UDC 532.5, 532.6

D. V. Shmeliova, S. V. Pasechnik*, S. S. Kharlamov, A. Sh. Saidgaziev, V. A. Podolsky

ELECTROKINETIC PHENOMENA IN HOMEOTROPIC LAYERS OF NEMATIC LIQUID CRYSTAL

MIREA – Russian Technological University, Problem Laboratory of Molecular Acoustics,
78 Vernadsky Av., Moscow, 119454, Russia. *E-mail: s-p-a-s-m@mail.ru

The work is devoted to the experimental studies of electrokinetic phenomena in oriented samples of a nematic liquid crystal (LC) 5CB, formed inside flat capillaries with a homeotropic surface orientation. A decay flow of the liquid crystal arising under the action of DC electric field and hydrostatic pressure gradient was experimentally realized and studied by the registration of meniscus' motion in the vertically oriented cylindrical capillary. The dependences of the maximal value of the meniscus' rise and characteristic decay time on the control voltage have been obtained. The analysis of the experimental data was performed in the framework of a simple model, taking into account the dependence of dielectric permittivity on the electrically controlled orientation of LC. The value of zeta potential as well as the effective shear viscosities at different voltages were determined. The obtained data were compared with the results of independent studies.

Key words: electrokinetic phenomena, nematic liquid crystal, zeta potential, anisotropic shear viscosity.

Д. В. Шмелева, С. В. Пасечник*, С. С. Харламов, А. Ш. Саидгазиев, В. А. Подольский

ЭЛЕКТРОКИНЕТИЧЕСКИЕ ЯВЛЕНИЯ В ГОМЕОТРОПНЫХ СЛОЯХ НЕМАТИЧЕСКОГО ЖИДКОГО КРИСТАЛЛА

МИРЭА – Российский технологический университет,
Проблемная лаборатория молекулярной акустики,
пр. Вернадского, д. 78, 119454 Москва, Россия. *E-mail: s-p-a-s-m@mail.ru

Работа посвящена экспериментальным исследованиям электрокинетических явлений в ориентированных образцах нематического жидкого кристалла (ЖК) 5CB, сформированных внутри плоских капилляров с гомеотропной граничной ориентацией. Затухающий поток жидкого кристалла, возникающий под действием постоянного электрического поля и градиента гидростатического давления, был экспериментально реализован и изучен путем регистрации движения менисков в вертикально ориентированных цилиндрических капиллярах. Получены зависимости максимальной величины подъема мениска и характерного времени затухания от управляющего напряжения. Анализ экспериментальных данных проводился в рамках простой модели с учетом зависимости значения диэлектрической проницаемости от ориентации ЖК, контролируемой электрическим полем. Были определены значения дзета-потенциала и эффективной сдвиговой вязкости при различных напряжениях. Полученные данные сравниваются с результатами независимых исследований.

Ключевые слова: электрокинетические явления, нематический жидкий кристалл, дзета-потенциал, анизотропная сдвиговая вязкость.

Introduction

It is well known that a static (or low frequency) electric field applied to micro and nano-channels may induce an overall flow of liquid through the channels [1–6]. These electrokinetic (EK) phenomena are of great interest for researchers in the field of bioengineering and microfluidics. In particular, EK effects can be used in the development of portable diagnostic chips and molecular sensors [6, 7], as well as in fine chemical technologies [8]. The main advantage of electrokinetic pumps, essentially for such applications, is the absence of moving parts, which provides precise pumping of micro (or nano) liter volumes of a liquid.

Up to now, a large number of experimental and theoretical studies were devoted to the study of EK phenomena in isotropic polar liquids and solutions. At the same time, there are only rare publications [9–12] of such type, referred to the electrically induced shear flows in flat capillaries and porous polymer films filled with nematic liquid crystals (NLC), which differ from isotropic liquids by orientational ordering of long molecular axes. As a result, NLC are characterized by high fluidity, which is typical for isotropic liquids, in combination with strong quasi crystalline anisotropy of different physical properties. It opens new perspectives for microfluidic applications of such anisotropic liquids.

In particular, the essential anisotropy of a refractive index of NLC and the intrinsic connection between an orientation and a velocity gradient made it possible to implement electroosmotic flow through polymer porous PET films [10] into a new type of the optofluidic device [13]. It also provided a registration of weak electroosmotic flow in the system of parallel-connected micron sized flat channels filled with NLCs [9]. In this case, the inner surfaces of channels were not treated, which resulted in arising of degenerate surface and bulk orientation of NLC. It prevented studying the nature of electrokinetic phenomena in anisotropic liquids with a controlled surface and bulk orientation.

This work is devoted to the experimental study of electroosmotic flows of a liquid crystal through the flat channels with a given (homeotropic) surface orientation. The main objective of our study is to reveal the applicability of the simple quasi isotropic model for the description of electroosmotic flows of strongly anisotropic liquid oriented by surfaces and electric field.

Experimental

The experimental study of electrokinetic phenomena in oriented samples of NLC was fulfilled by using the LC cell, shown in Fig. 1, *a*.
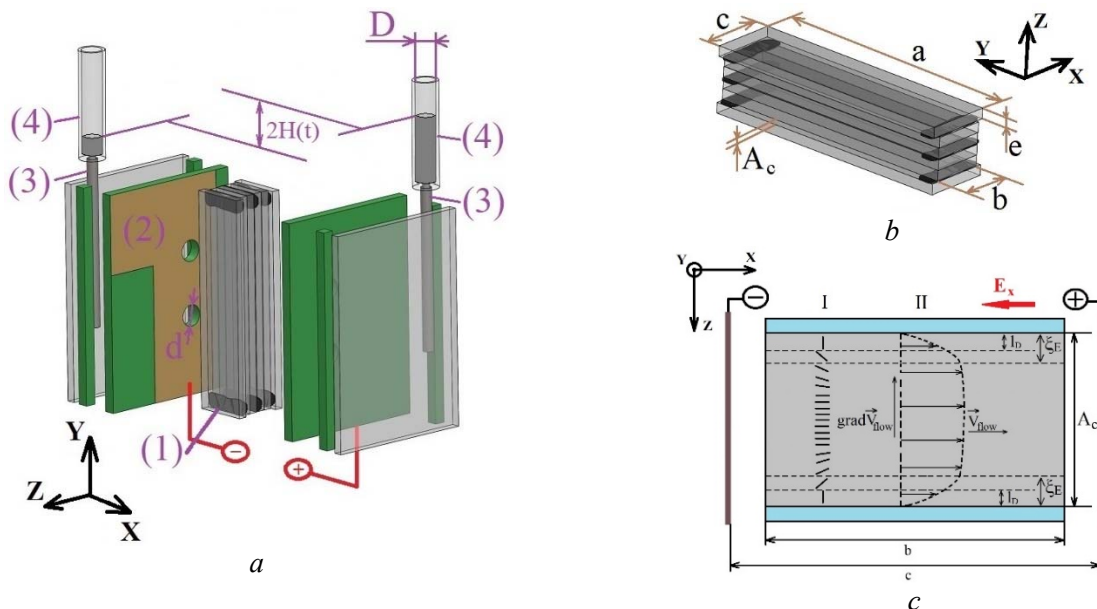

Fig. 1. Schematic representation of an experimental cell:
a – exploded 3D layout of the cell construction: *1* – multi layered package, *2* – copper electrodes, *3* – metal needles, *4* – open glass capillaries, $D = 2.8$ mm, $d = 2$ mm;
b – construction of the package assembled from glass substrates: $a = 20$ mm, $b = 4$ mm, $c = 5$ mm, $A_c = 60$ μm, $e = 1.1$ mm;
c – the scheme illustrating the theoretical model of LC reorientation (I) under the plug-shaped velocity profile (II) typical for electroosmotic flows, l_D – Debye length, ξ_E – electrical coherence length

In the central multilayer package (Fig. 1, *b*) of the experimental cell, three flat capillaries, each with the gap A_c = 60 µm, width a = 20 mm and length b = 4 mm, were formed with the help of nylon spacers, separating glass substrates, and an epoxy glue, which fixed the package.

The inner surfaces of the plates in the package were preliminary cleaned and then treated (using spin coating procedure) with 0,5 % solution of chromium stearyl chloride (chromolane) in isopropanole with further annealing at 90 ºC for 1 hour. As a result, the inner surfaces of flat channels formed inside the package were covered by thin solid layers of chromolane, which was needed to get a homeotropic surface orientation of LC. The package (1) was placed between two electrodes (2) (see at Fig. 1, *a*) made of fiberglass sheets (of 1 mm thickness), covered with a copper foil. Such construction made it possible to create the "in-plane" electric field after application of DC voltage, which was needed to induce electroosmotic flow of NLC through flat channels.

Two holes in the fiberglass sheets with the diameter d = 2 mm were drilled to provide the hydrodynamic connection between the central package and the peripheral parts of the cell. The latter included two rectangular chambers with metal needles (3) of the inner diameter 1 mm, connected with the vertically oriented open glass capillaries (4) of the inner diameter D = 2.8 mm. The cells were vacuumed and filled with the nematic liquid crystal 5 CB (4-cyano-4'-pentylbiphenyl). The constant temperature of the cell T = 26 ± 0.1 ºC was maintained during the entire time of measurements with the help of a water thermostat.

The measurements were based on recording the movement (with the help of a digital camera) of the liquid crystal meniscus in open cylindrical tubes under the action of applied DC voltage U. The obtained microscopic images were transmitted to a personal computer for further processing.

Results and discussion

Time dependences of the meniscus displacement $H(t)$ induced by application of different voltages, are shown in Fig. 2. The slope of each curve decreases with time and displacement H reaches the stationary level H_{max} at long enough time (t > 200 s). Such behavior corresponds to the decay flow of nematic liquid crystal LC taking place due to the compensation of an electroosmotic flow by Poiseuille flow of the opposite direction. The latter flow was induced by the hydrostatic pressure

gradient proportional to the difference of meniscus levels in the vertical capillaries.
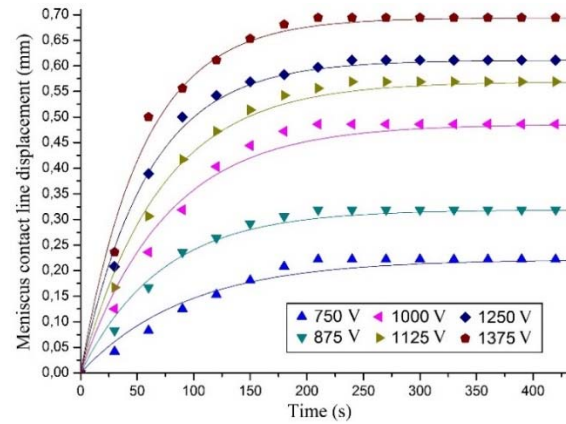

Fig. 2. Time dependences of the meniscus displacement $H(t)$ in open glass capillary at different DC voltages. Solid lines show the approximation of experimental data by equation (1)

As it can be seen from Fig. 2, in the entire range of control voltages the experimental data are satisfactory described by a simple exponential law:

$$H = H_{max}(1 - e^{-t/\tau}), \qquad (1)$$

where τ is a characteristic time of the rise.

The dependences of parameters $H_{max}(U)$ and $\tau(U)$ obtained as a result of approximation of the experimental data by expression (1) are shown in Fig. 3, *a* and Fig. 3, *b,* correspondingly. The presented dependence $H_{max}(U)$ demonstrates strong non-linear behavior at relatively low voltages. At the same time, the dependence $H_{max}(U)$ at relatively high voltages is close to the simple linear law, which is typical for electroosmotic flows of isotropic liquids [2]. This result and also strong decrease of the characteristic time τ with voltage, shown in Fig. 3, *b,* demand some explanation.

For this aim, we can use a theoretical expression for the volumetric rate of electroosmotic flow of an isotropic liquid under the additional action of a pressure gradient [2]:

$$\frac{Q}{A_c} = \frac{h^2 p_x}{3\eta} - \frac{\varepsilon \varepsilon_0 E_x \zeta}{\eta}\left[1 - \frac{\tanh(kh)}{kh}\right], \qquad (2)$$

where $A_c = 2h$ is the gap of a flat capillary, $Q = (1/a)(dV/dt)$ is the volumetric flow rate of liquid per unit width of a capillary, $p_x = \Delta p/b$ is the value of the pressure gradient created by the application of the pressure difference Δp to a capillary of length b, η and ε are the shear viscosity and dielectric permittivity of the liquid, ε_0 is the electric constant, $E_x \approx U/b$ is the strength of the

electric field, $k = (l_D)^{-1}$ is the parameter inverse to the Debye length l_D, ζ is the value of the zeta potential determined by the interaction of the surface and polar liquid.

In our experiment, the hydrostatic pressure gradient, caused by the appearance of a height difference in vertical tubes can be expressed in terms of the experimentally measured displacement $H(t)$ of one of the meniscus level relative to the initial zero value:

$$p_x = \frac{2H(t)\rho g}{b}. \quad (3)$$

Taking into account the fact that the integral flow of LC in a tube of radius R is provided by the action of three capillaries connected in parallel, the obvious relationship can be written:

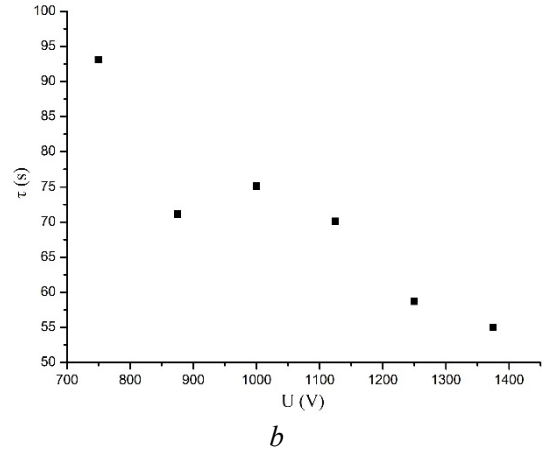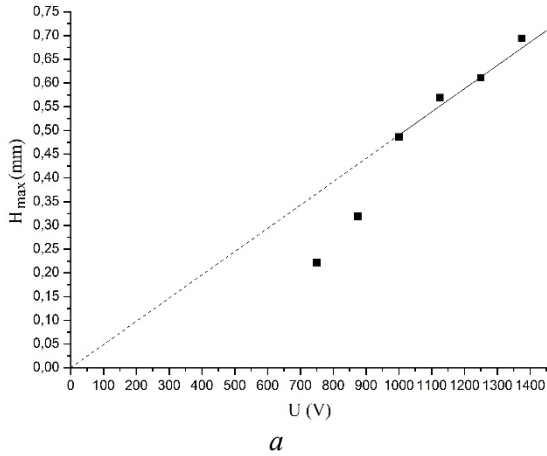$$\frac{dV}{dt} = \frac{1}{3}\frac{dH(t)}{dt}\pi R^2. \quad (4)$$

Fig. 3. The approximation parameters of experimental data by expression (1); *a* and *b* correspond to the dependences of the stationary value of the meniscus height $H_{max}(U)$ and the characteristic time of the rise (τ) on voltage

Using relations (3) and (4) and the approximation of the smallness of the Debye length with respect to the capillary gap ($kh \gg 1$), we can obtain the following differential equation describing the dynamics of a fluid rise using formulas (2–4):

$$\frac{dH(t)}{dt} = MH(t) - N, \quad (5)$$

where

$$M = \frac{4ah^3\rho g}{\eta b\pi R^2}, \quad 6)$$

$$N = \frac{6ah\varepsilon_0\varepsilon\zeta U}{\eta b\pi R^2}. \quad (7)$$

The solution of this equation has the form of function (1), where the characteristic relaxation time τ and the stationary value H_{max} are determined by the expressions:

$$\tau = \frac{1}{M} = \frac{\eta b\pi R^2}{4ah^3\rho g}, \quad (8)$$

$$H_{max} = \frac{3}{2}\frac{\varepsilon_0\varepsilon\zeta U}{h^2\rho g}. \quad (9)$$

As it follows from the expression (8), the characteristic time τ is directly proportional to the shear viscosity and does not depend on applied voltage as well as electrical characteristics of LC. While the stationary value of the rise height is directly proportional to the applied voltage and depends on both the dielectric constant of LC and the value of zeta potential. The contradiction between these conclusions and the experimental results presented above can be explained by the action of electric field on the orientation and material parameters of liquid crystal. In particular, the deviations of the experimental dependence $H_{max}(U)$ can be associated with an increase in the effective value of the dielectric constant due to partial reorientation of the boundary layer in the direction of electric field. Indeed, for 5CB the total reorientation of LC from the initial homeotropic orientation (normal to the field direction) to the planar orientation (parallel to **E**) results in the changes of the dielectric constant ε from 7 up to 18.5 [14]. Obviously, this mechanism can be realized in the case, when electric field effectively changes LC orientation

in the diffuse layer, which is responsible for the generation of electroosmotic flow. It means that the diffuse layer thickness characterized by Debye length l_D which has to be comparable with the electrical coherence length ξ_E, describing the near surface layer with an orientation controlled mostly by surface (Fig. 1, *c*). The latter parameter is described by the well-known expression [15]:

$$\xi_E = \frac{1}{E}\sqrt{\frac{K_{33}}{\varepsilon_0 \Delta\varepsilon}}, \qquad (10)$$

where K_{33} – Frank's module, $\Delta\varepsilon$ – anisotropy of dielectric permittivity.

The estimations made in accordance with the equation (10) using the values of material parameters of 5CB ($K_{33} = 8.2 \cdot 10^{-12}$ N and $\Delta\varepsilon = 11.5$) show that ξ_E varies from 2.4 μm to 1.3 μm with the increase of voltage from 750 V to 1375 V. It is obvious that this mechanism explaining the experimental data holds for the Debye length of the order of 1 μm. The above mentioned linear dependence $H_{max}(U)$ shown in Fig. 3, *a* approximately corresponds to a constant value of dielectric permittivity ε. In accordance with equation (9), it makes possible to estimate the value of zeta potential ζ. Using the value $\varepsilon \approx 18.5$ corresponding to the orientation of LC in diffuse layer close to the direction of electric field, one can get $\zeta = 19$ mV, which has the same magnitude order as the value $\zeta = 12$ mV [10] obtained during the investigations of electroosmotic flow through the porous PET film.

A partial orientation change in the boundary layers is also confirmed by the experimentally found decrease in the characteristic time with increasing voltage (Fig. 3, *b*). Indeed, taking into account strong anisotropy of shear viscosity, it is possible to expect the essential decrease of effective values η_{eff} of the shear viscosity coefficient η in the boundary layers, which determines main contribution to energy dissipation in the case of the plug-shaped profile flow [2] realized under the condition (*kh* >> 1).

The calculation results of η using the experimental data τ and the expression (8) are shown in Fig. 4. It can be seen that the values of this parameter are in the range between the previously determined [14] maximum and minimum shear viscosities of NLC (Miesowicz viscosities η_1 and η_2 correspondingly).
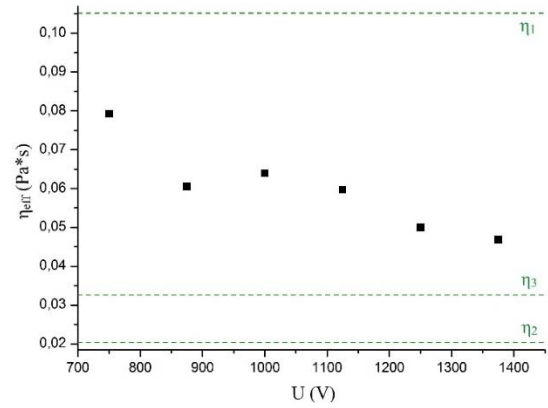

Fig. 4. The values of effective viscosity η_{eff} at different voltages determined from experimental data in accordance with the expression (8). Dashed lines correspond to the values of three Miesowicz viscosities η_1, η_2, η_3

Conclusion

The studies of electrokinetic phenomena in flat capillaries filled with nematic liquid crystal 5 CB with a homeotropic surface orientation have been performed. They made it possible to establish the following specific features of these phenomena:

1. For all used values of control voltage, the time dependences of the meniscus height rise are described by a simple exponential-type dependence arising from the decay flow model.

2. In general case, the dependence of the maximum meniscus' rise height on control voltage shows a nonlinear character. However, for the region of relatively high control voltages, the above mentioned dependence is close to the linear law, which allows to estimate the zeta potential value. Zeta potential of 19 mV is typical for other polar liquids contacting with glass surfaces and it slightly exceeds the value of 12 mV for the same liquid crystals confined to porous PET film.

3. The characteristic time of meniscus rise significantly decreases with voltage increase. The effective viscosities calculated from the experiments are in agreement with the results of independent measurements of the anisotropic viscosities (Miesowicz viscosities) of the liquid crystal 5CB, which confirms the adequacy of the decay flow model used for the explanation of the experimental data.

References

1. Tichomolova K.P., Kemp T.J. Electro-osmosis. New York : Ellis Horwood., 1993, 219 p.

2. Masliyah J.H., Bhattacharjee S. Electrokinetic and colloid transport phenomena. Hoboken (NJ) : John Wiley and Sons., 2006, 736 p.

3. Mao M., Sherwood J.D., Ghosal S. Electro-osmotic flow through a nanopore. *J. Fluid Mech.*, 2014, **749**, 167–183.

4. Rice C.L., Whitehead R. Electrokinetic flow in a narrow cylindrical capillary. *J. Phys. Chem.*, 1965, **69**, 4017–4024.

5. Chang H.-C., Yossifon G. Understanding electrokinetics at the nanoscale: a perspective. *Biomicrofluidics*, 2009, **3** (1), 012001.

6. Zaltzman B., Rubinstein I. Electro-osmotic slip and electroconvective instability. *J. Fluid Mech.*, 2007, **579**, 173–226.

7. Geschke O., Klank H., Telleman P. Microsystem Engineering of Lab-on-a-chip Devices. Willey-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, 270 p.

8. Manz A., Effenhauser C.S., Burggraf N., Harrison D.J., Seiler K., Fluri K. Electroosmotic pumping and electrophoretic separation for miniaturized chemical analysis systems. *J. Micromech. microeng.*, 1994, **4**, 257–265.

9. Tsvetkov V.A., Pasechnik S.V., Salov J.A. LC Electrohydrodynamic Pump. *Mol. Crys. & Liq. Crys.*, 2004, **409** (1), 483–491.

10. Pasechnik S.V., Chopik A.P., Shmeliova D.V., Drovnikov E.M., Semerenko D.A., Dubtsov A.V., Zhang W., Chigrinov V.G. Electro-kinetic phenomena in porous PET films filled with liquid crystals. *Liq. Cryst.*, 2015, **42** (11), 1537–1542.

11. Tovkach O.M., Calderer M.C., Golovaty D., Lavrentovich O., Walkington N.J. Electro-osmosis in nematic liquid crystals. *Phys. Rev. E*, 2016, **94** (1), 012702–012712.

12. Poddar A., Dhar J., Chakraborty S. Electro-osmosis of nematic liquid crystals under weak anchoring and second-order surface effects. *Phys. Rev. E*, 2017, **96** (1), 013114–15.

13. Shmeliova D.V., Saidgaziev A.Sh., Kharlamov S.S., Visotsky A.S., Safonov M.A., Konovalova A.A., Pasechnik S.V. Liquid crystal optofluidic device based on electrokinetic phenomena in porous polymer films. *Liq. Cryst. and their Appl.*, 2020, **20** (3), 72–29. **DOI:** 10.18083/LCAppl.2020.3.72.

14. Stewart I.W. The static and dynamic continuum theory of liquid crystals; a mathematical introduction. Tailor and Francis, 2004, 351 p.

15. Pasechnik S.V., Chigrinov V.G., Shmeliova D.V. Liquid Crystals: Viscous and Elastic Properties in Theory and Applications. Wiley: New York, USA, 2009, 424 p.