

*Mixed Liquid Crystals.*

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A number of binary systems have been investigated in which one component can form a nematic liquid-crystal phase and the other not. In all cases studied the liquid phase is apparently a homogeneous single phase which may or may not be anisotropic. There was no indication that two distinct liquid phases, one isotropic and the other anisotropic, could coexist over a range of temperature, for a binary mixture of a given composition. Thermodynamic arguments show, however, that such a situation is impossible for a normal first-order phase transition. Therefore, our results indicate either that the transition is not a first-order transition or that the two-phase region is extremely small. It seems likely that the same will be true in general for anisotropic liquids containing two components, such liquids being in general true solutions and not mixtures of phases.

It is now well known that a nematic liquid crystal is a system in which rod-shaped molecules have translational freedom, but only a restricted rotational freedom, and that such a liquid has a domain structure in which all the molecules in a given domain lie parallel. A second substance dissolved in such a liquid would then be in an anisotropic environment and this might clearly affect its chemical and physical properties in an interesting manner. Since it is our intention to investigate effects of this kind it became important to establish the conditions under which such solutions might be formed.

Very little work appears to have been done on binary liquid crystals. de Kock (*Z. physikal. Chem.*, 1904, **48**, 129) and Prins (*ibid.*, 1909, **67**, 689) studied binary systems in which one or both components could form liquid crystals and discussed the general problem in terms of the phase rule. They concluded that the transition from anisotropic liquid to isotropic liquid should not in general occur sharply in two-component systems, but that there should as a rule be a range of temperature over which two liquid phases (of different composition) could coexist. This suggestion is illustrated by Fig. 1*a* taken from de Kock's paper, giving his interpretation of the phase diagram for the system *p*-azoxyanisole-quinol; here quinol does not form a liquid crystal on fusion whereas azoxyanisole does, and in the shaded area two distinct liquids coexist, one isotropic and one anisotropic.

The experimental evidence on which these conclusions were based was however scanty. The transitions were followed mainly by observing the change in the liquid from cloudy to clear, without stirring or adequate temperature control; under these conditions it is not

surprising that the transitions were not sharp. Thermal analyses of the systems were also carried out, but with rates of cooling which according to our investigations appear much too high. Many of the phase diagrams, including Fig. 1a, seem to have been based largely on preconceived ideas rather than on direct evidence; thus no results are quoted for the critical range of composition corresponding to the horizontal break in the melting line in Fig. 1a.

Bogojawlensky and Winogradow (*Z. physikal. Chem.*, 1908, **64**, 228) and later Walter (*Ber.*, 1925, **58**, 2303) pointed out that in many cases the transition lines separating the anisotropic and the isotropic liquid regions in the phase diagrams are linear. When both components can themselves form liquid crystals, this implies that perfect mixed liquid crystals are being formed, analogous to a similar series of ideal solid solutions of two components. They deduced that in cases where only one component appears to form a liquid crystal, the other must have a potential or latent nematic form, but that this cannot normally be observed because the transition to isotropic liquid lies below the normal

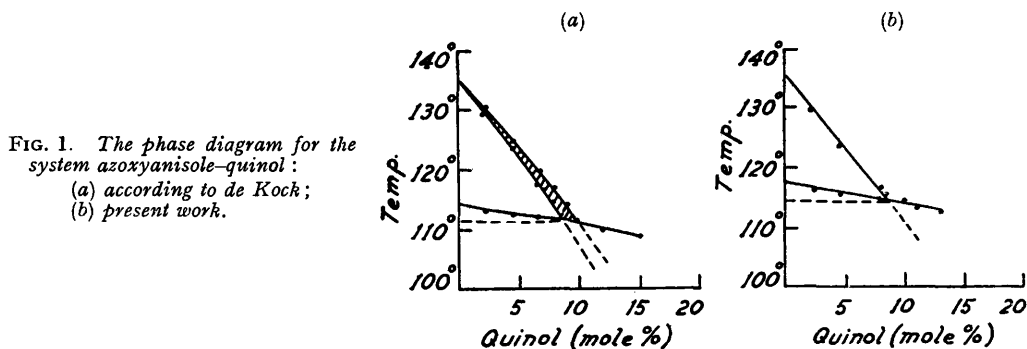


FIG. 1. The phase diagram for the system azoxyanisole-quinol:

(a) according to de Kock;  
 (b) present work.

melting point. The transition temperatures of these latent forms to normal liquids were deduced in a number of cases by extrapolation; and it even proved possible to obtain binary liquid crystals from pairs of substances which themselves showed no nematic phase, the melting points of the mixtures being depressed and so allowing the nematic mixed liquid to be observed. The latent transitions were also actually observed in some cases in supercooled melts. This work establishes clearly that in these ideal cases the transition from nematic to isotropic liquid is sharp; but it throws no light on cases where the transition lines are curved.

Most of the ideal systems involve mixtures in which both species of molecule have the features known to be necessary in nematic liquid crystals; that is, the molecules are rod-shaped with polar groups at each extremity (cf. Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1046). Since we were interested in systems of a more general type, in which an arbitrary solute is dissolved in a nematic liquid crystal, we wished to establish whether or not genuine mixed liquid crystals can be obtained in such cases over a useful range of concentration. It also seemed likely that the tendency of solutes to form mixed liquid crystals would throw light on the nature of the mesomorphic state. Here we describe an investigation of the first problem, and we shall give reasons for believing that the anisotropic liquids are in all cases homogeneous one-phase mixed liquid crystals. The regions where two liquid phases, one normal and one anisotropic, coexist must be at most extremely small.

#### EXPERIMENTAL

Temperatures are corrected, and were determined with thermometers calibrated against standard thermometers.

*Preparation and Purification of Materials.*—Equimolecular proportions of *p*-chlorobenzaldehyde and *p*-anisidine were heated slowly in a little alcohol until the mixture boiled; the residue on cooling was crystallised several times from alcohol, giving *N*-4-chlorobenzylidene-*p*-

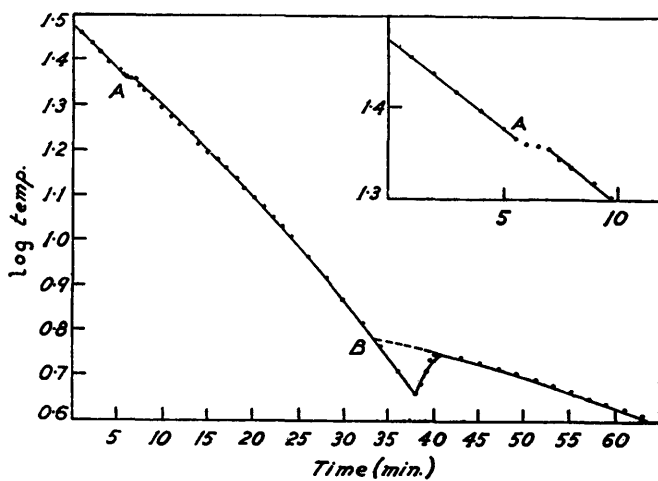


FIG. 2. A typical cooling curve (p-azoxyanisole-p-anisylidene-p-anisidine; 73 mole % of p-azoxyanisole; bath-temp. 100°).

A represents the liquid-liquid transition,  
B the normal melting point.

FIG. 3. The system p-azoxyanisole-phenanthrene.

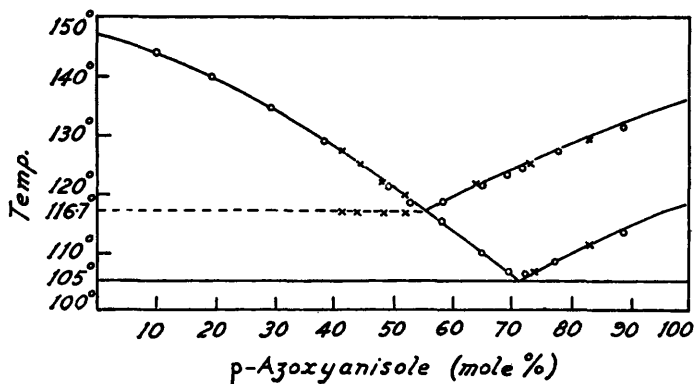
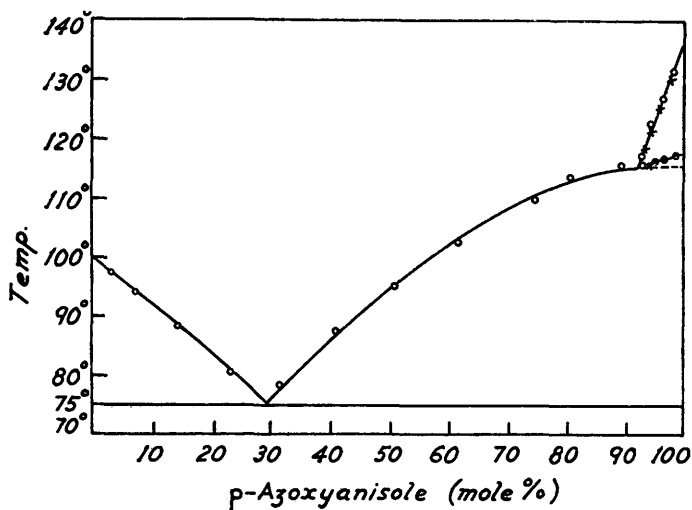


FIG. 4. The system p-azoxyanisole-p-anisylidene-p-anisidine.

*anisidine* in colourless plates, m. p. 124° (Found : C, 68.6; H, 5.0; N, 14.0; Cl, 5.7.  $C_{14}H_{12}ONCl$  requires C, 68.4; H, 4.9; N, 14.4; Cl, 5.7%).

*p*-Anisylidene-*p*-anisidine, *p*-bromoaniline, *p*-chloroaniline, and *p*-toluidine, and *p*-methylbenzylidene-*p*-anisidine were prepared similarly and crystallised from alcohol in colourless plates or needles; their m. p.s (147°, 120°, 93°, 92°, and 88°, respectively) agreed with those given in the literature. *p*-Azoxyphenetole (Gattermann and Ritschke, *Ber.*, 1890, 23, 1738) was recrystallised from alcohol (m. p. 137°, 168°; lit., 137°, 168°). 4 : 4'-Dichloroazoxybenzene (Willgerodt, *Ber.*, 1882, 15, 1004) was recrystallised from alcohol (m. p. 157°; lit., 158°).

FIG. 5. The system *p*-azoxyanisole-*p*-anisylidene-*p*-bromoaniline.

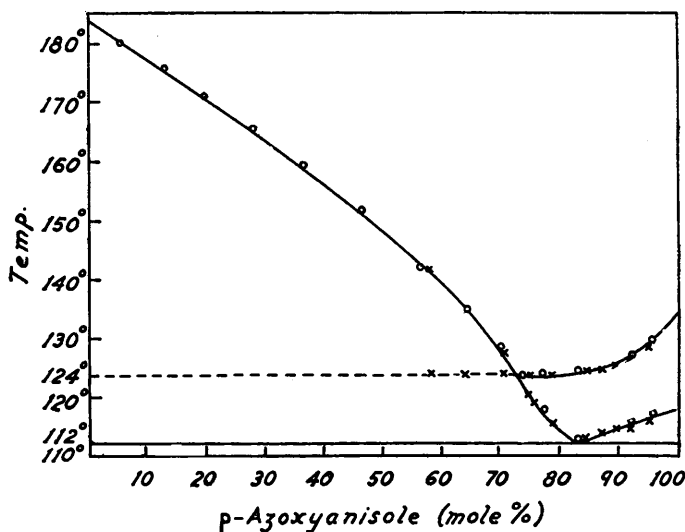
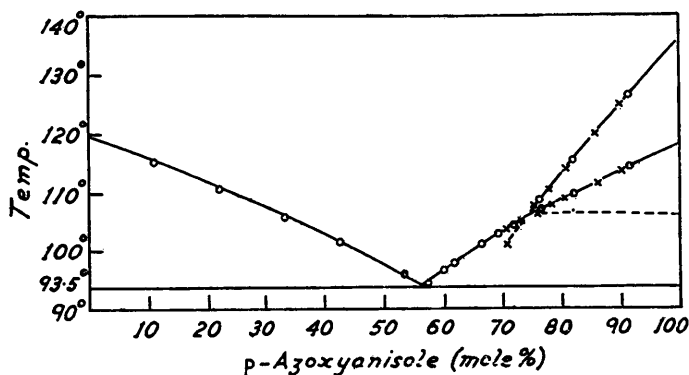


FIG. 6. The system *p*-azoxyanisole-*p*-anisic acid.

○ Melting curve points.  
× cooling curve points.

Phenanthrene was kindly provided by Mr. P. M. G. Bavin; it had been purified by treatment with maleic anhydride followed by chromatography and had m. p. 100° (lit., 100°).

The remaining materials were commercial products and were recrystallised; they then melted sharply at temperatures agreeing with those given in the literature, *viz.* (solvent in parentheses): *p*-azoxyanisole (alcohol), 118°, 136°; anisic acid (water), 184°; acetanilide (water), 114°; azobenzene (alcohol), 68°; azoxybenzene (alcohol), 36°; cinnamic acid (water), 133°;  $\beta$ -naphthylamine (alcohol), 110°;  $\alpha$ -naphthylamine (alcohol), 50°; quinol (water), 173°.

*Investigation of Phase Diagrams by the Optical Method.*—Intimate mixtures of the two components in known proportions were prepared in the usual way, by fusion and rapid cooling. The finely powdered residue was then heated in a wide capillary tube in a bath, and observed between crossed sheets of polaroid. The mixture was well stirred throughout with a thin glass rod. The bath consisted of a 1-l. beaker containing dibutyl phthalate and stirred

vigorously. The temperature was measured with a standardised thermometer graduated in  $0.1^\circ$ . The transitions from anisotropic to isotropic liquid were invariably very sharp, and reproducible within  $\pm 0.1^\circ$  whether the bath-temperature was rising or falling. The m. p. of the mixed solids could also be determined very accurately when the liquid phase formed was isotropic, from the disappearance of birefringence on fusion. It was not easy to determine m. p.s accurately when the liquid formed was anisotropic, but with care and experience they could be measured within  $\pm 0.2^\circ$ ; for this the bath-temperature must be changed exceedingly slowly, and the solid periodically allowed to settle.

*Investigation by the Thermal Method.*—In order to study the phase diagrams by the standard cooling-curve method, it is necessary to use very low rates of cooling since the heats of transition from mesomorphic to isotropic liquid are small. The measurements were carried out with 10-g. samples in a Dewar flask ( $6'' \times 1''$ ) immersed in an oil thermostat ( $\pm 0.05^\circ$ ). The flask was closed with a cork carrying a glass stirrer and a standardised thermometer. The bath-temperature was held within  $10^\circ$  of the temperature of the transition being observed; the various transitions were observed separately in different experiments for a given sample.

The temperature of the sample was observed at half-minute intervals, and the readings were plotted as logarithms of temperature differences against time. Fig. 2 shows a typical cooling curve, and illustrates the typical appearance of a liquid-liquid phase transition.

The liquid-liquid transition temperatures were reproducible within  $\pm 0.1^\circ$ . The solid-liquid transitions could not always be determined so accurately, since the melts readily supercooled, but the errors certainly did not exceed  $0.2^\circ$ .

*Results.*—Figs. 1b and 3—6 show the experimental results and inferred phase diagrams for the various transition temperatures in the binary systems, *p*-azoxyanisole plus quinol, phenanthrene, *p*-anisylidene-*p*-anisidine, *p*-anisylidene-*p*-bromoaniline, and anisic acid. A number of other systems have also been studied with similar results. The general form of the phase diagrams follows from results obtained by the optical method, but the critical regions were checked by careful thermal analysis.

#### DISCUSSION

In the systems reported here a substance (*p*-azoxyanisole) itself giving a mesomorphic phase is mixed with a "normal" second component. It will be observed that there are no invariant lines in the diagrams, implying that there are no two-phase liquid regions. Moreover the transitions from anisotropic liquid to isotropic liquid were in all cases quite sharp, and there was no indication whatsoever that any of the transitions took place over a range of temperature. The breaks in the cooling curves corresponding to such transitions were similar in form to the break observed in the cooling curve for *p*-azoxyanisole itself.

The case of quinol is interesting, since de Kock (*loc. cit.*) claimed this system as an example of a case where a two-phase liquid region occurred. It is clear from our investigation (cf. Fig. 1b) that the two-phase region, if it exists at all, is certainly very much smaller than de Kock inferred. His experimental methods could therefore evidently lead to misleading conclusions. We should add that preliminary investigations by the optical method suggested that invariant lines occurred in some of the systems which we examined; but this was not confirmed by detailed thermal analysis.

We have also studied the following systems, which appear similar in behaviour to those reported above; namely: azoxyanisole plus *p*-anisylidene-*p*-chloroaniline and *p*-toluidine, *p*-chlorobenzylidene-*p*-anisidine, *p*-methylbenzylidene-*p*-anisidine, 4 : 4'-dichloroazoxybenzene, acetanilide,  $\alpha$ - and  $\beta$ -naphthylamine, azoxybenzene, azobenzene, and cinnamic acid; azoxyphenetole plus 4 : 4'-dichloroazoxybenzene and  $\beta$ -naphthylamine.

For the equilibrium between the two liquid phases straightforward thermodynamic reasoning (cf. Guggenheim, "Modern Thermodynamics," North Holland Publ. Co., Amsterdam, 1949) leads to the relation :

$$(S_m^I - S_m^A) \frac{dT}{dx} = (x^I - x^A) \left( \frac{d\mu_1}{dx} - \frac{d\mu_2}{dx} \right) \dots \dots \dots (1)$$

where  $S_m^I$ ,  $S_m^A$  are the entropies per mole of the isotropic and anisotropic phases respectively,  $x^I$ ,  $x^A$  are the mole fractions of component 2 in the two phases,  $\mu_1$ ,  $\mu_2$  are the

chemical potentials of the two components, and  $T$  is the transition temperature. It follows that in general  $x^I = x^A$  only if  $dT/dx$  vanishes; that is, the two phases can have identical compositions only if the transition temperature is a maximum or minimum.

Equation (1) can be rewritten in the form

$$x^I - x^A = \frac{dT/dx}{T(d\mu_1/dx - d\mu_2/dx)} (H_m^I - H_m^A) \quad . \quad . \quad . \quad (2)$$

where  $H_m^I$ ,  $H_m^A$  are the heat contents of the two phases. Since the factor involving differentials should be much the same for transitions of this kind as for normal kinds of phase transition, the order of magnitude of  $(x^I - x^A)$  should tend to be proportional to the heat of transition. Since heats of fusion of anisotropic liquids are of the order of one-tenth of the heats of fusion of typical solids, the two-phase regions where the two liquids coexist should be correspondingly smaller than the regions where solid and liquid phases coexist in normal systems. It would not be surprising to find that the two-phase regions in the former case were too small to be detected by normal methods of investigation.

An alternative explanation of our results would be that the transition from anisotropic liquid to isotropic liquid is not a first-order transition. In that case the heat of transition would be zero and the two phases would necessarily have identical compositions. Our results do not distinguish between these two possibilities.

In the mixed liquid crystal, the liquid is presumably composed of oriented domains. These should presumably be formed more readily when the "normal" molecules are similar in shape and size to the molecules of the anisotropic component. If significant two-phase liquid regions are to occur, they should then do so in cases where the "normal" molecules differ in shape, size, or polarity from those of the anisotropic component. Our results show, however, no significant difference between the phase diagrams for "normal" components of different type. We feel therefore that the same will probably be generally true for such binary systems, and that systems with significant two-phase liquid regions will be rare if indeed they occur at all—except of course for pairs of substances which also give incompletely miscible isotropic melts.

The main qualitative difference between the various systems we have studied lies in the slopes of the liquid-liquid transition lines. These are steeper the more the second component departs from the criteria for mesomorphism. This might be expected; for the disturbing effect of a solute on the mesomorphic phase should be greater the smaller the tendency of the solute molecules themselves to give oriented melts. The slopes and shapes of the transition lines should therefore provide valuable information about the structure of the mesomorphic state and such investigations are now in progress.

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