotropic liquid. The method also makes it possible to monitor the time evolution of interfacial tension at a given temperature. The surface tension values we obtained for a liquid crystal indicated the method had a high degree of accuracy, matching those of standard methods for such measurements.

New data were obtained for the temperature dependence of the interfacial tension of the glycerol/5CB system.

ACKNOWLEDGMENTS

Some of the authors (T. B., I. Z., S. F.) are indebted to the Romanian Ministry of Education and Research for financial support (under CERES Program no. 3-86/2003).

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Received on November 9, 2005