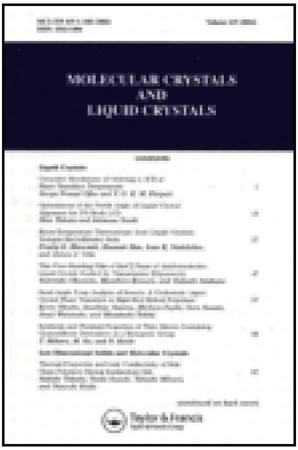

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Sorption and Diffusion of Gases in Liquid Crystalline Substances

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Sorption and Diffusion of Gases in Liquid Crystalline Substances

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Systematic studies on the sorption and diffusion behaviors of gases in low-molar-mass liquid crystalline substances (LCs) have been performed. The experiments were carried out in different gas atmospheres over temperature ranges which covered the phase transitions of the LCs under investigation, and at pressures of up to 15 bar. The equilibrium concentration and the diffusion coefficient of the sorbed gases were found to be strongly dependent on the LC phase state, gas type and gas pressure and temperature. Furthermore, the influence of gases on the phase transition temperatures of LCs and the reversibility of gas sorption have been studied.

Keywords: gas sorption; gas diffusion; liquid crystal

INTRODUCTION

Liquid crystalline substances (LCs) have gained considerable interest due to both their technological and theoretical importance. However, investigations on the gas sorption and diffusion properties of LCs, especially of low-molar-mass LCs, have been quite limited so far[1–5].

Chen et al.[1] have first investigated the solution and diffusion properties of CO_2 in a monomeric liquid crystal. Both properties were found to depend strongly on the LC phase state and interpreted in terms of molecular arrangements and the magnitude of free volume in different phases. The authors confirmed that liquid crystallinity can seriously limit the dissolution of gases even though the free volume in a liquid crystalline phase is usually close to that in the respective isotropic phase. They have also demonstrated that thermal behavior such as the isotropization temperature of the LC are influenced by the sorbed gas.

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The gas solubility and permeability of liquid crystalline polymers (LCPs) has received more attention due to their technological potential as polymeric membranes [2–4]. Generally, the LC order is expected to play an important role in reducing the gas solubility and gas permeability of polymers. Experiments on the CO_2 solubility in a series of LC side-chain polymers gave results similar to those obtained from the LC monomer mentioned above[2]. Significant discontinuities in the equilibrium concentration of the sorbed CO_2 were observed at various phase transitions (of the LC side-chain polymers). The magnitude of the change increased with increasing enthalpies of the transitions.

During our recent research on the surface tension of both low-molar-mass and polymeric LCs we found that the sorption of surrounding gases can seriously influence the surface-molecular arrangement of LCs [6–9]. Thus, systematic experimental studies on the gas sorption and diffusion behavior of liquid crystalline substances have been performed in our laboratory.

As a part of our report series, the goal of the present paper is to report some preliminary experimental results on both properties of different gases (N_2, CO_2, Ar and He) in several low-molar-mass LCs. We are not aware of any previous work on this subject. More detailed investigations considering physical/chemical interrelations are underway in our laboratory.

The paper is organized as follows: in the first part, the temperature-dependence of gas sorption will be reported. This is followed by measurements of the time-dependence of gas sorption, from which the corresponding diffusion coefficients are estimated. A correlation between the phase transition temperatures and the concentration of sorbed gases will be established. Finally, the reversibility of gas sorption is discussed.

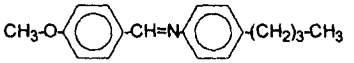
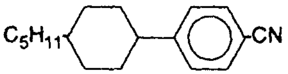
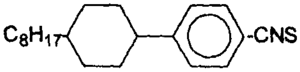
EXPERIMENTAL

(A) Materials

The low-molar-mass LC samples MBBA (*4*-methoxybenzylidene-*4'*-*n*-butylaniline) (purity > 98%, given by the manufacturer), *1*-isothiocyanato-*4*-(*trans*-octylcyclohexyl)-benzene (PCH8-CNS) (purity > 99%) and *4*-(*trans*-*4'*-penthylcyclohexyl)-benzonitrile (PCH5) (purity > 99%) obtained from Aldrich Chem. Company Inc. (USA) were recrystallized from ethanol for several times and then dried in vacuum. After evacuation they were stored at 0°C with dry nitrogen as protective gas.

The phase behavior of the LC samples 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 listed in Table I

TABLE I Results of phase characterization on MBBA, PCH5 and PCH8-CNS

Substance	*Phases and transition temperatures [°C]* [a]
MBBA 	**c** *ca.* 24 **n** 43.0 **i**
PCH5 	**c** *ca.* 30 **n** 55.2 **i**
PCH8-CNS 	**c** *ca* 28 **n** 47.8 **i**

a. **c**, **n** and **i** denote crystalline, nematic and isotropic phase, respectively.

The employed gases N_2, CO_2, Ar and He, purchased from the Company Messer Griesheim (Germany), had a purity > 99.99%.

(B) Gas sorption measurements

The sorption measurements were carried out by using a high pressure electro-microbalance (Model 4436, Sartorius, Germany). Details of the measurement set-up were given in an earlier paper[11]. Basically, it consists of a sorption chamber, a vacuum and gas supply system, a temperature controlled isolation body as well as a personal computer. The available temperature range, namely the calibrated temperature range of the microbalance, is from 0°C to 70°C, which is sufficient for locating phase transitions of the LCs under investigation.

Prior to the measurements the LC samples were degassed in vacuum by using an oil diffusion pump in connection with a rotary oil pump. In order to avoid the evaporation of the low-molar-mass samples, the degassing was carried out at 0°C, at which temperature all the samples were in the crystalline state.

After the sample had reached a constant weight, a desired pressure of gas 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 measure. Because of the thermal expansion of the gas in the microbalance on heating it was necessary to adjust the gas pressure from time to time.

For the kinetic study of the time-dependent sorption the following steps were performed: the LC samples were also first evacuated at 0°C. Subsequently, the samples were heated up to the desired temperature in vacuum. To ensure a homogeneous temperature over the whole microbalance a time of several hours was required for this. Finally, immediately after the introduction of gas into the microbalance the increase in weight of the samples by sorption was registered continuously as a function of time by the computer.

(C) Determination of diffusion coefficient

The time-dependence of gas solubility enables the determination of the diffusion coefficient D. For a plane sheet of thickness l in a gas atmosphere maintained at constant temperature and pressure the increase in weight of the sheet can be written as[12]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\}, (\mathrm{n} = 0, 1, 2, \ldots) \quad (1)$$

where M_t is the total amount of gas sorbed by the sheet at time t and M_∞ is the equilibrium sorption attained theoretically after infinite time.

Fitting the theoretical sorption curves from equation (1) to each of the experimental curves yields the concentration-independent, mean diffusion coefficient $\bar{D}$ which is defined by the following equation

$$\bar{D} = \frac{1}{c_a - c_b} \int_{c_b}^{c_a} D \cdot \mathrm{d}c, \quad (2)$$

where c_a to c_b is the concentration range existing in the sheet during the experiment. Normally, e.g. in our case, $c_a = 0$ and c_b is the equilibrium gas concentration (c_e) in sample after infinite sorption time.

In the present work, an initial mass of *ca.* 80 mg of each sample was chosen. The LC samples were located in a quartz pan with a diameter of 14 mm. This resulted in a cylindrical LC film of *ca.* 0.45 mm in depth. According to the schematic representation in Figure 1 this one-sided gas sorption process is obviously identical to the double-sided one taking place in a cylindrical film with a halved cross section yet a doubled thickness. Because of the wall of the quartz pan there

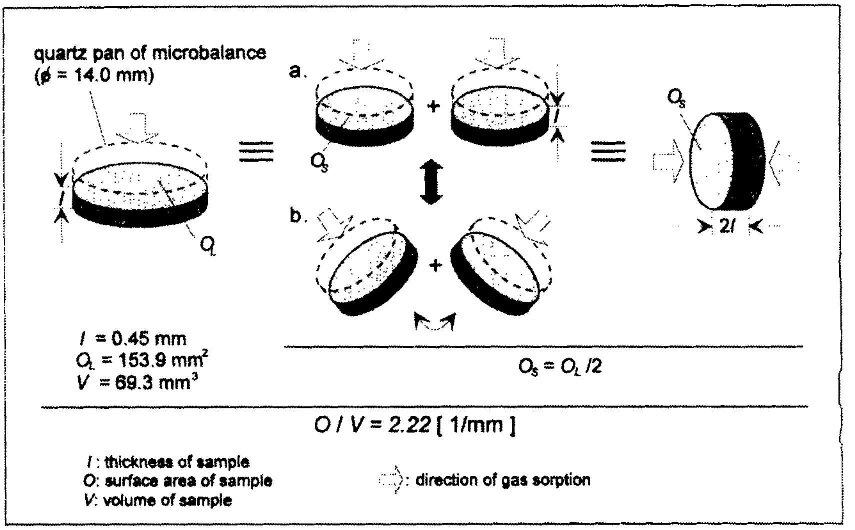


FIGURE 1 Schematic representation of sorption models for mathematical treatment to evaluate diffusion coefficient through curve-fitting

is no gas sorption through the edge. Therefore, in our case with $n = 6$ equation (1) can be changed into the following equation

$$\frac{c(t)}{c_e} = \frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{6} \frac{8}{(2n+1)^2\pi^2} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{0.0324}\right\}. \tag{3}$$

The curve-fitting was performed using the software *Origin 4.1* (Microcal Software, USA).

RESULTS AND DISCUSSIONS

Figures 2 –5 show the sorption of N_2, CO_2, Ar and He in MBBA at various pressures as function of temperature ($c(T)$-curves). The solubilities are as follows: $CO_2 > N_2 > Ar > He$.

In general, all gases exhibit a strong temperature- and LC phase-dependent solubility. Within the crystalline phase the equilibrium concentrations of the sorbed gases are relatively low. The influence of temperature is small. This is attributed to the fact that in the crystalline state gas molecules can only be adsorbed to the surface regions or in the defects between crystallites of the LC sample. In the isotropic phase the gas solubility is generally higher than in the LC (nematic) phase. For N_2, CO_2 and Ar this concentration increases dramatically at the c-n phase

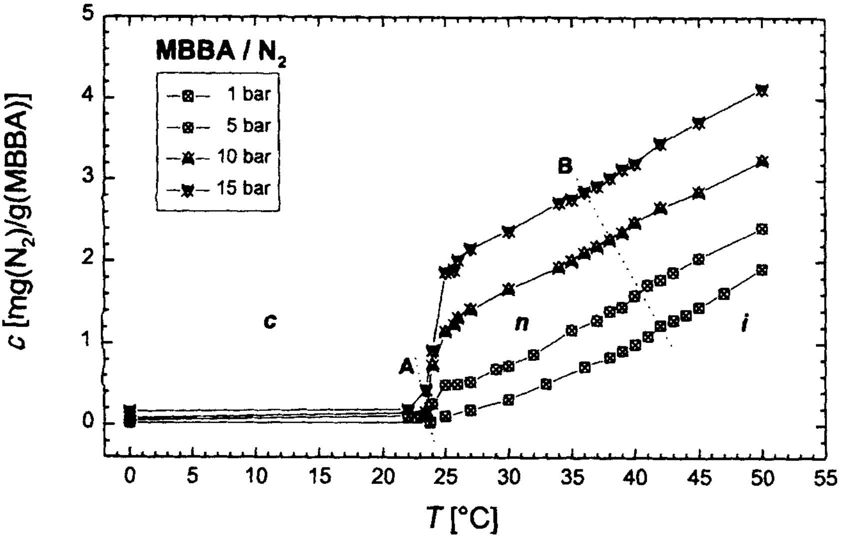


FIGURE 2 Temperature-dependence of the sorption of N_2 in MBBA at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

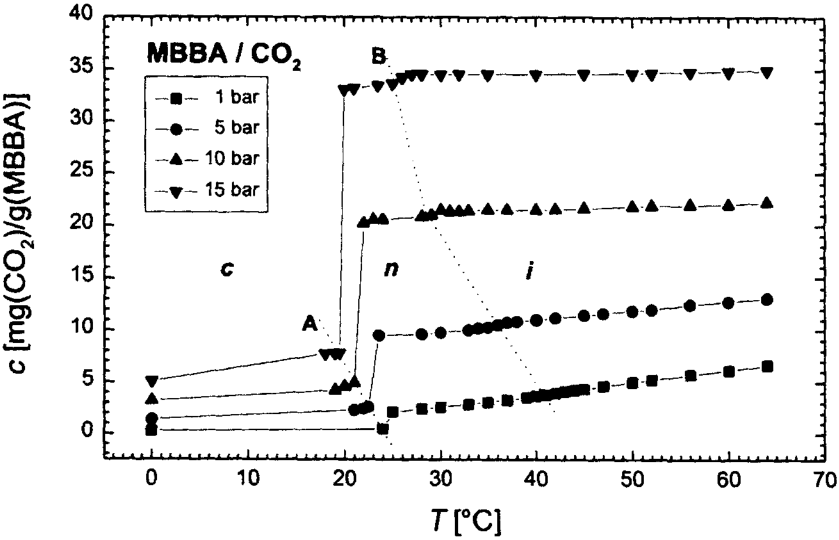


FIGURE 3 Temperature-dependence of the sorption of CO_2 in MBBA at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

transition. The upward trend of the $c(T)$-curves is maintained throughout the n- and i- phase. The discontinuity in the gas concentration at the transition n-i is rather small and in the case of N_2 even difficult to be recognized. However, this discontinuity becomes more obvious with the increase of gas pressure.

CO_2 possesses a considerably higher solubility than other gases, which compares well with the gas sorption behavior in normal liquids such as water. We suppose that the polar $\rangle C{=}O$-bond is mainly responsible for the intensive interaction between the gas and LC molecules and thus the high solubility. The sorption of the two noble gases Ar and He in MBBA is very low, and for He due to the small molar mass its equilibrium concentration within the crystalline and nematic states was beyond the accuracy limit of our microbalance and thus impossible to measure. On the contrary, in the isotropic phase, despite the relatively large errors the $c(T)$-curves for Helium confirm the increasing tendency with temperature. It is thus reasonable to infer that He possesses a sorption behaviour similar to the other gases under investigation.

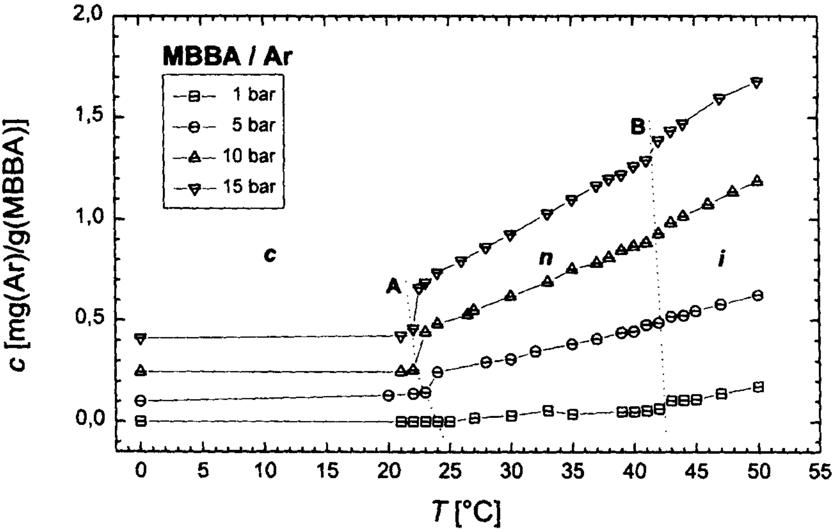


FIGURE 4 Temperature-dependence of the sorption of Ar in MBBA at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

The sorption isotherms in Figures 6 and 7 represent a direct comparison of the effect of pressure on the solubility of different gases, for the nematic and isotropic phase of MBBA, respectively. In both cases, the sorption of the gases is enhanced with increasing pressure. The strong pressure-dependence of CO_2 confirm again the high solubility of this gas.

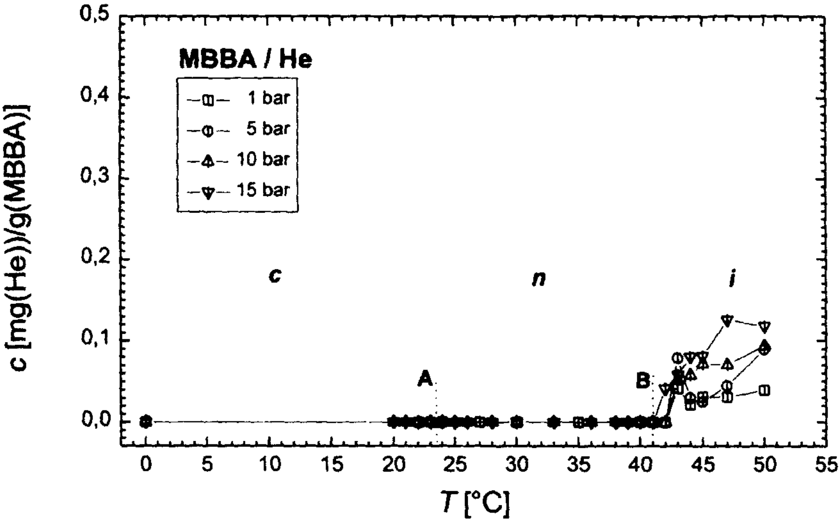


FIGURE 5 Temperature-dependence of the sorption of He in MBBA at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

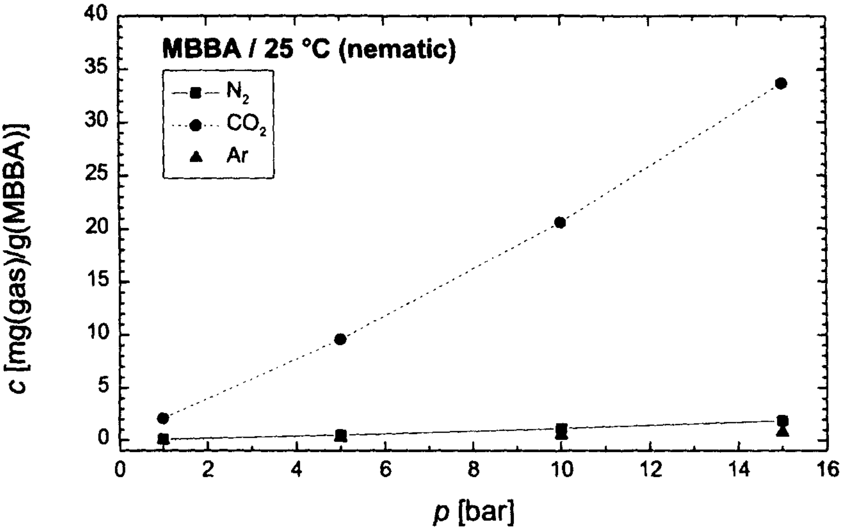


FIGURE 6 Pressure-dependence of the gas sorption in MBBA (25 °C, nematic phase)

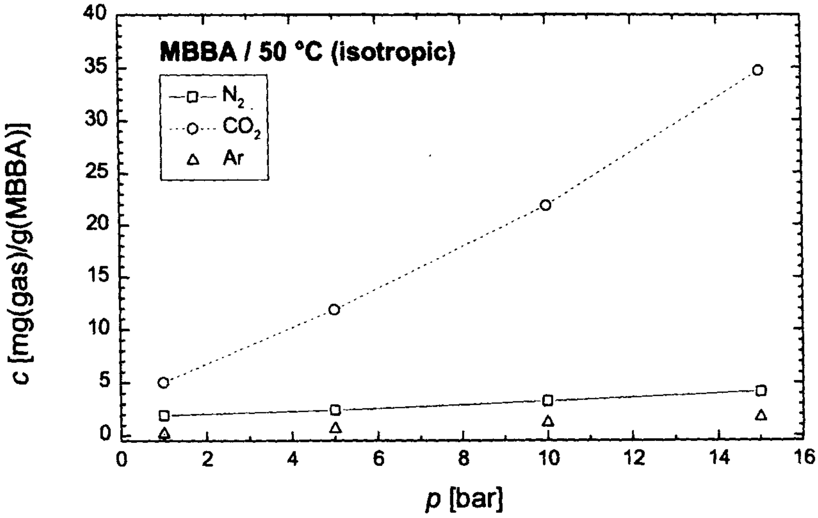


FIGURE 7 Pressure-dependence of the gas sorption in MBBA (50 °C, isotropic phase)

Therefore, according to the above observations, we conclude that the gas solubility in liquid crystals is a function of the LC phase state, temperature, gas type and gas pressure.

The same measurements have also been carried out on two other low-molar-mass liquid crystals: PCH5 and PCH8-CNS. Their c(T)-curves compare well to those obtained with MBBA. As an example, the sorption behaviors of CO_2 in both LCs are shown in Figures 8 and 9, respectively.

It is interesting to compare the sorption-temperature-characteristic of low-molar-mass LCs with that of LCPs. Chen et al. [2] have investigated the CO_2 sorption (under 1.2 bar gas pressure) in a series of side-chain LCPs. The gas solubility exhibits a discontinuous change at several types of first-order phase transition. The magnitude of the change increases with increasing enthalpies of the respective transitions. Also at the phase transition crystalline to LC mesophase a significant increase in the gas solubility can be seen. All these phenomena are in good agreement with those observed on low-molar-mass liquid crystals. The main difference in the sorption behaviors between the two LC-categories is that within a certain phase state, either of mesophases or not, low-molar-mass LCs possess an increasing tendency in gas solubility with temperature while the polymeric ones show a decreasing tendency. A further difference is that under the same experimental conditions the gas solubility in LCPs is generally lower than that in low-molar-mass ones. Obviously, the polymer backbone is mainly respon-

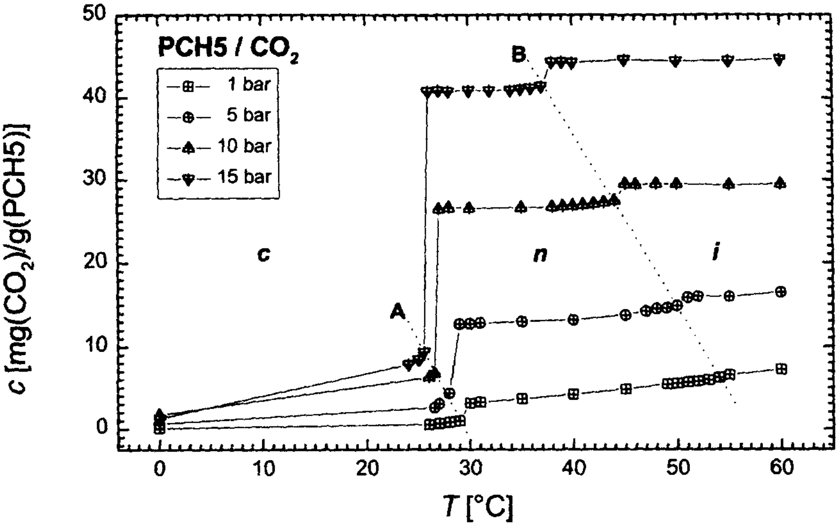


FIGURE 8 Temperature-dependence of the sorption of CO_2 in PCH5 at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

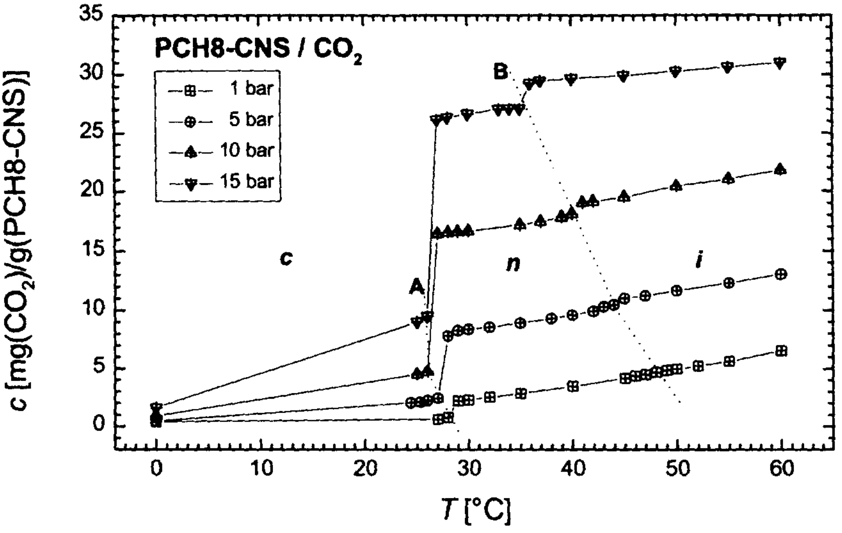


FIGURE 9 Temperature-dependence of the sorption of CO_2 in PCH8-CNS at various pressures (Line A and line B represent the c-n and n-i phase transition temperatures, respectively)

sible for these differences. Accordingly, further systematic studies on the gas sorption of polymeric LCs are essential for a full understanding/complete comparison and this is under way in our laboratory.

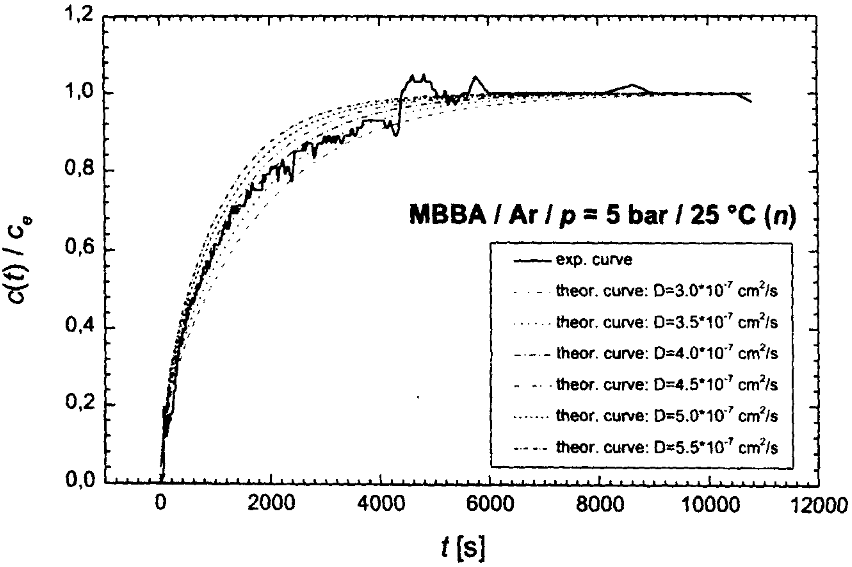


FIGURE 10 Determination of diffusion coefficient through graphic-fitting

The time-dependence of gas sorption ($c(t)$-curves) enables the estimation of the diffusion coefficient D through graphic-fitting. This has been performed in different phases of MBBA. As already noted, such D's are the concentration-independent mean values. However, in many cases this approximation is sufficiently accurate. Figure 10 represents, as an example, the fitting-process of the $c(t)$-curve obtained in 5 bar Ar-atmosphere. In this case, the diffusion coefficient is determined as $4.0^{*}10^{-7}$ cm^2/s. The D values obtained in this way are summarized in Table II. The diffusion coefficients decrease, independent on the phase state, from CO_2 via Ar to N_2, i.e. among the three gases, CO_2 possesses the highest diffusivity and N_2 the lowest.

Generally, at a constant temperature the diffusivity of all three gases rises with the increase of pressure. This tendency is much more easily observed in the case of CO_2 and N_2 rather than with Ar. The isotropic phase generally allows a higher diffusivity than the nematic. Compared with those for LC side-chain polysiloxane [13], the D-values for MBBA are higher but of the same order of magnitude.

TABLE II Diffusion coefficients of N_2, CO_2 and Ar in MBBA by different experimental conditions

T [°C]	*p [bar]*	*$D^{*}10^{7}$ [cm²/s]*		
		N_2	*CO_2*	*Ar*
25 (nematic)	1	1.7	5.0	4.0
	5	2.4	5.8	4.0
	10	2.9	6.5	4.2
	15	3.7	7.2	4.5
50 (isotropic)	1	2.5	5.5	5.3
	5	3.3	6.1	5.5
	10	4.2	8.0	5.8
	15	5.0	10.0	6.1

As can be seen from Figures 2–5, the phase transition temperature n-i (T_{ni}) decreases with increasing pressure and thus the concentration of sorbed gases. Figure 11 shows the T_{ni}'s of MBBA vs. pressure in different gas atmospheres*. The T_{ni}-values obtained from the $c(T)$-curves are in good agreement with those from the visual observation of the drop images of MBBA during surface tension measurement [7–10].

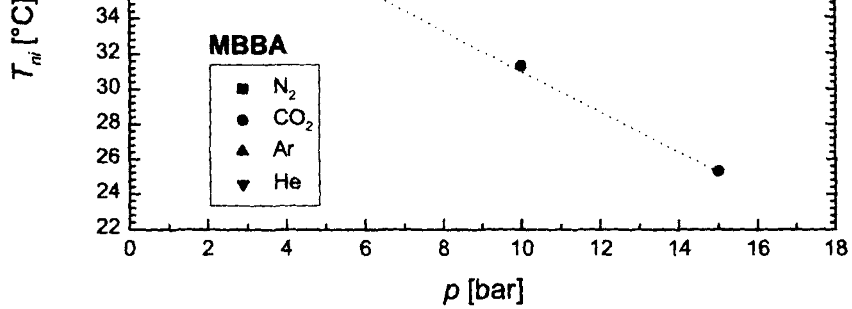


FIGURE 11 Influence of gas pressure on the n-i phase transition temperature of MBBA

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* Due to the complete gas sorption the T_{ni}-values presented here under normal pressure (1 bar) are a little lower than those determined by DSC and polarization microscopy (s. Tab. I).

Among the four gases, CO_2 has the strongest effect on the n-i phase transition of MBBA: a reasonable interpretation may attribute this 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)C=O-bond. In contrast to CO_2, due to the weak gas-LC interaction the sorption of the noble gases Ar and He affects the n-i phase transition only very slightly. Several effects are supposed to be responsible for the above phenomenon: first, the effect of pressure. For a one-component-system, namely LC without gas sorption, the transition n-i can be described by the *Clausius-Clapeyron* equation, which predicts a rise in isotropization temperature when the pressure increases. Numerous reports on this subject have been published[14–16]. Generally the pressure effect is quite low – it amounts to *ca.* +2 – +7 °C/100 bar, for both low-molar-mass and polymeric LCs. Therefore, in view of our experimental pressures this effect is considered to be small. Secondly, the effect of mixture. A LC-system including sorbed gases can be interpreted as a dilute solution. The reduction of a phase transition temperature is proportional to the concentration of solute. In the present study, a higher pressure corresponds to a higher concentration of sorbed gases, and accordingly the T_{ni} becomes lower. Third, the effect of molecular interaction. Since an important factor for the formation of LC phases is the anisotropy of intermolecular forces between LC molecules[17], 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 as the n-i phase transition temperature T_{ni}.

Compared to the n-i phase transition, the gas effect on the c-n transition seems to be similar but much smaller. In CO_2, e.g., the c-n phase transition is with a dT_{cn}/dp-rate of *ca.* −1.5°C/5 bar essentially less influenced by the gas sorption in comparison with the n-i transition, which exhibits 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. Finally, we have also investigated the reversibility of the gas sorption in MBBA. After the sorption measurements the saturated samples were measured again by DSC (in 1 bar N_2). Due to incomplete desorption during the preparation all the samples show the T_{ni}-values between those under gas pressure and pure materials. Such samples were then evacuated at 0°C. For an entire desorption of gases a long time(how long?) was required. After evacuation all of the recycled samples were able to regain a phase transition temperature of 43.0 °C, which indicated a reversible, physical sorption of the gases in MBBA. Additionally, this reversibility has been confirmed by the results of surface tension experiments [7–9].

SUMMARY

We have reported preliminary experimental results on the sorption and diffusion behaviors of different gases (N_2, CO_2, Ar and He) in several low-molar-mass LCs (MBBA, PCH5 and PCH8-CNS). The temperature-scanning sorption measurements reveal the correlation between the gas solubility and the temperature (LC phase). The time-dependence of gas sorption enables the determination of the diffusion coefficient of gases under various conditions. The influence of sorbed gases on the LC phase transitions has also been systematically studied. The results reveal that the equilibrium concentration, the diffusion of sorbed gases as well as the phase transition temperatures of LCs are a strong function of the LC phase state, temperature, gas type and gas pressure. Furthermore, the gas sorption is shown to be physical and reversible.

Acknowledgements

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