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Heat Capacity and Enthalpy of Transition of Aromatic Liquid Crystals

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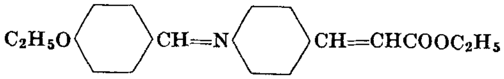
Abstract—Adiabatic calorimetry was applied to some liquid crystalline substances. Especial reference is made for the first time to the transition between smectic modifications of different types. The enthalpy of transition, including pre- and post-transition effects, is 2100 joules/mole for the smectic B to smectic A transition of ethyl *p*-(4-ethoxybenzylideneamino-)cinnamate, and only 100 joules/mole for the smectic C to smectic A transition of di-n-dodecyl 4,4′-azoxy-α-methylcinnamate.

In order to get information on energy changes connected with the appearance of the liquid crystalline state, calorimetric measurements were carried out by means of an adiabatic calorimeter. This method has the advantage of allowing the sample to be heated for limited periods and thus of allowing thermal equilibrium to be established after each heating period. Purity data can be gathered too. The details of the apparatus have already been described.[1] It makes possible a degree of precision within a few tenths per cent in caloric data.

Caloric Data of Substances Having Smectic–Smectic Transitions

The aim of our recent measurements was to make an investigation of the transition between two different smectic modifications. It was not easy to find suitable substances because of the tendency of decomposition which most of them show.

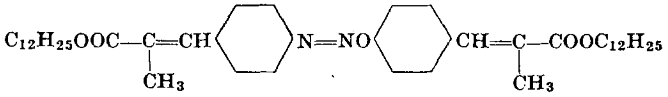
Two substances were selected:



ethyl *p*-(4-ethoxybenzylideneamino-)cinnamate

solid $\xrightleftharpoons{81^\circ}$ smectic B $\xrightleftharpoons{118.5^\circ}$ smectic A $\xrightleftharpoons{156.5^\circ}$ nematic $\xrightleftharpoons{159^\circ C}$ isotropic

(I)†



di-*n*-dodecyl 4,4′-azoxy-α-methylcinnamate

solid $\xrightleftharpoons{79^\circ}$ smectic C $\xrightleftharpoons{82.5^\circ}$ smectic A $\xrightleftharpoons{87.5^\circ C}$ isotropic

(II)

Thermal analysis indicated the formation of liquid and solid mixed crystals with impurities. Therefore exact values of impurity content were not obtainable. With the assumption of complete equilibrium between solid and liquid,[3] initial values for impurity concentration of

I: 1.4 mole % and II: 3 mole %

were estimated. During the measurement of heat capacities and enthalpies of transition some inevitable thermal decomposition occurred. The final values were

I: 1.5 mole% and II: 4 mole%.

Another treatment of thermal analysis data[4] excludes any diffusion in the solid. By application on substance I an initial value of 4 and an end value of 7 mole % impurity was obtained. No adequate treatment was possible for the data of substance II.

Figure 1 shows the "heat capacity", including enthalpy of transition, for compound I. The smectic A to nematic and the nematic to isotropic transition temperatures are rather close to each other, and the corresponding enthalpy effects thus overlap. The most important result is the considerable peak at the transition

† For details see Ref. 2.

between the two smectic modifications B and A. (For designating smectic modifications in general see Refs. 5 and 6.)

Because of the inevitable impurity content it is impossible to decide by calorimetric data whether a transition is of the first order or not.[7] However, in mixtures of I with a second compound three-phase equilibria have been observed in which modifications A and B participate together with a third phase, according to Gibbs' phase rule.[8] Heterogenous regions of the transition from smectic A to smectic B have been observed clearly.[8] We thus believe that there is a first order transition between smectic phases A and B, accompanied by pre- and post-transition effects, as this is also the case with other transitions of liquid crystalline substances.[10,11]

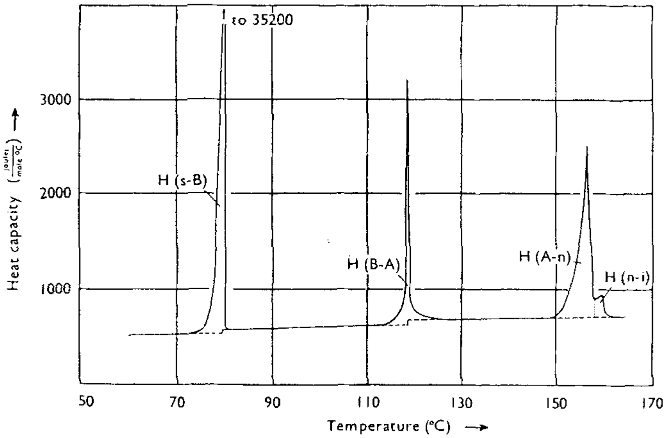


Figure 1. Caloric data of ethyl *p*-(4-ethoxybenzylideneamino-)cinnamate.

The area limited by the real curve to the peak and by the heat capacities extrapolated linearly as indicated in the diagram may be taken as representative of the sum of enthalpy of transition and pre- and post-transition enthalpy effects

$$\Delta H\,(\text{B–A}) = 2100 \text{ joules/mole.}$$

The areas indicated in the figure for the smectic A to nematic and for the nematic to isotropic transition correspond to

$$\Delta H\ (\text{A–n}) = 5100\ \text{joules/mole and}$$
$$\Delta H(\text{n–i}) = 500\ \text{joules/mole, respectively}$$

The enthalpy of melting is

$$\Delta H\ (\text{s–B}) = 27{,}300\ \text{joules/mole.}$$

Herrmann[12] concluded from his X-ray work on I, that the structure in the high temperature smectic modification (A) is of Friedels type,

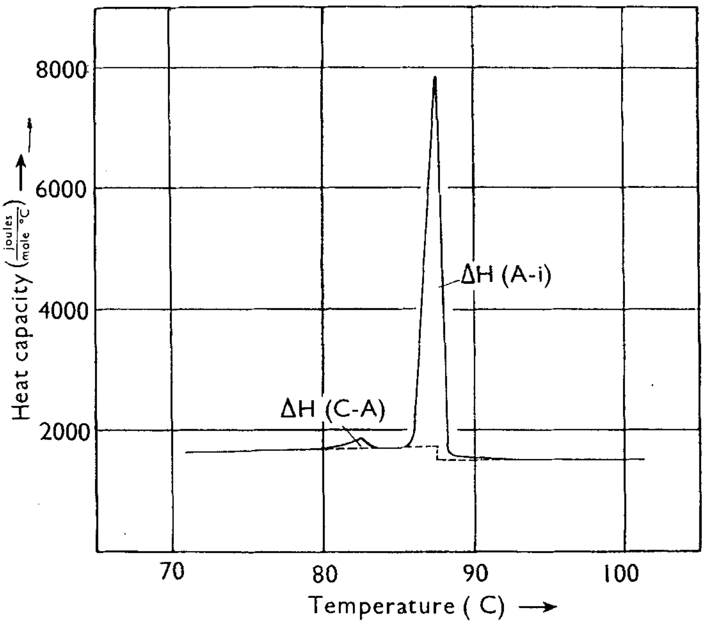


Figure 2. Caloric data of di-n-dodecyl 4,4′-azoxy-α-methylcinnamate.

but for the low-temperature smectic modification (B) he assumed a "smectic-hexagonal" structure. The region of transition between the two X-ray pictures ranged from 110°C to 125°C, and the deviation of the heat capacity from linearity lies in this region as well.

Figure 2 shows the "heat capacity", including enthalpy of transition, of compound II. For clarity, the heat capacity of the solid state has been omitted, and the liquid crystalline curve has been drawn downwards into the supercooled region (melting point 79° C).

The two smectic modifications are of the A- and of the C-type, respectively, the transition of which can be observed very well under the hot stage microscope (much better than the A–B transition of I). The peak corresponding to this transition in Fig. 2 is very small as compared with all other transitions of liquid crystalline substances we have studied so far. The indicated area corresponds to

$$\Delta H\ (\text{C–A}) = 100\ \text{joules/mole.}$$

For the smectic A to isotropic transition one obtains

$$\Delta H\ (\text{A–i}) = 8800\ \text{joules/mole}$$

and the enthalpy of melting is

$$\Delta H\ (\text{s–C}) = 75{,}200\ \text{joules/mole.}$$

In mixtures three-phase equilibria seem to occur in which modifications of the types A and C participate, but the restriction exists that a heterogenous A to C transition region has not been clearly observed so far.[9] This may be due to a very small latent enthalpy of transition or, alternatively, to a transition which is not of the first order. Further work is needed on the nature of this transition.

No X-ray studies on II, and in general on substances with smectic C modifications, seem to have been done so far. Since the difference in enthalpy between the smectic modifications C and A of II is much smaller than it is between B and A of I, the difference in molecular order is probably less significant between modifications of type C and type A than that between modifications of type B and type A. One may interpret in the same manner the fact that the succession is B, C, A with rising temperature, when the three modifications are present in the same substance.[5]

Comparison with the Enthalpies of Transition of Other Liquid Crystalline Substances

In Fig. 3 the enthalpies of transition so far discussed are compared with results which were obtained formerly on the well-known diethyl 4,4′-azoxybenzoate[2] with its single smectic phase (type A) and on the homologous series of 4,4′-di-n-alkoxy-azoxybenzenes[10,11] where nematic and smectic C phases occur. (The enthalpies of transition change much more from substance to substance than what the

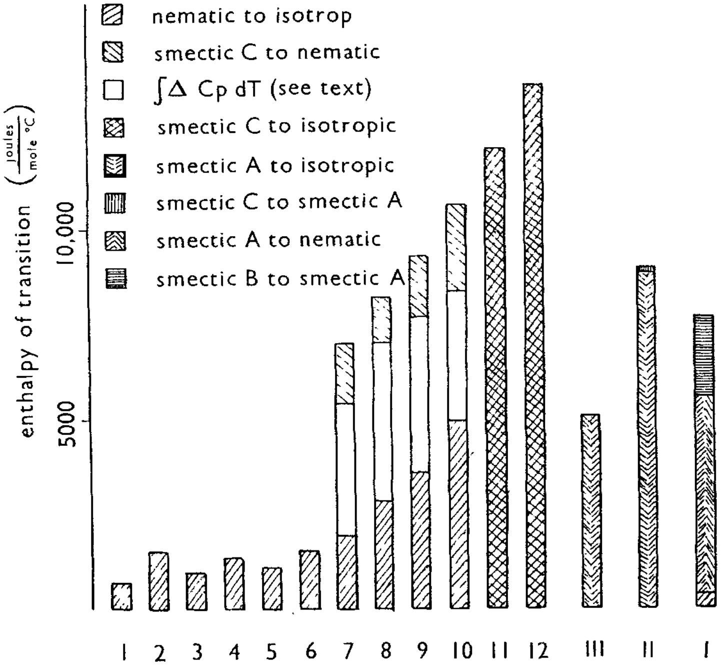
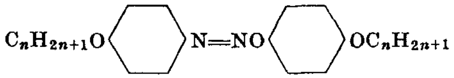


Figure 3. Enthalpies of transition of aromatic liquid crystalline substances:
I: Ethyl *p*-(4-ethoxybenzylideneamino-)cinnamate
II: Di-n-dodecyl 4,4′-azoxy-α-methylcinnamate
III: Diethyl 4,4′-azoxybenzoate[2]
1 to 12: 4,4′-Di-n-alkoxy-azoxybenzenes



with *n* varying from 1 to 12.[9,10]

transition temperatures change. Therefore the variation of entropies of transition is approximately parallel to that of the enthalpies in Fig. 3.)

As mentioned above, especially for the compounds I and II there are some difficulties when dividing the effects into heat due to transition and heat due to normal enthalpy change. But the resulting uncertainties are relatively small compared with the large change the values show from substance to substance even for transitions of the same type. In the homologous series this change occurs in a regular manner (values $\Delta H_{u,e}$ from Ref. 10).

For the nematic to isotropic transition this has been discussed previously[11] with respect to the statistical theory of the nematic state of Maier and Saupe. In the order of magnitude this theory is in accord with the experimental enthalpy of transition of the first member of the series, azoxyanisole.† The shift of the enthalpy of transition within the series is, however, not accounted for satisfactorily by this theory.

For the members 7 to 10 of the series, between the hatched areas representing the smectic to nematic and nematic to isotropic enthalpies of transition in Fig. 3 an additional amount of enthalpy $\int \Delta C_p dT$ is involved. This takes into account the fact that for these compounds the heat capacities are much higher in the nematic than in the isotropic and smectic states (see Fig. 5 in Ref. 11). This probably corresponds to the disintegration of residues of the smectic order above the smectic to nematic first order transition. $\int \Delta C_p dT$ is taken from the smectic–nematic to the nematic–isotropic transition temperature, and ΔC_p is the difference between the heat capacities of the nematic state and the corresponding values, linearly extrapolated from the isotropic state. The increase of the sum of these integrals and the enthalpies of transition is continued quite regularly by the values for the direct smectic C to isotropic transition for the members 11 and 12 of the series.

The great effect of the length of the alkyl residue is obvious. On the other hand, a change in the chemical nature of the residue connected with the azoxybenzene group has a still greater effect. For instance, the sum of the enthalpies of transition from smectic C to smectic A and from smectic A to isotropic for compound II is smaller than the di-dodecyloxy-azoxybenzene smectic C to isotropic value, in spite of a shorter residue of the latter. This may be

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† For new experimental work see Ref. 13.

due to the α-methyl group of II, which lowers the energy change connected with the formation of the liquid crystalline phase more than it is favoured by the conjugated cinnamic acid group.

It is to be hoped that further comparing study on broad experimental material will give us more information on the molecular sources of liquid crystalline behavior. For the smectic state there is a pressing need especially for X-ray investigations.

In our further calorimetric work we intend to examine substances with cholesteric modifications.

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REFERENCES

1. Arnold, H., *Z. phys. Chem.* (*Leipzig*) **225**, 45 (1964).
2. Arnold, H. and Roediger, P., *Z. phys. Chem.* (*Leipzig*), in press.
3. Mastrangelo, S. V. R. and Dornte, R. W., *J. Am. Chem. Soc.* **77**, 6200 (1955).
4. van Wijk, H. F. and Smit, W. M. *Analytica chim. Acta* **24**, 45 (1961).
5. Sackmann, H. and Demus, D., Liquid Crystal Conference, Kent, Ohio, 1965, to be published in *Molecular Crystals* **2** (1966).
6. Arnold, H. and Sackmann, H., *Z. Elektrochem., Ber. Bunsenges.* **63**, 1171 (1959).
7. Mayer, J. E. and Streeter, S. F., *J. Chem. Phys.* **7**, 1019 (1939).
8. Demus, D., Dissertation Halle/Saale 1963.
9. Arnold, H., Dissertation Halle/Saale 1959.
10. Arnold, H., *Z. phys. Chem.* (*Leipzig*) **226**, 146 (1964).
11. Arnold, H., *Zeitschrift für Chemie* **4**, 211 (1964).
12. Herrmann, K., *Z. Kristallogr.* **92**, 49 (1935).
13. Barrall, E. M. (II), Porter, R. S., and Johnson, J. F., *J. Phys. Chem.* **68**, 2810 (1964).