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Formation of spiral microstructures during crystallization of 4,4‘-azoxyanisole from a benzene solution

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Abstract. A phenomenon of formation of multiple ”coffee rings” consisting of microcrystals in the 4,4‘-azoxyanisole - benzene system was experimentally and theoretically investigated. It is shown that by changing of the geometry of a drop, for example, by placing a metal ball in its center it is possible to fundamentally change the geometry of the “coffee ring”. Assumptions were made about the physical nature of the effect of the formation of a ”coffee ring” of a spiral shape. The proposed geometric model of this phenomenon reflects well the physical processes occurring during spiral crystallization, and the model is in good agreement with the experimental data obtained by gravimetry. New approaches to the formation of microstructures of functional materials with a thermotropic liquid crystal phase on a glass substrate can be used to create devices for nano– and microelectronics and optical technology.

1. Introduction

Many modern electronic components, including those requiring optical transparency during operation, are printed using inkjet printing methods. One of the objectives of this technology is the uniform application of the functional component to the substrate. However, when the solvent dries, a phenomenon called the “coffee ring” effect is observed on the surface of the substrate. Particles of the dissolved substance are not distributed evenly over the surface of the coating during deposition from the solution, but are mostly located along the perimeter of the droplet [1–5]. It is traditionally considered [6–10] that this phenomenon is due to the presence of capillary flows in the droplet [11]. “Coffee rings” can be formed upon drying of various substances (true and colloidal solutions) – low molecular weight substances, protein molecules [12], carbon nanotubes [13–15], polymers [16–18]. This phenomenon is considered in detail in the technology of OLED displays in work [19–23]. The paper considers approaches to reduce the impact of this phenomenon. In [24], the effect of the “coffee ring”, on the contrary, is specially used for applying transparent conductive coatings based on carbon nanotubes to a flexible polymer substrate. It is interest to study of possibilities for controlling the shape of the “coffee ring” [13, 16, 25]. It is shown that the ring can be not one, but represent multiple ring structures or a spiral. Under the influence of phenomenon of various nature, a change in the shape of the coffee ring is observed. For example, acting on a drop with ultrasound during its drying, it is possible to achieve the disappearance of the “coffee ring” effect [26]. In a number of works, electrowetting [27, 28] or laser radiation [29] is used to uniformly coat the substrate. In [30], the effect of surfactants on the shape of the “coffee ring” was investigated. In [13], to obtain a spiral structure from single–walled nanotubes, a glass ball was placed in the centre of a drop. The aim of this work was to study the formation of spiral crystalline microstructures from 4,4‘ - azoxyanisolane and mathematical modelling of the processes.

2. Experimental part

A saturated solution of 4,4‘-azoxyanisole (N-4) in benzene was prepared at room temperature for the experiment. Compound N-4 has a thermotropic nematic liquid crystalline phase in the range of 118 – 136 °C. A metal ball with a diameter of 1 mm was placed on a glass and a drop of the solution with a diameter of ~ 10 mm was placed on the glass, so that the ball would appear in the centre of the drop. The experiment was carried out at room temperature.

The concentration of the solution at which N-4 begins to crystallize from benzene was determined by gravimetry. The experiment was carried out on an analytical balance (Gosmeter vl-220m, Russia). The concentration was determined from the mass difference between the solution and the crystals after drying of benzene. Polarization optical microscopy (POM) studies were performed using a POLAR 3 microscope (Altami, Russia).

3. Results and discussion

The effect of the formation of multiple spiral ”coffee rings” is observed visually. A photograph of a sample after the evaporation of benzene is in fig. 1. A metal ball with a diameter of 1 mm is in the middle.

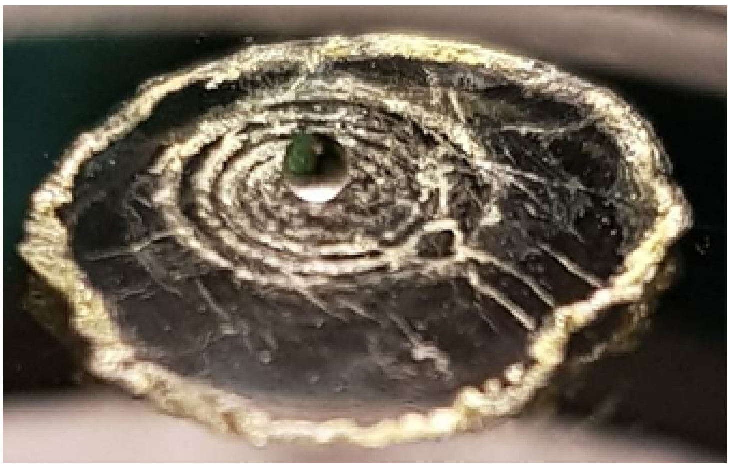


Figure 1. Photograph of sample of N-4 after evaporation of benzene. The diameter of the metal ball in the centre is 1 mm

It is assumed that the process of formation of the ”coffee ring” of this form occurs due to a number of physical phenomena. Evaporation occurs uniformly from the entire surface of the droplet, and the evaporation rate is directly proportional to the surface area of the evaporation. At a certain moment, the solution is supersaturated, and the crystals begin to crystallize. Crystals on the diameter of the droplet are wetted by the solution, so that the ensembles from the crystals are impregnated with the solution like a porous sponge due to the capillary effect. This “sponge” impregnated with a supersaturated solution obviously has a large evaporation surface of benzene, so evaporation from the “sponge” faster than from the surface of the droplet. This is confirmed by observations in POM. On relatively large crystals, which apparently appeared first, there are smaller crystals that appeared in the secondary process. Meanwhile, the droplet volume decreases and the solution recedes from the rim of the outer ring. At this moment, the system is similar to 2-communicating vessels connected by a thin flat capillary that feeds the external "sponge" due to the volume of the droplet solution. All this time, the drop's height is kept constant by wetting and holding by the surface of the metal ball. Then this thin capillary dries up, and the process begins again on a new ring.

The phenomenon of the formation of multiple spiral rings was investigated by the POM method. The result of polarization-microscopic investigation is presented in Fig. 2.

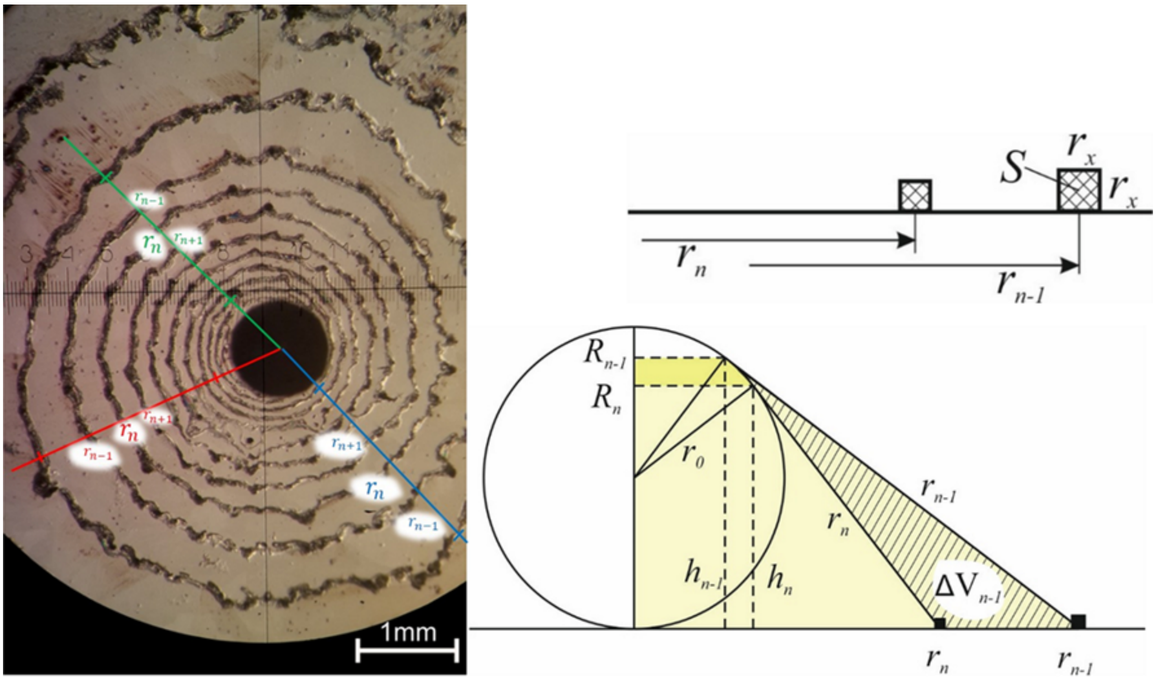


Figure 2. Microphotograph of a sample with N-4 crystallized in the form of a spiral (parallel polarizers, value of division is 40 m) and a geometric model for calculating the mass concentration

The geometric model for calculating the mass concentration at which crystallization occurs on each of the subsequent rings is shown in Fig. 2. The volume of the element (in Fig. 2 its cross section is shaded):

$$\Delta V_{n-1} = V_{n-1}^{bxt} - V_n^{int} - V^{sph}. \quad (1)$$

- V_{n-1}^{bxt} the volume of the truncated cone with the height h_{n-1} and radii of the bases R_{n-1} and r_{n-1},
- V_n^{int} the volume of the truncated cone with the height h_n and radii of the bases R_n and r_n,
- V^{sph} volume of a spherical layer with radii of the bases R_{n-1}, R_n, and height $h_{n-1} - h_n$.

Substituting the volumes of these bodies in (1), we obtain:

$$\Delta V_{n-1} = \frac{\pi}{3} r_0^3 A, \quad (2)$$

where

$$A = \frac{2x^2}{1+x^2}\left(x^2 + \left(\frac{2x}{1+x^2}\right)^2 + \frac{2x^2}{1+x^2}\right) - \frac{2y^2}{1+y^2}\left(y^2 + \left(\frac{2y}{1+y^2}\right)^2 + \frac{2y^2}{1+y^2}\right) - \\ - \frac{x^2-y^2}{(1+x^2)(1+y^2)}\left[3\left(\frac{2x}{1+x^2}\right)^2 + 3\left(\frac{2y}{1+y^2}\right)^2 + 4\left(\frac{x^2-y^2}{(1+x^2)(1+y^2)}\right)^2\right].$$

Here the normalized radii of the rings are introduced $x = \frac{r_{n-1}}{r_0}$, $y = \frac{r_n}{r_0}$, r_0 - the radius of the ball.

The volume of the part of the figure bounded by the angle φ (Fig. 3):

$$\Delta V_{n-1}^{\varphi} = \frac{\varphi}{2\pi}\Delta V_{n-1}. \quad (3)$$

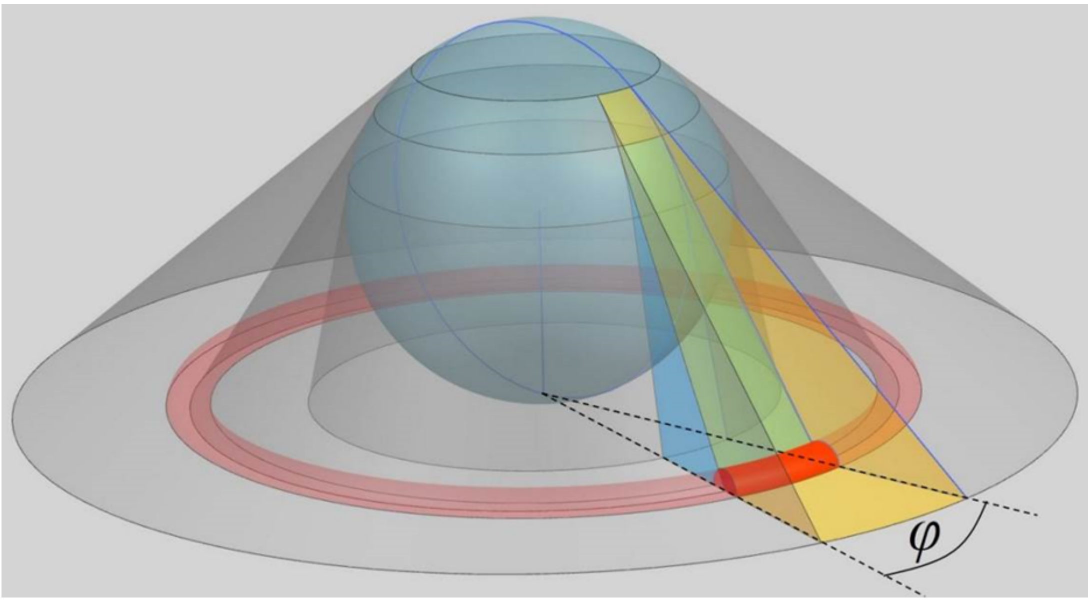


Figure 3. Volumetric model of a drop with a ball

We consider that after the evaporation of benzene from a solution with a volume ΔV_{n-1}^{φ} (indicated in yellow in Fig. 3). N-4 crystallizes on a strip of volume v_n^{φ} (indicated in red in Fig. 3). The volume of this strip can be estimated by the equation:

$$v_n^{\varphi} = S \cdot \varphi \cdot r_n, \quad (4)$$

Where S is the cross–sectional area (Fig. 3).

The ratio of volumes ΔV_{n-1}^{φ} and v_n^{φ} can be associated with the mass concentration of N-4 in solution:

$$\frac{\Delta V_{n-1}^{\varphi}}{v_n^{\varphi}} = \frac{1}{\omega} \cdot \frac{\rho_{LC}}{\rho_{sol}}. \quad (5)$$

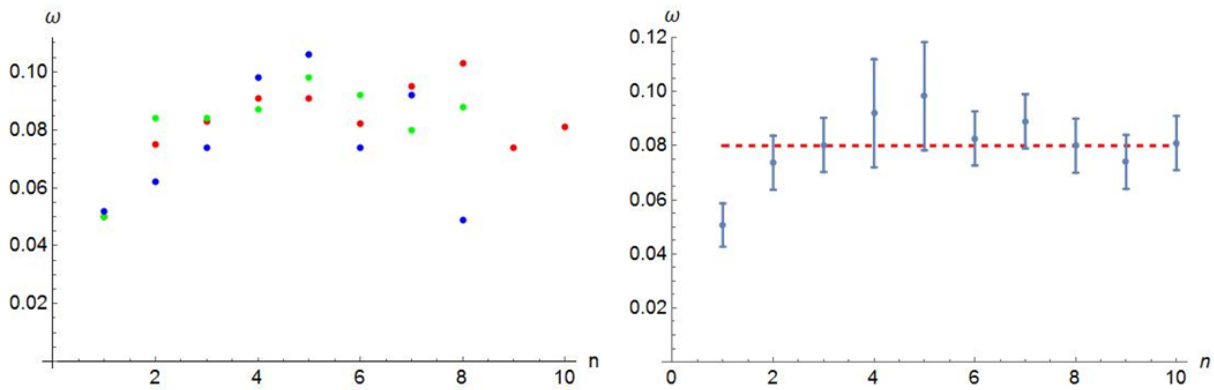
Here $\omega = \frac{m_{LC}}{m_{LC} + m_B}$ is the mass concentration, ρ_{LC}, ρ_{sol} – the density of the N-4 and the solution, respectively.

Substituting equations (2), (3) and (4) in (5), we obtain the equation for determining the concentration:

$$\omega = 6x\frac{\rho_{LC}}{\rho_{sol}}\left(\frac{r_x^2}{r_0^2}\right)A. \tag{6}$$

The calculation results by equation (6) are presented in Fig. 4. In the calculations, it is assumed that the height of the ring is equal to its width r_x.

In fig. 4a, red, blue, and green dots indicate mass concentration values calculated, respectively, along different directions of radii (see Fig. 2). In fig. 4b shows the mass concentration values averaged over the ring number. The dashed line is the mass concentration determined experimentally by gravimetry (8 wt. %).



a. b.

Figure 4. Mass concentration calculated according to the model (equation (6))

Thus, the presented geometric model of the formation of crystals of N-4 in the form of multiple rings reflects well the physical processes occurring during spiral crystallization and is in good agreement with experimental data obtained by an independent method.

4. Conclusion

The regularities of the formation of a microrelief from a solution of 4,4'-azoxyanisole in benzene using the "coffee ring" effect were studied. It is shown that by changing of the geometry of a drop, for example, by placing a metal ball in its center it is possible to fundamentally change the geometry of the "coffee ring". Microscopic studies in statics and dynamics were carried out and processes accompanying the formation of "coffee rings" were modeled. A geometric model is presented to explain the given processes. The equilibrium concentrations calculated by the model, at which the formation of each of the rings begins, are in good agreement with the data obtained by the gravimetric method. Thus, the developed new approaches to the formation of microstructures of functional materials with a thermotropic liquid crystal phase on a glass substrate can be used to create devices for nano- and microelectronics and optical technology.

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References

[1] Chen C T 2011 *Inkjet Printing of Microcomponents: Theory, Design, Characteristics and Applications, Features of Liquid Crystal Display Materials and Processes*

[2] Kozenkov V M, Spakhov A A, Chausov D N, Belyaev V V, Chausova O V and Chigrinov V G 2017 *J. Phys. Conf. Ser.* **867** 012039 DOI: 10.1088/1742-6596/867/1/012039
[3] Kozenkov V M, Spakhov A A, Belyaev V V, Chausov D N and Chigrinov V G 2018 *Techn. Phys.* **63** 576 DOI: 10.1134/S1063784218040138
[4] Chausov D N 2018 *J. Phys. Conf. Ser.* **996** 012019 DOI: 10.1088/1742-6596/996/1/012019
[5] Dadivanyan A K, Chausov D N, Belyaev V V and Bugaev A S 2014 *Doklady Phys.* **59** 457 ISSN 1562-6903 DOI: 10.1134/S1028335814100115
[6] Kazak A V, Usol'tseva N V, Bykova V V, Semeikin A S and Yudin S G 2011 *Mol. Cryst. & Liq. Cryst.* **541** 266 DOI: 10.1080/15421406.2011.569529
[7] Chumakov A S, Al-Alwani A J, Gorbachev I A, Ermakov A V, Kletsov A A, Glukhovskoy E G, Kazak A V, Usol'tseva N V and Shtykov S N 2017 *BioNanoSci.* **7** 666 DOI: 10.1007/s12668-017-0449-4
[8] Kazak A V, Zhukova L N, Kovaleva M I, Chausov D N, Kuznetsov M M and Gabdulsadykova G F 2018 *Liq. Cryst. and their Appl. (in Russ.)* **18** 74 DOI: 10.18083/LCAppl.2018.3.74
[9] Ermakova M V, Mashchenko V I, Chausova O V, Solomatin A S, Volosnikova N I and Chausov D N 2019 *Liq. Cryst. and their Appl. (in Russ.)* **4** 61 DOI: 10.18083/LCAppl.2019.4.61
[10] Mashchenko V I, Sitnikov N, Khabibullina I, Ermakova M V, Chausov D N and Chausova O V 2019 *J. Phys. Conf. Ser.* **1309** 012026 DOI: 10.1088/1742-6596/1309/1/012026
[11] Deegan R D, Bakajin O, Dupont T F, Huber G, Nagel S R and Witten T A 1997 *Nature* **389** 827
[12] Kistovich A V, Chashechkin Y D and Shabalin V V 2010 *J Tech. Phys.* **80**
[13] Mae K, Toyama H, Nawa-Okita E, Yamamoto D, Chen Y J, Yoshikawa K, Toshimitsu F, Nakashima N, Matsuda K and Shioi A 2017 *Sci. Rep.* **7** 5267
[14] Chausov D N, Kurilov A D, Kazak A V, Smirnova A I, Belyaev V V, Gevorkyan E V and Usol'tseva N V 2019 *J. Mol. Liq.* **291** 111259 DOI: 10.1016/j.molliq.2019.111259
[15] Chausov D N, Kurilov A D, Kazak A V, Smirnova A I, Velichko V K, Gevorkyan E V, Rozhkova N N and Usol'tseva N V 2019 *Liq. Cryst.* **46** 1345 DOI: 10.1080/02678292.2019.1566503
[16] Byun M, Hong S W, Zhu L and Lin Z 2008 *Langmuir* **24** 3525–31
[17] Dadivanyan A K, Noah O V, Chausov D N and Ignatov Y A 2008 *Polym. Sci. Ser. B* **50** 39 DOI: 10.1134/S1560090408010090
[18] Chausov D N, Dadivanyan A K and Belyaev V V 2015 *Mol. Cryst. & Liq. Cryst.* **611** 21 DOI: 10.1080/15421406.2015.1027991
[19] Eales A D, Dartnell N, Goddard S and Routh A F 2015 *J Colloid and Interface Sci.* **458** 53
[20] Belyaev V V, Solomatin A S, Chausov D N, Kurilov A D, Mazaeva V G, Shoshin V M and Bobylev Y P 2014 *App. Opt.* **53** H51–H57 DOI: 10.1364/AO.53.000H51
[21] Kazak A V, Usol'tseva N V, Smirnova A I, Bondarchuk V V, Sul'yanov S N and Yablonskii S V 2016 *Crystallography Rep.* **61** 493 DOI: 10.1134/S1063774516030159
[22] Chausov D N, Kurilov A D and Belyaev V V 2018 *Opto–Electron. Rev.* **26** 44 ISSN 1230–3402 DOI: https://doi.org/10.1016/j.opelre.2017.12.001
[23] Belyaev V V, Solomatin A S, Chausov D N, Suarez D A, Smirnov A G and Kuleshova J D 2017 *J. SID* **25** 561–567 DOI: 10.1002/jsid.606
[24] Shimoni A, Azoubel S and Magdassi S 2014 *Nanoscale* **6** 11084–89
[25] Li H, Luo H, Zhang Z, Li Y, Xiong B, Qiao C, Cao X, Wang T, He Y and Jing G 2016 *Phys. Chem. Chem. Phys.* **18** 13018–25
[26] Mampallil D, Reboud J, Wilson R, Wylie D, Klugb D R and Cooper J M 2015 *Soft Matter* **11** 7207
[27] Eral H B, van den Ende D and Mugele F 2012 *Phys. World* **25** 33
[28] Eral H B 2011 *Soft Matter* **7** 4954–58
[29] Yen T M, Fu X, Wei T, Nayak R U, Shi Y and Lo Y H 2018 *Scientific Rep.* **8** 3157
[30] Anyfantakis M, Geng Z, Morel M, Rudiuk S and Baigl D 2015 *Langmuir* **31** 4113–20