Photoinduced Spatiotemporal Oscillations and Self-Organization of Dissipative Structures in Polymer-Immobilized Dispersed Semiconductors

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This paper considers photoinduced reaction-diffusion processes in active medium containing polymer-immobilized dispersed semiconductors. The nature of both redox potential and ion concentration oscillations occurring in the microheterogeneous system under irradiation is discussed, and the role of a double electric layer on the surface of the microcompartments in generation and maintenance of electrochemical and concentration gradients is established. Formation of dissipative membranous microstructures within the active medium under light irradiation with the structural and phase inhomogeneity is described and their difference in chemical composition from the surrounding medium is proved to be due to the active redox transformations occurring in them which also involve the polymer matrix components.

Keywords: Photoinduced chemical oscillations, Reaction-diffusion kinetics, Dissipative structures, Polymer-immobilized silver halides, Dispersed semiconductors.

1. INTRODUCTION

At present, self-oscillatory reactions induced by photochemical and radiochemical methods are well-known. For example, Kuhnert [1, 2] describes a photoinduced Belousov-Zhabotinsky reaction with the use of a ruthenium photosensitive catalyst. This phenomenon, subsequently called the optochemical control, consists in the formation of a phase wave during transition from the dark cycle of the reaction to the stage of irradiation.

Within the framework of the reaction-diffusion model, the phenomenon of optochemical control can be described as the intersection point shift of zero isoclines as the isocline of the inhibitor shifts under irradiation. At a certain magnitude of illumination, this point undergoes transition from the oscillating to the excitable mode and the mode of a leading center. Thus, photochemical control of the reaction-diffusion kinetics of self-oscillatory reactions can be achieved. At the same time, the range of possible effects on the active photosensitive medium is not limited to the optical range, but depends on the spectral sensitization of a catalyst. The nomenclature of possible reactions is also not limited to the Belousov-Zhabotinsky reaction media, since there are different active media with photocatalysts that possess sensitivity in other spectral regions.

Thus, Horsthemke and Lefevr [3] describe noise-induced phase transitions in a Briggs-Rauscher reaction. As a source of perturbations, the authors used a radiation source with a fluctuating intensity, where the correlation time of fluctuations is small in comparison with the macroscopic time scale of the system. The bistability, detected by the photometric method and the redox potential measurements, indicates the presence of two phases corresponding to the oscillating and stationary system modes.

Since the formation of phases is controlled photo-

chemically, it is possible to form patterns of a predetermined shape in optically controlled autowave processes. This principle underlies the work on creating a reaction-diffusion processor for processing optical information, and the most studied active media of the Belousov-Zhabotinsky type [4] are most often used as the substrate. It follows that they are a particular case of a multitude of light-sensitive active media. Therefore, the mechanism of self-oscillating processes in optochemically controlled systems may drastically differ depending on the composition of the active medium and its individual response to the inducer. For example, in [5] the possibility of creating reaction-diffusion devices based on minor charge carriers in semiconductors is considered. Obviously, the nature of the self-organization processes in semiconductors is different – nonequilibrium phase transitions in them are due to recombination and generation phenomena [6]. As a result, the specific response of the active medium in the case of a semiconductor composition contains charge effects, which substantially changes the nature of the transport (interaction) between the medium particles.

As is known [7], the medium is considered as an active one when each point of it is a source of free energy and, as a consequence, participates in nonequilibrium processes, and is also conjugated to the neighboring points by means of transport processes. Being secondary with respect to activation, the transport process occurs either in the same or in derivative forms. Thus, nonequilibrium-thermodynamic reactions with diffusion of the Belousov-Zhabotinsky type, by definition, are sensitive to temperature [8] and external electric fields [9-11]. Accordingly, the transport processes in them can take the form of heat and mass transfer in a reaction-diffusion medium and migration of the charge carriers under the action of generated fields. This ensures the formation of dissipative structures in the active medium,

which depend on the nature of the transport in each point of the substrate. Thus, it is possible to select an active medium with a given complex of transport types, in which self-oscillatory reactions controlled by the response factors of a given medium will occur.

Based on the above, the authors attempted to implement controlled self-oscillating processes in the active medium based on an alternative substrate with a multifactor response. For this purpose, the authors studied self-organization processes in spectrally sensitized disperse systems based on inorganic semiconductors (in particular, silver halides or AgHal) with known sensitivity to the radiation in the optical range and further, possessing a set of properties providing the medium with numerous reaction channels. The properties of a multifactorial response of such systems include: photosensitivity, charge injection (charge coupling), thermal diffusion and a number of other secondary factors. Ionizing under the action of radiation, semiconductors of a similar composition exhibit the presence of mutually transient phases (multistability), charge accumulation and charge interactions (transport) between particles, which makes it possible to treat them as active media. Multistability is ensured by photoreduction of metallic silver alternating with the solarization process.

The phase transitions observed at that time are also insulator-conductor-type transitions in a partially ordered matrix [12]. Within the framework of the percolation model, with a small concentration of silver grains in a non-conducting dispersion medium, the system acts as an insulator, and at a high concentration, as a conductor. At the same time, if the concentration is small, the system is considered as a sol, and in the opposite case as a gel. This phenomenon is similar to the autowave switching between high and low-resistance states in semiconductor films exposed to radiation [13]. In this connection, the controlled formation of heterogeneous dissipative structures with different local conductivity on the basis of the dispersed semiconductor phase AgHal becomes feasible.

It is known that the efficiency of heterophase structuring in self-oscillating processes during the formation of Turing patterns of various dimensions increases when the reaction is performed in the inverse microemulsion (inverse micelles) [14-16]. This is due to the diffusion and mass-exchange advantages of disperse systems and membrane structures in the phenomena of chemical transport. Therefore, instead of using pure preparations of silver halides with simple kinetics for experiments, it is better to use gelatin matrix with the immobilized granules of silver halides in which, under irradiation, "bubble" boundaries are formed that separate local processes ("compartmentalizing" active medium pumped by the light radiation). Mikhailov named precursors of such microheterogeneous systems "polymer-immobilized matrix implants", or AgHal-GIM [17, 18]. Examples of such a system are nuclear emulsions, which are characterized by very high saturations of the AgHal layer (from approximately equal amounts of AgHal and gelatin to 85 % AgHal).

2. MATERIALS AND METHODS

2.1 Photosensitive Material

The dispersed phase selected was an AgBr semiconductor with a bandgap of 1.35 eV and a photoelectric threshold 3350-2400 Å immobilized in a gelatin
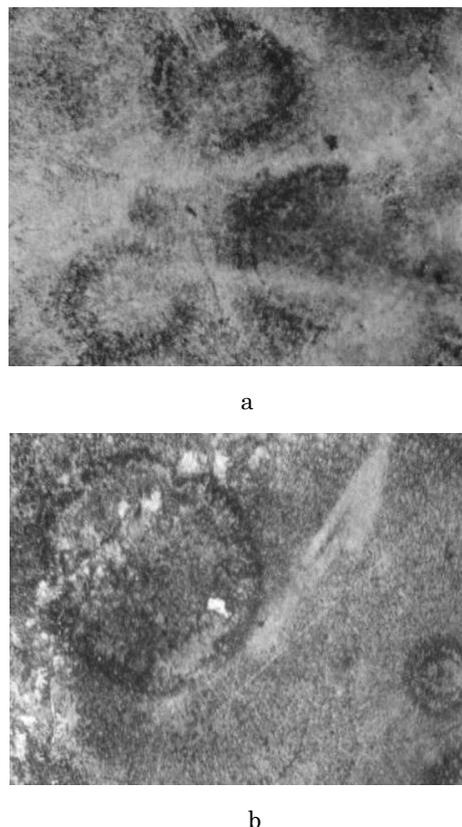

a

b

Fig. 1 – Membranous microstructures in AgHal-GIM (magnification: a – ×200, b – ×300)

matrix. In experiments, a nuclear gelatin-based photoemulsion was used with the concentrations of the component elements given in Table 1. The emulsions were irradiated using a mercury ultraviolet emitter DRB-8 ($\lambda = 253.7$ nm). After exposure, the photoemulsion was processed by the standard method [19], with the exception of the thermal regime.

2.2 Electrophysical and Electrochemical Measurements

Detection of the active medium parameters was carried out by the potentiometric method. Measurements of the redox potential Eh and the corresponding parameters (pH, pX) for individual ions were performed using the EXPERT-001 analyzer. On the surface of the emulsion, measurements were conducted by the probe method using solid-state ion-selective electrodes. To determine the pulse characteristics of the processes, a stand was built on the basis of reverse pulse counters and LC meters with computer output, which fixed the discharge of microstructures considered as carriers of an electrical double layer.

2.3 Microscopy and Chemical Mapping

The registration of microstructures, products of reaction-diffusion processes in the active medium, was performed optically with a trinocular microscope with
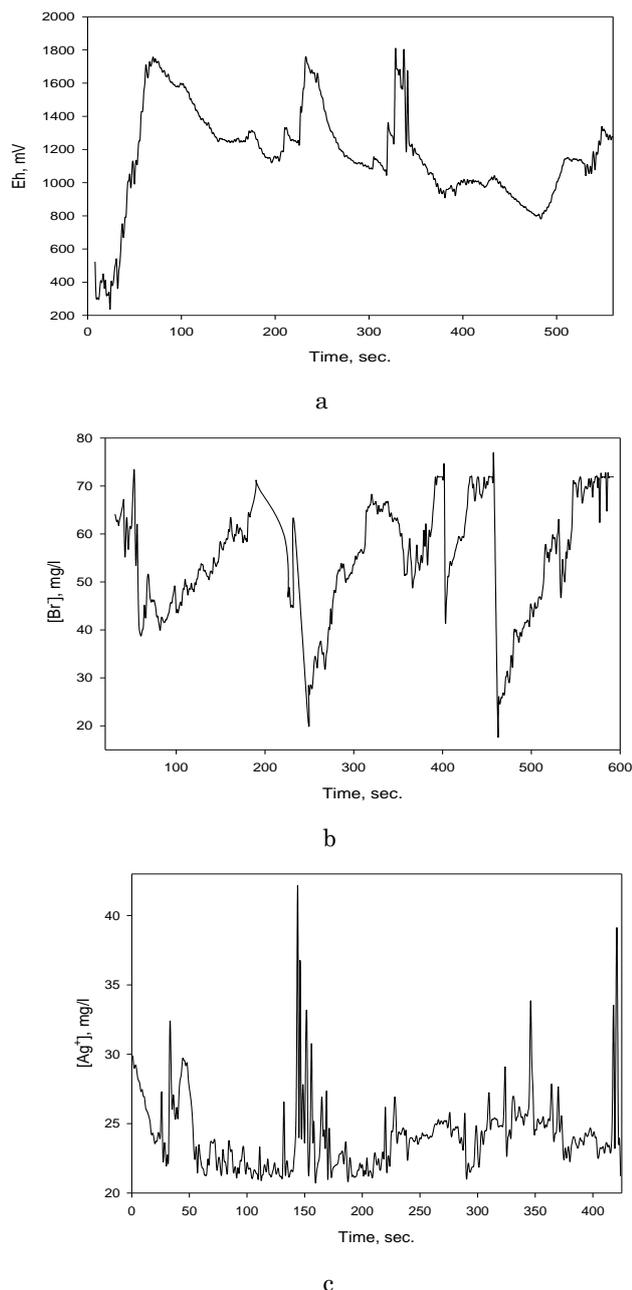
a

b

c

Fig. 2 – Photoinduced oscillations in AgHal-GIM: a – Eh oscillations, b – [Br⁻] oscillations, c – [Ag+] oscillations.

a photographic attachment CANON 590 IS with a bayonet lock. Secondary ion mass spectrometry and mapping of samples in secondary ions were carried out using a TOF-SIMS time-of-flight mass spectrometer by ION-TOF (Germany). Electronic photomicrographs of irradiated emulsions were obtained on a Scanning Electron Microscope Carl Zeiss LEO (Germany) at an accelerating voltage of 20 kV. Local element analysis of the samples was performed by the method of energy dispersive X-ray spectroscopy with an INCA 300 attachment detector.

3. RESULTS AND DISCUSSION

3.1 Morphological Characteristics of Microstructures in Active Media

Since radiation induces reaction-diffusion processes in a photosensitive active medium and, as a consequence, causes it to undergo structural changes, in all exposed photographic emulsions a pronounced structural heterogeneity was observed. Optical microscopy of the partially dehydrated photographic emulsions performed in a reflection mode revealed integral and fragmentary, partially perforated structures such as dynamic membranes and shells, probably formed during their dehydration (Fig. 1).

The dimensions of these structures (dozens of micrometers) relative to the grain size of nuclear emulsion (up to 0.3 microns) make it possible to hypothesize that dispersed particles of crystalline silver bromide are fixed on the surface of dynamic membranes and thus ensure their sensitization to radiation. Taking into account that the maximal blackening corresponds to the silver metal crystals in the developed nuclear emulsions, it can be concluded that the formation of optically dense silver-containing zones encrusting the membranes of these structures is well indicated on the resulting micrographs (Fig. 1). This effect is most likely due to the local accumulation and partial release of the microbubbles of molecular halogen formed during AgBr photolysis in a polymer matrix and due to parallel accumulation of a second product of photolysis – metallic silver, on their periphery.
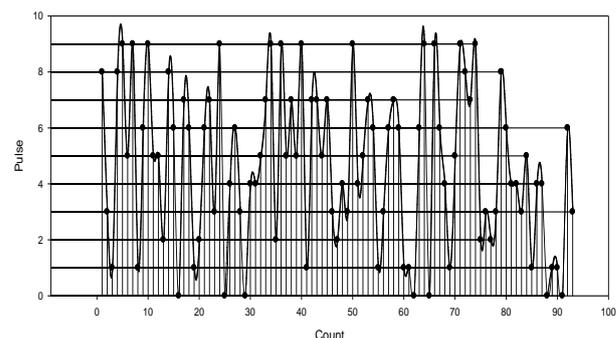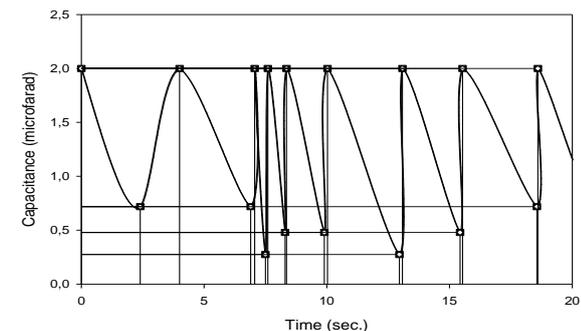

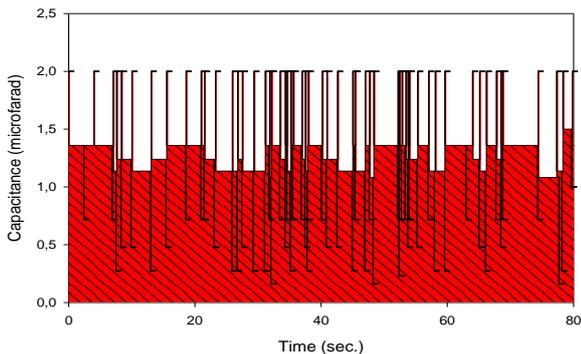**Fig. 3** – Reversive counting data in oscillating system (AgHal – GIM): Br⁻-selective electrode.

3.2 Results of Electrochemical Measurements

Given the presence of compartmentalized boundaries in the active medium, it is logical to assume the existence of concentration and potential gradients between the medium and the membrane bounded microvolumes. Figure 2 shows the results of measuring the electrochemical potential on the surface of the emulsion during the light exposure, confirming the existence of photoinduced oscillations in the above system.
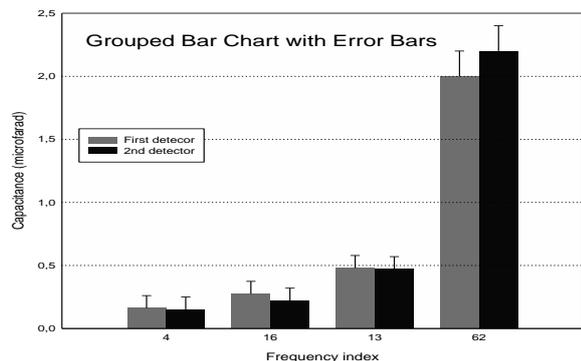
Figure 2a shows oscillations of the redox potential with an 1.7 V amplitude in AgHal-GIM. This is two orders of magnitude greater than the dark current and noise level in this system, and the shape of the curves differs significantly from the noise signal. Fluctuations in the concentrations of individual ions also contain a pronounced modulation that allows one to evaluate the kinetic regimes of the oscillatory processes in the system, most likely associated with the role of the dynamic membranes and the accumulation of individual ions in a heterogeneous medium with a subsequent ejection. Thus, oscillations in bromide ion concentration (Fig. 2b)
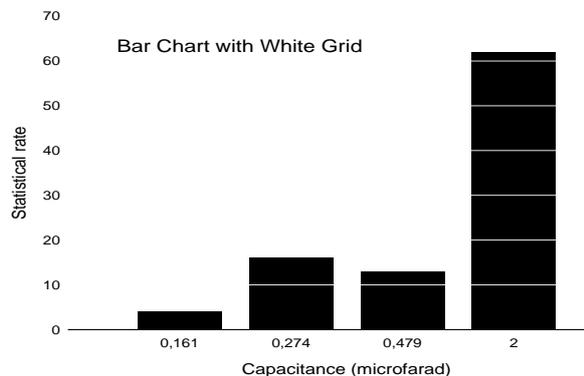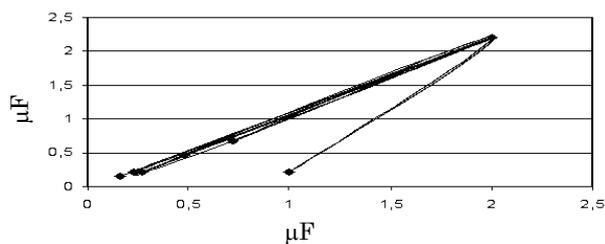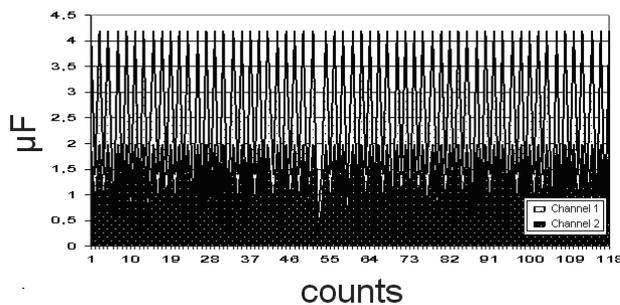
a

b

Grouped Bar Chart with Error Bars

c

Bar Chart with White Grid

d

Fig. 4 – Capacity oscillations in AgHal-GIM: a – direct registration of the capacity oscillations at $C_{max} = 2\mu F$, b – selected averaged components of the signal with the given variance; c, d – statistical processing of results

are characterized by a slow growth and rapid discharge, which indicates that Br^- is initially accumulated in the system as a part of AgBr, and then it is sharply released into the polymer matrix as a result of photooxidation to the free halogen. At the same time, the concentration of silver ions for a long time stabilizes at low level but when accumulated in the system, silver ions are injected into the medium in a pulse mode (Fig. 2c). This corresponds to the process of Ag_n^0 clusters solarization – the reversal of silver halide photolysis due to an equilibrium shift caused by the release of excess silver and the accumulation of molecular halogen with inversion of the optical density at the point or zone of overexposure.

a

b

Fig. 5 – Elements of chaotic dynamics in the electrical capacity of the active media: a – phase space of the electrical double layer discharge; b – recording of the electrical capacity

3.3 Reverse Pulse Counting

The "after-irradiation" phenomena similar to the one described above cannot be explained without taking into account the active role of membrane structures that "compartmentalize" their environment in the formation of the kinetics of this process. To test this hypothesis, it is necessary to accurately measure the rate of pulse generation and verify the presence of processes in the electrical double layer (if, in accordance with the notions of the membrane properties, we accept its presence as a necessary primary hypothesis) after irradiation. High-amplitude oscillations and dumps of concentrations can be regarded as pulses. Therefore, it is possible to find hidden periods of "frequency-pulse modulation" in oscillation modes by calibrating contact-fixed on the surface of the emulsion solid-state ion-selective electrodes of reverse counters used for counting outliers with amplitudes above a certain threshold. By means of reverse counting, with a 10 second accumulation time, a variable pulse count rate was detected in the active medium. It should be noted that in this case we are

talking about the counting rate, defined as a variable that depends on the flux density and the pulse frequency corresponding to the entry of particles onto the detector. The results of measurements are shown in Figure 3, on which oscillations of the counting rate in time can be observed.

Also the graph illustrates periods of the pulse activity that are not so obvious when the kinetics of the oscillation regimes in the medium is continuously registered. Thus, the technique and methods of reverse pulse count allow us to study the additive properties of oscillatory regimes in the active medium at comparatively wider macroscopic time intervals.

3.4 Processes in the Electrical Double Layer

It is obvious that electrochemical oscillations in this system have a source that is discharged during the generation of pulses. In a reverse microemulsion, such a source can be an electrical double layer of the inverse micelles with the properties of a capacitor. In a nuclear emulsion with the structures shown in Fig. 1, it is also possible to form an electrical double layer on their surface. In such a case, it is advisable to measure the electrical capacity of the structures in the photoemulsion in the course of the reaction. When capacity oscillations are detected in the system, one may speak of the source of the pulse activity in the structures and the surrounding medium. The measurements had $C_{max} = 2\mu F$ hardware limit; the results obtained are shown in Figure 4. It can be seen that some values in the sample are repeated (in particular the values of 0.161, 0.274 and 0.479 μF), which can indicate a clear structural dependence of these regimes (Fig. 4 c, d).

In this kind of measurements, mixing of trajectories of a nonlinear dynamical system in the phase space plays an important role. Mixing is the main factor in the ratio of the regular and chaotic dynamics of the system. To a certain extent, the Baker's transform procedure serves as an adequate model of the mixing process [20]. Since it is achieved within the phase spaces of non-linear dynamical systems, it is logical to explore the regularity of the beginning and completion points of the discharge by plotting the phase spaces of the signal. When measured by the two-electrode method, the phase space of the process can be considered as a phase portrait of the electrochemical reaction taking place in the system with the readings of each detector located along the axes. When registered from two points (from a control point of the medium and a zone with localized microstructures), a phase portrait of the system can characterize the transfer efficiency between the membraneous (or micellar) microstructures with a double electric charge-ion injection layer and the medium within which this layer is discharged.

Figure 5a shows the phase space of the discharging electrical double layer that participates in the oscillatory kinetics of photochemical processes on AgHal-GIM, registered by the method described above. It has a horseshoe shape and a multilayer contour of the orbit (at least on one side). In that respect, it is similar to such transformations as the Hénon map and Smale horseshoe [21]. The construction of the discharge curve

during long-term monitoring (in coordinates "count - capacity (μF)") indicates the existence of regions with chaotic dynamics in the reaction modes in the system under consideration (Fig. 5b). Thus, the described oscillatory system (or its electrochemical part) is characterized by the presence of both regular and chaotic dynamics (the medium being the source of noise in this case) and a portrait of the regularly discharged electrical double layer in the capacity- capacity phase coordinates.
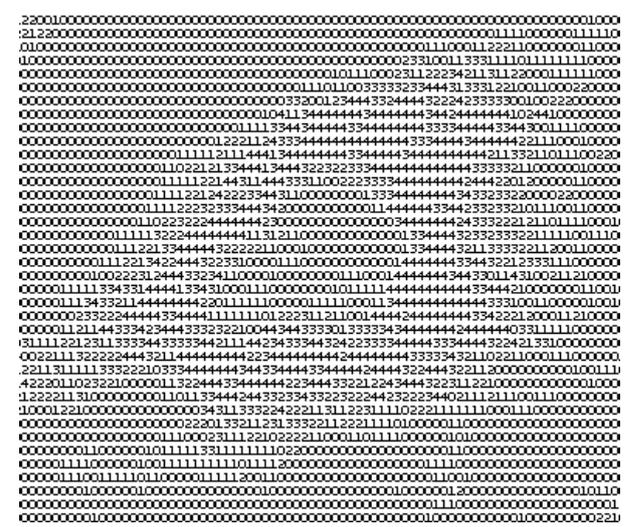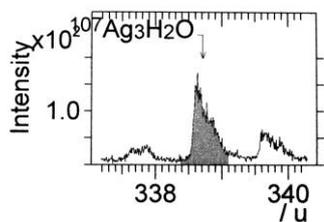

Fig. 6 – Matrix mapping of the optical density for the membraneous microstructures

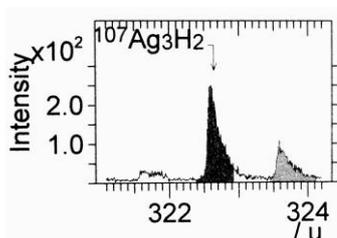### 3.5 Charge Properties of the Dynamic Membranes

Oxidation-reduction processes in photoemulsions are known to lead to an increased optical density in the zones of metallic silver accumulation and, in general, to the formation of an image where the local extinction is proportional to the concentration of reduced silver, that is, the reduction efficiency. In this connection, it is logical to conclude that it is also possible to map the charge distribution or redox characteristics of microstructures in the emulsion, based on their optical density. For extremely small structures (at the limit of the optical microscope resolution), a qualitative method of mapping the charge / redox characteristics of structures can be used: mapping an image of small dimensions ($n*10 \times n*10$ pixels) over several (usually 4-5) extinction gradients or densitometric scale, which compare the relative numerical value ranges (for example, from 0 to 4).

The periodic change in ion concentrations in the medium and the activity of the electrical double layer (see above) lead to inhomogeneity of the microstructure of the emulsion according to the redox criteria, and may be mapped in the way described above. Since the described process occurs in the medium whose microstructure changes during the irradiation, it is logical to map the resulting structures to the distribution of the oxidized and reduced zones. Figure 6 shows the results of matrix mapping of the optical density for the resulting structures, obtained by ASCII transformation of micrographs. The most reduced zones, characterized by the highest extinction, were encoded by identifier 4,

less reduced and more oxidized regions were given symbols from 3 to 1 (1 – the most oxidized points). The optical density of the background medium was measured and then subtracted (denoted by the symbol 0). As can be inferred from the illustrations and the data provided, the dynamic membrane structures formed by the above-mentioned way consist of an uncharged reduced region represented by the metallic silver clusters and the periphery with a more oxidized layer.
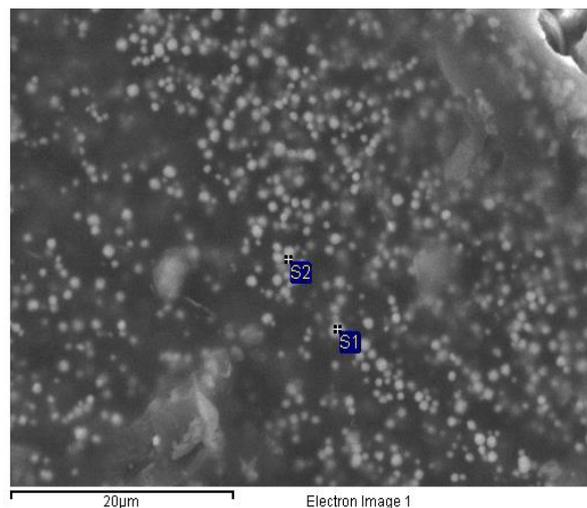

a

b

Fig. 7 – TOF-SIMS mass-spectra of the exotic intermediates (adducts) in AgHal-GIM: a – Ag_3H_2O, b – Ag_3H_2.

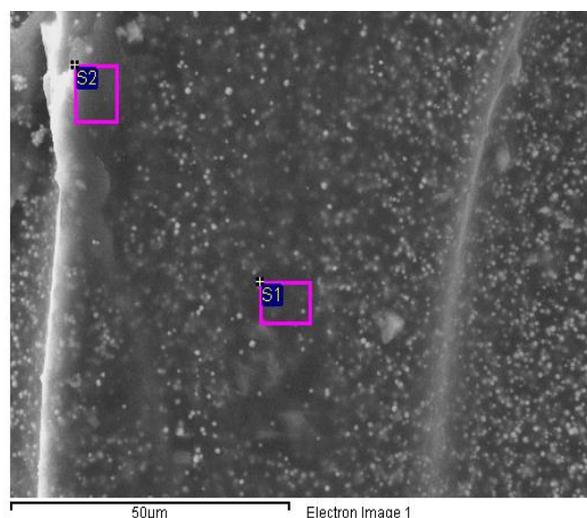### 3.6 TOF-SIMS and Elemental Analysis in Redox-active Zones

In addition to the structural and phase inhomogeneity, which are the consequence of the reaction-diffusion processes in active media based on AgHal-GIM under irradiation, it is logical to assume that the chemical composition of the emulsion after exposure will be also heterogeneous.

Time-of-flight mass spectrometry (producing "ion images" of individual sections of a sample with membrane structures in secondary ions) was used to show that apart from the typical components of AgBr photoemulsion and possible glass substrate artifacts some exotic intermediates were also detected in the active medium, in particular, Ag_3H_2O and Ag_3H_2 (Figure 7), which indicates the active participation of the polymer gelatin matrix in the reduction process.
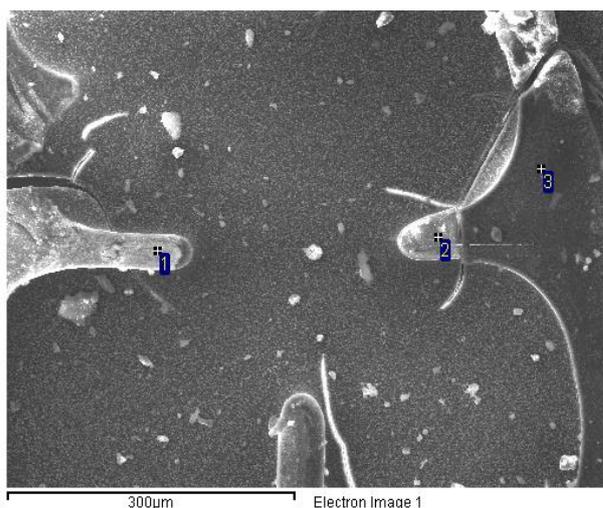
The results of estimating the local charge properties of membranes in combination with the preliminary TOF-SIMS data suggest the expediency of position-sensitive mapping of the atomic composition of these structures in the redox-active zones and beyond with reference to sufficiently high-resolution micrographs. Semiquantitative elemental analysis was carried out using energy-dispersive X-ray spectroscopy during electron microscopic studies of the samples. To better illustrate the effect in the polymer organogenes (which, judging by the time-of-flight mass spectra, actively participates in the redox processes on the dispersed phase particles), the experiment was repeated on a specially

a

b

c

Fig. 8 – Electronic micrographs of the microstructures formed in the active medium: a – the initial disperse medium, b – an autowave formed, c – the emerging antispiral waves.

Table 1 – Atomic composition of the nuclear emulsion

Element	$n_j \times 10^{-22}$, nuclei/cm³
H	3.148
C	1.412
N	0.396
O	0.956
S	0.004
I	0.002
Br	1.031
Ag	1.036

Table 2 – Elemental composition of AgHal-GIM

Atomic fraction, %	C	O	Br	Ag
Fig. 8a, zone S1	74.12	19.00	3.28	3.36
Fig. 8a, zone S2	75.19	17.72	3.84	3.25
Fig. 8b, zone S1	75.72	21.26	1.26	1.76
Fig. 8b, zone S2	73.22	25.49	0.70	0.59

Table 3 – Elemental composition of the structured sample (Fig. 8c)

Atomic fraction, %	C	O	Br	Ag
Zone 1	71.86	23.54	2.27	2.07
Zone 2	62.75	33.47	2.41	1.08
Zone 3	69.32	26.78	1.86	1.71
Average value	67.98	27.93	2.18	1.62
Standard deviation	4.70	5.07	0.28	0.50
Maximum	71.86	33.47	2.41	2.07
Minimum	62.75	23.54	1.86	1.08

prepared microphotographic emulsion with the reduced silver halide content.

According to the data obtained, the AgHal semiconductor filling is a photocatalyst and an electroinduction factor that triggers the oscillatory redox processes in the dispersion medium. The initial disperse system (Fig. 8a) has an atomic composition that differs little in different probing points, with the exception of hydrogen, nitrogen and minor impurities (Table 2). In respect of organogen content, the composition of the initial dispersion is practically the same (within the fluctuations) as the composition of the autowave recorded (Fig. 8b) and has an almost stoichiometric Ag: Br ratio, although the atomic fraction of silver and bromine decreases almost 3 times, as shown in Table 2.

For microstructures such as anti-spirals and Turing structures (Fig. 8c), on the contrary, a non-stoichiometric ratio of silver and halogen atomic fractions is observed (Table 3) as well as significant deviations of atomic fractions of organogens (zones 1 and 2, Table 3) and a change in their stoichiometric ratio. E.g., the carbon/oxygen ratio varies from 2/1 to 3/1, whereas in the control and "autowave" the ratio 3/1 is strictly maintained, which is consistent with the oxidation of organic carbon. In this case, the mass fractions of silver in large particles often significantly exceed the stoichiometry specified by the atomic fractions, which allows us to consider them as metal clusters. For instance, some particles on the edge of the aggregation front demonstrate the mass fraction of silver at 41.17 % with a mass fraction of bromine at 29.82 %. At the same time some polymer-immobilized particles inside the convective walls autowave have mass fraction of silver at 8.97 % with a mass fraction of bromine at 4.75 %. It should be noted that particles with small deviations (about several %) from the mean values were intentionally not taken into account.

4. RESUME

Thus, photoinduced reaction-diffusion processes in the polymer matrix with immobilized semiconductor particles lead to the formation of dissipative microstructures and chemical modification of the active medium facilitated by the redox processes in local microcompartments with an electrical double layer that helps to maintain the concentration gradients and the electrochemical potential on the membrane surface.

Фотоиндуцированные пространственно-временные колебания и структурная самоорганизация в полимер-иммобилизованных дисперсных полупроводниках

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В данной работе приводится описание фотоиндуцированных реакционно-диффузионных процессов в активных средах на основе дисперсных полупроводников, иммобилизованных в полимерной матрице. Исследован характер осцилляций редокс-потенциала и концентраций отдельных ионов в системе под действием излучения, показана роль двойного электрического слоя на поверхности микрокомпартментов в поддержании концентрационных и электрохимических градиентов на поверхности мембранных структур. Доказано формирование диссипативных микроструктур в активной среде

под действием излучения, обладающих структурной и фазовой неоднородностью и существенно отличающихся по химическому составу от окружающей их среды за счет активного протекания в них окислительно-восстановительных процессов с участием компонентов полимерной матрицы

Ключевые слова: Фотоиндуцированные химические колебания, Реакционно-диффузионные процессы, Диссипативные структуры, Полимер-иммобилизованные галогениды серебра, Дисперсные полупроводники.

Фотоіндуковані просторово-часові коливання і структурна самоорганізація в полімер-іммобілізованих дисперсних напівпровідниках

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У даній роботі наводиться опис фотоіндукованих реакційно-дифузійних процесів в активних середовищах на основі дисперсних напівпровідників, іммобілізованих в полімерній матриці. Досліджено характер осциляцій редокс-потенціалу і концентрацій окремих іонів в системі під дією випромінювання, показана роль подвійного електричного шару на поверхні мікрокомпартментов в підтримці концентраційних і електрохімічних градієнтів на поверхні мембранних структур. Доведено формування дисипативних мікроструктур в активному середовищі під дією випромінювання, що володіють структурної та фазової неоднорідністю і істотно отличающіхся за хімічним складом від навколишнього їхнього середовища за рахунок активного протікання в них окисно-відновних процесів за участю компонентів полімерної матриці.

Ключові слова: Фотоіндуковані хімічні коливання, Реакційно-дифузійні процеси, Дисипативні структури, Полімер-іммобілізовані галогеніди срібла, Дисперсні напівпровідники.

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