

On the possibility of a critical transition in para-azoxyanisole

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The values of the specific volumes of liquid-crystalline para-azoxyanisole are investigated experimentally in the temperature range 114.9–165°C at pressures up to 930 atm. Graphs of the V - P isotherms and V - T isobars are given in these ranges. Expressions are given for the temperatures of the phase transitions from the nematic phase to the isotropic and solid-crystalline phases as functions of the pressure. The values of the specific volumes of para-azoxyanisole in the region of the transition from the nematic to the solid-crystalline phase are given in a separate graph. On the basis of the experimental data, graphs are constructed for the variation of the discontinuities of the specific volume in the transition from the nematic phase to the isotropic liquid, and the critical values of the pressure and temperature are determined by an extrapolation method. Some conclusions concerning the possible types of phase transition in para-azoxyanisole are drawn.

Para-azoxyanisole (PAA) occupies a special place in the study of liquid-crystalline substances: in it, the liquid-crystalline state was discovered by one of the first investigators as long ago as 1889^[1]. Subsequent investigations have shown that PAA is the first member of the homologous series of dialkoxazoxybenzenes, with a nematic phase in the temperature range 115–135°C. PAA was one of the first liquid-crystalline substances to be studied by the ultrasonic method^[2], the orientational effect of electric and magnetic fields has been studied in it^[3], an x-ray structural investigation has been carried out^[4], and so on.

The thermodynamic properties of PAA under atmospheric pressure (the specific heat C_P ^[5], the heats of the transitions^[6,7], the effect of an electric field on the phase-transition temperature^[8], and also the changes of the phase-transition temperatures with pressure^[9-11]) have also been sufficiently well studied. However, until recently, there were no data on the behavior of the specific volumes of liquid crystals (including PAA) under pressure. Such results were first reported by us at the Second All-Union Conference on Liquid Crystals^[12]. The investigations were carried out on para-azoxyanisole in the temperature range 114.9–147°C and at pressures up to 400 atm, and then the temperature range was extended to 165°C and the pressures to 930 atm.

Our experimental setup^[13] made it possible to perform measurements of temperature with an accuracy of $\pm 0.005^\circ\text{C}$, of pressure with accuracy ± 4 atm, and of the specific volume with accuracy 10^{-5} cm³/g, but the process of measuring each isotherm took a rather long time (10–13 hours) and we rarely managed to maintain the thermostatic control with a precision better than $\pm 0.05^\circ\text{C}$, which we take as our estimate of the accuracy of the temperature measurement.

In all, we carried out measurements on 27 isotherms, 11 of which are shown in Fig. 1. As can be seen from the figure, the specific volume of the isotropic phase decreases practically linearly at low pressures, and appreciable nonlinearity appears at pressures above 400 atm; therefore, the initial measurements gave practically parallel straight lines in the isotropic phase. The error in the pressure measurements, as noted above, amounts to ± 4 atm, and therefore the measurements of the specific volumes at low pressures (~ 20 atm) are highly inaccurate and we obtained values of the volumes at normal pressure by the extrapolation method.

When we reach the temperature of the phase transition from the isotropic liquid to the nematic phase, which is determined by an equation of the form

$$t^\circ\text{C} = t_{p=0} + \frac{dt}{dP} P,$$

a substantial volume discontinuity is observed, which tells us that this phase transition is a first-order transition. This behavior of the isotherms is not unexpected, since we already knew previously about the heat of the transition^[6,7] and the discontinuity in the specific heat C_P ^[5].

The pressure dependence of the phase-transition temperature is described by a straight line, given by the above equation with $t_{p=0} = 135.8^\circ\text{C}$ and $dt/dP = 0.0325$ deg/atm. These data are in good agreement with the experimental data known in the literature^[9-11]. The slight discrepancy in the transition temperature under normal pressure can be explained by the purity of the substance (sample), by the technology of its synthe-

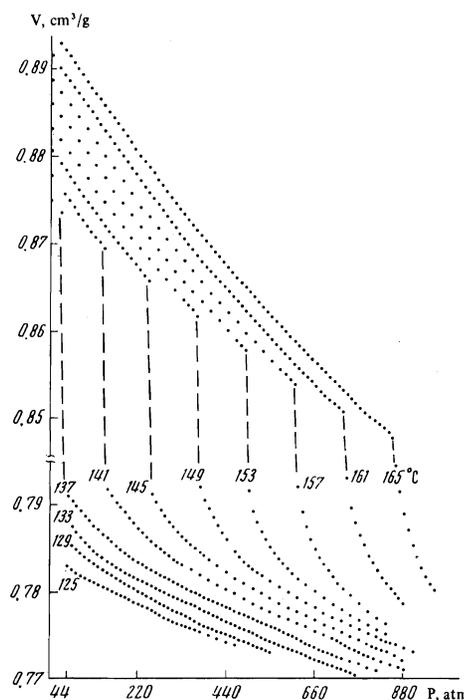


FIG. 1. Isotherms of the specific volumes of para-azoxyanisole in the range of pressures up to 930 atm.

sis and, in general, the previous history of the sample, and also by the method of measurement. Thus, in measurements by the method of lowering the temperature (each successive isotherm has a lower temperature than the preceding one) the value $t_{P=0} = 136.5^\circ\text{C}$, while the value of dt/dP also changes, on average, by 3%.

The values of the specific volumes of the nematic phase depend nonlinearly on the temperatures and pressures; this nonlinearity is especially important near the phase transition to the isotropic phase. Such behavior can be explained by the important pre-transition phenomena, which, in the given case, increase with rising temperature (Fig. 1) and pressure (Fig. 2). A further increase of the thermodynamic forces leads to equalization of the values of the specific volumes, which behave monotonically in the graphs up to the next phase transition, from the nematic to the solid-crystalline phase. In both graphs one can see fairly well that, as both the pressure and the temperature are raised, the discontinuities in the specific volumes decrease. Graphs of the dependence of the values of the specific-volume discontinuities on the temperature and pressure are given in Fig. 3. The graphs are straight lines and, consequently, can be extrapolated to the value $\Delta V = 0$, if the behavior of the specific volumes at the higher temperatures and pressures is the same as in the range investigated.

It is well known^[11] that PAA decomposes in air at a temperature $\sim 250^\circ\text{C}$, while in hermetic ampoules and in polysiloxane liquid the temperature range of existence of PAA is extended to 280°C and the pressure range to 6500 atm. Moreover, in the same experiment measurements of dt/dP were performed up to 6000 atm, and deviations of the measured quantity from linearity were not observed. All of this gives grounds for assuming that the change in the discontinuity of the specific volume may also be a linear function of the temperature and pressure, and, consequently, we can expect a critical phase transition from the isotropic liquid to the nematic phase at the extrapolations obtained ($P_{\text{cr}} = 2450$ atm and $t_{\text{cr}} \approx 218^\circ\text{C}$), i.e., before the substance begins to decompose.

We note that Hanus^[15], while studying the effect of an

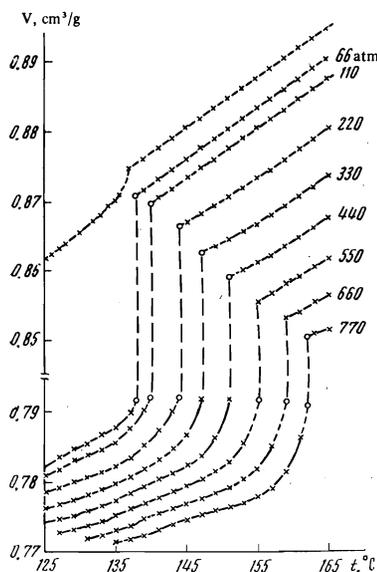


FIG. 2. Isobars of the specific volumes of para-azoxyanisole in the temperature range from 125 to 165°C (the upper curve is calculated from [14]).

electric field on liquid crystals, remarks that, since a strong electric field generates a preferred alignment of the molecules in the isotropic phase, values of the field, temperature and electric polarization are possible such that the isotropic and nematic phases should become indistinguishable above these values. If to this we add that most investigators of the optical properties of liquid crystals (LC) mention the considerable orienting action on LC by pressure on a glass cover, while studies under pressure show a substantial dependence of the phase-transition temperature on the pressure, the possibility of obtaining a critical point at certain pressures and at the corresponding temperatures becomes obvious.

Investigations carried out by a number of authors^[14, 16-18] on the density of PAA under normal pressure have given highly contradictory results for the values of the measured quantity in the region of the phase transition from the nematic to the solid-crystalline phase (NLC-SC) and results that are in good agreement for the isotropic phase and the isotropic-nematic (IL-NLC) phase transition. Thus, the authors of^[16] mention that, in the measurements of the molar volume of pure PAA in the temperature range $50-170^\circ\text{C}$, anomalies are detected in the transition from the nematic phase to both the solid-crystalline and the isotropic phase, the volume changes in the NLC-SC transition being almost 30 times greater than the volume change in the NLC-IL transition. The measurements reported in the papers^[14, 17] gave no noticeable special features at all in the NLC-SC transition.

The results of our investigations of this region are given in Fig. 4. The phase transition to the solid-crystalline phase is observed in six of the nine isotherms given, and in Fig. 1 this transition is noticeable, on a smaller scale, on the isotherms $129, 133, 137$ and 141°C . On all these isotherms the values of the specific volumes in the region of the transition fit on a smooth curve with no clearly pronounced discontinuities, even when the pressure steps are reduced to 1 or 2 atm. This can be seen particularly clearly on the isotherm 127°C , where eight points were measured in the transition region.

The pressure dependence of the phase-transition temperature is described by the same straight-line equation as for the transition to the isotropic liquid: $t^\circ\text{C} = 116 + 0.034OP$. Here, the discrepancy between the value of dt/dP and the data of other authors ($21.6 \times 10^{-3} - 25.6$

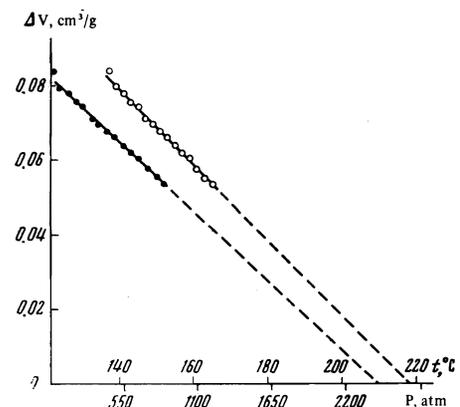


FIG. 3. Dependence of the magnitude of the specific-volume discontinuity on the temperature and pressure in the transition from the isotropic to the nematic phase of para-azoxyanisole: $\circ - \Delta V = f(t)$, $\bullet - V = f(P)$.

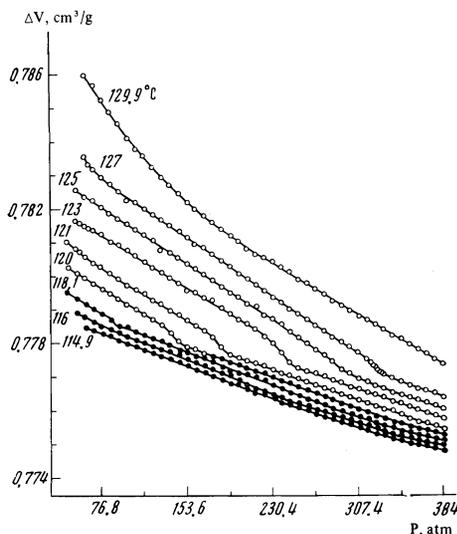


FIG. 4. Behavior of the specific volumes of para-azoxyanisole in the region of the phase transition from the nematic to the solid-crystalline phase.

$\times 10^{-3}$ deg/atm) is substantial. We explain this by the fact that the graph of the dependence $t_{tr} = f(P)$ was plotted from the average continuous-transition points, whereas the value of dt/dP obtained from the point of onset of the nonlinearity gives $dt/dP = 0.029$ deg/atm.

We note that, using the Clapeyron-Clausius equation, from which we obtain $\Delta V = (\Delta T/\Delta P)(\Delta Q/T)$, and the experimental data for the heats of the transitions^[5, 11] and values of dT/dP , from our data and the data of other authors we can estimate the magnitudes of the discontinuities of the specific volumes for the transitions from the nematic to the solid-crystalline and isotropic phases:

$$\Delta V_{NLC-IL} \approx 3 \times 10^{-3} \text{ cm}^3/\text{g}, \quad \Delta V_{NLC-SC} \approx 0.1 \text{ cm}^3/\text{g},$$

i.e., the volume discontinuity in the transition to the solid-crystalline phase should be two orders of magnitude greater than the volume discontinuity in the NLC-IL transition. The results of the measurements for the NLC-IL transition give values 25 times greater than the calculated value, at low pressures, while for the NLC-SC transition we obtained no volume discontinuity at all, even though the accuracy of the volume measurements made it possible to register an amount $\sim 10^{-5}$ cm^3/g .

Unfortunately, there are no data in the literature on the values of the heats of the transitions under pressure and we are denied the opportunity of carrying out an unambiguous comparison of the experimental values of ΔV with the calculated values for a given pressure. But the discrepancies between the estimated values of the specific-volume discontinuities and the experimental values can be attributed to the strong pressure dependence of the values of the specific volumes of the liquid-

crystalline phases; this is confirmed by comparing the specific volumes under normal conditions (the upper curve in Fig. 2, calculated from the data of Maier and Saupe^[14]) with the nearest isobar ($P = 66$ atm).

In conclusion, we remark that studies of the behavior of liquid crystals under pressure will also give valuable information about the features of phase transitions between liquid-crystalline phases. Thus, the measurements we have performed on cholesteryl valerate^[19] and also on eight members of the cholesteric series and the eighth dialkoxyazoxybenzene homolog have shown that transitions from the cholesteric to the smectic phase, from the nematic to the smectic phase, and from these mesophases to the isotropic liquid can occur continuously in a certain range of temperatures and pressures.

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