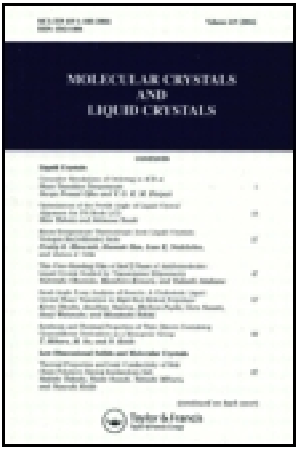

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Surface and Bulk Properties of Azoxyanisole

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Surface and Bulk Properties of Azoxyanisole

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p-Azoxyanisole has a nematic liquid crystal phase in addition to the normal isotropic liquid phase. In line with the rapid increase in interest in liquid crystals in recent years, its properties have been the subject of several investigations. As with nearly all initial explorations, however, these studies have raised questions as well as provided answers. Barrall, Porter and Johnson[1] measured specific heat as a function of temperature, using differential scanning calorimetry and reported an unexpected knee in the liquid-liquid transition peak. Neumann and Sell[2] studied the surface tension and density of azoxyanisole. A modified Wilhelmy technique which allowed continuous temperature scanning was used to make surface tension measurements. Temperature scanning density measurements were made by measuring the buoyancy of a glass bead suspended in the liquid from an electrobalance. Their results showed a step decrease at the liquid-liquid transition in both surface tension and density on heating. A split peak of the nature of that reported by Barrall, Porter and Johnson[1] was observed but not reported. Meanwhile, Robinder and Poirier[3] carried out a study of the solid phase of the same substance. They reported the existence of three crystalline solid phases, one of which had not been observed previously. More recently, Chow and Martire[4] reported dsc heats of the transition for the nematic-isotropic transition in close agreement with those of Barrall et al.[1] as well as those obtained by Arnold[5] who used conventional calorimetry. They observed only two solid phases, however. There seems, therefore, ample reason to attempt to obtain more detailed information regarding both the liquid-liquid and solid-solid transitions in azoxyanisole.

The present paper reports the results of a study of the nature of the liquid-liquid transition in azoxyanisole through measurements of the surface tension. Measurement of density allows the changes in surface properties reflecting bulk effects alone to be properly discounted. In addition, an attempt has been made to re-examine the results of Robinder and Poirier with regard to the number and kind of solid phases exhibited.

Surface properties can be significantly affected by the presence of an impurity if it happens to be adsorbed at the surface. Therefore, the purity of the samples used is of considerable importance. Since optimum purification procedures for liquid crystal-type materials have not yet been established three methods were tried. These were recrystallization from solution, zone refining, and a combination of the two. The zone-refining was carried out in a Fisher apparatus. Approximately 15 passes of a 20 cm. colum were made at a rate of the order of 0,5 cm/hr. The current through the heating coil was adjusted such that the width of the liquid zone was approximately 2 cm. The processed column was then separated into 5 segments.

An accurate, absolute value for purity is not easily determined. However, the width of the melting peak in a DTA scan is generally accepted as measure of relative purity. Samples of p-azoxyanisole obtained from Eastman Organic Chemicals and purified as described in the preceding paragraph were therefore compared with a sample of known high purity by this method. The reference sample used was purchased from Princeton Chemicals Corporation with a purity of 99.9%. Peak widths for samples from the center sections of the zone refined columns were very similar to those obtained with the Princeton material, with a tendency to be somewhat narrower. Samples of material which had been zone refined after recrystallization from n-pentanol exhibited the narrowest peaks. These comparisons thus provide a positive indication that the purity of the samples used in this study was at least 99.9%.

Isothermal surface tension measurements (see below) with the Princeton Chemicals product as well as the zone-refined-only Eastman product showed changes over periods of hours, strongly suggesting adsorption of impurities at the liquid/ vapour interface. Temperature scanning surface tension measurements for both samples resembled more the results reported by Neumann and Sell[2] for samples which had been recrystallized from solution than those reported below (Fig. 1 and 2) for our sample which was first recrystallized from solution and subsequently zone refined.

The apparatus and technique used in the surface tension and density measurements has been described in previous publications[2,6,7]. Briefly, it consist of a modified Wilhelmy technique in conjunction with an electrobalance and a temperature scanning device. The sample is held in a double-walled glass cell surrounded by a thermostating liquid and an argon atmosphere. A glass bead was used in place of the Wilhelmy plate for the density measurements. The bead was suspended from a thin platinum wire and completely immersed in the sample to minimize capillary effects. The density of the sample can be determined from

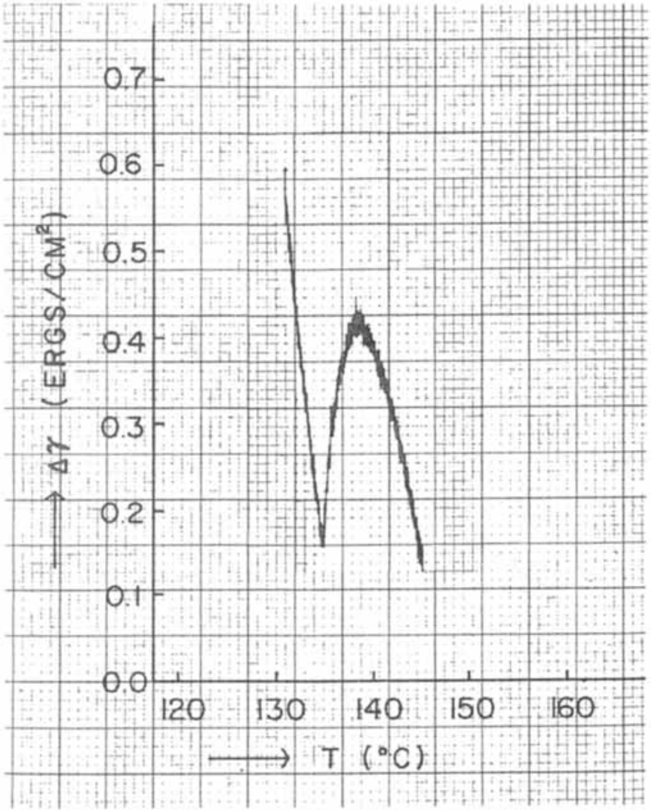


FIGURE 1 Change of surface tension of p-azoxyanisole on heating

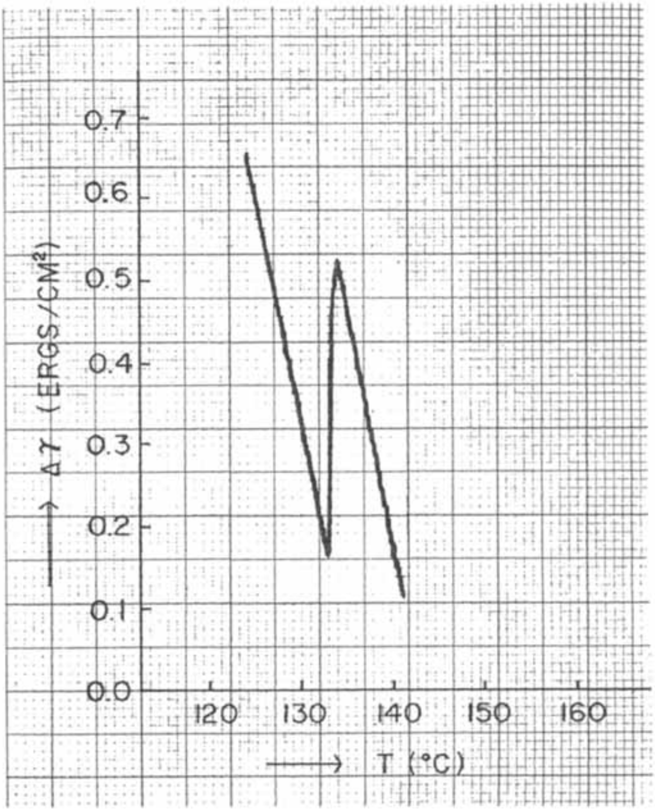


FIGURE 2 Change of surface tension of p-azoxyanisole on cooling

the balance readings when the bead is successively immersed in the sample, air and a liquid of know density. Glycerine was used in this study as the reference liquid.

The sample of highest purity from the central part of the column was, after the purity determinations, sufficient for two independent measurements of the temperature dependence of the surface tension. These two sets of runs were performed at different sensitivity settings of the electrobalance. Each of the two batches was run through several heating and cooling cycles. Typical surface tension data, for a heating and a cooling scan, respectively, are shown in Figures 1 and 2. Changes in surface tension rather than absolute values are shown. The variation in step height from one run to another was normally not more than 10%. The curves in Figures 1 and 2 are actual recorder outputs.

We conclude that the transition from the nematic phase to the isotropic liquid phase is, for a highly purified material, accompanied by a definite *increase* in surface tension. This is in contrast to the small *decrease* inferred by Neumann and Sell[2] for a material which had been purified only by recrystallization from solution.

Whereas some cholesteryl esters show drastic differences in surface tension between heating and cooling runs,[6,7] the traces of Fig. 1 and Fig. 2 are remarkably similar. The cause of the small, but reproducible, difference in this case cannot be definitely established at this time. As curious as this asymmetry may be it does not impinge on the basic finding regarding the direction of the surface tension change in the liquid-liquid transition.

A typical heating trace for the change in density with temperature is shown in Figure 3. The step height in the density due to the phase transition is 0.004 g/cm,[3] in agreement with the value obtained by Neumann and Sell.[2] The curve clearly shows that a sharp decrease in density accompanies the increase in surface tension. It is, therefore, clear that the effect shown in Figures 1 and 2 cannot be accounted for by a change in density alone. Density measurements were made with several grades of the zone refined material. The small amount of

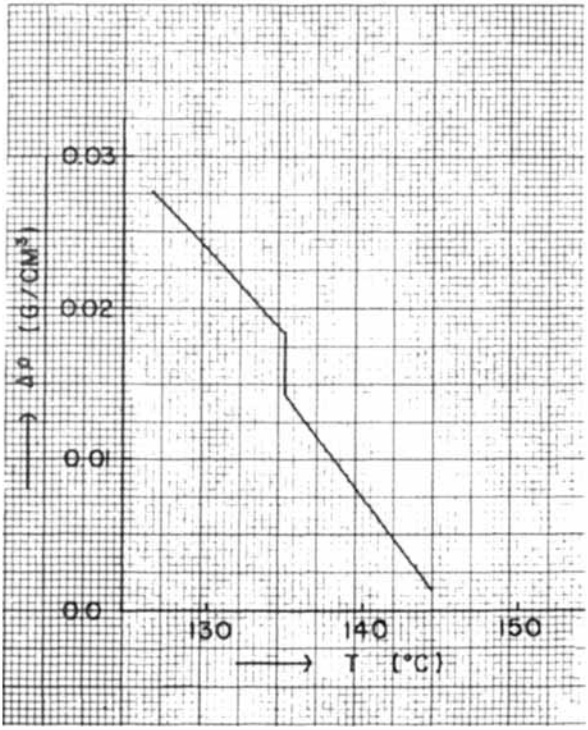


FIGURE 3 Change of density of p-azoxyanisole on heating

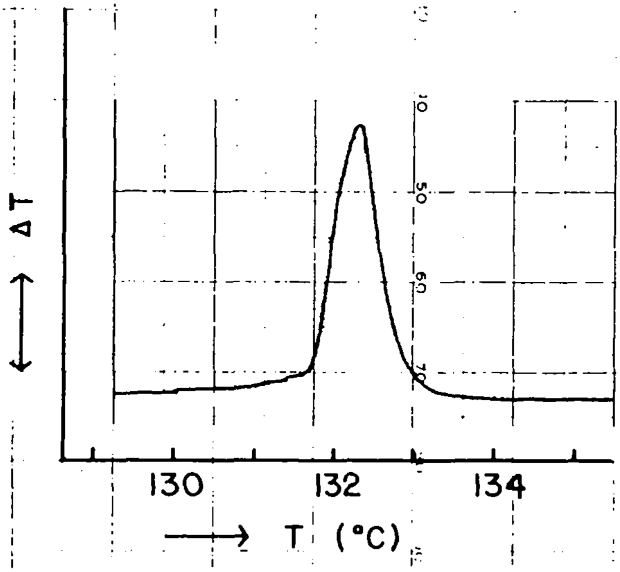


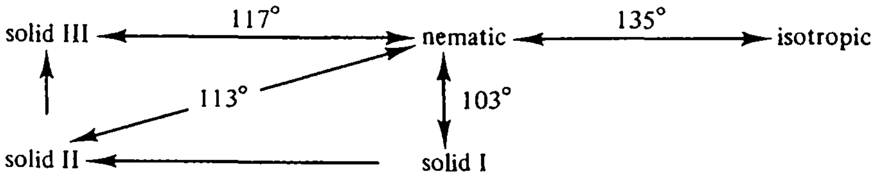
FIGURE 4 DTA peak for the nematic/isotropic liquid transition of p-azoxyanisole on heating

impurity present would not be expected to significantly affect measured values of a bulk quantity such as density. It is interesting to note that with our zone refined material there is no indication of pre-transformational density changes as reported by Price and Wendorff[10] in their study of the density of material which had been purified by recrystallization only.

A liquid-liquid transition peak for a zone refined sample is shown in Figure 4. The particular trace shown was obtained during a heating scan and clearly shows just one transition. This coupled with the fact that evidence of secondary peaks was seen on scans of the relatively impure substance, indicates that the secondary peak reported by Barrall, Porter and Johnson and also observed by Neumann and Sell was due to an impurity.

A number of DTA scans well below the nematic/solid transition temperature were also made. Only samples of zone-refined, and recrystallized and zone refined material of relatively high purity were used. Samples from the ends of the zone refining column, for example, were not used.

Results of these tests will be described using the nomenclature of Robinder and Poirier[3] which is most easily explained using their own schematic diagram:



The temperatures shown are transition temperatures obtained on heating. The single-headed arrows indicate that solid II is monotropic with respect to solid III and solid I is monotropic with respect to solid II. Chow and Martire[4] report only the solid phases I and III.

The results of the tests reported here confirm the existence of at least two solid phases. However, for many cooling runs with material which had been zone refined after recrystallization, three peaks were observed. A typical example is shown in Fig. 5. The amount of undercooling preceding each transition, and hence the relative spacing and size of the peaks, varied considerably from one scan to the next in the manner reported by Robinder and Poirier. Ultimate proof of the existence of the solid II could, however, not be obtained, since we in no case were able to observe the transition: solid II nematic. Heating immediately after the appearance of the second transition peak in a cooling run invariably resulted in melting at 117°C, indicating the presence of solid III.

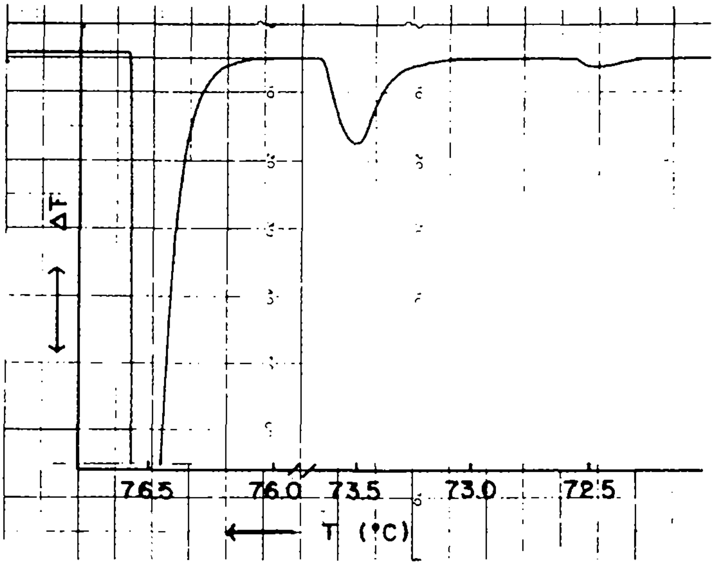


FIGURE 5 DTA peaks of p-azoxyanisole indicating the existence of three solid phases

A careful study of material which had been only zone refined without prior recrystallization from solution, as well as the Princeton Chemicals product, showed clearly the existence of two solid phases. No evidence for the existence of a third solid phase was obtained, i.e. cooling runs contained at most two peaks. These two types of samples hence gave results indentical with those reported by Chow and Martire.[4]

Acknowledgements

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