



# Diagrams of the Lamellar Liquid Crystal Phase in Systems Based on n-Alkyl-poly (ethylene) Glycols (C<sub>8</sub>E<sub>5</sub> and C<sub>12</sub>E<sub>5</sub>) and n-Octanol Determined by <sup>1</sup>H NMR Spectroscopy

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## Abstract

The two lyotropic liquid crystalline media based on n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub> and C<sub>12</sub>E<sub>5</sub>) and n-octanol for partial alignment of organic molecules and measured residual constants of dipole-dipole interaction between magnetic nuclei were studied. The paper presents the results of NMR studies of lyotropic properties of considered liquid crystalline media, and the boundaries (diagrams) of the existence of ordered lamellar phases (component concentrations, solution temperature) were determined.

**Keywords** NMR · N-alkyl-poly (ethylene) glycol · Lamellar phase · N-octanol

## 1 Introduction

It is known that in solutions, the dipole-dipole interaction between magnetic nuclei inside a molecule is completely averaged due to the random movement of molecules. If the molecular system is dissolved in a lyotropic liquid crystalline media, then the translational and rotational motion of the molecules stopped to be isotropic, as a result of a collision with magnetically oriented molecular formations [1, 2]. This anisotropy in the motion of molecules leads to the appearance of a “weak” dipole-dipole interaction between magnetic nuclei, which shows itself in the NMR spectra as residual dipole-dipole interaction constants, wherein no broadening of the NMR signals is observed [1, 3].

The nematic phase can be created on the basis of mixtures of n-cetyl-n,n-trimethylammonium, chloride or bromide of cetylpyridinium and n-hexanol [4, 5]; n-alkyl-poly (ethylene) glycols and normal alcohols [6], n-alkyl-poly (ethylene) glycol (C<sub>12</sub>E<sub>5</sub>) and dimethyl sulfoxide ((CD<sub>3</sub>)<sub>2</sub>SO) in water [7]. Under some conditions, these systems form lamellar liquid crystalline phases, designated as L<sub>α</sub>, in which the planes of

molecular formations are oriented along the direction of the magnetic field [1, 2] (the gel to liquid crystal phase transition), consisting of double layers that can be separated far enough from each other by adding solvent (Fig. 1).

The lyotropic liquid crystalline media partially orient organic molecules and let to measure the residual constants of the dipole – dipole interaction between magnetic nuclei, based on which the spatial structure of organic and bioorganic compounds can be determined (for example, see [7–15]). It is also known that micelles containing diacyllipid-polyethylene glycol in complex with <sup>111</sup>In or Gd metal ions are used as contrast agents for experimental gamma and MR imaging of various components of the lymphatic system [16, 17].

This paper presents original NMR studies of lyotropic liquid crystalline medias and their properties, which allowed us to determine the boundaries (diagrams) of the existence of lamellar phases (component concentrations, solution temperature) for mixtures based on n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub> and C<sub>12</sub>E<sub>5</sub>), n-octanol, and water.

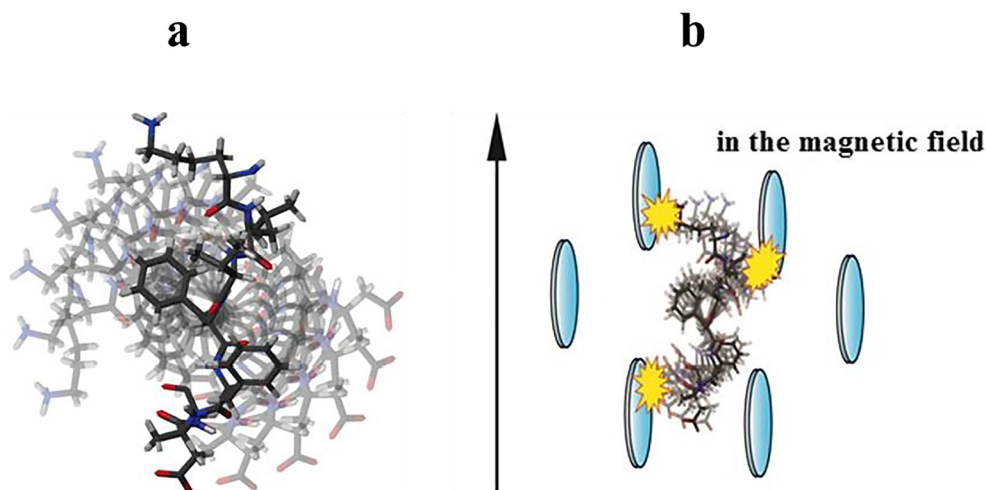
## 2 Materials and Methods

<sup>1</sup>H (300 MHz) and <sup>2</sup>H (46.05 MHz) NMR experiments of lamellar liquid crystalline phases based on n-alkyl-poly (ethylene) glycols, octanol, and water in isotropic and anisotropic states were carried out using NMR spectrometer “Unity 300” (“Varian” company). The spectrometer is equipped with a VTC-4 temperature prefix and works in the internal

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**Fig. 1** The demonstration of the mechanism of residual dipole-dipole interaction: **a** in solutions ( $^1J_{IJ} = 0$ ,  $D^J = 0$ ); **b** in lyotropic liquid crystalline media ( $^1J_{IJ} + D^J$ ,  $D^J = f(\theta, \phi, r^{-3}_{IJ})$ ).  $^1J_{IJ}$  and  $D^J$  are the scalar and dipole-dipole constants of spin-spin interaction;  $\theta$ ,  $\phi$ , and  $r$  are the parameters describing the spatial location of the internuclear vector  $\mathbf{I, J}$  relative to the external magnetic field [1]



stabilization mode by deuterium resonance line. The  $^1\text{H}$  NMR spectra were recorded to control the chemical purity of the studied mixtures. The pulses turning the magnetization vector by  $10^\circ$ – $15^\circ$  pulses and 2 s delays between pulses were used to obtain  $^1\text{H}$  NMR spectra; spectrum width 15 ppm; the number of scans 100; digital filtering was not applied. The  $^2\text{H}$  NMR spectra were recorded with  $10^\circ$ – $15^\circ$  pulses, 2 s delays between pulses, spectrum width 50 ppm, the number of scans from 40 to 100 and digital exponential filtering with the parameter ( $lb$ ) equal to 2–4 Hz. Studied samples were solutions of n-alkyl-poly (ethylene) glycols and octanol in water. The corresponding concentrations of the studied systems and the temperature of the solutions are shown in the figures. Chemical shifts in  $^1\text{H}$  NMR spectra were counted from the resonance lines of the reference liquids (TMS). Liquid crystalline medias based on n-alkyl-poly (ethylene) glycols and octanol in water were prepared as described in [4–7].

### 3 Results and Discussion

It is known that the orientation of particles is due to the stereospecific interaction of the studied organic or bioorganic molecules with strongly anisotropic, disk-shaped particles (bicelles, membrane fragments) or rod-shaped (phages, viruses) forms that are well oriented under the magnetic field. For weak orientation of the molecules, traditional lyotropic liquid crystalline systems, such as water-alcohol solutions of n-alkyl-poly (ethylene) glycols, quaternary ammonium salts, pyridinium, etc., were tried.

The study of lamellar liquid crystalline phases based on n-alkyl-poly (ethylene) glycols and normal alcohols in water is carried out by NMR. It should be noted that such studies using the NMR method are not described in the literature.

The existence of an ordered lamellar  $L_\alpha$  phase was confirmed by the polarized microscopy pictures (Fig. 2) and by the observation of quadrupole splitting of the  $^2\text{H}$  NMR signal

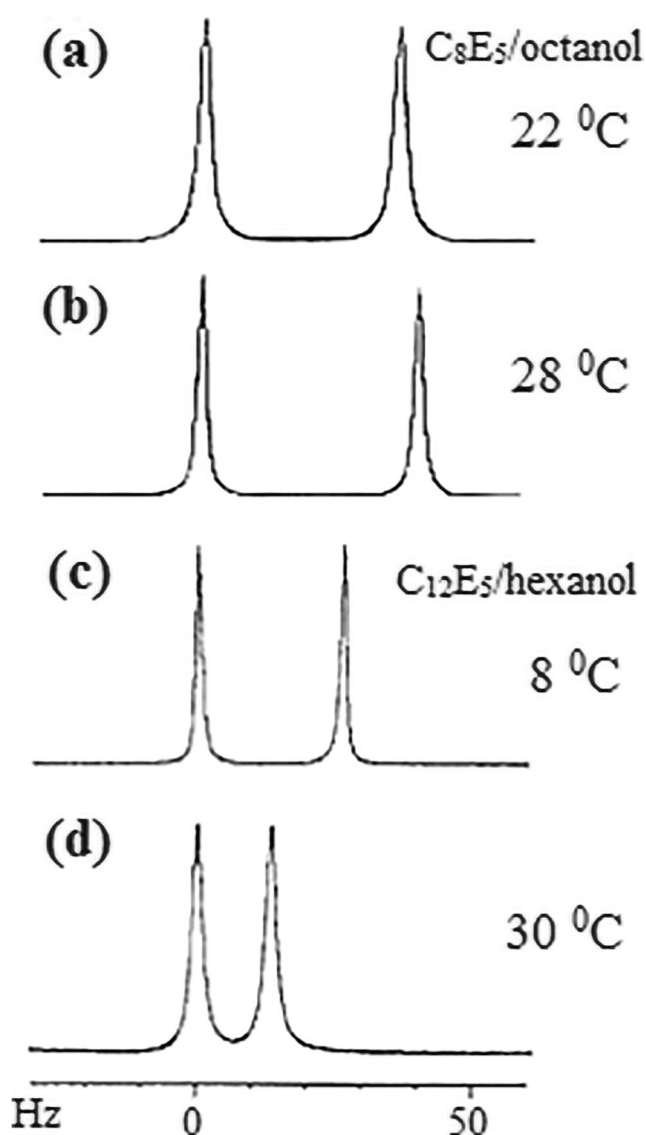
of deuterated water ( $\text{D}_2\text{O}$ ), which is part of liquid crystalline systems [3], as a consequence of the different orientations of the quadrupole deuterium nuclei that make up the water molecule. After placing a sample containing the lyotropic liquid crystalline system in the magnet at room temperature, a quadrupole splitting of  $^2\text{H}$  NMR signal from units to tens of Hz



**Fig. 2** The polarized microscopy pictures for two lyotropic systems based on  $\text{C}_8\text{E}_5$  (a) and  $\text{C}_{12}\text{E}_5$  (b)

appears for several minutes. An increase of solution temperature does not change the shape of the  $^2\text{H}$  NMR signal, and at some temperature or higher, the  $^2\text{H}$  NMR signal of  $\text{D}_2\text{O}$  is observed as a singlet. Lowering the solution temperature returns a quadrupole splitting of  $^2\text{H}$  NMR signal of deuterated water (Fig. 3).

Figure 3 shows the observed quadrupole splitting in the  $^2\text{H}$  NMR spectrum of deuterated water in two lyotropic systems based on n-alkyl-poly (ethylene) glycols ( $\text{C}_8\text{E}_5$  and  $\text{C}_{12}\text{E}_5$ , where  $\text{C}_n$  is the number of carbon atoms in the hydrocarbon chain and  $\text{E}_n$  is the number of glycol fragments in this molecular system) and normal alcohols (octanol and hexanol). Such splitting is averaged between different signals of deuterium water (the contribution of



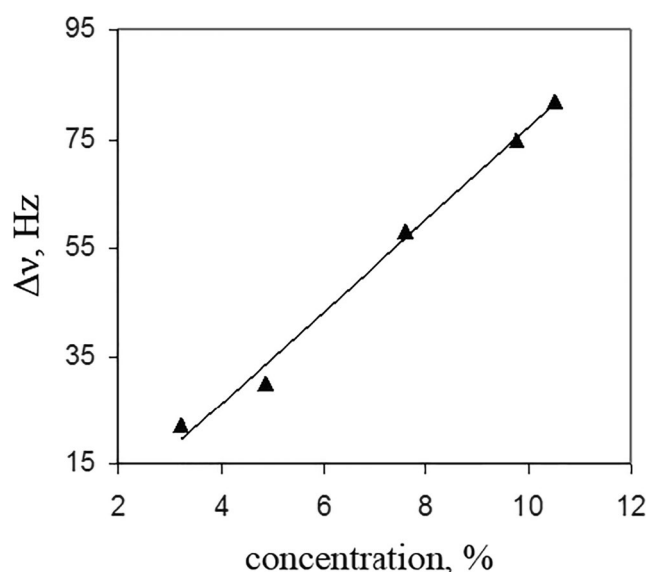
**Fig. 3** Observed quadrupole splitting of the deuterated water signal in two lyotropic systems based n-alkyl-poly (ethylene) glycols ( $\text{C}_8\text{E}_5$  and  $\text{C}_{12}\text{E}_5$ ) and normal alcohol (octanol) in the  $^2\text{H}$  NMR spectra at two temperatures [6]

the quadrupole moment of deuterium) located in the anisotropic part of the medium and the singlet signal of deuterium in the isotropic part.

Studied liquid crystalline lyotropic systems are mixtures of n-alkyl-poly (ethylene) glycols ( $\text{C}_8\text{E}_5$  or  $\text{C}_{12}\text{E}_5$ ), normal alcohol (octanol), and water. The mixtures are characterized by the weight (percent) content of n-alkyl-poly (ethylene) glycols in water and the molar ratio of n-alkyl-poly (ethylene) glycols and normal alcohols. The literature describes mixtures of  $\text{C}_8\text{E}_5$  (octanol and water), as well as  $\text{C}_{12}\text{E}_5$  (hexanol and water) [6]. However, phase diagrams of the liquid crystalline state for these systems are not given there. A mixture of  $\text{C}_{12}\text{E}_5$  (octanol and water) was developed and described by us for the first time. In this work, we present NMR study of two systems: (a)  $\text{C}_8\text{E}_5$  (octanol and water) and (b)  $\text{C}_{12}\text{E}_5$  (octanol and water).

We also carried out a comparative analysis of phase diagrams of liquid crystalline states for these two mixtures. As a determining test for the existence of ordered phase, we used the observation of quadrupole splitting of  $^2\text{H}$  NMR signal of  $\text{D}_2\text{O}$ , which is part of our liquid crystalline system.

Studies of the effect of n-alkyl-poly (ethylene) glycols ( $\text{C}_8\text{E}_5$  or  $\text{C}_{12}\text{E}_5$ ) concentrations in water on the observed quadrupole splitting of  $^2\text{H}$  NMR signal of deuterated water were carried out when the systems were in the liquid crystalline lyotropic state. In all cases, the dependences of quadrupole splitting in the  $^2\text{H}$  NMR spectrum of  $\text{D}_2\text{O}$  for n-alkyl-poly (ethylene) glycols and octanol systems versus the concentration of  $\text{C}_8\text{E}_5$  or  $\text{C}_{12}\text{E}_5$  were linear (Fig. 4). This explained by the fact that an increase in the concentration leads to an increase in the number of



**Fig. 4** The dependence of the quadrupole splitting ( $\Delta\nu$ , Hz) of  $\text{D}_2\text{O}$  signal in the  $^2\text{H}$  NMR spectrum versus  $\text{C}_{12}\text{E}_5$  concentration in water for n-alkyl-poly (ethylene) glycol ( $\text{C}_{12}\text{E}_5$ ) and octanol system at 288 K;  $r(\text{C}_{12}\text{E}_5/\text{octanol}) = 0.536$

lamellar particles in the solution, which in turn leads to an increase in the anisotropic part of the total volume and the corresponding contribution to the observed quadrupole splitting.

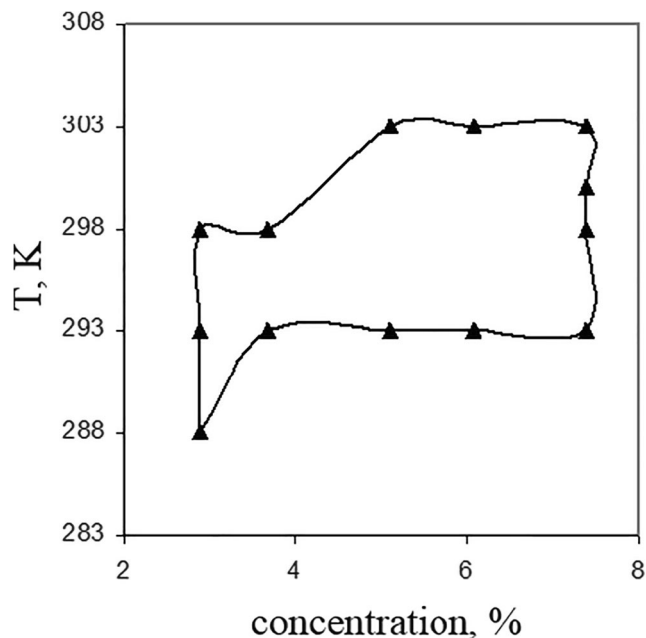
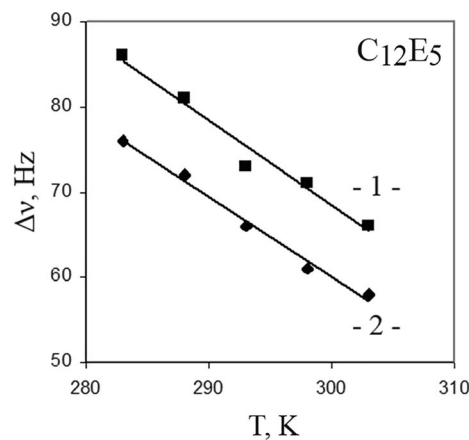
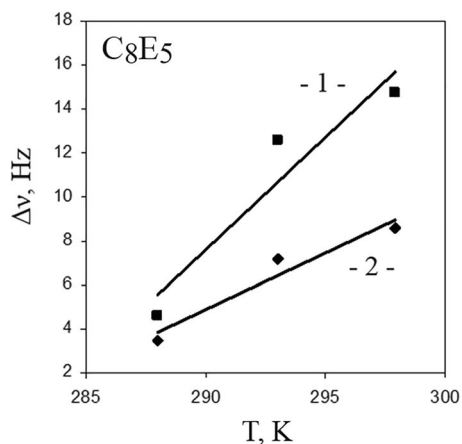
Then the temperature effect on the observed quadrupole splitting of D<sub>2</sub>O signal in the <sup>2</sup>H NMR spectrum in systems of n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub> and C<sub>12</sub>E<sub>5</sub>) and octanol in water when the media was also in the liquid crystalline lyotropic state was studied (Fig. 5).

C<sub>8</sub>E<sub>5</sub>, C<sub>12</sub>E<sub>5</sub> concentrations in water were 3.1%; r(C<sub>8</sub>E<sub>5</sub>/octanol, C<sub>12</sub>E<sub>5</sub>/octanol) = 1.06 (for line 1) and 0.92 (for line 2)

Figure 5 shows the linear temperature dependence of the quadrupole splitting of D<sub>2</sub>O signal in the <sup>2</sup>H NMR spectrum for the systems of n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub>, C<sub>12</sub>E<sub>5</sub>) and octanol. The observed dependence for the system C<sub>12</sub>E<sub>5</sub> (octanol and water) is explainable from the point of the inverse temperature dependence of the magnetic susceptibility of an ensemble of magnetic particles. A similar dependence is described by the Curie law [18], which postulates that with a change in temperature and at a constant external magnetic field, the degree of magnetization of magnets (dia- and para-) is inversely proportional to temperature. The last one, in turn, leads to a decrease in the fraction of the anisotropic part of the total volume and, accordingly, the contribution to the observed quadrupole splitting. On the other hand, the dependence for the system C<sub>8</sub>E<sub>5</sub> (octanol and water) was opposite, which can be explainable by competitive contributions, both by the temperature dependence of the magnetic susceptibility of the system and by a change in the ratio of the fractions of deuterated water molecules (isotropic and anisotropic part of the molecules) with temperature.

The study of the behavior of systems based on n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub> or C<sub>12</sub>E<sub>5</sub>) (octanol and water) by <sup>2</sup>H NMR revealed the boundaries of the existence of lamellar L<sub>α</sub> phases in the “temperature – concentration of C<sub>8</sub>E<sub>5</sub> or C<sub>12</sub>E<sub>5</sub>” coordinates. Figures 6 and 7 shows

**Fig. 5** The dependences of the quadrupole splitting ( $\Delta\nu$ , Hz) of D<sub>2</sub>O signal in the <sup>2</sup>H NMR spectrum versus solution temperature for n-alkyl-poly (ethylene) glycols (C<sub>8</sub>E<sub>5</sub>, C<sub>12</sub>E<sub>5</sub>) (octanol and water system);

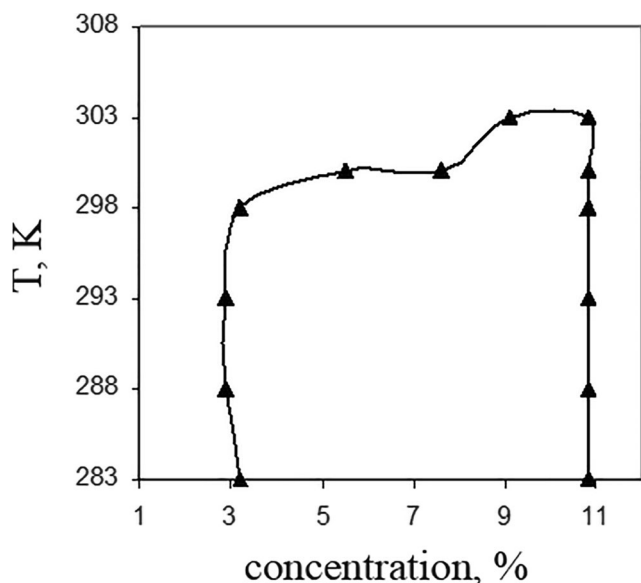


**Fig. 6** The effects of C<sub>8</sub>E<sub>5</sub> concentration and temperature on the phase behavior of the n-alkyl-poly (ethylene) glycol (C<sub>8</sub>E<sub>5</sub>)—octanol and water system; r(C<sub>8</sub>E<sub>5</sub>/octanol) = 1.06. Inside the marked line, the system is in the nematic L<sub>α</sub> phase

phase diagrams of the existence of liquid crystalline state for the studied systems.

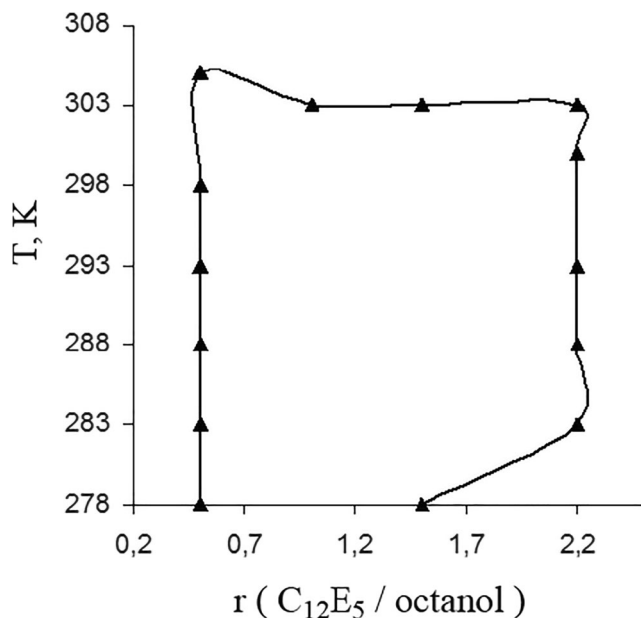
Comparing these two phase diagrams, it should be noted that our proposed system of n-alkyl-poly (ethylene) glycol (C<sub>12</sub>E<sub>5</sub>) (octanol and water) is more convenient because it is efficient in a wider range of temperatures and concentrations than the n-alkyl-poly (ethylene) glycol (C<sub>8</sub>E<sub>5</sub>) (octanol and water system).

<sup>2</sup>H NMR spectroscopy also revealed the boundaries of the existence of lamellar phases of the n-alkyl-poly (ethylene) glycol (C<sub>12</sub>E<sub>5</sub>) (octanol and water system) in the “temperature - molar ratio (r) of C<sub>12</sub>E<sub>5</sub> to octanol” coordinates (Figs. 8 and 9).

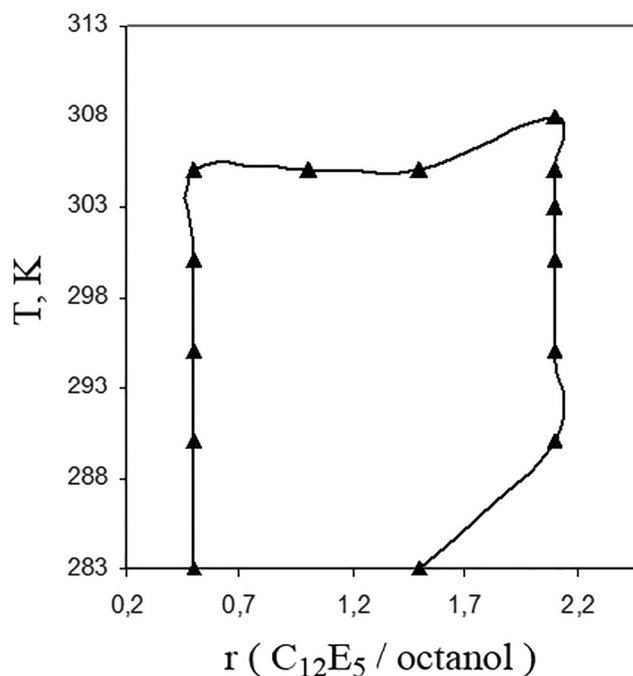


**Fig. 7** The effects of  $C_{12}E_5$  concentration and temperature on the phase behavior of the n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water system;  $r(C_{12}E_5/\text{octanol}) = 1.22$ . Inside the marked line, the system is in the nematic  $L_\alpha$  phase

The analysis of two presented phase diagrams means that our proposed system of n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water—retains its liquid crystalline properties in a wide range of the molar ratio of  $C_{12}E_5$  to octanol.



**Fig. 8** The effects of temperature and molar ratio ( $r$ )  $C_{12}E_5$  to octanol on the phase behavior of n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water system;  $C_{12}E_5$  concentration in water was 3.1% (w/w %). Inside the marked line, the system is in the nematic  $L_\alpha$  phase



**Fig. 9** The effects of temperature and molar ratio ( $r$ )  $C_{12}E_5$  to octanol on the phase behavior of n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water system;  $C_{12}E_5$  concentration in water was 7.3% (w/w %). Inside the marked line, the system is in the nematic  $L_\alpha$  phase

## 4 Conclusions

The system of n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water—is more convenient, because it is efficient in a wider range of temperatures and concentrations than the system of n-alkyl-poly (ethylene) glycol ( $C_8E_5$ ) (octanol and water). It was also shown that the n-alkyl-poly (ethylene) glycol ( $C_{12}E_5$ )—octanol and water system—retains its liquid crystalline properties in a rather wide range of the molar ratio of  $C_{12}E_5$  to octanol.

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## Compliance with Ethical Standards

**Conflict of Interest** Authors have no conflict of interest.

**Research Involving Humans and Animals Statement** None.

**Informed Consent** None.

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