Electrochemical processes in ultra-fine AgBr emulsion placed into redox system.

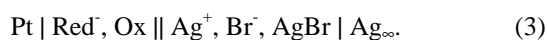V.N.Zakharov, I.K.Kudryavtsev, N.N.Alekhin,
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It is wellknown that reduction of silver is the main feature of the photographic process. Besides traditional ways of reducing sensitization (chemical sensitization, hydrogen hyper sensitization etc.) it is possible to use electrolytic treatment to increase the speed of photographic layers. This means that electrons are "injected" into the grains of fine-grain emulsion before exposure. As a rule the transfer of electrons is not direct and the reduction process may develop with the aid of a donor-acceptor impurity. During this process the absolute value of electric potential of emulsion grains is not essential, the main features of reduction are determined by relative values of electric potentials vs. equilibrium system $Ag_\infty/AgBr/Ag^+$. Increase of light sensitivity occurs when these values lie in the interval between -100 and -300 mV [1].

In this paper we consider some details of electrochemical process in AgBr emulsion microcrystals. In general case this process can be presented as:

$$Red^- \leftrightarrow Ox + e^-, \qquad (1)$$

$$Ag^+ + e^- \leftrightarrow Ag. \qquad (2)$$

We consider the galvanic element

$$Pt \mid Red^-, Ox \parallel Ag^+, Br^-, AgBr \mid Ag_\infty. \qquad (3)$$

The electromotive force of this element is equal to the difference of electric potentials of Pt and Ag electrodes, which can be found as

$$\varphi_{Ag} = \varphi^0_{Ag/AgBr} - RTF^{-1}\ln[Br^-], \qquad (4)$$

$$\varphi_{Pt} = \varphi^0_{redox} + RTF^{-1}\ln([Ox]/[Red^-]). \qquad (5)$$

Here $\varphi^0_{Ag/AgBr}$ and φ^0_{redox} are the values of standard electrochemical potentials.

For short circuit in this chain the condition of thermodynamic equilibrium gives

$$[Br^-][Ox]/[Red^-] = const. \qquad (6)$$

Condition (6) means that thermodynamic equilibrium in the system under consideration (Ag, AgBr, Ag^+, Br^-, Red^-, Ox) is possible only for strictly defined values of interconnected concentrations of ions of silver, bromine, red and ox agents. Under equilibrium the activity of silver has the same value for every part of the redox system and is equal to activity of bulk metal a = 1. For the Fe^{2+}/Fe^{3+} buffer Reinders [2] experimentally obtained that the potential of Pt electrode for short circuit element under equilibrium was equal to the potential of AgBr electrode placed into 0.01 N solution of KBr. Only for this value of the redox potential of buffer solution a change of optical density of partially reduced photographic emulsion was not observed. For any other value of potential a decrease or increase of initial blackening density was obtained.

The method of Reinders gave the possibility to determine perfectly the value of electric potential for equilibrium system Ag, AgBr, Ag^+, Br^-, Red^-, Ox. A deviation from equilibrium could be thus determined by the electric potential difference in the galvanic element chain.

A condition for correct determination of potential difference $\Delta\varphi = \varphi_{Ag} - \varphi_{Pt}$ and thus the correct value of overvoltage is identity of solution composition for bromine - silver comparison electrode and solution composition for different reducing agents (redox buffer solution, physical developer, regular reducing bath). If this condition is not valid the wrong values of potential difference $\Delta\varphi$ can be obtained.

The experimental values of overvoltage for typical processes of physical and chemical development were, as a rule, between 0 and - 200 mV. The higher absolute values can be a result of mistake in the comparison electrode choice. Such electrode has an electrolyte composition essentially differing from a composition of used developer or buffer solution by pH, ionic force, etc.

According to paper [3], the latent image specks must not appear if the potential of silver halide microcrystal under the action of powerful actinic light beam will be more positive than the potential of bulk silver. Nevertheless, even if the redox buffer potential is up to +300 mV the photographic material under investigation has a speed different from zero. The possible explanation is that actinic light sharply decreases the potential of emulsion microcrystals. The influence of redox buffers with positive potential comparing to the action of light is less effective.

The latent image specks under powerful actinic light appear in non-equilibrium conditions. According to the results of paper [4] and idea by Moizar and Granzer [5], the potential jump is determined by the relation

$$\Delta U = kTe^{-1}\ln\{[e]/[e]_\infty\}, \qquad (7)$$

where [e] is the stationary concentration of electrons producing supersaturation in the electron subsystem, and $[e]_\infty$ is the electron content at thermodynamic equilibrium, for instance in partly developed emulsion. The ratio (7) may be regarded as a measure of non-equilibrium of photographic systems.

References

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