Dynamic Processes during Phase Transitions and Structural Transformations in Oriented Liquid Crystal Systems

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Abstract: The dynamic parameters of liquid crystal (LC) systems in liquid crystalline and solid phases, such as orientation relaxation time and ordering of molecules, were studied by ESR technique with the help of spin probe. It was determined that, depending on the LC system, the rotatory diffusion correlation time (τ_c) changes in the same way as the rotational anisotropy. For investigated LC systems in liquid state $10^{-11} < \tau_c < 10^{-9} sec$ was found. In a frozen LC system, depending on the particular molecular structure of the system's component, the high molecular mobility of $\tau_c = 10^{-9} sec$ was managed to obtain. It's shown that such a high mobility of molecules, far beyond the LC—Crystal transition point, is caused by the structural features of component's molecules that lead to an increase in system polarity and changes in the activation energy for rotational motion of molecules.

Keywords: nematic and smectic liquid crystals, molecular structure, phase transition, ESR relaxation, molecular interactions, correlation time.

The aim of the study was to obtain numerical values of such dynamic parameters, as orientation relaxation time and ordering, which would offer new technical solutions that would expand the field of practical applications of liquid crystals (LC). In this paper, we managed to obtain high mobility of molecules in binary systems of nematogens in the solid phase.

As research objects for the present study we have chosen nematic LCs satisfying the following conditions:

a) molecules of the studied compounds should have electron-donor-acceptor and strongly polar end groups;

b) molecules of the selected compounds must have long alkyl chains to reveal the role of lateral interactions and steric factors in the mechanism of induction of the smectic phase [1];

c) in binary systems, the compounds must be unlimitedly mutually soluble;

d) selected objects should be of interest in terms of practical application.



Fig. 1. Structural Formula of Nitroxyl Radical

The mobility (rotatory diffusion) and ordering of molecules were investigated by electron spin resonance (ESR) technique with the help of spin probe (Fig.1) in such crystals, as 4-n-buthyl-4-n-heptanoiloxyazoxybenzene {I}; n-cyanophenil ether of n-heptylbenzoic acid {II}; n-cyanophenil ether of n-heptylbenzoic acid {II}; n-cyanophenil ether of n-heptylbenzoic acid {II}, (which possess nematic phase falling in the temperature range of $35-76^{\circ}C$; $44-58^{\circ}C$; and $44-56^{\circ}C$, accordingly) (Fig.2,3). Their systems: {I}/{II}; {I}/{III} with different concentration of components were also studied with the abovementioned technique. ESR measurements were carried out in the temperature range of $-27^{\circ}C - +70^{\circ}C$, which is far beyond LC→Crystal transition point.



Fig. 2. Phase diagram $\{II\}/\{I\}$

Fig.3. Phase diagram {III}/{I}

The use of a spin probe is based on the analysis of changes in the line widths of the ESR spectra caused by rotational and translational diffusion of radicals. As we know from [2-4], the mobility of a radical depends on the mobility of environmental molecules. Therefore, the radical is a kind of molecular sensor of structural and dynamic information about the local environment. The paramagnetic resonance spectra of nitroxyl radicals are sensitive not only to the molecular movements, but also to the nature of the medium in which they are dissolved. In this connection, the magnetic parameters of the radical are very sensitive functions of the electronic distribution in the molecule, and therefore they are affected by perturbations from the environment. These perturbations become especially strong in polar solvents due to the specific interaction of such solvents with a lone pair of electrons on the oxygen atom of the nitroxyl radical.

ESR measurements were carried out on a radio spectrometer P \ni -1301 in a microwave region of 9 *GHz*. To avoid the distortion of line shape, the amplitude of the high frequency modulation was set to be several times smaller than the line width, and the microwave power was chosen to be so small that the ESR signal was far from saturation. The magnetic parameters were measured with an accuracy of $\pm 0, 4G$. To minimize line broadening, due to the dipole – dipole interaction between the molecules of the spin probe, the concentration of the radical was determined to be as low as ~ $10^{-4} mol/l$. The samples under study were prepared by thoroughly mixing the LC components in the isotropic phase to obtain a homogeneous solution of the system. Uniformly oriented samples were obtained by the application of a sufficiently strong magnetic field ~ 3000 G. During the experiment, the samples were heated by a hot air stream, blowing through a quartz tube passing through the resonator of the spectrometer. At low temperatures (from ambient temperature to $27^{\circ}C$) spectra were recorded by blowing liquid nitrogen vapor through the resonator. The accuracy of temperature measurement was $\pm 0.1^{\circ}C$.

As known, the position and hyperfine splitting of the resonance lines of the spin are associated with the ordering of molecules of investigated objects and their dynamic properties related to the width and shape of these lines. Our analysis of the ESR spectra is based on well-developed theory of spin relaxation [5-7]. According to this theory the width of spectra $T(m)^{-1}$ is defined by the equation [5, 8]:

$$T(m)^{-1} = L + Bm + Cm^2$$
(1)

where, m = -1, 0, +1 -is nuclear quantum number characterizing the hyperfine splitting component; parameters *L*, *B*, *C* depend on the magnitude of magnetic anisotropy and the rate of molecular reorientation.

To simplify the analysis of ESR spectra, it is assumed that the rotational diffusion tensor is axially symmetric. The laboratory coordinate system (X, Y, Z) is chosen so that the Z – is the axis of symmetry and is directed by director. X, Y – axes are in the plane perpendicular to the Z – axis. The main values of the hyperfine splitting constant tensor: $A_{xx} = A_{yy} = A_{\perp}, A_{zz} = A_{\parallel}$.

 A_{\perp} - is the value of the hyperfine splitting constant of the experimental spectrum when magnetic field is normal to the Z axis; A_{\parallel} - is the value of the hyperfine splitting constant of the experimental spectrum when magnetic field is directed along the Z axis. The molecular coordinate system (X',Y',Z') relates to radical fragment as shown on Fig.1. In this coordinate system \hat{A} and \hat{g} tensors can be considered diagonal [9]. $A_{x'x'} = 31 G$, $A_{y'y'} = 5.2 G$, $A_{z'z'} = 5.2 G$ are the main values of the hyperfine splitting constant of radical in the molecular coordinate system.

For further calculations it is necessary to establish the orientation of Z – axis on the molecular coordinate system (X', Y', Z'). The idea of solving this problem is to compare the theoretically calculated ratio B/C with the experimentally derived (based on the analysis of line width) value $(B/C)_{exp}$. The B/C calculation results and their corresponding $(B/C)_{exp}$ experimental values are shown in Table1. $(B/C)_{exp}$ is observed to best coincide with the corresponding calculated value for the case when the Z – axis of the rotational diffusion tensor coincides with the Y' – axis of the molecular coordinate system. Small deviations between these quantities, apparently, are associated with various fluctuations, leading to a non-strict coincidence of Z – and Y' – axes .Thus, the radical in the LC medium is oriented in such way

that the Y' – axis of the molecular coordinate system becomes parallel to the Z – axis of the laboratory coordinate system.

Table1. Calculation results of the B/C for the binary systems with different orientations of the rotational diffusion tensor in the molecular coordinate system

Mol%	°C	(B/C)exp	(B/C) _{cal}	(B/C) _{cal}	(B/C) _{cal}
			Z=X'	Z=Y'	L=L'
100%{I}	35	0,29	0,54	0,29	0,24
	40	1,75	1,04	1,18	2,33
	48	1,13	1,10	1,40	2,49
	60	0,28	0,95	0,35	0,30
85%{II}/15%{I}	35	1,00	1,93	1,09	
	40	0,39	0,48	0,43	
	45	1,14	1,02	1,19	
	55	4,25	0,48	4,12	
70%{II}/30%{I}	30	0,40	0,50	0,42	0,34
	50	0,34	0,35	0,32	0,36
	60	1,97	1,15	1,81	
50%{II}/50%{I}	35	0,53	0,51	0,53	0,64
	50	0,61	0,56	0,63	0,64
	60	0,50	0,43	0,64	0,63
25%{II}/75%{I}	35	0,39		0,35	0,43
	45	0,58		0,53	0,63
	60	1,21		1,19	2,40
100%{II}	35	0,43	0,37	0,42	0,34
	40	1,13	1,05	0,11	2,40
	50	5,23	1,07	5,33	3,03
	60	0,49	0,51	0,44	0,64

The degree of ordering S and the angle θ between Z' – axis and the direction of magnetic field, were calculated using the following expressions [10]:

$$S = (\langle A \rangle - A) / \left[(A_{z'z'} - A_{x'x'}) \cos^2 \theta + A_{x'x'} - A \right]$$
(2)

$$\cos^{2} \theta = \frac{\left[\left(A_{x'x'} - A \right) (< g > -g) - \left(g_{x'x'} - g \right) (< A > -A) \right]}{\left[\left(g_{z'z'} - g_{x'x'} \right) (< A > -A) - (< g > -g) \left(A_{z'z'} - A_{x'x'} \right) \right]}$$
(3)

where $A = \frac{1}{3} (A_{x'x'} + A_{y'y'} + A_{z'z'}), g = \frac{1}{3} (g_{x'x'} + g_{y'y'} + g_{z'z'}), <A>$ and <g> - are experimental

values of the hyperfine interaction constants and g – factor in a liquid crystal medium.

As follows from Table 2, at a given temperature in the nematic phase the degree of ordering in {I} is greater than that in {II} and {III}. At the same temperature in the nematic phase the degree of ordering in $\{I\}/\{II\}$ and $\{I\}/\{III\}$ systems is greater than that in pure $\{II\}$ and $\{III\}$. In the range of temperatures when the systems $\{I\}/\{II\}$ and $\{I\}/\{III\}$ are in the smectic phase their degree of ordering is less than that in pure $\{II\}$ and $\{III\}$.

Mol %	°C	S
100% { II }	50	0,56
100% { III }	50	0,54
85%{II}/{I}	45	0,58
70% {II}/30% {I}	40	0,45
70% {II}/30% {I}	50	0,61
70% {III}/30% {I}	40	0,50
70% {III}/30% {I}	50	0,59
50% {II}/50% {I}	40	0,38
50% {II}/50% {I}	60	0,45
50% {III}/50% {I}	40	0,41
50% {III}/50% {I}	60	0,46
25% {II}/75% {I}	40	0,11
25% {II}/75% {I}	50	0,16
25% {III}/75% {I}	40	0,14
25% {III}/75% {I}	50	0,18
100% {I}	50	0,68

Table 2. Calculated values of the ordering parameter S.







ESR spectra of the mentioned systems in the liquid state represents a well-resolved triplet (Fig. 4, 5, 6). The analyses of ESR spectra shape and width showed that the rotatory diffusion correlation time was $10^{-11} < \tau_c < 10^{-9}$ sec in the liquid state. It was determined that the τ_c changes in the same way as the rotational anisotropy, depending on the system.

Remarkable reduction in the rotatory diffusion rate parallel to the decreasing temperature was observed in the abovementioned {I}, {II}, {III} LCs. The ESR spectra component, corresponding to m = -l, almost completely disappeared at the LCs' freezing temperature (Fig.7, 8, 9).



Fig.8. ESR spectrum of $\{II\}$ at $+6^{\circ}C$



At the same time, this rate was found to be considerably changed when {I} was added to {II} or {III}. In these systems the ESR spectra component, corresponding to m = -l, was clearly observed during freezing. In frozen systems, high molecular mobility of $-\tau_c = 10^{-9}$ sec was found to be preserved up to $t = -20^{\circ}C$ (Fig. 11). Such a high mobility of molecules far beyond the LC \rightarrow Crystal transition point indicates that in the solid phase these systems are either in the gas crystalline or glassy state, where the anisotropic rotation around the long axes of the molecules is preserved.



at +19°C

F**ig.11.** ESR spectrum of 54% {I}/46% {II at – 19°C

The mechanism of de-association and the formation of new associates presented in [11] makes the understanding of the "longevity" of the rotational degrees of freedom in the {II}/{I} system possible. This "longevity" is caused by the structural features of component molecules that lead to an increase in system polarity. The change in the splitting constant depending on the concentration of {I} (splitting constant increases with the increase of the number of the {I} molecules in system {II}/{I}[11]) serves as a confirmation of the increase in the system polarity. Changes in the activation energy for rotational motion can reflect the changes in the dynamic molecular structure experienced by the probe molecule as the LC undergoes phase transitions. According to [12, 13], the pair interaction energy in {II}{II} is greater than in {II}{I}. Indeed, the de-associative effect of {I} leads to the fact that the paired associates of {II} molecules are destroyed, and the activation energy of rotation in this system is significantly reduced before the new mixed associates are formed. These are equilibrium processes depending on the concentration of various types of the components of a LC system. This substantially complicates the pattern of the relationship between the splitting constant of the ESR spectra and the factors affecting it.

Conflict of Interest

There is no conflict of interest.

Author Contributions

Author L.S. Bezhanova invented and developed the experiment, carried out theoretical calculations. Authors L.S. Bezhanova and A.K. Atanesyan participated in data processing and in the writing of the text.

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