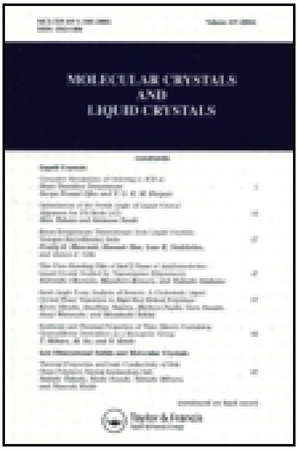

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Influence of Gas Sorption on Surface Tension of Liquid Crystalline Substances:—Influence of CO_2 on Time-dependence of Surface Tension

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Version of record first published: 04 Oct 2006

To cite this article: Gong-Hao Chen & JÜRgen Springer (1998): Influence of Gas Sorption on Surface Tension of Liquid Crystalline Substances:—Influence of CO_2 on Time-dependence of Surface Tension, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 312:1, 203-221

To link to this article: http://dx.doi.org/10.1080/10587259808042441

Mol. Cryst. Liq. Cryst., 1998, Vol. 312, pp. 203–221
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Influence of Gas Sorption on Surface Tension of Liquid Crystalline Substances

– Influence of CO_2 on Time-dependence of Surface Tension –

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(Received in final form 29 July 1997)

As one part of the experimental studies on the influence of gas sorption on the surface tension of liquid crystalline substances (LCs), this paper reports on the CO_2 sorption in low molecular LC MBBA (4-methoxybenzylidene-4′-*n*-butylaniline) and thus caused the time-dependence of surface tension. The experiments have been performed in the CO_2 atmosphere over the temperature range which covered the phase transitions of MBBA, and at pressures up to 15 bar.

Separately, the surface tension measurements and the gas sorption measurements have been carried out under the same experimental conditions, by using a computer-aided measuring set-up based on the pendant drop method and a high pressure electromicrobalance, respectively.

The paper provides experimental evidences for our previous suggestion, that the unusual time-dependence of surface tension of the freshly formed LC surfaces may be mainly attributed to the gas sorption processes, by comparing the results from above different measurements. The paper also reports the phase transition behaviors of MBBA as a function of the sorbed gas concentration, and the reversibility of the CO_2 sorption.

Keywords: Surface tension; gas sorption; time-dependence; temperature-dependence; pressure-dependence; phase transition; liquid crystals; MBBA; carbon dioxide

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INTRODUCTION

Recently we have reported the remarkable time-dependence of the surface tension of the freshly formed surfaces, which has been observed on various liquid crystalline substances (LCs), both of low molecular and polymeric, both in the mesophase and in the isotropic phase [1 – 3]. After discussing several possible processes which may lead to this time-dependence: such as the re-orientation or re-arrangement of the molecules at the surface, the chemical changes of the samples and the sorption of gases in the samples, we supposed that the gas sorption process taking place at the liquid surface as well as in the liquid bulk may be mainly responsible for this time-behavior.

Therefore, systematic experimental studies on the influence of gases on the surface tension of LCs have been performed in our laboratory. In our previous works [2, 3], we have determined the so-called *absolute* initial values of the surface tension ($\gamma_{0,a}$) of MBBA, both in the nematic (*n*) phase (25°C) and in the isotropic (*i*) phase (50°C), by using an indirect procedure via the pendant drop method. These $\gamma_{0,a}$ values enabled us to investigate the changes of the surface tension of the fresh MBBA drops during the time of drop formation, which have been next verified to be unnegligible in certain gas atmospheres (e.g. CO_2) and especially at higher gas pressures. We have also reported the surface tension behaviors of MBBA in the N_2 atmosphere of different pressures. The time-dependent surface tension of a freshly formed MBBA drop is proved to be a function of the gas type, gas pressure and LC phase. The suggestion, that the unusual time-dependence of surface tension of LCs may be mainly attributed to the gas sorption process, is supported by the results of our investigations. In the case of N_2 the sorbed gas concentration in MBBA doesn't critically affect the shape of the temperature-dependent surface tension ($\gamma(T)$-curves), but with increasing gas concentration in the sample the surface tension values of MBBA become generally lower. All the $\gamma(T)$-curves of MBBA obtained at different N_2 pressures show an *anomaly* near the phase transitions, which indicates the existence of higher ordered molecular states on the drop surface. Furthermore, the effect of the N_2 sorption on the *i-n* phase transition of MBBA has been also discussed, and the reversibility of the sorption process has been confirmed.

In continuation of our previously reported experimental studies on the influence of gas sorption on the surface tension of LCs, we will report in the present paper the time-dependence of the surface tension of MBBA at various CO_2 pressures correlated with the sorption behaviors of CO_2 in it, under the same experimental conditions. The influence of the sorbed gases on the phase transitions will be also discussed.

EXPERIMENTAL

(A) Materials

The MBBA (4-methoxybenzylidene-4′-*n*-butylaniline) sample obtained from Aldrich Chem. Company Inc. (USA) had a purity > 98%, given by the manufacturer. The sample was recrystallized from ethanol several times and then dried in vacuum. Immediately after evacuation it was stored at 0°C with dry nitrogen as protective gas. The phase behavior of the MBBA sample 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 results obtained in normal condition (at 1 bar N_2) are shown in Table I.

The employed gas CO_2 was purchased from the Company Messer Griesheim (Germany) and had a purity > 99.99%.

(B) Surface Tension Measurements

The surface/interfacial tension measurements of liquid/fluid-system were carried out by using a computer-aided pendant drop method, based on the principles discussed earlier [4]. 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.

(C) Preparation of Samples and Formation of Pendant Drops

All the surface tension measurements have been carried out in a gas-tight measuring chamber described in a previous paper [2]. After filled with a sample the syringe was heated under vacuum above the melting temperature of the LC. The syringe was then degassed in vacuum to remove gas bubbles

TABLE I Results of phase characterization of MBBA

Substance	*Phase Characterization* [1,2]
MBBA	*c* 24.0°C *n* 43.0°C *i*

[1] The *c-n* phase transitions were detected only by heating (monothermotropic).

[2] Due to the incompleteness of the N_2 sorption, the *i-n* phase transition temperature obtained by DSC as well as polarization microscopy are a little higher than those obtained during the surface tension measurements [3].

in the sample. After that the syringe had been cooled to room temperature, it was taken from vacuum and immediately inserted into the chamber. A reservoir of sample in the chamber was necessary to get a vapor-saturated atmosphere. The time-dependent measurements of surface tension has been described in other papers [1 – 3].

(D) Density

The temperature-dependence of the density ($\rho(T)$) of the two fluid phases is necessary by calculation of the surface/interfacial tension using the pendant drop method. The density of the gas phases was calculated using the normal gas law for ideal gases. Since MBBA is in liquid state within the experimental temperature range (25°C – 50°C), the temperature-dependence of its density, was measured at 1 bar air with a density meter DMA 48 from company Chempro/PAAR, GB. At every measuring temperature the density meter was calibrated with air and water. The accuracy of the measurement was estimated at $\pm 1.10^{-4}$ g/cm^3. The temperature-dependence of the density of MBBA under higher gas pressures has been discussed earlier [3].

(E) Gas Sorption Measurements

The sorption measurements of CO_2 in MBBA were performed by gravimetric method through use of a high pressure electromicrobalance (Model 4436, Sartorius, Germany). Details of the measuring set-up have been given in an earlier paper [5]. Basically, this set-up consists of a sorption chamber, a vacuum and gas supply system, a temperature controlled isolation body as well as a personal computer. The available regulation range of the temperature, namely the calibrated temperature range of the microbalance, is from 0°C to 70°C, which is sufficient for locating phase transitions of the LC under investigation.

Prior to the measurements the MBBA samples were degassed in vacuum using an oil diffusion pump in connection with a rotary oil pump. In order to avoid the evaporation of the low molecular LC, the evacuation was carried out at 0°C, at which temperature all the samples were in the crystalline state. After reaching a constant weight of a sample, a desired pressure of CO_2 was introduced into the chamber to start the temperature-dependent sorption experiments. All the measurements were performed with increasing temperature. Otherwise, with decreasing temperature, due to the strong retardation of the nematic-crystalline transition the corresponding sorption was very difficult to be measured. Due to the thermal extension of the gas in the microbalance by heating, it was necessary from time to time to control the gas pressure.

Following steps have been performed for the kinetic study of the time-dependent sorption measurements: to simulate the experimental condition as well as the state of a LC sample in the time-dependent measurements of the surface tension, the sample was firstly saturated with the gas at 0°C (crystalline (*c*) phase). Subsequently, the sample was very shortly (several minutes) evacuated with the rotary oil pump. A desorption of the sorbed gas from the sample during this evacuation was expected to be very limited. The sample was then heated up to the desired temperature in vacuum so as to avoid the gas sorption during the temperature-heating. It was necessary to wait for another several hours to ensure a homogeneous temperature over the microbalance, which could be confirmed by attaining a stable weight of the sample under investigation. Finally the time-dependent measurement was started immediately after the introduction of CO_2 into the microbalance.

In all sorption measurements the weight increase of sorbing samples was continuously registered as a function of time by the computer.

RESULTS AND DISCUSSIONS

Before we begin with our experimental results, some words are necessary for the concept *surface tension* used in our papers. Normally, in literature, the interfacial tension of a liquid in its own vapor or in a chemically indifferent gas up to a pressure of the order of normal atmosphere is called as the surface tension of this liquid. According to our knowledge so far, almost all of the surface tension measurements of various LCs reported by different authors [6–23] have been carried out in indifferent gases, so that the gas sorption was unavoidable. One of the main goals of our present works is to know how these gases indifferent are and how different the effects of these gases on the surface tension of LCs can be. Considering that the elevated gas pressures employed by us to vary the sorbed gas concentration in LCs are relative low (1 – 15 bar), and thus the effects of such gas atmospheres are widely different from that at very high pressures. Therefore, to continue the common naming of the concept *surface tension*, we call *here* the gases/LCs interfacial tension at all of the elevated pressures in our experiments also as the surface tension of the LCs.

Using the $\gamma_{0,\,a}$ values of MBBA reported in our previous paper [2]: 33.13 mN/m at 25°C and 32.18 mN/m at 50°C, Figures 1 and 2 show the time-

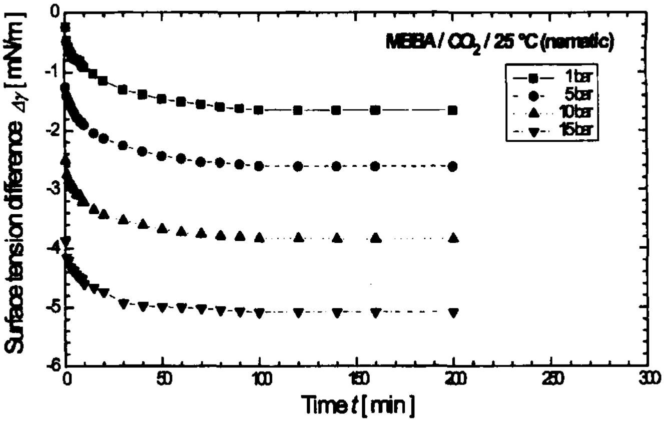

FIGURE 1 Time-dependence of the surface tension difference of MBBA in CO_2 at 25°C ($\Delta\gamma = \gamma(t) - \gamma_{0,\,a}$ with $\gamma_{0,\,a} = 33.13$ mN/m).

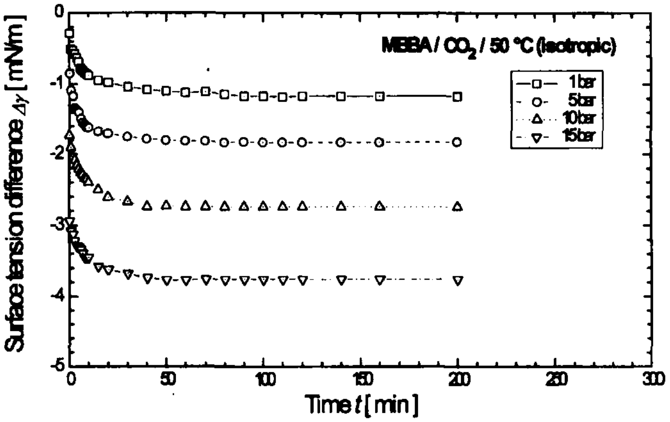

FIGURE 2 Time-dependence of the surface tension difference of MBBA in CO_2 at 50°C ($\Delta\gamma = \gamma\ (t) - \gamma_{0,\,a}$ with $\gamma_{0,\,a} = 32.18$ mN/m).

dependence of the surface tension difference ($\Delta\gamma = \gamma(t) - \gamma_{0,\,a}$) of the freshly formed MBBA drops at different CO_2 pressures, both for the *n*-phase (25°C) and for the *i*-phase (50°C). As mentioned, in using the pendant drop method, the first directly measured surface tensions of the freshly formed surfaces can be only obtained after having formed the stable drops (12 seconds in our case). These values are called by us as the *relative* initial values of the surface tension ($\gamma_{0,\,r}$) which are represented by each of the first points on the $\Delta\gamma(t)$-curves shown in the figures, respectively. The decrease of the surface tension during the drop formation at the pressure p is given by the difference $\Delta\gamma_{\mathrm{formation}} = \gamma_{0,\,r}(p) - \gamma_{0,\,a}$. Table II lists such decrease of the surface tension under various CO_2 pressures as well as under various N_2 pressures (obtained in the previous work [3]). Compared with in N_2, in CO_2 the surface tension of a fresh MBBA drop decreases much more strongly during the drop formation, especially at higher pressures. With increasing CO_2 pressure the proportion of such decrease in the total decrease of the surface tension ($\Delta\gamma_{\mathrm{total}} = \gamma_{\mathrm{equilibrium}}(p) - \gamma_{0,a}$), becomes more and more heavier. The $\Delta\gamma_{\mathrm{formation}}/\Delta\gamma_{\mathrm{total}}$ ratio increases from 14.5% to 76.2% at 25°C (nematic), and from 24.8% to 78.2% at 50°C (isotropic), as the pressure increases from 1 bar to 15 bar. These results confirmed our previous conclusion that change of the surface tension of MBBA during drop formation to be unnegligible and in some conditions dominant. Such a change is considered to be mainly caused by the gas adsorption at the drop surface, while the following time-dependence caused by the sorption (adsorption and diffusion), in which CO_2 shows also a much stronger but relative short-time effect than N_2. Similar to N_2, as the gas pressure becomes higher, each time-dependence curve, either in the *n*-phase or in the *i*-phase, systematically changes its shape with a more rapid and stronger decreasing rate to attain equilibrium: increasing the CO_2 pressure from 1 bar to 15 bar, the time needed to reach the equilibrium surface tension decreases from *ca.* 120 minutes to *ca.* 80 minutes at 25°C (nematic), while it decreases from *ca.* 90 minutes to *ca.* 50 minutes at 50°C (isotropic). Generally in the *n*-phase the time needed to reach the equilibrium value of the surface tension is longer and the time-dependence of the surface tension is stronger than in the *i*-phase. The obvious time-dependence of the surface tension of MBBA at 50°C (isotropic) indicates, that even at a temperature of *ca.* 7°C above the *i*-*n* phase transition (Tab. I) some higher-ordered structures might exist in the surface layers [24–29]. The time-dependence rate of the surface tension is a function of the gas type, gas pressure and molecular state.

TABLE II Decrease of the surface tension of the freshly formed MBBA drops during drop formation time as a function of the gas pressure*

$\Delta\gamma_{\mathrm{formation}} = \gamma_{0,r}(p) - \gamma_{0,a}$	CO_2				N_2			
[mN/m]	1bar	5 bar	10 bar	15 bar	1 bar	5 bar	10 bar	15 bar
25°C, nematic	−0.24	−1.26	−2.51	−3.87	−0.08	−0.13	−0.26	−0.43
50°C, isotropic	−0.29	−0.85	−1.73	−2.94	0	−0.10	−0.33	−0.55

* The $\gamma_{0,r}$ values were measured 12 seconds after formation of fresh drops. The accuracy of the results is estimated to be ±0.015 mN/m.

Figure 3 shows the equilibrium concentration of the sorbed CO_2 in MBBA as a function of the temperature ($c(T)$-curve) under normal pressure. This temperature-dependence covers the different phases of MBBA. The temperature marking these transitions, T_{cn} and T_{ni}[1], are defined at the beginning of the transitions. In the crystalline phase MBBA contains a very low concentration of the sorbed CO_2, which inceases as well only slightly with temperature within the crystalline phase (0°C-*ca.* 24°C). The equilibrium concentration of CO_2 increases dramatically at the transition of the crystalline to the nematic phase, which is well in agreement with the results obtained on another low molecular LC by Chen *et al.* [30]. The upward trend of the $c(T)$-curve keeps on throughout the nematic and the isotropic phase. Different from the LC investigated by Chen *et al.*, the change in the concentration of the sorbed CO_2 in MBBA at the *n-i* transition is much smaller but still recognizable. This infers that the gas sorption is strongly dependent on molecule structures of the LCs. Based on the above observation, it is reasonable to say that the MBBA sample which might have been saturated with gas (N_2) during the storage (0°C, crystalline state) is capable of sorbing more gas while our measuring its surface tension (25°C-50°C).

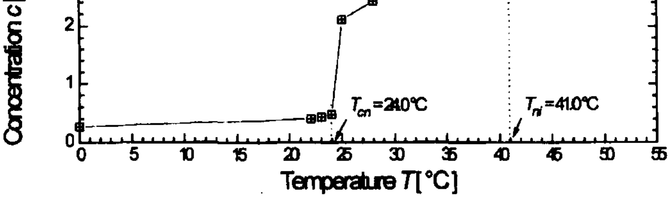

FIGURE 3 Temperature-dependence of the CO_2 sorption in MBBA at 1 bar.

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[1] Different from the measurements of the temperature-dependent surface tension, which were measured by cooling and thus the *i-n* phase transition temperature was defined as T_{in}, the temperature-dependent sorption measurements, as mentioned, have been performed by heating, so that we define in the present paper this temperature as T_{ni}. This applies also to the *c-n* phase transition temperature T_{cn}.

A comparison of the $c(T)$-curves of CO_2 in MBBA at various gas pressures is shown in Figure 4. All the curves show a similar form to that shown in Figure 3. In the crystalline phase the gas pressure influences only slightly the solubility of CO_2 in MBBA. This is attributed to the fact that crystalline regions are inaccessible; the gas can be only adsorbed to the surface regions or in the defects between crystallites. At higher temperatures, namely in the nematic and the isotropic phase, the difference between the $c(T)$-curves obtained at different pressures is generally much stronger. Compared with the *c*-*n* phase transitions, the *n*-*i* transitions show a considerably smaller discontinuity in the concentration of the sorbed CO_2. Yet this discontinuity enhances with the increase of gas pressure. At lower pressures, the dc/dT-value is in *i*-phase a little higher, while, at higher pressures, it turns, lower than that in the *n*-phase. Figure 5 shows the sorption isotherms of CO_2 in MBBA at 25°C and 50°C. The solubility of CO_2 shows a strong positive dependence with increasing pressure, both in the *n*-phase and *i*-phase. In the low pressure range the sorption values at 25°C (nematic) are obviously lower than those at 50°C (isotropic), and these values gradually approach the isotropic ones when the pressure increases. This means that with increasing pressure the constantly higher becoming transition sorption (Δc, the difference of gas concentration between the *i*- and *n*-phase) is offset by the changes of the dc/dT-slopes.

Analogous to the measurements on the time-dependent surface tension, the sorption kinetic of CO_2 to attain equilibrium states in MBBA has been also performed at different gas pressures. It's known that the kinetic of gas

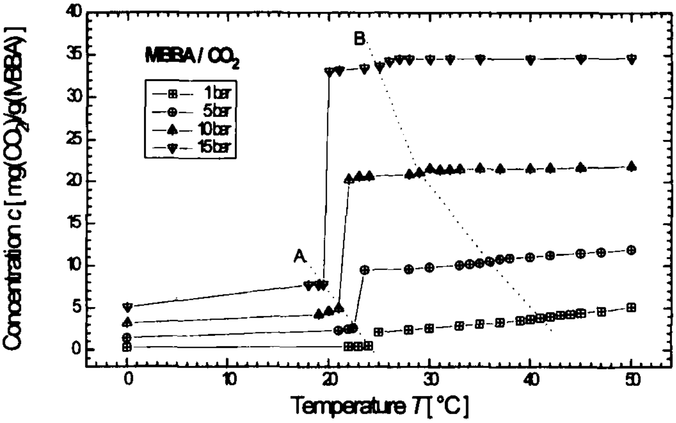

FIGURE 4 Temperature-dependence of the CO_2 sorption in MBBA at various pressures (Line A and line B represent the *c*-*n* and the *n*-*i* phase transition temperature, respectively).

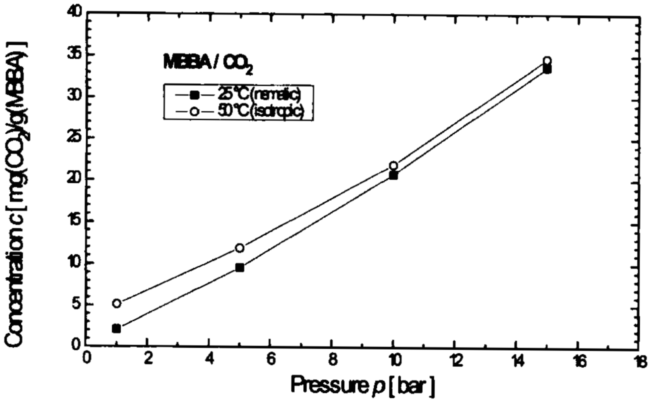

FIGURE 5 Sorption isotherms of CO_2 in MBBA at 25°C and 50°C.

sorption depends not only on the gas type, gas pressure, temperature as well as molecular properties, it is also strongly dependent on the surface/volume-ratios of samples. In order to have a possibly high accuracy, during the surface tension measurements, the pendant drops have been strictly controlled within a suitable size, typically for MBBA, of a volume of *ca.* 5.6 mm^3 and a surface of *ca.* 12.5 mm^2 (by using the needle with a outer diameter of 0.70 mm), which gave a surface/volume-ratio of *ca.* 2.2 [1/mm]. To simulate the situation of a drop in the surface tension measurements, it is essential to maintain the same surface/volume-ratio for the MBBA samples during the kinetic studies of the gas sorption. In our case, for a quartz pan employed in the microbalance with a diameter of 14 mm, a cylinder-shape liquid film of *ca.* 0.45 mm in depth was required for getting the above surface/volume-ratio. Thus, for MBBA a initial mass of *ca.* 80 mg of the samples was necessary.

The $c(t)$-curves of MBBA at 25°C (nematic) as well as at 50°C (isotropic) are shown in Figures 6 and 7 as a function of the CO_2 pressure. Similar to the results of the time-dependence of the surface tension, as the gas pressure becomes higher, each differential sorption curve systematically changes its shape with an increasing sorption rate to attain equilibrium, and this applies both to the *n*-phase and *i*-phase. Generally the time needed to reach the equilibrium is in the isotropic phase less than this in the nematic. That means, that the transport of CO_2 in the LC should be represented by a gas pressure, gas concentration (in the sample) and LC phase dependent diffusion coefficient. Some examples are shown in Figures 8–11 for a correlation between the $\gamma(t)$-curves and the $c(t)$-curves under analogous

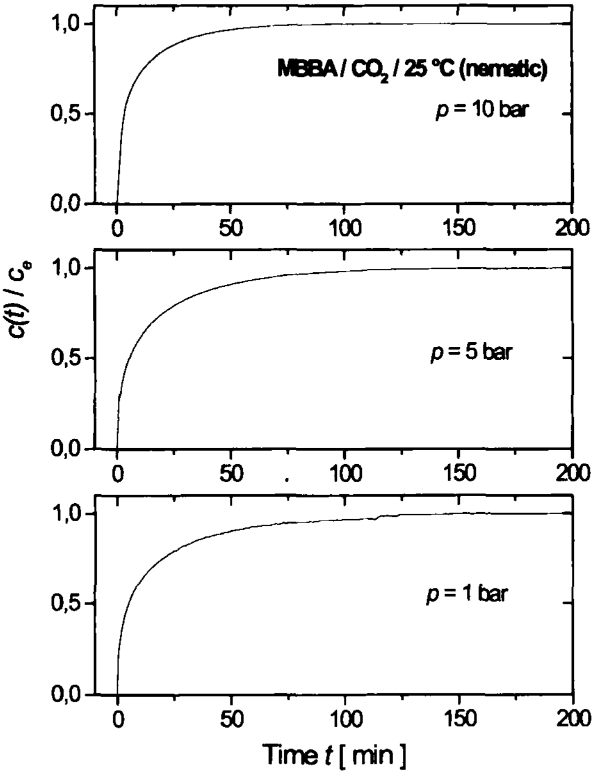

FIGURE 6 Reduced sorption curves of CO_2 for the nematic state of MBBA at various prssures (c (t) is the concentration of the sorbed gas at time t and c_e is the equilibrium value of the gas concentration).

experimental conditions. As seen, both in the *n*-phase and *i*-phase, both at normal gas pressure and at higher pressures, the time needed to reach the equilibrium which obtained from both kinds the curves is in good agreement with each other.

Previously, the possibility that the adsorption of surface active impurities, by which we meant all molecular species other than the liquid molecules themselves, from the drop liquid phase alone can lead to the observed time-dependence of the surface tension, has been excluded by us based on the following experiment [1]: after a freshly formed liquid drop has attained its steady-state the drop was destroyed by pulling it back into the syringe needle. After waiting for several minutes a new drop was formed again by driving the liquid out of the needle. Since a convective exchange of the liquid molecules vertically inside the needle was expected to be very limited due to

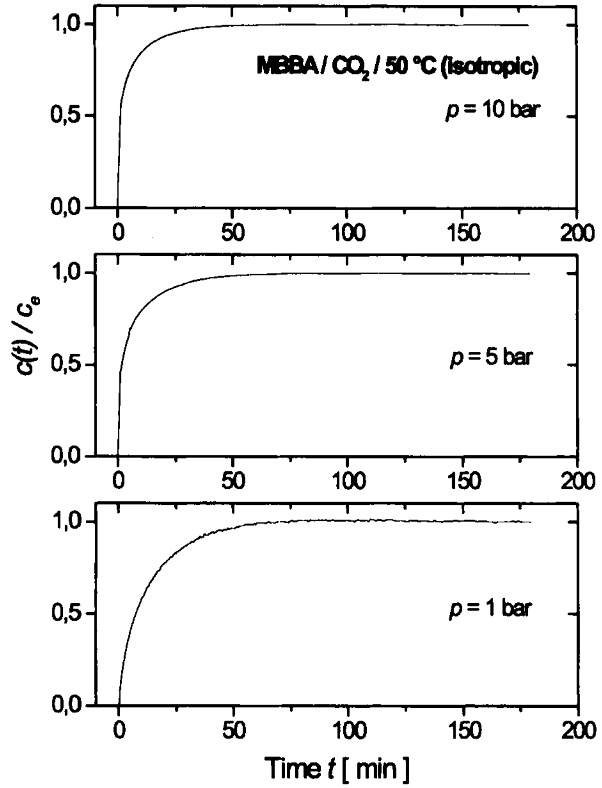

FIGURE 7 Reduced sorption curves of CO_2 for the isotropic state of MBBA at various pressures ($c(t)$ is the concentration of the sorbed gas at time t and c_e is the equilibrium value of the gas concentration).

its small diameters, the portion of the liquid used to form the new drop was nearly the same as that composed the previous one. The so formed new drop attained the steady-state value of the surface tension already in several seconds for low molecular LC-substances. The steady-state value of the surface tension of the new drop was found to be nearly identical with that of the previous one.

To confirm the above consequence, further experiments on the time-dependence of the surface tension of the with CO_2 saturated MBBA samples have been carried out at various pressures and temperatures. To avoid the desorption of the CO_2 from the saturated sample at preparation, which could later cause the sorption and thus the time-dependence of the surface tension once again, all of the processes should be done in the closed

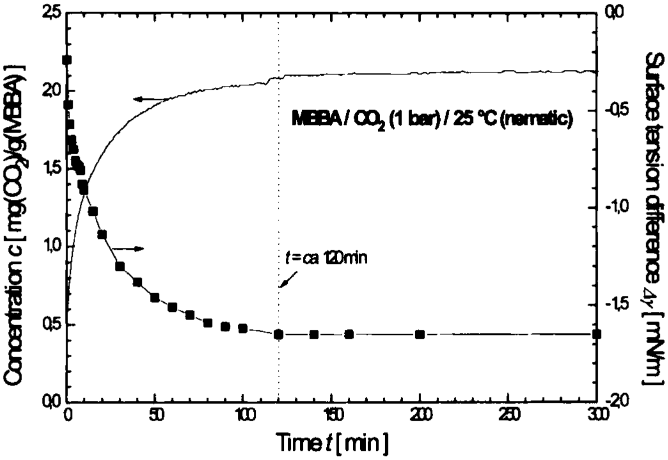

FIGURE 8 Comparison between the sorption curve and the time-dependence of the surface tension for the nematic state of MBBA (25°C, 1 bar CO_2).

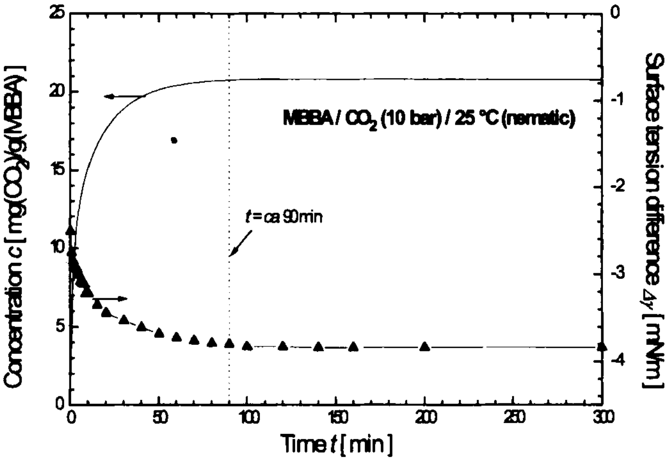

FIGURE 9 Comparison between the sorption curve and the time-dependence of the surface tension for the neamatic state of MBBA (25°C, 10 bar CO_2).

chamber. For this reason, the following method has been used to regain MBBA saturated with CO_2 (Fig. 12): in the gas-tight measuring chamber employed for the surface tension measurements, a small glass beaker was attached, at the bottom of it, with a very little among of paraffin to a metal supporter. The paraffin has been chosen with a melting point of *ca.* 56°C which was a little higher than the maximum experimental temperature on

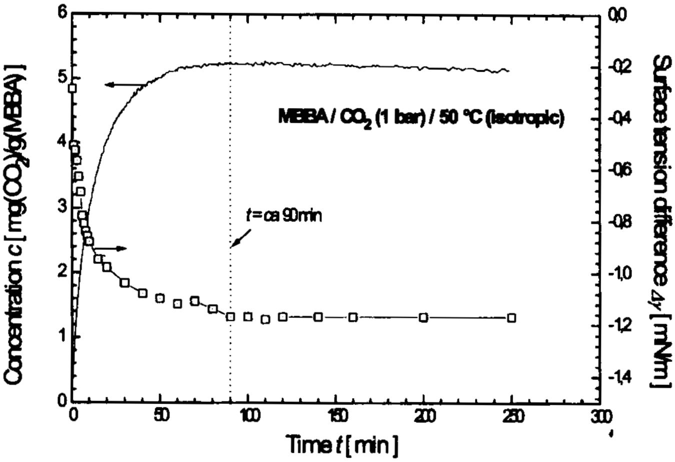

FIGURE 10 Comparison between the sorption curve and the time-dependence of the surface tension for the isotropic state of MBBA (50°C, 1 bar CO$_2$).

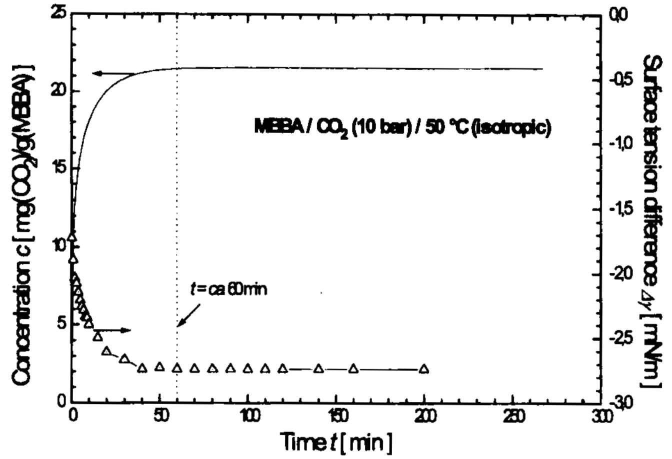

FIGURE 11 Comparison between the sorption curve and the time-dependence of the surface tension for the isotropic state of MBBA (50°C, 10 bar CO$_2$).

MBBA. The position of the glass beaker was so adjusted, that its bottom was as near as possible to the tip of the needle used for forming pendant drops. As a desired pressure as well as temperature had been reached, the MBBA sample was firstly driven into the beaker. A enough long time was waited to get the sample saturated with CO$_2$. Then the sample was pulled again into the syringe. Finally the measuring chamber was heated up very

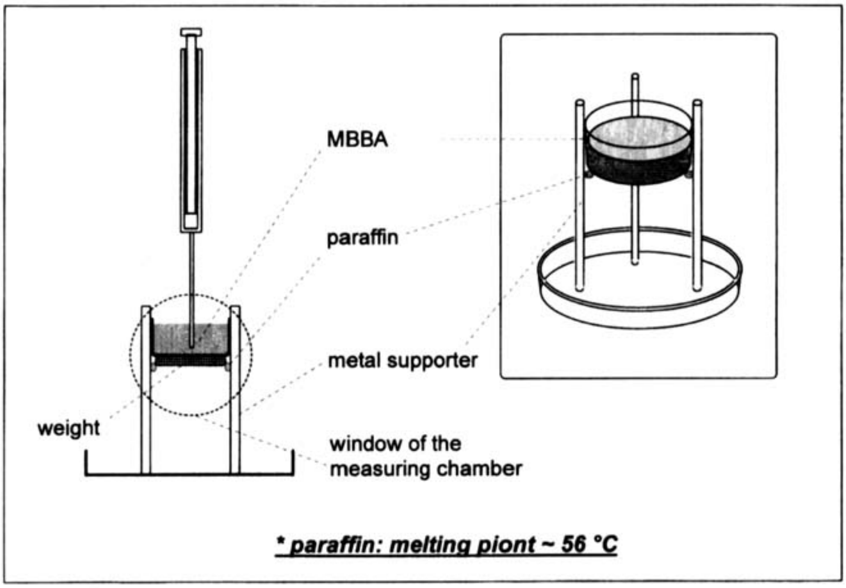

FIGURE 12 Schematic representaion of regaining MBBA samples, saturated with CO_2, in a closed measuring chamber.

shortly to the melting point of the paraffin, and the glass beaker fell to the bottom of the supporter, with the help of a metal weight. We measured the surface tension of the so prepared MBBA samples at various gas pressures, and both in the *n*-phase and *i*-phase. In all the cases, the samples didn't show the time-dependence of the surface tension any more. They reached the equiliburium states immediately after forming the drops. In addition, such samples were evacuated at 0°C again. Since an entire desorption of CO_2 from MBBA was quite difficult, a long time was required for the evacuation. As expected, the freshly formed drops of the desorbed samples showed once again a remarkable time-dependence of the surface tension, which was similar to the described in Figures 1 and 2. Based on the above observation, we confirmed the reversibility of the CO_2 sorption in MBBA. Different analyses (e.g. IR, NMR) on the recycled MBBA samples after the surface tension measurements showed no indications of chemical changes.

All the above results supported the suggestion, that the unusual time-behavior 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 molecules at the liquid surface or the gas-induced reordering and/or reorganization of the surface molecules. The transport of the CO_2 molecules in the MBBA under investigation should be represented by a gas type, gas concentration, temperature, substance structure and substance phase dependent diffusion coefficient, and thus the time-dependence of the surface tension is a function of the momentary distribution of the gas concentration in the surface region and in the bulk of the drop. The time-dependence of surface tension is supposed possibly to have confused the measurement of the early workers and may account partially for the inconsistencies of the results obtained so far [1, 6–13].

Finally we will discuss the influence of the sorbed CO_2 on the phase transitions of MBBA. Figure 13 shows the T_{ni}'s of MBBA *vs.* the gas pressure. In order to have a comparison, the results on the effect of N_2 reported in our previous paper [2] are also presented in this diagram. The T_{ni} values in various gas atmospheres can be obtained from the inflection points on the $c(T)$-curves (Fig. 4), or as described previously, can be obtained from the $\gamma(T)$-curves as well as from the visual observation of the drop images [2]. Generally with increasing gas pressure thus increasing sorbed gas concentration in the LC decrease the transition temperatures. A reasonable interpretation for this phenomenon is due to the interaction of the MBBA molecules with the sorbed gas molecules. Since a important factor for the formation of LC phases is the anisotropy of intermolecular forces between LC molecules [31], the introduction of the gas molecules reduces these intermolecular forces and the LC phases become destabilized. This can be expressed through the bulk properties of LCs such like the *n*-*i* phase transition temperature T_{ni}.

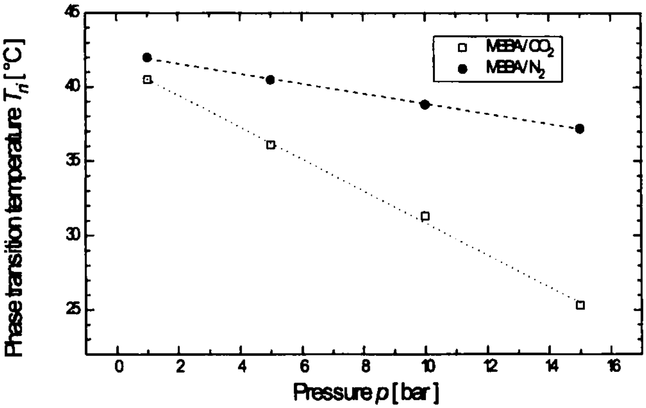

FIGURE 13 Influence of the gas sorption on the *i*-*n* phase transition temperature of MBBA.

Compared with N_2, CO_2 shows a much stronger effect on the *n-i* phase transition of MBBA: a reasonable interpretation may be attribute to the higher sorption rate of CO_2 and possibly a stronger interaction between CO_2 molecules and the LC molecules due to the polar CO-bond.

In CO_2, the *c-n* phase transition is with a dT_{cn}/dp-rate of *ca.* −1.5°C/5 bar in essential less influenced by the sorbed gas in comparison with the *n-i* transition, which has a dT_{ni}/dp-rate of *ca.* −5°C/5 bar. We suppose that this is mainly attributed to the difference of the CO_2 solubility between different LC phases of MBBA.

For a further understanding of the influence of gas sorption on the surface tension of LCs, it will be interesting to perform more experiments in other gas atmospheres, such as Ar and He. Such experiments are underway in our laboratory.

SUMMARY AND CONCLUSIONS

This paper highlights our investigation on the influence of the CO_2 sorption on the time-dependent surface tension of the freshly formed surface of the low molecular LC MBBA as a function of the gas pressure (1 – 15 bar) and the temperature (0 – 50°C).

Parallel to the surface tension measurements, the gas sorption measurements have been done in the same experimental conditions, which provided the possibility for the comparison between the surface tension values and the sorbed gas concentrations. A computer-aided measuring set-up based on the pendant-drop method and a high pressure electromicrobalance have been employed for the above measurements, respectively.

For MBBA, the CO_2 sorption shows a strong dependence on the LC phases, the temperature and the gas pressure: in the crystalline phase MBBA contains a very low equilibrium concentration of the sorbed CO_2, yet this concentration increases dramatically in the nematic phase as well as in the isotropic phase, and with increasing gas pressure this dramatic increase becomes more pronounced. The above phenomenon enables the MBBA samples, which might have been saturated with gas (N_2) during the storage (0°C, crystalline state), to sorb more gas while the surface tension measurements ($>$ 24°C, nematic or isotropic state). For the freshly formed MBBA surface, the time needed to attain the equilibrium of the surface tension is well in agreement with the needed to attain the sorption equilibrium in the same measuring condition, and this applies both to the nematic and the isotropic phase, and both to normal and higher gas pressures. Our previous suggestion, that the unusual time-dependence of surface tension of the freshly formed LC surfaces may be mainly attributed to the gas sorption processes, is supported by the experimental results. In addition, we have also verified the reversibility of the CO_2 sorption in MBBA.

Finally we have also investigated the influence of the CO_2 sorption on the phase transition temperatures of MBBA. In all cases, the depressions of the transition temperatures with increasing gas pressure have been observed, yet with different rates: for the *c-n* phase transition with a dT_{cn}/dp-rate of *ca.* −1.5°C/5 bar and for the *n-i* phase transition a dT_{ni}/dp-rate of *ca.* −5°C/5 bar.

Acknowledgements

Sincere thanks to *the Fonds der Chemischen Industrie* for financial support. One of the authors (G.-H. Chen) would like to thank the *Graduiertenkolleg "Polymerwerkstoffe" of the Deutsche Forschungsgemeinschaft at the TU Berlin* for the scholarship.

References

[1] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **293**, 39 (1997).
[2] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, in press (1997).
[3] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, in press (1997).
[4] B. Song and J. Springer, *J. Colloid Interface. Sci.*, **184**, 64 (1996); **184**, 77 (1996).
[5] L. Phan Thuy and J. Springer, *Colloid Polym. Sci.*, **266**, 614 (1988).
[6] J. E. Proust and L. Ter Minassian Saraga, *J. de. Physique*, **36**, C1-77 (1975)
[7] I. Haller, *Appl. Phys. -Lett.*, **24**, 349 (1974).
[8] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **35**, 253 (1976).
[9] L. T. Creagh and A. R. Kmetz, *Mol. Cryst. Liq. Cryst.*, **24**, 59 (1973).
[10] F. J. Kahn, G. N. Taylor and H. Schonhorn, *Proc. IEEE*, **61**, 823 (1973).
[11] B. Stryla, W. Kuczynski and J. Malecki, *Mol. Cryst. Liq. Cryst. Lett.*, **1**, 33 (1985).
[12] D. Pabitra, K. Grzegorz and W. L. Aaron, *J. Coll. Interf. Sci.*, **82**, 1 (1981).
[13] B. Tamamushi, in *Colloid and Interface Science* (M. Kerker, Ed.), **5**, p. 453, *Academic Press Inc.*, New York, 1976.
[14] F. M. Jeager, *Z. anorg. u. allg. Chem.*, **101**, 1 (1917).
[15] A. Ferguson and S. J. Kennedy, *Phil. Mag.*, **26**, 41 (1938).
[16] V. Naggiar, *Ann. Physique*, **18**, 5 (1943).
[17] W. M. Schwarz and H. W. Moseley, *J. Phys. Coll. Chem.*, **51**, 826 (1947).
[18] S. Krishnaswamy and R. Shashidhar, *Proc. Int. Liquid Crystals Conference*, Bangalore (India) 1973, No. 1, p. 247, Paramana Suplement, 1975.
[19] M. A. Bouchiat and D. Langevin-Cruchon, *Phys. Lett.*, **34A-6**, 331 (1971).
[20] K. Hatsuo and N. Huzio, *J. Phys. Soc. Japan*, **55-12**, 4186 (1986).
[21] M. G. Gannon and T. E. Faber, *Phil. Mag.*, **A-37**, 117 (1978).
[22] R. Schenck, *Z. Phy. Chem.*, **25**, 337 (1898).
[23] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **38**, 353 (1977).
[24] B. M. Ocko, A. Braslau, A. H. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev. Lett.*, **57**, 94 (1986).

[25] P. S. Pershan, A. Braslau, A. H. Weiss and J. Als-Nielsen, *Phys. Rev.*, **A35**, 4800 (1986).
[26] D. Beaglehole, *Mol. Cryst. Liq. Cryst.*, **89**, 319 (1982).
[27] J. W. Done, A. Golemme, J. L. West, J. B. Whitebread and B.-G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
[28] S. Immerachnitt, T. Koch, W. Stille and G. Strobl, *J. Chem. Phys.*, **96**, 6249 (1992).
[29] H. Elben and G. Strobl, *Macromolecules*, **26**, 1013 (1983).
[30] D.-S. Chen, G.-H. Hsiue, J. D. Schultze, B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **237**, 85 (1993).
[31] P. J. Flory, *Adv. Polym. Sci.*, **59**, 1 (1984).