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DSC CHARACTERIZATION OF NEMATIC-SMECTIC AND SMECTIC-SMECTIC PHASE TRANSITIONS IN N(p-n-alkoxy benzilidene)-p-n-alkylanilines (n O.m)*

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ABSTRACT

The DSC method of Navard and Haudin is applied to characterize the liquid-crystalline phase transitions in a series of n O.m compounds, which exhibit rich but subtle polymorphism. This method involves the measurement of the ratio $N = h_l/h$ (where h_l and h are the heights of DSC transition peaks at two heating rates, one being twice the other). The particular relevance to distinguishing the order of the nematic-smectic A (NA) phase transition is emphasized.

INTRODUCTION

Differential Scanning Calorimetry (DSC) is widely used for the study of phase transitions: i.e. relevant thermodynamic parameters such as transition temperatures, the enthalpy changes (ΔH) etc., are directly obtained. Additionally the elevation of transition temperatures during the successive stages of purification of liquid crystals may also be used to assess the purity of the samples. Recently Cox and Navard[1] proposed a method to characterize the order of a phase transition from the DSC peak heights obtained at two different scanning rates (one being twice the other). The important assumption of the method is that of a characteristic melting transition shape for the Cp vs T curve. This method was successfully applied in two cases,[2] viz. octyl and nonyl cyanobiphenyl (8CB, 9CB) and TBBA.

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The characterization of the NA phase transition in liquid crystals is a problem of current interest. Several theoretical[3-5] and experimental[6-9] studies have shown that this transition may be first-order or second order depending upon the extent of the nematic phase of the compound.

As part of a study determining the tricritical point in binary mixtures of n O.m compounds, we applied this convenient method to a number of n O.m compounds which possess a rich variety of liquid crystalline phases including the NA transition and which display a nematic phase of varying extent.

EXPERIMENTAL

The compounds used in this study were prepared according to standard procedures[10]. The transition temperatures and the identification of the phases were obtained with a polarizing microscope fitted with a Mettler hot stage. The DSC measurements were carried out using a Perkin Elmer DSC-4 controlled by a model 3600 data station. The enthalpy values and the transition temperatures of these compounds (n O.m) agree with the literature values[11].

RESULTS AND DISCUSSION

The method to determine the order of the phase transition requires the determination of the ratio $N = h_1/h$ where h_1 and h are the heights of the DSC transition peaks obtained with two temperature scanning rates: one (h_1) being twice the other (h), keeping the weight of the compound constant. The ratio N is $1<N<\sqrt{2}$ for an isothermal first-order transition and equals 2 for a second order transition.

The values of N for smectic-smectic smectic-nematic and nematic-isotropic transitions for the compounds are given in Table 1 along with the fractional density jumps at the various transitions and the extent of the nematic phase.

The smectic-nematic phase transition has been studied in detail with high temperature resolution for 40.8[12], 40.7[13], 40.6[14] and 70.7[15] using ac calorimetry, x-ray, and ESR, and the results show that for the first three compounds the transition is of second order, while in the compound 70.7[15] it is first order. A first-order

transition was observed in other compounds using density, refractive index, and ESR studies: 60.4[16], 70.4[17], 70.5[18], 60.5[19], 70.1[20a], and 60.8[20b]. Our results for N in Table 1 are in complete agreement with these assignments of transition order. However, from the previous data on these n O.m compounds, one could not determine where the tricritical point should occur.

It is interesting to note, that by the interchange of alkoxy and alkyl chain lengths, while keeping the total number of methylene groups constant, the NA transition can be changed from second order to first order. (This fact was used in our work for the cases of binary mixtures of 40.6/60.4; 40.7/70.4; 40.8/80.4; 50.7/70.5). This DSC method enabled us to determine the tricritical composition to at least 1% accuracy. But contrary to these results, a first-order transition was observed for compounds 50.6[21] and 60.5[19]. It appears that the decisive role is played by the alkoxy chain length in governing the order of the NA transition. For example in the 4 O-m series the NA transition is second order, while for the 6 O-m series the transition becomes first order. A particularly interesting case is the 5 O-m series, wherein for short alkyl chain lengths (i.e. $m \leq 5$) the transition is second order, and it switches to first order for m=6. Also, the compound 50.6 exhibits a rich sequence of smectic phases S_A, S_C, S_B, S_F, S_G in addition to the nematic phase.

To further test the validity of this DSC method, these compounds 50.6 and 60.5 were studied in detail using several temperature scanning rates (1·5, 2, 3, 4, and 6°C per (min.)). The value of N for 50.6 obtained for N-S_A transition was always $>\sqrt{2}$ even though this was not the case for other compounds which exhibit a first order transition. Since an impurity may cause an increase in the ratio[2], the compound was purified by repeated crystallizations, but the DSC data showed no variation either in the transition temperatures or the value of N. This anomalous value of N may be due to the NA transition being very weakly first-order[22]. Our ESR results on 50.6 confirm this transition as weakly first-order such that the jump in the order parameter observed at the N-S_A transition is smaller than for the other compounds 60.4, 70.4 and 70.5[22] exhibiting first order behavior.

Other observations in this DSC study are: 1. We could not detect the A-C transitions in these compounds despite the use of large samples, except for 70.5, for which the ΔH

value is very small, (~ 0.04 cal/mol).* 2. The value of N for the isotropic-nematic transition is virtually the same for all the compounds. 3. The S_B-S_F and S_B-S_G transitions in 50.6 are found to be first-order with N values 1.40 and 1.29 respectively, consistent with the density measurements[21].

In Table 1 we show the McMillan parameter (T_{NA}/T_{NI}) for the compounds studied. McMillan's theory predicts T_{NA}/T_{NI} to be >0.88 (<0.88) for a first (second) order NA transition and equal to 0.88 for the tricritical point. Quite clearly the simple McMillan mean field[4] model is inconsistent with the cases cited. A careful examination of the T_{NA}/T_{NI} values for the n O.m series reveals that T_{NA}/T_{NI} >0.955 for the first order NA transition. We suggest[22] that the extent of the nematic range as well as the T_{NA}/T_{NI} ratio are not universal parameters so they may not be very useful in comparing different homologous series of liquid crystals. The transition temperatures are dependent on the magnitude of various coupling coefficients in the Hamiltonian[25], so one expects that T_{NA}/T_{NI} will depend on the system.

In conclusion, our DSC study of n O.m compounds and the successful characterization of the N-S_A phase transition in these compounds show that the measurement of N is a convenient and reliable technique to characterize mesophase-mesophase transitions in liquid crystals and thus may be used to locate the tricritical NA point in (the n O.m) binary mixtures.

* This DSC observation for the AC transition in n O.m compounds is consistent with the ESR tilt angle measurements. ESR studies in the smectic C phase revealed a zero degree tilt at the AC transition, and the tilt angle increased with a decrease in temperature[22,24]. Subtle variation of C_p as a function of temperature near the AC transition requires a more sensitive Adiabatic Calorometric technique,[9] and it is not too surprising that DSC is unable to detect this transition.

REFERENCES

1. P. Navard and J.M. Haudin. J. Therm. Analysis 29, 405 (1984).
2. P. Navard and R. Cox. Mol. Cryst. Liq. Cryst. Letts. 101, 261 (1984); ibid 102, 265 (1986).

3. K.K. Kobayashi. Phys. Letts. A31, 125 (1970).
4. W.L. McMillan. Phys. Rev. A4, 1238 (1971).
5. K.K. Kobayashi. J. de Chimie Phys. 80, 1 (1983).
6. J. Thoen, H. Marynissen and W. Van Dael. Phys. Rev. Lett. 52, 204 (1984).
7. B.M. Ocko, R.J. Birgeneau, J.D. Litster and M.E. Neubert. Phys. Rev. Lett. 52, 208 (1984).
8. G.B. Kasting, C.W. Garland and K.I. Lushington. J. Phys. (Paris) 41, 879 (1980).
9. J. Thoen, H. Marynissen and W. Van Dael. Phys. Rev. A 26, 2886 (1982); Mol. Cryst. Liq. Cryst. 97, 149 (1983).
10. H. Kelker and B. Scheurle. Angew Chem., Int. Ed. Engl., 8, 884 (1969).
11. A. Wiegeleber, L. Richter, J. Deresch and D. Demus. Mol. Cryst. Liq. Cryst. 59, 329 (1980).
12. K.J. Lushington, G.B. Kasting and C.W. Garland. J. Phys. Lett. (Paris) 41, L 419 (1980).
13. R.J. Birgeneau, C.W. Garland, A.R. Korton, J.D. Litster, M. Meichle, B.M. Ocko, C. Rosenblatt, L.J. Yu and J. Goodby. Phys. Rev. A 27, 1251 (1983).
14. S.A. Zager and J.H. Freed, Chem. Phys. Letts. 109, 270 (1984); A. Nayeem, S.B. Rananavare, J.H. Freed (in preparation).
15. J. Thoen and A. Seynhaeve. Mol. Cryst. Liq. Cryst. 127, 229 (1985).
16. N.V.S. Rao and V.G.K.M. Pisipati. J. Phys. Chem. 87, 899 (1983).
17. N.V.S. Rao and V.G.K.M. Pisipati. Phase Transitions 3 317 (1983).
18. N.V.S. Rao, V.G.K.M. Pisipati, Y. Gouri Sankar and D.M. Polikuchi. Phase Transitions (in press) 1986.
19. K.R.K. Rao, J.V. Rao and P. Venkata Charuyulu. Acta Physica Polonica A69, 261 (1986).
20a. N.V.S. Rao, P.V. Datta Prasad, V.G.K.M. Pisipati. Mol. Cryst. Liq. Cryst. 126, 175 (1985); b. ibid (in press).
21. Y. Thiriet, J.A. Schulz, P. Martinoty and D. Guillon. J. Phys. (Paris) 45, 323 (1984).
22. V.G.K.M. Pisipati, S.B. Rananavare, and J.H. Freed (in preparation).
23. V.G.K.M. Pisipati and N.V.S. Rao. Phase Transitions 3, 169 (1983).
24. G.R. Luckhurst, B.A. Timimi, V.G.K.M. Pisipati and N.V.S. Rao. Mol. Cryst. Liq. Cryst. Lett. 1, 45 (1984
25. H.E. Stanley. Phase transitions and critical phenomena, p. 90, Ch. 6., Oxford UP, New York (1971).

TABLE 1.

Compound	Nematic Range (C)	T_{NA}/T_{NI}	N - Value				% Density Jump = $\Delta \rho/\rho \times 100$			
			I - N or I - A	N - A	A - B or A - C	B - G or C - G	I - N or I - A	N - A	A - B or C - B	B - G or C - G
60.4	7.8	0.978	1.37	1.41			0.42[c] 0.39	0.24 0.21	0.40	0.47
40.6[a]	22.4	0.936	1.34	2.02	1.53		0.23[d]	~ 0.[d]	0.30[d]	
70.4	2.1	0.994	1.38	1.37		1.5	0.28[e] 0.25	0.43 0.22		0.14 0.53
40.7[a]	27.1	0.925	1.31	2.05	1.07					
60.4	No Nematic	-	1.42	-	1.51	1.10		0.4[h]	0.06	

TABLE 1. (Cont'd.)

40.8[a]	15.7	0.955	1.38	2.05[b] 2.23	1.35					
70.5	2.8	0.990	1.31	1.32		1.41	0.34[f]	0.25	0.76	
50.7[a]	16.0	0.954	1.37	1.95[b] 2.04						
60.5	10.0	0.972	1.29	1.26	1.03	1.17	0.27[g]	0.22	0.49	0.47
50.6	12.1	0.967	1.31	1.53	1.37	B - F 1.40 F - G 1.29		0[i]		

a) Second order N-S_A Transition
b) The two values for N are due to the uncertainty of the base line.
c) Ref. 16
d) Pisipati et al (unpublished)
e) Ref. 17
f) Ref. 18
g) Ref. 19
h) Ref. 23
i) Ref. 21