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Do alkoxy chains behave like a solvent in the D phase? DSC study of binary systems, ANBC (n_C) ($n_C = 8$, 16 and 18)–*n*-tetradecane†

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The phase behaviour of the binary systems ANBC(n_C)–*n*-tetradecane, for $n_C = 8$, 16 and 18, was examined using DSC, paying special attention to the role of the alkoxy chain of the ANBC molecule in the D phase‡. The dependence of the SmC–D and D–isotropic liquid transition temperatures upon the apparent average number of paraffinic carbon atoms closely resembles the n_C dependence in the series of neat ANBCs, demonstrating that the alkoxy chain behaves, at least in part, like the solvent in lyotropic liquid crystals. The D phase was not detected in ANBC(8)–*n*-tetradecane.

1. Introduction

Since the discovery of an isotropic liquid crystal in a series of ANBC(n_C) (4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids, where n_C is the number of carbon atoms in the alkoxy chain) in 1957 [1], much attention has been paid to the structure and stability of the phase [2]. The molecule of ANBC consists of a nitrobiphenyl–carboxylic acid core and an alkoxy chain. In reality, however, the molecules are dimerized in the liquid crystalline phases [3, 4] via intermolecular hydrogen bonds. The system therefore consists of a 'molecule' that has a long core at its centre and two terminal alkoxy chains. A diffuse diffraction halo in the high angle region implies strong disorder of the terminal chains [5–10], and a well-resolved ¹H NMR spectrum [11] supports highly excited conformational motion of the chain. Recent rheological measurements [12] demonstrate that the D phase is rather stiff.

Isotropic liquid crystalline phases are widely observed in lyotropic systems [13, 14], in which spherical or rod-like micelles form a cubic lattice and the solvent (water) fills space between the micelles [13–16].

In analogy to isotropic liquid crystalline phases in lyotropic systems, models of the structure of the D phase have been proposed [5–10, 13]. Today, a longstanding debate concerning the structure of the D phase in ANBC seems to converge upon the model proposed first by Tardeau and Billard [6]. It is, however, evident that the establishment of the structural model is not the goal, but rather the starting point for statistical modelling of the D phase at the molecular level. Detailed thermodynamic study is crucial in such a context, because any molecular models of phase transition are assessed through a comparison with thermodynamic data, and especially because the unit cell of the D phase contains more than a hundred molecules, the number fluctuating both in space and time. This situation prompted the authors to begin a thermodynamic study of the D phase and related systems [17–21].

The structure of the ANBC molecule suggests that the nitrobiphenyl–carboxylic acid core and alkoxy chains play different roles in the formation of the D phase. Indeed, terminal chains are repeatedly claimed to resemble solvent [5, 6, 9–11, 22]. The examination of such a discrimination of the roles played by the core and the chains is very informative for constructing statistical models of the D phase. Curiously, however, no direct (i.e. experimental) assessment of the assumption that the chains behave like solvent has yet been carried out. The most naive though extreme way is to examine the behaviour of binary systems between ANBC and *n*-alkane. A similar dependence on the 'concentration' of the core would be observed if the terminal chains could play a role like the solvent in lyotropic systems. Moreover the D phase might be induced in a short chain ANBC if the melted chain governed the stability of the D phase. In this study, the

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phase behaviour of the binary systems of ANBC(n_C) compounds with $n_C = 8$, 16 or 18 and *n*-tetradecane were examined by using differential scanning calorimetry (DSC). The mesomorphic phase sequences of the ANBCs treated in the present paper are summarized as follows [1]:

ANBC(8)

     [Cr–445 K → SmC–462 K → SmA–480 K → I]

ANBC(16)

[Cr–401 K → SmC–446 K → D–471 K → SmA–472 K → I]

ANBC(18)

     [Cr–399 K → SmC–428 K → D–464 K → I]

2. Experimental

ANBC compounds were synthesized according to the method reported in the literature [1] and purified by repeated recrystallization from ethanol. *n*-Tetradecane was purchased from Tokyo Chemical Industry and used as received. Samples of about 2 mg in total were weighed into a DSC sample pan, which was sealed with its lid under N_2 gas. Measurements were performed using a Perkin-Elmer DSC7 at a cooling/heating rate of 10 K min^{-1}. The sample in the pan was heated to the isotropic liquid, kept there for 3 min to complete mixing, then cooled to the melting temperature for measurements in a cooling run, and reheated for a heating run. It is emphasized that the results described below are reproducible on repeating cooling/heating cycles for the same samples.

3. Results and discussion

The DSC traces for ANBC(8)–*n*-tetradecane in second heating runs are shown in figure 1, where x is the mole fraction of *n*-tetradecane. The SmA phase was detected only in the cooling run for the neat sample. The anomaly due to the liquid crystal to isotropic liquid transition is rather broad for the neat sample. Upon adding *n*-tetradecane, however, it becomes sharper, in contrast to the usual behaviour induced by impurity. In addition to its shift to the lower temperature side, an additional broad anomaly grows in the isotropic liquid state with increasing x. Similar humps are known to exist for ANBCs that exhibit the D phase [23] as exemplified in the following text. For comparison among the three systems with different ANBC(n_C), the average number of paraffinic carbon atoms per molecule (n_C^*) is defined by $n_C^* = n_C + 14[x/(1-x)]$. The n_C^* dependence of the temperatures of anomalies are summarized in figure 2.

Figure 3 shows the DSC traces for ANBC(16)–*n*-tetradecane in second heating runs. In the neat sample, all the phases are clearly detected, as well as a hump above the sharp anomaly due to the phase transition
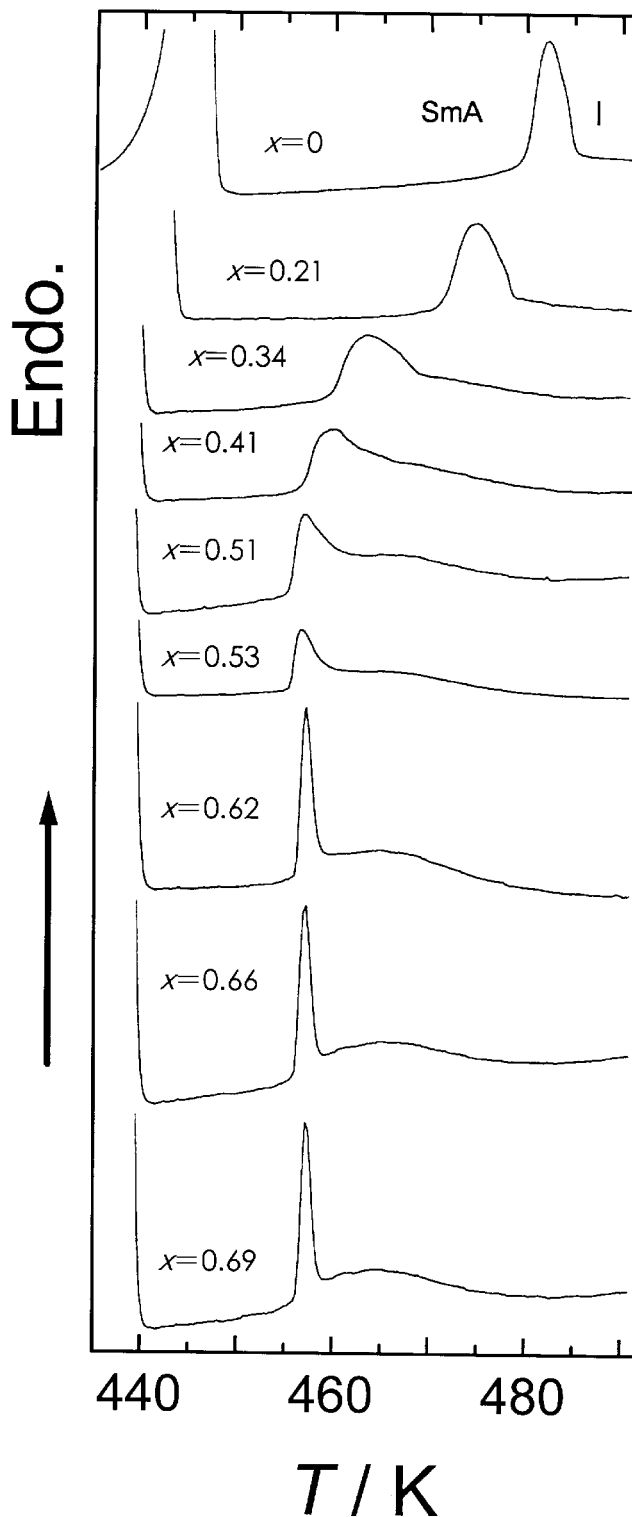

Figure 1. DSC traces from second heating runs for the ANBC(8)–*n*-tetradecane system. Traces are normalized to the amount of ANBC(8) in the system. x = mole fraction of *n*-tetradecane.
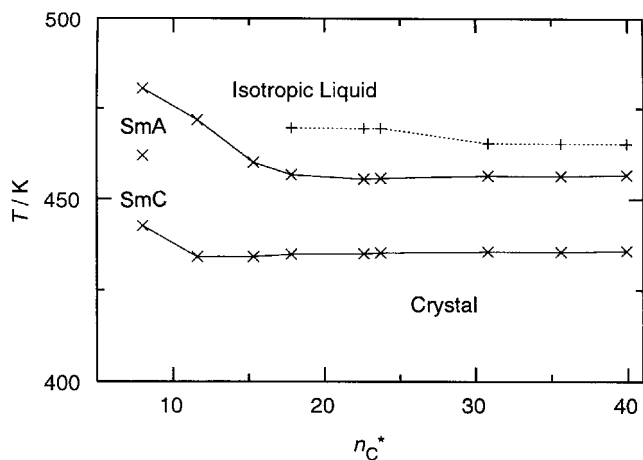
Figure 2. The n_C^* dependence of the phase transition temperatures (crosses) in the ANBC(8)–*n*-tetradecane system. The points given by the plus signs related to the peak temperatures for the broad anomaly above the transition to the isotropic liquid. In this and in figures 4 and 6, lines connecting the data points are merely given as guides for the eye and do not imply that phase boundaries are located on them.

from SmA to isotropic liquid. Although the anomaly due to this phase transition does not appear in other heating runs shown, probably due to superheating, the existence of the SmA phase was confirmed in cooling runs below $x = 0.07$ ($n_C^* = 17.1$). The anomaly due to the SmC–D transition gradually decreases with increasing x. For the system with $x = 0.21$ ($n_C^* = 19.7$), the anomaly due to the SmC–D transition is undetectable. The n_C^* dependence of the temperatures of the anomalies is summarized in figure 4. The hump appearing above the transition to the isotropic liquid shows no appreciable n_C^* dependence.

The DSC traces of ANBC(18)–*n*-tetradecane in second heating runs are shown in figure 5. In the neat sample, all the phases are clearly detected. A hump above the sharp anomaly due to the phase transition from the D phase to isotropic liquid is also clearly seen. The temperature of the anomaly due to the SmC–D transition decreases gradually with increasing x, and the anomaly is undetectable above $x = 0.12$ ($n_C^* = 20.0$). The n_C^* dependence of the temperatures of the anomalies is summarized in figure 6. The hump above the transition to the isotropic liquid again shows no appreciable n_C^* dependence.

The n_C^* dependences of the transition temperatures of the systems ANBC(n_C)–*n*-tetradecane ($n_C = 8$, 16 and 18) given above can be compared with the n_C dependence for the homologous series of neat ANBC given in figure 7 [23]. The n_C^* dependence of the ANBC(16) or ANBC(18)–*n*-tetradecane system is apparently similar to the n_C dependence of the neat ANBCs. Moreover,
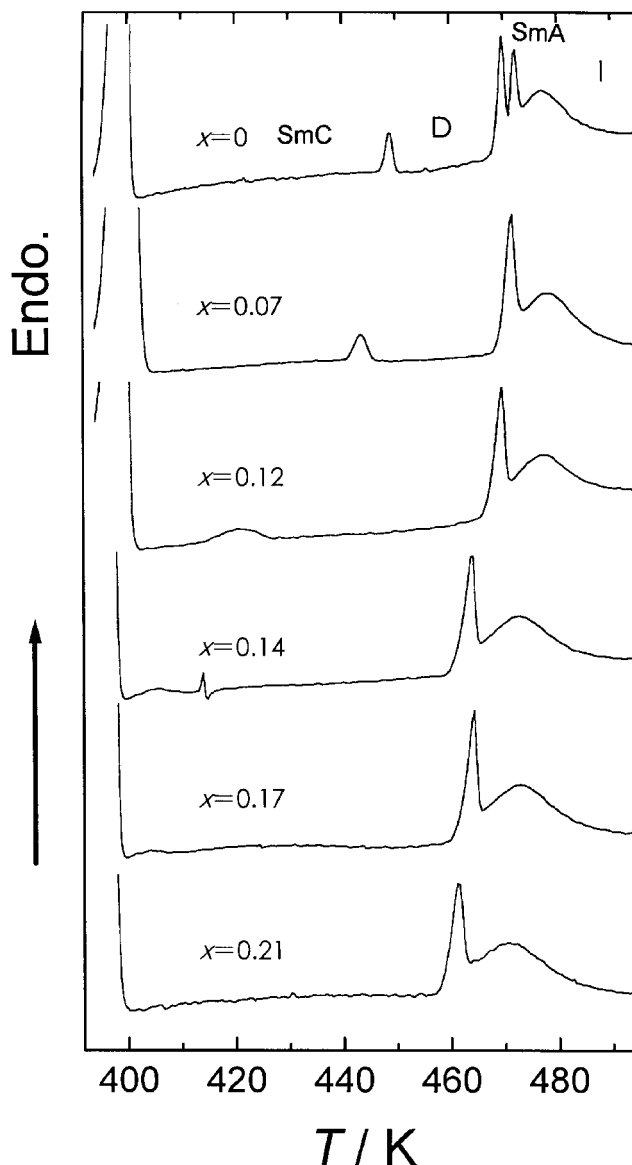

Figure 3. DSC traces from second heating runs for the ANBC(16)–*n*-tetradecane system. Traces are normalized to the amount of ANBC(16) in the system. $x =$ mole fraction of *n*-tetradecane.

the disappearance of the SmA phase between $n_C^* = 17$ and 18 is also similar to the absence of the SmA phase in neat ANBC(18), implying a quantitative equality between n_C and n_C^*. These facts clearly demonstrate that the terminal alkoxy chains behave, at least in part, like a solvent in the D phase. More precisely, the volume fraction of paraffinic carbon atoms (and hydrogen atoms attached) governs the temperatures of the SmC–D and the D–isotropic liquid phase transitions.

On the other hand, the D phase is not induced in the ANBC(8)–*n*-tetradecane system. It is plausible that only some part of terminal chains remote from the molecular
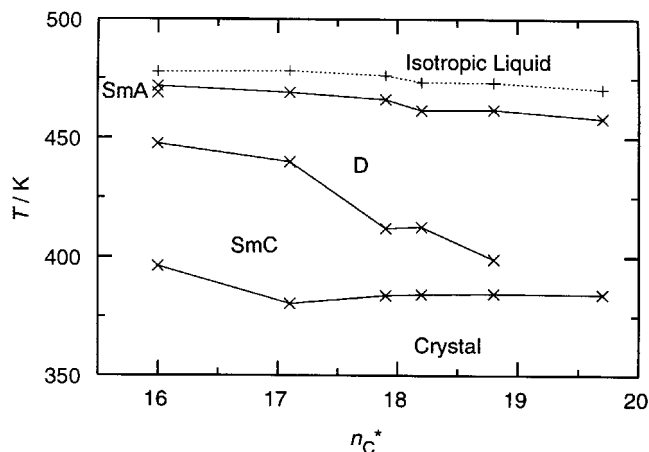
Figure 4. The n_C^* dependence of the phase transition temperatures (crosses) in the ANBC(16)–*n*-tetradecane system. The points given by the plus signs relate to the peak temperatures for the broad anomaly above the transition to the isotropic liquid.

core is highly disordered and behaves like a solvent in the D phase, while the methylene groups within a certain distance from the core are included into an effective 'core', which constitutes a three-dimensional structure with cubic symmetry. If a minimal dimension of the effective 'core' were larger than the size of the ANBC(8) dimer, addition of *n*-tetradecane as solvent would not induce the D phase in the system. In other words, an estimate of the effective 'core' will be obtained from such experiments on ANBC(n_C) with $n_C < 16$. It is noted that the effective 'core' assumed here is not necessarily rigid. In lyotropic systems, appearance of various topologies of micelles in phases, including cubic phases, is interpreted in terms of a conflict between the area occupied by the polar head and the (effective) sectional area of the paraffinic chain [14]. If this view also applies to the present system, the part of the chain included in the 'core' may correspond to the polar head and the rest to the solvent (water) in the lyotropic system.

A broad hump appearing in the temperature range above destruction of a higher order structure is observed in some liquid crystalline substances, and the possibility of assigning the hump to the destruction of shorter range order than the original unit length has been pointed out [24]. The appearance and growth of the hump in a system without the D phase, as in the case of the ANBC(8)–*n*-tetradecane system, may contradict such an idea, though the possibility still remains that the hump induced in the ANBC(8)–*n*-tetradecane system indicates a latent tendency of the D phase to exist in neat ANBC(8). It has been shown from an IR study at various temperatures [3] that the ANBC dimer appreciably dissociates in the temperature range of the
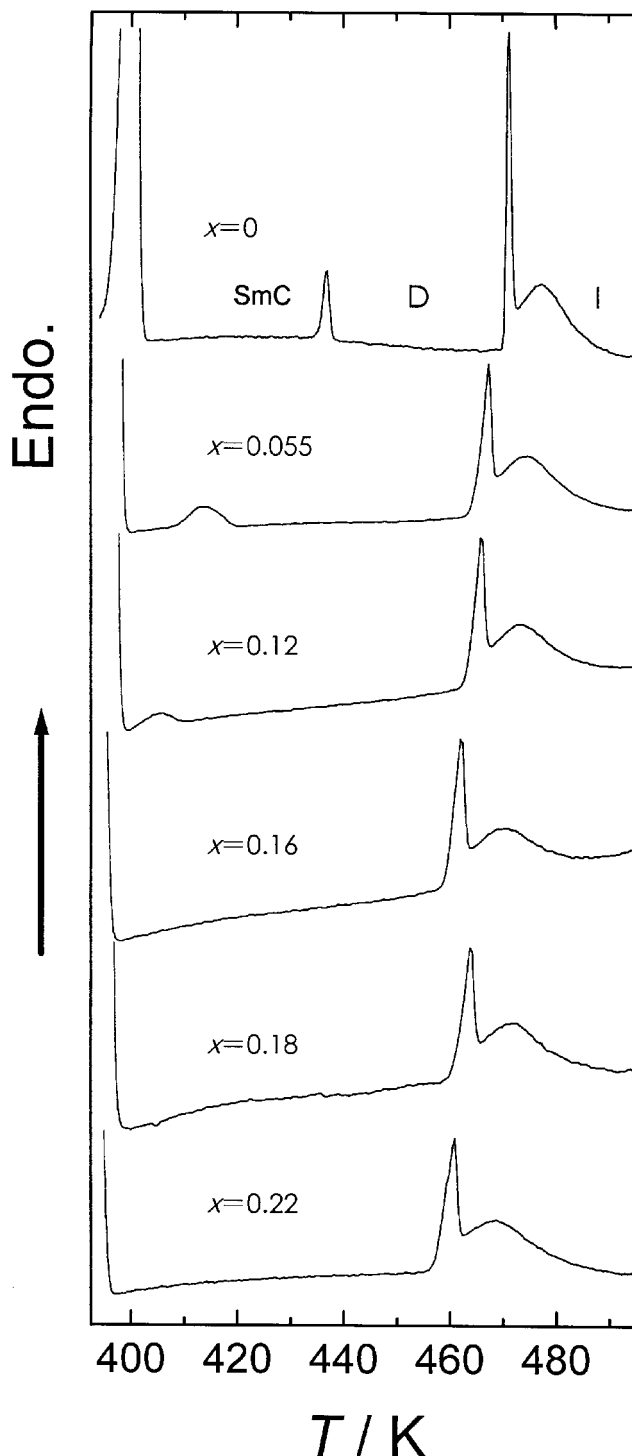

Figure 5. DSC traces from second heating runs for the ANBC(18)–*n*-tetradecane system. Traces are normalized to the amount of ANBC(18) in the system. $x =$ mole fraction of *n*-tetradecane.

broad hump. The enthalpy integrated over the hump remains almost constant for various n_C^* and is also in a reasonable range that would be expected for the
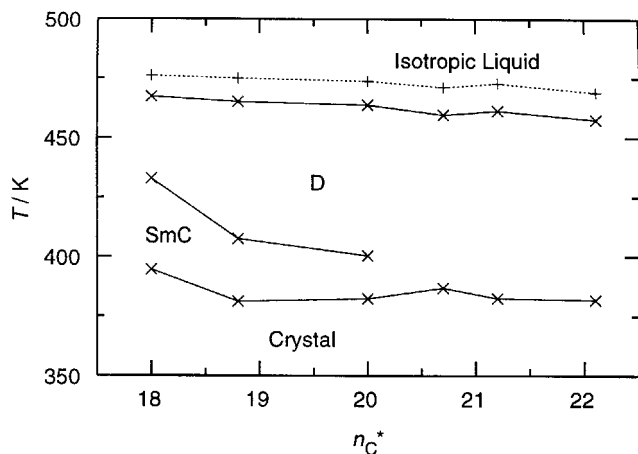
Figure 6. The n_C^* dependence of the phase transition temperatures (crosses) in the ANBC(18)–*n*-tetradecane system. The points given by the plus signs relate to the peak temperatures for the broad anomaly above the transition to the isotropic liquid.
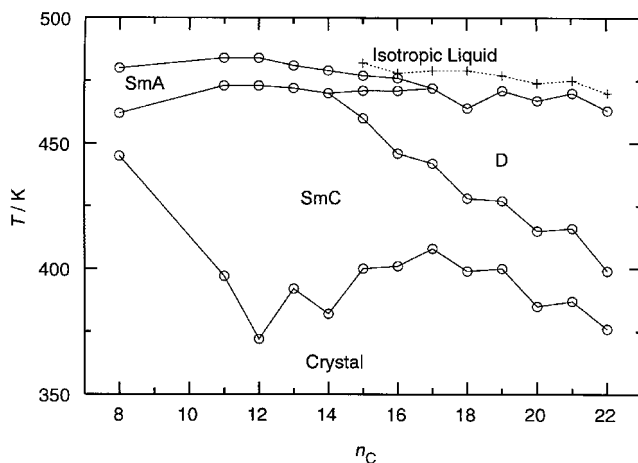

Figure 7. The n_C dependence of the phase transition temperatures (circles) and the peak temperature of the broad anomaly above the transition to the isotropic liquid (plus signs) in neat ANBCs [23].

dissociation of carboxylic acid dimers [23, 25]; however, the IR data do not reproduce the temperature dependence of the heat capacity anomaly.

The point to be discussed is then the mechanism of the growth in the peak height of the hump in the ANBC(8)–*n*-tetradecane system with increasing n_C^*. Since most of the molecules are thought to be dimerized in the SmC phase [3], the growth could be in terms of the tendency to dissociation with added *n*-tetradecane. The enthalpy of dissociation is expected to be roughly the same even upon the addition of *n*-tetradecane, because of the rather local nature of hydrogen bonds [25]. This is the trend observed. It is, therefore, natural to attribute the effect to the entropy term in the Gibbs

energy. The increase in the entropy term enhances the tendency towards dissociation of ANBC(8) dimers. The most simple mechanism is in terms of entropy of mixing, as *n*-tetradecane is nominally a solvent. The mechanism, however, cannot explain the growth with increasing n_C (not n_C^*) in neat ANBCs [23], because the number of molecules is identical for all the compounds. If the molecular identity of the ANBC molecules is abandoned, there appears another possibility. It is known that solvent behaves as an ideal gas in a dense polymer solution (polymers dissolved in a small amount of solvent) [26]. In other words, highly disordered and moving polymers play the role of 'vacuum' for a solvent ideal gas. Then, the entropy of mixing would be proportional to the logarithm of the system volume. Regarding the paraffinic carbon atoms (and hydrogen atoms attached) in the present systems as 'vacuum', the system volume increases with increase in n_C or n_C^*. It is natural to assume that the similarity of the alkoxy chains to solvent is enhanced more in the isotropic liquid than in the D phase, because the chains are more dynamically disordered in the isotropic liquid. Providing that the inner part of the terminal alkoxy chains is included in an effective 'core' and that the remaining part behaves like a solvent, the effect of the addition of *n*-tetradecane will be more conspicuous for the compounds with smaller n_C. This trend is observed experimentally. The idea given here, though qualitative, is therefore consistent with the solvent-like behaviour of alkoxy chains in the D phase.

In conclusion, the examination of the binary systems between ANBC and *n*-tetradecane has clearly shown that the terminal alkoxy chains behave like a solvent in the D phase. Not only the overall phase behaviour but also the growth of a broad hump in ANBC(8) can be explained qualitatively on the assumption that the chains play the role of a solvent. The examination of the binary systems between a long paraffin and ANBC(8), itself showing no D phase, gives valuable information about the size of the effective 'core' required for the establishment of the higher order structure in the D phase.

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