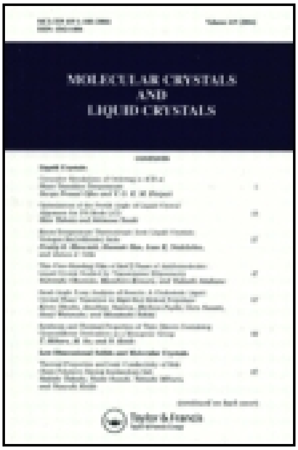

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Julian F. Johnson [a], Roger S. Porter [b] & Edward M. Barrall Ii [c]

[a] University of Connecticut Storrs, Connecticut, 06268
[b] University of Massachusetts Amherst, Massachusetts, 01002
[c] IBM Research Laboratories, San Jose, California

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Thermodynamics of Mesophase Transitions from Calorimetric Measurements‡

JULIAN F. JOHNSON
University of Connecticut
Storrs, Connecticut 06268

ROGER S. PORTER
University of Massachusetts
Amherst, Massachusetts 01002

and

EDWARD M. BARRALL II
IBM Research Laboratories
San Jose
California

Abstract—The increasing amount of research on mesophases (liquid crystals), the availability of differential scanning calorimetry for rapid, quantitative thermodynamic evaluation, and the availability of compounds in a number of homologous series of compounds have led to studies that attempt to interpret the nature of mesophase transitions. This paper collects and reviews data for two homologous series and provides the general conclusions which can be drawn from the therodynamics of mesophase formation.

Within the last few years a considerable body of thermodynamic information on mesophase forming systems has become available. This paper will review the data and draw some general conclusions about mesophase transitions. In particular, calorimetric data on mesophases formed by pure compounds in homologous series will be considered. Lyotropic mesophases, that is those where the disordering of the solid crystal is caused by solubility in contrast to thermal disordering, will not be discussed.

‡ Part XXI of a series on "Order and Flow of Liquid Crystals".

In reality virtually no calorimetry is available on lyotropic mesophases.

Calorimetric measurements have been made, using adiabatic calorimetry,[1–5] differential scanning calorimetry,[8–10] and differential thermal analysis.[6] Adiabatic calorimetry has a precision of about 0.2% although various calculation methods can introduce a considerably larger uncertainty. This technique is quite time consuming. The differential methods are more rapid, but precision is lower of the order of 2–10% with the larger errors at the lower transition heats.[6–10]

A number of homologous mesophase series have now been studied. Among the most completely investigated series are the aliphatic esters of cholesterol on the *p,p'-n*-alkoxyazoxybenzenes.

Cholesteryl Esters

Several transition temperature studies have been made on the mesophases formed by the aliphatic esters of cholesterol, see references 11–12. Calorimetric values have also been reported.[9] The lower members of the series exhibit only a cholesteric mesophase, the heptanoate, and higher members have two mesophases, a smectic and cholesteric. There is some question as to whether the formate exhibits a cholesteric mesophase so that liquid crystals may indeed first appear at the propionate ester. The cholesteric mesophase series may thus begin at the propionate ester with the formation of a second mesophase, smectic, becoming only general at higher molecular weights. The origin of the additional transitions in the propionate ester, see Table 1, are as yet unexplained. Table 1 lists the values reported. Calorimetric measurements obtained on mesophase systems are unusually difficult. Mesophases as a class exhibit the smallest known sets of first order transitions. It is therefore difficult to distinguish true calorimetric effects from instrumental variables. Also, among the reliable values, certain calorimetric events reported in Table 1 are monotropic, that is, they are observed only on cooling and not on heating.

TABLE 1 Cholesteryl Esters—Transition Temperatures and Calorimetric Data
(Data of Barrall *et al.*)

	Crystal–Cholesteric			*Crystal–Smectic*			*Smectic–Cholesteric*			*Cholesteric–Isotropic Liquid*		
	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K
Formate	50.0	3.56	11.0							97.1	0.083	0.025
Acetate												
Propionate	101.6	5.76	15.4	99.0	5.53	14.9	110	0.19	0.50	115.3	0.10	0.26
Heptanoate	87.0	8.38	23.3							‡		
Nonanoate	80.8	5.37	15.2				66	0.057	0.17	93.0	0.12	0.32
Decanoate	87.5	7.30	20.3				68.5	0.097	0.28	91.2	0.15	0.40
Myristate	87.2	7.19	19.9	73.6	11.2	32.3	79.7	0.31	0.88	85.5	0.24	0.67
Palmitate				47	10.0	34.2	64.0	0.36	1.07	70.0	0.29	0.84
Stearate				67.0	16.9	49.5				71.0	0.35	1.03

‡ Effect not reported or not resolved from other caloric events.

The values in Table 1 indicate an increase in entropy for the *cholesteric-isotropic transition* with increasing molecular weight with the trend becoming more prominent above C_9. Values for the smectic mesophase form a regular series at high molecular weight with the suggestion that this transition in the palmitate and stearate only depends on heating and cooling rate. This transition entropy is partially attributable to movement liberated in the ester tail. At the lower molecular weights the length of the tail does not appear to significantly affect the entropy of transition.

The *crystal–mesophase transition* exhibits irregularities and probably odd–even effects in transition entropy changes with molecular weight. For the myristate and higher esters the entropy increases markedly with chain length. It is of considerable interest to examine the interrelationships of the two mesophase transitions. Table 2 lists the percentage change of the highest temperature transition as a function of the total entropy and enthalpy. The enthalpy change is 1.97 ± 0.18% and that for the entropy 1.97 ± 0.15%. This very good empirical correlation suggests a relationship between the two transitions.

TABLE 2 Relationship between the Entropy and Enthalpy of the Highest Temperature Transition to the Total Entropy and Enthalpy Change for All Transitions for Cholesteryl Esters.

Ester	% ΔH	% ΔS
Formate	1.6	1.7
Propionate	1.8	1.7
Nonanoate	2.2	2.1
Decanoate	2.1	2.0
Myristate	2.1	2.0
Palmitate	2.0	2.1
Stearate	2.1	2.2
Average	1.97 ±0.15	1.97 ±0.18

p,p-n-Alkoxyazobenzenes

Table 3 lists transition temperatures and calorimetric data for a series of *p,p-n*-alkoxyazoxybenzenes.[1–4] The *nematic–isotropic*

TABLE 3 *p,p-n*-Alkoxyazoxybenzenes—Transition Temperatures and Calorimetric Data (Data of Arnold)

Ester	*Crystal–Smectic*			*Smectic–Nemantic*			*Crystal–Nemantic*			*Nemantic–Isotropic Liquid*		
	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K	T °C	ΔH Kcal/ mole	ΔS Cal/ mole/°K
Methyl							118	7.06	18.1	135	0.137	0.336
Ethyl							137	6.43	15.7	168	0.326	0.740
Propyl							116	6.44	16.5	124	0.161	0.406
Butyl							102	5.05	13.5	137	0.247	0.600
Pentyl							76	3.48	9.98	123	0.173	0.436
Hexyl							81	9.88	27.8	129	0.250	0.620
Heptyl	74	9.77	28.2	95	0.381	1.03				124	0.243	0.612
Octyl	80	10.08	28.2	108	0.283	0.742				126	0.343	0.860
Nonyl	76	9.11	26.1	113	0.395	1.02				122	0.423	1.07
Decyl	78	9.21	26.2	121	0.553	1.40				123	0.753	1.90
Undecyl	81	9.82	27.7							121‡	2.40	6.10
Dedecyl	82	10.05	28.3							122‡	2.86	7.24

‡ Smectic–isotropic liquid.

liquid transition shows a definite odd–even effect in the transition heats for the lower molecular weight members. This effect essentially disappears for molecular weights above C_8 at which point the change in transition heat with molecular weight becomes appreciably larger. By optical methods this is the same compositional condition where the phase change has been found to change from nematic–isotropic to smectic–isotropic.

The crystal–mesophase transition does not show an odd–even effect in transition heats. The transition entropy change decreases with increasing molecular weight with a minimum at C_5. There is relatively constant transition entropy region from C_6 to C_{10} after which it increases regularly with increasing molecular weight from C_9 to C_{12}.

For the terminal groups from heptoxy through decyloxy there is an additional mesophase transition. That is, there are two mesophases in this region, a nematic and a smectic. This represents an additional partitioning of order with the total transition entropy increasing regularly with molecular weight.

Discussion

If the transition entropies for all transitions are summed, the homologous series show a trend for increasing order with increasing molecular weight. Minor variations between adjacent members exist. The increment in total transition entropy for CH_2 group corresponds closely to Rln 3, the expected entropy increase for liberation of rotations through the three most probable minima in movement about a carbon–carbon bond.

The small percentage change, $\sim 2\%$, at mesophase–isotropic liquid transitions would appear to indicate an approximately equivalent partitioning of transition entropy for cases exhibiting either a nematic or cholesteric type mesophase. Entropy changes involving smectic–isotropic transitions are known to be much higher, up to 10 times higher, note last entries in Table 3. Thus calorimetry can serve as a method for identifying mesophase types in certain cases.

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