

Effect of nonmesogenic impurities on the liquid crystalline phase transitions of octylcyanobiphenyl

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The effect of the nonmesogenic solutes cyclohexane (CH), biphenyl (BP), and water (W) on the nematic-isotropic ($N-I$) and the nematic-smectic- A ($N-SmA$) phase transitions in the liquid crystal octylcyanobiphenyl (8CB) has been studied by means of adiabatic scanning calorimetry. For BP and CH a linear decrease of both transition temperatures was observed with increasing solute mole fraction. For water the transition temperature stayed nearly constant (after a slight decrease for mole fractions of water up to 0.1) over the entire investigated region. For all concentrations of biphenyl and water studied the $N-SmA$ transition remains second order. For 8CB+CH, however, crossover from second order to first order is observed at a tricritical point of the mole fraction x of CH around 0.046. For water it was found that for mole fractions of water above 0.1 phase separation between an 8CB rich and a water rich phase occurred. The changes in the transition temperatures and differences between the three systems, and in particular the crossover from second order to first order in the 8CB+CH system, is explained in terms of a mean-field free energy density expression including coupling terms of the solutes mole fraction with the nematic and smectic- A order parameters.

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I. INTRODUCTION

Liquid crystalline materials can exhibit a wide variety of mesophases with symmetry intermediate between that of solid crystals and of isotropic liquids. Such liquid crystalline phases possess orientational order but no or reduced positional order [1,2]. The many different phases and phase transitions make liquid crystals good model systems for testing general phase transition and critical phenomena concepts. In particular, the first-order or second-order (or continuous) character of the transition and the universality class of the critical exponents has been extensively investigated by many different techniques.

High resolution adiabatic and ac calorimetric techniques have contributed substantially by revealing subtle thermal features and fluctuation effects at the phase transitions [3–5]. In particular adiabatic scanning calorimetry has proven to be an important tool to discriminate between first-order and second-order transitions in addition to render high-resolution information on pretransitional specific heat capacity behavior.

The most common phase transition is the one between the isotropic (I) liquid phase and the nematic (N) phase possessing orientational but no positional order. This transition is weakly first order [1,2] with small latent heats and quite often substantial pretransitional fluctuation effects [6].

However, one of the most interesting and most extensively studied transitions is the nematic (N) to smectic- A (SmA) phase transition [7]. In addition to orientational order the SmA phase exhibits one-dimensional positional order. This positional order of the SmA phase can be described in terms of a two-component complex order parameter, and thus the $N-SmA$ transition was expected to be in the three dimensional (3D) XY universality class [8]. However, experi-

ments have revealed nonuniversal critical behavior and anisotropic divergences of correlation lengths [7]. In addition to that, coupling with the nematic order parameter [1] and nematic fluctuations may affect the order of the transition. It has been shown by de Gennes [1,8] that strong coupling (narrow nematic range) between the N and SmA order parameters results in a first-order $N-SmA$ transition, while weak coupling (wide nematic range) gives a continuous transition. High-resolution adiabatic scanning calorimetry (ASC) results on mixtures of alkylcyanobiphenyls (nCBs) are consistent with this picture [9]. However, it was predicted by Halperin *et al.* [10] that coupling between the SmA order parameter and the nematic director fluctuations may drive an otherwise continuous transition to a (weakly) first-order one. Two compounds for which this aspect was investigated in detail are 8CB (octylcyanobiphenyl) [11] and 8OCB (octyloxycyanobiphenyl) [12]. No evidence for a first-order latent heat could be found within an upper limit of 1.4 J/kg for 8CB and of 1.8 J/kg for 8OCB. However, optical investigations showed for 8CB some evidence for a very small two-phase region and a very small discontinuity in the SmA order parameter at the $N-SmA$ transition [13]. Estimates for a latent heat, if present, at the $N-SmA$ transition of 8CB, induced by the latter coupling, are apparently smaller than the upper limit obtained from ASC [14].

It was also suggested theoretically [15,16] that for chiral compounds the transition between the cholesteric or chiral nematic (N^*) phase and the smectic- A phase should also be first order. This prediction was experimentally confirmed by an investigation of mixtures of the nonchiral compound octyloxycyanobiphenyl (8OCB) (a compound with a continuous $N-SmA$ transition) and the chiral 4-(2-methylbutyl)-4'-cyanobiphenyl (CB15) [12].

Another type of coupling that potentially could drive the $N-SmA$ transition from second order to first order is the coupling with a nonmesogenic (impurity) solute, which has been occasionally invoked theoretically but never studied experi-

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mentally [17–19]. In order to investigate this possible coupling effect we carried out ASC measurements on a series of binary mixtures of the liquid crystal 8CB with three nonmesogenic solutes: cyclohexane (CH), biphenyl (BP) (a molecule identical to the aromatic core of 8CB), and water (W). A brief account of results for the N -SmA transitions of the biphenyl-8CB and cyclohexane-8CB systems has been given in a recent paper [20] where also an explanation in terms of a mean-field free energy density expression was put forward. Here we give full details of these investigations including additional measurements for the cyclohexane-8CB system and for a third system, water-8CB.

II. THEORETICAL BACKGROUND

The thermodynamic behavior near the nematic-isotropic transition (N - I) is usually described in terms of the mean-field Landau–de Gennes theory [1]. For the uniaxial nematic phase one obtains an expansion of the free energy density F in terms of the nematic order parameter S :

$$F - F_I = \frac{1}{2}A_0S^2 - \frac{1}{3}B_0S^3 + \frac{1}{4}C_0S^4 + \dots \quad (1)$$

In the isotropic phase $S=0$ and in the nematic phase $S \neq 0$. In Eq. (1) one has $A_0 = a(T - T^*)$ (with $a > 0$) and $B_0 > 0$ for uniaxial phases with positive anisotropy. The presence of the cubic term that does not disappear at T_{N-I} , leads to a first-order transition with a finite discontinuity in the order parameter [$S_{N-I} = 2B_0/(3C_0)$]. T^* is the lower stability limit of the isotropic phase. The nonzero value of B_0 results in a (typically quite small) enthalpy discontinuity (latent heat) at T_{N-I} ,

$$\Delta H_L = H_I - H_N = \frac{2aB_0^2}{9C_0^2} T_{N-I}. \quad (2)$$

Since the pure 8CB liquid crystal has a continuous N -SmA transition with an effective specific heat capacity critical exponent α value between the three-dimensional (3D) XY value and the tricritical value [7,11], the expression of the free energy density for this transition should include the Landau–de Gennes coupling between the N order parameter S and the SmA order parameter amplitude ψ [1,8],

$$F = F_N(S) + \frac{1}{2}\alpha(T)\psi^2 + \frac{1}{4}\beta\psi^4 - C\psi^2\delta S + \frac{1}{2\chi}\delta S^2 + \dots \quad (3)$$

F_N is the nematic free energy density given by Eq. (1). For $T < T_{N-SmA}$, one has $\delta S = S - S_0$, with $S_0(T)$ the nematic order parameter in the absence of smectic order. The temperature dependence of α is given by $\alpha(T) = \alpha_0(T - T_0)$, and $\chi(T)$ is a response function that is large near T_{N-I} but decreases with decreasing temperature. α_0 , β , and C are positive constants. Minimization of F with respect to δS gives

$$\delta S = C\psi^2\chi. \quad (4)$$

Substitution of Eq. (4) in Eq. (3) results in

$$F = F_N(S) + \frac{1}{2}\alpha(T)\psi^2 + \frac{1}{4}\beta'\psi^4 + \dots, \quad (5)$$

with

$$\beta' = \beta - 2C^2\chi. \quad (6)$$

Depending on the values of C and χ and the resulting sign of β' three different cases can be obtained. For $\beta' > 0$ one has a continuous transition with $T_0 = T_{N-SmA}$, $\beta' < 0$ corresponds to a first-order transition, and at $\beta' = 0$ one has a crossover from a (second-order) continuous transition to a first-order transition at a tricritical point.

The addition of nonmesogenic impurities to 8CB affects both the N - I transition as well as the N -SmA transition. Elements (see Sec. IV) that must be understood are as follows. For both transitions the decrease of the transition temperatures with solute mole fraction x must be understood. For the N - I transition the almost mole fraction independent latent heats (in the investigated mole fraction range) must be considered. For the N -SmA transition the crossover (with increasing x) from second order to first order for 8CB+CH and the absence of it for 8CB+BP and 8CB+W must be explained. Let us first look at the N -SmA transition. Considering different possibilities, it turned out that the following modification of Eq. (3) with two mole fraction x dependent terms is appropriate

$$F = F_N(S) + \frac{1}{2}\alpha\psi^2 + \frac{1}{4}\beta\psi^4 - C\psi^2\delta S + \frac{1}{2\chi}\delta S^2 + A\psi^2x + D\psi^2\delta Sx + \dots \quad (7)$$

Again minimizing with respect to δS and substitution in Eq. (7) gives

$$\delta S = (C - Dx)\psi^2\chi, \quad (8)$$

$$F = F_N(S) + \frac{1}{2}\alpha'(T)\psi^2 + \frac{1}{4}\beta''\psi^4, \quad (9)$$

with

$$\alpha' = \alpha + 2Ax, \quad (10)$$

$$\beta'' = \beta + 4DC\chi x = \beta - 2C^2\chi + 4DC\chi x, \quad (11)$$

$$T_{N-SmA}(x) = T_{N-SmA}(0) - \frac{2Ax}{\alpha_0}. \quad (12)$$

As it can be seen from Eq. (12), a coupling term with $A > 0$ would be needed to obtain a (linear) decrease of the N -SmA transition temperature with increasing x . A possible change of the order of the transition via the renormalization of β in Eq. (3) can be accounted for by the x -dependent term in Eq. (11). For $\beta' > 0$ (as in the case of pure 8CB), D would have to be negative to accomplish a transition from second-order to first-order.

In order to arrive at a (linear) transition temperature change for the N - I transition with increasing x , Eq. (1) must be extended also with a coupling term between S and x of the form ES^2x . This would result in

$$a(x) = \frac{a}{2} + Ex, \quad (13)$$

$$T_{N-I}(x) = T_{N-I}(0) - \frac{2Ex}{a}. \quad (14)$$

Assuming that E is a constant would result in a first-order approximation in a mole fraction independent latent heat given by Eq. (2). A coupling term between the mole fraction x and the nematic order parameter S also has a (small) effect on the renormalized β expression in Eq. (11). Adding in Eq. (7) a term $ES^2x = E(\delta S + S_0)^2x$ and minimization with respect to δS results in

$$\delta S = \chi'(C\psi^2 - D\psi^2x - 2ES_0x), \quad (15)$$

with

$$\chi' = \frac{\chi}{1 + 2ES_0x}. \quad (16)$$

Substitution in the adjusted Eq. (7) (with the additional term ES^2x) and further assuming $(\chi')^2/\chi \approx \chi'$ results (to lowest order in x) in

$$\alpha'' = \alpha + 2Ax \left(1 + \frac{2CES_0\chi'}{A} \right), \quad (17)$$

$$\beta''' = \beta - 2C^2\chi' + 4DC\chi'x(1 + 4EC\chi'), \quad (18)$$

$$T_{N-SmA}(x) = T_{N-SmA}(0) - \frac{2Ax}{\alpha_0} \left(1 + \frac{2CES_0\chi'}{A} \right). \quad (19)$$

For decreasing $N-I$ transition temperatures ($E > 0$) with increasing x (as the case for our systems), the fact that $\chi' < \chi$ reduces the second term in Eq. (18) in comparison with the corresponding one in Eq. (11) and thus takes the transition somewhat further away from the tricritical point on the second-order side of the phase transition line as a function of mole fraction.

III. EXPERIMENT

In order to study the effect of nonmesogenic impurities on the liquid crystalline phase transitions of octylcyanobiphenyl (8CB) we carried out adiabatic scanning calorimetry measurements. Adiabatic scanning calorimetry is designed to obtain continuously the evolution of the heat capacity C_p and the enthalpy H of a sample of interest as a function of temperature [3,4]. Both quantities can be studied with a very high precision and temperature resolution while maintaining thermal equilibrium inside the sample. To obtain C_p and H , a constant power P is supplied to the sample and the resulting change in temperature $T(t)$ is measured as a function of time. From these two quantities, the heat capacity can be easily calculated,

$$C_p = \frac{P}{\dot{T}(t)}, \quad (20)$$

with $\dot{T}(t) = dT/dt$ the time derivative of the temperature, to be calculated numerically. Besides information about C_p , the

exact knowledge of $T(t)$ allows one also to calculate directly the enthalpy H as a function of temperature by inverting the $T(t)$ data to

$$H(T) = H(T_0) + P[t(T) - t(T_0)], \quad (21)$$

with T_0 the starting temperature of the run. The continuous determination of the enthalpy as a function of temperature provides a unique tool for determining the order of the phase transition: if the enthalpy shows a jump at a certain temperature (i.e., a latent heat is present), the transition is first-order; if such a jump is absent, the transition is continuous (or second-order). In case of a broadened first-order transition, the two-phase region can be clearly identified. The fact that the direct ASC result is $H(T)$ allows one to define for second-order transitions the quantity

$$C = \frac{H - H_c}{T - T_c}, \quad (22)$$

with H, H_c being the enthalpy at the temperature T and at the critical temperature T_c , respectively. If the limiting specific heat capacity is of the form

$$C_p = A^\pm |\tau|^{-\alpha} + B, \quad (23)$$

with $\tau = (T - T_c)/T_c$, A^\pm the critical amplitudes above and below T_c , α the critical exponent, and B the background term, it can be shown that [11]

$$C - C_p = \frac{A^\pm}{1 - \alpha} |\tau|^{-\alpha}. \quad (24)$$

Thus, a log-log plot of $C - C_p$ versus τ shows a linear behavior with slope $-\alpha$.

In this paper we present high-resolution ASC results of 8CB diluted with three different nonmesogenic solutes: cyclohexane (CH), biphenyl (BP), and water (W). Cyclohexane (purity better than 99.9%) was obtained from VEL, Leuven, Belgium; biphenyl (purity better than 99.5%) was obtained from Sigma-Aldrich Chemie, Germany; and for the water mixtures we used triple distilled water. For the 8CB compound two different batches were used. The old (1999) batch 1 with purity of 99.9% was obtained from the laboratory of Dabrowski (Military University of Technology, Warsaw, Poland) and used initially for five mixtures (with mole fractions x_{CH} of 0.0104, 0.0183, 0.0368, 0.0467, and 0.0722) of 8CB + CH. For the other 8CB + CH mixtures and the subsequent measurements of 8CB + BP and 8CB + W mixtures a new (2006) high purity (better than 99.9%) batch 2 of 8CB, also synthesized at the laboratory of Dabrowski, was used. A tantalum cylindrical cell with a diameter of 10 mm and a length of 50 mm was used. The cell contained a stirring ball allowing continuous stirring in the usual way [3,4] by rolling the ball back and forth from one end to the other end of the cell by changing the inclination of the horizontally suspended cell. Sample masses in the cell were typically between 1.5 and 2.0 g. Both heating and cooling runs were executed.

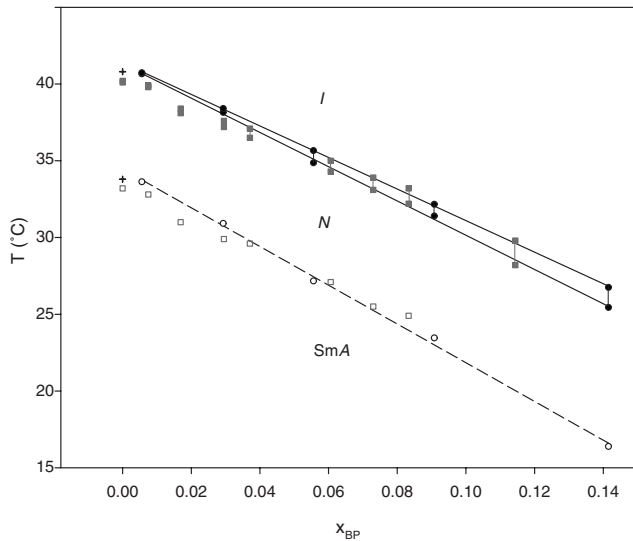


FIG. 1. Phase diagram of the system 8CB and biphenyl. The length of vertical line pieces indicates the width of the two-phase region. The solid and dashed lines are linear fits through the corresponding data points. The circles are present data, the crosses are literature values for pure 8CB [11], and the gray squares are from [21]. Full symbols represent a first-order phase transition and open symbols represent a continuous phase transition. The uncertainty on the temperatures is less than the symbol sizes.

IV. RESULTS AND DISCUSSION

A. Phase diagrams

For the three mixture systems there are changes observed for the N - I as well as for the N - SmA transition temperature by adding the solutes. In Fig. 1 for 8CB+BP, in Fig. 2 for 8CB+CH, and in Fig. 3 for 8CB+W the phase transition temperatures are given as a function of the solute mole fraction x . For the first system the decrease of T_{N-SmA} with x is somewhat stronger than for T_{N-I} . Our transition temperatures are in good agreement with literature values [21]. For 8CB+CH on the contrary T_{N-I} decreases substantially faster with increasing x than T_{N-SmA} .

With the exception of the largest mole fraction $x_{CH} = 0.0722$, it turned out that the (T_{N-I} and T_{N-SmA}) transition temperatures for the 8CB+CH mixtures prepared with batch 1 of 8CB (triangles in Fig. 2) were systematically lower than the ones prepared with the new batch 2. We believe the lower transition temperatures for the other samples with 8CB of batch 1 are a consequence of sample handling. The first sample of 8CB+CH ($x_{CH} = 0.0722$) was prepared by filling the cell with the required amounts of 8CB and CH. Since from the subsequent measurements it turned out that N - SmA transition was already strongly first-order, it was decided for the following measurements to stepwise reduce x_{CH} by evaporation of CH from the sample in the cell. This was done by heating the sample (in the open cell) with hot air from a heating gun. Four additional concentrations (with x_{CH} of 0.0104, 0.0183, 0.0368, and 0.0467) were obtained in this way and subsequently measured. Apparently, by this procedure some (unknown) type of impurity must have been introduced to these samples. Recent testing of a small left-over

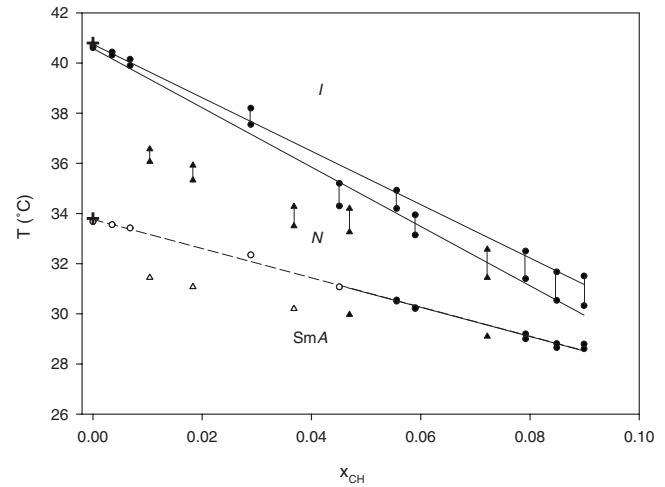


FIG. 2. Phase diagram for the system 8CB and cyclohexane. The length of the vertical line pieces indicates the width of the two-phase region. The triangles and circles are data corresponding with mixtures with 8CB of batch 1 and batch 2, respectively (see text). The crosses are for pure 8CB from [11]. Full symbols represent a first-order phase transition and open symbols a continuous one. The solid and dashed lines are linear fits through the corresponding data points of mixtures with 8CB from batch 2. The uncertainty on the temperatures is less than the symbol sizes.

(in the original bottle) of the pure 8CB of batch 1 by polarizing microscopy resulted in transition temperatures consistent (within 0.2 °C) with the well-established values of $T_{N-I} = 40.7$ °C and $T_{N-SmA} = 33.7$ °C [11]. The transition temperatures for the new batch 2 are also in very good accordance with the values for pure 8CB [11]. For 8CB+CH a second and a third series of samples was prepared with pure 8CB from batch 2 by adding small amounts of CH in steps. For the second series this is the CH mole fractions $x = 0.0451, 0.0590, 0.0849, 0.0899$ and for the third series the

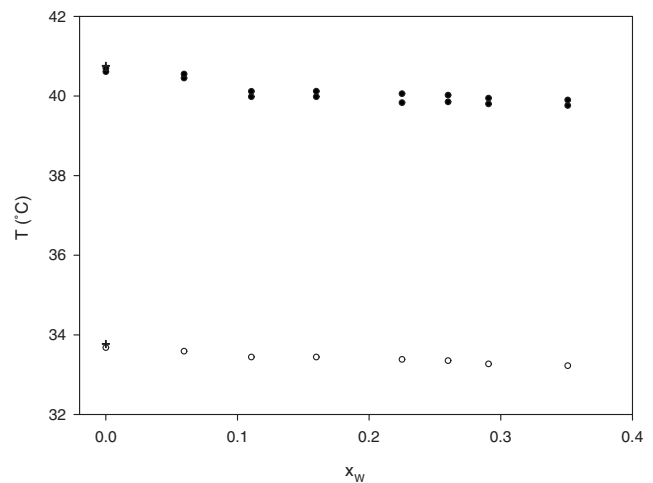


FIG. 3. Phase diagram of the system 8CB and water. The length of the short vertical line pieces indicates the width of the two-phase region. The circles are present data and the crosses are for pure 8CB from [11]. Full symbols represent a first-order phase transition and open symbols a continuous one. The uncertainty on the temperatures is less than the symbol sizes.

CH mole fractions of $x=0.0035$, 0.0068 , 0.0289 , 0.0556 , 0.0792 . The different mole fractions in the cases of 8CB+BP and 8CB+W were all prepared by adding in steps small amounts of BP or W. For the second-order transitions of all three systems there was (within experimental resolution of about 10 mK) no indication of hysteresis between heating and cooling runs. For the first-order transitions, depending on the scanning rates, differences of 0.1 to 0.2 °C were observed in some cases (quite similar to what can be seen in pure systems). The phase diagram for 8CB+W in Fig. 3 shows a different behavior. After a small (about 0.8 K for T_{N-I} and about 0.5 K for T_{N-SmA}) decrease for mole fractions up to about 0.10, the transition temperatures remain constant over the rest of the investigated x range. An explanation for the approximately constant transition temperatures for the mixtures with $0.10 < x_W < 0.35$ was found after a visual inspection of six newly prepared mixture samples with different mole fractions of water. For mixtures with $x > 0.10$, phase separation occurred: two phases, one mainly consisting of water and another one consisting mainly of 8CB, were clearly visible. Thus, there exists an upper limit for the mole fraction of water that is soluble in 8CB, and the liquid crystalline transitions observed for $x > 0.10$ are those occurring in the 8CB rich phase with a nearly constant composition of x around 0.10. Inspection of different 8CB+BP and 8CB+CH mixtures under the polarizing microscope did not give any indication of macroscopic segregation of BP or CH from 8CB.

An interesting question may arise regarding the distribution of the BP and CH impurity molecules between the 8CB liquid crystal host molecules, in particular in the smectic-A phase. Although this question cannot properly be answered by macroscopic heat capacity measurements, visual observation or inspection under the polarizing microscope, our results indicate homogeneous distribution (at least on a mesoscopic scale) of BP and CH in the different samples studied. For 8CB+W, however, clear macroscopic evidence was found that for $x_W > 0.1$, water molecules are expelled from the host liquid crystal. In an x-ray diffraction experiment Rieker [22] showed for a monolayer SmA and a monolayer SmC compound that the layer spacing increases with the addition of organic solvents (*n*-decane, *n*-hexane, and benzene) to the host materials. The rate of this increase was considered an indication of the formation of an organic lyotropic, lamellar liquid crystal phase with the solvent intercalated between the smectic layers of the host liquid crystal. For 8CB, exhibiting a SmA_d layer spacing, results were less clear. Visual inspection of 8CB+*n*-hexane and 8CB+benzene mixtures showed that the solvents were not uniformly distributed throughout the host liquid crystal. In both cases minimal or no swelling was observed. Thus, the question arises about the location in the 8CB host of the BP and CH molecules in our samples and whether intercalated impurity layers between the SmA_d layers could be present. First, it should be noted that our studies are for rather dilute solutions ($x_{BP} < 0.15$ and $x_{CH} < 0.10$) while in the x-ray experiment volume fractions of up to 0.8 were studied (in our cases volume fractions were more than an order of magnitude smaller). Although some layer swelling might also be present for 8CB+BP and 8CB+CH because the impurities

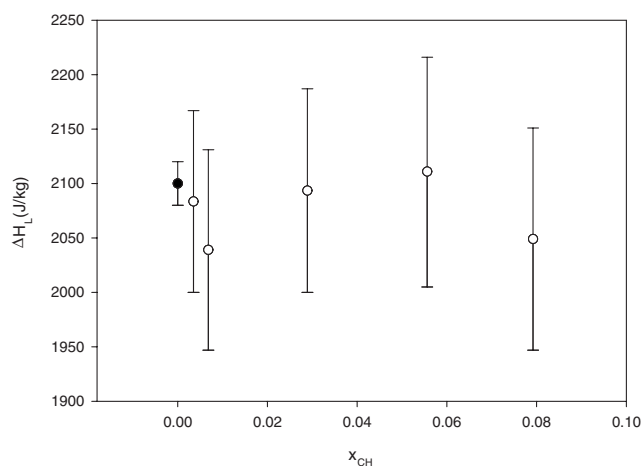


FIG. 4. Latent heats for the nematic to isotropic phase transition of the system 8CB and cyclohexane as a function of the mole fraction x of cyclohexane. The value for pure 8CB (solid dot) is from [11].

might preferably intercalate between the layers (or inside the layers for BP?), there are, for mole fractions below 0.1, not enough impurity molecules available to constitute a layer between each pair of smectic layers.

B. The nematic-isotropic transition

As observed in Fig. 1 for 8CB+BP and in Fig. 2 for 8CB+CH there is a rather strong decrease of T_{N-I} with increasing mole fraction. Also for the (small) x range where the amount of water in 8CB increases there is a decrease of the $N-I$ transition temperature with increasing x . This means that for these three cases the coefficient E in Eqs. (13) and (14) must be positive. In Sec. II it was pointed out that if E is a constant (and thus temperature independent) this would result in a first-order approximation in a $N-I$ latent heat that would not depend on the mole fraction of the solute. That this is, indeed, the case can be seen in Fig. 4 for a series of mixtures for the system 8CB with cyclohexane.

C. The nematic-smectic-A transition

For the three systems 8CB+BP (Fig. 1), 8CB+CH (Fig. 2), and 8CB+W (Fig. 3, in the range $x < 0.10$), a decrease of T_{N-SmA} is observed with increasing x . Considering Eqs. (12) and (19) it follows that (since all other parameters in these equations are positive) the parameter A in Eq. (7) is positive.

For the five mixtures of 8CB and biphenyl it was found that the N -SmA transitions are within experimental resolution, continuous with an upper limit for a latent heat (if present) of $\Delta H_L < 2$ J/kg. The specific heat capacity as a function of temperature near the transition was measured for all five mixtures and is depicted in Fig. 5. Also the effective critical exponent α was determined by plotting and fitting $\log_{10}(C - C_p)$ versus $\log_{10}|\tau|$. In Fig. 6 plots of $\log_{10}(C - C_p)$ versus $\log_{10}|\tau|$ for $T < T_{N-SmA}$ are given with linear fits for the data in the range $-3.9 < \log_{10}(C - C_p) < -2.5$. The effective critical exponent decreases from $\alpha = 0.25$ for $x_{BP} = 0.0056$ to $\alpha = 0.08$ for $x_{BP} = 0.1415$.

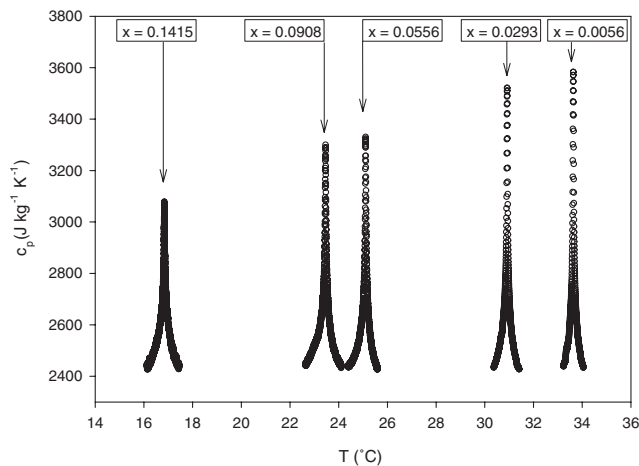


FIG. 5. Temperature dependence of the specific heat capacity for five mixtures of 8CB and biphenyl near the nematic to smectic-A phase transition. The mole fractions $x=0.0293$, 0.0556 , and 0.1415 are heating runs and $x=0.0056$ and 0.0908 are cooling runs.

For mixtures of 8CB and cyclohexane the picture is completely different. For the concentrations below $x_{CH}=0.046$, a continuous nematic to smectic-A transition was observed within the experimental resolution ($\Delta H_L < 2$ J/kg for $x_{CH}=0.0035$, $x_{CH}=0.0068$, $x_{CH}=0.0104$, and $x_{CH}=0.0183$; and $\Delta H_L < 5$ J/kg for $x_{CH}=0.0289$, $x_{CH}=0.0368$, and $x_{CH}=0.0451$). The effective critical exponent evolved from $\alpha = 0.33 \pm 0.03$ for $x_{CH}=0.0035$ toward $\alpha = 0.49 \pm 0.03$ for $x_{CH}=0.0451$. $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ plots for $T < T_{N-SmA}$ from which α values have been derived are shown in Fig. 7 for five concentrations. The $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ data for the mixtures $x_{CH}=0.0068$ and $x_{CH}=0.028$ resulted in effective critical exponents of $\alpha = 0.34 \pm 0.03$ and $\alpha = 0.43 \pm 0.03$, respectively. For clarity these data are not in-

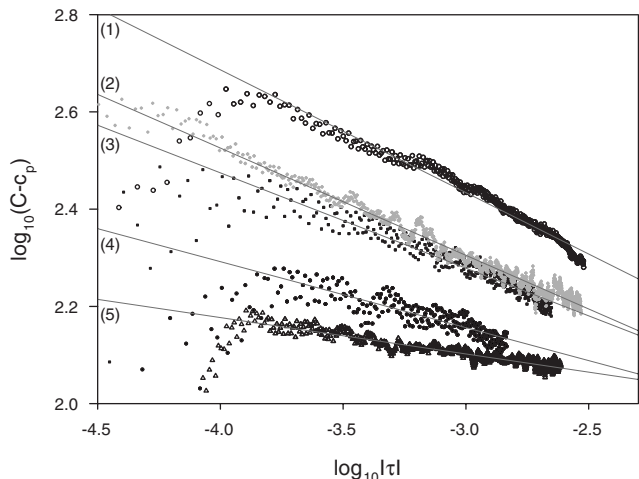


FIG. 6. Plots of $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ below T_{N-SmA} of the five mixtures of Fig. 5. The solid lines are linear fits (for $-3.9 < \log_{10}|\tau| < -2.5$) resulting in the indicated effective critical exponent α values. The uncertainty on α is ± 0.03 . (1) $x=0.0056$, $\alpha = 0.25$; (2) $x=0.0293$, $\alpha = 0.22$; (3) $x=0.0556$, $\alpha = 0.20$; (4) $x=0.0908$, $\alpha = 0.14$; (5) $x=0.1415$, $\alpha = 0.08$. The data (2), (3), and (5) are heating runs and (1) and (4) are cooling runs.

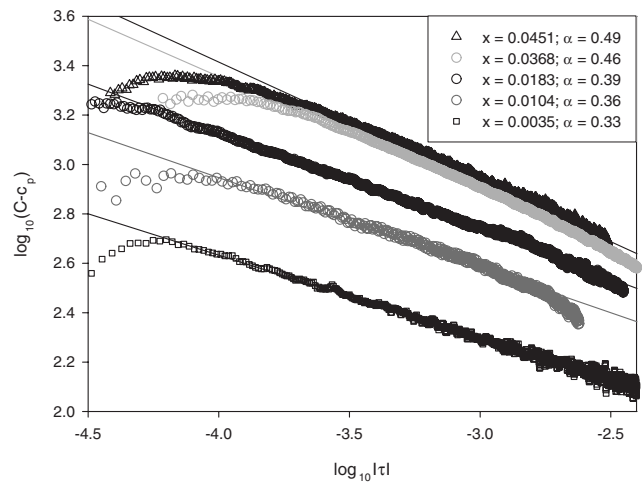


FIG. 7. Plots of $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ below T_{N-SmA} for five mixtures of 8CB and cyclohexane exhibiting a continuous phase transition. The mole fraction $x=0.0183$ is a heating run and $x=0.0451$, 0.0368 , 0.0104 , and 0.0035 are cooling runs. The solid lines are linear fits (for $-3.9 < \log_{10}|\tau| < -2.5$) resulting in the indicated effective critical exponent α values. The uncertainty on α is ± 0.03 .

cluded in Fig. 7. In Fig. 8 a plot of α as a function of x_{CH} shows clearly an evolution of α toward the tricritical value $\alpha = 0.5$.

For mole fractions of cyclohexane higher than $x_{CH}=0.046$, a first-order $N-SmA$ transition is observed. The enthalpy as a function of temperature for the mixture with a mole fraction of cyclohexane equal to 0.0470 is plotted in Fig. 9. A finite latent heat of 17 ± 5 J/kg and a two-phase region of ≈ 15 mK are clearly visible. In Fig. 10 it can be seen that for larger x_{CH} values the latent heat rapidly increases nonlinearly, reaching a value of 560 ± 10 J/kg for $x_{CH}=0.0899$.

As already pointed out for the mixtures of 8CB and water in the phase diagram of Fig. 3 at first a slight decrease of the $N-I$ as well as of the $N-SmA$ phase transition temperature

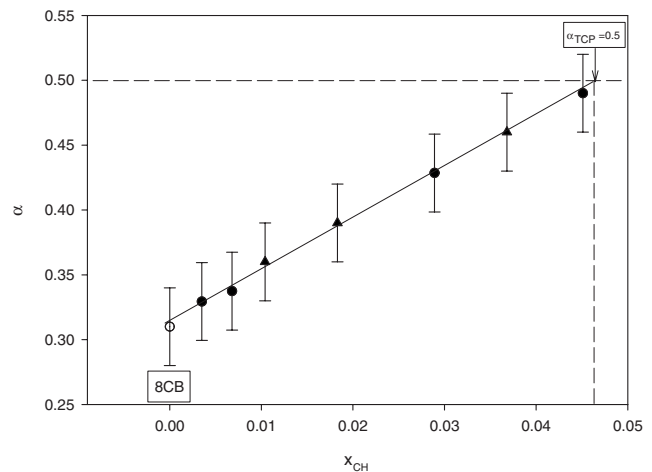


FIG. 8. Effective critical exponent α for the continuous phase transitions of the system 8CB and cyclohexane as a function of the mole fraction of cyclohexane. The value for pure 8CB is from [11].

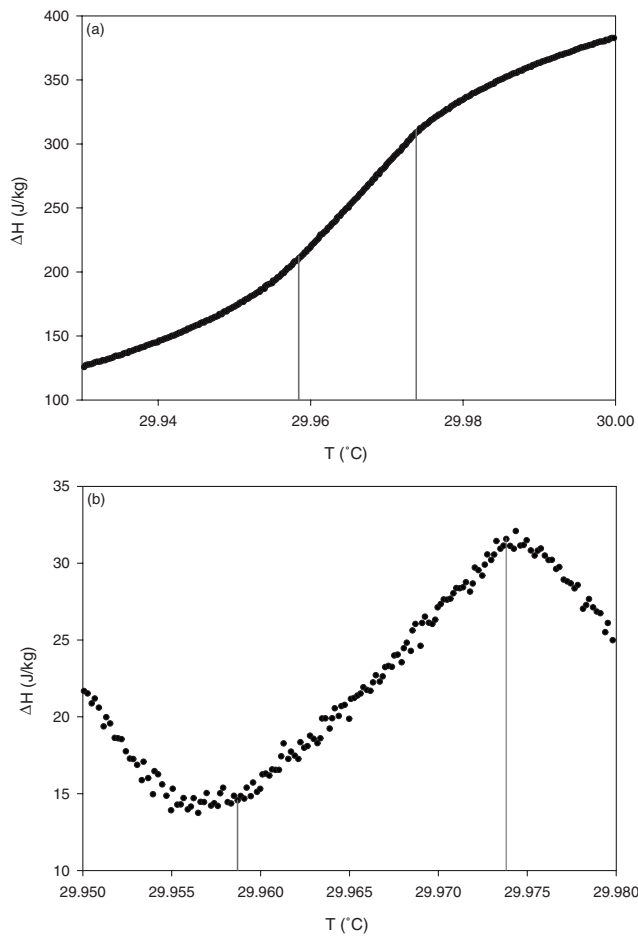


FIG. 9. Enthalpy near the N -SmA phase transition of a mixture of 8CB and cyclohexane with mole fraction of cyclohexane $x_{\text{CH}} = 0.0470$ with a linear background of (a) $3(T-T_0)$ J/g and (b) $8.8(T-T_0)$ J/g subtracted for clarity.

occurs over the range $0 < x_W < 0.10$, followed by nearly constant values for larger mole fractions. For these higher x_W values, phase separation in a water-rich and a 8CB-rich phase took place. In all the mixtures, however, quite sharp N -SmA heat capacity peaks could be observed, allowing the determination of effective critical exponent α values. A plot of the $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ results for five mixtures ($x_W = 0.0594$, $x_W = 0.1105$, $x_W = 0.1599$, $x_W = 0.2606$, and $x_W = 0.3509$) is shown in Fig. 11. Equal values of $\alpha = 0.36 \pm 0.03$ were obtained for all the mixtures from $x_W = 0.1105$ to $x_W = 0.3509$. For $x_W = 0.0594$ an intermediate value $\alpha = 0.32 \pm 0.03$ between this constant value of 0.36 ± 0.03 and the pure 8CB value of 0.31 ± 0.03 [11] was obtained.

The difference in the behavior of the three systems near the N -SmA transition can be understood by looking at the changes in the width of the nematic ranges with mole fraction of the solute. In Fig. 12 it can be seen that with respect to the width of the N range of pure 8CB it increases for 8CB+BP, decreases for 8CB+CH, and stays (after an initial small decrease) nearly constant for 8CB+W over the investigated x range. For 8CB+CH the narrowing of the nematic range results (at $x_{\text{CH}} \approx 0.046$) in a crossover at a tricritical

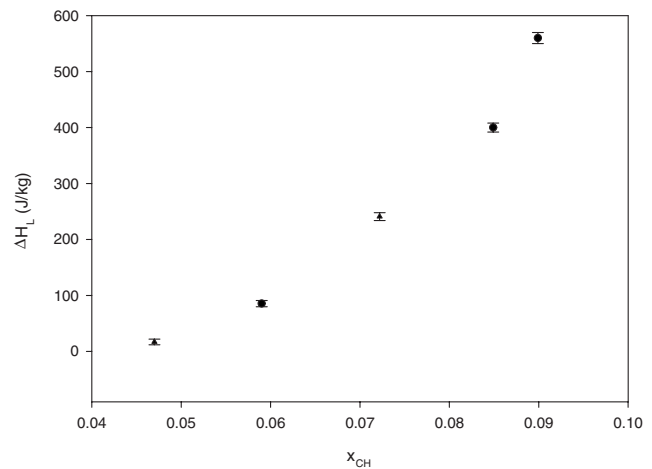


FIG. 10. Latent heat ΔH_L for the first-order N -SmA phase transitions of 8CB and cyclohexane as a function of mole fraction of cyclohexane x_{CH} .

point from continuous transitions (at low x_{CH} values) to first-order ones (at high x_{CH}) with nonlinearly increasing latent heats with increasing x_{CH} (Fig. 10). For the continuous transitions the effective critical exponent α increases from the pure 8CB value of 0.31 to the tricritical value of 0.5 (see Fig. 8). This means that β'' of Eq. (11) changes sign at the tricritical point. As a consequence the parameter D in that equation must be negative because for pure 8CB ($x=0$) one has $\beta'' = \beta' > 0$. In Eq. (7) the fourth and seventh term can be combined to a single one with a coefficient $(C-Dx)$ for the coupling term between the nematic and smectic- A order parameters. Thus, because $D < 0$ the addition of cyclohexane increases the coupling between these order parameters. The increasing width of the nematic range and the decreasing effective critical exponent α values for 8CB+BP, on the contrary, means that here D in Eq. (11) has the opposite sign,

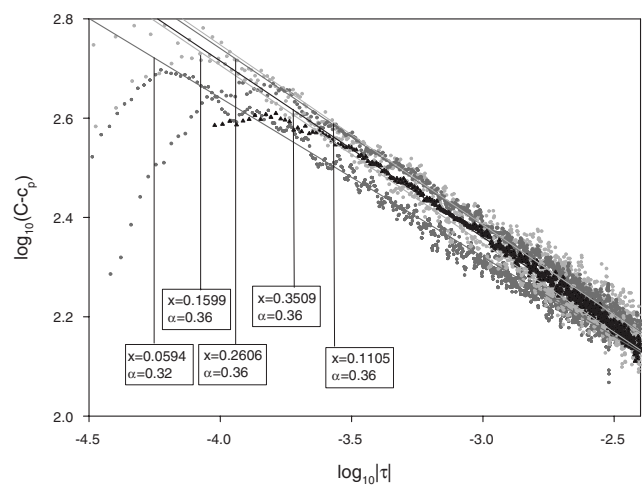


FIG. 11. Plots of $\log_{10}(C-C_p)$ versus $\log_{10}|\tau|$ below $T_{N\text{-SmA}}$ for five mixtures of 8CB and water exhibiting a continuous phase transition. The solid lines for $x_W = 0.02603$ and $x_W = 0.0594$ are linear fits for $-4.0 < \log_{10}|\tau| < -2.4$, and for the other mixtures linear fits are for $-3.7 < \log_{10}|\tau| < -2.4$, resulting in the indicated effective critical exponent α values. The uncertainty on α is ± 0.03 .

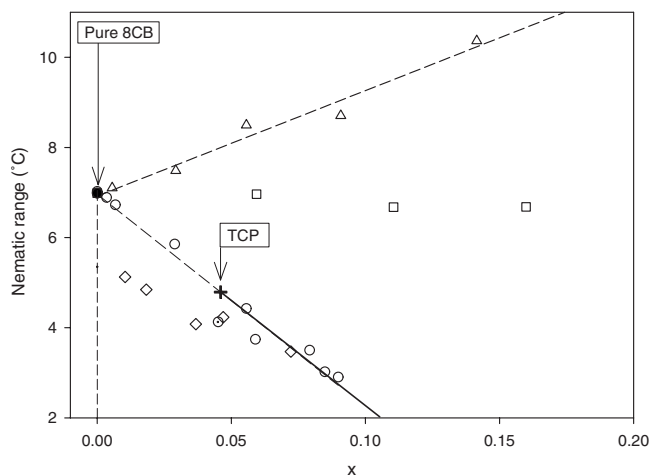


FIG. 12. The width of the nematic range as a function of the mole fraction of the nonmesogenic solutes. The solid dot is for pure 8CB. The triangles are the mixtures of 8CB and biphenyl. The dashed line is a linear fit through these data. The squares are the results for 8CB and water. The mixtures of 8CB and cyclohexane are represented by the diamonds (batch 1 of 8CB) and the circles (batch 2 of 8CB). The dashed-solid line is a linear fit through the data of the mixtures of cyclohexane with 8CB of batch 2. The tricritical point is indicated by the cross.

giving a decreasing coupling between the nematic and the smectic-A order parameters, consistent with an increase in the nematic range. For the 8CB+W system the initial small reduction in nematic range and the slight increase in effective critical exponent α for mole fractions up to $x_W \approx 0.10$ needs also a (small) negative value for D in Eq. (11). For larger x_W values there is no further addition of water to the 8CB rich phase and in Eq. (11) Dx keeps the value it attained at $x_W \approx 0.10$, consistent with the constant width of the nematic range. Although, we based the above arguments on Eqs. (7) and (11), on the basis of Eq. (18) and the extension of Eq. (7) with a term ES^2x (coupling between nematic order parameter and mole fraction) one reaches the same conclusions *albeit* with somewhat different coefficient values.

V. SUMMARY AND CONCLUSIONS

In this paper we reported on the effects of nonmesogenic solutes on the nematic to isotropic ($N-I$) and nematic to smectic-A ($N-SmA$) phase transitions of the liquid crystal octylcyanobiphenyl (8CB). Three different nonmesogenic impurities, being biphenyl (BP), cyclohexane (CH), and water (W), were added to 8CB.

The effects on the $N-I$ transition were rather straightforward. For BP and CH a linear decrease of the $N-I$ transition temperature T_{N-I} with the mole fraction of the solute was observed. For water as solute, T_{N-I} , at first slightly decreased for mole fractions of water up to $x_W \approx 0.10$ and stayed constant for higher values of x_W . From visual inspection of samples we found that at the higher mole fractions phase separation in a water rich and 8CB rich phase took place. In order to explain the linear decrease of T_{N-I} one needs to extend the mean-field free energy density expression [Eq.

(1)] for the nematic order parameter S with a coupling term between the solute mole fraction x and the nematic order parameter S of the form ES^2x , with E a positive constant. It was also found that the $N-I$ transitions remained first-order ones with latent heats that did not change with mole fraction x in the investigated range. This is to first-order consistent with a mean-field approximation and with E independent of temperature.

As far as the nematic to smectic-A transition temperatures T_{N-SmA} are concerned the observations are similar to those for T_{N-I} . This means a linear decrease for 8CB+BP and 8CB+CH and after a slight initial decrease (up to $x_W \approx 0.1$) a constant value for higher concentrations. To explain this decrease of T_{N-SmA} in the free energy expansion [Eq. (3)] for the smectic-A order parameter ψ also a coupling term of the form $A\psi^2x$ (A a positive constant) with the mole fraction x must be added. For the order of the transition as well as for the critical behavior of the specific heat capacity different results were obtained for the three systems. The $N-SmA$ transition for pure 8CB is continuous [11] and for all concentrations of biphenyl studied this transition remained continuous. The effective specific heat capacity critical exponent α decreased from 0.31 ± 0.03 for pure 8CB to 0.08 ± 0.03 for the highest mole fraction ($x_{BP} = 0.1415$) of biphenyl studied. For mixtures of 8CB and cyclohexane, however, with increasing x_{CH} crossover from continuous to first-order transitions is observed at a tricritical point of the mole fraction of cyclohexane around $x_{CH} = 0.046$. For the continuous part of the phase transition line the value of the effective critical exponent α increased from 0.31 ± 0.03 for pure 8CB to 0.5 at the tricritical point. Along the first-order part of the transition line a nonlinear increase of the latent heat with increasing mole fraction was observed. For the 8CB and water system in all the mixtures, second-order $N-SmA$ transitions with quite sharp heat capacity peaks could be observed, allowing determination of effective critical exponent α values. For mixtures with $x_W > 0.10$ a constant $\alpha = 0.36 \pm 0.03$ was derived, for $x_W < 0.10$ mixture, intermediate values between this α value and the pure 8CB ($\alpha = 0.31$) one were obtained.

The difference in the behavior of the three systems near the $N-SmA$ transition can be understood by looking at the changes in the width of the nematic ranges with mole fraction of the solute (see Fig. 12). For 8CB+BP the width of the nematic range increases with increasing mole fraction of BP, for 8CB+CH it decreases with x_{CH} , and for 8CB+W (after an initial small decrease up to $x_W \approx 0.10$) it stays constant over the investigated mole fraction range. Thus, one can conclude that depending on the type of impurity the coupling between the nematic and smectic-A order parameters can either be reduced (wider nematic range) or increased (smaller nematic range) or kept constant (no changes in the nematic range). We have shown that in terms of the mean-field free energy density expansion of Landau-de Gennes in Eq. (3) the difference in behavior of the three systems could be accounted for by adding an additional coupling term between the nematic and the smectic-A order parameters [see Eq. (7)] depending on the mole fraction of the solute with a coupling constant D depending on the system.

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