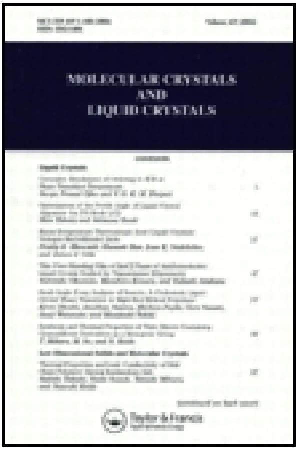

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Specific Volume Studies on p-Azoxyanisole

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Specific Volume Studies on *p*-Azoxyanisole

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The temperature variation of the specific volume of *p*-azoxyanisole was studied in the solid, nematic and isotropic phases. Sensitive measurements reveal that the specific volume does not vary linearly during solid–nematic phase transition, but is accompanied by an abrupt large jump of 7.74%. Specific volume jump at the nematic–isotropic transition is 0.35%. Pretransitional variations are found to occur only on the low temperature side of the phase transitions and are absent on the high temperature side. These results can be best explained on the basis of the Maier–Saupe theory.

Generally liquid crystalline phase transitions are regarded as first order phase transitions,[1–3] though recent investigations indicate that a few mesophase–mesophase transitions may be regarded as second order phase transitions.[2–5] Some investigators also believe that mesophase–isotropic transitions may be regarded as first order phase transition tending to second order.[6] Specific volume ($=1$/density) studies play an important role in deciding the order of a phase transition.[7] Though the specific volume (v) of PAA is widely studied,[8–18] yet in view of the marked controversy about the change of specific volume (Δv) at the solid–nematic transition,[8,9,11–18] it was thought fruitful to record a fresh set of careful observations.

The PAA was obtained in pure form from M/S Koch Light (England) and recrystallized 2 times each from ethanol and benzene. The transition temperatures were determined by a modified polarizing microscope similar to that of Gray.[19] The crystal–nematic and nematic–isotropic transition temperatures were found to be 117.4°C and 134.4°C respectively. The specific volume in the solid phase and around the solid–nematic phase transition was determined by using a dilatometer similar to that used by Price and Wendorff.[2,18,20,21] The level of the mercury in the capillary was read by a cathetometer (sensitivity ± 0.001 cm). The corrections for the temperature variation of the volume of the dilatometer and the thermal expansion of mercury were also made. In nematic and isotropic regions, the specific volume was determined by means of a sensitive pycnometer.[22] The thermal expansion of the volume of the pycnometer was also accounted for. The weighing was done by a sensitive balance (sensitivity = 10^{-4} gm). The correction for the mass of air present in the dilatometer and the pycnometer was also made.[2,23] For temperature variation a hot air oven (stability better than ±0.1°C), controlled by mercury-nitrobenzene regulator and hot wire tube 602, was employed. The temperature of the oven was kept uniform by continuously stirring the air within the oven. Void formation during the crystallization was avoided by annealing the PAA for ~20 hours at ~100°C before taking the final observations. Observations were taken when the level of the mercury or the substance in the capillary became perfectly stationary and constant.[18,20]

The temperature variation of v is shown in Figures 1 and 2. v increases linearly with increasing temperature in all the three phases, i.e. solid, nematic and isotropic phases except very near to the transition temperatures. In the

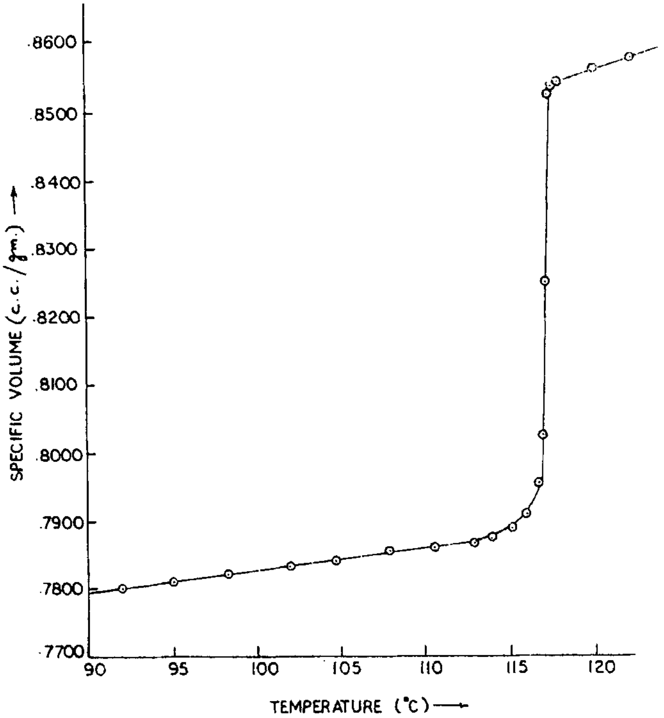

FIGURE 1 Specific volume (cc/gm) of PAA vs temperature (°C) in solid and nematic phases.

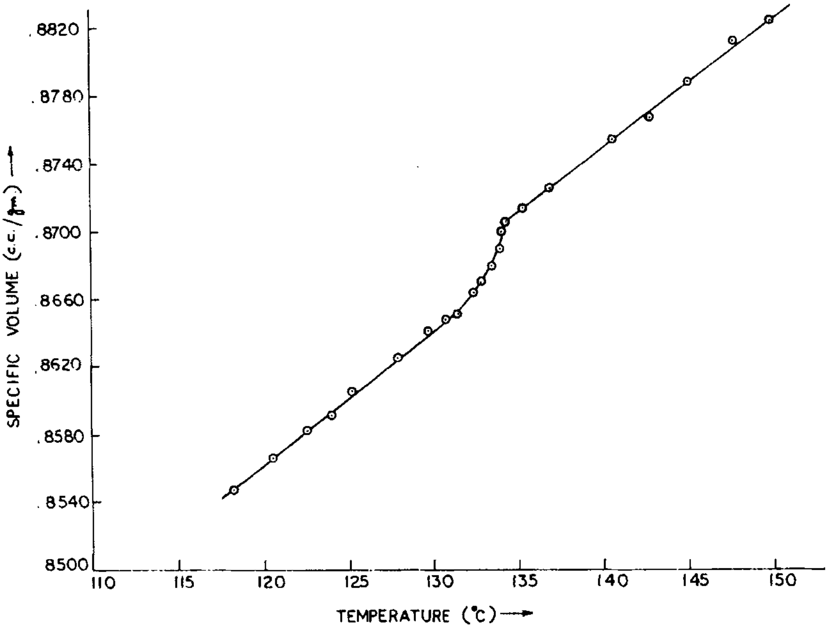

FIGURE 2 Specific volume (cc/gm) of PAA vs temperature (°C) in nematic and isotropic phases.

crystalline region the specific volume increases linearly up to ~4.5°C below the solid-nematic transition (Figure 1). The thermal expansion coefficient in the crystalline region is 4.11 × 10^{-4}/°C at 106.0°C and the volume jump at the crystal-nematic transition is 7.74%. It should be mentioned here that several previous workers[8,9,11-16] observed no appreciable change (i.e. volume jump <0.1%) at this transition. It seems that these authors could not obtain large volume changes due to some experimental flaws like supercooling, void formation etc. Recent measurements of Ubbelohde *et al.*[17] ($\Delta v/v$ = 11.03%), and Price and Wendorff[18] ($\Delta v/v$ = 6.9%) are in accordance with our observations. Price and Wendorff[18] have also pointed out that some voids may be left during crystallization leading to a low volume jump at the solid–nematic transition. The large value of 11.03% obtained by Ubbelohde *et al.*,[17] may be due to different calculational approach used by them. Perhaps Ubbelohde *et al.* have taken the value of molar volume at the crystal–nematic transition to be the value of molar volume in the crystalline phase at the transition (i.e. = 19.35 cc/mole). However, other authors including ourselves take it to be the specific volume at the transition on the nematic side, due to the reason that pretransitional effects in v are always found to occur on the low temperature side of the transition. From this

TABLE I.

Results of specific volume measurements on PAA by various workers

Sr. No. Investigators	Range of observations (°C)	Phase/phase transition	Temperature (°C)	Specific volume (gm/cc)	α (10^{-4}/°C)	$\Delta v/v$ (%)
1. (a) Schenk[a8] (b) Hoyer and Nolle[a13] (c) Runyan an Nolle[a14]	115–162	Solid	116	0.8534	8.71	
		Solid–Nematic	118.5			no change
		Nematic	128	0.8623	8.80	
		Nematic–Isotropic	135.0 (135.5)[b]			~0.5
		Isotropic	144	0.8783	7.13	
2. Jaeger[a9]	115.5–211	Solid	116	0.8543	9.09	
		Solid–Nematic	118.5			no change
		Nematic	128	0.8637	9.19	
		Nematic–Isotropic	135.0			0.38
		Isotropic	144	0.8796	7.14	
3. Becherer and Kast[a11]	116.5–145	Solid	116	0.8543	9.09	
		Solid–Nematic	118.5			no change
		Nematic	128	0.8637	9.19	
		Nematic–Isotropic	135.0			0.38
		Isotropic	144	0.8796	7.14	
4. Eichwald[a10]		Nematic–Isotropic	135.0			~0.31
5. Maier and Saupe[a15]	100–144	Solid	100	0.8457	7.54	
			116	0.8557	7.63	
		Solid–Nematic	118.5			$\lesssim 0.1$[c]
		Nematic	128	0.8640	9.20	
		Nematic–Isotropic	135.0 (135.8)[b]			0.35
		Isotropic	144	0.8796	7.14	

6. Porter and Johnson[a16]	119–160	Solid	116	0.8546	9.10	
		Solid–Nematic	118.5			no change[d]
		Nematic	128	0.8640	9.20	
		Nematic–Isotropic	135.0			0.36
		Isotropic	114	0.8796	7.14	
7. Mclaughlin, Shakespeare and Ubbelohde[17]		Solid–Nematic	118.2			11.03 (9.94)[e]
		Nematic–Isotropic	135.2			0.36
8. Price and Wendorff[18]	30–135	Solid	70.0	0.7839	4.1	
		Solid–Nematic	117.0			6.9
		Nematic	128	0.8626	9.4	
		Nematic–Isotropic	134.2			0.34
		Isotropic	135.0	0.8712	8.4	
9. Bahadur	90–150	Solid	106	0.7845	4.11	
		Solid–Nematic	117.4			7.74
		Nematic	128.0	0.8625	9.26	
		Nematic–Isotropic	134.4			0.35
		Isotropic	140.0	0.8749	8.61	

[a] Values are extrapolated from Figure 2 of Reference 16.

[d] Original transition temperature. In Porter and Johnson's paper the values of various workers are levelled taking the nematic-isotropic transition temperature to be 135.0°C.

[c] Maier and Saupe have mentioned nothing about the volume change at solid–nematic transition. However the value 0.1% has been extrapolated from the slopes of the specific volume plot in solid and nematic regions.

[d] Porter and Johnson merely extrapolated the specific volume curve of nematic region in solid phase. None of their values lies in the solid phase. It seems that on the basis of the observations of other previous workers they concluded that no volume change occurs at solid–nematic transition.

[e] Calculated value of the volume jump assuming that the pretransitional phenomenon occurs only on the low temperature side of the transition.

value (221.35 cc/mole) the recalculated value of Ubbelohde *et al.*,[17] for $\Delta v/v$ comes to be 9.94% (instead of 11.03%). Our value (7.74%) lies in between 9.94% and 6.9%. The pretransitional effect in PAA also occurs on the low temperature side of the transition, i.e. towards the crystalline region. A large volume change at the solid–nematic transition is naturally expected as the structure changes abruptly from a three dimensional closely packed crystalline state to a less packed nematic state.

A sudden jump (0.35%) in specific volume occurs at the nematic–isotropic transition (Figure 2), manifesting it to be a first order phase transition. The value of the thermal expansion coefficient (α) in the nematic phase ($= 9.26 \times 10^{-4}$/°C at 128.0°C) being higher than that in the isotropic phase ($= 8.61 \times 10^{-4}$/°C at 140.0°C) indicates that the tendency of increasing order with decreasing temperature is stronger in the liquid crystalline phase than in the isotropic phase (and also in the solid phase). This is the general case with the liquid crystals.[2,18,20,24]

The breadth of the nematic–isotropic transition is large in the case of PAA ($\sim$3.0°C). This value is smaller than the value ($\sim$4.0°C) obtained by Price and Wendorff.[18] Pretransitional effects at nematic–isotropic transitions are found to occur only on the nematic side. This shows that Frenkel's theory,[25–27] requiring the pretransitional effects on both the sides of the transition, fails to explain the specific volume results and the Maier–Saupe theory[15,18,29] is perhaps the best one to be applied in this case.

The calculated values[15] of A (i.e. the characteristic constant of the substance) and S_k (i.e. the degree of order at the nematic–isotropic transition temperature) are found to be 13.0×10^{-9} erg cm^6 and 0.443 respectively.

The results of various workers along with our own findings are summarized in Table I.

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