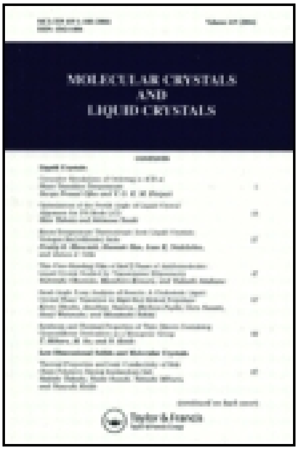

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Surface Phenomena of Liquid Crystalline Substances: -Time Dependence of Surface Tension-

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Surface Phenomena of Liquid Crystalline Substances

-Time Dependance of Surface Tension-

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The presently available experimental results on the measurement of the surface tension of liquid crystals have been shortly reviewed. They are inconsistent either in view of the temperature-dependence behavior of the surface tension near the phase transition temperatures or with respect to the absolute values of the surface tension. As one of our papers to report the results obtained in our laboratory on the investigation of the interfacial phenomena of liquid crystalline substances, we reported in this first paper the remarkable time-dependence of the surface tension of a freshly formed surface, observed on several liquid crystalline substances, both of low molecular and polymeric, both in the mesophase and in the isotropic phase. After discussed several possible processes, which may lead to a time-dependence of the surface tension of a freshly formed liquid surface, we suppose that the gas sorption process taking place at the liquid surfaces may be mainly responsible for this unusual time-behavior. It has been further suggested in the paper that such a remarkable time-dependence may occur on a liquid surface where the molecules are relatively highly ordered or have some particular structures and such ordering or structures will be influenced sensitively by the presence of certain gas molecules, perhaps either as a result of the interaction between the gas molecules and the molecules at the liquid surface or as a consequence of the gas-induced re-organization of the molecules in the liquid surface region. It is inferred that such time-dependence phenomena may have confused the measurements of the surface tension of liquid crystalline substances performed by the early workers and may have contributed to some of the inconsistencies in the obtained results so far.

Keywords: Review; surface tension; liquid crystals; temperature and time dependence

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INTRODUCTION

Surface phenomena in liquid crystal systems have attracted a great deal of attention recently, on account not only of their technological importance but also of their interest as a fundamental problem in the statistical mechanics of no-uniform, ordered fluids [1–11]. 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 liquid crystal-liquid crystal interactions. Anchoring phenomena [12, 13], which concern the alignment of a liquid crystal by a substrate or on its free surface, are in particular crucial in the fabrication of display devices. Many basic properties of interfaces, such as the excess interfacial free energy (interfacial or surface tension) and excess surface entropy as well as their relationships to the variation of the interface structure and to the temperature, have, nevertheless, not yet been well either experimentally investigated or explained on microscopic theoretical grounds.

Recently we have carried out a series of measurements on the surface tension of liquid crystals (LCs), both of low molecular and polymeric. The aim of our work is to reveal the specific characters of the molecular organizations in the surface of LCs through the measurement of the temperature- and time-dependence of their surface tensions. During the work we have observed many interesting behaviors of the surface tension of LCs. In the present paper we will report the observed novel time-dependence of the surface tension on LCs. Other results will be published in the forth coming papers.

The paper is organized as follows. First, to demonstrate the inconsistency of the presently available results, a brief review of prior studies on the measurement of surface tension of LCs will be given. This is followed by the measurements we have carried out on studying the time-dependence of the surface tension of several LCs. The observed phenomena are then discussed to reveal the possible underlying grounds, and is supposed to be at least partially responsible for the inconsistency of the presently available results on the surface tension of LCs.

A BRIEF REVIEW

In the past years the surface tension (γ) of some low molecular LC-substances has been studied using a variety of techniques. Most of the attentions have been paid to the behavior of the surface tension change at the phase transitions nematic-isotropic, smectic-isotropic and cholesteric-isotropic.

The results obtained so far are inconsistent in several respects. Whilst some workers have found the temperature dependence of the surface tension ($\gamma(T)$-curve) of the LCs to be normal (in the sense that the slope of a $\gamma(T)$-curve $d\gamma/dT$ is negative and nearly constant throughout a wide temperature range), many others have found that the temperature dependence of the surface tension of LCs are peculiar, just around the clearing point of a LC-substance $d\gamma/dT$ can be positive and there may even exist a discontinuous change of the surface tension at the phase transition temperatures. These unusual characters are often referred to the so-called "anomaly" of the surface tension behavior of the LC-substances. Many of the measurements have also revealed that the negative value of $d\gamma/dT$ is larger in the mesophases than in the corresponding isotropic phase on $\gamma(T)$-curves of the LCs. Another inconsistency, which has so far not got so much attention as the discussion about the existence or reality of the anomalies, may be the remarkable differences that are often to be noticed between the absolute values of the surface tension of LC-substances, obtained by different workers using different techniques. They seem to us not to be explainable alone from the aspect of the measurement errors. To make these discrepancies more clearly, we want at first to briefly review on the measurements of the surface tension of LCs. Certainly such a review will be limited to our knowledge. An earlier short review on this subject is available in [14].

The measurement on the temperature dependence of the surface tension ($\gamma(T)$-curve) of LCs began with the works of Schenck [15] and Jaeger [16]. In 1917 by using the maximum bubble pressure method Jaeger [16] had, with special interest in the determination of the magnitude of the Eötvös constant, measured the $\gamma(T)$-curves of five LCs: *p*-azoxyanisole (PAA), *p*-azoxyphenetole (PAP), *p*-anisaldazine, ethyl *p*-azoxybenzoate and ethyl *p*-ethoxybenzalamino-α-methylcinnamate. For all the substances he measured the obtained γ (T)-curves (see Fig. 1) had always larger negative slopes in the anisotropic phase than those in the corresponding isotropic phase and shown more or less sharp maximums just near the phase transitions. In 1938 Ferguson and Kennedy [17] repeated the measurements of Jaeger for three (PAA, PAP and *p*-anisaldazine) of the five substances by using a modified capillary rise method and confirmed the results of Jaeger. They found that the $\gamma(T)$-curves of those substances had a van der Waals form near the clearing point and shown exceptionally positive slopes near the phase transitions. Ferguson [18] later called attention to the fact that this behavior demands further investigation.

In 1947 Schwartz and Moseley [19] measured the $\gamma(T)$-curves of three LC-substances (PAA, PAP and ethyl *p*-azoxybenzoate) using a du Noüy-ring

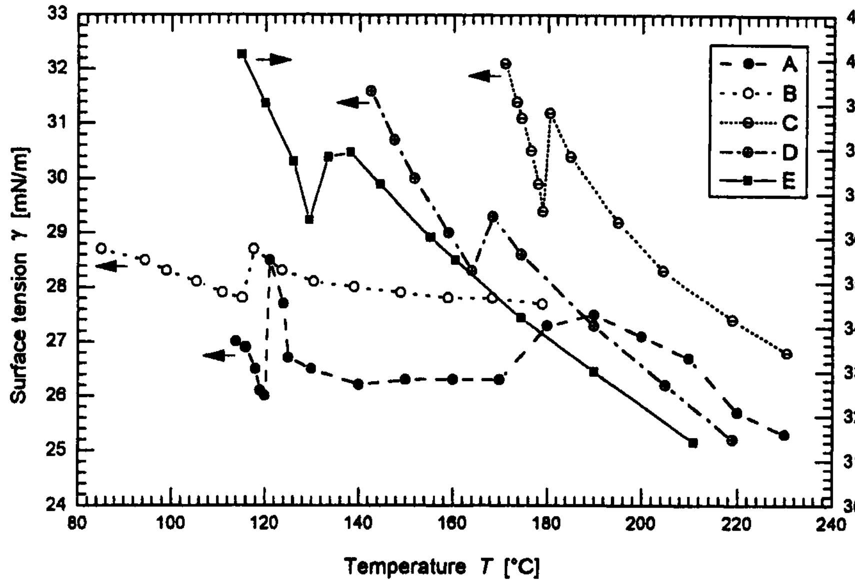

FIGURE 1 Temperature-dependence of the surface tension of LCs after Jaeger [16].
A–Ethyl *p*-azoxybenzoate (*k* 114°C *s* 121°C *i*)
B–Ethyl *p*-ethoxybenzalamino-α-methyl-cinnamate (*k* 95°C *n* 118°C *i*)
C–*p*-Anisaldazine (*k* 169°C *n* 180°C *i*)
D–*p*-Aazoxyphenetole (PAP) (*k* 138°C *n* 168°C *i*)
E–*p*-Azoxyanisole (PAA) (*k* 114°C *n* 135°C *i*).

tensionmeter. In opposition to Jaeger and Ferguson and Kennedy they found no unusual by the $\gamma(T)$-curves of these three LC-substances near their phase transitions. The sole distinguishing mark they could find was that the surface tension of these substances seems to stay constant just near the phase transition (see curve D in Fig. 2). They meant that the observed anomalies by the former investigators may probably be due to the use of non-equilibrium values, owing perhaps to superheating, and referred the importance of the time factor that could affect the determination of the surface tension of these substances. Similar results were obtained by Gorskii and Sakevich [20] as well.

The measurement on the $\gamma(T)$-curve of PAA was also repeated by Neumann *et al.* [21, 22]. By using a modified Wihelmy-plate method, which allowed the $\gamma(T)$-curve of a liquid to be registered continuously within a certain temperature range, they found that the behavior of the surface tension vs. temperature near the phase transition nematic-isotropic is very sensitive to the purity of substance employed for the measurement. Whereas the $\gamma(T)$-curve of a highly purified PAA-sample shows the similar anomaly behavior as observed by Jaeger and Ferguson and Kennedy, the one obtained from a relatively less purified PAA-sample has a rather normal course. Moreover they also noticed that the surface tension of the less purified PAA-sample changed with time over a period of several hours under a constant temperature, which was supposed by these authors to be caused by the strong adsorption of impurities on the liquid surface. Meanwhile measurements of the $\gamma(T)$-curves of LC-substances have also been carried out by Churchill and Bailey [23] on cholesteryl myristate (with cholesteric mesophase) and by Tamamushi [24, 14] on ammonium alkanoates (with smectic mesophase) and *p*-methoxybenzylidene-*p*′-butylaniline (MBBA). Their results agreed quite well with those of Jaeger and Ferguson and Kennedy. All the measured LC-substances, independent of the nature (i.e. nematic, cholesteric or smectic) of the liquid crystals, exhibited anomalies on their $\gamma(T)$-curves. Nevertheless, the behavior of the $\gamma(T)$-curves of MBBA showed in two papers of Tamamushi [24, 14] is quite different.

Krishnaswamy and Shashidhar [25–28] have taken, by using the pendant-drop method, a series of investigations on the behavior of the $\gamma(T)$-curves of LC-substances as well. Their measurements were performed under the "equilibrium conditions" as suggested by Croxton and Chandrasekhar [29, 30]. By equilibrium conditions is meant here to measure the surface tension of a liquid with the liquid in equilibrium with its saturated vapor phase so that there is no net flux of particles (atoms or molecules) across the liquid-vapor interface. According to Croxton and Chandrasekhar [29, 30] a net transport of particles from a liquid surface has a disruptive effect on the structural features there are in its transition zone, so it is crucial to carry out the measurements under the equilibrium conditions (e.g. by ensuring the liquid in equilibrium with its own vapor) in order to observe such positive regions over limited temperature ranges on the $\gamma(T)$-curves of LC-substances. For all the measured substances (*p*-anisaldazine, PAA, PAP, MBBA *p*-cyanobenzylidene-*p*′-*n*-octyloxyaniline (CBOOA), *p*-azoxybenzoate and 4-*n*-pentyl-4′-cyanobiphenyl (5CB)) Krishnaswamy and Shashidhar could observe the anomalies in the $\gamma(T)$-curves near the phase transitions. By most of the substances they found the anomalies appeared some degrees before or after the (bulk) phase transition temperatures. For CBOOA their measurements showed that the $\gamma(T)$-curve has a positive slope in the whole studied smectic temperature range [27]. In opposition to Neumann *et al.* [8, 9] the purity of a sample seemed not to have critical effects on the behavior of the $\gamma(T)$-curves they obtained.

By using the Wihelmy-plate technique Gannon and Faber [31] have carried out a careful study on two LCs (4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB)). Due to their chemical stability 5CB and 8CB should be less likely to undergo chemical changes during the study. It was observed during the measurements that, whenever the temperature of the sample was changed, a period of relatively rapid drift of surface tension would ensure, followed (after ca. $1 \sim 3$ days) by a slow drift with a relative steady rate of ca. $-0.002 \sim -0.005$ mN/m per day for 5CB and ca. -0.05 mN/m per day for 8CB at the end of the measurement. Such a drift was found to be even much more troublesome by measuring MBBA so that the authors were not able to obtain reproducible and reliable surface tension values for this substance.

Unfortunately these authors did not give any values about the rates for those beginning rapid drift periods. The observed drift rates in the followed slow periods of ca. $-0.002 \sim -0.005$ mM/m per day may be considered as very small and seem to be near the accuracy limit of most of the surface tension measuring methods currently in use. Due to the adsorption processes taking place at a liquid surface such a small change of the surface tension values should be normally counted for the most of liquid surfaces. The $\gamma(T)$-curves of 5CB and 8CB obtained by them (after correction for the slow drifts during the accumulation of γ-values used in the curves) show clearly anomalies over the phase transitions. In the case of 5CB the authors were sure that the surface tension changes discontinuously at the phase transition.

To make a more close comparison, the presently available results on the four most frequently investigated LC-substances in the past years, obtained by the different workers with various measuring methods, are shown in Table I and in Figures $2 \sim 4$.

It can be seen that the results are inconsistent either in view of the behavior of the $\gamma(T)$-curves or from the aspect of the absolute surface tension values at given temperatures. Although nearly all the authors have

TABLE I Values of the surface tension of MBBA obtained by different workers using various measuring methods

Reference	14	32	33	34	35	26	36	41
Method[1]	Wihelmy	Ring	?	PD	?	PD	Capillary	PD
γ [mN/m][2]	32	32–34	28.8	35.8	38	35.5	20, 32.5[3]	28.5–32[4]

1) Wihelmy = Wihelmy-plate method; Ring = Du Noüy-ring method; ? = unknown method; PD = pendant-drop method; Capillary = capillary rise method.

2) By temperatures between 22–25°C.

3) γ-value is dependent on the orientation of the molecules at the surface. If the molecules at the surface are orientated perpendicularly to the surface a value of 20 mN/m was obtained; if they are ordered parallel to the surface a value of 32.5 mN/m was measured.

4) γ-value is time-dependent. The surface tension of a freshly formed surface decreased from 32.0 mN/m to 28.5 mN/m within a period of about one hour.

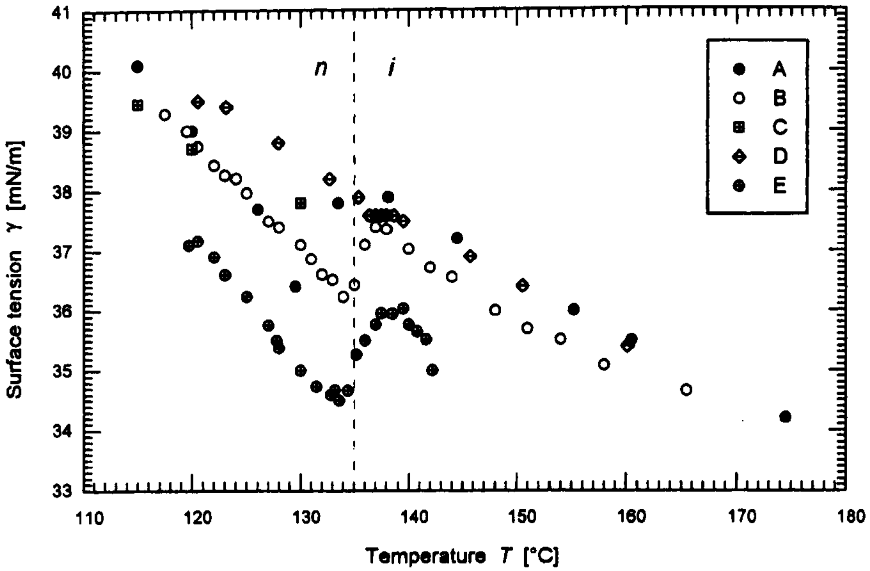

FIGURE 2 Temperature-dependence of the surface tension of *p*-azoxyanisole (PAA) (after literature).
A–Jaeger [16], bubble pressure method
B–Ferguson & Kennedy [17], capillary rise method
C–Naggiar [42], drop profile method
D–Schwartz & Moseley [19], ring method
E–Krishnaswamy & Shashidhar [25], pendant drop method.

given for their measuring methods an absolute error of ca. 1 ~ 1.5%, the values of the surface tension of most substances differ quite largely. For MBBA this difference amounts to about 30%, for PAA and *p*-anisaldazine to about 13 ~ 15% in the nematic phase and 7 ~ 10% in the isotropic phase. Besides from the difference in the absolute accuracy of the used methods, which amounts only to 1 ~ 1.5%, one may try to explain these discrepancies from the aspect of the sample purity used by the different authors for their measurements. The values of the phase transition temperatures may give indications of their sample purity. Among the four substances the samples of PAA used by the different authors have nearly the same nematic-isotropic transition temperature (T_{ni}) of 135°C and the difference in T_{ni} values of *p*-anisaldazine may be considered to be small. However, the differences in the surface tension values for these two substances are much more large than that in *p*-azoxyphenetole, whose T_{ni} values differ most distinctly among the samples used by different authors. Usually a higher surface tension value is to be expected for a more pure sample. Nevertheless

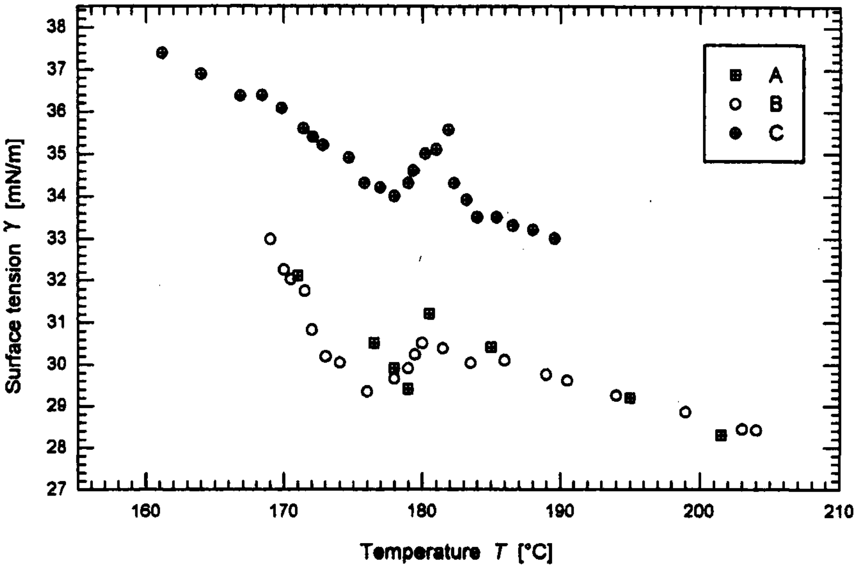

FIGURE 3 Temperature-dependence of the surface tension of *p*-anisaldazine (after literature).
A–Krishnaswamy & Shashidhar [25], pendant drop method ($T_{ni} = 182.2$°C)
B–Ferguson & Kennedy [17], capillary rise method ($T_{ni} = 180.5$°C)
C–Jaeger [16], bubble pressure method ($T_{ni} = 180.0$°C).

Tamamushi [14] obtained at 25°C a value of ca. 32.0 mN/m for a MBBA sample with $T_{ni} = 47$°C, whereas Krishnaswamy and Shashidhar measured at the same temperature a nearly identical value of ca. 32.4 mN/m but for a MBBA sample with $T_{ni} = 43.2$°C [26]. It seems thus to us to be difficult to explain the remarkable differences in the surface tension values obtained by different authors alone from the respects of the measurement errors and the purity of the employed samples.

The tremendous inconsistency observed so far by the measurement of the $\gamma(T)$-curves of LC-substances suggests the complication of such kind of measurements associated with LC-substances and may be considered as a manifestation of the structural peculiarities of the surface of LCs. The appearance of the anomalies in their $\gamma(T)$-curves is certainly of great theoretical interest for the theories considering the liquid crystal interfaces [5, 29, 30, 37, 38]. Thermodynamically the negative slope of a $\gamma(T)$-curves is related to the surface excess entropy through $\Delta S = -d\gamma/dT$. For the ordinary liquids the molecules at the surface, due to spatial delocalization across the liquid/vapor-transition zone, have large degree of freedoms and are thus less ordered than those in the bulk phase. Surfaces of such liquids have positive

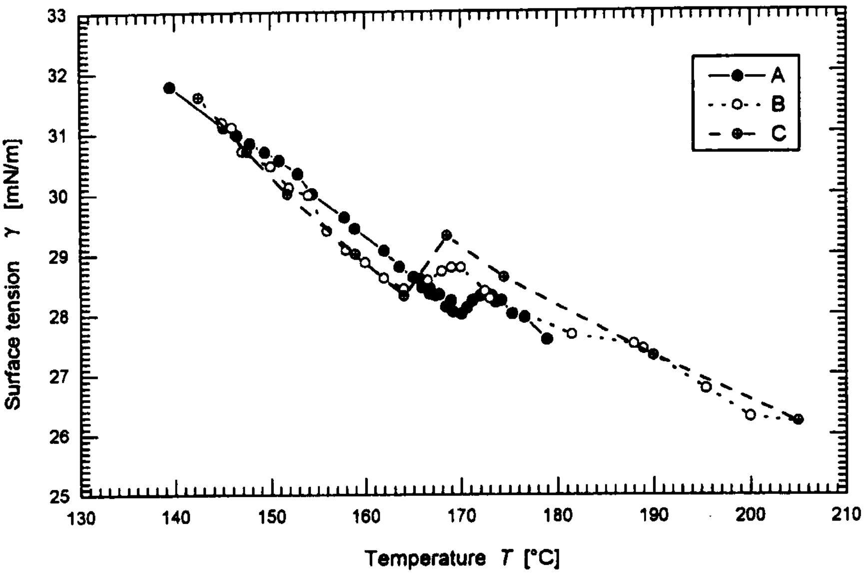

FIGURE 4 Temperature-dependence of the surface tension of p-azoxyphenetole (PAP) (after literature).
A–Krishnaswamy & Shashidhar [26], pendant drop method (T_{ni} = 166.6°C)
B–Ferguson & Kennedy [17], capillary rise method (T_{ni} = 162°C)
C–Jaeger [16], bubble pressure method (T_{ni} = 168°C).

ΔS-values and their $\gamma(T)$-curves show negative slopes in the nearly whole temperature range below the critical temperature. The appearance of maximums in the $\gamma(T)$-curves of LC-substances near phase transitions and the associated curve segments of positive slope indicate that the surfaces must have negative ΔS-values in the corresponding temperature ranges. It must be, therefore, suggested that a certain molecular arrangement or organization must occur at those surfaces so that the surface molecules are *relatively* higher ordered than their counterparts in the corresponding bulk phases in a defined temperature range near phase transitions. The properties of such highly ordered structures and how they vary with temperature are surely of theoretical interest. Unfortunately little experimental data have been reported on this subject since the measurement of Gannon and Faber [31], although much more careful investigations in this area are surely desirable to make some insights into the origin of the complications associated with such measurements and to gather much more experimental data from well-purified LC-substances of various types. Such a trial has been now carrying out in our laboratory.

EXPERIMENTAL

(A) Measurements

The surface (or 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 [39, 40] and is outlined shortly as follows: At a preset temperature a drop of a to be studied liquid was formed in another phase, which was a gas phase (saturated with the vapor of the liquid substance) in the case where the surface tension of the liquid was measured or another immiscible liquid phase when the determination of interfacial tension was concerned. After the formation of the drop, drop profiles were extracted from its image and recorded with the time. The surface or interfacial tensions were then determined (as a function of time) by fitting these recorded drop profiles to the Laplace-Young equation, which governs the profile of a liquid drop at its hydromechanical equilibrium. The method reaches a relative accuracy of ca. 0.05% error and an absolute accuracy of ca. 0.5% error. For the measurements presented in this paper only the relative accuracy is to be taken into account. Among the commonly employed methods, used for the determination of surface or interfacial tension of liquid/fluid-systems, the pendant-drop method is possibly the most suitable one to measure the equilibrium values of the surface or interfacial tension of LC-substances, since by this method the contact area between a liquid drop and the supporting solid phase is so small that the possible molecular orientation effect of the solid phase on the measured surface tension of the liquid may be neglected. Such an effect, if it is to occur, will be certainly much more large by the other commonly available methods, especially by the method of the capillary rise, Wihelmy hanging-plate and Du Noüy-ring as well as with the method of sessile drop.

All of the measurements have been carried out in a measuring chamber from Ramé Hart Inc. (New Jersey, USA). The to be measured sample (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 and degassed 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 the elevated temperature syringe 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 keep the substances from the possible chemical changes.

After the wished temperature in both the chamber and the syringe attachment was reached, another 10 to 20 minutes, before a fresh drop of liquid was formed and measured, were waited to ensure a uniform temperature within the measuring room. For a solid sample, the sample was first heated above its melting point and then cooled to the wished temperature for measurement. The size of a drop can be controlled by turning a screw attached to the piston of the sample syringe. All the time-dependence curves were determined using one each *freshly* formed drop.

(B) Materials

The employed MBBA and 5CB sample were purchased from Aldrich Chemical Company Inc. (USA) and had both a purity of 98% given by the manufacturer. Other than MBBA, which was received as a crystalline solid at the room temperature, the obtained 5CB-sample was a nematic liquid. EBBA (4′-ethoxybenzylidene-4-*n*-butylaniline) was purchased from TCI (Tokyo Chemical Industry Co., Ltd., Japan), and had a purity > 99% (TCI Guaranteed Reagent). The other samples were synthesized in our laboratory [41] after the known procedures given in the literature. Their structures and the corresponding designations, which will be used through the following text of the paper, are shown in Figure 5. M11-CN and M11-OCH_3 were purified using recrystallizations (in Ethanol/H_2O) and through column chromatography; the side-chain liquid crystalline polymer PAC_n-series ($n = 2, 4, 6$) were purified to monomer-free using repeated dissolution (in toluene) and precipitation (in methanol).

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 II.

RESULTS AND DISCUSSIONS

The results on the time-dependence of the surface tension ($\gamma(t)$-curve) are shown in Figures 6, 7, 8, 9, 10, 11 and 12 for the studied LC-substances EBBA, 5CB, M11-CN, M11-OCH_3, PAC_6, PAC_4 and PAC_2 respectively.

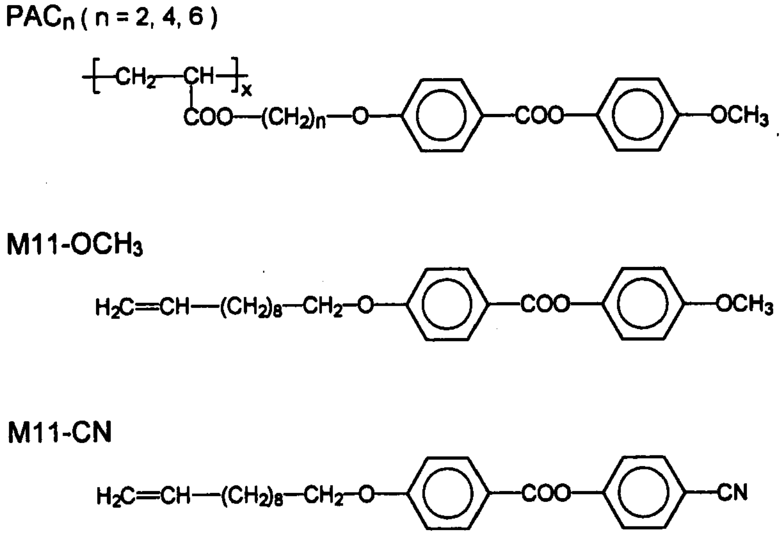

FIGURE 5 Structures and designations of the self-synthesized LC-substances.

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

Substance	*Phase Characterization*[1]
MBBA	*k* ? *n* 43.2°C *i*
EBBA	*k* 38 *n* 79°C *i*
5CB	*k* ? *n* 35.5°C *i*[2]
$M11\text{-}OCH_3$	*k* 70°C (s_A 46°C) *n* 72°C *i*[3]
M11-CN	*k* 74°C *n* 78°C *i*
PAC_6	*g* 22 ~ 29°C s_A 95 ~ 96°C *n* 123°C *i*[4]
PAC_4	*g* 51 ~ 52°C s_A 75 ~ 76°C *n* 122 ~ 123°C *i*[5]
PAC_2	*g* 60°C *n* 114.5°C *i*[6]

1) *k*, s_A, *n* and *i* denote crystalline, smectic A, nematic and isotropic phase, respectively; *g* stands for the glassy state of a polymer.
2) The received sample of 5CB lay as a nematic liquid.
3) The smectic phase and the corresponding phase transition temperature were detected only by cooling (i.e. monothermotropic).
4) The used PAC_6 has a weight average mole mass (M_w) of 183 000 g/mol and a M_w/M_n – ratio of 1.15 (M_n = number average mole mass).
5) M_w = 150 000 g/mol
6) M_w = 98 000 g/mol, M_w/M_n = 1.19

Except for 5CB we have observed for all other studied LC-substances a remarkable time-dependence of the surface tension, both in their nematic and in their isotropic phases. The surface tension of a freshly formed MBBA-surface at room temperature (ca. 23°C) dropped from 32.0 mN/m to 28.5 mN/m within about one hour (see Tab. I), followed then by a much slower drift with the time.

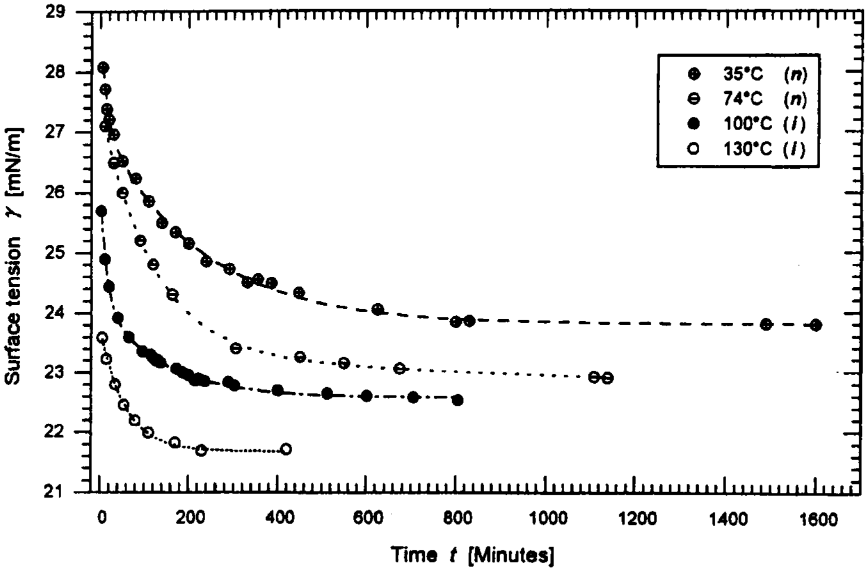

FIGURE 6 Time-dependence of the surface tension of EBBA.

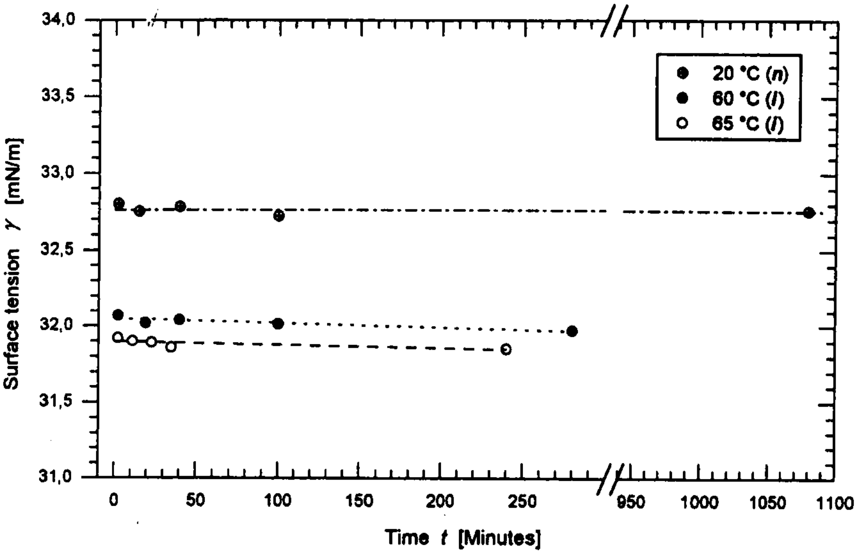

FIGURE 7 Time-dependence of the surface tension of 5CB.

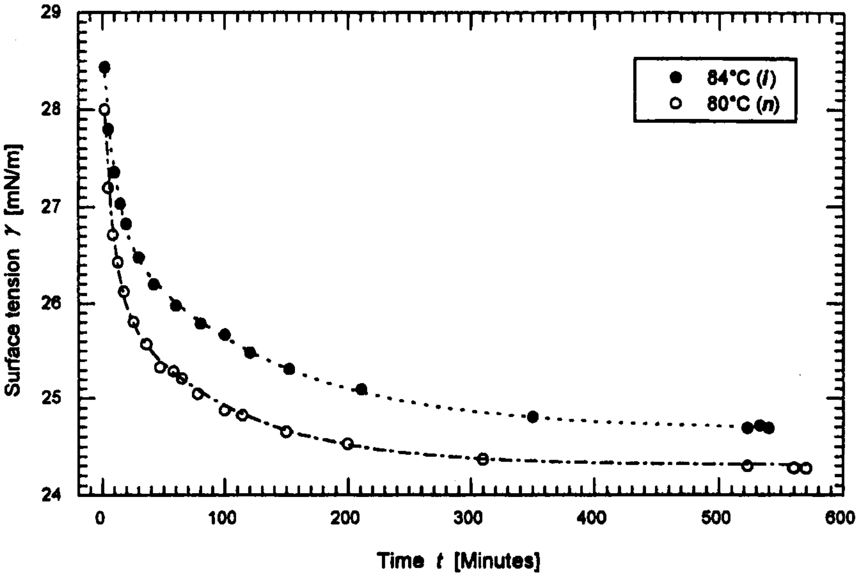

FIGURE 8 Time-dependence of the surface tension of M11-CN.

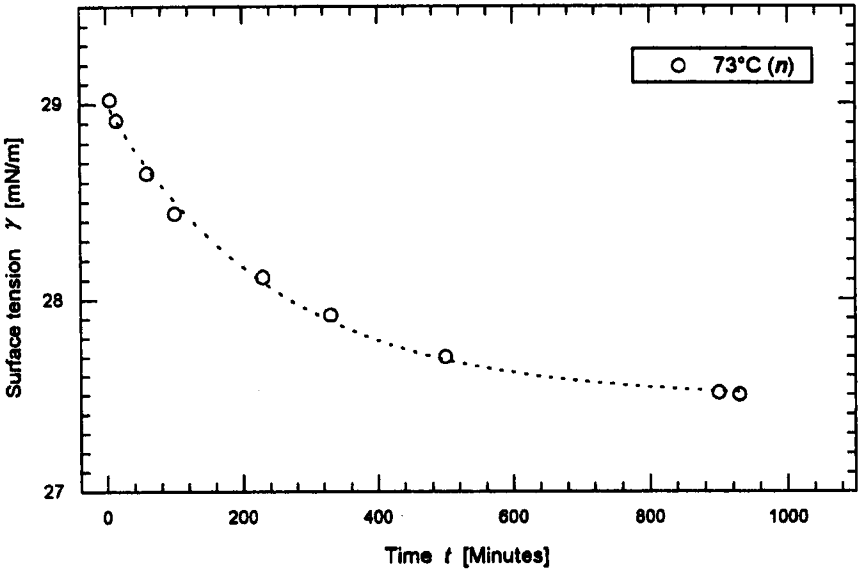

FIGURE 9 Time-dependence of the surface tension of M11-OCH$_3$.

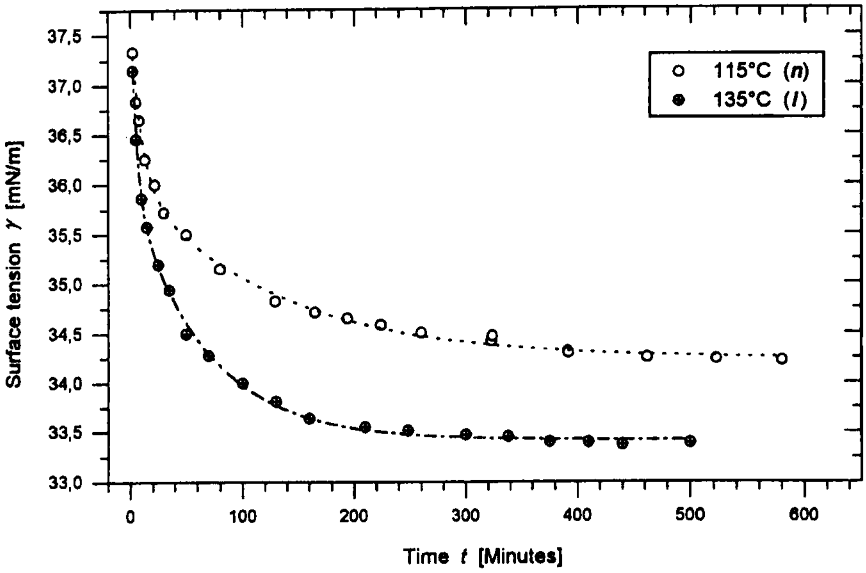

FIGURE 10 Time-dependence of the surface tension of PAC_6.

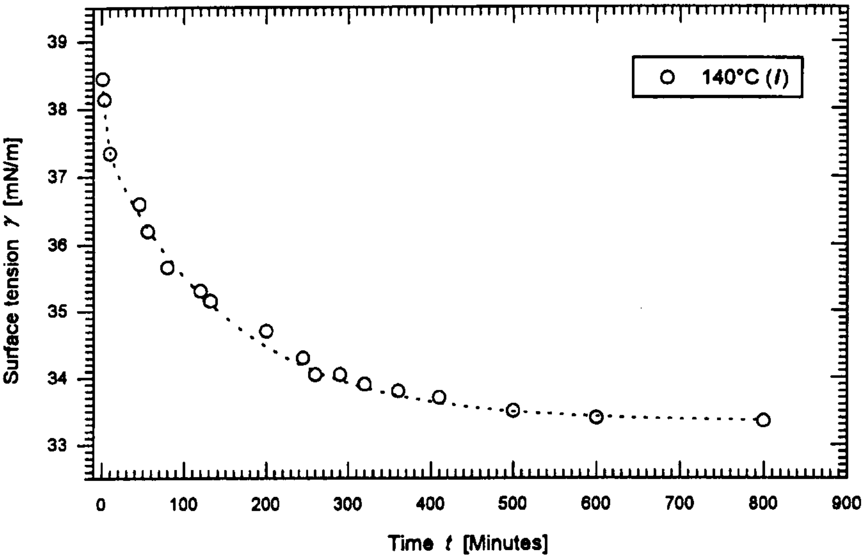

FIGURE 11 Time-dependence of the surface tension of PAC_4.

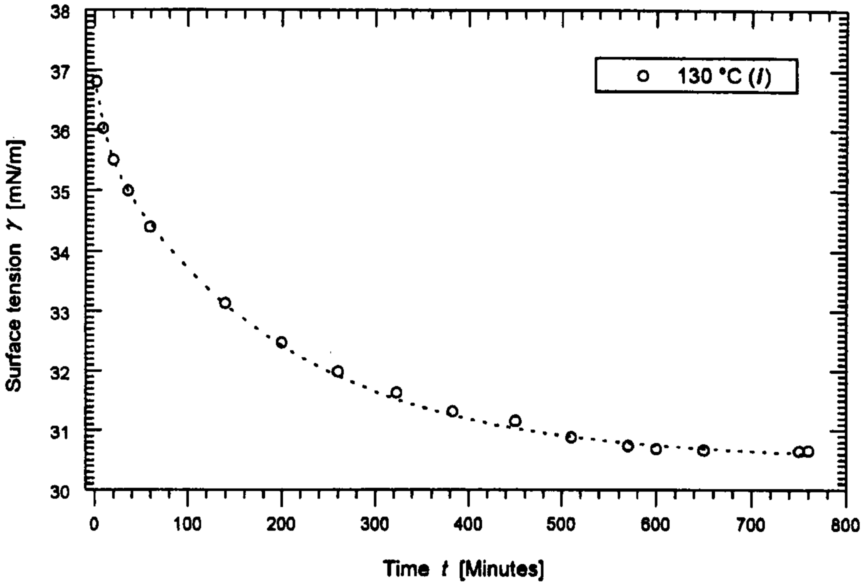

FIGURE 12 Time-dependence of the surface tension of PAC_2.

Similar phenomena were observed by other LC-substances. The decrease of the surface tension from the formation of a fresh drop to the attainment of a steady-state value at a constant temperature amounts to about 10 ~ 16% for EBBA, 15% for M11-CN, 5% for M11-OCH_3, 10% for PAC_6, 15% for PAC_4 and 20% for PAC_2 of their corresponding end values. The time required for reaching the steady-state lies in order of 4 ~ 10 hours and is, to certain extent, substance- and phase-dependent. The process slows down by decreasing temperature. A freshly formed drop of EBBA, for example, reached the steady state after annealing for ca. 4 hours at 130°C (in isotropic phase), whilst about 15 hours was needed for a freshly formed drop of the same substance to attain its equilibrium state at 35°C (in nematic phase). Among the side-chain LC-polymer series PAC_n ($n = 2, 4, 6$) more time was necessary for PAC_4 and PAC_2 to reach the steady-state than for PAC_6, possibly due to the differences in their molecular structures and the resulted substance properties such as glass temperature and viscosity. In opposition to other LC-substances the time-dependency of the surface tension of freshly formed drops of 5CB was found to be negligible small.

The observed time-dependence of the surface tension on these LC-substances is remarkable in view of its duration and the resulted change in the value of the surface tension. It is now of interest to explore its possible grounds. Generally there are many known processes, which may take place at a freshly formed liquid surface and lead to certain time-dependence of its surface tension:

(A) re-orientation or re-arrangement of the molecules at the surface;
(B) re-adjustment of possible molecular association equilibriums at the surface;
(C) adsorption (positive or negative) at the liquid surface (re-distribution of the molecular components between the surface and bulk);
(D) chemical changes of the sample.

For the polymer melt samples of PAC_n-series we may not, without any considerations, exclude the possibility that a freshly formed drop of polymer melt requires certain time to reach its hydromechanical equilibrium before the profile of the drop fulfills the Laplace-Young equation and the value of the surface tension can be thus calculated correctly through the optimization of the drop profile to the Laplace-Young equation as done by the measurements. However, such a suspect can be cleared away here. Firstly, all the drop profiles used for the calculation fulfilled the Laplace-Young equation very well, as indicated by the very small mean residuals ($< 2\ \mu m$) between the measured drop profiles and the optimized theoretical ones. Secondly, no similar phenomena could be observed by carrying out the same kind of measurements with conventional (ordinary) polymer melts like polyethylene (PE) and poly(ethylene glycol) (PEG) [41] (see Fig. 13). Thirdly, Wu [43] has measured the surface tension of a lot of viscous polymer melts using the pendant drop method. He estimated about 20 minutes are generally enough for a drop of ordinary viscous polymer melts to reach its hydromechanical equilibrium by this method. Among the common methods for determining the surface tension of liquids the pendant-drop method is believed to be the one, by which the equilibrium of a measurement can be reached most rapidly due to its small contact area between the supporting solid phase and the measuring liquid. Based on these considerations and also in view of the fact that such a strong time-dependence has been observed not only by the polymer samples but also by the low molecular substances as well, we may conclude that the high viscosity of a sample alone can by no ways be the essential ground, which will lead to such a time-dependence. We want here also to rule out the process (D) listed above for the responsibility of the observed time-dependence, at least for the duration of a typical such measurement (ca. 10 hours), based on the following

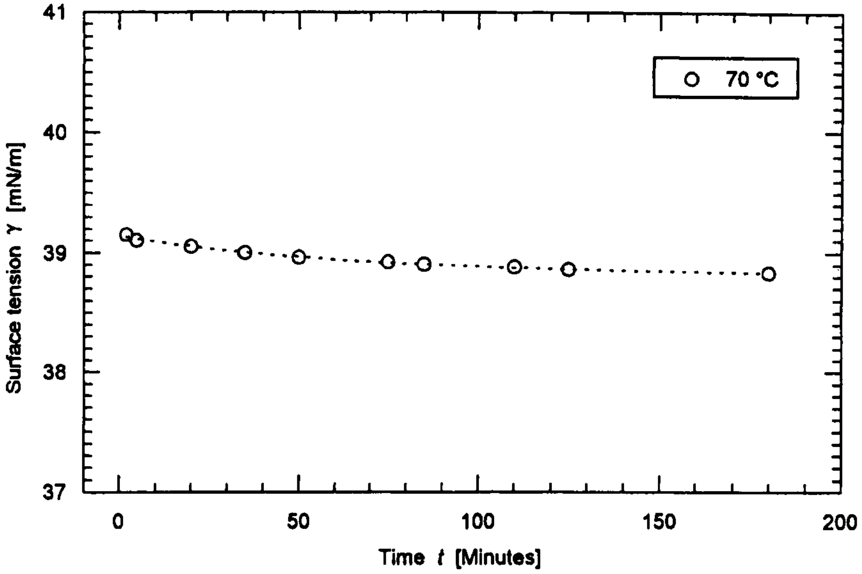

FIGURE 13 Time-dependence of the surface tension of poly (ethylene glycol) (PEG6000 with $M_w = 6000$ g/mol).

considerations: First, the samples of MBBA and EBBA shown at room temperature stronger time-dependence than at higher temperatures. If the slow chemical changes which may take places on a sample during the measurement accounted for the observed time-dependence, one would expect that such chemical processes would affect the value of the surface tension much more strongly at higher temperatures rather than at lower ones. Moreover it seemed to be little conceivable that the samples like MBBA and EBBA underwent chemical changes under N_2-atmosphere even at room temperature. Secondly, we have carried out the same measurements at room temperature with MBBA and EBBA under air-atmosphere as well. The results obtained under air-atmosphere are similar with that measured under N_2-protection (at room temperature). If the chemical processes played a role in the observed time-dependence, the presence or the concentration of water and oxygen molecules should be expected to play also a role. Thirdly, if a freshly formed liquid drop reached its steady-state, its equilibrium value of surface tension could be repeated even after several heating/cooling runs with the same drop.

A freshly formed liquid surface, particularly when there are other surface active components in the liquid, e.g. in cases of liquid solutions, will generally have the different surface tension as that obtained after sufficient time has elapsed to establish equilibrium, mostly due to the processes A, B and C mentioned above, which take place at a freshly formed liquid surface and change the structure and constitution of the molecules at the surface, from that resembling the disrupted bulk properties to the equilibrium surface properties, and thus affect the value of its surface tension. Most of such processes, nevertheless, run very rapidly out (typically in order of milliseconds to seconds) so that it is normally difficult, and special measuring equipment is often required, to determine the values of such "unsteady state" surface tension (i.e. dynamic surface tension). The processes A and B are believed to be run in general rapidly [44] and should be normally completed within a range of milliseconds to seconds. Consequently, these two processes alone will be expected most likely to affect the value of surface tension of a freshly formed drop only in its very beginning period after its formation, over a maximum time range of several seconds [44].

The process C–adsorption at the liquid surface–may be now the most likely one, which accounts for the here observed time-dependence phenomena. The adsorption process is a transport process and is generally assumed to be either diffusion controlled [45] or regulated by certain adsorption energy barriers in the region of the interface [46, 47]. The time needed for a adsorption process to attain its equilibrium state depends, among others, on the nature of a surface as well as on the molecular species to be adsorbed onto the surface and lies usually in a order of $1 \sim 10^2$ seconds for surface active substances [48]. It takes, however, generally much longer for the adsorption processes, by which adsorption energy barrier presents, than those that are simply diffusion-controlled. In the former cases the time scale may be extended to several hours [48]. An adsorption process which may be expected to be involved by most surfaces of liquids or liquid solutions is the adsorption of surface or interfacial active impurities. The adsorption of impurities is usually a slow, long time process due to their very low concentrations [48].

Since the surface of a pendant liquid drop is in contact simultaneously with two bulk phases: the liquid bulk phase of the drop itself and the gas atmosphere (phase) around it, adsorption processes at the drop surface are to be expected to occur from both of the surrounding bulk phases. That is, in our cases, the adsorption of possible surface active impurities from the drop liquid phase and the adsorption of gases from the surrounding gas phase. Impurities are always unavoidably presented in any liquids and may be enriched with the time during a measurement. However, if the time-dependence of the surface tension observed in the present work was caused by the adsorption of surface active impurities from the drop liquid phase, it should be reasonable to expect that the value of surface tension must be very sensitive to every action that will disturb the surface layer and change the composition or concentrations of molecular species at the surface. Therefore we would await that such a time-dependence should be repeated if we destroy a liquid drop (after it has attained its steady-state) and re-form a new one with the same portion of the liquid of the previous drop. In reality we could not observe such a repetition as demonstrated by the following experiment: After a freshly formed liquid drop has attained its steady-state the drop was destroyed by pulling it back into the syringe needle through the fine turning of the micrometric screw attached to the piston of the sample syringe. After waiting for several minutes a new drop was formed again by driving the liquid out of the syringe needle. The portion of the liquid used to form the new drop was nearly the same as that composed the previous one, since an exchange of the liquid molecules vertically inside the syringe needle was expected to be very limited within such a short period of time due to the small diameter of the syringe needle used (interior diameter $\approx 1.7\,\text{mm}$). Such a destruction and re-formation action should be strong enough to destroy completely the surface layer structures of the previous drop and the fresh surface of the newly formed drop should have the same character as that of the previous drop just after its formation. For such a fresh surface we should await a similar time-dependence behavior as that observed on the previous one if the adsorption of surface active impurities from the drop liquid phase was responsible for the observed time-dependence. In contrast to this expectation the freshly formed new drop attained the steady-state value of the surface tension already in several seconds for low molecular LC-substances or in maximum ca. 20 minutes for polymeric substances. The equilibrium value of the surface tension of the newly formed drop was found to be nearly identical with that of the previous one. Based on these considerations and observations we thus exclude here also the possibility that the adsorption of surface active impurities, by which we mean all molecular species other than the liquid molecules themselves, from the drop liquid phase alone can lead to the time-dependence observed here.

The most likely process, which will lead to the here observed time-dependence behavior of the surface tension, seems now to be the other kind of adsorption, i.e. the adsorption at a liquid drop surface from its surrounding gas phase. Since all of the measurements were performed under N_2-protection, there existed, besides the vapor molecules of a measuring liquid (if the liquid is a low molecular one), N_2-molecules in the gas phase. Moreover some amounts of air molecules might also present in the measuring chamber due to its limited air-tightness. The adsorption of gas molecules at a liquid surface changes the molecular composition in the surface layer and may induce some other orientational and/or structural changes of the molecules near the surface (see below), and thus leads to a change in the surface tension. The adsorbed gas molecules may be further adsorbed into the bulk phase of the liquid drop. A steady-state is then reached when an equilibrium of the sorption of gas molecules at the liquid surface and into the liquid bulk as well as an equilibrium between the surface and the bulk phase has been reached. Such a process may be so slow that it causes the surface tension to change over a long period of time. The time required for the adsorption process to be completed may be estimated from the gas-sorption measurements. Such a measurement recently carried out with the low molecular LC-substance M11-OCH_3 (the same sample as used in the present work) by Chen *et al.* [49] shows that about 8 hours is required for the substance to reach its sorption equilibrium under 1 atm CO_2-gas phase both in its nematic and in its isotropic phase, which agrees quite well with the duration of the time-dependence of the surface tension observed here. Their experiments also indicate that the equilibrium gas concentration in the crystalline phase is much lower than that in the nematic or isotropic phase, which suggests that if a sample used for the surface tension measurement is stored previously in its crystalline state, the gas concentration, which may have been reached in the sample through its contact with air during the storage, is much lower than the concentration, which is to be reached at the equilibrium in its nematic or isotropic phase. Thereafter, a gas sorption process will still take place for a nematic or isotropic drop, freshly formed from a crystalline substance, even that the substance in its crystalline state may have been saturated with gas (e.g. air).

Under the suggestion that the gas-sorption process accounts for the observed time-dependence of the surface tension of a freshly formed liquid drop, we may now easily explain the phenomena associated with the destruction and reformation of a drop described above, which has led us to rule out the possibility that the time-dependence can be caused by the adsorption of surface active components at the surface from the drop liquid bulk phase. After a freshly formed liquid drop had attained its steady-state, it had, under the assumption that the time-dependence is caused by the gas-sorption, reached the equilibrium gas concentration in both its surface and bulk phase. When such a "gas saturated" steady-state drop was destroyed and reformed using the procedure described above, the previous equilibrium gas concentrations at its surface layer and in its bulk phase could be rashly reestablished through the redistribution and adsorption processes between its newly fresh formed surface layer and its bulk phase, which was already saturated with gas. In such a case no extra gas sorption process from the surrounding gas-atmosphere may be more needed to be involved for the liquid drop to reach its equilibrium gas concentration. The redistribution and adsorption processes between the surface layer and the bulk phase are to be expected to be proceeded much more quickly than the gas sorption process from the surrounding gas-phase, which was needed by the previous freshly formed drop to reach its equilibrium gas concentration at its surface layer as well as inside its bulk phase. So the equilibrium value of the surface tension may be immediately reached after such a destruction and re-formation procedure, so long as the previous liquid drop had reached its steady-state before. The maximum time period of about 20 minutes, which was needed for a drop of polymer melt to re-reach its previous steady-state value of surface tension after such a procedure, was possibly conditioned, to a significant extent, by its high viscosity.

Similarly, the absence of such a time-dependence of the surface tension on the sample of 5CB used for this study may be also well explained under this assumption. Other than the rest of the materials used in the present work the received 5CB sample lay as a nematic liquid at room temperature and was kept in a normal glass bottle. The nematic liquid of 5CB should have been already saturated with air before the measurement was done. Consequently, no significant gas-sorption was to be awaited for a freshly formed drop of this sample, and thus no remarkable time-dependence has been observed on this sample.

The suggestion that the gas sorption process plays a governing role in the here observed time-dependence of the surface tension of a freshly formed liquid drop is supported by the measurements of interfacial tension of side-chain polymeric liquid crystals of the PAC_n-series in polyethylene (PE) and in poly(ethylene glycol) (PEG) [41]. In opposition to freshly fomed drops of PAC_n-series in N_2-atmosphere, which all show a strong, long time-dependence of the surface tension, the drops of these polymers, when freshly formed in the liquid phase of another polymer (i.e. PE or PEG) phase, reached their equilibrium values very rashly, just in about 30 minutes. One of such curves is shown in Figure 14. In such cases the liquid drops were exposed no longer immediately to the gas-atmosphere but through the other intermediate polymer melt phase, in which the gas equilibrium concentration was very limited and must be slowly established as well.

If the gas-sorption process can be truly made for accounting for the observed remarkable time-dependence of the surface tension of LC-substances,

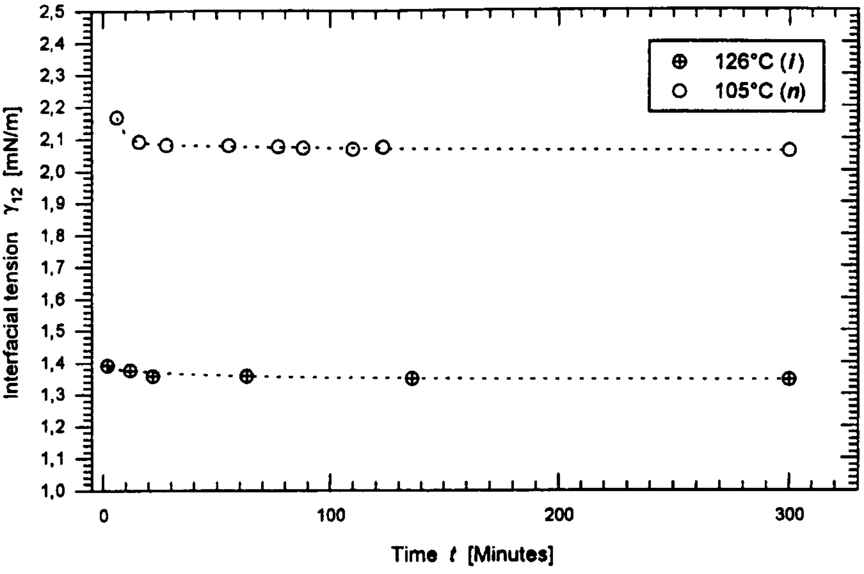

FIGURE 14 Time-dependence of the interfacial tension of PAC_4 in PEG.

it is now of interest to discuss the possible effect of gas molecules on the surface tension of a liquid, particularly on the surface tension of a liquid crystalline substance. Surface tension determinations are commonly performed under air- or a protection gas-atmosphere (usually N_2). Therefore gas-sorption process should be generally expected to be involved over a liquid surface during the measurement. Nevertheless, such a remarkable time-dependence is generally not to be observed by the measurement of the surface tension of the most of the ordinary pure liquids. Why does such a process seem now to excise a particular effect on the surface tension of freshly formed surfaces of LC-substances? The crucial properties which distinguish the surface of a LC-substance liquid from that of an ordinary (i.e. non-liquid crystalline) liquid, are the tendency and capability of the molecules of a LC-substance to orientate themselves to a certain direction and to build up a relative highly ordered-state in the surface layer, which will certainly affect the surface tension behavior of a LC-substance. It may thus be reasonable to explore the reason of such a particular effect of gas molecules on the surface tension of LC-substances, if it is to occur, in the possible influences that the adsorbed gas molecules may exert on the structure or order of the molecules in or near the surface layer. The experiments of Chen *et al.* [49] have shown that the sorbed gas can influence the physical properties of a LC-substance significantly. It was found by them that the isotropization temperature of the M11-OCH_3 sample dropped from the original value of 71.8°C under normal atmosphere to about 67°C under 7.5 bar CO_2-gas pressure, which is an indication of the strong interactions presented between the sorbed CO_2-molecules and the liquid crystal molecules. The presence of foreign molecules may also affect the surface anchoring of the liquid crystalline molecules [50, 51] and thus affect its surface tension. Moreover the presence of a small amount of gas molecules may cause an induction effect on the ordering or organization structure of the liquid molecules as suggested for the liquid water. [52]

We may therefore further suppose that the presence of a limited amount of adsorbed gas molecules in a liquid surface layer may cause a change of its surface tension remarkably when the molecules in the liquid surface have a particular structure or order and this structure or order can be affected (enhanced or depressed) strongly by the presence of certain gas molecules. A similar phenomenon, which has been observed on surfaces of non-liquid crystalline liquids, is the surface aging behavior of water/air-system as reported by Sobol *et al.* [52] They have observed in air-saturated and deaerated water/air-systems a dramatic time-dependence of the surface tension, by which the surface tension of a freshly formed water/air-surface was observed to decrease within a period of one hour by as much as 15%. The phenomenon has been discussed correlatively with the various types of water molecular organization that is supposed to be present in the bulk and in the interfacial region. It was considered that such organizations may be highly sensitive to the presence of certain foreign (e.g. O_2, N_2) molecules, whose initial content in the liquid water phase can have a drastic influence on the behavior of its surface aging. "Ice-like" structure has been supposed to be presented for some most outer layers in the water surface [53], just similarly to what has been observed on the surfaces of LC-substances that the surfaces of some LC-liquids seem to have relatively high-ordered or "smectic-like" layer structures [54–59], which may be maintained even in a temperature range high above their clearing points [59]. This seems to be true particularly for those LC-substances, which have low-temperature smectic phases [54, 55, 59]. The fact, that such high ordering or structures on the surface of LC-substances may still stably exit in the isotropic phase [59], explains also the seeming contradiction between our suggestion and the experimental observations that the time-dependence phenomenon has been observed for the studied LC-substance in their isotropic phases as well.

Based on the observations we have made on these LC-substances in this work, it may be reasonable to infer that the time-dependence of the surface tension observed here may be shared by many of the LC-substances. This phenomenon may has troubled some of the early works on this subject and may, at least partially, account for the inconsistencies in the results obtained so far by different authors on the surface tension of LC-substances. Under the presence of such a time-dependence the value of surface tension of a liquid crystal is strongly dependent on the time allowed for equilibration to take place. Consequently, depending on time of measurement or on the method used, the values obtained for the surface tension of a substance may vary. Moreover, if the assumption we suggested above about the effect of the gas-sorption on the surface tension of a LC-substance is revealed to be reasonable, the value of the surface tension of a liquid crystal will certainly depend on the initial gas content of the sample used for the measurement, on the surface age and possibly on the used gas environment as well, depending on the particular effect of certain gas molecules on this specific LC-substance.

CONCLUSIONS

We have briefly reviewed the presently available experimental results on the measurement of the surface tension of liquid crystals. They are inconsistent either in view of their temperature-dependence behaviors near the phase transitions or with respect to their absolute values. The time-dependence of the surface tension of a freshly formed surface has been studied using the computer-aided pendant-drop method on several liquid crystalline substances, both of low molecular and polymeric. By most of the studied LC-substances the surface tension of freshly formed surface was found to change over a long period of time. After considering several possible processes, which may lead to such a time-dependence, we have supposed that the observed unusual time-behavior may be mainly attributed to the gas-sorption process taking place at the liquid surfaces. It has been further suggested that such a remarkable time-dependence may occur on a liquid surface when the molecules at the surface are relatively highly ordered or have some particular structures and such ordering or structures will be influenced sensitively by the presence of certain gas molecules, perhaps either as a result of the interaction between the gas molecules and the molecules at the liquid surface or as a consequence of the gas-induced reordering or reorganization of the surface molecules. It was inferred that such time-dependence phenomena may have confused the measurements of the prior workers on the surface tension of liquid crystalline substances and may account for some of the inconsistencies in the presently available results.

In order to gain experimental evidences of the effect of gas molecules on the surface tension of LC-substances, further studies on the dependence of the surface tension of LCs on gas concentration and on gas sort are now underway in our laboratory.

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