

Gas Chromatographic Characterization of Liquid Crystalline Cholesteryl Nonanoate

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Gas chromatography (GC) has been applied to observe the liquid crystalline behavior of cholesteryl nonanoate (CHON) under conditions approaching infinite dilution of the volatile component. The specific retention volumes (V_s^0) were calculated from the retention volumes of the CHON/solvent systems. The retention diagrams (RDs), which were plotted as $\ln V_s^0$ vs. reciprocal temperature, corresponded with the thermodynamic phase transition of CHON. The molar heat of sorption of the solvent (ΔH_i) absorbed by CHON, which is calculated from the retention values, indicated that the characteristics of the interaction between CHON and solvents (probes) varied with the probe properties. The results of GC of CHON/solvent systems are discussed in relation to CHON phase transitions.

Key words: liquid crystal, cholesteryl nonanoate, gas chromatography, phase transition

1. INTRODUCTION

Cholesteryl nonanoate (CHON) is a typical liquid crystal. The properties of CHON, particularly, the thermal phase transition behavior, was investigated by McMillan (1), by measuring the X-ray Bragg-scattering intensity versus temperature. Hande et al. (2) studied the solvent effect on the thermal performance of cholesteric liquid crystals. However, the thermodynamics of CHON/organic solvent systems remains to be fully clarified.

Gas chromatography (GC) is a useful method (3) to observe the interaction between solutes and solvents. This technique, which measures the interaction between pure solvents (mobile phase, probes) and the stationary phase (CHON), utilizes conventional gas chromatography with minor modifications in terms of the retention time of the probes. The term "solute" is used to represent a low-molecular-weight volatile solvent that is usually injected into a gas chromatographic column.

In this study, the GC method was applied to investigate the thermodynamic interaction between CHON and solvents (probes) and in addition to determine the phase changes by plotting the natural logarithm of specific retention volume ($\ln V_s^0$) versus reciprocal temperature.

2. EXPERIMENTS

2.1 Materials

Cholesteryl nonanoate and solvents (probes) used in this work were commercially obtained and used without further purification. Chromosorb (WAW DMCS, 60 ~ 80 mesh) was used as a support of CHON. The solvents (probes) used are listed in Table I. They are aliphatic or aromatic hydrocarbons, and

ethyl acetate.

Table I Solvents (probes) used in this work

Solvents (Probes)	Abbrev.	M_i g · mol ⁻¹	bp °C
n-Hexane	HEX	86.2	68.7
n-Octane	OCT	114.2	125.7
Benzene	BEN	78.1	80.1
Toluene	TOL	92.1	110.6
Ethyl acetate	EA	88.1	77.1

2.2 Column preparation

The column was prepared as follows: A calculated amount of CHON was completely dissolved in HEX, and a known amount of Chromosorb (WAW DMCS, 60 ~ 80 mesh) was immersed in the solution. A soaking method (3) for coating the stationary phase on the support was used. The HEX was allowed to evaporate at 40 °C by gentle and continuous stirring of the solution followed by drying at ambient temperature under reduced pressure. The CHON loading (wt %) was calculated from the weight of CHON and the Chromosorb. A weighted amount of the CHON-loaded Chromosorb was tightly packed into a 2 m (length) x 3 mm (i.d.) stainless steel column. The column was dried for 24 h at ambient temperature under a constant stream of helium.

2.3 Instrumentation and procedures

All chromatographic measurements were carried out on a Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector. The temperature of the injection port and the detector was 140 °C. Helium was introduced at a flow rate of 25 ml/min,

and measurements were performed using a soap bubble flow meter at room temperature. Injection of probe vapor at infinite dilution mixed with air as a marker was performed manually using a Hamilton microsyringe (full scale $1 \mu\text{l}$).

Table II Column specification and GC conditions

Column no.	Cholesteryl nonanoate	Support weight	Loading
	g	g	%
1	0.1662	3.154	5.01
2	0.2192	3.285	6.26
3	0.2204	3.292	6.27

Column: Stainless steel, inner diameter x length = 3.0 mm x 2 m; Carrier gas: He; Flow rate: 25 ml/min; Marker: Air; Detector: TCD; Injection volume: < 0.1 μl ; Support: Chromosorb (WAW DMCS 60 ~ 80 mesh).

The chromatograms were recorded by a Shimadzu C-R6A Chromatopac. Usually, the retention volume is obtained using the experimental peak maximum to define the retention time. Differential scanning calorimetry (DSC) was performed using a Shimadzu heat flux, Model DSC-50. DSC experiments were carried out at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

2.4 Calculation

In GC, unretained gas, such as methane or air which is inert to the stationary phase, is used as the marker. The time spent by the probe during its passage through the stationary phase is expressed as

$$t_N = t_R - t_M \quad [1]$$

where t_N is the net retention time of the probe, at a given temperature, t_R is the probe retention time, and t_M is the marker retention time. The measured net retention volume of the probe is

$$V = t_N \cdot F \quad [2]$$

where F is the volume flow rate of the carrier gas measured at room temperature (T_r) at outlet pressure P_o . However, the volume flow rate is not constant along the column, i.e., it is higher at the outlet than at the inlet, because the inlet pressure P_i is greater than P_o . Therefore, the volume flow rate measured at P_o should be corrected to the volume flow rate in the column due to the compressibility of the gas. The correction factor (4) is as follows.

$$J = (3((P_i/P_o)^2 - 1)) / (2((P_i/P_o)^3 - 1)) \quad [3]$$

Then, the net retention volume in the column is

$$V_N = t_N \cdot F \cdot J \quad [4]$$

The specific retention volume (V_s^0) is calculated using the equation,

$$V_s^0 = \frac{\bar{V}_N \cdot 273.15 \cdot (P_o - P_w)}{w \cdot P_o \cdot T_r} \quad [5]$$

where w is the mass of the stationary phase, and P_w is the vapor pressure of water at T_r . The specific retention volume is related to the enthalpy of absorption. The molar heat of sorption (ΔH_s^0) (5) of the probe was calculated as follows:

$$\Delta H_s^0 = -R \cdot \delta \ln V_s^0 / \delta (1/T) \quad [6]$$

3. RESULTS and DISCUSSION

3.1 Specific retention volumes

We prepared three columns (Table II). The retention times for hexane were obtained for the three columns. The specific retention volumes (V_s^0), however, were independent of column loading. Consequently, we used column no.2 (Table II) to obtain the retention times for BEN, OCT, EA, and no.3 for OCT. Figure 1 shows the RDs of hydrocarbons measured at various temperatures (from 60 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$) of CHON. The natural logarithm of the specific retention volumes ($\ln V_s^0$) of hydrocarbons such as HEX, BEN and OCT, shows the absorption when they were injected into the column as the probes to measure the interaction between CHON and solvents.

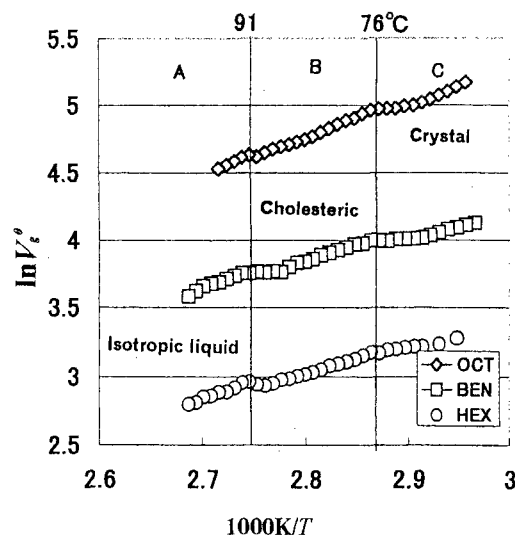


Figure 1 Natural logarithm of specific retention volume versus reciprocal column temperature for cholesteryl nonanoate, using n-octane (OCT), benzene (BEN), and n-hexane (HEX).

There are three retention mechanisms that could affect the GC results. These mechanisms include dissolution of the probe in the stationary phases. The observed retention behaviors differ according to the column temperature. The plots of $\ln V_s^0$ versus $1/T$ are divided into three regions based on the slopes of the curves shown in Figure 1. For the case of a liquid crystal (LC), it exists as a crystal in the lower temperature region (C) in Figure 1. The temperature at which

upward deviation from the straight line portion of the RD is observed corresponds to the transition temperature of the CHON. It is evident from Figure 1, that the transition temperature (T_i) from crystal to LC and the transition temperature (T_l) from LC to isotropic liquid of CHON were about 76 and 91 °C, respectively. With increase of the temperature from 76 °C to about 86 °C, the V_g^0 decreased gradually and monotonously to that at about 86 °C for HEX, OCT, and BEN.

In regard to the polar solvents such as EA, the RD of EA is shown in Figure 2. The RD is also divided into three regions as in Figure 1. However, the $\ln V_g^0$ in region (C) could not be obtained as a straight line as in HEX ($\ln V_g^0$ of HEX is also shown in Figure 2).

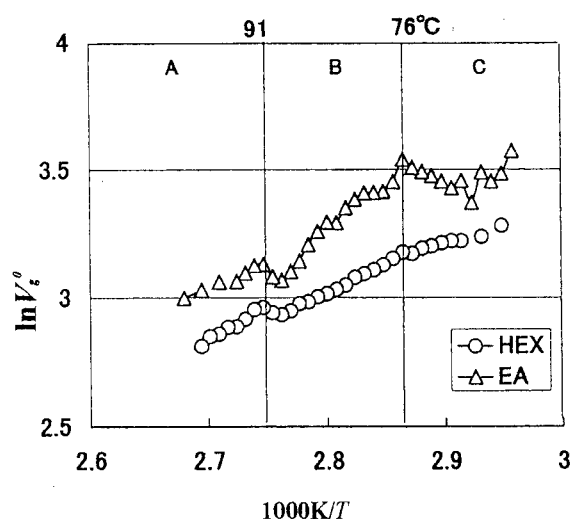


Figure 2 Natural logarithm of specific retention volume versus reciprocal column temperature for cholesteryl nonanoate, using ethyl acetate (EA) and n-hexane (HEX).

This implies that CHON has a more variable interaction with the polar solvent. Hande and coworkers (2) studied spectral distributions as a function of the dipole moment of a solvent used in casting the film of cholesteryl liquid crystal. The use of nonpolar solvents does not affect the interactions between liquid crystal molecules. As the polarity of the solvent increases, the rotation of the helical arrays of cholesteryl molecules is inhibited with a resultant decrease in sensitivity. In region (C) in Figure 2, CHON exists as a crystal, and the possible variation in retention volume would be due to differences in interactions between CHON and EA, the injection size of which could not be controlled precisely (6). At any time, in order to discuss the detailed mechanism of interaction between crystalline CHON and EA, it is necessary to observe another behavior (for example, solubility of CHON in such solvents). The thermogram of CHON obtained by differential scanning calorimetry (DSC) shows the corresponding deviations. Figure 3 shows the thermogram of CHON, together with that of RD of HEX.

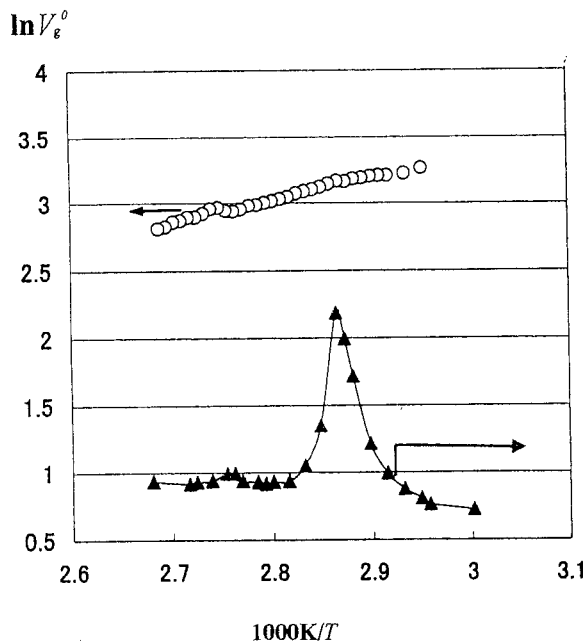


Figure 3 Natural logarithm of specific retention volume (n-hexane) and differential scanning calorimetric thermogram versus reciprocal temperature for cholesteryl nonanoate.

3.2 Molar heat of sorption (ΔH_i^s) of the probe

The RD yields a slope proportional to H_i^s changes in the thermodynamics of retention shown as discontinuities in the straight line in Figure 1. The molar heat of (enthalpy) sorption (ΔH_i^s) (5) of the probes was calculated, using equation [6]. Table III shows the values of sorption enthalpies for n-alkane and aromatic hydrocarbons with respect to CHON. When CHON is at an equilibrium phase, exothermic values for all the used probes were obtained. ΔH_i^s values of HEX are almost the same regardless of whether the CHON phases are crystal, liquid crystal (cholesteric), or isotropic liquid. Differences in molar heat of sorption between CHON and solvents are probably due to the differences in solvent properties rather than the CHON phase, except for ethyl acetate.

Table III Molar heat of sorption (ΔH_i^s) of various probes with respect to cholesteryl nonanoate $-\Delta H_i^s$ (kJ/mol)

Probes	Phase		
	Crystal	Liquid crystal	Isotropic liquid
HEX	18.2	18.2	19.8
EA	-	31.5	14.1
BEN	17.7	22.9	24.6
TOL	24.3	24.2	27.0
OCT	29.9	25.8	31.1

CONCLUSIONS

Gas chromatography (GC) was applied for the characterization of the thermodynamics of liquid crystalline cholesteryl nonanoate (CHON). Using this method, information regarding the interaction between

CHON and organic solvents, such as esters and hydrocarbons, could be obtained over a wide temperature range, including the phase transitions of CHON. The specific retention volumes in CHON/solvents systems indicated the phase transitions of CHON. The sorption of CHON was discussed in relation to the molar heat of sorption of the probes absorbed by CHON.

Polymer dispersed liquid crystal (PDLC) (7) possesses many aspects which make them attractive for practical developments such as display application. PDLC could be concerned with the interaction between LC and polymer surface. While gas chromatography has been applied to observe the interaction polymer/solvent or polymer/polymer systems (8). Therefore, the notable information in this work could give a useful approach to study PDLC.

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