A Systematic Study of Effect of Cyanine Dyes on Ionic Conductivities of AgBr Grains

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Abstract

A systematic knowledge of effect of cyanine dyes on ionic conductivity of silver bromide grains was given by dielectric loss measurements of cubic, octahedral, and tabular grains which adsorbed the dyes with different adsorption preference to {100} and {111} faces. The obtained result has supported a Jagannathan's model of a tabular grain with (100) faces on its side surfaces.

Introduction

A large variety of cyanine dyes are used as spectral sensitizers for silver halide emulsions. It is therefore important to know the nature of the interaction between cyanine dyes and silver halide grains in emulsions. Silver halide grains are characterized by their ionic conductivity with interstitial silver ions as electric carriers, and the dependence of the conductivity on their adsorbates reflects the nature of their interaction with the adsorbates.[1] Although it is known that the adsorption of cyanine dyes to cubic silver bromide grains increases their ionic conductivity and therefore the concentration of interstitial silver ions in the grains,[2] our knowledge of the effect of cyanine dyes on the ionic conductivity of silver halide grains is still limited.

This paper is undertaken to obtain a systematic knowledge of the effect of cyanine dyes on ionic conductivity of silver bromide grains by studying octahedral and tabular silver bromide grains in addition to cubic ones, which adsorbed cyanine dyes with different adsorption preference to {100} and {111} faces.

Experiments

The cyanine dyes used in this study were 3,3'-disulfobutyl-9-methyl-thiacarbocyanine dye (Dye 1) with adsorption preference to {100} face[3,4] and 3,3'-disulfopropyl-5,5'-dichloro-9-ethyl-thiacarbocyanine dye (Dye 2) with adsorption preference to {111} face.[4] The adsorption preference of Dyes 1 and 2 was determined on the basis of the analysis of the desorption process of adsorbed dyes on silver bromide grains by CHP Resin.[5]

The photographic emulsions used in this study were composed of octahedral silver bromide grains with average

equivalent circular diameter of 0.24, 0.40, and 0.66 μm, and tabular silver bromide grains with average projective equivalent circular diameter of 1.0 μm and average thickness of 0.1 μm.

The ionic conductivity of the above-stated grains were measured by means of a dielectric loss method.[1] It is known that the frequency at the maximum dielectric loss gives the ionic conductivity of cubic silver bromide grains with interstitial silver ions as electric carriers. In the case of octahedral silver bromide grains, two maximums are usually observed in their dielectric loss vs. frequency curves. It has been revealed in the previous paper[6] that the lower-frequency maximum corresponds to the ionic conductivity with interstitial silver ions as electric carriers, while the higher-frequency maximum corresponds to the ionic conductivity with mobile silver ions on the grain surface as electric carriers.

Adsorption Preference of Dyes to {100} and {111} Faces

When CHP resin was added to a dyed silver bromide emulsion, dye molecules on the emulsion grains were desorbed and adsorbed to CHP resin. The analysis of the desorption process provided the evidence that Dye 1 was adsorbed to cubic grains more preferably than to octahedral ones, and that Dye 2 was adsorbed to octahedral grains more preferably than to cubic ones.

Namely, the desorption rate of Dye 1 on the cubic grains was smaller than that of the dye on the octahedral ones, and the activation energy of the former was larger than that of the latter. On the other hand, the desorption rate of Dye 2 on the octahedral grains was smaller than that of the dye on the cubic ones, and the activation energy of the former was larger than that of the latter.

Ionic Conductivity of Octahedral Silver Bromide Grains

The dielectric loss vs. frequency curves of all the octahedral grains studied exhibited two maximums, as already described in the previous paper.[6] Neither Dye 1 nor Dye 2 could influence the frequency of the lower-frequency maximum, which corresponds to the ionic conductivity with interstitial silver ions as electric carriers, on the contrary to

the case of the ionic conductivity of cubic silver bromide grains, which was increased by their adsorption of both Dyes 1 and 2.[2] On the other hand, both Dyes 1 and 2 increased the frequency of the higher-frequency maximum, which corresponds to the ionic conductivity by mobile silver ions on the grain surface.

It is already known that cyanine dyes increase the ionic conductivity of cubic silver bromide grains, pushing silver ions at kink sires into interstitial positions.[2] In contrast to the case of cubic grains, the result obtained in this paper revealed that cyanine dyes pushed silver ions at surface sites on octahedral grains, not into interstitial positions, but into surface positions where silver ions are mobile, giving rise to the higher-frequency peak in their dielectric loss vs. frequency curve.

Ionic Conductivity of Tabular Silver Bromide Grains

The ionic conductivity of tabular silver bromide grains with interstitial silver ions as electric carriers was given by the frequency at the lower-frequency maximum in their dielectric loss vs. frequency curve, and is shown as functions of the added amounts of Dyes 1 and 2 to tabular silver bromide emulsions in Figure 1.

The conductivity increased and then became to be constant with increasing the added amount of Dye 1 within the amount needed for the saturation of the surface of the grains by the dye, whereas it was kept constant and then increased with increasing the added amount of Dye 2 within the amount for the saturation.

A model for a tabular grain with (100) faces on its side surfaces was proposed by Jagannathan and others,[7] and supported by Hosoya and Tani,[8] and by Urabe and Hosoya.[9] It is considered that the above-stated result could provide an additional evidence for the model. With increasing the added amount, Dye 1 with adsorption preference to {100} face was adsorbed to the (100) face on the side surfaces of tabular grains, causing the increase in the ionic conductivity of the grains, and then to (111) faces on the surfaces of the grains, causing little influencing on the ionic conductivity.

On the other hand, with increasing the added amount, Dye 2 was adsorbed to (111) faces on the surface of the grains, causing little influence on the ionic conductivity, and then to the (100) faces on the side surfaces of the grains, increasing the ionic conductivity of the grains.
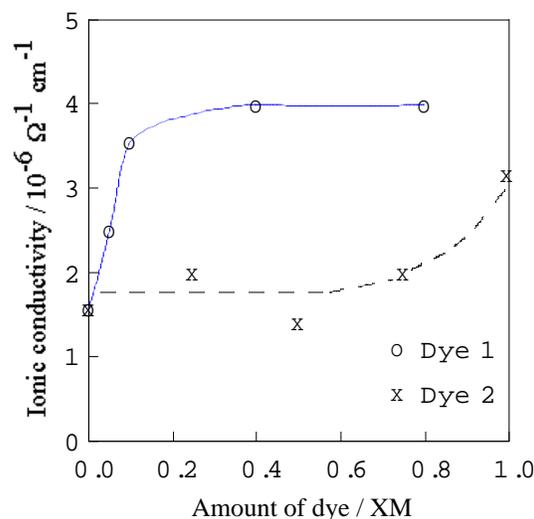
Figure 1. Ionic conductivities of dyed tabluar silver bromide grains with equivalent diameter of 1.0 μm, which were given by the frequencies of the lower frequency maximums of their dielectric loss curves. M refers to the saturated amount of adsorbed dyes.

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