

Thermodynamics of phase transition from a nematic liquid crystal into an isotropic liquid in para-azoxyanisole (PAA) at high pressures

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A piston piezometer is used to investigate, for the first time, the phase transition from a nematic liquid crystal to an isotropic liquid in para-azoxyanisole at high pressures. It is shown that the nematic–liquid phase transition is of first order in the entire interval of investigated temperatures and pressures. Evidence is presented favoring the concept that the dominant role is played by repulsion between particles in the nematic ordering.

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The present investigation was undertaken to study the laws governing the behavior of the thermodynamic quantities in a first-order phase transition from an isotropic liquid to a nematic liquid crystal at high pressures, using para-azoxyanisole (PAA) as an example.¹⁾ Of particular interest was the possibility of observing an isolated critical point.^[4]

The investigation method consists of measuring the volume of the coexisting phases and the coordinates of the equilibrium curve with the aid of a piston piezometer with an intermediate liquid.^[5,6] To determine the initial volume of the piezometer, we used the data of^[2]. The errors in the measurement of the volume V , the pressure P , and the temperature T were respectively $\sim 10^{-2}$ cm³/mole, ~ 2 kgf/cm², and ~ 0.01 °K.

The experimental results enable us to determine the volume discontinuity ΔV in the phase transition and to calculate, by using the Clausius–Clapeyron

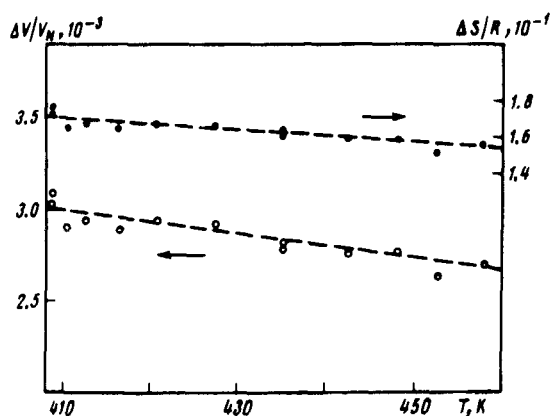


FIG. 1.

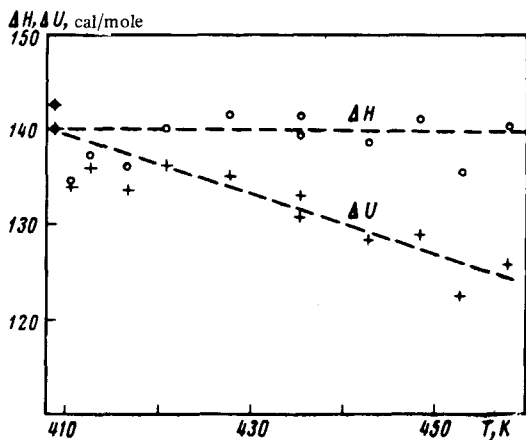


FIG. 2.

equation, the corresponding changes in the entropy (ΔS), enthalpy (ΔH), and internal energy (ΔU).

Owing to the smallness ΔV the error in the determination of this quantity was $\sim 5\%$. The errors in the calculated values of ΔS , ΔH , and ΔU were in fact of the same order.

In the experiments we used PAA multiply recrystallized from benzene, with a melting temperature at atmospheric pressure 118.3°C . The regions of the investigated temperatures and pressures were determined by the thermal stability of the PAA molecule. At temperatures $\sim 185^\circ\text{C}$, noticeable effects attesting to the decomposition of the substance were observed.

The results of the measurements and calculations are listed in the table and are illustrated in Figs. 1 and 2. As seen from Figs. 1 and 2, the phase transition from the nematic liquid crystal to the isotropic liquid is of first order at all temperatures and pressures. The rather weak temperature dependence of the thermodynamic quantities characterizing the phase transition leaves practically no hope for the existence of an isolated point, even if the PAA molecule were to be more stable. It must also be indicated that, according to our observations, the pretransition anomaly of the compressibility of PAA in the nematic phase becomes less and less pronounced with increasing pressure.

A few words concerning the form of the interaction that determines the ordering of the nematic type. The rather weak temperature dependences of the volume discontinuity and of the entropy discontinuity in the phase transition and the practically linear dependence of the transition temperature on the pressure may indicate that in this case we are dealing with a short-lived repulsion interaction. Then, if we consider the van der Waals attraction in the spirit of the average-field theory and approximate the repulsion by a power-law function of the type $\phi(r) \sim (r^n)^{-1}$, then we easily obtain for the temperature dependences of the transition pressure and the relative volume discontinuity the following relations^[7]

$$P = aT^{1+3/n} + \beta T^{6/n} \quad (1)$$

TABLE I.

T_N	P_N	V_N	ΔV	$\Delta V/V_N$ 10^{-3}	$\Delta S/R$	ΔH	ΔU
408.75	1	225.04	0.68	3.04	0.172	140.0	140.0
408.85	1	225.02	0.69	3.09	0.176	142.6	142.7
410.61	40	224.80	0.65	2.90	0.165	134.6	134.0
412.70	85	224.53	0.66	2.94	0.167	137.2	135.8
416.55	167	223.97	0.65	2.89	0.164	136.0	133.5
420.78	255	223.49	0.66	2.94	0.167	140.0	136.1
427.55	405	222.70	0.65	2.92	0.166	141.4	135.2
435.25	572	221.92	0.64	2.82	0.164	141.4	132.9
435.23	578	221.92	0.63	2.78	0.161	139.3	130.8
442.63	732	221.19	0.61	2.76	0.158	138.7	128.3
448.21	857	220.65	0.61	2.76	0.158	141.1	128.9
452.66	955	220.29	0.58	2.63	0.151	135.6	122.6
457.77	1068	219.83	0.59	2.69	0.154	140.4	125.6

T_N —phase-transition temperature ($^{\circ}\text{K}$), P_N —phase-transition pressure (kgf/cm^2), V_N —volume of the nematic phase (cm^3/mole), ΔV —change of volume in the phase transition (cm^3/mole), ΔS —change of entropy, R —universal gas constant, ΔH —change of enthalpy (cal/mole), ΔU change of internal energy (cal/mole).

where n is the exponent in the law governing the interparticle interaction that determines the phase transition. In the case of repulsion, $n > 6$;

$$\Delta V/V_N = (\Delta V/V_N)_0 \exp^{\epsilon/T} \quad (2)$$

where ϵ is an energy constant equal in order of magnitude to the depth of the potential well of the total interparticle-interaction function. For PAA we have $\epsilon \times 550^{\circ}\text{K}$.^[8] Calculations using the experimental data (see the table) yield $n \approx 20$ and $\epsilon \approx 450^{\circ}\text{K}$.

Thus, even though the rather narrow region of investigated temperatures does not allow us to make any definite statements, the experimental data confirm the idea that in the nematic ordering the decisive role is played by the short-range repulsion. The results of numerical experiments^[8,9] yield additional evidence favoring this concept.

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¹This question was dealt with earlier in^[1], but the material given in that reference does not lend itself to a reasonable interpretation. In particular, the volume discontinuities in the transition from the nematic phase to the liquid phase at pressures close to atmospheric, cited in^[1], exceed by more than one order of magnitude the corresponding published data.^[2,3]

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