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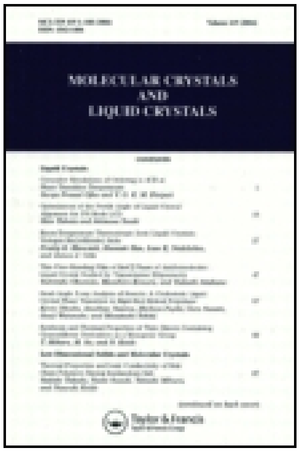

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Surface Phenomena of Liquid Crystalline Substances: Temperature-Dependence of Surface Tension

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Surface Phenomena of Liquid Crystalline Substances: Temperature-Dependence of Surface Tension

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The temperature dependence curve of surface tension has been measured using computer-aided pendant drop method for several low molecular liquid crystalline substances (LCs) near their phase transition temperatures. The results reveal anomalies (positive $(\partial\gamma/\partial T)$-values and discontinues change) in the surface tension vs. temperature curve for all the studied substances, which may indicate the development of highly ordered molecular state in the surface layer in the defined temperature ranges. Furthermore, a sharp decrease of surface tension has been observed for two LCs by approaching their crystallization points from higher temperatures, which seems to suggest that something like surface induced freezing occurs at the liquid surface of those substances by nearing their crystallization temperatures. The resulst are discussed on the basis of statistical thermodynamic models proposed in the literature.

Keywords: Surface tension; temperature dependence of surface tension; anomaly of temperature dependence of surface tension; surface phenomena; liquid crystals

INTRODUCTION

During recently years surface/interfacial phenomena in liquid crystal systems have attracted a great deal of attention, on account not only of their technological importance but also of their interest as a fundamental problem in the statistical mechanics of non-uniform, ordered fluids [1–11].

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However, some basic properties of interfaces, such as the thermodynamic properties of the interfaces and their dependence on temperature, particularly near bulk (first order) phase transitions, and on changes of the interface structure, have not yet been well investigated experimentally, nor been well explained on microscopic theoretical grounds. A study of the free surface may yield information on molecular interactions that are averaged out in the bulk phase, and thus provide invaluable insight into the nature of molecular interactions.

In a preceding paper [12] we have given a brief review on the presently available experimental results on the temperature-dependence of the surface tension of liquid crystalline substances (LCs) and reported our observations about the remarkable time-dependence of the surface tension of freshly formed surfaces of some LCs. After considering several possible mechanisms that may lead to such time-dependence, we have ascribed the observed phenomena mainly to the gas-sorption process taking place at surfaces of LC-liquids. The presence of a certain particular order or structure of molecular organizations, which could be sensitive to the presence of certain gas molecules, at a liquid surface has been suggested to be essential for the occurrence of such a novel surface tension phenomenon. It has been inferred that this time-dependence of the surface tension could have confused the measurement of the early workers and may account partially for the inconsistencies of the results obtained so far.

Despite the inconsistencies existing in the available data of different authors, most of the results revealed the occurrence of anomalies in the surface tension vs. temperature curve ($\gamma(T)$-curve) of LCs (see the references cited in [12]). Such anomalies (e.g. positive or relatively small negative slope in the $\gamma(T)$-curve), if they really exist, would be indicative of a particular structural ordering of molecules in the surface zone of LCs at the liquid-vapor interface and are thus of general theoretical interests. Molecular ordering in the surface zone is likely to occur for the LCs due to the asymmetric field conditions at the interface and the strong anisotropic characters of the LC-molecules, concerning both the geometric shape and the molecular interaction forces.

Due to the liquid character of the LC-mesophases, direct measurement of the temperature dependence of surface tension across bulk phase transitions can be precisely carried out under certain circumstances with LCs, which provides us a novel experimental method to understand the surface behavior at the bulk phase transitions. We report in this paper the results of the temperature dependence of surface tension measured on several low molecular LC-substances, particularly concerning the occurrence of anomalies in their $\gamma(T)$-curves.

EXPERIMENTAL

(A) Measurements

The surface (and interfacial) tension of liquid/fluid-systems was measured using a computer-aided pendant-drop method. The method was developed in our laboratory and has been applied successfully to investigate the time- (in a time order of seconds to hours) and temperature-dependence of a various of liquid/fluid-systems. Its principle has been given in detail elsewhere [13, 14] and outlined in a previous paper [12]. We describe in the following therefore only the measurement procedure concerning the determination of the temperature dependence of the surface tension of LCs with this method.

All of the measurements have been carried out in a measuring chamber from Ramé Hart Inc. (New Jersey, USA). The sample to be measured (liquids or solids) was filled at room temperature into a 1 cm^3 – glass syringe. If the sample was solid at room temperature, the filled syringe was then heated under vacuum above the melting point of the sample to remove gas bubbles in the resulted melts, followed by cooling it under vacuum again to the room temperature. The thus prepared syringe was inserted into a syringe temperature control attachment (Ramé Hart Inc., New Jersey, USA), which was always maintained at the same temperature as the measuring chamber itself to avoid the thermal gradient and to reduce the possible thermal convection of the liquid in the sample tube. All of the measurements have been carried out under the protection of N_2-atmosphere (99.999% pure) to preserve the substances from the possible chemical changes.

After the wanted measurement temperature in both the chamber and the syringe attachment was reached, a fresh drop was formed. Due to the time-dependence of the surface tension of LCs reported before [12], it was impossible to carry out a reliable temperature-dependence measurement with a freshly formed drop before it had reached its steady-state (or equilibrium state). The freshly formed drop had to be annealed at a certain temperature, usually for several hours, before the measurement with it could be began. After the drop came to the equilibrium state at a certain temperature, however, it did not show noticeable time-dependence any more when the measurement temperature was varied. The measurement of the temperature dependence of surface tension could be thereafter carried out with the drop by increasing or decreasing the measuring temperature. To ensure that the recorded surface tension value corresponds its equilibrium value at a given temperature, the drop was let to be annealed for about 20–30 minutes at every measuring temperature before the value of surface tension was determined from the drop image. Efforts were made to record the temperature-dependence of the surface tension with one and the same drop by changing (decreasing or/and increasing) the measuring temperature. Due to the thermal contraction and expansion of the liquid volume along with varying measuring temperature, it was necessary from time to time to control the drop within a stable size through finely turning the screw attached to the piston of the sample syringe. The measurements were repeated several times, each time with newly formed fresh drops.

By calculation of the temperature-dependence of the interfacial tension using the pendant-drop method, the temperature-dependence of the density ($\rho(T)$) of the two fluid phases is required. We have neglected the density of the gas phase (1 atm) in the calculation and determined the $\rho(T)$-curves of the liquid phases (expect for 5CB, for which we used the $\rho(T)$-curve reported by Gannon and Faber [15] in the calculation) using an automated precision capillary mercury dilatometer equipped with a PC for registering data [16]. With a sample size of ca. 0.25 g the $\rho(T)$-measurements can be done with an absolute accuracy of ca. $\pm 1{\cdot}10^{-3}\,\mathrm{g/cm^3}$ and a relative accuracy of ca. $\pm 2{\cdot}10^{-4}\,\mathrm{g/cm^3}$ within a certain $\rho(T)$-curve at different temperatures [17].

(B) Materials

The employed 5CB (4-*n*-pentyl-4′-cyanobiphenyl) sample was purchased from Aldrich Chemical Company Inc. (USA) and had a purity of 98% as given by the manufacturer. The received sample was a nematic liquid at room temperature. EBBA (4′-ethoxybenzylidene-4-*n*-butylaniline) was purchased from TCI (Tokyo Chemical Industry Co., Ltd., Japan), and had a purity > 99% (TCI Guaranteed Reagent). These two samples were used as received without further purification. The other samples were synthesized in our laboratory after the known procedures given in the literature [18]. Their structures and the corresponding designations, which will be used through the following text of the paper, are shown in Figure 1. They were purified using recrystallizations (in Ethanol/H_2O) and through column chromatography.

The phase behaviors of the used substances were determined by DSC (DSC-7 from Perkin-Elmer) and using polarization microscopy (PM-10 ADS, Olympus, Japan) equipped with a heating table (THM 600, Linkam Scientific Instruments, Ltd., Surrey, GB). The results are summarized in Table I.

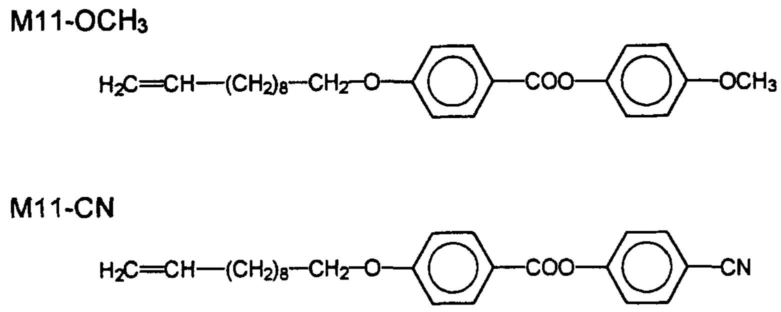

FIGURE 1 Structures and designations of some LC-substances used in this work.

TABLE I Results of Phase Characterization of the Used LC-Substances

Substance	*Phase Characterization*[1]
EBBA	*k* 38°C *n* 79°C *i*
5CB	*k* ? *n* 35.5°C *i*[2]
M11-OCH_3	*k* 70°C (s_A 46°C) *n* 72°C *i*[3]
M11-CN	*k* 74°C *n* 78°C *i*

[1] *k*, s_A, *n* and *i* denote crystalline, smectic A, nematic and isotropic phase, respectively.

[2] The sample of 5CB was received as a nematic liquid.

[3] The smectic phase and the corresponding phase transition tempera ture were detected only by cooling (i.e. the LC-substance is monothermotropic).

RESULTS

The density-temperature-dependence curve ($\rho(T)$-curve) of EBBA, M11-CN and M11-OCH_3 are shown in Figures 2, 3 and 4, respectively. As seen from the figures, the density changes at the phase transition ***n–i*** amount only to about 0.003 to 0.004 g/cm^3 and are thus generally much more small than that occur at melting.

The results of the temperature-dependence of the surface tension ($\gamma(T)$-curve) are shown in Figures 5, 6, 7 and 8 respectively for the studied LC-substances EBBA, 5CB, M11-CN and M11-OCH_3.

For all the measured LC-substances we observed the anomalies near the phase transitions, and for some substances the anomalies appear in the whole nematic phase range studied.

Compared to MBBA (4′-methoxybenzylidene-4-*n*-butylaniline), whose $\gamma(T)$-curve has been measured by Krishnaswamy and Shashidhar [19] using the classic pendant drop method, EBBA has a much lower surface tension in

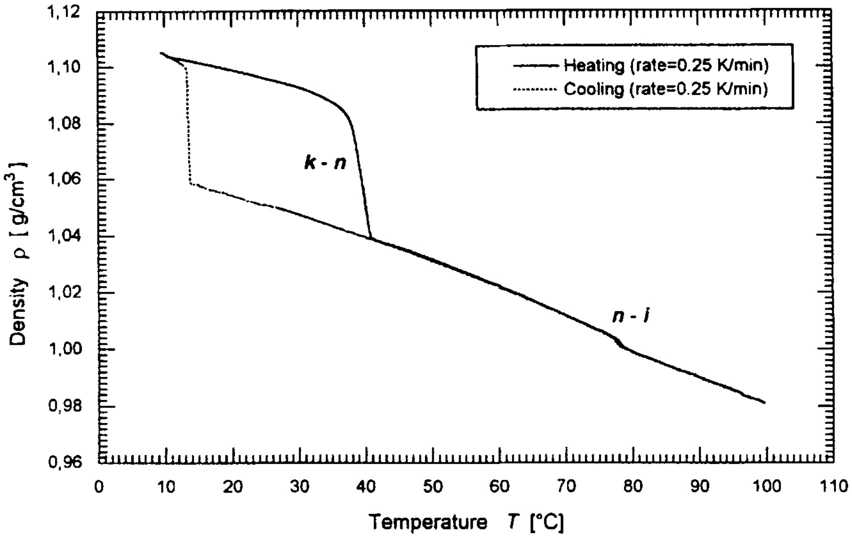

FIGURE 2 Temperature-dependence of density ($\rho(T)$-curve) of EBBA.

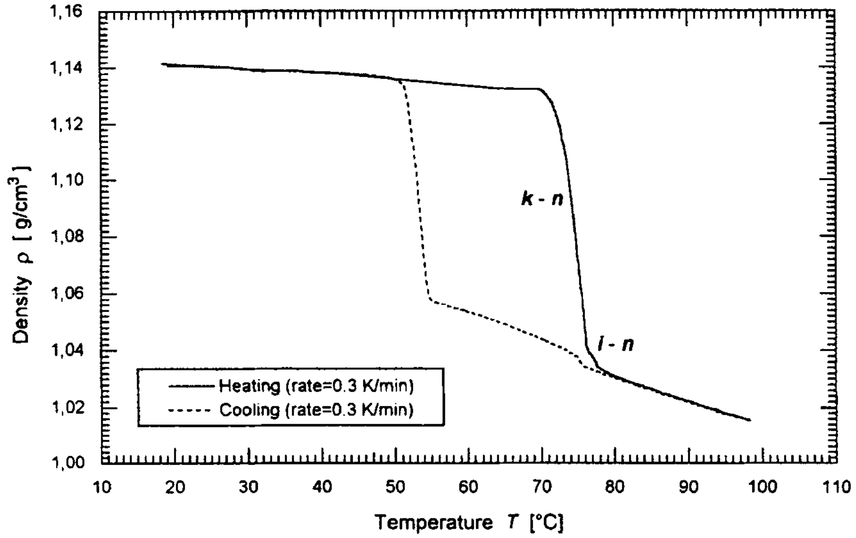

FIGURE 3 Temperature-dependence of density ($\rho(T)$-curve) of M11-CN.

the whole temperature range, which can be closely related to the ethyl-group of the EBBA-molecule. The course of the obtained $\gamma(T)$-curve of EBBA is yet well comparable to that of MBBA, both in the isotropic and in

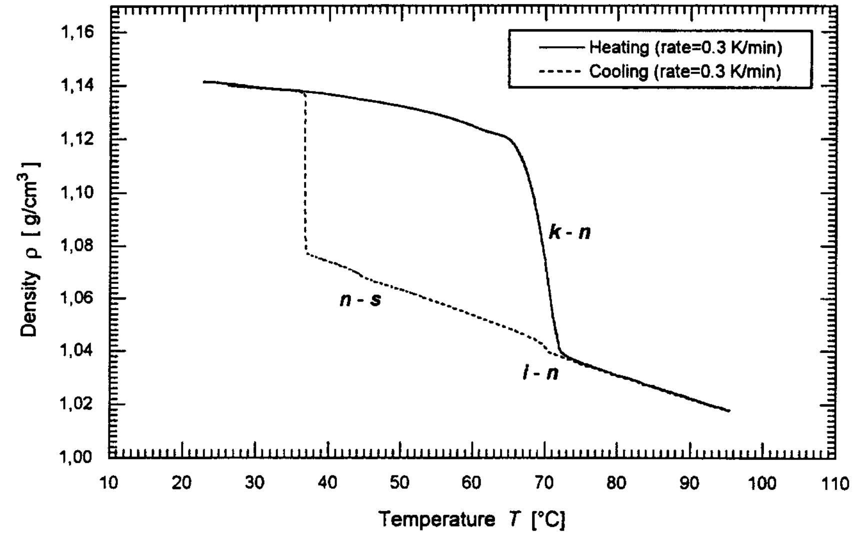

FIGURE 4 Temperature-dependence of density ($\rho(T)$-curve) of M11-OCH_3.

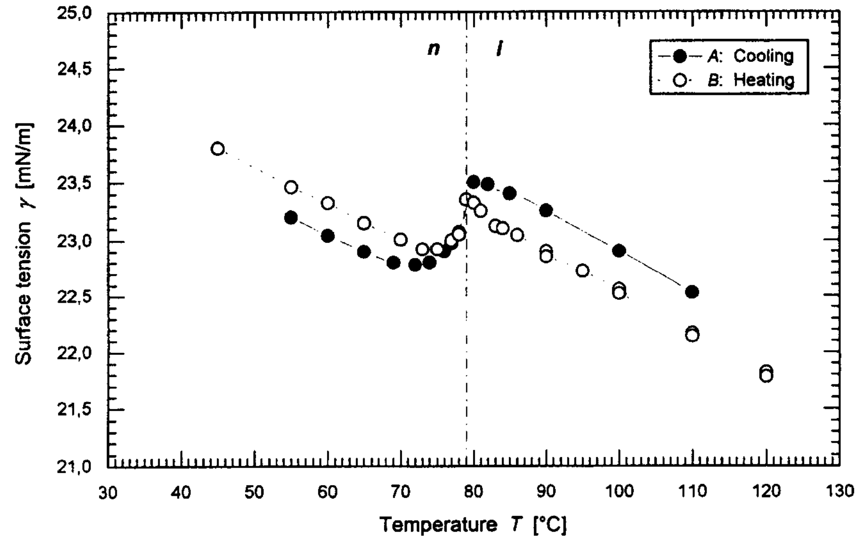

FIGURE 5 Temperature-dependence of the surface tension ($\gamma(T)$-curve) of EBBA.

the nematic phase. However, at the phase transition *n–i* the surface tension seems to change more likely discontinuously, as may be seen from Figure 5, for EBBA, whereas the result of Krishnaswamy and Shashidhar [19] shows a rather continuous, increasing temperature dependence for MBBA.

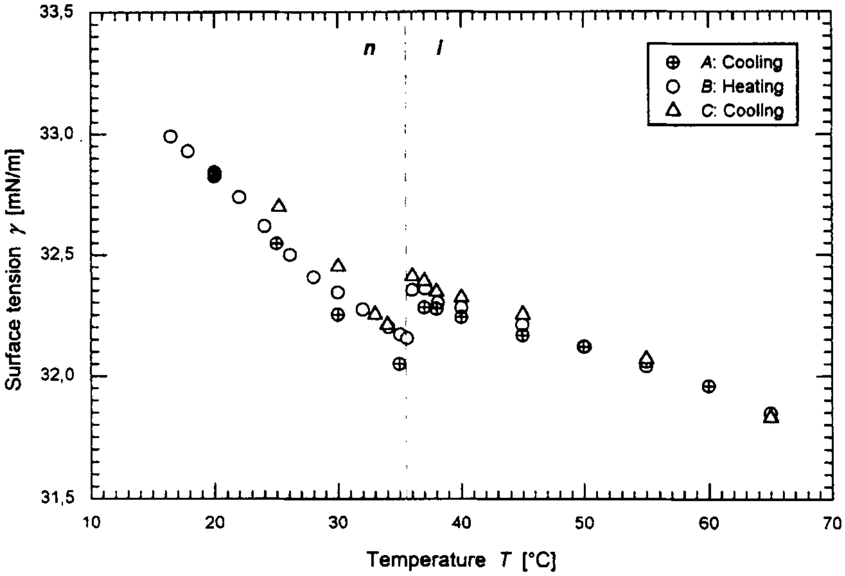

FIGURE 6 Temperature-dependence of the surface tension ($\gamma(T)$-curve) of 5CB.

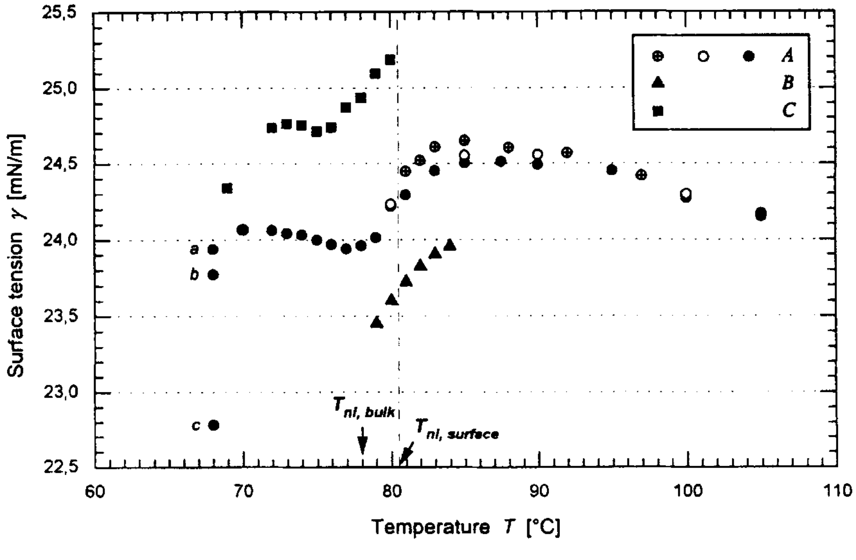

FIGURE 7 Temperature-dependence of the surface tension ($\gamma(T)$-curve) of M11-CN. (Note: *A*, *B* and *C* are three different measurement series and the γ-values of *B* and *C* have been shifted respectively by -0.5 and $+0.8$ mN/m; see text for the explanation of *a*, *b* and *c*).

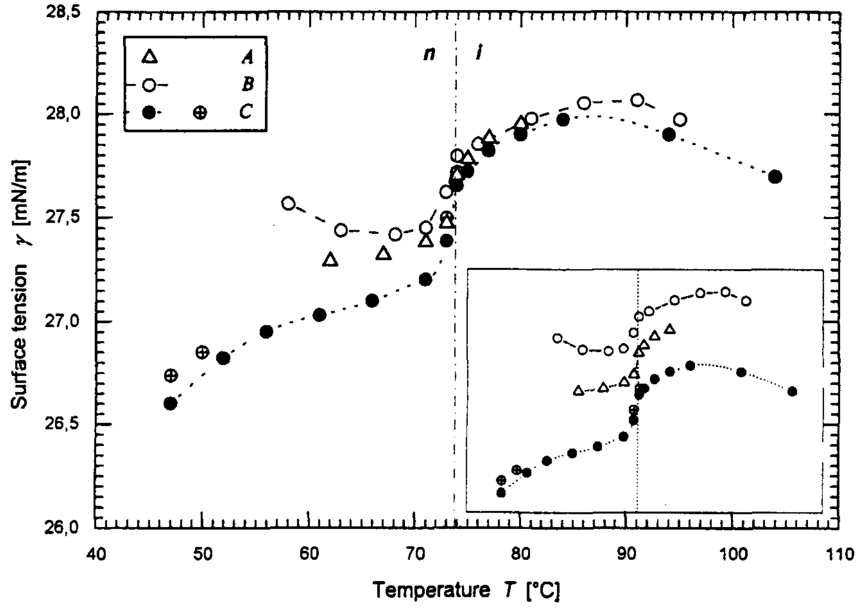

FIGURE 8 Temperature-dependence of the surface tension ($\gamma(T)$-curve) of M11-OCH$_3$ (Note: *A*, *B* and *C* are three different measurement series: the small diagram in the right-bottom corner shows the series again after the γ-values of each series have been shifted for a defined value).

The $\gamma(T)$-curves of 5CB shown in Figure 6 were obtained using two liquid drops. One drop was formed at 60°C. The drop was thereafter cooled (and measured) stepwise to 20°C (curve *A*). After one night annealing at 16°C the drop was heated stepwise to 65°C (curve *B*). The curve *C* in Figure 6 was obtained by using another freshly formed drop. As can be seen from the figure, the curves obtained with different drops, and by heating or cooling, are well comparable, both in their absolute values and in their course. The substance 5CB was found to be quite stable under the measuring conditions. The value of surface tension of a drop at 35°C, for example, was found to fall from 32.12 mN/m to 31.90 mN/m after 64 hours annealing at this temperature. A typical $\gamma(T)$-curve measurement took about 8 hours, so the influence of the surface tension drift on the measurement result may be considered as negligible small, in relation to the available precision of the measuring method employed (ca. ± 0.015 mN/m in this case). To demonstrate the decrease of the surface tension at the phase transition $i \rightarrow n$, we have repeatedly measured the surface tension of a 5CB-liquid drop at two discrete temperatures (just across the ***n–i*** phase transition temperature) several times by heating/cooling the same drop. The results are as follows:

$$35^\circ\text{C}\ (\textit{nematic})\ \gamma = 32.32\ \text{mN/m} \rightarrow 36^\circ\text{C}\ (\textit{isotropic})\ \gamma = 32.45\ \text{mN/m} \rightarrow$$

$$35^\circ\text{C}\ (\textit{nematic})\ \gamma = 32.23\ \text{mN/m} \rightarrow 36^\circ\text{C}\ (\textit{isotropic})\ \gamma = 32.41\ \text{mN/m}$$

The change of the surface tension between these two temperatures (across the phase transition) amounts to ca. 0.15 to 0.2 mN/m.

The temperature dependence of the surface tension of 5CB has been studied by Gannon and Faber [15] using the Wilhelmy-plate method and by Krishnaswamy [20] with the classic pendant-drop method (i.e. the surface tension was calculated with the classic selected-plane method). The result obtained by Krishnaswamy later was in excellent coincidence with that of Gannon and Faber, both in view of the absolute value of surface tension and of the whole $\gamma(T)$-curve course. However, the results of our measurement reveal a much higher absolute value for the surface tension of 5CB in the whole studied temperature range. For example, the γ-values at 30°C fall between 28.1 and 28.3 mN/m from their measurements, whereas the present work yields a value of 32.3 mN/m. This difference can not be explained alone from the aspect of the absolute accuracy of the measuring methods involved, since the absolute accuracy is estimated to be 1% (for the methods used by Gannon, Faber and Krishnaswamy) or better (for the present work). By comparison, for the same substance at room temperature (22 to 23°C), Dubois *et al.* [21] and Proust *et al.* [22] measured a value of 30 mN/m and 40 ± 1 mN/m, respectively by using the Wilhelmy-plate method. As pointed out above, the sample of 5CB was received as a nematic liquid, which must have been already saturated with air. As an exception among the LCs studied by us no remarkable time-dependence of the surface tension could be observed on the freshly formed drops of this sample as reported in our preceding paper [12]. The time-dependence could here not be the cause of this difference (unless the surface tension would increase with sorption of air). Although the sample used for the present work has nearly the same clearing temperature (ca. 35.5°C) as that used by Gannon and Faber, it may be still likely that such a difference could be caused by the different purity of samples used. A further study using carefully prepared substance will be necessary to explain this difference.

The $\gamma(T)$-curves reported by the former authors show a distinct jump at the phase transition ***n→i***, whose extent (about 0.3 to 0.4 mN/m) was yet comparable with that observed in this study (ca. 0.2 mN/m). Nevertheless the occurrence of the positive slope in the $\gamma(T)$-curve in the whole nematic phase as found by the former authors could not be observed by the present work. In contrast the $\gamma(T)$-curves shown in Figure 6 have negative slopes with values of ca. -0.04 mN/m pro degree.

The results shown in Figure 7 for M11-CN were obtained with three different drops. To make the figure more obviously, the values of the measurement series *B* and *C* in the figure have been shifted in the γ-axis respectively by -0.5 and $+0.8$ mN/m. The measurement series *A* was obtained with a drop, which was freshly formed at 84°C. The drop was then annealed for about 9 hours at the temperature, then cooled to 81°C and stayed overnight at this temperature. The surface tension values were recorded at the second day by heating the drop stepwise to 105°C (see the values in the figure represented by the symbol ⊕). The drop was then stepwise cooled to 68°C (just before the crystallization temperature of the substance), the thereby recorded surface tension values were represented by the symbol ● in the figure. In order to check the reproducibility of the surface tension values, the drop was thereafter heated stepwise again to 100°C (see the values represented by the symbol ○). The measurement series *B* and *C* around the phase transition ***n–i*** were obtained with another two different drops and determined by cooling. In the figure we have also shown the clearing temperature of the substance determined by DSC and polarization microscope (denoted by $T_{ni,\,bulk}$) and the ***n–i*** phase tansition temperature determined through the observation of the morphology changes taking place at the drop surface (denoted by $T_{ni,\,surface}$).

As seen from the figure, the $\gamma(T)$-curves of this substance show distinctly the anomalies in a relative wide temperature range (ca. 7K) around the phase transition ***n–i***. The change of the surface tension at the phase transition ***n–i*** is rather continuous than abrupt. Furthermore the substance reveals in the temperature range above the clearing temperature very small $(-d\gamma/dT)$-values (ca. -0.01 (mN/m)/K) near the phase transition and ca. -0.035 (mN/m)/K far above it). In the nematic phase the $\gamma(T)$-curve exhibits at first a very small negative slope (ca. -0.01 to -0.005 (mN/m)/K) and by approaching the crystallization point of the substance the surface tension began to decrease again by further decreasing temperature. The values marked by *a*, *b* and *c* in the measurement series *A* in Figure 7 were determined from the liquid drop images respectively 8, 4 and 1.5 minutes before the drop crystallized. It is remarkable that the surface tension falls sharply just before the crystallization. Doubts may arise about the validity of these values determined just before the drop crystallized. However, the crystallization was found to be a process with a time order of several seconds in this case. Just before the crystallization began, the drop was totally in a fluid state (see

Fig. 9) and all the drop profiles extracted form the drop image fulfilled the Laplace-Young's equation very well [17]. So the values calculated from these drop profiles should represent the real, instantaneous surface tension of the drop at these moments (or states), although these states seemed to be thermodynamically unstable.

Another remarkable point on this substance is the difference between its bulk clearing temperature ($T_{ni,bulk}$), as determined by DSC and polarization microscope, and its surface ***n–i*** phase transition temperature ($T_{ni,\,surface}$) as

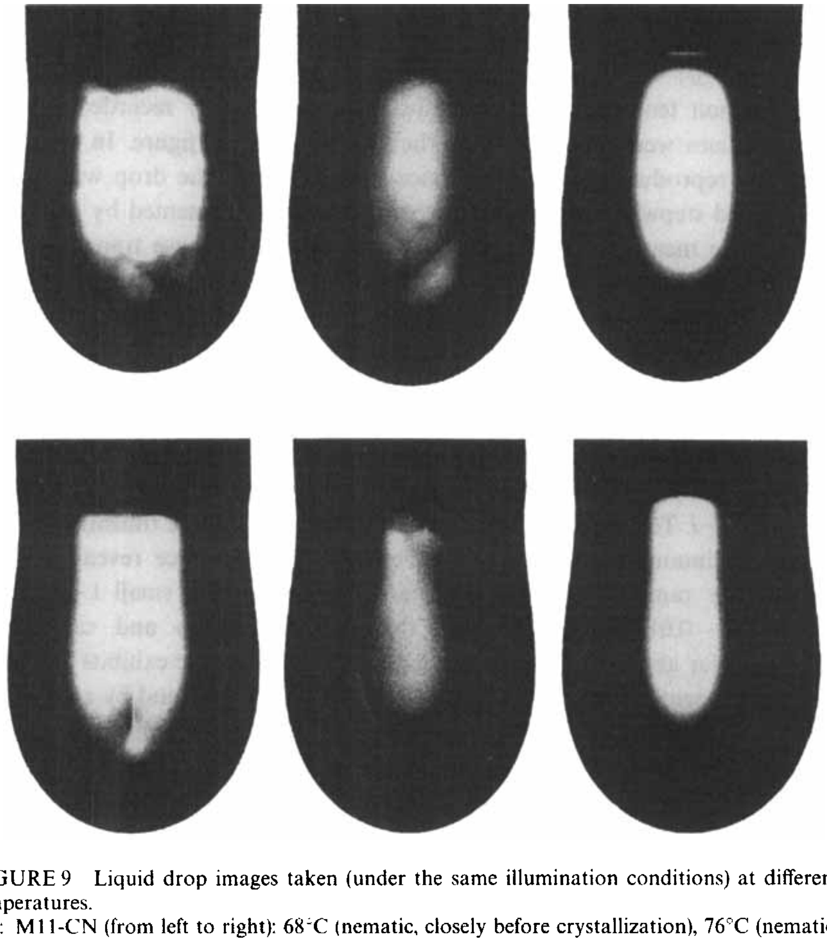

FIGURE 9 Liquid drop images taken (under the same illumination conditions) at different temperatures.
top: M11-CN (from left to right): 68°C (nematic, closely before crystallization), 76°C (nematic) and 85°C (isotropic).
bottom: M11-OCH$_3$ (from left to right): 47°C (nematic, ca. 5 minutes before crystallization), 50°C (nematic) and 74°C (isotropic).

determined by the direct observation of the liquid drop surface during the measurement. $T_{ni,\,surface}$ was found to be about 1.5 to 2 K higher than $T_{ni,\,bulk}$. Such a phenomenon was nevertheless not observed by the substances of EBBA and 5CB.

The values shown in Figure 8 for M11-OCH$_3$ were obtained from one and the same liquid drop. After the freshly formed drop was annealed to reach its equilibrium state, the measurement series *A* was firstly recorded (by heating). After annealing the drop at 58°C overnight, the measurement series *B* was obtained by heating the drop stepwise to 95°C. The drop was then cooled and annealed again at 58°C overnight. On the second day the drop was at first cooled further to 47°C, and by heating it stepwise to 104°C the measurement series *C* was recorded. The drop was cooled thereafter rapidly at first to 74°C and subsequently stepwise to 47°C. During this cooling procedure the values represented by the symbol ⊕ of the measurement series *C* were recorded. Only after annealing the drop at this temperature (47°C) for ca. 40 minutes it began to crystallize. The values of the surface tension at 47°C were measured from drop profiles extracted about 20 and 10 minutes before the crystallization happened. They were found yet to be quite stable, i.e. nearly independent of the annealing time at this temperature (cf. Fig. 9).

Similarly to M11-CN, the $\gamma(T)$-curve of M11-OCH$_3$ shows in a relative wide temperature range the anomalies. The surface tension values in the isotropic phase were found to be much more repoducible than in the nematic phase. In the latter phase not only the absolute values of the surface tension but also the course of the $\gamma(T)$-curve revealed to change from measurement series to series. They seemed to be sample-history dependent. The surface tension values obtained by measurement series *B* and *C* show an increasing dependence function of temperature in the nematic phase as well.

Analogously to M11-CN, the ***n–i*** phase transition temperature at the drop surface ($T_{ni,\,surface} = 73.8$°C) of M11-OCH$_3$ was found to be located about 1.8 K higher than that in the bulk phase ($T_{ni,\,bulk} = 72.0$°C).

DISCUSSION

It is certainly of general theoretical interest to explain the appearance of such anomalies by LC-substances or, carefully expressed, to discuss the reasonableness and underlying grounds of such phenomena theoretically. Thermodynamically the slope of a $\gamma(T)$-curve, $\partial\gamma/\partial T$, for a pure liquid-vapor system is, when the vapor pressure is comparatively low, related to its surface excess entropy, ΔS^s, and to the absorption of heat by surface formation, ΔQ^s, by the following thermodynamic expressions: [23]

$$\Delta S^s = -\frac{\partial\gamma}{\partial T}, \quad \Delta Q^s = -T\cdot\frac{\partial\gamma}{\partial T}.$$

For the most ordinary liquids the molecules at the surface, due to spatial delocalization across the liquid/vapor-transition zone, are less ordered than those in the bulk phase, i.e. $\Delta S^s > 0$, and extension of the surface is therefore in general associated with an absorption of heat. The $\gamma(T)$-curve of such liquids has a negative slope in the nearly whole temperature range as described by the following relation proposed by Eötvös: [24]

$$\gamma V^{2/3} = k(T_c - T),$$

where V is the molar volume of the substance in the liquid bulk phase, T_c is the critical temperature and k is a constant (Eötvös constant). The surface tension approaches to zero by nearing the critical temperature as described by $\gamma(T) \sim (T_c - T)^\mu$ with $\mu = 1.28 \pm 0.06$ [25]. The appearance of local maximums or curve segments with positive slope in the $\gamma(T)$-curves of LC-substances near phase transitions indicates, however, that the surface of these LCs must have negative ΔS^s -values in the corresponding temperature ranges. It must be, therefore, suggested that a certain molecular arrangement or organization occurs at the surface so that the surface molecules are *relatively* more ordered than their counterparts in the corresponding bulk phases in those defined temperature ranges. It may be stressed here that the positive slopes in the $\gamma(T)$-curves depend only upon the *relative* values of the surface and the bulk phase entropy (or ordering), not on their absolute values.

Since the experimental observation of such anomalies in the LC-substances (see references cited in [12]) many suggestions have been given to explain such an apparent more ordered organization of molecules in the surface layer. Jaeger [26] and Wolf [27] have suggested, for example, that the observed phenomena may be ascribed to the formation of molecular associations in the surface layer. Tamamushi [28] pointed out that a certain molecular orientation of higher order – something like "surface smectic structure" – should take place at the free surface of liquid crystals when their anisotropic melts transform into isotropic liquids.

During the recent years many theoretical efforts have been made, based on the basis of the statistical thermodynamic models [2, 4, 5, 9, 29, 30] and of the phenomenological Landau theory [1, 15], to interpret those anomalies observed in the $\gamma(T)$-curves of LCs. Most of the attentions so far have been nevertheless only paid to account for the anomalies just near the phase transition ***n–i***.

Croxton and Chandrasekhar [29, 30] discussed these phenomena based on statistical thermodynamics using an local effective order parameter, which is determined as a competition between the spatial disorder which develops at the liquid surface and the orientational order, which is to be expected (particularly for molecules having anisotropic shape forms) due to the development of a surface field that may impress an orienting torque on the surface molecules. The former effect serves to diminish the local order, whilst the latter will enhance it. Just beyond the crystal-nematic (melting) point (T_m), the spatial delocalisation may be sufficiently low and the surface orientational field correspondingly high such that the local effective order at the liquid surface may be higher than in its bulk for a limited temperature range just above T_m, which will lead to the positive slope in the $\gamma(T)$-curves immediately after the melting transition (see Fig. 10). As temperature rises the increasing spatial delocalisation of the surface and the corresponding relaxation of the surface field diminish the surface local order much more strongly than its bulk value decreases. The molecules at the surface are now relatively less ordered than in the bulk and the $\gamma(T)$-curves show the usual monotonic decreasing function of temperature. At the nematic-isotropic transition temperature the bulk order parameter will change discontinuously (first order transition) from a certain value to 0, whereas the weak surface field may be able to establish a small residuum of orientational order at the isotropic liquid surface over a short thermal range. In such a case, a discontinuous change of the absolute surface tension value and/or a second positive region in the $\gamma(T)$-curves may be observed (cf. Fig. 10).

The considerations made by Croxton and Chandrasekhar seem to be, at least phenomenally, reasonable. At the time these considerations were made most of the features suggested by them have been observed experimentally. However the appearance of positive slope in the $\gamma(T)$-curve just above the melting transition (the so-called "inversion temperature") seemed to be only observed by liquid metal system [30–33] at that time. The $\gamma(T)$-curves shown in Figures 7 and 8 reveal that such anomalies may occur also by organic substances near the crystallization temperature. However, these considerations seem to be not sufficient enough to interpret the pre-transitional positive ($\partial\gamma/\partial T$)-values, which appear in the $\gamma(T)$-curve of some LCs well before T_{ni} (cf. Fig. 8), although they have proposed a second possibility, trying to embrace this phenomenon in their considerations [29]. For those LC-substances it seems that the surface induced ordering of molecules in the surface layer becomes so strong that it not only offset the disorder due to the spatial

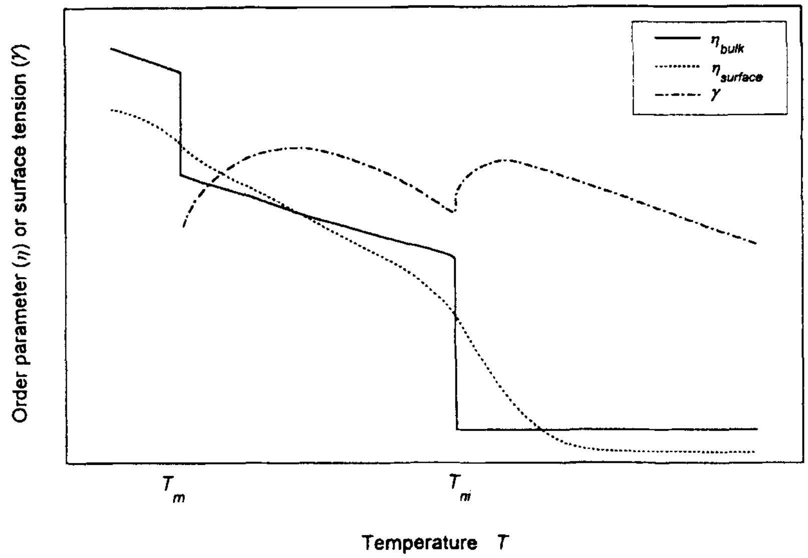

FIGURE 10 Schematic variation of the effective order parameter and the surface tension of a liquid crystal across phase transitions (according to [29]).

delocalisation but cause the molecules in the surface layer to be arranged more orderly than the molecules in the bulk phase as well, even in nematic phase.

Telo da Gama [4] has tried to interpret the experimentally observed $\gamma(T)$-characteristics of the liquid-vapor surface of LC-substances using a microscopic statistical-mechanical model. According to this model, the characteristic of the $\gamma(T)$-curve of a LC-substance near the phase transition is closely related to the structure of the liquid-vapor interface at the nematic-isotropic transition and the wetting behavior of a system of three fluid phases (i.e. nematic, isotropic liquid and the vapor phase) in equilibrium. The model predicates a discontinuous gap of the surface tension at the phase transition ***n–i***. Depending on the situation whether a nematic wetting of the isotropic-vapor interface or an isotropic wetting of the nematic-vapor interface presents at the surface near T_{ni}, the gap can be positive or negative. However, its largest possible magnitude is limited to the interfacial tension between the nematic and isotropic phase, γ_{NI}, at the triple point temperature for any LC-vapor systems as suggested by Gama [4, 5]. γ_{NI} is believed to be in order of 10^{-2} mN/m [34, 35], which is one order smaller than the surface tension gaps (0.1 to 0.4 mN/m) observed experimentally so far for most of the LCs studied. Telo da Gama ascribed this discrepancy to experimental errors [4]. The uncertainty by the direct measurement of the surface tension gap at ***n–i*** transition lies in the fact that the phase transition takes place in a more or less diffuse manner respecting to the time scale involved in the surface tension determination, and the measurements can thus only be made at two discrete temperatures across T_{ni}, which must lie at least 0.1K away from the triple point to ensure the liquid at one temperature is completely nematic and at the other isotropic. Since the magnitude of $\partial\gamma/\partial T$-value near T_{ni} is rather large, the surface tension gap determined as the difference of the values measured at these two discrete temperatures may be overestimated largely. The model was later refined by Tjipto-Margo *et al.* [5] and the refined model can be used to interpret the non-monotonic variation (i.e. positive $(\partial\gamma/\partial T)$) of the surface tension vs. temperature near the phase transition above T_{ni}, just as a consequence of the approach to complete nematic wetting. The model is yet also insufficient to explain the positive $(\partial\gamma/\partial T)$-values appeared in the nematic phase (cf. Figs. 7 and 8).

The unusual phenomenon, that the surface tension decreases with decreasing temperature below T_{ni}, seems to be more often observed for the LC-substances, which have a low temperature higher ordered meosphase (e.g. smectic phase, crystalline phase), located not very away from T_{ni} [36]. Among the four studied LCs, the melting points of the substances M11-CN and M11-OCH_3 are only some degrees away from T_{ni} (cf. Tab. I), and the latter substance has a low-temperature smectic phase as well. In comparison the melting points of EBBA and 5CB ($T_m \approx 20$°C) are far below their T_{ni}. It seems thus the existence of a nearby low-temperature high-ordered phase will induce or favorite the formation of a high-ordered molecular layer at the surface, which agrees well with the recent experimental evidences obtained through the direct measurement of the molecular order at the liquid surface using X-ray reflectivity. Those experiments indicate that high-ordered or "smectic-like" layer structures [37–42] may exist in the surface layer, and be maintained even in a temperature range high above their clearing points [42], which seems to be true particularly for those LC-substances, which have low-temperature smectic phases [37, 38, 42]. The observed higher T_{ni}-values at the drop surface of these two substances may be also an indication of such an enhancement in the molecular ordering at the surface.

The values determined for M11-CN from the liquid drop just before the crystallization (see values marked as *a*, *b* and *c* in Fig. 7) do not represent the equilibrium value at this temperature, since the drop was not in a thermodynamic stable state. However these values may reflect the true surface tension values at these thermodynamic non-stable states. Because, as pointed out above, the drop images, from which these values were calculated, were still in liquid state and their profiles fulfilled the Laplace-Young equation very well (cf. Fig. 9). In certain sense they may be considered as the "dynamic" surface tensions just before the crystallization happened. The sharply decreasing trend of the surface tension near the crystallization point (T_k) suggests that the molecules at the surface were induced to be highly-ordered as approaching T_k and the crystallization process might originate at the liquid surface layer, i.e. the so-called surface freezing [43] occurred at the liquid drops of these substances, as may be morphologically observed at the liquid drop surfaces just before the crystallization took place (see Fig. 9).

The result shown in Figure 8 indicates that the course of the $\gamma(T)$-curve in the nematic phase was less reproducible than in the isotropic phase, and seems to be sample-history-dependent, which may explain the difference between the $\gamma(T)$-curve of 5CB obtained in this study and by the former authors [15, 20]. A plausible explanation of this less reproducibility may lie in the possibility that for this substance there may exist several meta-stable states in the nematic phase, and the different $\gamma(T)$-courses in the nematic phase may reflect these different states. Such a phenomenon has been also observed recently by us for some other substances, the results of which will be published later.

CONCLUSIONS

We have reported the surface tension vs. temperature dependence curve of several low molecular liquid crystalline substances near their phase transition temperatures, measured by the computer-aided pendant drop method. For all the studied substances anomalies in the $\gamma(T)$-curve were observed, which may indicate the existence of highly ordered molecular state in the surface layer in the defined temperature ranges. Unusually, a sharp decrease of surface tension has been observed for two LCs (M11-CN and M11-OCH_3) as their crystallization points were approached from higher temperatures, which seems to suggest the occurrence of surface induced freezing at these liquid surfaces. The results have been discussed on the basis of statistical thermodynamic models currently proposed in the literature. More experimental as well as theoretical studies are necessary to clarify the novel surface phenomena involved in the liquid-vapor systems of LC-substances, which may reveal much important information regarding the nature of the intermolecular interactions, ordering of the molecules in the surface, etc. of the LCs.

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