Iron in Photographic Gelatin—I.The Influence of Fe^{2+} Ions in Gelatin Medium on Chemical Sensitization of Silver Halide

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Abstract

In this paper the influence of Fe^{2+} ions in Gelatin Medium on the sensitivities of silver halide emulsions with sulfur or sulfur plus gold sensitizers is studied. The drop of emulsion sensitivity is shown because of doped Fe^{2+} ions in gelatin medium. In addition its influence mechanism is also explored.

Preface

There are various chemical forms[1] and several valences of iron in gelatin[2], which may exert different influences on photographic emulsion. According to earlier studies, the desensitizing effect of iron with +3 valence has been undoubtful[3-5]. However, the influence of iron with lower valence on photographic sensitization of silver halide emulsion is hazy due to the lack of exploration. It was reported that Fe^{2+} ions doped prior to emulsion coating have no effect on photosensitivity and but more of Fe^{2+} ions doped during chemical ripening of emulsion do that[7]. In this paper our attention is focused on the effect of Fe^{2+} ions in gelatin medium on silver halide emulsion sensitized with sulfur and sulfur plus gold salt. In addition its influence mechanism is also explored.

Experiment

At first a series of 10% gelatin solutions doped with different amount of Fe^{2+} are prepared. A silver iodobromide emulsion is made according to China GB method. Added a certain amount of the above 10% gelatin solution doped with Fe^{2+}, the emulsion is ripened at 50°C for 90 minutes while chemical sensitizer (e.g., sulfur of sulfur plus gold) is added. The chemically ripened emulsion is immediately coated on the film-base and the film is dried. Exposed for 0.05 second, the film is developed and fixed. Lastly, the densities are measured successively.

Fe^{3+} and Fe^{2+} contents in 10% gelatin solution are determinated by spectrophotonmetric method, respectively.

The 10% test gelatin solution is prepared according the following operation: 3 grams of photographic gelatin are taken into a beaker and dissolved with 25ml of ultra-pure water at 50°C. Some volume of a standard solution of $(NH_4)_2Fe(SO_4)_2$ is added into this gelatin solution in such a way that doped amount of Fe^{2+} is 1.5μg of 3.0μg per milliliter. 0.5ml of 5% Na_2Co_3 solution, 0.5ml of 20% $C_6H_5SO_2Na_2 \cdot H_20$ solution and some chemical sensitizer (e.g. sulfur of sulfur plus gold salt) are introduced into the above gelatin solution doped with Fe^{2+} successively. The mixed solution is diluted to 30ml end stands at 50°C for 90 minutes. On this base, the 10% test gelatin solution doped with Fe^{2+} approaching chemical ripening condition of silver halide emulsion is prepared. Lastly, its Fe^{3+} content is determined.

Result

1. The effects of Fe^{2+} doped in gelatin medium on photographic sensitivities of emulsions with various chemical sensitizers are shown in Table 1. Sr means the relative sensitivity of emulsion with gelatin medium containing doped Fe^{2+} to that without doped Fe^{2+}
2. The valence changes of $Iron^{2+}$ in test gelatin solutions doped with Fe^{2+} under the condition approaching chemical ripening of silver halide emulsion are shown in Table 2.

Discussion

The curves in Figure l indicate the effects of Fe^{2+} doped in gelatin medium of emulsions tested, i.e. Fe^{2+} ions make photographic sensitivity decrease in its degree. It is worthy to note that in the case of emulsions with sulfur of sulfur plus gold salt sensitizer, less of Fe^{2+} doped in gelatin medium cause photosensitivity to decrease significantly. But only if more of Fe^{2+} doped in gelatin medium do so for unsensitized emulsions. BP gelatin sample is taken for example. Relative photographic sensitivities are reduced to 0.46 and 0.30 due to addition of 1.5μg Fe^{2+} per milliliter of 10% gelatin solution for the emulsions with sulfur and sulfur plus gold salt sensitizer, respectively. However, the desensitizing effect of Fe^{2+} concerning unsensitized emulsions is not observed practically under the same condition. It is also clear in Figure l that the desensitizing effect becomes more serious as amount of doped Fe^{2+} increase. The similar features are also discovered in the GF gelatin sample.

It is considered that Fe^{2+} in a solution may be oxidized to Fe^{3+} and Fe^{3+} damages photographic performance because of the deep electron trap effect[5]. It is possible that the desensitizing effect of Fe^{2+} in gelatin medium has relation to the valence change of Fe^{2+} in the process of chemical ripening. For this reason, the content of Fe^{3+} in the 10% gelatin solution, i.e. the original content of Fe^{3+} in Table 2. and one in the 10% test gelatin solution are determined further in order to explore the mechanism of Fe^{2+} effect. Comparing content of Fe^{3+} in the test gelatin solution after chemical ripening to its original content of Fe^{3+} in Table 2, it is found that the former is obviously increased. This means that Fe^{2+} ions in the test gelatin solution doped with Fe^{2+} are indeed in part oxidized to Fe^{3+} ions in the process of chemical ripening. It appears that an oxidation of Fe^{2+} in gelatin medium to Fe^{3+} is one of factors influencing sensitivity of emulsion. It is worthy to note the situation of gelatin medium with chemical sensitizer, i.e. sulfur of sulfur plus gold salts. Observing changes of emulsion sensitivities in Figure l and percentage data of oxidized Fe^{2+} in the test gelatin solution with the chemical sensitizer are near to ones without any chemical sensitizer, the drops of relative photographic sensitivity of corresponding emulsions with sulfur or sulfur plus gold sensitizer are much more significant than that of unsensitized emulsion due to doped Fe^{2+} in gelatin medium during the emulsion making. Take the test solution of BP gelatin doped with 1.5μg Fe^{2+}/ml for example yet. The percentage of oxidized Fe^{2+} in the case containing S or (S+Au) sensitizer is 34% or 31% and that without the sensitizer is 30%, i.e. they are nearly equal to each other. However, relative photographic sensitivity of corresponding emulsion sensitized with S or (S+Au) salt is reduced to 0.46 or 0.30, which is obviously lower than one of unsensitized emulsion (i.e. about 1.0). This implies that the oxidation of Fe^{2+} is not only mechanism of Fe^{2+} effect in the case of emulsion with sulfur plus gold salt sensitizer. A further study will be reported later.

Table 1. Effect of Fe2+ doped in gelatin medium on photosensitivity of AgBr/I emulsion

Amount of doped Fe^{2+}(μg/ml)	Sensitizer No	Sensitizer S	Sensitizer S+Au
BP Gelatin Sample			
0.0	1.0	1.0	1.0
1.0	---	0.58	0.48
1.5	1.0	0.46	0.30
3.0	0.67	0.35	0.26
GF Gelatin Sample			
0.0	1.0	1.0	1.0
1.0	---	0.86	0.60
1.5	---	0.64	0.70
3.0	1.0	0.64	0.66

Table 2. Valence change of iron in the test gelatin solution after approaching chemical ripening[(a)]

Sensitizer		No		S		S+Au	
Original content of Fe^{2+} (μg.ml)	BP Gel.	0.34	0.34	0.34	0.34	0.34	0.34
	GF Gel	0.23	0.23	0.23	0.23	0.23	0.23
Doped amount of Fe^{2+} (μg.ml)	BP Gel.	1.5	3.0	1.5	3.0	1.5	3.0
	GF Gel						
Original content of Fe^{3+} (μg.ml)	BP Gel	0.13	0.13	0.13	0.13	0.13	0.13
	GF Gel	0.31	0.31	0.31	0.31	0.31	0.31
Content of Fe^{3+} after chemical ripening (μg.ml)	BP Gel.	0.69	1.47	0.75	0.96	0.70	0.98
	GF Gel	1.21	2.68	1 17	2.30	1.31	2.55
Percentage of oxidized Fe(%)[(b)]	BP Gel.	30	40	34	25	31	25
	GF Gel	52	73	50	60	58	69

(a) 10% gelatin solution is used in this test.

(b) It's the ratio of increased amount of Fe3+ to the sum of original Fe2+ and doped Fe2+ in the 10% test gelatin solution.

References

1. J. Yue, B. X. Huang, X.Fang, J.Y. Ai and A.B. Yue, *J. Photogr. Sc.* **39**, 130-132, 1991.
2. X. Li and B. X. Peng, *Chinese Acta of Photogr. Sci . and Photochem.*, **11**(3), 193 - 197, 1993.
3. V. Platikanova and J. Matinowski, *J. Photogr. Sci* **16**, 235-240,1968.
4. J. W. Mitchell, *J. Imaging Sci.*, **31**(6), 239-243, l987.
5. R. Q. Wang and B. X. Peng, *Chinese Acta of Photogr. Sci. Photochem.*, *(***2***)* 33-37,1988.
6. T. Tani and Mistuo Saito, *Photogr. Sci. Eng.*, **17**(5), 434 441, 1973.
7. B. X. Huang, X. D. Cao, G. F. Xu and J. Yue, *IS&T's 48th Annual Conference Proceedings*, 298-330, 1995.
8. D. Wang, J. P. Gan and B. X. Huang, *IS&T's 47th Annual Conference Proceedings*, 269,1994.