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Phase diagrams of new lamellar liquid crystalline systems based on ^{2}H NMR spectroscopy data

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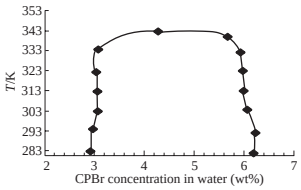
Lyotropic liquid crystals based on cetylpyridinium chloride (or bromide) and *n*-hexanol were examined by NMR spectroscopy. The partial molecule ordering, residual dipolar couplings as well as the conditions (component concentrations and temperatures) under which lamellar phases exist were determined.



Keywords: NMR, cetylpyridinium chloride, cetylpyridinium bromide, lamellar phase, *n*-hexanol.

Dipolar interaction between magnetic nuclei inside a molecule is completely averaged to zero in solutions due to the random movement of molecules. If a molecular system is dissolved in a lyotropic liquid crystal, the translational and rotational motions of molecules become anisotropic due to collisions with magnetically oriented molecular aggregates.[1,2] This molecular motion anisotropy leads to the appearance of a weak dipolar interaction between magnetic nuclei, which manifests itself in NMR spectra as residual dipolar coupling (RDC) constants.[3,4]

Nematic phases can be prepared using the mixtures of *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide, cetylpyridinium chloride (CPCl) or cetylpyridinium bromide (CPBr) and *n*-hexanol;[5,6] *n*-alkyl polyethylene glycol ethers and normal alcohols,[4,7] and *n*-alkyl polyethylene glycol ($C_{12}E_5$) and dimethyl sulfoxide $(CD_3)_2SO$ in water.[8] Under certain conditions, these systems form lamellar liquid crystalline phases (L_α), in which the planes of molecular aggregates are oriented along the magnetic field direction.[1,2]

Lyotropic liquid crystalline media make it possible to partially orient organic molecules and measure RDC values between magnetic nuclei, which can be used to determine the spatial structure of organic and bioorganic molecules.[8–12] An increase in the concentration of CPCl or CPBr in solution leads to a phase transition from a lamellar liquid crystalline phase to a micellar solution. The phase behavior (micelle formation) of an aqueous solution of CPCl in the presence of NaCl and C_9–C_{13} *n*-alcohols was studied depending on alcohol and salt concentrations and temperature.[13] The CPCl/NaCl system exists in the form of micelles, as confirmed by dynamic light scattering. The alcohol chain length affects micelle formation in this system.[13] Thus, micelles based on CPCl in the presence of NaCl and long-chain alcohols can be used as cell surface models to study the interaction of organic or bioorganic systems with cell surface models.[14–18]

In this work, we studied lyotropic liquid crystalline systems and their properties by NMR spectroscopy to determine the limits of existence of lamellar phases (component concentrations and solution temperature) for mixtures based on cetylpyridinium chloride (or bromide) and hexanol in water, which were prepared as described previously.[4–8]

The ^{2}H NMR spectra† (46.1 MHz) of lamellar liquid crystalline phases based on CPCl (or CPBr) and hexanol and an alternative system based on *n*-alkyl polyethylene glycols, octanol and water in isotropic and anisotropic states were recorded.

Lyotropic systems based on charged CPCl or CPBr, normal hexanol, water and a corresponding salt (NaCl or NaBr) were described,[4,5] but no phase diagrams of these liquid crystal systems were determined by NMR spectroscopy so far. An ordered lamellar phase was detected by the quadrupole splitting of a ^{2}H NMR signal of deuterated water in liquid crystal systems,[3] which appeared due to different orientations of quadrupole deuterium nuclei in water molecules (Figure 1). After placing a lyotropic liquid crystal sample in a magnet at room temperature, a quadrupole splitting of units to tens hertz appeared within several minutes.

We studied the effects of temperature and CPCl (CPBr) concentration in deuterated water on the observed splitting in the ^{2}H NMR spectrum when the systems were in a liquid crystalline state (Figure 2).

The temperature dependence of the quadrupole splitting of D_2O signal in the ^{2}H NMR spectra of the CPBr/*n*-hexanol/water/

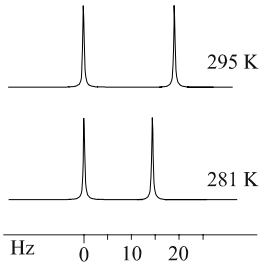


Figure 1 Quadrupole splitting of deuterated water signals in ^{2}H NMR spectra at two temperatures.

† ^{2}H NMR spectra were acquired on a Varian Unity-300 NMR spectrometer with 10–15° pulses, and delays between pulses were 1–2 s; the spectrum width was 50 ppm; the number of accumulations varied from 40 to 100; digital exponential filtering was used with a line broadening factor of 2–4 Hz. The spectrometer was equipped with a VTC-4 temperature control unit. The internal field stabilization relies on ^{2}H lock signal.

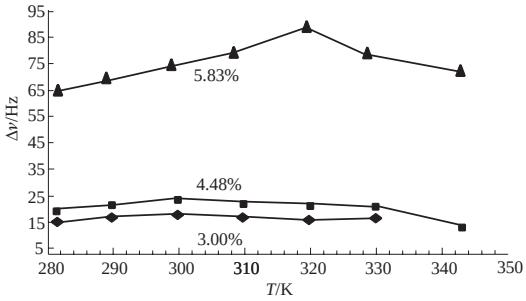


Figure 2 The temperature dependence of quadrupole splitting in the ^{2}H NMR spectrum of deuterated water for the cetylpyridinium bromide/*n*-hexanol/water/NaBr system; CPBr concentrations in water, 3.00, 4.48, and 5.83 wt%; CPBr : hexanol molar ratio, 1.31; and NaBr concentration, 30 mM.

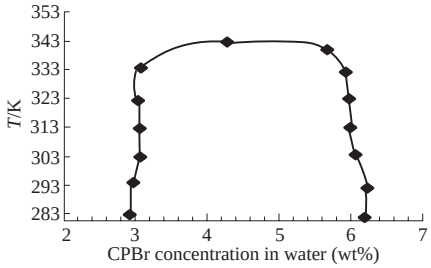


Figure 3 Phase diagram of the lamellar state of CPBr/*n*-hexanol; the CPBr/hexanol molar ratio, 0.203; NaBr concentration in water, 30 mM.

NaBr and CPCl/*n*-hexanol/water/NaCl liquid crystal systems can be explained based on the inverse temperature dependence of the magnetic susceptibility of an ensemble of magnetic particles (see Figure 2). A similar dependence is described by the Curie law,[19] according to which the degree of magnetization of dia- and paramagnets is inversely proportional to temperature at a constant external magnetic field.

Note that no significant differences between the effects of concentration and temperature on quadrupole splitting were observed in the ^{2}H NMR spectrum of D_2O in these two systems. Previously, we studied the linear dependence of quadrupole splitting in the ^{2}H NMR spectra of D_2O in *n*-alkyl polyethylene glycols and octanol systems on the concentration of C_8E_5 or $C_{12}E_5$.[4] An increase in the concentration led to an increase in the number of lamellar particles in the solution and, in turn, to an increase in the anisotropic part of the total volume and a corresponding contribution to the observed quadrupole splitting.

Figure 3 shows the effects of CPBr concentration in water and temperature on phase behavior of the CPBr–hexanol system. Area inside a contour corresponds to conditions under which the mixture existed as a lamellar L_α phase. An analogous diagram was obtained for the CPCl/hexanol/water/NaCl system.

A comparison between the phase behaviors of CPBr(CPCl)/*n*-hexanol/water/NaBr and previously studied C_8E_5($C_{12}E_5$)/octanol/water liquid crystal systems[4] showed that the former systems have a wider contour for the existence of a lamellar liquid crystal phase due to a wider temperature range; therefore, they are more efficient.

Thus, the systems based on cetylpyridinium chloride (or bromide)–hexanol and water work in wide ranges of temperatures and concentrations, and they can be efficient lyotropic liquid crystal media for the partial alignment of organic molecules and the measurement of the constants of residual dipole–dipole interactions between magnetic nuclei.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.044.

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