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High-pressure measurements in a homologous series of liquid crystals

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Pressure-volume-temperature measurements throughout the nematic phase for the first six members of the homologous series of di-alkoxyazoxybenzenes are reported. These data represent the first investigation of thermodynamic parameters in an homologous series, thus demonstrating the role of the end chains in a specific molecular geometry. Measurements at constant volume permit the conversion of previous orientational order studies at atmospheric pressure to constant-volume conditions. Measurements at constant temperature at the nematic-isotropic phase transition reveal the behavior of the specific volume, volume discontinuity, and volume dependence of the mean-field potential in this series. Finally, the implication of these data on several liquid-crystal theories is explored.

I. INTRODUCTION

Theories of the liquid-crystalline state are best tested by experiments which produce basic thermodynamic measurements such as transition temperatures and enthalpies, transition densities and density changes, and order-parameter measurements. Even more useful are measurements under pressure, where data on all of the previously mentioned variables can be generated, along with information on pressure derivatives, order-parameter behavior at constant volume, and the volume dependence of the mean-field potential. An excellent review of liquid-crystal measurements under pressure can be found in Ref. 1. Two examples of more recent work are *P-V-T* measurements in three nematic and one cholesteric liquid crystal,[2] and investigations of phase transitions in cholesteric and smectic liquid crystals.[3]

One shortcoming of all these measurements under pressure is that they have been done on liquid crystals from various homlgous series. The importance of data from a single homologous series cannot be underestimated; only through such measurements can the role of molecular geometry and endchain flexibility be examined. We therefore present basic thermodynamic measurements on the first six members of the homologous series of di-alkoxyazoxybenzenes (denoted *n*OAB where $n=1,2,3,4,5,6$). Data were taken throughout the liquid-crystal phase at constant volume for all six compounds. In addition, constant-temperature data near the nematic-isotropic phase transition were obtained for the third through sixth members of the series. These measurements result in data which (1) show the volume dependence near the nematic-isotropic transition, (2) give the volume dependence of the mean-field potential, and (3) can be used to correct for volume changes at constant pressure. As an illustration of this last aspect of the data, order-parameter results at constant volume are generated using previous studies at constant pressure. Finally, we briefly discuss how these measurements compare with the predictions of several theoretical models of the liquid-crystal state.

II. EXPERIMENTAL METHOD

The experimental apparatus allowed simultaneous measurement of sample pressure, volume, and temperature. The liquid crystal was confined in a stainless-steel bellows holding about 4.5 cm^3 of sample. The pressure was measured with either a 0—10 000 psi or 0—100 000 psi Heise bourdon-tube pressure gauge, while the temperature was measured using a Chromel-Alumel thermocouple located next to the sample vessel. The sample was inside a pressure-vessel—double-oven arrangement, with the oven temperature regulated by a proportional servomechanism using a sensor thermocouple. The pressure was generated by a hydraulic pump and intensifier system. The Bridgman bellows and slide-wire technique[4] was employed to measure the volume of the sample. The position of the slide wire was measured using an ac bridge arrangement, resulting in an accuracy of 0.000 15 cm^3/g in measurements of the specific volume. This figure was determined by utilizing water as the sample.

All the liquid-crystal samples, except 3OAB, were purchased from Eastman Kodak and recrystallized several times in an ethanol-toluene mixture. The sample of 3OAB was synthesized using the procedure of van der Veen,[5] and then recrystallized several times. The sample bellows was filled by evacuating the vessel and then introducing dry nitrogen above the liquid crystal, forcing the fluid up a tube into the sample bellows.

The constant-volume measurements were made by starting at a pressure and temperature near the nematic-solid transition; the temperature was raised a degree or two, after which the pressure was raised until the volume was equal to its previous value. This procedure was repeated until the isochor line intersected the nematic-isotropic coexistence line. This method produced measurements of pressure and temperature at which the specific volume varied by no more than 0.015%.

The nematic-isotropic phase transition was investigated by starting at a temperature and pressure in the isotropic phase, and then increasing the pressure in steps of 50 or 100 psi, recording the volume each time. The increase in pressure was done slowly so the sample would remain at the equilibrium temperature. These pressure increments were repeated until the sample was well into the nematic phase; this entire procedure was performed at three points along the nematic-isotropic coexistence curve.

III. EXPERIMENTAL RESULTS

The result of a typical constant-volume run is shown in Fig. 1. Measurements of this type have been reported once before for a cholesteric liquid crystal.[6] The isochors for all six members of the series are shown in Fig. 2. Notice that the lines of constant volume are fairly straight, with some curvature evident near the nematic-isotropic phase transition. Notice also that the temperature range of the nematic phase is considerably larger at constant volume than at constant pressure. In these six compounds, the enhancement of liquid-crystallinity ranges from about 2.8 for 1OAB to 1.8 for 6OAB. Using this data, any experiment done along one of these isochors would be one in which the volume did not vary during the experiment.

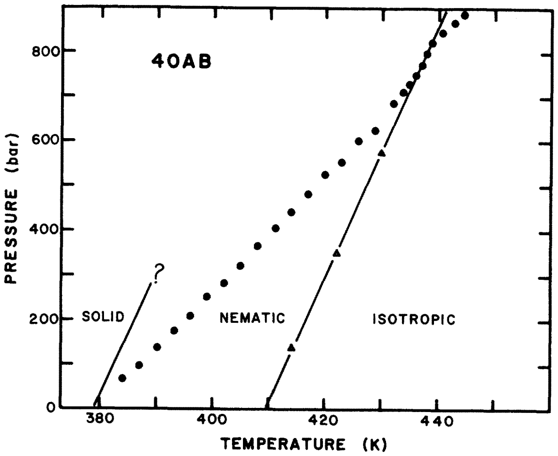

FIG. 1. Constant-volume data for 4,4′-bis(butyloxy)azoxybenzene. The solid circles represent points of specific volume 0.9511 cm^3/g; the open triangles represent measurements of the nematic-isotropic phase transition.

A typical result for the constant-temperature runs on one member of the series is shown in Fig. 3. Results of this type have been reported once before.[2] During each run the change of phase was very evident, as only then did the volume reading continue to change for a few minutes after the pressure was increased. This effect occurred at one or sometimes two pressure readings (separated by either 50 or 100 psi) but never at more than two readings. These constant-temperature runs not only provided data about volume changes near the phase transition, they also served to locate the nematic-isotropic coexistence curve and confirm the nematic-isotropic transition line observed in the constant-volume runs. The transition points plot-

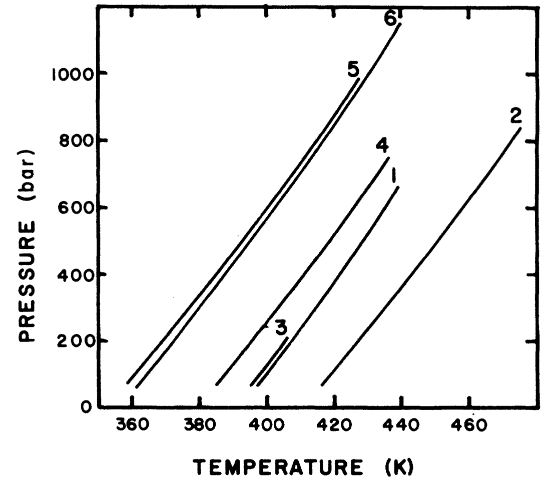

FIG. 2. Constant-volume data in the nematic phase for the first six members of the homologous series of di-alkoxyazoxybenzenes.

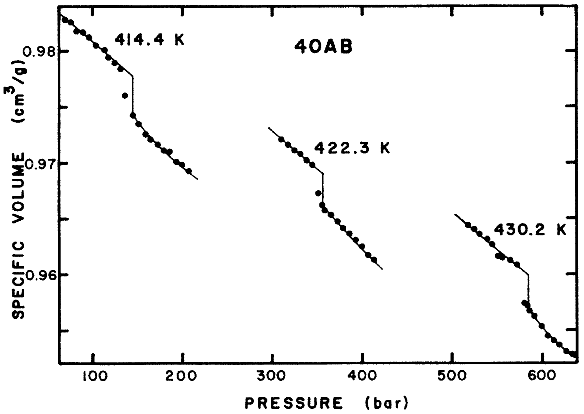

FIG. 3. Constant-temperature data across the nematic-isotropic transition in 4,4′-bis(butyloxy)azoxybenzene. The solid lines have been drawn to aid the eye.

ted in Fig. 1 come from each of the constant-temperature runs.

The results of all the constant-temperature runs have been compiled in Table I. The change in volume at the transition, ΔV, was found by fitting the data in the isotropic phase to a straight line and measuring the volume change from this line to the first point in the nematic phase. The transition volume for members of the series have been plotted in Fig. 4; the fractional change in volume has been plotted in Fig. 5. Data from the experiments of others have also been presented in Figs. 4 and 5 to demonstrate the behavior of all six members of the series.[7,8] Several general trends are evident from these two figures: (1) both the volume and the fractional volume change decrease as one moves up in temperature and pressure along the coexistence curve; (2) an odd-even effect is clearly evident as one moves up the homologous series; (3) the volume at the transition increases as one moves up either the odd members or the even members of the series; and (4) the fractional volume change at the nematic-isotropic transition decreases as one goes up either the odd or even members of the series.

The volume dependence of the mean-field potential is another theoretically important property which can be examined using these results. This quantity γ describes the relative sensitivity of the order parameter to changes in density versus changes in temperature and may be a sensitive probe of the relative importance of attractive and repulsive interactions.[9] All one must assume is that the order parameter at the nematic-isotropic transition does not vary to any great extent along that part of the coexistence curve studied in these experiments. Evidence that this is the case is quite ample.[10–13] The coexistence curve is therefore nearly a curve of constant-order parameter, and γ,

TABLE I. Nematic-isotropic transition data for the third through sixth members of the homologous series of di-alkoxyazoxybenzenes.

Compound	T(K)	P(bar)	V(cm^3/g)	ΔV(cm^3/g)	$\Delta V/V$
30AB	402.2	117.2	0.9213	0.0027	0.0029
30AB	405.2	189.0	0.9185	0.0018	0.0020
30AB	408.1	258.6	0.9153	0.0016	0.0017
40AB	414.4	144.8	0.9742	0.0032	0.0033
40AB	422.3	355.9	0.9667	0.0028	0.0029
40AB	430.2	583.4	0.9581	0.0028	0.0029
50AB	400.2	172.4	0.9526	0.0018	0.0019
50AB	414.2	586.2	0.9389	0.0013	0.0014
50AB	427.2	993.1	0.9272	0.0013	0.0014
60AB	407.3	144.8	0.9974	0.0024	0.0024
60AB	419.2	500.3	0.9837	0.0018	0.0018
60AB	441.0	1227.6	0.9618	0.0011	0.0011

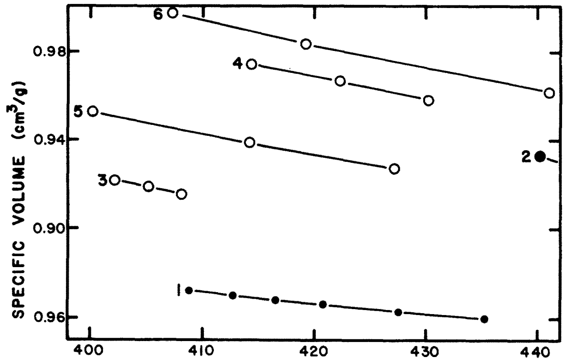

FIG. 4. Specific-volume data at the nematic-isotropic phase transition for the di-alkoxyazoxybenzenes. Data for the first and second members of the series are taken from Refs. 7 and 8, respectively.

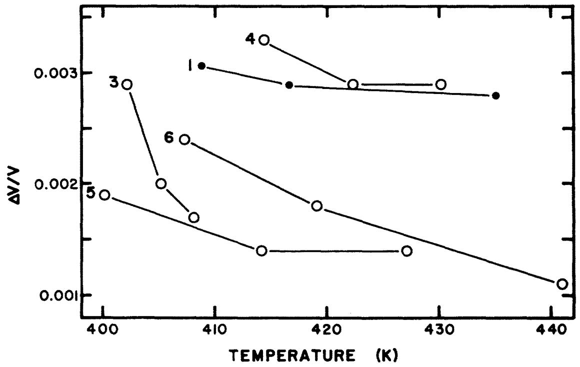

FIG. 5. Fractional-volume discontinuity at the nematic-isotropic phase transition for the di-alkoxyazoxybenzenes. Data for the first member of the series are taken from Ref. 7. Data for the second member of the series fall much higher on this graph at about 0.006 (Ref. 8).

the exponent of the volume of the mean-field potential, can be determined. Two equivalent methods may be employed[11,14] and the results are presented in Table II. It is evident from these results that γ for 10AB is much higher than the other members of the series, with perhaps a slight decreasing trend as the higher members of the series are examined.

As an illustration of how these data may be employed, the constant-volume data have been used to transform prior measurements at constant pressure to measurements at constant volume. This may be accomplished by realizing that the isochors are fairly straight, indicating the temperature range of the nematic phase is expanded linearly at constant volume. To test the validity of this approach, the constant-volume data on 10AB from McColl and Shih[14] have been plotted in Fig. 6 along with the properly expanded constant pressure data on 10AB from McColl.[15] The fairly good agreement indicates this method does produce data which closely resemble actual constant-volume data. Constant-pressure order-parameter data on all six members of the series have been generated by deJeu and Claassen,[8] and we have plotted their results after transformation to constant volume in Fig. 7.

TABLE II. High-pressure thermodynamic data on the homologous series of di-alkoxyazoxybenzenes. γ is the exponent of the volume in the mean-field potential, i.e., $U \propto V^{-\gamma}$.

Compound	T(K)	$(dP/dT)_{\text{coex}}$ (bar/K)	$(dP/dT)_V$ (bar/K)	γ^{a}	γ^{b}
10AB	419	22.2	14.2	4.2	4.4[c]
20AB	445	24.6	12.9	2.5	
30AB	403	26.0	13.4	2.6	2.2
40AB	410	27.9	12.9	2.1	2.3
50AB	395	30.3	13.2	2.0	2.4
60AB	398	32.3	13.7	1.9	2.2

[a] Using $\dfrac{1}{\gamma}=T\alpha_p\left[\dfrac{(dP/dT)_s}{(dP/dT)_v}-1\right]$ with $\alpha_p=0.001\ \text{K}^{-1}$.

[b] Using $\dfrac{1}{\gamma}=-\dfrac{T}{V}\left[\dfrac{dV}{dT}\right]_s$.

[c] Using data from Ref. 7.

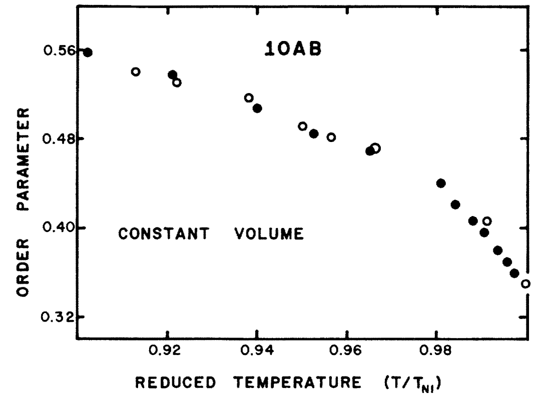

FIG. 6. Order-parameter data for *p*-azoxyanisole at constant volume. Open circles are data actually taken at constant volume (Ref. 14); closed circles are data taken at constant pressure (Ref. 15), but transformed to constant-volume conditions using the results contained in this paper.

Perhaps the most striking feature evident in the figure is the fairly small spread in the order-parameter curves for these members of the series. This feature is also present in the constant-pressure results, but it is not lost after transformation to conditions of constant volume. Although there may be a slight trend to higher-order-parameter values in going up the homologous series, it certainly is masked by the individual differences between each member of the series.

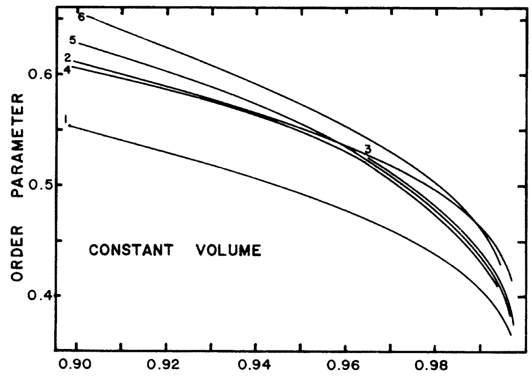

FIG. 7. Order-parameter data for the first six members of the homologous series of di-alkoxyazoxybenzenes. The data are from constant-pressure measurements (Ref. 8), but transformed to conditions of constant volume using the results contained in this paper.

IV. DISCUSSION

Previous work by other investigators have determined a few of the results presented in this paper. For instance, the phase diagram of 10AB reported here agrees well with prior results.[10,11] Constant-volume experiments on 10AB by McColl[14] also agree with our results. Some discrepancies do seem to exist between the fractional change in volume results under pressure as compared to experiments done at atmospheric pressure. Specifically, our results are consistent with the results of deJeu and Claassen[8] for the first members of the series, but are significantly less than their results for 50AB and 60AB. Recent work on 50AB by Phaovil, Pongthana-Ananta, and Tang[16] also shows a larger volume discontinuity than we find. Part of the reason for these discrepancies could very well be the analytical method used to determine ΔV once the data have been collected. All curves of volume near the phase transition show significant curvature just inside the nematic phase. If these points are considered to be due to a mixture of both phases, a higher ΔV will result. Our method gave an excellent indication of exactly when the phase transition was taking place. Keyes and Daniels[2] also considered this problem and their volume changes for other liquid crystals are equal to or smaller than our results. Needless to say these are difficult measurements; the need to proceed in small steps keeping the sample in equilibrium with its surroundings is very great. It may be that pressure experiments done slowly at constant temperature might achieve these conditions better than measurements done at atmospheric pressure.

Rather than try to compare various theoretical models to our measurements, we prefer to discuss general trends evident in our data. These general trends are specific enough to point out problems in many theories. First of all, it has already been pointed out that as the temperature and pressure increase, the volume at the nematic-isotropic transition and the fractional change in volume at the transition both decrease. Both of these trends have been seen before in other compounds,[2] and are predicted by Ågren and Martire in their lattice model of rigid, rodlike central cores with semiflexible pendant tails. However, a more important trend is the increase in volume and decrease in fractional volume change at the nematic-isotropic transition evident in our data as the length of the flexible tails is increased. The theory of Ågren and

Martire[17] predicts just the opposite in each case. The theory of Dowell and Martire utilizing rigid cores and completely flexible tails[18] also predicts the wrong volume dependence at the transition, while the the theories of Wulf and DeRocco[19] (long semiflexible molecules) and Cotter[20] (lattice model) both predict the wrong fractional volume change as one increases the length of the molecule. Two theories which predict both the increase in volume and the decrease in the volume change are those of Baron and Gelbart[21] (van der Waals theory) and Dowell and Martire[22] (lattice model of rigid cores and semiflexible tails). The latter theory predicts either volume trend depending on the tail-bending energy. It is clear that the general trends evident in our data are specific enough to point out problems in many of the liquid-crystal theories cited.

V. CONCLUSIONS

We have presented important thermodynamic measurements under pressure for an homologous series of liquid crystals. The results enable researchers to see the effect of increasing molecular length in a single molecular geometry on various characteristics of the liquid-crystal phase. Data of this kind have been lacking up to now, and we hope it will provide important checks for researchers working in liquid-crystal theory. For this series of di-alkoxyazoxybenzenes, trends are clearly present and these trends imply important constraints for theoretical models. At this point one can only speculate if such trends are universal.

Another result which stems from this data is that 1OAB (PAA) is not very typical of the other members of the series. Keyes and Daniels[2] found the same to be true for MBBA when compared to other liquid crystals. It is obvious that the shortness of these molecules coupled with the lack of flexibility produce unique effects. Perhaps it is unfortunate that so much experimental work has been done on these two liquid crystals, when they may in fact not be typical of the majority of liquid crystal forming compounds.

For those researchers who would like to see the collection of original data in its entirety, the authors will send a copy of all their data to those who request it.

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