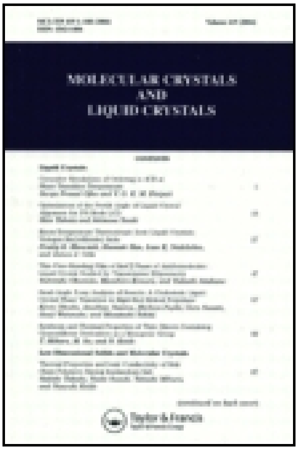

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Binary Phase Diagrams for Mixtures by Long Chain Esters

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Binary Phase Diagrams for Mixtures by Long Chain Esters

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Binary phase diagrams for mixtures of the ester tetradecyl tetradecanoate with dodecyl octadecanoate, dodecyl hexadecanoate and dodecyl tetradecanoate and of dodecyl tetradecanoate with hexadecyl decanoate and tetradecyl dodecanoate are reported. They are compared with phase diagrams for paraffin mixtures and related to dielectric absorption in the esters.

It has been established that the intensity of dielectric absorption in crystalline long chain aliphatic esters is strongly influenced by the presence of impurities, whether the ester group be at the end[1] or near the middle[2] of the chain. The application of zone refining for the removal of homologous impurities appeared to be feasible, but difficulties were encountered whose understanding required some knowledge of representative phase diagrams.

Although several phase diagrams have been reported[3,4] for mixtures of ethyl and methyl esters, only one system involving esters having the ester group near the middle of the chain appears to have been described.[5] It is notable for the presence of a maximum in the liquidus curve, suggesting the formation of a 1:1 compound. The present report is a preliminary examination of several systems based on tetradecyl tetradecanoate and dodecyl tetradecanoate, selected as typical of the esters whose dielectric properties have been studied.[2]

The phase diagrams have been determined by visual observation in polarised light, using a microscope fitted with a Mettler FP2 hot stage. Only liquidus curves, defined as the temperature of fusion of the last crystal in the field of view at a standard heating rate of 1° mm, were recorded. The beginning of fusion, defining the solidus curve, was difficult to observe and has not been recorded. Observation of fusion rather than solidification avoids problems associated with supercooling.[1] Nevertheless, the solidification

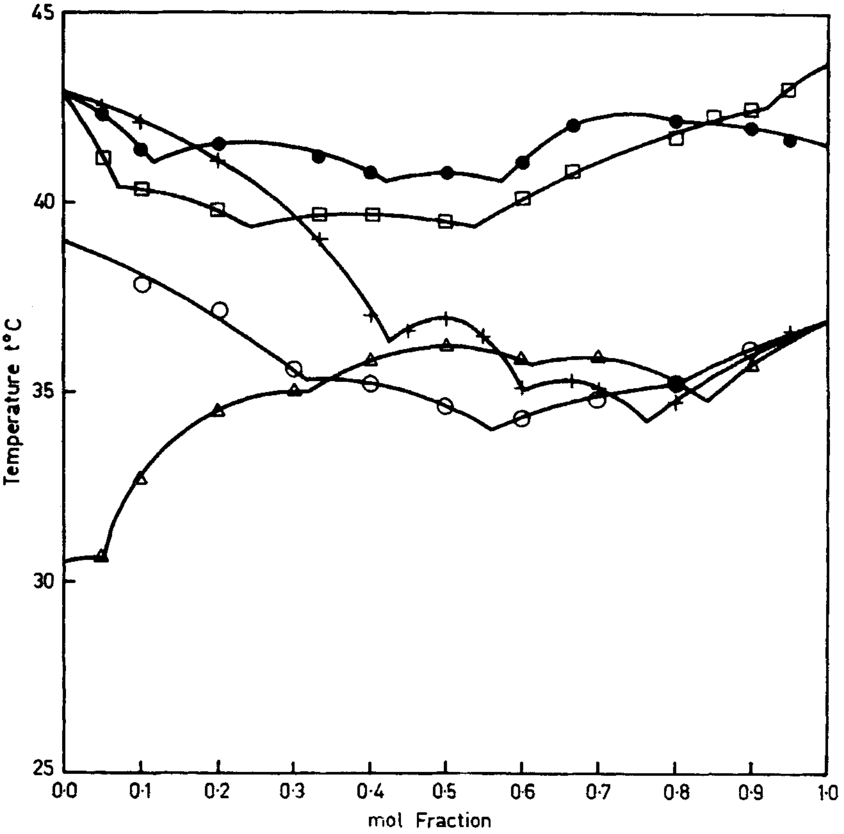

FIGURE 1 Phase diagrams for binary mixtures of long chain esters. Concentrations are given as mole fractions of the material listed second for each system.
□——□ tetradecyl tetradecanoate-dodecyl octadecanoate
■——■ tetradecyl tetradecanoate-dodecyl hexadecanoate
+——+ tetradecyl tetradecanoate-dodecyl tetradecanoate
○——○ tetradecyl dodecanoate-dodecyl tetradecanoate
△——△ hexadecyl decanoate-dodecyl tetradecanoate

of all systems was examined to check the formation of metastable phases. All the esters were synthesised in this Laboratory. The main limitation on the diagrams (Figure 1) is the purity of materials, particularly of esters other than the key pair.

The phase diagrams are complex, generally suggesting the presence of several intermediate phases. The present measurements for the system dodecyl tetradecanoate-hexadecyl decanoate agree qualitatively with the previous report,[5] but suggest the presence of three rather than one intermediate phase, primarily because more mixtures have been observed. The data for the additional systems demonstrate the generality of the difference in behaviour of mixed esters and mixed ketones noted in the earlier report.[5]

In none of the systems was there evidence of metastable phases such as observed[3,4] in ethyl and methyl esters nor of a stable high temperature phase such as found[6] in paraffin mixtures. However there is a striking resemblance between the general features of the ester liquidus curves and the structure of the phase boundaries between high and low temperature forms of the paraffins. Although it seems possible to interpret the ester diagrams in terms of the formation of several compounds, as has been done for mixtures of acids,[7] caution is necessary until more detailed data are obtained.

For the interpretation of dielectric properties, the most interesting feature is the presence of phase boundary intersections for additions of 0.05 to 0.10 mole fraction in many if not all systems. This is just the concentration range in which the effect of annealing on dielectric absorption changes sign.[2] At low concentrations, absorption in quenched samples decreases on annealing, at high concentrations it increases. The present work suggests correlation of this phenomenon with the presence of a phase boundary. The presence of a phase boundary, in some cases associated with little change in solidification temperature, may also account for the difficulties encountered in the application of the zone refining technique.

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