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NUCLEAR MAGNETIC RELAXATION NEAR THE NEMATIC-TO-ISOTROPIC TRANSITION IN MICELLAR SYSTEMS

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Abstract Using the NMR ^{19}F technique, decay of the transverse magnetization (DTM) is studied over the nematic-to-isotropic liquid transition region for aqueous micellar solutions of cesium perfluorononanoate. Transverse magnetization decay appears to be single-component in both nematic and isotropic phases and two-component in the two-phase region. Componental composition of the DTM changes fastly near the low-temperature border of the coexistence region but slowly near the high-temperature border. Long exposition at fixed temperature leads to spatial phase separation of the micellar system: the isotropic phase moves up while the nematic one drowns. It is argued that this fact is due to a difference in micellar concentrations between the two phases.

INTRODUCTION

Solutions of anisometric micelles are known to form the liquid crystalline nematic phase at certain temperatures and concentrations. The well-studied examples of such systems are solutions of cesium perfluorononanoate and cesium perfluorooctanoate in water. The structural units of such nematics are small discoid micelles[1,2].

It is well established that transformation between nematic and isotropic phases falls into the first order transitions. In thermotropic systems, doping the liquid crystalline sample with non-mesogenic impurity lowers the transition temperature[3]. Then in place of the only transition point one can observe a line of transition points at the temperature – composition plane. Moreover, in such binary systems the phase consolution region appears due to the existence of an additional degree of freedom associated with the ability of mesogenic particles to redistribution between different parts of the solution. In the case of lyotropic liquid crystals, the consolution region is an obligate attribute of phase diagrams[1]. Experimental research in this region is quite complicated in view of two main reasons. First, the region is usually confined in the narrow temperature interval and, second, almost every physical measurement requires solution of the additional problem on separa-

tion of contributions from two phases. Possibly because of these reasons, two-phase region attracts no considerable attention in literature. Mechanisms controlling the lyotropic nematic–to–isotropic liquid transition are not perfectly clear, but without the understanding of nature of two-phase states in these systems the concept of formation of micellar mesophases does not seem complete.

The goal of the present work is to investigate the behavior of the nuclear magnetization measured in pulse NMR-experiment near the nematic–to–isotropic phase transition in lyotropic liquid crystals.

EXPERIMENTAL

In this work we used three solutions of cesium perfluorononanoate $CF_3(CF_2)_7COO$-Cs (CsPFN) in water with weight fractions c of amphiphile of 12.6% (1), 19.7% (2) and 30.0% (3) and a solution of cesium 2,2-dihydrofluorononanoate $CF_3(CF_2)_6CH_2COO$-Cs in heavy water (CsFNH-D_2O) with c=58.0% (4). Initial cesium salts were obtained from NIOPIK (Moscow) and kindly presented by Prof. A.S. Sonin. Water used as the solvent was obtained by double distillation. Heavy water (99.9% D_2O) was kindly presented by the Russian Federal Nuclear Center (VNIITF – Snezhinsk).

Before the dissolution of the salts, the water was boiled to remove paramagnetic molecular oxygen. Cylindrical ampoules containing the solutions were sealed. Similarity in the structure of amphiphilic molecules CsPFN and CsFNH and in behavior of nuclear magnetization allows one to suggest that micelles in the mixture CsFNH-D_2O are also oblate ellipsoids.

The measurements were fulfilled on a pulse NMR spectrometer operating at frequency 25 MHz that corresponds to the ^{19}F resonance. The decay time of the free induction signal due to inhomogeneity of the magnetic field was about 1.5 ms. Duration of the 90°-pulse was 4 μs. Dead time after a high-frequency pulse was 6 μs.

Air thermostat provided temperature control within 0.1 K. Temperature drop inside the sample did not exceed 0.1 K. In order to prevent moisture condensation in higher parts of the ampoules, their temperature was held by the special heater to be slightly higher than that in the working part of the samples.

In experiments, there were measured the decay of the transverse magnetization (DTM) either from a signal of the free induction after a single 90°-pulse in nematic phase or an envelope of the spin-echo signals after application of the Carr–Parcell–Meiboom–Gill (CPMG) pulses sequence[4] in the isotropic phase. In the coexistence region DTM was measured simultaneously from a signal of the free induction after the first 90°-pulse and spin-echo signals after 180°-pulses in CPMG pulse sequence.

In the nematic phase, DTM is single-component and has a gauss-like form, which is characteristic for solid state, with the decay time $T_{2N} \leq 150$ μs. In the isotropic liquid, DTM is also single-component but has near-exponential form with the decay time $T_{2I} > 600$ μs. In the mixed phase region, DTM is two-component and consists of the fast-decaying gauss-like and the slow-decaying near-exponential parts. The fast-decaying component is associated with the nematic while the slow-decaying one with the isotropic phase. Each component was characterized by the two parameters: the initial amplitude A_i ($i = I, N$) and the transverse relaxation time T_{2i}. The initial amplitude of the signal related to the isotropic phase was estimated by extrapolation of the slow-decaying component to the starting moment. The extrapolation was performed according to the principle of preservation of the shape of DTM near the transition. Since the initial amplitudes are proportional to the number of fluorine atoms in the corresponding phase, mass fraction of the isotropic liquid was calculated as the fraction of amplitudes $A_I/(A_I+A_N)$.

The pulse interval τ in the CPMG sequence was chosen to be equal to 200 μs. This value corresponds to the maximal meaning of τ, at which the dependence disappears of the DTM shape on the pulse frequency due to chemical exchange.

Before the beginning of the experiment the samples were heated up to ~100°C for homogenization and thoroughly stirred by shaking. After that the ampoules were placed into the spectrometer and exposed for 20 min. at the given temperature. After 20 min. the DTM parameters became time-independent. While working in the two-phase region, this procedure was repeated before each measurement.

RESULTS

The DTM time in nematic is connected with the orientational ordering of micelles and independent on either temperature or initial amphiphile concentration within the biphasic region[5]. In contrast, time T_{2l} is determined by several types of micellar motions and comprises a complex function of temperature and composition[5]. For each temperature the values of P_l and T_{2l} were computed. Their temperature dependencies for the three samples of CsPFN-H_2O are represented on Figs. 1-3.

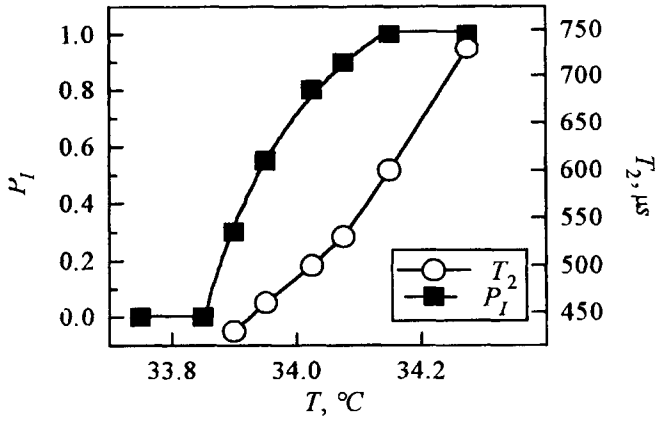

FIGURE 1 Temperature dependencies of the fraction of the isotropic liquid P_l and the relaxation time T_{2l} in the sample 1.

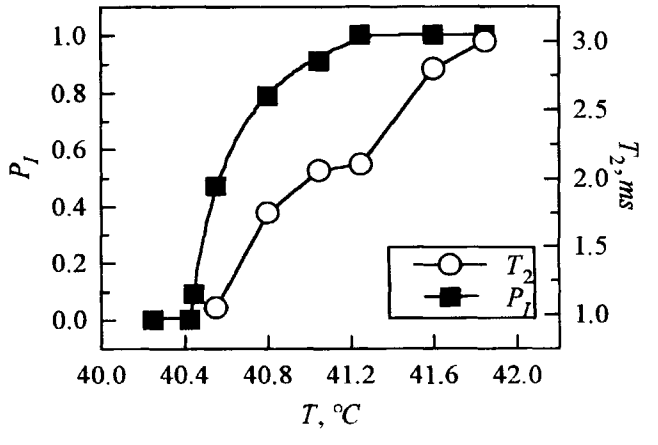

FIGURE 2 Temperature dependencies of the fraction of the isotropic liquid P_l and the relaxation time T_{2l} in the sample 2.

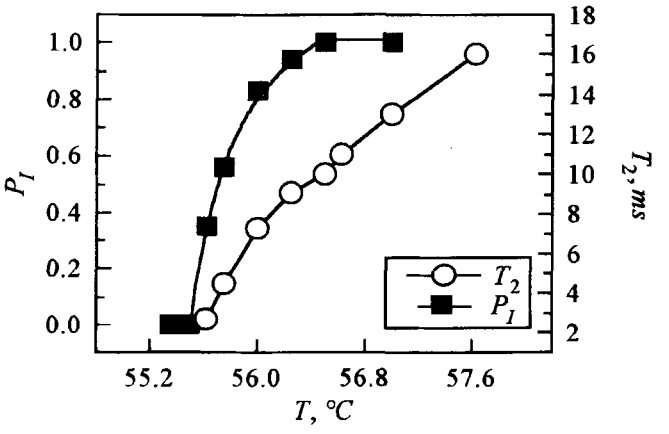

FIGURE 3 Temperature dependencies of the fraction of the isotropic liquid P_I and the relaxation time T_{2I} in the sample 3.

Temperature difference between T_{NI} and T^*, which are correspond to P_I=0 and P_I=1 meanings, respectively, defines the temperature interval of stability of biphasic states. It is readily seen from the Figs. 1-3 that curves $T_{2I}(T)$ have singularities at T^*. It is also seen that the width of the coexistence region depends on the initial composition. It equals to 0.3°C, 0.8°C and 1.0°C for the 1, 2 and 3 specimens, respectively. It should be noted that the transition width for the sample 1 is comparable with the uncertainty of its experimental determination. The extrapolation of the lines of $T_{NI}(c)$ and $T^*(c)$ shows that the coexistence region becomes narrower when c decreases and vanishes at $c \approx 11.2\%$. At higher amphiphile contents the width of the region tends to a finite meaning when c reaches the upper border of existence of the nematic.

As compared to the above described solutions, the sample 4 has wider coexistence region that makes the research easier and allows one to perform the measurements to a higher precision. Temperature dependencies of P_I and T_{2I} for this sample are represented on Fig. 4. Besides, Fig. 5. illustrates the behavior of P_I in the modified experimental conditions, in which heating and cooling were carried out without additional stirring. The curves obtained on heating (a) and cooling (b) approximately repeat the shape of the equilibrial curve but are shifted relative to this along the temperature axis.

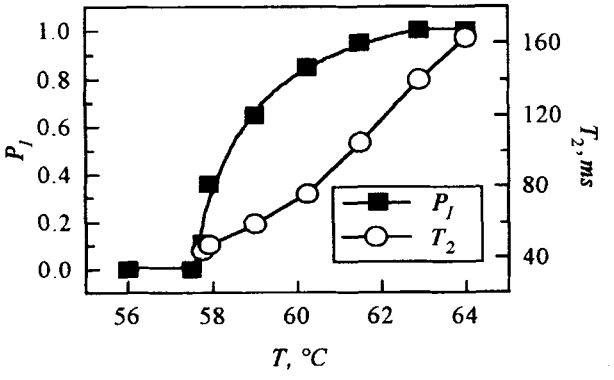

FIGURE 4 Temperature dependencies of the fraction of the isotropic liquid P_I and the relaxation time T_{2I} in the sample 4.

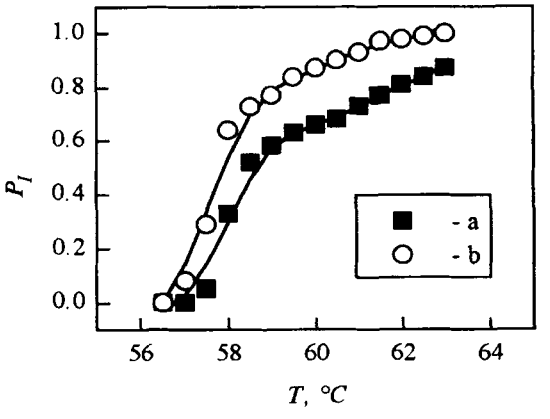

FIGURE 5 Temperature dependencies of the fraction of the isotropic liquid P_I in the sample 4 on heating (a) and cooling (b).

On long standing at fixed temperature, the spatial phase separation of the samples in height into two distinct parts was observed. By the character of light scattering, the lower part was identified as the nematic and the higher part as the isotropic phase. The fraction of their volumes was in accordance with the fraction of initial amplitudes of the NMR signals. This fact was also checked in the following way: partial bringing the sample out from the transceiving inductance coil affected the componental composition of DTM. The signal from the isotropic phase disappeared on shifting the sample up but the signal from the nematic disappeared on shifting the sample down.

DISCUSSION

In describing the *N-I* transition in thermotropic mesogens, it is commonly accepted that near the transition temperature there exist the regions of metastable states[6]. The region enclosed with the upper border of the superheated nematic and the lower border of supercooled isotropic liquid is then called biphasic region. It should be noted that these states are not normally observed[1,6]. In some works, the same concept of biphasic region was applied by analogy to lyotropic systems[1]. However, in contrast to thermotropic systems, in lyotropic ones the two-phase state is stable. Portions of the coexisting phases take the finite equilibrium values which depend on the temperature and the initial composition[3].

The spatial phase separation, which is observed in the present investigation, evidently stems from the density difference between the nematic and the isotropic liquid. This difference cannot be explained from only change in orientational ordering of micelles because the intermicellar space is filled by water and the density is not considerably influenced by the micelles orientation. At the same time, the density of the used amphiphile is more than the density of water and, hence, the density of the corresponding phase increases with growing the amphiphile content. Therefore, the phase separation by height rather indicates the difference in composition between the coexisting phases.

One more evidence of the redistribution of micelles between the nematic and the isotropic phases follows from the widening of temperature interval of the nematic state upward to higher temperatures at the cost of the biphasic region. Since the *N-I* transition temperature increases with the amphiphile concentration, this points to the increase of amphiphile content in the nematic phase.

It is important that the two coexisting phases differ from each other not only by concentrations but also by the character of micelle ordering. According to the Landau – de Gennes theory[6] the nematic order parameter behaves near the transition to isotropic phase as

$$Q = a + b\tau^{1/2}, \qquad (1)$$

where $\tau = (T^{**}-T)/T_{NI}$, T^{**} is the upper border of stability of the nematic, a, b are temperature-independent coefficients. Since T_{NI} and T^{**} depend on concentration, the order parameter (1) should be considered as a function of the temperature and composition of

the nematic phase c_N. If concentration variation is not too large, the transition temperature T_{NI} can be described by a linear function of c_N

$$T_{NI}(c_N) = T_{NI}(c) + \Delta c_N \frac{\partial T_{NI}}{\partial c}. \tag{2}$$

By analogy,

$$T^{**}(c_N) = T^{**}(c) + \Delta c_N \frac{\partial T^{**}}{\partial c}. \tag{3}$$

In view of Eq.(3), the order parameter takes the form

$$Q = a + bt^{1/2}, \tag{4}$$

where

$$t = T^{**} + \Delta c_N \left(\frac{\partial T^{**}}{\partial c}\right) - T. \tag{5}$$

On heating the lyotropic nematic, Q gradually decreases, then reaches its minimal meaning corresponding to the transition point and then remains fairly constant within the biphasic region[1,5]. Taking into account that this minimal meaning does not considerably depend on initial composition, we found from the requirement of constancy of the t value that excess amphiphile content in the nematic phase should linearly increase with temperature

$$\Delta c_N = c + k_1(T - T^{**}), \tag{6}$$

where the coefficient k_1 coincides with the derivative $(\partial T_{NI}/\partial c)$. The lever rule for this system can be represented as

$$P_I = \frac{c_N - c}{c_N - c_I} = \frac{\Delta c_N}{\Delta c}. \tag{7}$$

Let us assume that amphiphile concentration in isotropic liquid Δc_I is also linear function of the temperature

$$\Delta c_I = c_0 + k_2(T - T_{NI}), \tag{8}$$

where c_0 is the amphiphile concentration in the isotropic phase at $T \to T_{NI}+0$. The slope of the line $\Delta c_I(T)$ jumps at exit from the coexistence region that agrees with the behavior of the relaxation time T_{2I} (Figs. 1-4). Then one can readily obtain an equation for P_I

$$P_I = \frac{k_1 \Delta T}{(c - c_0) + (k_1 - k_2)\Delta T}. \quad (9)$$

where $\Delta T = T - T_{NI}$. According to Eq. (9), we carried out an approximation of the experimental curves $P_I(T)$ with the fitting function

$$P_I = \frac{d_1 \Delta T}{1 + d_2 \Delta T}. \quad (10)$$

The results are represented in Table 1.

TABLE 1 Fitting parameters for the experimental curves $P_I(T)$.

Sample	d_1, K^{-1}	d_2, K^{-1}	k_1, K^{-1}	k_2, K^{-1}	c–c_0, weight %
1	8.03	4.55	0.93	0.40	0.12
2	5.85	4.72	1.20	0.23	0.20
3	3.91	2.85	1.47	0.40	0.38
4	1.79	1.39	≈2.2	0.47	1.18

It follows from the data of the Table 1, that difference in concentrations between the coexisting phases grows up with temperature. The difference (c - c_0) is found to be less than the expected value corresponding to the distance between the lines $T_{NI}(c)$ and $T^*(c)$. As a consequence, the portion of the isotropic phase inside the coexistence region appears to be higher than one prescribed by Eq. (9) at $k_1 \approx k_2$ that would agree with the relative positions of these lines on the phase diagram. From the above reasoning, one can conclude that there occur processes with a release of energy in the nematic – isotropic liquid system, which are responsible for growing the portion of the isotropic phase. It is important to note that this phenomenon cannot be explained either by the barometric distribution of micelles in height or by the ordering action of the constant magnetic field[7]. Besides, the used technique excludes the influence of concentration fluctuations.

CONCLUSION

The main results of the investigation of behavior of parameters of nuclear magnetic relaxation near the nematic–to–isotropic transition are the follows

1) There is a region of stable biphasic states of the micellar system at the temperatures higher than the nematic–to–isotropic transition temperature.

2) On long standing at fixed temperature and concentration corresponding to the coexistence region, spatial separation of the system by height occurs. The nematic phase therewith drowns and the isotropic one moves up.

3) The phase separation of the system is accompanied by the difference in concentrations between the coexisting phases: amphiphile content in the nematic grows up approximately in a straight line with temperature while the concentration in the isotropic phase jumps down at the transition point and then also linearly increases.

4) The character of variation of the mass fractions of the coexisting phases allows to suggest that there occur processes with a release of energy in the nematic – isotropic liquid system, which lead to additional growing the portion of the isotropic phase.

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