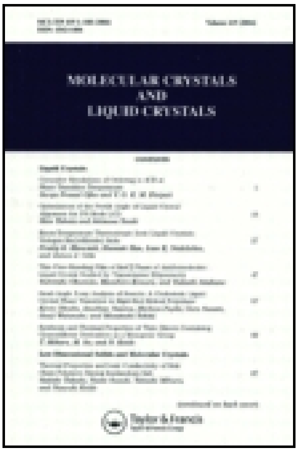

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Gas Sorption Properties and Molecular States of a Liquid Crystal

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Gas Sorption Properties and Molecular States of a Liquid Crystal

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The solution and diffusion properties of CO_2 in a monomeric liquid crystal have been investigated through use of an electromicrobalance apparatus. Both kinds of properties have been shown strongly dependent on the phase states of the liquid crystal. The results are interpreted in terms of molecular arrangements and the magnitude of free volume in different phases. Effects of the sorbed CO_2 on the thermal behavior of the liquid crystal were also investigated. A correlation between the isotropization (clearing) temperature of the liquid crystal and the concentration of the sorbed gas has been established.

Keywords: gas sorption, gas diffusion, liquid crystalline phases, free volume, carbon dioxide

INTRODUCTION

Diffusion and solution behavior of gases in organic solids, especially in polymers, is of interest from both theoretical and technological points of view. The behavior is generally associated with the molecular characteristics of material, in particular flexibility of molecular chains, configuration, interactions between adjacent molecular segments and the overall morphology.[1-4]

In comparison to liquid and gaseous states, an organic solid in a crystalline state generally possesses very little translational or rotational freedom. It is generally believed that gases and vapors are dissolved in the noncrystalline regions.[5-7] In the case of a liquid crystal, the molecular motion is highly increased in its liquid crystalline (LC) phase. The values of diffusivity and solubility of gases in LC phases are much higher than those in crystalline phases.[8,9] Despite this, the effect of LC phase structures on transport properties is still unclear; experimental data decisive

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for the elucidation of differences between LC and isotropic phases are not available. Different activation energies of permeation between both phases have been reported[10-12] for the side-chain (comb) polymer liquid crystals (PLCs). However, a quantitative description of the behavior of LC phase can not be obtained due to the complicated permeation systems existing in polymers.

Following Samulski,[13] we need to distinguish between monomeric liquid crystals (MLCs), which may or may not be able to polymerize, and PLCs. Under the circumstances described above, we have studied transport properties of a MLC through the use of the gas sorption method. The structure of the MLC and its phase behavior is shown in Figure 1. Due to much simpler permeation systems for MLCs than for polymers, the measurements of transport properties taken at different phases can quantitatively provide us the necessary information regarding the role of LC order in gas permeation process. The sorbed gas has been also known to be able to influence the physical properties of organic materials such as melting point and the glass transition, as well as molecular motions.[14,15] Therefore, the present work was aimed at finding how the sorbed gas affects transport and

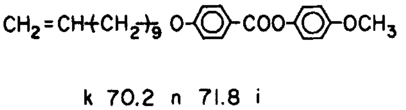

FIGURE 1 Structure of the liquid crystal and its thermal behavior.

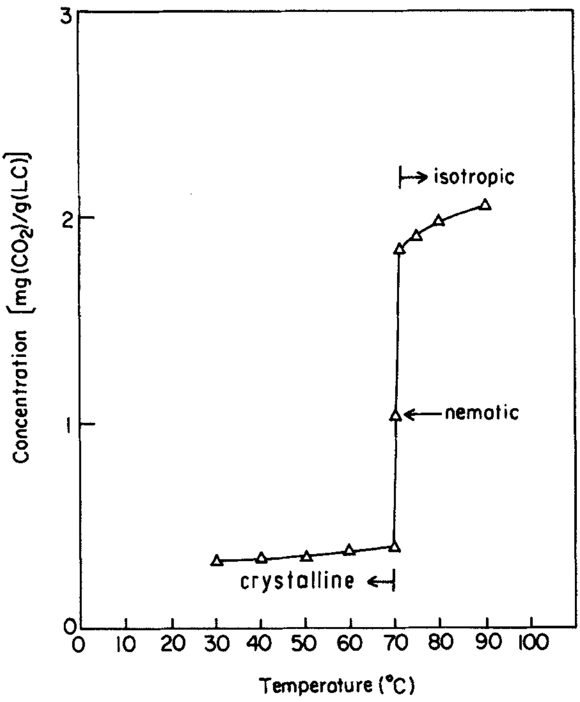

FIGURE 2 Equilibrium concentration of sorbed CO_2 at 1 bar as a function of temperature.

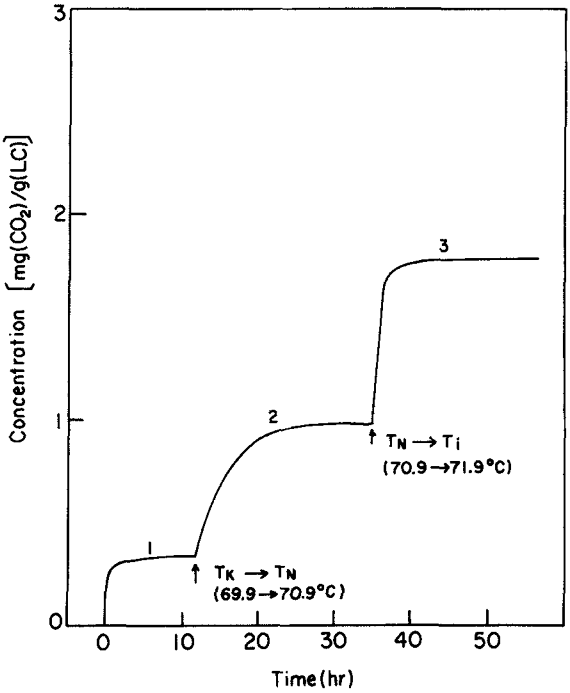

FIGURE 3 Sorption curves for the liquid crystal at various temperatures (pressure: 1 bar). The sorption value changed abruptly due to the transformation of phase states of the liquid crystal: Curve 1: 69.9°C (crystalline), Curve 2: 70.9°C (nematic) and Curve 3: 71.9°C (isotropic).

thermal behavior of the MLC. We are not aware of any previous work on this subject. Given certain similarities between MLCs and PLCs, in their phase structures in particular,[16,17] we expect that these results will become helpful also in understanding the transport mechanism of gases in PLCs.

EXPERIMENTAL

The MLC used in this study was synthesized by using a standard method.[18] The product was purified through column chromatography by using chloroform as a diluent and followed by recrystallization in ethanol. A Nikon optical polarizing microscope equipped with a Mettler FP82 hot stage was used for locating phase transitions and analyzing the anisotropic textures.

The solubility of CO_2 in the liquid crystal was determined by gravimetric method through use of a Sartorius high pressure electromicrobalance (Model 4436). Details of the equipment were reported in an earlier paper[19]; essential elements include a sorption chamber, a vacuum and gas supply system, as well as a temperature-controlled thermobath. The thermobath permitted a regulation of a temperature range from ambient to 100°C, which was sufficient for locating phase transitions of the MLC under investigation. The gas sorption measurement was preceded by

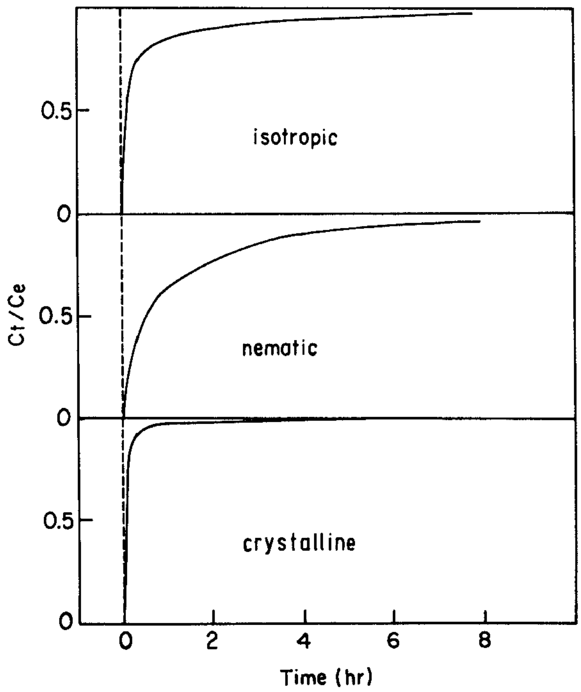

FIGURE 4 Reduced sorption curves for the crystalline (69.9°C), nematic (70.9°C) and isotropic (71.9°C) states (pressure: 1 bar). C_t is the concentration of the sorbed gas at time t and C_e is the equilibrium value of the gas concentration.

degassing the sample until a constant weight was indicated by the balance. A given pressure of a gas was then introduced into the chamber to start the sorption experiment. The weight increase of the sorbing sample was continuously registered as a function of time.

RESULTS

Gas Sorption and Molecular States

The equilibrium concentrations of sorbed CO_2 at various temperatures, which cover different phases of the liquid crystal, are shown in Figure 2. The values increase dramatically at the transitions of the crystalline to a nematic and the nematic to an isotropic phase. The detailed characteristics regarding this sorption change can be seen more clearly from the sorption curves taken at the temperatures around both transitions, as shown in Figure 3. The sorption behavior occuring at 69.9°C (crystalline state) is represented by the Curve 1, obtained by exposing an evacuated sample to the CO_2 environment. After a equilibrium value had been attained, the temperature was raised to 70.9°C, so as to obtain a nematic phase. An apparent sorption occurs at this time as a result of this phase transformation (Curve 2). Similarly, another apparent sorption has been observed as the phase changes from

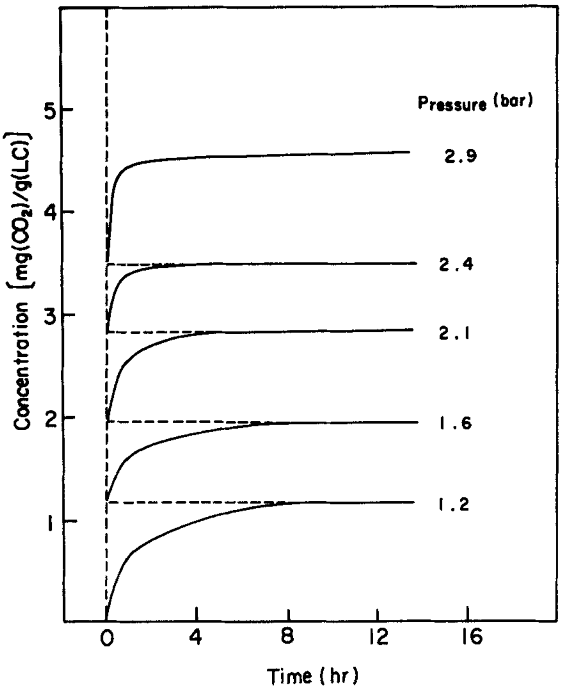

FIGURE 5 Successive differential sorptions of CO_2 in the liquid crystal at 70.9°C.

nematic to isotropic. The change in sorption values at the nematic-isotropic transition is a little higher than that at the crystalline-nematic transition.

The diffusion rate, as well as the equilibrium sorption values, is also dependent on the molecular states of the liquid crystal. This is seen from the reduced sorption curves shown in Figure 4. The diffusion rate can be related to the initial slopes of the reduced curves.[20] The higher the values of the initial slopes, the faster is the diffusion. Among the three curves, the one in crystalline state exhibits the highest value of the initial slope. 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. Since the adsorption involves little diffusion process which requires the cooperative molecular motion of the sorbing liquid crystal, the gas can quickly saturate the material. In the nematic and isotropic phases, however, the gas has dissolved in the liquid crystal in the ordinary way. The initial slopes of reduced sorption curves can, as a result, represent the real diffusion rate of the gas during sorption process. From a comparison of both sorption curves, the substance in the isotropic phase is seen to have an obviously higher initial sorption rate. This indicates that the gas diffuses significantly easier in the isotropic phase than in the LC phase since the respective diffusion temperatures differ only by 1°C, a virtually negligible difference.

Concentration Effect of Sorbed Gas

As already noted, physical properties of organic materials are known to be altered by the presence of a sorbed gas. Different sorption pressures have been used here

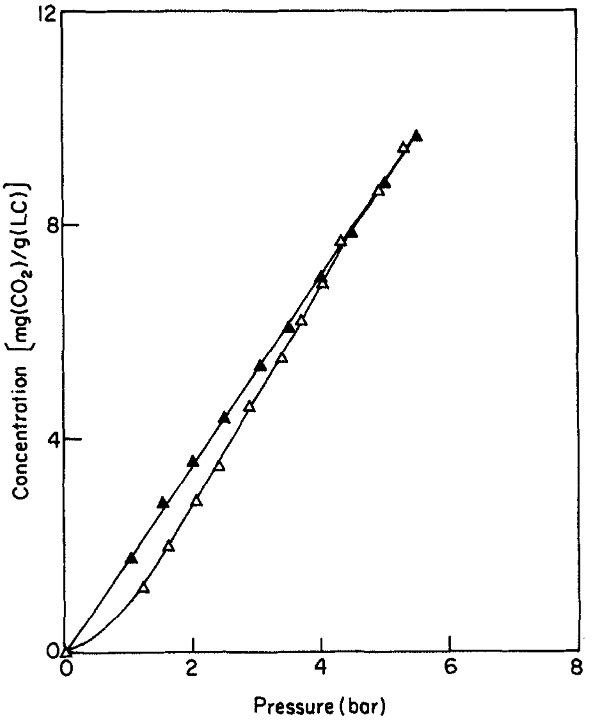

FIGURE 6 Sorption isotherms of CO_2 in the liquid crystal at 70.9° (Δ) and 71.9°C (▲).

to investigate how the sorbed gas influences the physical properties of the liquid crystal. The effect of initial pressure on the sorption curves at 70.9°C (nematic phase) is shown in Figure 5. As initial pressure becomes higher, each differential sorption curve systematically changes its shape with an increasing sorption rate to attain equilibrium. The same phenomenon is also observed in isotropic phase. This means that the transport of CO_2 in the MLC under investigation should be represented by a concentration dependent diffusion coefficient.

The sorption isotherms at 70.9°C (nematic) and 71.9°C (isotropic) are shown in Figure 6. The plot for the isotropic phase can be represented by a straight curve; we infer that gas dissolution in the isotropic phase follows Henry's law, at least in our experimental pressure range. A sigmoid curve exhibiting an inflection point is, however, observed in the nematic phase. In the low pressure range the sorption values in the nematic phase are lower than that in the isotropic phase. These values then gradually approach the isotropic one when the pressure increases, with an intersection point located approximately at 3.7 bar. From the shape of both curves, the transition sorption (ΔC, the difference of gas concentration between the phases) at the nematic-isotropic phase transformation is seen to decrease with an increasing pressure; it finally becomes zero at approximately 3.7 bar. To check this further, the transition sorption occuring as a result of this phase transformation has been measured here at various pressures using sorption-desorption characteristics of the liquid crystal. The typical procedure is illustrated in Figure 7. The sample temperature was first kept at 70.9°C (nematic) and the pressure was then increased

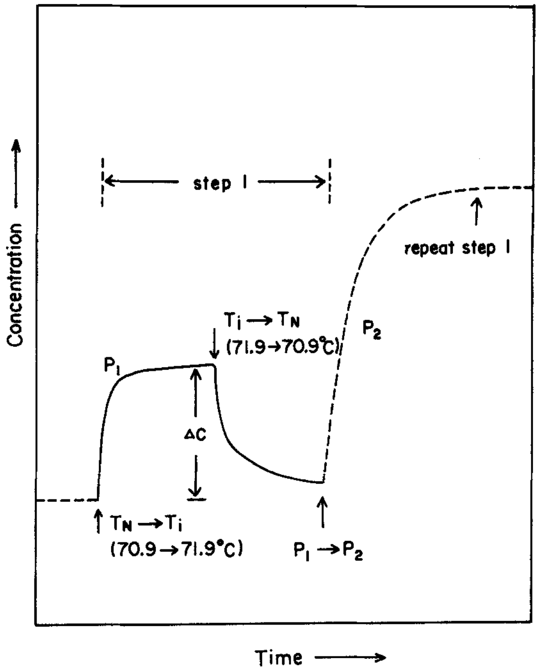

FIGURE 7 Procedures for the measurements of transition sorption (ΔC) from nematic to isotropic at different pressures.

stepwise. The temperature was raised at each step to 71.9°C (isotropic) to measure the transition sorption when the sorption reaches equilibrium at a specific pressure P_1. After the equilibrium of this new sorption was attained, the temperature was reduced to 70.9°C. Due to the lower capacity of gas dissolution in the nematic phase, the sorbed gas was at this time forced to leave the liquid crystal into the surroundings, so that a desorption process occurs. The pressure was increased from P_1 to P_2 when the desorption process approached equilibrium. The same procedure was repeated at P_2 to attain a new transition sorption. The transition sorptions at various pressures can be easily determined using this method. The pressure effect on transition sorptions is shown in Figure 8. The transition sorption values (ΔC) gradually decrease as the pressure increases. They becomes zero at approximately 3.7 bar, which coincides with the results shown in Figure 6. The phase state of the liquid crystal at the condition of 70.9°C and 3.7 bar is characterized by lowering the temperature from 70.9° to 69.9°. An obvious desorption occurs, caused by the temperature change. This suggests that the liquid crystal at the above condition has become an isotropic phase. The isotropization temperature of the liquid crystal is indicated by these results to be located between 69.9 and 70.9°C, approximately 1°C lower than the original one. Further depression of the isotropization (clearing) temperature can be similarly achieved by setting the sample temperature just below the new isotropic transition. The isotropization temperature as a function of the pressure and concentration of CO_2 is shown in Figure 9 and 10, respectively. An almost linear depression can be found in the high pressure and high sorbed concentration range.

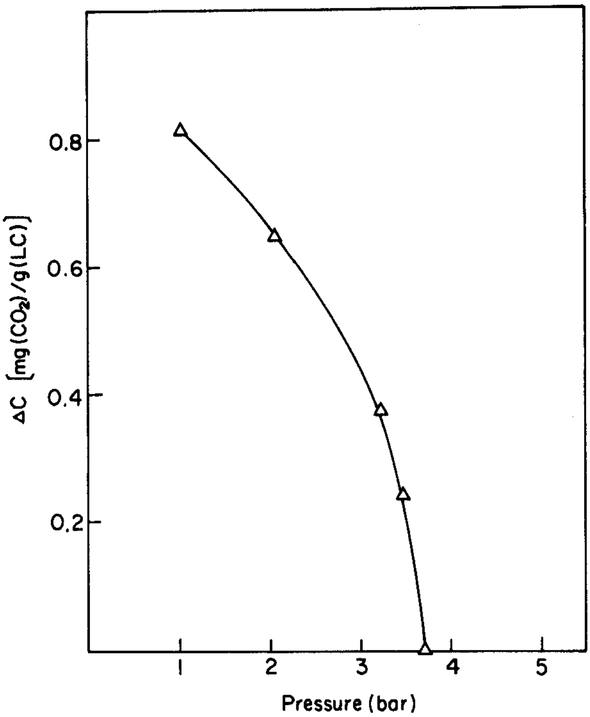

FIGURE 8 Effect of CO_2 pressure on the transition sorption (ΔC) from nematic to isotropic.

DISCUSSION

We find that gas sorption is strongly dependent on the phase states of the LC material. In order to clarify this phase effect, two factors associated with phase transformation should be considered at the same time. One is the magnitude of the free volume in the substance and the other is the arrangement of the molecules. The free volume is related to the magnitude of the specific volume of a material.[21] Therefore, a change in free volume at the transition of the liquid crystal may be found from the measurement of the specific volume. The specific volume of a MLC as a function of the temperature was measured by Frenzel and Rehage.[22] A dramatic increase in specific volume at the phase transition of crystal to nematic has been found. It has, however, increased only a little from nematic to isotropic phases. The volume change at the former transition may be ten times larger or even higher than that occuring at the later transition. This indicates that the increase in free volume at the crystal-nematic transition is much higher than that occuring at the nematic-isotropic transition. If the free volume were the only factor playing a role here, the values of transition sorption would differ significantly for the transitions in question. However, as seen from Figures 2 and 3, both transition sorptions exhibit similar values. We conclude that the LC phase structure plays also an important role in gas sorption. This demonstrates that gas sorption is closely related to the thermodynamic states of a substance. A limitation applied towards the

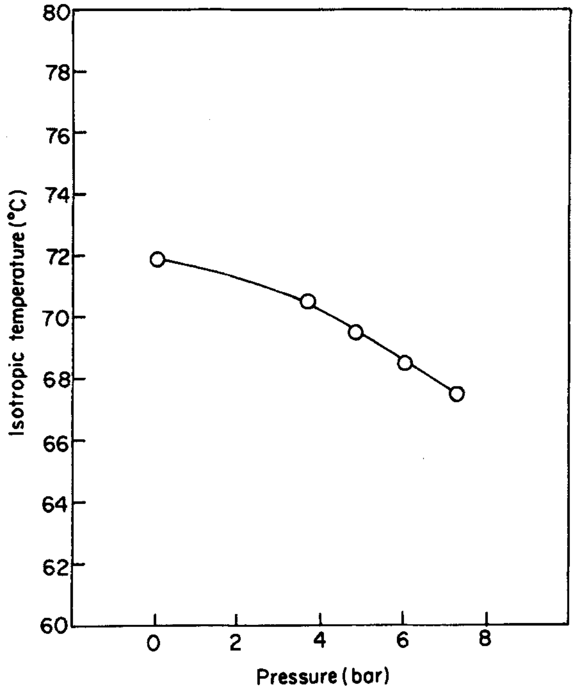

FIGURE 9 Effect of CO_2 pressure on the isotropization temperature of the liquid crystal.

freedom of chain motion as the orientational order of liquid crystal, would result in a large decrease in the value of gas sorption and diffusion rate of gases.

The concentration of a sorbed gas is, however, an important factor which needs to be considered when characterizing the effect of LC order on gas sorption. The transition sorption and the isotropization temperature of the liquid crystal have been shown in Figures 8–10 to decrease with increasing pressure and concentration of sorbed gas. The depression of the clearing temperature contradicts the Clausius-Clapeyron equation, which predicts a rise in isotropization temperature when the pressure increases. A reasonable interpretation for this phenomenon may be attributed to the interaction of the MLC with the sorbed CO_2.[14,15] According to Raucher and Sefcik,[14] the interaction between a gas and a polymer can significantly enhance the cooperative motion of molecular chains; in turn, this results in an increase of gas permeability and diffusivity. This phenomenon is more pronounced when the concentration of sorbed gas becomes higher. The same effect is seen in Figure 5 for the present CO_2/MLC system, showing that diffusivity becomes highly increased through an increasing sorbed concentration. One important factor for the formation of LC phases is the anisotropy of intermolecular forces between LC molecules.[23] It seems that the anisotropy is affected by the interactions of liquid crystal with sorbed CO_2. As a consequence, the LC phase becomes destabilized and the isotropization temperature is depressed.

In conclusion, the present study confirms that liquid crystallinity can seriously limit the dissolution of gases even though the free volume in a liquid crystalline

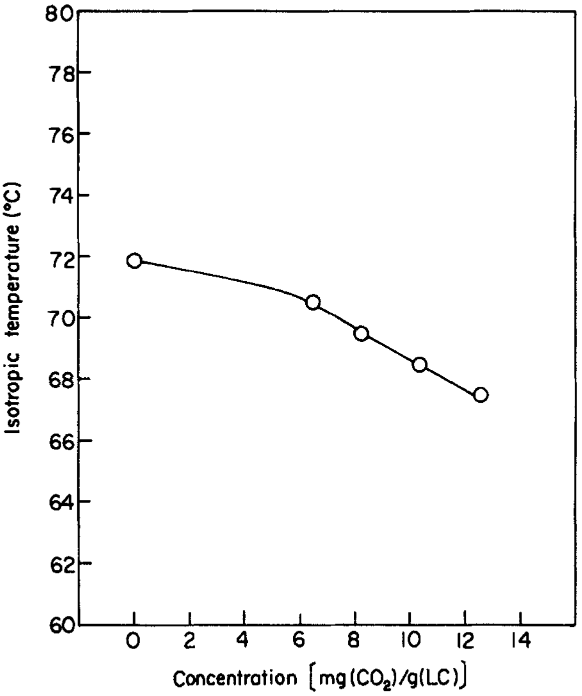

FIGURE 10 Effect of the concentration of sorbed CO_2 on the isotropization temperature of the liquid crystal.

phase is usually close to that in the respective isotropic phase. The thermal behavior of our MLC appears to be influenced by the sorbed gas. Further work is needed to correlate the thermodynamic properties of transitions, i.e. enthalpy and entropy, with the concentrations and the nature of sorbed gases.

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