Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Unusual Character of Some Liquid Crystal Mixtures Exhibiting Induced Smectic Mesophases

A. Boij [a] & P. Adomenas [a]
[a] Chemistry Department of Vilnius V., Kapsukas University, 232006, Vilnius, Partizanu 24, USSR
Version of record first published: 20 Apr 2011.

To cite this article: A. Boij & P. Adomenas (1983): Unusual Character of Some Liquid Crystal Mixtures Exhibiting Induced Smectic Mesophases, Molecular Crystals and Liquid Crystals, 95:1-2, 59-62

To link to this article: http://dx.doi.org/10.1080/00268948308072408

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 59–62
0026-8941/83/9502–0059/$18.50/0

Printed in the United States of America

Unusual Character of Some Liquid Crystal Mixtures Exhibiting Induced Smectic Mesophases

A. BOIJ and P. ADOMENAS

Chemistry Department of Vilnius V. Kapsukas University, 232006, Vilnius, Partizanų 24, USSR

(Received December 2, 1982)

The phase diagram of the binary system 4-*n*-pentyl-4′-*n*-pentyloxytolane and 4-(4′-*n*-pentylbicyclo[2.2.2]octyl) benzonitrile exhibiting induced smectic mesophases was determined. The unusual character of this system is emphasized by: a) the formation of two types of smectic — A and E, b) the thermal stability maximum of the smectic mesophases corresponds not to an equimolar composition, but to the formation of molecular associates between the polar and the low-polarity component in the ratio 1:2 and 1:4, respectively.

It is known that mixtures of nematic liquid crystal materials with a large difference in polarity in many cases produce an induced smectic mesophase,[1–5] generally of type A,[3–5] and sometimes of type B or E.[5] In all investigated cases, the thermal stability maximum of the induced smectic mesophase corresponded to an approximately equimolar composition of polar and low-polarity components.

We have examined mixtures containing the recently synthesized[6] 4-(4′-*n*-pentylbicyclo[2.2.2]octyl) benzonitrile and shown that this compound exhibits an induced smectic mesophase of type A with many low-polarity compounds (see Table I). For example, the equimolar mixture of 4-(4′-*n*-pentylbicyclo[2.2.2]octyl) benzonitrile and 4-*n*-hexyloxyphenyl 4-*n*-butylbenzoate exhibits a transition from the smectic A mesophase to the nematic mesophase at 25°C and a transition between the nematic and isotropic states at 67°C.

However, a more detailed study of the bicyclo-octylbenzonitrile-tolane system has indicated that the thermal stability maximum of the smectic A

TABLE I

Formation of induced S_A phases in equimolar binary mixtures of 4-(4′-n-pentylbicyclo[2.2.2]octyl) benzonitrile and low-polarity components

Low-polarity component, 50 mol %	Transition temperatures (°C)		
	S_A	N	I
1. C_4H_9-⟨⟩-COO-⟨⟩-OC_6H_{13}	25	67	
2. C_4H_9-⟨⟩-N=N-⟨⟩-OC_4H_9	44	48	
3. C_5H_{11}-⟨⟩-C(CN)=CH-⟨⟩-OC_6H_{13}	26	55	
4. C_5H_{11}-⟨⟩-C≡C-⟨⟩-OC_5H_{11}	50	84	

mesophase corresponds not to an equimolar composition, but to 33 mol% of the polar component (see Figure 1). Furthermore, at lower temperatures, another type of smectic appeared with a thermal stability maximum at 20 mol% of the polar component. From the textures observed, this smectic is of type E (striped focal-conic texture).[7]

So in the investigated system the formation of associates between polar and low-polarity components in the ratio 1:2 leads to the induction of the S_A mesophase and in the ratio 1:4 of the S_E mesophase.

The measured value of the enthalpy for the transition S_E—S_A at the composition 30 mol% of the polar component is 1.21 cal/g, and for the transition from S_A to nematic phase −0.95 cal/g. At the point of disappearance of the S_A phase (20 mol% of the polar component), the value of the enthalpy for the transition smectic to nematic is 2.92 cal/g.

It is characteristic that this system exhibits two eutectics with m.p. 22°C and 29.5°C. The temperature curve for the transition from the nematic to the isotropic state reflects the temperature-concentration boundaries of the smectic region: this line exhibits a slight concavity at concentrations 50–100 mol% of the polar component and a slight convexity — from 0–50 mol%. So the formation of associates also increases the thermal stability of the nematic phase. We have examined two other systems containing tolanes and have again established the formation of S_A and S_E phases (Table II).

For example, a mixture of 40 mol% 4-(4′-*n*-octylbicyclo[2.2.2]octyl) benzonitrile 30 mol% 4-*n*-hexyloxyphenyl 4-*n*-butylbenzoate and 30 mol% 4-*n*-heptyl-4′-*n*-butyloxytolane is characterized by the transition temperatures: S_E — S_A at 58°C, S_A — I at 63°C. The same systems without the added tolane form only induced S_A mesophases.

We hope that the observed influence of the composition of the molecular associates on the type of induced smectic mesophase may be useful for an

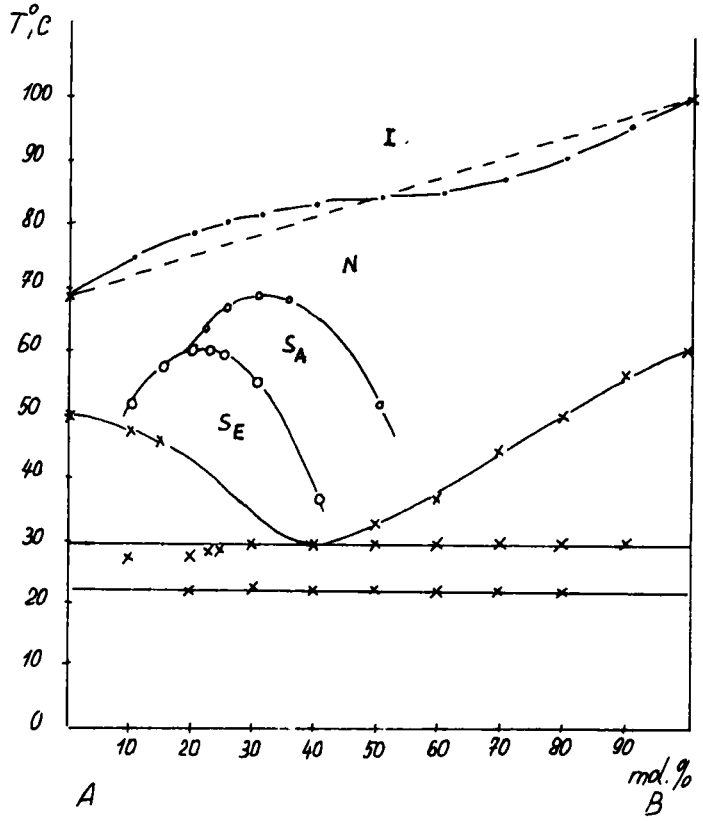

FIGURE 1 The phase diagram of the system 4-*n*-pentyl-4′-*n*-pentyloxytolane (A) and 4-(4′-*n*-pentylbicyclo[2.2.2]octyl benzonitrile) (B).

TABLE II

Formation of S_A and S_E phases in liquid crystal mixtures

Mixture	Mol %	Transition temperatures (°C) S_E	S_A	N	I
C_8H_{17}-(cyclohexane)-(benzene)-CN	40		58	—	63
C_4H_9-(benzene)-COO-(benzene)-OC_6H_{13}	30				
C_7H_{15}-(benzene)-C≡C-(benzene)-OC_4H_9	30				
C_5H_{11}-(benzene)-(benzene)-CN	40		37	53.2	58
C_4H_9-(benzene)-COO-(benzene)-OC_6H_{13}	30				
C_5H_{11}-(benzene)-C≡C-(benzene)-OC_5H_{11}	30				

understanding of the nature of this phenomenon which certainly needs further investigation.

References

1. B. K. Vainshtein, I. G. Chistiakov, G. G. Maidachenko, L. A. Gusakova, V. D. Belilovskij, V. M. Chaikovskij, L. K. Vistinj, and S. R. Chumakova, *Dokl. AN SSSR, Phys. chem. (rus.)*, **220**, 1349 (1975).
2. J. W. Park, C. S. Bak, and M. M. Labes, *J. Amer. Chem. Soc.*, **97**, 4398 (1975).
3. G. Heppke and E. J. Richter, *Z. Naturforsch.*, **33a**, 185 (1978).
4. Ch.S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).
5. B. Engelen, G. Heppke, R. Hopf, and F. Schneider, *Ann. Phys.*, **3**, 403 (1978).
6. G. W. Gray and S. M. Kelly, *J. Chem. Soc. Perkin II*, 27 (1981).
7. D. Coates and G. W. Gray, *Microscope*, **24**, 117 (1976).