

# Nematic order parameter as determined from dielectric relaxation data and other methods

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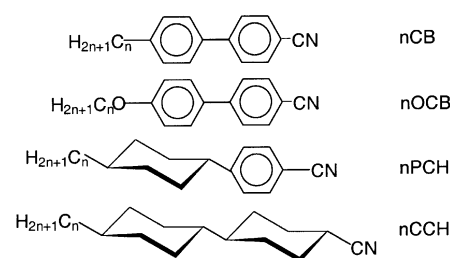
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The nematic order parameter  $S = \langle P_2(\cos\theta) \rangle$  was calculated from the dielectric relaxation time characterizing the molecular rotation around the short axes using formulae derived by Coffey *et al.* (W. T. Coffey, Yu. P. Kalmykov and J. P. Waldron, *Liq. Cryst.*, 1995, **18**, 677; W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov and J. P. Waldron, *Physica A*, 1995, **213**, 551; Yu. P. Kalmykov and W. T. Coffey, *Liq. Cryst.*, 1998, **25**, 329). In order to test the approximations on which the theory is based (rod-like shape of molecules, the diffusional model of reorientational motion in the presence of an ordering Maier–Saupe potential) several nematogens were chosen for which the  $S(T)$  behaviour is known from other experimental techniques as well. These molecules (1OCB, 5OCB, 7CB, 5PCH, 3CCH, 5CCH and 7CCH) have rigid or flexible cores, strongly polar –CN group at one side and the alkyl or alkoxy tail at the other side. A common analysis of the results coming from different experimental methods show large differences between data. Using the Haller-type formula a re-scaling of the  $S$ -values was proposed which reduced the scatter of experimental sets of points to a reasonable range. It was established that the Coffey *et al.* approach leads to the order parameter being consistent with other data if the molecular cores are sufficiently rigid.

## 1. Introduction

The order parameter  $S = \langle P_2(\cos\theta) \rangle$  is the fundamental quantity which characterises the physical properties of the nematic state. Practically each experimental method measuring an anisotropic property of the nematic can be used in determining  $S$ . On the other hand, the knowledge of the order parameter and its dependence on the temperature and/or pressure is essential for testing any model of liquid-crystalline behaviour. Several text-books and review articles deal with the subject (for example refs. 1–5). However, in ref. 6 we have turned attention to the fact that if one compares the data obtained in different experiments for the same substance a large disagreement of  $S(T)$  behaviour can be noted. This happens in spite of the fact that in most cases the relationships between  $S$  and measured quantities are quite straightforward (optical, magnetic and dielectric anisotropy, quadrupole splitting, Raman scattering, *etc.*). In refs. 4 and 6 (and references therein) we have explored another approach in determining the order parameter  $S$  as a function of temperature and pressure. It is based on the Meier *et al.*<sup>7</sup> and Coffey *et al.*<sup>8–10</sup> theories linking  $S$  with the retardation factor given by the ratio of the longitudinal relaxation times measured in the nematic ( $\tau_{||}$ ) and isotropic ( $\tau_0$ ) phases as obtained from dielectric relaxation spectroscopy. Certainly, this approach is based on an indirect connection between  $S$  and the measured quantities. Nevertheless, the  $S(T)$  and  $S(p)$  behaviours seemed to be reasonably close to the other results.<sup>6</sup> Recently Bates and Luckhurst<sup>11</sup> criticised this approach arguing that the use of the results of dielectric relaxation theories is doubtful due to drastic assumptions concerning

the diffusional model of reorientational motion in the presence of an ordering potential (the authors did not mention the results quoted in ref. 6, however). Moreover, in the theoretical models the molecules are treated as rigid rods which is hardly realised in reality. In order to shed more light on the problem we have undertaken a comparative investigation of several additional substances belonging to the well known homologous series:  $n$ CB,  $n$ OCB,  $n$ PCH and  $n$ CCH:



In these molecules the strongly polar CN group gives a predominant longitudinal dipole moment which allows for an easy determination of the longitudinal relaxation times in both the nematic and isotropic phases. Their cores and tails have different flexibility: (i) molecule with “no tail” and rigid core: 1OCB; (ii) molecules having flexible tails and rigid cores: 7CB, 5OCB; (iii) molecules having flexible tails and cores: 5PCH, 3CCH, 5CCH and 7CCH.

This should allow us, at least, to find how a deviation of the molecule’s shape from the rigid rod “ideal”, as considered in the theories, influences the results obtained. The present

investigation is a continuation of the studies presented in ref. 6.

## 2. Theoretical background

The existing theories of the low frequency relaxation process<sup>7–10</sup> are based on the model assuming that the symmetric top molecules perform rotational diffusion in the self-consistent mean field potential  $U(\theta)$  proposed by Maier and Saupe<sup>12</sup>

$$U/k_B T = -\sigma \cos^2 \theta, \quad (1)$$

where  $\theta$  is the angle between the symmetry axis of the molecule and the director  $\mathbf{n}$ . The nematic potential barrier parameter is defined as  $\sigma = q/k_B T$ , where  $q$  is the height of the barrier separating two minima corresponding to  $+\mathbf{n}$  and  $-\mathbf{n}$  directions and  $k_B$  is the Boltzmann constant. This barrier hinders the molecular reorientations around the short axes and thus the longitudinal relaxation time  $\tau_{\parallel}$  must be slowed down in comparison with the situation when the potential  $q = 0$ . In order to describe the reduction of the molecular reorientation rate Meier *et al.*<sup>7</sup> introduced the concept of a retardation factor  $g_{\parallel} = \tau_{\parallel}/\tau_0$ , where  $\tau_0$  corresponds to a hypothetical state with  $q = 0$ . This is usually extrapolated from the isotropic data assuming an exponential dependence of  $\tau_{is}$  upon  $T^{-1}$  or  $p$ <sup>4,6,7</sup> and was proved by the theoretical calculations.<sup>11</sup> Meier *et al.* have found a relation between  $g_{\parallel}$  and  $q$  by considering the parallel relaxation process in the Maier–Saupe potential (eqn. (1)). Using several simplifications they derived the following formula

$$g_{\parallel} = \frac{\tau_{\parallel}}{\tau_0} = \frac{e^{\sigma} - 1}{\sigma}. \quad (2)$$

The same problem was recently solved in a more rigorous mathematical way by Coffey *et al.*<sup>8–10</sup> The molecular rotation motion in the presence of the Maier–Saupe ordering potential was treated as a Brownian rotational diffusion. Using sophisticated mathematical procedures the authors obtained the exact analytical solutions for the retardation factors  $g_{\parallel}$  and  $g_{\perp} = \tau_{\perp}/\tau_0$  in terms of  $\sigma$ . The following formula for the parallel retardation factor renders a close approximation to the exact solution for all  $\sigma$

$$g_{\parallel} = \frac{\tau_{\parallel}}{\tau_0} = \frac{e^{\sigma} - 1}{\sigma} \left( \frac{2}{1 + 1/\sigma} \sqrt{\sigma/\pi} + 2^{-\sigma} \right)^{-1}, \quad (3)$$

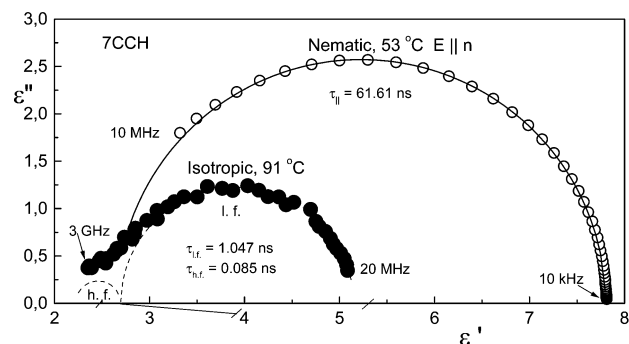
which is eqn. (2) with a correction term. For  $\sigma > 1$  the Meier and Saupe formula considerably overestimates  $g_{\parallel}$ , which causes the  $q$  values calculated with the use of eqn. (3) to be approximately 25% greater than those obtained by eqn. (2).

In the mean-field theory of the nematic state Maier and Saupe (MS) have calculated the order parameter  $S$  using a simplified form of the orientational distribution function,  $f(\theta)$ , which is related to the strength parameter  $\sigma$ .

More recently Kalmykov and Coffey (KC)<sup>10</sup> have derived the relation between  $S$  and  $\sigma$  in a more general way. Starting from the Maier and Saupe interaction potential the authors applied the effective eigenvalue method and obtained a complex analytical equation which can well be approximated by the relation

$$\sigma \approx \frac{3S(5 - \pi S)}{2(1 - S^2)}. \quad (4)$$

Combining the experimental  $\sigma$ -values as deduced from eqn. (2) and (3), respectively, with formula (4) it is possible, in principle, to calculate the order parameter  $S$  for the nematic phase. However, in order to be in accord with the assumed approximations the following conditions should be fulfilled: (1) the molecules can be approximated by rigid rods; (2) the dipole moment should be directed along the long axis of the molecule;



**Fig. 1** Cole–Cole plots for the isotropic (TDS) and nematic (Agilent) phase of 7CCH. The solid semicircle is the fit of the Debye equation, the dashed line corresponds to eqn. (5).

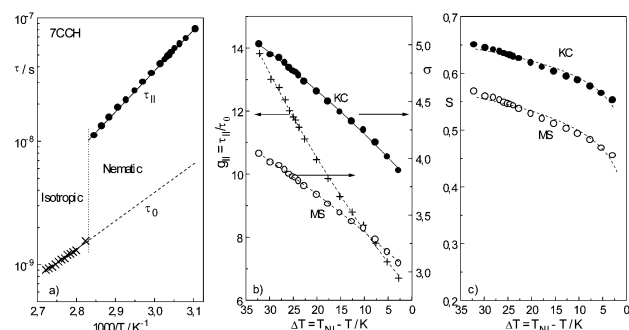
(3) the low frequency relaxation process can unambiguously be extracted from the spectra in both the isotropic and nematic phase; (4) the nematic range is sufficiently broad in order to avoid the pretransitional effects.

The first point will be especially tested in the present work, while the other conditions seem to be well satisfied for the chosen substances. (The angle between the –CN dipole and the long molecular axis was estimated to be *ca.* 15°–30° for different compounds, see for example refs. 13 and 14.)

## 3. Experimental and results

The dielectric relaxation measurements in the nematic phase have been performed with the aid of impedance analysers (Agilent 4194A or Novocontrol). The samples were aligned parallel to the measuring field. A DC electric field of *ca.* 2000 V cm<sup>−1</sup> was used in the case of substances having the cyclohexyl group(s), whereas those with two benzene rings were oriented by a magnetic field of 0.8 T. In the isotropic phase a time domain spectroscopy (TDS) method was applied as was described in ref. 15. The measurements of the optical birefringence and the way of calculating the order parameter were the same as in refs. 16 and 17. All substances studied were synthesized in the Institute of Chemistry, Military University of Technology, Warsaw.

The relaxation spectra for 7CCH (which are typical for all substances studied) are presented in Fig. 1 in the form of Cole–Cole diagrams. They were analyzed with the equation



**Fig. 2** (a) The longitudinal dielectric relaxation times *versus* inverted temperature determined for the isotropic and nematic phases of 7CCH. The dashed line shows the way of establishing  $\tau_0$  in the nematic phase. (b) The retardation factor  $g_{\parallel}$  (left hand scale) and the strength parameter  $\sigma$  calculated with the use of eqn. (2), MS, and eqn. (3), KC (right hand scale) *versus* the reduced temperature. (c) The order parameter  $S$  calculated with formula (4) from the above  $\sigma$ -values *versus* the reduced temperature. The dashed lines are fits of eqn. (6).

**Table 1** The clearing temperatures  $T_{\text{NI}}$ , the preexponential factor  $\tau_0$  and the activation enthalpy  $\Delta H$  according to the Arrhenius equation,  $\tau = \tau_0 \exp(\Delta H/RT)$ , in the isotropic and nematic phases of the substances studied

Substance	$T_{\text{NI}}/\text{K}$	Isotropic		Nematic	
		$\tau_0/\text{s}$	$\Delta H/\text{kJ mol}^{-1}$	$\tau_0/\text{s}$	$\Delta H/\text{kJ mol}^{-1}$
1OCB	359 <sup>a</sup>	$1.32 \times 10^{-14}$	33.1	$1.57 \times 10^{-19}$	70.4
5OCB	341.2	$8.87 \times 10^{-15}$	34.5	$2.44 \times 10^{-19}$	65.4
7CB	314.7	$1.20 \times 10^{-16}$	50.3	$1.90 \times 10^{-18}$	63.9
5PCH	328.2	$1.47 \times 10^{-14}$	32.7	$3.77 \times 10^{-20}$	71.7
3CCH	352.2	$1.12 \times 10^{-14}$	32.6	$1.65 \times 10^{-19}$	69.4
5CCH	358.1	$1.52 \times 10^{-14}$	32.8	$3.79 \times 10^{-19}$	68.7
7CCH	354.2	$1.47 \times 10^{-15}$	40.7	$4.06 \times 10^{-18}$	63.6

<sup>a</sup> The melting point is 378 K. The N phase is obtained by a deep supercooling of the isotropic phase. Details of the dielectric studies of 1OCB (static and dynamic) will be published separately.<sup>39</sup>

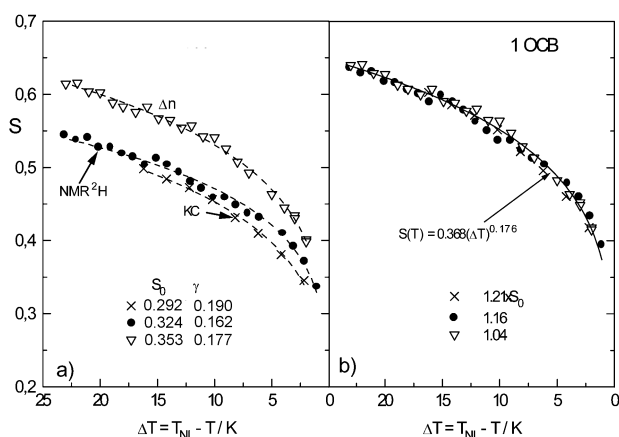
$$\varepsilon^* - \varepsilon_\infty = \frac{\delta_1}{(1 + i\omega\tau_1)^{1-\alpha_1}} + \frac{\delta_2}{(1 + i\omega\tau_2)^{1-\alpha_2}}, \quad (5)$$

where  $\delta_1 = \varepsilon_s - \varepsilon_2$ ,  $\delta_2 = \varepsilon_2 - \varepsilon_\infty$ , are the strengths (increments) of two relaxation processes,  $\varepsilon_s$  and  $\varepsilon_\infty$  are the static and high frequency permittivity, respectively, and  $\alpha$  characterises a distribution of the relaxation times. In the case of the nematic phase the spectra obeyed the Debye equation excellently (one part of eqn. (5) with  $\alpha = 0$ ). Fig. 2 presents: (a) the l. f. relaxation times, (b) the retardation factor  $g_{\parallel}$  and the strength parameters  $\sigma$  according to formulae (2), MS, and (3), KC, and (c) the order parameters  $S(T)$  as derived using eqn. (4) for 7CCH (high pressure study of this substance was reported in ref. 18). The MS theory leads to considerably lower  $S$ -values than the Coffey *et al.* approach (Fig. 2c) and will not be analysed further. The data on the l. f. relaxation process observed in the isotropic and nematic phases of particular substances studied are collected in Table 1.

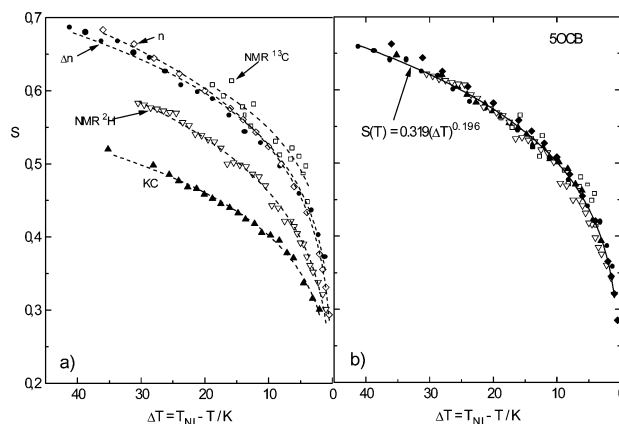
Figs. 3–7 (left hand sides) present the obtained results together with other data available in the literature. The functional form of  $S(T)$  is often approximated by the formula proposed by Haller<sup>19</sup>

$$S(T) = S_0(T_{\text{NI}} - T)^\gamma \quad (6)$$

with two adjustable parameters  $S_0$  and  $\gamma$ . Heeks and Luckhurst<sup>20</sup> have found that eqn. (6) works rather well for



**Fig. 3** (a) The order parameter for 1OCB derived from different experiments: NMR ( $^2\text{H}$ ),<sup>22</sup> optical birefringence ( $\Delta n$ ) and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6) with the parameters shown in the insert. (b) The same data multiplied by factors shown in the insert (see text).



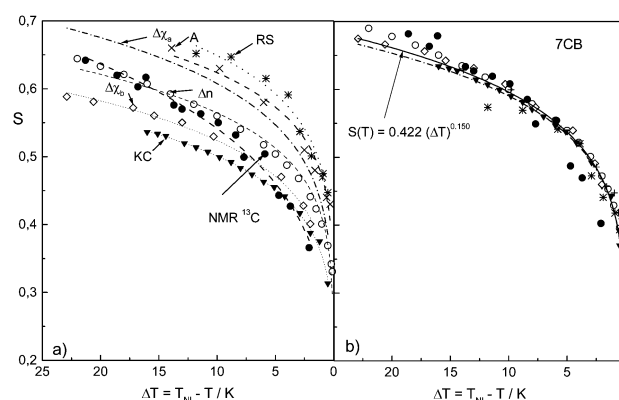
**Fig. 4** (a) The order parameter for 5OCB derived from different experiments: NMR ( $^2\text{H}$ ),<sup>20</sup> NMR ( $^{13}\text{C}$ ),<sup>23</sup> optical birefringence ( $\Delta n$ ),<sup>16</sup> refractive indices ( $n$ ),<sup>24</sup> and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as before.

$S$ -values determined for 5OCB from the NMR measurements (compare Fig. 4). However, points closer to  $T_{\text{NI}}$  than  $\sim 1.5$  K must be omitted in the fitting procedure because  $\gamma$  strongly depends on  $T$  in this region. This formula will be used for the discussion of the  $S(T)$  behaviour observed experimentally. Other approaches, like that based on the mean-field extrapolation<sup>21</sup> are less appropriate for the present aim.

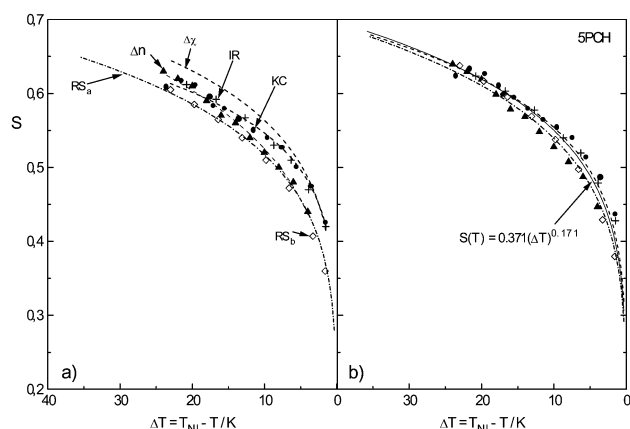
## 4. Discussion

Several features can be pointed out looking at Figs. 3a–9a:

1. A large disagreement of  $S(T)$  behaviour coming from different experimental methods.
2. In most cases the differences between particular sets of the data are markedly larger than the experimental errors (usually *ca.* 5% or less).
3. The NMR measurements usually yield smaller  $S$ -values than the magnetic susceptibility and optical anisotropy methods; this is especially drastic in the case of the *n*CCH series (Figs. 7a–9a).
4. The data according to the Coffey *et al.* (KC) theory obtained for rigid molecules are fairly close to the results coming from experimental methods giving a more straightforward connection of  $S$  with the measured quantity.



**Fig. 5** (a) The order parameter for 7CB derived from the different experiments: NMR ( $^{13}\text{C}$ ),<sup>23</sup> magnetic susceptibility ( $\Delta\chi_a$ ,<sup>25</sup>  $\Delta\chi_b$ ),<sup>26</sup> Raman scattering (RS),<sup>27</sup> infrared absorption (A),<sup>28</sup> optical birefringence ( $\Delta n$ ) (according to data reported in ref. 29), and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as before.



**Fig. 6** (a) The order parameter for 5PCH derived from the different experiments: magnetic susceptibility ( $\Delta\chi$ ),<sup>25</sup> birefringence ( $\Delta n$ ),<sup>30</sup> Raman scattering ( $RS_a$ ,<sup>31</sup>  $RS_b$ ),<sup>32</sup> infrared dichroism (IR),<sup>33</sup> and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as previously.

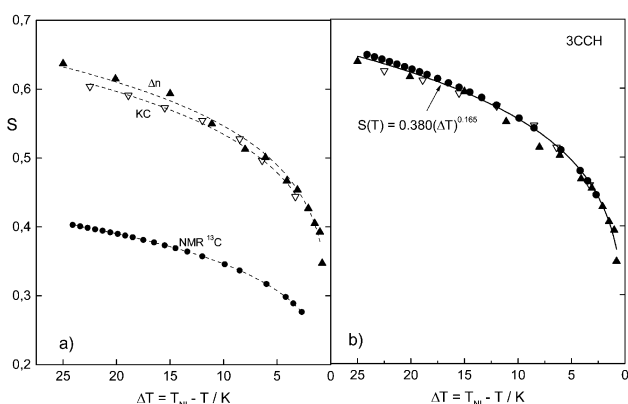
5. Most of the  $S(T)$  behaviour can well be approximated by the Haller formula (6).

6. The more rigid the molecule, the larger the KC-values and thus they are closer to the  $\Delta\chi$  and  $\Delta n$  results.

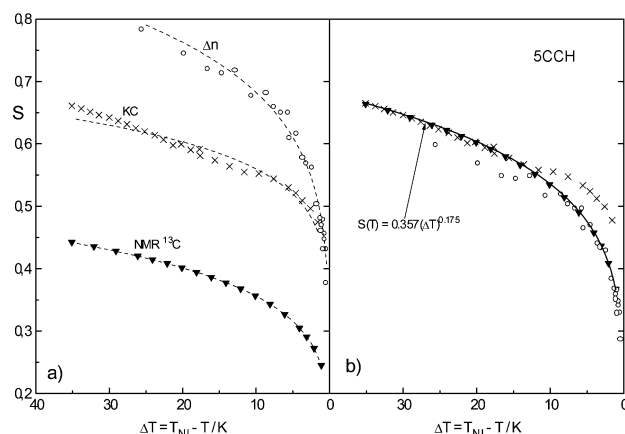
7. In the case of molecules with flexible cores and long tail (5CCH and 7CCH) the agreement with other experimental data is bad.

The points 1–3 seem not to be astonishing taking into account the details of particular methods applied for the determination of the order parameter. None of them can provide the absolute value of  $S$  because in each case some theory that relates the measured property to the molecular orientational order must be engaged<sup>1–3,34</sup> and thus some unknown parameters of the theory need to be fitted. Moreover, each method provides its own order parameter since the measured quantities are connected with different parts of molecules (selected pairs of atoms, a given atomic vibration, dipolar groups, *etc.*) or with whole molecules (polarisability and susceptibility anisotropy). Additionally, they observe the molecular behaviour in different time and/or length scales. In such a situation the question arises: is it possible to “normalize” in some way all the data yielded by different experiments for a given substance in the nematic phase?

In our previous paper<sup>6</sup> we have suggested that the  $S_0$  parameter of the Haller formula can be used for this. It is supposed that  $S_0$  is related to the clearing temperature:



**Fig. 7** (a) The order parameter for 3CCH derived from the different experiments: NMR ( $^{13}C$ ),<sup>33</sup> optical birefringence ( $\Delta n$ ), and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as previously.



**Fig. 8** (a) The order parameter for 5CCH derived from the different experiments: NMR ( $^{13}C$ ),<sup>33</sup> optical birefringence ( $\Delta n$ ), and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as previously.

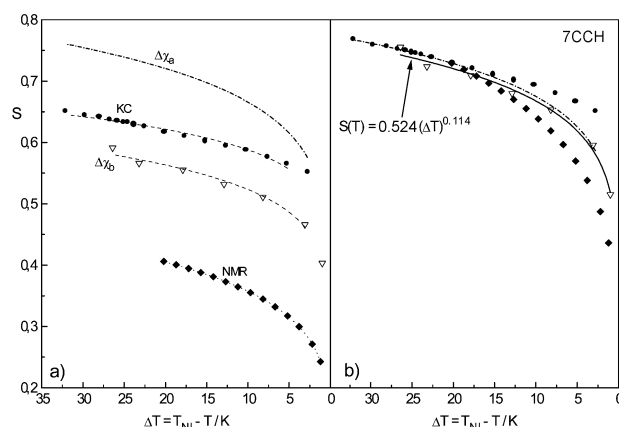
$S_0^t = T_{NI}^{-\gamma}$ .<sup>19,22,25,35</sup> Using this idea the following scaling procedure was applied. To each set of experimental points formula (6) was fitted giving the  $S_0$  and  $\gamma$  values.  $S_0^t$  was calculated taking  $T_{NI}$  from Table 1 and the mean  $\gamma$  value from the fits as is shown in Fig. 3. Then the particular sets of points were multiplied by the factor  $S_0^t/S_0$ . Such scaling procedure gives the results presented in Figs. 3b–9b.

It is clear that this procedure leads to a considerable reduction of the deviation of experimental sets of points, including the KC values. A similar feature was found for 5CB.<sup>36</sup> However, it does not apply to the substances having flexible core and long alkyl chain (5CCH and 7CCH, see Figs. 8 and 9).

A common analysis of a large number of experimental results obtained for different substances allows us to conclude as follows:

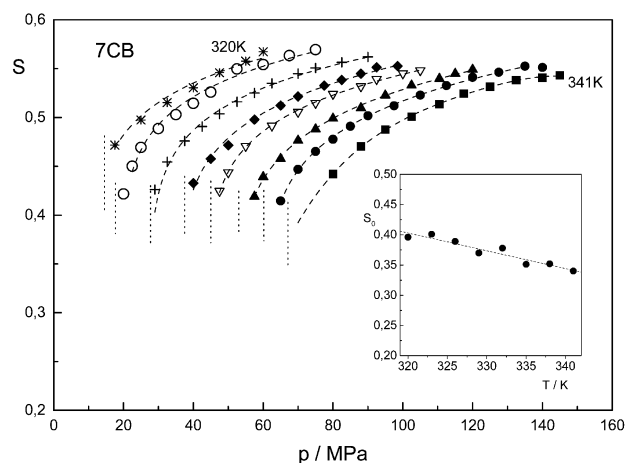
(i) A scaling procedure based on the Haller formula (6) reduces the scatter of experimental sets of points to a reasonable range; this means that the temperature variation of the order parameter,  $S(T)$ , is properly established in most of experiments.

(ii) The mean field theory of the low frequency dielectric relaxation process established by Coffey *et al.* can successfully be applied for determination of the order parameter if the molecular structure satisfies the conditions on which the theory is based. This justifies the use of this method for determining the pressure dependence of the order parameter as it was done



**Fig. 9** (a) The order parameter for 7CCH derived from the different experiments: NMR ( $^{13}C$ ),<sup>33</sup> magnetic susceptibility ( $\Delta\chi_a$ <sup>25</sup> and  $\Delta\chi_b$ <sup>26</sup>), and dielectric relaxation data according to formulae (3) and (4). The lines are fits of eqn. (6). (b) The same data scaled as previously.





**Fig. 10** Order parameters *versus* pressure for several isotherms between 320 K and 341 K with 3 K steps in the nematic phase of 7CB (according to ref. 38). Dashed lines are fits of the Haller-type formula  $S(p) = S_0(p - p_{NI})^b$ , where  $p_{NI}$  corresponds to the clearing pressure (dotted vertical lines).  $p_{NI}$  values are marked by vertical dotted lines. The fits gave  $b = 0.105$  and  $S_0$  as is displayed in the insert.

in several our papers (for example in refs. 4, 6 and 37). New calculations for 7CB which are based on the old results<sup>38</sup> are presented in Fig. 10.

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