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Thermodynamic analysis of the low frequency relaxation time in the smectic *A* and *C* phases of a liquid crystal

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Pressure-temperature-volume (pVT) measurements were carried out on 2-(4-hexyloxyphenyl)-5-octyl-pyrimidine, a substance exhibiting nematic and smectic *A* and *C* polymorphism. Analysis of the longitudinal relaxation times obtained recently for elevated pressures [Czub *et al.*, Z. Naturforsch. A: Phys. Sci. **58**, 333 (2003)] was performed for isobaric, isothermal, and isochoric conditions within the two smectic phases. Several relationships linking the dynamical and thermodynamical quantities, derived recently for isotropic glass formers [Roland *et al.* Rep. Prog. Phys. **68**, 1405 (2005)], were found to hold for the liquid crystal, revealing a striking similarity of behaviors for these two types of materials. The parameter γ characterizing the steepness of the interaction potential was derived in different ways. It is interesting that the liquid crystal gives relaxation time versus $TV^{-\gamma}$ plots that are linear, unlike results for glass formers, implying that the dynamics of the former is thermally activated. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2759488]

INTRODUCTION

Rotational motion of elongated molecules around the short axes in the liquid crystalline (LC) phases is possible due to coupling with the translational movements (fluctuations) of their centers of mass. X-ray studies indicate that the distance between the centers of molecules in smectic phases are approximately 30%–40% of their lengths on average.[1–3] External pressure reduces the intermolecular distances and thus must influence considerably the dynamical characteristics of molecules in LC phases. Dielectric relaxation is well suited to study the dynamical properties of dipolar molecules in LC phases subjected to elevated pressures,[4–6] especially the low frequency relaxation time $\tau_{\|}$ characterizing the flip-flop motions of elongated molecules in a given LC phase. This relaxation time is sensitive to the temperature (T), pressure (p), and volume (V), and can be parameterized in terms of the activation quantities:

- Activation enthalpy,

$$\Delta^{\#}H = R\left(\frac{\partial \ln \tau}{\partial(1/T)}\right)_p, \tag{1}$$

- Activation energy,

$$\Delta^{\#}U = R\left(\frac{\partial \ln \tau}{\partial(1/T)}\right)_V = \Delta^{\#}H - T\left(\frac{\partial p}{\partial T}\right)_V \Delta^{\#}V, \tag{2}$$

- Activation volume,

$$\Delta^{\#}V = RT\left(\frac{\partial T \ln \tau}{\partial(p)}\right)_T. \tag{3}$$

It is seen from Eq. (2) that $\Delta^{\neq}U$ is smaller than $\Delta^{\neq}H$; for many studied nematics and smectics the activation energy is roughly half the value of the activation enthalpy $\Delta^{\neq}H$.[4–8] This indicates that the energy barriers hindering the flip-flop molecular motions are equally determined by the thermal and volume effects in the LC phases. Such behavior indicates application of the thermodynamic scaling procedure,[9,10] which yields a parameter characterizing the steepness of the intermolecular repulsive potential.[11–15]

In the present paper we examine results of dielectric relaxation studies of 2-(4-hexyloxyphenyl)-5-octyl-pyrimidine (6OPB8, $M = 388.3$ g/mol) under elevated pressure.[16] The longitudinal relaxation time $\tau_{\|}$ characterizing the flip-flop molecular motions in two liquidlike smectic phases (smectic A and smectic C) are reanalyzed in light of new pVT measurements and the obtained equation of state, $V = f(p, T)$. In particular, the isochoric activation energy in both phases could be calculated, which completed the data on the isobaric activation enthalpy and the isothermal activation volume derived previously.[16] Several relationships linking the

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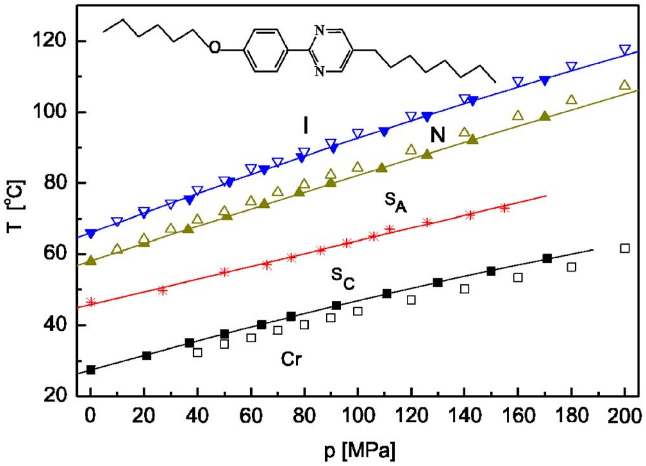

FIG. 1. Phase diagram of 6OPB8 (structure as indicated) from calorimetric (DTA) measurements (full symbols) (Ref. 16) and by PVT measurements (open symbols)—see Fig. 2.

relaxation time with thermodynamic quantities, developed recently for isotropic liquids and polymers,[9,11–15,17–19] will be employed for the two smectic phases.

EXPERIMENT

The 6OPB8 was obtained from the Institute of Chemistry, Military University of Technology in Warsaw, Poland, and used as received. Its structure is shown in Fig. 1.

The volumetric (pVT) measurements were performed with the apparatus described elsewhere.[15] Changes in sample volume were measured in the isobaric and isothermal modes. For the isobaric runs, at a given pressure in the range between 10 and 200 MPa, the measurements started at high temperature with the system cooled at 0.5 °C/min. The volume change was detected every 30 s, until the temperature 20 °C was reached. For the isothermal runs, at a constant temperature in the range of 25–105 °C, the ΔV values were collected with increasing pressure in 10 MPa increments up to 200 MPa.

The density $\rho = 1/V_m$ (V_m—specific volume) was measured at atmospheric pressure with the Anton Paar densitometer. The sample was cooled from the isotropic liquid to the LC phases. The obtained data enabled rescaling of the $\Delta V(p,T)$ results to the corresponding specific volumes.

RESULTS

Figure 1 shows the $p(T)$ phase diagram of the 6OPB8 as determined by calorimetric (differential thermal analysis, DTA) measurements[16] (full symbols and lines). In Fig. 2 the pVT data established for the 6OPB8 are presented. The small volume jumps observed at the I-N, N-S_A, and S_C-Cr (crystalline) phase transitions are denoted by the open symbols in Fig. 1. The line corresponding to the S_A-S_C transition in both figures comes from analysis of the relaxation times;[16] no change of the heat capacity or the density was observed at this transition due to its second order character. Figure 3 shows the longitudinal relaxation time $\tau_{\parallel}$ versus pressure at several isotherms within the S_A phase (open symbols) and the S_C phase (full symbols). These data were analyzed with Eqs. (1) and (3) leading to the activation enthalpy and activation volume, respectively.[16] Using the pVT data the relaxation times could now be determined for isochoric conditions, giving the activation energy. Figure 4 shows an example of an Arrhenius plot for one isochor. Similar to the data for isothermal and isobaric conditions,[16] a small but marked change of slope is observed, reflecting a smaller value of $\Delta^{\neq}U$ for the S_C than for the S_A phase. The two activation quantities, $\Delta^{\neq}H$ and $\Delta^{\neq}U$, are presented in Fig. 5 together with the activation volume data. As can be seen, the activation energy is approximately 65% of the activation enthalpy, while the activation volume is approximately 20% of the molar volume of the 6OPB8. These results indicate a greater contribution of volume to the dynamics for the molecules in the LC phase.

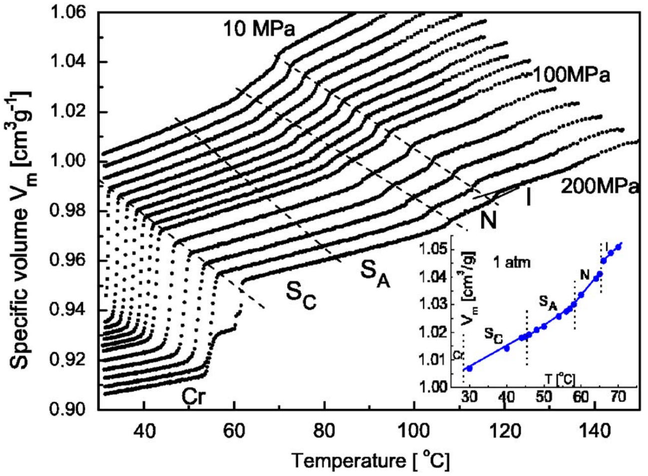

FIG. 2. Volume changes as a function of T and p, normalized by the specific volume at atmospheric pressure (see inset) for 6OPB8. The dashed lines indicate the phase transitions observed as steps in the isobars (no step is seen at the S_A-S_C transition; in this case the line was drawn according to Fig. 1). Isobars were measured every 10 MPa up to 100 MPa, and every 20 MPa above this pressure.

DISCUSSION

Liquid crystalline phases are formed by molecules having strongly anisotropic (usually rodlike) shapes, which lead

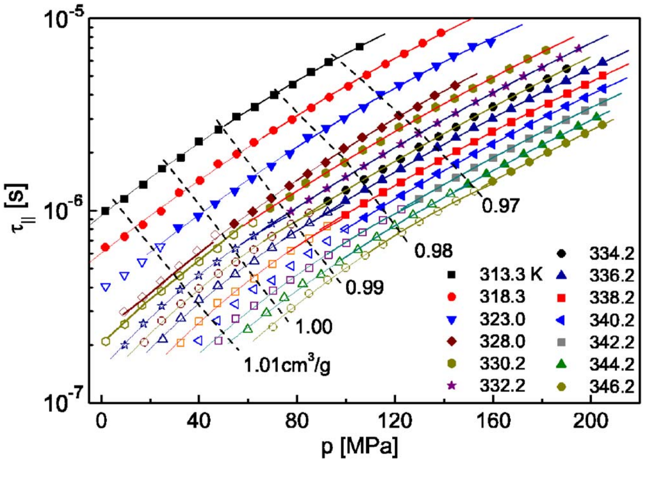

FIG. 3. Longitudinal relaxation time plotted logarithmically vs pressure for several isotherms within the smectic A phase (open symbols) and smectic C phase (full symbols) of 6OPB8 (Ref. 16). Dashed lines correspond to the isochors with the indicated specific volumes.

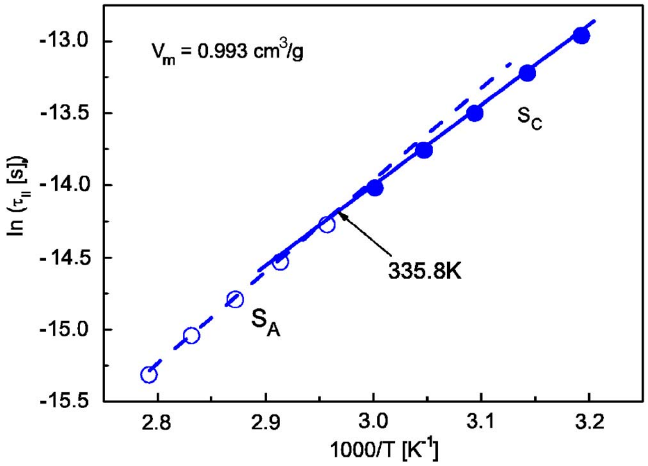

FIG. 4. Representative analysis of the relaxation time for one isochore within the smectic *A* and smectic *C* phases of 8OPB8.

to the anisotropy of molecular interactions indispensable for long range ordering of their symmetry axes. For simple isotropic liquids most of the physical properties can be well described by the Lennard-Jones intermolecular pair potential,[20]

$$U(r) = Ar^{-12} - Br^{-6}, \tag{4}$$

where A and B are constants and r is the intermolecular distance. In the case of LC substances consisting of asymmetric molecules, the mutual orientations of the neighboring molecules must be taken into account. This is realized by the potential proposed by Gay and Berne,[21] which has been successfully applied in many studies (for example, Refs. 22–24). The Gay-Berne potential can be written in the form

$$U(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\boldsymbol{r}) = 4\varepsilon(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\boldsymbol{r})(R^{-12} - R^{-6}), \tag{5}$$

where

$$R = [r - \sigma(\hat{\boldsymbol{u}}_i,\hat{\boldsymbol{u}}_j,\boldsymbol{r}) + \sigma_0]/\sigma_0. \tag{6}$$

The unit vectors $\hat{\boldsymbol{u}}_i$ and $\hat{\boldsymbol{u}}_j$ describe the orientations of a pair of particles in the laboratory frame, the vector $\boldsymbol{r}$ links the centers of mass of two particles, ϵ is the well depth, σ an orientation-dependent molecular shape parameter, and σ_0 is the contact distance when the particles are orthogonal to the interparticle vector. In general, the Lennard-Jones and the Gay-Berne potentials both include the attractive and repulsive parts. However, it is difficult to find properties of a liquid crystal phase that provide a clear distinction between the attractive and repulsive contributions to the interaction potential. For consideration of this problem, the pVT data are indispensable. Especially intriguing is the fact that the activation barriers hindering the flip-flop motions in the LC phases differ considerably for isobaric versus isochoric conditions.

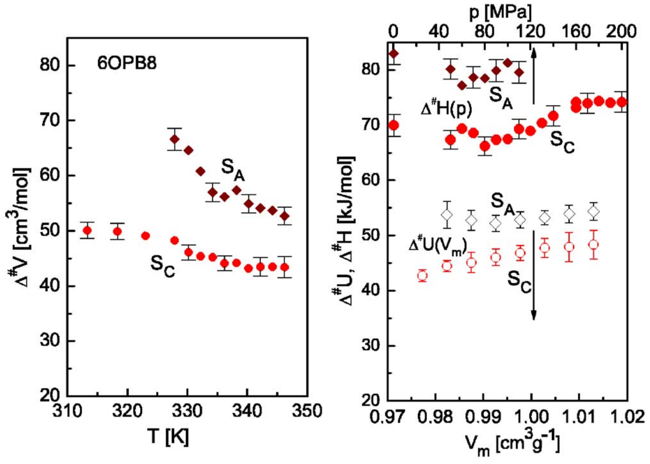

FIG. 5. Activation volume as a function of temperature, activation enthalpy as a function of pressure, and activation energy as a function of specific volume in the smectic *A* and smectic *C* phases of 6OPB8.

The well known Maier and Saupe mean field theory of the nematic state[25] assumes the stability of the phase to be due to anisotropic dispersion forces. The orientational energy of a single molecule in a field generated by its neighbors is

$$U_i(\theta_i) = -AS(3\cos^2\theta_i - 1)/2V^2, \tag{7}$$

where A depends solely on molecular properties, $S = \langle 3\cos^2\theta - 1\rangle/2$ is the second rank order parameter, θ is the angle between the long axis and the optical axis of the mesophase (the director), and V is the volume. The theory can be used to calculate the orientational contribution to all thermodynamic quantities.[26] In particular, the nematic-isotropic transition temperature T_{NI} is given by

$$T_{\mathrm{NI}} = A/4.541k_B V_{\mathrm{NI}}^2. \tag{8}$$

It should be noted that the Maier-Saupe theory was criticized by Cotter[27] who argued that in any mean field theory the thermodynamic consistency requires proportionality of the strength of potential to the density (inversely to the volume). However, Luckhurst[26] explains that "this particular failure of the Maier-Saupe theory stems from the form of the mean field approximation and not necessarily from the form of the intermolecular potential." High pressure experiments performed on nematics make clear that the repulsive part of the interaction potential cannot be ignored.[28–32] Also the theoretical slope $dT_{\mathrm{NI}}(p)/dp$ can be close to the experimental ones if the strong repulsive part is introduced to the interaction potential.[33] This means that the interaction potential depends more strongly on the intermolecular distances r than predicted by Maier-Saupe theory. Therefore it is useful to introduce the parameter γ to characterize the steepness of the interaction potential, $U(r) \sim V^{-\gamma} \sim r^{-3\gamma}$, whereby relation (8) can be replaced by

$$T_{\mathrm{NI}}(p) \sim V_{\mathrm{NI}}^{-\gamma}(p). \tag{9}$$

Using the results for $T_{\mathrm{NI}}(p)$ (Fig. 1) and $V_{\mathrm{NI}}(p)$ (Fig. 2) for 6OPB8, double logarithmic plots can be constructed, Fig. 6, with the slope yielding $\gamma = 2.5 \pm 0.2$; this is significantly higher than the quadratic dependence on volume in Eq. (8). For cyanobiphenyls and related compounds γ attains values of 4 and larger (see Refs. 10, 29, 31, and 32 and references therein). A similar relation was derived for glass formers, with the clearing line replaced by the temperature T_g corresponding to the glass transition.[11–14] T_g corresponds to a constant time characterizing the dynamics of molecules in the system (structural relaxation times, viscosity, ionic conductivity, and so on). In the case of the *N-I* transition in LC

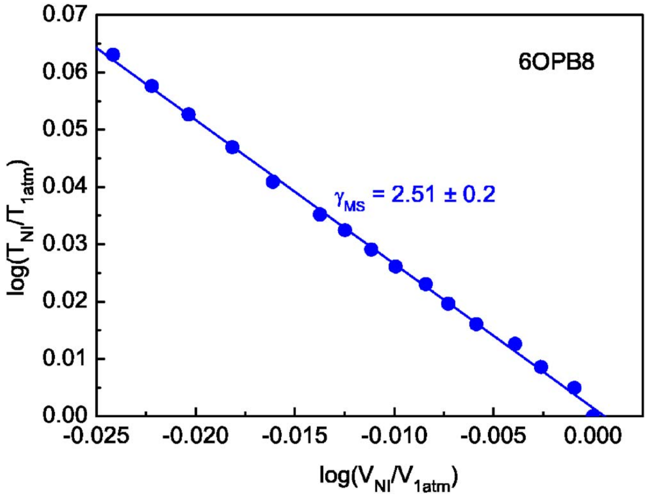

FIG. 6. Double logarithmic plot of the clearing temperature vs molar volume for 6OPB8 at different pressures (both scales normalized to the respective value at atmospheric pressure).

compounds, the longitudinal relaxation time has been found to be almost constant along the $T_{NI}(p)$ line (see Refs. 4–8 and references therein).

Casalini and Roland[9] have proposed for supercooled liquids and polymers the following formula, relating the relaxation time for the α-process with the temperature and volume:

$$\tau(V,T) = f(TV^{\gamma}), \tag{10}$$

where f is a function. It allowed rescaling of the relaxation data obtained at different thermodynamical conditions to a common master line with one adjustable parameter γ (see Refs. 8 and 15 and references therein). If the origins of the scaling behavior in Eq. (10) were thermally activated dynamics with an activation barrier varying as V^{γ}, the Arrhenius form would obtain

$$\tau(V,T) = \tau_0 \exp(C/TV^{\gamma}), \tag{11}$$

with τ_0 and C constants. However, unlike the results in Fig. 7(c), the structural relaxation times of supercooled, isotropic liquids are not proportional to $\exp(T^{-1}V^{-\gamma})$. On the other hand, Eq. (10) was recently applied by Urban and Würflinger[10] to accurately describe the longitudinal relaxation times of several LC substances measured under different thermodynamic conditions. This scaling procedure can be applied to the dynamics of 6OPB8 in the smectic *A* and *C* phases as well. In Fig. 7(a) and 7(b) the relaxation times determined for 6OPB8 in the *A* and *C* phases are plotted versus p and inverse T, respectively. The data, corresponding to different isothermal, isobaric, and isochoric conditions, fan out across the graph; neither p nor T uniquely defines τ.

When the same data are rescaled using $\gamma = 2.7 \pm 0.1$, the τ collapse to a single, straight line [Fig. 7(c)]. The small scatter of the points arises mainly from the interpolation procedure

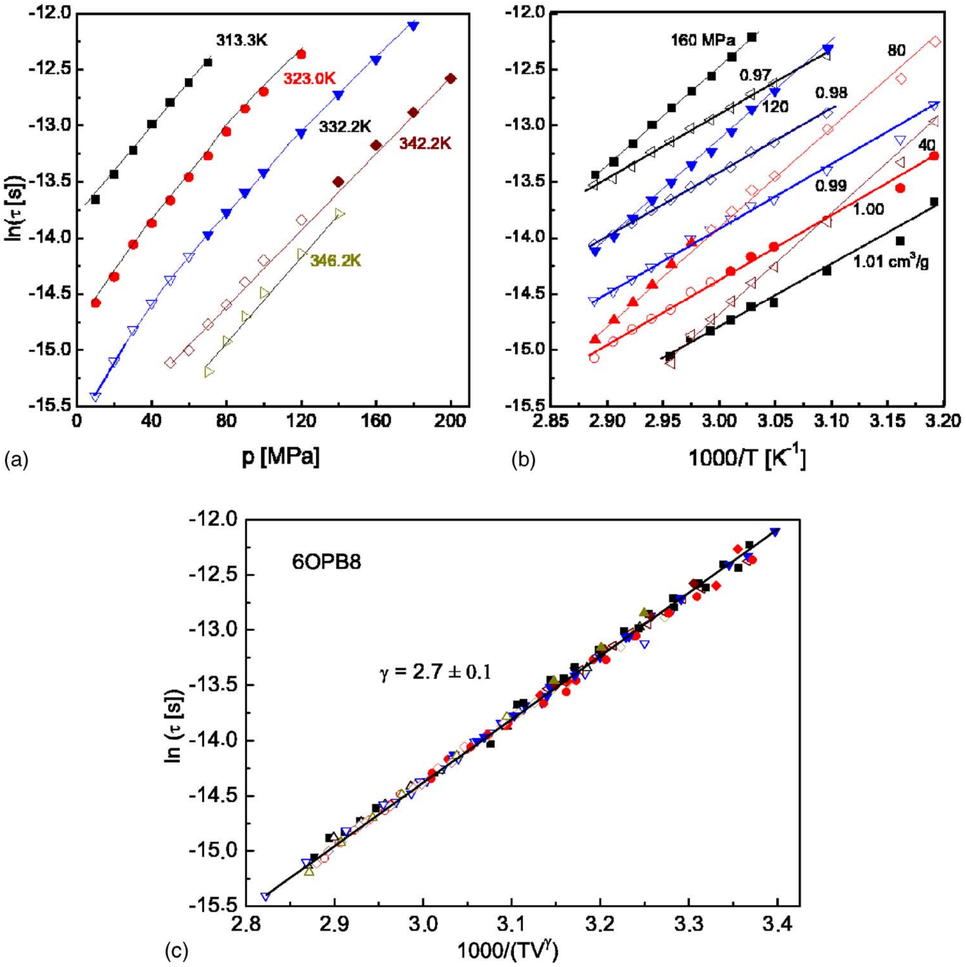

FIG. 7. Analysis of the data for the smectic *A* (open symbols) and smectic *C* (full symbols) of the 6OPB8. (a) Pressure variation of the relaxation time at five temperatures. (b) Arrhenius plots at four pressures and five specific volumes. (c) Variation of the relaxation time with $1/(TV_m^{2.7})$ for all data in (a) and (b).

TABLE I. Parameters derived for LC substances from the analysis of the longitudinal relaxation time at different thermodynamic conditions. Except for 6OPB8, data were taken from the results of Urban and co-workers (see Refs. 4–8 and 10 and references therein).

Substance	Phase	$-\alpha_\tau/\alpha_p$	$\Delta^{\neq}U/\Delta^{\neq}H$		γ		
			Expt.	Eq. (13)	Eq. (9)	Eq. (11)	Eq. (14)
5CB	*N*	0.95	0.44	0.49	5.3	4.1	4.8
6CB	*N*	1.06	0.45	0.51	6.3	4.1	4.0
7CB	*N*	1.16	0.43	0.54	4.7	3.3	3.1
8CB	*N*	1.00	0.50	0.50	4.0	4.2	3.8
	A		0.52			4.2	
5PCH	*N*	1.39	0.58	0.58	5.2	3.5	3.4
7PCH	*N*	1.01	0.51	0.50		3.9	3.9
8PCH	*N*	1.33	0.51	0.57	3.4	3.6	3.3
6OPB8	*N*				2.5		
	A, *C*	1.63	0.65	0.62		2.7	2.7
6DBT[a]	*A*	0.70	0.38	0.41		4.0	4.6
8BT[b]	*E*	0.96	0.44	0.49		4.1	4.6

[a] 6DBT-5-*n*-hexyl-2-(4′-isothiocyanato-phenyl)-1,3-dioxane.

[b] 8BT-4′*n*-octyl-4-isothiocyanato-biphenyl.

used to obtain the molar volumes from the data in Fig. 2. No differences can be noted between the data for the two smectic phases; one common straight line describes all the points. For other LC compounds the parameter γ is larger (see Table I), which may be attributed to greater molecular rigidity. Note that the *n*CBs (alkyl-cyanobiphenyls) have larger γ than the *n*PCHs (alkyl-cyanophenyl cyclohexanes), the latter having a flexible cyclohexyl ring instead of the benzene ring in *n*CB. The same trend was observed in the homologous series of dialkoxyazoxybenzenes.[30]

Conformance to the scaling of Eqs. (10) and (11) implies that the repulsive term in the interaction potential dominates the attractive part. Evidently the attractive forces acting on a molecule from neighbors effectively cancel, so that for local properties the attractions exert primarily just a mean field, density dependent pressure.[12] This simplification, $U(r) \sim V^{-\gamma}$, seems to be valid for many liquid crystalline substances. Recently Roland and co-workers[11–14] have argued that for glass formers γ can be related to the Grüneisen parameter and have shown that Eq. (10) can be derived from any model that expresses the relaxation times as a function of the entropy.

The similarity of the dynamic behavior of glass-forming liquids and liquid crystals described above suggests employing another relationship between the relaxation time and thermodynamic quantities. Recently Ferrer *et al.*[17] and Casalini and Roland[18,19] considered the thermal expansivities for supercooled liquids and polymers under different conditions. The isochronic and isobaric expansivities,

$$\alpha_p = V^1(\partial V/\partial T)_{\underset{\wedge}{\cancel{V}}} \quad \text{and} \quad \alpha_\tau = V^1(\partial V/\partial T)_\tau, \tag{12}$$

near the glass transition were compared for various materials. A ratio $|\alpha_\tau|/\alpha_p = 1$ connotes equal contributions from volume and temperature to the relaxation time; $|\alpha_\tau|/\alpha_p > 1$ implies that temperature dominates; and $|\alpha_\tau|/\alpha_p < 1$ when volume dominates. This approach can be applied to the 6OPB8. Figure 8 shows volume-temperature plots for several isobars and isochrones within the S_A and S_C phases. The slopes yield $\alpha_\tau = -(11.1 \pm 0.2) \times 10^{-4}$ K^{-1} and $\alpha_p = (7.0 \pm 0.3) \times 10^{-4}$ K^{-1}. The ratio $|\alpha_\tau|/\alpha_p = 1.63 \pm 0.15$ is larger than in the case of other LC substances (~ 1.1).[10] Casalini and Roland[18] derived a simple relation between these expansion coefficients and the two activation quantities,

$$\Delta^{\neq}U/\Delta^{\neq}H = 1/(1 - \alpha_p/\alpha_\tau). \tag{13}$$

Using the expansion coefficients reported above and the data in Fig. 5, we have for $\Delta^{\neq}U/\Delta^{\neq}H$ comparable values, 0.62 and ~ 0.65, respectively. Table I contains these and other quantities derived for several LC substances in different phases.

Yet another relation between γ and the isochronic expansivity α_τ was derived by Roland *et al.*,[12]

$$\gamma = -1/(T\alpha_\tau(T)). \tag{14}$$

The calculated values of γ according to this formula are also listed in Table I (for LCs the α_τ can be assumed independent

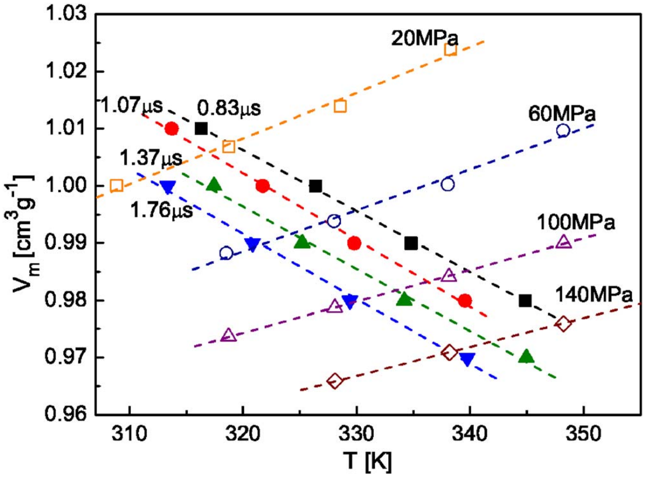

FIG. 8. Molar volume vs temperature at constant pressures (open symbols) and constant relaxation time (full symbols) for the *A* and *C* phases of 6OPB8. The slopes yield the respective isobaric and isochronic thermal expansivities.

of temperature—see Fig. 8; the values of T correspond to a midrange of the phase). Results obtained recently for many other LC substances (see Refs. 4–8 and references therein) were also evaluated using Eqs. (13) and (14). The results (Table I) show full consistency for $\Delta^{\neq}U/\Delta^{\neq}H$ and γ from different determinations methods.

CONCLUSIONS

Knowledge of the equation of state for molecular systems such as liquid crystals allows deconvolution of the volume and temperature effects governing the rotational dynamics. From such an analysis the details of the interaction potential can be investigated. The results presented herein reveal a striking similarity in the dynamical behavior of glass-forming (isotropic) liquids and liquid crystalline compounds having different degrees of molecular order. The relaxation time for flip-flop motion con~~fi~~rms to the thermodynamic scaling found quite generally for isotropic materials. This result is consistent with the repulsive part of the interaction potential being dominated by the local LC structure. Molecular flexibility reduces the steepness of the interaction potential, whereby the attractive part may no longer be negligible. The present findings suggest that similar studies on a compound exhibiting both liquid crystalline and glass-forming behavior would be particularly insightful.

ACKNOWLEDGMENTS

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