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Calorimetric study of heptyloxybenzylidene butylaniline in silica aerogels

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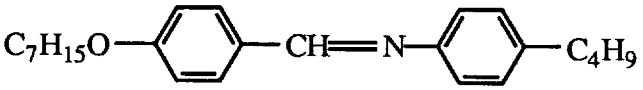
A high resolution a.c. and relaxation calorimetric study has been carried out on heptyloxybenzylidene butylaniline (7O.4) in two silica aerogels with mass densities $\rho = 0{\cdot}08$ and $0{\cdot}17\,\mathrm{g\,cm^{-3}}$. Bulk 7O.4 exhibits strongly first order N–I, N–S_A and S_C–Cr G transitions as well as a mean-field second order S_A–S_C transition. The 7O.4/aerogel samples exhibit three first order transitions (N–I, N–S_A, S_A–crystal) that are appreciably shifted and broadened relative to bulk 7O.4. The S_A–S_C transition is not observed in either of the aerogel samples.

1. Introduction

A wide variety of studies have been made on liquid crystals confined in porous media [1]. Heat capacity measurements have been used to characterize the phase transitions of several compounds—octylcyanobiphenyl (8CB), octylphenylthiolpentyloxybenzoate (8S5), butyloxybenzylidene octylaniline (4O.8)—in silica aerogels [2–4], additional calorimetric work has been done on liquid crystals in porous glasses [5].

The present work involves a thermal study of *N*-(4-*n*-heptyloxybenzylidene)-4′-*n*-butylaniline (7O.4)



in two of the same aerogels that were used in [2–4]. Bulk 7O.4 exhibits N–I, N–S_A, S_A–S_C, and S_C–Cr G transitions [6], where Cr G is the tilted plastic crystal G phase and N, S_A, S_C are the familiar nematic, smectic A and smectic C phases. The features that distinguish 7O.4 from previously studied aerogel systems is the fact that the N–S_A bulk transition is strongly first order (due to a small nematic range of ~2 K) and the bulk S_A–S_C transition is very close to a classical Landau tricritical point with a large excess heat capacity peak [6]. The principal goal of this investigation was to characterize the effect of quenched disorder associated with high porosity aerogels on these two transitions.

2. Procedures

The aerogels were from the same batches as those used previously for other liquid crystal/aerogel studies [2–4]. The two aerogels used in this study were the highest porosity (lowest density) gels with mass densities of $0{\cdot}08$ and $0{\cdot}17\,\mathrm{g\,cm^{-3}}$. They have a fractal network structure where the internetwork voids ('pores') have average pore chords L of 700 ± 100 Å ($\rho = 0{\cdot}08$) and 430 ± 65 Å ($\rho = 0{\cdot}17$); the volume fractions ϕ_P of pores are 0·945 and 0·90, respectively. Further details about these aerogels are given in [2].

Samples were prepared by first vacuum drying at 300°C a thin aerogel slab prior to filling, which was also carried out in vacuum by heating 7O.4 into the isotropic phase and allowing the slab to fill slowly by capillary action. Three samples were prepared from the $\rho = 0{\cdot}08$ aerogel. In one case, the filled sample was unwiped so that a small surface excess of bulk 7O.4 remained. In a second case, the surface of the filled aerogel was gently wiped dry with filter paper to remove excess bulk liquid crystal that might be present. In a third case, a considerable excess of 7O.4 was used so that there was appreciable bulk 7O.4 left on the surface of the sample. For the sample prepared from the $\rho = 0{\cdot}17$ aerogel, the amount of 7O.4 was smaller than that needed to completely fill this gel; it is estimated that this sample was ~80 per cent full.

Once filled, the samples were weighed and sealed in a silver cell having a cold-weld indium seal. The handling procedure was such that the 7O.4 does not transform into the rigid crystal K phase, thus avoiding damage to the fragile aerogel network [3].

The calorimeters used in this investigation have been described elsewhere [7]. Two distinct modes of operation were used. One was a conventional a.c. calorimetry mode, and the other was a ramped relaxation (or non-adiabatic scanning) mode that uses d.c. heating and is

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capable of determining enthalpy changes including latent heats at first order transitions. Even the a.c. technique can provide a qualitative indication of two-phase coexistence. The a.c. power input causes a sample temperature response $\Delta T_{\mathrm{a.c.}}\, e^{i(\omega t+\phi)}$. The amplitude $\Delta T_{\mathrm{a.c.}}$ determines the heat capacity C_p, and anomalous peaks in the phase shift ϕ indicate two-phase coexistence. All C_p(a.c.) data were acquired at $\omega = 0{\cdot}196\,\mathrm{Hz\ s^{-1}}$ (f=31·25 mHz).

3. Results and discussion

Heat capacity data for 7O.4 in an aerogel with density $\rho = 0{\cdot}08\,\mathrm{g\,cm^{-3}}$ is given in figure 1. This sample is the unwiped $\rho = 0{\cdot}08$ aerogel, which exhibits clear indications of a surface excess of bulk 7O.4. Sharp spike-like features associated with N–I, N–S_A, and S_C–Cr G first order bulk transitions are denoted by arrows. Shifted to lower temperatures are three broad peaks associated with transitions involving 7O.4 inside the aerogel pores. The assignment of the three spikes as due to excess bulk 7O.4 is confirmed by data on the $\rho = 0{\cdot}08$ aerogel containing substantial excess 7O.4 and the wiped $\rho = 0{\cdot}08$ aerogel sample. In the former case, the spikes grow appreciably in size while the rounded intragel peaks do not change. In the latter case, the spikes almost completely vanish but the intragel peaks are only slightly modified.

A comparison of C_p data in the 330–338 K range for wiped and unwiped $\rho = 0{\cdot}08$ aerogel samples is given in figure 2. This shows that wiping the surface almost completely eliminated the sharp S_C–Cr G spike and also the small S_A–S_C second order C_p feature. It should be noted that a very small surface excess still remained on the wiped sample since tiny N–I and N–S_A surface spikes were observed. The temperatures of the N–S_A and S_C–Cr G surface spikes agreed well with bulk 7O.4 transition temperatures. The N–I surface spike was located 0·6 K below the bulk transition temperature and the S_A–S_C peak was 1·0 K below the bulk values, indicating that these transitions are sensitive to perturbations by the surface, perhaps due to anchoring. Even larger differences between the temperature of surface spikes and bulk transitions were observed for 4O.8/aerogel samples [4].

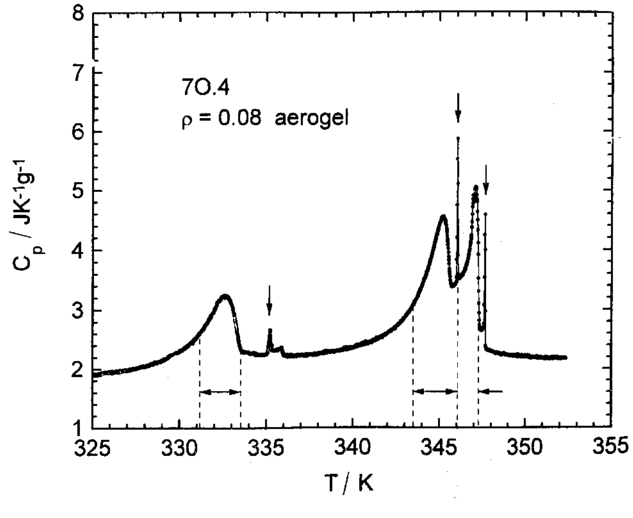

Figure 1. C_p(a.c.) for 7O.4 in a $\rho = 0{\cdot}08$ silica aerogel. This sample was unwiped and contained a small excess of bulk 7O.4 on the surface. The sharp spikes marked by arrows correspond to first order transitions in this surface excess. The dashed lines and horizontal arrows at the bottom of the figure indicate the widths of two-phase coexistence regions associated with the broad 7O.4/aerogel peaks.

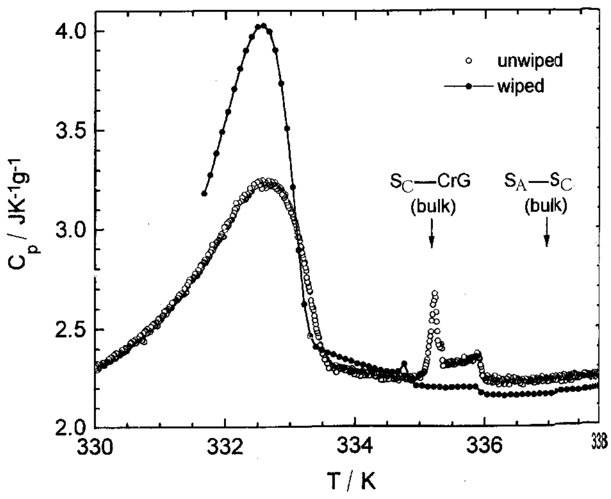

Figure 2. Detailed view of C_p(a.c.) data for 7O.4 in two $\rho = 0{\cdot}08$ aerogels. The unwiped sample is the same as that shown in figure 1, and the wiped sample was dried with filter paper to remove excess 7O.4 bulk on the surface.

The conclusion drawn from figure 2 is that 7O.4 inside the aerogel network does not undergo a S_A–S_C transition. This is confirmed by figure 3, which shows the heat capacity of 7O.4 in a $\rho = 0{\cdot}17$ aerogel that is ~80 per cent filled. In this case, there are no sharp spikes related to first-order bulk-like surface transitions and no indications of a S_A–S_C feature.

The three broad 7O.4/aerogel peaks represent smeared first order transitions with wide coexistence regions. This is indicated for both the $\rho = 0{\cdot}08$ and 0·17 samples by large characteristic peaks in the phase shifts ϕ at all three transitions. The widths of the coexistence ranges, as determined by these ϕ anomalies, are given in the table along with the temperatures of the center of the broad 7O.4/aerogel peaks. Additional confirmation of the smeared first order character of these transitions was provided by a non-adiabatic scanning (relaxation) run on the unwiped $\rho = 0{\cdot}08$ sample. For the 7O.4/aerogel peaks, the C_p(relax) curves were higher near the maxima than the respective C_p(a.c.) curves, which is consistent

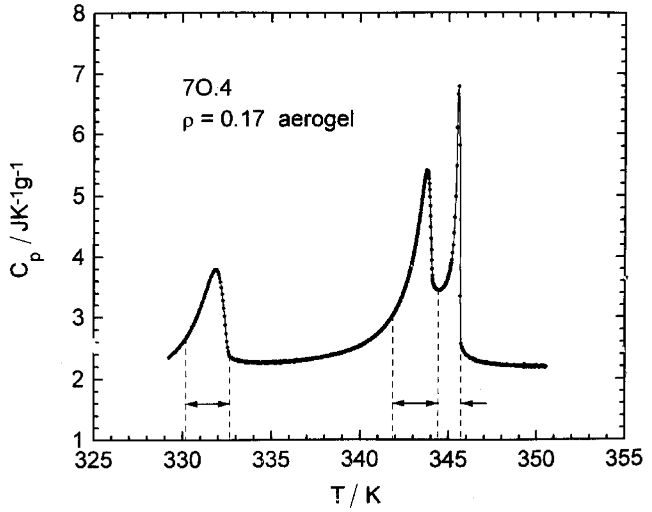

Figure 3. C_p(a.c.) for 7O.4 in a $\rho = 0.17$ silica aerogel that is ~80 per cent filled. In this case, the absence of sharp spikes like those in figure 1 indicates that no surface excess of bulk 7O.4 is present. The dashed lines and horizontal arrows at the bottom indicate the widths of two-phase coexistence regions.

Table Transition temperatures and widths of two-phase coexistence regions for bulk 7O.4 and 7O.4 in two aerogels. For the $\rho = 0{\cdot}08$ aerogel, the data correspond to the unwiped sample shown in figure 1. Also given are the shifts $\Delta T = T(\text{aerogel}) - \text{T}(\text{bulk})$. All quantities are in degrees kelvin.

Material	Bulk	$\rho = 0{\cdot}08$ aerogel	$\rho = 0{\cdot}17$ aerogel
T_{NI}	348·28	347·07	345·55
coex. width	0·18	1·22	1·28
ΔT_{NI}	—	−1·21	−2·73
T_{NA}	346·19	345·21	343·78
coex. width	0·20	2·51	2·55
ΔT_{NA}	—	−0·98	−2·41
$T_{\text{S}_\text{A}\text{S}_\text{C}}$	336·96	none	none
T_{SCr}	335·15	332·64	331·85
coex. width	0·85	2·50	2·46
ΔT	—	−2·51	−3·30

with effective C_p(a.c.) peaks that miss part of the latent heat at first order transitions.

Also given in the table is the shift in temperature between a 7O.4/aerogel transition and the respective bulk transition. As in the case of 4O.8/aerogel samples [4], the N–I transition is shifted more than the N–S_A transition. This is opposite to the trend observed for 8CB/aerogel samples [2]. It should be noted that the temperature shifts differ substantially for the two aerogels but the widths of the two-phase coexistence regions are essentially independent of aerogel density. In the case of the smectic-to-plastic crystal freezing transition, this is a S_C–Cr G transition in bulk 7O.4 but the 7O.4/aerogel samples do not exhibit a S_A–S_C transition. Thus the aerogel freezing transition is a S_A–Cr X transition, where Cr X is probably plastic crystal Cr B (but might be the tilted analogue Cr G). The table combines these different types of freezing transitions under the notation T_{SCr}, but the shifts ΔT may not be too relevant in this case since the nature of the smectic and plastic crystal phases differ.

In conclusion, the sharp first order transitions in bulk 7O.4 remain first order for 7O.4/aerogel samples, but the C_p peaks are shifted significantly and the two-phase coexistence regions are greatly broadened. Although bulk 7O.4 exhibits a large second order $C_p(\text{S}_\text{A}\text{–}\text{S}_\text{C})$ peak, the 7O.4/aerogel samples do not undergo a S_A–S_C transition.

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