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The Entropy Effects in Binary Mixtures of Polar Mesogenic Solvent/Nonpolar Solute

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The paper concerns two aspects of the entropy in mesogenic systems: (i) the entropy jump (ΔS^0_{NI}) at the phase transition from the isotropic liquid (I) to the nematic liquid crystalline state (N), and (ii) the entropy increment (ΔS) caused by the ordering action of the probing electric field applied to the dipolar system. The system studied are the mixtures of strongly polar mesogenic solvent *n*-hexylcyanobiphenyl ($C_6H_{13}PhPhCN$, 6CB) and the nonpolar nonmesogenic admixture 4-ethylcyclohexyl-4′-*n*-nonylphenyl ($C_2H_5CyHxPhC_9H_{19}$, 2CyPh9). The entropy jump at the I−N phase transition in pure 6CB [$\Delta S^0_{NI} = 1.52$ J/(mol K)] was evaluated from the analysis of the phase diagram of the mixture 6CB + 2CyPh9 with use of the Landau−Lifshitz theory; the resulting value of the transition enthalpy ($\Delta H^0_{NI} = T_{NI}\Delta S^0_{NI} = 0.50$ kJ/mol) agrees well to that obtained with the calorimetric methods. The field-induced entropy increment (ΔS) was calculated, at the given temperature, from the static dielectric permittivity derivative value ($d\varepsilon_s/dT$), with use of the Fröhlich theory. The singularities in dependence of the entropy increment on the temperature and on the mixtures composition are discussed in terms of the prenematic molecular self-organization extent in mesogenic liquids of different density of dipoles.

Introduction

The entropy change in liquids and thermotropic liquid crystals reflects a change in the molecular order resulting either from spontaneously occurring phase transitions or due to the application of external fields to the system. Especially important is the entropy behavior at the given phase transition in relation to the order of the transition.

Phase transitions can be classified as first or second order depending on the behavior of the first and second derivatives of the thermodynamic potential relevant to the system studied.[1,2] In the case of liquids (or liquid crystals), where the phase transitions are studied mainly in the isothermal or isobaric conditions, a behavior of the derivatives of the Gibbs function $G(T,p)$: $(\partial G/\partial p)_T = V$, $-(\partial G/\partial T)_p = S$, $(\partial^2 G/\partial T^2)_p = C_p/T$, $(\partial^2 G/\partial p^2)_T = VK$, and $\partial^2 G/\partial T\partial p = V\alpha$ is under consideration. The first order phase transitions are accompanied with the discontinuity of the Gibbs function first derivatives, so the jumps in the specific volume, ΔV_{tr}^0, and the entropy, ΔS_{tr}^0, are recorded. At a second order transitions, these quantities are continuous, but jumps in the heat capacity at a constant pressure (ΔC_p), the isothermal compressibility (ΔK), and the expansion coefficient ($\Delta\alpha$) are observed.

As the entropy jump is related to the latent heat: $\Delta H_{tr}^0 = T_{tr}\Delta S_{tr}^0$, where T_{tr} is the phase transition temperature, the calorimetric measurements are the main tool for determination of the phase transition order. At typical first order transitions, namely, in the melting from the crystalline solid to the isotropic liquid (or to the liquid crystalline phase), the enthalpy change attains quite high values $\Delta H_{tr}^0 = 20$–50 kJ/mol, so, from the experimental point of view, there are no problems with detection of such heating effects. The problem arises for transitions which are accompanied by a small (or very small) latent heat.[3–5] This is just the case of transitions from one to other liquid crystal phase or from liquid crystal phase to isotropic liquid, where the enthalpy changes are of the order of 1 kJ/mol and often much less. Such type of phase transitions are called a weakly first order or close to the second order, and for their detection, scanning calorimeters of high resolution have to be used.[6,7]

The entropy jump ΔS^0_{NI} (even of a relatively small value) occurring at the transition from the isotropic liquid (I) to the nematic phase (N) of a given mesogenic compound has its consequences in mixtures of that compound with a nonmesogenic solute; the two-phase region (I + N) appears. In this paper, we present the phase diagram of binary mixtures of polar mesogenic solvent and nonpolar admixture. A simple analysis of the diagram allows one to determine the entropy jump ΔS^0_{NI} for the I−N transition in pure mesogenic solvent.[8,9]

The another interesting aspect of the entropy in mesogenic systems is related to the interaction of the system with external fields. As it was shown by Fröhlich,[10] the electric field applied to dipolar liquid induces the entropy increment, ΔS, which is directly related to the derivative of the static dielectric permittivity:

$$\frac{\Delta S}{E^2} \equiv \frac{S(T,E) - S_0(T)}{E^2} = \frac{\varepsilon_0}{2}\frac{\partial\varepsilon_s}{\partial T} \qquad (1)$$

where E denotes the strength of the probing electric field, S_0 is the value of the entropy (per unit volume) in the absence of the electric field, T is the absolute temperature, and $\varepsilon_0 = 8.85$ pF/m is the permittivity of free space. As it was shown recently,[11–13] the entropy increment measured in the isotropic phase of the mesogenic liquid in the vicinity of the transition to the nematic liquid crystalline phase allows one to gain important information on the prenematic spontaneous molecular organization. In this paper, we analyze an evolution of that self-organization process in conditions of a decreasing number of the molecular dipoles in unit volume.

Experimental Section

The compounds studied, the mesogenic solvent *n*-hexylcyanobiphenyl ($C_6H_{13}PhPhCN$, 6CB) and nonpolar admixture 4-*n*-

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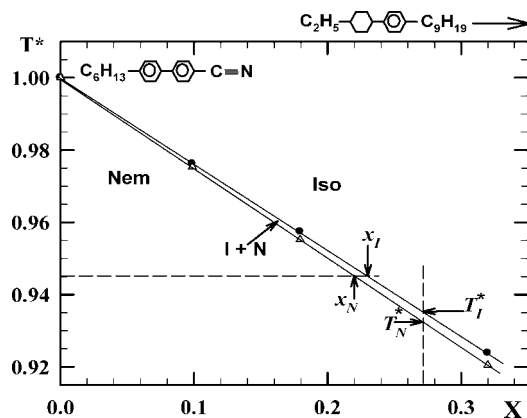

Figure 1. Phase diagram for mixtures of mesogenic 6CB and nonmesogenic 2CyPh9. $T^* = T/T_{NI}$ is the reduced temperature and x is the mole fraction of nonmesogenic solute.

Figure 2. The temperature extent of the two-phase N + I region in the mixtures of 6CB + 2CyPh9 as a function of the mole fraction of nonmesogenic admixture.

Figure 3. The concentration extent of the two-phase N + I region in the mixtures of 6CB + 2CyPh9 as a function of the reduced temperature.

ethylcyclohexyl-4'-*n*-nonylphenyl ($C_2H_5CyHxPhC_9H_{19}$, 2CyPh9), were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by the chromatography, was better than 99%. The temperature of the transition from the isotropic liquid (I) to the nematic (N) liquid crystalline phase in pure 6CB (T_{NI} = 302.4 K) and in the solutions were determined using the polarizing microscope. 6CB is a strongly polar mesogenic compound with the molecular dipole moment equal to about 5D.[7]

The static dielectric characteristics of the compounds were measured with an HP 4194A impedance/gain phase analyzer at the frequency of about 100 kHz, where, in the dielectric spectrum, a plateau of the real part of the complex dielectric permittivity is recorded. The measuring capacitor consisted of three plane electrodes, one central and two grounded on each side with a distance between them of about 0.5 mm. The probing electric field intensity E was equal to about 1 V/mm. The use of electrical heating of high performance with a Scientific Instruments temperature controller, model 9700, assured a good temperature stabilization (at milikelvin level) with the possibility of varying the temperature by steps of 10^{-2} K. Such equipment allows one to determine the permittivity with a relative accuracy better than 0.5%.

Results and Discussion

Figure 1 presents the phase diagram of the 6CB + 2CyPh9 binary mixtures, where $T^* = T/T_{NI}$ is the reduced temperature and x is the mole fraction of the nonpolar admixture 2CyPh9. The mixtures exhibit the nematic phase in rather unusually large range of the nonmesogenic admixture contents (for the x values up to somewhat higher than 0.4), which undoubtedly results from the similarity of the shape and structure of 6CB and 2CyPh9 molecules. The extent of the two-phase I + N region appearing in the mixtures (as a result of the first order in nature of the I−N phase transition) can be represented in two ways, as depicted in Figure 1: as the temperature extent, $\Delta T_{N+I} = (T^*_I - T^*_N)T_{NI}$, at a constant concentration of admixture or as an admixture concentration extent, $\Delta x_{N+I} = x_I - x_N$, at a constant temperature T^*. Both representations are important and interesting as they give a different look at the transition from the isotropic liquid to the nematic phase. The temperature extent of the two-phase region, ΔT_{N+I}, can be observed directly with the polarizing microscope, and it gives an answer on the role of the molecular parameters of admixture on the stability of
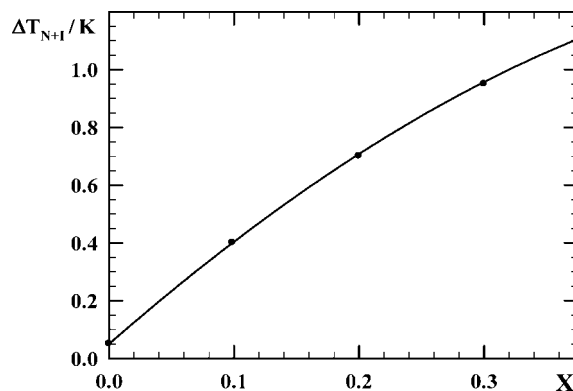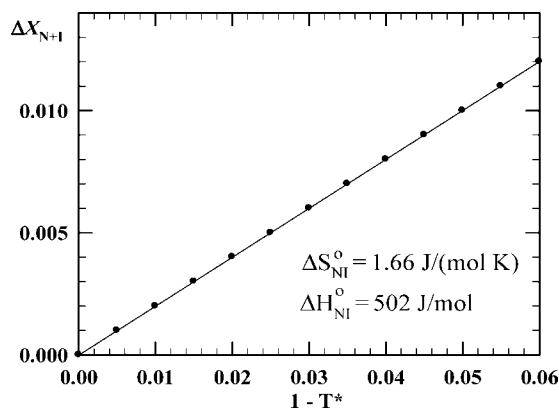
the nematic phase of the mixture studied. The results presented in Figure 2 show an exceptional thermodynamic stability of the nematic phase in the mixtures of 6CB + 2CyPh9, where the molecular length and structure of the solute is highly compatible to those of the mesogenic solvent.

An importance of the concentration extent of the two-phase I + N region results from the Landau and Lifshitz statistical theory of binary mixtures of mesogenic + nonmesogenic compounds.[8,9] According to the theory, the concentration extent of the two-phase region (Δx_{N+I}), as a function of the reduced temperature, does not depend on type of the solute used but it depends only on the magnitude of the entropy jump ΔS^0_{NI} at the I−N phase transition in pure mesogenic solvent:

$$\Delta x_{N+I} = \frac{\Delta S^0_{NI}}{R}(1 - T^*) \tag{2}$$

where R is the gas constant. Figure 3 shows that the linear dependence predicted by eq (2) is fulfilled in the case of 6CB + 2CyPh9 solutions. The entropy jump ΔS^0_{NI}, estimated from the data presented in the figure, is equal to 1.66 J/(mol K), which gives for the latent heat ($\Delta H^0_{NI} = T_{NI}S^0_{NI}$), the value of about 0.5 kJ/mol. This value is situated within the limits of those obtained with the calorimetric methods for the I−N transition in pure 6CB (from 0.3 kJ/mol[6] to 0.9 kJ/mol[14]). So, the presented results clearly show that an analysis of the phase diagram, which, in principle can be obtained in a simple way, can lead to quite important thermodynamic conclusions concerning the nature of the I−N phase transition.
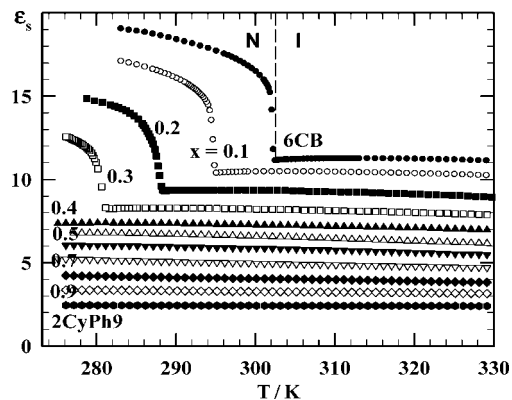
Figure 4. Temperature dependences of the static dielectric permittivity measured for 6CB + 2CyPh9 mixtures in the isotropic (for the whole concentration range) and the nematic (for $0 \leq x \leq 0.3$) phases.
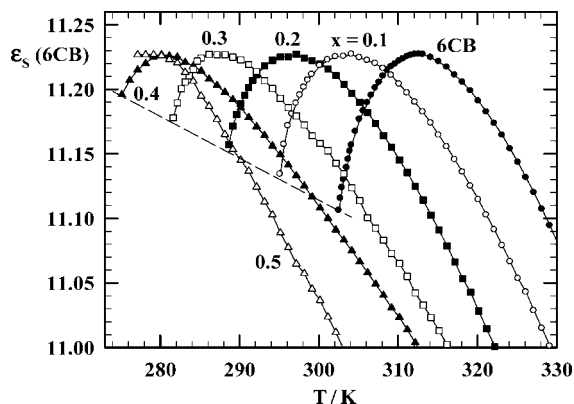

Figure 5. Anomalous temperature behavior of the static permittivity in the isotropic phase of the 6CB + 2CyPh9 mixtures in the vicinity of the I−N phase transition. For solutions, the dependences $\varepsilon_s(T)$ are shifted to have the same maxima level as those for the pure mesogenic solvent 6CB.
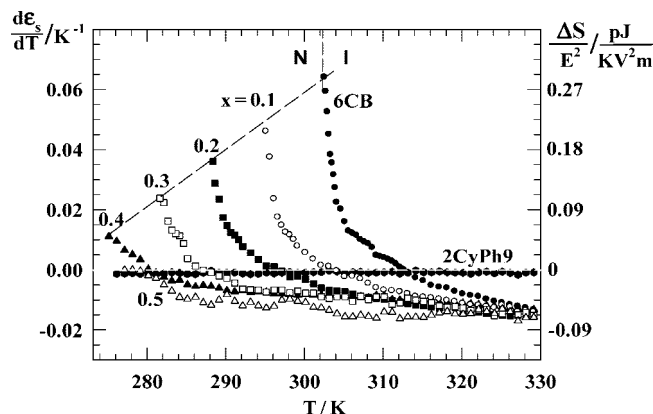

Figure 6. Critical-like temperature dependence of the static permittivity derivative and the corresponding field-induced increment of the entropy for 6CB + 2CyPh9 solutions in the prenematic region.
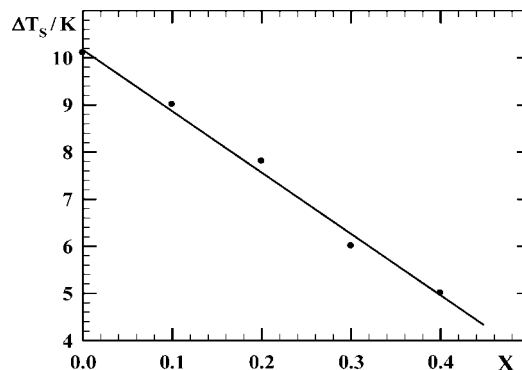

Figure 7. Temperature distance ΔT_S between the point of the I−N phase transition (T_{NI}) and the point of $\Delta S = 0$ ($T_{\Delta S=0}$) as a function of the mole fraction of nonmesogenic (and nonpolar) compound 2CyPh9 dissolved in mesogenic (and strongly polar) 6CB.

Figure 4 presents the temperature dependence of the static dielectric permittivity measured for 6CB + 2CyPh9 mixtures in the whole concentration range $0 \leq x \leq 1$ of nonpolar admixture. As the biasing dc electric field was applied to the samples, the transition from the isotropic liquid to the nematic phase manifests itself in strong increase of the permittivity to the value corresponding to the parallel component of the permittivity tensor of the nematic liquid crystal. Figure 5 shows, that in the isotropic phase of the solutions which exhibit the transition to the nematic phase ($0 \leq x \leq 0.4$), the static permittivity presents a strong anomaly in its temperature dependence in the vicinity of the transition. For comparison of the extent of that anomaly for mixtures of different nonpolar additive contents (different permittivity value), the maxima of the $\varepsilon_s(T)$ dependences for $x = 0.1$–0.4 (and 0.5 where the traces of the pretransitional effects occur) are shifted to the same level as for $x = 0$ (pure 6CB). The presented data show that with increasing of the amount of the nonpolar component of the mixtures, i.e., as the number of dipolar mesogenic molecules in the unit volume decreases, the pretransitional anomalous effect in the static dielectric permittivity loses its strength markedly.

A physical significance of the pretransitional effects observed can be discussed in terms of the entropy increment (ΔS) induced by the probing electric field in the particular mixture. According to the Fröhlich eq (1), the entropy increment is represented by

the static permittivity derivative. The corresponding data for the mixtures studied are presented in Figure 6. Far from the I−N phase transitions, the field-induced entropy increment is negative, which means the applied electric field causes an increase of the molecular order in liquids. It is a usual orientational effect expected for dipolar liquids. It is worthy to notice in Figure 6 of an extremely low, but still negative, entropy increment, corresponding to the electric field ordering of the nonpolar 2CyPh9 molecules due to their anisotropic electronic/atomic polarizability.

Figure 6 shows that as the temperature of a given solution approaches the temperature of transition to the nematic phase, the entropy increment shows a critical-like increase from negative values, goes through zero, and then becomes positive. The positive increment of the field-induced entropy, occurring close to the I−N phase transition, denotes that the electric field applied to a given polar liquid generates a decrease of the molecular ordering, contrary to the field action far from that transition. So, the same isotropic polar liquid can produce the opposite field-induced entropy effects depending on the temperature distance from the phase transition to the nematic phase. As it was discussed previously,[11–13] singular entropy behavior is a consequence of the spontaneous molecular self-organization process, leading to the pseudonematic domains formation in the isotropic liquids in the vicinity of the transition to the nematic phase. In the domains, the mesogenic molecules are arranged preferably antiparallel to each other, so an application of the probing electric field, which always forces the parallel arrange-

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ment of the dipoles, leads to destruction of the domains. This process is a source of the positive increment of the entropy ($\Delta S > 0$).

Of course, as in the prenematic region of mesogenic liquid, the pseudonematic domains and the free molecules are in equilibrium,[13] both the positive and the negative field-induced entropy effects occur simultaneously, and, in the experiment, at a given temperature, one records the resultant effect. In particular, in some distance from the transition to the nematic phase, the resultant entropy increment is equal to zero, indicating an equilibration of the two entropy constituents. At that particular temperature, $T_{\Delta S=0}$, the mesogenic polar liquid behaves as a nonpolar one. The analysis of the data presented in Figure 6 shows that the value of $T_{\Delta S = 0}$ in relation to the temperature of the I−N phase transition T_{NI}:

$$\Delta T_S = T_{NI} - T_{\Delta S=0} \tag{3}$$

can be taken as a measure of an ability of a given mesogenic system to the spontaneous molecular self-organization in the prenematic region.

The results of such an analysis performed for 6CB + 2CyPh9 solutions, are presented in Figure 7. The temperature distance (ΔT_S) between the point where $\Delta S = 0$ and the point of the phase transition decreases approximately linearly as the concentration of the nonpolar additive in the mixtures increases. So, as the number of polar molecules in the unit volume decreases, the self-organization process quite rapidly reduces its extent but even for the mole fraction $x = 0.4$, where (in the solution) there are 3 mesogenic 6CB molecules per 2 nonpolar 2CyPh9 molecules, the self-organization ability, measured in ΔT_S, equals to a relatively high value of 5 K. In the case of recently studied[11] pure mesogenic compound 6CHBT [4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene] of an average

polarity (molecular dipole moment is equal to 2.5D[7]), the pretransitional aggregation ability, measured in the ΔT_S scale, is equal to 0 K; the entropy increment of the value $\Delta S = 0$ is realized just at the temperature of the I−N phase transition in 6CHBT. The presented result points out for an essential role of the polarity of mesogenic molecules in their ability to spontaneously form the pseudonematic domains in isotropic liquids in the vicinity of transition to the nematic phase.

References and Notes

(1) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: Oxford, 1971.

(2) Callen, H. B. *Thermodynamics and an Introduction to Thermostatics*; Wiley: New York, 1985.

(3) Thoen, J. In *Phase Transitions in Liquid Crystals*; Martellucci, S., Chester, A. N. Eds.; NATO Advanced Study Institute Series B: Physics Plenum: NY, 1992.

(4) Anisimov, M. A. *Critical Phenomena in Liquids and in Liquid Crystals*; Gordon and Breach: Reading, MA, 1992.

(5) de Gennes, P. G. *Physics of Liquid Crystals*; Oxford University Press: Oxford, 1974.

(6) Thoen, J. *Int. J. Mod. Phys. B* **1995**, *9*, 2157.

(7) Van Roie, B.; Leys, J.; Denolf, K.; Glorieux, C.; Pitsi, G.; Thoen, J. *Phys. Rev. E* **2005**, *72*, 041702.

(8) Landau, L.; Lifshitz, E. *Statistical Physics*; Pergamon Press: London, 1959.

(9) Martire, D. E. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R. ; Gray, G. W. Eds.; Academic Press: London, 1979.

(10) Fröhlich, H. *Theory of Dielectrics*, 2nd ed.; Clarendon Press: Oxford, 1958.

(11) Jadżyn, J.; Czechowski, G. *J. Phys. Chem. B* **2007**, *111*, 3727.

(12) Jadżyn, J.; Czechowski, G.; Déjardin, J.-L. *J. Phys. Chem. A* **2007**, *111*, 8325.

(13) Jadżyn, J.; Czechowski, G.; Déjardin, J.-L. *J. Phys. Chem. B* **2008**, *112*, 4948.

(14) Barrall, E. M.; Cox, R. J.; Doelman, A.; Clecak, N.; Logan, J. A.; Gregges, A. R. *Anal. Calorim.* **1977**, *4*, 19.