Reports of the Academy of Sciences of the USSR

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1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1963. Volume 149, No. 2

PHYSICAL CHEMISTRY

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ON THE DISCRETE CHARACTER OF IMPURITY SPECTRAL PHOTOSENSITIVITY OF PHOTOGRAPHIC EMULSIONS

Earlier investigations ([1,2]) showed that the long-wavelength photosensitivity $S_{\lambda>500}$ of optically unsensitized emulsions is caused by the electron-donor function of impurity centers. However, it remained unclear, first, whether centers of the molecular-colloidal type, responsible for the fine structure in the impurity absorption spectrum, exhibit this function, and, second, whether such centers also create short-wavelength impurity photosensitivity superposed on the intrinsic photosensitivity of silver halide. At the same time, there are facts indicating photoelectric properties of this type of silver centers. These include, on the one hand, the correspondence between the fine structure of the impurity absorption spectrum and the bands in the spectrum of the photoelectric ([3,4]) and photovoltaic effects ([5]), and, on the other hand, the phenomenon of "bleaching" of photochemically colored silver halide ([6,7]). In order to prove the effective role of primary centers as electron donors, it is evidently necessary to show the discrete character of impurity spectral photosensitivity and its connection with the fine structure of the impurity absorption spectrum. To study impurity spectral photosensitivity, a differential method was used (by analogy with the observation of fine structure ([8])), consisting in the determination of the relative photosensitivity

$$S'_\lambda = S_{\lambda,t}/S_{\lambda,0} = H_{\lambda,0}/H_{\lambda,t},$$

where S_λ is the spectral photosensitivity and H_λ is the energy of monochromatic radiation producing a definite photographic effect (the sensitivity criterion), respectively in the initial state of the emulsion (0) and at a certain moment (t) of chemical sensitization.

To determine the presence and character of short-wavelength impurity photosensitivity ($\sim \lambda < 500$ mμ), a Lippmann bromosilver emulsion was taken and subjected to gold sensitization (the layers were immersed for $2^1/_2$ to 10 min in

Fig. 1

Figure 1: Fig. 1

a 10^{-2}% solution of gold chloride). For comparison, the long-wavelength photosensitivity of a normal emulsion was studied (purely bromide and iodobromide with 1 to 5 mol.% AgI). Chemical sensitization in this case was carried out by ordinary chemical ripening. Absolute values of the spectral photosensitivity S_λ ($\mathrm{cm}^2\,\mathrm{erg}^{-1}$) were determined by the standard spectrosensitometric method ([9]).

Figure 1 gives the curves of impurity spectral photosensitivity (S'_λ, λ) for the Lippmann emulsion, from which three features are visible: 1) the presence of selective bands with coincident maxima at different degrees of sensitization; 2) the ambiguous change with sensitization time in the intensity of the bands; 3) the sharp increase in impurity photosensitivity beyond the long-wavelength boundary of the intrinsic absorption of the solid phase of the emulsion ($\sim \lambda 460$ mμ). Table 1 compares the positions of the bands of impurity absorption and relative spectral photosensitivity; these data show satisfactory agreement of the indicated quantities, which testifies to their close interrelation.

The positions of the maxima in the impurity-absorption spectrum of a Lipmann emulsion sensitized with gold were specially determined on Kirillov' s spectrophotometric apparatus with a light-measuring sphere ([10]). The observed coincidence of the fine-structure bands in the absorption spectrum of silver centers with the bands in chemical sensitization by gold, which is reduced to the formation of gold centers, is in agreement with measurements of gold deposits on quartz ([11]) and its hydrosol ([12]).

Fig. 1. Curves of impurity spectral photosensitivity (S'_λ, λ) of a bromosilver Lipmann emulsion for different durations of bathing in a solution of gold chloride: **1** –2.5 min., **2** –5 min., **3** –7.5 min., **4** –10 min.

The curves of the relative spectral photosensitivity of normal emulsions showed analogous results: low values of S'_λ in the region up to $\lambda = 530$ mμ (the approximate limit of intrinsic absorption)

Table 1

Positions of band maxima (λ, mμ)

Impurity silver centers (data ([8]))	416	422	432	441	450	463	471	480	490	500

Centers of Lippmann emulsion sensitized with gold	414	423	430	440	450	464	473	481	490	498
Impurity spectral photosensitivity of the same emulsion	413	423	433	441	450	465	475	—	488	498

and, conversely, large values in the long-wavelength region, especially with an increase in the time of chemical ripening; the presence of a number of discrete bands with close positions of the maxima for different emulsions and ripening times. Table 2 shows the same satisfactory agreement—

Table 2

Positions of band maxima (λ, mμ) (mean values according to data from 28 emulsions)

Impurity silver centers (data ([8]))	521	541	555	570	595	615	635	650	671

Figure 2

Figure 2: Figure 2

Relative spectral photosensitivity	527	—	554	574	594	623	—	648	670

coincidence of the maxima of the fine structure and of the bands of long-wavelength sensitivity that was observed in the short-wavelength region in Lippmann emulsions.

Thus, the discrete character of the impurity spectral photosensitivity of optically unsensitized emulsions and the coincidence of the selective bands with the bands of fine structure in the absorption spectrum of impurity centers indicate that the short-wavelength S'_{λ}, like the long-wavelength one, has an impurity nature, i.e., is due to the electron-donor function of silver (or gold) centers. At the same time, a kinetic difference is observed, associated with the evolution of the centers: thus, in normal emulsions (see Fig. 2) the long-wavelength photosensitivity, for example $S'_{\lambda 680}$, increases strongly, whereas the short-wavelength, for example $S'_{\lambda 450}$, after passing through a maximum, falls as a result of a decrease in the concentration of molecular-colloidal centers ([13]). From this it may be concluded that, before the optimum of chemical ripening, when the maximum total photosensitivity is reached, the long-wavelength photosensitivity is probably produced by the absorption bands of molecular-colloidal centers lying in this region; beyond the optimum, secondary, precolloidal centers act predominantly, being responsible only for the long-wavelength photosensitivity.

Fig. 2. Curves of variation of $S'_{\lambda 450}$ (1), $S'_{\lambda 680}$ (2), and S'_{Σ} (3) of an iodobromide emulsion (3 mole % AgJ) as a function of the time of the second ripening (t_2— hours)

As a very characteristic feature, one should note the sharply expressed increase in spectral photosensitivity in the long-wavelength region, where its absolute values are very small, and, conversely, the small increase shown in the region of intrinsic absorption of the solid phase of the emulsion, where the spectral photosensitivity is several orders of magnitude higher. This indicates that, in addition to the electron-donor function of impurity centers, other factors act which increase the short-wavelength and the overall photosensitivity. First of

all, these apparently include the electron-donor function of bromide ions. It may be thought that precisely for this reason, in that spectral region where the intrinsic donors of the emulsion microcrystals act, additional donors in the form of impurity centers exert little influence.

However, when bromide ions serve as electron donors, this process must be accompanied by the emergence of bromine atoms at defects of the microcrystals. Consequently, for the effective utilization of photoelectrons, binding of bromine must be ensured in order to prevent recombination. Therefore, in accordance with the considerations expressed earlier ([14]), it may be assumed that the second factor increasing the photosensitivity of a photographic emulsion is another, parallel function of the primary centers, namely the bromine-acceptor function. This is also confirmed by the greater increase in the relative integral photosensitivity S'_{Σ} with ripening time in comparison with the short-wavelength photosensitivity (for example, $S'_{\lambda 450}$), caused by the electron-donor function of impurity centers (see Fig. 2).

It follows from the data presented that the scheme of the photographic process proposed earlier ([15]), in which a definite individual function is assigned to silver centers of different dispersity, requires

in clarifying the role of primary molecular-colloidal centers. In accordance with the considerations set forth, these centers apparently perform a dual function in the formation of the latent image—electron-donor and bromine-acceptor.

B. G. Varshaver and L. P. Mel' nichuk took part in the work, to whom the authors express their gratitude.

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Received
30 XI 1962

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Note: Figure translations are in progress. See original paper for figures.