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Density Studies in Terephthalylidene-bis-p-n-Octylaniline TBOA

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The temperature dependence of density ρ, in terephthalylidene bis-p-n-octylaniline (TBOA) is carried out to probe the phase transitions, associated volume jumps, order of the transitions and pretransitional effects. The compound exhibits smectic A, smectic C, smectic F, smectic G and smectic H phases. The smectic A-isotropic and smectic F-smectic C are found to be first order. The smectic C-smectic A and smectic G-smectic F transitions are second order and the calculated thermal expansion coefficient, α, also supported the density results.

INTRODUCTION

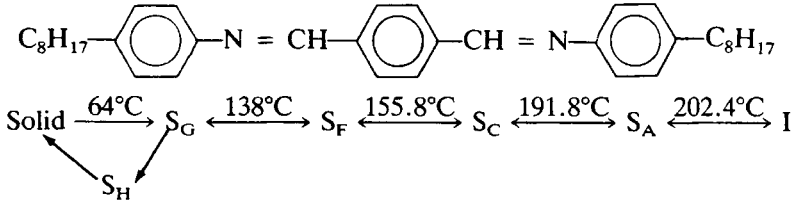
After the first synthetic report of terephthalylidene-bis-p-n-butyl-aniline (TBBA) along with temperature dependence of the tilt angle by Taylor et al.[1] in 1970 followed by the first noteworthy investigation of differentiating S_G and S_H phases in a single compound by Sakagami et al.,[2] several other reports[3–10] appeared in the last decade by different workers regarding the polymorphism and phase identification, the molecular structure in different phases, the pretransitional effects, the nature of the phase transitions, the zig-zag model in S_C phase and different (core and chain) tilt angles, using X-ray, inelastic coherent neutron scattering, calorimetry, thermal microscopy, ultrasonic velocity and absorption, density and optical experimental techniques. Following these experimental exploitation of different results in TBBA, Weigeleben et al.[5] reported the synthesis, characterisation of phases and associated thermal behaviour while Diele et al.[6] investigated the physical properties by X-ray studies in the homologous series of compounds terephthalylidene-bis-p-n-alkyl-anilines TBAA's, (where Al-

kyl = ethyl to decyl) exhibiting rich polymorphism. These compounds exhibit widely known nematic, smectic A, smectic C, smectic G and smectic H phases along with the uncommon smectic F and smectic I phases. In recent years much progress has been made in phase transition studies, order of the transition and pretransitional effects. Several reports appeared on the N-I, N-S_A, S_A-S_C and S_A-S_B phase transformation studies by different techniques. Recently Thiriet et al.[11] reported S_F-S_G transition in N(p-n-pentyloxy benzylidene)p-n-hexyl aniline, 50.6 by dilatometry and acoustic methods. Except the above lone report of dilatometric study across S_F-S_G transition in 50.6 no density studies are reported so far at this transition. Hence we report here the density studies in terephthalylidene-bis-p-n-octyl aniline, (hereafter referred as TBOA) which exhibits smectic A, smectic C, smectic F, smectic G and smectic H meso phases.

EXPERIMENTAL

The densities were carried out with a bicapillary pyknometer[12] containing a sample of approximately 3 ml. The diameter of the capillary is about 0.35 mm and the accuracy in density is ± 0.1 kg.m^{-3}. The permitted cooling rate in the present experiment is 1°C/hr. The pyknometer was filled with the sample in an inert atmosphere, keeping the pyknometer surroundings at a temperature around 205°C ~ 215°C.

The sample was prepared by condensation of p-n-octyl aniline (0.2 mole) and terephthaldehyde (0.1 mole) in refluxing absolute ethanol in the presence of a few drops of glacial acetic acid. After refluxing the reactants for four hours the solvent was removed by distillation under reduced pressure and later the pure compound was recrystallized from absolute alcohol-benzene mixture until the observed transition temperatures were constant. The transition temperatures were determined using a polarizing microscope. Special precautions were taken to keep the sample away from atmospheric hydrolysis since the sample has shown a tendency to decompose at high temperature because of prolonged heating. The decomposition was indicated by a change in colour, transition temperatures, widening in transition temperature range and density values. The observed transition temperatures in °C by thermal microscopy are as follows



RESULTS AND DISCUSSION

The results of the density variation with temperature in TBOA in the isotropic, smectic A, smectic C, smectic F and smectic G phases are illustrated in Figure 1. The density in all the phases, excluding the vicinity of transition regions, increases with the decreasing temperature. No hysteresis was observed in density in the heating and cooling cycles in isotropic, smectic A and smectic C phases. There is a significant change in density associated with the transition from isotropic liquid to smectic liquid crystal. The vertical distance between the density values of the extrapolated curves from the isotropic and smectic A regions is taken as density change at the observed transition temperature. The observed jump in density across this transition is $(\Delta\rho/\rho) = 0.9\%$ and is in agreement with the reported values[13-15] across this transition. The minimum[13] and maximum[14] values of density change reported so far across S_A-I transition are 0.35% and 2% respectively. The material in the bulb was not homogeneous in the vicinity of the transition temperature but rather appeared as a two phase coexisting mixture of isotropic and smectic phases demarked by an interface. The total transition region ranges about 1.5°C, how-

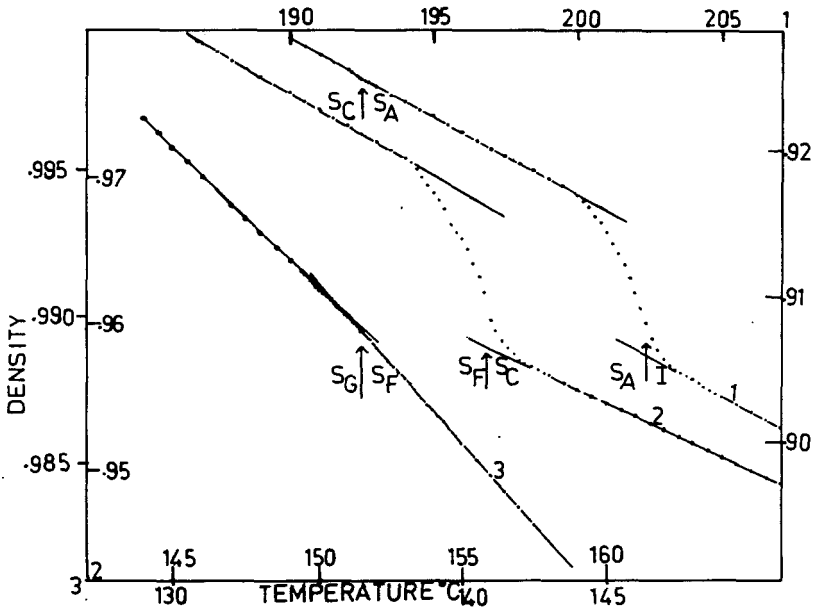


FIGURE 1 Temperature dependence of density ρ in smectic A, smectic C, smectic F and smectic G phases F and smectic G phases of Terephthalylidene-bis-p-n-octyl aniline, TBOA.

ever 90% transition is complete within 0.3°C. Prolonged heating at a constant temperature in the vicinity of transition region, indicated a change in colour of the sample, which is due to deterioration of purity of the sample. Similar studies of coexistence of two phases of S_A and I for about 2.5°C in azoxy benzoate have already been reported. However Demus and Rurainski reported molar volume data at and above 1°C temperature interval. Hence from their data the observation of two phase coexistence cannot be realised.

The determination of the thermal expansion coefficient α = (d ln V/dT), where V = molar volume, is carried out and the results are illustrated in Figure 2. A maximum in α indicated a first order S_A-I transition. The pretransitional effects are found to occur in smectic A phase at this transition. An estimate of the pressure dependence of the isotropic-smectic A transition temperature can be given using the Clausius-Clapeyron equation. $(dT_t/dP) = T_t(\Delta V/\Delta H)$ where T_t is the transition temperature, ΔV the molar volume change associated with the transition and ΔH is the heat of transition. The estimated value of dT_t/dP is 42 K/k.bar. This value is in good agreement with the estimated value of 43 K/k.bar found for diethyl 4,4'-azoxy dibenzoate from the density results.

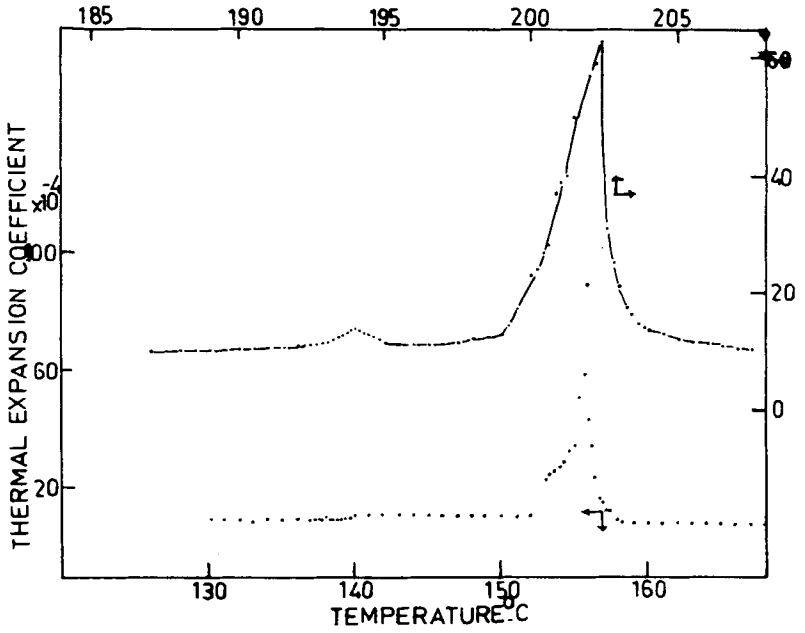


FIGURE 2 Temperature dependence of thermal expansion coefficient α in smectic A, smectic C, smectic F and smectic G phases of Terephthalylidene-bis-p-n-octyl aniline, TBOA.

The smectic A-smectic C transition is inferred by a change in slope of the density versus temperature. However, the reported heat of transition,[5] $\triangle H$ = 260 J/mole, across this transition is an interesting point for discussion; suggests a first order $S_A - S_C$ transition. The true latent heat, which should be related to a purely first order transition in a realistic way, is diffferent from the heat of transition, which may also include, besides a latent heat, pretransitional effects. Hence the 260 J/mole across the $S_C - S_A$ transition is probably due to the large pretransitional effects effecting the molecular arrangement in the transformation. Recently Thoen et al.[16] also reported analogous anomaly in p-n-octyl cyanobiphenyl, with a total enthalpy change of 218 J/mole obtained from adiabatic scanning calorimetry. They assigned it as entirely due to pretransitional enthalpy change and is in agreement with the interpretation of Kasting et al.[17] who obtained 228 J/mole from a.c. calorimetric technique. Leadbetter et al.[18] reported 200 J/mol from differential scanning calorimetry and with concurrent small volume change at the $S_A - N$ transition interpreted the results as an indication of very weak first order. However Thoen et al., Kasting et al. suggested that the reported volume jump as pretransitional volume change.

The thermal expansion coefficient variation with temperature suggests the presence of pretransitional effects on both sides of the transition temperature. The thermal expansion coefficient which is higher in S_A phase than in S_C phase indicates a slightly closer molecular packing in S_C phase than in S_A phase. It is well known that the smectic C phase possesses the analogous molecular packing as that in smectic A except to an additional layer tilt obtained with a displacement along the long molecular axes or by tilting of fixed layers. The liquid like order is also present within the layers. Hence the change in the value of thermal expansion coefficient compliments the phase transformation. The smectic C-Smectic F transition is an example of disordered-ordered smectic transition. The S_C-S_F transition sequence is present from pentyl homologue to octyl homologues of the terephthalylidene-bis-p-n-alkyl aniline homologous series. This sequence is also found in derivatives of pyrimidine series.[19] We are not aware of any other report of density studies across this transition. The smectic F phase has a monoclinic symmetry with a hexagonal molecular packing in the plane normal to the long axes of the molecules which are tilted to the layer planes. Lattice orientation and tilt direction have long range order but the molecular positions are situated with relatively short range order. Hence the smectic F phase is represented as a weakly coupled 2-D system having long range bond orientational order but with a short range positional order. Thus the transition

from smectic C phase, possessing one dimensional translational order of tilted molecules with disordered centres of mass positions and fluid layers, to smectic F is expected to be a first order transition. The distinct jump in density ($\Delta\rho/\rho$ = 1.04%) across the S_F-S_C transition and the maxima in thermal expansion coefficient suggest a first order transition. Our results are in good agreement with the reported heat of transition across this transition.

It should be emphasized that the estimated pressure dependence of the transition temperature ($dt_t/d\rho$) = 43 K/k.bar, from the volume change from our results and heat of transition (5460 J/mol) from literature, is of the same order obtained for S_A-I transition. Further the pretransitional effects are found to be present in the smectic F phase below the S_F-S_C transition. It should be mentioned here that the indicated results for $\Delta\rho/\rho$ and for ρ below the transition temperature could be slightly high due to some material in smectic F phase sticking to the walls of the capillary during cooling.

Wiegeleben et al.[5] reported small enthalpies at the smectic G-smectic F transition, the transition between ordered phases. For TBOA they reported[5] a heat of transition of 7 Joules/mol which is an indication of second order transition. Diele et al.[6] found that the layer thickness does not change discontinuously at the S_G-S_F phase transition. In this work also we found no discontinuity in density at the S_G-S_F transition. This observation is in good agreement with the reported enthalpy data. The change in thermal expansion coefficient and change in slope of density versus temperature indicate a second order transition rather than first order one. However our results are at variance with the lone report of a small jump in volume in N(p-n-pentyloxy benzylidene)p-n-hexyl aniline 50.6 at this transition. Any conclusion at this stage will be superfluous and we cannot offer any explanation for this discrepancy until we carry out further work on the other compounds exhibiting S_G-S_F transition.

CONCLUSIONS

The S_A-I and S_F-S_C transitions are found to be first order and these experimental results are obeying the Clausius-Clapeyron equation. The S_C-S_A and S_G-S_F transitions are found to be second order and these results are concurring with D.S.C. data reported for this compound. Further work is in progress in other compounds of this homologous series terephthalylidene-bis-p-n-alkyl anilines to establish the order of the phase transitions and pretransitional phenomena.

Acknowledgments

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