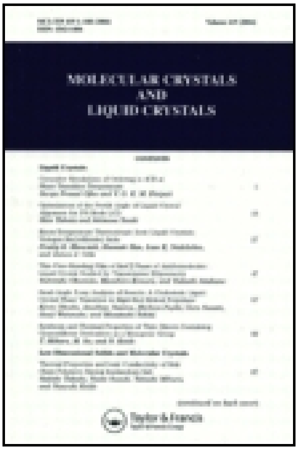

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Dilatometric Properties of p-Azoxyanisole (PAA), p-p-di-n-Pentyloxyazoxybenzene (PPAB) and Their Mixtures

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Dilatometric Properties of *p*-Azoxyanisole (PAA), *p*-*p*-di-*n*-Pentyloxyazoxybenzene (PPAB) and Their Mixtures

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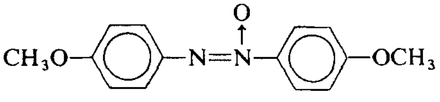
Dilatometric properties of two nematic liquid crystals, *p*-azoxyanisole (PAA), *p*-*p*-di-*n*-pentyloxy azoxybenzene (PPAB) and their mixtures have been measured with an Anton Paar digital density meter. It has been found that in both the nematic and isotropic phases of all the compositions, the density varies linearly with the temperature except in the region 2°C below the nematic isotropic transition. The density data have been used to determine the value of the thermal expansion coefficient.

I INTRODUCTION

The densities of relatively few mixed liquid crystals systems have been measured. Yet knowledge of densities which in turn implies knowledge of the molar volumes, is fundamental for the understanding of the phase behavior and other dilatometric properties of the mixed system. Density data can be used along with the refractive index data to obtain the polarizability and orientational order parameters of the liquid crystal mixtures. Several techniques have been employed to measure the densities of liquid crystals, viz. using a pycnometer,[1] a capillary dilatometer,[2] and using a density meter.[3]

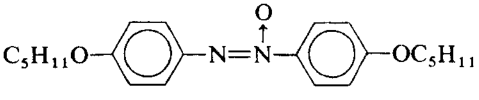
This work is concerned with the study of the densities of *p*-azoxyanisole, (PAA), *p*-*p*-di-*n*-pentyloxyazoxybenzene (PPAB) and their mixtures using the latest technique, the density meter, to measure the densities. The structural formulas and transition temperatures are:

p-azoxyanisole (PAA)



118°C nematic → 135.3°C isotropic

p-*p*-di-*n*-pentyloxyazoxybenzene



79°C nematic → 123°C isotropic

II EXPERIMENTAL PROCEDURE

The *p*-azoxyanisole (PAA) and *p*-*p*-di-*n*-pentyloxyazoxybenzene (PPAB) were obtained from Riedel (Hannover, Germany) and Eastman (Rochester, New York), respectively. The PAA and PPAB liquid crystals were recrystallized three times in ethanol and dried under vacuum before they were prepared into mixtures with mole fraction ratios of 0.02 increments. An indication of the purity of the PAA and PPAB liquid crystals was the microscopic observation of the two phase regions at the nematic-isotropic transition over a temperature of 0.1°C. For the mixtures, the two phase region occurred over a range of 0.2°C to 2°C. In the experiments, samples of about 1.5 gm were used.

The densities were measured using an Anton Paar Digital Density Meter Model DMA 02D. Using glycerol and quinoline as standards, various apparatus constants were determined at different temperatures to an accuracy of 0.04%. The temperatures were measured with a Mettler TM16 thermometer and maintained with a Poly Corp. Model 80 constant temperature circulator. The temperature stability during the measurements could be controlled to within ±0.1°C. The error in the measured density was estimated to be 0.08%.

III RESULTS AND DISCUSSION

The densities and expansion coefficients at various temperatures for PAA, PPAB and their mixtures all exhibit curves similar to the ones shown in Figure 1. Figure 2 displays the temperature dependences of the densities of all the

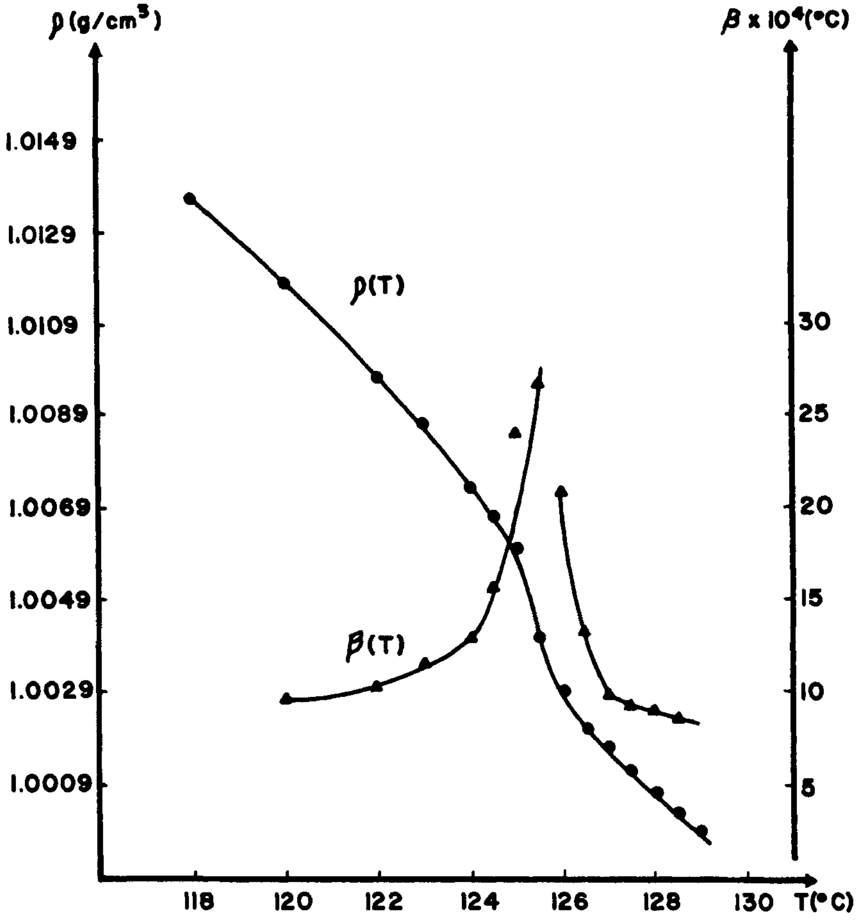


FIGURE 1 The densities and expansion coefficients of pure PPAB in the nematic and isotropic phases. The temperature dependent density and expansion coefficient curves for PAA and mixtures of PAA and PPAB exhibit behavior similar to that shown.

compositions studied. The sharp discontinuity in the expansion coefficients and sudden drop in the densities at the neematic-isotropic transition temperature clearly shows that the transitions are all first order. The sudden decrease of the density with temperature near the transition point can be attributed to the sudden change from the ordered nematic phase to the disordered isotropic phase, since the two phases differ mainly in the degree of molecular orientations. It was observed by microscopic studies that the nematic-isotropic phase transition was not sharp because the phase transition began with the formation of clusters which increased in size to give nematic droplets, then they

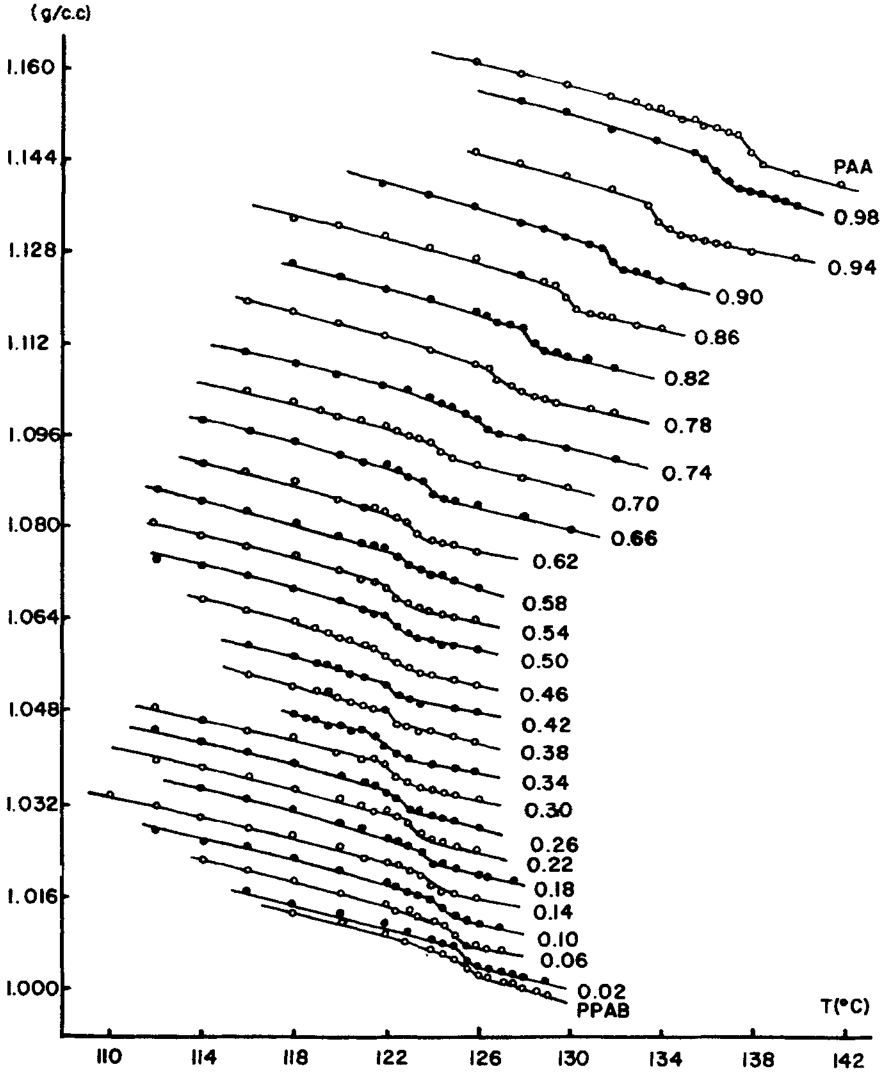


FIGURE 2 Temperature dependence of the densities of PAA, PHAB and their mixtures.

finally coalesced to complete the transition. For the pure PAA and PHAB samples, the two phase regions occurred over a 0.1°C range while for the mixtures, the two phase regions ranged from 0.2° to 2.0°C. In Table I, we have listed the densities of PPAB near the nematic isotropic transition temperature measured in this study and compared them to the densities reported in Ref. 4. As we see, the two sets of data are in good agreement. Our measured

TABLE I

Specific densities of *p*-*p*′-di-*n*-pentyloxyazoxybenzene

This study (accuracy 0.08 %) Temperature (°C)	Density (gm/cc)	De Jeu and Classen's study Temperature	Density
115.4	1.01362	115.8	1.0101
117.4	1.01178	117.5	1.0085
119.4	1.00973		
120.4	1.00870	120	1.0060
121.4	1.00732	121.2	1.0048
121.9	1.00668	121.7	1.0042
122.4	1.00409		
122.9	1.00288	122.6	1.0015
123.4	1.00211		
123.9	1.00166		
124.4	1.00120		
124.9	1.00070		
		126.0	0.9983

value of 0.8642 cc/gm for the specific volume of PAA at 128°C is close to the values quoted by Bahadur[7] (0.8623–0.8640 cc/gm).

The transitional density change $\Delta\rho/\bar{\rho}$ is defined as

$$\frac{\Delta\rho}{\bar{\rho}} = \frac{2(\rho_N - \rho_I)}{\rho_N + \rho_I}$$

where ρ_N and ρ_I are the densities of the nematic and isotropic phases at the transition temperature, respectively. In this study, the two densities at the

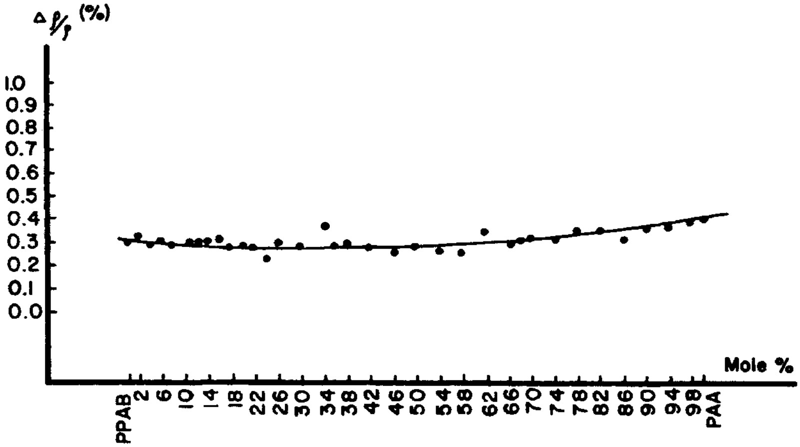


FIGURE 3 The plot of the transition density change $\Delta\rho/\bar{\rho}$ versus composition of PAA, PPAB and their mixtures.

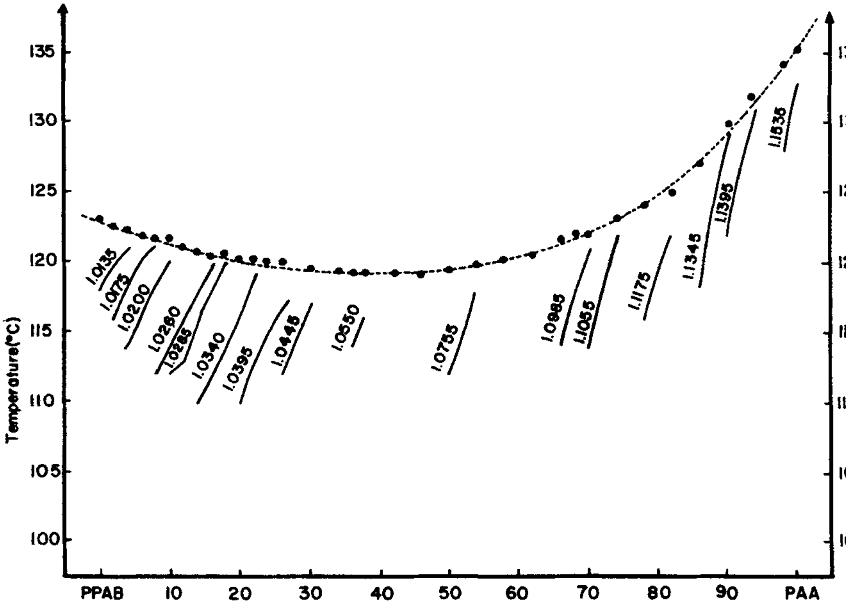


FIGURE 4 Contour plot of density in the temperature compositional plane of PAA, PPAB and their mixtures. This curve also represents the nematic-isotropic phase boundary for the PAA-PPAB system.

transition were obtained by an extrapolating of the linear portions of the density curves in both the nematic and isotropic phases to the transition temperatures. The transition density changes of all the mixtures had values within the range of 0.25 % to 0.40 %. The plot of the density changes versus composition is shown in Figure 3. The values for the density changes of PAA and PPAB, 0.40 % and 0.30 %, obtained in this work are close to the values, 0.35 % and 0.27 %, reported in a recent study of the p-p-alkoxyazoxybenzene homologous series.[4]

Figure 4 gives the nematic-isotropic phase boundary for the PAA-PPAB system. The phase boundary is very smooth and starts at $T = 122.9$°C for pure PPAB and slowly drops to a minimum at $T = 119.2$°C for 42 % PAA–58 % PPAB and 46 % PAA–54 % PPAB mixtures and slowly bends upwards. This behavior is in contrast to the phase boundary of PAA and PAP (*p*-Azoxyphenetole) system which is linear based on the transition temperatures reported by Chatelain and Germain,[5] but is similar to the behavior of the phase boundary of PAA and PHAB (*p*-*p*-di-*n*-hexyloxyazoxybenzene) systems.[6] On Figure 4, the densities of the mixtures at the transition are indicated. A better indication of the densities is given in Figure 5 which shows a three dimensional phase diagram of PAA–PPAB systems.

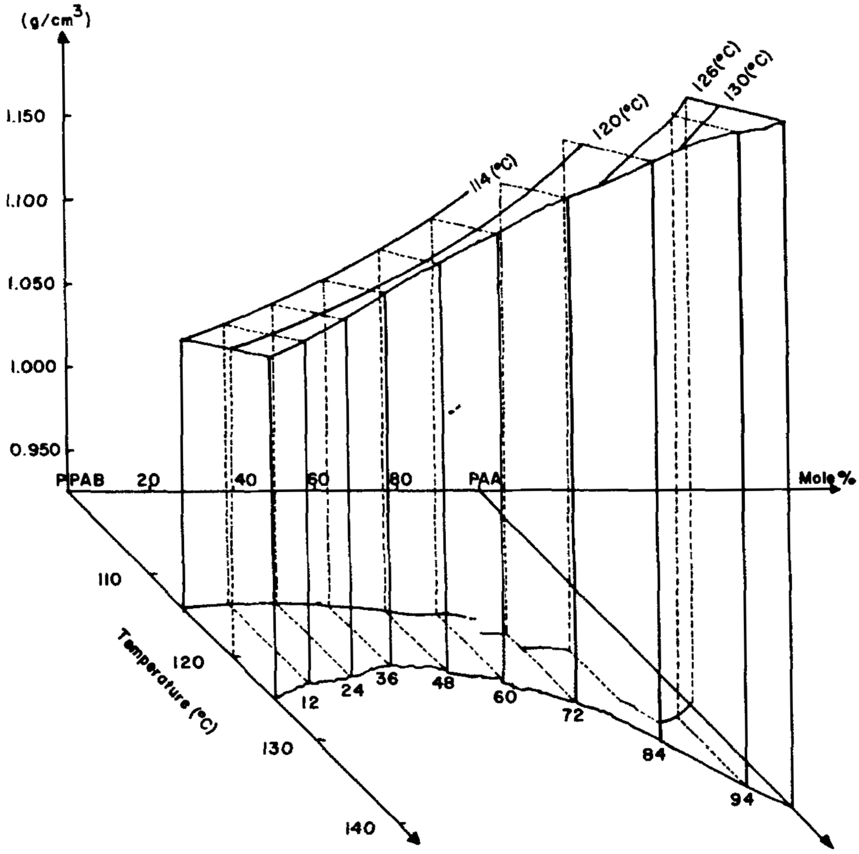


FIGURE 5 Perspective plot of the density surface above the temperature-composition plane of PAA-PPAB system.

The results of this study can be used along with the refractive indices data to determine the degree of ordering the liquid crystal mixture. We do not feel that the fractional volume change data can be used by itself to determine the values of the order parameters of the mixture since the errors between the observed order parameters of the different members of a homologous series[4] and those predicted by Maier and Saupe[8] volume change theory are greater than the differences between the order parameters of the members of the series.

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