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# Influence of UV Radiation on Structure of Lyotropic Liquid Crystals

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*Molecular mechanisms of the impact of ultraviolet (UV) rays on biological systems can be divided into three categories: structural and functional changes of DNA, photoinactivation of proteins and structural damage of cell membranes. Though a large number of studies have explored the first two categories of UV ray impacts on biological systems and have proposed various feasible models for the pathways of these impacts, few studies have explored structural damage of cell membranes and the only proposed mechanisms for this UV impact is that of lipid, peroxide, and amino acid oxidation with the impact of various wave lengths of UV rays, A (400–320 nm), B (300–275 nm), and C (275–180 nm) being explained by these mechanisms. In the present work, we have studied the biological impact of UV rays on the phospholipid bilayer by using simultaneous small and large angle X-ray diffraction method.*

**Keywords** Amphiphilic compound; DNA, membrane; lyotropic liquid crystals; ultraviolet (UV) radiation; X-ray

## Introduction

To date, most research findings have reported a high sensitivity of DNA to ultraviolet (UV) radiation, including UV radiation of different wavelengths [1–6]. However, few publications have addressed the effect of UV radiation on cell membranes [7, 8], which may lead to the death of the cell through structural damage of its membrane. The impact of UV radiation on the erythrocytes (red blood cells), which are responsible for overall physiological regulation, has not been studied. Erythrocytes are not homogeneous but include cells of different masses, states, and ages. Studying the effects of UV radiation on erythrocytes may shed light on UV radiation impacts on the entire biological system.

One of the peculiarities of ionizing UV radiation is that different doses of radiation have different impacts on biological systems, including erythrocytes. The impact of UV radiation on erythrocytes also depends on their structure and mass. However, the mechanisms of membrane damaged by UV radiation are not clear. Clarifying the mechanisms and

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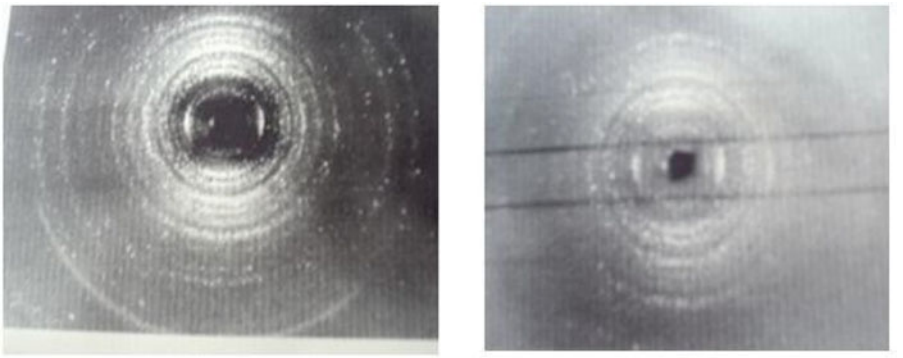


**Figure 1.** The diffraction pattern of X-rays at small and large angles for the lecithin-water system before exposure to UV rays (Fig. 1(a)) and after exposure (Fig. 1(b)).

consequences of UV radiation exposure may provide opportunities for better understanding protective biological mechanisms.

## Results and Discussions

We used the lecithin-water system as the physical model of membrane. X-ray diffraction reflexes are expanded by using the two-parameter Luzatti formula [9]

$$d = l_0 \frac{(k + 2M/\rho_0 s_0)c_w}{c_a} \tag{1}$$

where $d$ is the period of identity, $l_0$ is the length of a single amphiphilic molecule, $k$ is the swelling coefficient, $M$ is the molar mass of amphiphilic matter, $\rho_0$ is the density of water, $s_0$ is the partial area per molecule head, $c_{\mathrm{w}}$ is the water concentration, and $c_{\mathrm{a}}$ is the concentration of amphiphilic matter. From the small angle X-ray diffraction pattern of the lecithin-water system we determine the parameter $d$. From the large angle reflex, we determine $s_{\mathrm{o}}$. The diffraction pattern of X-rays at small and at large angles for the lecithin-water system is given in Fig. 1.

By studying the influence of UV rays for various concentrations of water, the dependence of $d$ on $C_w/C_a$ is plotted. The corresponding angle $\beta$ is given by

$$tg\beta = k + 2M/\rho_0 s_0 \tag{2}$$

from which we derive $k = tg\beta - 2M/\rho_0 \mathrm{s}_0$, where $\beta$ is the angle between the dependence curve $d$ between $c_w/c_a$ (1) and the axis $c_w/c_a$ (see Fig. 2).

Thus, experimentally obtaining the structural characteristics such as period of identity $d$ and the area per molecule head for amphiphilic matter $s_{0,}$ by determining tg$\beta$ and having $\rho_0$ and $M$, we can determine the swelling coefficient $k$. By using the acquired data, we plot $s_0$ versus $C_w/C_a$ (a) and $L/l_0$ – versus $C_w/C_a$ (b) (see Fig. 2).

As shown in Fig. 2(a), the influence of UV rays leads to an increase of partial area. The same is the case for the relative width. In all cases, the influence of UV rays on the

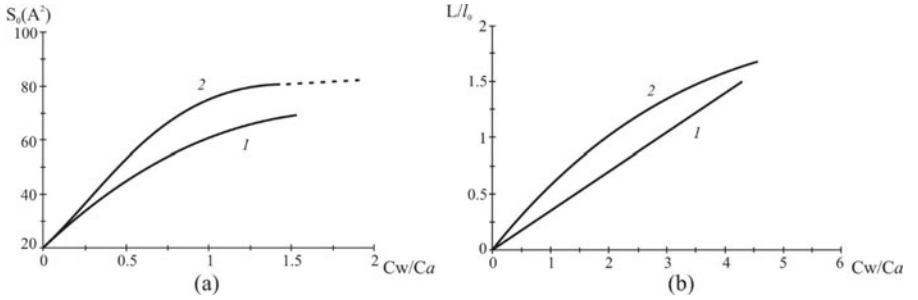


**Figure 2.** The dependence of the partial area (a) and phospholipid bilayer relative width (b) on the $\frac{C_w}{C_a}$ : 1 – before the radiation, 2 – after the radiation; $L$ – bilayer width, and $l_o$ – phospholipid molecule width.



phospholipid bilayer leads to swelling, whereas in the case of infrared (IR) radiation a wrinkling of the bilayer occurs. We further investigated the impact of UV rays on the structure of the bilayer using mathematical modeling. For this purpose, we have employed the method of free energy minimization. First we determined the change $\Delta F$ for free energy:

$$\Delta F = F_2 - F_1, \tag{3}$$

where $F_1$ and $F_2$ are the free energies before and after radiation exposure respectively. The system of lecithin-water has the following form:

$$\Delta F = \Delta E_e + \Delta E_w + \Delta E_s - kTN \ln(V_{2f}/V_{1f}), \tag{4}$$

where $\Delta E_e$ is the change of electric energy, $\Delta E_{vv}$ the change of Van der Vaals energy [10], $\Delta E_s$ the change of surface energy, and $kTN \ln(V_{2f}/V_{1f})$ is the change of entropic energy:

$$\begin{aligned} E_e = \frac{q^2}{2\pi\varepsilon_0\alpha}\left(\frac{L\rho N_A}{m}\right)^{1/2}\Bigg\{ & \left(\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}\right)\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2\right)^{1/2}} \\ & +\frac{1}{2\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(L+2d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L+2d\sin\theta}\right] \\ & +\frac{1}{\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+L^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L}\right] \\ & +\frac{1}{\varepsilon_1}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{d\sin\theta}\right] \\ & +\frac{1}{2\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(L+d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L+d\sin\theta}\right]\Bigg\}, \end{aligned}$$

$$E_{vv} = A\left(31 - 15^{L}/_{l_0}\right)\frac{\xi^5 N}{l_0^4}\left(\frac{L\rho N_A}{m}\right)^4 - B\left(7 - 4^{L}/_{l_0}\right)\frac{\xi^2 N}{l_0^2}\left(\frac{L\rho N_A}{m}\right)^2,$$

$$E_s = \sigma\frac{Nm}{\rho L N_A},$$

$$E_{en} = kTN\ln\left(\frac{m}{\rho N_A}\right).$$

Substituting the values for separate energies, we have:

$$\begin{aligned}
F = {} & \frac{q^2}{2\pi\varepsilon_0\alpha}\left(\frac{L\rho N_A}{m}\right)^{1/2}\left\{\left(\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}\right)\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2\right)^{1/2}}\right. \\
& +\frac{1}{2\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(L+2d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L+2d\sin\theta}\right] \\
& +\frac{1}{\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+L^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L}\right] \\
& +\frac{1}{\varepsilon_1}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{d\sin\theta}\right] \\
& \left.+\frac{1}{2\varepsilon_2}\left[\sum_{i=0}^{(N/2)^{1/2}}\sum_{k=0}^{(N/2)^{1/2}}\frac{4\left((N/2)^{1/2}-i\right)\left((N/2)^{1/2}-k\right)}{\left(i^2+k^2+(L+d\sin\theta)^2\right)^{1/2}}-\frac{3}{2}\frac{N}{L+d\sin\theta}\right]\right\} \\
& +A\left(31-15L/l_0\right)\frac{\xi^5 N}{l_0^4}\left(\frac{L\rho N_A}{m}\right)^4 - B\left(7-4L/l_0\right)\frac{\xi^2 N}{l_0^2}\left(\frac{L\rho N_A}{m}\right)^2 \\
& +\sigma\frac{Nm}{\rho L N_A} - kTN\ln\left(\frac{m}{\rho N_A}\right). \qquad (5)
\end{aligned}$$

where $L$ is bilayer thickness, $\xi$ is the number of CH-groups in the amphiphilic molecule, $\rho$ is the density of lamella, $\sigma$ is the coefficient of surface tension, $q$ is the charge of the head of the dipole fragment of phospholipid, $\alpha$ is the distance between the nearby heads in phospholipid molecule, $\theta$ is the angle between the dipole fragment and the lamella plane, $\varepsilon_0$ is the electric constant, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric permittivities for the water and phospholipid, $N$ is the number of molecules in the bilayer, $N_A$ is Avogadro's number, $m$ is the mass of phospholipid, and $A$ and $B$ are the Leonard-Jones constants. With exposure to UV rays, the electrostatic repulsive forces are increased due to ionization, whereas the Van der Vaals forces are reduced due to lipid, amino-acid, and peroxide oxidation. In the case of peroxide oxidation, free radicals are formed on the outer part of the radical particle a where an unpaired electron is created; this activates an interaction on an intramolecular level and decreases the *Van der Waals* interaction on the intermolecular level. Consequently, the *Van der Waals* force between hydrocarbon chains is decreased.

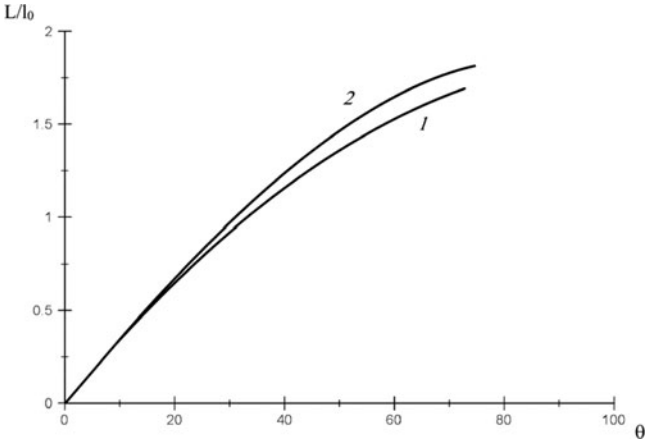


**Figure 3.** The dependence of the $\frac{L}{l_0}$ on the angle $\theta$ between the dipole fragment of phospholipid and the bilayer surface: 1 – before the radiation, 2 – after the radiation.

In the case of amino-acid oxidation, the destruction of the link C=O is possible, which would lead to the creation of unsaturated amino acids and as a result reduce the *Van der Waals* interaction. A similar situation takes place in the case of lipid oxidation.

For all three cases of ionizing radiation, charges are formed which increase the repulsive forces due to Coulomb's (electrostatic) interaction, and radicals are created which decrease the *Van der Waals* attraction forces. As a result, the balance between the electrostatic and the *Van der Waals* forces is lost. The electrostatic repulsive force prevails over the *Van der Waals* attraction force, leading to the swelling of the phospholipid bilayer.

The latter also is a consequence of the change of the angle $\theta$ between the phospholipid dipole fragment and the bilayer surface (see Fig. 3). $F$ is the common formula of free energy. Using (5), an expression for free energy for the states 1 and 2 is obtained with reference to the previously listed variables $\sigma_1$, $\rho_1$, $\alpha_1$, etc.

Using the condition of minimization for free energy, namely, $\frac{\partial F}{\partial L} = 0$, $\frac{\partial F}{\partial \alpha} = 0$, $\frac{\partial F}{\partial N} = \mu$, where $\mu$ is the chemical potential, a ratio between $L/l_0$ and $\theta$ can be obtained, as shown in Fig. 3.

As is shown in Fig. 3, the impact of UV radiation exposure leads to an increase in angle $\theta$ between the dipole fragment of phospholipid and the bilayer surface, due to the increase of repulsive forces and, hence, produces swelling.

To distinguish between the contributions of the separate oxidations (lipid, amino acid, and peroxide) in the bilayer swelling, we used quantum-mechanical modeling and determined the chemo-luminescence wavelengths for various oxidations. The program *HyperChem-8* provided the means of obtaining the spectra of the system by quantum-mechanical calculations, both in the visible and the UV region. The calculation shows that while forming radicals, the system radiates chemiluminescent rays of various wavelengths, including that for amino-acid oxidation wavelength of $\lambda = 540$ nm, for lipid oxidation $\lambda = 420$ nm, for peroxidation $\lambda = 580$ nm, and for singlet oxygen $\lambda = 1270$ nm.

By using an interference filter, we separated out the integral intensity of the radiation corresponding to the given oxidations (Fig. 4), the result of amino-acid oxidation.

As a result of UV rays exposure amino-acid oxidation takes place, which through chemiluminescence emits electromagnetic waves in an optical range $\lambda = 540$ nm. During

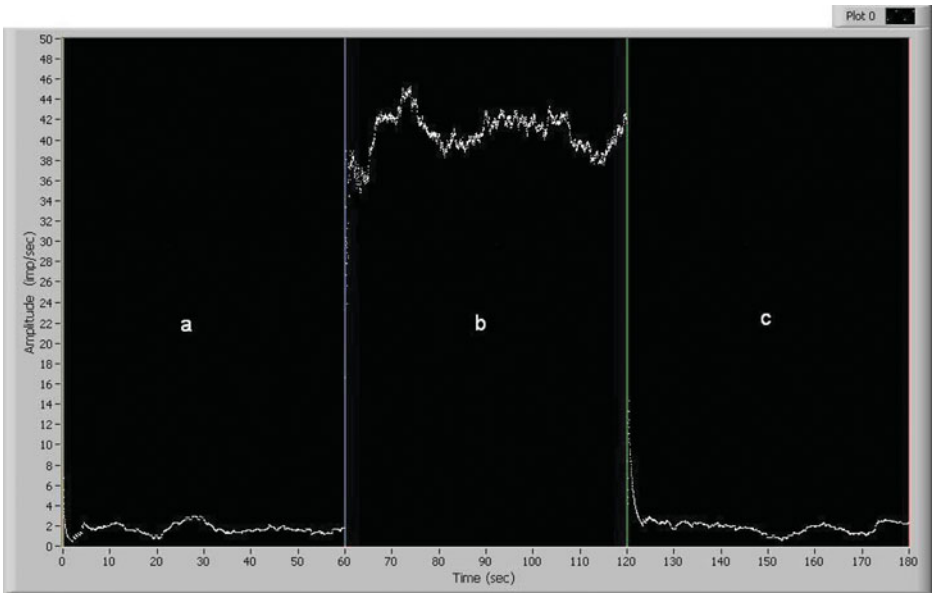


**Figure 4.** Chemoluminescence radiation for (a) lipid, (b) amino acid, and (c) peroxide oxidations.

the experiment, an interference filter of a narrow band (wavelength of $\lambda = 540$ nm) was installed in front of a photomultiplier.

As shown in Fig. 4, the chemiluminescent signal is revealed only in diagram (b) with a narrow wavelength transmission band of around $\lambda = 540$ nm. Diagram (a) shows the results for smaller wavelengths of $\lambda < 540$ nm, and diagram (c) shows results for larger wavelengths $\lambda > 540$ nm. For neither of these two wavelength ranges, a signal was detected.

Comparing the experimental and theoretical results, we concluded that the UV rays cause amino-acid oxidation, where *Van der Waals* interaction decreases and, consequently, disrupts the balance between the forces of attraction and repelling. As a result, the bilayer swells with the increase in the thickness of the bilayer $L$ as well as in the partial area $S$ in one head of the molecule.

In summary, on the bases of this experimental data and the theoretical modeling, we concluded that UV radiation leads to the swelling of the phospholipid bilayer, whereas IR radiation results in the wrinkling of the bilayer.

## Experimentation

### *Methods*

The experimental results were produced by applying X-Ray diffraction methods to the smaller and larger angles simultaneously, using a polarization optical microscopy and computer simulation methods. X-Ray diffraction for the smaller and larger angles and the method of computer simulation were the essential experimental methods applied. These methods allowed us to acquire information about the structure and the orientation of the amphiphilic compounds, the electronic density (which differed from the normal electronic density), and to confirm the existence of the hydrocarbon "tails." The concentrated water

solutions of the amphiphilic compound formed the liquid crystal lamellar phase. The previously mentioned methods can be applied for the study of changes in the structure of the lyotropic liquid crystals (LLC) under the influence of the external actions such as the electrical and magnetic fields of the UV bandwidth.

### *The Materials Applied*

The current study investigated the changes of the mesophase structures in lecithin-water due to ultraviolet radiation exposure for different concentrations. Egg lecithin was a local standard produced in a factory in Kharkov. It is in a 10% alcohol solution, which was exposed to vacuum evaporation to produce a dry powder-like substance. Experiments were carried out by the X-ray simultaneous diffraction method for small and large angles, as is described in Ref. [9]. Our experimental URS-2 X-ray device and a *BSV-29 Cu* X-ray tube were used in the experiment. The sample was prepared in the form of a cylindrical quartz glass in the presence of different liquid crystals of various concentrations.

## Conclusions

On the base of experimental data and theoretical modeling we conclude that:

The influence of UV radiation exposure leads to the increase of the partial area and the width of the lamella.

As a result of the impact of UV radiation exposure, the balance between the electrostatic and Van der Waals forces was disrupted, causing structural changes of the lamella.

We also defined the coefficient of bilayer swelling, which is very important for the investigation of the behavior of biomembranes exposed by UV radiation.

UV radiation leads to the swelling of the phospholipid bilayer, whereas IR radiation produces wrinkling of the lamella.

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