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Electrolyte effects on the nematic–isotropic phase transition in lyotropic liquid crystals

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A phenomenological approach to the description of the electrolyte effect on the nematic–isotropic phase transition in lyotropic liquid crystals is proposed. The influence of the electrolyte is discussed by varying the coupling between the concentration variables and the orientational order parameter. The analysis shows that the discontinuity in the first order nematic–isotropic phase transition as measured by $T_{\mathrm{NI}}-T_{\mathrm{NI}}^{0}$ increases as a function of the weight fraction of the electrolyte. Here T_{NI} is the first order nematic–isotropic phase transition temperature and T_{NI}^{0} is the extrapolated supercooling limit. The electrolyte dependence of the Cotton–Mouton coefficient and the non-linear dielectric effect in the isotropic phase above the nematic–isotropic phase transition are calculated. The theoretical predictions are found to be in good agreement with experimental results.

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1. Introduction

Lyotropic mesophases are formed by supramolecular aggregates of surfactant molecules in a suitable solvent. Nematic lyomesophases are formed by the long range orientational ordering of the symmetry axes of non-spherical micelles, either rod-like or disk-like. The lyotropic nematic phases of disc-like micelles are designated as $\mathrm{N}_{\mathrm{D}}^{+}$ or $\mathrm{N}_{\mathrm{D}}^{-}$ according to whether the diamagnetic susceptibility is greater along or transverse to the nematic director. In experimental studies [1–3], binary mixtures of cesium perfluorooctanoate (CsPFO) and water were found to produce an $\mathrm{N}_{\mathrm{D}}^{+}$ phase, whereas ternary mixtures of decylammonium chloride (DACl), water, and ammonium chloride (NH_4Cl) form the $\mathrm{N}_{\mathrm{D}}^{-}$ phase.

There is a one-to-one correspondence in the symmetries of the phases involved in lyotropic and thermotropic nematic to isotropic transitions. The lyotropic nematic to isotropic (N_{D}–I) transition has been studied extensively by several authors [1–18]. Rosenblatt *et al.* [6, 8] measured the Cotton–Mouton coefficient on the isotropic side of the N_{D}–I transition in aqueous CsPFO solutions. They showed that the equilibrium N_{D}–I transition temperature T_{NI} decreases strongly with the decrease of surfactant concentration, and concluded a value of $T_{\mathrm{NI}}-T_{\mathrm{NI}}^{*}<20\,\mathrm{mK}$, where T_{NI}^{*} is the supercooling limit. This remarkably low value of $T_{\mathrm{NI}}-T_{\mathrm{NI}}^{*}$ indicates that the N_{D}–I transition is very close to being second order and suggests the possibility of a Landau point at the N_{D}–I transition line with a cross-over from uniaxial to biaxial symmetry. However, very recently Jolley *et al.* [17, 18] observed in the binary system cesium pentadecaflurooctanoate (CsPdFO)/water a very weak first order N_{D}–I transition over the entire range of experimentally accessible concentrations, which, at least for this system, rules out the possibility of a Landau point.

Rosenblatt *et al.* [19] also studied the N_{D}–I transition of aqueous CsPFO solutions in the presence of an added salt, CsCl. The pretransitional behaviour, reflected by the magnetically induced birefringence close above the I–N_{D} transition, was found to be strongly influenced by the presence of the CsCl electrolyte, and the discontinuity in the first order transition as measured by $T_{\mathrm{NI}}-T_{\mathrm{NI}}^{*}$ increased as a non-linear function of the electrolyte concentration. In the light of these most interesting results, this paper aims to provide a phenomenological Landau-type description of the N_{D}–I transition in the presence of an electrolyte added to the lyotropic solution.

On the theoretical side there have been relatively few attempts to study the N_{D}–I transition in lyotropic liquid crystals [20–24]. In a recent paper Mukherjee [24] treated this problem within the Landau phenomenological approach and discussed in detail the possibility of a Landau point in the N_{D}–I transition. The present paper now focuses on the electrolyte effect on the N_{D}–I transition in lyotropic liquid crystals. It is shown that

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the coupling between the surfactant concentration variable, the orientational order parameter and the concentration of the electrolyte shifts the N_D–I transition temperature. We further analyse the effect of the electrolyte on the Cotton–Mouton coefficient and on the non-linear dielectric effect (NDE) in the pretransitional regime of the I–N_D transition. The theoretical results are found to agree with the experimental results obtained for the $N_D^+ - I$ transition by Rosenblatt *et al.* [19] and with our own results on the $N_D^- - I$ transition in aqueous solutions of dodecylammonium chloride (DDACl) in the presence of additional ammonium chloride (NH_4Cl).

2. Model

2.1. *The order parameters*

We start by describing the order parameters involved in the N_D–I transition for a micellar solution. Since thermotropic and lyotropic nematic phases have the same symmetry, they are described by the same orientational order parameter that was originally proposed by de Gennes [25] as a symmetric, traceless tensor given by $Q_{ij}=\frac{S}{2}\left(3n_in_j-\delta_{ij}\right)$ where the scalar quantity S defines the strength of the nematic orientational ordering. Following Mukherjee [24] and Anisimov *et al.* [26] we define another dimensionless parameter, $\phi=(x-x_1)$, where x_1 is the molar fraction of the free surfactant molecules and x is the total molar fraction of surfactant. Here $x=N_{sr}/(N_{sr}+N_s)$, where N_{sr} and N_s denote the numbers of surfactant and solvent molecules, respectively. According to this definition, ϕ measures the concentration of those surfactant molecules which are aggregated in micelles. In the lyotropic nematic phase $\phi>0$, in the isotropic micellar phase $\phi>0$ and in the isotropic liquid (molecular) phase $\phi=0$. A very schematic phase diagram of the different phases and the corresponding values of the order parameters is depicted in figure 1. Our choice of the order parameter ϕ is not unique, and different definitions of the order parameter will lead to different coefficients in the free energy expansion; but the thermodynamic quantities calculated thereof will not be affected by the definition of the order parameter ϕ. Thus Q_{ij} and ϕ are taken as the two order parameters involved in the N_D–I transition.

2.2. *The free energy*

We start by using a standard Landau expansion for the free energy in powers of the order parameters Q_{ij} and ϕ. Keeping homogeneous terms up to the fourth order, the free expansion near the N_D–I transition can be written as [24]:

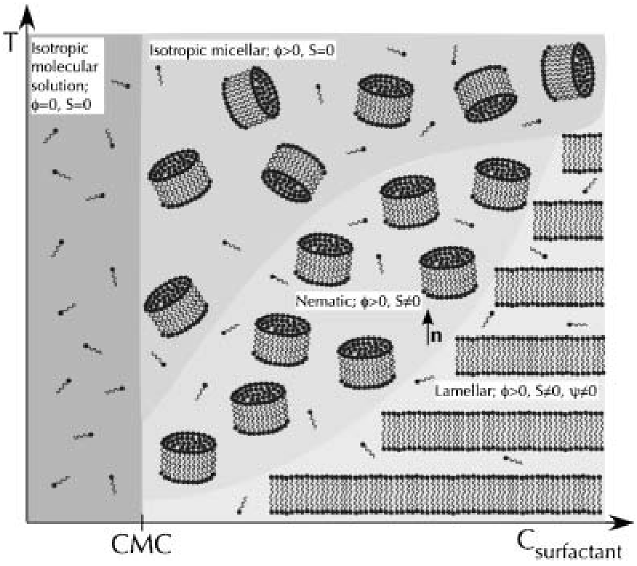

Figure 1. Schematic phase diagram of the different phases considered: for explanations see the text. ψ is the translational order parameter needed for describing lamellar phases; it is not considered in the present analysis.

$$\begin{aligned}F\left(Q_{ij},\phi,T\right)=F_0&+\frac{1}{2}aQ_{ij}Q_{ij}-\frac{1}{3}bQ_{ij}Q_{jk}Q_{ki}+\frac{1}{4}c\left(Q_{ij}Q_{ij}\right)^2\\&+\frac{1}{2}p\phi^2-\frac{1}{3}q\phi^3+\frac{1}{4}r\phi^4+\frac{1}{2}\delta Q_{ij}Q_{ij}\phi\qquad(1)\\&+\frac{1}{3}\eta Q_{ij}Q_{jk}Q_{ki}\phi+\frac{1}{2}\gamma Q_{ij}Q_{ij}\phi^2\end{aligned}$$

where F_0 is the free energy of the molecularly dispersed isotropic liquid phase, $a=a_0\left(T-T^*_{NI}\right)$ and $p=p_0\left(T-T^*_1\right)$ with a_0 and p_0 being positive constants. T^*_{NI} and T^*_1 are the hypothetical second order transition temperatures, the latter referring to the direct isotropic liquid to isotropic micellar transition. The parameters δ, η and γ are coupling constants and the coefficients b, c, q and r are assumed to be concentration dependent. The sign of η determines the sign of the cubic coefficient b and, thereby, decides whether the nematic phase is N_D^+ or N_D^-. The free energy equation (1) describes the three types of transition [24]: (i) isotropic molecular liquid to isotropic micellar; (ii) isotropic micellar to discotic nematic; and (iii) isotropic molecular liquid to discotic nematic.

Our aim is now to study the effects of an electrolyte on the N_D–I transitions. Let y be the concentration (e.g. the weight fraction) of the electrolyte. In order to obtain the effect of an electrolyte on the N_D–I transition, we have to introduce the coupling of the order parameters Q_{ij} and ϕ with the electrolyte concentration y. Since the N_D–I transition is close to being second order [6, 18, 19]

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we assume that ϕ is small in the neighbourhood of the N_D–I transition and neglect the higher order terms in ϕ. Defining ϕ_0 as the equilibrium value of ϕ in the isotropic micellar phase at the N_D–I transition point, the free energy F for the ternary mixture of the micellar liquid crystal with the electrolyte can be expanded around $T = T_{NI}$ and $\phi = \phi_0$ as:

$$F = F_I(\phi_0) + \frac{1}{2}aQ_{ij}Q_{ij} - \frac{1}{3}bQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}c\left(Q_{ij}Q_{ij}\right)^2 + \frac{1}{2}\alpha_0(\phi - \phi_0)^2 + \frac{1}{2}\delta Q_{ij}Q_{ij}\phi + m\phi y \tag{2}$$

where $F_I(\phi_0)$ is the corresponding free energy of the isotropic micellar phase. The coupling constants δ and m are assumed to be negative and the material parameter a is rewritten as $a = a_0\left[T - T^*_{NI}(y)\right]$. The coefficient α_0 determines the response of ϕ to external pertubations, i.e. $-m/\alpha_0$ is a generalized susceptibility which describes the change in ϕ imposed by a change of the concentration variable y in the isotropic micellar phase.

In accordance with the experimental phase diagram [19], $T^*_{NI}(y)$ is expanded as:

$$T^*_{NI}(y) = T^0_{NI} + uy + vy^2 \tag{3}$$

where u and v are constants. T^0_{NI} is the temperature (mean-field) of the absolute stability limit of the isotropic phase in the absence of any electrolyte–order parameter coupling. Thus the N_D phase is always stable for $T < T^0_{NI}$.

The substitution of Q_{ij} into equation (2) leads to the free energy expansion:

$$F = F_I(\phi_0) + \frac{3}{4}aS^2 - \frac{1}{4}bS^3 + \frac{9}{16}cS^4 + \frac{1}{2}\alpha_0(\phi - \phi_0)^2 + \frac{3}{4}\delta S^2\phi + m\phi y. \tag{4}$$

In the case of the isotropic micellar phase ($S = 0$), the minimization of equation (4) with respect to ϕ gives:

$$\phi_I(y) = \phi_0 - \frac{m}{\alpha_0}y. \tag{5}$$

This result shows that the value of ϕ in the isotropic micellar phase increases with the addition of an electrolyte, which agrees well with the experimental observation that the critical micelle concentration x_{CMC} decreases on the addition of an electrolyte.

To find out the variation of ϕ with y in the N_D phase ($S > 0$), the minimization of equation (4) with respect to ϕ results in:

$$\phi_N(y) = \phi_0 - \frac{1}{\alpha_0}\left(\frac{3}{4}\delta S^2 + my\right) \tag{6}$$

Substitution of equation (6) into the free energy equation (4) then gives:

$$F = F^*_0 + \frac{3}{4}a^*S^2 - \frac{1}{4}bS^3 + \frac{9}{16}c^*S^4 \tag{7}$$

where the renormalized coefficients are:

$$a^* = a - \frac{\delta m}{\alpha_0}y + \delta\phi_0,\ c^* = c - \frac{\delta^2}{2\alpha_0},$$

$$F^*_0 = F_I(\phi_0) - \frac{m^2}{2\alpha_0}y^2 + m\phi_0 y.$$

From the conditions $F = F^*_0$ and $\partial F/\partial S = 0$, the N_D–I transition transition temperature T_{NI} can now be calculated to be:

$$T_{NI} = T_0(y) + \frac{b^2}{27a_0c^*} \tag{8}$$

where $T_0(y)$ is defined as:

$$T_0(y) = T^0_{NI} - \frac{\delta\phi_0}{a_0} + u'y + vy^2 \tag{9}$$

with $u' = u + \frac{\delta m}{\alpha_0 a_0}$. Equations (8) with (9) predict that the N_D–I transition temperature T_{NI} increases with the concentration y of an added electrolyte.

Finally, the variation of the orientational order parameter $S(y, T)$ with y in the N_D phase is given by:

$$\left[S(y) - S^+_{NI}\right]^2 = \left(S^+_{NI}\right)^2 - \frac{2a_0}{3c^*}\left[T - T_0(y)\right] \tag{10}$$

where $S^+_{NI} = b/6c^*$ is the order parameter value in the superheated nematic phase.

2.3. *Cotton–Mouton coefficient*

In this section we will analyse the electrolyte effect on the magnetically induced birefringence (Cotton–Mouton effect) in the isotropic phase of a lyonematic material close to its I–N_D transition. The orientational order of the micelles induced by the application of a static magnetic field $\mathbf{H}$ gives rise to the additional free energy density $-\Delta\chi\mathbf{H}^2/3$ where the anisotropy of the diamagnetic susceptibility $\Delta\chi$ depends linearly on the (field-induced) orientational order parameter S. Writing $\Delta\chi = (\Delta\chi)_{max}S$ we obtain the free energy density in the presence of a magnetic field $\mathbf{H}$ as:

$$f_{\mathbf{H}} = F^*_0 + \frac{3}{4}a^*S^2 - \frac{1}{4}bS^3 + \frac{9}{16}c^*S^4 - \frac{1}{3}(\Delta\chi)_{max}\mathbf{H}^2S \tag{11}$$

where $(\Delta\chi)_{max}$ denotes the maximum anisotropy of the magnetic susceptibility, which is observed under the condition of perfect orientational order, i.e. $S = 1$. Since the orientational order induced by the magnetic field in the isotropic phase ($T > T_{NI}$) is assumed to be small, the third and fourth order terms in S can be omitted in a first approximation, and the order parameter, $S(H)$ measuring the field-induced orientational order of the isotropic phase is obtained to be:

$$S(\mathbf{H}) = \frac{2}{9}\frac{(\Delta\chi)_{\max}}{a^*}\mathbf{H}^2. \tag{12}$$

The anisotropy of a physical property such as the dielectric permittivity ε is proportional to the induced orientational order:

$$\Delta\varepsilon' = \varepsilon_{\parallel} - \varepsilon_{\perp} = S(\mathbf{H})(\Delta\varepsilon)_{\max} \tag{13}$$

where $(\Delta\varepsilon)_{\max}$ is the maximum anisotropy of the dielectric permittivity in the case of perfect orientational order. Following Stinson *et al.* [27] it is readily shown that a magnetic field applied to the isotropic phase will induce the optical birefringence:

$$\Delta n = \frac{(\Delta\varepsilon)_{\max}(\Delta\chi)_{\max}}{9na_0[T - T_0(y)]}\mathbf{H}^2 \tag{14}$$

where $n = (\bar{\varepsilon})^{1/2}$. The Cotton–Mouton coefficient $C(y, T)$ of the isotropic phase is then given by:

$$C(y, T) = \frac{\Delta n}{\mathbf{H}^2} = \frac{\Phi}{T - T_0(y)} \tag{15}$$

where $\Phi = \frac{1}{9na_0}(\Delta\varepsilon)_{\max}(\Delta\chi)_{\max}$ and the electrolyte-dependent temperature $T_0(y)$ is defined by equation (9). The addition of an electrolyte increases T_0 and, thereby, tends to increase the Cotton–Mouton coefficient C which is observed at a certain temperature $T > T_{NI} > T_0$. At lower temperatures in the range $T_{NI} > T > T_0$ the free energy (11) has two minima in S representing the metastable isotropic and the stable nematic states. Under the action of a magnetic field both minima are shifted to higher values of the order parameter S.

2.4. *Non-linear dielectric effect*

The non-linear dielectric effect (NDE) denotes the change in the dielectric permittivity of a material that originates from the application of a strong (static) electric field **E**. This field-induced shift in the dielectric permittivity is measured by a weak a.c. electric field, the frequency of which is typically in the range of radio frequencies. Except for the measuring frequency, the NDE is widely analogous to the electro-optic Kerr effect which applies to the case of optical frequencies.

Transitions from the isotropic to the nematic state are associated with a pronounced pretransitional NDE since the aligning electric field **E** couples to the critical fluctuations and, thereby, induces a certain long range orientational order $S(\mathbf{E})$ of the mesogenic units in the originally disordered isotropic phase [28]. This electric field-induced orientational order gives rise to an induced dielectric anisotropy which in turn changes the dielectric permittivity observed in the direction of the measuring field. With $(\Delta\varepsilon_f)_{\max}$ being the maximum anisotropy of the dielectric permittivity at the frequency f of the measuring field, the NDE in the isotropic phase of a (lyotropic) nematic liquid crystal is written as [29–31]:

$$\varepsilon(\mathbf{E}) - \varepsilon(0) = \left(\Delta\varepsilon_f\right)_{\max} S(\mathbf{E}) \tag{16}$$

where $\varepsilon(\mathbf{E})$ and $\varepsilon(0)$ are the dielectric permittivities observed with and without the strong static aligning field $\mathbf{E} \gg 0$. The amplitude of the measuring electric field is assumed to be so small that it has no additional effect on the orientational order parameter $S(\mathbf{E})$ which therefore depends on the strength of the (static) aligning field **E** only.

We shall now calculate how the addition of an electrolyte changes the NDE in the isotropic phase of a lyotropic liquid crystal. In the presence of a static electric field **E** the free energy density is given by:

$$f_{\mathbf{E}} = F_0^* + \frac{3}{4}a^*S^2 - \frac{1}{4}bS^3 + \frac{9}{16}c^*S^4 - \frac{1}{3}\varepsilon_0(\Delta\varepsilon)_{\max}\mathbf{E}^2 S \tag{17}$$

where ε_0 is the vacuum permittivity and $(\Delta\varepsilon)_{\max} = (\varepsilon_{\parallel} - \varepsilon_{\perp})_{\max}$ is the maximum anisotropy of the static dielectric permittivity in the case of perfect orientational order, see equation (13). Since the dielectric permittivities depend on the frequency f, the static $(\Delta\varepsilon)_{\max}$ differs from $(\Delta\varepsilon_f)_{\max}$. Similarly to the procedure in the preceeding section, the orientational order parameter $S(\mathbf{E})$ induced by the static field **E** in the isotropic phase of the lyotropic liquid crystal is calculated in a first approximation to be:

$$S(\mathbf{E}) = \frac{2}{9}\frac{\varepsilon_0(\Delta\varepsilon)_{\max}\mathbf{E}^2}{a^*}. \tag{18}$$

Combining equations (18) and (16) we find:

$$\varepsilon_{NDE} = \frac{\varepsilon(\mathbf{E}) - \varepsilon(0)}{\mathbf{E}^2} = \frac{\eta}{T - T_0(y)} \tag{19}$$

where $\eta = \frac{2\varepsilon_0}{9a_0}\left(\Delta\varepsilon_f\right)_{\max}(\Delta\varepsilon)_{\max}$. In complete analogy to what was found for the Cotton–Mouton effect, the addition of an electrolyte increases T_0 and, thereby, also tends to increase the ε_{NDE} which is observed at a certain temperature $T > T_{NI} > T_0$.

3. Comparison with experimental results

In this section we will compare some of the theoretical results with experimental data. The $T_{NI} - T_{NI}^0$ vs. y

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phase diagram of ternary mixtures of CsPFO/H_2O/CsCl was experimentally studied by Rosenblatt *et al.* [19]. Equation (8) shows that the N_D–I transition temperature increases with addition of electrolyte. Equation (8) is fitted to the experimental data of Rosenblatt *et al.* [19] taking $(\frac{b^2}{27a_0c^*}-\frac{\delta\phi_0}{a_0})$, u' and v as fit parameters. The fit (solid) line and the measured data (points) are shown in figure 2. The fit yields $\left(\frac{b^2}{27a_0c^*}-\frac{\delta\phi_0}{a_0}\right)=0.0338\,\text{K}$, $u'=0.007\,\text{K}$ and $v=87.53\,\text{K}$. The agreement between the measured data and the theory is reasonably good and the non-linearity is clear even within the relatively large scatter of the experimental points. For further checking our theoretical results, we have fitted equation (8) with our measured data of T_{NI} as a function of the NH_4Cl concentration in DDACl/H_2O solutions. The fit (solid) line and the measured data (points) are shown in figure 3. The fit yields $\left(T_{NI}^0+\frac{b^2}{27a_0c^*}-\frac{\delta\phi_0}{a_0}\right)=327.2\,\text{K}$, $u'=1.4\,\text{K}$ and $v=6.0\,\text{K}$. It is clearly seen that T_{NI} drastically increases with the NH_4Cl concentration.

Regarding the Cotton–Mouton coefficient C, the quantity $C[T-T_0(y)][\equiv\Phi]$ in lyonematic CsPFO/H_2O/CsCl mixtures was experimentally found to decrease at increasing weight fraction y of the CsCl electrolyte [19]. Our equation (15) also suggests a decrease of $C[T-T_0(y)]$ since $T_0(y)$ increases with increasing y. Accordingly $C^{-1}(y, T)$ would decrease with the increase of y. As for the temperature dependence the mean-field value of the susceptibility exponent in $C(y, T)\propto[T-T_0(y)]^{-\gamma}$ gives $\gamma=1$, which agrees with the experimental observations.

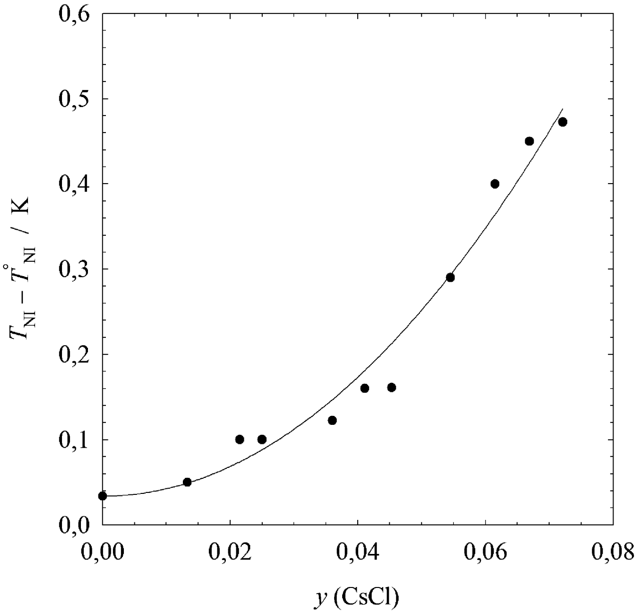

Figure 2. Dependence of $T_{NI}-T_{NI}^0$ of lyonematic CsPFO/water solutions on the weight fraction y of added CsCl electrolyte. The solid points are the experimental data from [19]. The solid line is the best fit of equation (8).

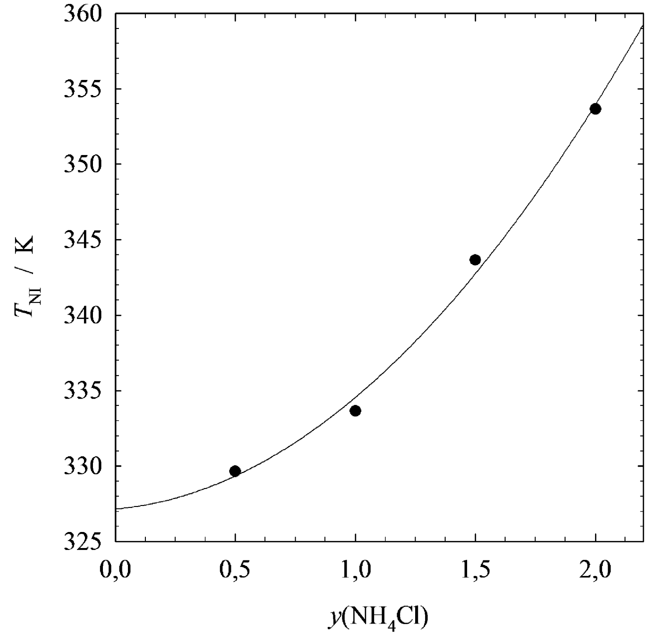

Figure 3. Dependence of the clearing temperature T_{NI} of lyonematic DDACl/water solutions on the weight fraction y of added NH_4Cl electrolyte. The solid line is the best fit to equation (8).

The fluid-like analogy in the isotropic phase of the calamitic N–I transition has been successfully investigated theoretically [32, 33] and experimentally [34–36]. The quasicritical fluid-like equation applied to this case results in the exponents $\alpha=0.5$ and $\gamma=1$ [34–36]. It was also shown [37–39] that on approaching the critical consolete point, $\varepsilon_{NDE}\propto\langle S^2\rangle\propto\chi$, where $\langle S^2\rangle$ is the mean square fluctuation of the orientational order parameter S, and $\chi\propto(T-T_0)^{-\gamma}$ denotes the susceptibility with a critical exponent of $\gamma=1$. Indeed, the current theoretical analysis of the lyotropic case also results in $\gamma=1$, cf. equation (19). To the best of our knowledge there has been no such measurement of the NDE in the isotropic phase of the N_D–I transition in lyotropic liquid crystals due to the experimental problem with the significant electrolytic d.c. conductivity.

4. Conclusions

We have presented a simple Landau theory to describe electrolyte effects on the N_D–I transition in lyotropic liquid crystals, the electrolyte increasing the N_D–I transition temperature. The theory predicts a weakly first order character of the N_D–I transition even in the presence of electrolytes. This weak first order character of the N_D–I transition, which is measured by $T_{NI}-T_{NI}^0$,

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is further weakened by decreasing the electrolyte concentration. The Cotton–Mouton coefficient, as well as the NDE, decreases with increasing electrolyte concentration. The pretransitional behaviour at the N_D–I transition in lyotropic liquid crystals is strongly influenced by the presence of an electrolyte. Furthermore, the critical exponents $\alpha=0.5$ and $\gamma=1$ indicate the fluid-like analogy in the isotropic phase of the N_D–I transition, similar to that at the calamitic N–I transition.

We hope that the present theoretical analysis of the NDE in the isotropic phase of the N_D–I transition in lyotropic liquid crystals will stimulate a closer look at this problem. Although we have made some progress in explaining different phenomena related to the critical properties of the N_D–I transition, a more fundamental molecular theory is clearly needed to gain a better understanding of the intriguing physics, namely the role of coulombic interactions on the micellar solution of the N_D–I transition in the presence of an electrolyte.

Acknowledgments

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