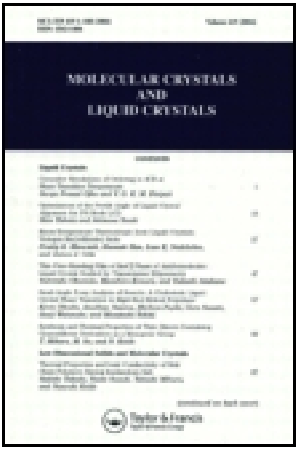

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Gong-Hao Chen [a] & Jürgen Springer [a]

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

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Influence of Gas Sorption on Surface Tension of Liquid Crystalline Substances

Influence of CO_2 on Temperature-dependence of 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

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We report for the first time a gas-induced molecular excess order at the surface of the low molecular liquid crystalline substance MBBA (4-methoxybenzylidene-4′-*n*-butylaniline), revealed from its surface tension-temperature characteristic in CO_2 at elevated pressures. Such gas-induced surface excess order has been observed both in the nematic and isotropic phase, which can be enhanced by increasing the gas pressure. It is unusual for a low molecular liquid crystal, that this surface order can be even in the isotropic phase over a wide temperature range stable when the gas pressure is high enough.

Experimentally, the surface tension measurements and the gas sorption measurements have been carried out separately under the same conditions which cover a temperature range of 0–80°C and a pressure range of 1–15 bar, by using a computer-aided measuring set-up based on the pendant drop method and a high pressure electromicrobalance, respectively.

Keywords: Gas-induced surface excess order; temperature-dependence of surface tension; temperature coefficient; gas sorption; liquid crystals; MBBA; carbon dioxide

INTRODUCTION

Recently, systematic experimental studies on the influence of gas sorption on the surface tension of liquid crystalline substances (LCs) have been performed in our laboratory [1–3].

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*Corresponding author. Tel.: +49 30 314 22262, Fax: +49 30 314 79237.

In our previous papers, we have firstly reported a remarkable time-dependence of the surface tension of the freshly formed surfaces of various LCs, which has been supposed by us in consequence of the gas sorption process taking place at the liquid surface as well as in the liquid bulk [4]. We have investigated 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), especially at higher gas pressures [1]. We have also reported the surface tension behaviors of MBBA in the N_2 atmosphere of different pressures [2].

In our last paper [3], the influence of the CO_2 sorption on the time-dependent surface tension of the freshly formed surface of MBBA has been studied as a function of the gas pressure (1 – 15 bar) and the temperature (0 – 50°C). For MBBA, the CO_2 sorption shows a strong dependence on the LC phases, temperature and 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 (n) phase as well as in the isotropic (i) phase, and with increasing gas pressure this dramatic increase becomes more pronounced. For the freshly formed MBBA surface, the time needed to attain the equilibrium of the surface tension is well in agreement with that needed to attain the sorption equilibrium under the same measuring conditions, this applies both to the n- and i-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 investigated the influence of the CO_2 sorption on the phase transition temperatures of MBBA as well as the reversibility of the CO_2 sorption in it.

As the second part of the investigation on the influence of the CO_2 sorption on the surface tension of MBBA, we will report in this paper the temperature-dependent behaviors of the surface tension ($\gamma(T)$-curves) in CO_2 of various pressures. The observed phenomena are discussed to reveal the possible underlying grounds.

EXPERIMENTAL

(A) Materials

Before the experiments we recrystallized the MBBA (4-methoxybenzylidene-4′-*n*-butylaniline) sample (purity > 98%, from Aldrich Chem. Company Inc.

USA) several times with absolute ethanol. Immediately after evacuation it was stored at 0°C with dry nitrogen as protective gas.

The n – i transition temperature of the MBBA sample was 43.0°C (in 1 bar N_2), 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 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 have been performed by using a computer-aided pendant drop method which defined a relative accuracy of ca. 0.05% and an absolute accuracy of ca. 0.5% [5]. For our measurements presented here more interest is to be given to the relative accuracy.

Detail descriptions on the sample preparations and the measurements have been given in our earlier publications [1 – 4]. Briefly, a gas-tight measuring chamber [1] has been employed for the surface tension measurements, with a reservoir of sample used to get a vapor-saturated atmosphere. All the temperature-dependent measurements have been carried out by cooling and repeated several times, each time with a new drop.

(C) Gas Sorption Measurements

The sorption measurements were performed by gravimetric method through use of a high pressure electromicrobalance (Model 4436, Sartorius, Germany). A description of the experiments and details of the measuring set-up have been reported elsewhere [3, 6], so that we will restrict ourselves to a brief description of the temperature-dependent measurements. To prevent the evaporation during the evacuation, all the MBBA samples were degassed in the crystalline (c) state (0°C) by using an oil diffusion pump in connection with a rotary oil pump. By attaining a constant mass of a sample, a desired pressure of CO_2 was introduced into the chamber to start the measurements. It was essential that all the measurements should be performed by heating. Otherwise, due to strong supercooling the gas sorption at the nematic-crystalline transition were impossible to determine. Needle valves were employed to control the gas pressure against the thermal extension of the gas in the microbalance by heating.

The change of mass of sorbing samples *vs.* time was continuously recorded by the computer.

(D) Density

By using the pendant drop method, it is necessary to determine the density difference between the two fluid phases ($\Delta\rho$) for calculating the surface/interfacial tension. Therefore, in the present case the temperature scanning densities ($\rho(T)$) of the gas phase (CO_2) and MBBA are necessary. The density of the gas phase was calculated by using the normal gas law for ideal gases.

The temperature scanning density of MBBA has been measured under normal condition (in 1 bar air) by cooling 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 $\pm 1 \cdot 10^{-4}\,\mathrm{g/cm^3}$. Since the i–n phase transition temperature (T_{in}) varies with the gas pressure, corresponding corrections for the density–temperature characteristic were necessary [2]. Briefly, we determined firstly the i–n transition temperatures of MBBA at various CO_2 pressures by taking the inflection points from the uncorrected $\gamma(T)$-curves ($\rho = 1\,\mathrm{g/cm^3}$) as well as by observation of the phase change *via* video during the surface tension measurements [3]. Then we shifted the discontinues part (near the T_{in}) of the originally measured $\rho(T)$-curve to the T_{in}'s obtained. Figure 1 shows the original $\rho(T)$-curve and the $\rho(T)$-curves

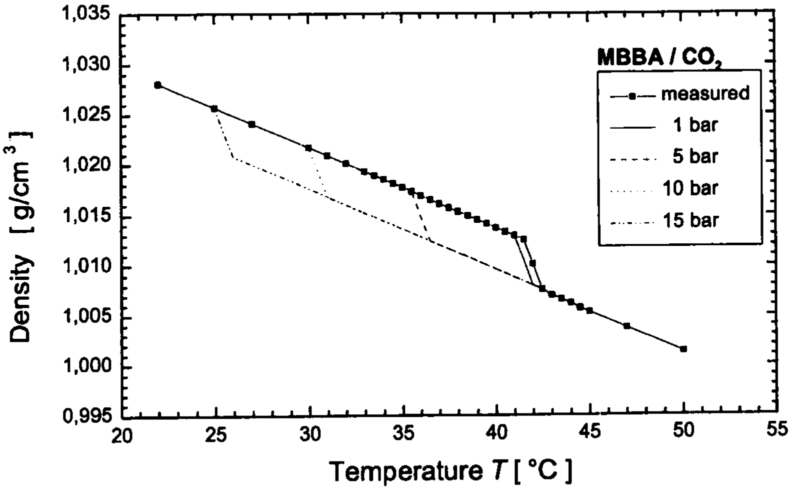

FIGURE 1 Temperature scanning densities of MBBA in CO_2 at various pressures.

in 1, 5, 10 and 15 bar CO_2, respectively. The $\rho(T)$-curves related to other pressures have been handled similarly.

RESULTS AND DISCUSSIONS

The primary intention of this paper is to report a gas-induced excess order at the surface of MBBA observed through the temperature-dependent surface tension measurements. A previous work revealing this phenomenon is to our knowledge not aware.

Figure 2 shows the surface tension–temperature characteristic ($\gamma(T)$-curves) of MBBA in CO_2 at various pressures. In all cases the anomalies of the surface tension can be observed near the i–n phase transition temperatures. The i–n transition temperatures are a function of the sorbed CO_2 concentration in the LC: they show a downward trend with increasing gas pressure [3]. At lower gas pressures, *e.g.*, 1 bar and 3 bar, the $\gamma(T)$-

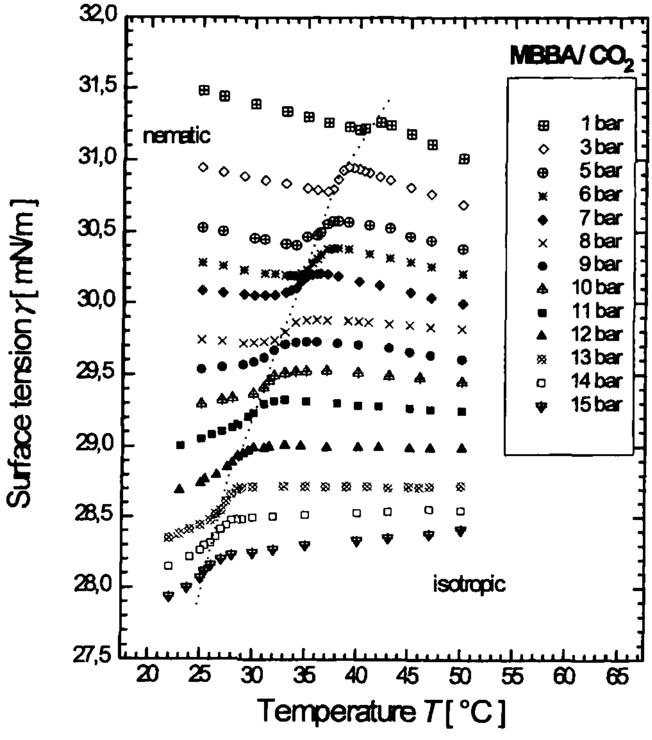

FIGURE 2 Temperature-dependence of the surface tension of MBBA in CO_2 at various pressures. (The dotted lines refer to the i–n phase transition).

curves show well comparable course to those determined in the N_2 atmosphere [2, 7]. Yet compared with the $\gamma(T)$-curves determined in N_2 the $\gamma(T)$-curves in CO_2 have generally lower values, which is supposed to be attribute to the higher solubility of CO_2 in the LC as well as the stronger interaction between CO_2 molecules and the LC molecules.

Originally the $\gamma(T)$-curves were measured by us only at the pressures of 1, 5, 10 and 15 bar. At first time, a remarkable change of the temperature coefficient $d\gamma/dT$ with the CO_2 pressure has been observed both before and after the i–n phase transition. Further $\gamma(T)$-measurements at other pressures confirmed this change definitely. Figure 3 shows that the $d\gamma/dT$-values *vs.* the CO_2 pressure for the nematic and isotropic phase respectively, they are resulted from the linear regression on the corresponding parts of the $\gamma(T)$-curves. In the i-phase the $d\gamma/dT$-values increase with gas pressure practically linearly, whereas they seem to increase with different slopes in the n-phase, with the inflection locating at $d\gamma/dT = 0$.

Since, as seen at higher pressures, the monotonic increases of the $\gamma(T)$-curves in the i-phase contradict the physical rules [7], further surface tension measurements have been carrried out up to the temperature of 80°C. Figure 4 shows such results together with the previous ones. As expected, all $\gamma(T)$-curves (except the ones measured under normal pressure) change the $d\gamma/dT$-values again at temperatures between 45–50°C above which they exhibit values about −0.03 mN/m·K and thus lie within the normal range of

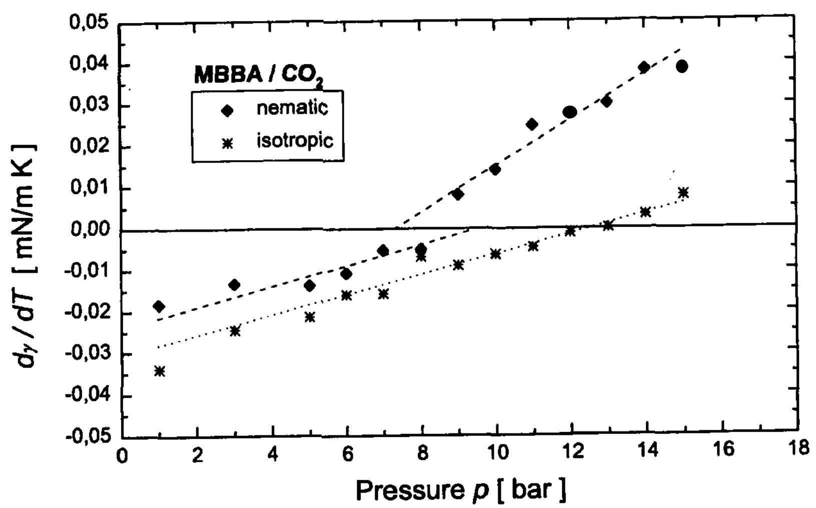

FIGURE 3 Temperature coefficient $d\gamma/dT$ *vs.* the CO_2 pressure.

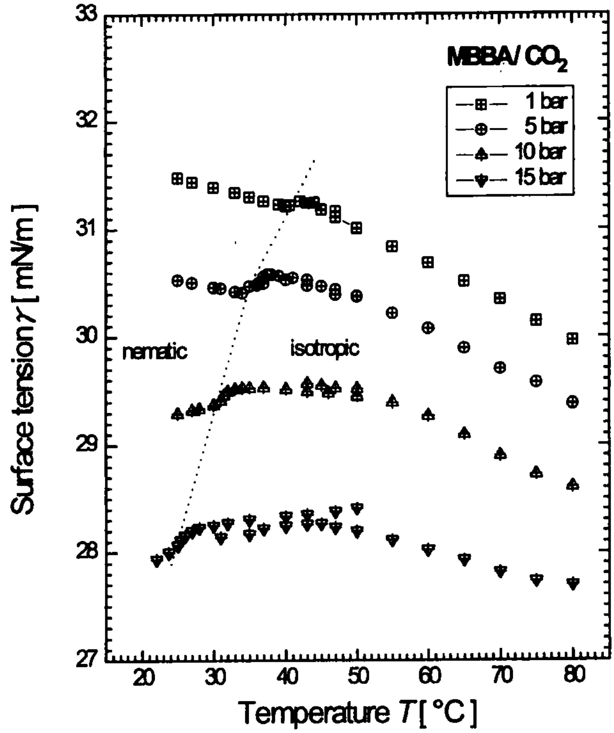

FIGURE 4 Temperature-dependence of the surface tension of MBBA in CO_2 up to 80°C. (The dotted lines refer to the i – n phase transition).

conventional liquids. The deviation of the results from the two measurement series are identifiable yet within the range of the absolute error of our method, they are caused by the different adjustments of the measuring setup, which can essentially influence the measuring accuracy [5].

In an earlier paper we have concluded in our case ($p_{max} = 15\,\text{bar}$) the effect of pressure self on surface tension can be neglected [1], so that the above revealed increase of the $d\gamma/dT$-values (at the both sides of the i – n transition) has to be attributed to the CO_2 sorption in the LC. This phenomenon exist at either lower or higher gas pressures: in the n-phase it can be observed throughout the whole experimental temperature range, while in the i-phase it takes place over a temperature range more than 20 K. Moreover, the intensity of the phenomenon is able to be enhanced by heightening the CO_2 pressure, and as the result, at sufficient pressure it implies also positive $d\gamma/dT$-values: for the n-phase $p > 8$ bar and for the i-phase $p > 12$ bar (Fig. 3). Therefore, in the latter circumstance due to the sign change of the $\gamma(T)$-slope at the temperatures between 45 – 50°C the corresponding temperatures can be called as the inversion temperatures (T_i,'s).

The question arises whether the above phenomenon is directly caused by the change of the CO_2 concentration in the LC samples, which normally displays the molecular reorganization in the LC bulk. Figure 5 shows the equilibrium concentration of the sorbed CO_2 in MBBA at various pressures. In all cases, within the crystalline phase MBBA contains relative low concentrations of the sorbed CO_2, these equilibrium concentrations increase yet dramatically at the transition of the crystalline to the nematic phase. The upward trend of the c(T)-curve keeps on throughout the n- and i-phase. Compared with the c – n phase transition, the n – i transitions show a considerably smaller but still recognizable discontinuity in the concentration of the sorbed CO_2. This discontinuity enhances with the increase of gas pressure.

Figure 6 shows, as an example, a direct correlation between the $\gamma(T)$-curves and the c(T)-curve measured at 15 bar. The cause for the deviation between the both $\gamma(T)$-curves has been mentioned above. Comparing the both $\gamma(T)$-curves, in the i-phase a retardation of the T_i, towards lower temperature is recognizable by the curve measured by cooling from 80°C, yet near the T_i shows the c(T)-curve normal linearity. It is known, for the

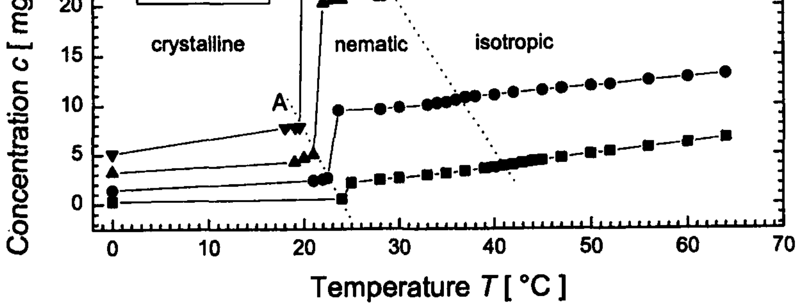

FIGURE 5 Temperature-dependence of the CO_2 sorption in MBBA at various pressures. (Line A and line B represent the c – n and n – i phase transition, respectively).

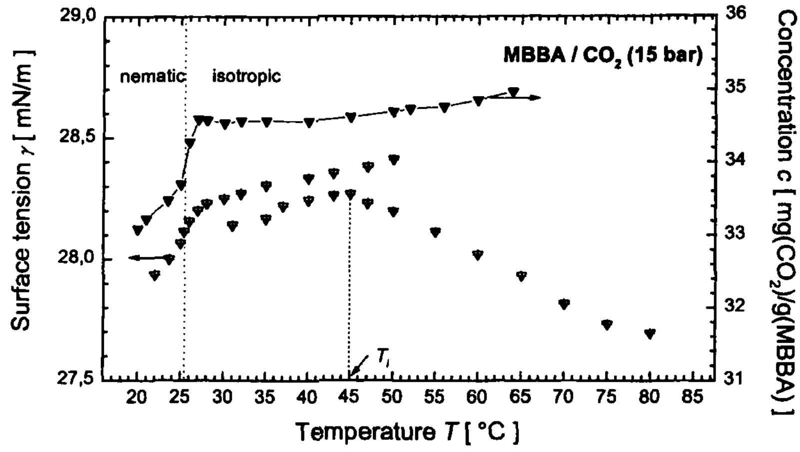

FIGURE 6 Comparison of the $\gamma(T)$-curves and the c(T)-curve in 15 bar CO$_2$. (The dotted line refers to the i–n phase transition).

surface of a system containing N components the temperature coefficient of its surface tension can be written as [8, 9]:

$$\frac{\partial\gamma}{\partial T} = -S^s - \sum_{i=1}^{N} \Gamma_i^s \left\langle \frac{\partial \mu_i}{\partial T} \right\rangle, \tag{1}$$

where S^s and Γ_i^s are the surface excess entropy and the surface excess mole number of component i per unit area respectively, and μ_i the chemical potential of i. For one-component systems the second term of the above equation is zero, and thus their temperature coefficients can be expressed as:

$$\frac{d\gamma}{dT} = -S^s \tag{2}$$

with $S^s = S_s - S_b$, where S_s and S_b refer to surface and bulk entropy per unit area states, respectively. In situation $d\gamma/dT$ is positive, the liquid is more ordered at the surface than in the bulk. For the most conventional liquids yet, due to spatial delocalization across the liquid/vapour-interfacial zone, the molecules at the surface are less ordered, and thus with negative $d\gamma/dT$-values.

Due to the ultra thin surface region the amount of sorbed gas at the LC surface is negligiblely small compared with that in the bulk. Therefore, the c(T)-curve shown in Figure 6 (as well the ones in Fig. 5) describes mainly the temperature-dependent CO$_2$ sorption in the bulk of MBBA. However, it gives also the evidence of the CO_2 sorption at the LC surface. As known from our earlier experimental results the CO_2 sorption in MBBA is purely physical and reversible, and the MBBA surface is far from the saturated state of gas sorption [1 – 3, 10], which means that there is no reason to expect a discontinue change in the surface CO_2 concentration at the temperature range near the T_i. Thus, the second term at the right side of Eq. (1), which directly reflects the gas sorption property at the surface, can be considered as a monotonically changing term. For these reasons, the change of the sorbed CO_2 concentration is obviously not directly responsible for the remarkable behavior of the $\gamma(T)$-slopes.

Thus, we attribute the change of the temperature coefficient $d\gamma/dT$ to a surface-molecular excess order resulted from the gas-induced reorganization and/or reorientation of the LC molecules. Under normal conditions (1 bar air or N_2), in the case of low molecular LCs some specific surface structures of molecular ordering at surface boundaries can be observed within a narrow temperature range above the i – n phase transition ($T - T_{in}$ = several K) [11 – 14]. A respective large temperature range can be observed only on polymeric LCs [15]. In our case yet, when the CO_2 pressure is high enough (*e.g.*, $p > 12$ bar), the gas-induced surface excess order can be quite strong and obvious, and especially this can be even over a wide temperature range ($T - T_{in} \geq 20$ K) stable.

Assuming that the limited sorbed CO_2 only indirectly influences the surface tension by inducing some reorganization and rearrangement of the MBBA molecules, the thermodynamic expression Eq. (2) should be still approximately available in our cases.

The different behaviors of $d\gamma/dT$ *vs.* the CO_2 pressure before and after the i – n transition (Fig. 3) are interpreted with the following consideration: since, in the i-phase, the bulk MBBA molecules are in statistical state, the sorbed CO_2 molecules influence (induce) primarily the molecular order or orientation at the surface region, and this effect is able to be enhanced with increasing concentration of the sorbed CO_2. The $d\gamma/dT$-values are approximately only a function of the surface entropy, therefore, they show a monotonous increase with increasing gas pressure. In the n-phase, however, there are certain molecular orders existing both at the surface and in the bulk of the LC, which can be changed through the invasion of the gas molecules. Obviously, the influence of the gas molecules effects differently on the surface and bulk molecules, thus, the $d\gamma/dT$-values are no more only a function of the surface entropy but also a function of the bulk entropy. As seen in Figure 3, at lower pressures the negative $d\gamma/dT$-values indicate lower orders of the surface molecules than those of the bulk molecules. When the

CO_2 pressure becomes higher, the surface molecules in general tend to have a better order than the bulk ones. At the pressure by 9 bar the inversion takes place, *i.e.*, the surface molecules become better ordered, the corresponding discontinuity is characterized by the inflection point on the $d\gamma/dT$-pressure curve. After the inversion the increase of the surface excess entropy seems to accelerate with the pressure.

We have also performed the temperature-dependent surface tension measurements of MBBA in other gas atmospheres such like N_2, Ar and He, in which yet the above described gas-induced surface order could not be observed. We suppose that the polarity of the C—O bonds in the sorbed CO_2 molecules plays the essential role in inducing this surface excess order.

Very recently similar investigations have been also performed on other low molecular LCs such as 1-isothiocyanato-4-(*trans*-octylcyclohexyl)-benzene (PCH8-CNS) and 4-(trans-4′-penthylcyclohexyl)-benzonitrile (PCH5), the results confirmed again the gas induced surface excess order described above.

The generalize the above phenomenon further experiments are necessary. The related studies with reflection ellipsometry as well as X-ray reflection are planed in our laboratory.

SUMMARY

We have studied the influence of the CO_2 sorption on the surface tension–temperature characteristic of the low molecular liquid crystal MBBA. The surface tension and the gas sorption measurements have been performed separately under the same experimental conditions, by using a computer-aided measuring set-up based on the pendant drop method and a high pressure electromicrobalance. A remarkable increase of the temperature coefficient $d\gamma/dT$ with increasing CO_2 pressure has been observed, both below and above the isotropic–nematic phase transition temperature T_{in}, yet with different increasing rates. When the pressure is sufficiently high, $d\gamma/dT$ becomes definitely positive and can be even over a wide temperature range in the isotropic phase stable. At more higher temperatures it changes into negative again and shows the values comparable to conventional liquids. A comparison of the temperature scanning surface tension with the temperature scanning sorption shows that there isn't a direct correlation between the sorbed CO_2 concentration and the above phenomenon. We suppose this results from a excess order of the surface molecules, induced by the sorbed CO_2 molecules.

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References

[1] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 89 (1997).
[2] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, in press (1998).
[3] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, **312**, 203 (1998).
[4] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **293**, 39 (1997).
[5] B. Song and J. Springer, *J. Colloid Interface. Sci.*, **184**, 64 (1996); **184**, 77 (1996).
[6] L. Phan Thuy and J. Springer, *Colloid Polym. Sci.*, **266**, 614 (1988).
[7] R. Eötvös, *Wied. Ann.*, **27**, 448 (1886).
[8] S. Flügge (Ed.), *Handbuch der Physik*, Band 10, Springer-Verlag, Berlin 1960.
[9] L. Dufour and R. Defay, *Thermodynamics of Clouds*, Academic Press, New York and London 1963, Chapter 3.
[10] G.-H. Chen, *Ph.D. Thesis*, Technical University of Berlin (D83), 1998.
[11] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **35**, 253 (1976).
[12] M. G. Gannon and T. E. Faber, *Phil. Mag.*, **A-37**, 117 (1978).
[13] D. Beaglehole, *Mol. Cryst. Liq. Cryst.*, **89**, 319 (1982).
[14] S. Immerschitt, T. Koch, W. Stille and G. Strobl, *J. Chem. Phys.*, **96**, 6249 (1992).
[15] H. Elben and G. Strobl, *Macromolecules*, **26**, 1013 (1993).