^{2}H NMR Studies of the Temperature Dependence of Lyotropic Liquid Crystal

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Abstract: *A detailed temperature dependence diagram of tetradecyltrimethylammonium bromide (TTAB)/n-decanol (DeOH)/water system was determined for representative samples at fixed water/TTAB mole ratio and various decanol/TTAB mole ratios by ^{2}H NMR. The variation of the deuterium quadrupolar splittings N-CD_3 group and of HOD with temperature indicated various phase transitions of the first order in this series of samples. The results show an interesting behavior of this system with temperature variation and represent an important contribution to r understanding changes in micellar shape in lyotropic liquid crystal systems.*

Amphiphilic molecules in aqueous solution assemble into micellar aggregates (lyotropic liquid crystals), which, under certain conditions of temperature and concentration, may present nematic mesophases (calamitic N_C, discotic N_D and biaxial N_{BX}), characterized by diamagnetic and optical anisotropies, but no translational order.[1] The long-standing popularity of nematic mesophases within the NMR community derives largely from the fact that the magnetic field used to polarize the nuclear spin system also acts to align the nematic phase. Spectroscopic studies of spectral line shapes provide information about the symmetry of the mesophase, the sign of magnetic susceptibility anisotropy and the orientational ordering of the nematogens (or solutes).

Recently, a detailed phase diagram of tetradecyltrimethylammonium bromide (TTAB)/decanol (DeOH)/water system was determined.[2] This ternary system presents all the possible micellar shapes (hexagonal H $\rightarrow$ calamitic nematic N_C $\rightarrow$ positive biaxial nematic N_{BX}^+ $\rightarrow$ negative biaxial nematic N_{BX}^- $\rightarrow$ discotic nematic N_D $\rightarrow$ lamellar L mesophases) that may be present in noncholesteric lyotropic mesophases. The distinct biaxial mesophases with diamagnetic and optical opposite anisotropies stand out this system.

To investigate the temperature dependence of this lyotropic system, a series of representative samples at fixed water/TTAB (M_w = [H_2O]/[TTAB] ≈ 25.7) mole with decanol/TTAB (M_d = [DeOH]/[TTAB]) mole ratio ranging from 0.20 to 0.42 were prepared, characterized and studied by ^{2}H NMR. These samples were prepared with 3.0 wt. % TTAB substituted with a N-CD_3 group (TTAB-d_3) and 0.2 wt. % D_2O. ^{2}H NMR measurements were performed with a Varian Gemini 2000 spectrometer at 46 MHz in 5mm sample tubes in the temperature range from 4 to 95ºC.

Figure 1 presents a temperature dependence diagram of this series. In general, all nematic mesophases were stable between temperatures of approximately 5 and 12 ºC to temperatures of 25-45 ºC or higher. Hexagonal mesophases were more stable as lamellar mesophases availed. The variation of the deuterium quadrupolar splittings of N-CD_3

group and of HOD with temperature variation indicated the discontinuous first order nature of phase transitions in this series of samples. The N_C–H, nematic–isotropic (I), N_{BX}^+–N_{BX}^-, lamellar-isotropic phase transitions were clearly first order. Complementary X-ray experiments of nematic lyotropic mesophases are being carried out to characterize the biaxial mesophases in the transition phase region.

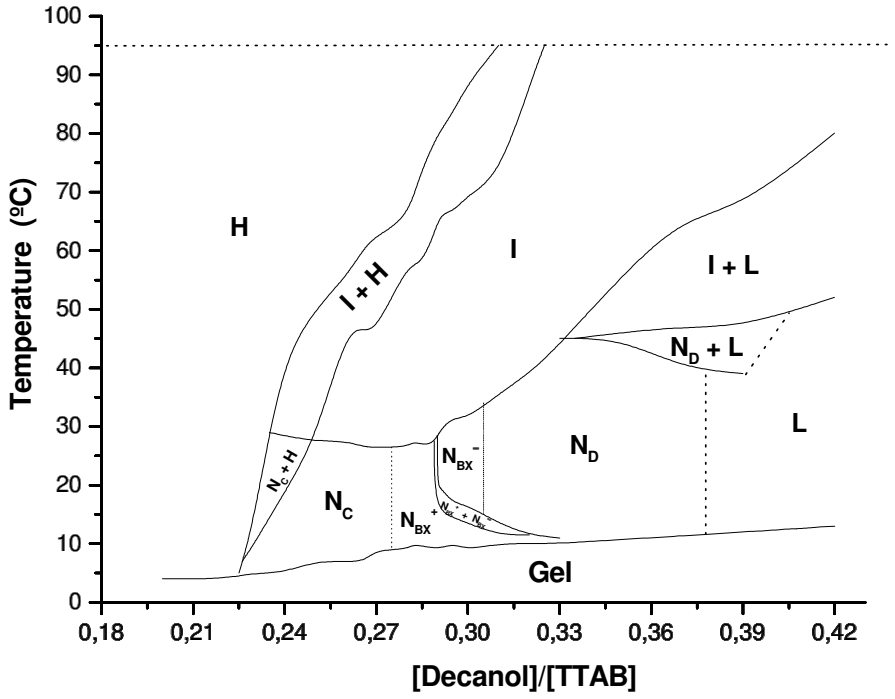

Figure 1. Temperature dependence diagram of a series of the representative mesophase samples of TTAB/DeOH/H_2O system. The water/TTAB ratio was maintained constant.

An unusual behavior was observed for nematic mesophases at higher temperatures. On increasing temperature, a more highly ordered hexagonal mesophase appears.

Our results show an interesting behavior of this system with temperature variation and represent an important contribution for understanding changes in micellar shape in lyotropic liquid crystal systems.

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References

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