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Nematic–isotropic phase transition in lyotropic liquid crystals

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We propose a Landau–de Gennes phenomenological model to describe the nematic–isotropic phase transition in lyotropic liquid crystals. The possibility of a first or second order transition is explored by means of the variation of the concentration of surfactant. We show that a Landau point on the nematic–isotropic phase transition line can be achieved under certain conditions. The theoretical predictions are found to be in good qualitative agreement with available experimental results.

1. Introduction

Although the nematic–isotropic (NI) phase transition in thermotropic liquid crystals (TLCs) has been a topic for the last few decades [1], it is surprising that until now there has been very little progress on the theory of NI transition in lyotopic liquid crystals (LLCs). Since its discovery in 1967 [2], the nematic micellar phase has been found in many binary systems. A large number of experimental studies are devoted to the nature of the NI transition in LLCs [3–18]. The nematic phases of all LLCs are formed by the interaction of non-spherical micelles. The micelles can be either rod-like or disk-like exhibiting long-range orientational ordering of their symmetry axis. The corresponding lyotropic nematic phases are designated as N_R and N_D. The disk-like nematic phase is also designated as N_D^+ and N_D^- according to whether the diamagnetic susceptibility is greater along or transverse to the nematic symmetry axis. In experimental studies [3, 19, 20], the binary mixture of a caesium perfluorooctanoate (CsPFO) and water produces an N_D^+ phase, and the binary mixture of decylammonium chloride (DACl) micelles and water–ammonium chloride (NH_4Cl) solution produces an N_D^- phase.

The transition between N_D^+ to isotropic (N_D^+–I) has been studied extensively by several authors [3, 6–18]. The conclusion of all these studies indicates that the N_D^+–I transition in LLCs is very similar to the nematic–isotropic (N–I) transition in TLCs, and the N_D^+–I transition is very close to a second order transition. Rosenblatt *et al.* [6, 8] measured the concentration and temperature dependences of the Cotton–Mouton coefficient and the magnetic birefringence in the isotropic phase above the N_D^+–I transition for the binary mixture of CsPFO and water. They showed that the transition temperature decreases strongly with the decrease of concentration and measured a low value for $T_{NI} - T^* < 20$ mK, where T_{NI} is the N_D^+–I transition temperature and T^* is the supercooling limit. This low value of $T_{NI} - T^*$ indicates that N_D^+–I is close to being second order. Finally they concluded that a Landau point may be achieved at the N_D^+–I transition line with the possibility of a crossover from uniaxial to biaxial behaviour. Shin *et al.* [12, 14] measured the specific heat at the N_D^+–I transition for the same binary mixture. They observed a vanishing latent heat and coexistence range at low concentration on the first order N_D^+–I transition line, indicating the existence of a Landau point. According to X-ray and neutron scattering studies by Johannesson *et al.* [17] the orientational order parameter in the nematic phase increases with concentration at a fixed temperature but it decreases rapidly while approaching the transition temperature T_{NI} at a very low concentration, with a jump of the order parameter <0.2 at T_{NI}. In a recent study Jolley *et al.* [18] observed a very weakly first order N_D^+–I transition of the binary cesium pentadecafluorooctanoate (CsPdFO)–water system over the entire range of experimentally accessible concentrations $\sim$0.07–0.40, which of course rules out the possibility of a Landau point. The lowest value of $T_{NI} - T^*_{NI}$ is obtained as 0.01 K at a concentration 0.15.

The main result of all of the above experimental results is that the low value of $T_{NI} - T^*_{NI} = 0.01$ K at the N_D^+–I transition which is a much lower value than $T_{NI} - T^*_{NI} \approx 1$ K for TLCs. The low value of $T_{NI} - T^*_{NI} \approx 1$ K in TLCs is a long-standing puzzle [21]. In order to gain insight into this problem several workers showed how the inclusion of fluctuations can give considerable improvement. However, the reason for the low value of $T_{NI} - T^*_{NI}$ in LLCs is not very clear. This low value shows that the transition is very close to being second order. But the most interesting feature is that this low value decreases with the decrease of the concentration

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of surfactant. On the other hand, the value of the critical exponent of the order parameter in the nematic phase gives [13] $\beta = 0.34$ which is different from the mean-field exponent $\beta = 0.50$. All of these facts comprise an interesting feature of the N_D^+–I transition in LLCs.

On the theoretical side there have been a few attempts to study this transition. Kuzma *et al.* [22] studied the $T_{NI} - T^*_{NI}$ problem in terms of the competition between attractive and repulsive forces in the nematic phase. Shin *et al.* [14] tried to fit their experimental data by the Landau–de Gennes model [1, 23]. They calculated the Landau coefficients and showed that they decreased with concentration as expected. Taylor *et al.* [24, 25] discussed the problem of lyotropic liquid crystalline ordering in systems of self-assembled molecular aggregates. In a recent paper Moldovan and Puica [26] reproduced some experimental results with the inclusion of a concentration dependent term in the Landau–de Gennes model.

In none of the theoretical studies undertaken so far were the key features of the N_D–I transition characterized. The purpose of the present paper is to develop a Landau model to investigate the key features of the N_D–I transition and to determine the influence of the surfactant concentration on this transition. We describe different possibilities for this transition as suggested by the experiments. The observed theoretical results are found to be in good agreement with experimental results.

2. Model

2.1. *The free energy*

The starting point of our approach is to write down the Landau–de Gennes free energy near the N_D–I transition for a micellar solution. In the literature there are some attempts [27, 28] to study the micellation as a phase transition and the phase transition in LLC [29] in the context of Landau theory. We follow the same ideas [27–29] while developing the model. The thermotropic nematic phase and the lyotropic nematic phase have the same symmetry. Hence the lyotropic nematic order parameter originally proposed by de Gennes [23] is a symmetric, traceless tensor described by $Q_{ij} = S/2(3n_i n_j - \delta_{ij})$. The quantity S defines the strength of the nematic ordering. We define another parameter $\phi = (x - x_c)$, where x_c is the critical micellar concentration and x is the concentration of surfactant molecules (say, CsPFO). $x = n_{sr}/(n_{sr} + n_s)$, where the n terms are the number densities of surfactant and solvent, respectively. Therefore ϕ is the concentration of surfactant molecules aggregated in micelles. In the lyotropic nematic phase $\phi > 0$, in the isotropic micellar phase $\phi < 0$ and in the isotropic liquid phase $\phi = 0$. Thus one can define ϕ as an order parameter.

Then the free energy expansion near the N_D–I transition can be written as:

$$F_1(Q_{ij}, \phi, T) = F_0 + \frac{1}{2}aQ_{ij}Q_{ij} - \frac{1}{3}bQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}c(Q_{ij}Q_{ij})^2 + \frac{1}{2}p\phi^2 - \frac{1}{3}r\phi^3 + \frac{1}{4}q\phi^4 + \frac{1}{2}\delta Q_{ij}Q_{ij}\phi + \frac{1}{3}\eta Q_{ij}Q_{jk}Q_{ki}\phi + \frac{1}{2}\gamma Q_{ij}Q_{ij}\phi^2 \quad (1)$$

where F_0 is the free energy of the isotropic phase, $a = a_0(T - T^*_{NI})$ and $p = p_0(T - T^*_\phi)$. T^*_{NI} and T^*_ϕ are the hypothetical second order transition temperatures. a_0 and p_0 are constant but the coefficients b, c, q, δ, η and γ are concentration dependent and independent of temperature; δ, η and γ are coupling constants. As we shall see, a negative value of δ favours the nematic phase over the isotropic micellar or isotropic liquid phase. A positive or negative value of η changes the sign of the cubic coefficient b for which the nematic phase becomes N_D^+ or N_D^-. We choose $\gamma > 0$. Thus the nematic phase would be stable for $a < 0$ and $p < 0$.

The substitution of Q_{ij} in equation (1) leads to the free energy expansion

$$F = F_0 + \frac{3}{4}aS^2 - \frac{1}{4}bS^3 + \frac{9}{16}cS^4 + \frac{1}{2}p\phi^2 - \frac{1}{3}r\phi^3 + \frac{1}{4}q\phi^4 + \frac{3}{4}\delta S^2\phi + \frac{1}{4}\eta S^3\phi + \frac{3}{4}\gamma S^2\phi^2. \quad (2)$$

Minimization of equation (2) with respect to S and ϕ yields the following three phases:

Isotropic liquid phase: $S = 0$, $\phi = 0$ (3)

Isotropic micellar phase: $S = 0$,

$$\phi_I = \frac{r}{2q}\left[1 + (1 - 4pq/r^2)^{1/2}\right] \quad (4)$$

Nematic phase: $\phi_N > 0$,

$$S = \frac{(b - \eta\phi_N)}{6c}\left\{1 + \left[1 - \frac{24(a + \delta\phi_N + \gamma\phi_N^2)c}{(b - \eta\phi_N)^2}\right]^{1/2}\right\} \quad (5)$$

where ϕ_N is defined by: $p\phi_N - r\phi_N^2 + q\phi_N^3 + 3/4\,\delta S^2 + 1/4\,\eta S^3 + 3/2\,\gamma S^2\phi_N = 0$.

Thus it is clear from the solutions (3), (4) and (5) that three types of transition are possible: (i) isotropic liquid to isotropic micellar; (ii) isotropic micellar to discotic nematic; (iii) isotropic liquid to discotic nematic.

Equation (5) gives the variation of the orientational order parameter with temperature and concentration in the N_D phase.

The sufficient conditions for the N_D phase to be stable are

$$\frac{\partial^2 F}{\partial\phi^2}\,\frac{\partial^2 F}{\partial S^2}-\left(\frac{\partial^2 F}{\partial\phi\partial S}\right)^2$$
$$=\frac{3S}{16}\{[4rb\phi_N-4(r\eta+2qb)\phi_N^2+8\eta q\phi_N^3]$$
$$+S[-24(rc+2\gamma\delta)\phi_N+48\Delta\phi_N^2-12\delta^2]$$
$$+S^2(3\delta b/\phi_N-24\gamma\eta\phi_N-15\delta\eta)$$
$$+S^3(-18\delta c/\phi_N+b\eta/\phi_N-4\eta^2)\}>0 \qquad (6)$$

$$\frac{\partial^2 F}{\partial S^2}=\frac{3}{4}(-bS+6cS^2+\eta\phi_N S)>0 \qquad (7)$$

$$\frac{\partial^2 F}{\partial\phi^2}=p-2r\phi_N+3q\phi_N^2+\frac{3}{2}\gamma S^2>0 \qquad (8)$$

where $\Delta=qc-\gamma^2$. These three conditions determine the stability of the N_D phase explicitly. The condition (7) shows that $S>(b-\eta\phi_N)/6c$. The sufficient condition for the stability of the isotropic micellar phase reads (taking $S=0$)

$$\frac{\partial^2 F}{\partial\phi^2}=p-2r\phi_I+3q\phi_I^2>0. \qquad (9)$$

For the isotropic liquid phase the stability conditions are $a>0$ and $p>0$.

To find the variation of the orientational order parameter with concentration as well as with temperature in the nematic phase, we have plotted S, equation (5), versus T for two fixed concentrations in figure 1. This is done for a set of parameters for which the N_D to isotropic micellar phase transition is possible. Figure 1 shows that for a lower value of concentration ($\phi=0.15$), the orientational order parameter S near the transition point falls rapidly with temperature. For a fixed set of parameter values, we find that the value of the jump of the order parameter at T_{NI} is $S_{NI}=0.023$ and the value of $T_{NI}-T^*_{NI}=0.016$ K. But the value of the orientational order parameter S and the N_D phase increases with increasing concentration. In figure 1 the jump of the order parameter increases for the higher concentration. The above phase behaviour of the N_D–I transition is in agreement with all of the experimental results described in § 1.

2.2. *Possibility of a Landau point*

As discussed in § 1 some experiments suggested the possibility of a Landau point on the N_D–I transition line for a lower value of the concentration of surfactant. Hence in the neighbourhood of the Landau point of the N_D–I transition, ϕ would be small. We will now turn

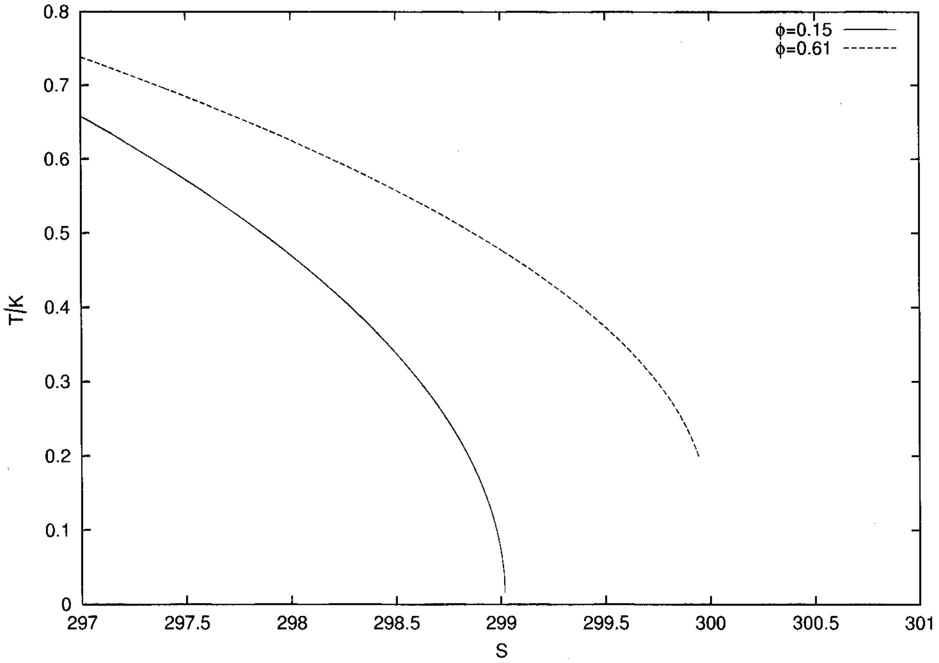

Figure 1. Temperature (T) variation of the orientational order parameter (S) in the nematic phase obtained from equation (5) for fixed concentrations $\phi=0.61$ and $\phi=0.15$. The values of the parameters are taken to be $a_0=0.1$, $b=0.4$, $c=0.53$, $\delta=-0.6$, $\gamma=0.01$ (for $\phi=0.61$) and $a_0=0.1$, $b=0.02$, $c=0.32$, $\delta=-0.12$, $\gamma=0.01$ (for $\phi=0.15$).

our attention to this problem. Since in the neighbourhood of the N_D–I transition ϕ is small, the higher order terms in ϕ can be neglected. In this case free energy (2) near the N_D–I transition (neglecting the higher order terms in ϕ) can be rewritten as

$$F(S,\phi,T) = F_0 + \frac{3}{4}aS^2 - \frac{1}{4}bS^3 + \frac{9}{16}cS^4 + \frac{1}{2}p\phi^2 + \frac{3}{4}\delta S^2\phi + \frac{1}{4}\eta S^3\phi + \frac{3}{4}\gamma S^2\phi^2. \tag{10}$$

From the condition

$$\frac{\partial F}{\partial \phi} = p\phi + \frac{3}{4}\delta S^2 + \frac{1}{4}\eta S^3 + \frac{3}{2}\gamma S^2\phi = \mu \tag{11}$$

where μ is the quantity thermodynamically conjugate to ϕ, we get

$$\phi = \frac{\mu\left(1 - \frac{3}{2p}\gamma S^2\right) - \frac{3}{4}\delta S^2 - \frac{1}{4}\eta S^3 + \frac{9}{8p}\gamma\delta S^4}{p}. \tag{12}$$

On transforming $F(\phi, S, T)$ to the free energy depending on the field variable μ

$$\begin{aligned} F_1(S,\mu,T) &= F(S,\phi,T) - \mu\phi \\ &= F_0 + \frac{3}{4}a_1 S^2 - \frac{1}{4}b_1 S^3 + \frac{9}{16}c_1 S^4 \\ &\quad + \text{higher order terms} \end{aligned} \tag{13}$$

with the renormalized coefficients:

$$a_1 = a + \frac{\mu\delta}{p} + \frac{\mu^2\gamma}{p^2} \tag{14a}$$

$$b_1 = b - \frac{\mu\eta}{p} \tag{14b}$$

$$c_1 = c - \frac{\delta^2}{2p} - \frac{2\mu\gamma\delta}{p^2} - \frac{2\mu^2\gamma^2}{p^3}. \tag{14c}$$

We notice from equations (14 *a*)–(14 *c*) that taking into account the coupling between S and ϕ leads to the renormalization of the coefficients a, b and c. Hence the coefficients b and c change with the change of concentration x. Then the order of the N_D–I transition also changes. When $b > \mu\eta/p$ and $c > (\delta^2/2p + 2\mu\gamma\delta/p^2 + 2\mu^2\gamma^2/p^3)$, a first order N_D^+–I transition is possible which occurs in the binary CsPFO–water system [3]. When $b < \mu\eta/p$ and $c > (\delta^2/2p + 2\mu\gamma\delta/p^2 + 2\mu^2\gamma^2/p^3)$, again a first order N_D^-–I transition is possible which occurs in the binary mixtures of the DACl/NH_4Cl–water system [4, 5]. Again for $b > \mu\eta/p$ (or $< \mu\eta/p$) and $c < (\delta^2/2p + 2\mu\gamma\delta/p^2 + 2\mu^2\gamma^2/p^3)$, a first order N_D^+–I (N_D^-–I) transition is still possible with the addition of a sixth order term in the free energy expansion, equation (10). Thus the model free energy, equation (10), shows the competition of the first order transitions between a N_D^+–I and a N_D^-–I transition depending on the sign of the cubic coefficient b, which changes sign due to the changes of x. The cubic coefficient b decreases with decreasing concentration of surfactant. Thus the coupling constant η plays an important role for the determination of the order of the transition. Now when $b = \mu\eta/p$ and $c > (\delta^2/2p + 2\mu\gamma\delta/p^2 + 2\mu^2\gamma^2/p^3)$, then a second order N_D–I transition occurs and a Landau point is obtained with a possibility that the system is crossing over from uniaxial to biaxial behaviour. To achieve this condition, a fifth and a sixth order terms are to be added to the free energy expansion (10)—these which already appear in F_1, equation (13). The experimental observations by Melnik *et al.* [30] showed that such a crossover from uniaxial to biaxial is possible for the ternary system potassium laurate(KL)–1-decanol–D_2O and indicate the existence of a Landau point on the NI transition line. If CsPFO is analogous to KL the existence of a Landau point on the N_D–I transition is possible, as suggested by experiment [4–6, 8–10, 12, 14].

Thus for the second order N_D–I transition $a_1 = 0$ and $S = 0$. Then we have from equation (14 *a*) (lowest order in ϕ)

$$T_c(\phi) = T^*_{NI} - \frac{\delta\phi}{a_0} \tag{15}$$

where

$$\delta = -a_0 \frac{dT_c}{d\phi}. \tag{16}$$

Thus the coupling between the two order parameters S and ϕ also shifts the transition temperature. Equation (15) shows that the critical temperature increases with increase of the concentration of surfactant. Thus the conditions $a_1 = 0$ and $b_1 = 0$ correspond to the Landau point. For fixed ϕ the coordinates of the Landau point are ($a = -\delta\phi - \gamma\phi^2$, $b = \eta\phi$). The above analysis shows that if a Landau point is not achieved at all then the N_D–I transition should be very weakly first order due to smallness of the cubic coefficient b. Thus for $T \geqslant T_C(\phi) = T^*_{NI} - \delta\phi/a_0$, one has an isotropic micellar phase (I) and for $T < T_C(\phi)$ one obtains a N_D phase. When $b = \mu\eta/p$ and $c = (\delta^2/2p + 2\mu\gamma\delta/p^2 + 2\mu^2\gamma^2/p^3)$ then a tricritical point is obtained. But the experimental results do not show such a point.

2.3. *First order N_D^+–I transition*

Most of the experimental results so far available are for the weakly first order N_D^+–I transition. In this section we will therefore turn to the first order N_D^+–I transition.

Rosenblatt [8] pointed out that the supercooling temperature of the isotropic phase strongly depends on the concentration of surfactant and decreases with concentration. We start by using a standard Landau–de Gennes free energy expansion [23] while taking into account the concentration dependence of the supercooling temperature. Keeping spatially homogeneous terms up to the fourth order, the free energy near the N_D^+–I transition can be written as:

$$F(T, P, S, x) = F_0(T, P, x) + \frac{3}{4}aS^2 - \frac{1}{4}bS^3 + \frac{9}{16}cS^4 \tag{17}$$

where $a = a_0(T - T^*_{NI}(x))$, with a_0 a constant. The material parameters are assumed to be functions of concentration (as we noticed in the previous section). We assume $b = b(x)$ and $c = c(x)$. Here x is the concentration of surfactant.

From the experimental phase diagrams [3, 11, 18] one observes that the T vs x curve of the N_D^+–I transition is a straight line. We therefore assume a linear form for T^*_{NI},

$$T^*_{NI} = T^*_0 + m(x - x_c). \tag{18}$$

Here m is a positive constant and x_c is the critical micellar concentration. T^*_0 is the temperature (mean field) of the absolute stability of the isotropic phase in the absence of any concentration–order parameter coupling. Thus the N_D phase is stable for $T < T^*_0$ and $x > x_c$.

The jump of the order parameter S_{NI} and the transition temperature T_{NI} is given by

$$S_{NI} = \frac{2b}{9c} \tag{19}$$

$$T_{NI}(x) = T^*_0 + \frac{b^2}{27a_0c} + m(x - x_c). \tag{20}$$

The order parameter $S(x, T)$ in the N_D^+ phase is given by

$$(S - S^+_{NI})^2 = (S^+_{NI})^2 - \frac{2a_0}{3c}(T - T^*_0) + \frac{2a_0}{3c}m(x - x_c) \tag{21}$$

where $S^+_{NI} = b/6c$ is the order parameter value in the superheated nematic phase and the corresponding temperature T^+_{NI} is given by

$$T^+_{NI}(x) = T^*_0 + \frac{b^2}{24a_0c} + m(x - x_c). \tag{22}$$

From equation (21), when S is fixed, T vs x should be a straight line. Equation (21) may be written as

$$T - T_S(S) = m(x - x_c) \tag{23}$$

where

$$T_S(S) = T^*_0 - \frac{3c}{2a_0}S(S - 2S^+_{NI}). \tag{24}$$

The jump of the enthalpy density at the transition point is

$$\Delta H_{NI} = \frac{b^2}{27a_0c^2}T_{NI}. \tag{25}$$

2.4. *Comparison with experiment*

In this section we will compare some of our theoretical results with experimental results. For the T_{NI} vs x phase diagrams of CsPFO–H_2O and CsPFO–D_2O, there exist several experiments by Boden *et al.* [3], Jolley *et al.* [11], Shin *et al.* [12, 14] and Jolley *et al.* [18]. All the above experimental phase diagrams for $T(T_{NI})$ vs x give a straight line (figure 1). From equation (23), when S is fixed, T vs x should be a straight line, which agrees well with the experiments [3, 11, 12, 14, 18]. The experimental data for the heat capacity measurements [12, 14] near the N_D^+–I transition show that the measured values of T_{NI} and T^+_{NI} are the same, which indicates the existence of a Landau point on the N_D^+–I transition line. Hence in principle, equations (20), (22) and (23) are the same. We therefore fitted equation (20) with the experimental data of Shin *et al.* [12, 14]. The fit (line) and measured data (points) are shown in figure 2. The fit to the measured values is found to be good. The values obtained for fit parameters are $T^*_0 + b^2/27a_0c = 298.55$ K and $m = 12.26$ K mol^{-1}.

We already noted in the previous section that the Landau coefficients decrease with a decrease of concentration. This can easily be verified by calculating the coefficients b, c and m using the relations (19), (20) and (25), with the corresponding experimental data for each concentration. But we have not repeated the calculations since such calculations are already available in the literature [14, 26]. In order to check equation (21), we see that for fixed T, the order parameter increases with increasing concentration and S vs x looks like a parabola which agrees with the experimental curve shown in figure 15 of Johannesson *et al.* [17]. Again for fixed concentration x, equation (21) shows that the order parameter decreases with increase of temperature and the curve S vs T looks like a parabola, which also supports the experimental curve, figure 11, of Johannesson *et al.* [17]. The data ΔH vs x in [12, 14] also satisfy our theoretical equation (25). Using equations (20) and (22) we get $T^+_{NI} - T_{NI} = b^2/216a_0c$, which decreases with concentration as the coefficients b and c decrease, which agrees with the experimental results of Boden *et al.* [13].

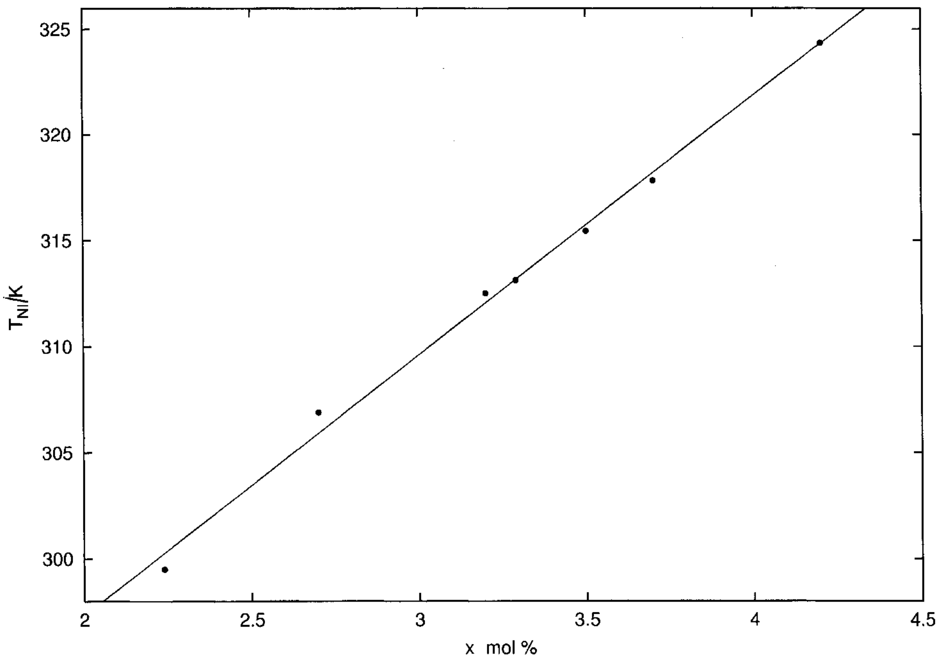

Figure 2. The concentration (x) dependence of the N_D^+–I transition temperature of CsPFO–water system. The measured data are from [12], and the line is best fit of equation (20).

3. Conclusions

We have presented a Landau theory analysis of the N_D–I transition in lyotropic liquid crystals. We have shown how a single model can explain various possibilities of the N_D–I transition depending on the coupling between the order parameter and the concentration of surfactant. Thus the coupling between the order parameter and concentration is found to play a crucial role in determining the phase behaviour and the order of the transition. The proposed interpretation of the N_D–I transition allows us to explain all of the various types of phase behaviour observed experimentally. The present analysis clearly indicates the possibility of the existence of a Landau point on the N_D^+–I transition line for a lower value of the concentration of surfactant. Since the Landau coefficients b and c decrease with concentration, when b becomes small then higher order terms like $\sim Tr(Q^5)$ and $\sim Tr[(Q^3)]^2$ are needed for a better description of the N_D–I transition. The most puzzling aspect of the N_D^+–I transition is the very low value of $T_{NI} - T^*_{NI}$ for lower concentrations, which indicates the almost second order character of the N_D^+–I transition. But the weakness of this transition is characterized by the expression $\Delta = (T_{NI} - T^*_{NI})/T^*_{NI} \propto b^2$. Since b decreases with concentration, Δ takes a lower value. We also point out that density fluctuations which change with concentration may influence the character of the N_D^+–I transtion. We observe a very low value of $T_{NI} - T^*_{NI} = 0.016$ K for the low concentration 0.15. However, a proper identification of the order parameter of the micellar phase and a coupling with the orientational order parameter may give new insight into this transition. In addition, the suitable choice of the functional forms of $b(x)$ and $c(x)$ will provide better ideas for the construction of the free energy.

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