Phase Diagrams of Binary Mixtures of Liquid Crystals

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Summary Preliminary studies indicate that some mixtures of liquid crystal compounds may exhibit unusual features in their phase diagrams.

PREVIOUS investigations of mixtures of liquid crystals have shown that the nematic mesophase to isotropic liquid transition temperatures often vary linearly with the composition of the mixtures, but can show regular deviations from linearity.[1-6] Normally, dissimilar compounds show more deviation from linearity than similar compounds,[1,7,8] but in all cases the curves are reported to be continuous. Recently, a theory for nematic–isotropic phase transitions has been developed which explains very satisfactorily the regular experimental data.[9] In contrast to the nematic–isotropic change, the solid-nematic phase diagrams usually exhibit a eutectic, and not a smooth curve.[2-4]

In the course of studying mixtures of liquid crystals suitable for the n.m.r. investigation of solutes partially orientated in the nematic mesophase we have encountered some compounds whose phase diagrams indicate some differences from those normally found. Whilst our observations are incomplete we report our empirical findings in order that they may aid the theoretical understanding of phase changes in mixtures of liquid crystals.

The compounds used in the investigations were 4,4′-dimethoxyazoxybenzene (A), azoxybenzene (B), 4,4′-di-n-hexyloxyazoxybenzene (C), 4-n-pentyloxybenzoic acid (D), 4-n-hexyloxybenzoic acid (E), and 4-n-octyloxybenzoic acid (F), and the binary mixtures studied were A–B, A–C, D–E, D–F, E–F, A–D, A–E, A–F, C–D, C–E, and C–F. Some of these mixtures show regular or near regular phase diagrams and little further comment will be passed on them.

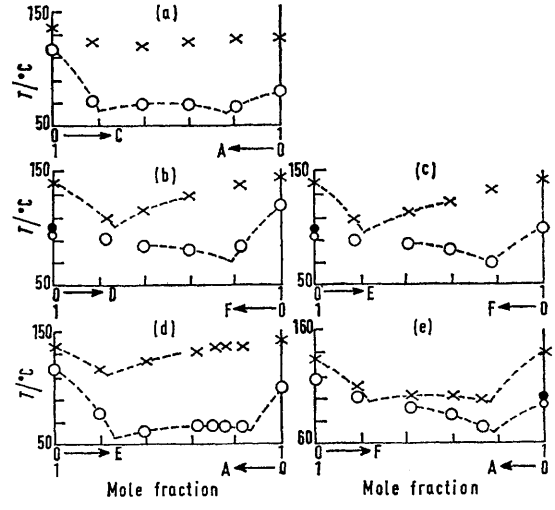

FIGURE. *Phase diagrams of binary mixtures of some liquid crystals. Solid-nematic (or smectic), smectic–nematic, and nematic–isotropic transitions are symbolised by* ○, ●, *and* × *respectively. Broken lines are used merely to illutrate the possible interpretations of the phase changes referred to in the text and should not be taken as accurate assessments of eutectic points.*

The accuracy of our experimental procedure was assessed by studying mixtures of A and B, for which data have been reported previously;[8] the maximum error in our data corresponds to ± 2°C.

Mixtures of C and A showed [Figure (a)] the normal negative deviation from the ideal (linear) nematic-isotropic phase change, as established previously.[1] The present data show that a regular curve cannot be drawn for the solid–nematic transition, but indicate 'eutectic' points.

The 4-n-alkoxybenzoic acids were also examined. These compounds largely owe their nematic character to their ability to exist as dimers.[10] In view of this it is expected that mixtures of them should show double eutectics indicating the formation of weak compounds between unlike acids. In the Figure, (b) and (c), the solid–nematic data clearly show one eutectic with the possibility of a second. More interesting than these observations, however, is that in the Figure, (b) and (c), the nematic–isotropic phase lines appear to show well defined 'eutectics,' in complete contrast to that for D–E mixtures which may be represented by a smooth curve; it is interesting that in the last case the compounds involved have similar lengths.

For the binary mixtures between three 4-n-alkoxybenzoic acids and two 4,4′-di-n-alkoxyazoxybenzenes, strong evidence for eutectics in the solid–nematic phase line was found for the A–E and A–F mixtures [Figure, (d) and (e)]. So far as the nematic–isotropic transition is concerned Figure (e) provides strong evidence for a double eutectic and Figure (d) may be interpreted as showing a regular phase change but arguably shows a eutectic.

Recently, Bernheim and Shuhler have reported phase diagrams for a limited number of liquid crystal mixtures.[11] In common with us, they found that the solid–nematic transition is lowered in temperature over a rather wide range of composition. However, they did not comment on the irregularities in the nematic–isotropic phase diagrams which are quite prominent in two of the four binary mixtures studied by them and concur with our observations. Consequently, despite the limited data available, it appears that some mixtures of liquid crystals may show unusual discontinuities in the nematic–isotropic transition, and that further investigations of them are necessary.

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