Critical Exponents for Thermal Expansion and Isothermal Compressibility near the Nematic to Smectic-A Phase Transition

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High-resolution measurements of the molar volume, *V*, measured as a function of temperature at two different pressures allowed the calculation of the isobaric thermal expansion coefficient, $\alpha_p(T)$, and isothermal compressibility coefficient, $\beta_T(T)$. Critical exponents for observed singularities in both thermodynamic quantities were found. It was confirmed that the same critical exponent α, usually assigned to heat capacity, describes singularities of the thermal expansion and the isothermal compressibility coefficients. Two compounds from the two different homologous series, *n*CB and *m̄*S5, were studied. *V*(*T*) and $\beta_T(T)$ variations in 8CB showed a continuous phase transition with the effective critical exponent $\alpha = \alpha' = 0.32 \pm 0.02$. For 10S5 a weakly first-order transition with a volume jump $\Delta V = 0.127 \pm 0.001$ cm³/mol ($\Delta V/V = 2.6 \times 10^{-4}$) was observed and an exponent $\alpha = \alpha' = 0.50 \pm 0.02$ was found.

I. Introduction

The nematic (N) to smectic-A (SmA) phase transition is the one most frequently studied and still not fully understood from a theoretical point of view. In both phases the long axes of the rodlike molecules are oriented along one direction. In the smectic-A phase they are additionally organized in layers perpendicular to the molecular orientation. The order parameter characterizing this transition is an amplitude of the density wave related to the layers observed in the smectic-A phase.

There are theoretical models that predict that this transition belongs to the three-dimensional (3D) *XY* universality class.[1,2] A broad theoretical overview of the SmA–N phase transition was given by Lubensky.[3] In spite of universality predicted by theories, the numerous experimental studies, analyzed and summarized in a detailed overview by Garland and Nounesis,[4] show that experimental critical exponents are not universal. Also the order of the transition is hard to predict from the theory. Halperin *et al.*,[2] considering a coupling between the density wave represented by a smectic order parameter, ψ, and the director fluctuations, δn, found that the N–SmA phase transition is always first order. Recent work by Patton and Andereck[5] utilizing self-consistent one-loop theory and the same $\psi-\delta n$ coupling predicts a crossover of the critical exponents from isotropic to anisotropic behavior, but there is no conclusion about the order of the transition. Theory developed by Nelson and Toner[6] assuming that the ordering in the SmA phase is perturbed by a growth of the dislocation loops predicts a continuous phase transition. A model proposed by de Gennes[1] assuming coupling of the smectic order parameter, ψ, and the nematic orientational order parameter, φ, also predicts a crossover from the first-order transition to continuous. These two theories[1,5] seem to be the closest to the real systems. Such a crossover was already confirmed experimentally[7–9] in two different homologous series of liquid-crystalline materials (known as *m̄*S5 and *n*CB), and the tricritical points were found. In each series the compounds are characterized by a McMillan ratio defined as T_{AN}/T_{NI}, where T_{AN} is the nematic–smectic-A critical temperature and T_{NI} is the nematic to isotropic transition temperature. When the T_{AN}/T_{NI} ratio is increasing (the nematic range is decreasing), then the nematic order parameter, φ, is less saturated and its coupling

with smectic order parameter, ψ, is enhanced because of an increasing susceptibility.[1] It leads the transition from continuous to tricritical and next to discontinuous. The values of T_{AN}/T_{NI} at which the tricritical point occurs in these two homologous series cannot be compared because they form different types of smectics. The series of nonpolar compounds, denoted as *m̄*S5, which exhibits the monomeric smectic, SmA_m, was studied by ac calorimetry[7] and X-ray technique.[8] The polar compounds can exhibit monolayer smectic, SmA_1, partially bilayer smectic, SmA_d, and bilayer smectic, SmA_2. The *n*CB series belongs to the SmA_d type and was studied in an adiabatic calorimeter[9] as well as by X-ray scattering.[8]

Among thermodynamic quantities that have singularities at the phase transitions, the thermal dependence of the isobaric heat capacity, $C_p(T)$, is the one most frequently investigated. The singularity in $C_p(T)$, characterized by critical exponent α, is usually described with the following expression:

$$C_p = At^{-\alpha}(1 + Dt^\Delta) + B \tag{1}$$

where $t = |(T - T_c)/T_c|$ is the reduced temperature, T_c is the transition temperature, and Dt^Δ is the correction-to-scaling term with exponent $\Delta = 0.5$.

Heat capacity data complemented with molar volume, *V*, measured as a function of temperature and, what would be especially important, as a function of pressure, could give a full thermodynamic description. Precise *V*(*T*) data, if available close enough to the phase transition for at least two different pressures, allow for estimation of the isobaric thermal expansion coefficient, $\alpha_p(T)$, and the isothermal compressibility coefficient, $\beta_T(T)$, and the critical exponents characterizing their divergences can be calculated. It can be proved that critical exponents for $C_p(T)$, $\alpha_p(T)$, and $\beta_T(T)$ should be the same.

All above thermodynamic quantities are related by thermodynamic identities (Maxwell relations) which are valid far from the singular points. Similar relations were derived by Pippard[10] (and later in generalized form by Garland[11]) for the vicinity of a λ-point transition:

$$C_p/T = V\alpha_p\left(\frac{dp}{dT}\right)_\lambda + \text{const} \tag{2}$$

and

Critical Exponents for Thermal Expansion

J. Phys. Chem. B, Vol. 101, No. 35, 1997 **6971**

TABLE 1: Transition Temperatures (K) for 8CB and $\overline{10}$S5. For the First Order Transition, the Coexistence Range Is Reported

	T_{AC}	T_{AN}	T_{NI}
8CB		307.09	314.32−314.35
$\overline{10}$S5	337.30	354.35−354.38	359.62−359.65

$$\alpha_p = \beta_T \left(\frac{dp}{dT}\right)_\lambda + \text{const} \tag{3}$$

where $(dp/dT)_\lambda$ is a derivative along the λ-line. Equations 2 and 3 clearly show that the singularities of $C_p(T)$, $\alpha_p(T)$, and $\beta_T(T)$ should diverge with the same critical exponent α. Pippard's equations had to be confirmed experimentally[11] because their derivation was based on a cylindrical approximation for $V(T,p)$ and $S(T,p)$. It seems to be worth testing the validity of the above assumptions in the vicinity of the SmA−N phase transition.

In this paper we present the critical exponents found for divergences of the thermal expansion and the compressibility coefficients obtained from the precise volumetric measurements carried out for the compounds 4-cyano-4′-(*n*-octyl)biphenyl (8CB) and 4-(*n*-pentyl)phenylthiol-4′-(*n*-decyloxy)benzoate ($\overline{10}$S5) exhibiting different smectic phases as mentioned above. The exponents will be compared with exponents α found by others[7,9] from $C_p(T)$ for the same compounds.

Both compounds, 8CB and $\overline{10}$S5, were synthesized and purified by "ZD Chemipan", Warsaw, and further purification by slow fractional crystallization from methanol was done by us. The high purity of the samples was confirmed by a very narrow temperature range of the two-phase region at the nematic-to-isotropic phase transition. Transition temperatures or coexistence ranges observed for both compounds are given in Table 1. A thin-layer chromatography of our samples did not reveal any impurities.

II. Experiment and Results

In our earlier papers[12,13] we demonstrated that it is possible to obtain the critical exponents from precise volumetric measurements. Since then the experiment was adapted for simultaneous measurements of volume as a function of either temperature or pressure in a narrow pressure range (up to 2 bar). A new glass dilatometer with a pressure jacket and an assembly of manometers as well as the experimental procedure was described[14] and successfully applied for studies of the smectic-C to smectic-A phase transition in $\overline{10}$S5. It should be mentioned that in all experiments the size of the samples was about 8 cm^3, the temperature of a 70 dm^3 water bath was controlled with ±0.2 mK precision, and the resolution of volume measurements was a little better than 0.1 ppm. A pressure jacket around a container of the dilatometer maintained approximately equal pressures inside and outside the container and prevented errors caused by glass elasticity. Corrections for the small pressure differences were made.

The results of the volumetric measurements calculated as the temperature dependence of the molar volume at $p = 1.013$ bar are presented in Figures 1, 4, and 5. It occurred in the data analysis that the mean values of $\overline{\alpha_p}$ calculated successively from the pairs of neighboring data points are too scattered, especially when the points are measured at rather small temperature steps, *i.e.* 5−10 mK, as required for investigations of the phase transitions. Therefore eq 1 was integrated and applied to describe the molar volume as a function of temperature:
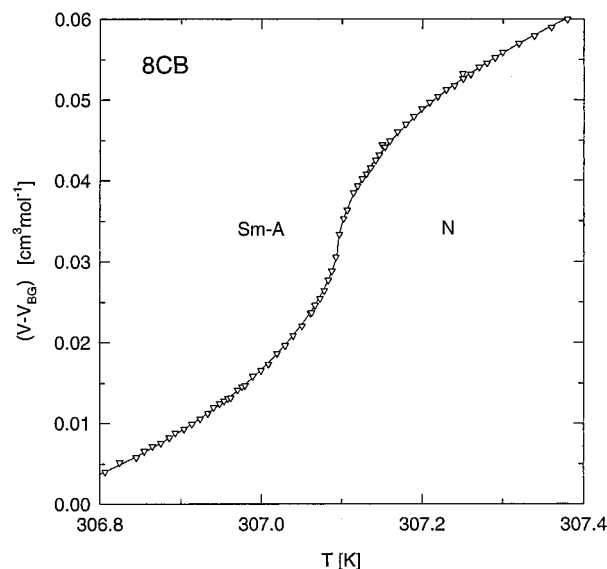
Figure 1. Molar volume near the smectic-A to nematic phase transition in 8CB, with linear background $V_{BG} = a + bT$ subtracted, plotted against temperature; $a = 125.840$ cm^{3}mol^{-1}, $b = 0.292$ cm^{3}mol^{-1}K^{-1}, ($\triangledown$) experimental points; solid line was calculated from eqs 4, fits 7 and 8 in Table 3.

$$V_T(T) = \begin{cases} At^{(1-\alpha)}(1 + Dt^{0.5}) + Bt + C, & T > T_{AN} \\ A't^{(1-\alpha')}(1 + D't^{0.5}) + B't + C', & T < T_{AN} \end{cases} \tag{4}$$

where $t = |(T - T_{AN})/T_{AN}|$ is the reduced temperature and T_{AN} is the transition temperature.

Critical exponents α and α' together with other adjustable parameters were calculated in a fitting procedure using a standard nonlinear least squares method.[15] These parameters can be used for calculation of the thermal expansion coefficient $\alpha_p = V^{-1}(dV/dT)_p$ as derivatives of eqs 4:

$$\alpha_p(T) =$$

$$\begin{cases} \dfrac{1}{V(T)T_{AN}}\left[(1-\alpha)At^{-\alpha}\left(1 + \dfrac{1.5-\alpha}{1-\alpha}Dt^{0.5}\right) + B\right], & T > T_{AN} \\ \dfrac{-1}{V(T)T_{AN}}\left[(1-\alpha')A't^{-\alpha'}\left(1 + \dfrac{1.5-\alpha'}{1-\alpha'}D't^{0.5}\right) + B'\right], & T < T_{AN} \end{cases}$$
$$\tag{5}$$

An advantage of our direct volumetric measurements with respect to, for example, differential scanning calorimetry is that we are able to find the volume change, ΔV_{AN}, at the phase transition, if it exists (analogous to a latent heat, ΔH_{AN}, measured directly by adiabatic calorimetry[16,17]), and to give an answer whether the transition is continuous or first order.

From measurements of volume at two pressures (about 1.0 and 1.8 bar) and at constant temperature we directly have the isothermal compressibility coefficient calculated as

$$\beta_T = -\frac{1}{\overline{V}}\left(\frac{\Delta V}{\Delta p}\right)_T \tag{6}$$

where $\overline{V}$ is a mean value of volumes measured at two different pressures.

The pressure difference $\Delta p \leq 0.8$ bar, which in case of liquids of low compressibility can be considered as a differential increment, dp, allows for very precise measurements of the isothermal compressibility coefficient, β_T. A small increment of pressure allows one also to measure β_T close to the transition temperature without change of phase due to the change of

pressure. Close to the transition temperature measurements were taken at temperature increments of 5–10 mK.

The temperature dependence of the isothermal compressibility coefficient, $\beta_T(T)$, calculated according to eq 6, was described with the equations similar to eq 1 for C_P

$$\beta_T(T) = \begin{cases} A|t|^{-\alpha}(1 + D|t|^{0.5}) + B, & T > T^{AN} \\ A'|t|^{-\alpha'}(1 + D'|t|^{0.5}) + B', & T < T_{AN} \end{cases} \quad (7)$$

with $t = T/T_{AN} - 1$. In numerical analysis of the data, eqs 7 were simplified by the constraint $D = D' \equiv 0$.

The quality of all fits is represented by standard deviation, σ, and by weighted value χ_v^2 defined as

$$\chi_v^2 = \frac{1}{n-p}\sum_{i=1}^{n} w_i(X_i^{expt} - X_i^{calc})^2 \quad (8)$$

where X_i is replaced by V_i or β_{Ti}, w_i is the weight of each point, n is the number of experimental points, and p is the number of adjustable parameters. The calculations were carried out twice: for $w_i = 1$ (then "chi-square" is the square of the standard deviation of the fit, $\chi_v^2 = \sigma^2$) and for $w_i = 1/\sigma_i^2$, where $\sigma_i^2 = \sigma_X^2 + \sigma_T^2(dX/dT)^2$ with σ_X being an experimental error of V or β_T and $\sigma_T = 0.0002-0.0005$ K.

In following parts of the paper our new results for the smectic-A to nematic phase transition in 8CB and in $\overline{10S5}$ are presented and a comparison with the results obtained by other experimental techniques is discussed.

A. 8CB. Most reliable and detailed studies of the SmA–N transition in 8CB were done by Thoen *et al.*[17] using adiabatic scanning calorimeter of very high resolution. They proved undoubtedly that a discontinuity in enthalpy at the SmA–N phase transition, if present, is less than 0.4 J/mol, so they concluded that the transition is continuous. Density[18] and molar volume[19] were also measured by other authors in the vicinity of this transition, and a volume jump was estimated. A wide discussion of these discrepancies was given by Thoen *et al.*[17] with the conclusion that pretransitional increase of volume was included in the estimated volume change because of unjustified extrapolation. The volume jump, ΔV_{AN}, estimated this way does not seem very reliable.

We measured about 120 points of volume within the temperature range 305.35–308.65 K and at two different pressures. Close to the transition temperature volume was measured with 5 mK temperature steps. To show the $V(T)$ curve on the graph with a resolution comparable to the resolution of our experiments, an arbitrary background, linear with temperature, had to be subtracted. The results are shown in Figure 1 as the deviations of the volumetric data from a linear background. In the numerical analysis we fitted the molar volume data with eqs 4. The result of the lack of singularity in volume changes at the transition (inflection point, not divergence nor maximum) was that the transition temperature could not be treated in the fitting procedure as an adjustable parameter (the optimizing procedure could not reach a convergence). The transition temperature T_{AN} was established during preliminary fits of the following differential quotients,

$$Q_i = \frac{V_i - V(T_{AN})}{T_i - T_{AN}} \quad (9)$$

to the equations

TABLE 2: Results of the Preliminary Fits of Molar Volume Data for 8CB near the Smectic-A to Nematic Transition for Different Transition Temperature T_{AN}[a]

T_{AN} (K)	$V(T_{AN})$ (cm³/mol)	α,α'	A, A' (cm³/mol)	B, B' (cm³/mol)	$10^4\sigma$ (cm³/mol)	χ_v^2
307.0930	294.3921	0.344	0.015	0.227	1.51	
		0.183	0.078	0.107	2.74	1.79
307.0940	294.3930	0.304	0.022	0.206	1.74	
		0.279	0.025	0.211	1.48	1.45
307.0942	294.3932	0.297	0.024	0.203	1.67	
		0.297	0.021	0.223	1.26	1.35
307.0944	294.3934	0.281	0.028	0.191	1.85	
		0.310	0.018	0.231	1.26	1.41
307.0954	294.3944	0.219	0.055	0.133	2.34	
		0.357	0.012	0.250	1.16	1.56

[a] Data from the temperature range 306.70–307.40 K were fitted with the eqs 9 and 10; σ is the standard deviation and χ_v^2 is the mean weighted value of the square deviations calculated from eq 8 for each pair of fits above and below T_{AN}

$$Q(T) = \begin{cases} \dfrac{A}{T_{AN}}\left|\dfrac{T - T_{AN}}{T_{AN}}\right|^{-\alpha} + \dfrac{B}{T_{AN}}, & T > T_{AN} \\ \dfrac{A'}{T_{AN}}\left|\dfrac{T - T_{AN}}{T_{AN}}\right|^{-\alpha'} + \dfrac{B'}{T_{AN}}, & T < T_{AN} \end{cases} \quad (10)$$

with T_{AN} being changed by iterations with steps of 0.0002 K. This procedure is similar to that applied by Thoen *et al.*[17] in their analysis of the enthalpy data. The criteria of choosing the best value of T_{AN} were a minimum of χ_v^2 calculated for both fits below and above T_{AN} and also an equality of critical exponents, $\alpha = \alpha'$. The results of some fits established this way at $T_{AN} = 307.0942$ K are presented in Table 2.

Next we have fitted the $V(T)$ data from three different temperature ranges with eqs 4 and with $T_{AN} = 307.0942$ K fixed. The results are shown in Table 3. For narrow ranges with $t_{max} \cong (0.5$ and $1.0) \times 10^{-3}$ the correction-to-scaling term did not make any improvement to the fits (fits 1–4), so we set $D = D' \equiv 0$. For the range $t_{max} \cong 2 \times 10^{-3}$ the correction-to-scaling term was introduced, and the results are given as fits 5–8. The values of calculated critical exponents are insensitive to the range shrinking and can be averaged to $\alpha = \alpha' = 0.32 \pm 0.02$, as shown in fits 7 and 8. In all fits the standard deviations $\sigma = (1.0-1.6) \times 10^{-4}$ cm³/mol were obtained. The line representing fits 7 and 8 is shown in Figure 1. The temperature dependence of the thermal expansion coefficient, $\alpha_p(T)$, was calculated from eqs 5 with parameters of fits 7 and 8 in Table 3 and is shown in Figure 2 together with $\alpha_p(T)$ for $\overline{10S5}$, for comparison. Experimental points given in the plot were calculated from the pairs of neighboring data points as $\overline{\alpha_p} = (1/\overline{V})(\Delta V/DT)_p$.

From the values of parameters $C = V(T_{AN}^+)$ and $C' = V(T_{AN}^-)$ it is possible to estimate the volume jump at the transition as $\Delta V_{AN} = C - C'$. Because in our fits we obtained $C \cong C' = V(T_{AN}^{\pm}) = 297.3932 \pm 0.0002$ cm³/mol, we concluded that the transition is continuous. It should be mentioned that the error of our estimation $\delta V = \pm 0.0002$ cm³/mol can be related to $\delta H = \pm 0.3$ J/mol by Clapeyron's equation taking a value of $(dp/dT)_{coex} = 41.6$ bar/K, as we estimated from a few isotherms of volume against pressure.[20]

Isothermal compressibility coefficients, β_T, for 8CB were calculated according to eq 6, and the results are shown in Figure 3. In preliminary calculations the data from the range 306.76–307.40 K ($|t|_{max} \cong 10^{-3}$) were fitted to eqs 7 with the constraint $D = D' \equiv 0$ and with different values of T_{AN}. The temperature T_{AN} was changed by iterations with steps of 0.0005 K to find its best value, giving an equal exponent, $\alpha = \alpha'$, and a minimum

Critical Exponents for Thermal Expansion

J. Phys. Chem. B, Vol. 101, No. 35, 1997 **6973**

TABLE 3: Parameter Values Obtained from the Fitting of Molar Volume Data for 8CB above and below the Smectic-A to Nematic Transition with Eqs 4[a]

fit	phase	$10^3 t_{max}$	α, α'	A, A' (cm³/mol)	B, B' (cm³/mol)	C, C' (cm³/mol)	D, D'	$10^4 \sigma$ (cm³/mol)
1	N	0.510	0.304 ± 0.010	6.297 ± 0.696	61.950 ± 2.519	294.3931 ± 0.0001		1.26
2	Sm-A	0.500	0.304 ± 0.029	−5.911 ± 1.861	−69.833 5.932	294.3933 ± 0.0001		1.00
3	N	0.994	0.321 ± 0.012	5.457 ± 0.534	68.681 ± 1.729	294.3931 ± 0.0001		1.27
4	Sm-A	1.066	0.320 ± 0.016	−4.952 ± 0.789	−73.221 ± 2.335	294.3933 ± 0.0001		1.13
5	N	1.974	0.331 ± 0.016	5.739 ± 0.792	44.895 ± 3.093	294.3929 ± 0.0001	10.300 ± 3.149	1.30
6	Sm-A	2.101	0.306 ± 0.015	−4.045 ± 0.499	−108.693 ± 2.502	294.3928 ± 0.0001	−23.075 ± 1.251	1.62
7	N	1.974	(0.320)	6.452	41.802	294.3929	10.106	1.30
8	Sm-A	2.101	(0.320)	−3.348	−116.132	294.3928	−29.951	1.61

[a] Constraint $D = D' \equiv 0$ was made in fits 1–4; transition temperature $T_{AN} = 307.0942$ K was chosen from fits shown in Table 2 and was held fixed in all fits; σ is the standard deviation. Values in parentheses were held fixed during the fit. $t_{min} = |T/T_{AN} - 1| = 8.14 \times 10^{-6}$ for $T > T_{AN}$ and $t_{min} = 5.86 \times 10^{-6}$ for $T < T_{AN}$.

TABLE 4: Results of the Preliminary Fits of Isothermal Compressibility for 8CB in the Vicinity of the Smectic-A to Nematic Transition for Different Transition Temperatures T_{AN}[a]
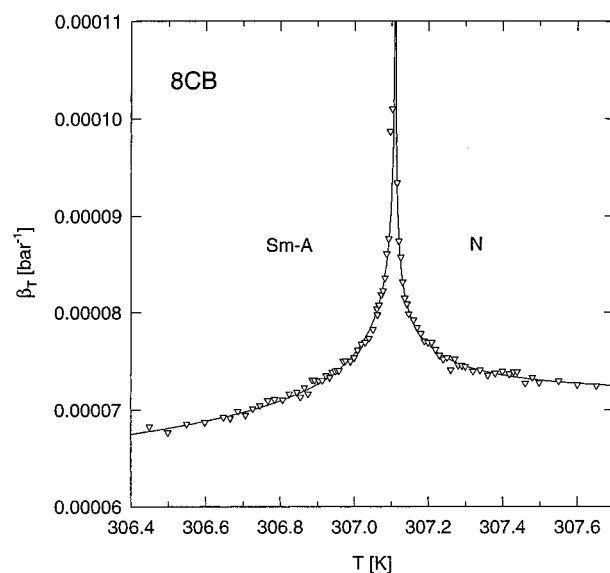
T_{AN} (K)	phase	α, α'	A, A' (10^{-6}bar^{-1})	B, B' (10^{-6}bar^{-1})	σ (10^{-6}bar^{-1})	χ_v^2
307.1090	N	0.352 ± 0.033	0.559 ± 0.292	66.94 ± 1.49	0.38	
	Sm-A	0.316 ± 0.040	1.215 ± 0.555	60.71 ± 2.07	0.37	0.929
307.1095	N	0.336 ± 0.027	0.662 ± 0.209	66.60 ± 1.05	0.37	
	Sm-A	0.327 ± 0.037	1.073 ± 0.453	61.13 ± 1.81	0.37	0.921
307.1100	N	0.311 ± 0.029	0.875 ± 0.310	65.82 ± 1.29	0.38	
	Sm-A	0.337 ± 0.040	0.965 ± 0.426	61.53 ± 1.84	0.38	0.935

[a] Data from the temperature range 306.76–307.40 K were fitted with eqs 7 with the constraint $D = D' \equiv 0$; σ is the standard deviation and χ_v^2 is the mean weighted value of the square deviations calculated from eq 8 for each pair of fits above and below T_{AN}.
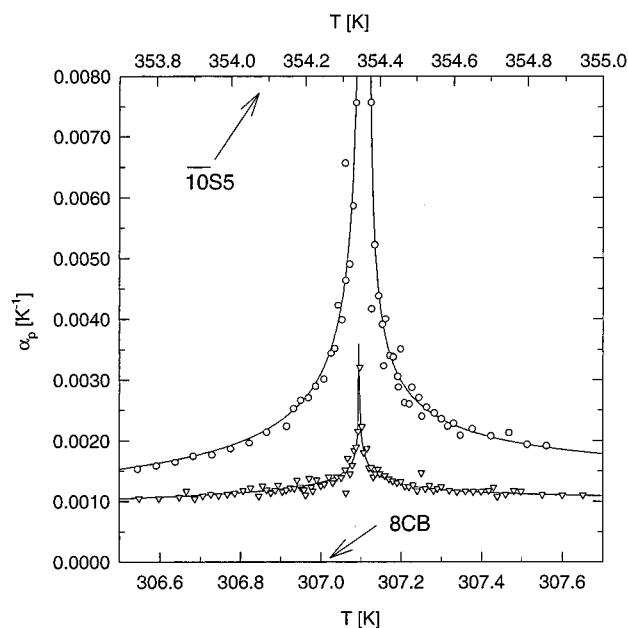
Figure 2. Thermal expansion coefficient, α_p, near the smectic-A to nematic phase transition. Lower part for 8CB: ($\triangledown$) results calculated from pairs of neighboring data points, solid line was calculated from eqs 5 with parameters from fits 7 and 8 in Table 3. Upper part for 10S5: ($\bigcirc$) results calculated from pairs of neighboring data points, solid line was calculated form eqs 5 with parameters from fits 1 and 2 in Table 7.

Figure 3. Isothermal compressibility coefficients, β_T, versus temperature for 8CB in the vicinity of the smectic-A to nematic phase transition. Solid line was calculated from eqs 7, fits 3 and 4 in Table 5.

of χ_v^2. The transition temperature $T_{AN} = 307.1095$ K was established as shown in Table 4. This value differs slightly from that established in analysis of $V(T)$ data because the data of $\beta_T(T)$ must be treated as measured at slightly higher pressure, *i.e.* average between 1.0 and 1.8 bar. Only four points from the range 307.095–307.110 K for which an increase of pressure caused the transition from nematic to smectic-A were excluded in all calculations. To extract the best value of the critical exponent α, the two other temperature ranges of data with $|t|_{max} \cong (2$ and $5) \times 10^{-3}$ were analyzed, and results are given in

Table 5. The values of α and α' obtained in fits 1 and 2 with $D = D' \equiv 0$ differ from those in Table 4 obtained for the range $|t|_{max} \cong 10^{-3}$ and for the same $T_{AN} = 307.1095$ K, but a correction-to-scaling term introduced in fits 3 and 4 gave the same values of effective critical exponents $\alpha = \alpha' = 0.33 \pm 0.04$. Fits 5 and 6 for $|t|_{max} > 5 \times 10^{-3}$ gave also a very good description of the data with similar standard deviations $\sigma = (0.34$ and $0.43) \times 10^{-6}$ bar^{-1}, but the obtained critical exponents $\alpha = \alpha' = 0.28 \pm 0.03$ are much lower because of too much weight put on the points far from the phase transition.

B. $\overline{10S5}$. The SmA–N phase transition in $\overline{10S5}$ was studied by Brisbin *et al.*[7] in an ac calorimeter. The critical exponent $\alpha = 0.45$ was found with the suggestion that the transition might be of the first order. The jump of the entropy

TABLE 5: Parameter Values Obtained from the Fitting of Isothermal Compressibility Data for 8CB above and below the Smectic-A to Nematic Phase Transition with Eqs 7[a]

| fit	phase	n, n'	$10^3 t_{max}$	α, α'	A, A' (10^{-6}bar^{-1})	B, B' (10^{-6}bar^{-1})	D, D'	σ (10^{-6}bar^{-1})
1	N	38	2.088	0.361 ± 0.022	0.484 ± 0.123	67.60 ± 0.65		0.39
2	Sm-A	45	2.151	0.230 ± 0.017	3.509 ± 0.753	53.87 ± 1.70		0.42
3	N	38	2.088	0.315 ± 0.025	0.912 ± 0.284	62.58 ± 2.66	10.97 ± 4.79	0.36
4	Sm-A	45	2.151	0.333 ± 0.036	0.798 ± 0.345	71.74 ± 3.90	-34.37 ± 7.23	0.40
5	N	48	5.015	0.281 ± 0.019	1.524 ± 0.372	57.77 ± 2.53	15.31 ± 4.17	0.34
6	Sm-A	53	5.737	0.290 ± 0.030	1.331 ± 0.273	68.03 ± 3.39	-22.15 ± 7.82	0.43

[a] Transition temperature $T_{AN} = 307.1095$ K was held fixed in all fits; n and n' are the numbers of experimental points; σ is the standard deviation.
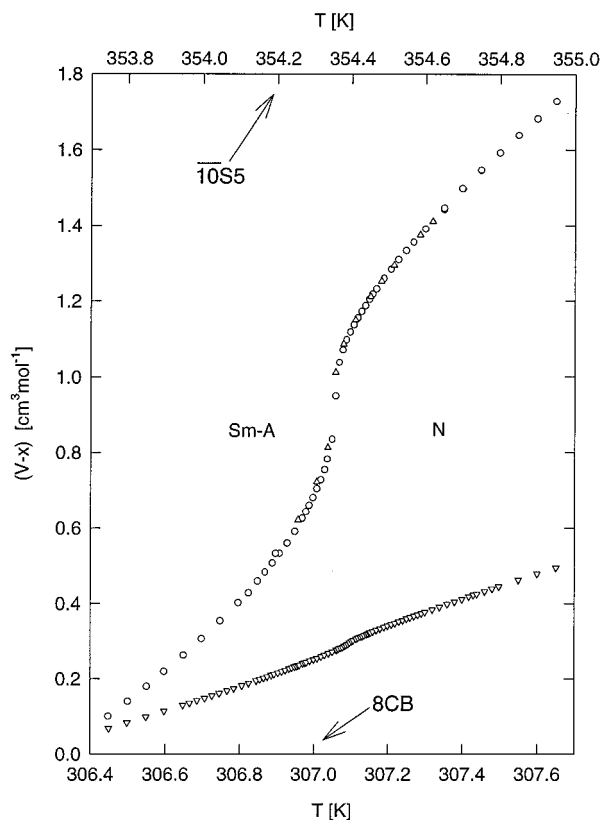
Figure 4. Temperature dependence of molar volume near the first-order smectic-A to nematic phase transition for $\overline{10S5}$ (upper curve); the data are shifted down by a constant value $x = 479.94$ cm³/mol. For comparison, the direct $V(T)$ data for 8CB (lower curve) shifted by $x = 294.10$ cm³/mol are shown.

at this transition, $\Delta S_{AN} = 0.05R$, was estimated. High-resolution X-ray scattering measurements showed that this transition is continuous and a tricritical point occurs in a mixture 0.8 mol $\overline{10S5}$ + 0.2 mol $\overline{11S5}$. In our studies we would like to clarify the above discrepancies and to compare the heat capacity exponents α with those determined by us from molar volume and, for the first time, from the compressibility measurements.

The volumetric and compressibility measurements near the SmA−N phase transition in $\overline{10S5}$ have been done using the same procedure as described above. The $V(T)$ results reveal pretransitional effects much stronger than that in 8CB that is shown in Figure 4. For comparison the $V(T)$ curves for $\overline{10S5}$ and 8CB without subtracted background but shifted by a constant "x" are drawn in this figure. The molar volumes of $\overline{10S5}$ were measured in two runs, during heating and cooling. A small horizontal shift about 10 mK between these two runs was found and can be seen in Figure 5 drawn against an expanded temperature scale. This "hysteresis", although not certain because of temperature shift comparable with the distance between particular points, together with the two-phase
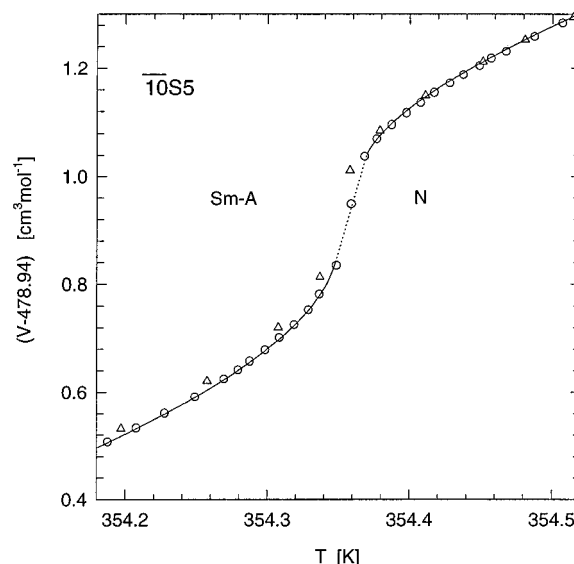
Figure 5. Details of the molar volume changes in the vicinity of the smectic-A to nematic transition in $\overline{10S5}$: (O) heating run, (△) cooling run; the solid line was calculated from eqs 4 with parameters from fits 1 and 2 in Table 7; dotted line denotes a two-phase region.

TABLE 6: Standard Deviations, σ, Obtained from the Preliminary Fits of Molar Volume Data for $\overline{10S5}$ near the Smectic-A to Nematic Phase Transition for Different Transition Temperatures, T_{AN}^-, T_{AN}^+, and Exponents α, α': Data from the Temperature Ranges 353.25−354.34 K for Smectic-A Phase and 354.38−355.55 K for Nematic Phase Were Fitted with Eqs 4 with Constraint $D = D' \equiv 0$

	$10^4 \sigma$ (cm³/mol)				
	$\alpha = 0.40$	$\alpha = 0.45$	$\alpha = 0.50$	$\alpha = 0.55$	$\alpha = 0.60$
			Smectic-A Phase		
T_{AN}^-/(K)					
354.348	20.2	9.6	5.3	15.2	26.8
354.350	24.4	13.9	4.5	9.6	20.5
354.352	28.5	18.2	8.1	5.2	15.1
			Nematic Phase		
T_{AN}^+/(K)					
354.366	13.2	7.8	2.9	4.9	10.5
354.368	11.5	6.1	2.8	7.1	12.9
354.370	9.8	4.6	4.2	9.5	15.6

region observed in the range about 30 mK, proves that this transition is of first order. Only the data obtained during the heating run were considered in further analysis.

Different transition temperatures, T_{AN}^- from the SmA side and T_{AN}^+ from the N side, were considered. The preliminary fits, in which "a map" of standard deviations was made for different values of T_{AN} and α, are given in Table 6. The lowest values of standard deviation were obtained for $\alpha = \alpha' = 0.50$ and for the transition temperatures $T_{AN}^- = 354.350$ K and $T_{AN}^+ = 354.368$ K from the side of SmA and N, respectively. The $V(T)$ data of four temperature ranges with $|t|_{max} = (0.5,$

Critical Exponents for Thermal Expansion

J. Phys. Chem. B, Vol. 101, No. 35, 1997 **6975**

TABLE 7: Parameter Values Obtained from the Fitting of Molar Volume for $\overline{10}$S5 above and below the Smectic-A to Nematic Transition with Eqs 4 with Constraint $D = D' \equiv 0^a$

fit	phase	n, n'	$10^3 t_{max}$	α, α'	A, A' (cm^3/mol)	B, B' (cm^3/mol)	C, C' (cm^3/mol)	$10^4 \sigma$ (cm^3/mol)	ΔV_{AN} (cm^3/mol)
1	N	34	3.341	0.500 ± 0.017	10.45 ± 1.30	180.27 ± 9.10	479.9463 ± 0.0035	2.8	0.1276
2	Sm-A	27	3.111	0.496 ± 0.016	-16.38 ± 1.80	-72.12 ± 9.40	479.8186 ± 0.0062	4.3	
3	N	30	2.214	0.495	10.81	178.32	479.9472	2.8	0.1259
4	Sm-A	24	2.262	0.497	-16.47	-69.13	479.8313	3.4	
5	N	23	1.075	0.494	10.90	178.27	479.9477	2.6	0.1260
6	Sm-A	17	0.993	0.498	-16.23	-71.12	479.8217	3.8	
7	N	13	0.548	0.492	10.79	186.14	479.9496	3.0	0.1284
8	Sm-A	13	0.512	0.491	-17.54	-55.78	479.8212	3.5	

^{a} Transition temperatures $T_{AN}^- = 354.350$ K and $T_{AN}^+ = 354.368$ K were fixed in the calculations; n and n' are numbers of the experimental points used in calculations; σ is the standard deviation; $\Delta V_{AN} = C - C'$ is the estimated volume jump at T_{AN}. $t_{min} = |T/T_{AN}^+ - 1| = 5.475 \times 10^{-5}$ for the nematic phase and $t_{min} = |T/T_{AN}^- - 1| = 3.753 \times 10^{-5}$ for the smectic-A phase.

TABLE 8: Parameter Values Obtained from the Fitting of Isothermal Compressibility Data for $\overline{10}$S5 above and below the Smectic-A to Nematic Phase Transition with Eqs 7 with the Constraint $D = D' \equiv 0^a$

fit	phase	n, n'	$10^3 t_{max}$	α, α'	A, A' (10^{-6}bar^{-1})	B, B' (10^{-4}bar^{-1})	σ (10^{-4}bar^{-1})
1	N	32	3.329	0.508 ± 0.017	0.661 ± 0.106	0.810 ± 0.012	0.015
2	Sm-A	28	3.147	0.517 ± 0.021	1.001 ± 0.107	0.598 ± 0.013	0.011
3	N	19	0.922	0.501	0.715	0.798	0.011
4	Sm-A	18	1.029	0.502	1.186	0.567	0.013
5	N	13	0.496	0.498	0.750	0.790	0.012
6	Sm-A	13	0.494	0.502	1.181	0.571	0.013

^{a} Transition temperatures $T_{AN}^- = 354.363$ K and $T_{AN}^+ = 354.372$ K were held fixed in all fits; n and n' are the numbers of experimental points; σ is the standard deviation; deviations of the parameters for fits 3–5 are omitted because they are the same as for fits 1 and 2.

1.0, 2.2, and 3.3) $\times 10^{-3}$ were next fitted with eqs 4 with T_{AN}^- and T_{AN}^+ fixed and α treated as a freely adjustable parameter. The correction-to-scaling term was neglected in all fits; that is, the assumption $D = D' \equiv 0$ was made. Results collected in Table 7 show that $V(T)$ data are very well described by effective exponents $\alpha = \alpha' = 0.50 \pm 0.01$ and all parameters are insensitive to the range shrinking. Standard deviations of the fits, $\sigma = (2.8–3.8) \times 10^{-4}$ cm^3/mol, are slightly worse than for 8CB because of greater temperature fluctuations (about ± 0.5 mK) at higher temperatures. The last column of Table 7 gives the volume jump at the transition estimated from the C and C' parameters as $\Delta V = C - C' = 0.127 \pm 0.001$ cm^3/mol ($\Delta V_{AN}/V_{AN} = 2.6 \times 10^{-4}$), *i.e.* 3 orders of magnitude greater than the resolution of our experiment. There is no doubt that the SmA–N phase transition in $\overline{10}$S5 is of the first order.

The thermal dependence of the isothermal expansion coefficient $\alpha_p(T)$ was calculated according to eqs 5, with parameters of fits 1 and 2 given in Table 7, and the results are presented in Figure 2 along with the results of $\alpha_p(T)$ for 8CB.

The thermal dependence of the isothermal compressibility coefficient $\beta_T(T)$ near the SmA–N phase transition in $\overline{10}$S5 is shown in Figure 6. For comparison the curve of $\beta_T(T)$ for 8CB is drawn also in the figure. The strong divergence was described with eqs 7 with $D = D' \equiv 0$. Different transition temperatures $T_{AN}^- = 354.363$ K and $T_{AN}^+ = 354.372$ K were found in preliminary fits performed the same way as for 8CB but for both phases separately. The critical exponents as well as other adjustable parameters calculated from $\beta_T(T)$ data are stable to the range shrinking, as can be seen from the results given in Table 8. The same value of the effective exponent, $\alpha = \alpha' = 0.50 \pm 0.02$, consistent with theoretical predictions for the tricritical point,[21] was obtained from $\beta_T(T)$ as well as from $V(T)$ fits. Although this transition is definitely first order, it is also close to the tricritical point. We can expect that the tricritical point should occur in a mixture of $\overline{9}$S5 + $\overline{10}$S5 rather than in $\overline{10}$S5 + $\overline{11}$S5, as suggested by Ocko *et al.*[8]
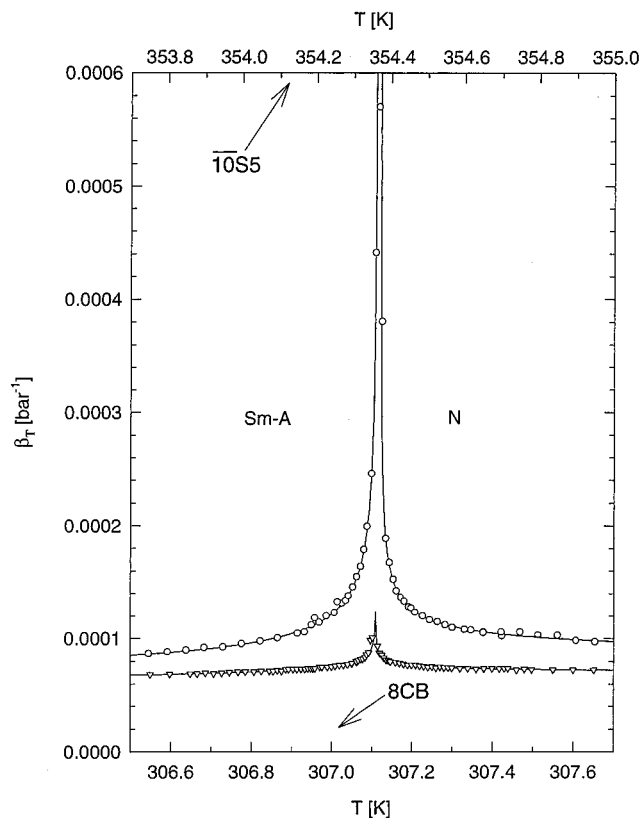
Figure 6. Isothermal compressibility coefficients, β_T, versus temperature for $\overline{10}$S5 near the smectic-A to nematic transition (upper part); solid line was calculated from eqs 7 with parameters from fits 5 and 6 in Table 6. For comparison, $\beta_T(T)$ results for 8CB (from Figure 3) are drawn in the same scale.

III. Discussion and Conclusions

In this paper we have presented new experimental results of temperature dependence of molar volume, thermal expansion, and isothermal compressibility near the smectic-A to nematic
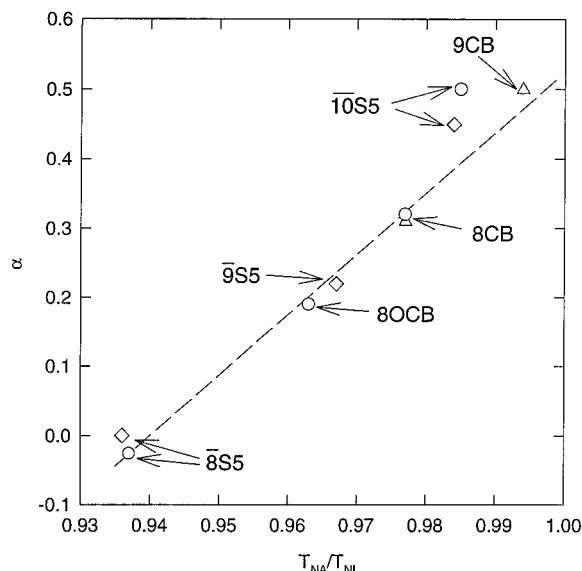
Figure 7. Critical exponents α for the smectic-A to nematic phase transition for different liquid crystals determined by different authors: ($\diamond$) Brisbin *et al.*;[7] ($\triangle$) Marynissen *et al.*[9]; ($\bigcirc$) this work and Żywociński *et al.*;[13] the straight line is a guide for the eye.

phase transition. The compounds studied, 8CB and $\overline{10}$S5, belong to different homologous series exhibiting different smectic-A phases, *i.e.* SmA$_d$ and SmA$_m$, respectively. The McMillan's ratios T_{AN}/T_{NI} are equal to 0.977 for 8CB and 0.985 for $\overline{10}$S5.

The experimental critical exponent, α, obtained from $V(T)$ and $\beta_T(T)$ measurements for 8CB near the SmA−N phase transition can be averaged to $\alpha = \alpha' = 0.32 \pm 0.02$. Kasting *et al.*[22] using their ac calorimeter and Thoen *et al.*[17] in adiabatic scanning calorimetry have obtained for 8CB similar values of critical exponents, $\alpha = 0.30 \pm 0.05$ and $\alpha = 0.31 \pm 0.03$, respectively. All these exponents are consistent with correlation-length exponents[23] $\nu_{\parallel} = 0.67 \pm 0.03$ and $\nu_{\perp} = 0.51 \pm 0.03$ satisfying the anisotropic scaling relation

$$\alpha + \nu_{\parallel} + 2\nu_{\perp} = 2 \qquad (11)$$

within the experimental error.

For $\overline{10}$S5 a weak first-order transition with a volume jump $\Delta V_{AN} = 0.127 \pm 0.001$ cm^3/mol was found, in contradiction to the results of high-resolution X-ray scattering measurements[8] where the tricritical point was found in a mixture 0.8 mol $\overline{10}$S5 + 0.2 mol $\overline{11}$S5. We found that pretransitional effects at this transition can be described with the exponent $\alpha = \alpha' = 0.50 \pm 0.02$. The anisotropic critical exponents for correlation lengths, $\nu_{\parallel} = 0.61 \pm 0.03$ and $\nu_{\perp} = 0.51 \pm 0.05$, have also been determined[8] for pure $\overline{10}$S5. The above exponents as well as $\alpha = 0.45$ found by Brisbin *et al.*[7] are consistent with the scaling relation, eq 11, within limits of experimental uncertainty.

Although nonuniversality of the smectic-A to nematic phase transition is not fully explained, the dependence of critical exponents α on the McMillan's ratios T_{AN}/T_{NI} is evident. Our present and earlier[13] results are compared with others[7,9] in Figure 7. Only the best literature values for nCB and $\bar{m}$S5 homologous series are shown together with our results obtained from volumetric measurements (except, our result[13] for 8OCB

exhibiting SmA$_d$ phase is added). More data can be found in a similar graph in an overview by Garland and Nounesis.[4] However, effective critical exponents α determined from $V(T)$, $\beta_T(T)$, and $C_p(T)$ measurements and shown in Figure 7 lie almost on a straight line (except those for $\overline{10}$S5), and it is obvious that an extrapolation to $\alpha = 0.5$ cannot give the McMillan's ratio for the tricritical point $(T_{AN}/T_{NI})_{TCP}$. The above results as well as careful investigations by Ocko *et al.*[8] have shown that $(T_{AN}/T_{NI})_{TCP}$ must be different in different homologous series. McMillan's parameter is greater for 9CB (very close to tricritical) than for $\overline{10}$S5 (first order). It cannot be said whether the dependence of α on T_{AN}/T_{NI} in the crossover region, *i.e.* for $0.93 < (T_{AN}/T_{NI}) < 1$, is simply linear or more complicated.

In summary we would like to remark that the singularities in isobaric thermal expansion α_p, isothermal compressibility β_T, and isobaric heat capacity C_p in the vicinity of the smectic-A to nematic phase transition are described by the same critical exponent α. Our improved volumetric method can be successfully applied to study the pretransitional effects near the phase transitions in liquid crystals or other systems. The results of isothermal compressibility coefficients near the continuous phase transition in liquid crystal are the first of such resolution.

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