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G. Voets[a]; H. Martin[a]; W. Van Dael[a]
[a] Laboratorium voor Molekuulfysika, Katholieke Universiteit Leuven, Leuven, Belgium

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Calorimetric investigation of phase transitions in cholesteryl oleate

by G. VOETS, H. MARTIN and W. VAN DAEL
Laboratorium voor Molekuulfysika, Katholieke Universiteit Leuven,
Celestijnenlaan 200 D, 3030 Leuven, Belgium

An adiabatic scanning calorimeter has been used to investigate the temperature dependence of the enthalpy and the heat capacity near phase transitions in the cholesteric liquid crystal cholesteryl oleate (CO). It is found that the blue phases in CO are thermodynamically stable and that the observed enthalpy differences between the phases are small.

1. Introduction

In recent years, much attention has been paid to the investigation of the so-called blue phases of cholesteric liquid crystals. These liquid-crystalline blue phases (BPs) exist in a very small temperature range just below the clearing point of cholesterics of sufficiently short pitch. Stegemeyer *et al.* established that cholesteric liquid crystals of short pitch may form up to three distinct blue phases [1], indicated in order of increasing temperature as follows: blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII).

A survey of both the theoretical and the experimental aspects has been given by Belyakov and Dimitrienko [2]. As far as the thermal properties of these phase transitions are concerned, several differential scanning calorimetry results have been reported. High-resolution data allowing a detailed analysis of each of the transitions are, however, only available for cholesteryl nonanoate [3, 4]. Even in this case, some uncertainty remains about the order of the transition. In order to extend those data, we report in this paper high-resolution adiabatic scanning calorimetric measurements for cholesteryl oleate. For CO, the temperature range goes between 35°C and 56°C including a solid, smectic, cholesteric and at least two blue phases. From the measurements, the temperature dependence of the enthalpy and of the heat capacity is obtained.

2. Experimental method

The experimental results were obtained by means of an adiabatic scanning calorimeter. Full details of the construction and the possible modes of operation can be found elsewhere [5]. Some aspects of the measuring procedure may be mentioned, since they can be important for the interpretation of the results. The measuring cell contains about 17 g of the sample. A constant heating power P is applied to the cell from the time t_S and during a period of several days. The cell is surrounded by a shield that is intended to be at each moment at the cell temperature T so that heat leaks are negligible. The temperature is measured and recorded every 20 s. If the pressure is a constant, the enthalpy $H(t)$ of the system will increase linearly with time,

$$H(t) - H(t_S) = P(t - t_S),$$

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but the function $T(t) - T_S(t_S)$ will have a time-dependent slope inversely proportional to the heat capacity at the actual T value

$$\frac{\delta T}{\delta t} = \frac{P}{C_p^{\mathrm{tot}}(T)}$$

This $C_p^{\mathrm{tot}}(T)$ value has to be transformed by subtracting the heat capacity of the container and by normalizing to one mole of sample.

At an ideal first-order transition $\delta T/\delta t$ should be zero during a time interval Δt at a time-independent value $T = T_{\mathrm{tr}}$: the corresponding latent heat amends to $\Delta H = P\,\Delta t$. In reality, transitions occur over a certain interval ΔT, which is partly a result of experimental circumstances (temperature gradients, local non-equilibrium etc.) and partly a result of the properties of the sample (impurities, surface effects etc.).

In our experimental arrangement special care has been taken in order to avoid the former effects, which, incidentally, are the reason why most of the D.S.C. data are unreliable for a detailed analysis. The phenomena related to sample impurities are more difficult both to avoid or to take into account. They result in a two-phase coexistence region: if it is detected, it forms a sufficient proof of the first-order character, but it is not evident which part of the involved latent heat has to do with the phase separation and which, if any, with the orientational order transition. On the other hand, if, as is often the case for liquid crystals, the latent heat is small and the pretransitional effects large, and if the purity of the sample is rather good so that the coexistence region is very narrow, it may be extremely difficult to disentangle both effects.

3. Results and discussion

We have investigated the temperature dependence of the enthalpy and of the heat capacity of CO in the temperature range between 35°C and 56°C. In this range, we observed five phase transitions (see figure 1). If we identify the transition temperatures with the maxima in the specific-heat curves, we obtain

crystalline–smectic A	at 41·37°C,
smectic A–cholesteric	at 49·09°C,
cholesteric–BPI	at 53·58°C,
BPI–BPII	at 54·39°C,
BPII–isotropic	at 54·87°C.

The sample was obtained from Van Schuppen Chemicals (Holland) and used without further purification. A comparison with previous experimental investigations on CO is made in table 1. The differences in the reported values of the transition temperatures may largely be due to the different degree of purity of the samples investigated. The high value of the clearing temperature in this experiment could be an indication that this sample is purer than those studied before. On the other hand, the very broad melting peak may suggest a rather high impurity concentration. There may, however, be another explanation for this experimental fact. As shown by Krzewki and Porter [12] and Armitage [8], there are at least four different crystal phases in CO: the dynamics of the mutual transitions are strongly influenced by metastability and by glass formation. Our melting data are consistent with this picture: the reproducibility of the data is to some extent influenced by a hysteresis effect depending on the cooling–heating cycle, and some fine structure is apparent in the melting peak. We

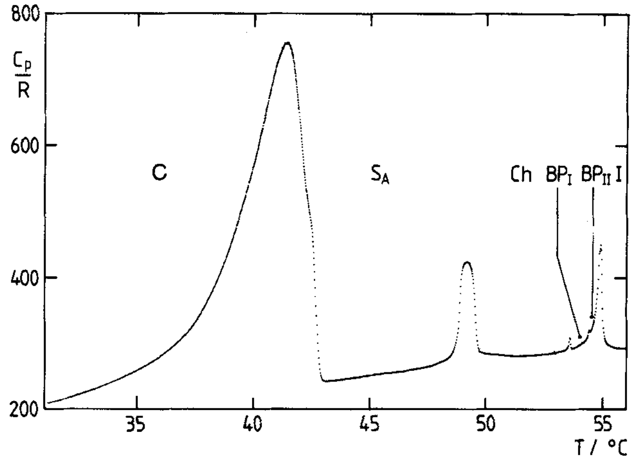

Figure 1. General overview for the reduced heat capacity per mole C_p/R for CO in the region from 31°C to 56°C.

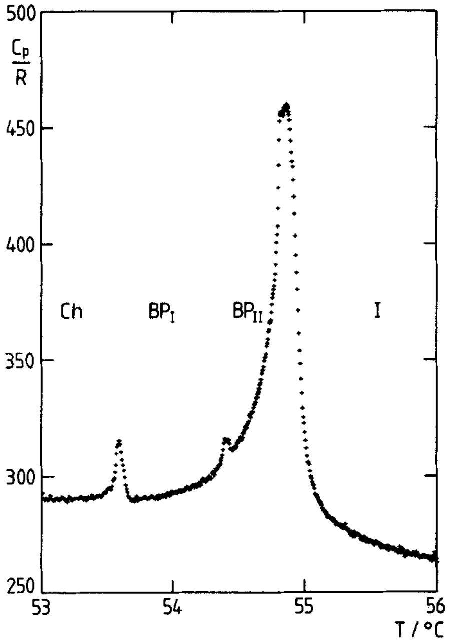

Figure 2. Detailed plot of the reduced heat capacity per mole C_p/R for CO in the region from 53°C to 56°C.

intend to discuss these phenomena elsewhere: here we concentrate further on the blue phases.

In figure 2 the general behaviour of the heat capacity per mole of CO is shown in the region from 53°C to 56°C. It is clear that a few relatively small C_p peaks are superposed on a much larger peak associated with the gradual disappearance of chiral nematic order.

Taking into account the difficulty of separating first- and second-order contribution, we made a preliminary estimation of the total enthalpy difference between subsequent

Table 1. Transition temperatures in CO.

		Crystalline	↓	Smectic A	↓	Cholesteric	↓	BPI	↓	BPII	↓	Isotropic
1. This work	T/°C		41·37		49·09		53·58		54·39		54·87	
	ΔT/°C			7·72		4·49		0·81		0·48		
2. Davis *et al.* [6]	T/°C		—		41·8		—		—		46·4	
	ΔT/°C			—		⟵			4·6		⟶	
3. Armitage and Price [7]	T/°C		44·8		46·3		50·8		—		51·3	
	ΔT/°C			1·5		4·5		⟵	0·5	⟶		
4. Armitage [8]	T/°C		32		39·2		44·6		—		45·1	
	ΔT/°C			7·2		5·4		⟵	0·5	⟶		
5. Albertini *et al.* [9]	T/°C		—		42		—		—		47·5	
	ΔT/°C			—		⟵			5·5		⟶	
6. Dubini *et al.* [10]	T/°C		—		38·8		—		—		44·4	
	ΔT/°C			—		⟵			5·6		⟶	
7. Clark *et al.* [11]	T/°C		—		42	—	47·5		—		48·7	
	ΔT/°C			—		5·5		⟵	1·2	⟶		

Table 2. Heats of transition in CO.

		$C \to S_A$	$S_A \to Ch$	$Ch \to BPI$	$BPI \to BPII$	$BPII \to I$
This work	$\Delta H/J\,mol^{-1}$	19 500	980	18	12	485
Davis *et al.* [6]	$\Delta H/J\,mol^{-1}$	21 800	1530		680	
		30 600	1010		490	
Armitage and Price [7]	$\Delta H/J\,mol^{-1}$	22 100	1010	27	680	
Armitage [8]	$\Delta H/J\,mol^{-1}$	21 800	930	27	550	
Albertini *et al* [9]	$\Delta H/J\,mol^{-1}$	—	960		545	

phases, both extrapolated to the transition temperature. This ΔH includes a summary of all pretransitional effects together with the latent heats. The results have been collected in table 2 and are compared with earlier data. In general the agreement is satisfactory: it should be pointed out that all of the older data are obtained by D.S.C. and that one ΔH value may be a global result of several unresolved transitions.

In table 2, an overview of the heats of transition has been given and has been compared with other experimental results.

4. Conclusions

The thermal properties of cholesteryl oleate have been measured from the solid to the isotropic phase, including the mesophases. The transition from the chiral nematic phase to the isotropic occurs with a gradual increase of C_p on which at least two blue phase transitions are superposed. The general behaviour of this $C_p(T)$ curve resembles more the data obtained by Thoen [4] in cholesteryl nonanoate than those by Kleiman *et al.* [3] in the same fluid. The final conclusion may be that the blue phases, although isotropic, are, as far as their thermal properties are concerned, closer to the chiral nematic phase than to the isotropic. For the transition to the isotropic phase, a thermal energy is required that is comparable to what is needed for the nematic–isotropic transition.

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