RHEOLOGICAL PROPERTIES OF LIQUID CRYSTAL 4-PENTYL 4′-CYANOBIPHENIL

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Rheological properties of liquid crystal 4-pentyl 4'-cyanobiphenyl (5CB) were investigated using the picnometer technique and method of capillary viscometer and Stokes method in temperature interval from 298 to 333 K. Experimental data reveal a non-monotonic temperature behavior of the kinematics viscosity coefficient. It because that viscosity consist from regular and fluctuating parts. The fluctuating part is determined by anomaly development of order parameter fluctuations in the vicinity of the phase transition point. In nematic and isotropic phase it obeys power dependence. In nematic phase value of exponent of power is close to the value of critical parameter of isothermal compressibility for a liquids in the vicinity of critical point. In isotropic phase value of exponent of power is close to the critical parameters for correlation radius. It was shown that in the vicinity of phase transition point viscosity attains finite value.

Keywords: liquid crystal; kinematics viscosity; phase transition point

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1. INTRODUCTION

Liquid crystals (LC) constitute an important class of organic compositions and are widely used in scientific and engineering researches. However, the structure of these substances in liquid phase, kinetics and molecular mechanisms of disbalansed processes, which take place during thermal movement are not studied at all. Nevertheless, study of kinetics of such processes as well as determination of their molecular mechanisms are necessary for the further development of various branches of physics, chemistry, biology and for solving plenty of engineering tasks.

The most common acoustic methods of viscoelastic properties investigation of liquid crystals (LC) add up to measurements of corresponding mechanical parameters (acoustic impedance), reflectance coefficients etc. One of the most commonly used methods of LC acoustic impedance determination - method of reflectance - is based on intensity measurements of shear wave reflected from solid - LC interface. Reflection coefficients are given by formula [1]

$$r = (Z_{SB} - Z)(Z_{SB} + Z)^{-1},$$

where Z_{SB} and Z are impedance for solid and nematic LC.

If impedance Z_{SB} is known, then measurement of the reflectance coefficient provides mechanic impedance value $Z = R + iX$, which is related to the dynamic shear viscosity (η') by

$$\eta' = 2RX (\rho\omega)^{-1} = 2R^2 (\rho\omega)^{-1}.$$

It was established that temperature and frequency dependencies of dynamic viscosity obtained through measurements of real and imaginary parts of the impedance for certain typical LC have much in common both in the region of isotropic-nematic transition and in isotropic and nematic states. As evidenced in [2], the dynamic viscosity of 5CB is independent of frequency in the frequency range of 70 kHz - 15.4 MHz. In isotropic phase far from the clearing point its value coincides with static shear viscosity η_0. On cooling the sample down with approaching phase transition isotropic phase - namatic LC the dynamic viscosity falls as compared to static viscosity, while their
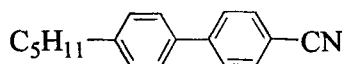
difference $\eta_0 - \eta'$ attains maximum value in the vicinity of the clearing point. In the region of clearing temperature the greatest difference of the static and dynamic viscosity values for 5CB is observed at frequency 15,4 MHz, and the smallest one - at frequency 69,6 kHz. They equal correspondingly 0,046 and 0,007 P.

Measurements of the LC static shear viscosity are usually made by known method of capillary viscometer at low shear rates (10 - 50 s^{-1}), commonly with capillary of 0,73 - 1,0 mm in diameter [3-5].

It was established that in nematic and isotropic phases far from the phase transitions the static viscosity diminishes exponentially with temperature increase. All studies of NLC have shown qualitative identical temperature dependence of the shear viscosity, with its maximum located in the clearing point, while the viscosity value at maximum exceeds by 0,03 - 0,06 P the minimal viscosity value observed before its transition to isotropic phase. There remains a problem to solve on the reasons for differences in experimentally observed temperature dependencies of viscosity in the nematic and isotropic liquid crystal phases. In this paper have been made attempt to explain it difference.

2. EXPERIMENTAL PROCEDURES

Nematic liquid crystal of 4-pentyl 4`-cyanobiphenyl (5CB) has been used in experiments, which has following structural formula

$$C_5H_{11} \text{—} \bigcirc \text{—} \bigcirc \text{—} CN$$

with transition temperature ($T_{N\text{-}I}$) of nematic phase - isotropic phase (clearing point $T_{cl} = T_{N\text{-}I}$) equal to 307,8 K.

Measurements of density (ρ) and shear viscosity η_s for 5CB were conducted in the temperature interval of 298 - 333 K.

Density of 5CB was determined by standard picnometry method. Coefficient of shear viscosity was measured by method of capillary viscometer with different capillary diameters, as well as by falling weight method. The weights used were both of spherical and cylindrical shape. Hepler type viscometer has been used with tube diameter equal

to 4 mm. This construction of the viscometer provides for tube slope of 45°, so that the weight slides down the wall. The viscometer is supplied with a set of cylindrical weights of different diameter and balls. Viscosity is measured by the time of weight fall in the calibrated tube. Measurements of the shear viscosity coefficient were conducted both for vertical and sloped fall of the weight.

The accuracy of the density and shear viscosity experimental measurements was better than 0.05% and 3%, correspondingly.

3. RESULTS AND DISCUSSION

The results of density measurements are shown in Fig.1. It is seen from Fig.1 that density for both nematic and isotropic phase behaves as linear function of temperature.
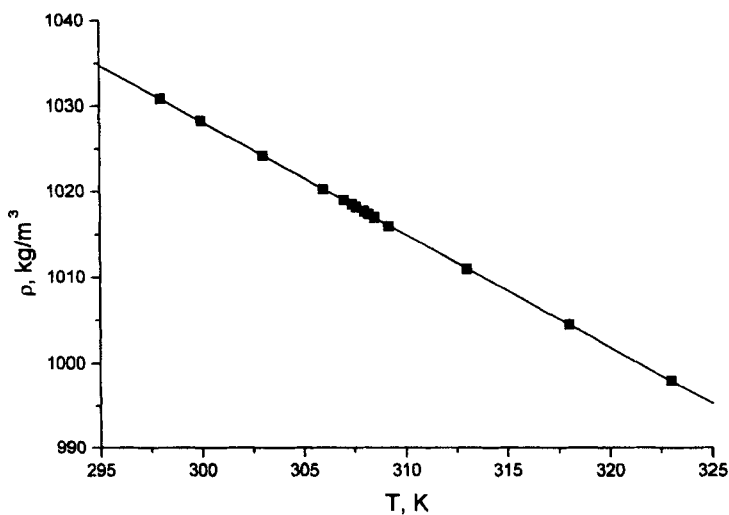

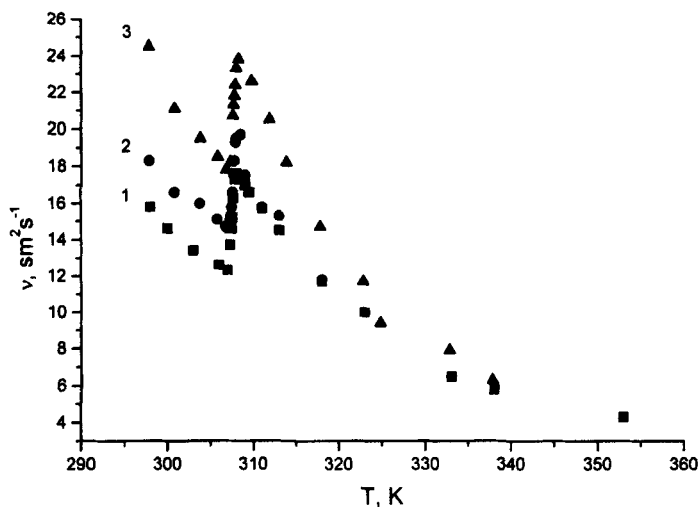FIGURE 1   Temperature dependence of density for liquid crystal 5CB.

FIGURE 2   Coefficient of kinematics viscosity *vs.* temperature:
1 - capillary viscometer, Ø3 mm ball, small weight;
2 - measurements with Ø3 mm ball, slope 45°;
3 - measurements with cylindrical weight Ø3,95 mm.

Results of measurements of coefficient of kinematics viscosity $v = \eta_s / \rho$ with capillary viscometer and falling weight method depending on temperature and weight dimensions are shown in Fig.2. It is seen from Fig.2 that temperature dependence of the coefficient of kinematic viscosity is of non-monotonic nature. In the beginning, in temperature region of 298 to 307 K, viscosity decreases with temperature, reaching minimal value at T = 307 K. In temperature region of 307-308,5 K viscosity rises steeply. Maximum value $v(T_M)$ is situated in the vicinity of nematic phase - isotropic phase transition temperature, T_{N-I} = 307,8 K. Analysis of experimental data shown in Fig.2 indicates that calculated values of liquid crystal viscosity in the vicinity of phase transition point are obviously dependent on external experimental conditions, such as mass and dimensions of the weight, fall slope, etc. Simultaneously, values of v obtained in three different

experiments using capillary viscometer and Stokes method with ball and cylinder $\varnothing \leq 3$ mm coincide within the limits of experimental mistake. We assumed that these values of viscosity coefficient $v(T)$ are the true ones. In our opinion, the dependence of v value on the weight diameter and slope of its fall (weight dimensions being the same) is conditioned by so called wall effect. According to de Gennese [6], in a certain wall «transition layer» having thickness $h \sim \sqrt{\dfrac{K}{\langle v \rangle \nabla v}}$, (K - constant value, $\langle v \rangle$ - mean viscosity, ∇v - rate gradient), the long and rigid LC molecules, aligned against one another, are gradually changing their orientation under the influence of tube walls. So, if viscosity measurements use large weights or ball sliding on sloped tube wall, the wall effect generates additional energy dissipation. This is the reason for dependence of the calculated v values on weight dimensions and slope.

The sharp rise of 5CB viscosity in the temperature region of 307 - 307,8 T, in our opinion, is related to intensive development of order parameter fluctuations in nematic phase and density fluctuations in isotropic phase. On further increase of temperature 5CB viscosity starts to decrease again.

Taking into account effect of fluctuations in LC on the viscosity value, the experimental data obtained ($v(T)$, Fig.2) can be presented as binomial:

$$v(T) = v_r(T) + v_{fl}(T).$$ (1)

Here $v_r(T)$. and $v_{fl}(T)$ - regular and fluctuating parts of viscosity, correspondingly.

Experiment demonstrates that in temperature region 298 - 307 T temperature dependence of regular viscosity contribution Δv_r follows Frenkel-Eyring equation [7,8]

$$v_r = A\exp\left(\frac{\Delta H_\eta^* - T\Delta S_\eta^*}{RT}\right) = A_1 \exp\left(\frac{\Delta H_\eta^*}{RT}\right),$$ (2)

$(A_1 = A\exp\left(-\dfrac{\Delta S_\eta^*}{R}\right)$ - exponential factor, ΔH_η^* - and ΔS_η^* - activation

enthalpy and entropy of viscous flow, R - absolute gas constant, T - temperature). In this temperature region fluctuating part of viscosity $v_{fl}\,(T)$ can be discarded ($v_r \gg v_{fl}$).

On basis of parameters appearing in equation (2), only activation enthalpy of viscous flow can be calculated directly from experimental values as slope of logarithmic plot of viscosity *vs.* temperature $\Delta H_\eta^* = \dfrac{\partial \ln(v_r)}{\partial(T^{-1})}$. The results have shown that ΔH_η^* value equals to 20

kJ/mole, being independent of measurement method. Regular part of viscosity v_r is determined by extrapolation of relationship (2) to the high temperature region. After obtaining v_r value in such a way, contribution of fluctuating part of total viscosity in the vicinity of N - I phase transition temperature is calculated as $v_{fl} = v - v_r$. Fig.3 shows plot of $\left(v_{fl}\right)^{-1}$ value against temperature. It is seen in Fig.3 that curves meet in the point of maximal $v(T_M)$ value. This intersection means that in the vicinity of phase transition point viscosity attains finite value.

On withdrawal from phase transition temperature the reciprocal viscosity value increases. As shown in Fig.3, temperature dependence of viscosity difference $\Delta v_{fl}^{-1}(T) = v_{fl}^{-1} - v_m^{-1}$ is essentially asymmetric for phase transition temperature $T_M = 307{,}8K$. So, for equal values of temperature difference $|\Delta T| = |T - T_M|$

$\Delta v_{fl}^{-1}(T > T_M) \gg \Delta v_{fl}^{-1}(T < T_M)$. Besides, in the nematic phase $\Delta v_{fl}^{-1}(T > T_M)$ value is changing more strongly than $\Delta v_{fl}^{-1}(T < T_M)$.

Analysis of the results obtained has demonstrated that in the nematic phase fluctuating part of viscosity $\Delta v_{fl}(T)$ in singular region is given by power dependence

$$\Delta v_{fl}(T) = \Delta v_{01} t^{-n_1},\qquad (4)$$

where $t = \dfrac{T_M - T}{T_M}$, $n_1 = 1{,}25 \pm 0{,}05$, and $\Delta v_{01} = (1\pm0{,}1)\cdot 10^{-4}$ sm^2/s.
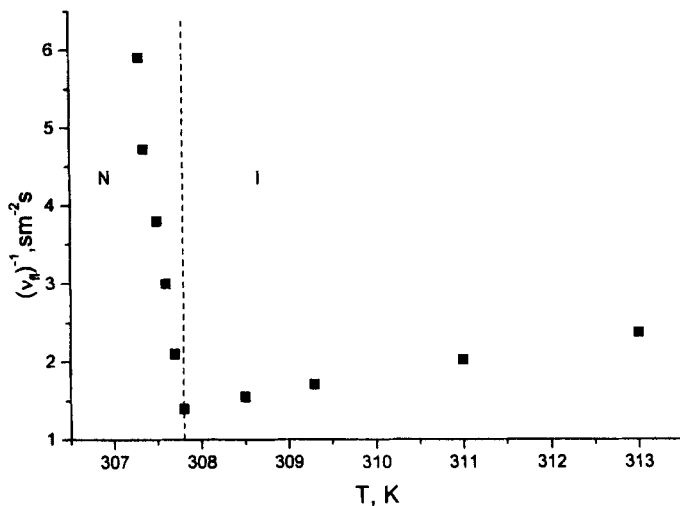
FIGURE 3　　Plot of reciprocal value of fluctuating part of kinematic viscosity coefficient, measured with capillary viscometer and by Stokes method with ball and small weight: N - nematic singularity region; I - isotropic phase region.

It means that exponent of power $n_l = 1,25 \pm 0,05$, within the limits of experimental and calculation mistake is close to the value of critical parameter $\gamma = 5/4$ of isothermal compressibility for a liquid in the vicinity of critical point $(\beta_T \sim t^{-\gamma})$ [9].

The obtained value $n_l = 1,25 \pm 0,05$ is in good compliance with γ values obtained from measurements of magnetic birefringence and intensity of light-scattering [6].

Unlike viscosity behavior in the nematic phase, it follows from Fig.3 that in isotropic liquid phase at $T > T_M$ singular part of viscosity $\Delta \nu_{fl}^{-1}(T > T_M)$ is given by power dependence

$$\Delta \nu = \Delta \nu_{02} |t|^{-n_2} .$$

(5)

Here $n_2 = 0,65 \pm 0,05$; and $\Delta v_{02} = (7 \pm 1) \cdot 10^{-2}$. Obviously, value of the parameter $n_2 = n_1/2$ is close to the critical parameter for correlation radius $R_c(t) \sim t^{-\nu}$ ($\nu \approx 2/3$) [9].

There is no long-range order in the direction of molecular orientation in isotropic phase. Tensor order parameter Q_{ij} on the average disappears [9]. Nevertheless, if we consider molecules in small volumes, we will find that locally they remain parallel to one another. This local ordering holds up to certain intrinsic distance $\xi(T)$, which is called correlation radius $(R_c(t))$.

It means that in isotropic phase we can speak about nematic clusters - small nematic inclusions (having dimension of $\xi(t)$ with continual orientation in adjacent inclusions). So at temperatures above T_{N-I} the important role should belong to short-range effects. It was demonstrated in [6] that correlated regions of $\xi(t) > 200 \overset{o}{A}$ dimensions exist in isotropic phase just above T_{N-I}.

Generally, analysis of the viscosity coefficient behavior in the region of phase transitions presents complex problem. The viscosity increase may be caused by pre-transitional fluctuations of the order parameter. There are nematic phase nuclei near the NLC - isotropic liquid transition [1,10]. Size of these formations (clusters) $R_c \sim t^{-\nu}$ increase continuously on approaching phase transition.

4. CONCLUSION

Rheological properties of liquid crystal 4-pentyl 4`-cyanobiphenyl (5CB) were investigated using the picnometer technique and method of capillary viscometer and Stokes method in temperature interval from 298 to 333 K. Experimental data reveal a non-monotonic temperature behavior of the kinematics viscosity coefficient. It because that viscosity consist from regular and fluctuating parts. The fluctuating part is determined by anomaly development of order parameter fluctuations in the vicinity of the phase transition point. In nematic and isotropic phase it obeys power dependence. In nematic phase value of exponent of power is close to the value of critical parameter of isothermal compressibility for a liquids in the vicinity of critical point. In isotropic phase value of exponent of power is close to the critical parameters for correlation radius. It was shown that in the vicinity of phase transition point viscosity attains finite value.

ACKNOWLEDGMENTS

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