A Color-forming Reaction in a Reversed Microemulsion System

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As a reaction sequence, the color-forming process in color photographic chemistry has been studied in the system of AOT (*bis*-(2-ethylhexyl)sulphosuccinate sodium) reversed micelles. At the beginning of the reaction, a color developer was oxidized into quinonediimine, the oxidation product for the color developer, by the AgCl particle in the water phase of AOT reversed micelles. A subsequent color coupling reaction of quinonediimine with a photographic color coupler proceeded at the interface of the surfactant and hydrophobic outer phase of the reversed micellar system. The color dye thus formed distributed itself into the continuous hydrophobic outer phase of the reversed micellar system. The experiments showed that the complicated sequential reaction in color photographic chemistry could be controlled by adjusting surfactant concentration, the molar ratio of $[H_2O]/$ [surfactant], and a reagent concentration in the water phase of the system.

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Introduction

Since 1950s, the mechanism and kinetics for the formation of imaging dyes in the color photographic process have been studied and elucidated.¹⁻⁷ In earlier works, however, the investigation was carried out either in a homogeneous aqueous solution using optical methods¹⁻⁵ or a photographic film.^{6,7} Actually, color photographic reactions occur in a microheterogeneous environment. For example, the formation of latent image by exposure is an evolution from silver ions to silver clusters. During developing, latent image grows into silver image, which is an evolution process from silver cluster to bulk metallic silver. The color-forming process in color photography involves an autocatalytic reduction of silver halide followed a coupling reaction for the oxidation product of a color developer (quinonediimine, QDI) with a coupler in a microheterogeneous environment. Therefore, the research insights obtained in a homogenous system may not be relevant to practical issues to some extent, while in studies using processed film it is difficult to get results both in situ and in real time during color development. Therefore, since the 1970s, the process of color forming reactions has been simulated in various microheterogeneous systems using silver nanoparticles as a catalyst.⁸⁻¹⁰ The present work attempted to investigate the color-forming process based on nanoparticles of silver halide in a system of reversed micelles, a microheterogeneous environment.

Recently, nanoparticles of silver halide have attracted considerable attention. It is difficult, however, to obtain stable and monodispersed nanoparticles of silver halide by convenient methods in the absence of

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stabilizers. Micelle solutions, particularly reversed micelles are thermodynamically stable and also optically transparent, which can offer a unique microenvironment, in which water soluble reactants are isolated in different water cores, and oil soluble reactants are present in the hydrophobic outer phase of the reversed micelles. The water cores are an ideal nanoreactor. Therefore, reversed micellar systems are currently being explored to produce nanoparticles of metals and semiconductors.^{11–13} The formation of nanoparticles of silver halide in reversed micelles containing ionic or non-ionic surfactants has also been reported.^{14–16}

Additionally, reversed micelles can also provide a favorable microenvironment for study of a photosensitization process. The photosensitization of colloidal TiO₂ and AgCl particles in water-in-oil microenvironment by organic dyes has been studied in our laboratory¹⁷⁻¹⁹ and by others.^{20–22} However, characteristics of small particles and chemical species in reversed micelles are still not understood perfectly. To our knowledge, a sequential microheterogeneous reaction in a reversed micellar system has not yet been elucidated. Herein, as a model of sequential reactions occurring both in hydrophilic and hydrophobic phases of the microenvironment, a colorforming reaction representing the color photographic process is studied in the AOT reversed micellar system. However, it should be noted that the research results introduced here are only a preliminary attempt. Because this research area is still developing,²³⁻²⁵ there are many indefinite factors, e.g., the aggregation and growth of particles, interparticle interaction, exchange kinetics of reaction species in micelles, the dissociation of a proton or hydroxide ions from acidic or alkaline compounds in the water core of reversed micelles, etc. Further work is therefore required.

Experimental

In the present work, all chemicals were analytical grade reagents, *bis*-(2-ethylhexyl)sulphosuccinate sodium

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Figure 1. Transmission electron micrographs of the silver chloride samples formed in AOT reversed micelles. For image a: AOT = 0.2, $\omega = 10$, AgNO₃ = 0.25 mol/L; for image b: AOT = 0.1, w = 10, AgNO₃ = 0.25 mol/L; for image c: AOT = 0.5, $\omega = 10$, AgNO₃ = 0.25 mol/L; for image d: AOT = 0.2, $\omega = 70$, AgNO₃ = 1.7 × 10⁻² mol/L, and Cl⁻ excess 10% relatively to silver nitrate for every experiment.

(AOT) was obtained from Aldrich Chemical Company, and used as received.

The reversed micelles consist of a water core in AOT (0.2 mol/L) surfactant, and isooctane as the continuous hydrophobic phase. The molar ratio of $[H_2O]/[AOT] = 10 = \omega$. A photographic cyan color coupler $(1 \times 10^{-3} \text{ mol/L})$; see Eq. 2 for structure) was first dissolved in isooctane. The particles of silver chloride were prepared by mixing two individual reversed micelle dispersions both containing AOT-isooctane with the coupler and the aqueous solution of either silver nitrate or potassium chloride (excess 1% or 10% relative to silver nitrate). The reversed micelles containing the AgCl particles in the water phase and the photographic cyan color coupler in the continuous hydrophobic phase can be stable for one month at room temperature. A representative transmission electron microscope (TEM) image of AgCl particles

thus prepared on a copper grid covered with Formvar film, recorded in a JEM-100 CX TEM is shown in Fig. 1. The particles seemed quasi-spherical under TEM. According to the preparation conditions, the size of AgCl particles varied. The average diameter of AgCl particles in Fig. 1a is about 10 nm. Particles in this size range were used to study the color-forming reaction in the present work.

The reversed micelles containing a color photographic developer in the water phase were independently prepared. The developer used in this work is a derivative of p-phenylenediamine (CD-2, 4×10^{-4} mol/L).

Results and Discussion

The color-forming reaction during the color photographic process can be shown in Eqs. (1) through (3):



On replacement of the cyan color coupler with yellow or magenta color coupler, a yellow or magenta color dye can in principle form.

Figure 2 is a schematic diagram for the cyan colorforming reaction occurring in the AOT-isooctane reversed micellar system. Several processes are included. (1) AgCl is reduced to silver and CD-2 is oxidized into

- quinonediimine (QDI) in the water phase (Eq. 1).
- (2) Because the coupler is oil-soluble and quinonediimine is water-soluble,¹⁻³ cyan color coupler anions should react with QDI and form the cyan dye (Eqs. 2 and 3) at the interface of the AOT surfactant film and the continuous hydrophobic phase of the reversed micellar system.
- (3) Due to the hydrophobic property of the dye formed from the cyan coupler, the cyan dye should diffuse into the continuous hydrophobic phase of the reversed micellar system after formation.
- (4) Some basic kinetic processes should be included, e.g., the collision and fusion-fission of water cores, as well the intermicellar exchange of aqueous phase contents.

The color-forming reactions in AOT reversed micelles are monitored by absorption spectroscopy. Figure 3 shows the spectral evolution of the system with the re-



Figure 2. Schematic diagram for the color-forming processes proceeded in the AOT-isooctane reversed micellar, where dotted circle represents a water core.

action time. As shown in this figure, with increasing reaction time, the absorption peak at 652 nm increased. Compared with the absorption of the pure cyan dye formed of the CD-2 oxide and the cyan color coupler, it can be confirmed that this peak corresponds to the cyan dye.



Figure 3. The absorption evolution during the color-forming reaction in reversed micelles, the reaction times for curves a to i are 5 to 45 min, with a time interval of 5 min.

In practical color photographic development, accompanying the formation of imaging dyes, a silver image, i.e., black silver is formed simultaneously. However, under the same conditions as in Fig. 1, the observation by TEM showed, after the color-forming reaction, no silver particles could be observed in the sample. The silver cluster produced during the above redox reaction may be too small to be detected by TEM.

Based on the analysis of Pileni²⁴ and Joselevich and co-workers,²⁵ the molar concentration of AOT micelles in the present work was about 2.4×10^{21} micelles/L (0.2 mol/L AOT). The molar concentration of AgCl particles for the given concentration of silver nitrate, $4.3 imes 10^{-4}$ mol/L for example, was 1.5×10^{17} particles/L. Thus, the probability finding one AgCl particle in one micelle was only 6.2×10^{-5} . In our experiments, the CD-2 concentration was 1.1×10^4 mol/L, i.e., 6.6×10^{19} mol/L. The probability of finding one CD-2 molecule in one micelle was about 2.8×10^{-2} . Therefore, each micelle contains generally no more than one CD-2 molecule. If the CD-2 molecule is distributed into the water core with one AgCl particle, the redox reaction between CD-2 and AgCl could occur. According to Eq. (1), the oxidation of one CD-2 molecule produces two silver atoms. When a second developer molecule from another water core reacts with the above AgCl particle, the two silver atoms produced previously may already be separated from the water core by fusion-fission. For this reason, bigger silver clusters could only form through fusion-fission among micelles containing silver atoms. Due to statistical factors, there was thus little possibility to form bigger silver clusters. Moreover, the AOT film may protect the small silver clusters from aggregation.

Obviously, the reactions described by Eqs. 1, 2 and 3 are redox reactions involving electron transfer; therefore, these reactions are relatively fast. However, the time scale for diffusion controlled collision and species exchange among micelles is respectively 0.1 - 1 ms and 0.1 - 1 ms.¹³ Thus, the rate-limiting step of the color-forming reaction under our conditions is assumed to be the process of exchange of reactive species among water cores. Therefore, the color-forming reaction proceeds



Figure 4. The change of the absorption at 652 nm with the reaction time; for experimental details see Table I.

TABLE I. Experimental Conditions for Kinetic Runs

	AOT	Excess of Cl	NaOH
а	0.2	10%	0.002
b	0.2	1%	0.002
С	0.2	1%	0.004
d	0.1	1%	0.002

more slowly in reversed micelles than in a practical color photographic process (Fig. 3).

Various factors may influence the color-forming reaction. As shown in Fig. 4, for the conditions given in Table I, decrease in AOT concentration led to increase in the rate of dye formation. Keeping other parameters invariant, a decrease in AOT concentration should lead to a decrease of the micelle concentration, which results in an increase of a reagent concentration in the water phase. The increase of the Cl⁻ ion concentration may however lead to a decrease of the reaction rate, because Cl⁻ ions inhibit the reaction between AgCl and the developer (see Fig. 4(a) and (b)). Changes in micelle concentration and particle size also affect kinetics of interparticle intreraction and of exchange of reactive species among micelles, leading to complex alterations of the rate profile (see Fig. 4 (b) and (d)).

As is well known, the reduction of silver halide by a developer is a spontaneous process thermodynamically. Keeping other factors as a constant, differential between developable and undevelopable grains of silver halide in a photographic film depends dynamically on the activity of a developer. During a normal color photographic development, the concentration of alkaline compounds in a photographic developer can influence developing activity of the developer by change of the redox potential of the photographic developer. Moreover, only in an alkaline solution, can a cyan color coupler form a coupler anion that reacts with the oxidation product of a developer to form dye. The experiments here showed that the concentration of sodium hydroxide is very important to the colorforming reaction in the reversed micellar system. Although AgCl particles in reversed micelles were unexposed to light, the color-forming reaction still proceeded, as long as the concentration of NaOH was suitable. Also, the greater the concentration of NaOH, the faster the reaction proceeded (see Fig. 4 (c) and (d)). Based on Eqs. (1) through (3), the complete reaction for one developer molecule needs two hydroxide ions to neutralize two protons. In principle, the hydroxide ions should take part in the color forming reaction here in a stoichiometric relationship. However, the behavior of hydroxide ions in reversed micelles is not very clear, owing to dissociation of hydroxide ions or protons from other compounds in the reversed micelles, as will be discussed elsewhere.

Clearly, micelle solutions, particularly reversed micelles can offer a unique microenvironment, in which water soluble reactants are isolated in different water cores, and oil soluble reactants are present in a continuous hydrophobic phase. In a reversed micelle system, a complicated color-forming reaction in photographic chemistry can be controlled by factors, such as a surfactant concentration, the ratio of [H₂O]/[surfactant], and reagent concentration. These advantages, together with the ability to tailor freely the particle size of metal and semiconductor in reversed micelles, suggest a rich use to study the sequential reaction occurring both in the hydrophilic and hydrophobic phases of this microenvironment. Most importantly, the work here demonstrates a possibility for studing the color imaging chemistry of silver halide in a controlled microheterogeneous system.

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