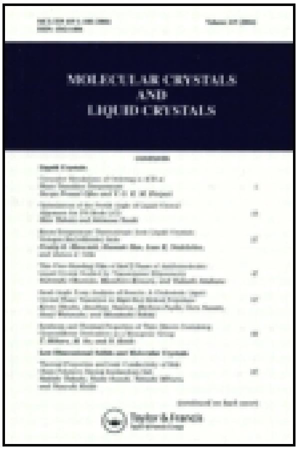

Molecular Crystals and Liquid Crystals

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

Mixed Dimer Formation in Binary and Ternary Mixtures of Liquid Crystalline 4-Substituted Benzoic Acids

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Version of record first published: 20 Apr 2011.

To cite this article: S. Takenaka & M. M. Labes (1983): Mixed Dimer Formation in Binary and Ternary Mixtures of Liquid Crystalline 4-Substituted Benzoic Acids, Molecular Crystals and Liquid Crystals, 90:3-4, 365-371

To link to this article: http://dx.doi.org/10.1080/00268948308072462

Mol. Cryst. Liq. Cryst., 1983, Vol. 90, pp. 365–371
0026-8941/83/9004-0365$18.50/0

Printed in the United States of America

Mixed Dimer Formation in Binary and Ternary Mixtures of Liquid Crystalline 4-Substituted Benzoic Acids

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(*Received July 6, 1982*)

Mixed dimer formation is studied for a wide variety of 4-substituted benzoic acids that form liquid crystalline phases. The solid–mesophase transitions can show double eutectics when mixed dimer formation occurs, but in many cases the equilibrium constant for such a mixed dimer is extremely small. The mesophase–isotropic transitions are essentially linear over the entire phase diagram. Ternary mixtures can be created having nematic ranges of over 80° by virtue of eutectization.

INTRODUCTION

There have been a number of studies of the mesomorphic properties of 4-alkyl-[1] and 4-alkoxybenzoic acids[2–4] and also some investigations of the corresponding trans-cyclohexanecarboxylic acids.[5] Both in the solid state and in the mesophase, these compounds are almost completely dimerized (1).[6] Upon mixing two such compounds, an equilibrium is established with a mixed dimer (2).[7,8]

When mixed dimer formation is favored, the phase diagram might be expected to reflect an enhancement of the thermal stability of the solid phase at ~0.5 mole fraction of each component and two eutectic temperatures. When essentially no mixed dimer formation occurs, simple eutectization might be anticipated. The purpose of this work

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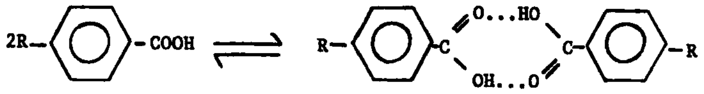

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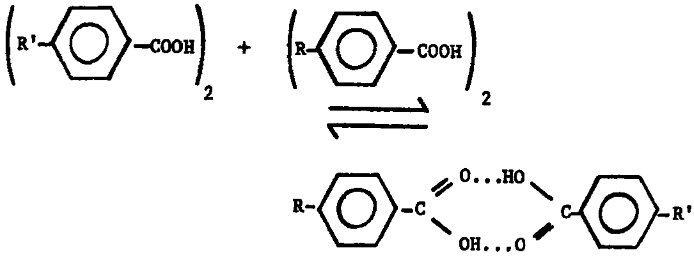

was to examine how the nature of substituent might affect the tendencies to these extrema. Phase diagrams are presented involving the highly polar substituents —CN, RNH—, as well as the more classically studied cases of RO— and R— substituents. Taking advantage of these tendencies, two ternary compositions are formulated having extremely large nematic temperature ranges.

EXPERIMENTAL

Synthesis

Alkoxybenzoic acids were purchased from Frinton Laboratories and used without purification, since their melting points were in agreement with literature values. Alkylbenzoic acids were prepared by hydrolysis of the corresponding acid chlorides, which were purchased from Eastman Kodak Company, followed by crystallization from benzene. Alkylaminobenzoic acids were prepared by the method described by Weissflog *et al.*[9]

Phase diagram studies

All phase diagrams were determined by both optical microscopy, using a Mettler Hot Stage on a polarizing microscope, and thermodynamically by using a Perkin-Elmer DSC-2C-TADS system. These phase diagrams are presented in Figures 1 and 2.

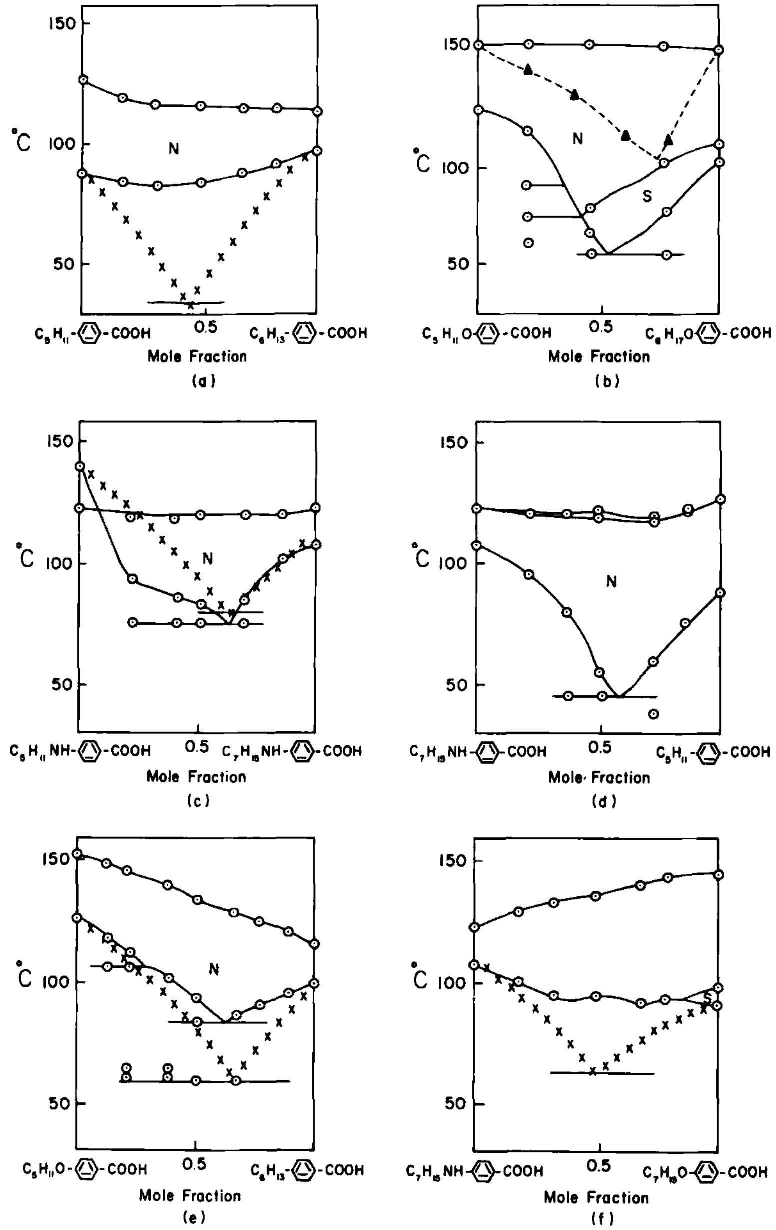

FIGURE 1 Phase diagrams of binary mixtures of some liquid crystalline carboxylic acids. ⊙ observed values. X values calculated from the Schroeder-vanLaar equation. ▲ values reported by Homer and Dudley.[7] (N—nematic, S—smectic phases).

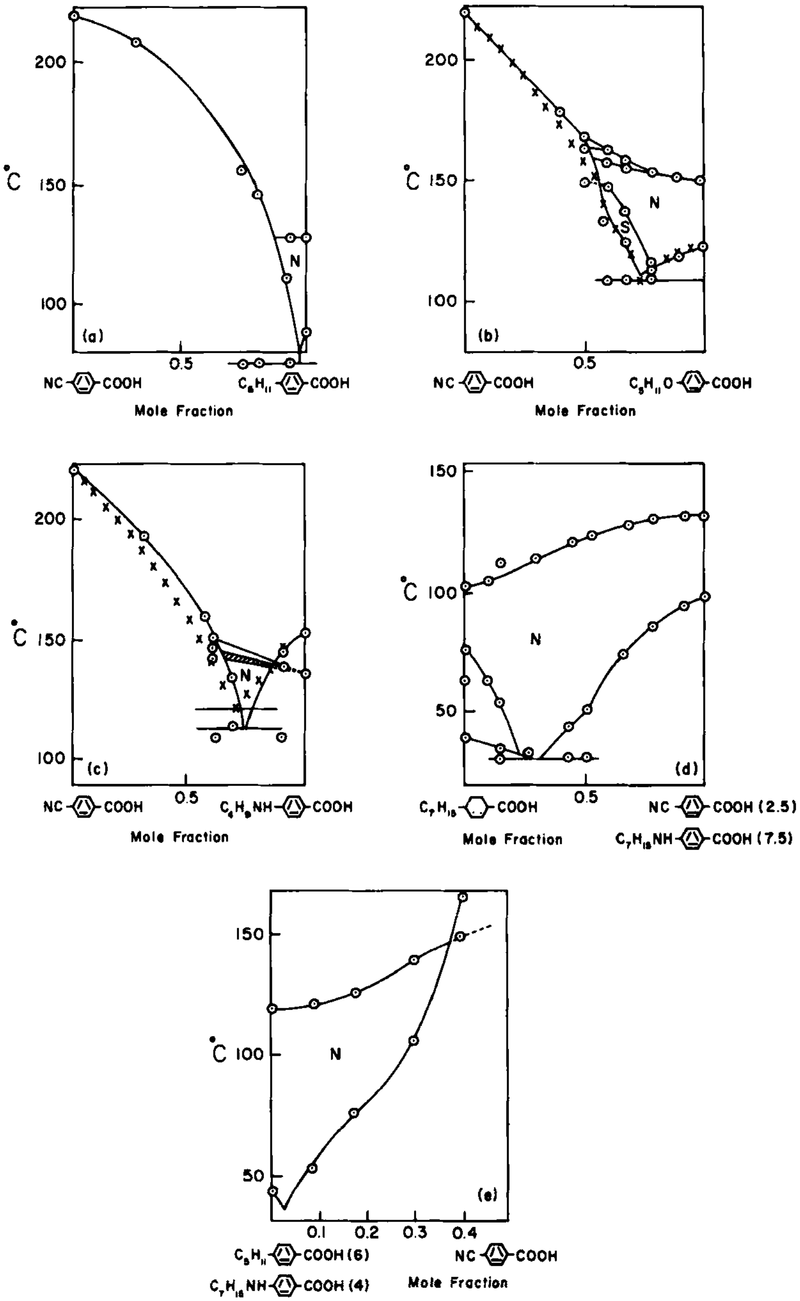

FIGURE 2 Phase diagrams of binary and ternary mixtures. ⊙ observed values. × values calculated from the Schroeder-vanLaar equation.

DISCUSSION

Figures 1a–1c show the typical behavior of binary mixtures of 4-alkyl-, 4-alkoxy-, and 4-alkylaminobenzoic acids. The solid–nematic transitions for the 4-alkylbenzoic acid mixture are much higher than those calculated from the Schroeder-vanLaar equation.[10,11] Such mixtures are, clearly, tending away from simple eutectization to a mixed dimer phase. This tendency is also observed in mixtures of 4-heptylamino- and 4-heptyloxybenzoic acids (Figure 1f). In mixtures of 4-alkylamino- and 4-alkoxy-benzoic acids (Figures 1b and 1c), on the other hand, a single eutectic indicating a very small amount of mixed dimer is observed. The binary phase diagram of 4-pentyloxy and 4-hexylbenzoic acids (Figure 1e) shows two eutectics at 107 and 79°C. The shape of the eutectic curve, however, bears a strong resemblance to the calculated single eutectic behavior. Furthermore, on heating, DSC measurements reveal an endothermic event at 61°C, exactly coinciding with the calculated single eutectic temperature, and indicating that mixed dimer formation is not favored. The eutectic temperature for the mixture of heptylamino- and pentylbenzoic acid (Figure 1d) is almost in agreement with the calculated value.

All other systems studied (Figure 2) are cases in which mixed dimer formation is negligible. These include mixtures of the non-mesogen 4-cyanobenzoic acid with mesogenic 4-substituted benzoic acids. Solid–nematic transitions agree quite well with calculated values. As is evident from Figure 2b, the mixture of pentyloxy- and cyanobenzoic acids induces a smectic phase, and the thermal stability is dependent on the ratio of the acids. A similar phenomenon has been reported in a mixture of 4-cyano-4′-pentylbiphenyl and 4-pentylbenzoic acid.[12]

This phase behavior might be a consequence of hydrogen bonded dimer–mixed dimer equilibria (Equations 1 and 2). Dimer formation (Equation 1) is known to be the cause of liquid crystallinity in 4-substituted benzoic acids.[6] In fact, dimer formation in the nematic phase has been confirmed by infrared absorption spectroscopy.[13,14] On the other hand, Homer and Dudley[7] reported that mixtures of pentyloxy- and octyloxy-, or heptyloxy- and octyloxybenzoic acids form mixed dimer (Equation 2), giving rise to notable double eutectic phenomena not only in the solid–nematic but also in nematic–isotropic transitions. We reinvestigated the pentyloxy-octyloxy system, and our results are not in agreement with those reported by Homer and Dudley.[7] As shown in Figure 1b, this mixture shows a single eutectic in the solid–nematic transition, and the nematic–isotropic transition line is almost linear.

Although the deviations recognized in Figure 1a and 1f are assumed to arise from mixed dimer formation (Equation 2), the formation constant is probably small. Furthermore, the nematic–isotropic transition line for all systems studied here can be approximated by a straight line. The thermal stability of hydrogen bonded dimers might be dependent on the acidity of the carboxyl group. The *pka* value is 4.36 for *p*-toluic acid, 4.47 for *p*-anisic acid, and 4.92 for *p*-aminobenzoic acid. However, there is no evident correlation of these values to the phase behavior of the mixtures.

In Figures 2d and 2e, data are presented on ternary mixtures in which wide temperature range nematics are created, in one case by adding an alkyl substituted trans–cyclohexanecarboxylic acid. A measurement of the dielectric properties of the eutectic composition in Figure 2d at 82°C gave $\epsilon_{\parallel} = 4.96$ and $\epsilon_{\perp} = 4.43$ at 1 kHz.

We have not as yet discussed the degree of mixed dimerization which occurs in the nematic phases of these mixtures. Since none of the phase diagrams show any significant enhancements of N–I transition temperature over the expected linear relationship, it is doubtful that mixed dimer equilibria are of significance in the mesophases.

CONCLUSIONS

Mixed dimer formation is of significance in the solid phases of binaries of alkylbenzoic acids or alkylamino- with alkoxybenzoic acids, where as alkoxy–alkyl mixtures have a slight tendency to show this effect. On the other hand, alkylamino–alkyl mixtures, alkoxy–alkoxy mixtures, or the mixtures of the virtual mesogen 4-cyanobenzoic acid with any 4-substituted benzoic acid of the above classes show negligible amounts of mixed dimer formation and, therefore, simple eutectic behavior. The mesophases of all these binary systems do not favor mixed dimer formation.

Wide range nematic ternary systems can be formulated from carboxylic acids by taking advantage of these eutectization principles, and their dielectric properties can be controlled by adding the virtual mesogen 4-cyanobenzoic acid with its strong positive dielectric anisotropic contribution.

Acknowledgment

This work was supported by the National Science Foundation under Grant No. DMR81-07142.

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