DOI 10.31489/2019No2/83-88

UDC 535.37; 535.47; 537.635; 543.544.2; 539.194; 541.18

OPTICAL SYSTEMS FOR REMOVAL OF POLARIZATION SPECTRA

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In the article optical systems are presented that are developed by the authors and have been used for many years to remove the polarization properties of anisotropic molecules. Both systems are designed for visible and close to ultraviolet spectral regions. In this case, the double Fresnel parallelepiped plays the role of an achromatic quarter of the wave plate. They are used in the Jasco-20 dichrograph after the Pockels cell. As a result, the sensitivity of the device increases from $\theta \cong 10^{-3} degree \cdot cm^{-1}$ *to* $10^{-5} degree \cdot cm^{-1}$ *of the value of the differences in optical density.*

Keywords: *optical systems, anisotropic molecules, polarization, ultraviolet spectral area, quarter wave plate, sensitivity, optical density.*

Introduction

Polarization spectra provide information on the orientation of the molecules of dissolved substances, and also these spectra are more informative with respect to electronic spectra [1]. The photophysical and photochemical properties and processes occurring in solutions of vitamin preparations were studied in [2-6]. Molecules of plant origin have such characteristics that determine their photostability and thermal stability, these characteristics are a guarantee of their use in pharmaceuticals and medicine. In [7–9], the results of a research on the study of photochemical processes occurring in solutions Some medications are water-soluble, which allows them to be prepared on the basis of various drugs used in pharmaceuticals [10, 11] in the form of their concentrated aqueous solutions [12, 13].

The creation of new drugs based on plant pigments requires further research on their self-assembly. The identification of the conditions for the formation of self-assembly of molecules is one of the urgent problems of pharmaceuticals, as a result of which it becomes possible to test drugs [14, 15]. The determination of the structure of self-assembled molecules allows their targeted usage in medicine [16, 17]. Carrying out these studies allows us to identify the relationship of anisotropic - optical spectra with the structure of self-aggregates. These research methods are highly sensitive in detecting the delicate details of optical transitions.

1. The spectral-optical method to polarization measurement

The first optical system includes a mirror system. The scheme of the mirror system is shown in Fig. 1, which contains a bi-mirror 1 with an angle of 270^0 between its working faces a and b, bi-mirrors 2 and 3 with an angle of 90^0 between their own working faces c, d, e, and g-d. We will consider the polarization transformation in successive reflections in the system. Let a light beam be incident on the input face of the system in the general case of an arbitrary ellipticity of polarization.

We denote by E_p and E_s the components of the electric field of the incident light lying in the plane of incidence and perpendicular to it, respectively. After reflection from the face *a*, the ellipticity of light changes - the components of the electric field become equal to E_p^I and E_s^I. The incidence planes for the faces *a* and *c* are mutually perpendicular, therefore the S-component on the face *a* is the P-component on the face *c*. Similarly, P-component on a face *a* is P-component on *c*. Such a transformation of the components of the electric vector is described by the matrix y = (*G*-*b*).

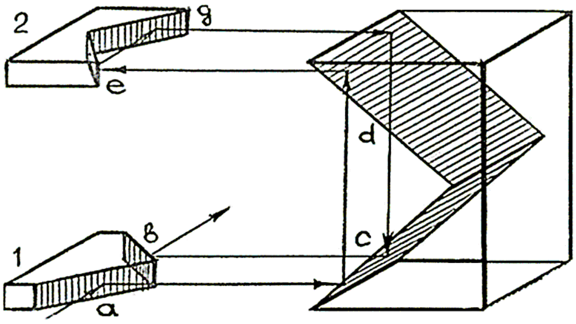

Fig. 1. Mirror system for spectral-optical polarization measurements.

After successive reflection from the faces *a* and *c*, the resulting vector of the electric field $\vec{E}'$ equal to

$$\vec{E}' = A\vec{E}, \quad (1)$$

where $\vec{E}$ –the electric vector of the light wave incident on the system, A – the transformation matrix.

In matrix A it is taken into account that the changes in the phases δ_p and δ_s, δ_s and δ_p of the oscillations of *p* and *s* components of the electric field of the light wave upon reflection from the faces a and c, are pairwise identical due to the equality of the angles of incidence of light on the faces. It follows from the form of matrix A that successive reflection from the faces of a and from the system of bi-mirrors introduces the same phase shifts (δ_p+δ_s) into both components of E_p and E_s. The ellipticity of the light does not change here, and the axis of the polarization ellipse rotates by 90^0. Successive reflections of the light beam from the faces *d* and *l* restore its initial state of polarization, since this reflection is identical to the reflection from the faces *a* and *c*. Further reflection of light from the faces *d, g, c,* and *b* does not change the state of polarization of the light wave due to the symmetry of the mirror system relative to the bisector plane of the bi-mirrors 1 and 2. The ellipticities of the light beams entering and between the faces *c-d* and *d-c* are equal. This device is used: as a universal prefix to a variety of optical and spectral devices for measuring optical activity, circular and linear dichroism. In this case, it is necessary to get rid of the scattered light, since it is possible to increase the optical path length without significant changes in the dimensions of the devices and without violating the initial polarization of the measuring light beam; as a reflecting system similar to multi-way ditches for increasing the optical density of discharged gas mixtures, vapors, and solutions. In addition, this optical device allows measurements of optical anisotropy in substances whose anisotropy is induced by the Earth's gravitational and magnetic fields, allows to isolate and identify these effects, which is achieved by placing the studied samples in different optical channels of the mirror system, since it is possible to ensure reciprocal passage of light beams with the same polarization

2. Fresnel double parallelepiped

The spectrum-polarimeter *Spektropol*-1, in which the compensation method of measuring the optical rotation of the plane of polarization of light is applied, has a sensitivity of $2\cdot10^{-3}$ – $8\cdot10^{-2}$ angular degrees [19]. Another method for measuring the linear dichroism of weakly oriented systems was implemented by us in serial circular dichrographs. The fundamental possibility of measuring linear dichroism with help of serial dichrographs, in which the electro-optical method for measuring circular dichroism was used, have been predicted in a number of works [18, 19]. One of these possibilities can be realized on Jasko-20, using an optical prefix - Fresnel double parallelepiped designed for the visible and near ultraviolet spectral area [19].

Figure 2 shows the optical scheme of the Fresnel double parallelepiped, a device that plays in our measurements the role of an achromatic quarter-wave plate and zero dichrograph lines, which we use to measure the linear dichroism of weakly oriented anisotropic and gyro anisotropic systems.

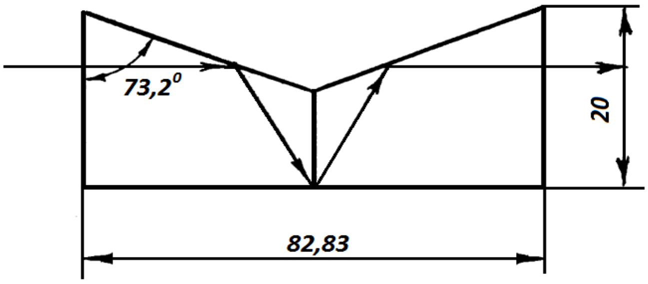

Fig.2. Fresnel double parallelepiped.

Figure 3 shows the data on the measurement of linear dichroism of the same linear dichroic sample using Spektropol-1spectropolarimeters and a Jasko-20 circular dichrograph according to the methods described above. As an anisotropic linear-dichroic object, a polymer film of polymethyl-methacrylate containing rhodamine 6G and its base, stretched uniaxially 4 times, was chosen. Both dyes in the polymer film are in an aggregated state and are easily oriented when stretched. Curves 1 and 2 were recorded on Spektropol-1 and Jasko-20 spectro-polari-meters, respectively, on the scales of these instruments: φ and θ. Nearby on the vertical axes are marked, the scale according to linear dichroism recalculated according to the above formulas.

The linear dichroism spectra were measured on a spectropolarimeter when the film was oriented with its axis of extension at an angle of 45^0 to the polarization vector of the light incident on it. The linear dichroism spectra were measured on a circular dichrograph when the film was oriented with its axis of extension at an angle of 0^0 to the linear polarization vector converted by a Fresnel double parallelepiped from a circular rhodamine 6G and its base, stretched 4 times. Film thickness is 0.3 mm.

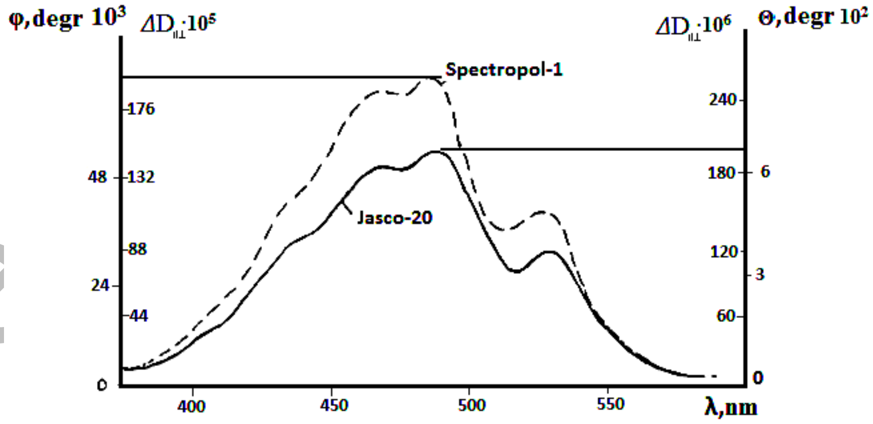

Fig. 3. Spectra of linear dichroism of a polymethylmethacrylate film containing.

The positions of the films in both cases corresponded to the maximum amplitudes of the bands of the recorded curves. In this case, there is good correspondence between the two spectra of linear dichroism. So, at the maximum of both curves $\lambda^{\varphi}_{\max}$ = 490nm, the amplitudes recorded on Spektropol - 1 and Jasko-20 are respectively $2.03 \cdot 10^{-3}$ and $2.04 \cdot 10^{-3}$ units of difference optical density. As the electro-optical element in a serial Jasko-20 dichrograph, a Pockels cell with a KDP crystal (KH_2PO_4) is used [20].

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In practice, the measure of circular dichroism is the ellipticity value, determined by the ratio of the minor and major axes of the ellipse and equal for small θ;

$$tq\theta \approx \theta = tq\frac{\pi}{\lambda}(X_L - X_R)\cdot l \approx 33C\cdot l(\varepsilon_l - \varepsilon_R), \tag{2}$$

where x_L, x_R, ε_L, ε_R – are absorption coefficients and molar extinction coefficients of a substance for light with a wavelength λ polarized in a circle to the left (L) and to the right (R); C- concentration of optically active substance; *l* - the thickness of the sample.

It is known that

$$\Delta\varepsilon = \varepsilon_l - \varepsilon_R = \frac{1}{Cl}\log_{10} {}^{I_R}\!\big/_{L_L}, \tag{3}$$

where I_R, I_L- the intensities of the light, transmitted through the sample, polarized in a circle to the right and left.

By virtue of this

$$\theta = 33\cdot\log_{10} {}^{I_R}\!\big/_{I_L} = 33\cdot\log_{10}\frac{1+I_2/21}{1-I_2/21}, \tag{4}$$

where $I_1 = \frac{1}{2}(I_R + I_L), I_2 = I_R - I_L$ a-priory.

As $\frac{I_R - I_L}{I_R + I_L} = \frac{I_2}{2I_1} \leq \mathrm{I}$ (for small optical activity), so

$$log_{10}\frac{1+{}^{I_2}/_{2I_1}}{1-{}^{I_2}/_{2I_1}} \approx log_{10}\frac{e+{}^{I_2}/_{2I_1}}{e-{}^{I_2}/_{2I_1}} = \frac{I_2}{I_1}\cdot log_{10}e \tag{5}$$

hence,

$$\theta = 33\cdot\frac{I_2}{I_1}\cdot log_{10}e \tag{6}$$

That is, the ellipticity value (in degrees) is proportional to the ratio of intensities I_2, I_1, which are recorded [21] by the Jasko-20 dichrograph photoelectric system. In the transition from circular to linear dichroism, it is convenient to use the formula for θ in another form:

$$\theta_{CD} = 28{,}6\frac{I_R - I_L}{I_R + I_L}. \tag{7}$$

When circular light polarization is incident on a Fresnel double parallelepiped, it is converted to linearly polarized light, and, for R and L, circular polarizations are orthogonal. Consequently, the Jasko-20 dichrograph, which measures θ_{KD} in degrees, is equipped with an optical prefix in the form of a double Fresnel parallelepiped, located after the Pockels cell in front of the sample, and measures linear dichroism

$$\theta_{LD} = 28{,}6\cdot\left|\frac{I_\perp - I_\parallel}{I_\perp + I_\parallel}\right| \tag{8}$$

where I_I, I_{II} - intensities of linearly polarized light transmitted through the sample and incident on the dichrograph photodetector:

$$\frac{I_\perp - I_\parallel}{I_\perp + I_\parallel} = \frac{10^{-D_\perp} - 10^{-D_\parallel}}{10^{-D_\perp} + 10^{-D_\parallel}} = \frac{e^{-D_\perp log_e 10} - e^{-D_\parallel log_e 10}}{e^{-D_\perp log_e 10} + e^{-D_\parallel log_e 10}} =$$

$$= th\left[(D_\perp - D_\parallel)log_e {}^{10}\!/_{2}\right] \approx \frac{(D_\perp - D_\parallel)\cdot log_e 10}{2} \tag{9}$$

(for small argument values). Thus, the dichroism measured by the dichrograph

$$\Delta D_{\perp,\parallel} = D_\perp - D_\parallel = \frac{\theta_{LD}}{32{,}98} \tag{10}$$

at the maximum sensitivity of the dichrograph

$$\theta_{CD} = 10^{-3} degr \cdot sm^{-1} \tag{11}$$

corresponds to its linear dichroism sensitivity

$$\Delta D_{\perp,\parallel} \cong 3 \cdot 10^{-5} \tag{12}$$

values of difference optical density.

The Spektropol-1spectropolarimeter allows measurements in the spectral area 200 - 610 nm, and the Jasko-20 dichrograph - in the spectral area 200-700 nm. The zero line of the spectrum of the polarimeter (through the air) has an ideal rectilinear character, while the zero line of a linear dichrograph based on the Jasko-20 is not quite ideal: the deviation of this line from the straight line in the spectral areas 200-320 and 640-700 nm, apparently, is associated with the imperfection of the Pockels cell of the dichrograph, which gives in these spectral areas values as in the circular polarization of light. As a result of this, after the light transmits through the Fresnel double parallelepiped, it acquires a polarization close to linear, with a very large ellipticity. Thus, if a linear dichroic sample has a small linear birefringence, it is preferable to measure the linear dichroism on the spectrum of a Spektropol-1polarimeter. In all other cases, especially when the sample is gyro-anisotropic and has significant optical activity, it is convenient to use Jasko-20.

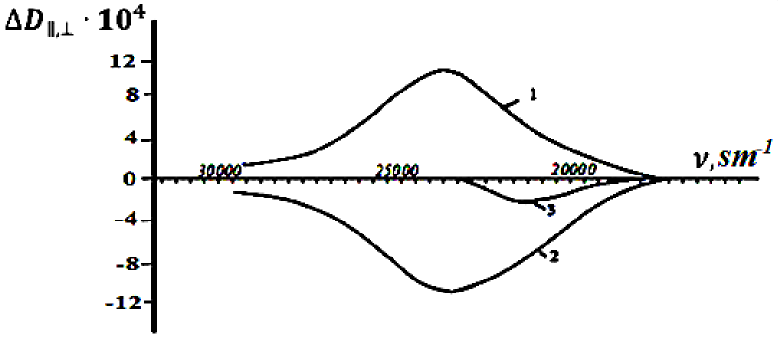

Fig. 4. The spectra of linear dichroism of tartrazine associates under the conditions of the hydrodynamic flow of its solution at an angle between the flow velocity vector and the transmitted light polarization vector + 45 ° (1) and –45 ° (2). Curve 3 is the difference between spectra 1 and 2. C = 2 · 10^{-4}M. *l* = 0.1 cm.

As an example, we studied solutions of tartrazine in a laminar hydrodynamic flow. It was found that they show significant linear dichroism, its value at the maximum of the absorption band at ν=23500 cm^{-1}makes$\Delta D_{\parallel,\perp}=10^{-3}$units of dichroic optical density.

Figure 4 shows the spectrum of linear dichroism of tartrazine associates oriented in the hydrodynamic flow of a binary mixture of a water-dioxane solution, obtained from the corresponding spectrum of the non-gyrotropic rotation of the plane of polarization at an angle between the flow velocity vector and the polarization vector, transmitting perpendicular to the linearly polarized light flow equal to +45° C (curve 1), and the linear dichroism spectrum of the same solution, recorded at an angle of -45° C (true linear dichroism spectrum) (curve 2). Just at these angles of orientation of the flow velocity vector relative to the polarization vector of transmitted light the maximum amplitudes of the main bands are observed in the corresponding non-gyrotropic rotation spectra of the plane of polarization, which is a necessary condition for recording the linear dichroism curves $\Delta D_{\parallel,\perp}$= (λ) on the spectropolarimeter [22] .

The algebraic sum of spectral curves 1 and 2 gives a curve 3, from which, by applying the decomposition into Lorentzian contours, it is possible to distinguish two different amplitude bands of linear dichroism. The positions of maxima and FWHM of which corresponds to that position of the maxima and half-widths of the absorption bands associated tartrazine, which confirms the correctness of measurements and calculations. The fact that tartrazine associates show linear dichroism, being easily oriented in a laminar hydrodynamic flow, indicates a strong anisotropy of dye microcrystals having a needle (rod-like) shape.

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Conclusion

The results show that both in concentrated aqueous solutions and in binary mixtures of solvents, the association of food dyes shows itself as a result of combining the molecules of the studied compounds directly between themselves. In this case, the structures of the combined molecules are determined by the use of optical systems, obtaining spectra of linear dichroism. In these cases the sensitivity of the device increases by about two orders of magnitude

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Article accepted for publication 22.11.2019