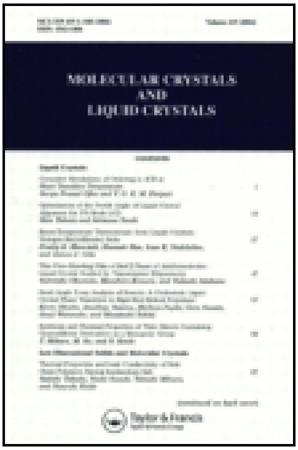

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Surface Phenomena of Liquid Crystalline Substances

Gong-Hao Chen [a] & Jürgen Springer [a]

[a] Institut für Technische Chemie der Technischen Universität Berlin, Fachgebiet Makromolekulare Chemie, Straße des 17. Juni 135, D-10623, Berlin, Federal Republic of Germany

To cite this article: Gong-Hao Chen & Jürgen Springer (1999): Surface Phenomena of Liquid Crystalline Substances, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 326:1, 1-14

To link to this article: http://dx.doi.org/10.1080/10587259908025401

Mol. Cryst. Liq. Cryst., Vol. 326, pp. 1 – 14
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Surface Phenomena of Liquid Crystalline Substances

Influence of N_2 Gas Sorption on Surface Tension

GONG-HAO CHEN and JÜRGEN SPRINGER*

Institut für Technische Chemie der Technischen Universität Berlin,
Fachgebiet Makromolekulare Chemie, Straße des 17. Juni 135, D-10623
Berlin, Federal Republic of Germany

(Received 3 April 1997; In final form 26 September 1997)

The influence of the sorbed N_2 on the surface tension of the low molecular liquid crystal MBBA (*p*-methoxybenzylidene-*p*′-*n*-butylanilin) has been investigated using the pendant drop method. The time- and temperature-dependent measurements of the surface tension of MBBA have been carried out under different N_2 pressures (1 – 15 bar). The time-dependence of the surface tension is interpreted in terms of the sorption process of N_2. The results depend strongly on the liquid crystal (LC) phase, the gas pressure and the gas type. All the temperature-dependence curves of the surface tension of MBBA, obtained at different N_2 pressures, show a similar shape within the experimental temperature range (25 – 50°C), yet with a systematic decrease of the phase transition temperature isotropic(*i*)/nematic(*n*) by the increasing N_2 pressure and thus the increasing concentration of the sorbed gas in the sample. The positive slope of the surface tension-temperature characteristic near the phase transition temperature indicates the development of higher ordered molecular states in the surface layer. The correlation between the *i-n* phase transition temperature of LCs and the concentration of sorbed gases, the gas type and the impurities in LCs has been also discussed.

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

INTRODUCTION

Since the pioneering work of Schenck [1] and Jaeger [2] there have been numerous reports of surface/interfacial phenomena on LCs [3 – 15].

---

* Corresponding author.

However, not only some basic questions such as the thermodynamic properties of interfaces and their dependence on temperature, particularly near phase transitions and on changes of the interface structure, remain unanswered, but also the results obtained by different authors are rather conflicting.

Recently we have given a series of reports on properties of surface tension of different low molecular as well as polymer LCs [16–18]. In these papers we have given a brief review on the prior studies on measurements of surface tension of LCs. We have also reported the remarkable time-dependence of surface tension of freshly formed surface of LCs. This phenomenon has been supposed by us to be mainly attributed to the gas sorption taking place at the liquid surface as well as in the liquid bulk, 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 reorganization of the molecules in the surface region. It is inferred that such time-dependent phenomena may have confused the measurements of surface tension of LCs performed by different groups and may have contributed to some of the inconsistencies in the obtained results.

As the first step of the systematic study of surface tension of LCs in different gas atmospheres we reported an indirect procedure to determine the so-called *absolute* initial values of the surface tension $\gamma_{0,a}$, which corresponds the surface tension values of the liquid in its own vapor [17]. The $\gamma_{0,a}$ values of the low molecular LC MBBA have been determined: 33.13 mN/m for 25°C (*n*-phase) and 32.18 mN/m for 50°C (*i*-phase), and they are to be used in the present paper for the time-dependent study of the surface tension of MBBA in N_2. We have also reported the change of the surface tension of MBBA during the time of drop formation and concluded that it is unnegligible in certain gas atmospheres (*e.g.*, CO_2) and especially at higher gas pressure.

Furthermore, we have reported the temperature-dependence of surface tension of several low molecular LCs near their phase transition temperatures. The results were discussed on the basis of statistical thermodynamic models currently proposed in the literature.

In continuation of our systematic study on surface tension behaviors of LCs in different gas atmospheres, the present work is aimed at studying how the adsorbed/sorbed N_2 gas affects on the surface tension of MBBA, with emphasis on the gas pressure. We expect that these results will be also helpful in understanding the transport mechanism of gases in LCs.

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 *i-n* phase transition temperature of the MBBA sample is 43.0°C (at 1 bar N_2).

The employed gas N_2 was purchased from the Company Messer Griesheim (Germany) and had a purity $> 99.99\%$. The gas was used without any further purification.

(B) Surface Tension Measurements

The surface/interfacial tension of liquid/fluid-system was measured using a computer-aided pendant drop method, developed in our laboratory. Its principle has been given in detail elsewhere [19–20]. Briefly, a pendant drop is formed in a gas-tight thermostatic chamber saturated with the vapor of the liquid. After the extraction of the drop profile from its image the surface tension is determined by fitting this profile to the Laplace 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 the relative accuracy is to be taken more into account.

(C) Preparation of Samples and Formation of Pendant Drops

All the measurements have been carried out in a gas-tight measuring chamber described in the prior paper [17]. At room temperature the MBBA sample 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. Having been cooled to room temperature, the syringe was taken from vacuum and immediately inserted into the with N_2 filled measuring chamber. A reservoir of sample was placed into the chamber to get a vapor-saturated atmosphere before starting the experiment. According to Chen *et al.* [21], 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). Due to the rapid computer-aided pendant drop method we had the possibility for the time dependent study of surface tension, in a time of the order of seconds such drops to choose, which were still without sorbed gas during the time of preparation [17]. The temperature-dependent measurements of surface tension were carried out only after the drops had reached their steady-state (or equilibrium state). All the temperature-dependent measurements were carried out with decreasing temperature. At every experimental temperature about 20–30 minutes has been waited to ensure that the recorded surface tension value corresponds its equilibrium value. Due to the thermal contraction of the liquid volume by decreasing the temperature, it was necessary from time to control the drop within a stable size. All the measurements have been repeated several times, each time with a new drop.

(D) Density

The MBBA sample is in liquid state within the experimental temperature range (25°C – 50°C). The temperature-dependence of the density of MBBA, in normal condition (at 1 bar air), was measured 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 will be discussed below.

RESULTS AND DISCUSSIONS

The temperature-dependence of the densities ($\rho(T)$) of the two fluid phases is necessary by calculation of the temperature-dependence of the interfacial tension using the pendant drop method. The density of the gas phases was calculated using the normal gas law for ideal gases. The $\rho(T)$-curve of MBBA in normal experimental condition (at 1 bar N_2) in shown in Figure 1.

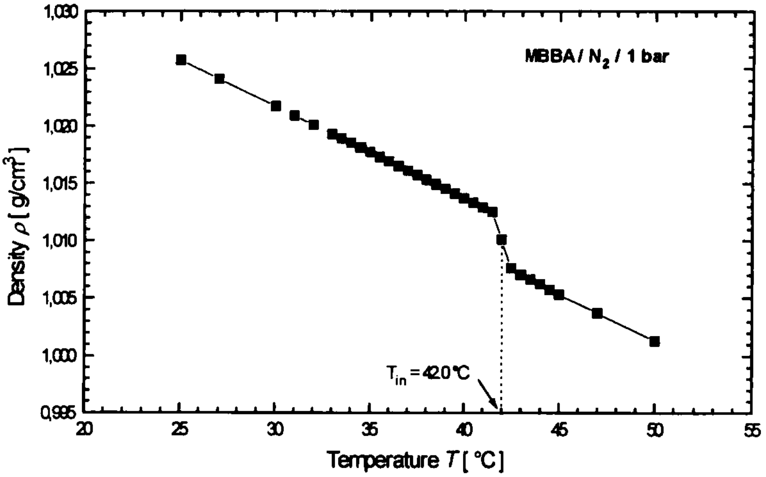

FIGURE 1 Temperature-dependence of the density of MBBA measured in normal condition (at 1 bar N_2).

Our result in terms of the relative change of the density within the experimental temperature range gives a good agreement with that reported by Press and Arrott [22]. The density change at the *i-n* phase transition is very small, it amounts to about $0.005\,g/cm^3$.

As mentioned in the prior papers [17, 21], the *i-n* phase transition temperatures (T_{in}) of LCs decrease with increasing gas pressure and thus the increasing concentration of sorbed gases in them. Figure 2 shows the pressure-dependence of the T_{in} on MBBA in N_2. The T_{in} values could be obtained from the inflection points on the temperature-dependence curves of the surface tension ($\gamma(T)$-curves), which yet had not been corrected with the temperature-dependent density difference (normally with the assumption $\Delta\rho = 1\,g/cm^3$ for all temperatures). Because of the small change of the density of MBBA within the experimental temperature range such uncorrected $\gamma(T)$-curves showed a similar tendency to those corrected $\gamma(T)$-curves (Fig. 9). The T_{in} values could be also obtained from the visual observation of the drop image. Figure 3 shows the images of a MBBA drop at different temperatures, from which the phase states of the LC could be well distinguished. The results on the T_{in} values from the above two methods agreed well with each other.

Due to the pressure-dependent T_{in} it is obvious, that the in Figure 1 shown $\rho(T)$-curve is only available for the calculation of temperature-dependence of the surface tension of MBBA in 1 bar N_2 atmosphere. A direct way to measure the $\rho(T)$-curves at different gas pressures and in fact with the sorption of the

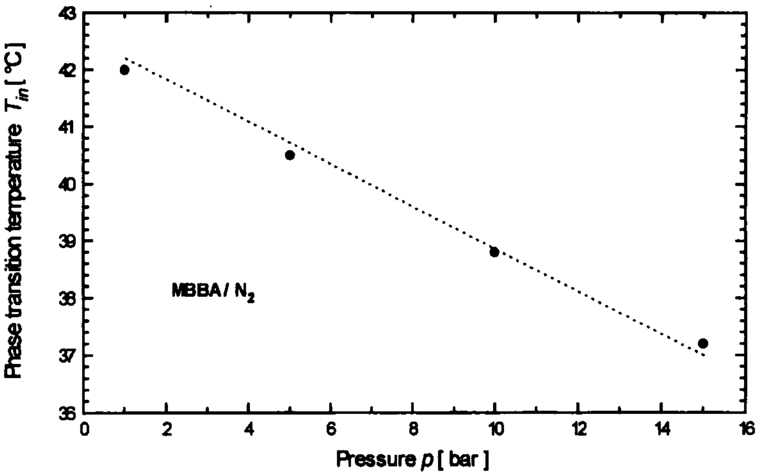

FIGURE 2 Influence of the pressure of N_2 on the *i-n* phase transition temperature of MBBA.

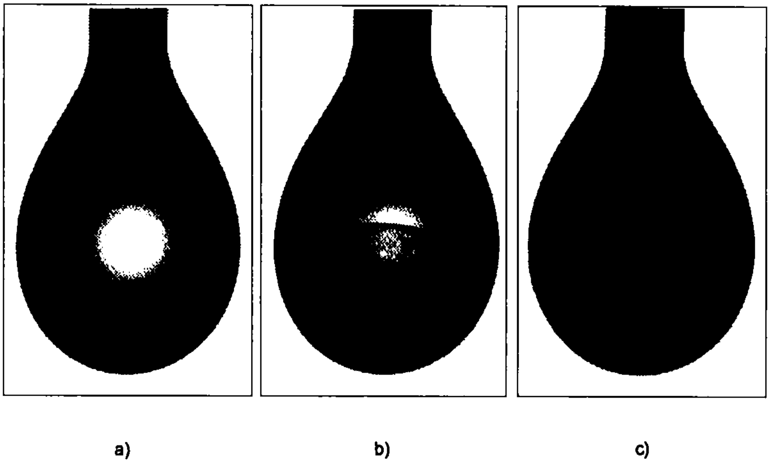
a) b) c)

FIGURE 3 Video images of a MBBA drop at various temperatures (at 1 bar N_2). (a) 43.0°C (isotropic), (b) 42.1°C (phase transition isotropic-nematic), (c) 41.0°C (nematic).

N_2 gas during the measurement, which corresponds the experimental condition of the $\gamma(T)$-measurement, is unfortunately not available. Therefore, a indirect way is used to gain such $\rho(T)$-curves. This method bases on the following two facts: first, a liquid can be considered incompressible under our experimental condition; second, the concentration of the sorbed gas in LCs is quite limited [21]. Thus it is reasonable to assume, that the parts of

$\rho(T)$-curves, which are not in the changing range of the T_{in}, remains for the different measuring pressures the same. Through shifting the discontinues part (near the T_{in}) of the $\rho(T)$-curve shown in Figure 1 to the corresponding T_{in}'s (Fig. 2) the $\rho(T)$-curves for the different N_2 pressures can be obtained, respectively. Figure 4 shows the so obtained $\rho(T)$-curves of MBBA for the higher experimental pressures. Finally the uncorrected $\gamma(T)$-curves of MBBA, obtained with the assumption $\Delta\rho = 1\ g/cm^3$, are to be corrected with the temperature-dependent density difference $\Delta\rho(T) = \rho(T)_{MBBA} - \rho(T)_{N_2}$ (see below).

Figure 5 shows the relationship between the so-called *relative* initial value of surface tension ($\gamma_{0,r}$) of the freshly formed MBBA drops, both at 25°C (*n*-phase) and at 50°C (*i*-phase), as a function of the pressure of N_2. The $\gamma_{0,r}$ values are namely the first values of the surface tension directly measured after drop formation using the pendant drop method [17]. With increasing gas pressure the adsorbed gas concentration at the drop surface increases, and thus decreases more strongly the surface tension after the drop formation time (here 12 seconds). The $\gamma_{0,r}$ values at the both temperatures show a similar dependence on the N_2 pressure with a $d\gamma_{0,r}/dp$ value of ca. $-$ 0.03 mN/m · bar. The *absolute* initial values of the surface tension ($\gamma_{0,a}$), of the freshly formed MBBA drops: 33.13 mN/m at 25°C and 32.18 mN/m at 50°C, have been obtained by using a indirect procedure by extrapolation of the pressure-dependent $\gamma_{0,r}$ values to $p=0$ [17]. The time-dependence of the

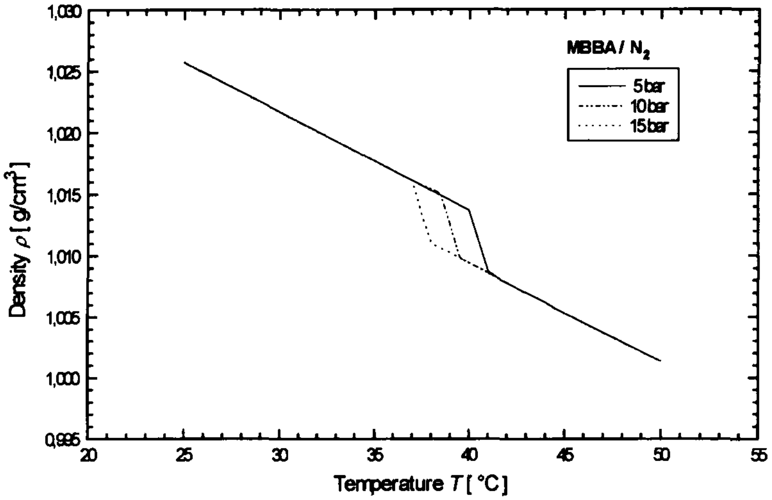

FIGURE 4 Temperature-dependence of the density of MBBA for the surface tension calculation in different N_2 atmospheres.

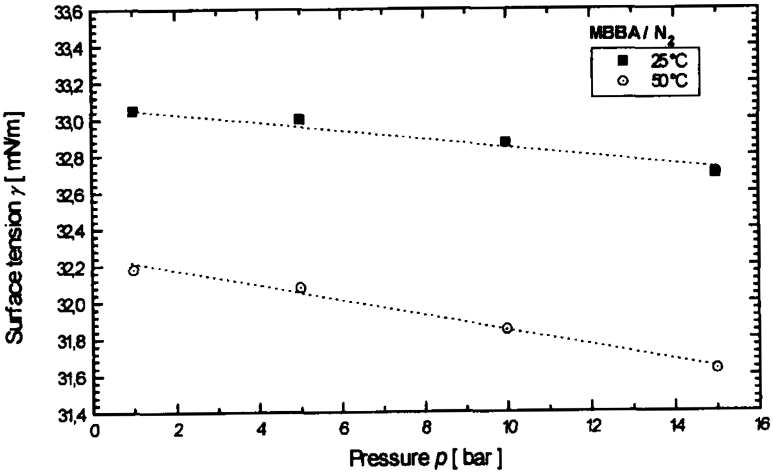

FIGURE 5 Pressure-dependence of the *relative* initial values of the surface tension of MBBA ($\gamma_{0,r}$) in N_2.

surface tension difference ($\Delta\gamma = \gamma(t) - \gamma_{0,a}$) of the freshly formed MBBA drops at different N_2 pressures is represented in Figures 6 and 7, for the *n*-phase (25°C) and for the *i*-phase (50°C), respectively. The time-dependence rate of the surface tension is a function of the molecular state as well as the N_2 gas pressure. As the gas pressure becomes higher, each time-dependence curve, either in the *n*-phase or in the *i*-phase, systematically changes its shape

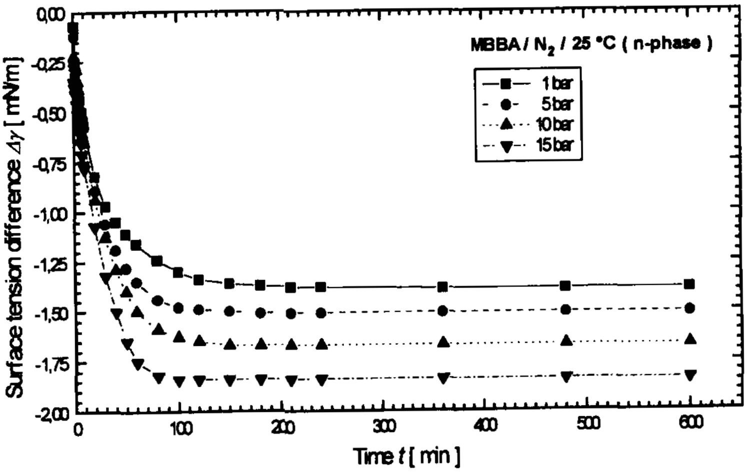

FIGURE 6 Time-dependence of the surface tension difference of MBBA in N_2 at 25°C ($\Delta\gamma = \gamma(t) - \gamma_{0,a}$ with $\gamma_{0,a} = 33.13\,\mathrm{mN/m}$).

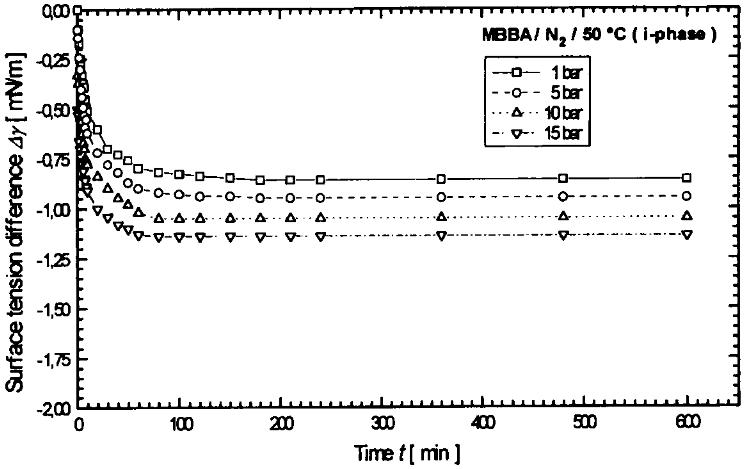

FIGURE 7 Time-dependence of the surface tension difference of MBBA in N_2 at 50°C ($\Delta\gamma = \gamma(t) - \gamma_{0,a}$ with $\gamma_{0,a} = 32.18\,\mathrm{mN/m}$).

with a more rapid and stronger decreasing rate to attain equilibrium. The time needed to reach the equilibrium surface tension decreases from ca. 240 minutes at 1 bar N_2 to ca. 120 minutes at 15 bar N_2 in the *n*-phase (25°C), while it decreases from ca. 180 minutes at 1 bar N_2 to ca. 80 minutes at 15 bar N_2 in the *i*-phase (50°C). 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 under the same experimental condition. The obvious time-dependence of the surface tension of MBBA at 50°C (*i*-phase) indicates, that even at a temperature of ca. 7°C above the *i*-*n* phase transition some high-ordered structures may exist in the surface layer [23–28]. The transport of the N_2 molecules in the MBBA drop under investigation should be represented by a gas type, gas concentration, temperature, substance 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 decrease of the surface tension during the drop formation time is given by the surface tension difference $\Delta\gamma = \gamma_{0,r}(p) - \gamma_{0,a}$ (Tab. I). This decrease is considered to be mainly caused by the gas adsorption on the drop surface, and the following long time-dependence of the surface tension by the gas sorption (adsorption + diffusion). The equilibrium surface tension values of MBBA at 25°C as well as at 50°C are shown in Figure 8 as a function of the N_2 pressure. These pressure-dependent equilibrium values are presented by a $d\gamma/dp$-slope of $-0.04\,\mathrm{mN/m \cdot bar}$ at 25°C and $-0.02\,\mathrm{mN/m{\cdot}bar}$

TABLE I Decrease of the surface tension of the freshly formed MBBA drops during drop formation time as a function of the N_2 pressure*

$\Delta\gamma = \gamma_{0,r}(p) - \gamma_{0,a}$ (*mN/m*)	1 *bar*	5 *bar*	10 *bar*	15 *bar*
25°C, nematic phase	−0.08	−0.13	−0.26	−0.43
50°C, isotropic phase	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.

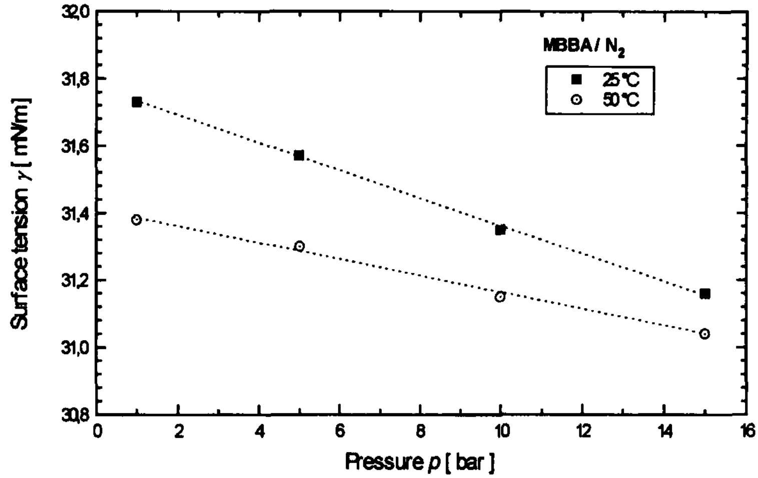

FIGURE 8 Pressure-dependence of the equilibrium values of the surface tension of MBBA in N_2.

at 50°C. Also the equilibrium values of the surface tension are in the *n*-phase more strongly influenced by the gas pressure than they in the *i*-phase. 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.

The temperature-dependence of the surface tension of MBBA at different N_2 pressures is shown in Figure 9. Due to the time-dependence of the surface tension all the temperature-dependent measurements have been carried out after the freshly formed MBBA drops reached their steady-state (or equilibrium state). The $\gamma(T)$-curve obtained by us at 1 bar N_2 is in qualitative agreement with the result of Krishnaswamy and Shashidhar [7]. In all the cases the surface tension decreases initially with increasing temperature, changes slope around the T_{in} and finally regains the decreasing trend at high temperatures. The discontinuity of the anomaly near the phase transition is not so marked. This *anomaly* indicates the development of

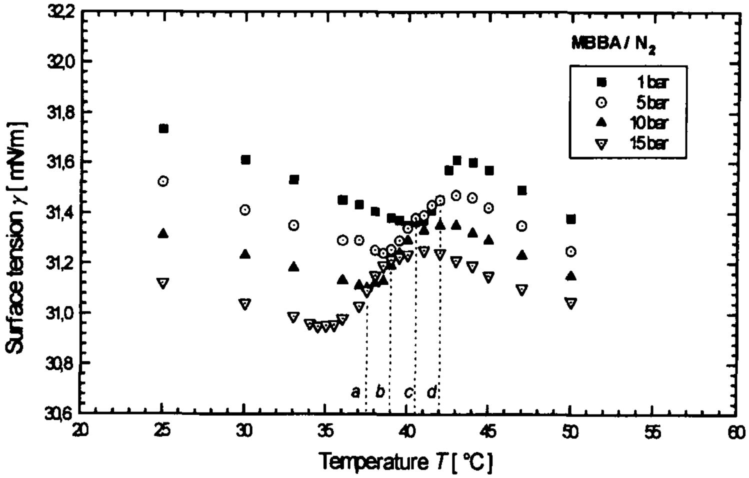

FIGURE 9 Temperature-dependence of the surface tension of MBBA in different N_2 atmospheres. (a) $T_{in} = 42.0°C$ ($p = 1$ bar), (b) $T_{in} = 40.5°C$ ($p = 5$ bar), (c) $T_{in} = 39.0°C$ ($p = 10$ bar), (d) $T_{in} = 37.5°C$ ($p = 15$ bar).

higher ordered molecular states in the surface layer. The positive $d\gamma/dT$ takes place in a temperature range from ca. 4°C to ca. 6°C around the T_{in}, with a jump of ca. $+0.3\,mN/m$, in different N_2 atmospheres. It shows a trend, that the temperature range of the positive $d\gamma/dT$ increases with the increasing N_2 pressure and thus the increasing N_2 concentration in the MBBA sample. With the increasing N_2 pressure the $\gamma(T)$-curves become generally smaller, they differ from each other in the T_{in} values. Even in normal condition (at 1 bar N_2) the T_{in} of MBBA obtained by taking the inflection point on the $\gamma(T)$-curve as well as by the observation of the pendant drops with video camera (see above) is about 1°C lower as the T_{in} determined by DSC (43.0°C). This difference can be explained with the consideration of the state of the N_2 sorption in the MBBA samples. The DSC investigation has been carried out on the MBBA sample immediately after leaving its storage at 0°C in refrigerator, so that such sample had not enough time to reach a N_2 saturated state in it. The sorbed N_2 concentration in such sample was smaller than it in the drop forming sample, which had been already annealed for long time (several hours) in the enclosed measuring chamber during the temperature-dependent measurement of the surface tension. The DSC-investigation on the recycled MBBA sample (after the temperature-dependent measurement) gave a T_{in} value of 42.0°C in 1 bar N_2 atmosphere. Since one important factor for the formation of LC phases is the anisotropy of intermolecular forces between LC molecules [29], it seems that the anisotropy of MBBA is affected by the interactions of the MBBA molecules with the sorbed gas molecules. As a consequence, the LC phase becomes destabilized and the phase transition temperature is depressed (Fig. 2). Different analyses (*e.g.*, IR, NMR) on the recycled MBBA samples after the surface tension measurements showed no indications of chemical changes.

We have also investigated the T_{in} of the recycled MBBA samples after the surface tension measurements at the higher N_2 pressures. The T_{in} values of such samples were determined by DSC and polarization microscopy. The results remained the trend of the depression of the T_{in} values with the increasing pressure, under which the samples had been investigated. Compared to the T_{in} values shown in the Figure 2, all the T_{in} values of the recycled samples are a little higher. This indicates a slow desorption of the N_2 gas in the samples during the transport and the preparation of the DSC-measurement. After a longtime evacuation in vacuum all of the recycled samples were able to regain a phase transition temperature of 43.0°C, which indicated a physical sorption of the N_2 molecules in the MBBA samples. Similar phenomena have been observed on different LCs by other authors [9, 30]. However, neither of the authors have considered the influence of the gas sorption (air).

Our recent experimental results, which will be published later, show that the phase transition temperature T_{in} as well as the surface tension of MBBA depend strongly on the type of sorbed gases. For example, CO_2 has a much larger influence than N_2. Taking the sorbed gases as one kind of the impurities in LCs, one can reason that different impurities will have different effects on the surface tension of LCs. Therefore, it is easy to understand, why some authors [5, 9] considered that the presence of impurities can significantly affect on the surface tension of LCs, while others didn't [31]. Our results of the surface tension of MBBA obtained under different N_2 pressures showed that the purity of the sample (the concentration of the sorbed N_2 in the sample) does not critically affect the shape of the $\gamma(T)$-curves.

The effects of other gases, such like CO_2, He and Ar, on the surface tension of LCs as well as the kinetic study of gas sorption in LCs are underway in our laboratory.

CONCLUSIONS

We have investigated the surface tension behaviors of the low molecular liquid crystal MBBA in the N_2 atmosphere of different pressures using the pendant drop method. The time-dependent surface tension of a freshly formed MBBA is a function of the gas type, gas pressure and the LC phase. The suggestion, that the unusual time-dependence of surface tension of LCs may be mainly attributed to the gas sorption processes, is supported by the results of our investigation. In the case of N_2 the sorbed gas concentration in MBBA doesn't critically affect the shape of the $\gamma(T)$-curve, but with the increasing gas concentration in the sample the absolute surface tension values of MBBA become 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. The effect of N_2 sorption on the phase transition temperature of MBBA has been also discussed. Furthermore, the reversibility of the sorption process has been confirmed.

Acknowledgment

We thank *the Fonds der Chemischen Industrie* for financial support. We also thank Dr. B. Song for useful discussions. One of the authors (G.-H. Chen) is grateful to *the Graduiertenkolleg "Polymerwerkstoffe" of the Deutsche Forschungsgemeinschaft at the TU Berlin* for the scholarship.

References

[1] Z. R. Schenck, *Z. Physik. Chem.*, **25**, 337 (1898).

[2] F. M. Jaeger, *Z. Anorg. u. Allg. Chem.*, **101**, 1 (1917).

[3] D. Langevin and M. A. Bouchiat, *Mol. Cryst. Liq. Cryst.*, **22**, 317 (1973).

[4] C. A. Croxton and S. Chandrasekhar, *Proc. Int. Liquid Crystals Conf.*, Bangalore (India) 1973, Pramana Supplement, **1**, 237 (1975).

[5] A. W. Neumann, R. W. Springer and R. T. Bruce, *Mol. Cryst. Liq. Cryst.*, **27**, 23 (1973).

[6] J. E. Proust, E. Perez and L. Ter Minassian Saraga, *Coll. Polym. Sci.*, **256**, 666 (1978); **254**, 672 (1976).

[7] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **35**, 253 (1976); **38**, 353 (1977).

[8] J. D. Parsons, *J. Physique*, **37**, 1187 (1976).

[9] C. A. Gannon and T. E. Faber, *Phil. Mag. A*, **37**, 117 (1978).

[10] C. A. Croxton, *Mol. Cryst. Liq. Cryst.*, **59**, 219 (1980); **66**, 223 (1981).

[11] W. J. A. Goossens, *Mol. Cryst. Liq. Cryst.*, **124**, 305 (1985).

[12] H. Kimura and H. Nakano, *J. Phys. Soc. Japan*, **54**, 1730 (1985); **55**, 4186 (1986).

[13] H. Kimura, *J. Phys. Soc. Japan*, **62**, 2725 (1993).

[14] W. E. Mcmullen and B. G. Moore, *Mol. Cryst. Liq. Cryst.*, **198**, 107 (1991).

[15] T. Sugiyama, S. Kuniyasu and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **231**, 119 (1993).

[16] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **293**, 39 (1997).

[17] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 89 (1997).

[18] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 69 (1997).

[19] B. Song and J. Springer, *J. Colloid Interface. Sci.*, **184**, 64 (1996).

[20] B. Song and J. Springer, *J. Colloid Interface. Sci.*, **184**, 77 (1996).

[21] D.-S. Chen, G.-H. Hsiue, J. D. Schultze, B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **237**, 85 (1993).

[22] M. J. Press and A. S. Arrott, *Physical Review A*, **8-3**, 1459 (1973).

[23] B. M. Ocko, A. Braslau, A. H. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev. -Lett.*, **57**, 94 (1986).

[24] P. S. Pershan, A. Braslau, A. H. Weiss and J. Als-Nielsen, *Phys. Rev.*, **A35**, 4800 (1986).

[25] D. Beaglehole, *Mol. Cryst. Liq. Cryst.*, **89**, 319 (1982).

[26] J. W. Done, A. Golemme, J. L. West, J. B. Whitebread Jr. and B.-G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).

[27] S. Immerschitt, T. Koch, W. Stille and G. Strobl, *J. Chem. Phys.*, **96**, 6249 (1992).

[28] H. Elben and G. Strobl, *Macromolecules*, **26**, 1013 (1993).

[29] P. J. Flory, *Adv. Polym. Sci.*, **59**, 1 (1984).

[30] D. Langevin and M. A. Bouchiat, *Phys. Lett.*, **34A**, 331 (1971).

[31] S. Krishnawany and R. Shashidhar, *Proc. Int. Liquid Crystals Conf.*, Bangalore (India) 1973, Pramana Supplement, **1**, 247 (1975).