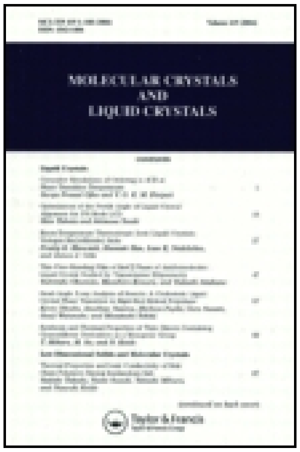

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Surface Phenomena of Liquid Crystalline Substances: Surface Tension of Freshly Formed Droplets

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Surface Phenomena of Liquid Crystalline Substances: Surface Tension of Freshly Formed Droplets

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A procedure is described to determine the initial value of the surface tension of a freshly formed MBBA (*p*-methoxybenzylidene-*p*′-*n*-butylaniline) drop using the pendant drop method. A gastight measuring chamber was constructed for the measurements in different gas atmospheres. The relationship between the initial value of surface tension and gas sorption, with emphasis on the effect of gas type and gas pressure, is presented. The determined initial values of the surface tension are used to study the time-dependence of the surface tension of MBBA, both in its nematic (*n*) phase and in its isotropic (i) phase, and will be used for the further time-dependent studies. The observed behaviors of the surface tension of MBBA in different gas atmospheres are discussed.

Keywords: Surface tension; pendant drop method; time-dependence of surface tension; gas sorption; liquid crystals; MBBA

1. INTRODUCTION

A great deal of attention has been attracted to surface phenomena in liquid crystal substances (LCs), 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 [1–10]. However, the results obtained by the different authors are rather conflicting. To demonstrate the

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inconsistency of the presently available results, we [11] have recently given a brief review of the prior studies on the measurement of surface tension of LCs. We have also discussed the possible reasons of the remarkable time-dependence of the surface tension of a freshly formed LC surface. We supposed this behavior may be mainly attributed to the gas sorption process taking place at the liquid surface, 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 surface region. 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. It is inferred that such time-dependent phenomena may have confused the measurements of the surface tension of LCs performed by different groups and may have contributed to some of the inconsistencies in the obtained results.

In order to gain experimental evidences of the gas effect, we have performed a systematic experimental study of time-dependence of surface tension of LCs as a function of gas type and gas pressure. As the very first step it is necessary to determine the initial value of surface tension of a freshly formed drop of the LCs. This initial value is namely the surface tension value of the drop at the moment when it has been just formed ($t = 0$). But unfortunately with the pendant drop method, which being used by us as the standard method for surface tension measurements, it can not be measured directly. In the present paper we will discuss an indirect way to determine the initial value of surface tension of a freshly formed drop using this method. The low molecular LC MBBA is chosen as the model substance. We will also report some behaviors of the surface tension of MBBA in different gas atmospheres. This is followed by some time-dependent measurements of the surface tension of MBBA as an example for the necessity of gaining such initial values of the surface tension. The observed phenomena are discussed to reveal the possible underlying grounds.

EXPERIMENTAL

(A) Materials

The MBBA (*p*-methoxybenzylidene-*p*′-*n*-butylaniline) sample was purchased form Aldrich Chemical Company Inc. (USA) and had a purity of 98% given by the manufacturer. The sample was purified by several recrystallizations from ethanol and was stored at 0°C with dry nitrogen as protective gas immediately after evacuation. MBBA is a crystalline solid at room temperature with a melting temperature of ca. 24°C. Its phase behavior was determined by differential scanning calorimetry (DSC 7 from Perkin-Elmer) and polarization microscopy (PM-10 ADS, Olympus, Japan) equipped with a hot stage (THM 600, Linkam Scientific Instruments. Ltd., Surrey, GB). The nematic-isotropic transition temperature of the MBBA sample is 43.0 °C (at 1 bar N_2).

The employed gases N_2, CO_2, He and Ar were purchased from the Company Messer Griesheim (Germany) and had all a purity $>$ 99.99%. These gases were used without any further purification.

(B) Measurements

After comparison of various experimental techniques, it was decided to use the pendant drop method. This method has several advantages: a) Only a very small fraction of the total surface area of drop is in direct contact with the supporting solid phase. Therefore in comparison with the other commonly available methods, e.g. Wilhelmy plate method and the method of sessile drop, the molecules of the measured liquid are rather small influenced by the solid phase. b) It is a static method so that the viscous drag of liquid drop does not play any part.

For the measurements a gastight chamber (Fig. 1), which can be heated up to 110°C with a maximum gas pressure of 20 bar, was constructed. The temperature is controlled with a thyristor unit (Model 425A from EUROTHERM, Germany) with eight heating elements. The accuracy of the temperature control is within ± 0.1°C. The gas pressure in the measuring chamber can be controlled with a digital Manometer (Mano Gauge-4266 from Keller, Germany) and needle valves, with an accuracy of ± 0.01 bar. A gastight syringe (Unimetrics Silverline from Alltech, USA) is used to form pendant drops under pressure. The syringe attachment and the screw spindly form the company Rame Hart Inc. (New Jersey, USA) are modified and further used.

The surface tensions of liquid/fluid-systems were measured using a computer-aided pendant drop method. The method was developed in our labroatory and has been applied successfully to investigate the time- and temperature-dependence of various liquid systems. Its principle has been given in detail elsewhere [12, 13]. But some aspects should be repeated briefly. A drop of a to be studied liquid is formed in a gas atmosphere which is saturated with the vapour of the liquid. The time for drop formation and for relaxation of oscillation phenomena of freshly formed drop

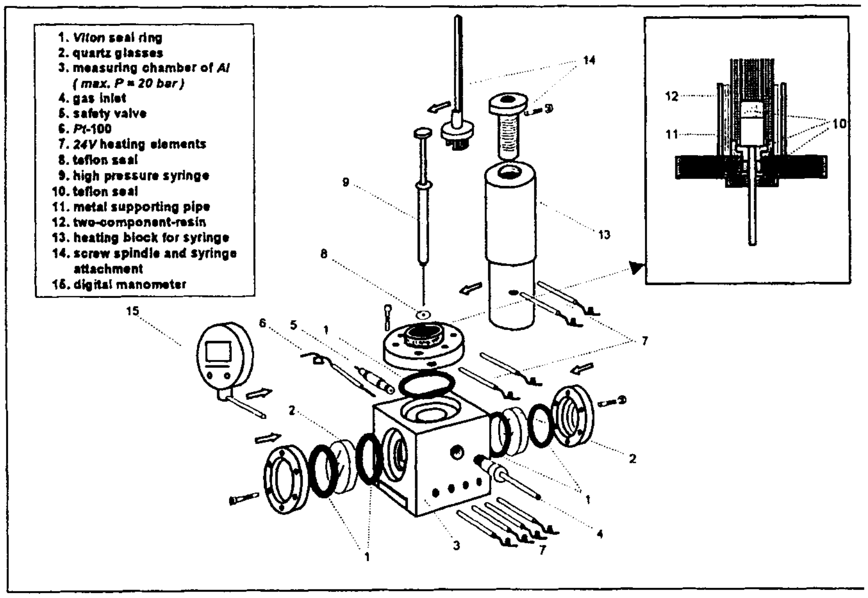

FIGURE 1 Schematic representation of the gastight measuring chamber for the pendant drop method.

takes ca. 10 seconds. After the formation of the drop, the drop profile is extracted from its image and the surface tension is determined by fitting this recorded profile to the Laplace equation, which governs the profile of a liquid drop at its hydromechanical equilibrium. The input parameters of this method are the total magnification factor, the gravitational acceleration, the density difference between the fluid phases at the measuring temperature, and the drop profile coordinates. The resulting output are the surface tension, the drop value and the drop-vapor surface area. 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 the relative accuracy is to be taken more into account.

At room temperature the MBBA sample we used is a solid. The with MBBA filled syringe was heated under vacuum above the melting temperature (ca. 24 °C) and degassed to remove gas bubbles from the melt. To prevent the decomposition of the compound by oxygen and moisture, after the sample had been cooled to room temperature the syringe was taken from vacuum and immediately inserted into the measuring chamber, which was filled with dry test gas (N_2, CO_2, He or Ar). A reservoir of sample was placed into the chamber to get a vapor-saturated atmosphere before starting an experiment. According to Chen *et al.* [14], the equilibrium gas concentration in the crystalline phase of LCs is much lower than that in the nematic or isotropic phase. For this reason the so prepared MBBA sample is capable of sorbing more gas, even if the sample in its crystalline state might have been saturated with gas (N_2).

To reach the optimal condition of the measuring set-up, it took 1.5–2 hours for preparation as well as for adjustment. After reaching the given temperature and pressure, it was necessary to wait for another 20 minutes before the steady state between the sample and its vapor could be attained. During this time gas sorption began to occur in the sample at the tip of the needle. At the moment of starting the measurement there was a concentration gradient of the sorbed gas in the sample, yet due to the slender needle of the syringe we used (ca. 0.4 mm inner diameter and ca. 40 mm in length) the diffusion of the sorbed gas into the inner of the syringe was considered to be very slowly and thus the concentration of the gas in the liquid sample decreased rapidly with the depth of this sample in the syringe. As an example, Figure 2 shows the influence of the sorbed gas on the surface tension of the freshly formed MBBA drops. The MBBA sample was filled in the syringe and annealed at 50°C and 15 bar CO_2 for 4 hours before

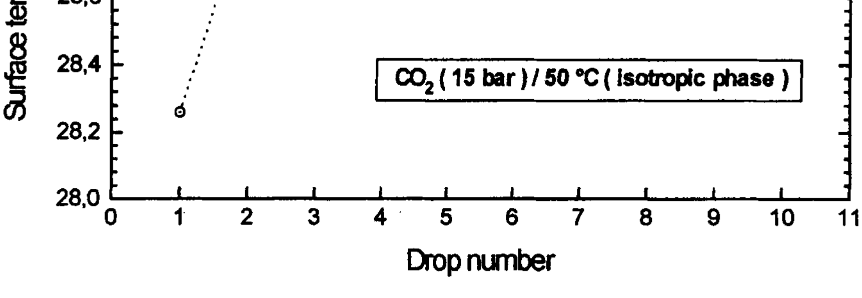

FIGURE 2 The surface tension of MBBA from the same filling in a syringe (1st drop measured after 4 hours hanged in CO_2, 2nd–10th drops measured ca. 20 seconds one after another).

starting the measurement. Except for the first drop, the initial values of the surface tension of the other freshly formed drops from the same filling were measured one after another in the above atmosphere. The relationship between the gas sorption and the surface tension can be clearly inferred: the more sorbed gas in a drop, the smaller its surface tension. Since a convective exchange of the liquid molecules vertically inside the needle as well as the syringe is expected to be very limited due to their small diameters, the intial values of surface tension of the freshly formed drops increase rapidly with the drop number, namely the depth in the needle as well as in the syringe, where the drops forming sample had been located. The sample, which was not so close to the tip of the needle, was still "unpolluted" by the gas during the time before drop formation, so that the drops formed from such sample had almost the same and the highest surface tension value. A similar but stronger phenomenon like described above could be observed in the nematic phase. It is supposed that the influence of sorbed gas molecules on the surface tension of LCs depends more on the substance phase as on the amount of sorbed gas, and thus a higher order phase is easier to be influenced by the sorbed gas than a lower order phase.

The above mentioned measurement is used to choose the MBBA drops for our time-dependent studies of surface tension. With the computer-aided pendant drop method we have the possibility to distinguish a MBBA drop in a time of the order of seconds, whether it has been during the time of preparation "polluted" by gas or not. During the preparation time "unpolluted" pendant drops (e.g. in Fig. 2: from the 7th drop on) are then chosen for the time-dependent studies of surface tension.

RESULTS AND DISCUSSIONS

For the following measurements the fresh MBBA drops are chosen with the procedure described in the previous section (Fig. 2). In order to get an uniform start of the measurements, for each drop a time of 12 seconds is taken for the drop formation as well as for the relaxation of oscillation phenomena. Because of the spontaneous gas adsorption of the surface of the drop even a so-called "unpolluted" drop would be after the 12 seconds partially covered by gas molecules. With the pendant drop method the change process of the surface tension during this time interval, which mainly caused by the adsorbed gas molecules, is impossible to be measured, simply because of the instability of the drop. The first value of the surface tension of a freshly formed drop can only be measured after having formed a stable pendant drop (here after 12 seconds), and this value is called here the *relative* initial value of surface tension $\gamma_{0,r}$. In the previous work of us [11], the time-dependent behavior has been studied only with the *relative* initial values since the measurements were performed at normal gas pressure and only the relative changes of surface tension were taken into account. Such results showed yet no information of the change of surface tension during the time of drop formation. But for the systematic studies of time-dependence of surface tension of LCs, especially at higher gas pressure, such a change may be unnegligible. Therefore it is necessary to determine the initial value of the surface tension of a freshly formed liquid drop without any influence of adsorbed gas molecules. Here we call such an intial value the *absolute* initial value of surface tension $\gamma_{0,a}$. Obviously, the so-called *absolute* initial value $\gamma_{0,a}$ is namely the surface tension of the liquid in its own vapor, which seems able to be measured at reduced pressure ($p = p_{\text{vapor}}$). But unfortunately, due to its low vapor pressure within the range of experimental temperatures a pendant drop of MBBA is out of mechanical balance and can not be hanged at the reduced pressure. The ideal of taking measurements by using the sessile drop method, which in contrast to the pendant drop method can meet the measuring condition, was due to its limited accuracy in the actually experimental condition [15] abandoned. Therefore, an indirect way should be found to determine the $\gamma_{0,a}$ values. In normal experimental condition (1 bar N_2) the nematic-isotropic transition temperature of MBBA is about 43.0°C, but it may decrease with increasing pressure and thus the concentration of sorbed gas in it. A reasonable interpretation for this phenomenon may be attributed to the interaction of MBBA with sorbed gas, and as a consequence the mesophase becomes destabilized. A similar phenomenon was reported by Chen *et al.* [14] for a low molecular LC. To ensure the measurements from this phenomenon, we chose 25°C, which was much lower from the isotropization temperature, as the experimental temperature for the study of the nematic phase of MBBA.

The results on the gas pressure-dependence of the $\gamma_{0,r}$ values of MBBA in different gas atmospheres, both in the nematic (n) phase and in the isotropic (i) phase, are shown in Figures 3 and 4 respectively. Except for He we have observed for the other gases the negative gas pressure-dependence of the $\gamma_{0,r}$ values. For He a positive gas pressure-dependence of the $\gamma_{0,r}$ values is shown. The effect of the pressure itself on the surface tension is so small [16], that it can be neglected. Otherwise, if the pressure effect were dominant, a similar tendency of the gas pressure-dependence for all the gases should be observed, what in reality is not so. What Figure 3 and Figure 4 really show, are the relationship between the *relative* initial values of the

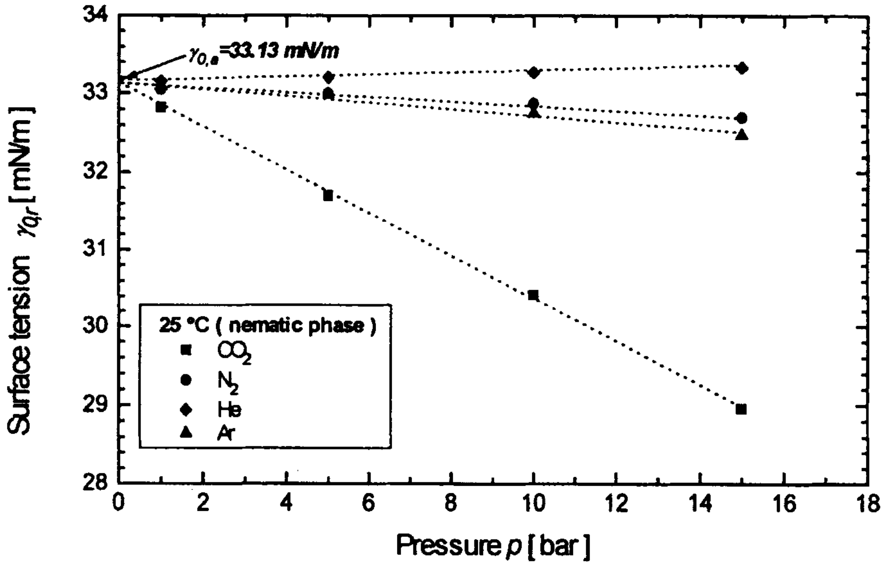

FIGURE 3 Pressure-dependence of the *relative* initial values of the surface tension of MBBA ($\gamma_{o,r}$) at 25°C in different gas atmospheres.

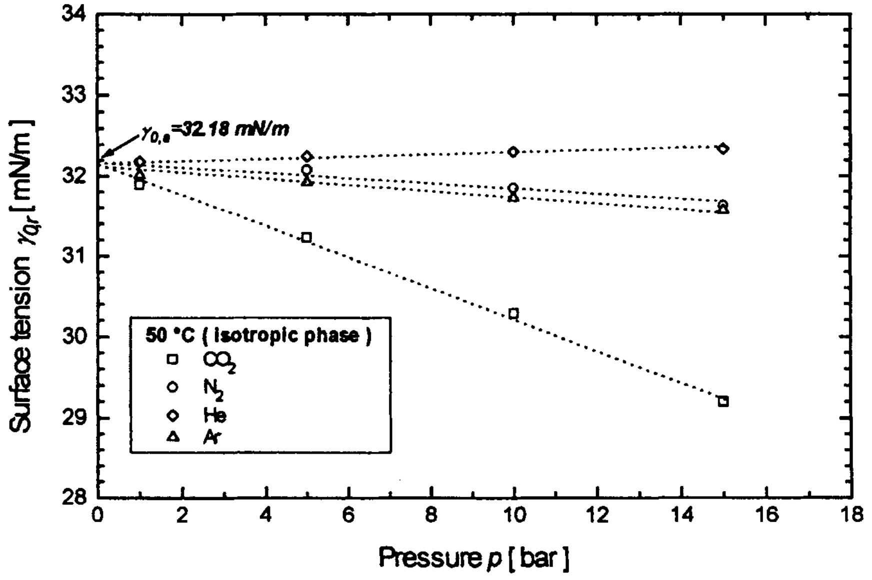

FIGURE 4 Pressure-dependence of the *relative* initial values of the surface tension of MBBA ($\gamma_{o,r}$) at 50°C in different gas atmospheres.

surface tension and the gas adsorption: with the increasing gas pressure, more gas molecules are adsorbed during the time of drop formation in the surface region of the drops, and thus a stronger increase (for He) as well as stronger decreases (for N_2, CO_2 and Ar) of the surface tension can be observed. The relationship shows very good linearity for each gas. After extending the line to $p=0$ bar for each gas respectively, a confluent surface tension of 33.13 mN/m is then obtained for 25°C (*n*-phase) of MBBA, and 32.18 mN/m for 50°C (*i*-phase). Now that all the $\gamma_{0,r}$ values in the diagrams have been measured in equilibrium with the saturated MBBA vapor, the pressure scales in these diagrams represent the sum of the vapor pressure of MBBA and the gas pressure. Strictly speaking, we should take the surface tension at the point $p=p_{\text{vapor}}$ as the $\gamma_{0,a}$ values of the surface tension. But the vapor pressures of MBBA at the experimental temperatures are so small, that both values of surface tension at $p=0$ can be well approximately taken as the $\gamma_{0,a}$ values for 25°C and 50°C, respectively. The accuracy of the method is estimated to be ± 0.015 mN/m.

The effect of gas adsorption on the surface tension depends on gas concentration-, gas type- and substance phase (Tab. I). Among the four gases CO_2 has the largest effect on a fresh drop with a $d\gamma_{0,r}/dp$ value of -0.28 mN/m·bar at 25°C and -0.20 mN/m·bar at 50°C, while He the smallest but positive $d\gamma_{0,r}/dp$: $+0.01$ mN/m·bar for both 25°C and 50°C. These results supported that: the adsorption of gas molecules at a liquid surface with a particular structure (e.g. liquid crystals) causes the change of the molecular composition in the surface layer and may induce some other orientational and/or structural changes of the molecules near the surface [11]. Since the processes of such re-orientation and structural changes are in general believed to run rapidly (milliseconds to seconds) [17], they can be at least partially finished and thus cause the change of the surface tension during the time of drop formation. A similar phenomenon to the positive $d\gamma/dp$ in He was observed by Wigand and Franck [18]. They have measured the adsorption

TABLE I Gas pressure-dependence of the *relative* initial values of the surface tension of the freshly formed MBBA drops in different gas atmospheres*

	N_2	CO_2	He	Ar
$d\gamma_{0,r}/dp$ [mN/m.bar] (25°C, nematic phase)	-0.03	-0.28	$+0.01$	-0.04
$d\gamma_{0,r}/dp$ [mN/m.bar] (50°C, nematic phase)	-0.03	-0.20	$+0.01$	-0.03

*The $\gamma_{0,r}$ values were measured 12 seconds after formation of fresh drops.

isotherms of He, N_2 and CH_4 on the water surface within a wide pressure range (0–2000 bar). In contrast to N_2 and CH_4, in which a decrease of the surface tension with the increasing gas pressure occurred, He caused an increasing surface tension. Although water is no liquid crystalline substance, it was suggested to have a particular structure some how like "ice" in outer layers of the water surface [19, 20], and thus could be also affected by certain gas molecules.

Two examples of the time-dependence of the surface tension difference ($\Delta\gamma = \gamma - \gamma_{0,a}$) of the freshly formed MBBA drops in He as well as in CO_2 are shown in Figure 5 and Figure 6, for the nematic phase (25°C) and the isotropic phase (50°C), respectively. For both temperatures a strong time-dependence can be observed. At a pressure of 10 bar the *relative* initial values $\gamma_{0,r}$, which can be directly measured, have a value of 30.62 mN/m in CO_2 and 33.27 mN/m in He at 25°C, while 30.45 mN/m in CO_2 and 32.31 mN/m in He at 50°C. The increase of the surface tension of MBBA in He during the formation time of a stable drop indicates a particular effect of Helium molecules on the liquid surface, compared with the other gases (e.g. CO_2), in which a decrease occurs. In CO_2 the surface tension of a fresh MBBA drop decrease very rapidly during drop formation for 2.51 mN/m at 25°C and 1.73 mN/m at 50°C, which corresponded to about 65.4% and

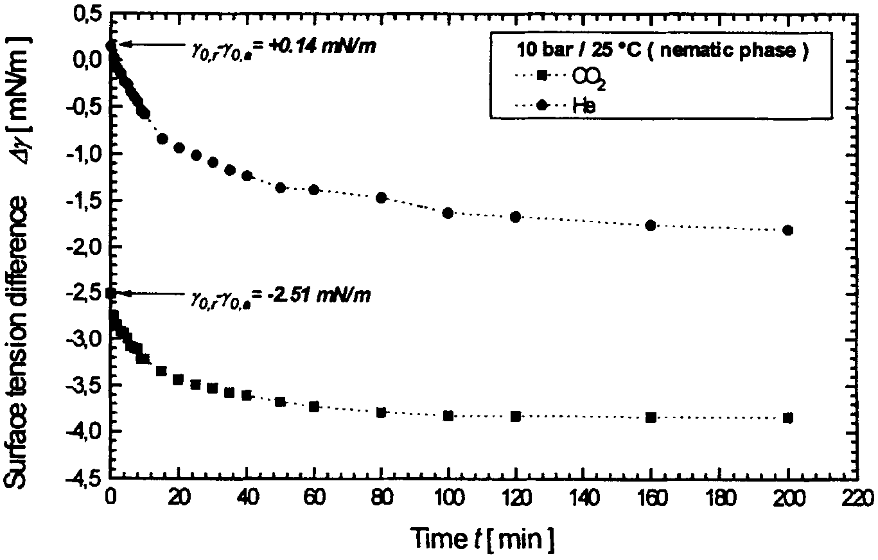

FIGURE 5 Time dependence of the surface tension difference of MBBA at 25°C ($\Delta\gamma = \gamma - \gamma_{0,a}$ with $\gamma_{0,a} = 33.13$ mN/m).

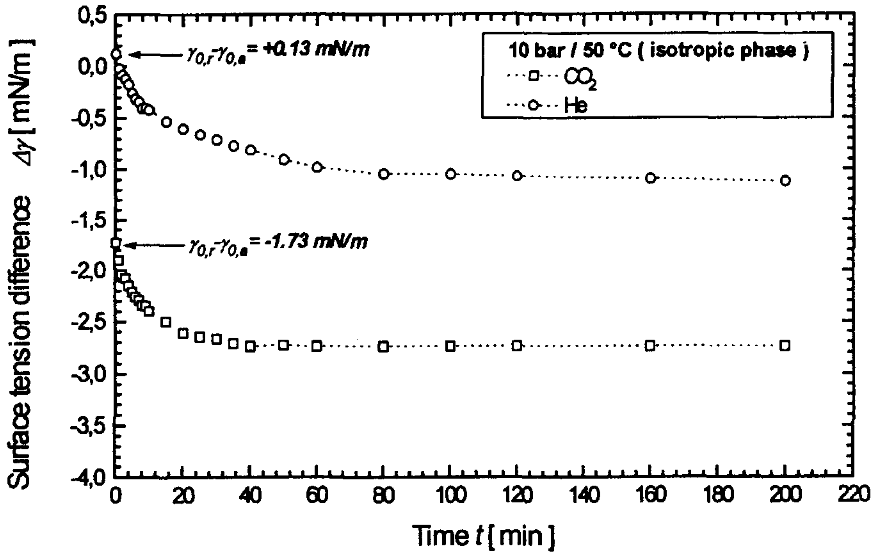

FIGURE 6 Time dependence of the surface tension difference of MBBA at 50°C ($\Delta\gamma = \gamma - \gamma_{0,a}$ with $\gamma_{0,a} = 32.18$ mN/m).

63.1% of the total decrease after reaching the steady-state, respectively. Such a change of the surface tension is considered to be mainly caused by the gas adsorption, while the following time-dependence by the sorption (adsorption and diffusion). The above results predicate the change of surface tension during drop formation to be unnegligible and in some conditions dominant. The similar long time-dependent phenomena of the surface tension of a freshly formed drop, without concerning the time period of drop formation, were reported by us for different LCs [11] 'at normal pressure, we have also discussed the possibility of chemical changes during measurements and the effect of surface active impurities in samples. According to our results these both possibilities can not be essentially responsible to the time-dependent phenomena of surface tension. Systematic experimental studies of the time-dependence of surface tension of LCs on gas pressure and on gas type will be published later.

CONCLUSIONS

We have described a gastight measuring chamber for gas pressure- and gas type-dependent studies of the surface tension of liquid crystalline substances using the pendant drop method. The so-called *relative* initial values of the surface tension of the freshly formed surface of MBBA ($\gamma_{0,r}$) in different gas atmospheres have been measured, both in the nematic phase and in the isotropic phase. An indirect procedure has been used to determine the *absolute* initial values of the surface tension of MBBA ($\gamma_{0,a}$): 33.13 mN/m for 25°C (*n*-phase) and 32.18 mN/m for 50°C (*i*-phase). These values are essential for the systematic time-dependent studies of the surface tension of MBBA. As an example the time-dependent phenomena of the surface tension in various experimental conditions, with consideration of the above $\gamma_{0,a}$ values, are shown. The change of surface tension of MBBA during the time of drop formation is proved to be unnegligible in certain gas atmospheres (e.g. CO_2) and especially at higher gas pressure. The results supported the suggestion, that the unusual time-behaviour of surface tension of LCs may be mainly attributed to the gas sorption processes taking place in the liquid drops, possibly brought about by the interaction between the gas molecules and the moelcules at the liquid surface or the gas-induced reordering and/or reorganization of the surface molecules. Further studies on time- and temperature-dependence of surface tension of LCs on gas pressure and on gas type are now under way in our laboratory.

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